Biotesting as a Method of Evaluating Waste Hazard in Metallic Mineral Mining

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Abstract. As the result of identifying content of each chemical element it has been revealed that metallic mineral wastes have a considerable amount of valuable useful metals. Thus, large-tonnage inorganic wastes are considered to be an additional raw source of metal production. This paper highlights the necessity of supplementary biotesting metallic mineral wastes in order to bring into correlation with corresponding hazard classes and facilitate efficient recycling of these wastes in future. It has been found out that determined in this way waste class can be dumped or used after recycling. It has been also indicated that mill tailings are to be stored according to contained metals without messing up dissimilar metal-containing wastes. After winning metals these wastes are similar to the group of inorganic non-metallic wastes and can be used in building material production, for filling mined-out spaces, in road construction etc.

The notion "waste" is defined in Waste Frame Directive as any substance or object utilized by an user on his own or in terms of national legislation [1]. This definition is too generalized so in appendix of the Directive there is a list of certain substances that can be regarded as wastes. This list is constantly changed, supplemented and currently contains more 600 waste types.

The amount of industrial wastes rises every year because of ore-dressing and processing enterprises. Anthropogenic load arising in the course of mineral deposit exploitation includes grounds beneath overburdens, mine dumps and waste banks. Extracted raw materials are delivered to processing plants affecting the environment negatively. Processing plants majoring in iron ore dressing destroy Earth surface via mining, discharge air pollutants into atmosphere, dump contaminated wastewater and produce used fine-grained burden, that is, industrial wastes. Used materials are delivered by hydraulic conveying into tailing dumps. Tailing dumps are aggregated wastes of ore-dressing and processing enterprises. The scales of aggregated material are rather considerable.

Any waste operations produced as the result of mining, processing and storing mineral resources and opencast mine activities are legislatively regulated in Mining Waste Directive.

In terms of up-to-date legislation [1, 3, 4] all industrial wastes are to be classified according to their impact on the environment and mankind. Therefore, all wastes are divided into hazard classes.

Investigation into wastes is necessary for identifying optimal technologies of their processing, storing and utilizing, as well as for compiling standards on waste generation and limits of their licenses, waste certificates.

International classification of industrial wastes accepted in all organizations-members of World Bank of industrial wastes highlights solid (S), liquid (L) and paste-like (F) wastes. Each waste is specified to eight parameters (waste state, basic component of the waste, attending substances, acid or alkaline nature of wastes, inflammability of wastes, and possibility of recycling or mixing up with household wastes for disposal). Industrial wastes are coded according to the System based on International Standard of Industry Classification.

If wastes contain chemical substances in a definite concentration they are singled out in a separate class and called hazardous. However, all waste classifications are conventional and can vary with time. In some cases wastes are classified according to the possibility of their utilization [5].

Resolution of waste problem necessitates, first, separation of so-called large-tonnage wastes, because they have the heaviest contaminating impact on the environment.

In EU countries wastes are principally divided in hazardous and nonhazardous. The key difference between them is the extent of harmful effect on the environment and technologies required for their recycling and utilization. The list of hazardous wastes and decision criteria of their hazardous character are provided in Directive 91/689/EEC on hazardous wastes [1]. The Directive determines 40 hazardous wastes and 14 criteria to consider them hazardous.

An integrated laboratory study is to carry out for identifying the class of waste hazard. Methods for investigation of industrial wastes include:
 - quantitative and chemical analysis (component content and concentration);
 - toxicological research (toxicity degree);
 - biotesting (hazard revealing from the standpoint of ecology, by means of protozoa).

Computational method to put wastes into a hazard class is applied provided quantitative and qualitative composition of a waste is known.

Experimental method on the base of biotesting is applied in the following cases:
 - confirmation of nonhazardous class determined computationally is required;
 - qualitative and quantitative composition of wastes can't be determined.

To sum up the stated above, if a waste is computationally determined as a nonhazardous one; its nonhazardous nature is to be confirmed via biotesting. Unless the hazard class is experimentally confirmed, wastes are considered non-hazardous substances [7, 8].

Computational determination of waste hazard class in metallic mineral mining

Therefore, our work was focused on determination of waste hazard class computationally and via biotesting. As the object of research we chose the enterprise majoring in iron ore dressing by wet magnetic separation and sintered ore production. The reference material is waste from a tailing dump.

Abagur processing factory specializes in recycling primary concentrate located in Tashelgin, Telbes, Tersin and other groups of West Siberian Plain. The deposits are rich in iron ore minerals and fluxing limestone used for secondary concentrate production. There is an extensive network of railway and automobile approach lines on the factory ground. As the result of enterprise activity large-tonnage inorganic metal containing wastes are produced and their further recycling needs separation and classification.

