GEOCHEMISTRY, MINERALOGY AND PETROLOGY • SOFIA
ГЕОХИМИЯ, МИНЕРАЛОГИЯ И ПЕТРОЛОГИЯ • СОФИЯ
2009, **47**, 51-63.

Efflorescent minerals from the metallurgical waste heaps of the KCM non-ferrous metal smelter, Plovdiv, Bulgaria

Radostina Atanassova, Thomas Kerestedjian

Abstract. Alteration processes in the waste dumps of the KCM non-ferrous metal smelter near Plovdiv and their environmental impact have been focussed in this study. The waste materials from the metallurgical production (weltz-clinker) expected to be relatively insoluble were found to be affected by spontaneously initiated burning processes, turning the chemically resistant glassy phases into highly water soluble mineral phases. Newly formed minerals occur predominantly as efflorescent masses or deposited around gas and vapour exhalations in the dump. Various soluble sulphates of Cu, Fe, Al, Ca, Mn and Zn (chalcanthite, antlerite, melanterite, copiapite, halotrichite, apjohnite, dietrichite, gypsum etc.) and native sulphur were identified.

The measured physical and chemical parameters of the mineral transforming processes allowed determination of the forming conditions of the observed specific mineral assemblages.

The role of newly formed minerals for the remobilization of heavy metals in the environment is clarified. The detected phenomenon results in significant increase of the ground and surface water pollution and also in airborne soil contamination in the investigated area. The knowledge of the described processes became an important starting point for management plan realised in the area.

Key words: sulphate minerals, native sulphur, metallurgical wastes, environmental mineralogy

Address: Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria;
E-mail: radi@geology.bas.bg

Радостина Атанасова, Томас Керестеджиян. Ефлоресцентни минерали от отвалите за металургични отпадъци на комбината за цветни метали (КЦМ), Пловдив, България

Резюме. Изследвани са променителните процеси протичащи в отпадните отвалите на комбината за цветни метали (КЦМ) край Пловдив и влиянието им върху компонентите на околната среда. Отпадъчните материали от металургичното производство (велц-клинкер), смятани за относително инертни, се оказват засегнати от спонтанно инициирани процеси на горене. Получените резултати показат, че химически устойчивите стъклообразни материали се превръщат в силно водоразтворими минерални фази. Преобладаващата част от новообразуваните минерали се отлагат като ефлоресцентни маси или се наблюдат отложени около газови и парови ексхалации в депонираните маси. Идентифицирани са разнообразни разтворими сулфатни минерали на Cu, Fe, Al, Ca, Mn и Zn (халкантит, антлерит, мелантерит, копиапит, халотрихит, апджонит, дитрихит, гипс и други) както и самородна сяра.

Регистрираните физични и химични параметри на протичащите процеси позволиха да бъдат установени условията на формиране на наблюдаваната специфичната минерална асоциация.

Изяснена е ролята на новообразуващите се минерали за ремобилизацията на тежки металите в околната среда. Резултатът от установения феномен е значително повишаване на замърсяването на подземните и повърхностните води, а също и аерозолното замърсяване на почвите в изследваната област. Познаването на описаните процеси, стана отправна точка за взетите управленски решения в района.

Introduction

The mining and smelting of metallic ores result in large amounts of waste, including slags, ash, industrial constructions, among others. Metallurgical residue materials are important sources of potentially toxic elements and may constitute a serious environmental problem in the area where they are stored (Manz & Castro 1997; Sidenko et al. 2001). The release of toxic elements from the waste materials during weathering leads to contamination of surrounding soils, ground and surface waters (Gieré et al. 2003; Kierczak et al. 2009). The evaporation of water during dry seasons produces efflorescences, which consist of a large variety of metal hydrosulphates (Zodrow et al. 1979, Jambor *et al.* 2000, Romero et al. 2006).

The salts, effloresced on mining wastes, tailings, stock piles and outcrops, include minerals that incorporate heavy metals in solid solution, primarily the highly soluble members of the melanterite, rozenite, epsomite, halotrichite, and copiapite groups. The predominantly efflorescent occurrences of these minerals are characterized by a great variety of sulphate mineral species. Some minerals are the same as those encountered in coal fire environments or around volcanic fumaroles and in areas of geothermal activity (Masalehdani et al. 2009).

Studies about efflorescent sulphates are of increasing interest because they provide information about reactions occurring in the environment, water chemistry, and the potential impact on water quality following rains. The formation and paragenesis of efflorescent sulphates, as well as the release of metals to stream waters, have been widely studied (Keith et al. 2001, Sánchez España et al. 2005, Romero et al, 2006). Other studies about the mineralogy of efflorescences, parageneses and transformations have been also carried out recently (Alpers et al. 1994; Jambor et al. 2000; Buckby et al. 2003; Jerz & Rimstidt 2003; Hammarstrom et al. 2005, Joeckel et al. 2005; Romero et al. 2006; Kierczak et al. 2009; Farkas et al. 2009).

Furthermore, efflorescent sulphates play an important role in the storage of acid components, metals and trace elements. The accumulation of Cu, Fe, Zn and Mn in sulphate minerals and their dissolution may impact the environment (Keith et al. 2001; Hammarstrom et al. 2005). The storage of other elements such as As, Cd, Co, Ni or Pb in these salts is presented in several studies (Buckby et al. 2003; Jamieson et al. 2005, Sánchez España et al. 2005). The ability of melanterite to sequester Cu and Zn is well known (Frau 2000; Jambor et al. 2000; Hammarstrom et al. 2005).

