Минно-геоложки университет “Св. Иван Рилски”
Годишник, том 47, свитък I, Геология и геофизика, София, 2004, стр. 147-153

MINERALOGICAL CHARACTERISTICS OF COPPER FLOTATION PRODUCTS FROM CAYELI MINE, TURKEY AND THEIR INFLUENCE TO MINERAL PROCESSING

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ABSTRACT. The paper presents mineralogical characteristics and peculiarities of mineral distribution in products from Cu cycle of clastic ore mineral processing from Cayeli VHMS Cu-Zn deposit of Upper Cretaceous age located in the Black Sea Pontide belt, Northern Turkey. The study covers 16 samples from Cu flotation feed, Cu rougher concentrate, Cu final concentrate and Cu rougher tail sieved in 4 classes each (> 36 µm, 36 – 20 µm, 20 – 9 µm and < 9 µm). Special attention had been drawn to the mineralogical and geochemical peculiarities of sphalerite as it is one of the main ore minerals presenting in ores.

It is found out that relatively high amount of chalcopyrite is concentrated in the finest fractions as particles below 9 µm, especially in copper rougher and copper final concentrate. Class 20 – 36 for all samples (except Cu rougher tail) contains low chalcopyrite and the highest pyrite content due to the better pyrite flotation. Significant quantity of sphalerite characterised by higher Cu and Fe content as isomorphic impurities or extremely fine crystals of chalcopyrite presents in Cu final concentrate. This trend is very well evident for the class > 36 of Cu final concentrate where the total amount of Fe + Cu is 11.29 wt. % compared to 7.60 wt. % for the whole Cu final concentrate and 6.24 wt. % compared to clastic ore flotation feed. Based on the mineralogical data obtained it is suggested that improvement of mineral processing should be expected after grinding and hydrocycloning optimisation – rendering the circuit to operate in more pronounced “scalping mode”. Elimination the influence of copper containing inclusions in sphalerite is suggested through pH regime optimisation or testing new reagents in flotation processes.

МИНЕРАЛОЖКА ХАРАКТЕРИСТИКА НА ПРОДУКТИ ОТ МЕДНАТА ФЛОТАЦИЯ НА РУДИ ОТ НАХОЩЕ ЧАЙЕЛИ, СЕВЕРНА ТУРЦИЯ И ТЯХНОТО ВЛИЯНИЕ ВЪРХУ ПРОЦЕСИТЕ НА ОБОГАТЯВАНЕ

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РЕЗЮМЕ. Статията представя минераложка характеристика и особенности в разпределението на минералите в продукти от обогатяване на “кластични” Cu руди от горнокредното масивно-сулфидно Cu-Zn находище Чайели (във вулканити), локализирано в Понтидите на Северна Турция. Изследванията са проведени върху 16 образци от входяща Cu руда, колективен Cu концентрат, краен Cu концентрат и отпадък от колективния Cu концентрат, разделени в четири класи (> 36 µm, 36 – 20 µm, 20 – 9 µm and < 9 µm). Специално внимание е обърнато върху минераложките и геохимични особености на сфалерита, който е един от главните рудни минерали в находището.

В резултат на изследванията е установено, че относително голямо количество халкопирит като частици с размери под 9 µm се концентрира в най-фините фракции, най-вече в крайния Cu концентрат и колективния Cu концентрат. Клас 20 – 36 за всички продукти (без отпадъка от колективния Cu концентрат) е с най-ниско халкопиритово и най-високо пиритово съдържание, дължащо се на по-добрата флотация на пирита. Значително количество сфалерит, характеризиращ се с по-високо съдържание на Cu и Fe (като изоморфни примеси или изключително фини включения от халкопирит) присъства в крайния Cu концентрат. Тази тенденция е добре изразена за клас > 36 на крайния Cu концентрат, където общото количество Cu и Fe е 11.29 тегл. % сравнено с 7.60 тегл. % за целия меден концентрат и 6.24 тегл. % във входящата руда. Изхождайки от минераложките изследвания се предлага подобряване на обогатителния процес чрез оптимизация на смилането и хидроциклониране – насочване на цикъла в ясно изразен режим тип “scalping mode”. Елиминиране на влиянието на медсъдържащите включения в сфалерита може да се осъществи също така и чрез оптимизиране на pH на средата и изпробване на нови реагенти в процеса на обогатяване.

Introduction

The main purpose of the recent study includes mineralogical investigation and quantitative evaluation of distribution of minerals in products from mineral processing of copper ore from Çayeli Copper mine (Turkey). Special attention had been drown to the mineralogical and geochemical peculiarities of sphalerite as it is one of the main ore minerals presenting in ores. Based on mineralogical data obtained it is suggested some optimisation of mineral processing of ores.

