Physicochemical Problems of Mineral Processing, 40 (2006), 89-98
Fizykochemiczne Problemy Mineralurgii, 40 (2006), 89-98

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PETROGRAPHICAL AND MINERALOGICAL CHARACTERISTICS OF THE METALLURGICAL SLAG FROM THE DÖRSCHL FURNACE (GŁOGÓW FOUNDRY, POLAND)

Received March 15, 2006; reviewed; accepted May 15, 2006

Lead metallurgical slag from the Dörschl furnace resembles magmatic rocks with respect to the mineral composition and petrographic structure. The majority of mineral phases in lead metallurgical slag are not 'stoichiometric' chemical compounds present in natural conditions. The slag studied contains Cu and Cu+Fe sulfides, i.e. cubanite, covellite, bornite and chalcopyrite. The most Cu-rich phase in the lead metallurgical slag is cubanite (16 - 20 % wt.). Cu is present also in the form of inclusions of metallic copper in silicates. Zinc is mostly present in the form of sulfides (sphalerite) and silicates (willemite). Iron occurs mainly as metallic iron of various composition, magnetite, phayalite and pyrrhotite. Magnetite forms tiny inclusions in silicates of phayalite type and in rhombic pyroxenes. Lead is mostly present in the form of Pb alloys with Ag, Cu, Zn. Arsenic present in the slag was captured by the crystallizing metallic iron and incorporated in its crystal lattice. The slag contains also a minor quantity of metallic silver and molybdenite. The knowledge of mineral phases composed of non-ferrous metals, i.e. Zn, Cu and Pb may facilitate the design of methods for their recovery. Thus a waste product that is arduous to the environment and deposited on a heap may become a valuable anthropogenic source of these metals.

Key words: metal alloys, ore minerals, metallurgical slag, furnace Dörschl, industrial waste, petrography and mineralogy of lead metallurgy slag

INTRODUCTION

Lead metallurgical slag from the Dörschl furnace resembles magmatic rocks with respect to the mineral composition and petrographic structure. The slag is an analogue of magmatic rocks present in the Earth’s crust. The majority of mineral phases in the lead metallurgical slag are not 'stoichiometric' chemical compounds present in natural conditions. Due to their fast crystallization process these mineral phases may be regarded as unstable. The elemental composition of the chemical compounds under study is much different from that of their analogues present in ores. Due to their

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physical and optical properties, the metal-bearing mineral phases will be referred to in this paper as ore mineral by analogy to mineral present in ores.

The studies were concentrated on the description of ore minerals and metal compounds in slag from the Dörschl furnace in the “Głogów” Foundry (copper metallurgy), and on the determination of crystallographic forms in which the main chemical elements are concentrated in the process of lead smelting. The knowledge of mineral phases composed of non-ferrous metals, i.e. Pb, Zn and Cu may facilitate the design of uncomplicated methods for their recovery. Thus a waste product that has been deposited on a heap may become a valuable anthropogenic source of these metals. The transition from waste to a component of anthropogenic deposit shall reduce negative impact on the environment and decrease the related cost of waste disposal.

METHODS

Samples of these slags were obtqined for investigations in 2002 and 2003, during the study of metallurgic dusts in the vicinity of “Głogów” Foundry (Grech 2002, Wójcik 2003, Muszer 2004). Samples from 2002 and 2003 years were mixed in the proportion of fifty to fifty per cent. Also 1.5 kg sample of the lead metallurgical slag was taken to petrographical and mineralogical investigations.

Table 1. Outputs of a lead metallurgical slag sample

Fraction	γ %	non-magnetic fraction	γ % 0.6 T	γ % 0.9 T
>0.125	63.83	14.61	11.65	73.74
<0.125	36.17	----	4.52	95.48
total	100,00			

In order to prepare the lead metallurgical slag for the investigations it was ground in a crush mill (Fritz’s Mill) and separated into two grain-size fractions: >0.125 mm and < 0.125 mm (Tab. 1). In order to determine the character of ore minerals that reveal magnetic properties, magnetic concentration was carried out (in dry state; 5 cycles of concentration). The enrichment was performed with the use of permanent magnets with magnetic induction 0.6 T and 0.9 T. After separation with the magnet of components revealing strong and weak magnetic properties, polished sections for microscopic investigations in the reflected light were prepared from individual grain-size fractions, i.e. >0.125 mm and <0.125 mm, from five products received for the study. The sections were prepared according to the standard method for metal ore samples (Muszer 2000). Polishing of the study material was performed on polishing cloths (Struers DP-Mol, DP-Dur and DP-Nap) while applying strictly defined grain sizes of diamond polishing pastes.

