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Features of Geocoprotective Properties' Manifestation of Some Silicate-containing Waste Products

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Abstract. The relevance of the problem is caused by contamination of the biosphere with heavy metal ions, which are called «super-toxicants of the 21st century». The aim of the work is to detect and evaluate the ability of silicate-containing waste products to absorb heavy metal ions. Such silicate-containing waste products can be called mineral geoantidotes. The leading method of researching and evaluating the mineral geoantidotes' ability to absorb heavy metal ions is to determine their capacity in relation to contamination. The value of the capacity allows to compare known sorbents used in practice with those proposed in the article. The static and dynamic capacities of mineral geoantidotes have been determined as a result of the research; it has been shown that the ion exchange of calcium ions into heavy metal ions is a possible mechanism for the absorption of heavy metal ions. The conducted experiments showed the absence of absorbed metals' leaching into the aqueous solution from mineral geoantidotes, the lack of selectivity with respect to various heavy metal ions, and the absence of the organic pollution's influence on the ion exchange. The questions of mineral geoantidotes' regeneration or its further safe utilization into burning technologies are considered. The materials of the article can be useful for developing technological solutions for reducing the negative impact of heavy metal ions on the hydrosphere, as well as on the useful utilization of solid mineral silicate-containing waste products.

1. Introduction

Available and effective scientific and technological solutions which would simultaneously reduce the negative impact on various elements of the biosphere are needed taking into account the existing scale of anthropogenic pollution. For today the following environmental problems can be singled out from the actual problems of the national economic complex of the Russian Federation [1-4]:

firstly – wastewater pollution with heavy metal ions,

secondly – solid mineral waste formation and storage from various industries.



One of the ways to solve these problems in a complex can be solid mineral waste usage for wastewater treatment. According to this, the detection of solid mineral waste's sorption properties in relation to heavy metal ions is of fundamental importance [5-7].

The nature of nascent mineral waste in the form of various silicates of calcium and magnesium often unites many different industries. More than 2.5 billion cubic meters including silicate-containing rocks, 250 million tons of silicate-containing waste from concentrating and metallurgical industries and about 100 million tons of slag and ash from thermal power plants were accumulated in dumps only in the Chelyabinsk region. About 15 million hectares of useful land is occupied by dumps.

The volume of silicate-containing waste accumulation is presented in Table 1, along with such known waste generation processes as mining, steelmaking, construction materials, additional is represented: breakdown of building structures [9-16].

Table 1. Silicate-containing waste products.

Example of solid mineral waste	Active component	Process of formation	Quantity of formation (mln.t / year)	Geographical region
Blast furnace slag	$2\text{CaO} \cdot \text{SiO}_2$	Cast iron smelting	0.5-4.7 (from 1 combine)	North-Western Russia, Eastern Siberia
Crushed concrete	$x\text{CaO} \cdot y\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Breakdown of building structures	10-12 (Moscow)	Ubiquitously
Foam concrete waste		Production of foam concrete	0.06 (from 1 plant)	North-Western and Central Russia

The solid minerals given in the Table 1 are contained in the form of large-tonnage technogenic wastes in great quantities. If these wastes have a sorption capacity in relation to heavy metal ions, they can be called the mineral geoantidotes.

2. Material and methods

Sorption capacity estimation (mg / g) is the main method for determining the ability of silicate-containing waste products to absorb. The sorption capacity shows how many mg of contaminants (in this case heavy metal ions) one gram of the sorbent can absorb. The capacity was determined with relation to various heavy metal ions and was calculated by an equation (1):

$$a = (C_{fin} - C_{ini})V/m \quad (1)$$

where a – the sorption capacity (mg / g)

C_{ini} , C_{fin} – the initial and the final concentration of metal ions in the sample (mg / l)

V – the volume of the sample (l)

m – the mass of the sorbent (g)

Breakthrough threshold concentration was considered at the level of MPC of fishery for each of the metals. The grain size of the sorbent was less than 0.114 mm to determine the static capacity. Taking into account the low specific surface area of the studied materials, it can be assumed that the greatest effect of their usage can be achieved in the case of low initial concentrations of heavy metal ions in the waste water, so the initial concentration of heavy metal ions in model solutions was at the level of 10 MPC.

It is known from the practice of wastewater treatment that the filtration rate and the grain size of the sorbent oscillate within a fairly wide range [17-18], therefore, researches have been carried out to

select the optimum filtration rate and grain size of the sorbent. All the studied materials were preliminarily grounded and dispersed into a number of fractions ranging from 0.114 to 5 mm, the filtration rate of the solution varied from 1 to 9 meter per hour.

