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Development of oxidation in Zn-Pb deposits in Olkusz area

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ABSTRACT: *Based on data obtained from drilling and on the analysis of samples taken from Pomorzany Mine, the author described intensity of the secondary alterations in ores (the level of oxidation of sulphide minerals including zinc, lead, and iron). The impact was shown of some geological factors (mineral composition, the depth of the ore nests, structural characteristics of rock mass) on the intensity and the pace of the secondary alterations in ores. The impact of tectonic systems on water circulation in the zone of oxidation and on the development of secondary mineralization was also discussed. Based on the analyses of chemical composition of several hundred Zn-Pb ore samples and on macroscopic analysis of selected samples, the primary origin of some of cerussite in the ores was pointed out. The content of selected elements (Cd, Ag, and As) as well in oxidised ores as in sulphide ores was presented. Finally, changes in mineral composition of ores in the region and their negative impact on ore processing were also indicated.*

1 INTRODUCTION

Zn-Pb ore deposits in the Silesia-Cracow region are of Mississippi Valley type (Viets et al., 1996). These ores occur in the carbonate sediments of Triassic and Devonian. The process of oxidation of Zn-Pb ores in Olkusz region (southern Poland) was already analysed by W. Zabinski (1960, 1964) and B. Radwanek-Bak (1981). Initially, oxidized ores in the horst areas were analysed and documented. The richest deposits of oxidized ores were extracted in open pits until the mid 1980s.

It is widely assumed that ore deposits at larger depths in the fault graben areas under impermeable layers of argillaceous sediments of Keuper, are only marginally oxidized. The richer deposits of ores were depleted forcing the mines to reach for deposits occurring on the peripheries. Due to the increased level of oxidation of the primary sulphides and other mineralogical changes such as enriched ores with clay minerals, the efficiency of metal extraction from the ores in the ore dressing process decreases. Determination of the changes in the mineral composition of ores occurring in the highly oxidized fault belts and karst zones and near the surface allows a more accurate assessment of the size of metal reserves in selected parts of the ore deposits.

In addition, the determination of the direction and preferred zones for the development of oxidation in rock mass delivers a useful tool for the reconstruction of hydrogeological conditions and paleomorphology of areas with ore deposits.

1.1 *Location of the investigation*

To compare the extent of secondary alterations, the chemical and mineral composition of ores from seven ore deposits in the Olkusz-Zawiercie area were analysed (Fig. 1).

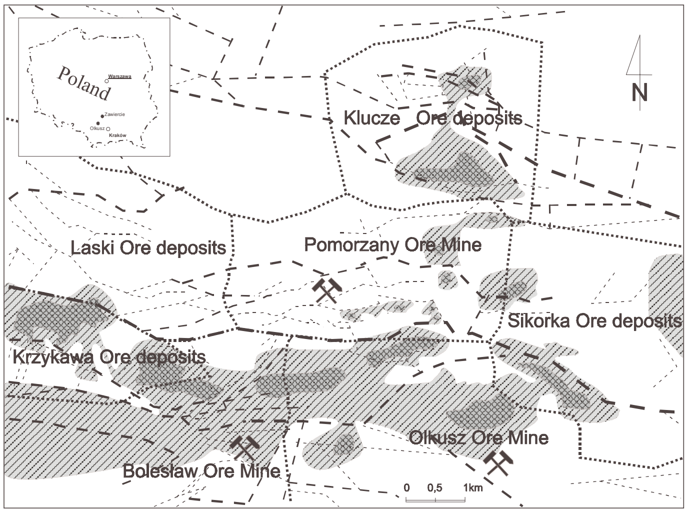

Fig. 1. Location of ore deposits in Olkusz region. The areas with oxidized ores are denoted with grey colour.

In this paper, data from 580 complete analyses were taken into account. The analyses were conducted on samples collected from both bore-holes and the Pomorzany Mine.

2 LOCATION OF OXIDATION ZONES

Heavily oxidized segments of the ore deposits can be found in horst faults that are not isolated by impermeable roof sediments of Keuper. This is a well-known phenomenon and the author chose not to discuss it in this paper.

2.1 *Tectonic fault graben areas*

The presence of ore deposits is associated with graben and horst fault structures running approximately or evenly with a parallel of latitude (W-E, WNW-ESE). Long-term impact of tectonic movements is visible through several stages of brecciation (Dzulynski & Sass-Gustkiewicz, 1978). Breccias, that have been sealed up by ores of the later stages of mineralization are not conductive to oxidizing water and oxidation of sulphides in such areas is weak.

