



# STUDY OF HEAVY METAL EMISSION FROM GRINDING SLUDGE

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## ABSTRACT

The paper presents the results of a study of the environmental impact of industrial waste - grinding sludge. Atomic emission spectroscopy was used to determine the content of 25 elements in aqueous and acetate-ammonium waste extracts. It was found that, in terms of mass content, the priority elements in the water extract are Ca, B, Mg, Fe, Si, Sr, the priority elements in the acetate-ammonium extract are Fe, Ca, Mn, Cr, Si, Ni, B. To assess the environmental hazard of the analyzed elements for environmental objects, the calculations of the multiplicity of exceeding the standard indicators, as well as the indices of environmental impact were carried out. According to the results of calculations, it was determined that the water extract of grinding sludge is characterized by the level of toxic water pollution as "highly toxic (dirty)", acetate-ammonium - "extremely toxic (extremely dirty)". In the case of aqueous extracts of grinding sludge, the main contribution to the pollution of drinking water is made by soluble compounds B, Ca and Fe, to the pollution of natural water - Fe, B, Mn and Zn, in acetate-ammonium extracts - heavy metals - Fe, Cr, Mn, Ni, Pb and Cd. The most significant increase in the acetate-ammonium buffer is the increase in the environmental impact indices for six priority elements on the water of water bodies for domestic drinking and cultural and domestic water use (by 2734 times) and on water of water bodies of fishery significance (by 9648 times). Accordingly, the contact of grinding sludge with natural water, which exhibits buffering and complex-forming properties with respect to heavy metals, leads to its significantly greater contamination with the studied heavy metals in comparison with tap, distilled or non-contaminated natural water. The placement of grinding sludge in soil (soil) with filtration soil water, in wet soil, in soil with rain and melt water will lead to significant emission of mobile forms of heavy metals and pollution of the soil landscape and adjacent environments, which in turn requires the introduction of additional measures aimed to reduce the toxicity of the above waste.

**Keywords:** production waste, grinding sludge, heavy metals, atomic emission spectroscopy, emission of heavy metals, disposal of production waste.

## 1. INTRODUCTION

Recycling and disposal of industrial waste, taking into account their diversity in composition and properties, indicators of hazard and requirements for storage and transportation, means the development of a technology for their processing, as well as the creation of a material and labor base for the implementation of these technologies.

The final product of processing should not only have a certain set of useful qualities, but also should not be a source of secondary environmental pollution, and should also be economically beneficial for use. And this means that, first of all, it is necessary to study the emission of potentially harmful ingredients into the environment, both waste and the product of its processing. If the volumes of this emission for the processed product is less or at least of the same order as that of the waste, or does not exceed the relevant standards of the environmental object or does not exceed the corresponding emission indicators for similar products from primary raw materials, then the processed product can be considered relatively safe for the environment and person.

As for grinding sludge (GS) and metallurgical production waste, the technologies for their processing and enrichment are currently insufficiently developed for successful implementation in production. Enterprises with large volumes of grinding production accumulate up to 1000 tons of GS per year. The solution to the problem is known - it is necessary to decompose the sludge into its components. The economic feasibility of separating grinding slimes is obvious: a ton of ultra dispersed metal

costs from 60 to 250 thousand rubles, a ton of abrasive ~ 12 to 33 thousand rubles. Thus, utilization of GS can turn into profitable production for the enterprise [1]. The above considerations determine the relevance of the topic of work devoted to the development of a technological process for the separation of grinding slimes and further return to the production of recoverable materials.

As part of the work presented, studies of the environmental impact of GS were carried out. The results of this work can serve as an environmental justification for further research into the possibility of processing GS into products with useful properties.

## 2. METHODS

GS is a waste from the mechanical production of the engineering industry and is usually formed during metalworking [2]. Most often they are black powders with varying moisture content and an inconsistent content of petroleum products. The main components GS, apart from the already mentioned oil and water, are the products of grinding processes - particles of abrasive materials and the processed alloy in the form of both metal and its compounds, mainly oxides, including mixed ones [3].

Considering the wide range of alloys used in metal products, the variety of grinding technologies used for grinding materials, it is possible to assume both the complexity of the GS composition and the diversity and inconsistency of the GS composition. On the one hand, this complicates the procedure for studying the composition of sludge and water extracts from them, and



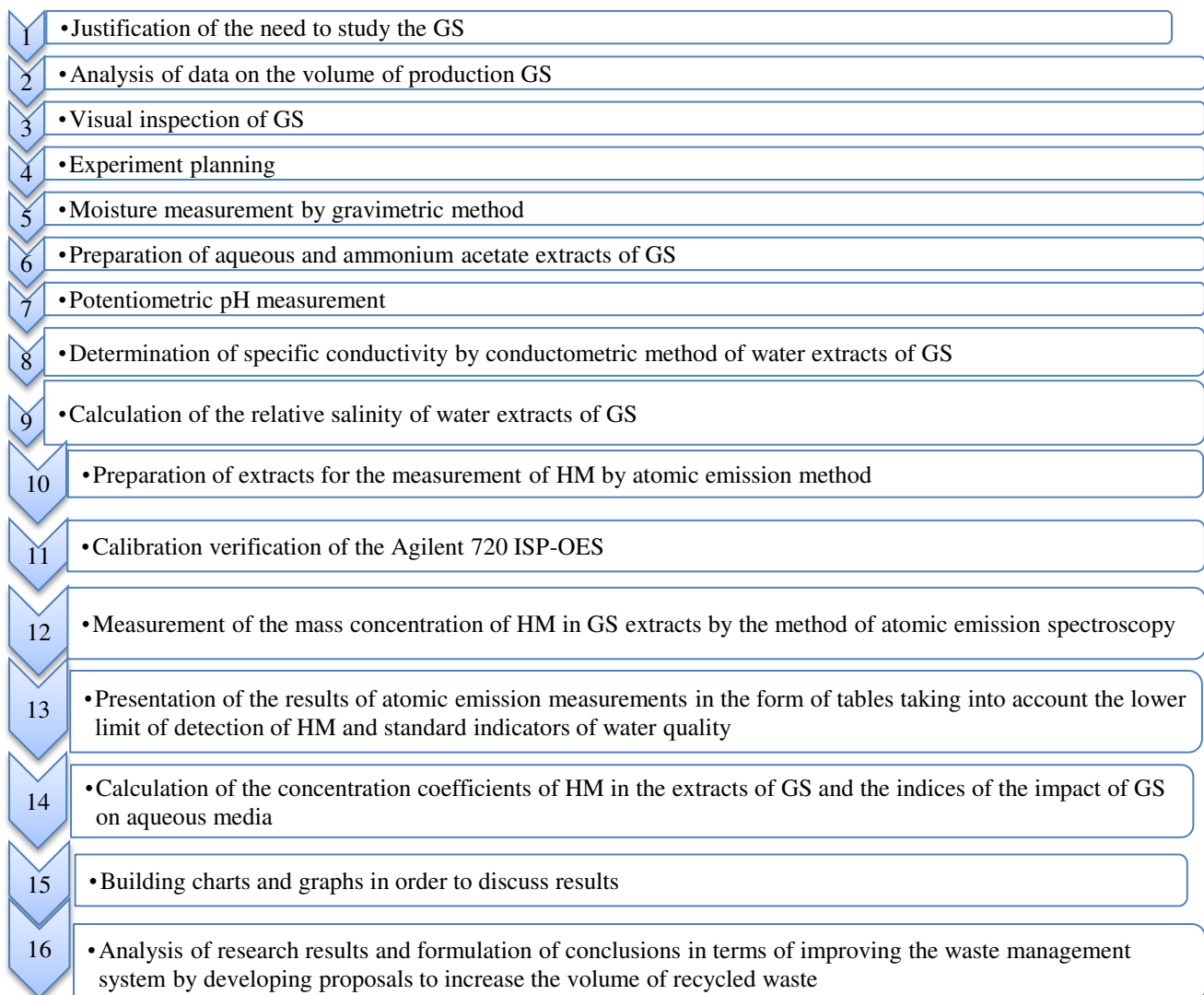
on the other hand, it makes it necessary to study the impact of GS on environmental objects during temporary or permanent placement, as well as transportation, processing and disposal.