Geolological setting

The Cayeli mine is on of the largest copper-zink deposits (19.5 Mt @ 4.2% Cu, 6.4% Zn, 65 g/t Ag) located in the eastern part of Eastern Black Sea Pontides belt, Northern Turkey (Fig. 1). It is typical representative of the VMS Kuroko type Upper Cretaceous deposits hosted in basalt-rhyolite-dacite submarine volcanic complex (Leaman and Staude, 2002). This complex forms a strip elongated in NE direction and it is set up by basalts, gabbroic intrusions, rhyolite flows and intrusions, dacite flows and intrusions. The main ore body has column to lense-like shape and size 800 m x 600 m deeping 55 – 70° NW and it is divided by scissor fault to two parts – “Main” and “Deep” respectively. Ore mineralization includes chalcopyrite (chp), sphalerite (sp) and pyrite (py) as main ore minerals, galena (ga), bornite (brn), covellite (cov), tennatite-tetrahedrite (ten), chalcocite and other sulphides in minor quantities developed in massive ore-shots, rarely as stockwork dissemination around them.

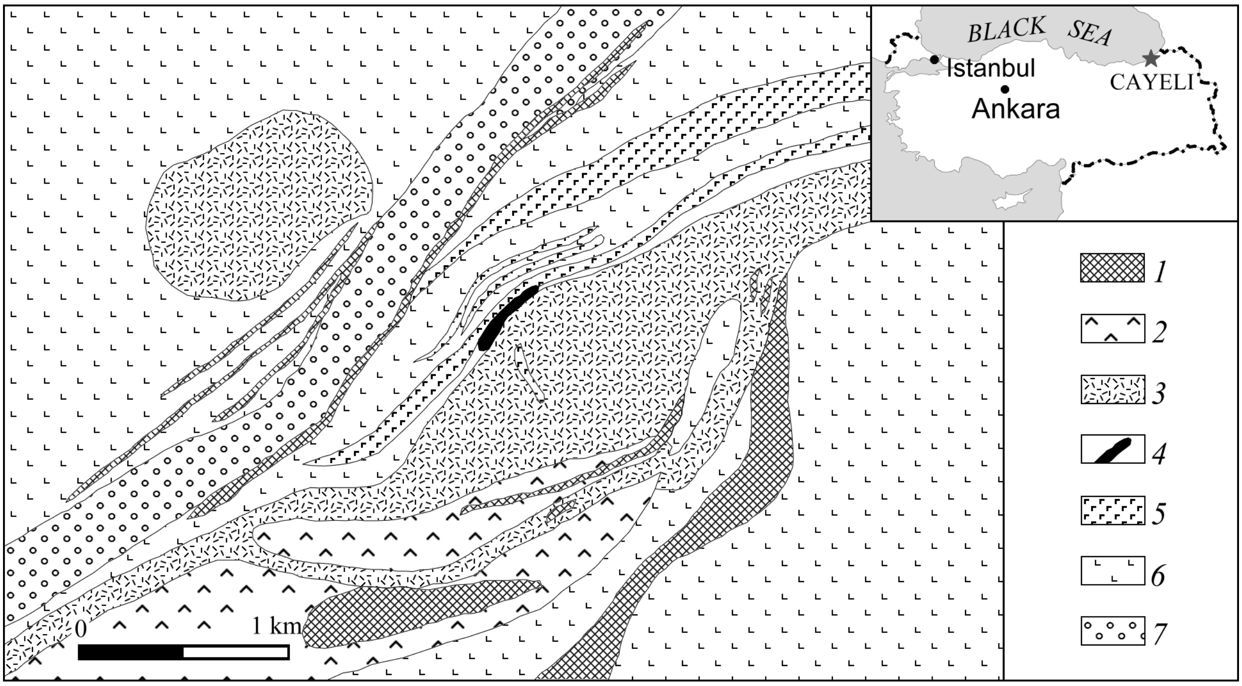

Fig. 1. Geological map of Cayeli deposit (modified after Leaman and Staude, 2002).
1 – dacite subvolcanuc bodies and dykes; 2 – dacite flows; 3 – rhyolite flows, breccias; 4 – massive sulphides; 5 – gabbroic intrusions; 6 – basalts; 7 – sediments

Material and methods

The study is performed on 16 polished briquettes prepared from 4 main products – Clastic Ore Flotation Feed (TK 1), Clastic Ore Cu Final concentrate (TK 2), Clastic Ore Cu Rougher concentrate (TK 3) and Clastic Ore Rougher Tail (TK 4), including 9 classes each: a) > 63, 50 and 36 (particle size in μm); b) > 28 and 20; c) > 15, 11 and 9; d) < 9. The respective single samples from these classes are labelled as follows: TK 1-1, TK 1-2; TK 1-3 and TK 1-4, etc. (Table 1.)

The prepared 16 samples are studied through an optical microscope under magnifications from x250 up to x1000 including immersion liquid in the cases when magnification is x1000. The distribution of ore mineral particles is evaluated through the use of Panasonic CCD colour camera (model GP KR22 2E) fitted to an universal microscope NU – 2 and computer program for image analysis installed on IntelliStation Z pro IBM computer, Matrox Rainbow Runner Studio, iPhoto Express and PhotoShop 5.0 programs for processing images, controlled by visual measuring of mineral particles. The evaluation of participation of different minerals as liberated particles and in intergrowths is based on the principles of area measurements discussed by Jones (1987). The measurements of areas of different particles in the first two classes from every product cover between 300 000 and 600 000 μm^2 and for the last two between 200 000 – 300 000 μm^2. Area ratio provides a good presentation of the participation of different minerals as liberated particles and as locked particles. In case the volumetric proportions are required, then these percentages should be precise by adding coefficients considering the specific gravity of participated minerals, but due to the relatively similar specific gravity of the minerals studied the corrections will not be very significant.

