IJIRSS
International Journal of Innovative Research & Scientific Studies

ISSN: 2617-6548

URL: www.ijirss.com

Ecological assessment of the environmental state in the area of Polymetal waste storage in the Southern of Kazakhstan

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Abstract

The territory of Kazakhstan is rich in various minerals, which, unfortunately, during Soviet times were developed only for 1-2 components. The result of this attitude towards natural resources was the emergence of "man-made" deposits from the formed and stored waste of the mining and metallurgical complex. Due to erosion processes, waste storage sites have become sources of negative impact on the environment. The purpose of this study was to conduct an environmental assessment of the state of the environment in the area where polymetallic waste is stored in the south of Kazakhstan. An assessment of the ecological state of polymetallic waste revealed the presence of a number of toxic components that negatively affect the decrease in the biodiversity of microflora, represented only by the genera *Thiobacillus, Pseudomonas, Penicillium, and Aspergillus* in an amount of 10.0 CFU/g. It has been established that the projective cover and species diversity of phytocenoses of dumps and technosoils are in a correlative relationship with the distance to the storage site of polymetallic waste. Toxicotolerant species of native flora, *Dodartia orientalis* L. and *Capparis spinosa* L., were identified, growing in single copies on the surface of toxic waste. As the distance from toxic waste heaps increases, phytocenoses become enriched with species of *Poaceae, Asteraceae, Polygonaceae, and Fabaceae*. A complete absence of representatives of lumbric fauna was revealed in the residential area, which were found only sporadically 5.0±0.5 km from waste heaps. A negative impact of polymetallic waste on the health of the population of various age groups in a nearby village was noted, with a predominance of respiratory diseases, metabolic, and digestive disorders.

Keywords: Polymetallic waste storage, Public health, Vegetation of dumps.

DOI: 10.53894/ijirss.v8i1.4675
Funding: This study received no specific financial support.
History: Received: 30 December 2024/**Revised:** 4 February 2025/**Accepted:** 12 February 2025/**Published:** 14 February 2025

Competing Interests: The authors declare that they have no competing interests.
Authors' Contributions: All authors contributed equally to the conception and design of the study. All authors have read and agreed to the published version of the manuscript.
Transparency: The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.
Publisher: Innovative Research Publishing

1. Introduction

The territory of Kazakhstan is rich in mineral deposits, including barite, lead, zinc, phosphorites, copper, and molybdenum. Unfortunately, mining and processing technologies have been focused on the extraction of only one or two components. As a result, areas with stored waste, which have various chemical, mineralogical, and elemental compositions, have begun to form. Currently, the south of Kazakhstan is a concentration of areas with phosphorus-containing [1], lead-zinc [2], polymetallic, and oil-containing waste.

Unfortunately, due to the processes of water and wind erosion on one hand and high rates of urbanization on the other, waste sites are becoming local hotspots of environmental hazards. These wastes contain valuable metals such as copper, zinc, aluminum, iron, and others that can be extracted and used in modern industry. Lim, et al. [3] described that generally, the focus is on the potential environmental problems associated with the environmental impact of waste, but little research has been done on its further utilization. Competent utilization of industrial waste will not only contribute to solving the problem of waste storage but also to the creation of new marketable products [4, 5]. However, the chemical and mineralogical composition of mining waste depends on the metallurgical process, which can determine whether any slag can be a reusable product or not. At present, slags from steel production are well analyzed by several techniques such as X-ray diffraction, ICP-OES, leaching tests, and many others. In terms of further industrial applications, they are mainly reused as aggregate for road construction or as filler material for hydraulic structures.

There are a number of ways to extract valuable components from mining and metallurgical wastes using cyanidation, thiourea leaching, sulfuric acid leaching, etc. [6]. On the other hand, the requirements for environmental safety in production dictate the need to use environmentally friendly technologies. Such technologies include bacterial leaching or selective extraction of chemical elements from multicomponent compounds through their dissolution by microorganisms in an aqueous medium [7, 8]. The most frequently described studies are those conducted with thiobacteria, in particular Acidithiobacillus ferrooxidans, which has proved to be an active agent in the bioleaching of copper sulfide minerals [9] and other refractory ores and concentrates.

