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ECOLOGICAL ASPECTS OF REMADIATED POST-MINING AREAS AFTER ZINC AND LEAD EXPLOITATION IN SOUTHERN POLAND

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EKOLOGICZNE ASPEKTY REKULTYWACJI TERENÓW PO EKSPLOATACJI RUD CYNKU I OŁOWIU W POŁUDNIOWEJ POLSCE

Na obszarach eksploatacji rud cynku i ołowiu na Górnym Śląsku w Polsce, najpospolitszym elementem krajobrazu są hałdy górnicze, zwałowiska związane z metalurgią żelaza, cynku i ołowiu oraz osadniki po flotacji rud. Te ostatnie, zlokalizowane są w północnej części województwa katowickiego, na linii Piekary – Bytom – Bukowno – Olkusz i zajmują obszar ok. 350 ha. Powierzchnia jednego osadnika waha się od 15 do 40 ha. Osadniki w znacznym stopniu deformują krajobraz. Ich głównym materiałem jest drobnoziarnisty dolomit. Osady zawierają maksymalnie do 8,0% Zn, 1,5% Pb i zwykle powyżej 100 mg/kg Cd. Pomimo ich wysokiego zasolenia i wysokich zawartości Zn, Pb i Cd, osadniki te mogą być rekultywowane metodą bezglebową. Ich rekultywacja wpływa na zahamowanie erozji wodnej i wietrznej. Dla celów rekultywacji biologicznej wykorzystano kilka mieszanek traw, jak również wiele gatunków drzew i krzewów. Jednakże prawie trzydziestoletnie doświadczenia potwierdziły, że pobór metali ciężkich z podłoża przez trawę, jak również ich akumulacja w ściółce jest znaczna. Niska i wysoka roślinność jest wykorzystywana jako pokarm przez dziką zwierzynę, co powoduje zagrożenie ekologiczne. W celu ograniczenia przedostawania się metali ciężkich, poprzez łańcuch gleba – rośliny – zwierzęta, do otaczającego środowiska, wydaje się konieczne przykrycie osadników innym substratem. Sugeruje się wykorzystanie odpadów z górnictwa węgla kamiennego, zawierających mało metali ciężkich, które są dostępne w regionie w prawie nieograniczonej ilości.

Summary

In area of zinc and lead exploration the most common elements of landscape are mine spoil-heaps and also dumps and settling tanks connected with zinc and lead metallurgy and ore flotation. They are located in the northern part of Katowice Province, on a line Piekary – Bytom – Bukowno – Olkusz and cover area of about 350 hectares. The individual settling tank in this area is between 15 and 40 hectares and considerably deforming landscape. A fine-grained dolomite is main material of tank sediments. The sediment contains maximally up to 8.0% of Zn, 1.5% of Pb and Cd in content usually over 100 mg/kg. In spite of high salinity and high Zn, Pb and Cd content the settling tanks can be soil-less reclamated but the first stage of the reclamation should be trying to stop weathering and erosion processes. For the soil-less reclamation some grass mixtures as well as many tree and shrub species have been used. However, almost 30 years of study proved that heavy metal uptake from a substratum into grass as well as into leaf litter is considerably high. Low- and high-growing vegetation is used as food by wild animals, what causes an ecological hazard. Considering this, the settling tanks must be covered by another material. The most suitable seems to be mining waster stored in a large amount in the same area.

INTRODUCTION

Two kinds of zinc and lead ores occur in Poland. A hydrothermal ores are very poor in metal. They were explored in Lower Silesia (Miedzianka, Bogoszów, and Srebrna Góra) and in Kielce area (Karczówka). In the area of Upper Silesia occur metal-rich metasomatic ores connected with Triassic dolomites. This kind of Zn and Pb ores is of great economic importance in Poland. They are explored in Bytom area (Orzeł Biały Mine), in Olkusz area (Olkusz and Pomorzany Mines) and in Chrzanów area (Trzebionka Mine). About 5 millions Mg of Pb and Zn ores is produced annually. The ores occur in carbonate and sulphide forms. For technological reasons only sulphide ores are economically used. To increase the metal content the ores are subjected to flotation process. As a by-product of such process a large amount of waste material is produced. This material is stored in so-called after flotation settling tanks, located in areas of ore exploration. In Katowice Province the area covered by the settling tanks exceeds 350 hectares. The other kind of waste materials are rocks from the roof and bottom of a bed. The waste rock material is stored in dumps containing mostly dolomites with a stony grain-size fraction. The dumps of carbonate material in Katowice Province cover about 150 hectares of the area of Pb and Zn exploration. The third kind of wastes are variety of sintered products being a result of Zn and Pb metallurgy, which are stored in dumps covering area of about 60 hectares. The first experiments on methods of biological reclamation of after flotation wastes were started in 1972 in Bytom area where 8 settling tanks are located (covering the area of about 15 – 40 hectares) [5, 8]. Their highest over the local ground level is from 4 to 20 m.

