THE USE OF NUCLEAR-PHYSICAL METHODS FOR THE ANALYSIS OF WASTES FROM MINING AND PROCESSING INDUSTRY

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The topic of using nuclear-physical methods for the analysis of waste mining and processing industry is shown by the example of the analysis of the dry part (beach zone) of the Unal tailings Mizur concentrator, located in the Central part of the Alagir district, the Republic of North Ossetia-Alania, in the valley of the river Ardon. Analytical identifications were performed at the Joint Institute for Nuclear Research (JINR) in Dubna, Moscow region. X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA) were used to identify the composition of multi-element samples, which allows us to obtain data on the content of 39 elements in the composition of the tails. The content of Ca, Ti, Cr, Mn, Cu, Sb in tails was determined by two methods. The results obtained by XRF and INAA are the same within the measurement uncertainties The Unal tailing dump is a geochemical anomaly with the content of Zn, As, S, Cu, Sb, Se, Ag, In, Pb, Cd exceeding the Clark more than hundreds and thousands of times. The composition of tails in different parts of the tailing dump varies considerably, including the content of useful components, due to different distance from the mirror of water. As a result of the impact of flotation processes, the upper 10 cm of the dry part of the beach area of the tailing dump is enriched, including highly toxic elements (Zn, As, Cu, Sb, Ni, Pb), which poses a danger to the environment and public health. The presence of useful components in the tailings indicates the need for the use of waste under consideration as a source of minerals

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1. INTRODUCTION

In the Sadonsky ore district of the Republic of North Ossetia-Alania (RSO - Alania), about 300 vein lead-zinc deposits and ore occurrences are known. Prospecting, exploration, mining and processing of polymetallic ores have been conducted in this area since the middle of the XIX century. The entire infrastructure of mining enterprises (mines, processing plants, tailing dumps, roads) is confined to the densely populated valleys of the main water systems of the Republic [1]. In RSO-Alania, 10 million tons of metal-containing tails of Mizur and Fiagdon concentrators and metallurgical plants have been accumulated on the area of 250 hectares [2, 3]. Since 1984, waste from processing ore materials (tails) of the Mizur concentrator has been placed on the territory of the Unal tailings storage facility. The tailing dump is located in the Central part of the Alagir district, the Republic of North Ossetia-Alania, in the valley of the river Ardon, on its left bank between the villages of Unal and Zintsar. The area of the Unal tailings pond is about 0.2 km2. According to [6] in Unal tailings is 2600000 t. tails with a content of lead 0.21%, zinc 0.9%, copper 0.10%, etc.

Most of the surface of the tailing dump is occupied by a pond. The storage depth ranges from 12 to 15 m. The volume of tails is about 3.2 million tons. Currently, the tailing dump has a beach area (about 40% of its area) and water-filled one (60% of the area) due to continuous irrigation with water sprinklers. The tails represent the crushed rock mass, which is similar to fine-grained dusty sand on grain-size composition. In dry hot weather, this dust gets into the air pool area from the beach area. The dust in the area of tailings ponds in summer time is more than ten times the maximum permissible concentration (MPC) [2].

According to the results of comprehensive studies on the geoecological situation in the Sadon ore district [4, 5], the decisive role of the Unal tailings in the formation of technogenic anomalies of lead on the lower terraces of the Ardon river was revealed. The purpose of this study is to analyze the elemental composition of waste from the surface of the Unal tailings.

2. OBJECT AND METHODS OF RESEARCH

Sampling the surface with a dry portion of the tailings was conducted in 2015-2016. Sampling was carried out in accordance with conventional methods [7] in 10 points. Each sample was formed by mixing 5 spot samples, taken at a depth of 0-10 cm. Also in point 8 were further selected the sample from a depth of 15-20 cm. Positions of sampling points are shown in the figure.

Analytical identifications were performed at the Joint Institute for Nuclear Research (JINR) in

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Dubna, Moscow region. Multi-element determination of the composition of samples by x-ray fluorescence (XRF) was carried out in The Laboratory of nuclear reactions named after G. N. Flerov (JINR FLNR), instrumental neutron activation analysis (INAA) - in the laboratory of neutron physics named after I. M. Frank (JINR FLNP). The x-ray spectra of the samples were measured using a standard Canberra spectrometer.

Ring radioisotope sources ^{109}Cd (E =22.16 keV, $T_{1/2}$= 453 days) and ^{241}Am (E = 59.6 keV, $T_{1/2}$= 458 years) with a total activity of 20 µCi were used to excite x-ray radiation. The characteristic x-ray radiation was recorded by a semiconductor Si (Li) detector with an area of 30 mm^2 and a thickness of 3 mm, with a beryllium window thickness of 25 µm and a resolution of 145 eV on the 5.9 keV line. The WinAxil Canberra x-ray fluorescence analysis software was used to process spectra and calculate element concentrations. Concentrations of elements were determined by comparison with standard samples with similar matrix effects (SG-1A, GnA, soil-5, GM, Sch-ST, Fe_2O_3, etc.). The method of simultaneous determination of all elements excited by radioisotope sources in saturated layers of matter by a single calibration curves, constructed on the basis of measurements of standard samples [8], was used to determine the elements absent in the reference samples.