In 2000-2004 under Science for Peace NATO Program (project WATMETAPOL 973739) extensive hydrogeological and geochemical investigations were conducted in order to establish potential risk to the environment created by metallurgical activities in the Asenovgrad-Plovdiv district. The obtained analytical results, hydro-geochemical modelling and software, created by the project were implemented by the responsible authorities for environmental management and monitoring. Later, after the completion of the project, the waste dumps, highlighted as important sources of secondary metal and As pollution in the area, were neutralised. One part of the new dump was removed and the rest was moved on hydro-isolated ground, covered by earthy material, re-vegetated and safety protected against meteoric impact. Seasonal water monitoring is conducted in the vicinity of the KCM area by the environmental authorities of the factory (Pentcheva et al. 2004).

In this paper, we describe newly formed mineral phases resulting from the underground burning of the metallurgical residue materials. In our study, we have focused on minerals formed on the surface and their important role in environmental cycling of metals and acids.

Although native sulphur is *sensu stricto* not an efflorescent mineral, because it is formed by gas and vapor exhalations, unlike the strictly efflorescent ones, formed by fluid dehydration, we use this term *sensu lato* for addressing the "bloom" and incrustations of minerals newly formed on the investigated dump materials, during the dry seasons.

Description of the studied object

Non-ferrous metals smelter KCM near the town of Plovdiv (Fig. 1) is the largest producer of non-ferrous metals and alloys in Central and Eastern Europe. It starts its activity in early 60-ies. Main industrial products of the smelter are lead, zinc and cadmium ingots as well as various alloys. Sulphuric acid is also an important component of its production. Classical pyro-metallurgical flow sheet, comprising sintering, shaft furnace reduction smelting and pyro-refining is applied for the lead production. The flow sheet for the zinc production is classical hydro-metallurgical one, comprising roasting of zinc concentrates, treatment of gases to sulphuric acid, conventional two stage calcine leaching, weltz process to treat residues, solution purification, electrolysis, and melting and casting of zinc ingots.

The production wastes of the KCM smelter, produced during its over 50 years of activity, have been deposited in large heaps (waste dumps) in a neighbouring area. The main residue product in the heaps is weltz-clinker. The clinker is a loose, coarse-grained and heterogeneous material resembling slag. According to previous investigations (Donchev & Mitov 1997; Donchev 2000) it consists mainly of Fe and Cu sulphides, oxides and silicates, as well as up to 12% coke (carbonaceous material). Pb, Zn and precious metal minerals are rare. Non-stoichiometric (partially destructed, vitrified) sulphides are the most characteristic content of the investigated materials.

Two unsecured heaps (old and new dumps) contained residue materials corresponding to a long period of metallurgical activity (Kerestedjian et al. 2003; Pentcheva et al. 2004). The old dump is the smaller one, about 80 000 m^3 in size and is not in use since 1970. The main part of the dump is built up by old weltz-clinker, highly agglomerated and petrified (Fig. 2a). Large cracks up to 30 m long and 1 m wide break up the heap surface. Degraded sulphides are the most characteristic content of this material. A separate part of the dump contains black slag.

The new dump is bigger and is the one used until now. It is located near the Chepelarska River (Fig. 1) which regularly recharges and discharges ground waters of the underlying aquifer.

The filtration parameters of this aquifer are much higher compared to that of the old heap site. Conductivity coefficient here is from 20 to 100 m/d while at the old heap it is only about 5 m/d (Hristov et al. 2004). The groundwater level here is shallower and the leaching

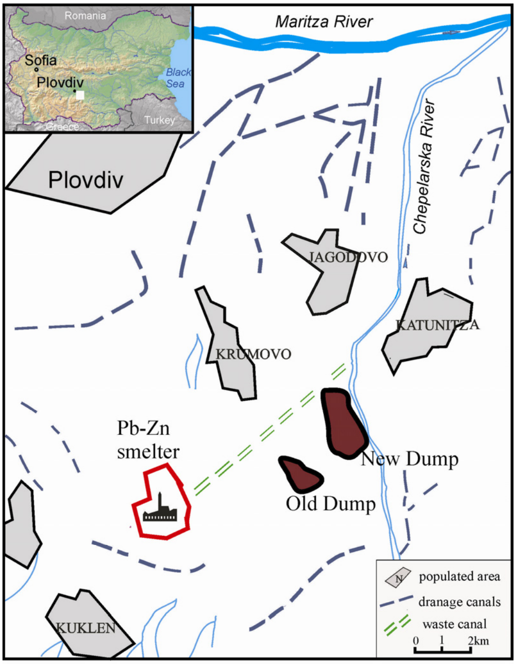


Fig. 1. Sketch map showing the location of the KCM non-ferrous metal smelter near the town of Plovdiv, Bulgaria

processes are more intensive. This causes higher pollutant concentration. The As content is relatively stable (0.5-0.9 mg/l) excluding the spring period when water levels reach their maximum and comparatively clean river water recharges the aquifer (Pentcheva et al. 2004).

In the course of the study the new dump contained about 205 000 m^3 of clinker material. Our field observations revealed that the waste material can be grouped into three visibly different types (Fig. 2):

a) Fresh residue. The main constituent is weltz-clinker material, rusty-brown in colour, non-agglomerated. No chemical activity is observed, except gypsum formations on the surface, few days after deposition.

b) Chemically active material. Older residue, slightly agglomerated, with some highly cemented spots. Chemical activity is noticed by intensive exhalation of acid (pH 2) gases and vapour and high temperature – mostly ~40 °C, but up to 211 °C measured in some active spots. The highly altered by fumarole gases areas are covered by efflorescent crusts.

c) Materials with moderate chemical activity. Older residue, with no external signs of chemical activity, but with temperatures up to 110 °C at a depth of 1 m or more. Different efflorescent phases occur in the weakly altered waste which is very poorly cemented together with goethite and small amount of hematite.

During the routine maintenance works, all described types of waste materials were periodically mixed to form flat heap surface.

