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MINERALOGICAL CHARACTERISTICS OF METALLURGICAL DUST IN THE VICINITY OF GŁOGÓW

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The investigations of the atmospheric dusts in the Głogów-Żukowice area detected the presence of unaltered grains and fragments of ore minerals characteristic of the ore from the Legnica Głogów Copper District. Industry in the Żukowice area emits not only sulphides and arsenides of such metals as Cu, Pb, Zn, and Ni but also alloys of Pb and Pb-Cu as well as precious metals. Size of the dust particles varies considerably from submicroscopic grains to several hundreds of micrometers. The particles are usually xenomorphic grains or crystals and ore fragments (mainly shale ore). Intergrowths of ore minerals are rare. The biggest grains consist of semigraphite blades and unaltered fragments of bituminous shale. Bornite, chalcopyrite, goethite, chalcocite, hematite, covellite, marcasite, arsenides of Ni-Co (rammelsbergite-safflorite), fragments of Bessemer and shaft furnace slag, metallic silver and copper, metallic iron, ilmenite, magnetite, malachite, cuprite, pyrrhotite, metallic lead and lead alloys were detected in the polished samples.

Key words: metallurgical dust, ore minerals, silver, ore microscopy, sulphides, metals alloy

INTRODUCTION

The research aimed mainly at characterising the mineralogical composition of metallurgical dusts falling in the neighbourhood of the copper smelters and refineries Głogów I and II near the Żukowice village. It has been carried out systematically since 1999 and the results were presented in several MSc thesis (Gruszka 2001, Grech 2002, Wójcik 2003). The observations allow evaluating the efficiency of filters installed on the factories' chimneys.

Dusts are generated on various technological stages of extracting copper and accompanying metals and carried out by smelter gases as well as air that are pumped out of the factory buildings. The dusts are mobilised mechanically by a stream of

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ventilation air from materials under processing (transport, mixing, drying etc.) and by smelter gases in roasting and sintering devices as well as in furnaces (Krupkowski 1974, Byrdziak 1996). They are also generated as a result of partial escaping and subsequent condensation of some constituents of metallurgical load.

The investigations of the atmospheric dusts, which fall on the ground and vegetation in the Głogów-Żukowice area, detected the presence of unaltered grains and fragments of the ore minerals characteristic of the Legnica Głogów Copper District metal deposits. The presence of various alloys was also detected. Not only sulphides and arsenides of such metals as Cu, Pb, Zn, and Ni but also alloys of Pb, Pb-Cu and precious metals are emitted from the smelters and refineries near Żukowice. Presence of metallic compounds in the atmospheric dusts is an indicator of pollution that was not eliminated entirely in the last period of the factories activity. Most of all the research was to answer the problem to what extent Głogów is subjected to falls of metallurgical dusts from the Żukowice area and how far anthropogenic dusts generated during smelting activity in the Głogów area may travel.

METHODS

Sampling of the dusts was carried out in autumn – winter and spring – summer cycles. The dusts were caught in basins with a diameter of 40 cm. The investigations presented in the article cover the period of time from 1999 to 2003. Depending on the place in which the basins were installed collecting of the dusts took about 4-8 weeks in autumn-winter and spring. The basins were installed in various distances from the Głogów smelter and refinery in accordance with wind directions dominating in the area. Material for the investigations comes from Żukowice (in the proximity of the metallurgical complex) Bogomice, Biechów, Głogów, Drożów and Nielubie (Fig. 1).