This does not take into account the possibility of emission of harmful GS ingredients into aqueous media in the form of mobile forms of heavy metals (HM), which is theoretically difficult to predict without comprehensive data on the composition of the GS solid phase with an accuracy of thousandths of a percent.

The grinding processes themselves, which often occur with the heating of the metal surface, can be accompanied by thermochemical reactions that increase the list of water-soluble components in GS. It is possible that some of these components, to one degree or another, provide the transfer of toxic HM into the aqueous phase when the corresponding GS suspensions are shaken, simulating the effects of GS contact with water or soil objects of the environment.

The study of water extracts (WE) based on distilled water can provide information on the level of water pollution in water bodies of various uses. The study of ammonium acetate extracts (AE) provides primary data on the level of soil cover sludge pollution.

A block diagram of the work is shown in Figure-1. This diagram implies the use of modern methods of physicochemical analysis of research objects - potentiometry, conductometry, atomic emission spectroscopy. The work execution algorithm provides for the intelligent analysis of the initial data on GS waste; planning an experiment; obtaining primary data on GS indicators, such as moisture, pH of the aqueous extract and salinity; preparation of the Agilent 720 ISP-OES instrument and GS samples for quantitative measurements; cooking WE and AE; quantitative measurements; obtaining and processing results using applied and statistical software tools; construction of diagrams and graphs.



**Figure-1.** Block diagram of work execution.



### 3. RESULTS AND DISCUSSIONS

According to the information provided by the customer's enterprise for performing the submitted work GS, which is received by the enterprise from a large machine-building plant, the sludge contains oil products in the amount of 12.6%. According to available data, the amount of GS waste generated in 2019 was almost 468 tons, in 2017 - 1233 tons and in 2020 - 1400 tons.

In accordance with the Federal Classification Catalog of Wastes (FCCW) [4], this waste is referred to as "grinding sludge containing petroleum products in an amount of less than 15%" and belongs to the IV hazard class (low hazardous waste). In accordance with the criteria for classifying waste as a hazard to the environment [5], the degree of harmful impact on environmental objects is low, which corresponds to a violation of the ecological system with a self-recovery period of 3 years.

The approved component composition of GS is characterized by a relatively small list of ingredients that can affect the hazard class: aluminum - 4.94%, iron - 3.85%, manganese - 1.85%, petroleum products - 12.56%, silicon dioxide - 62.90 %, moisture - 13.90%.

Based on the foregoing, it becomes necessary to study the composition of GS in more detail, implying a

quantitative chemical analysis of aqueous and ammonium acetate extracts GS to determine the mass concentration of a wider list of elements. The above studies will subsequently help to characterize the volumes of emission of pollutants into the water or storage environment, causing subsequent pollution of the environment.

At the initial stage of research, the primary indicators of GS were determined, such as humidity pH, electrical conductivity and salinity of water extracts. According to the data obtained, the moisture content of the studied GS samples is about 20%, the pH varies in the range from 7.0 to 7.5 units. pH, specific electrical conductivity - 50-70  $\mu\text{S}/\text{cm}$ , salinity (by NaCl) - 25 - 40 mg/l.

The results of atomic emission quantitative determination of elements in aqueous and ammonium acetate extracts GS are given in Table-1. Here, reference data on the lower limit of detection of elements ( $C_{LLD}$ ) by atomic emission spectroscopy on the "Agilent 720 ISP-OES" spectrometer are given, the maximum permissible concentration of water in water bodies of domestic drinking and cultural and domestic water use ( $MPC_d$ ), and the maximum permissible concentration of water in water bodies of fishery significance ( $MPC_f$ ).



**Table-1.** Mass concentration of an element in aqueous and acetate-ammonium extracts of grinding sludge, the lower limit of detection of elements ( $C_{LLD}$ ) by atomic emission spectroscopy on an Agilent 720 ISP-OES spectrometer, the maximum permissible concentration of water in objects of household drinking and cultural domestic water use ( $MPC_d$ ), maximum permissible concentration of water in fishery water bodies ( $MPC_f$ ).

