Original Research

Geochemical and Geophysical Study of Historical Zn-Pb Ore Processing Waste Dump Areas (Southern Poland)

J. Cabala*, B. Zogala**, R. Dubiel***

Faculty of Earth Sciences, University of Silesia, Bedzinska 60, 41-200 Sosnowiec, Poland

Abstract

This paper presents the results of mineralogical, geochemical and geophysical studies of Zn-Pb processing waste dump stored at the turn of the 19th and 20th centuries. The mineral composition of wastes was identified using the XRD method, the contents of Zn, Pb, Fe, Mn, Cd, and Tl were determined using the AAS method, whereas the characteristic features of metalliferous grains were examined using the ESEM method. High geochemical mobility of these metals reduces plant succession and brings about the pollution of the former Zn-Pb ores mine areas. High contents of Zn-Pb-Fe sulfides and unstable, hydrated Pb, Fe, Pb-Fe sulfates result in distinctly raised levels of heavy metals (Zn 121,501 mg kg^{-1}, Pb 208,869 mg kg^{-1}, Cd 477 mg kg^{-1}). Various waste types and surrounding Triassic or Quaternary deposits differ significantly in mineral composition, and consequently in physical properties such as electrical conductivity of top soil horizons. This enabled using geoelectric methods for the purpose of this study, and contouring mine wastes in the polluted areas. The field geophysical survey was carried out with a high-resolution conductivity meter (Geonics EM31-MK2).

Introduction

In Poland, lead and silver ore mining has been carried out since the 12th century in the Silesia-Kraków region (Fig. 1). Since the early 19th century zinc ore has been extracted as well. The regions where shallow Zn-Pb mineral deposits occur have been considerably transformed by mining activity.

The mining and processing wastes have been stored on the surface of numerous sites (Fig. 1). Metal-rich wastes related to historical ore mining and processing, even after several hundred years, are sources of pollutants transported to waters and soils [1, 2].

Biological and geochemical studies have shown that the impact of heavy metals stored in tailings and metallurgical piles on the environment have been considerable [3-5]. Heavy metals affect soils and biota (especially plant roots, microorganisms and meso-fauna). Pb, Zn and Cd concentrations in soils formed in polluted areas are usually very high and consequently jeopardize human and animal health [6]. Due to the reclamation, metalliferous wastes are covered by a soil layer. The remains of past mining activity are obliterated by urban and agricultural development.

Long-lasting hypergenic factors affect the changes of physical and chemical properties of mine wastes [7]. The mineral composition, granulation, shallow occurrence and

*e-mail: jerzy.cabala@us.edu.pl;
** e-mail: bogdan.zogala@us.edu.pl;
*** e-mail: ryszard.dubiel@us.edu.pl

most of all specific physical properties of these wastes enable to apply geophysical methods for pinpointing their locations. The geophysical measurements are an excellent tool for studying mine and processing wastes, detecting the acid mine drainage effects, and contouring the polluted areas. Of the various geophysical methods, the following are commonly applied, including resistivity [8-10], GPR [11-13], magnetic susceptibility measurements [14, 15] and EM [16-18].

The principal objective of our study was to present the mineral composition of historical mine wastes and to determine the possibility for using field EM methods to investigate these wastes, especially to contour the polluted zones.

Material and Methods

Studied Area

The Silesia-Kraków Zn-Pb ores were recognized as Mississippi Valley type ores (MVT) (Fig. 1). Their mineral composition is simple, including sphalerite, galena, wurtzite, pyrite and marcasite [19]. They occur in ore-bearing dolomites of Middle Triassic age.

The study area is situated in the former washing plant "Józef" near Olkusz. The wastes were derived from the Zn-Pb ore washing and flotation (Fig. 2). At the beginning, from 1896 to 1918, oxide ores (supergene type) were processed with a gravity separation method. During 1918 – 1931 most of the wastes resulted from sulfide ore flotation. The Zn-Pb ores were extracted in a shallow supergene type ore mine in Olkusz Stary.

In the middle of the 20th century the total waste reserves in this washing plant area were estimated at 177,000 tons. Metals occurred mostly in oxide minerals such as carbonates, hydroxides and oxides, and sulfates. The average metal contents were high: Zn was 7.82% (13,800 tons), whereas Pb was 1.45% (25,000 tons) [7]. Every year, approximately 7,000 tons of wastes were put in charge in hot processing at Bukowno zinc smelter. At present more than 10,000 tons of wastes are stored in the studied washing plant area. The area of 6 ha is covered by irregular tailing piles. Local depressions are filled with clayey fractions of wastes as a result of erossion and surface flow processes.

Two kinds of wastes, i.e. red and light grey are observed. The light grey wastes are related to the sulfide ore flotation, whereas the red ones are the product of the oxide ore washing process.

