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OXIDATION PRODUCTS OF ARSENOPYRITE AND OTHER SULFIDES FROM THE ORE DEPOSIT SASTAVCI, SERBIA

Ivana Jelić[1a], Jovica Stojanović[1b], Aleksandar Pačevski[2a], Nikola Vuković[1c], Alena Zdravković[2b], Ana Radosavljević-Mihajlović[1d], Vladan Kašić[1e]

[1] Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey 86, Belgrade, Serbia

[2]Faculty of Mining and Geology, University of Belgrade, Đušina 7, Belgrade, Serbia

[1a] i.jelic@itnms.ac.rs, https://orcid.org/0009-0000-9901-9323;
[1b] j.stojanovic@itnms.ac.rs, https://orcid.org/0000-0002-2752-6374;
[2a] aleksandar.pacevski@rgf.bg.ac.rs, https://orcid.org/0009-0001-9682-4738;
[1c] n.vukovic@itnms.ac.rs, https://orcid.org/0000-0002-3607-5907;
[2b] alena.zdravkovic@rgf.bg.ac.rs, https://orcid.org/0000-0001-5048-4769;
[1d] a.radosavljevic@itnms.ac.rs, https://orcid.org/0000-0002-9194-161X;
[1e] v.kasic@itnms.ac.rs, https://orcid.org/0000-0002-4430-567X

Abstract

The dominant sulfide minerals of the Pb-Zn deposit Sastavci are arsenopyrite, galena, and sphalerite. Oxidation of arsenopyrite can lead to the release of arsenic, a highly toxic environmental element. Oxidation products of arsenopyrite and other sulfides, present in the ores themselves as well as on the surfaces of samples, were analyzed by the OL microscopy in reflected light, SEM-EDS, and XRPD methods. It was established that scorodite and Fe sulfo-arsenates are the main alteration products of arsenopyrite. The Zn- and Mn-sulfates form crusts and aggregates on the surfaces of some samples. The conclusion is that the main concentrations of released As are found in scorodite, a relatively stable mineral in the surface conditions, and to a lesser extent in arsenolite.

***Keywords**: oxidation products, scorodite, Fe sulfo-arsenate, sulfates, Sastavci*

1. INTRODUCTION

Sulfide and sulfosalts of arsenic are considered as the primary natural environmental pollutants of this highly toxic element. Through their oxidation, As reaches hydrothermal and meteoric solutions, and then it can migrate, be transported and re-precipitate depending on the existing geochemical conditions of the environment [1]. Arsenopyrite, as the main carrier of arsenic among all sulfides, is a frequent companion of Pb-Zn deposits and other types of ore in which it represents tailings and even a harmful component that is deposited in the ore tailings during ore processing. Like most other sulfides, under the influence of atmospheric conditions, i.e., in an oxidizing environment, the transition of As(-I) to As(III) or As(V) occurs enabling the formation of certain secondary arsenic minerals [2]. As a result, arsenic, a serious environmental pollutant, is released. Scorodite is one of the main alteration products of arsenopyrite. Therefore, it is important to study the oxidation products of arsenopyrite both in the ore and in tailings. Its origin is attributed to the dissolution of arsenopyrite under conditions of surface oxidation (by weathering), while the hydrothermal origin of this secondary

mineral is suggested in the paper [3]. Scorodite, as a secondary phase in the ore tailings, is the subject of numerous studies [4,5,6], mainly because it represents the most suitable phase for arsenic scalding due to its stability in a wide range of surface conditions [7,8,9].

This study presents the mineralogical characterization of weathering alteration products of sulfide paragenesis from the Sastavci ore deposit.

2. MATERIALS AND METHODS

2.1 Materials

Sampling of the Pb-Zn ore deposit Sastavci was carried out during a field visit in 2017. The surface mine of this deposit consists of four horizons (levels). In the middle of the first level, there are piles of excavated material. For this study, samples were collected both from the mentioned piles and different parts of the surface mine.