No	Index E	Grinding sludge				
		$C^E$ , mg/l		$C_{LLD}$ , mg/l	$MPC_d$ , mg/l	$MPC_f$ , mg/l
		WE, $C^E_{WE}$	AE, $C^E_{AE}$			
1	2	3	4	5	6	7
Sample weight per hood volume		5 gr. per 0,15 l of water	5 gr. per 0,15 l buffer	-	-	-
1	Al	0,002	3,83	0,0001	0,2	0,04
2	Ba	<0,00003	0,100	0,00003	0,7	0,74
3	Be	<0,0000	<0,00001	0,00001	0,0002	0,0003
4	Cd	<0,00005	0,034	0,00005	0,001	0,005
5	Co	<0,0002	<0,0002	0,0002	0,1	0,01
6	Cr	<0,00015	69,1	0,00015	0,05	0,02
7	Cu	<0,0003	0,150	0,0003	1	0,001
8	Fe	0,155	2592	0,0001	0,3	0,05
9	Mn	0,0056	126	0,00003	0,1	0,01
10	Mo	<0,0005	0,490	0,0005	0,25	0,001
11	Ni	<0,0003	7,64	0,0003	0,1	0,01
12	Pb	<0,0008	0,505	0,0008	0,01	0,006
13	Sb	<0,002	0,838	0,002	0,05	0,005
14	Se	<0,002	0,073	0,002	0,01	0,002
15	Si	0,047	23,0	0,001	10	-
16	Sr	0,015	1,13	0,00001	7	0,4
17	Ti	<0,0001	<0,0001	0,0001	0,1	0,06
18	V	<0,0002	<0,0002	0,0002	0,1	0,001
19	Zn	0,0045	3,40	0,0002	1	0,01
20	Ca	2,08	263	0,00001	3,5	180
21	B	1,51	5,18	0,00010	0,5	0,5
22	Mg	0,190	2,82	0,00001	50	40
23	Ag	<0,0003	<0,0003	0,0003	0,05	-
24	Tl	<0,0015	<0,0015	0,0015	0,0001	-
25	As	<0,001	<0,001	0,001	0,01	0,05
$\Sigma^n C^E$		4,0	3099,3	-	-	-
$\Sigma^k C^E (>LLD)$		4,0	3099,3	-	-	-
$\Sigma^6 C^E$		4,0	3080,7			

Figure-2 shows a diagram of the priority of GS elements by mass content in the GS water extract. For plotting the diagram, data were selected for six elements from Table-1 (column 3) with the highest mass concentration in WE, numerically exceeding the lower limit of detection (LLD) of the corresponding element by atomic emission spectroscopy on an Agilent 720 ISP-OES

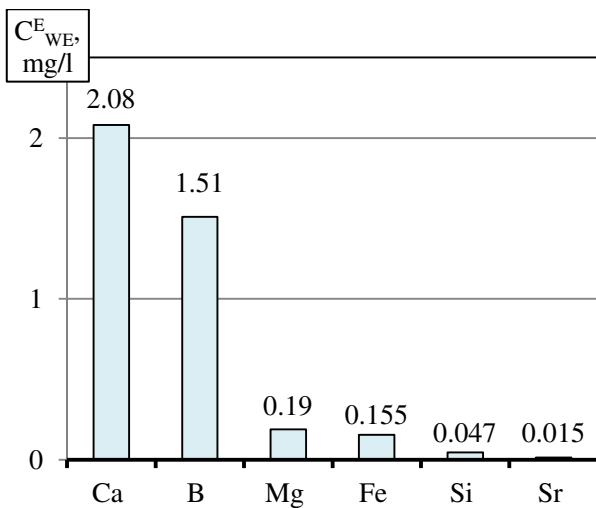
spectrometer. There are 9 such elements (Ca, B, Mg, Fe, Si, Sr), 6 are present in the diagram, there are no Mn, Zn and Al, the bars of which in this diagram will not appear due to the relatively low concentration value.

On the diagram, the elements are arranged in order of decreasing mass concentration of elements in WE GS, that is, the more to the left of the diagram the column

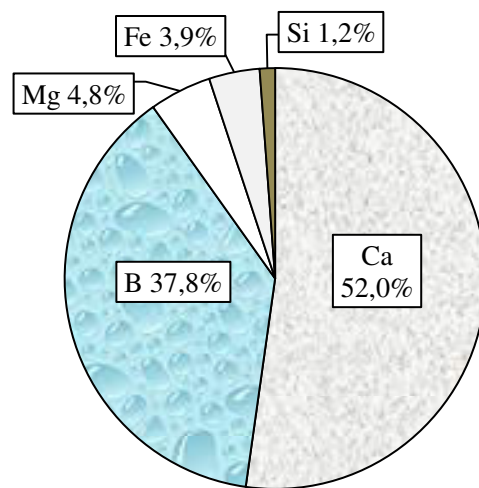


of an element is located, the greater its content in WE GS, since the emission of its compounds from GS to distilled water is greater by weight, the more "problematic" is the element in terms of mass concentration in water. From this point of view, Ca and B are the most "problematic". Their share of the mass content of elements leached from GS in WE turned out to be much higher than all other heavy metals GS mobile for transfer to distilled water (Figure-3).

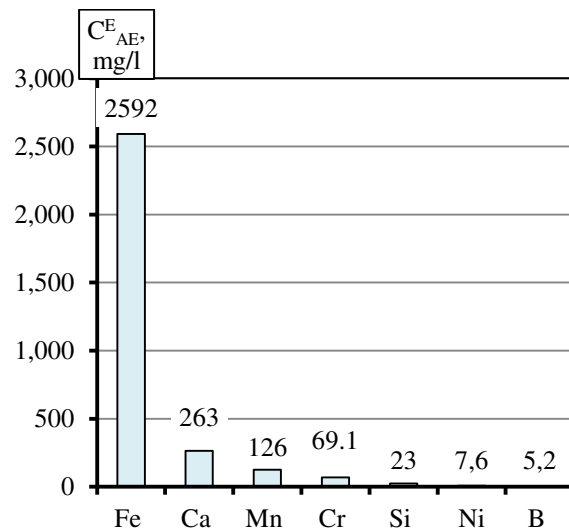
The transfer of heavy metals from GS to the aqueous phase increases sharply in quantitative terms (almost 800 times in total) if, instead of distilled water, an ammonium acetate buffer solution is taken to shake the suspension (Table-1, column 4). The sums of  $\Sigma^n C^E$ ,  $\Sigma^k C^E$  (>LLD),  $\Sigma 6C^E$  increased from 4.0 mg / L to about 3100 mg / L. This situation is probably due to the complexing properties of an aqueous solution of ammonium acetate with respect to compounds of many elements, including HM [6]. Acetate-ammonium buffer solution acts as a more effective extractant compared to distilled water. As a result, not only the quantitative, but also the qualitative picture of the priority and proportion of the mass contribution of elements to the mineralization of filtrate of GS powder suspensions changes (Figures 4 and 5).



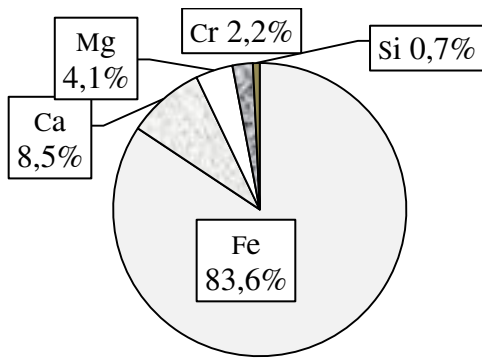
**Figure-2.** Priority by mass content in the water extract of six elements with the highest mass concentration  $C^E_{WE}$ .