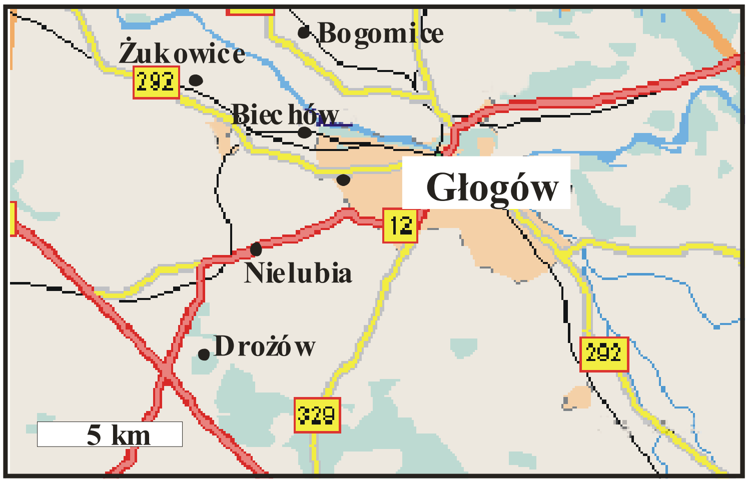

Fig. 1. Location of sampling points

It was sifted on the 250 µm and 125 µm Fritz sieves. Polished samples for reflectance microscopy and electron microscopy were then prepared. Reflectance microscopy was performed using an Optiphot 2-Pol Nikon microscope equipped with a Photometr 100 for reflectance measurements. Ore identification followed a standard procedure based on reflectance microscopy observations (Ramdohr 1975, Piestrzyński 1992, Muszer 2000). They were carried out at the Laboratory of Ore Minerals Microscopy, University of Wrocław. Chosen polished samples abundant in metallic compounds were coated with graphite and analysed with a scanning microscope Philips-515 equipped with a microprobe and an EDX spectrometer at the Institute of Low Temperature and Structure Research, Polish Academy of Sciences in Wrocław.

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SOURCES OF POLLUTION

Industry in the Żukowice area generates various dust wastes depending on a technological process. During copper smelting convector gases (N_2, SO_2, O_2) mobilise fine silica grains, cold solid additions, and fragments of slag and metallic copper. Together with these particles some volatile metals (Zn, Pb, As, Bi etc.) are ejected. According to Chodkowski (1976) the amount of dust generated in technological processes constitutes about 0,5 to 1 % of the volume of the processed material. According to Byrdziak (1996) on the other hand, after application of methods of wet de-dusting of gases in 1970-1980's and installation of bag and cassette filters (in 1995) operating at 99,9 % efficiency the amount of dusts does not exceed 5 mg/Nm^3.

During drying of copper concentrate in the "Głogów I" smelter and refinery the "Mikropul" wet de-dusting installation operates with the efficiency of 94.7 % and in the "Głogów II" electrofilters reach the efficiency of 98 %. In "Głogów I" de-dusting systems were not installed in reloading sections, which are not attended by workers, but bag filters were applied and operate at 99.9 % efficiency in loading sections of shaft furnaces. In "Głogów II" hermetisation of the technological line was applied instead of de-dusting. Shaft furnace gases are de-dusted with a Venturi tube with a regulated valve. Then all the shaft furnace gases are transported to the heat plant and combusted. In emergency shaft furnace gas is released through 150 m high chimneys and in case of de-dusters malfunctioning untreated gas is emitted through the technological chimney of a shaft furnace. Furnace loading is done through a bell shaped valve. Filters (e.g. in "Głogów II") de-dust with 99,9 % efficiency reaching the level of 5 mg/Nm^3 of dust in the gases. Flush furnace gases are de-dusted with the efficiency of 99,9 %. According to the data presented by KGHM Polska Miedź S.A. converter gases do not contain dusts after application of converter flaps.

CHARACTERISTICS OF ANTHROPOGENIC DUSTS

Dusts generated during metallurgical activity are not homogeneous and depend on the character of the technological process of copper extraction and solid wastes generated in this process (Muszer 1996, 1998). Their abundance and composition depend on the season of a year and distance from the smelter and refinery in Żukowice. Dusts collected in the basins installed in the same places but in different time periods show different mineralogical compositions. Size of the dust particles varies considerably from submicroscopic grains to particles with a diameter of several hundred micrometers. They are represented mostly by separate xenomorphic grains or crystals and fragments of ore (mainly shale ore). Intergrowths of ore minerals are rare (Fig. 2). The biggest fragments consist of semigraphite blades and unaltered parts of bituminous shale. However semigraphite and graphite were not taken into account in the current work as their presence results from the activity of heat plants operating in the Głogów area.