The polished sections were investigated under the microscope in the Laboratory of Mineral Raw Materials at the Institute of Geologic Studies of the Wrocław University.

The studies in reflected light were performed with the use of Nikon Optiphot 2-Pol microscope. Planimetric analysis and the Lucia M programme was used in the quantitative analysis of ore minerals. The proportion of metals in sulfides and orthosilicates was determined with the use of microchemical analysis. The elemental composition of minerals was studied with the use of scanning microscopes SEM 515 (Philips) and JOEL JSM-55800LV equipped with an X-ray spectrum analysis attachment. These investigations were carried out at the Institute of Low Temperature and Structure Research (Polish Academy of Sciences) in Wrocław and at the Wrocław University of Technology.

THE QUALITATIVE AND QUANTITATIVE CHARACTERISTICS OF THE LEAD METALLURGICAL SLAG

The charge for lead smelting consists of lead slag from the shaft process, converter ashes, electro-furnace ashes, converter slag and lead slag from Kaldo furnace (Table 2). The per cent share of individual components in the smelting process varies in relation to the quantity of the furnace charge.

Table 2. The contents of metals in metallurgical waste (Pluciński et al. 1996)

Component	Slag from shaft furnaces	Converter ashes	Electro-furnace ashes	Converter ashes	Slag from Kaldo furnace
Pb	44.4	46.37	44.58	64.24	56.4
Cu	1.67	0.87	1.72	1.01	1.06
Zn	6.1	8.17	16.34	1.82	-
As	3.22	2.59	0.98	6.67	1.24
Sb	0.03	0.01	0.052	0.09	4.9
Bi	0.034	0.02	0.0078	0.021	0.24
S_{og}	10.9	11.3	1.85	4.58	-
Fe	0.7	0.2	0.23	0.06	-
SiO_2	4.4	0.2	4.72	2.56	9.04
Na_2O	0.4	0.4	1.2	0.23	-
K_2O	1.9	0.4	12.7	0.18	-
C_{org}	13.55	-	1.83	0.22	-
C_{org}	11.27	-	-	-	-
Cl	1.5	-	0.03	0.1	0.2
Cd	0.015	-	0,12	-	-
Ag	0.012	0.045	0.007	0.007	0.21
Hg	0.001	-	-	-	-
Re	0.013	0.003	0.0006	-	-
Main Pb-bearing component	PbS	$PbSO_4$	PbO	PbO	$PbO \cdot SiO_2/2PbO \cdot SiO_2$

During the process of smelting of crude lead, there forms a slag characterized by varied elemental and mineralogical composition (Bielankin et al. 1957; Ptak, Nowakowski 1978).

The lead metallurgical slag composition depends on the share of individual components in the furnace charge (Table 2). The proportion of shaft furnace slags in the charge amounts to 30-60%, converter ash 10-40%, oxide ash and slag 5-20%, and of the 'own' slag from the foundry 0-10% (Pluciński et al. 1996). The slag formed in the Dörschl furnace (lead metallurgy slag) is a mixture of slag, copper-lead matte and waste from Ni-Co refining. The proportion of individual metals varies strongly (Tab. 3).

Table. 3. An average composition of the lead metallurgy slag, after Pluciński et al. (1996)

Component	Contents [%]
Pb	4.2-8.0
Cu	2.2-4.3
Ag	0.004-0.008
Fe	15.0-25.0
Zn	6.0-12.0
SiO_2	10.0-18.0
S_{og}	10.0-12.0

The following mineral phases were determined in the lead metallurgy slag sample: metallic iron, cubanite, covellite, bornite, chalcopyrite, metallic copper, sphalerite-willemite, Pb alloys, magnetite (+hematite), pyrrhotite, cuprite and trace amounts of metallic silver and molybdenite. The major transparent constituents are phayalite (Fe_2SiO_4), silicates and silicate alloy. The majority of ore minerals of the tabular or scaly morphology (covellite, cubanite) are strongly structurally intergrown with other copper sulfides or silicates parallel or perpendicular to the crystallization planes.

Almost total amount of metallic iron present in the sample was taken out with a weak magnet (magnetic induction 0,6 T). A characteristic feature of the alloy is its high reflectance and isotropism. The size of iron grains in the slag ranges from several to several tens of μm in diameter. The shape of this mineral is frequently irregular; intergrowths with phayalite are common.