**Figure-3.** The proportion (%) of five priority elements of grinding sludge from the total mass concentration of pollutants in distilled water in terms of elements.



**Figure-4.** Priority by mass content in the ammonium acetate extract of seven elements with the highest mass concentration  $C^E_{AE}$ .



**Figure-5.** The proportion (%) of five priority elements of grinding sludge from the total mass concentration in the ammonium acetate (buffer) solution of pollutants in terms of elements.

Iron is now in first place in terms of mass emission. The mass concentration of iron in AE GS is five times higher than the transfer of all other analyzed elements. On the one hand, iron in AE GS is higher in mass concentration than any other d-element of GS in a mobile form, and on the other hand, iron, as a d-element, is much more prone to the formation of complex compounds in aqueous solution than s-elements (for example Ca and Mg) or p-elements (for example B and Al). Hence, the proportion of iron ions by weight of the total amount passed into the HM acetate-ammonium solution was more than 83% (Figure-5). Among the priority elements in the ammonium acetate solution, the d-elements Mn, Cr and Ni appeared, of which Cr and Ni were not detected at all in the aqueous extract by atomic emission spectroscopy.

Accounting for the emission of polluting compounds into the aquatic environment by mass concentration in the resulting extract does not provide true information about the level of environmental pollution, since it does not take into account the danger of elements or heavy metals for environmental objects, which is reflected by the numerical values of such regulatory indicators as the maximum permissible concentration of HM in water water bodies of drinking and cultural and household water use and water of water bodies of fishery significance. In this case, the multiplicity of the excess of the concentration of heavy metal in aqueous and ammonium acetate extracts GS relative to the MPC<sub>d</sub> standard (calculated according to equations 1 and 2) and the MPC<sub>f</sub> standard (calculated according to equations 3 and 4) are indicative:

$$K_d^{WE} = \frac{C_{WE}^E}{MPS_d}, \quad (1)$$

$$K_d^{AE} = \frac{C_{AE}^E}{MPS_d}, \quad (2)$$

$$K_f^{WE} = \frac{C_{WE}^E}{MPS_f}, \quad (3)$$

$$K_f^{AE} = \frac{C_{AE}^E}{MPS_f}, \quad (4)$$

The results of calculating the multiplicity of excess concentration are shown in Table-2. There are also given the results of summing up the multiplicity of excess concentration of elements, which are calculated by the equations (5-16):

$$\sum^n K_d^{WE} = K_d^{WE}(E_1) + K_d^{WE}(E_2) + \dots + K_d^{WE}(E_{n-1}) + K_d^{WE}(E_n), \quad (5)$$

$$\sum^k K_d^{WE} (>LLD) = K_d^{WE}(E_a) + K_d^{WE}(E_b) + \dots + K_d^{WE}(E_{(k-1)}) + K_d^{WE}(E_k), \quad (6)$$

$$\sum^6 K_d^{WE} = K_d^{WE}(E_c) + K_d^{WE}(E_d) + K_d^{WE}(E_e) + K_d^{WE}(E_f) + K_d^{WE}(E_g) + K_d^{WE}(E_h), \quad (7)$$

$$\sum^n K_d^{AE} = K_d^{AE}(E_1) + K_d^{AE}(E_2) + \dots + K_d^{AE}(E_{n-1}) + K_d^{AE}(E_n), \quad (8)$$

$$\sum^k K_d^{AE} (>LLD) = K_d^{AE}(E_a) + K_d^{AE}(E_b) + \dots + K_d^{AE}(E_{(k-1)}) + K_d^{AE}(E_k), \quad (9)$$

$$\sum^6 K_d^{AE} = K_d^{AE}(E_c) + K_d^{AE}(E_d) + K_d^{AE}(E_e) + K_d^{AE}(E_f) + K_d^{AE}(E_g) + K_d^{AE}(E_h), \quad (10)$$

$$\sum^n K_f^{WE} = K_f^{WE}(E_1) + K_f^{WE}(E_2) + \dots + K_f^{WE}(E_{n-1}) + K_f^{WE}(E_n), \quad (11)$$

$$\sum^k K_f^{WE} (>LLD) = K_f^{WE}(E_a) + K_f^{WE}(E_b) + \dots + K_f^{WE}(E_{(k-1)}) + K_f^{WE}(E_k), \quad (12)$$

$$\sum^6 K_f^{WE} = K_f^{WE}(E_c) + K_f^{WE}(E_d) + K_f^{WE}(E_e) + K_f^{WE}(E_f) + K_f^{WE}(E_g) + K_f^{WE}(E_h), \quad (13)$$

$$\sum^n K_f^{AE} = K_f^{AE}(E_1) + K_f^{AE}(E_2) + \dots + K_f^{AE}(E_{n-1}) + K_f^{AE}(E_n), \quad (14)$$

$$\sum^k K_f^{AE} (>LLD) = K_f^{AE}(E_a) + K_f^{AE}(E_b) + \dots + K_f^{AE}(E_{(k-1)}) + K_f^{AE}(E_k), \quad (15)$$

$$\sum^6 K_f^{AE} = K_f^{AE}(E_c) + K_f^{AE}(E_d) + K_f^{AE}(E_e) + K_f^{AE}(E_f) + K_f^{AE}(E_g) + K_f^{AE}(E_h), \quad (16)$$

where  $K_d^{WE}$ ,  $K_d^{AE}$ ,  $K_f^{WE}$ ,  $K_f^{AE}$  – calculated by equations (1-4); E - designation of an element or heavy metal; n - the number of analyzed in the work of the elements in the hoods; k is the number of analyzed elements in extracts with a mass concentration exceeding LLD; a,b,...,k<n - indices for the K values of elements with a heavy metal mass concentration exceeding LLD; c,d,e,f,g,h<n - indices for the Ke values of six priority elements with a heavy metal mass concentration exceeding LLD, for which the K values exceed the other elements in terms of K; LLD - lower limit of detection;  $\sum^n K_d^{WE}$  – the sum of the