MATERIALS AND METHODS

114 samples from 21 pits excavated on a surface of settling tanks were taken. The following analysis were made according to Ostrowska et al. [6]:

- Grain-size composition on a base of Casagrande method with Proszynski modification;
- Specific and spatial density;
- Actual humidity and hygroscopic water content;
- Calcination loss (in 550°C);
- Carbonate content (Scheibler method);
- Phosphorous and potassium content (Egner method);
- Total nitrogen (Kjedahl method);
- pH in H_2O and 1 n KCl (potentiometric method);
- Water extracts 1:5 (Gedroic method);
- Heavy metal content in water extract 0.1 n HCl and 60% $HClO_4$ (AAS – 1100 Perkin Elmer).

In 1972 the following tree species were introduced into the same part of settling tanks: birch (*Betula verruscosa L.*), maple (*Acer platanoides L.*), red oak (*Quercus rubra L.*), common oak (*Quercus robur L.*), linden (*Tilia cordata Mill.*), alder (*Alnus glutinosa (L) Gaertn.*), robinia (*Robinia pseudoacacia L.*), pine (*Pinus sylvestris L.*) and larch (*Larix eurolepis Henry*). The tree seedlings were introduced directly into sediment without any agrochemical measures improving the substratum. In 1978–1979 a possibility of some grass mixtures introduction on settling tanks was studied [7]. From 4 tested grass mixtures only one was chosen to be sown on settling tanks. The composition of the grass mixture was as follows: darnel, fescue and bent grass. In 1989 the following poplar cuttings were introduced on settling tanks: Hybrid-275, Hybrid-194, Italica-214, Robusta, Serotina. The grass mixtures and poplar cuttings were fertilised using different doses of nitrogen, phosphorus and potassium.

In 1994 samples of grass mixtures as well as leaves and needles from tree species mentioned above were collected for determination of heavy metal content. The grass samples were taken in June from 6 places within the area of 1 m^2, located on settling tank surface. Leaves and needles were washed 2 times in distilled water, then dried and dry-combusted in temperature 450°C. Ashes were dissolved in 10% HCl. Each heavy metal was determined using AAS method [6]. The grass was not washed up before treatment. It was combusted after initial drying.

RESULTS AND DISCUSSIONS

The flotation process of broken up ores takes place in water environment. Also the wastes after flotation are transported to settling tank using a hydraulic transport. During the sedimentation in the tank a natural separation of waste material occurs and a grain-size diversification on the surface and in profile can be observed. Many kinds of different sediments, such as sands, loams and clays can be found in uppermost layers of the tank (Tab. 1). The other sediment profiles had a similar granulometry. Such grain-size variety is not facilitation for biological reclamation process. Before the settling tank becomes completely dry in some places a gleying process, which in some cases forms even a gley-horizonts with a thickness about 20 – 40 cm, takes place.

Former studies pointed to many differences between sediments from the settling tanks and natural soils. The specific gravity of sediments is increased because of the presence of ore-minerals. Also a bulk density of sediment from the tank in many cases is higher than that of soil. It is the result of their compaction and can be observed mostly in deeper layers. Porosity of tank sediments also forms an unfavourable air-water condition for reclamation. In spite of the fact that the waste material after flotation has a mechanical composition similar to loams, the porosity is typical of sand [9].

A laminar structure of tank sediments has a great influence on such parameters as momentary porosity and sediment moisture. Values of these parameters suggest that drying out of uppermost layers and great difficulties with capillary rise water from deeper layers can be expected during reclamation. Such structure of wastes causes their wind erodibility in dry periods and water erodibility during rainfall [9].

