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POLSKA AKADEMIA NAUK

ARCHIVES of FOUNDRY ENGINEERING

DOI: 10.1515/afe-2017-0045

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

DE GRUYTER OPEN

ISSN (2299-2944)
Volume 17
Issue 2/2017

25 – 30

Metallurgical Slags as Traces of a 15th century Copper Smelter

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Received 19.07.2016; accepted in revised form 22.09.2016

Abstract

The research focuses on assessing the metal content, mainly copper, lead, iron and also silver in metallurgical slag samples from the area where historical metallurgical industry functioned. In the smelter located in Mogiła, near Krakow (southern Poland), whose operation is confirmed in sources from 1469, copper was probably refined as well as silver was separated from copper. Based on the change of chemical and soil phase content and also taking cartographic and historical data into account, considering the restrictions resulting from the modern land use the area was determined whose geochemical mapping can point to the location of the 15th century Jan Thurzo's smelter in Mogiła near Krakow. Moreover, using the same approach with the samples of this kind here as with hazardous waste, an attempt has been made to assess their impact on the environment. Thereby, taking the geoenvironmental conditions into account, potential impact of the industrial activity has been assessed, which probably left large scale changes in the substratum, manifested in the structure, chemical content and soil phase changes. Discovering areas which are contaminated above the standard value can help to identify historical human activities, and finding the context in artefacts allows to treat geochemical anomalies as a geochronological marker. For this purpose the best are bed sediments, at present buried in the ground, of historical ditches draining the area of the supposed smelter. Correlating their qualities with analogical research of archeologically identified slags and other waste material allows for reconstructing the anthropopressure stages and the evaluation of their effects. The operation of Jan Thurzo's smelter is significant for the history of mining and metallurgy of Poland and Central and Eastern Europe.

Keywords: Environment protection, Archaeometallurgy, Metallurgy of copper, Environment pollution, Copper, Lead, Silver

1. Introduction

In the Middle Ages there were shaft furnaces used for smelting copper and its concentrates, as well as furnaces for separating lead from silver and refining metals [1, 2].
If copper ores contained an increased amount of silver, lead was introduced into the furnace already at the beginning of the process so that silver flowing down the furnace could combine with it. The rest of the silver remained in so called black copper. During the next stage, lead with silver was melted away from the copper, and the last step was separating silver from lead by cupellation method [3, 4, 5].

One of the most important copper and silver production centre in Europe was created in the 15th century in Poland. At that time a significant role was played by copper imported from the area of present Slovakia (then Hungary), which was most effectively obtained from mines located near Banska Bystřica in the area of Stare Hory-Špana Dolina [6, 7]. A mining and trading association started to operate in this area, belonging to the Thurzos and

Fuggers, which gradually monopolized copper and silver production in central Europe, as well as trade in these metals and copper. The sources inform that during the 50 years of its operation the association obtained about 30 000 tons of copper and 115 tons of silver [1, 3, 8, 9].

Jan Thurzo (1437-1508) from Lewocza in Spisz was a valued engineer, an expert in mining and metal obtaining techniques. He exploited rich ores in the area of what was Hungary then, and in Poland he conducted exploration of copper ores in the Tatra Mountains, also he established a copper smelter near Krakow, in the area belonging to the Cistercian monks, in the village of Mogiła [2]. He became famous as the importer of copper from mines and Hungarian smelters to Poland and other European countries. He traded Hungarian copper as well as purchased copper in Krakow, Olkusz, Trzebinia and Tarnowskie Góry. He established a new path for copper trade (so called Thurzo's road), which, through Orawa, joined Krakow and Slowakia, enabling trading in metals. The copper and lead trade significantly helped the economic development of Poland and strengthened its position in Europe [10,11,12]. Jan Thurzo introduced modern and efficient technology of obtaining metals based on separating silver from copper with the help of lead. He brought to Mogiła (now belonging to the area of Krakow-Nowa Huta) Hungarian copper with silver, so called black copper, to conduct the technological process there, with the goal of obtaining silver from copper. Silver extracted in this way was sold to the royal mint and the copper was floated on the Vistula to Gdańsk and next to Western Europe [9,11].