As it was found during the observation in classes 3 and 4 for products TK 1, TK 2 and TK 3 the presence of very small mineral particles (1 – 4 μm^2 or less) is very common. It these cases optical observation is not sufficiently effective because minerals (especially pyrite and chalcopyrite) could not be determined distinctly on the basis of their optical properties in reflected light microscope even when the most powerful observation available (x 1000 + immersion) is used. To avoid this problem, optical observation for these classes is combined with area quantitative electron microprobe analyses, which could very precisely determine the type of mineral particles on the basis of specific radiation of elements under the beam of focused accelerated electrons. JEOL JSM 35 CF microprobe with X-ray microanalyser (TRACOR NORTHERN TH 2000) of JEOL company and set of standards are used for quantitative measurements of chemical composition of particles studied. Data obtained from the measurements are proceeded through computer program SSPS and the percentage distribution of minerals as liberated grains and intergrowths is calculated.

Mineral distribution in different products

a) Clastic ore flotation feed (TK 1)

Analyses established that during the grinding of ore the percentage of chalcopyrite locked in intergrowths significantly decreases, compared to those of pyrite and sphalerite (Table 1). In class TK 1-1 intergrowths between two, three or even four minerals are very common (Fig. 2, Plate A), The most frequently met intergrowths are of py + sp and py + chp. In class TK1-4 almost all of the particles are liberated (Plate B). Total chalcopyrite quantity in the finest class (TK1-4) is practically liberated and the number of its intergrowths is below 0.05 %. Compared to the findings from the other classes it should be acknowledged that here chalcopyrite has the highest concentration which means that about one third of it reports in the finest fraction from all the fractions studied.

Table 1.

Distribution of ore minerals as liberated particles and locked as intergrowths (in area %)

Sample No	Size [μm]	**Chp** Total	Chp (liber)	Chp in intergr	**Sp** Total	Sp (liber)	Sp in intergr	**Py** Total	Py (liber)	Py in intergr	**Ga** Total	**Brn** (±**Cov**) Total	**Ten** Total
TK1-1	> 36	**16.2**	6.7	9.5	**23.7**	9.8	13.9	**59.5**	49.0	10.5	**0.5**	**0.1**	**-**
TK1-2	20 – 36	**12.1**	8.7	3.4	**16.8**	11.7	5.1	**70.2**	64.7	5.5	**0.7**	**0.2**	**-**
TK1-3	9 – 20	**16.1**	15.4	0.7	**18.6**	16.9	1.7	**64.2**	61.8	2.4	**0.6**	**0.5**	**-**
TK1-4	< 9	**22.4**	22.97	0.03	**19.5**	18.5	1.0	**56.7**	55.9	0.8			
TK2-1	> 36	**61.2**	45.5	15.7	**10.9**	3.2	7.7	**25.5**	17.6	7.9	**2.0**	**0.2**	**0.1**
TK2-2	20 – 36	**48.8**	41.5	7.3	**11.3**	3.6	7.7	**35.8**	29.9	1.9	**3.1**	**(+) 0.1**	**0.2**
TK2-3	9 – 20	**56.3**	53.7	2.6	**17.2**	12.9	4.3	**23.5**	21.9	1.6	**1.2**	**2.0**	**-**
TK2-4	< 9	**71.4**	70.1	1.3	**16.2**	15.4	0.8	**11.0**	10.3	0.7	**0.4**	**1.0**	**-**
TK3-1	> 36	**45.7**	28.2	17.5	**12.0**	2.7	9.3	**37.7**	23.4	14.3	**2.1**	**1.9**	**0.6**
TK3-2	20 – 36	**35.1**	28.5	6.6	**14.2**	7.4	6.8	**47.1**	42.2	4.9	**2.2**	**(+) 1.3**	**-**
TK3-3	9 – 20	**45.8**	43.5	2.3	**16.3**	12.8	3.5	**36.1**	33.3	2.8	**0.7**	**1.3**	**-**
TK3-4	< 9	**53.0**	52.4	0.6	**16.2**	14.9	1.3	**29.9**	28.6	1.3	**0.3**	**0.6**	**-**
TK4-1	> 36	**6.8**	4.4	2.4	**25.7**	20.7	5.0	**66.8**	59.5	7.3	**0.4**	**0.2**	**0.1**
TK4-2	20 – 36	**7.1**	5.1	2.0	**22.1**	17.6	4.5	**69.5**	65.1	4.4	**1.0**	**0.4**	**-**
TK4-3	9 – 20	**5.1**	4.1	1.0	**21.3**	19.7	1.6	**72.9**	70.9	2.0	**0.4**	**0.3**	**-**
TK4-4	< 9	**9.2**	8.9	0.3	**22.4**	21.6	0.8	**67.7**	67.0	0.7	**0.3**	**0.4**	**-**