Metallic iron contains high proportion of As. Its quantity is within a range from 1 to 24 % wt. Iron contains also high amounts of sulphur - up to 2.5 % wt. Metallic iron forms growths with pyrrhotite, silicates and silicate alloy. In places continuous transition from metallic iron to iron-lead alloy is observed (Fig. 1).

Cubanite has physical properties typical of its natural counterpart. It forms tabular crystals very strongly intergrown with silicate minerals and silicate alloy. The size of individual crystals does not exceed 100 μm in diameter. Its optical properties depend on the Cu content in the ore mineral and vary within wide limits. A particular feature is its brownish-yellow to brass-brown colour and strong anisotropy related with the elemental composition. Cu content in natural cubanite is around 23.4% In the Cu sulfide under study it amounts to 16 - 20% wt. of Cu (Fig. 2).

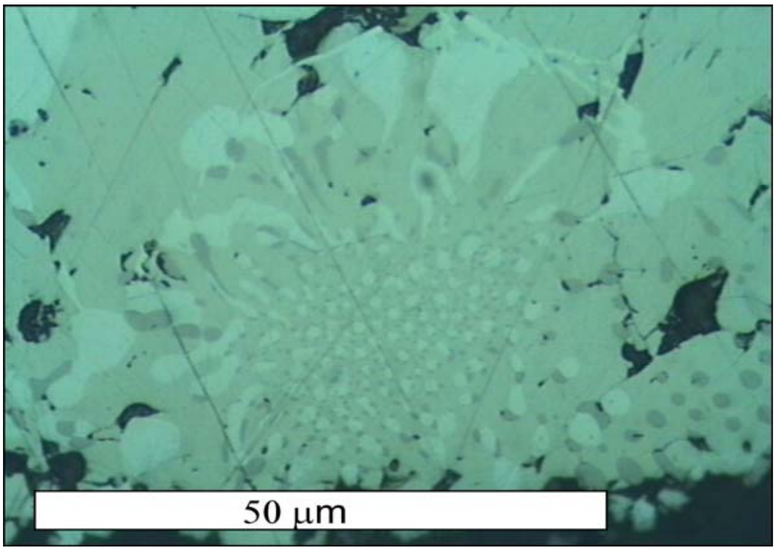

Fig. 1. Metallic iron with variable elemental composition (Fe-As to Fe-Pb). Reflected light; plane polarized light

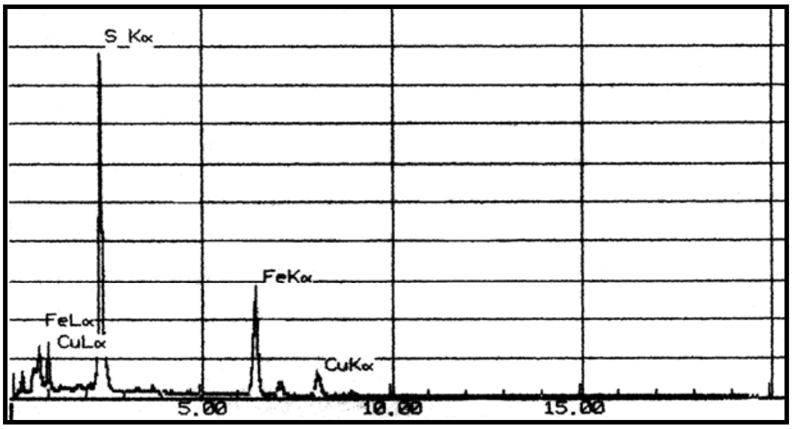

Fig. 2. Characteristic X-ray spectrum of "cubanite"

This is a feature indicative of sulphur deficiency and fast crystallization of this mineral. Cubanite is most commonly present in the form of tabular intergrowths with covellite, bornite or silicates (Figs. 3, 4).

