Cabała J & Bzowska G: 2008. Sulphate speleothems in Pomorzany Zn-Pb ore mine, Southern Poland. Kras i Speleologia 12 (XXI): 59-76.

Jerzy Cabała, Grażyna Bzowska

University of Silesia, Faculty of Earth Sciences

41-200 Sosnowiec, Będzińska 60

3 tab, 2 figs, 8 phots, 20 p

Sulphate speleothems in Pomorzany Zn-Pb ore mine, Southern Poland

Abstract

Underground mining of Zn-Pb ore deposits stimulates the development of acid mine drainage (AMD) processes. In conditions of high humidity (92-95%) sulphate forms such as stalagmites, stalactites and others are found on side walls of excavations. They can increase in size up to 2 m and their colours are white, greenish or yellow. These forms comprise mainly epsomite and melanterite minerals including other sulphates such as hexahydrite, pentahydrite, chvaleticeite, starkeyite, szomolnokite, rozenite, copiapite, boyleite, bianchite, anglesite and gypsum. A lowering of the humidity level may cause a change in the mineralogical composition of sulphate minerals, e.g., hexahydrite can transform into pentahydrite and quite often into tetra-hydrous starkeyite and rozenite. These minerals are only stable in conditions of high mine air humidity and an increase in mine water inflow results in dissolution and water pollution with sulphate ions and heavy metals. ESEM analyses revealed that sulphate speleothems included numerous sub-microscopic sulphides (up to 200 μm) such as galena, sphalerite, piryte, markasite and carbonate such as smithsonite, cerrusite and also hemimorfite and native sulphur. Sulphate contents in non-exploited Zn-Pb ores range from 0.05 to 4% mass fraction and even up to 8% in oxide ores occurring near the drainage zone (e.g., Klucze ore). The sulphates are characterized by high contents of metals such as Zn (up to 11 594 $mg{\cdot}kg^{-1}$), Fe (78 709 $mg{\cdot}kg^{-1}$), Cd (24.8 $mg{\cdot}kg^{-1}$) and Mn (322.4 $mg{\cdot}kg^{-1}$), which is why these metals can be activated during the sulfide oxidation phase.

Introduction

Site description

The aim of the study is to examine the present sulphate dripstones occurring in the underground excavations in the Pomorzany Zn-Pb mine. The Pomorzany ore deposits are situated in the area of the Pomorzany graben (Fig.1). The ore deposits are exploited using pit shafts which are located several kilometres west of the town of Olkusz. The mine has been under operation since 1968 and the constant decrease in recoverable reserves results in imposing limitations on the prospects of further exploitation in the next 10-12 years. In the mine two main systems of the exploitation have been applied - a pillar-chamber system and a shortwall one. The distinct advantage of applying these is to obtain a greater mobility of mine faces as well as almost complete exploitation of ore deposits. The exploitation activity is carried out using a hydraulic filling. The pillar-chamber systems are applied to exploit a single layer up to 6 m in thickness, whereas the shortwall systems can be used for a multilayer deposit. Before the 1990s there were other systems in use, for example a chamber system with a falling roof and others such as a 'subshelf' system with a falling roof and an "85 Pomorzany" which were peculiar to the Pomorzany mine only (Cabała, Konstantynowicz, 1999).

The excavation are conducted mainly in ore-bearing dolomites, and rarely in limestones and marls. When exploiting a new part of a deposit, it is very important to drain it before the mine activity takes place. The exploitation is connected with draining the water in large amounts out of the fissured and karstic rock mass (Różkowski et al., 1997). The water is pumped and drained into the water-course. In consequence of mining activities the secondary fracturing in roof rocks occurs and the fissuring of the rock mass increases simultaneously. The considerable hydration of the rock mass, the permeable nature of rock overlayers as well as fissured and karstic rock mass make a substantial contribution to foster the development of sulfide oxidation and the dissolution of carbonate rocks.

Methods

Forty samples of sulphate minerals were collected from dripstone forms, sulfide ores, oxidized ores and internal sediments of karst space. These materials were examined using an Environmental Scanning Electron Microscope (ESEM) with a back-scattered electron (BSE) detector (30 XL Philips type). The use of Electron Dispersive Scanning (EDS) analytical unit was used in this research. In micro-zones 160 EDS analyses were done.