Five sphalerite particles in class TK 1-1 (1 liberated particle and 4 as intergrowths) are studied quantitatively by microprobe analyses for trace elements, but Fe and Cu concentration above the average for the series TK 1 (Table 2, an. #2) is registered only in one of them. Four particles of liberated sphalerite in class TK 1-2 are analysed by microprobe and it is found out that Cu + Fe content is very close to the average one for the series TK 1 (Table 2). Two of the analyses indicate Cd, one of which (an. # 8, Table 2) carries the highest amount (0.82 wt. %) of this element among all the samples measured in this study. Fe participates probably partly in sphalerite as isomorphic impurities and partly as chalcopyrite of submicronic size, while Cu is expected only as submicronic inclusions of chalcopyrite. Galena, bornite, covellite and tennantite-tetrahedrite are in very minor quantity (< 1%) in the clastic ore flotation feed.

b) Clastic ore rougher concentrate (TK3)

The content of chalcopyrite significantly increases when compared to this found in the same fractions of TK 1 (Ore flotation feed) and it is the dominated mineral in this product. The presence of intergrowths in class TK 3-1 is high, but these are mainly intergrowths between two minerals and very rarely they integrate three minerals. Their distribution is irregular. For the chalcopyrite and pyrite they are less than the liberated particles (Table 1), but for sphalerite they are dominating. The presence of tennantite is typical for this product met both as liberated particles and equally as intergrowths with chalcopyrite or sphalerite. This mineral is determined by qualitative microprobe analysis, which has established high content of As and no presence of Ag – an element found very often in tennantite from similar deposits. Previous studies of De Priesco (1997 and 1999) established presence of tetrahedrite, but our analyses found the member of tennantite-tetrahedrite mineral row being closer to the position of tennantite. Secondary copper minerals are presented by bornite which takes between 0.6 and 1.9 % from all the area measured (Table 1). Galena presents also between 0.3 – 2.1 % of all the area measured for ore minerals and one third of galena is in intergrowths mainly with sphalerite. Two particles of sphalerite in class TK 3-2 are analysed for trace elements content and one of them indicates the highest Fe wt. % found in all samples studied (Table 2). As Cu is only 1.5 wt. %, it could be concluded that about 10 wt. % of Fe is as an isomorphic impurities in sphalerite. One particle containing relatively higher quantity of Fe and Cu (Table 2, # 32) is studied at magnification x 4300 by SEM (Plate C), but no evidence for presence of chalcopyrite and pyrite is found. The surface of the particle studied under SEM COMPO regime looks absolutely clear of mineral inclusions, so this is leading to confirmation of the suggestion that if there are any mineral inclusions in it, they should be sized hundreds part of the micrometer – which is below the accuracy level of the device used at present.

c) Clastic Ore Final Concentrate (TK 2)

The sample TK 2-1 hosts the largest variety of intergrowth types and about 20 combinations of ore minerals are identified in it. The intergrowths including two minerals are dominant, but cases when 3 minerals are also typical for the sample. Plates D, E, F illustrate some of the most often found intergrowths in the sample. Chalcopyrite content in intergrowths gradually decreases from 15.7 % (TK2 -1) to 1.3 % (TK2 -4) and reaches the highest quantity as liberated particles in the finest class – 70.1 %. Chalcopyrite emulsion in sphalerite is not typical for this product and it is found relatively rarely. During the study, it is found out that classes 3 and 4 for products TK 2, TK 3 (less in TK 1 and TK 4) contain a lot of agglomerated aggregates including many very fine mineral particles with size less then 9 μm. Plate G illustrates SEM photo of such agglomerate, shoot at magnification x 100. Agglomerates are also observed in classes 1 and 2 but their relative participation in products is not so emphasised and fine particles in them are rarely found.