In the area of Mogiła in 1953 copper slag was discovered accidentally at the site no 28 explored by the Archeological Museum in Krakow [13]. The research conducted so far has aimed to prove that the slag is a waste material resulting from copper production processes [14, 15].

2. Issues and research methodology

The basic goal of this research is pointing at the location of the Thurzo's smelter, because there is no data concerning the placement of the buildings or the elements of the smelter infrastructure, besides the general naming of the Mogiła village area, at the public road [9]. The factor which erased all traces of its operation is the land use and the present ownership structure, not conducive to archaeological research or metallographic and geochemical prospection. Because of these reasons, at the present stage of research, the aspects of the smelter location were analyzed on the basis of cartographic sources, including historical materials, and especially geoenvironmental conditions assessed with the help of lithological changes of the substratum. The indicated area, at the next stage of research, will be used for geochemical analysis of the ground at the sites selected for conducting test low-invasive and small diameter boreholes (Fig.1). In this way it will be possible to assess the pollution level of the soil and water environment and determine the areas of geochemical anomalies whose location will point to the location of Jan Thurzo's copper smelter. Lithological pictures of the terrain and the layout of copper and lead concentrations in them will be helpful, supported by interdisciplinary interpretations. The identification of the kind of ground and the transformation of its phase and chemical content will become the basis for assessing the impact of this kind of activity on the environment of this 15the century village of Mogiła near Krakow. The research starting point is the detailed analysis of the metallurgical slag from Mogiła, the find which is treated as the proof of Jan Thurzo's smelter, functioning from 1469 to 1529 [9].

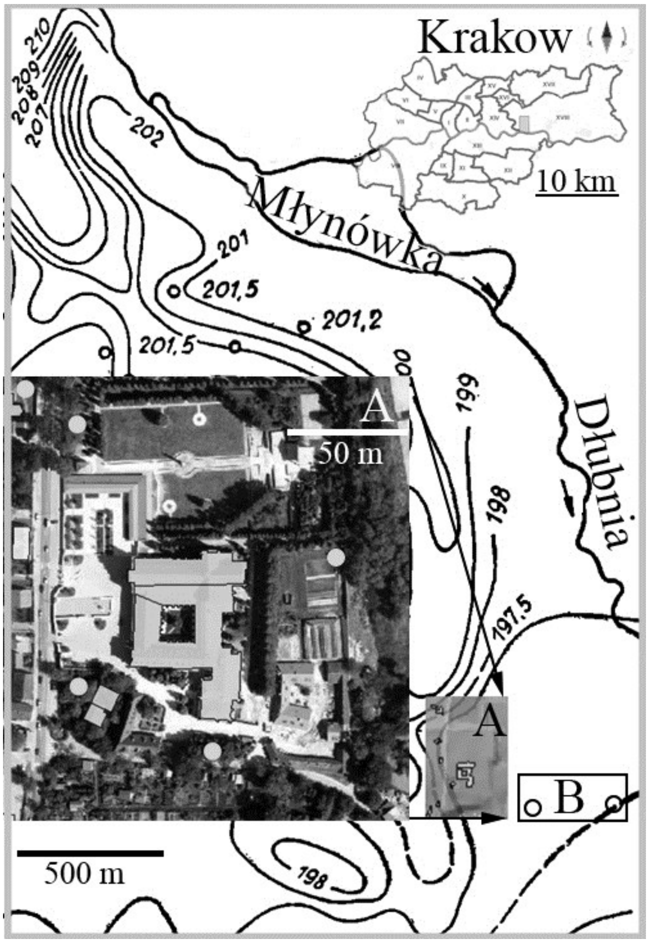

Fig. 1. The sites of planned archeological and geochemical prospection in the area of Cistercian monastery in Mogiła (Nowa Huta), against the background of hydroizohypses [16]; the research of the background (A), the contamination level tests (B)