The systems of tectonic fissures are essential determinants of the degree of water permeability in Triassic sediments and as such they play a key role in the development of zones of oxidation. Faults are epigenetic with respect to primary mineralization and therefore their impact on the consequent development of the zones of oxidation with in ore deposit is significant. Faults and accompanying fissure systems create paths of hydraulic contact through which vertical and/or horizontal permeation of descending oxidized water occur (Fig. 2a and Fig. 2b).

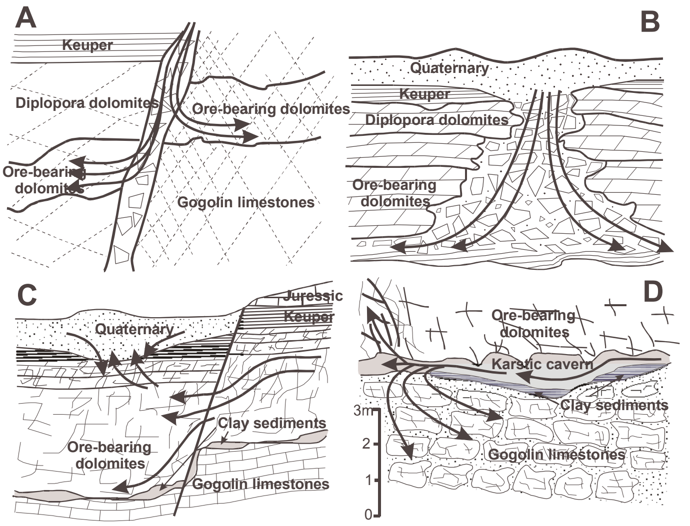

Fig. 2 Direction of oxidation development in ore deposits. A- in fault zone, B- in collapse breccia, C- in erosion gaps and sinkholes D-in surrounding of karstic cavern

It is noteworthy that the accumulation of oxidized minerals in fault fissures as well as in horizontal and vertical karst dykes is not significant, only in some distance from them irregular pockets of oxidized ores can be found. This is because the speed of the passing water and the absence of dissolved metal ions made the development of secondary Zn-Pb-Fe carbonates or oxides impossible.

The systems of fissures in the upthrown blocks of faults are characterized by a greater width than similar systems within downthrown blocks. (Cabala, 1995). This fact is of significance for oxidation - an unimpeded seepage of water into the deposits caused the creation of irregular pockets of oxidized ore within sulphide ore deposits. Orebodies within upthrown blocks of faults are more likely to occur within aeration zones where the process of oxidation develop much faster than in zones of saturation. Within the Pomorzany deposit, the majority of the isolated oxidized zones can be found in upthrown blocks of normal or pivotal faults, also in zones of fault terminations (horse tail or echelons).

Ore pockets with an enhanced galena content can be found in the peripheral areas of the deposits which can be seen on the example of the eastern parts of the Pomorzany deposit that are already being industrially explored. These ores are characterized by higher levels of oxidation than those in the central parts of the deposit.

2.2 *Oxidation of ores in vertical profile of deposit*

Oxidized ore nests are associated with: isolate faults (Fig. 2A), collapse breccias or tectonic breccias (Fig 2B), caverns (Fig. 2D), or with the presence of erosion gaps and sinkholes in Keuper cover rocks (Fig. 2C).

Oxidized ores can also be found underneath impermeable Keuper formations (Sikorka, Pomorzany) or at considerable depth in Roethian and Devonian formations (Klucze, Zawiercie). Their origin is associated with horizontal flows (fissures, interlayer joints, karst systems) of oxidizing water, and sometimes with ascent of these waters in a regime of the confined acquifer.

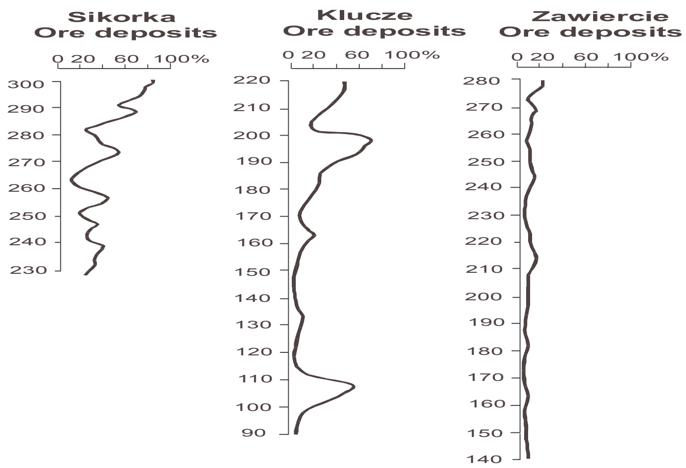

Fig. 3 Distribution setting of oxidation degree of zinc sulphides in profiles of ores.