Taking into account the nature of silicate-containing waste products [19-24], it can be assumed that the absorption of heavy metal ions proceeds by the ion exchange mechanism. Additional research for the detection of possible exchange ions in the filtrate were carried out to substantiate ion exchange during the sorption of heavy metal ions. Presumably ions of alkaline and alkaline-earth metals - potassium, sodium and calcium - can be released into the aqueous solution. The research consisted in determining the concentration of these metals in water passed through the sorbents. The background content of these metals in pure water passed through the sorbent layer was previously defined in the determination of exchange ions.

3. Results of the research

The results of preliminary research on the choice of the optimum filtration rate and the grain size of the sorbent are given in Table 2.

Table 2. Data on the choice of the sorbent grain size and the filtration rate.

Sorbent grain size (mm)	Volume of the passed model solution (L)											
	Foam concrete waste				Crushed concrete				Blast furnace slag			
	Filtration rate (meter per hour)											
	1	3	6	9	1	3	6	9	1	3	6	9
0.114-0.315	30	29	28	-	24	22	22	-	23	22	22	-
0.315-0.630	30	29	28	23	23	22	22	20	23	22	22	21
0.630-1.25	18	18	17	10	11	10	9	5	10	6	5	5
1.25-2.5	10	10	10	8	8	8	7	2	8	5	4	3
2.5-5.0	8	8	6	6	5	4	4	2	5	3	3	2

According to the results of the experiment, a filtration rate of 6 m / h and a grain size of 0.315-0.63 mm were chosen to determine the dynamic capacity of the sorbents.

The research of solid silicate-containing wastes products included the determination of static and dynamic capacities. The results of the research are given in Tables 3 and 4.

Table 3. The static capacity of silicate-containing waste products (mg / g).

Name of the material	Heavy metal ions					
	Cu^{2+}	Cd^{2+}	Fe^{3+}	Mn^{2+}	Ni^{2+}	Cr^{3+}
Foam concrete waste	2.2	2.5	2.7	2.3	2.1	2.2
Crushed concrete	1.1	1.2	1.3	1.1	1.0	1.2
Blast furnace slag	1.0	1.0	1.2	1.2	0.9	0.9

Table 4. The dynamic capacity of silicate-containing waste products (mg / g).

Dynamic capacity of crushed concrete					
Mn^{2+}	Fe^{3+}	Ni^{2+}	Cu^{2+}	Cd^{2+}	Cr^{3+}
0.78	0.45	0.98	0.60	0.79	0.98
Dynamic capacity of foam concrete waste					
2.05	2.32	1.90	2.06	2.12	2.12
Dynamic capacity of blast furnace slag					
0.65	0.9	0.5	0.75	0.85	1.10

To research the possibility of simultaneous sorption of several heavy metal ions, the dynamic capacity of sorbents was determined for one of the metals in the presence of the other two. The results of the research are given in Table 5.

Table 5. The results of selective sorption research.

Sorbent	Dynamic capacity for each of the metals in the presence of the other two (mg / g)		
	Mn²⁺	Fe³⁺	Cr³⁺
Blast furnace slag	0.23	0.44	0.52
Foam concrete waste	0.98	1.22	1.10
Crushed concrete	0.35	0.22	0.50

According to the data in Table 5, the selective sorption was not observed for any of chosen metals with the simultaneous presence of metal ions in solution.

To justify the ion exchange the research of the exchange ions detection in the filtrate were carried out. It turned out that the ions of calcium, potassium and sodium leaching out into water when it passes through the sorbent (Table 6).

Table 6. The results of exchange metal ions leaching from a sorbent during the sorption of heavy metal ions.

Sorbent	Concentration of exchange metal ions (mg / l)					
	background content			passage of heavy metal ions		
	Ca²⁺	K⁺	Na⁺	Ca²⁺	K⁺	Na⁺
Blast furnace slag	2	2	0.5	9.8	2	0.5
Foam concrete waste	3	0	0	10.2	0	0
Crushed concrete	3.9	0	0	10.1	0	0

The strength of the formed bonds between the sorbent and heavy metal ions is indirectly confirmed by testing the possibility of "leaching" heavy metal ions into the aqueous medium from its surface. The research wastes were pre-saturated with iron ions. Analysis of the water extracts of each "saturated" waste was carried out after that (Table 7).

Table 7. The results of the analysis of "saturated" waste's water extracts.

Name of waste	pH	Concentration of Fe (III) in water extract (mg / l)	Concentration of Ca (II) in water extract (mg / l)
Crushed concrete	7.8 - 8.2	-	1.8 - 2.0
Foam concrete waste	7.8 - 8.2	-	1.5 - 1.8
Blast furnace slag	7.3 - 7.6	-	0.5 - 0.8

The results of the research given in Table 7 exclude the possibility of heavy metal ions leaching from the surface of the sorbent.