The studied sediments have mostly alkaline pH. A very significant is the fact that there are small differences between pH values measured in 1 n KCl and in distilled water. It is certainly the result of alkaline reaction and a very small content of particles below 0.002 mm (Tab. 1 and 2).

Table 1. Grain-size composition and pH value

Sample No.	Profile No.	Depth [cm]	Grain-size composition [in %] 1 – 0.1	0.1 – 0.02	<0.02	<0.002	pH H_2O	KCl
79		1–10	65	26	9	3	7.9	7.6
80		15–30	57	39	4	0	7.7	7.4
81	14	45–60	21	76	3	0	7.7	7.4
82		75–100	24	71	5	0	7.9	7.5
83		100–110	13	34	53	0	7.9	7.6
84		0–10	29	47	24	2	8.4	8.0
85		10–20	5	76	19	0	8.0	7.7
86	15	45–60	20	79	1	0	8.0	7.7
87		60–75	10	83	7	0	7.9	7.6
88		90–100	1	34	65	0	7.9	7.5
89		0–10	72	27	1	0	7.9	7.5
90		15–30	10	58	32	0	7.9	7.7
91	16	30–45	9	57	34	0	8.0	7.6
92		60–75	7	44	49	0	8.0	7.7
93		100–110	68	26	6	0	7.9	7.5

Table 2. Carbonate content, calcination losses and chemical composition of water extracts

Sample No.	$CaCO_3$ [%]	Calcination loses [%]	Water extract 1:5 [μS cm^{-1}]	Na (mg/100 g)	K	Ca	Mg	Cl	SO_4	HCO_3
79	81.02	2.28	1808	5.2	0.7	92.0	31.4	9.1	302.9	18.3
80	85.07	2.30	1322	6.3	0.5	165.8	53.1	9.1	581.7	18.3
81	93.98	2.06	1776	7.4	0.7	256.0	38.0	9.1	771.8	18.9
82	76.97	2.50	1712	7.0	0.7	234.4	66.5	11.8	819.3	18.9
83	78.99	3.13	1871	3.8	1.4	268.0	52.7	9.1	895.6	28.1
84	90.05	1.83	454	1.0	0.8	21.6	77.4	9.1	353.2	27.4
85	88.40	3.35	1966	4.6	1.5	304.0	18.2	6.4	713.1	36.6
86	87.58	2.77	1903	4.5	1.2	310.4	32.4	9.1	891.7	28.9
87	80.18	2.42	1934	5.3	1.9	316.0	26.8	9.1	817.5	42.7
88	83.47	3.49	1776	3.8	1.7	249.6	36.8	9.1	683.5	33.5
89	87.17	2.08	627	0.6	0.2	9.6	75.7	1.0	264.2	26.8
90	79.36	3.18	1776	4.1	0.9	256.0	15.2	10.0	818.8	36.6
91	78.95	2.43	1776	4.4	1.0	260.0	26.4	13.6	705.1	36.6
92	76.09	2.95	1649	6.3	1.4	224.0	65.5	20.0	736.8	39.6
93	83.88	2.37	1039	2.9	0.4	75.2	47.4	10.9	293.6	28.1

In some cases considerable differences in calcination losses have been noticed. They are not connected with a high organic matter content but they are due to gypsum and iron oxides presence in different hydration state. The studies confirmed also the high carbonate content, which is also unfavourable for biological reclamation, especially taking into consideration a grain-size of waste sediments. What is worse, most parts of carbonates are dolomites, which weather more slowly than calcium carbonate.

Determination of phytoavailable P and K forms in a presence of considerable amount of carbonates using the Egner method gives only approximate results. However, carbonate sediments are rather poor in available forms of potassium compounds, but they contain more P, also in hardly available form, which is not extractable in Egner extract.

The waste sediment contains a considerable amount of mineral salts (Tab. 2). In some sediment samples a relatively high value of electrolytic conductivity (2000 μS cm^{-1}) was measured. Among the salts the most common is gypsum ($CaSO_4.2H_2O$) which is non-toxic. The presence of gypsum was confirmed by dependence of increase of electrolytic conductivity on time of water contact of the sediment. The conductivity increases after a longer water contact. The concentration of mineral salts in sediments was probably a result of using waste mine waters for hydraulic transport. The mine waters with of different mineralization have an increased content of sodium, magnesium, chlorides and sulphates. Sodium chloride (NaCl), which is present in mine waters, is probably easily leached out from sediment because it was not noticed in tank sediment.