In any case, before the rational use of any waste, it is necessary to carry out preliminary studies to create a general picture of the ecological state of the waste. Studies aimed at examining the impact of anthropogenic wastes on flora and fauna are known, where molecular, cytological, population, and species-level criteria are used as bioindicative features [10-14]. A correlation between the accumulation of heavy metals such as lead, zinc, cadmium, copper, manganese, chromium, and nickel in different plant species and the distance from the emission source has been found [15, 16]. In addition, it has been revealed that individual physiological characteristics of different plants determine the barrier function in the distribution of heavy metals in the phytomass of the plant, and the accumulators of heavy metals are the species *Ambrosia artemisiifolia L., Artemisia austriaca Pall. ex. Wild., Achillea nobilis L., and Tanacetum vulgare L.*

The purpose of this study was to conduct an environmental assessment of the polymetallic waste storage area in southern Kazakhstan.

2. Materials and Methods of Research

Polymetallic wastes from Yuzhpolymetal JSC (YuPM JSC), stored near the village of Achisai in the Turkestan region of southern Kazakhstan, were used as the subject of research (Figure 1).

Figure 1.
Map of Kazakhstan and the location of polymetallic waste storage sites of Yuzhpolymetal JSC (68053'45.92"): 1. Polymetallic slag; 2. Localization of the old extraction plant; 3. Achisay village.

Water and ore samples were taken aseptically using special samplers in accordance with the methodological recommendations.

Infrared spectroscopy was used to determine the chemical composition of ore using the spectrophotometer SPECORD 75 IR with mass spectrometric detection Varian-820 MS (Australia), and the elemental composition was analyzed by atomic absorption on the spectrometer AAnalyst 800 (Perkin-Elmer) and on the high-performance liquid chromatograph Varian-Pro (Holland).

X-ray diffractometric analysis was carried out on an automated diffractometer DRON-4 with Cu Ka-radiation and a β-filter. Conditions for diffractogram shooting were: U=35kV; I=20 mA; scale: 2000 imp; time constant 2s; shooting theta-2theta; detector 2 grad/min.

X-ray phase analysis on a semi-quantitative basis was performed on powder sample diffractograms using the method of equal suspensions and artificial mixtures. Quantitative ratios of crystalline phases were determined. The interpretation of diffractograms was carried out using the data from the ASTM Powder Diffraction File and diffractograms of minerals free of impurities. Content calculations were performed for the major phases. Possible impurities, the identification of which cannot be unambiguous due to low content and the presence of only 1-2 diffraction reflections or poor crystallization, were noted.

The fractional composition of slags was determined by the granulometric method using sieves of different diameters. Video fixation of the material was carried out using a digital camera 'Samsung' and a video card of the electron scanning microscope JSM 649LV manufactured by JEOL (Japan) with the system of energy dispersive microanalysis INCA Energy 350 manufactured by OXFORD Instruments (Great Britain), connected with the system of structural analysis of polycrystalline objects HKL Basis.

Scout-Pro scales were used in the preparation of the nutrient medium, and a SPGA-100-1-NH autoclave was used for sterilization.

Taxonomic analysis of microorganisms was carried out using Bergey B's Bacterial Identifier [17]. Microscopy of microbiological preparations was conducted using microscopes 'Mikmed-5' (Russia) and 'Tayda' (Japan) at magnifications of x40, x600, x1000, and an electron scanning microscope at magnifications of up to x3300 times. The morphology of the micromycetes was determined by colonies on Petri dishes. The shape, cross-section, margins, texture, color, and pigment diffusion on agar were considered while describing the colonies. Statistical processing of the study results was carried out by calculating the arithmetic mean and standard deviation. The data were processed using a personal computer IBM 'Pentium' based on application software packages 'Excel'.