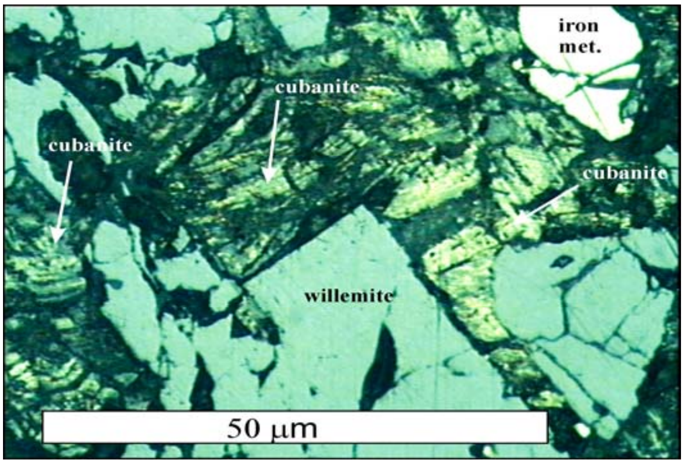

Fig. 3. Cubanite structure in lead metallurgy slags. Reflected plane polarized light.

Covellite is a common sulfide in the slag under investigation. Its physical and optical properties are so distinct that it is difficult to mistake it for any other chemical compound. It is characterized with a typical tabular morphology and fiery-orange-red anisotropy. In individual covellite grains one may observe continuous transitions from 'cubanite' to 'semi-bornite' (Fig. 4). Along crystallization planes of covellite alloys and silicates of Fe-Na are frequently encountered.

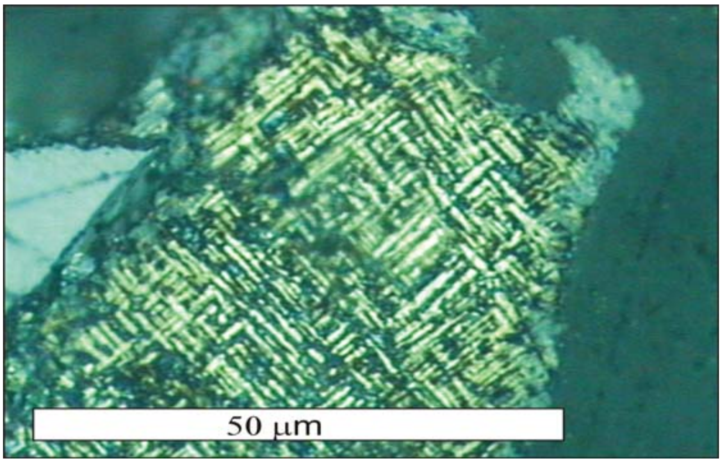

Fig. 4.Cubanite-bornite-covellite structure in lead metallurgy slag. Reflected plane polarized light

The content of copper in covellite under study is different from Cu proportion in natural covellites. Covellite present in copper ores contains around 66.5% Cu. In the samples analyzed the copper content is much lower and ranges from 46 to 53% wt.

Cu. This varied Cu content is related with the presence of Fe ions in the structure of covellite. Iron content may in places reach up to 18.5% wt. On the basis of observation of grains and crystals one may state that they have optical and physical properties of covellite, but their chemical composition shows phase transitions from bornite to cubanite (Fig. 4).

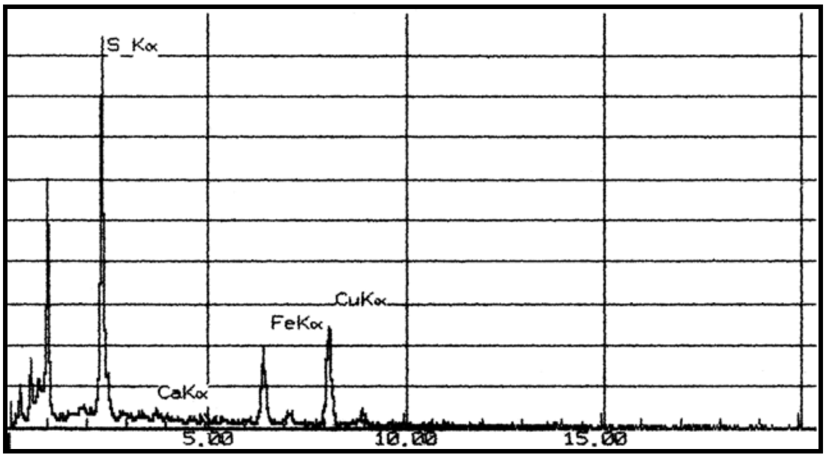

Fig. 5. X-ray spectrum of 'covellite'

Bornite is characterized by a varied colour from brown to blue-heather colour. It reveals very weak anisotropy and its chemical composition is different from the one of the natural bornites. Bornite does not form a uniform crystalline phase. Microchemical analyses confirmed that most commonly it is a mixture of transition phases from semi-bornite to covellite-cubanite with an addition of chalcopyrite (Fig. 6). In places bornite contains small oval forms of 'pure' metallic copper. The Cu concentration varies in individual grains from 31.5 to 59.5 % wt. Cu and never reaches the proportion observed in natural bornites 63.3 % wt. Cu. Its chemical composition is more similar to that of the compound Cu_3FeS_3 or $CuFeS_6$, than the one of Cu_5FeS_4.