Macro and micro observations of the slags marked as NH1-NH8 (Fig. 2) were performed, using light and scanning microscopy. Additionally, defectoscopic radiographic tests (RT) were conducted. The X-Ray Fluorescence method was used for the analysis and on its basis representative samples for qualitative determination of the slag chemical composition were chosen. The indirect assessment of the metal content was conducted using spectrometers: atomic absorption (Thermo Scientific ICE 3500) and emission spectrometer with inductively coupled plasma (Optima 7300DV) and mass spectrometer with inductively coupled plasma (ELAN 6100), first having extracted the elements from the samples of the chosen slags with concentrated nitric acid [14, 15].

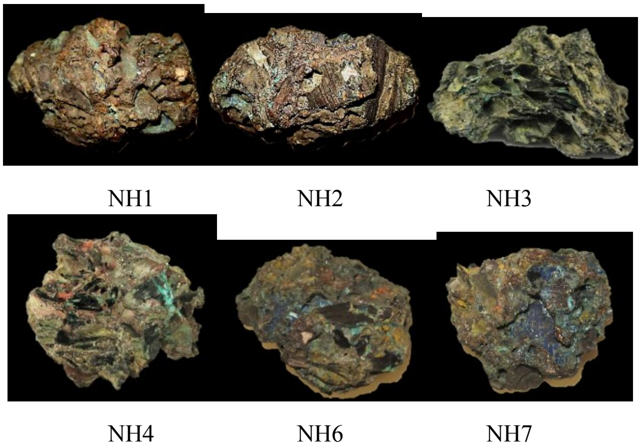

Fig. 2. Copper slags from Mogiła archaeological site (Kraków-Nowa Huta)

For two particularly rich in metals slag samples, NH1 and NH7, with the help of scanning microscopy SEM/EDS (FEI Quanta 200 FEG), interesting microareas were pointed out, where the elements were identified using the X-Ray Fluorescence method. Phase content of the slag samples were determined by X-Ray Diffraction method (SmartLab (9kW) RIGAKU). This enabled the assessment whether, in the conditions of disrupting the geochemical balance, they can be susceptible to be released into the environment. The evaluation of the physicochemical properties of the slag containing metals is also helpful when determining the forms of their chemical bonding. To this effect their pH, conductivity (PEW) and redox potential (Eh) were analyzed in water solutions of the suspension (1:3) prepared from slag samples crushed down to the <0,18 mm fraction [17]. Based on the susceptibility to release contaminants an attempt was made to determine if historical slags deposited in the Mogiła area could have created geochemical aureole in the subsoil, which would be an indicator confirming the location of the smelter.

3. The results of slag observations and research

The presence of numerous metallic drops in the structure of archeological slags was confirmed in RT defectoscopic tests (Fig 3). The radiographic analysis confirmed amorphous structure of the sample, permeable for X-rays, as well as numerous porosities inside the material tested. In the sample structure there are visible areas of metallic inclusions, mainly or approximately spherical in shape, irregularly distributed.

Macro and microscopic observations showed amorphous structure typical of slags, containing numerous metallic inclusions in the glassy phase (Fig. 4-6) and considerable share of charcoal fragments (Fig. 4b).

In the slags there were revealed a structure containing considerable amounts of irregularly distributed spherical, metallic inclusions. Small inclusions with the diameter of 3.61÷4.94 μm, dominated there, and the inclusion with maximal diameter was 43.79 μm.