Sample collection and analytical methods

Solid samples were collected from zones of fumarole activity and from inactive parts of the waste heaps in different seasons during the period 2000 and 2004. The accumulations of efflorescent phases were more abundant during dry periods and less common in autumn and winter. The materials collected were heterogeneous and show various macroscopic features.

The samples were transported and stored in closed polyethylene bags, to avoid dehydration. Nearly all sulphate minerals are hydrous and the number of water molecules is controlled by relative humidity and temperature (Jambor et al. 2000) hence it is not surprising that some of the samples consist of a mixture of phases. Some post sampling changes may be unavoidable, but if samples are examined carefully at every step in the analytical procedure, these changes can be documented (Jamieson et al. 2005).

All species are identified both by chemical analyses and X-ray diffraction (XRD). A sequential leaching procedure was used to determine the contents of soluble and mobile metal forms. The techniques and results of the leaching test analyses were reported previously (Kerestedjian et al. 2003; Pentcheva et al. 2004).

The minerals were initially identified using X-ray diagram patterns (Debye-Scherrer method) compared with PDF cards in the 2001-2002 set of samples. The X-ray method was chosen because it is the only one allowing registration of diffraction pattern from very small amounts of material. A digital Guiner Camera G670 (at the Geological Institute, BAS) was also used for a precise identification when it was possible to separate slightly larger amount of material. The measurement patterns were then matched with ICDD files to characterize the sample.

Selective samples were analyzed using microprobe JEOL JSM 35 (at Evrotest Control AD) with an accelerating voltage of 20 kV, a probe current of 30 nA and a beam diameter of 1 μm. Chemical analyses with electron microprobe (EPMA) were difficult owing to the small grain-size and variable quality of polished surfaces.

Scanning electron microscopy and energy-dispersive spectrometry (SEM-EDS) were used for analyses of the phases in selected undisturbed samples. We used a JEOL JSM 6390 equipped with INCA analytical system under accelerating voltage of 10 kV (at the Institute of Physical Chemistry, BAS). Selected

Fig. 2. The waste dump sites: a) efflorescent accumulations, preserved in shelter places of the old dump site; b) dark brown fresh residue; c) slightly agglomerated older residue with some highly cemented spots; d) view of the zone of fumarole activity on the waste heap; e) efflorescent gypsum masses on fresh clinker material; f) parts of the recultivated terrains and the water collector of the new solid waste landfill; b-f) new dump site

samples were examined using Bruker S2 PICOFOX XRF (X-ray fluorescence) instrument (at GI, BAS).

In addition, combined thermo-gravimetric and derivative thermal measurements of 100 mg of sample, were performed on a MOM thermograph (at GI, BAS), operated at heating rate of 10°/min from 20 to 900 °C to determine the water and SO_3 contents in the minerals from copiapite and halotrichite groups.

Mineral deposition observed

The chemical composition and glassy structure of the clinker was an evidence for the KCM authorities to claim that these dumps do not present any serious thread for the environment, since the solubility and mobility of the metallic content is expected to be very low. And this was indeed the situation for the recently produced clinker. The amount of coke and the concentrations for all the elements both in the clinker and its water solutions were below the maximum permissible limits (MPL) in Bulgaria. However, clinkers produced even just 4-5 years ago were significantly above the allowed limits. The old dump materials, after almost 30 years of coke burning and natural rain leaching, used to show concentrations of about 10 times above MPL (Pentcheva et al. 2004). The worst situation was with the materials 5-20 years old (on the new dump). The Leaching test results (Atanassova et al. 2004, Pentcheva et al. 2004) used to show concentrations of hundreds times above MPL: f. ex. Cu 800 mg/l = 3200 times MPL; Zn 270 mg/l = 20 times MPL; As a matter of fact, the silicate-sulphide agglomerate (weltz clinker) with the burning coke in it represents an active chemical reactor, mobilizing the metallic contents from the hardly soluble glasses into easily soluble recent phases on the heap surface.

Most of these phases are sulphate minerals of Cu, Zn, Fe, Mn and Al (Fig. 3) and all of them are highly soluble. As stated above, efflorescent mineral accumulations were found around specific gas exhalations in the metallurgical clinker heaps. These fumaroles are generated by a process of coke burning inside the heap mass. The high temperatures at combustion points cause decomposition of the glassy clinker mass and uplift of chemical components, forming new mineral phases on the heap surface. The measured temperature of the gas varies from 40°C in the oldest parts of the heap up to ~ 200°C in some hot spots on the new dump. The pH of the gas also varies from 3 in relatively exhausted parts of the heap to ~1 in the hot spots. As a matter of fact, almost the entire heap mass is more or less affected by the burning process and the respective chemical transformations connected with it. However, the intensity of the process depends on the composition of the clinker at the specific location, the amount of water, drainage conditions etc.

Atmospheric water plays important role in the overall environmental picture. On one hand, each time a long enough rain comes, it dissolves and takes away all the newly formed minerals; on the other hand, the water drained inside the heap intensifies the chemical processes there and new quantities of recent phases are formed on the surface over and over again.

The main result of the chemical activity of the dumps is the deposition of significant amounts of sulphate phases close to smoke or water outlets. During the course of the field investigation (2000-2004) abundant newly formed mineral accumulations were observed in shelter places of the dump sites (Fig. 2). They contained all enumerated mineral species listed in Table 1.

Old dump

On the slopes of the waste pile efflorescent masses, consisting mainly of Cu and Fe-sulphates, were observed (Fig. 2a). The following salt minerals were identified in these crusts, formed through evaporation of pore solutions:

Chalcocyanite occurs as white to pale bluish stalactite like rims. This anhydrous sulphate is only registered in the old dump materials, probably due to its extremely hygroscopic behaviour.