Considering a specificity of investigated waste sediment and possibility of their toxic influence on revegetation three forms of heavy metal occurring were found. The total content of heavy metals, determined on the basis of their solubility in 60% $HClO_4$ is very high. Zinc content exceeds 8% and Pb content is already 1% (Tab. 3). A relationship between heavy metal content and a depth of layer sediment was not determined. However, a tendency towards concentration of heavy metals in sediments, which contain much coarser fraction was observed. It refers especially to total Zn and Zn soluble in 0.1 n HCl. An average Zn content in main types of sediment depends on their grain-size (Tab. 4).

Table 3. Heavy metal content

Samples No.	Depth [cm]	Horizon	60% $HClO_4$			Water extract 1:5		
			Zn	Pb	Cd	Zn	Pb	Cd
			mg/kg					
79	1–10	C	32300	4690	127	2.0	1.0	0.20
80	15–30	C	38700	6110	196	5.5	2.8	0.25
81	45–60	C	28400	3250	101	6.5	0.9	0.20
82	75–100	C	26000	3980	106	1.5	1.0	0.10
83	100–110	Gyr	31500	4310	93	25.5	0.0	0.60
84	0–10	C	29600	4110	130	0.0	1.6	0.10
85	10–20	C	30800	4350	135	5.0	2.1	0.15
86	45–60	C	24000	3600	98	3.5	0.0	0.08
87	60–75	C	30200	3040	88	4.0	0.0	0.09
88	90–100	Gyr	85800	3840	255	30.5	2.3	0.85
89	0–10	C	26800	2420	116	1.5	0.0	0.05
90	15–30	C	25600	2830	119	3.0	0.0	0.07
91	30–45	C	24800	2960	121	4.5	0.0	0.10
92	60–75	C	16700	3370	107	7.0	0.0	0.12
93	100–110	Gyr	14100	3060	100	14.2	0.8	0.25

These data suggest decrease of total Zn and Zn soluble in 0.1 n HCl together with increase of shore of loamy fraction in sediments, whereas increase of sandy fraction in loams increases the total Zn content and content of Zn soluble in 0.1 n HCl. The relationship is not so clear for other heavy metals. This effect is probably caused by imperfection of technological process which aims at metal recovery from Zn and Pb

Table 4. An average Zn content in main types of sediment distinguished in waste material

Fraction	Zn total (mg/kg)	Zn soluble in 0.1 n HCl (mg/kg)
loose sand	39 500	4 230
dusty loose sand	26 070	3 900
loamy light dusty sand	23 530	4 500
common sandy loams	29 630	4 310
common loams	19 370	3 790

ores. A comparison of content of such heavy metals as Zn, Pb and Cd in waste sediments that values defined as a "tolerated in arable soils" are exceeded several times. For the biological reclamation important is comparison of some heavy metals soluble in water, which are present in waste sediments with content of the same metals in natural soils. These values should not be higher than 0.1 ppm for Zn, 0.0 for Pb and 0.00 for Cd [3]. The concentrations found in waste sediments are considerably higher but it does not mean that they must be phytotoxic. The amount of Zn soluble in water, defined as toxic is between 72 and 130 ppm [4]. It was also confirmed by study of sewage sludge rich in heavy metals. A chlorosis effect was observed in plants growing on sewage sludge only when the content of Zn soluble in HCl exceeded 600–1000 ppm. These values are lower than those noticed in waste sediments. Such concentration of heavy metals certainly causes metabolic disorders in plants revegetated on settling tank, however not to such degree as to stop vegetation at all. It was confirmed by vegetation experiments [5]. This ability is connected with forms of metal occurring in waste sediments. A condition in sediment makes it impossible for a large amount of heavy metals to pass into solution to be toxic for vegetation. Environmental hazard appears only when the increased concentration of heavy metals is observed in low- and high-growing vegetation. The studied samples had inordinate Zn, Pb and Cd concentration. The highest one was observed in all poplar clones and also in birch, oak and robinia that is in pioneer species used for biological reclamation of many industrial wastes. Worth mentioning is a considerable low heavy metal concentration in larch needles and low Pb content in common oak leaves. A cadmium content is increased in all species except of larch needles. The high content of heavy metals was observed in grass mixtures (Tab. 5). Limits of some elements content in forages are given in table 6 [1].