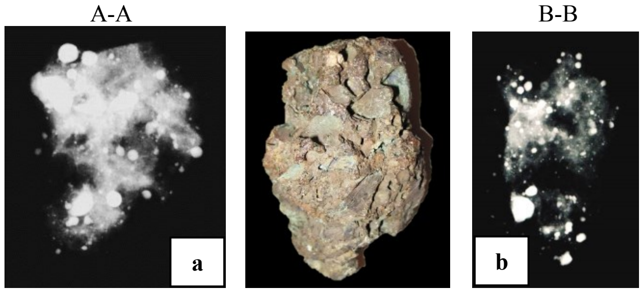

Fig. 3. X-ray picture of NH1 object in two perpendicular planes: A-A (a) and B-B (b)

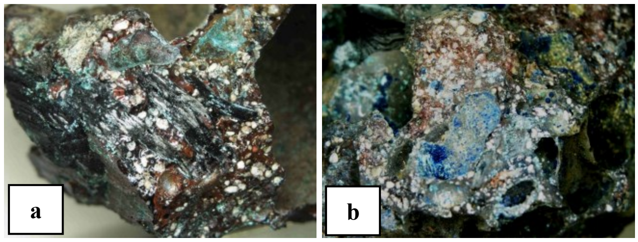

Fig. 4. Macroscopic picture of the slag surface: (a) NH4, (b) NH7, 6.7x magnification

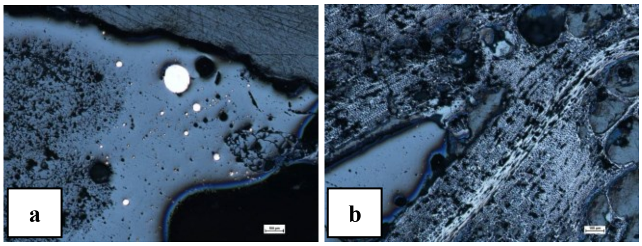

Fig. 5. Microscopic picture, NH4 object structure: 50x (a), 100x (b) magnification

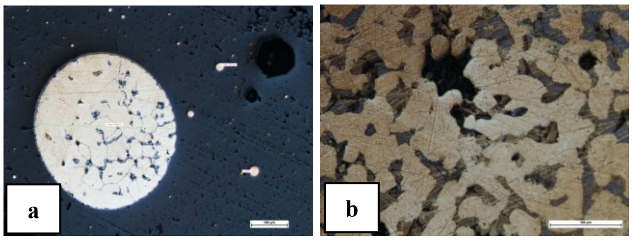

Fig. 6. Microscopic picture, NH4 object structure: 100x (a), 200x (b) magnification

Microstructure analysis was conducted with a scanning microscope. A structure characteristic of slag was revealed, with visible areas of an amorphous phase and numerous porosity zones, which remain after gas emissions. Also fractures were noticed, resulting from shrinkage during the slag solidification. In order to identify the chemical composition, especially the content of metallic inclusions, there were analyses conducted in microareas using SEM-EDS method (Fig.7-8, Tab.1, 2). The results obtained from the analyses confirmed that the main phase forming the sample consists of SiO_2, with three oxide phases located inside (Fig. 7). The structure of charcoal was revealed and areas characteristic of alloys (Fig. 8). These are mainly multicomponent solutions consisting of copper, antimony and lead, with small content of iron and silver.