Laboratory Study

Mineral composition was determined by the X-ray diffraction (Philips PW 3720 X-ray diffractometer; tube Co kα, 45 KV, 30 mA; impulse counting time 1÷2 seconds at 0.02° increments).

The waste components were determined using the spectral emission analysis (SEA) and atomic absorption spectroscopy (AAS). Heavy metals concentrations in waste or
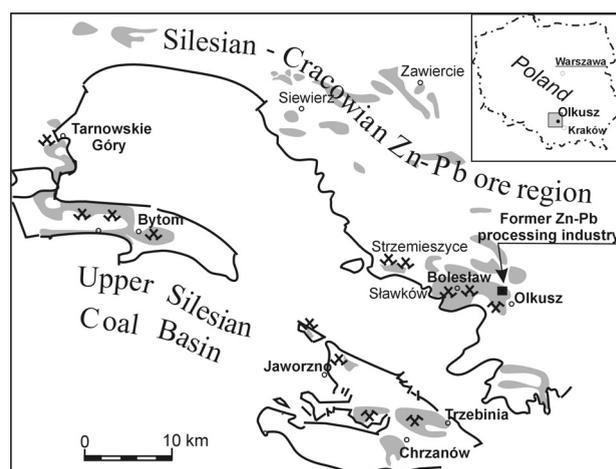

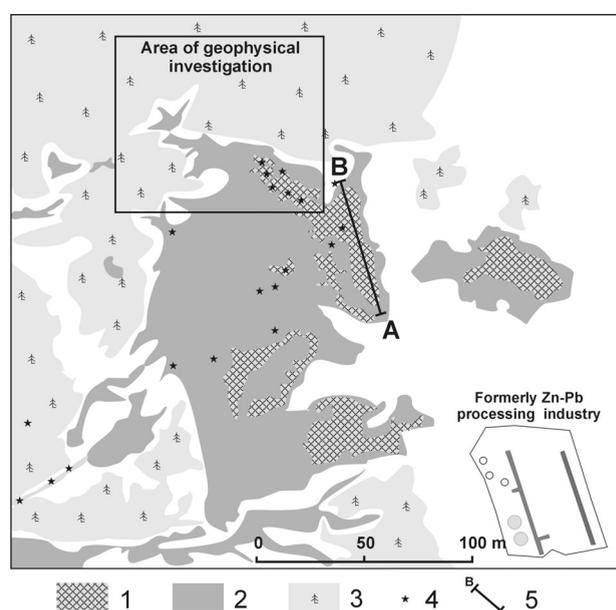Fig. 1. Areas of historical mining in the Silesia-Kraków Zn-Pb ore region.

Fig. 2. Area of historical Zn-Pb washing plant "Józef". Explanation: 1 – light grey waste, 2 – red waste, 3 – woodland (mostly Scots pine stands), 4 – sampling locations, 5 – A-B geophysical profile.

soil samples were measured by atomic absorption spectroscopy (SOLAAR M6). After drying at 110°C, samples (0.2g) were digested in a microwave oven (Milestone MLS 1200 Mega). A mixture of HF, HNO$_3$ and HCl acids was used to mineralize the samples.

The ESEM study was performed with the Environmental Scanning Electron Microscope (Philips XL 30 with EDAX analyzer). Waste or soil particles were attached to the 1 x 1 cm carbon tape and fixed to aluminium stubs. The soil and waste samples were examined using back scattered electrons (Centaurus). The semiquantitative microanalyzes (EDS) of mineral grains were done using the EDAX analyzer (accelerating voltage – 15 kV, environmental mode, H$_2$O pressure – 0.2 torra).

The laboratory analyzes were done at the Faculty of Earth Sciences, University of Silesia.

Table 1. Mineral composition of wastes in the area of historical Zn-Pb ore mining activity. Identification was made with XRD methods.

Type of waste	Primary minerals	Ore minerals	Secondary minerals
(1) light grey waste	quartz SiO_2, kaolinite $Al_2Si_2O_5(OH)_4$, illite $(K,H_3O)(Al,Mg,Fe)_2$ $(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	galena PbS, sphalerite ZnS, pyrite FeS_2, marcasite FeS_2, barite $BaSO_4$	gypsum $Ca(SO_4)\cdot2(H_2O)$, bassanite $Ca(SO_4)\cdot0.5(H_2O)$, anglesite $Pb(SO_4)$, jarosite $KFe^{3+}3(SO_4)_2(OH)_6$, plumbojarosite $PbFe^{3+}6(SO_4)_4(OH)_{12}$,
(2) red waste	ankerite $Ca(Fe^{2+},Mg)(CO_3)_2$, quartz, kaolinite, illite, dolomite $CaMg(CO_3)_2$	sphalerite, galena	goethite $Fe^{3+}O(OH)$, smithsonite $Zn(CO_3)$, cerussite $PbCO_3$, minrecordite $CaZn(CO_3)_2$, plumbojarosite, hemimorphite $Zn_4Si_2O_7(OH)_2\cdot(H_2O)$, gypsum
(3) clayey fraction	dolomite, quartz, kaolinite, feldspar $(Ca,Na)Al_2Si_2O_8$	pyrite, sphalerite, marcasite, galena	gypsum, plumbojarosite hydronium jarosite $(H_3O)Fe_3(SO_4)_2(OH)_6$, minrecordite, goethite, hemimorphite, Mg and Pb chloride, sylvite KCl, srebrodolskite $Ca_2Fe^{3+}_2O_5$