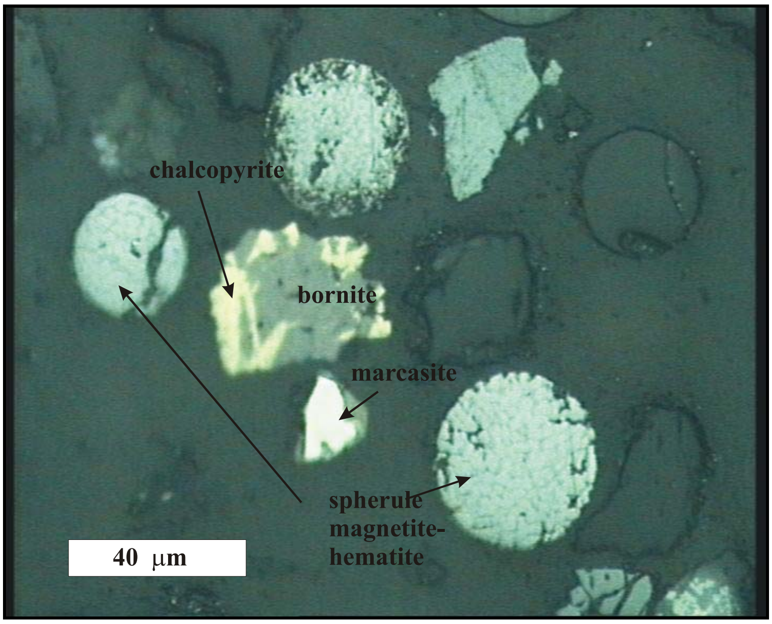

Fig. 2. Forms of anthropogenic dusts near Bogomice. Reflected light, uncrossed nicols. Grey minerals: quartz and silicates of metals

The greatest concentration of metallurgical dusts was observed in Żukowice (in the protective zone of the copper smelter and refinery) and northeastwards, in Bogomice and Biechów. In the other places the amount of the material collected in the basins decreased with the distance from the smelter and refinery. In the polished samples the following phases were detected: Ni-Co arsenides (rammelsbergite-safflorite), bornite, chalcopyrite, goethite, chalcocite, hematite, covellite, marcasite, silver and metallic copper, fragments of Bessemer and shaft furnace slag, metallic iron, ilmenite, magnetite, malachite, cuprite, pyrrhotite, metallic lead and lead alloys.

The greatest fall of anthropogenic dust occurs near the Głogów I and II smelters and refineries, i.e. at the fences, northeastwards towards the Odra River and in the forested protective zone. The material collected in this area resembled rich ore concentrate with minor amount of wind-blown quartz (Fig. 3). In the polished samples from this area the following phases were detected: chalcocite, chalcopyrite, metallic copper, cuprite, covellite, bornite, magnetite, sphalerite, chromite, goethite, pyrite, marcasite, Pb-Cu alloys, metallic lead, fragments of Bessemer and shaft furnace slag. The size of the ore phases varies from 0,1 µm to 75 µm in diameter. The copper ore minerals display structures typical of copper ores. This indicates the lack of thermal influence. Lead and lead-copper alloys show irregular forms up to 20 micrometers in diameter. Exsolutions of lead are present within the spheres of metallic copper. Lead, together with metallic copper, iron and traces of gold are also present in cristobalite spheres (Fig. 4). Those spheres contain 50 wt.% of lead and 26,45 wt. % of copper.

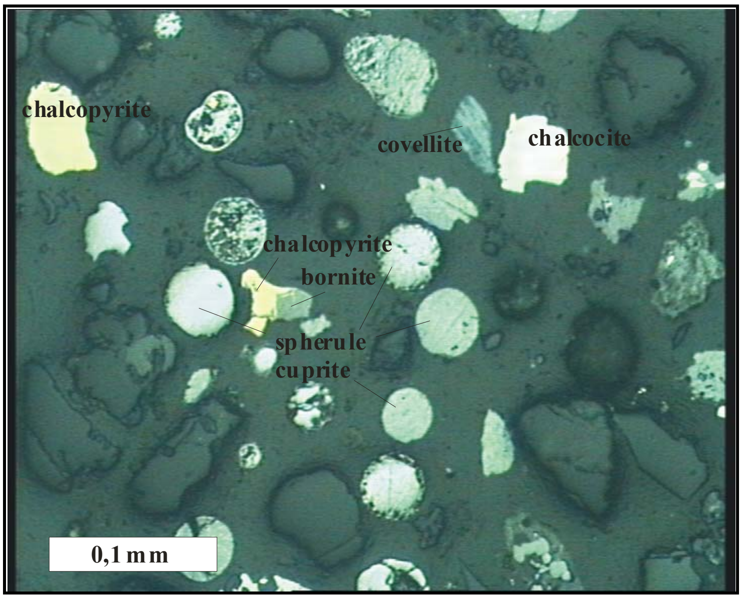

Fig. 3. Forms of anthropogenic dusts near Żukowice. Reflected light, uncrossed nicols. Grey minerals: quartz and silicates of metals

Apart from cristobalite spheres also silicate spheres with diameters below a hundred micrometers fall around the smelter and refinery. They contain steel metals, i.e. Ni up to 4,5 wt. %, Co up to 6,5 wt. %, Cr up to 24,5 wt. % and non-ferrous metals: Zn up to 3,5 wt. %, Cu up to 1,5 wt. % (Fig. 5).