multiplicities of the excess  $MPC_d$  of all quantitatively measured elements in the water extract in this work;  $\Sigma^n K_d^{AE}$  - the sum of the multiplicities of the excess  $MPC_d$  of all quantitatively measured elements in the acetate-ammonium extract in this work;  $\Sigma^n K_f^{WE}$  - the sum of the multiplicities of the excess  $MPC_f$  of all quantitatively measured elements in the water extract in this work;  $\Sigma^n K_f^{AE}$  - the sum of the multiplicities of the excess  $MPC_f$  of all quantitatively measured elements in the acetate-ammonium extract in this work;  $\Sigma^k K_d^{WE} (>LLD)$  - the sum of the multiplicities of the excess  $MPC_d$  of all quantitatively measured elements in the water extract in this work with an excess of the mass concentration of the lower detection limit;  $\Sigma^k K_d^{AE} (>LLD)$  - the sum of the multiplicities of the excess  $MPC_d$  of all quantitatively measured elements in the acetate-ammonium extract in this work with an excess of the mass concentration of the lower detection limit;  $\Sigma^k K_f^{WE} (>LLD)$  - the sum of the multiplicities of the excess  $MPC_f$  of all quantitatively measured elements in the water extract in this work with the excess of the mass concentration of the lower detection

limit;  $\Sigma^k K_f^{AE} (>LLD)$  - the sum of the multiplicities of the excess  $MPC_f$  of all quantitatively measured elements in the acetate-ammonium extract in this work with an excess of the mass concentration of the lower detection limit;  $\Sigma^6 K_d^{WE}$  - the sum of the multiplicities of exceeding the  $MPC_d$  of six priority quantitatively measured elements in a water extract in this work with an excess of the mass concentration of the lower detection limit;  $\Sigma^6 K_d^{AE}$  - the sum of the multiplicities of exceeding  $MPC_d$  of six priority quantitatively measured elements in the acetate-ammonium extract in this work with an excess of the mass concentration of the lower detection limit;  $\Sigma^6 K_f^{WE}$  - the sum of the multiplicities of exceeding the  $MPC_f$  of six priority quantitatively measured elements in a water extract in this work with an excess of the mass concentration of the lower detection limit;  $\Sigma^6 K_f^{AE}$  - the sum of the multiplicities of exceeding the  $MPC_f$  of six priority quantitatively measured elements in the acetate-ammonium extract in this work with an excess of the mass concentration of the lower detection limit.



**Table-2.** Mass concentration and concentration factor of an element (relative to the maximum permissible concentration of elements in the water of water bodies of household and drinking and cultural and domestic water use and water of water bodies of fishery significance) in water and acetate-ammonium extracts of grinding sludge.

No	Index	Grinding sludge			
		$K_d$ (HM)		$K_f$ (HM)	
		Water extracts $K_d^{WE}$	Acetate extracts $K_d^{AE}$	Water extracts $K_f^{WE}$	Acetate extracts $K_f^{AE}$
1	2	3	4	5	6
Sample weight per hood volume		5 gr. per 0,15 l of water	5 gr. per 0,15 l buffer	5 gr. per 0,15 l of water	5 gr. per 0,15 l buffer
1	Al	0,0088	19,1	0,044	95,7
2	Ba	< 0,000043 <sup>a)</sup>	0,034	< 0,00004 <sup>a)</sup>	0,13
3	Be	< 0,050 <sup>a)</sup>	< 0,050 <sup>a)</sup>	< 0,033 <sup>a)</sup>	< 0,033 <sup>a)</sup>
4	Cd	< 0,050 <sup>a)</sup>	33,7	< 0,01 <sup>a)</sup>	6,75
5	Co	< 0,0020 <sup>a)</sup>	< 0,0020 <sup>a)</sup>	< 0,02 <sup>a)</sup>	< 0,02 <sup>a)</sup>
6	Cr	< 0,0030 <sup>a)</sup>	1382	< 0,0075 <sup>a)</sup>	3454
7	Cu	< 0,0003 <sup>a)</sup>	0,16	< 0,3 <sup>a)</sup>	150,5
8	Fe	0,518	8641	3,110	51846
9	Mn	0,056	1258	0,562	12576
10	Mo	< 0,002 <sup>a)</sup>	1,98	< 0,5 <sup>a)</sup>	490
11	Ni	< 0,0030 <sup>a)</sup>	76,4	< 0,03 <sup>a)</sup>	764
12	Pb	< 0,08 <sup>a)</sup>	50,5	< 0,13 <sup>a)</sup>	84,1
13	Sb	< 0,040 <sup>a)</sup>	16,8	< 0,4 <sup>a)</sup>	168
14	Se	< 0,200 <sup>a)</sup>	7,3	< 1 <sup>a)</sup>	36,6
15	Si	0,0047	2,3	-	-
16	Sr	0,0022	0,16	0,038	2,83
17	Ti	< 0,001 <sup>a)</sup>	< 0,001 <sup>a)</sup>	< 0,0017 <sup>a)</sup>	< 0,0017 <sup>a)</sup>
18	V	< 0,002 <sup>a)</sup>	< 0,002 <sup>a)</sup>	< 0,2 <sup>a)</sup>	< 0,2 <sup>a)</sup>
19	Zn	0,0046	3,39	0,455	340
20	Ca	0,593	75,0	0,012	1,46
21	B	3,02	10,4	3,02	10,4
22	Mg	0,0038	0,07	0,005	0,071
23	Ag	< 0,006 <sup>a)</sup>	< 0,006 <sup>a)</sup>	-	-
24	Tl	< 0,001 <sup>a)</sup>	< 0,001 <sup>a)</sup>	-	-
25	As	< 0,100 <sup>a)</sup>	< 0,100 <sup>a)</sup>	< 0,02	< 0,02 <sup>a)</sup>
$\Sigma^n K_d$ или $\Sigma^n K_f$		4,8	11579	9,9	70027
$\Sigma^k K_d (>LLD)$		4,2	11578	7,2	70026
$\Sigma^6 K_d$ или $\Sigma^6 K_f$		4,2	11483	7,2	69470

<sup>a)</sup> the “<” sign is given at the numerical value of the concentration and the concentration factor corresponding to the lower detection limit of the element in cases where the element is not detected by atomic emission spectroscopy.