Table 2. Contents of heavy metals in wastes in the area of "Józef" washing plant in Pomorzany [7].

pH (H_2O)	Zn	Pb	Fe	Mn	Cd	Tl
	mg kg^{-1}					
Light grey wastes (1)						
Min-max	2.5-3.9	10315-27814	20352-208869	23363-146909	8-968	44-180	1-513
Average	2.89	17331	119147	72315	163	120	219
SD (σ)	0.46	7355	68210	37812	356	51	158
Red wastes (2)						
Min-max	5.5-5.7	33835-121501	8550-19381	47571-114194	183-781	152-477	5-79
Average	5.66	67763	13420	79962	556	285	35
SD (σ)	0.10	47071	5497	33350	325	171	39
Wastes (clayey fraction) (3)						
Min-max	5.5-5.2	21503-94532	9176-53239	37333-161319	54-416	151-238	38-209
Average	5.1	56769	32193	98737	247	185	126
SD (σ)	0.1	36579	22098	62001	182	47	86

Geophysical Measurements

The electromagnetic induction (EM) measurements with Geonics EM31-MK2 conductivity meter were carried out. The on-site measurements were carried out in the area of 0.6 ha, along parallel profiles situated 5m away from each other with both vertical (VD) and horizontal (HD) measuring dipole orientations. The apparent electrical conductivity was recorded every 0.5 s and the coordinates of each measuring profile were estimated using GPS.

The variations of apparent electrical conductivity to the depth of 3m (HD) and 6m (VD) in the area of 0.6ha were studied. Furthermore, the reference electromagnetic measurements were carried out along a 65m long A-B profile. The results of field measurements were processed statistically and graphically with Oasis Montaj software.

For optimal visualisation, both maps of apparent electrical conductivity are presented in the same standardized colour scale.

Results

Mineralogical Investigation

Various metalliferous minerals such as Zn-Pb-Fe sulfides, Zn-Pb carbonates, Fe oxides, Ca-Pb and Fe-Pb sulfates were noted in the examined wastes. The flotation wastes **(1)** and washing ones **(2)** differ from each other in chemical composition (Table 1). Chemical and physical weathering processes caused the washing out of fine-grained material **(3)** which was settled in local depressions around the tailings pile. Ca-Mg, Zn carbonates, Fe oxides,

Fe-Pb sulfates, and minerals, such as srebrodolskite, chlorides and hemimorfite were observed among the clayey fraction deposit (Table 1).

(1) light grey wastes. A significant content of Pb-minerals (to 14.5% by weight) consists mainly of galena, anglesite, plumbojarosite (Table 1). Fe oxide and hydroxide particles are bounded on sulphide (pyrite and marcasite) surfaces. The contents of Zn-sulfides and carbonates reach several percent. The typical constituent is gypsum. Its concentration exceeds 10%. Moreover, barite, clayey minerals and silica are observed. The Ca and Ca-Mg carbonates occur in minor amounts.

(2) red wastes. They consist of Fe oxides and hydroxides, mainly goethite (11.9 to 28.5% by weight). There is a significant content of Zn minerals: carbonates, smithsonite, minrecordite and sulfides. In addition, many gangue minerals occur: quartz, dolomite, ankerite, kaolinite, illite (Table 1).

Geochemical Investigation

The light grey and red wastes differ in metal concentrations as well. The common feature of these wastes is very high Pb content varying from 78,423 to 201,414 mg kg^{-1}. The Zn content in other wastes is subordinate and varies in the range of 10,315 to 27,814 mg kg^{-1}.

The high Zn concentrations (33,835 to 121,501 mg kg^{-1}) and lower Pb concentrations are characteristic of the red wastes (Table 2). Moreover, the high average Cd and Tl concentrations are observed. They exceed standards established for industrial soils by several orders of magnitude. Thus, the toxicity of red and light grey wastes is very high.

The light grey wastes represent both incoherent sediments (dusty sands) and cohesive sediments (compact clays). The cohesive sediments are observed mainly in local depressions. The contents of clayey, dusty and sandy fractions in cohesive sediments are comparable with each other and amount to about 30%. The carbonate content is very low (CaCO$_3$ < 1%). The light grey wastes are chemically very active. Their pH averages 2.89 (Table 2).