3. Results of the Studies and Their Discussion

3.1. Retrospective Analysis of Polymetallic Waste Status

Achisai polymetallic combine was founded in 1927 based on the Achisai lead-zinc deposit and was actively functioning for 60 to 70 years. In 1941, the Mirgalimsaiskoye deposit was developed, where barite production started in 1953. The combine consisted of the Zapadnaya and Skipovaya mines, the Kentauskaya mining and processing plant, and the zinc plant. From 1984 to 1995, the Achisai polymetallic combine comprised four mines and three concentrating plants. The shape of the ore bodies is plate-shaped, and the deposit itself is divided by tectonic disturbances into nine geological blocks, with the dip of ore bodies ranging from 5 to 10 degrees to 70 to 80 degrees and a depth of occurrence of up to 900 meters. The mineralogical composition is represented by galena, pyrite, sphalerite, and barite, while the host rocks are dolomite and dolomitized limestone. After the collapse of the USSR, the factory ceased its activities, but a significant amount of waste in the form of slag and slimes remained, most of which is stored in the open air near the settlements of Achisai, Kentau, Kantagi, Bayaldyr, and others.

Waste used to fill mine voids is a separate environmental impact. Analyses of the polymetallic waste stockpile site revealed the main sources of groundwater contamination:

- Underground: contaminated backfill material from mine workings,
- Surface: tailings waste used as suffusion void fillers.

The backfill material is represented by various-sized pebbles, the fraction of which is more than 5.0 mm – 36.1±2.2%, 1.0-5.0 mm - 7.0±0.1%, and less than 1.0 mm - 57.0±2.6%. It was revealed that the fillings below the G horizon are made with 6.0% cement, as a result of which water solutions gradually leach pollutants contained in the fillings. In several places, ore dressing tailings were used to fill the spent mines, which contained up to 22.5±2.5% of flotation agents from their total consumption. It is established that throughout the entire period of operation of enrichment plants, there was a large amount of flotation agents in the tailings, namely: sodium sulfide, xanthogenate, oleic acid, sodium silicate, phenols, cyanides, and shale resin. In total, from 12.0 to 14.8 million tonnes of tailings were deposited in mine workings.

3.2. Physical and Chemical Characterisation of Polymetallic Wastes

The results of chemical analyses showed that the maximum amount of cyanide was found in horizon B (0.13 mg/kg). In horizons A, B, and D, the cyanide content is 0.045±0.002, 0.06±0.003, and 0.047±0.003 mg/kg, respectively. The maximum amount of rhodanides was detected in horizon D at 0.60±0.03 mg/kg; in other horizons, their content varies from 0.210±0.001 to 0.05±0.003 mg/kg. Oleic acid in maximum amounts is found in the tailings of horizon G at more than 15.0±0.8 mg/kg, and in horizons A, B, and C at 0.05±0.004, 0.04±0.001, and 5.0±0.03 mg/kg, respectively. In open tailings, the oleic acid content does not exceed 0.05±0.005 mg/kg. Xanthogenates were not detected in any of the samples, which is probably due to their easy conversion to other organic forms. However, chemical analyses of the groundwater at the polymetallic waste disposal site have shown that the water is environmentally benign and can be used for agricultural purposes.

As a result of ICS analysis of polymetallic slags, in addition to the main elements, %: Ti - 1.04 ± 0.1; Fe - 8.21 ± 0.5; Mn - 0.23 ± 0.01; C - 29.10 ± 2.12; Ca - 14.20 ± 1.22; K - 3.41 ± 0.30; Al - 7.23 ± 0.55; Mg - 3.23 ± 0.25; Na - 2.22 ± 0.12; Si - 32.21 ± 3.15; S - 1.03 ± 0.01; traces of Ba, Zn, V, La, Ce, Nd, Zr, Y, Hf, Th, U were noted. The presence of active forms of toxic metals such as aluminum, manganese, and iron, in combination with arid conditions of waste storage, suggests their dominant role in the formation of toxic conditions for the vital activity of biological organisms. A number of studies [18, 19] have shown that metal concentration in plants growing on anthropogenic substrates can cause oxidative stress, genotoxicity, and programmed cell death, disrupting physiological processes. This leads to a decrease in the intensity of growth processes, reduction in the size and weight of organs, seed productivity of plants, suppression of the root system, and wilting of leaves, which is a response of plants to the entire complex of negative factors of dumping.