The level of oxidation of zinc, iron, and lead sulphides in different deposits varies, which is shown by the different slopes on the diagrams (Fig. 3 and Fig. 4). In some of these deposits (Klucze) a significant level of oxidation of zinc sulphides can be observed up to the depth of 270 meters below surface (Fig. 3).

In this case oxidized zones include Devonian formations. Significant vertical differentiation of oxidation with in Klucze deposit is associated with unusually complex structure of this deposit, with the development of karst systems, breccia zones, and with a raised (in comparison to other deposits) horizontal extent of mineralisation.

Iron sulphides are the fastest oxidizing component of ores. Analysis of the level of their oxidation allows for the determination of the stage of development of the oxidation zone. Sometimes, as it is in the case with Goluchowice deposit, almost 100 per cent of the iron sulphides have turned into iron oxides. More typically, the average level of oxidation of iron sulphides varies between 40 and 80 per cent. Oxidation of iron sulphides progresses frontally from the roof to the floor of the deposit In some parts of the floor of the deposit an increased level of oxidation of iron sulphides can also be observed. This is associated with karstic and fissured development of floor sections of the deposit (Fig. 4).

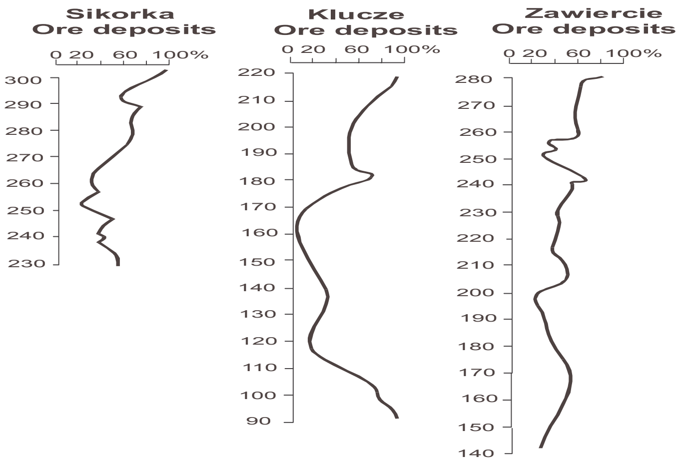

Fig. 4 Distribution setting of oxidation degree of iron sulphides in profiles of ores.

3 MINERAL COMPOSITION OF OXIDIZED ORES

Oxidized ores are defined as the types of ores in which over 30 per cent of zinc and lead occur in combination with oxygen as minerals of carbonates, sulphides or oxides.

3.1 *Primary minerals*

Zinc, lead, and iron sulphides in relic amount are present among oxidized mineral components. The proportion of content of zinc, lead, and iron sulphides in oxidized ores are different that in unchanged ore sulphides.

Galena content in the oxidized ore is 2-3 times higher than sphalerite content. Pyrite and marcasite occur only in limited quantities (Tab. 1).

Baryte is a typical primary mineral whose content does not vary due to oxidation process. In the examined samples the typical parageneses of cerussite and shell type marcasite were found. Because of the weak mobility of lead ions, there is a possibility of the development of lead carbonates during the initial phases of the oxidation. This occurs because of the influence of acidic solutions that allow the migration of Pb^{2+}ions.

Table 1. Average content of oxidized ores and sulphide ores (in percentages)

Minerals and elements	Average content in ores [%]	
	Oxidized ores n=75	Sulphide ores n=410
ZnS -sphalerite	1,57	10,91
PbS - galena	9,38	1,91
FeS_2 – marcasite & pyrite	1,27	7,67
$PbCO_3$ - cerusite	2,87	0,52
$ZnCO_3$ - smithsonite	7,59	0,51
Fe_2O_3 - limonite	3,53	1,40
$BaSO_4$ - barite	0,367	0,51
Cd & CdS - greenockite	0,0346	0,0448
Ag	0,0049	0,0028
As	0,0441	0,0451

The presence of cerussite (up to 1%) in the samples with no traces of secondary transformation of zinc and iron sulphides is difficult to explain. It is possible that a part of the cerussite has a primary origin and it developed during one of the stages of ore mineralization. Such a possibility was raised earlier by W. Zabinski (1964).

3.2 *Secondary minerals*

Smithsonite, cerussite, goethite, and lepidocrocite forming limonite accumulations belong to the group of minerals that have developed in the secondary process. Also monheoimite, hydrozincite, jarosite, thallium jarosite, gypsum, epsomite, copiapite and unstable sulphates such as melanterite and goslarite are typical for oxidized zones.

