Preventive geochemical barriers during transport construction

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Abstract. The article discusses the possibility of using chlorite crushed stone as part of geochemical barriers in transport construction. It has been shown that during the construction of railways and during their operation, the main pollutants are petroleum products and heavy metal ions. To substantiate and study the neutralizing properties of chlorite crushed stone, infrared spectroscopy, ionomer, atomic absorption spectrometry and the gravimetric method for determining petroleum products were used. Research has shown that chlorite crushed stone is a quartz-albite-chlorite shale with a small inclusion of carbon; its physical and mechanical characteristics are not inferior to granite crushed stone. The oil capacity of chlorite crushed stone depends on the concentration of petroleum products in the model solution and ranges from 0.03 to 0.5 g/g. Chlorite crushed stone has a capacity towards nickel, iron and cadmium ions, while their simultaneous presence in the model solution does not have selectivity towards these ions. It has been proven that when the capacity of chlorite crushed stone is fully realized in relation to one of the heavy metal ions, it is not washed out and replaced by another metal ion (for example, nickel and iron ions). It has been proven that the presence of organic contaminants in the model solution does not significantly affect the capacity of chlorite crushed stone for heavy metal ions. It has been shown that chlorite crushed stone, due to its physical, physical-mechanical and chemical properties, can be used in geochemical barriers to protect the environment from pollution.
Keywords: Chlorite crushed stone, mineral waste, geochemical barrier, pollutant, petroleum products, heavy metal ions, capacity, oil capacity.

1 Introduction

The development of transport communications, including railway transport, significantly affects the deterioration of the geo-ecological state of the natural environment [1-6]. The negative impact of the construction and operation of railways on environmental components is multifaceted, however, among the chemical pollution caused by the use of railways, especially attention should be paid to the emission into the environment of such pollutants as heavy metals and petroleum products [7-12]. The cause of contamination of the right-of-way with heavy metals is exhaust gases from diesel locomotive engines, abrasion of the chassis and rails, transportation of mineral fertilizers, the use of chemicals for weed control, etc.

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Table 1 shows the gradation of soils according to contamination with heavy metal ions in the railway right-of-way.

Table 1 – Contamination of soil with heavy metal ions in the railway right-of-way

Heavy metal ion	Soil gradation by degree of contamination, mg/kg					
	I	II	III	IV	V	VI
Mn^{2+}	50	100	150	200	250	300
Cr^{3+}	10	20	30	40	50	60
Ni^{2+}	2	3	6	8	10	12
Cu^{2+}	1	2	3	4	5	6
Pb^{2+}	0,8	1,5	2,3	3,2	4	5
Co^{2+}	0,5	1,0	1,5	2	2,5	3
Cd^{2+}	0,1	0,2	0,5	1,0	1,5	2,0
Fe^{3+}	10	20	30	40	50	60

Contamination of the right-of-way with petroleum products occurs primarily due to spills, leaks and faulty boilers. Table 2 shows data on the degree of soil contamination with petroleum products at railway enterprises.

Table 2 - Share of territories of railway enterprises contaminated with petroleum products

Business name	Area of contaminated territory, %	Total area, ha	Content of petroleum products, mg/kg
Car maintenance companies	10	50	300
Depot (locomotive/wagon)	20/20	5/4,5	400/200
Sleeper impregnation plants	24	10	600
Washing and steaming stations	25	12	500

In general, the technogenic impact of the railway transport route on the environment cannot be uniform and depends on many factors:

- duration and intensity of operation of the transport route;
- type and volumes of cargo transported;
- availability of modern methods of cargo transportation;
- operating mode (travel speed, braking distance, etc.).

The most promising solution to the problem of environmental pollution during transport construction is the creation of geochemical barriers. Through the use of substances capable of interacting with contaminants of various natures, such barriers will prevent contaminants from entering the environment, binding them into safe compounds [13-21].

The purpose of this study was to test the possibility of using chlorite crushed stone in the geochemical barrier of a railway embankment to reduce environmental pollution by heavy metal ions and petroleum products.