The red wastes represent medium- and coarse-grained sands. However, the content of clayey fraction is relatively high (10 to 15%). The cohesive red wastes are observed only in local depressions. The red wastes are calcareous-rich (CaCO$_3$ > 5%).

The ESEM study demonstrated a high content of Zn-Fe sulfides in association with Zn-carbonates and Fe-oxides (Fig. 3a). Isolated metalliferous mineral grains of 100 µm in size occur in fine-grained groundmass consisting of clayey minerals, quartz and dolomite. Polimineral sulfide aggregates (sphalerite, galena, marcasite) are frequently observed. They are coated by Zn-Pb carbonates (smithsonite, cerussite) and Fe oxides and hydroxides (including goethite) due to primary sulfide oxidation. Metalliferous mineral aggregates are fractured and porous. Etching traces are observed occasionally.

In the light grey wastes metalliferous, both unstable sulfate minerals, and barite crystallize on a mass scale. Gypsum is also commonly observed. The size of its grains varies from several to several hundred µm (Fig. 3b-d). Moreover, hydrated Fe-sulfates (Fig. 3b), Pb-sulfates (Fig. 3c) and dolomites associated with Zn-Fe (Fig. 3d) minerals were identified. Mineral grains are sub-microscopic in size.
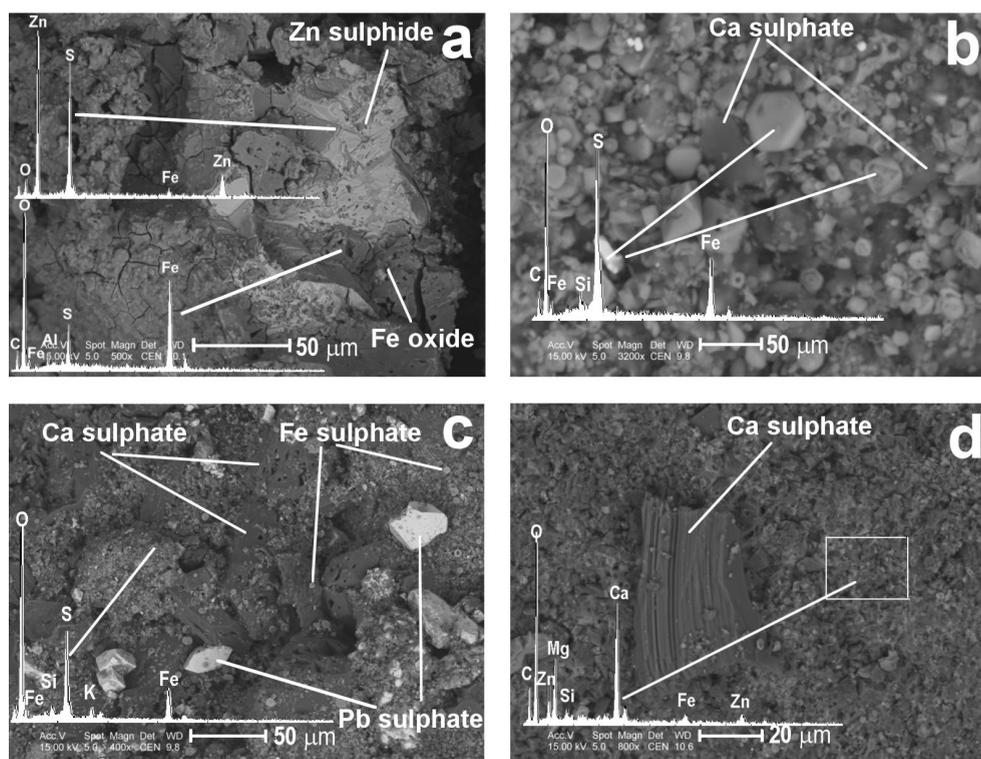

Fig. 3. BSE images of metal-bearing components in the waste from historical Zn-Pb ore processing.

Geophysical Investigation

The area of geophysical investigation is covered by sands and both light grey and red wastes. The boundaries between particular waste types are not distinctly seen on the surface because they are obliterated by wind-blown deposits and vegetation cover. Therefore, the EM measurements were applied to pinpoint these boundaries. First, one reference measurement along the A-B profile was performed. The A-B profile is situated on the neighbouring flotation tailings pile (Fig. 5). It is covered by red and light grey wastes along its length and the boundaries between different waste types are visible on the surface.

