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SPATIAL DISTRIBUTION OF ELEMENTS, ENVIRONMENTAL EFFECTS, AND ECONOMIC POTENTIAL OF TECHNOGENIC WASTE MATERIALS OF PAVLODAR ALUMINUM PLANT (PAVLODAR, KAZAKHSTAN)

Abstract. The utilization of technogenic waste or more productive secondary use of the waste is a relevant problem for both economic and sustainable development. A study of content, as well as spatial distribution of elements, is needed when assessing the environmental and economic potential of technogenic objects. Moreover, it is necessary to reveal the tendencies of the spatial distribution of some indices such as the pollution coefficient. The characteristics of spatial distribution can give information about peculiarities of accumulation and amounts of dangerous or valuable components kept in the technogenic object. The objects of this research are sludge storages of the Pavlodar aluminum plant located in Pavlodar city, Kazakhstan; the elemental contents of 75 ground samples from three sludge storages were analyzed. The data were placed on an electronic map, using GIS. Average gross contents, hazard quotients, concentration coefficients of each metal, as well total pollution coefficients (Zc) at each sample point were calculated. The maps of the spatial distribution of element concentrations as well as synthetic maps of the spatial distribution of total pollution coefficients were created. The research showed that from an environmental point of view the territory of the studied objects by the level of soil contamination should be considered as a territory with a relatively satisfactory situation. The studied ground is of iron-vanadium geochemical specialization. The calculated overall volume is approximate 135 117 349.28 m^3. Knowing the average bulk density of the ground samples the approximate weight of the accumulated waste was calculated and was equal to 136 787 399.7171 tons, including 15 248 984.09 tons of iron, 209 413.3 tons of manganese, 16 487 875.77 tons of calcium. The huge amounts of valuable components retained in the waste mass led us to conclude that studied technogenic objects can be considered as a secondary field for the production of various technological products, as well valuable components can be extracted as metal concentrate.

Key words: Pavlodar aluminum plant; bauxite sludge; spatial distribution; elemental content; economic potential.

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ПАВЛОДАР АЛЮМИНИЙ ЗАУЫТЫ ТЕХНОГЕНДІК ҚАЛДЫҚТАРЫНЫҢ ҚОРШАҒАН ОРТАҒА ӘСЕРІ ЖӘНЕ ЭКОНОМИКАЛЫҚ ӘЛЕУЕТІ, ЭЛЕМЕНТТЕРІНІҢ КЕҢІСТІКТЕ БӨЛІНУІ (ҚАЗАҚСТАН, ПАВЛОДАР)

Аннотация. Техногендік қалдықтарды кәдеге жарату немесе екінші реттік өнімді қалдықтарды пайдалану экономикаға, сондай-ақ тұрақты даму үшін де өзекті мәселе болып табылады. Элементтердің мазмұнын зерттеу, сонымен қатар кеңістікте бөлінуі техногендік нысанның экологиялық және экономикалық әлеуетін бағалау кезінде қажет. Бұдан бөлек, ластану коэффициенті сияқты кейбір көрсеткіштердің кеңістікте бөліну үрдісін анықтау керек. Элементтердің кеңістікте бөліну сипаты техногендік нысанда қамтылатын қауіпті немесе құнды құрамдас бөліктерінің жинақталу ерекшеліктері және саны туралы ақпарат беруі мүмкін. Осы зерттеудің нысаны Қазақстандағы Павлодар қаласында орналасқан Павлодар алюминий зауытының қалдық қоймасы болып табылады. Зерттеу барысында үш қалдық қоймасынан топырақтың 75 сынамасының элементтік құрамы талданды. Деректер геоақпараттық жүйелердің қолданылуымен электронды картаға енгізілді. Орташа жиынтық мөлшері, қауіптілік коэффициенті, әр металдың шоғырлану коэффициенттері, сондай-ақ сынама алудың әр нүктесінде ластанудың жалпы коэффициенттері (Zc) есептелінді. Элементтердің шоғырлануының кеңістікте бөліну карталары, сондай-ақ ластанудың жалпы коэффициенттерінің кеңістікте бөлінуінің жинақтамалы картасы құрылды. Зерттеу топырақтың ластану деңгейі бойынша зерттелетін нысанның аумағын салыстырмалы қанағаттанарлық жағдайы бар аумақ ретінде экологиялық көзқараспен қарастырған жөн екендігін көрсетті. Зерттелетін топырақтың темірлі-ванадийлі геохимиялық мамандануы бар. Қалдықтардың есептік жалпы көлемі шамамен 135 117 349,28 $м^3$ құрайды. Топырақ үлгілерінің орташа үйінділік тығыздығын біле отырып, жинақталған қалдықтардың жуық салмағы 136 787 399,7171 тоннаны, оның ішінде темір 15 248 984,09 тоннаны, марганец 209 413,3 тоннаны, кальций 16 487 875,77 тоннаны құрады. Қалдықтардың массасында қамтылатын құнды құрамдас бөліктердің көп мөлшері зерттелетін техногендік нысан технологиялық түрлі өнімдер өндірісі үшін екінші реттік кен орны ретінде қаралуы мүмкін, құнды құрамдас бөліктер металл шоғыры түрінде алынуы мүмкін деген қорытындыға әкеледі.

Түйін сөздер: Павлодар алюминий зауыты; боксит қоқыры; кеңістікте бөліну; элементтік құрам; экономикалық әлеует.

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ПРОСТРАНСТВЕННОЕ РАСПРЕДЕЛЕНИЕ ЭЛЕМЕНТОВ, ВОЗДЕЙСТВИЕ НА ОКРУЖАЮЩУЮ СРЕДУ И ЭКОНОМИЧЕСКИЙ ПОТЕНЦИАЛ ТЕХНОГЕННЫХ ОТХОДОВ ПАВЛОДАРСКОГО АЛЮМИНИЕВОГО ЗАВОДА (ПАВЛОДАР, КАЗАХСТАН)

Аннотация. Утилизация техногенных отходов или более продуктивное вторичное использование отходов является актуальной проблемой как для экономики, так и для устойчивого развития. Изучение содержания, а также пространственного распределения элементов необходимо при оценке экологического и экономического потенциала техногенного объекта. Кроме того, необходимо выявить тенденции пространственного распределения некоторых показателей, таких как коэффициент загрязнения. Характер пространственного распределения элементов может дать информацию об особенностях накопления и количествах опасных или ценных компонентов, содержащихся в техногенном объекте. Объектом данного исследования являются шламохранилища Павлодарского алюминиевого завода, расположенные в городе Павлодар, в Казахстане. В ходе исследования был проанализирован элементный состав 75 проб грунта из трех шламохранилищ. Данные были нанесены на электронную карту с использованием ГИС. Были рассчитаны средние валовые содержания, коэффициенты опасности, коэффициенты концентрации каждого металла, а также общие коэффициенты загрязнения (Zc) в каждой точке отбора проб. Были созданы карты пространственного распределения концентраций элементов, а также синтетическая карта пространственного распределения общих коэффициентов загрязнения. Исследование показало, что с экологической точки зрения территорию исследуемого объекта по уровню загрязнения почвы следует рассматривать как территорию с относительно удовлетворительной ситуацией. Исследуемый грунт имеет железо-ванадиевую геохимическую специализацию. Расчетный общий объем отходов составляет приблизительно 135 117 349,28 м^3. Зная среднюю насыпную плотность образцов грунта, был рассчитан приблизительный вес накопленных отходов, который составил 136 787 399,7171 тонн, в том числе 15 248 984,09 тонн железа, 209 413,3 тонн марганца, 16 487 875,77 тонн кальция. Огромное количество ценных компонентов, содержащихся в массе отходов, приводит к выводу, что исследуемый техногенный объект может рассматриваться как вторичное месторождение для производства различных технологических продуктов, ценные компоненты могут быть извлечены в виде металлических концентратов.