It is logical to call the sums of the K values the environmental impact indices (IEI) and from all the K sums we choose the sums  $\Sigma kK$  as such, as taking into account all the elements, the mass concentration of which

in GS extracts numerically exceeds LLD. Then we have the following environmental impact indices:

a) the index of the environmental impact on water of objects of household and drinking and cultural and





household water use through distilled or ordinary drinking water:  $IEI_{d}^{WE} = \sum^k K_{d}^{WE} (>LLD)$ ;

b) the index of the environmental impact on water of objects of household, drinking and cultural and household water use through buffer or complex-forming water environments:  $IEI_{d}^{AE} = \sum^k K_{d}^{AE} (>LLD)$ ;

c) the index of the environmental impact on water of water bodies of fishery importance through distilled or ordinary drinking water, or natural water without buffer or complex-forming properties:  $IEI_{WEf} = \sum^k K_{WEf} (>LLD)$ ;

d) Index of environmental impact on water of water bodies of fishery importance through buffer or complex-forming aquatic environments:  $IEI_{AEf} = \sum^k K_{AEf} (>LLD)$ .

Taking into account the values of the K sums, at least for AE, it is easy to assume that the placement of GS on unsettled landfills can be associated with an emergency (ES). The hazard of toxic contamination in ES cases is assessed in accordance with the guidelines [7-202]. The danger is established by the signs of high pollution and extremely high pollution of a water body. At the same time, the excess of the concentration ratio has a different threshold value for pollutants, including HM, 1st hazard class (for example, Be, Hg, Ga), 2nd hazard class (for example, Al, Ba, B, Cd, Mo, As, Pb, Se, Sr) and the 3rd hazard class (for example, Ni, Cr, Cu). Metals of 1 hazard class Hg and Ga are absent in Table-1, Be has a concentration lower than LLD. Among metals of the 2nd hazard class, WE have Al, Sr, B, the mass concentration of which does not exceed MPC by 5 or more times. At the same time, according to the recommendations [7-202], if  $K = 3 \div 5$ , then the level of toxic water pollution is "highly toxic (dirty)". This is exactly what the WE corresponds to according to Table-2 (column 3).

AE of the GS is significantly more contaminated than WE. So, for aluminum  $K_{d}^{AE} = 19.1$ , boron  $K_{d}^{AE} = 10.4$ , cadmium  $K_{d}^{AE} = 33.7$ , lead  $K_{d}^{AE} = 50.5$ , selenium  $K_{d}^{AE} = 7.3$ , which is more than 5. And this means according to the recommendations [202] that the level of toxic pollution AE is "extremely toxic (extremely dirty)", which is also reflected in the excess of MPC for metals of the 3rd hazard class - chromium  $K_{d}^{AE} = 1382$ , nickel  $K_{d}^{AE} = 76.4$ , for which the "red line" is  $K > 15$ .

In the methodology [8-201], the ecological situation is classified according to the increasing degree of ecological trouble as follows: 1) relatively satisfactory; 2) tense; 3) critical; 4) crisis (or zone of ecological emergency); 5) catastrophic (or zone of ecological disaster). Extreme degrees of environmental distress [8-201] are environmental crises and environmental disasters. A critical ecological situation is answered by persistent negative changes in the environment, a threat to public health, persistent negative changes in the state of ecosystems (for example, a decrease in diversity). Ecological disaster, as the highest degree of ecological trouble, is associated with profound irreversible changes in the natural environment, a significant deterioration in the health of the population, and the destruction of natural

ecosystems. The level of water pollution as "extremely toxic" corresponds to the ecological situation "catastrophic (or zone of ecological disaster)". The obtained results of the study of the emission of heavy metals from GS indicate that: 1) grinding sludge is much more dangerous for environmental objects than wastes of IV hazard class, to which they are assigned in accordance with information from production; 2) the fact that grinding sludge is classified as hazard class IV waste contradicts the results obtained in this work; 3) it is unacceptable to place grinding sludge on specially equipped landfills, where a special storage regime is provided with isolation from atmospheric air, precipitation and soil moisture; 4) grinding sludge is subject to processing with preliminary extraction of toxic metals with K exceeding 3. One way to extract HM from GS is to shake the GS suspension in an aqueous or ammonium acetate buffered dispersion medium. In this case, the extraction proceeds more efficiently under the action of an acetate-ammonium buffer solution. The quantitative differences in the extraction of HM from GS with distilled water and ammonium acetate buffer solution are shown in Table-3.

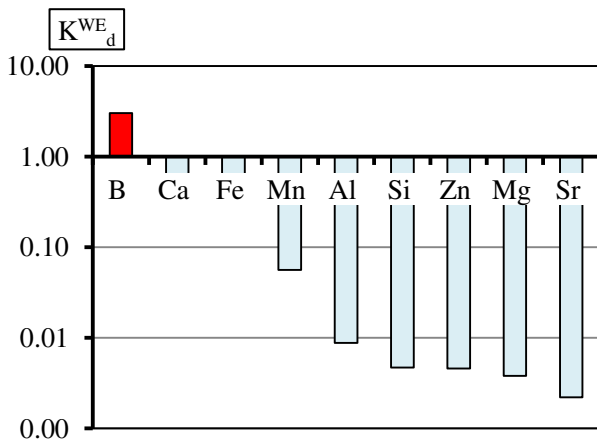
**Table-3.** Comparison of aqueous and ammonium acetate extracts of grinding sludge by the sum of the concentrations of six priority elements, the total number of analyzed elements (n), the number of elements with a mass concentration exceeding the lower detection limit of elements (k), the number of elements exceeding MPC<sub>d</sub> or MPC<sub>f</sub> (q), Environmental Impact Indices for Drinking Waters (IEI<sub>d</sub><sup>6</sup>) and Natural Waters (IEI<sub>f</sub><sup>6</sup>).

No	Index	WE	AE	WE / AE
1	$\sum^6 C^{E a)}$	4,0	3080,7	770
2	$n^{(6)}$	25	25	25
3	$k_d^{(6)}$	9	18	2
4	$k_f^{(6)}$	8	17	2,125
5	$q_d^{(6)}$	1	14	14
6	$q_f^{(6)}$	2	15	7,5
7	$IEI_d^6 = \sum^6 K_d^{(6)}$	4,2	11483	2734
8	$IEI_f^6 = \sum^6 K_f^{(6)}$	7,2	69470	9648