The values of apparent electrical conductivity were very high for the whole profile. In the case of the light grey wastes, these values reached 280 mS/m (VD) and 200 mS/m (HD). The course of electrical conductivity curves are in good concordance to the boundaries between the red and light grey wastes. These boundaries correspond to distinct change of conductivity value for the 140-to-175 mS/m (HD) level. The difference in electrical conductivity between these two waste types is linked to different concentrations of heavy metals and clayey material, and to mineral composition (Tables 1, 2). The reference profile data were used for interpretation of conductivity variations in the study area.
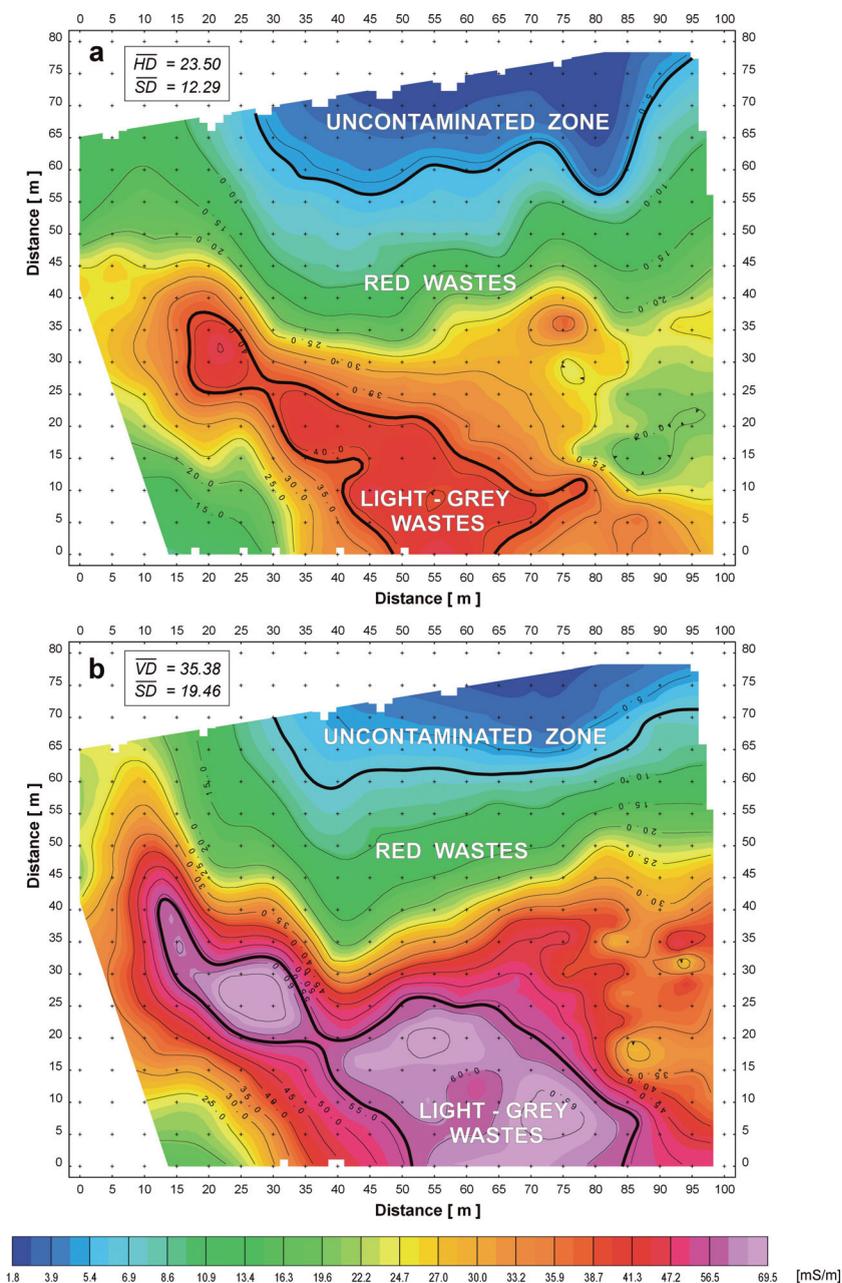

Fig. 4. Maps of apparent electrical conductivity to a depth of:
a - approx. 3 m (HD)
b - approx. 6 m (VD)
(EM31-MK2 conductivity meter)

The values of electrical conductivity in the study area varied in a range of 2–40 mS/m and 2–65 mS/m (Figs. 4a, b). The zone of high conductivity related to the waste flow is evident on both maps.

The electrical conductivity values are considerably lower in the study area in relation to the reference profile due to decreased metal concentration. The thickness of wastes (mixed with sands) is lower, and the light grey wastes thin out towards northwest. The area is partially covered by soils and plants (trees, shrubs and grass) that are not observed along the reference profile.

The boundaries between the light grey and red wastes were placed on maps of apparent electrical conductivity according to the following assumptions:

- the boundary between two waste types on the reference profile corresponds to the average value of 157 mS/m,
- the average electrical conductivity value (HD) in the reference profile is 4 times greater than in the study area. Thus, we assumed that the boundary between these two waste types corresponds to the value of about 39 mS/m,
- the average electrical conductivity value (VD) is 1.5 times greater than that (HD) in the study area. Thus, the boundary between these two waste types on the HD map corresponds to the value of 58 mS/m.