Ключевые слова: Павлодарский алюминиевый завод; бокситовый шлам; пространственное распределение; элементный состав; экономический потенциал.

Introduction. The issue of industrial waste accumulation is relevant to regions, where active production complexes and industrial zones are located. So, in Kazakhstan, the main industrial regions are the Karaganda region, East Kazakhstan region, and Pavlodar region (Adno, 2021; Aubakirova et al., 2021; Yermolayeva et al., 2020; Berdenov et al., 2015). The main industrial branches in these regions are metallurgy, mining, and oil refining. It is well known, that metallurgical production gives a huge amount of waste – mainly sludges. As a result of the constant increase in the volume of accumulated waste there can occur migrations of pollutants into the environment (FAO and UNEP, 2021; Ministry of Energy of the Republic of Kazakhstan, 2016). From the other point, the investigation of the contents of the sludges shows the possibilities of their return into the technological process for deep recycling or obtaining new products. At the same time, the metallurgical branch is mainly raw material oriented (Ni, 2005). The productions are not aimed at deep processing of waste. Currently, there is a stable need to find new ways to dispose of waste, as well as to reveal and study the economic potential of industrial waste deposits placed on enterprises of the metallurgical industry.

In the Pavlodar region, one of the largest metallurgical enterprises is the Pavlodar Aluminum Plant (PAP) — a Kazakhstan enterprise producer of alumina. This enterprise, being a part of JSC “Aluminum of Kazakhstan”, is located in the city of Pavlodar. The capacity of the enterprise is 1.4-1.5 million tons of alumina per year. The raw materials come from Turgai (Arkalyk, Kazakhstan) and Krasnooktyabrsky (Lisakovsk, Kazakhstan) bauxite ore departments, as well as from the Keregetas limestone deposit in the Pavlodar region. The resulting alumina is sent to the Kazakhstan Electrolysis Plant for the production of aluminum metal in ingots. In 2015, the company produced 1.448 million tons of alumina (metalmininginfo.kz, n.d.).

Among CIS alumina plants, the alumina plant of JSC “Aluminum of Kazakhstan” is in the 1st place by realized capacity. The Pavlodar alumina plant occupies a special place in the world hierarchy of alumina producers. It has a positive experience of processing low-quality bauxite raw materials to alumina under the world’s only technological scheme “series-parallel version of Bayer sintering with achieving good economic performance.

As a result of the work of all processing of alumina production, harmful substances are released into the atmosphere: suspended solid particles (dust of bauxite, limestone, coal, alumina), alkaline steam, and gases: sulfur dioxide, oxides of nitrogen, and carbon. All alumina production equipment is equipped with gas purification devices for capturing harmful emissions.

The enterprise has four accumulators of waste from the production: a slurry collector consisting of three cards, an ash collector of the heat power plant, and an administrative landfill of household waste.

As world aluminum consumption increases, so does the amount of waste generated by the Bayer process - the red mud, also known as bauxite tailings, red sludge, and bauxite sludge. Depending on the composition of the original bauxite and the technology, 1 ton of alumina is produced from 0.9 to 1.5 tons of this waste (Evans, 2016; R. Zhang et al., 2011). Usually, red mud is not processed but stored in special slurry storage.

The chemical composition of the bauxite red mud of the Pavlodar aluminum plant was investigated with the optical emission spectrometer for metal analysis DFS 500 (OKB Spektr, Russia) (Kasenov et al., 2018). The study results are shown in Table 1.

Table 1 – Content of red mud from the Pavlodar aluminum plant (Pavlodar, Kazakhstan) (Kasenov et al., 2018)

Compound	Fe_2O_3	CaO	Al_2O_3	SiO_2	Na_2O	K_2O
Content, wt.%	21	40-45	4	23	1.75	0.27

To protect groundwater from pollution, there is an anti-filtration curtain around the perimeter of the sludge storage – a “wall in the ground”.

Red mud recycling research is underway worldwide and hundreds of disposal methods have been developed. The multi-component composition of these wastes allows their use in different industries (Cakici et al., 2004; Gräfe et al., 2011; Gräfe & Klauber, 2011; Klauber et al., 2011; Liu et al., 2011; Liu & Naidu, 2014; Power et al., 2011; Siverio Lima et al., 2017; Tsakiridis et al., 2004; Shomanova et al., 2018). Red mud treatment methods can be divided into pyrometallurgical, hydrometallurgical, and direct use methods, for example in construction (Tsakiridis et al., 2004) or as a catalyst for chemical reactions (Cakici et al., 2004). This separation is conditional because in most cases the proposed technologies include both pyrometallurgical and hydrometallurgical transformations. There are many critical reviews in the literature on how red mud is treated, both considering all applications (Gräfe et al., 2011; Gräfe & Klauber, 2011; Klauber et al., 2011; Power et al., 2011) and describing specific areas, such as their use for pollutant treatment (Liu et al., 2011) extraction of metals from them (Liu & Naidu, 2014), pyrometallurgical processing (Zinoveev et al., 2018), use in construction (Siverio Lima et al., 2017). Despite numerous studies, only a small proportion of red mud is still recycled, owing to the low profitability of most technologies, the high capital cost of the development of new products, and the complexity of sales.

The secondary use of deposited waste mass is a relevant issue (Ilieş et al., 2021; Šajn et al., 2022; Xu et al., 2022). For solving the problem, it is necessary to study the technogenic object from environmental and economic points of view (Mendybayev et al., 2015; Safarov et al., 2019). For that, it is required to assess environmental indices, such as the total pollution coefficient, as well as to define the gross amounts of valuable waste components. The most significant metals in the studied waste were Al, Mn, and Fe. As well the study of the spatial distribution of elements allows us to conclude the total volume and weight of the deposited waste, however, before that it is necessary to assess the gross amounts of the target components. Meanwhile, there are no recent studies regarding the spatial distribution of elements for sludge storages of PAP.

Thus, this research aims to reveal the elemental content of ground samples taken from different locations of the sludge storage of PAP, show the distribution of the elements on the territory of the storage, calculate the average elemental content, as well the total pollution coefficient Zc (Allayarova et al., 2021; Linnik et al., 2020; Sivukhin et al., 2020; Solodukhina et al., 2021), to calculate the approximate volume of waste which has been accumulated in the storage and to calculate the approximate amounts of the element reserves deposited in the studied technogenic object. Hereinafter, using local prices for some valuable metals to calculate the average economic potential of the waste utilization.

Material and methods. Study area. The objects of this research are three sludge storages of the Pavlodar aluminum plant (Pavlodar, Kazakhstan). The storages are more or less rectangular territories with areas of approximately 4 407 405 m^2, 3 471 518 m^2, and 5 770 919 m^2 correspondingly (Fig. 1).