Instrumental neutron activation analysis (INAA) was performed at the IBR-2 reactor of the JINR LNP using a pneumatic transport unit REGATA [9]. To determine short-lived isotopes Of al, Cl, Ca, Ti, V, Mn, Cu, In elements, the samples were irradiated for 1 minute in the reactor channel with a neutron flux density of 1.3x10^{12} neutrons/(cm^2 • s). To determine the long-lived isotopes of elements Na, Sc, Cr, Co, Ni, As, Se, Sb, Cs, La, Ce, Tb, Ta, Ag, Th, U, the samples were irradiated for about three days in the channel of the reactor with a cadmium screen and a flux density of resonance neutrons 1.6x10^{12} neutrons/(cm^2 • s). After irradiation, the samples were repackaged in clean containers for the measurement. Induced gamma activity of the samples was measured twice: 4-5 days after extraction from the irradiation channel for 45 minutes and 20 days later for 1.5 hours. The software package developed in FLNP, JINR [10] was used for processing of gamma spectra and to calculate concentrations of elements. The quality of the analysis was ensured by certified reference materials Coal fly ash (NIST, 1633c), Montana Soil (NIST, 2710), Estuarine sediment (BCR, 667), which were irradiated under the same conditions as the samples under study.

3. RESEARCH RESULTS AND THEIR DISCUSSION

The use of XRF and IINAA allows us to obtain data on the content of 39 elements in the composition of mining waste (tailings of the Mizur concentrator). The content of Ca, Ti, Cr, Mn, Cu, Sb in tails was determined by two methods. The results obtained are the same within the measurement uncertainties. The results of the analytical identifications are presented in table 1.

Unal tailing dump is a technogenic geochemical anomaly with the content of a number of elements exceeding their Clarks in the earth's crust (table 1). The content of elements such as Zn, As, S, Cu exceeds the Clark concentration by more than a hundred times, the content of Sb, Se, Ag, In, Pb exceed the Clark values by thousands of times. Attention is drawn to the enrichment of technogenic formations of the Unal tailings by Cd, the content of which is more than twenty thousand times higher than its Clark in the earth's crust, while Cd is not included in the association of chemical elements (Pb, Zn, Fe, Cu, Ag, Bi, Al, Si), which are in high concentrations in lead-zinc deposits [11].

The composition of tails in different parts of the tailing dump varies considerably, including the content of useful components [12]. A significant variation in the content of a number of elements at different points of testing is probably due to different distance from the water mirror, and the impact of flotation processes. The average content (median) of elements in technogenic formations of the tailing dump (at a depth of 10 cm) is (in descending order) %: S – 13;Fe- 6,19; Zn- 4,32; Al – 3,9; Pb - 2,71; Ca – 2,5; K - 1,2;Cu - 1,1; Na - 0,92; As -0,47; Sb - 0,39; Ba - 0,38; Ti – 0,28; Sn - 0,234; Mn – 0,21; Cr – 0,08; In - 0,07; Te - 0,056; Cd – 0,028; Cl - 0,028; Ni – 0,019, Se -0,01; Sr -0,0095; hereinafter in ppm: Nd – 94; Zr - 44; V – 33,7; Ce -33; Ag – 30; La – 25; Co – 22; Th – 8; Sc – 6,4; U – 6,2; Rb – 3; Nb – 3; Ta-1,2; Tb – 1,04; Mo. – 1.

It should be noted that most of the elements present in the dry part of the tailings are toxic and highly toxic ones.

In the absence of moisture dispersed particles spread over long distances, polluting the soil, surface water, vegetation. The greatest dangers to human health are fine particles (with a diameter less than 1 μm) as they reach the lower respiratory tract and settle in the alveoli of the lungs. The analysis of stale tails taking into account granulometric composition [5] revealed high variability of element content. The maximum contents of Pb, Zn, Cu, As are noted in the clay fraction.