The boundary between the red wastes and unpolluted soils was determined according to the tabular conductivity value for dry, unpolluted sands [20] as 5 mS/m (HD and proportionally 7.5 mS/m (VD).

Both "conductivity" boundaries are in accordance with those observed in several filled sites, where the wastes are visible on the surface.

Discussion

The historical Zn-Pb ore processing dumps are rich in Fe-sulfides and carbonates, which in oxidizing conditions produce SO_4^{2-}, CO_3^{2-}, OH^- ions, humic, fulvic and other acids [21]. Wong et al. [22] demonstrated that high sulfur values (> 15%) resulted in acid drainage proccess even for environment with high carbonate contents.

Acid Waste Drainage (AWD) occurs mainly in surficial parts of the examined dumps and is highlighted by the occurrence of hydrated sulfates such as gypsum, bassanite, anglesite, jarosite and Fe-sulfate crystallization. Mass sulfate crystallization indicates that historical wastes are very susceptible to secondary changes related to weathering.

Sulfides and sulfates are unstable, particularly in low pH value conditions. Heavy metals, such as Zn, Pb, Fe, Cd, Tl are principal constituents of primary and secondary minerals or form isomorphic replacements (Fig. 3). Sulfate ions are relatively tightly bounded by Zn or Pb ligands. Therefore, heavy metals mobility is significant and influence water and soil pollution and their high bioavailabilty. Pb mobilizing is a result of galena oxidation in carbonate-depleted environments. This leads to crystallization of Pb-sulfates such as anglesite and plumbojarosite. In the study area these alterations are typical of wastes related to historical ore processing that took place during 1915-31. Crystallization of anglesite in mine wastes is an important indicator of Pb mobilization that jeopardizes the environment [23].

The exact assessment of heavy metal mobilization related to weathering susceptibility can be based on mineral composition study [23]. In order to assess the chemical activity of metalliferous wastes, the ESEM investigations should be performed as well.

The high element mobility in the examined wastes is also stimulated by biotic factors. It was confirmed by the bacterial microflora study. Waters draining the historical wastes usually contain the active chemolithotrophic bacterium species Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans. Their reproduction ability is higher than the other related bacteria living in present day proccessing waste dumps [24].

The similar mineral changes and high contents of heavy metals carried away to waters and soils have been reported in historical mining areas in England [1, 2], Spain [25], USA [6, 26] and Australia [3]. Thus, mining wastes are still a source of water and soil pollution in spite of several hundred years of storage [2, 5].

The very high toxic Pb concentration (15,000 mg kg⁻¹) [26] is observed in historical Zn-Pb processing wastes.
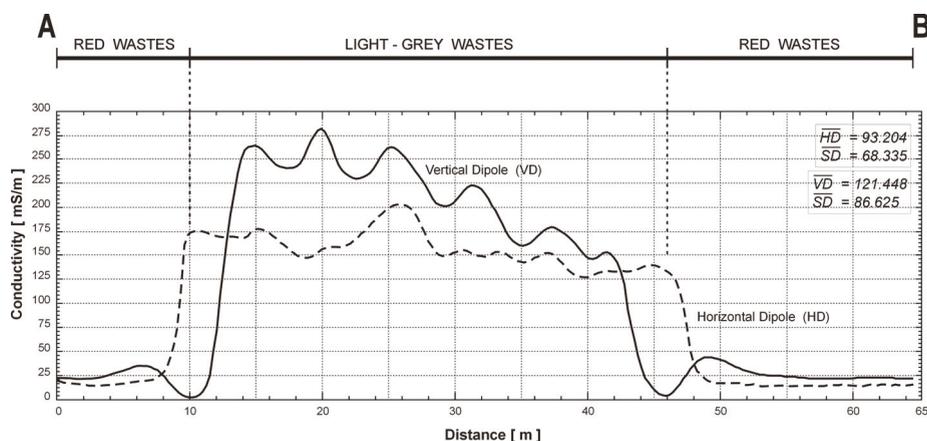

Fig. 5. Variations of apparent electrical conductivity along A-B reference profile to a depth of approx. 3 m (HD) and approx. 6 m (VD). (EM31-MK2 conductivity meter).

It was confirmed for the studied area (Table 1). Zn, Pb, Cd concentrations are higher than permissible limits of soil pollution several times. In Poland and many EC countries, permissible metal concentrations for industrial soils are significantly lower. It amounts to 1000 mg kg-1 for Zn, 600 mg kg^{-1} for Pb, and 15 mg kg^{-1} for Cd [27]. In the areas of Zn-Pb ores mining and processing, the soils with the highest (IV) metal pollution degree are observed. They contain up to 8000 mg kg^{-1} (Zn), 7000 mg kg^{-1} (Pb) and 20 mg kg^{-1} (Cd) [28]. They are the sources of metals transferred to waters, soils and the food chain [25, 26]. Moreover, high toxic thallium concentrations (Table 1) in Silesia-Kraków Zn-Pb mining and smelting area induce negative changes in plants [29] and animals [30].