Figure 1. Studied technogenic objects – sludge storages of Pavlodar aluminum plant (Pavlodar, Kazakhstan) with sampling locations. (coordinate system: WGS 84: Pseudo-Mercator EPSG:3857, satellite map: ESRI Satellite ArcGIS/World_Imagery), scale: 1:32 278)

Sludge storages are open locations partly covered by water containing the bauxite sludge obtained during the production process. Upper layers of bauxite sludge (red mud) are partly oxidized. Oxidized layers differ by color, they are of a gray hue, and another part is brown (Fig. 2).

Figure 2. View of upper and lower layers of bauxite sludge on sludge storages of Pavlodar aluminum plant

Sampling. From every object 25 samples of the ground, the weight of each at least 1 kg were sampled from different ground layers from the surface to about 50 cm in depth. In total 75 samples were collected. The coordinates of sampling points are presented in Table 2. Sampling was performed using plastic equipment, and a sampling map is shown in Fig 1. The distance between the sample points was not less than 200 m. The samples were transported and stored in plastic containers for preservation from the direct sunbeams. Before the analyses, the waste samples were air-dried.

Table 2 – Coordinates of sampling points (coordinate system: WGS 84: Pseudo-Mercator EPSG:3857)

Sludge storage 1			Sludge storage 2			Sludge storage 3		
id	X	Y	id	X	Y	id	X	Y
1	8581689	6847580	1	8584676	6847933	1	8585063	6849175
2	8580497	6848040	2	8583400	6849108	2	8585290	6846992
3	8582018	6847656	3	8583917	6848684	3	8586299	6847352
4	8580350	6849045	4	8583484	6848236	4	8586958	6848889
5	8581381	6847183	5	8584699	6847400	5	8586446	6848799
6	8582460	6848504	6	8583459	6848721	6	8586287	6847636
7	8581215	6848120	7	8583619	6847295	7	8586093	6848801
8	8582313	6847532	8	8583142	6847681	8	8586545	6847656
9	8580380	6847655	9	8583902	6847601	9	8586985	6846810
10	8581114	6847783	10	8584341	6847953	10	8586161	6847040
11	8580703	6848035	11	8584287	6848516	11	8585270	6848433
12	8582241	6847943	12	8583436	6848018	12	8585529	6847753
13	8581620	6847994	13	8583848	6848921	13	8586676	6848348
14	8582143	6847425	14	8583621	6849077	14	8587115	6847584
15	8580768	6847677	15	8584670	6847655	15	8586961	6847181
16	8581568	6848273	16	8583917	6847132	16	8585856	6848694
17	8582233	6848798	17	8584389	6847345	17	8585921	6849041
18	8582132	6848314	18	8583644	6848442	18	8586993	6848640
19	8581245	6847360	19	8583676	6847882	19	8586273	6846860
20	8581744	6847796	20	8584520	6848796	20	8587234	6848577
21	8581342	6847835	21	8584294	6847167	21	8585201	6848043
22	8580753	6847298	22	8584061	6848109	22	8587367	6847304
23	8581074	6848899	23	8584292	6848790	23	8586979	6848225
24	8581904	6847413	24	8584573	6848529	24	8585100	6847596
25	8581548	6847726	25	8583115	6848661	25	8585226	6847314

Elemental analysis. The elemental contents of samples were analyzed using an X-Ray fluorescent analyzer BRA-18 (Russia). The analyzer allowed us to detect the content of some chemical elements (Cl, K, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Pb), some of which belongs to a group of heavy metals. The XRF method is convenient when it is needed to work with a lot of samples without labor-intensive sample preparation in solid, powder, and liquid samples (Brutch et al., 2022). The method uses the measurement of the wavelength and intensity of fluorescent radiation (X-Ray) from the excited atoms of the sample (Pohrebennyk et al., 2017).

Result and discussion. Elemental analysis. The results of the elemental analysis were following the presented earlier results of the waste chemical content (Table 1) (Kasenov et al., 2018). Despite the fact, that aluminum was not detected, it can be referred to as the undefined part of the content. The sums of contents of detected elements were about 26-29%. The maximum Ca content is 13.2300 wt. %, Fe – was 11.9193 wt. %, and K – was 3.5140 wt. % (Table 3). Overall, the results show that the Mn content is not higher than 0.1722 wt. %, Ti varies in the range of 1.7770 - 1.6369 wt. %, contents of V, Co, Ni, and Cu are even and are approximately 0.0250, 0.0029, 0.0043, and 0.0060 wt. % respectively. The largest amount of Zn was 0.0128 wt. %, and Pb – was 0.0017 wt. %. Thus, the high content of valuable metals such as V, Ti, and Fe provides opportunities to use the studied waste material to obtain new products or in the processes of obtaining metal concentrates.

Table 3 – Elemental content (wt. %) of ground samples from sludge storages of Pavlodar aluminum plant