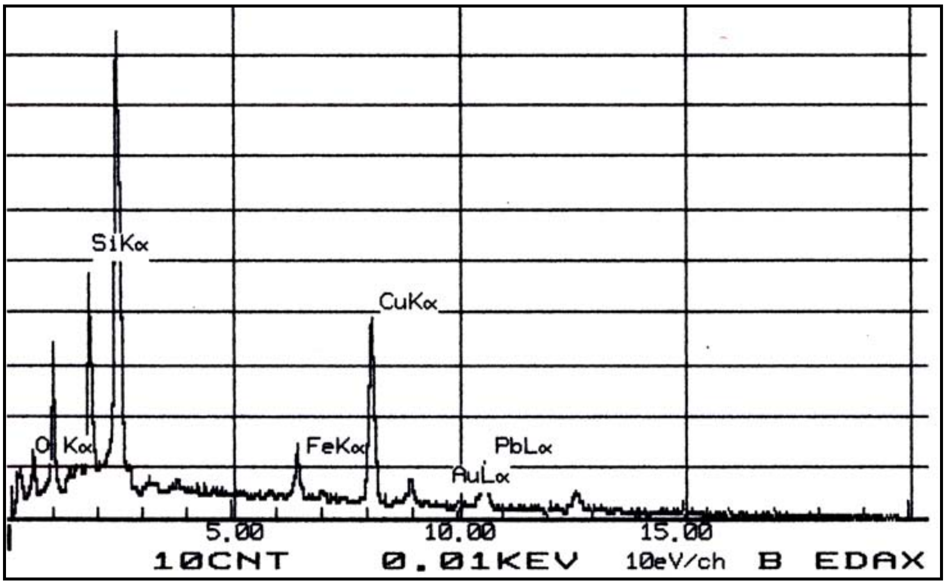

Fig. 4. EDS spectrum of a cristobalite sphere with exsolutions of Pb, Cu, Fe and Au alloys

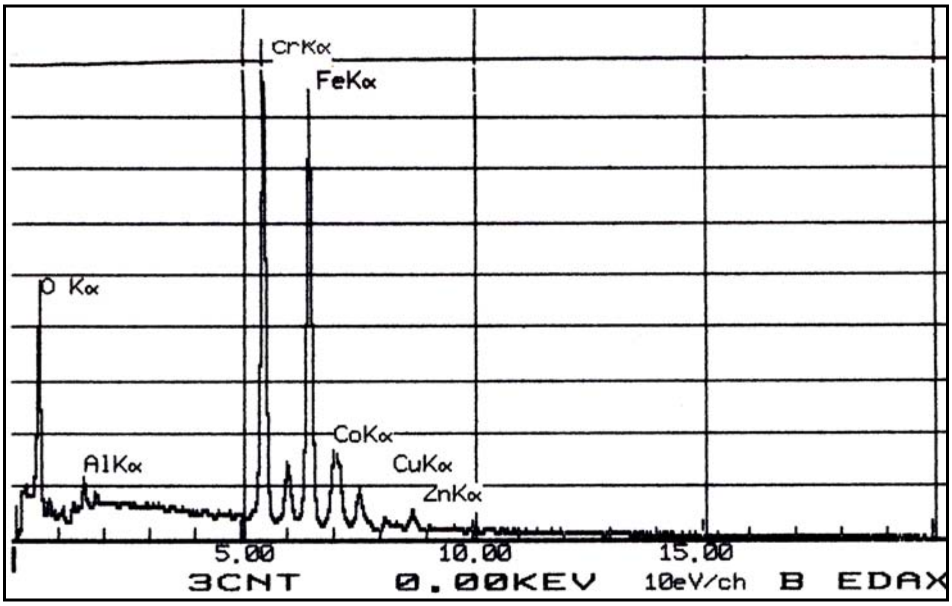

Fig. 5. EDS spectrum of a silicate sphere with exsolutions of metallurgical alloys