Our study has revealed high geochemical activity of metalliferous wastes after more than 80 years of storage. Both the mineral composition and structural features undergo changes in wastes. Fine-grained aggregates of metalliferous and clayey minerals are formed. They reveal large specific surfaces and considerable sorption capacity. Water is bonded into an inter-granular space of clayey minerals and into sulfate structure. The mineral, chemical and structural changes significantly influence electrical conductivity and magnetic susceptibility of deposits.

Of the many geophysical methods, the EM one has not been widely used to investigate mine processing wastes so far. One of the most detailed studies was presented by Wynn [31], who demonstrated the close relationship between the occurrence of heavy metals in soils and measured electrical conductivity.

Our geophysical investigation showed that even a thin layer of wastes of about several centimetres in thickness significantly increases the values of measured electrical conductivity of soils. However, these values depend on the mineral and chemical composition of wastes, but especially on heavy metal concentrations.

Conclusions

The long-lasting geochemical changes occurring in the areas of Zn-Pb mining activity put some constraints on plant succession and processes of natural revitalization.

The occurrence of metalliferous sulfates (anglesite, plumbojarosite, jarosite and Fe sulfates) and gypsum in historical mine wastes triggers low pH values (2.0–4.0) and favours intense geochemical interactions. Needless to say, toxic metals such as Cd, Pb, and Tl are carried away from tailings piles into waters, soils and biota.

The unstable hydrated mineral phases affect physical properties of surface parts of wastes and polluted soils. Of the many physical properties, electrical conductivity, which can be easily measured with geophysical instruments, is very sensitive to chemical composition. Therefore, the geophysical measurements can be successfully applied for studying polluted mine waste areas.

This study demonstrated the efficacy of EM investigation. The boundaries between the two types of mine wastes, and between the polluted and unpolluted soils were determined based on the variations of electrical conductivity values.

References

1. MERRINGTON G., ALLOWAY B.J. The transfer and fate of Cd, Cu and Zn from two historic metalliferous mine sites in the UK. Appl. Geochem., **9**, 677, **1994**.
2. MASKALL J., WHITEHEAD K., GEE C., THORNTON I. Long-term migration of metals at historical smelting sites. Appl. Geochem. **11**, 43, **1996**.
3. HARRISON J., HEIJNIS H., CAPRARELLI G. Historical pollution variability from abandoned mine sites, Greater Blue Mountains World Heritage Area, New South Wales, Australia. Environ. Geol. **43**, 680, **2003**.
4. CABALA J., TEPER L. Metalliferous constituents of rhizosphere soils contaminated by Zn-Pb mining in southern Poland. Water, Air, & Soil Pollution, **178**, (1-4): 351, **2007**.
5. DEGRYSE F., SMOLDERS E. Mobility of Cd and Zn in polluted and unpolluted Spodosols. European J. Soil Sci., **57**, 122, **2006**.
6. ECKEL W.P., RABINOWITZ M.B., FOSTER G.D. Investigation of unrecognized former secondary lead smelting sites: confirmation by historical sources and elemental ratios in soil. Environ. Pollut. **117**, 273, **2002**.
7. CABAŁA J., IDZIAK A., KONDRACKA M., KLECZKA M. Physical and chemical properties of wastes occurring in areas of historical Zn-Pb ore processing. Central Mining Institute Quaterly, Katowice, Special Issue **3**, 141, **2007** [In Polish].
8. BENSON A.K., ADDAMS, C.L. Detecting the presence of acid mine drainage using hydrogeological, geochemical, and geophysical data: applications to contrasting conditions at mine sites in Little Cottonwood and American Fork Canyons, Utah. Environ. Geosciences, **5**, (1), 17, **1998**.
9. BUSELLI G., HWANG H.S., LU K. Minesite groundwater contamination mapping. Explor. Geophysics, **29**, 296, **1998**.
10. EBRAHEEM A.M., HAMBURGER M.W., BAYLESS E.R., KROTHKE N.C. A study of acid mine drainage using earth resistivity measurements. Ground Water, **28**, 361, **1990**.
11. CAMPBELL D.L., WYNN J.C., BOX S.E., BOOKSTROM A.A., HORTON R.J. Tests of ground penetrating radar and induced polarization for mapping fluvial mine tailings on the floor of Coeur d'Alene River, Idaho. Proc. of the Symposium on the Application of Geophysics to Engineering and Environmental Problems, March 23-26, Reno, Nevada, pp. 81-87, **1997**.
12. CAMPBELL D.L., HORTON R.J., BISDORF R.J., FEY D.L., POWERS M.H., FITTERMAN D.V. Some geophysical methods for tailings/mine waste work. Proc. of the 6th International Conference: Tailings and Mine Waste '99, January 24-27, Fort Collins, Colorado, Rotterdam, A.A. Balkema, pp. 35-43, **1999**.
13. MONIER-WILLIAMS M., MAXWELL M., SCHNEIDER G. Preparing for waste: geophysics in geotechnical and environmental assessments of proposed mine waste facilities. Proc. of the 4th Decennial International Conference on Mineral Exploration, Toronto, pp. 893-904, **1997**.
14. STRZYSZCZ Z, MAGIERA T. Heavy metal contamination and magnetic susceptibility in soils of Southern Poland. Physics and Chemistry of the Earth, **29** (9-10), 1127, **1998**.
15. MAGIERA T., STRZYSZCZ Z., KAPIČKA A., PETROVSKÝ E. Discrimination of lithogenic and anthropogenic influences on topsoil magnetic susceptibility in Central Europe. Geoderma, **130** (3-4), 299, **2006**.
16. MC DOUGAL R.M., SMITH B.D., CANNON M.R., FEY D.L. Integrated geophysical, geochemical, and hydrological study of the Buckeye mine tailings, Boulder watershed,