2 Materials and methods

Chlorite crushed stone is a by-product of shungite mining. Pure shungite is found quite rarely in nature, mainly in the form of thin veins, up to 30 cm wide. It is present as an impurity in shungite shales and dolomites distributed in Karelia on the territory of the Zaonezhsky Peninsula and around the northern tip of Lake Onega. Inferred resources for all fields are about 1 billion tons. To date, the Koksu deposit in Kazakhstan has been explored with a confirmed reserve of 49 million tons. Up to 200 thousand tons of shungite are mined annually per plant, but the main product makes up no more than 15% of the total amount of processed rock, so when shungite is mined, up to 170 tons of waste is generated in the form of chlorite crushed stone.

The size of the fractions of chlorite crushed stone ranges from 0.114 to 40 mm; the crushed stone has a dark gray color and slatey texture (Fig. 1).

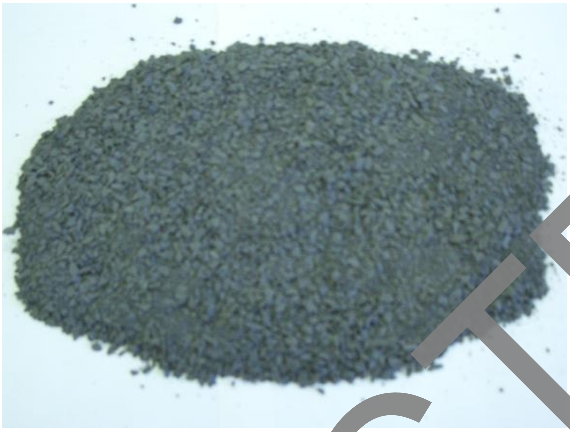

Fig. 1 – Chlorite crushed stone

According to the passport data, crushed stone is represented by granite with a small content of shungite in the amount of 1-3% and limestone in the amount of 1-3%, the presence of these impurities is confirmed by physical and chemical studies. According to the Federal Waste Classification Catalog (2023), chlorite crushed stone has a waste code of 2 00 110 01 20 5 “Silicate overburden rocks are practically not dangerous”, hazard class 5.

To study the properties of chlorite crushed stone, the following research methods were used:

- IR-Fourier spectroscopy

Laboratory Fourier transform infrared (FTIR) spectrometers are used to record and study optical spectra in the infrared (IR) region, as well as for qualitative and quantitative analysis of substances and elements. The method refers to optical methods of physical (instrumental) analysis for the identification of substances. The IR-Fourier spectrometer IRTracer-100 from SHIMADZU was used in this work.

- determination of the pH value of the environment

Determination of the degree of acidity of the aqueous extract of chlorite crushed stone was carried out using a pH-meter-ionomer. It is designed to determine pH, temperature, concentration of heavy metal ions. To use the Expert-001 device, ion-selective electrodes and a reference electrode are required. When measuring pH, a glass electrode is used as a measuring electrode, and a silver chloride electrode is used as an auxiliary electrode.

- gravimetric method for determining emulsified and film oil products

Today, there are many different instrumental methods for determining the mass concentration of emulsified and film oil products in wastewater, however, as a rule, such methods make it possible to determine fairly low concentrations of up to 10-50 mg/l. To determine the concentration of emulsified and film oil products, the gravimetric method was used. When determining the concentration of emulsified and film oil products, the mixture was settled, oil products were separated from water using a separating funnel, their volume was measured and converted to weight, taking into account the density of oil products in model effluents according to formula 1:

$$m_{n.p.} = V_{n.p.} \cdot \rho_{n.p.}, \qquad (1)$$

where:

m $_{n.p.}$ – mass of petroleum products, kg
V $_{n.p.}$ – volume of petroleum products, m^3
ρ $_{n.p.}$ - density of petroleum products, kg/m^3
- atomic absorption method for determining heavy metal ions

When studying the neutralizing properties of chlorite crushed stone in relation to ITM, the analysis of aqueous solutions was carried out by atomic absorption spectrometry (AAS). The AAS method is an instrumental method of quantitative elemental analysis. It is based on fixing the absorption value of optical radiation by free atoms. The concentration in the sample is determined using the established relationship between the analytical signal and its value. The concentration of heavy metal ions was monitored using an MGA-915MD atomic absorption spectrometer. The concentration of nickel, iron and cadmium ions was determined using the AAS method.