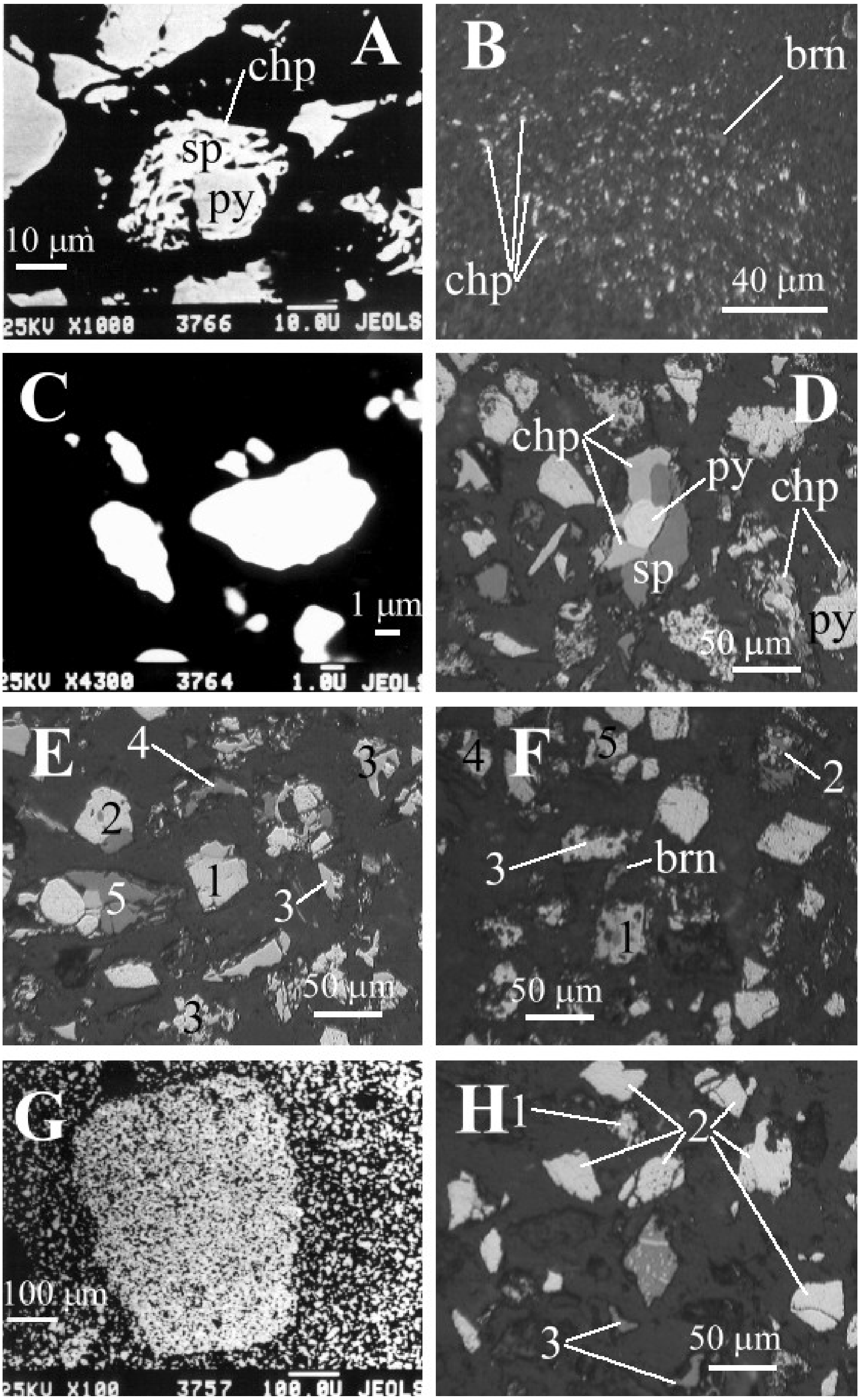

Fig. 2. Microphotograhs (SEM and polarised reflected light).

Plate A. Triple intergrowth sphalerite + chalcopyrite + pyrite (centre). – *SEM, Regime COMPO*; Plate B. A general view of TK 1-4 in optical microscope. The largest part of the ore particles is liberated and intergrowths are very rare. Liberated particles are of pyrite (white yellow), chalcopyrite (yellow), sphalerite (grey) and bornite (brown); Plate C. Several sphalerite particles observed in SEM at magnification x 4300. The largest particle was analysed by microprobe analyses and it was found that copper and iron presents in it (Table 3, an # 32). No any other mineral was found as mineral inclusion in it. Bar size on photo is 1 μm and if there are any mineral particles above 0.2 μm they must be seen in sphalerite particle, but the surface is free of any inclusions. – *SEM, Regime COMPO*; Plate D. A large pyrite + chalcopyrite + sphalerite intergrowth (centre) and smaller one below it. Chalcopyrite + pyrite in the right bottom corner; Plate E. Intergrowths galena + sphalerite (1) – in the centre, sphalerite + pyrite (2), chalcopyrite + pyrite (3), sphalerite + chalcopyrite (4) and sphalerite + pyrite + chalcopyrite (5); Plate F. Different types of intergrowths in the sample TK 2-1. Tennantite + chalcopyrite + sphalerite (1), sphalerite + chalcopyrite + gangue mineral (2), chalcopyrite + pyrite (3), sphalerite + pyrite (4) and pyrite + sphalerite + chalcopyrite (5) intergrowth. Liberated bornite also presents; Plate G. A general view of agglomerate aggregate in the sample TK2-3. – *SEM, COMPO Regime*; Plate H. Chalcopyrite inclusions and small veinlet in sphalerite (centre), intergrowth chalcopyrite + pyrite (1), liberated pyrite (2) and liberated sphalerite (3)

Table 2.
Chemical composition of sphalerite in different products results from Electron Microprobe Analysis (in wt. %)