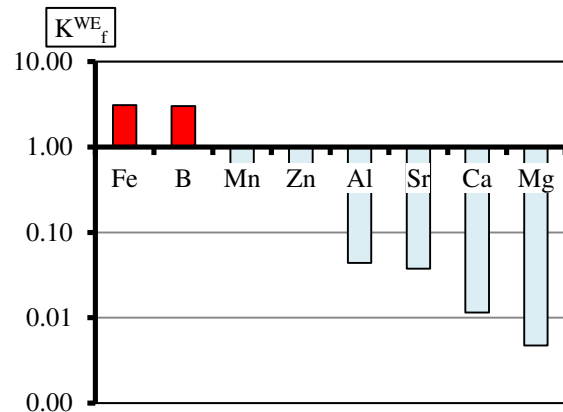
In the acetate-ammonium buffer, both the amount and weight of the recoverable elements and the amount of elements with an excess of LLD and with an excess of standards both for water of water bodies of domestic drinking and cultural and domestic water use, and for water of water bodies of fishery significance increase. The most significant increase in the acetate-ammonium buffer is the increase in the environmental impact indices for six priority elements on the water of water bodies for domestic drinking and cultural and domestic water use (by 2734 times) and on water of water bodies of fishery significance (by 9648 times). Consequently, the higher extraction capacity in relation to HM and a number of other elements of the ammonium acetate buffer solution in



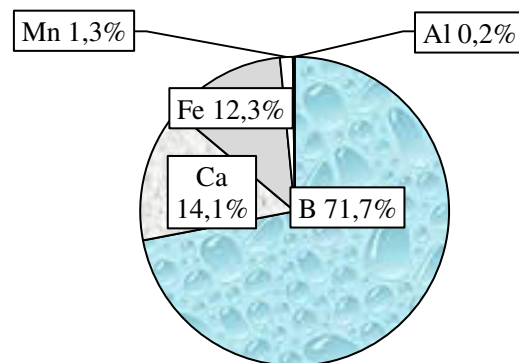
comparison with distilled water requires taking into account the following points when handling waste such as GS: 1) contact of GS with natural water, which exhibits buffering and / or complex-forming properties in relation to HM, means that it is significantly more (thousands of times) contaminated with the studied HM in comparison with tap, distilled or unpolluted natural water; 2) placement of GS in soil with filtration soil water, in moist soil, in soil with rain and melt water will lead to significant emission of mobile forms of HM from GS and contamination of the soil landscape and adjacent environments. Based on the foregoing, there is a requirement for a transition from the practice of accumulating waste, even less hazardous, to the practice of their disposal and recycling. In terms of neutralization, utilization, recycling, as well as temporary placement, it is also important to know about the priority of GS elements in a mobile form in terms of the multiplicity of exceeding MPC<sub>d</sub> and MPC<sub>f</sub>, that is, in fact, the environmental hazard in water of water bodies of different water use. Figures 6 and 7 show the diagrams of the priority of elements in the WE GS by the multiplicity of exceeding MPC<sub>d</sub> ( $K^{WE}_d$ ) and MPC<sub>f</sub> ( $K^{WE}_f$ ), respectively. In the first case, the standard is exceeded only for boron, which, as you know, is controlled when assessing the quality of drinking water. In the second case, iron is of the highest priority, since for iron the standard for natural water is six times more stringent, and for boron MPC<sub>d</sub> and MPC<sub>f</sub> have the same values.



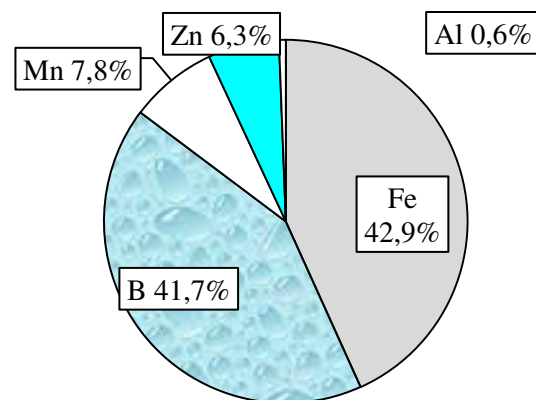
**Figure-6.** Priority according to the concentration coefficient ( $K^{WE}_d$ ) in the water extract of grinding sludge of nine elements with the highest value of  $K^{WE}_d(HM)$ .



**Figure-7.** Priority according to the concentration coefficient ( $K^{WE}_f$ ) in the water extract of grinding sludge of eight elements with the highest value of  $K^{WE}_f(HM)$ .



**Figure-8.** Share (%) of five priority elements of grinding sludge in contamination of distilled water by the value of the magnitude of the excess ratio MPC<sub>d</sub> ( $K^{WE}_d$ )



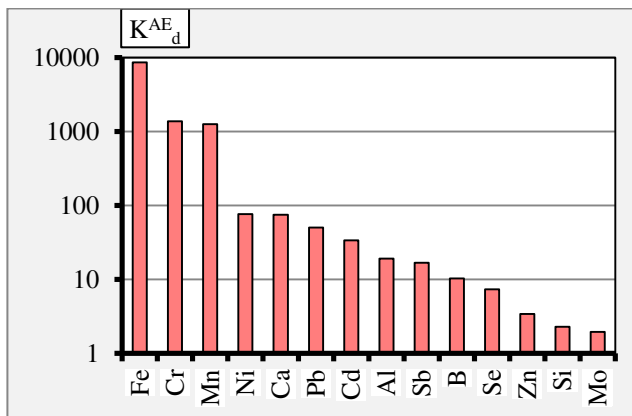
**Figure-9.** Share (%) of five priority elements of grinding sludge in contamination of distilled water by the value of the magnitude of the excess ratio MPC<sub>f</sub> ( $K^{WE}_f$ ).

Contributions in fractional percent of pollution of the water extract by GS elements by the magnitudes of the multiplicity of excess MPC<sub>d</sub> and MPC<sub>f</sub> are shown in the diagrams of Figures 8 and 9. The main contribution to the

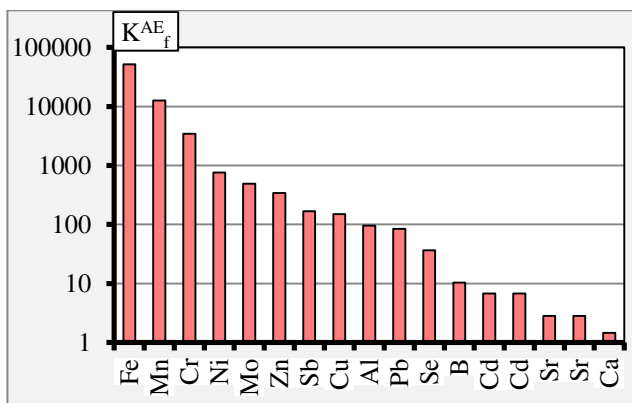


drinking water pollution is made by soluble compounds of boron, calcium and iron, in the pollution of natural water - iron, boron, manganese and zinc.