3 Research results

The infrared absorption spectrum of chlorite crushed stone is presented in Figure 2.

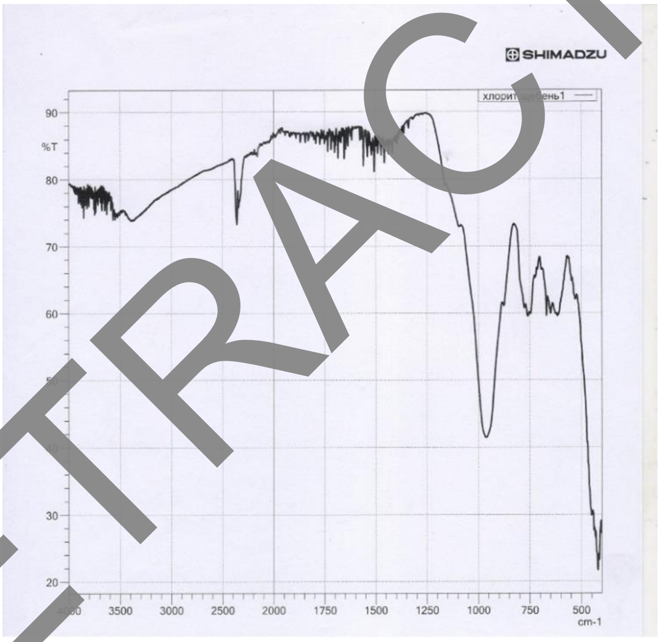

Fig. 2 - IR spectrum of chlorite crushed stone

The band at 471 cm^{-1} corresponds to bending vibrations of Me-O bonds. The band in the range of 779 cm^{-1} corresponds to Si-O-Si vibrations of rings of SiO4 tetrahedra. The absorption band in the region of 702 cm^{-1} is associated with an admixture of calcite. The spectrum contains a band at 600 cm^{-1}, characteristic of the C-C bond. Absorption bands in the frequency range 400...1200 cm^{-1} correspond to the fundamental vibrations of aluminum-silicon tetrahedra of the frame structure. The appearance of a clear shoulder at 1183 cm^{-1} is associated with vibrations of the carbon atoms of fullerene-like clusters; this band is characteristic of the C60 fullerene. Two narrow maxima at 760 and 680 cm^{-1} are associated with local maxima of the G(ν) function of graphite-like structures in which the carbon atoms are in a state close to sp^3 hybridization.

The physical and mechanical properties of chlorite crushed stone in accordance with the requirements for crushed stone as a building material are presented in Table 3.

Table 3 - Physical and mechanical properties of crushed stone

Index	Test results (average value)
Content of flaky and needle-shaped grains, %	24,5
Crushing grade, weight loss, %	5,3
Abrasion grade, weight loss during testing, %	A-1 (16,7)
Content of soft rock grains, % by weight	Not detected
Frost resistance grade	F 200 (2,8)
Content of dust and clay particles, % by weight	0,01
Clay content in lumps, % by weight	Not detected
Resistance against all types of decay, mass loss during decay, %	1,0

Studies to determine the pH of the aqueous extract of chlorite crushed stone were carried out using a pH meter-ionomer of the Expert-001 brand. An aqueous extract was prepared from the sample, which was analyzed for pH using ion-selective electrodes. The total relative error is 0.1 pH units. The essence of the method is to extract water-soluble salts from the soil with distilled water at a soil-to-water ratio of 1:5 and determine the pH using a pH meter.