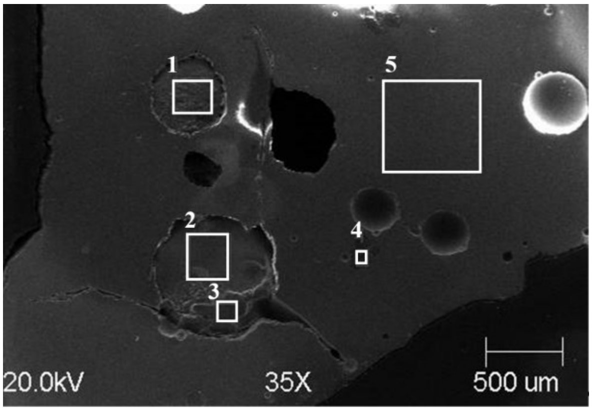

Fig. 7. SE picture, the surface topography of object NH3

Table 1.
SEM-EDS results of slag NH3 for Fig. 7

Element	Cu	Sb	Fe	Al	Ag	Si	O	C
	Concentration (wt%)							
1	15, 94	3,76	2,05	0,00	0,81	0,00	59,94	17,51
2	8,70	4,27	0,86	0,00	0,05	0,00	63,64	22,18
3	0,00	4,75	0,00	0,00	1,70	0,00	65,46	28,09
4	0,00	1,12	0,00	0,00	0,81	22,91	60,01	15,15
5	0,00	4,82	4,02	4,29	1,94	32,32	48,42	4,18

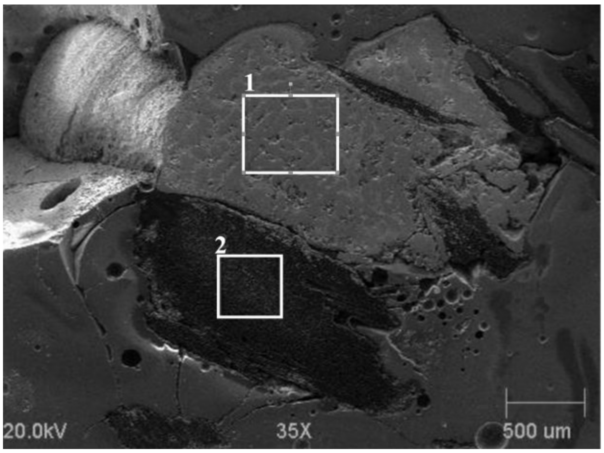

Fig. 8. SE picture, the surface topography of object NH1

Table 2.
SEM-EDS results of slag NH1 for Fig. 8

Element	Cu	S	Sb	Pb	Fe	Ag	O	C
	Concentration (wt%)							
1	66.58	0.62	15.96	9.99	0.55	0.67	7.24	0.00
2	0.00	0.00	0.00	0.00	0.14	0.00	3.55	95.97

The results of concentrations of metallic elements extracted from the samples determined by spectrometric methods and the measurements of physiochemical markers in water solutions of the slags (1:3) are presented on the graph (Fig. 9) and in Table 3. The biggest silver content, compared to other slags from Mogiła, is shown for NH1 and NH7 samples.

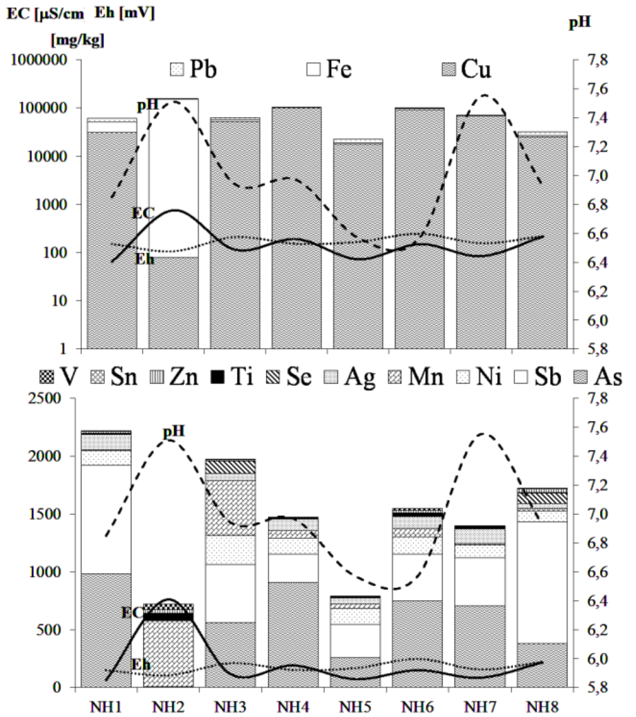

Fig. 9. Changes of metal contents and physiochemical properties of water solutions (1:3) of slag samples