Bonattite and *Poitevinite* are hard to be distinguished macroscopically. They are registered by chemical analyses in hand specimen from bright blue vermiform masses and probably represent dehydration products of chalcanthite.

Table 1. *Minerals present in studied samples and methods of identification*

Mineral	Formula	Method
Chalcocyanite	$CuSO_4$	XRD, EPMA
Poitvenite	$CuSO_4.H_2O$	EPMA
Bonattite	$CuSO_4.3H_2O$	XRD, EPMA
Chalcanthite	$CuSO_4.5H_2O$	XRD, EPMA, SEM-EDS
Antlerite	$Cu_3SO_4\ (OH)_4$	XRD, EPMA
Rozenite	$Fe^{2+}SO_4.4H_2O$	XRD
Siderotil	$Fe^{2+}SO_4.5H_2O$	EPMA, SEM-EDS
Melanterite	$Fe^{2+}SO_4.7H_2O$	XRD, EPMA,
Halotrichite	$Fe^{2+}Al_2(SO_4)_4.22H_2O$	XRD, SEM-EDS
Apjohnite	$Mn^{2+}Al_2(SO_4)_4.22H_2O$	XRD, XRF, EPMA , DTA
Dietrichite	$Zn^{2+}Al_2(SO_4)_4.22H_2O$	XRD, XRF, SEM-EDS
Copiapite	$Fe^{2+}Fe^{3+}_4\ (SO_4)_6(OH)_2.20H_2O$	XRD, SEM-EDS, DTA
Gypsum	$CaSO_4.2H_2O$	XRD, EPMA
Native S	α-S	XRD, EPMA, SEM

Chalcanthite. Macroscopically, chalcanthite is represented by kidney-like aggregates with typical blue colour. As observed in SEM, the aggregates are composed of tabular on {111} crystals with rough surfaces. Corroded appearance witnesses that many of these crystals are partly dissolved (Fig. 5a).

Antlerite. Anhydrous sulphate, sampled for this study, typically forms fine grainy or acicular rims with greenish colour, often mixed with chalcanthite. Both species are distinguished by semi-quantitative microprobe and X-ray (Debye-Scherrer method) analyses.

Halotrichite. Since no chemical evidence was obtained for the presence of Mg in the studied samples, the most common phase found at the old dump site is halotrichite, whereas *aluminocopiapite* is less widespread. It occurs as dusty or earthy yellowish to greenish masses, sometimes with visible tiny fibrous or acicular crystals. The efflorescent crusts further contain the Mn member *apjohnite*, which was identified by powder XRD and which contains small amounts of Zn (~1.2 at.%). It is represented by white rims or shapeless masses, often together with halotrichite.

New dump

In addition to the minerals described from the efflorescences on the old dump site the following minerals in the new dump materials were identified:

Gypsum. Gypsum is the earliest forming efflorescent mineral, observed as dusty masses on fresh clinker material, even just few hours after the heap deposition (Fig. 2c). Another variety of gypsum is found growing around smoke exhalation outlets or as incrustations on different porous substrates. This type represents both chemical and structural evidence of a transition to anhydrite (Table 2).

Sulphur. Native sulphur is found exclusively around active smoke exhalation outlets and is represented by acicular crystals up to 1 cm long, but less than 1 mm wide, bright yellow in colour (Fig. 3c,d). Sometimes fine droplets of sulphuric acid (14%) are found on the sulphur crystal surfaces (Kerestedjian et al. 2003; Atanassova & Kerestedjian 2004). These droplets are hygrostatic and do not evaporate. Recorded XRD patterns determine the mineral as orthorhombic *a*-sulphur variety.

Table 2. *Representative compositions of efflorescent minerals*

wt.%	CaO	FeO	Al_2O_3	CuO	ZnO	MnO	SO_3	Totals*
Old dump site								
Poitvenite		1.16		39.63			45.56	86.35
Chalcanthite		1.69		30.86	1.02	0.89	32.45	66.91
Bonattite		0.59		35.49	1.03	0.84	40.87	78.82
Apjohnite			17.03	1.38	5.09	11.37	33.42	68.29
Chalcocyanite		0.39		50.67			45.39	96.45
New dump site								
Gypsum	32.50						42.27	74.77
Gypsum (Anhydrite)	26.96	1.46					37.25	65.67
Melanterite		24.88		0.34	2.43	1.60	30.73	59.98
Siderotil		26.05		0.51	1.36	1.18	39.76	68.13
Halotrichite		4.42	10.49	1.10	2.95	3.10	32.49	54.55
Copiapite		27.56	0.36	1.96	0.34	1.26	39.41	70.89

*Totals below 100% indicate light elements invisible for the microprobe. Typically this reflects the presence of: O, H, F, Cl, H_2O molecules, OH groups, etc.