Part of the soil suspension, with a volume of 15–20 cm3, was poured into a beaker with a capacity of 50 cm3 and pH measurements were carried out. The pH meter is adjusted using three buffer solutions with pH = 4.01, pH = 6.86 and pH = 9.18. Buffer solutions were prepared from standard titres. The pH meter readings were recorded 1.5 minutes after the electrodes were immersed in an aqueous extract when the pH meter readings stopped drifting. The research results are shown in Table 4.

Table 4 - determination of pH of aqueous extract of chlorite crushed stone

Sample number	Settling time	pH
1	5	5,5
2	30	5,5
3	4	5,6
4	12	5,7
5	24	5,7

To describe the efficiency of purifying contaminated water using various filter materials, the concepts of sorption and capacity (the mass of contaminants that 1 kg of substance can absorb) are used [22-23], which also applies to materials capable of collecting petroleum products.

The most promising method for determining the oil capacity of film and emulsified petroleum products for bulk filter materials is the method of filtering a model solution with a known concentration of petroleum products through an active load, determining their final concentration after filtration and calculating the oil capacity using formula 2:

$$\mathrm{N} = \frac{\mathrm{C}_{out.} - \mathrm{C}_{final}}{m_3},\ \mathrm{g/g} \qquad (2)$$

$\mathrm{C}_{\mathrm{out.}}$ – initial concentration of petroleum products in the sample, g/l

$\mathrm{C}_{\mathrm{final.}}$ – final concentration of petroleum products in the sample after filtration through the loading layer, g/l

$\mathrm{m}_{3.}$ – loading weight, g

The residual concentration of emulsified and film oil products was determined by measuring the volume of oil products in the filtrate.

The cleaning effect was calculated using formula 3:

$$E = \frac{V_{out.} - V_{final.}}{V_{out.}} \cdot 100, \% \qquad (3)$$

$V_{out.}$ – initial volume of petroleum products in the sample, ml

$V_{final.}$ – final volume of petroleum products in the sample after filtration, ml

Research was carried out to select the optimal conditions for determining the oil capacity of chlorite crushed stone, namely, the optimal fraction size and the optimal filtration rate were determined (the results are presented in Tables 5 and 6).

Table 5 – Dependence of the oil capacity of chlorite crushed stone on the fraction size (filtration speed 3 cm/min)

Fraction size, mm	Cleaning effect, %	Oil intensity, g/g
7,5-10	11,1	0,09
5-7,5	14,0	0,13
3-5	15,1	0,18
2,5 - 3	20,0	0,28
2,5 – 1,25	23,3	0,31
1,25 – 0,63	43,3	0,49
0,114-0,63	no filtering	

Table 6 – Dependence of the oil capacity of chlorite crushed stone on the filtration rate of oil products

Filtration speed, cm/min	Fraction size, mm	Cleaning effect, %	Oil intensity, g/g
1	1,25 – 0,63	46,7	0,52
	2,5 – 1,25	33,3	0,40
	2,5 - 3	26,7	0,34
3	1,25 – 0,63	43,3	0,49
	2,5 – 1,25	23,3	0,31
	2,5 - 3	20,0	0,28
7	1,25 – 0,63	40,0	0,46
	2,5 – 1,25	20,0	0,28
	2,5 - 3	13,3	0,22
10	1,25 – 0,63	33,3	0,4
	2,5 – 1,25	16,7	0,25
	2,5 - 3	10	0,19
15	1,25 – 0,63	26,7	0,34
	2,5 – 1,25	13,3	0,22
	2,5 - 3	6,7	0,16

Based on the research results, the optimal filtration speed of 3 cm/min (1.8 m/hour) and the optimal fraction size of 0.63-1.25 mm were selected. Under optimal conditions, studies were carried out on the dependence of the capacity of chlorite crushed stone on the concentration of petroleum products in the model solution. The results are presented in Table 7.