The mineral composition of the samples was identified by an X-ray diffractometer (Philips PW 3710) using Co Kα X-ray (at 45 kV of voltage and 30 mA of intensity). The impulse counting time was 1-2 sec and the counter track was 0.02°. The amount of sulphate content in Zn-Pb ores was determined on the basis of 618 chemical analyses (spectroscopic and rentgenographic ones) of the samples taken from Olkusz-Zawiercie area and were done in the Laboratory of Geological Company in Cracow, whereas X-ray and microscopy examinations were carried out at the Faculty of Earth Sciences, Silesia University in Sosnowiec.

References

Alpers C.N., Blowes D.W., Nordstrom D.K., Jambor, J.L., 1994: Secondary minerals and acid mine-water chemistry, In: The Environmental Geochemistry of Sulfide Mine-wastes. Eds Blowes, D.W. and Jambor, J.L.,., Mineral. Assoc. Canada Short Course Notes, v. 22: pp. 249-269.

Andrejchuk V.N. Klimchuk A.B., 2001: Geomicrobiology and Redox Geochemistry of the Karstfield Miocene Gypsum Aquifer, Western Ukraine: The Study from Zouloushka cave. Geomicrobiology Journal, 18, pp. 275-295.

Buckby T., Black S., Coleman M.L., Hodson M.E., 2003: Fe-sulphate evaporative mineral precipitates from the Rio Tinto, southwest Spain. Mineralogical Magazine, vol. 67 (2), pp. 263-278.

Cabała J., Konstantynowicz E., 1999: Silesian-Cracowian Zn-Pb ore deposits: Character and prospects for exploitation (in Polish). In: Perspective of ore and economic geology in Poland. Prace Naukowe UŚ nr 1809, pp. 76-98.

Cabala J., 2001: Development of oxidation in Zn-Pb deposits in Olkusz area. In: Mineral Deposits at the Beginning of the 21st century. Balkema, pp. 121-124.

Cabala J., E. Teper, Teper L., 2004a: Mine-waste impact on soils in the Olkusz Zn-Pb ore district (Poland). In: Mine Planning and Equipment Selection 2004. Balkema Publ, pp. 755-760.

Cabala J, Teper E., Teper L., Małkowski E. Rostański A., 2004b: Mineral composition in rhizosphere of plants grown in the vicinity of a Zn-Pb ore flotation tailings pond. Preliminary Study. Acta Biologica Cracoviensia Series Botanica 46, pp. 65-74.

Cabała J., 2005: Acid drainage of postflotation wastes from Zn-Pb ores; changes of mineral composition in rhizosphere zones developed on tailings pond. (in Polish). Zesz. Nauk. Polit. Śl. 1690, Górnictwo, 267 pp. 63-70.

Chou, I.-M., Seal II R. R., 2003: Determination of epsomite-hexahydrite equilibria by the humidity-buffer technique at 0.1 MPa with implications for phase equilibria in the system $MgSO_4$-H_2O. Astrobiology 3, pp. 619-630.

Da Silva G., 2004: Relative importance of diffusion and reaction control during the bacterial and ferric sulphate leaching of zinc sulphide. Hydrometallurgy 73, pp. 313-324.

Edwards K.J., Bond P.L., Druschel G.K. McGuire M.M., Hamers R.J., Banfield J.F. 2000: Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California. Chemical Geology, 169, pp. 389-397.

Fowler T.A., Holmes P.R., Crundwell F.K., 2001: On the kinetics and mechanizm of the dissolution of pyrite in the presence of Thiobacillus ferrooxidans. Hydrometallurgy 59, pp. 257-270.

Hill C., Forti P., 1997: Cave Minerals of the World. National Speleological Soc., Inc.

Jambor, J.L., Nordstrom, D.K., And Alpers, C.N., 2000: Metal-sulfate salts from sulfide mineral oxidation: In: Sulfate minerals: crystallography, geochemistry, and environmental significance, Reviews in Mineralogy and Geochemistry. Eds Alpers, C.N., Jambor, J.L., Nordstrom, D.K., v. 40, pp. 305-350.