Object name	id	Cl	K	Ca	Ti	V	Mn	Fe	Co	Ni	Cu	Zn	Pb	Sum	Other
Sludge storage 1	1	0.0036	3.3511	12.7133	1.7210	0.0251	0.1470	11.1528	0.0027	0.0042	0.0060	0.0121	0.0011	29.1400	70.8600
	2	0.0036	3.3583	12.6029	1.7212	0.0251	0.1453	11.1683	0.0028	0.0042	0.0060	0.0121	0.0012	29.0510	70.9490
	3	0.0036	3.3636	12.6350	1.7213	0.0251	0.1460	11.1687	0.0028	0.0041	0.0061	0.0121	0.0012	29.0895	70.9105
	4	0.0036	3.3420	12.7365	1.7206	0.0251	0.1492	11.1175	0.0024	0.0042	0.0060	0.0121	0.0012	29.1204	70.8796
	5	0.0036	3.3560	10.2082	1.7225	0.0252	0.1489	11.4733	0.0049	0.0047	0.0055	0.0119	0.0016	26.9664	73.0336
	6	0.0036	3.3545	12.9745	1.7206	0.0251	0.1494	11.0899	0.0022	0.0042	0.0061	0.0121	0.0011	29.3433	70.6567
	7	0.0036	3.3553	12.7075	1.7207	0.0251	0.1483	11.1232	0.0024	0.0041	0.0062	0.0121	0.0011	29.1095	70.8905
	8	0.0036	3.3444	13.0206	1.7205	0.0250	0.1479	11.0856	0.0021	0.0042	0.0061	0.0121	0.0011	29.3731	70.6269
	9	0.0036	3.3528	12.7504	1.7208	0.0251	0.1465	11.1538	0.0027	0.0042	0.0060	0.0121	0.0011	29.1792	70.8208
	10	0.0036	3.3451	12.7768	1.7209	0.0250	0.1469	11.1314	0.0026	0.0042	0.0060	0.0121	0.0012	29.1756	70.8244
	11	0.0035	3.3832	12.4973	1.7198	0.0250	0.1456	11.0190	0.0026	0.0041	0.0059	0.0124	0.0011	28.8195	71.1805
	12	0.0035	3.2859	12.2459	1.7160	0.0245	0.1486	10.9785	0.0028	0.0040	0.0059	0.0116	0.0012	28.4284	71.5716
	13	0.0035	3.3637	12.5925	1.6966	0.0254	0.1414	11.3064	0.0028	0.0042	0.0061	0.0124	0.0011	29.1561	70.8439
	14	0.0035	3.3613	13.1609	1.7453	0.0246	0.1472	11.3400	0.0025	0.0041	0.0060	0.0120	0.0011	29.8085	70.1915
	15	0.0036	3.4970	10.3818	1.7385	0.0242	0.1459	11.5460	0.0048	0.0048	0.0057	0.0113	0.0017	27.3653	72.6347
	16	0.0037	3.2725	12.4079	1.6856	0.0243	0.1494	11.5335	0.0023	0.0043	0.0061	0.0116	0.0011	29.1023	70.8977
	17	0.0036	3.4032	13.0248	1.7299	0.0257	0.1473	11.2011	0.0025	0.0042	0.0062	0.0116	0.0011	29.5612	70.4388
	18	0.0035	3.3834	12.9119	1.7324	0.0251	0.1470	10.8969	0.0022	0.0041	0.0058	0.0120	0.0011	29.1254	70.8746
	19	0.0035	3.3484	12.4400	1.6658	0.0244	0.1483	10.9864	0.0027	0.0042	0.0059	0.0116	0.0011	28.6423	71.3577
	20	0.0036	3.4733	13.1178	1.7449	0.0258	0.1401	11.0905	0.0025	0.0041	0.0060	0.0119	0.0011	29.6216	70.3784
	21	0.0035	3.3308	12.9625	1.7677	0.0254	0.1524	10.6671	0.0024	0.0041	0.0062	0.0120	0.0011	28.9352	71.0648
	22	0.0037	3.4661	13.1077	1.7502	0.0256	0.1549	10.9077	0.0021	0.0042	0.0060	0.0118	0.0011	29.4411	70.5589
	23	0.0036	3.5116	12.7894	1.7014	0.0258	0.1477	10.7151	0.0027	0.0044	0.0059	0.0116	0.0011	28.9203	71.0797
	24	0.0037	3.2111	12.2871	1.6767	0.0246	0.1453	10.7603	0.0027	0.0042	0.0059	0.0122	0.0012	28.1350	71.8650
	25	0.0036	3.4499	12.9598	1.7443	0.0255	0.1410	11.4245	0.0026	0.0041	0.0062	0.0120	0.0012	29.7747	70.2253
Sludge storage 2	1	0.0036	3.3840	12.4170	1.7194	0.0251	0.1514	11.1169	0.0025	0.0042	0.0062	0.0122	0.0011	28.8436	71.1564
	2	0.0036	3.3903	12.6072	1.7184	0.0249	0.1608	11.0388	0.0020	0.0042	0.0063	0.0122	0.0012	28.9699	71.0301
	3	0.0036	3.3898	12.6720	1.7188	0.0249	0.1517	11.0591	0.0021	0.0041	0.0063	0.0122	0.0011	29.0457	70.9543
	4	0.0036	3.3881	12.6440	1.7196	0.0250	0.1498	11.0706	0.0022	0.0041	0.0063	0.0122	0.0011	29.0266	70.9734
	5	0.0036	3.3832	12.8624	1.7192	0.0250	0.1556	11.0597	0.0021	0.0042	0.0062	0.0122	0.0012	29.2344	70.7656
	6	0.0036	3.3796	12.9794	1.7182	0.0248	0.1567	11.0033	0.0018	0.0042	0.0062	0.0122	0.0011	29.2911	70.7089
	7	0.0036	3.2929	12.2134	1.7755	0.0248	0.1514	10.6795	0.0025	0.0043	0.0060	0.0119	0.0012	28.1670	71.8330
	8	0.0037	3.3540	12.7576	1.7557	0.0257	0.1656	10.7554	0.0021	0.0043	0.0060	0.0125	0.0012	28.8438	71.1562
	9	0.0035	3.4565	12.9939	1.7257	0.0246	0.1511	10.9671	0.0020	0.0041	0.0062	0.0126	0.0010	29.3483	70.6517
	10	0.0036	3.4185	12.7404	1.6921	0.0248	0.1474	11.4102	0.0021	0.0042	0.0064	0.0123	0.0011	29.4631	70.5369
	11	0.0035	3.3854	12.6869	1.7416	0.0248	0.1492	10.7538	0.0021	0.0040	0.0060	0.0122	0.0012	28.7707	71.2293
	12	0.0036	3.3774	12.9589	1.7171	0.0249	0.1587	10.6724	0.0018	0.0043	0.0064	0.0123	0.0011	28.9389	71.0611
	13	0.0036	3.3524	12.8225	1.6792	0.0251	0.1465	11.0468	0.0026	0.0040	0.0063	0.0122	0.0012	29.1024	70.8976
	14	0.0035	3.2817	12.2250	1.7442	0.0242	0.1640	10.9174	0.0020	0.0044	0.0064	0.0124	0.0012	28.3864	71.6136
	15	0.0037	3.4859	12.8444	1.7738	0.0256	0.1516	10.9856	0.0021	0.0040	0.0065	0.0123	0.0011	29.2966	70.7034