The results of chemical and spectral analyses of mine waters and aqueous extracts of hard rocks from the G horizon showed high concentrations of residual flotation agents, which suggests that in the event of flooding of the mine below this horizon, leaching of the backfill material and penetration of toxic elements into groundwater is possible (Tables 1,2). The fractional composition of polymetallic waste, including slag and clinker, at the disposal sites was studied (Table 3).

Table 1.
Chemical composition of waters and aqueous extracts of hard rocks of G horizon.

Sampling location	Component content, mg/dm3								
	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	H_2SO_4	NO_3^-	P
Total mine water inflow at surface discharge.	8.1	78	25	24	1.4	171	153	10.2	0.44
Total water inflow of the horizon.	8.2	70	24	23	1.5	165	160	11.5	0.43
Wastewater of the horizon	8.1	339	24	45	4.0	37	897	150	10.75
Tails	7.0	68	12	7	4.0	31.0	173	4	-
G horizon laying test	7.1	236	0	60	21	49	625	19	-

Table 2.
Results of spectral analysis.

Sampling location	Sr, 10^{-2}	Co, 10^{-4}	Zn, 10^{-3}	Cu, 10^{-3}	Mo, 10^{-4}	Ba, 10^{-2}	Ni, 10^{-3}	Mn, 10^{-2}	V, 10^{-3}	Ti, 10^{-1}	Pb, 10^{-3}	Cr, 10^{-3}	Ag, 10^{-5}
Tails	-30	15	8	6	1	>100	0.5	100	2	0.3	300	1.5	150
G horizon laying test	30	10	8	6	1	>100	0.5	100	1.5	0.2	250	1.0	150

Table 3.
Fractional composition of polymetallic waste from Turkestan region, %.

Waste type	Weight of averaged sample, g	Fractional composition, cm*							
		Dust	0.14	0.315	0.63	1.25	2.5	4.0	5.0
Polymetallic slags**	996.3±3.69	0.37	0.45	4.4	4.29	6.56	16.72	9.76	57.4

Note: * δ - relative error <10.0% ** dense and loose pelletized clinker samples up to 1.2 m and larger are visually marked at storage sites.

It was revealed that the fractional composition of waste is influenced not only by production conditions but also by weather, climatic conditions, and time characteristics of storage. The largest waste samples, up to 2.5-3.0 m, were formed due to long-term (more than 30 years) storage at landfills. SEM and ICS analyses of the average clinker sample showed that the samples contain a variation of metals such as Fe, Mg, Pb, Cu, Ba, Cr, Al, Mn, Zn, and Ti (Figure 2).

Environmental impact of polymetallic waste.

The impacts of polymetallic slag on the biosphere are poorly understood, and data are often contradictory due to the diversity of the surrounding ecosystem [20], primarily associated with deep-sea sites. In areas of offshore polymetallic mining, biodiversity of inhabitants has been found to depend on the availability of carbon [21] and topography [22]. Some studies have described potential threats in the processing of polymetallic nodules [23, 24], such as possible radioactive contamination, which requires particular caution in research.

Despite the prolonged exposure of polymetallic waste to the open air, the surface of most areas remains unvegetated, with projective cover of the surface of the dumps ranging from 0% to 5%. Individual specimens of Dodartia orientalis L. and Capparis spinosa L. occur only on the waste surface with small soil layers. In the area around the waste, at a distance of 50 to 100 m, phytocenoses are formed from ruderal flora, seeds of which are carried by the wind and which have developed resistance to available toxicants. The projective coverage of the techno-soil surface is within 10% to 25%. The dominant part of the formed phytocenosis is represented by herbaceous plants of the Poaceae family: Bromus tectorum L., Poa bulbosa L., Agropyron trichophorum (Link.) Richt., and Cynodon dactylon L. Pers. As the distance from the waste storage site increases to 100 to 300 m, the diversity of phytocenosis composition increases due to the appearance of perennial plants from the Asteraceae, Polygonaceae, and Fabaceae families, with the projective coverage of the techno-soil surface increasing up to 30% to 35%.