Komosa A., 1994: Flotation investigation markasite-galena-sfalerite system. (in Polish) Rudy Metale 39, 7 pp.184-187.

Kubisz J., 1964: Studies on supergene sulphate minerals occurring in Poland (in Polish). Prace. Geol., 26, Wyd. Geol. 73 p.

Kubisz J., Żabiński W., 1958: The jarosites from the Silesia-Cracow zinc and lead ore deposits. *Bull. Acad. Pol. Sc.,* vol VI, 12.

Mayer W, Sass-Gustkiewicz M., 1998: Geochemical characterization of sulphide minerals from the Olkusz lead-zinc ore cluster, Upper Silesia (Poland), based on laser ablation data. *Mineralogia Polonica* 29, 2, pp. 87-105.

3

Różkowski A., Chmura A., Siemiński A., 1997: Utilizable underground water of the Upper Silesian Coal Basins and its borders (in Polish). Prace PIG CLIX Warszawa.

Sracek O., Choquette M., Gelinas P., Lefebvre R., Nicholson R.V., 2004: Geochemical characterization of acid mine drainage from a waste rock pile, Mine Doyon, Quebec, Canada. Journal of Contaminant Hydrology, 69, pp. 45– 71.

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 IG, 154, pp. 51-71.

Żabiński W., 1958: Epsomite and melanterite from Bolesław near Olkusz. Bull. Acad. Polon. Sci., Ser. Sci. chim. , geol. et geogr. VI.

Żabiński W., 1960: The mineralogical characteristic of the oxidation zone of Silesia-Cracow Zinc and Lead ore deposits. (in Polish) Prace Geol., 1, Wyd. Geol. 99 p.

Figure captions

Fig. 1 Location of the Pomorzany ore deposit and its cross-section, the sketch of a heading with sulphate speleothems. Q- Quaternary, J – Jurassic, T_3- Keuper, T_2^2- Diplopora dolomites, T_2 obd - Ore-Bearing dolomites, T_2^{1III-V} Górażdże, Terebratula and Karchowice Beds, T_2^{1I-II} - Gogolin limestones, T_1^3- Roet, dolomites, P – Permian.

Fig. 2. Bar charts of Ca-Mg-Fe-Zn sulphate content in Zn-Pb ores. Klucze n = 46, Pomorzany n = 91, Zawiercie n = 106 (n - numbers of observation).

Phot. 1 Sulphate speleothems occurring in exploited excavations in the Pomorzany Zn-Pb mine. A – epsomite stalactites (white), B - epsomite stalactites (white), copiapite and ferrohexahydrite (yellow), C - a melanterite stalactite (green), copiapite and siderotile (yellow and red), D – a melanterite stalagmite.

Phot. 2 Sulphate speleothems occurring in exploited excavations in the Pomorzany Zn-Pb mine. A – Mg-sulphates & Fe-sulphates. B – halotrichite, C – epsomite stalactites (white) and melanterite stalaktites (green), D – epsomite and melanterite stalactites, E – Fe-sulphates with rosenite and szamolnokite composition, F – blooms and efflorescence of Mg-sulphates with pentahydrite composition (white) formed in excavations where mining machines were used.

Phot. 3 Sulphate speleothems. A- Mg sulphate, B- Mg,Fe sulphate, C – native sulphur

Phot. 4 Sulphate speleothems. A- Mg sulphate, B- Mg,Fe,K sulphate, C – Mg,Fe sulphate

Phot. 5 Sulphate speleothems. A- Mg,Ca,K sulphates, B - Mg,Ca,K sulphates

Phot. 6 Sulphate speleothems. A - K,Mg sulphates, B- Mg sulphates.

Phot. 7 Sulphate speleothems. A- Mg sulphate, B- Ca sulphate, C – Fe sulphate with Cl.

Phot. 8 Sulphide minerals in sulphate speleothems. I: A –Zn sulphides, B - Zn sulphates, C – Mg sulphates, II: A - Pb sulphates & Pb sulphides, B – Zn sulphates & Zn sulphides, C – Mg sulphates, III: A - Sn oxide, B- Mg sulphates, IV: A- Pb sulphides & Pb carbonate with Ag.