Table 1 – Composition and content of wastes

Sample	Index	Test results		MPC mg/kg
		%	mg/kg	
Wastes of metallic material mining (wastes of wet magnetic separation)	Moisture	4.77		
	Cadmium		< 0.05	1.0
	Lead	0.00116	11.60	32.0
	Vanadium	0.00370	37.02	150.0
	Manganese	0.13770	1377.00	1500.0

Sample	Index	Test results		MPC mg/kg
		%	mg/kg	
	Copper	0.05126	512.60	132.0
	Arsenic	0.00604	60.40	2.0
	Mercury	0.00002	0.16	2.1
	Cobalt	0.01276	127.60	
	Nickel	0.00857	85.72	40.0
	Zinc	0.02431	243.10	220.0
	Petrochemicals	0.00149	14.9	
	Nitrates	0.00275	27.5	130.0
	Cyanides		<0.5	
	Benzapyrene		<0.001	0.02
	Phenol		<0.01	
	Carbon	1.42		
	Hydrogen	0.76		
	Silicon dioxide	41.22		
	Aluminum oxide	9.21		
	Ferrum trioxide	17.04		
	Titanium dioxide	0.44		
	Calcium oxide	12.45		
	Magnum oxide	8.80		
	Phosphor oxide (V)	0.41		
	Potassium oxide	0.62		
	Sodium oxide	0.96		
	Sulphur total	1.650	16500.0	160.0
	Fluorine	0.00020	2.0	6.0

The index "Hazard rate" of waste component for the environment Ki is calculated on the base of data on waste composition and content and from the formula:

$$K_i = \frac{C_i}{W_i},$$ (1)

where   Ci   –   concentration   of   i-component   in   the   waste   (mg/kg   of   waste);
Wi – coefficient of hazard rate of i-component for the environment, (mg/kg) [8,9].
Consolidated index is calculated from the formula:

$$\sum_{i=1}^{m} K_i = \sum_{i=1}^{n} \frac{C_i}{W_i},$$ (2)

The hazard class of wastes depending on the hazard rate is determined on the base of data from Table 2.

Table 2 – Hazard class - hazard rate correlation (K)

Hazard class	Waste hazard rate, K
I	106≥ K >104
II	104≥ K >103
III	103≥ K >102
IV	102≥ K >10
V	K=10

Results of calculation are in Table 3.

Table 3 – Reference data to calculate waste hazard class

№	Component	C_i (mg/kg)	W_i (mg/kg)	K_i
1	Cadmium	0.050	215.443	0.00023
2	Manganese	1377	5878.016	0.23426
3	Copper	512.6	1930.698	0.26550
4	Arsenic	60.4	803.086	0.07521
5	Nickel	85.72	1550.516	0.05528
6	Benzapyrene	0.001	59.97	0.00002
7	Mercury	0.16	17.013	0.00940
8	Lead	11.6	701.704	0.01653
9	Water	47699.839	1000000	0.04770
10	Phenol	0.01	215.44	0.00005
11	Silicon dioxide	412200	1000000	0.41220
12	Aluminum oxide	92100	1000000	0.09210
13	Titanium dioxide	4400	1000000	0.00440
14	Calcium oxide	124500	1000000	0.12450
15	Manganese oxide	88000	1000000	0.08800
16	Potassium oxide	6200	1000000	0.00620
17	Sodium oxide	9600	1000000	0.00960
18	Phosphorus oxide (V)	4100	1000000	0.00410
19	Cobalt	127.6	1000	0.12760
20	Petrochemicals	14.9	1000	0.01490
21	Carbon	14200	1000000	0.01420
22	Hydrogen	7600	1000000	0.00760
23	Cyanides	0.5	215.443	0.00232
24	Ferrum trioxide	170400	1000000	0.17040
25	Zink	243.1	3727.594	0.06522
26	Vanadium	37.02	2404.099	0.01540
27	Sulphur	16500	8576.959	1.92376
28	Fluorine	2	464.159	0.00431
29	Nitrates	27.5	13111.339	0.00210
	Total:	1000000		3.79309

Consolidated index $\Sigma K = 3.79309$, as the consequence, waste is in the 5th hazard class ($\Sigma K < 10$).

Biotesting determination of waste hazard class
As it was stated above an experimental method based on biotesting is used to confirm nonhazardous waste class defined computationally.

Experimental determination of waste hazard class requires at least two test-objects from various groups (Daphnia and Infusorian, Ceriodaphnia, bacteria, algae etc.). Hazard class revealed on a bio-object, which was the most sensitive to the analyzed substance, is accepted as an ultimate result.

The mostly used objects of bio-tests are as follows: Chlorophyta - Scenedesmus (Scenedesmus quadricauda) and Chlorella (Chlorella vulgaris); Crustacea - Daphnia (Daphnia magna Straus) and Ceriodaphnia (Ceriodaphnia affinis Lilljeborg); protozoa - Infusorian (Paramecium caudatum Erenberg).