Considering the period of 30 years which has passed from the time of starting revegetation experiment on studied settling tanks and the fact that the area was permanently penetrated by wild animals (roe deers, hares, rabbits, pheasants, partridges), the high concentration of heavy metals in plants causes a permanent ecological hazard. This hazard needs to be eliminated. From the economic and technological (the settling tanks could be explored again in the future) points of view the most sensible seems to be covering of this area by at least 2 m layer of mining wastes and starting again a new biological reclamation. The mining wastes contain a small amount of heavy metals (Tab. 7) and their annual production is about 80–100 millions Mg (0.5 Mg of wastes for 1 Mg of coal).

Table 5. Heavy metals in leaves and needles of tree species and in grass mixtures

Species	Fe	Mn	Zn	Pb	Cd
	mg/kg				
Pop. H 275	100–400	50–150	1150–1950	10–100	2–12
Pop. 194	75–100	50–70	1250–1800	10–90	4–6
Pop. I 214	75–130	60–80	1350–1900	10–50	2–8
Pop. Robusta	75–95	60–90	1300–1750	40–110	2–6
Pop. Serotina	60–105	60–70	1450–2050	70–90	4–12
birch (*Betula verrucosa* L.)	115	70	1250	110	2
maple (*Acer platanoides* L.)	105	20	455	80	2
red oak (*Quercus rubra* L.)	90	20	265	60	2
common oak (*Quercus robur* L.)	70	120	200	10	2
linden (*Til;ia cordata* Mill.)	110	70	185	50	2
alder (*Alnus glutinosa* (L) Gaertn.)	205	90	800	80	2
robinia (*Robinia pseudoacacia* L.)	115	40	550	60	2
pine (*Pinus sylvestris* L.)	210	30	225	70	2
larch (*Larix eurolepis* Henry)	275	80	155	5	0.5
grass mixture	–	91	694	454	19

Table 6. A boundary values of some elements in forages

Element	According to Underwood [1]	According to [1]
As		5
Be		1
Cd	> 0.5 – 1	1
Co	<10 – 50	10
Cr	<10 – 50	20
Cu	< 30 – 100	15
F		30
Fe		500
Hg	1	<1
J		1
Li		50
Mn		1000
Mo		3
Ni	< 50 – 60	100
Pb	> 10 – 30	25
Se	> 4 – 5	3
Sn		100
Tl	> 1 – 5	1
V		<5
Zn	> 500	500

Table 7. An average content of some heavy metals soluble in 10% HNO_3 in mining wastes from Upper Silesian Coal Basin in comparison to boundary values occurring in soils [2]

Rock series	Rock type	Fe	Co	Cr	Mn	Zn	Pb	Cd
limnic	coal shale	1820	1	6	52	22	6	<0.5
	claystone	2340	1	14	88	94	10	<0.5
	mudstone	2040	2	24	82	51	6	<0.5
	sandstone	2400	1	16	95	42	12	<0.5
	siderite	18 000	2	12	500	29	8	0.5
paralic	coal shale	1060	2	8	12	14	2	<0.5
	claystone	6620	2	14	290	21	12	<0.5
	clystone with siderite	9960	1	10	310	22	10	0.8
	mudstone	2080	3	14	155	29	12	<0.5
	sandstone	6980	3	24	1050	34	12	<0.5
soil pollution standard [10]		–	25	75	–	200	50	0.8

CONCLUSIONS

From the study it appears that, in spite of high Zn, Pb and Cd content, the settling tanks could be reclamated using a soil-less method. However, because of environmental criteria, the a tanks surface must be covered by at least 30 cm of soil layer for a low-growing revegetation or 150–200 cm of soil in the case of introducing shrubs and trees. The other waste material with a low content of heavy metals can be also utilised for this purpose. In Upper Silesia there are many kinds of suitable waste materials remaining after hard coal exploration.

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