The priorities of elements in AE GS in terms of exceeding rates  $MPC_d$  ( $K^{AE}_d$ ) and  $MPC_f$  ( $K^{AE}_f$ ) are shown in Figures 10 and 11, respectively. In both diagrams for AE, only HM are taken into account in excess of the standard values for drinking and fishery waters. In both cases, the main HM pollutants are d-elements: Fe, Cr, Mn, Ni. Among metals with  $K \geq 1$ , such toxic ones as Pb and Cd are also manifested.

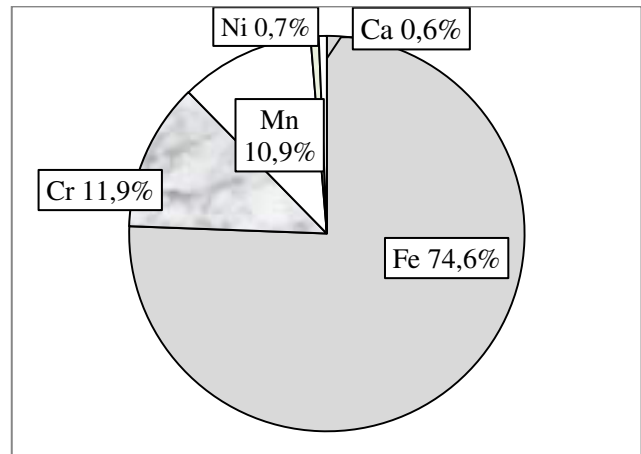


**Figure-10.** Priority according to the coefficient of concentration ( $K^{AE}_d$ ) in the ammonium-acetate extract of grinding sludge of fourteen elements with the highest value of  $K^{AE}_d$ .

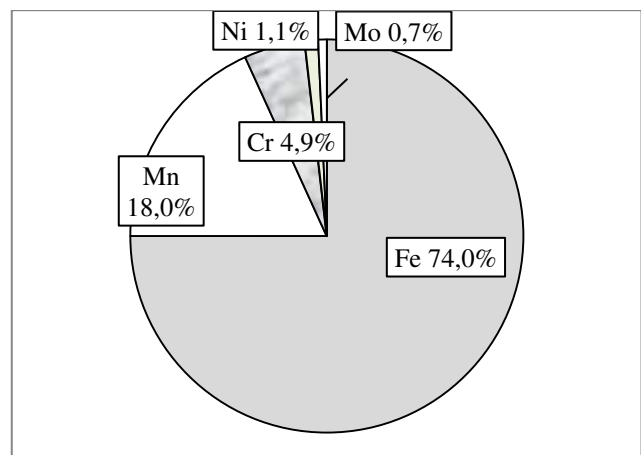


**Figure-11.** Priority according to the coefficient of concentration ( $K^{AE}_f$ ) in the ammonium-acetate extract of grinding sludge of fifteen elements with the highest value of  $K^{AE}_f$ .

Contributions of HM contained in GS to buffer contamination are shown in Figures 12 and 13. Iron accounts for over 74% of AE contamination.



**Figure-12.** The share (in percent) of five priority elements of grinding sludge in the contamination of the acetate-ammonium extract by the value of the magnitude of the multiplicity of exceeding the  $MPC_d$  ( $K^{WE}_d$ ).



**Figure-13.** The share (in percent) of five priority elements of grinding sludge in the contamination of the acetate-ammonium extract by the value of the magnitude of the multiplicity of exceeding the  $MPC_f$  ( $K^{WE}_f$ ).

## SUMMARY

As part of the work presented, studies of the environmental impact of industrial waste - grinding sludge were carried out. At the initial stage of research, the primary indicators of waste were determined, such as humidity pH, electrical conductivity and mineralization of water extracts. According to the data obtained, the moisture content of the studied samples is about 20%, the pH varies in the range from 7.0 to 7.5 units. pH, specific electrical conductivity - 50-70  $\mu S/cm$ , salinity (by NaCl) - 25 - 40 mg/l.

Atomic emission spectroscopy was used to determine the content of 25 elements in aqueous and acetate-ammonium waste extracts. It was found that, in terms of mass content, the priority elements in the water extract are Ca, B, Mg, Fe, Si, Sr. When using an acetate-ammonium buffer solution, there is a sharp increase in the emission of elements into the aqueous phase, as a result, not only the quantitative, but also the qualitative picture of



the priority and the proportion of the mass contribution of elements to the mineralization of filtrate suspensions of the grinding sludge powder changes. The priority elements in the ammonium acetate extract are Fe, Ca, Mn, Cr, Si, Ni, B.

To assess the environmental hazard of the analyzed elements for environmental objects, the calculations of the multiplicity of exceeding the standard indicators, as well as the environmental impact indices, were carried out. According to the results of calculations, it was determined that the water extract of grinding sludge is characterized by the level of toxic water pollution as "highly toxic (dirty)", acetate-ammonium - "extremely toxic (extremely dirty)". In the case of aqueous extracts of grinding sludge, the main contribution to the pollution of drinking water is made by soluble compounds of boron, calcium and iron, to the pollution of natural water - iron, boron, manganese and zinc, in acetate-ammonium extracts - heavy metals - iron, chromium, manganese, nickel, lead and cadmium.

The most significant increase in the acetate-ammonium buffer is the increase in the environmental impact indices for six priority elements on the water of water bodies for domestic drinking and cultural and domestic water use (by 2734 times) and on water of water bodies of fishery significance (by 9648 times).

Accordingly, the contact of grinding sludge with natural water, which exhibits buffering and / or complex-forming properties with respect to heavy metals, leads to its significantly greater contamination with the studied heavy metals in comparison with tap, distilled or non-contaminated natural water. The placement of grinding sludge in soil (soil) with filtration soil water, in wet soil, in soil with rain and melt water will lead to significant emission of mobile forms of heavy metals and pollution of the soil landscape and adjacent environments, which in turn requires the introduction of additional measures aimed to reduce the toxicity of the above waste.

#### 4. CONCLUSIONS

Thus, the procedure of mathematical processing of the results of quantitative chemical analysis of aqueous and acetate-ammonium extracts of grinding sludge waste used in this work made it possible to:

- To determine the volumes of emission of heavy metals of grinding sludge into the water and water-buffer medium;
- To determine the level of contamination of drinking and natural waters by mobile forms of heavy metals of grinding sludge;
- To assess the level of contamination by heavy metals of sludge of the grinding natural landscape;
- To show that grinding sludge is a much more hazardous waste for the environment than it follows from its classification as low hazardous waste (IV hazard class).
- Point out the inadmissibility of placing this waste on non-equipped landfills, which do not exclude

its contact with rain and melt water and soil (ground);

- To justify the need for disposal and / or processing of grinding sludge.

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