2.2 Methods

The polished sections were first investigated by the polarized light microscopy in reflected light (OM: Leitz wetlzar – ORTOLUX II pol-MK), to determine the association of minerals. During this analysis, a more intense presence of arsenopyrite oxidation products was found. As their reliable determination is not possible only with the method of polarization microscopy, the separation of these minerals was done by a manual selection under a stereomicroscope on previously crushed material. This separation was necessary in order to obtain the purest possible concentrates, which were later used for the XRPD and SEM analyses.

2.2.1 Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS)

The SEM analysis was carried out at the Institute for Technology of Nuclear and Other Mineral Raw Materials (ITNMS), using a JEOL JSM–7001F field emission scanning electron microscope (SEM), equipped with an INCA energy–dispersive X–ray analysis unit (EDS). An acceleration voltage of 20 kV and internal standards with detection limit ~0.1 wt. % were used for the analyses. The analyzed samples were coated with carbon (15 nm thick layer, density 2.25 g/cm^3).

2.2.2 X-Ray Powder Diffraction (XRPD)

The X-ray diffraction method was used to determine the qualitative mineralogical composition. The XRPD pattern was obtained using a PW 1710/1820 automated diffractometer (Philips, Eindhoven, The Netherlands) using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite

monochromator and Xe-filled proportional counter. The diffraction data were collected over the range 5 ─ 65° 2θ, counting for 1 s per 0.02° step. The divergence and receiving slits were fixed at 1 and 0.1, respectively. All the XRPD measurements were performed at room temperature in a stationary sample holder.

3. RESULTS AND DISCUSSION

Studied samples from the Sastavci ore deposit contain arsenopyrite, galena, and sphalerite as the dominant sulfides, while pyrite and chalcopyrite occur to a lesser extent. Significantly subordinate, Pb-sulfosalts (with or without As and Sb) and bournonite are present. The tailing minerals are represented mainly by silicates. The secondary oxidation products of arsenopyrite and other sulfides were determined both in the ore samples themselves and in the form of thin crusts and aggregates on the surface of samples.

The optical microscopy in reflected light and SEM-EDS method showed that scorodite ($Fe^{3+}AsO_4 \cdot 2H_2O$) is one of the main oxidation products of arsenopyrite. Scorodite occurs in the form of cryptocrystalline aggregates that cement the arsenopyrite crystals and fill cracks and cavities in this mineral. Anglesite is determined as the micro-secondary product of oxidation that occurs in the small amounts.

Scrums separated under stereomicroscope from the surface of samples were analyzed by the SEM-EDS method as well as by X-ray diffraction on the powdered samples (XRPD). The yellowish-orange scrums are represented by the thin crusts and botryoidal- to plate-like aggregates forming the clusters. Morphology of white scrums can be described by the appearance of spherical aggregates, feathery and efflorescence-like.

According to these analyses, except for certain sulfide phases and gypsum (fig. 1a), Fe-arsenate as scorodite or its dimorph - parascorodite, as well as iron sulfo-arsenate and probably the amorphous phases of this composition, are the main constituents of the yellowish-orange scrums (table 1). Phases that, according to their semi-quantitative chemical composition and morphology, could correspond to tooeleite $Fe^{3+}_6(As^{3+}O_3)_4(SO_4)(OH)_4 \cdot 4H_2O$ or pitticite $Fe^{3+}_2(AsO_4)(SO_4) \cdot (H_2O)$, sarmientite $Fe^{3+}_2(AsO_4)(SO_4)(OH) \cdot 5H_2O$ and angelellite $Fe^{3+}_4(AsO_4)_2O_3$ occur in a lesser extent. The mentioned phases could not be recorded by the XRPD method, either due to their too low concentration in the analyzed sample (below detection limits for this method), or due to the low degree of crystallinity. The analyzed white scrums (Figure 1b, Table 2) mainly consist of gunningite $ZnSO_4 \cdot H_2O$, apjohnite $Mn^{2+}Al_2(SO_4)_4 \cdot 22H_2O$, phases between apjohnite and dietrichite $(Zn,Fe^{2+},Mn^{2+})Al_2(SO_4)_4 \cdot 22H_2O$, while gypsum $CaSO_4 \cdot 2H_2O$, arsenolite As_2O_3 and anglesite $PbSO_4$ occur in smaller amount.