The distribution of the atmospheric dust is similar in the areas of Biechów (Fig.6) and Bogomice (Fig. 7). Hematite, covellite, goethite, marcasite, chalcopyrite, bornite, metallic copper, alloys of Pb and magnetite occur in both places. The main difference between the places lies mostly in the presence of fragments of Bessemer slag and metallic iron in the Bogomice area. Main ore minerals are represented by copper phases unaltered by influence of high temperature. Their structures and intergrowths are typical of the processed copper ore. The size of ore dust particles rarely exceeds 40 µm. The diameter of the main ore grains varies from 2 to 35 µm.

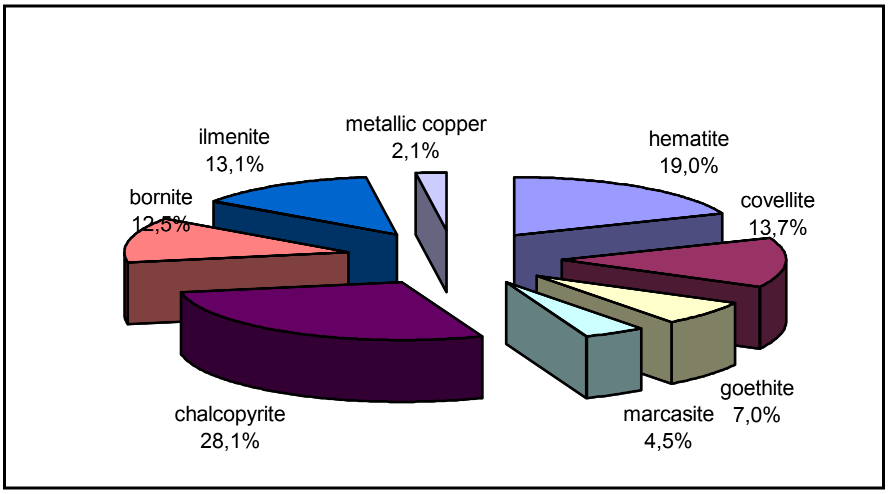

Fig. 6. Percentages of ore minerals in the Biechów area.

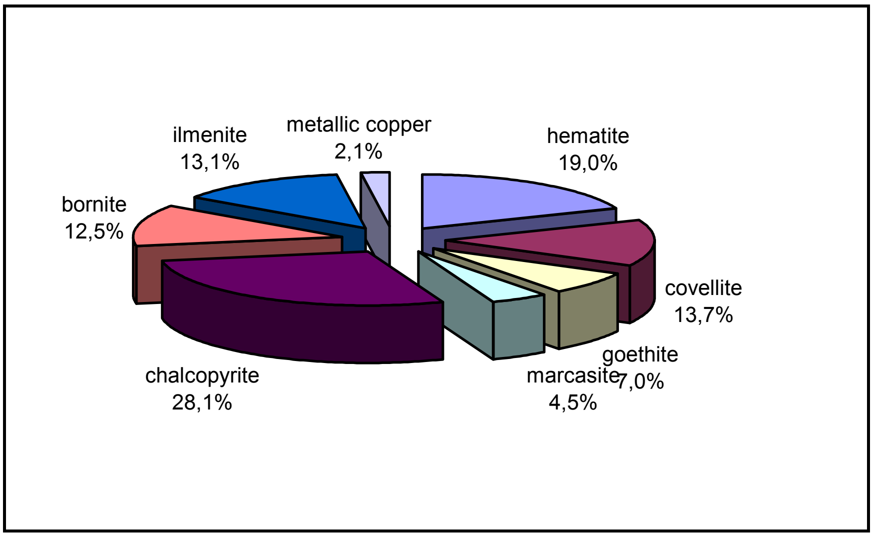

Fig. 7. Percentages of ore minerals in the Bogomice area.