Table 7 – Dependence of the oil capacity of chlorite crushed stone on the concentration of petroleum products

Concentration, g/l	Oil intensity, g/g

500	0,49
257	0,31
125	0,16
100	0,12
53	0,08
31	0,03

The capacity of chlorite crushed stone under static conditions with respect to heavy metal ions is presented in Table 8.

Table 8 - Static capacity of chlorite crushed stone with respect to heavy metal ions, mg/g

Metal ion	Fraction size, mm			
	0,114…0,315	0,315…0,63	0,63…1,25	>1,25
Mn^{2+}	0,50	0,55	0,55	0,45
Fe^{3+}	0,60	0,60	0,55	0,45
Ni^{2+}	0,45	0,50	0,55	0,55
Cu^{2+}	0,60	0,50	0,50	0,40
Cr^{3+}	0,56	0,60	0,55	0,45
Cd^{2+}	0,50	0,50	0,40	0,40

In development of studies of the neutralizing properties of chlorite crushed stone, additional studies were carried out to determine the possible selectivity when cleaning a model solution containing several different metal ions simultaneously. For this purpose, waste capacities were determined for the simultaneous presence of metal ions in solution, for each metal ion.

To prepare a model mixture, soluble salts of heavy metals were used:

- $NiSO_4*7H_2O$;
- $FeCl_3 * 6H_2O$;
- $Cd(NO_3)_2 * 4 H_2O$.

The concentration of metal ions in the model solution was 10 MAC:
for nickel (II) ion –0.2 mg/l,
for iron (III) ion - 3 mg/l,
for cadmium (II) ion – 0.01 mg/l.

250 ml of prepared model solutions were placed in flasks, and crushed chlorite stone weighing 5 g was also placed there. The solution was stirred periodically, the contact time was 3 hours.

After this time, the material was separated from the model solution on a paper filter, and the final concentration of ITM in each sample was determined. The capacity was calculated using formula 4:

$$a = \frac{(C_{out.} - C_{final.}) \cdot V}{m} \tag{4}$$

a – static capacity, mg/g
Cout. – initial concentration of model solution, mg/l
Cfinal.- final concentration of model solution, mg/l
V- volume of model solution interacting with waste, l
m – waste mass, g
The results are presented in Table 9.

Table 9 - Static capacity of chlorite crushed stone

Static capacity for each metal separately, mg/g			Static capacity for each of the metals, in the presence of the other two, mg/g		
Ni^{2+}	Fe^{3+}	Cd^{3+}	Ni^{2+}	Fe^{3+}	Cd^{3+}

0,55	0,55	0,40	0,19	0,18	0,13

Since it was discovered that crushed stone is capable of sorption of several metals from a solution simultaneously, it was necessary to investigate the possibility of replacing an ion of one metal with ions of another metal located in the solution.

A study was conducted in which a solution containing a nickel ion with a concentration of 10 MAC was filtered through chlorite crushed stone until the crushed stone was completely saturated under dynamic conditions, i.e. until the breakthrough concentration in the source water and in the filtrate is equal. Next, a solution containing iron ions with a concentration of 10 MAC (3.0 mg/l) was filtered through crushed stone contaminated with nickel ions. Analysis of the filtrate showed the presence of iron ions at the level of the initial concentration, with the complete absence of nickel ions (Table 10).

Table 10 - Results of studies on the possibility of replacing nickel ions with iron ions

Volume of filtered model solution, l	Nickel ion concentration,		Concentration of iron ions, MPC fraction	
	Initial	In filtrate	Initial	In filtrate
0,25	0	0	10	9,7
0,5	0	0	10	9,8
1	0	0	10	10,0
3	0	0	10	9,9
5	0	0	10	10,0

Studies were also carried out on the capacity of chlorite crushed stone under the condition that contaminants of various natures were present in the model solution. A model solution was prepared containing iron ions with a concentration of 10 MPC and emulsified petroleum products with a concentration of 25 mg/l.