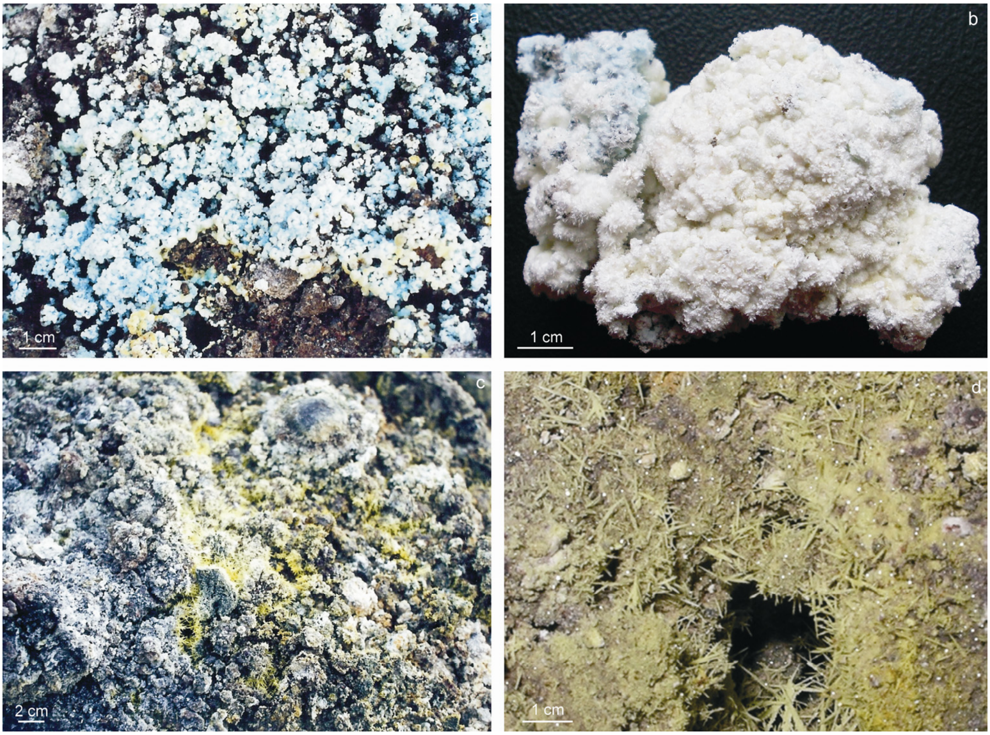


Fig. 3. Selected mineral samples: a) melanterite efflorescences; b) hand specimen of dietrichite; c) native sulphur aggregates around gas exhalations; d) sulphur crystals with droplets of sulphuric acid

Several morphological types of native sulphur appear: 1) isometric bipyramidal {111} crystals; 2) barrel-formed crystals; 3) c-elongated needles; 4) threads of parallel twinned along c-axis bipyramids; 5) complex skeletal crystals (Fig. 6a-c). Flat faces of layer-by-layer growth are prevailing, but hopper faces indicative for morphological instability are not rare too. In many cases crystals have rounded apexes and edges, a result of partial corrosion (sublimation and melting). In the intensively corroded skeletons nets of small voids, formerly fluid inclusions, is well revealed, and the process of skeletal growth is clearly traced (Fig. 6b-c). Some crystal aggregates are covered by thicker molten crusts with later recrystallized mosaic surface. The morphologies of the sulphur crystals observed are clearly dependent on local conditions.

The observed features of sulphur crystals are similar to those described by Maleev (1976) from underground coal fire sites in the Brejane deposit, Bulgaria.

Melanterite. Melanterite is observed as light-blue masses, changing to yellowish upon exposure to dry air and is commonly found around smoke exhalation outlets (Fig. 3). According to EPMA it contains Zn up to 0.40 at.% and some minor amounts of Mn – 0.20 at.% and Cu – 0.10 at.%. Also, siderotil pseudomorphs after melanterite are observed. SEM-EDS data confirm that our melanterite-bearing samples, that dehydrated to siderotil, are Zn and Mn-bearing.

Halotrichite group minerals. Extensive formation of solid solutions is characteristic for these monoclinic hydrated sulphates, thus they typically produce complex XRD patterns, with many overlapping peaks (Jambor et al. 2000). This is the case at new dump site, as some samples were mixtures of minerals of the halotrichite group and only few matched exactly the powder patterns of the nominal end-members. Along with *halotrichite* the Zn-bearing member *dietrichite* was detected by XRD and SEM-EDS analyses. It occurs either as a white crusts or as a delicate aggregates of sub-millimetric acicular whitish crystals (Figs. 3; 6d-e).

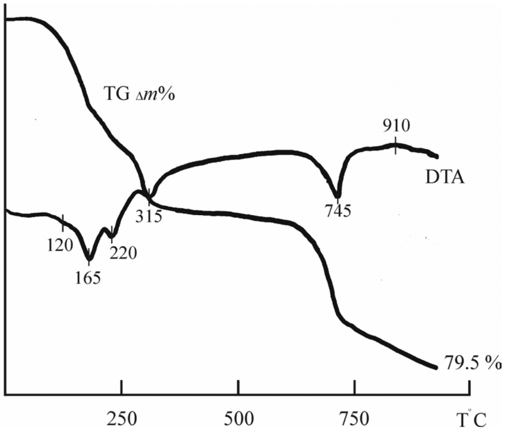
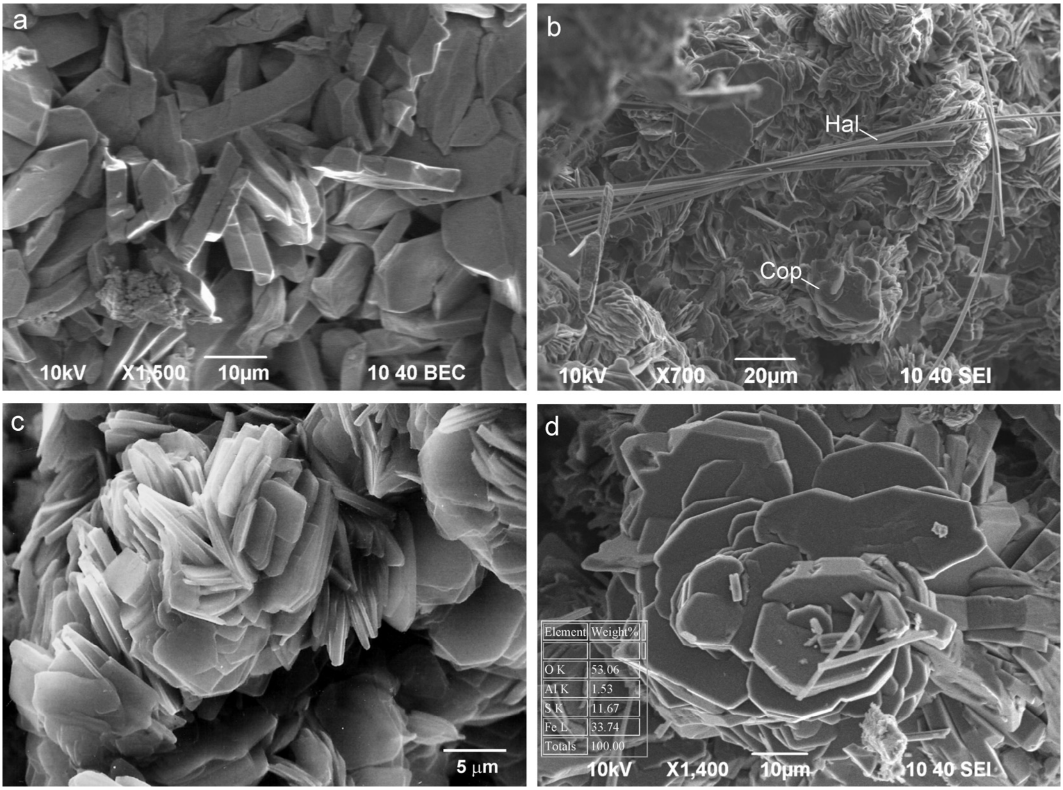