Table

The results of the analysis of Unal tailings by means of INAA and XRF methods

Elem.	Analysis Method	Depth up to 10 cm (median)	Depth 15-20 cm	By data of [3]	By data of [4]	By data of [5]
		Concentration, %				
Na	INAA	0,92±0,09	0,36±0,04	0,12		
Al	INAA	3,4±0,2	4,6±0,3	5,24		
S	INAA	6,2±1,8	7±2	7,39		1,2-18,9
Cl	INAA	0,048±0,014	0,017±0,005			0,012-0,058
K	XRF	1,2±0,2	1,7±0,2	2,07		
Ca	XRF INAA	1,9±0,1	1,22±0,09	1,97		
Ti	XRF INAA	0,23±0,03	0,21±0,03	0,31	0,17	
Cr	XRF INAA	≤0,1	≤0,1		0,016	0,005-0,07
Mn	INAA	0,20±0,01	0,096±0,005		0,19	
Fe	XRF	5,83±0,03	2,34±0,02	8,86		
Cu	XRF INAA	1,1±0,3	0,08±0,02		0,04	0,04-2,74
Zn	XRF	4,32±0,01	0,758±0,005		0,235	9,03-0,18
As	INAA	0,82±0,06	0,022±0,002		0,028	0,014-0,175
Se	INAA	0,0103±0,0016	0,0040±0,0006			
Sr	XRF	0,0078±0,0003	0,0029±0,0002			0,0010-0,0069
Cd	XRF	0,028±0,0003	0,0032±0,0001		0,0006	
In	INAA	0,07±0,02	0,0005±0,0001			
Sn	XRF	0,2294±0,0003	0,0085±0,0001		0,0023	0,12-0,57
Sb	XRF INAA	0,7387±0,0002	0,1336±0,0001			0,09-3,83
Te	XRF	0,0443±0,0004	≤0,0002			
Ba	XRF	0,3857±0,0002	0,1416±0,0001			0,11-1,16
Pb	XRF	2,93±0,04	1,18±0,03		0,193	0,11-12,42
		Concentration, ppm (10^{-4} %)				
Sc	INAA	6,8±1,7	7,8±2,0			
V	INAA	89±6	38±4		40	14-78
Co	INAA	29±4	12,0±1,8		28	4-13
Ni	INAA	256±77	23±7		20	4-49
Rb	XRF	≤3	90±3			
Zr	XRF	15±3	69±3		140	
Nb	XRF	2±1	6±1			
Mo	XRF	3±1	3±1		5	
Ag	INAA	30±2	5,7±0,4		4	
Cs	INAA	3,9±0,8	4,9±1,0			
La	INAA	21±5	22±6			
Ce	XRF INAA	33±3	43±2			
Nd	XRF	71±5	28±2			
Tb	INAA	2,5±0,2	0,5±0,4			
Ta	INAA	1,2±0,2	1,6±0,2			
Th	INAA	6,9±0,8	14,5±1,2			
U	INAA	6,7±1,3	5,9±1,2			

Analysis of the composition of tails selected at different depths of the tailing dump showed that on the surface of the dry part of the tailing dump there is a sharp increase in the content of such components as: Te (221 times) from 0.0002 to 0.0443 %, In (140 times), from 0.0005 to 0.07 %, As (37 times) from 0.022 to 0.82%, Sn (27 times) from 0.0085 to 0.2294 %. To a lesser extent, but significantly increases the content of Cu (13.7) from 0.08 to 1.1 %, Ni (10.8 times) from 23 to 250 ppm, Cd (8.7 times) from 32 to

280 ppm. From 5 to 5.5 times the content of Zn (5.7 times) increases from 0.758 to 4.32%, Sb (5.5 times) from 0.1336 to 0.7387%, Ag (5.2 times) from 5.7 to 30 ppm, Tb (5 times) from 0.5 to 2.5 ppm. From 2.1 to 2.8 times the content of Fe (2.5 times) increases from 2.34 to 5.83%, Ba (2.7 times) from 0.1416 to 0.3857%, Pb (2.5 times) from 1.18 to 2.93 %, Na (2.6) from 0.36 to 0.92%, Cl (2.8 times) from 0.017 to 0.048%, Mn (2.1 times) from 0.096 to 0.2 %, Se (2.6 times) from 0.004 to 2.7 times) from 29 to 78 ppm, Nd (2.5 times) from 28 to 71 ppm, V (2.3 times) from 38 to 89 ppm, Co (2.4 times) from 12 to 29 ppm. The Ca content increases slightly (1.5 times) from 1.22 to 1.9% and U (1.1 times) from 5.9 to 6.7 ppm.

The results of the analysis showed that the content of such highly toxic elements as Cd, Ni, As, Ag, Cu in samples from the surface of the beach area of the tailing dump is tens and hundreds of times higher than the data available in the literature [3, 4, 5, 6]. Deflationary processes, developing in the dry part of the beach area, pose a serious threat to the surrounding areas.

Despite the fact that the content of useful components in the composition of tailings is extremely uneven, the average content of Pb and Zn in the upper part of the beach area of the Unal tailings corresponds to ordinary ores (Pb + Zn from 7 to 4%). A radical way to protect the environment from the impact of the tailing dump is the leaching of tails with the utilization of useful products of processing, and subsequent recultivation.

Involvement in the production of non-traditional technologies can become a priority direction of the mining industry not only in the RSA, but also in the entire North Caucasus region.

4. SUMMARY

1. The use of RF and INAA for the analysis of waste from the Mizur mining and processing plant made it possible to quantify the content of 39 elements.

2. The content of Zn, As, S, Cu, Sb, Se, Ag, In, Pb Cd in the composition of technogenic formations of the Unal tailing dump is abnormally high and exceeds the Clark values by more than hundreds and thousands of times.

3. The content of elements in the upper part of the beach zone is uneven, a significant variation in the content of a number of elements at different points of testing is probably due to different distances from the water mirror, and the impact of flotation processes.

4. The high content of highly toxic elements (Zn, As, Cu, Sb, Ni, Pb) in the surface layers of the beach area of the tailing dump poses a danger to the environment and public health.

5. The presence of useful ore components in the tailings indicate the need for recycling of waste Mizur concentrator**.**

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