Studies on the impact of heavy metals on terrestrial organisms are mainly concentrated within several taxonomic groups, where representatives of Hymenoptera, Coleoptera, and Lepidoptera predominate [25]. Insects with a social level of life organization not only have good criterion characteristics of the environment but also contribute to its health improvement [26]. On the other hand, insect population recovery processes and their seasonal changes [27] in different disturbed ecosystems are poorly understood. Among soil mesofauna, earthworms are most often used as bioindicators, the number of which directly correlates with the content of heavy metals in the soil. Issayeva [28] found that earthworms accumulate heavy metals in their tissues, which imitates the situation with the behavior of metals in higher organisms. A reduction of earthworms in ecosystems with high levels of cadmium (0.25±0.0024 mg/kg) and lead (more than 16.0 mg/kg) was found [29]. The studies showed a complete absence of lumbricofauna in the polymetallic slag stockpile area, with isolated specimens of earthworms found 5.0±0.5 km from the heaps in small settlements.

Microbiological examination of the samples showed that Acidithiobacillus ferrooxidans were absent in all samples, indicating the cessation of their oxidative activity, confirmed by neutral or slightly alkaline pH values, which are limiting factors for their vital activity. The sulfur-oxidizing bacteria Thiobacillus thiooxidans were observed mainly in aqueous solutions. The cyanide-oxidizing bacteria T. thiocyanooxidans occurred in low numbers in most of the samples analyzed due to the presence of carbon sources (xanthogenates) and cyanide compounds (Table 4). Heterotrophic microorganisms of the genus Pseudomonas were detected only in horizons 0-10 and 10-20 cm in the amount of 102-103 CFU/g (colony-forming units). Micromycetes Penicillium sp. and Aspergillus sp. were found in these horizons in the amount of (8.0±0.5)×10 CFU/g.

The data from statistical analyses of medical examinations of the residents of the neighboring settlements show that diseases of the respiratory organs, metabolic disorders, and digestive organs prevail. An analysis of cases of primary visits by residents over 60 years old in 2020 indicates that 6.5±0.2 visits to medical organizations are related to diseases of the endocrine system and metabolism, 9.5±0.5% of cases are related to diseases of the eye and its appendage apparatus, and 47.8±2.5% of visits are for diseases of the circulatory system, including high blood pressure, ischemic heart disease, and angina pectoris. Additionally, 14.7±1.2% are for diseases of the respiratory organs, including chronic obstructive pulmonary diseases; 6.5±0.5% are for diseases of the digestive organs, including gastric and duodenal ulcers, liver fibrosis and cirrhosis, cholecystitis, and pancreatic diseases; 7.5±0.2% are for diseases of the genitourinary system, with a predominance of renal tubulointerstitial diseases; 1.4±0.1% are for skin diseases; and 3.4±0.1% are for diseases of the musculoskeletal system and connective tissue, including various arthroses.

In the young population over 18 years of age, the primary referrals to a medical institution for diseases of blood and hematopoietic organs account for 4.4±0.2%; endocrine and metabolic diseases - 5.3±0.3%; circulatory system diseases, including high blood pressure, ischemic heart disease, cardiomyopathy, and cerebrovascular diseases - 49.4±3.4%; diseases of the nervous system - 1.2±0.1%; eye diseases - 3.3±0.2%; respiratory diseases - 5.0±0.4%; skin diseases and allergic reactions - 0.9±0.4%; nervous system diseases - 1.2±0.1%; eye diseases - 3.3±0.2%; respiratory diseases - 5.0±0.4%; skin diseases and allergic reactions - 0.9±0.0%; congenital anomalies, deformities, and chromosomal disorders were noted in 0.8±0.0% of young people; and neoplasms were detected in 0.4±0.0%. The obtained statistical data correspond to trends and characteristics of morbidity in other disadvantaged regions of Kazakhstan. Thus, in the Shymkent megacity with heavy metal air pollution, T-lymphopenia was detected in 42.1% of children, and B-lymphopenia in 46.3% of children, which shows a high level of adaptation processes of the immune system to altered environmental conditions [30] and causes disorders in the respiratory and circulatory systems [31]. In general, there is a decrease in the quality of life in the inhabitants of settlements located in close proximity to polymetallic waste storage areas, which is noted regardless of age categories.