Fig. 4. Thermogravimetric (TG) and Differential Thermal (DTA) curves of copiapite

Copiapite. Found as shapeless yellowish masses usually in association with melanterite and other Fe sulphates in efflorescent encrusttations. Copiapite was less common in exposed settings relative to the halotrichite-group minerals, and apparently forms in more sheltered environments.

Thermogravimetric (TG) and differential thermal analysis (DTA) curves for copiapite were obtained, to further support the determination. All endothermic peaks correspond to loss-in-weight steps as shown in Fig. 4. DTA curve registered shows endotherm at 315°C with weight loss about 45%, corresponding to simple dehydratation. The second 745°C endotherm corresponds to major loss of sulphur probably as SO_3 gas.

Regardless of the XRD pattern complexity, caused by both the presence of mixtures and preferred orientation problems, (similar to those faced by Jamieson et al. 2005), the dominant mineral species in our samples could be determined as ferricopiapite. SEM-EDS analyses confirmed copiapite-group mineral with strong peaks for Fe, and S and minor peak for Al. Under SEM copiapite display a platy habit with crystals from 3-5 up to 10- 20 μm in size (Fig. 5).



Element	Weight%
O K	53.06
Al K	1.53
S K	11.67
Fe L	33.74
Totals	100.00

Fig. 5. SEM microphotographs of efflorescent minerals: a) chalcanthite tabular crystals with corroded surfaces; b) rosette-like aggregates of copiapite (Cop) and acicular crystals of halotrichite (Hal); c-d) various platy crystals of copiapite

Discussion and conclusions

The represented data form the following overall picture of the observed process:

1. The sulphides (already destabilized by the metallurgical treatment) are decomposed with the formation of H_2SO_4; the coke is oxidized using atmospheric oxygen and probably agitated by the sulphuric acid. Initially insoluble phases, as also noted by Sidenko et al. (2001) are metamorphosed into highly soluble material. The observed processes according to the resulting products are characterized by different stages of oxidation of the sulphide sulphur (S^{2-}), through zerovalent elementary S and fourvalent (SO_2) to sixvalent (SO_4). Bacteria are supposed to take an important part in this process (Satchanska et al. 2003; Trifonova et al. 2003).

2. Minerals found here have also been reported for volcanic, coal-fire and geothermal environments (Martin et al. 1999; Hall et al. 2003; Masalehdani et al. 2009). The common acicular and skeletal forms for many of the described minerals indicate rapid crystallization. This should be thought to happen in non-equilibrium conditions and thus depends a lot on minor local differences. Similar conditions are suggested by the fine-grained nature of many efflorescent occurrences. This is compatible with rapid cooling, or rapid evaporation of solutions, which can be expected to occur along the surface of a waste heap with subsurface combustion.