	16	0.0035	3.3835	12.3070	1.6657	0.0253	0.1475	11.0597	0.0022	0.0041	0.0063	0.0121	0.0012	28.6181	71.3819
	17	0.0037	3.3336	12.9020	1.7272	0.0250	0.1591	11.4431	0.0020	0.0041	0.0061	0.0123	0.0011	29.6193	70.3807
	18	0.0035	3.3063	12.6496	1.6575	0.0251	0.1515	11.2661	0.0018	0.0040	0.0061	0.0122	0.0011	29.0848	70.9152
	19	0.0036	3.3202	12.6927	1.7213	0.0249	0.1621	10.8768	0.0021	0.0043	0.0062	0.0118	0.0012	28.8272	71.1728
	20	0.0037	3.4973	12.6010	1.6369	0.0241	0.1481	10.8231	0.0021	0.0040	0.0064	0.0120	0.0011	28.7598	71.2402
	21	0.0035	3.3925	13.1455	1.7058	0.0247	0.1487	10.9303	0.0021	0.0041	0.0062	0.0124	0.0011	29.3769	70.6231
	22	0.0037	3.4000	12.8411	1.7714	0.0247	0.1643	11.0005	0.0021	0.0042	0.0061	0.0121	0.0011	29.2313	70.7687
	23	0.0036	3.4460	13.1129	1.7331	0.0248	0.1548	10.8785	0.0017	0.0042	0.0063	0.0124	0.0011	29.3794	70.6206
	24	0.0035	3.2644	12.4618	1.7618	0.0249	0.1498	11.0763	0.0026	0.0043	0.0060	0.0124	0.0011	28.7689	71.2311
	25	0.0036	3.3486	12.8759	1.6909	0.0252	0.1581	10.9358	0.0020	0.0042	0.0064	0.0122	0.0012	29.0641	70.9359
Sludge storage 3	1	0.0036	3.3900	12.5996	1.7184	0.0249	0.1647	11.0379	0.0019	0.0042	0.0063	0.0122	0.0010	28.9647	71.0353
	2	0.0036	3.3927	12.5252	1.7188	0.0250	0.1577	11.0787	0.0022	0.0042	0.0061	0.0122	0.0011	28.9275	71.0725
	3	0.0036	3.3864	12.6858	1.7180	0.0249	0.1645	11.0241	0.0018	0.0041	0.0062	0.0122	0.0011	29.0327	70.9673
	4	0.0036	3.3865	12.6564	1.7184	0.0249	0.1625	11.0355	0.0019	0.0041	0.0062	0.0122	0.0011	29.0131	70.9869
	5	0.0036	3.3880	12.6667	1.7180	0.0249	0.1620	11.0333	0.0019	0.0042	0.0062	0.0122	0.0011	29.0221	70.9779
	6	0.0036	3.3907	12.8112	1.7182	0.0249	0.1634	11.0046	0.0017	0.0041	0.0062	0.0122	0.0011	29.1418	70.8582
	7	0.0036	3.3560	12.6694	1.7321	0.0245	0.1616	10.8649	0.0019	0.0041	0.0064	0.0122	0.0010	28.8377	71.1623
	8	0.0037	3.3292	12.1873	1.7400	0.0256	0.1574	10.7500	0.0021	0.0042	0.0063	0.0127	0.0011	28.2196	71.7804
	9	0.0036	3.4518	12.5423	1.7002	0.0261	0.1656	11.1453	0.0017	0.0041	0.0063	0.0128	0.0010	29.0608	70.9392
	10	0.0036	3.4619	12.5258	1.6674	0.0246	0.1620	11.0540	0.0019	0.0041	0.0063	0.0120	0.0011	28.9247	71.0753
	11	0.0036	3.4818	12.5303	1.6871	0.0249	0.1666	10.9670	0.0019	0.0042	0.0063	0.0122	0.0011	28.8870	71.1130
	12	0.0037	3.2913	13.2300	1.7268	0.0260	0.1655	10.9607	0.0016	0.0040	0.0061	0.0126	0.0011	29.4294	70.5706
	13	0.0036	3.3595	12.0246	1.6868	0.0250	0.1719	11.1556	0.0020	0.0042	0.0064	0.0126	0.0010	28.4532	71.5468
	14	0.0036	3.3734	12.6762	1.7130	0.0245	0.1636	11.0012	0.0022	0.0043	0.0061	0.0120	0.0011	28.9812	71.0188
	15	0.0036	3.3399	12.8672	1.7077	0.0246	0.1697	11.1782	0.0018	0.0040	0.0062	0.0118	0.0010	29.3157	70.6843
	16	0.0036	3.3516	13.1411	1.7676	0.0248	0.1595	10.8769	0.0019	0.0040	0.0063	0.0122	0.0011	29.3506	70.6494
	17	0.0037	3.5032	12.4046	1.7741	0.0253	0.1635	11.3533	0.0019	0.0043	0.0064	0.0122	0.0011	29.2536	70.7464
	18	0.0036	3.4970	12.6505	1.7279	0.0248	0.1669	10.9054	0.0017	0.0042	0.0062	0.0123	0.0011	29.0016	70.9984
	19	0.0038	3.3787	13.1749	1.7687	0.0241	0.1624	10.7435	0.0019	0.0041	0.0061	0.0122	0.0011	29.2815	70.7185
	20	0.0035	3.3081	12.1625	1.6804	0.0254	0.1628	11.3151	0.0022	0.0041	0.0064	0.0125	0.0010	28.6840	71.3160
	21	0.0038	3.4777	12.8466	1.6642	0.0251	0.1722	10.9543	0.0018	0.0042	0.0061	0.0126	0.0011	29.1697	70.8303
	22	0.0035	3.4848	13.2009	1.6926	0.0247	0.1653	11.4953	0.0020	0.0041	0.0063	0.0122	0.0011	30.0928	69.9072
	23	0.0037	3.3541	12.5731	1.7106	0.0242	0.1615	11.0481	0.0020	0.0042	0.0061	0.0121	0.0010	28.9007	71.0993
	24	0.0037	3.5140	13.1314	1.7056	0.0250	0.1700	10.6562	0.0017	0.0039	0.0062	0.0121	0.0010	29.2308	70.7692
	25	0.0037	3.2355	12.3618	1.7182	0.0255	0.1557	11.3778	0.0022	0.0043	0.0062	0.0124	0.0011	28.9044	71.0956
	18	0.0035	3.1950	10.3606	1.7522	0.0250	0.1517	11.9193	0.0046	0.0048	0.0056	0.0118	0.0014	27.4355	72.5645
	19	0.0036	3.2883	10.3547	1.6456	0.0247	0.1507	11.5946	0.0048	0.0044	0.0056	0.0121	0.0015	27.0906	72.9094
	20	0.0038	3.3894	10.4809	1.7291	0.0245	0.1464	11.3556	0.0051	0.0046	0.0053	0.0116	0.0015	27.1578	72.8422
	21	0.0036	3.3557	9.9562	1.6617	0.0255	0.1439	11.1986	0.0051	0.0046	0.0057	0.0119	0.0015	26.3740	73.6260
	22	0.0037	3.4117	10.6319	1.6891	0.0254	0.1451	10.9135	0.0048	0.0045	0.0055	0.0117	0.0015	26.8484	73.1516
	23	0.0035	3.3755	10.1264	1.6944	0.0250	0.1454	11.4459	0.0047	0.0045	0.0056	0.0115	0.0016	26.8440	73.1560
	24	0.0037	3.4311	10.2104	1.7652	0.0248	0.1505	11.5466	0.0049	0.0047	0.0054	0.0118	0.0016	27.1607	72.8393
	25	0.0037	3.3868	9.8235	1.7150	0.0248	0.1483	11.4849	0.0050	0.0046	0.0052	0.0117	0.0016	26.6151	73.3849
Max		0.0038	3.5140	13.2300	1.7755	0.0261	0.1722	11.5460	0.0049	0.0048	0.0065	0.0128	0.0017	-	-
Min		0.0035	3.2111	10.2082	1.6369	0.0241	0.1401	10.6562	0.0016	0.0039	0.0055	0.0113	0.0010	-	-
Average		0.0036	3.3808	12.6516	1.7186	0.0250	0.1551	11.0517	0.0022	0.0042	0.0062	0.0122	0.0011	-	-

According to the value of the average gross content, the studied elements were arranged in the following descending order: Ca > Fe > K > Ti > Mn > V > Zn > Cu > Ni > Cl > Co > Pb.

The coefficient of variation of the average gross contents of the studied elements ranged from 1.69 wt. % (Ti) to 24.19 wt. % (Co). That points to the high degree of uniformity of the accumulated waste. That is because the origin of the technogenic material is the stable production process – obtaining the alumina.

A complect of maps was created to demonstrate the distribution character of detected elements (Fig. 3-5).