In the Głogów area there are ore minerals of Fe: goethite, magnetite, hematite, and Cu: covelline, bornite, chalcopyrite, chalcocite, metallic copper, cuprite, malachite as well as marcasite, pyrite framboids, Bessemer slag, pyrrhotite, metallic iron, ilmenite and metallic silver. The biggest grains in the collected materials consist of goethite and reach 250 μm in diameter. The other ore minerals do not exceed 70 μm and their average diameter is 16 μm. The copper ore minerals do not reveal signs of melting opposite to metallic copper, cuprite, magnetite and metallic iron. The copper phases of cuprite and metallic copper are related to each other. Cuprite is usually present as rims around metallic copper spheres (Fig. 8). Metallic iron on the other hand forms tiny, below twenty micrometers in diameter, spheres in silicates (pyroxenes).

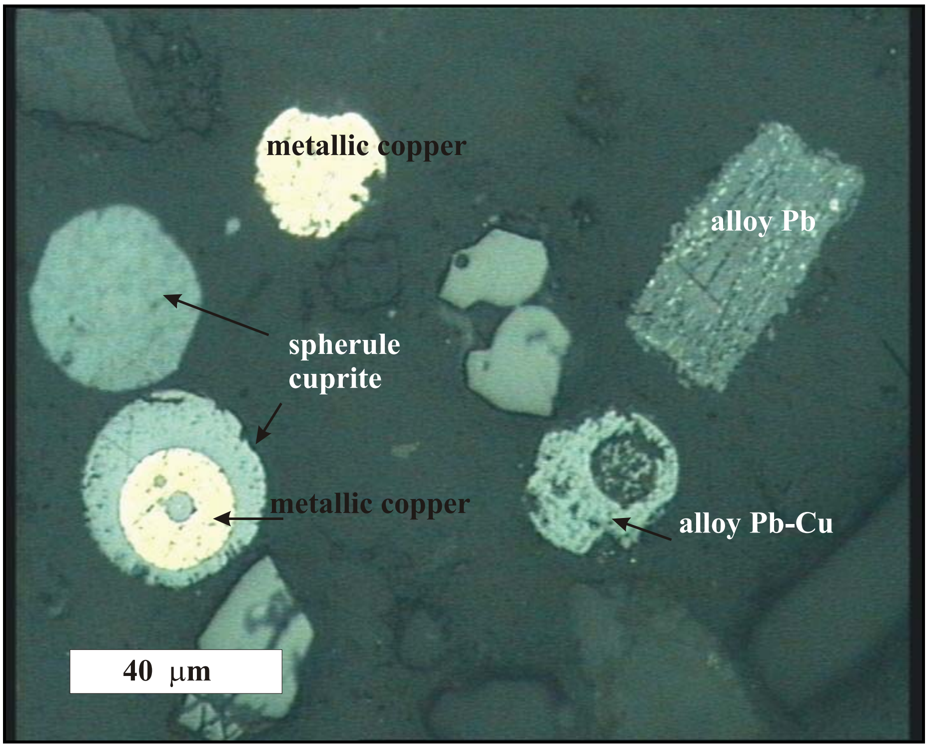

Fig. 8. Forms of anthropogenic dusts near Głogów. Reflected light, uncrossed nicols. Grey minerals: quartz and silicates

In the Głogów area a clear difference in the character of dust falls between autumn-winter and spring-summer periods (Fig 9). In autumn-winter the main ore minerals are covellite, goethite and metallic iron with bornite while during spring-summer the relative percentage changes and hematite and covellite become major constituents (Fig. 9).