In the slags, the highest concentration was shown for copper (max. 10.01%), lead (max. 1.07%) and iron (max. 15.33%). Moreover, there is a significant content of arsenic (max. 0.09%) and antimony (max. 0.10%). Also silver (max. 0.01%) and nickel (max. 0.02%) are present in concentrations often higher than 100 mg/kg. Only slag NH2 is significantly poorer in this respect. Slags do not show a strong tendency for solving and for this reason their water solution conductivity is comparatively low, which can result from the process of slag aging. The pH of about 7 can suggest that the samples lack chemical agents causing acidity (of sulfide types), but there are alkalizing elements, e. g. charcoal found in the samples. Its presence can also be confirmed by a lowered value of oxidation reduction potential. Phase tests of the samples of NH1 and NH7 slags (Fig. 10) testify to the presence of metallic forms in them, also of secondary carbonate and sulfate character [18, 19]. Their occurrence in acidic environment at the storage stage of this kind of waste materials from metallurgic processes was probably responsible for comparatively weak bonding of heavy metals. Because of that it is expected that around the historical smelter belonging to Thurzo there was created a geochemical anomaly in the substratum, connected with the presence of copper and lead, and maybe also of arsenic and antimony, which can testify to the operation of this copper smelter and reveal its location in the area.

Table 3.
Concentration results [mg/kg] of the elements and the physiochemical marker values of the water solutions (1:3) of the slag samples [17]

Element	NH1	NH2	NH3	NH4	NH5	NH6	NH7	NH8
	Concentration [mg/kg]							
Ag	137,27	0,88	63,96	97,99	57,15	99,69	126,20	43,08
As	987,00	0,30	561,96	908,74	261,04	752,51	709,74	380,39
Bi	<0,10	0,09	<0,10	<0,10	1,13	20,31	<0,10	9,95
Cd	0,62	<0,10	<0,10	<0,10	<0,10	2,10	<0,10	0,16
Co	48,96	11,38	26,93	4,64	19,87	6,96	6,75	7,06
Cr	<0,20	3,25	<0,20	<0,20	<0,20	4,81	0,19	<0,20
Cu	31372,65	79,20	53116,50	100988,50	17800,05	94868,48	69299,83	25796,58
Fe	20177,99	153343,82	4617,81	1115,55	1201,16	5131,21	884,93	1663,14
Mn	3,12	565,95	478,65	65,63	34,47	75,18	10,05	22,88
Ni	126,72	9,04	248,68	137,15	136,74	151,24	112,53	94,26
Pb	10721,34	36,50	5912,52	1279,73	3869,98	1777,03	2053,24	4706,93
Sb	936,13	1,96	501,56	246,57	288,82	402,22	413,82	1053,27
Se	1,58	<0,20	103,81	2,43	0,99	0,05	4,16	89,58
Sn	<0,20	<0,20	1,08	0,14	<0,20	0,64	0,43	0,59
Ti	8,39	63,74	1,98	3,17	5,57	32,19	10,75	4,96
V	2,32	48,17	2,12	3,75	2,95	11,48	0,92	3,86
Zn	13,09	32,01	9,98	6,47	1,61	21,54	6,96	29,25
pH	6,85	7,51	6,94	6,97	6,57	6,57	7,55	6,93
Eh [mV]	151	107	212	153	168	248	157	221
PEW [µS/cm]	65	762	116	192	73	151	85	217