Montana. Proc. of the 22nd Annual National Association of Abandoned Mine Land Programs Conference, September 24-27, Steamboat Springs, Colorado, pp. 411-428, **2000**.

17. VANHALA H., RAISANEN M.L., HUOTARI T., VALJUS T., LEHTIMAKI J., SUPPALA I. Characterizing tailings impoundment at the closed Hammaslahti Cu-Zn mine, Finland. Proc. of the 10th European Meeting of Environmental and Engineering Geophysics, B-035, **2004**.

18. PERSSON L. HOLMSTRÖM H., LAX K., MAXE L., RIPA M., STRÄNG T. A multidisciplinary study of an old mine waste site in Sweden using geophysical, geological and geochemical methods. Proc. of the 12th European Meeting of Environmental and Engineering Geophysics, P-024, **2006**.

19. CABALA J. Prospects for Zn-Pb ore mining in Poland with regard to ore quality in discovered deposits. Mine Planning and Equipment Selection. Balkema, pp. 177-182, **2000**.

20. SCHÖN J.H. Physical properties of rocks: fundamentals and principles of petrophysics. Pergamon – Elsevier Science Inc., New York. pp. 393, **1996**.

21. EVANS L.J. Fractionation and aqueous speciation of zinc in a lake polluted by mining activities, Flin Flong, Canada. Water, Air and Soil Pollution, **122**, 299, **2000**.

22. WONG J.W.C., IP C.M., WONG M.H. Acid – forming capacity of lead-zinc mine tailings and its implications for mine rehabilitation. Environmental Geochemistry and Health, **20**, 149, **1998**.

23. FANFANI L., ZUDDAS P., CHESSA A. Heavy metals speciation as tool for studying mine tailings weathering. J. Geochem. Explor., **58**, 241, **1997**.

24. PACHOLEWSKA M., CABAŁA J., CWALINA B., SOZAŃSKA M. Environmental conditions of the metals (bio)leaching from zinc-lead post-flotation tailings. Rudy Metale **6** (52), 337, **2007** [In Polish].

25. MARQUES M.J., MARTINEZ-CONDE E., ROVIRA J.V., ORDONEZ S. Heavy metals pollution of aquatic ecosystems in the vicinity of a recently closed underground lead-zinc mine (Basque Country, Spain). Environ. Geol. **40**, 1125, **2001**.

26. BALISTRIERI, L.S., FOSTER, A.L., GOUGH, L.P., GRAY, FLOYD, RYTUBA, J.J., STILLINGS, L.L. Understanding metal pathways in mineralized ecosystems: U.S. Geological Survey Circular **1317**, 12, **2007**.

27. JOURNAL OF LAWS, Poland, Dz.U. 165 item 1359, **2002**.

28. KABATA-PENDIAS A., PIOTROWSKA M., MOTOWIC-KA-TERELAK T., MALISZEWSKA-KORDYBACH B., FILIPIAK K., KRAKOWIAK A., PIETRUCH C., Estimation Base of Soil Pollution, Warsaw, pp. 20, **1995** [in Polish].

29. WIERZBICKA M. SZAREK-ŁUKASZEWSKA, GRODZIŃSKA G. Highly toxic thallium in plants from the vicinity of Olkusz (Poland). Ecotoxicology and Environmental Safety **59**, 84, **2004**.

30. DMOWSKI K., KOZAKIEWICZ A., KOZAKIEWICZ M. Search for thallium in the areas of southern Poland by means of bioindication methods. Kosmos. Problemy Nauk Biologicznych **51** (2), 151, **2002** [In Polish].

31. WYNN J. Ground electromagnetic survey used to map sulfides and acid sulfate ground waters at the Abandoned Cabin Branch Mine, Prince William Forest Park, Northern Virginia Gold-Pyrite Belt. U.S. Geol. Surv. Open-File Raport 00-360, **2001**.