FLOTATION OF A TETRAHEDRITE ORE

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Recently, a deposit of tetrahedrite ore has been discovered in the Alps, north Italy (Monte Avanza Mine). The ore contains valuable elements as copper, antimony and silver - but also undesirable elements as arsenic and mercury - in a single polymetallic sulphide. The processing of the ore gives problems as pyrometallurgical or hydrometallurgical methods are necessary for separating the valuable elements. However, the first processing step has to be the flotation of the raw ore in order to collect a high grade tetrahedrite concentrate to be subjected to the above mentioned further treatments. In this paper, the studies carried out for the characterization of the ore and its flotation are reported and discussed. For the characterization of the different types of ore of Monte Avanza Mine, systematic sampling, mineralogical studies, microprobe analysis, localization of the metals and of the impurities were done in order to make a distribution balance of the metals into the carrier minerals. The flotation tests were conducted using conventional laboratory flotation cells on different samples and in different operating conditions.

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INTRODUCTION

In the European countries and outside Europe there exist significant reserves of polymetallic sulphides, in many cases containing also precious metals, whose processing is very difficult. Two main cases may be mentioned:

(a) complex polymetallic sulphides in which the non ferrous metal sulphides are found finely disseminated in the matrix (often a pyritic matrix) with a high degree of association;

(b) polymetallic sulphides in which the non ferrous metal elements are the constituents of a single sulphide mineral, for example the tetrahedrite.

In case (a) it is theoretically possible to separate the single sulphides, because they are single minerals even if associated in intergrowths which sometime are very complex. However, using conventional processing systems the recovery may be very poor and dissatisfactory from an economic point of view. Therefore, the option of producing bulk concentrates and separating the different metals by a metallurgical process should be preferred.

In case (b) the single elements cannot be separated by physical or physico-chemical methods. It is only possible to produce a mono-mineral polymetallic concentrate and the following alternatives may be considered: (i) selling the concentrate having high content of impurities as Hg, As, Sb, a non-economic solution considering the heavy penalties generally applied by the smelter, or (ii) treating the bulk concentrate by a novel metallurgical process. For the latter alternative there are two possibilities which can be taken into consideration:

- a process for the removal of the impurities, particularly those connected to higher penalties, in order to obtain a Cu-Ag, or a Cu-Ag-Sb concentrate easy to sell to a smelter, and possibly also allowing the recovery of such impurities to produce saleable metals or by-products;
- a complete process for the separation and the production of all valuable metals contained in the ore.

As far as case (a) is concerned, it is possible to find in literature some studies related to the processing of these types of sulphides [1,2,3,4].

As far as case (b) is concerned, even if some studies are reported in the literature [5,6,7,8], a simple method for the valorization of tetrahedrite ores, suitable for small mines is not available at present.

THE MONTE AVANZA DEPOSIT

The deposit is situated in the eastern Alps near Forni Avoltri (Udine) at a height between about 1600 and 1900 meters o.s.l. The geology is characterized by two stratigraphic units which develop in an E - W direction: (a) the carbonatic unit which includes the Devonic limestone (395-345 million years) and (b) the Carboniferous flyschoid unit (345-280 million years). The two stratigraphic units are separated through a sub-vertical contact surface, plunging towards the South. The main useful mineral is argentiferous tetrahedrite. Associated minerals in very small quantities are sulphides such as pyrite, chalcopyrite and sphalerite. Tetrahedrite can be found disseminated, in veins and in milli-centimetrical thick "kidneys", often associated with calcite, in fragmented and recrystallized limestone. The most important metals in the ore are copper, silver, antimony and mercury, all contained in tetrahedrite.

CHARACTERIZATION OF THE ORE

The systematic sampling of the deposit has shown that two principal types of ore are present: No. 1 associated with the Carboniferous flyschoid, and No. 2 associated with the Devonic limestone. Samples of both types of ore have been studied.

Screen and Chemical analysis

The screen and chemical analysis of the size ranges are reported in Table I for ore type No. 1 and in Table II for ore type No. 2. Table III reports the ratios Cu/Zn, Cu/Sb and Cu/Ag.

Table I Screen and chemical analysis for ore type No. 1.