No of an.	No of MPA	No of sample	Type of particle	Zn wt.%	Fe wt.%	Mn wt.%	Cu wt.%	Cd wt.%	Ag wt.%	S wt.%	Total wt.%
1	54	TK1-1	liber	62.87	1.66	0.00	2.47	0.58	0.00	32.20	99.77
2	55	TK1-1	sp+py+chp	54.31	6.79	0.11	7.06	0.00	0.00	31.34	99.61
3	55a	TK1-1	sp+py+chp	62.00	2.58	0.00	1.88	0.35	0.00	33.14	99.95
4	56	TK1-1	sp+py+brn	61.10	3.17	0.00	2.51	0.00	0.18	32.95.	99.91
5	56a	TK1-1	sp+py+brn	61.10	3.17	0.00	3.09	0.00	0.00	31.94	99.37
6	50	TK1-2	sp+chp	62.07	3.01	0.00	2.56	0.00	0.00	32.40	100.04
7	51	TK1-2	liber	63.19	1.73	0.00	1.68	0.35	0.00	32.62	99.57
8	52	TK1-2	liber	60.69	3.23	0.15	3.06	0.82	0.00	32.25	100.20
9	53	TK1-2	liber	60.46	5.64	0.10	1.13	0.00	0.00	33.17	100.50
10	49	TK1-3	liber	59.69	3.34	0.23	2.53	0.63	0.38	32.62	99.42
11	45	TK1-4	liber	59.66	3.53	0.13	2.93	0.00	0.00	34.37	100.63
		TK 1	average		**3.44**	**0.07**	**2.80**	**0.24**	**0.05**		
12	1	TK 2-1	liber	53.01	5.68	0.00	6.36	0.50	0.00	34.46	100.01
13	2	TK 2-1	liber	55.93	6.91	0.11	2.23	0.00	0.00	34.15	99.33
14	3	TK 2-1	sp+chp	57.73	4.73	0.11	4.89	0.00	0.00	32.05	99.51
15	4	TK 2-1	sp+py	51.12	10.49	0.00	3.59	0.00	0.00	35.28	100.48
16	5	TK 2-2	liber	58.69	3.80	0.00	5.23	0.00	0.00	31.53	99.25
17	7	TK 2-2	sp+py	64.22	2.20	0.10	1.15	0.00	0.00	32.21	99.88
18	8	TK 2-2	sp+py	61.72	3.26	0.00	2.35	0.44	0.00	31.97	99.74
19	9	TK 2-2	sp+chp	63.53	2,45	0.00	1.35	0.00	0.00	32.53	99.86
20	10	TK 2-3	liber	62.94	2.74	0.09	2.06	0.00	0.00	31.98	99.81
21	11	TK 2-3	liber	61.74	1.74	0.00	1.75	0.00	0.00	34.19	99.42
22	31	TK2-4	liber	55.51	5.14	0.00	4.65	0.59	0.00	33.03	98.92
		TK 2	average		**4.46**	**0.03**	**3.14**	**0.14**	**0.00**		
23	19	TK3-1	liber(c)	65.44	1.36	0.12	1.33	0.00	0.00	32.50	100.75
24	20	TK3-1	liber(p)	65.19	1.21	0.00	1.44	0.54	0.00	31.47	99.85
25	21	TK3-1	liber(c)	60.77	3.14	0.06	4.18	0.47	0.00	31.74	100.36
26	22	TK3-1	liber(p)	60.10	3.06	0.00	4.15	0.00	0.00	33.31	100.62
27	23	TK3-1	sp+py+chp	62.43	2.76	0.00	2.79	0.32	0.24	32.21	100.75
28	24	TK3-1	sp+chp+brn	64.54	1.41	0.00	1.47	0.00	0.00	32.52	99.94
29	25	TK3-2	liber	55.71	11.83	0.00	1.50	0.00	0.00	31.77	100.81
30	26	TK3-2	liber	64.54	2.44	0.35	2.56	0.00	0.00	31.07	100.96
31	27	TK3-3	sp+py	58.10	4.10	0.10	3.65	0.00	0.00	33.72	99.67
32	35	TK3-4	liber	54.54	4.96	0.15	5.22	0.00	0.00	36.22	101.09
		TK 3	average		**3.62**	**0.08**	**2.83**	**0.13**	**<0.005**		
33	18a	TK 4-1	liber	61.32	3.15	0.00	1.69	0.00	0.00	33.78	99.94
34	57	TK4-1	liber	64.88	1.17	0.00	1.15	0.51	0.00	31.84	99.55
35	58	TK4-1	liber	63.34	2.55	0.00	0.93	0.71	0.00	32.09	99.62
36	59	TK4-1	liber	59.30	4.18	0.00	4.65	0.00	0.00	31.87	100.00
37	43	TK4-2	liber	62.33	2.75	0.12	0.80	0.39	0.00	32.87	99.26
38	42	TK4-3	liber	63.10	3.17	0.00	0.65	0.36	0.00	33.01	100.29
39	44	TK4-2	liber	60.71	3.58	0.08	2.80	0.23	0.00	32.70	100.17
40	39	TK4-4	liber	59.54	2.44	0.00	0.46	0.44	0.33	36.74	99.95
41	38	TK4-4	liber	57.04	3.68	0.09	2.07	0.49	0.30	37.56	100.93
		TK 4	average		**2.96**	**0.03**	**1.68**	**0.34**	**<0.005**		

These agglomerate aggregates are probably precipitated during separation of different classes and this finding should be taken into account when using the chemical analyses especially of classes 3. This is confirmed by the fact that in class 9 – 20 µm it is found aggregates much larger than 20 µm. Practically the chemical analyses of obtained fractions cover particles with sizes 15, 11 and 9 µm, but also many particles with sizes less then 9 µm. Quantitative electron microprobe analyses of representative fields are performed in areas of normal distribution of mineral particles as well as in areas of agglomerate aggregates and it is found that copper content in agglomerates is 2 – 4% higher. It is due probably to the larger presence of fine chalcopyrite particles in the agglomerates.

d) Clastic ore rougher tail (TK 4)

This product is characterised with relatively stable distribution of minerals in different classes as liberated particles and intergrowths. Intergrowths are very rare compared with the other products (Plate H). Pyrite is dominating mineral in quantity between 66.8 and 72.9 %. Chalcopyrite is less then 10 % but the quantity of sphalerite is relatively high within 21.3 to 25.7 %. Fe + Cu content in sphalerite varies within the range of average for all samples, but it should be mentioned that as a total, estimated sphalerite in the rougher tail contains iron and copper less than in the other products.