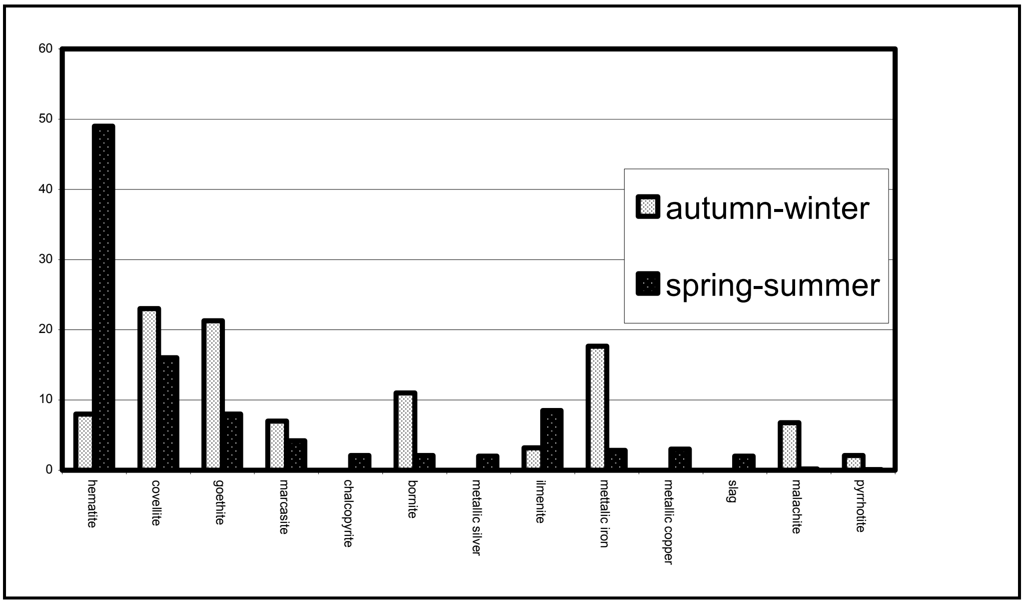

Fig. 9. Percentages of ore minerals in the investigated samples from the Głogów area

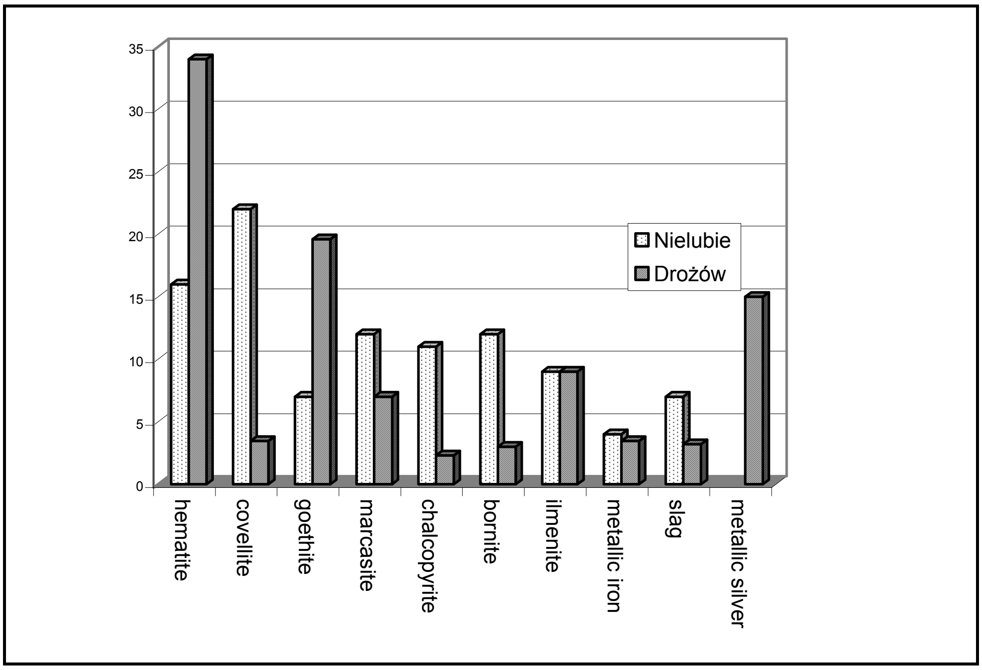

Fig. 10. Percentages of ore minerals in samples from Nielubie and Drożów

Villages of Nielubie and Drożów lie North of the metallurgical complex of Żukowice. They are located about 5 and 10 km respectively away from the metallurgical complex. Identical composition of ore minerals was detected in both places in summer 2002 and 2003. The collected dusts are dominated by fragments and spheres of hematite, ilmenite, goethite, marcasite, metallic iron, chalcopyrite, bornite, covellite, granulated (Bessemer) slag and pyrite framboids. Moreover the presence of metallic silver was detected near the Drożów village. Southern direction of metallic silver transportation was already confirmed four times since 2000. All ore minerals, except metallic iron, show typical forms. Usually they are xenomorphic due to ore milling. Only iron and metallic silver display forms different from the other phases. Metallic iron is present as spheres in magnetite or silicates while metallic silver forms broken dendrites or flat blades. Statistic relations between ore minerals are depicted in Figure 10.