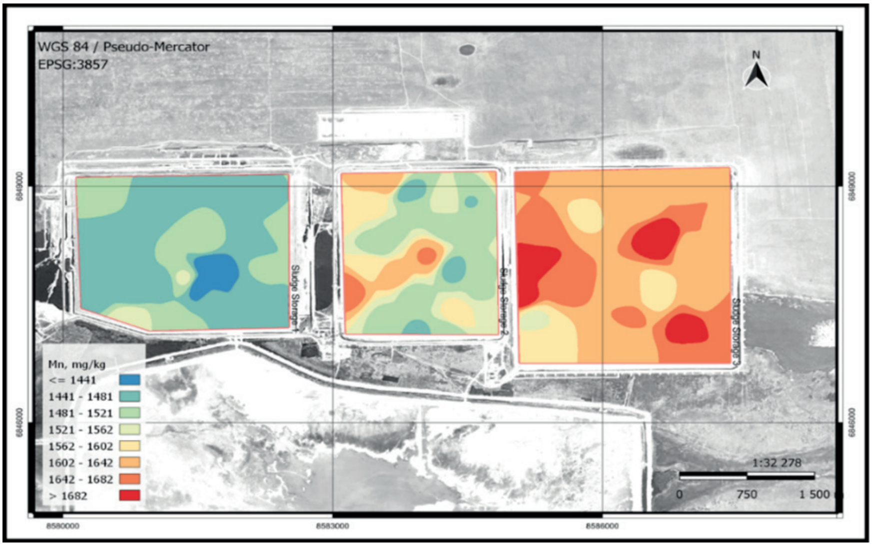

Figure 3. Spatial distribution of Mn on the sludge storages of PAP. Coordinate system: WGS 84 : Pseudo-Mercator EPSG:3857, satellite map: ESRI Satellite (ArcGIS/World_Imagery), scale: 1:32 278, method of interpolation: QGIS IDW, distance coefficient = 5.0, pixel size = 1.0

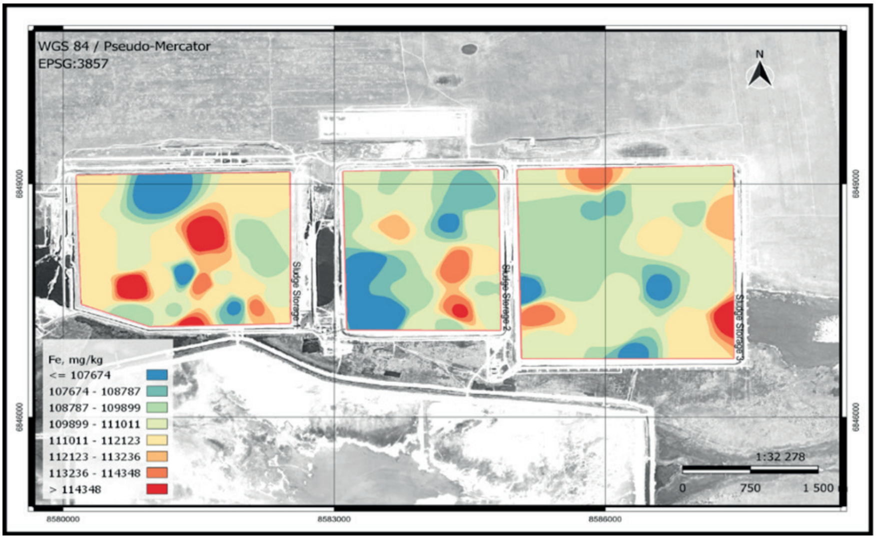

Figure 4. Spatial distribution of Fe on the sludge storages of PAP. Coordinate system: WGS 84 : Pseudo-Mercator EPSG:3857, satellite map: ESRI Satellite (ArcGIS/World_Imagery), scale: 1:32 278, method of interpolation: QGIS IDW, distance coefficient = 5.0, pixel size = 1.0

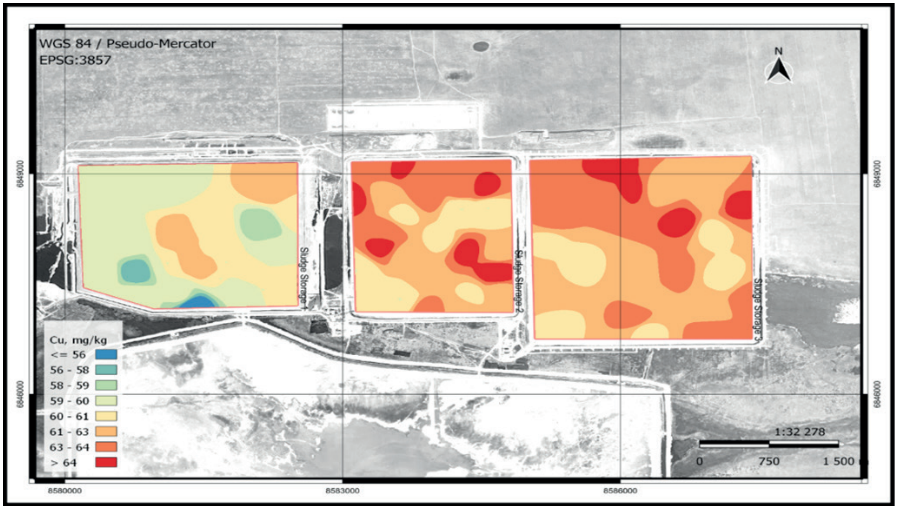

Figure 5. Spatial distribution of Cu on the sludge storages of PAP. Coordinate system: WGS 84: Pseudo-Mercator EPSG:3857, satellite map: ESRI Satellite (ArcGIS/World_Imagery), scale: 1:32 278, method of interpolation: QGIS IDW, distance coefficient = 5.0, pixel size = 1.0

Environmental assessment. The environmental effects were assessed by calculation of total pollution coefficients Zc (Allayarova et al., 2021; Linnik et al., 2020; Sivukhin et al., 2020; Solodukhina et al., 2021), both the average value and the value of Zc in every studied point. The last allows us to create a map of spatial Zc distribution. As well comparing with the levels of maximum permissible concentrations (MPC, mg/kg) in the ground has been carried out.

Analysis in comparison with MPC (Table 4) showed that all waste samples exceed the declared Kazakhstan levels of MPC based on the heavy metal contents.

Table 4 – Assessment of gross content of heavy metals in waste samples regarding MPC (n = 75).

Metal	Average gross content, wt.%	Average gross content, mg/kg	Range of gross content (Lim), mg/kg	Variation Coefficient, %	MPC, mg/kg	Average HQ	Share of samples where HQ > 1, %
Ca	12.053651	120536.51	102082 - 132300	3.8	-	-	-
Fe	11.147945	111479.45	106562 - 115460	1.93	-	-	-
K	3.37518	33751.8	32111 - 35140	1.96	-	-	-
Ti	1.718264	17182.64	16369 - 17755	1.69	-	-	-
Mn	0.153094	1530.94	1401 - 1722	5.34	1500	1.02	58.7
V	0.025012	250.12	241 - 261	1.71	150	1.67	100

Zn	0.012079	120.79	113 - 128	2.22	23	5.25	100
Cu	0.006005	60.05	55 - 65	2.92	33	1.82	100
Ni	0.004285	42.85	39 - 48	3.3	4	10.71	100
Cl	0.003602	36.02	35 - 38	1.99	-	-	-
Co	0.00291	29.1	16 - 49	24.19	5	5.82	100
Pb	0.001224	12.24	10 - 17	9.36	32	0.38	0

The excess value was expressed by hazard quotients (HQ) (Ikhajiagbe & Ogwu, 2020; Pokorska-Niewiada et al., 2022; Pongpiachan et al., 2018), where HQ = actual gross content (mg/kg) / MPC (mg/kg). The HQ levels were very high and achieve 10.71 in the case of nickel. In the case of lead, the MPC level was not exceeded, the content of Mn exceeded the MPC in 58.7% of studied samples, and the content of other heavy metals, excluding Pb, was over the MPC level in 100% of samples.