Since the ion exchange process can be in equilibrium, it is necessary to research the possibility of replacing heavy metal ions (for example manganese) with calcium ions on the surface of the used sorbent. For this purpose, a crushed concrete treatment was carried out under dynamic conditions with

a solution of manganese salt with an initial concentration of 10 MPC. A calcium salt solution was passed through the used sorbent until the concentration of calcium ions in the initial water and in the filtrate stabilized. The concentration of the calcium salt solution was assumed equal to the molar manganese content in the used sorbent and referred to the liter of the solution. After stabilization of the calcium ions concentration in the sorbent, i.e. when the complete process of manganese ions replacement with calcium ions was completed, the process was repeated again, i.e. calcium ions was replaced with manganese ions. This operation of direct and reverse replacement was carried out several times. It was noticed that the sorbent capacity was steadily decreasing after each subsequent operation for the manganese ion. The results of the experiment confirm that the chemical bond formed between heavy metal ions and the sorbent is stronger than between the sorbent and the calcium ions. The increase in the number of cycles was impractical because after the first cycle the capacity of the sorbent was 0.45 mg / g, and after the second cycle - 0.1 mg / g. The results of research on the heavy metal ions reverse replacement on calcium ions allow us to talk about the possibility of regenerating such sorbents for their reuse.

Since experiments have shown that the process of partial replacement of sorbed heavy metal ions in the presence of calcium ions is possible, other research have been carried out to determine the capacity of sorbents in solutions with varying degrees of hardness. The results showed that when the hardness of solutions exceeds 10 mME / l, the capacity of sorbents decreases significantly.

It is important for practical purposes to research sorption with the simultaneous presence of various nature contaminants (organic and inorganic) in water. The research of the sorbents' sorption capacity determination with simultaneous presence of heavy metal ions and dissolved petroleum products in the water were carried out. Since it was previously shown that the sorbents do not possess selectivity for the heavy metal ions sorption, the model solution contained ions of only one metal (manganese ions) with a concentration of 10 MPC and dissolved petroleum products with a concentration of approximately 2 mg / l. The concentration of heavy metal ions and dissolved petroleum products at the level of the corresponding MPC was accepted as a breakthrough. The results of the research showed that the capacity of sorbents for manganese is not decreased with the presence of dissolved petroleum products in the model solution. Such results indicate that the heavy metal ions sorption does not depend on the presence of organic contaminants in water.

It is important to know the dependence of the sorbent capacity on the initial concentration for the operational characteristics of the sorbent. Since concentrations of not less than 10 MPC are interesting for industrial operation, the capacities of granulated blast furnace slag have been researched with the following initial concentrations of the manganese solution: 10 MPC, 20 MPC, 40 MPC, 60 MPC, 80 MPC, 120 MPC. The results of the research are given in Table 8.

Table 8. The data of the dependence of sorbent capacity on the manganese concentration in the initial solution.

Concentration of Mn^{2+} (mg / l)	Concentration of Mn^{2+} (share of MPC)	Capacity (mg / g)
1.0	10	0.76
2.0	20	0.8
4.0	40	0.8
6.0	60	0.036
8.0	80	0.016
12.0	120	0.01

The question of the beneficial utilization of the used sorbent can be solved as part of its use in firing ceramics. For example, the used blast furnace slag can be introduced qua additive into raw materials as a replacement for the waste component (natural sand) and a fluxing component to increase the formation of the liquid phase, which makes it possible to increase the flexural strength

limits. The experiments have shown the possibility of used sorbent application in the method of plastic molding. Bending and strength tests were carried out with samples (160 · 40 · 40 mm) which were made of cambrian clay and used blast furnace slag in laboratory conditions. The results of the research showed that the strength of the samples corresponds to the brick brand M150, and the bend of the samples corresponds to the M300, i.e. there is an increase in flexural strength, which leads to an increase of water resistance, which is especially important for semi-dry pressing technology. In this regard, the usage of mineral geoantidotes could be considered as one of the aspects of non-waste technology in the hydrosphere protection and purification.

4. Conclusions

1. Solid mineral silicate-containing waste products could be considered as a mineral geoantidotes in relation to heavy metal ions.
2. Solid mineral waste products, for example blast furnace slag, foam concrete waste and crushed concrete, have static and dynamic capacity in relation to heavy metal ions.
3. Systematic research of exchange ions have shown that a possible mechanism for the absorption of heavy metal ions is the ion exchange of calcium ions for heavy metal ions.
4. The results of the research have shown the absence of absorbed metals leaching into the aqueous solution from the sorbent, the absence of selectivity with respect to various heavy metal ions, and the absence of the organic pollution effect on the ion exchange.
5. The issue of the possible sorbent regeneration and its further safe utilization into burning technologies is considered.
6. According to the results of the research, patents for wastewater treatment from heavy metal ions [25-26] and hygienic certificate for foam concrete as a sorbent for wastewater treatment No. 78.01.03.033.P.009887.12.01 are received.

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