300 ml of a model solution was placed in the flask, and chlorite crushed stone weighing 5 g was poured into it. The solution was stirred periodically, the contact time was 3 hours. After this time, the material was separated from the model solution on a paper filter, and the concentration of iron ions was determined (Table 11).

Table 11 - Capacity of chlorite crushed stone in the presence of organic contaminants

Concentration of petroleum products, mg/l	Capacity, mg/g		
	in relation to iron ions	in relation to nickel ions	in relation to cadmium ions
25	0,50	0,50	0,35

4 Analysis of results

IR spectroscopy data confirms the chemical composition of chlorite crushed stone, which includes aluminosilicates of various metals in the form of chlorite minerals ((Mg,Fe)3(Si,Al)4O10(OH)2·(Mg,Fe)3(OH)6) and albite (Na[AlSi3O8]), as well as quartz (SiO2) and carbon (C). Thus, in terms of mineral composition, chlorite crushed stone can be classified as quartz-albite-chlorite schist with a small inclusion of carbon (Table 12).

Table 12 – Mineral composition of chlorite crushed stone

Mineral	Contents, volume %	Chemical formula
Chlorite	40-45	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$
Albite	35-40	$Na[AlSi_3O_8]$
Quartz	15-20	SiO_2

Calcite	1-3	$CaCO_3$
Shungite	1-2	C

According to Table 3, it can be seen that the physical and mechanical properties of chlorite crushed stone are close to granite crushed stone. The data presented allow us to conclude that, from a technical point of view, large waste fractions can be used in the construction industry, including in transport construction in the ballast prism of railway tracks.

The research results showed that the oil capacity significantly depends on the size of the filter material fraction, the filtration speed and the initial concentration of the pollutant in the solution.

The results of the study showed that chlorite crushed stone does not have selectivity towards heavy metal ions (for example, nickel, iron and cadmium ions) and when the capacity of chlorite crushed stone towards one of the heavy metal ions is fully realized, it is not washed out and replaced by another metal ion . The presence of organic contaminants in the model solution does not significantly affect the capacity of crushed chlorite stone for heavy metal ions (for example, iron, nickel, cobalt ions).

5 Conclusion

It has been determined that chlorite crushed stone can be classified as quartz-albite-chlorite shale with a small inclusion of carbon; its physical and mechanical characteristics are not inferior to granite crushed stone.

The optimal filtration speed of 3 cm/min (1.8 m/hour) and the optimal fraction size of 0.63-1.25 mm of chlorite crushed stone were determined to determine its oil capacity. The oil capacity of chlorite crushed stone under selected optimal conditions significantly depends on the concentration of petroleum products in the model solution and ranges from 0.03 to 0.5 g/g.

The static capacity of chlorite crushed stone with respect to nickel, iron and cadmium ions with their simultaneous presence in the model solution was determined, reaching values of 0.19 mg/g, 0.18 mg/g and 0.13 mg/g, respectively. It has been proven that crushed chlorite stone does not have selectivity towards heavy metal ions (for example, nickel, iron and cadmium ions).

The possibility of replacing an ion of one metal with ions of another metal located in a model solution has been studied and it has been proven that when the capacity of chlorite crushed stone is fully realized in relation to one of the heavy metal ions, it is not washed out and replaced by another metal ion (using the example of nickel and iron ions).

The influence of the presence of organic petroleum products in a model solution on the ability of chlorite crushed stone to neutralize heavy metal ions was studied.

It has been proven that the presence of organic contaminants in the model solution does not significantly affect the capacity of crushed chlorite stone for heavy metal ions (for example, iron, nickel, cobalt ions).

Thus, chlorite crushed stone, being a large-scale waste from shungite mining, in terms of its mineral composition can be classified as quartz-albite-chlorite shale with a small inclusion of carbon, in terms of physical and mechanical characteristics it is not inferior to granite crushed stone, it has neutralizing properties in relation to ITM and dissolved petroleum products and can be used in geochemical barriers to protect the environment from pollution.

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