The level of technogenesis can be assessed by comparing with indices of the normal content of elements in the ground like MPC by Kloke, Clarke in the soil, and Clarke in the lithosphere (Table 5). In the ground samples, the V content exceeds the MPC by Kloke by 5 times, soil Clarke by 2.38 times, and lithosphere Clarke by 2.78 times. The Fe content exceeds soil Clarke by 5 times, and lithosphere Clarke by 2.4 times. The Mn content exceeds the soil Clarke by 2.1 times, and lithosphere Clarke by1.53 times.

Table 5 – Values of average gross content of heavy metals in waste samples in comparison with conventional indicators

Metal	Average gross content, mg/kg	MPC by Kloke, mg/kg (Kloke et al., 1984)	Clarke in soil, mg/kg (Alekseenko & Alekseenko, 2013)	Clarke of the earth's crust, mg/kg by P. Vinogradov (1962) (Kasimov & Vlasov, 2015)	Background, mg/kg	Kc
Cu	60.05	100	39	47	17.9	3.35
Fe	111479.45	-	22300	46500	19274	5.78
Zn	120.79	300	158	83	42.4	2.85
Pb	12.24	100	54.5	16	15.7	0.78
Mn	1530.94	-	729	1000	525.8	2.91
V	250.12	50	104.9	90	47.8	5.23
Co	29.1	50	14.1	18	7.2	4.04
Ni	42.85	50	33	58	28.8	1.49

The summary indicator of pollution (Zc) is calculated it is the sum of excess coefficients of concentrations of chemical elements accumulating in technogenic anomalies and is calculated using the formula of the Saeta index (formula 1) (Solodukhina et al., 2021).

$$Z_c = \sum_i Kc_i - (n-1) \qquad (1)$$

where Kc is the concentration coefficient of the substance; n is the number of analyzed contaminant elements with Kc > 1. Kc was calculated using the following formula 2:

$$Kc = \frac{C}{C_0} \qquad (2)$$

where C is the content of the contaminant element at a given point; C_0 is the content of the contaminant element in the background soil. Background samples were taken at 80 km from the object in a pollution-free territory.

In the formulas for geochemical specialization (Kovalev et al., 2017; Parafilov et al., 2020), the numerical index attached to the symbol of the chemical element refers to the multiplicity of the average values of the concentration coefficients (Kc) for the entire set of points included in the contour of the object (Parafilov et al., 2020). The formula for geochemical specialization (Panin, 2002) of ground samples from the sludge storage of PAP is $Fe_{5.78}V_{5.23}Co_{4.04}Cu_{3.35}Mn_{2.91}Zn_{2.85}Ni_{1.49}Pb_{0.78}$. On average, the studied ground is of iron-vanadium geochemical specialization.

The assessment of the potential level of danger of soil contamination by a complex of pollutant elements was carried out using indicator Zc. For Zc level calculation Kc by metals Cu, Zn, Pb, Mn, V, Co, Ni, and Fe were used.

Gradations of the assessment scale are developed based on the study of indicators of the health status of the population living in the territory with different levels of pollution. The Zc indicator calculated from the average contents of detected metals in the ground from three sludge storages of PAP is 17.43. According to the Criteria for assessing the environmental situation of territories to identify an environmental emergency and environmental disaster zones, the Zc level is lower than 32 and can be considered as a territory with a relatively satisfactory situation. However, the result should be considered correctly with the understanding, that the Zc indicator was calculated by the defined list of elements and the normal parameters of soils (the salt content, the content of organic mass in soil, pH, the content of nutrients, soil humidity, microbial activity) haven't been considered.

The Zc values were calculated for every sample to create the 3D maps of Zc distribution on the studied territories (Fig. 2). The analysis of the distribution of geochemical indicators, obtained from the results of ground sampling, gives the spatial structure of pollution.

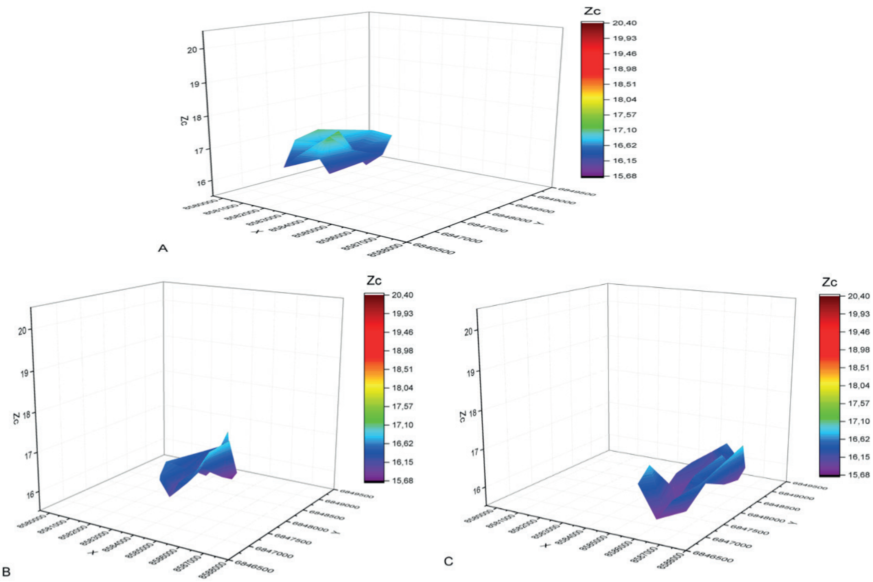

Figure 6. 3D spatial distribution of Zc levels on the sludge storages of PAP. A – Sludge storage 1, B – Sludge storage 2, C- Sludge storage 3. Coordinate system: WGS 84 : Pseudo-Mercator EPSG:3857

As well Zc spatial data were overlapped as a layer on the map using GIS technologies. Data visualization was performed using interpolation by inverse distance weighting (IDW) in QGIS Software (v. 3.24.2-Tisler). The radius of influence of each of the starting points on the interpolated variable is determined by the value of "weights" (Fig. 7).

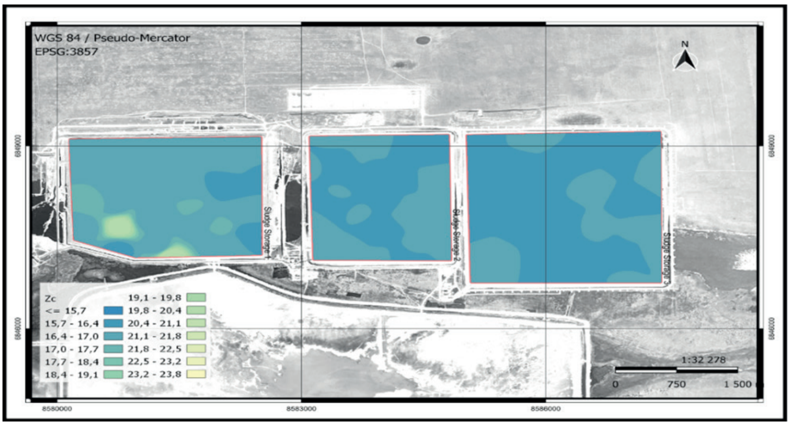

Figure 7. 2D spatial distribution of Zc levels on the sludge storages of PAP. Coordinate system: WGS 84 : Pseudo-Mercator EPSG:3857, satellite map: ESRI Satellite (ArcGIS/World_ Imagery), scale: 1:32 278, method of interpolation: QGIS IDW, distance coefficient = 5.0, pixel size = 1.0

When analyzing the spatial distribution of metals it is required to consider variation coefficients to assess the degree of uniformity in the dissemination of elements (Suleimenov et al., 2017; J. Zhang & Shi, 2010). Variation coefficient allows us to compare the uniformity of the values even with different scales of data. Variation coefficient (%) is calculated by the formula 3 (J. Zhang & Shi, 2010):

$$c = D \cdot 100 / \overline{x} \qquad (3)$$

where D - standard deviation, $\overline{x}$ - the medium value.