Chemical peculiarities of sphalerite

The analyses are performed on liberated sphalerite particles as well as on intergrowths of sphalerite with other minerals. The areas studied in sphalerite by microprobe analysis are found clear of mineral inclusions visible under optical microscope at magnification up to x1000. SEM observations under magnification up to x4300 do not establish inclusions of single mineral grains in sphalerite as well. The sphalerite chemical studies realised through electron microprobe analysis have established Fe and Cu as main trace elements in it. These elements are found in different quantity in every single sphalerite particle that was studied. Mn, Cd, Ag and In are found in some of the sphalerite particles in very minor quantity. Iron could be present as isomorphic inclusions in sphalerite up to 20 %, but it could be also found together with copper as very fine (hundred parts of micrometers) crystals of chalcopyrite intergrowths in sphalerite (Bonev and Radulova, 1996). A presence of smaller inclusions not visible even at magnifications up to x4300 used in this study could be presumed for the Cayeli ore on the basis of our microprobe analyses. The main and probably the only possible presence of copper in sphalerite is due to the very fine (micronic and submicronic sizes) mineral inclusions of chalcopyrite rather than as an isomorphic inclusions inside the crystal lattice crystallised after decomposition of solid solution between sphalerite and chalcopyrite (Petrovskaya, 1977, Kojima and Toshiro, 1994, Gu et al., 1999 and others). In some recent studies, copper found in sphalerite analysis is labelled as "lattice" copper (Mielcsarski et all. 2000), underlying that in fact it is not copper from the real crystal lattice of sphalerite, but is due to the "invisible" chalcopyrite inclusions in it. The so called "chalcopyrite disease" often found in many deposits as epigenetic deposition of visible chalcopyrite grains (> 2 μm) in interstitial spaces of sphalerite is not very typical for the samples studied. Chalcopyrite grains (> 2 μm) in sphalerite are observed relatively rarely in the products studied by now (Plate C). Our studies suggest that the presence of Cu and partly of Fe in sphalerite for the Cayeli Mine products is due mainly to submicronic inclusions of chalcopyrite in sphalerite and to a lesser extent to the presence of small (1 – 4 μm^2) optically visible chalcopyrite inclusions in it. Part of Fe is, at no doubts, present as isomorphic impurities in sphalerite. Several cases are found in which concentration of Fe is much higher than Cu presence and the additional Fe quantity not included in chalcopyrite is supposed to be present as an isomorphic form replacing Zn in the sphalerite crystal lattice (an. ## 9, 15, 29, 37, 38, 40, Table 2). Part of the Cu and Fe could reach sphalerite grains as well, resulting from diffusion between sphalerite and chalcopyrite and pyrite contacting with it. In some samples, such as an. ## 2 (TK 1-1), 15 and 14 (TK 2-1) this could be expected (Table 2), but it should be underlined that these occurrences are found very rarely within the range of the samples studied. Some of the particles are studied for possible zonal distribution of Fe and Cu (an. ## 23, 24, 25 and 26, TK 3-1, Table 2), but no zonality in distribution is found for them. This fact supports the idea for a limited presence of Fe and Cu in sphalerite as a result from diffusion processes between sphalerite and the neighbouring minerals surrounding it. If we take as a basis the average concentration of Cu + Fe (6.24 wt. %) for product TK 1 (Clastic ore flotation feed), the content of Fe + Cu increases up to 7.60 wt. % for TK2 product (Clastic ore Cu concentrate) and decreases to 3.64 wt % in the rougher tail. That means that the flotation behaviour of the relatively rich in Cu and Fe sphalerite particles stimulates their reporting towards copper concentrate. This trend is very well pronounced for the coarser sphalerite particles in TK 2-1 (an. ## 12, 13,14,15, Table 2) which mean content is higher (11.22 wt. % Fe + Cu) compared to the 7.60 wt. % (Fe + Cu) mean content found for the rest classes copper final concentrate (TK 2). Cadmium content in the samples studied is relatively low, but the element has a stable presence in the most of sphalerite grains studied. It is distributed as isomorphic admixture in sphalerite. Inclusions of greenockite (CdS) or any other single Cd-bearing mineral are not observed. It should be mentioned that Cd concentration is lower for products TK 2 and TK 3 and slightly increases in the copper rougher tailing TK 4 (0.34 wt. %). Mn and Ag have very rare distribution for the products studied and the analyses obtained do not provide basis for sound interpretation of their behaviour. Indium is found in only one single sample (an. # 35, TK 4-1), as 0.31 wt. % and it is not included in Table 2.