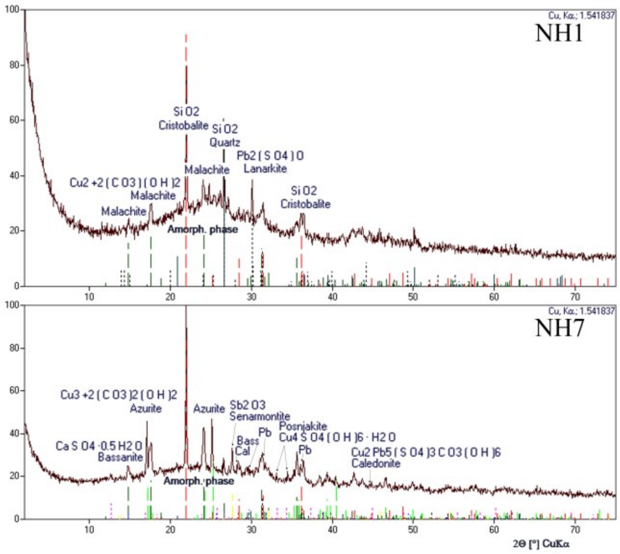

Fig. 10. Phase analysis (XRD) of slags NH1 and NH7

4. The research summary

The research of the archaeological slags from Mogiła showed a significant inhomogeneity of the material tested in respect of its structure, texture and chemical composition. The structure analyses of these objects reveled internal composition with amorphous phase, being the filling of the sample. Tests of chemical composition proved the presence of SiO_2 and numerous oxides. Numerous metallic inclusions in the form of drops point to the metallic character of the finds. These inclusions have the character of complex intermetallic compounds: Cu-Sb and Cu-Sb-Pb with the presence of Ag. In the slags tested copper, iron and lead reach the highest concentrations. Also the presence of arsenic, antimony, nickel and silver was confirmed. The results of chemical analysis of the slags from the perspective of their metallic elements content show the character of this material as metallurgical slag resulting from copper production.

Microscopic observations showed a similar character of metallic inclusions in archaeological and modern slags. However, significant differences were noticed in chemical composition, especially in antimony, arsenic, silver and nickel content, which are not present in slags resulting from current metallurgical processes. The differences in elements concentrations depend on the characteristics of the ore deposits used, as well as on the kind of copper production process (solution or converter process) or its stage (converter I or II) [14, 18, 19, 20, 21].

The variety of chemical composition, especially the concentrations of metallic elements, can signify inhomogeneity of the material used for copper smelting, in this case copper matte with different content of silver, nickel, antimony and arsenic pointing at its origin from ores. Because of significant waste rate of specific processes of extracting copper, the by-product can differ in chemical content for successive stages of the process. This confirms the multi-stage character of medieval processes of copper and silver production. High concentration of copper in slags means that old metallurgical processes did not entail a high yield of copper. The presence of lead confirms using it in an advanced process of silver recovery from copper. A low content of silver in slags points to efficiency of the method used.

Taking into account the place where the analyzed objects were discovered, the area of Nowa Huta and the results of the analyses, the tested metallurgical slags need to be acknowledged as material proofs of the operation of Jan Thurzo's copper smelter. This smelter, taking advantage of advanced metallurgical processes, operated in the 15th century in Mogiła, near Kraków.

Recognized based on the subsoil example of the Main Market Square in Krakow [10, 12] consequences for the environment resulting from depositing in the substratum the waste coming from the process of copper and lead confectioning in the building of the Great Scales can become the comparative testing ground. A similar correlation of physiochemical characteristics of the slags with the geochemistry of the subsoil, especially the sediments from the historical watercourses, draining the area of the supposed 15th century copper smelter near Krakow, can point to the traces of its operation and in this way determine its location.

The collected materials have made it possible to recognize the old metallurgical processes of copper and silver production. Metallic elements identified in slags confirm the purposefulness of conducting detailed geochemical and metallurgical research around the probable historical area of Thurzo's smelter, where significant geochemical anomaly developed in the subsoil connected with the presence of copper and lead. In this way environmental pollution can help to identify historical manufacturing processes, which will precede the planned fieldwork.

Acknowledgements

The work has been implemented within the framework of statutory research of AGH University of Science and Technology, contracts No 11.11.170.318-11 AGH and 11.11.140.199 AGH.

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