SUMMARY AND CONCLUSIONS

Pollution resulting from metallurgical processes poses a threat not only on a local but also regional scale as it may be seen in the areas around metallurgical complexes in Mancziegorsk in the Kola Peninsula (Ni-Cu smelter and refinery) and Karabash (Ni-Cu smelter and refinery in the Ural Mts.). These areas belong to the most polluted zones in Europe.

According to the published data (Byrdziak et al. 1996) the main source of dust emission in the whole area of the Legnica Głogów Copper District is the HM Głogów heat plant. It emits 700Mg of dusts a year. Those dusts display a characteristic composition (Piestrzyński, Ratajczak 2000). The dusts analysed with a microscope in the present study are not related to the heat plant but to metallurgical activity. It seems however that a part of hematite observed in the polished samples may come from magnetite weathered during transport in the air. Hematite spheres display sieve structure with preserved relicts of magnetite. Such spheres are typical of coal burning processes. Structures of the other ore minerals and their chemical composition suggest their formation either as a result of copper concentrate melting or forceful ejection of milled ore fragments. The presences of intergrowths of framboidal pyrite and covellite or intergrowths of chalcopyrite with bornite clearly indicate that they are grains of copper concentrate.

Due to migration of elements in nature pollution of water, soil and air affects eventually plants and human. In the case of dust fall from metallurgical industry contamination will last in the near surface zone of the earth crust much longer than gaseous pollution. This a result of slow migration of elements incorporated in the minerals that build dust particles. The process of releasing the elements and their entering the biozone was treated in detail in geochemical publications (Polański, Smulikowski 1969; Kabata-Pendias 1993). These processes however are mostly governed by pH and Eh of the environment and proceed according to the diagrams for individual element systems (Garrels 1960; Garrels, Christ 1965; Barnes 1982, Bułach et al. 1995). Knowledge of the crystallographic form of the dust substance may allow determining the rate of migration of such pollution to the environment. The rate is related to resistance of mineral phases to weathering processes. Metals shielded by silicate cover will be cumulated in the environment longer. If however dusts are composed of fragments of ore exploited from a deposit, they will oxidise immediately, transform into soluble phases, migrate to aquifers and will be incorporated by plants. In the cases presented in the article all forms of ore minerals are unstable and disintegrate easily.

Wide spread of metallic silver on great distances from the smelter and refinery in Żukowice (Głogów, Drożów) is noteworthy. The presence of gold and silver in lead alloys from the metallurgical dusts has been monitored since 1999. The investigations carried out in the same places in 2004 confirmed that the situation had not changed. Nevertheless it still remains not clear which of the two metallurgical complexes, "Legnica" or "Głogów", is responsible predominantly for the metallic silver emission to the atmosphere.

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Głównym celem badań było scharakteryzowanie składu mineralogicznego pyłów hutniczych, opadających w rejonie hut miedzi Głogów I i II, położonych w okolicy wsi Żukowice. Badania pyłów atmosferycznych wykonane w rejonie Głogowa-Żukowic wykazały obecność niezmienionych ziarn i okruchów kruszców charakterystycznych dla rud znajdujących się w złożu LGOM. Z zakładów przemysłowych w rejonie Żukowic nie tylko wydostają się siarczki i arsenki metali: Cu, Pb, Zn, Ni ale także stopy Pb, Pb-Cu oraz metale szlachetne. Wielkość pyłów waha się w szerokich granicach od ziarn submikroskopowych do kilkuset mikrometrów średnicy. Badane pyły są niejednorodne. Najczęściej są to pojedyncze ksenomorficzne ziarna lub kryształy oraz fragmenty rudy łupkowej. Rzadziej spotykane są zrosty kruszców ze sobą. Największe okruchy składają się z blaszek semigrafitu i niezmienionych fragmentów łupka smolistego. W preparatach polerowanych stwierdzono obecność: bornitu, chalkopirytu, goethytu, chalkozynu, hematytu, kowelinu, markasytu, arsenków Ni-Co (ramelsbergitu-safflorytu), fragmentów żużla konwertorowego i szybowego, srebra i miedzi metalicznej, żelaza metalicznego, ilmenitu, magnetytu, malachitu, kuprytu, pirotynu, ołowiu metalicznego oraz różnych stopów ołowiowych. Struktury kruszców oraz ich skład pierwiastkowy świadczy o tym, że powstały albo w wyniku przetopienia koncentratu miedziowego, albo w wyniku wyrzucenia w powietrze z dużą siłą zmielonych okruchów rudy.