4. Conclusion

As a result of the assessment of the ecological state of polymetallic production wastes in the south of Kazakhstan, the chemical and fractional composition of polymetallic slag wastes and the spectral composition of groundwater in the places of polymetallic waste storage were established. The composition of microflora of polymetallic slag and contaminated water, in species and quantitative terms, is poor and is represented by the genera Thiobacillus, Pseudomonas, Penicillium, and Aspergillus. The results of floristic analysis showed that the projective cover and species diversity of vegetation on dumps and technoposhes are in correlative dependence on the distance to the site of polymetallic waste disposal, with only isolated specimens of Dodartia orientalis L. and Capparis spinosa L. noted in the immediate vicinity and on the surface of dumps. Successional processes around the territory of slag heaps are formed at the expense of representatives of the Poaceae family; as the distance from toxic slag heaps increases, phytocenoses are enriched at the expense of species of the Poaceae family. Studies have shown that representatives of lumbricofauna in the residential zone are completely absent and are sporadically found only 5.0±0.5 km from the spoil heaps in small settlements. The negative impact of polymetallic waste was also noted on the health of the population of the nearby village, where the prevalence of respiratory, metabolic, and digestive diseases was found.

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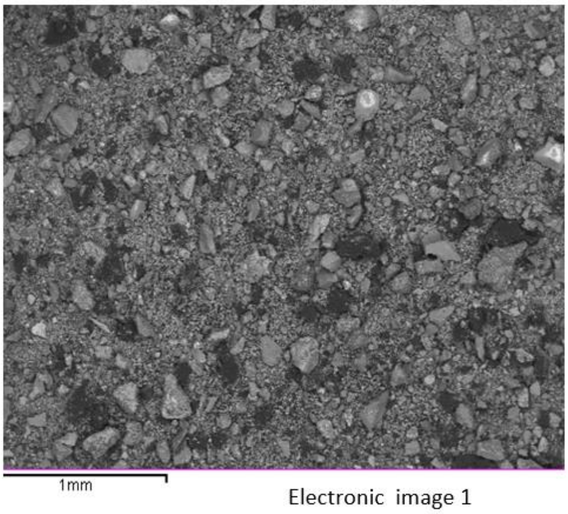
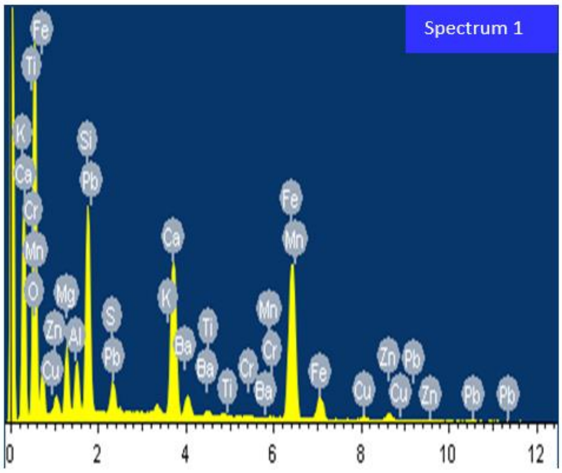
Table 4.
Results of microbiological examination of waste and water samples from the polymetallic deposit

Sampling location	**Thionic bacteria, CFU/g, CFU/ml***		
	A. ferrooxidans	***T.thiooxidans***	***T.thiocyanooxidans***
Laying of horizon A	0	0	10
Horizon B	0	0	10
Horizon B	0	0	10
Horizon D	0	10	10
Tailings	0	0	0
Total mine water inflow at surface discharge	0	10	10
Total water inflow of G horizon	0	10	10
Wastewater of G horizon	0	10	10
Groundwater (above the G horizon)	0	0	10

Note: * δ - relative error <10.0%





a b

Figure 2.
SEM image (a) and Spectrogram(b) of polymetallic clinkers.