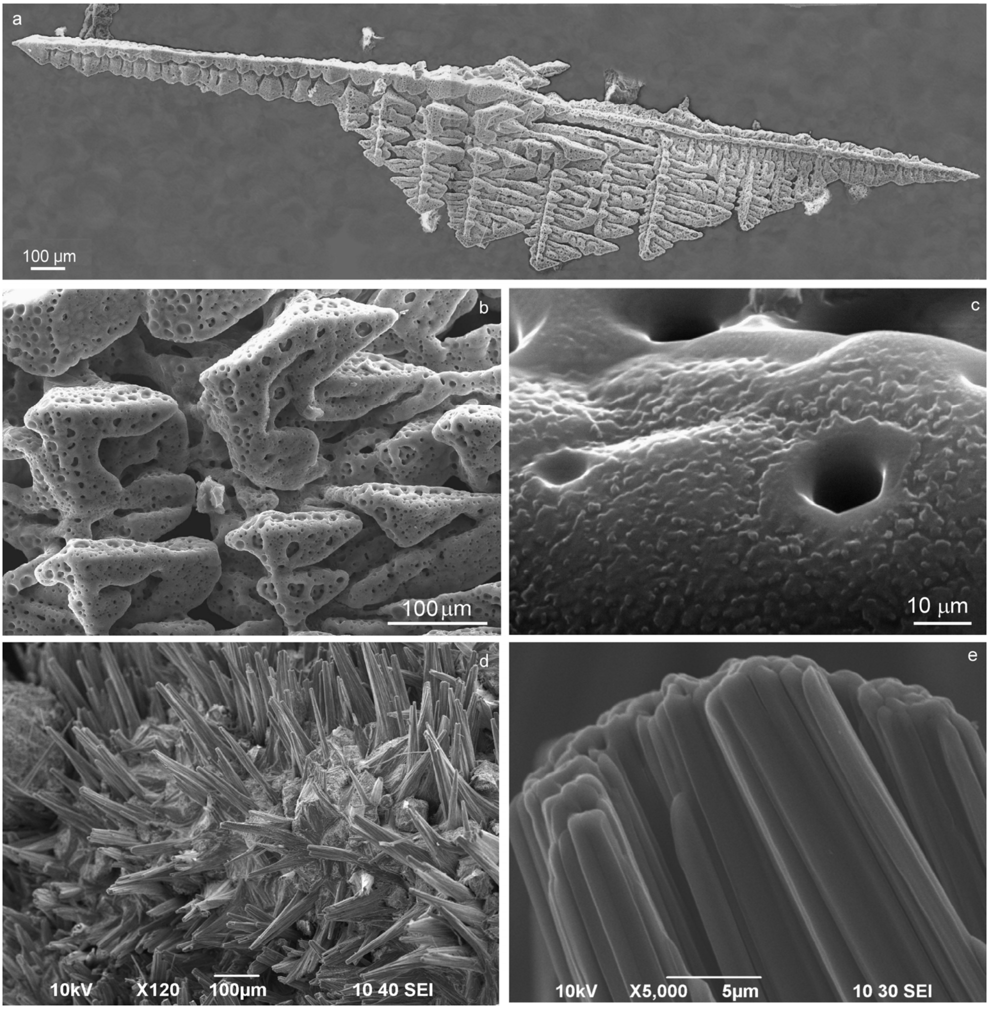


Fig. 6. Morphology of native sulphur (a-c) and dietrichite (d-e): a) a complex skeletal crystal with intensive growth of bipyramidal edges; b) intensively corroded skeletons with a network of small voids; d) a detailed view of skeleton surface; d) radiating bunches of acicular dietrichite; e) a tip of a sub-parallel aggregate (bunch) of dietrichite crystals. SEM

3. The oxidation of sulphides is an exothermic process, and this heat modifies the conditions within the waste dump materials. Formed gases SO_2 and CO_2 elevate the metallic components, mobilized during sulphide decomposition. On the surface, both gases and liquid solutions deposit sulphate minerals. Due to the pronounced affinity of SO_2 towards concentrating in the liquid phase, we suppose that liquid solutions are responsible for the formation of sulphate efflorescent minerals mainly. Contrary, the native sulphur seems to be deposited from gas exhalations.

4. The self-initiated combustion process is the main reason for the redistribution of various elements. Primary metal-bearing waste material appears to be more resistant to weathering than the secondary phases as a result of combustion.

Without a combustion process, the removal of metals from the waste material by water would not be as pronounced as it was observed. Sulphates were found in abundance in places less affected by atmospheric influence. However, heavy rainfalls easily dissolve formed masses, leaving place for new amounts of them to form. Thus, quantities of sulphates are continuously mobilized and their components enter into the surface and ground waters, causing both an increase of metallic pollution and acidification of the surrounding environment.

Recently, the KCM Company has undertaken environmental management measures by implementing several procedures. In 2005 waste water purification system was built to eliminate the underground water pollution in the surroundings of the smelter. The recultivation of the terrains and the settlement of new solid waste landfill were finished in 2008 by a successful certification. At present, the comparative surface and ground water analytical data show an improvement of the ecological state (Benderev et al. 2009). The comparison of soil samples, however, does not show any change which makes sense, given that natural soil remediation is known to take longer period.

Acknowledgements: The main part of research has been carried out in the framework of the NATO Science for Peace Program (WATMETAPOL 973739 project). This study was also funded in part through the Bulgarian National Science Fund and the Bulgarian Ministry of Education and Science (BIn7/07; DO1-904/MON).

References

Alpers CN, Blowes DW, Nordstrom DK, Jambor JL (1994) Secondary minerals and acid mine-water chemistry. In: The Environmental Geochemistry of Sulfide Mine-Wastes, Jambor JL & Blowes DW (Editors). Mineralogical Association of Canada, Short-Course Handbook **22**, 247-270.

Atanassova R, Kerestedjian T (2004) Native sulphur: A product of anthropogenic fumaroles. *32nd International Geological Congress,* Florence, Abstracts, 633.

Atanassova R, Kerestedjian T, Donchev I (2004) Mineralogy and remobilization processes in the weltz-clinker dump site, Plovdiv region, Bulgaria. In: Pecchio M et al. (Editors) *8th International Congress for Applied Mineralogy ICAM 2004*, Aguas de Lindoia, Brasil, 387-389.

Benderev A, Mihaylova B, Kerestedjian T, Atanassova R, Singh V (2009) Assessment of the ecological state of the art in the area of KCM Plovdiv smelter, after the measures undertaken for environmental improvement. In: *Proceeding of GEOSCIENCES 2009*,123-124.

Buckby T, Black S, Coleman ML, Hodson ME (2003) Fe-sulfate-rich evaporative mineral precipitates from the Río Tinto, southwest Spain. *Mineralalogical Magazine*, **67**, 263-278.

Donchev I (2000) Mineralogy of weltz-clinker waste – ways for useful component extraction and environmental decisions. *Acta Mineralogica-Petrographica*, **XLI**, Szeget, Hungaria, Abstracts, 21.

Donchev I, Mitov K (1997) Mineralogy of clinker waste and opportunities for its useful components extraction. *Geology and Mineral Resources*, **2-3**, 26-29.

Farkas IM, Weiszburg TG, Pekker P, Kuzmann E (2009) A half-century of environmental mineral formation on a pyrite-bearing waste dump in the Mátra Mountains, Hungary. *Canadian Mineralogist,* **47**, 509-524.