Discussion and conclusions

The data and findings obtained allow us to figure out the following conclusions:

Relatively high amount of chalcopyrite is concentrated in the finest fractions as particles below 9 μm, especially in Cu Rougher and Cu Final concentrates. Agglomerated aggregates are often found in 9 - 20 and < 9 classes for the Cu rougher and Cu final concentrate similar to p. 1 above. Aggregates are characterised by relatively high presence of very fine (< 9 μm) chalcopyrite particles. We suppose that aggregates are formed due to the processes of the separation of the material in classes because in class 9 – 20 there are aggregates larger than 50 – 60 μm. Class 20 – 36 for all the samples (except in copper rougher tail) contains relatively low quantity of chalcopyrite and higher pyrite content compared to the rest three classes. The implication is that this is due to the better pyrite flotation in this class. Thus its increased concentration is leading to a concomitant decrease in the respective chalcopyrite presence. Secondary copper minerals are very limited in distribution. The quantity of bornite, which is the most often, found secondary copper mineral increases for 9 – 20 classes. Significant amount of sphalerite is present in the copper final concentrate. It is characterised by higher Cu + Fe content - as isomorphic impurities or extremely fine crystals of chalcopyrite. This trend is very well evident for the class > 36 of Cu Final Concentrate (TK 2-1) where the total amount of Fe + Cu is 11.29 wt. % compared to 7.60 wt. % for the whole Cu Final Concentrate (TK 2) and 6.24 wt. % compared to Clastic ore Flotation Feed (TK 1). Chalcopyrite emulsion in sphalerite is not typical for the products studied. In the previous studies of ore mineral composition (De Priesco, 1997, De Priesco, 1999) it is mentioned that chalcopyrite emulsion forms "cloud"-like textures involving numerous chalcopyrite grains (< 2 μm), however such textures are not very often found in the samples studied. It could be argued that during sphalerite grinding, as the destruction of aggregates usually starts from the interstitial spaces, such a chalcopyrite is liberated immediately on a "first-come first-serve" basis and it reports in the finest range, together with the fine particles formed during larger chalcopyrite grain size reduction. Sphalerite in the Copper Rougher Tail is characterised by lower content of Fe + Cu compared to the other products. Characteristic for it is the constant Cd content (0.34 wt. % average). Intergrowths are very limited in distribution for classes 9 – 20 and < 9.

One of the major findings derived from the mineralogical studies described above is that whilst for all the products examined there is a well emphasised presence of copper in sphalerite grains, this could be attributed merely to submicronic inclusions of chalcopyrite in sphalerite, rather than to the so called "chalcopyrite disease". This important characteristic do provide an avenue for searching possible technological solutions for bringing about a further reduction in the content of zinc in copper concentrate for the clastic ore which seems a tangible objective. In the case of Çayeli clastic ore, two directions, which could be studied in parallel, deserve attention.

The first one is grinding and hydrocycloning optimisation - rendering the circuit to operate in a more pronounced "scalping" mode. Taking into consideration the frequently reported agglomerated particles the actual reconstitution of the size distribution figures for the sieved classes of Cu rougher and Cu final concentrates with no doubts will result in increase in class –9 µm yield up to 40-45 %. Needless to say is that such a significant presence of fine slimes (involving mainly chalcopyrite in our case) is known to have a pronounced unwanted influence leading to complications in flotation selectivity. In support of this is the insufficient degree of Cu/Zn selection evident for these size classes belonging to both Cu concentrates studied (TK 2 and TK 3), regardless of the almost complete mineral liberation observed. In such cases selective Cu/Zn flotation could be hampered principally in two ways – on a "mechanical" grounds due to the vast amount of slimes and by introducing Cu ions leading to sphalerite activation in copper circuits. Both phenomena are interconnected, however the first reason seems more relevant for the case of Çayeli clastic ore since in the studied samples secondary copper minerals which could supply Cu ions were rarely found.

Mineralogical studies have revealed that below 36 µm sufficient degree of liberation occurs and the amount of intergrowths drops significantly in classes under 20 µm. The implication is that the factors contributing to ore overgrinding during first stage grinding should be eliminated, if technologically possible, in order to lower to a maximum possible extent the overall yield of class –9 µm in the flotation feed which significant presence suggests material overgrinding. Our suggestion is that such a situation is feasible and will be beneficial for Cu/Zn selection in the following flotation stages. Attempts in this direction are evident in ÇBI grinding circuit where two-stage hydrocycloning is implemented, however we feel further studies and optimisation of their configuration will be beneficial in view elimination of regrinding and re-circulation in mill circuit of the ready-to-float particles.

The second direction is modifications in the reagent regime. Here as a major objective the elimination of factors leading to sphalerite activation should be pursuit. As a first step two directions could be investigated for limitation or elimination the influence of copper inclusions in sphalerite – pH optimisation and testing new reagents.

For establishing the practical limits for improving metallurgy in terms of achievable concentrate grades and recovery, the best way will be both directions to be studied in parallel.

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Препоръчана за публикуване от
катедра "Геология и проучване на полезни изкопаеми", ГПФ