Some types of oxidized ores (e.g. cerussite ores) are characterized by a high content of non-oxidized galena and silver. For 80 per cent of analised samples the content of cerussite for 1 per cent weight content of lead is constant and falls between 0.22 and 0.26 per cent [%] (Cabala, 1996). Because of the fact that in the process of flotation grains of cerussite become waste material, the loss of lead can be expected to remain constant at the level of between 20 and 25 per cent.

3.3 *Accompanying elements*

Primary ores contain varying content of trace minerals (Viets et al., 1996). The most important of them are silver and cadmium, both of which can be recovered during processing. Silver does not create its own mineral phases. It occurs in the form of substitutions in the crystal lattice of zinc, lead, and iron sulphides. Average content of silver in oxidized ores is slightly higher than in ore sulphides (Tab. 1). This is due to the increased content of galena.

Cadmium is present mainly in the crystal structure of zinc sulphides. Only rarely does it create (in combination with sphalerite) its own isostructural sulphide - greenockite. During the process of ore oxidation cadmium is dissolved and then it can enter crystal lattice of zinc carbonate - smithsonite. In oxidized ores the concentration of cadmium can be slightly diminished due to the possibility of removal of some of the Cd^{2+} ions by the waters of the oxidation zone (Tab. 1).

Arsenic is a typical element in the ore deposits from Silesia-Cracow area. It is present with high regularity in marcasite and pyrite. Within the oxidation zone the arsenic content does not change. Because it is not released, no arsenides are formed. The arsenic is absorbed by the secondary iron oxides. The geochemical compounds of arsenic with thallium are also of interest. Both of these elements associate with iron sulphides. Because in the ore dressing all iron minerals are treated as waste, all of the elements that are associated with them (including arsenic and thallium) become flotation tailings.

4 CONCLUSIONS

Depletion of ore resources in the central parts of deposits is the main reason for undertaking the exploitation of workable reserves on the peripheries.

Deposits such as Klucze, Sikorka and neighbouring the already exploited Pomorzany Mine show higher oxidation and a considerable variability of zinc and lead sulphides oxidation. Both the mineral composition of the ore and the content of particular metals vary. The identification and development of oxidation zones allows for more accurate estimation of metal reserves and the value of deposits. Mineralogical studies of forms and modes of the occurrence of oxidised minerals can also be helpful in an ongoing adjustments of the process of ore dressing to improve the productivity of flotation of useful minerals. Exploration of oxidation zones can also be helpful to reproduce the hydrogeological conditions existing in periods just after ore deposits were formed. The change of rock tint associated with iron oxidation facilitates to follow tectonic zones in difficult mining conditions. Based on oxidation levels it is possible to assess whether tectonic zones were permeable to water passing through. Moreover, it is also indirectly possible to classify some faults as open (tension) or closed (compression) ones.

5 REFERENCES

Cabala J., 1995: Structural characteristics of tectonic horsts and grabens in the area of zinc and lead ore occurence near Olkusz. In *Mechanics of Jointed and Faulted Rock*. Balkema edited by H.P. Rossmanith .Institute of Mechanics, TU Vienna p. 335-340.

Cabala J., 1996c: Occurrence of cerussite and oxidation degree of lead sulphides in zn-pb ores of the Olkusz-Zawiercie area (in Polish, English summary) *Zesz. Nauk. Polit. Śląsk. Górnictwo* z. 230 Nr 1343 s. 223-242

Dzulynski, S. & M. Sass-Gustkiewicz 1978. Ore breccias in the Triassic rocks of the Cracov-Silesian region (Poland). Oesterreichi- sche Akadem. *der Wiss. Schriftr. der Erdwiss. Komm*. 3:125-130. Wien-New York.

Radwanek B., 1981: Characteristic of watering zone of Zn-Pb ores in Boleslaw and Olkusz region. *PhD Th*. (in Polish, English summary). Arch. AGH Kraków.

Viets J.G., Leach D.L., Lichte F.E., Hopkins R.T., Gent C.A., Powell J.W., 1996: Paragenetic and minor-and trace-element studies of Mississippi Valley-type ore deposits of the Silesian-Cracow district, Poland. *Prace Inst. Geol.,* 154, p. 51-71.

Zabinski W., 1960: The mineralogical characteristic of the oxidation zone of Silesia-Cracow zinc and lead ore deposits. (in Polish, English summary). *Prace Geol.,* nr 1, Wyd.Geol. W-wa.

Zabinski W., 1964:Geochemical studies of lead and zinc ores in oxidation zones from Silesian-Cracow region. (in Polish, English summary)] *Prace Geol.,* nr 19, Wyd. Geol. W-wa.