Chalcopyrite is a very rare ore mineral constituent of the samples. It is very distinctly visible at the background of grey silicates and sphalerite. Its yellow colour is typical of natural chalcopyrite and its anisotropy is very weak. It forms intergrowths with other copper sulfides. The grain sizes do not exceed several tens of μm in diameter.

Metallic copper in the lead metallurgy slag is rare. It is most frequently present in the form of oval or round inclusions in bornite and metal silicates. The copper exsolutions reach up to a dozen or so micrometers in diameter. Bigger forms of a wire type are not grown with silicates but they are covered with a thin coat of cuprite. The copper grains analyzed are of an extraordinary 'purity'. The proportion of other metals' additions is below 0.5% wt.

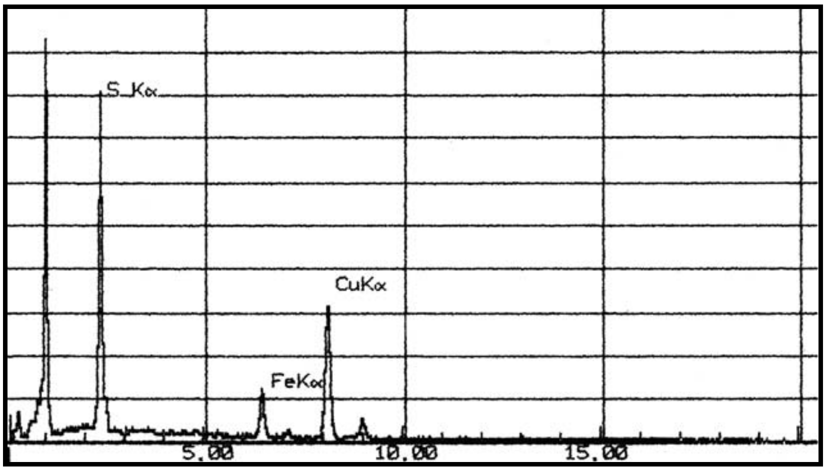

Fig. 6. X-ray spectrum of 'bornite'

Sphalerite present in the material under study contains high amounts of Fe. It is characterized with a low reflectance and grey colour which is a feature distinguishing it clearly from natural sphalerites. The surface of sphalerites studied is easy to polish - this is yet another difference from their natural counterparts. The mineral colour is uniform grey on the whole surface. It forms irregular shapes or grains intergrown with phayalite, willemite and Mg-Ca silicates. Their physical and optical properties are typical of sphalerite. Its chemical composition could be expressed with a formula (Zn,Fe)S. The content of Fe ranges from 9 to 17.1% wt. of Fe. Sphalerite is accompanied by willemite that forms growths and intergrowths with it. Because of difficulty in separation of these two minerals from one another they have been treated together in the course of the quantitative analysis.

Pb alloys are easy to distinguish in the material as they have very high reflectance when compared with the other ore minerals. The reflectance points to a low amount of metal admixtures in the alloys. Pb alloys have various complicated forms: drop-like, vermicular and oval. In places there are transitions from a pure Pb alloy to the alloy containing Pb and Fe. The majority of Pb alloys grains are grown-together with other metal compounds or silicates.

Magnetite is most commonly present in the form of tiny crystals within phayalite or silicate alloy. The size of individual crystals ranges from 0.2 μm to 60 μm in diameter. This mineral forms automorphic or hypautomorphic crystals. It also forms inclusions in sphalerite. Large magnetite grains bear traces of martitization (hematite formation). This process advanced from the outer rim of the grains. Microchemical analyses revealed no presence of admixtures in this mineral.

Pyrrhotite is present in the samples mainly in the form of growths with metallic iron, cubanite or phayalite. This mineral has typical optical parameters, distinct anisotropy and brown-creamy colour.