Methods of biotesting:
1.   Methods to test algae bases on registration of falling chlorophyll fluorescence level and decreasing quantity of algae cells exposed to toxic substances in aqueous extract of wastes and comparison with a reference sample in tests without toxic substances.

The criterion of acute toxicity is reducing quantity of algae cells by more 50 % as compared with the reference quantity in 72 hours.

The experiments are to identify:

1) acute toxicity or inhibiting concentration (further - IC50-72) of particular substances or inhibiting order of dissolution (further - IOD50-72), that is, such quantity of toxic substance, which causes reducing chlorophyll level by more 50% as compared with the reference quantity or decreasing number of algae cells in 72 hours;

2) nonhazardous (conditioning no effect of acute toxicity) concentration (further - NH20-72) of some substances and nonhazardous order of dissolution (NOD - BKR 20-72), that is, such quantity of toxic substance, which causes 20% reducing chlorophyll level as compared with a reference quantity or decreasing number of algae cells in 72 hours [15].

2. Methods to calculate death rate and change in fertility of Daphnia (Daphnia magna Straus, Cladocera, Crustacea) affected by toxic substances of wastes base on their lethality over a particular period of exposure.

The criterion of acute toxicity is death of more 50 % Daphnia for 96 hours in water under consideration provided that the death rate doesn't exceed 10% in reference experiment.

In short-termed experiments aimed at determining acute toxic effect one identifies:

1) acute toxicity or mean lethal concentration (here and further LC 50-96) of particular substances (order of waste dissolution), conditioning death of more 50 % test-organisms;

2) nonhazardous (causing no effect of acute toxicity) concentration of particular substances, conditioning death less 10 % test-organisms (NHC10-96, NHC-96) [6].

To determine acute toxicity of the tested solution the percentage of the dead in water under consideration is calculated in comparison with the reference sample. If the death rate of life forms in the solution is ≤ 10%, the tested sample doesn't have an acute toxic effect (nonhazardous order of dissolution). If the death rate is ≥50% the tested aqueous extract has an acute toxic impact [16].

Hazard class is identified according to the order of dissolving waste aqueous extract, which doesn't affect life forms as on order of dissolution provided in Table 4.

Table 4 – Dependence of waste hazard class on dissolution order of aqueous extract

Waste hazard class	Dissolution order of hazardous waste aqueous extract without harmful effect
I	>10000
II	10000 – 1001
III	1000 – 101
IV	<100
V	1

The obtained results of bio-tested waste aqueous extract were recorded in the form of tested samples presented in Table 5.

Table 5 – Record form of bio-tests

	Test-object	Observation period	Biotesting results	Order of water dissolution (aqueous extract) without any effect on test-object	Tested sample estimation
	Crustacea *Daphnia magna* Straus FR.1.39.2007.03222	96 hours (4 days)	Daphnia death rate		No pronounced toxic effect
			100% solution = 10%	1	
			50% solution = 0%		
			25% solution = 0%		
			10% solution = 0%		
			$NHC_{10-96}=1$		

	Test-object	Observation period	Biotesting results	Order of water dissolution (aqueous extract) without any effect on test-object	Tested sample estimation
	Algae *Scenedesmus quadricauda* FR.1.39.2007.03223	72 hours (3 days)	Reducing number of algae		No pronounced toxic effect
			100% solution = 4%	1	
			50% solution = 0%		
			25% solution = 0%		
			10% solution = 0%		
			NHC $_{20-72}$=1		

Therefore, we can sum up the results of carried out bio-test.

1. The death rate of Daphnia in singly dissolved sample is 10 %, that is the waste under consideration has no toxic impact;

2. The decrease in population of algae in 100% dissolution is 4 %, so there is no toxic effect on life forms.

3. The bio-tests of two waste samples produced in metal mineral mining have revealed that the tested sample has no toxic effect on algae and Daphnia $C_{nonhazardous}$ 1. As the result, hazard class to be recommended is a nonhazardous one.

Conclusions

1. International classification says that wastes of metallic mineral mining are large-or-middle-grained solids; their main component is heavy-density metal that can be used after recycling.

2. As the result of identifying content of each chemical element it has been revealed that metallic mineral wastes have a considerable amount of valuable useful metals. Thus, large-tonnage inorganic wastes are considered to be an additional raw source of metal production.

3. The analysis of obtained data of bio-tests and computations has shown that metallic mineral wastes of tailing dump №3 are environmentally nonhazardous substances.

4. The wastes have a slight impact on the environment. This waste class is allowed to be dumped. Collecting wastes of this class contributes to nature resource preservation because they can be used after recycling.

5. Wastes of this class are to be stored in the way facilitating their further recycling. Tailings are to be stored according to the metals they contain, no messing up different metal containing wastes is allowed. Various dressing methods are used for recycling these wastes, among them is pyrometallurgy, chemical methods and biotesting. After winning metals these wastes are similar to the group of inorganic non-metallic wastes and can be used in building material production, for filling mined-out spaces, in road construction etc.

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