In statistics, it is accepted that if the value of the coefficient of variation is less than 33%, then the set is considered uniform, else it is random (33-64%) or cluster distributed (>64%) (Li et al., 2014). In general, the coefficient of variation is used to estimate the relative spread of the data in the sample. So, the colors on the maps represent the relative concentration dispersion divided into eight equal classes. The classifications for each element are shown in the corresponding maps.

The analysis showed the value of the variation coefficient for the Zc index was 4.4%, which indicates high uniformity of the index. The result can be explained by the technogenic character of the genesis of the studied ground. The waste is produced by a steady production process for many years.

Technogenic resource assessment. Knowing the elemental content, it is possible to calculate the storage ability of valuable raw materials as a secondary field. First, the total weight of waste deposited in the storage must be calculated. The total weight could not be calculated quite precisely, which is why we used the approximated value. The approximate total weight was calculated using the following formula 4:

$$m = \rho \cdot V \qquad (4)$$

where ρ - bulk density (kg/m^3), V – volume (m^3).

The storage is an industrial facility that is an embankment with an approximate form of a truncated pyramid. Thus, a truncated pyramid-shaped model of the storage geometry was used to calculate the volume of waste deposited in the studied storage. The volume of the truncated pyramid was calculated by the formula 5:

$$V = 1/3 \cdot h \cdot (S_{top} + S_{base} + \sqrt{S_{top} \cdot S_{base}}) \qquad (5)$$

where h – the height of the figure (m), S_{top} – the area of the top trapezoid, S_{base} – the area of the pyramid basement. The truncated pyramid parameters are shown in Table 6.

Table 6 – Geometry parameters of studied storage for calculation of waste volume

Storage	Height, m	S_{top}, sq.m.	S_{base}, sq.m.	Volume, cub.m.
Sludge storage 1	17	2 469 670.00	3 058 282.00	46 898 549.39
Sludge storage 2	17	1 686 727.00	2 367 446.00	34 297 392.65
Sludge storage 3	15	3 413 748.00	3 778 864.00	53 921 407.24
Total				135 117 349.28

The sum of obtained volumes gives the total volume of the waste mass deposited in the storage. The obtained volume was 135 117 349.28 m^3. The average bulk density of the samples from the studied sludge storage was 1.01236 g/cm^3 or 1 012.36 kg/m^3. Thus, the total mass of the deposited waste is 135 117 349.28 · 1 012.36 = 136 787 399 717.1 kg or 136 787 399.7171 ton.

Using the data on the elemental content the approximate deposit of every detected element (in the elemental state) was calculated (Table 7). Thus, we can see that storage has great economical potential. Studying technogenic objects can be considered a secondary field for the production of various technological products like additives to building mixes, catalysts, additives for steel production, and valuable metals that can be extracted as metal concentrate.

Table 7 – Assessment of gross content of heavy metals in waste samples regarding maximum permissible concentrations (MPC) (n = 75)

Metal	Average gross content, wt.%	Approximate content in the sludge storage, tons	Prices of metals, USD/t on 11.08.2022	Approximate cost of the deposit, USD
Ca	12.053651	16 487 875.77	-	-
Fe	11.147945	15 248 984.09	395.00 (metallicheckiy-portal.ru, n.d.)	6 023 348 715.55
K	3.37518	4 616 820.96	-	-
Ti	1.718264	2 350 368.65	-	-
Mn	0.153094	209 413.3 Corresponds to 329 078 t. of MnO_2	1 440 000.00 (MnO_2) (Alerts, n.d.)	473 872 320 000.00
V	0.025012	34 213.26 Corresponds to 61 047.19 t. of V_2O_5	16 314.19 (V_2O_5) (vanadiumprice.com, n.d.)	995 935 456.63
Zn	0.012079	16 522.55	3 575.00 (metallicheckiy-portal.ru, n.d.)	59 068 116.25
Cu	0.006005	8 214.08	7 971.00 (metallicheckiy-portal.ru, n.d.)	65 474 431.68
Ni	0.004285	5 861.34	21 350.00 (metallicheckiy-portal.ru, n.d.)	125 139 609.00
Cl	0.003602	4 927.08	-	-

Co	0.00291	3 980.51	48 490.00 (metallicheckiy-portal.ru, n.d.)	193 014 929.90
Pb	0.001224	1 674.28	2 182.00 (metallicheckiy-portal.ru, n.d.)	3 653 278.96
Other	71.496749	97 798 543.84	-	-
Total	100	136 787 399.7171	-	481 337 954 537.97

Conclusion. In this study, the analysis of the elemental content of waste placed on the sludge storages of the Pavlodar aluminum plant (Pavlodar, Kazakhstan) sampled in 75 locations was carried out. The maps of spatial concentration distribution were created for every metal. As well summary indicator of pollution (Zc) was calculated for every point and these data were placed on the map. The environmental assessment was carried out, as well the assessment of the reserve of valuable components presented in the waste was performed. The valuable metals revealed in the waste are Cu, Fe, Zn, Pb, Mn, V, Co, and Ni. The studied ground is characterized as iron-vanadium geochemical specialization.

The studied technogenic objects – sludge storages of Pavlodar aluminum plant are typical products of technogenesis. As technogenic objects, they can negatively affect the environment. The territory taken for the placement of these facilities is alienated. By the level of content of detected elements, the contamination level is relatively satisfactory. However, the investigation can be widened using other more sensible instruments. The proper conditions of storage, using facilities preventing the leaching of pollutants into groundwater, like anti-filtration curtain “wall in the ground”.

It was revealed that the studied waste has great economic potential. Utilization of the waste can bring in approximate calculations up to 481 billion USD. The most valuable components are Mn, which is selling as MnO_2, and Fe. The total cost of iron concluded in the waste can reach up to 6 billion USD.

Thus, the investigation has revealed that the studied technogenic waste can be a valuable origin of raw materials and can be involved in new production cycles. A significant amount of such valuable metals as Mn, Fe, V, Co, and Ni can be used for extracting them as metal concentrates or can be used for direct recycling. This approach leads to finding new ways to modification of production schemes by including new co-productions using the bauxite sludge waste as a raw material. One of the most prospective ways for utilization of the studied type of waste is the production of construction and refractory mixtures, commercial crushed stone and sand, catalysts, and obtaining metal concentrates.

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