Table. 4. Quantity of main ore minerals in % vol

Cubanite	Metallic iron	Metallic copper	sphalerite- willemite	Bornite	Covellite
19.07	19.60	0.67	26.72	1.37	3.52
Chalcopyrite	Magnetite	Pb alloy	Pyrrhotite	Cuprite	Covellite-cubanite
0.40	13.04	8.52	4.60	0.07	2.42

The main useful mineral in the slags is sphalerite, which is most frequently intergrown with willemite. These both minerals constitute 26.72% vol. of all ore minerals (Tab. 4). The second most common mineral is cubanite. Its quantity amounts to 19.07% vol. The third one is metallic iron of varied elemental composition. These four minerals make up 65.39% vol. of the ore minerals in the slag. The quantity of the other ore minerals ranges from 0.07 % vol. (cuprite) to 13.04% vol. (magnetite). Apart from the ore minerals mentioned earlier, the sample contained accessory amount of molybdenite and tiny exsolutions of metallic silver.

CONCLUSIONS

The lead metallurgy slags from the Dörschl furnace from the 'Głogów' Foundry contain Cu and Cu+Fe sulfides, i.e. cubanite, covellite, bornite and chalcopyrite. The first mineral is the main Cu carrier in the lead metallurgy slag. Its optical and physical properties resemble the properties of natural cubanite present in metal ores. The copper concentration in cubanite ranges from 16 to 20%. The rest of copper occurs in the form of metallic Cu. Zinc is mainly concentrated in the sulfide (sphalerite) and silicate (willemite) forms. These both minerals frequently form intergrowths. Iron is present mostly as metallic iron, magnetite and pyrrhotite. Iron alloy grains have irregular shapes and form gradual transitions to alloys of Fe-Pb-As. Magnetite is present in the form of tiny inclusions in silicates of phayalite type and in rhombic pyroxenes. The main Pb carriers are lead alloys with various admixtures such as Fe, Ag, Cu, Zn. Arsenic in the slag was intercepted by metallic iron during crystallization. The microchemical analyses revealed no presence of arsenic in other minerals of the lead metallurgical slag.

The determination of mineral phases composed of non-ferrous metals (Zn, Cu, Pb) may help in designing of a recovery technology. Thus a waste material, regarded as arduous to the environment, may become a valuable anthropogenic source of these metals.

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Głównym celem niniejszych badań było scharakteryzowanie kruszców i związków metali w żużlach pochodzących z pieca „Dörschla" z huty miedzi „Głogów" oraz określenie, w jakich formach krystalograficznych gromadzą się najważniejsze pierwiastki przechodzące podczas wytopu ołowiu. Znajomość faz mineralnych złożonych z metali kolorowych, tj. Pb, Zn, Cu może przyczynić się do opracowania łatwego sposobu ich odzysku i zminimalizowania negatywnego skutku oddziaływania ich na środowisko, a tym samym obniżenia kosztów jego składowania. W próbce żużla poołowiowego stwierdzono obecność: żelaza metalicznego, kubanitu, kowelinu, bornitu, chalkopirytu, miedzi metalicznej, sfalerytu-willemitu, stopów Pb, magnetytu (+ hematytu), pirotynu, kuprytu oraz śladowe ilości srebra met. i molibdenitu. Dominującym składnikiem przeźroczystym jest fajalit (Fe_2SiO_4), krzemiany oraz stop krzemianowy (szkliwo). Większość kruszców o budowie tabliczkowej lub łuseczkowej (kowelin, kubanit) są silnie przerośnięte strukturalnie z innymi siarczkami miedzi lub krzemianami zgodnie z powierzchniami krystalizacyjnymi lub prostopadle do nich. Głównym nośnikiem Cu w żużlach poołowiowych jest kubanit w którym ilość miedzi waha się w zakresie od 16 do 20 % wag. Ponadto Cu gromadzi się w formie miedzi metalicznej w postaci wrostków w krzemianach. Cynk zgromadzony jest głównie w formie siarczkowej (sfaleryt) i krzemianowej (willemit). Żelazo koncentruje się głównie w żelazie metalicznym o różnym składzie, magnetycie, fajalicie oraz pirotynie. Magnetyt obecny jest w formie drobnych wrostków w krzemianach typu fajalit i w piroksenach rombowych. Głównym nośnikiem Pb są stopy ołowiu z domieszkami Ag, Cu, Zn. Arsen obecny w żużlu został przechwycony przez krystalizujące żelazo metaliczne i w budowany w sieć krystaliczną. Żużle poołowiowe, uciążliwe dla środowiska a obecnie składowane na hałdzie, stać się mogą cennym złożem antropogenicznym.