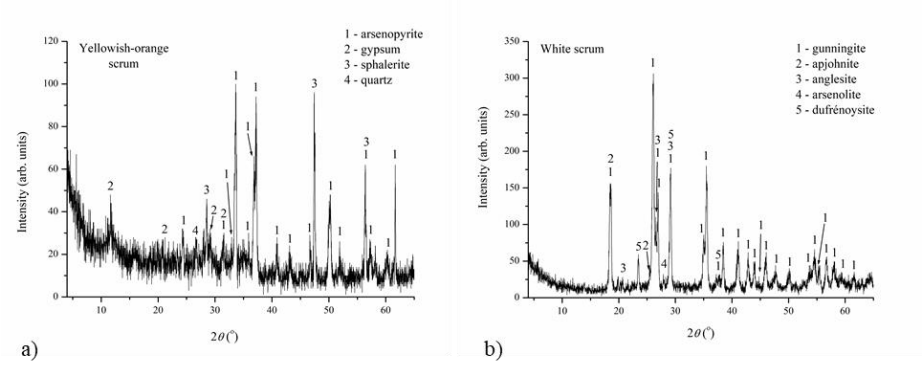

Figure 1. *XRPD diffractograms of the scrums separated from the surface of representative samples from the Sastavci ore deposit: (a) Yellowish-orange scrum; (b) White scrum*

Table 1. *SEM-EDS analysis of the yellowish-orange scrum separated from the surface of representative sample from the Sastavci ore deposit*

Element [wt %]	O	S	Ca	Fe	As	Sb	Total
Scorodite/Parascorodite	43.38			23.84	32.78		100.00
Fe sulfo-arsenate	13.39	17.34	0.22	32.01	36.37	0.67	100.00
Tooeleite/Pitticite	36.65	6.68	0.48	29.61	26.58		100.00
Sarmientite	40.34	6.70		31.17	21.79		100.00
Angelellite	28.76	2.66		41.97	26.00		100.00

Scorodite or its dimorph–parascorodite occurs in the form of spherical and plate grains intergrown with other phases present in the studied sample. Tooeleite and/or amorphous pitticite, sarmientite and angelellite are present in the aggregates, made of similar forms. Fe sulfo-arsenate occurs in the form of phases with different ratios of constituent elements, mostly in the form of coatings and cryptocrystalline aggregates on arsenopyrite.

Table 2. *SEM-EDS analysis of white scrum separated from the surface of the representative sample from the Sastavci ore deposit*

Element [wt %]	O	Al	S	Ca	Mn	Fe	Zn	As	Pb	Total
Gunningite	52.78		15.71		5.05	0.87	25.59			100.00
Gypsum	53.33		18.99	22.80			4.87			100.00
Apjohnnite-Dietrichite	60.66	9.28	17.40		4.51	0.79	5.15	2.21		100.00
Arsenolite	74.72							25.28		100.00
Anglesite	22.91		10.94						66.15	100.00

Gunningite occurs in the form of cryptocrystalline aggregates closely intergrown with the other phases, present in the studied sample. Arsenolite is observed in the form of irregular grains and crystals up to 15 μm in size. The apjohnite-dietrichite matrix occurs in the form of phases with different proportions of constituent elements. A precise determination of this phases could not be done due to close intergrowth and small grain size of its constituents.

4. CONCLUSION

Based on the above, it can be concluded that the arsenopyrite oxidation products are significantly present in the Sastavci ore deposit. According to the results, obtained by the optical and electron microscope studies, the most abundant secondary minerals are represented by scorodite and Fe sulfo-arsenates, while arsenolite occurs to a lesser extent. Furthermore, using the XRPD method, the presence of Zn- and Mn-sulfates were determined, among which gunningite occurs in the largest amount. On the basis of the structural-textural characteristics of the investigated mineral assemblage, it can be concluded that the products of oxidation in the Sastavci ore deposit were formed due to the weathering processes. The main concentrations of arsenic, released during oxidation processes, are found in scorodite, a relatively stable mineral in the surface conditions, and arsenolite, but to a lesser extent.

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