Frau F (2000) The formation-dissolution-precipitation cycle of melanterite at the abandoned pyrite mine of Genna Luas in Sardinia, Italy: Environmental implications. *Mineralogical Magazine,* **64**, 995–1006.

Gieré R, Sidenko NV, Lazareva EV (2003) The role of secondary minerals in controlling the migration of arsenic and metals from high-sulfide wastes (Berikul gold mine, Siberia). *Applied Geochemistry*, **18**, 1347–1359.

Hall AJ, Fallick AE, Perdikatsis V, Photos-Jones E (2003) A model for the origin of Al-rich efflorescences near fumaroles, Melos, Greece: enhanced weathering in a geothermal setting. *Mineralogical Magazine*, **67**, 363-379.

Hammarstrom JM, Seal RR II, Meier AL, Kornfeld JM (2005) Secondary sulfate minerals associated with acid drainage in the eastern US: Recycling of metals and acidity in surficial environments. *Chemical Geology*, **215**, 407-431.

Hristov V, Atanassova R, Benderev A (2004) Heavy metal pollution of soil and groundwater in vicinity of the two slag-dumps near a smelter "KCM" (Bulgaria). *Proc. 5th Intern. Symp.*

Eastern Mediterranean Geology ISEMG, Thessaloniki, Greece, 994-997.

Jambor JL, Nordstrom DK, Alpers CN (2000) Metal-sulphate salts from sulphide mineral oxidation. In: Alpers et al. (Editors) *Reviews in Mineralogy and Geochemistry,* **40***,* 303-350.

Jamieson HE, Robinson C, Alpers CN, McCleskey RB, Nordstrom DK, Peterson RC (2005) Major and trace element composition of copiapite-group minerals and coexisting water from the Richmond mine, Iron Mountain, California. *Chemical Geology*, **215**, 387-405.

Jerz JK, Rimstidt JD (2003) Efflorescent iron sulphate minerals: Paragenesis, relative stability, and environmental impact. *American Mineralogist*, **88**, 1919-1932.

Joeckel RM, Ang Clement BJ, Vanfleet Bates LR (2005) Sulfate-mineral crusts from pyrite weathering and acid rock drainage in the Dakota Formation and Graneros Shale, Jefferson County, Nebraska. *Chemical Geology,* **215**, 433-452.

Keith DC, Runnells DD, Esposito KJ, Chermak JA, Levy DB, Hannula SR, Watts M, Hall L (2001) Geochemical models of the impact of acidic groundwater and evaporative sulfate salts on Boulder Creek at Iron Mountain, California. *Applied Geochemistry*, **16**, 947-961.

Kerestedjian T, Atanassova R, Piperov N (2003) Recent mineral formation and heavy metal remobilization in clinker waste heaps of KCM smelter, Plovdiv, Bulgaria. *7th biennial SGA meeting*, *Athens, Greece*, Mill. Press Rotterdam, Netherlands, 29-32.

Kierczak J, Néel C, Puziewicz J, Bril H (2009) The mineralogy and weathering of slag produced by the smalting of lateritic Ni ores, Szklary, southwestern Poland. *Canadian Mineralogist*, **47**, 557-572.

Maleev M (1976) Morphological features of a-Sulfur crystals formed during underground coal fires in the Brezhane deposit. *Geochemistry Mineralogy and Petrology*, **4**, 8-26.

Manz M, Castro LJ (1997) The environmental hazard caused by smelter slags from the Sta. Maria de la Paz mining district in Mexico. *Environmental Pollution*, **98**, 7-13.

Martin R, Rodgers KA, Browne PRL (1999) The nature and significance of sulphate-rich, aluminous efflorescences from the Te Kopia geothermal field, Taupo Volcanic Zone, New Zealand. *Mineralogical Magazine*, **63**, 413-419.

Masalehdani M N-N, Mees F, Dubois M, Coquinot Y, Potdevin J-L, Fialin M, Blanc-Valleron M-M (2009) Condensate minerals from a burning coal-waste heap in Avion, Northern France. *Canadian Mineralogist*, **47**, 573-591.

Pentcheva E, Fouillac C, Gijbels R (2004) Final report WATMETAPOL 973739 NATO Science for Peace Project: Dynamics, evolution and limitation of heavy metal water pollution in the Plovdiv region (Bulgaria), 123 p.

Romero A, González I, Galán E (2006) The role of efflorescent sulfates in the storage of trace elements in stream waters polluted by Acid Mine-Drainage: The case of Peña Del Hierro, Southwestern Spain. *Canadian Mineralogist*, **44**, 1431-1446.

Sánchez-España J, López Pamo E, Santofimia E, Aduvire O, Reyes J, Barettino D (2005) Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochemistry,* **20**, 1320-1356.

Satchanska G, Pentcheva EN, Atanassova R, Trifonova R, Ivanova I, Groudeva V (2003) Effect of heavy metal pollution in the microbial community, environmental impact and isolation of heavy metal- and 2,4-D resistant bacteria from soils and waters in industrial area. *6th International Symposium on Environmental Contamination in Central and Eastern Europe*, Prague, Czech Republic. Abstracts, 98.

Sidenko NV, Giere R, Bortnikova SB, Cottard F, Pal'chik NA (2001) Mobility of heavy metals in self-burning waste heaps of zinc smelting plant in Belovo (Kemerovo Region, Russia). *Journal of Geochemical Exploration,* **74,** 109-125.

Trifonova R, Kerestedjian T, Atanassova R, Satchanska G, Groudeva V (2003) Strains resistant to heavy metals in polluted soils and waters from the Pb-Zn smelter in Bulgaria. *Biotechnology and Biotechnological Equipment,* **17** (2), 91-97.

Accepted September 25, 2009