		Cu %	Zn %	Sb %	Ag g/ton
Size Range	Weight %		ORE TYPE	NO. 1	
-8+4 mm	57.90	3.70	0.45	1.60	96
-4+2 mm	17.92	5.70	0.72	2.90	155
-2+1 mm	8.77	7.40	0.90	3.80	184
-1+0.5 mm	5.71	9.60	1.10	5.20	246
-500+212 μm	3.74	12.00	1.40	5.90	286
-212+75 μm	2.97	12.50	1.15	6.40	250
75 μm	2.99	11.50	1.30	5.60	237
Feed	100.00	5.52	0.66	2.65	139

Table II Screen and chemical analysis for ore type No. 2.

		Cu %	Zn %	Sb %	Ag g/ton
Size Range	Weight %		ORE TYPE	NO. 2	
-8+4 mm	58.11	2.96	0.52	1.60	99
-4+2 mm	17.18	2.99	0.52	1.31	119
-2+1 mm	9.07	3.30	0.54	0.80	144
-1+0.5 mm	5.86	3.56	0.58	1.84	165
-500+212 µm	3.63	4.48	0.79	2.70	128
-212+75 µm	2.74	4.28	1.03	3.36	78
-75 µm	3.41	5.20	0.94	3.10	64
Feed	100.00	3.20	0.56	1.63	110

From Tables I and II, it can be observed, particularly for the ore type No. 1, that a selective comminution occurs (the grade of Cu, Zn and Sb increases as the particle size decreases). The same trend for the ore type No. 2 is much less significant.

Table III Values of the ratios Cu/Zn, Cu/Sb and Cu/Ag.

	Cu/Zn	Cu/Sb	Cu/Ag
Size Range		ORE TYPE NO. 1	
-8+4 mm	8.22	2.31	385
-4+2 mm	7.92	1.97	368
-2+1 mm	8.22	1.95	402
-1+0.5 mm	8.73	1.85	390
-500+212 µm	8.57	2.03	420
-212+75 µm	10.87	1.95	500
-75 µm	8.85	2.05	485
Feed	8.31	2.16	392
Size Range		ORE TYPE NO. 2	
-8+4 mm	5.69	1.85	299
-4+2 mm	5.75	2.28	251
-2+1 mm	6.11	4.13	229
-1+0.5 mm	6.14	1.93	216
-500+212 µm	5.67	1.66	350
-212+75 µm	4.16	1.27	549
-75 µm	5.53	1.68	813
Feed	5.72	2.11	306

Optical microscope and microprobe analysis

The study by the optical microscope has been carried out by Casari [9] on a large number of sections of the ore types No. 1 (associated with the Carboniferous flyschoid) and No. 2 (associated with the Devonic limestone). This study evidenced in the samples a large prevalence of tetrahedrite, and a small occurrence of pyrite-marcasite-bravoite, chalcopyrite, galena, blenda and rarely bournonite, boulangerite, barite and fluorite.

The macroscopic ore texture may be of the stockwork type, disseminated and banded type.

The tetrahedrite can be easily liberated at a comminution size suitable for flotation. In addition, the associated minerals are in such a small amount that their influence on the flotation and on the results can be neglected.

The microprobe analysis has been carried out on a number of sections of the two ore types. Typical results for the two ore types are reported in the Tables IV and V.

Table IV Microprobe analysis, ore type No. 1 - Sample 1-Test 1.

Element	Weight %	S.D.%	% Atom
Hg	5.45	2.25	1.53
S	25.50	0.48	44.99
Pb	0.17	26.01	0.05
Bi	0.14	27.14	0.04
Ag	0.17	14.97	0.09
Sb	21.92	0.40	10.18
As	4.61	1.15	3.47
Ni	0.00	0.00	0.00
Cu	38.86	0.24	34.60
Zn	4.87	0.68	4.21
Fe	0.79	1.98	0.80
Co	0.04	15.85	0.04
	102.52		100.00

Table V Microprobe analysis, ore type No. 2 - Sample 1-Test 1.

Element	Weight %	S.D.%	% Atom
Hg	1.70	4.48	0.45
S	26.94	0.48	44.82
Pb	0.07	59.02	0.02
Bi	0.16	23.82	0.04
Ag	0.13	19.56	0.06
Sb	13.16	0.51	5.77
As	11.15	0.75	7.95
Ni	0.00	0.00	0.00
Cu	41.43	0.23	34.79
Zn	6.83	0.55	5.57
Fe	0.52	2.51	0.49
Co	0.04	14.93	0.04
	102.13		100.00

Microprobe analysis work has shown that some variations occur in the tetrahedrite composition for the different ore types. However, within an ore type the variation is limited. Table VI shows the order of magnitude of the percentage of the main elements, as results from all the microprobe analyses made, for the different ore types.

Table VI Order of magnitude of the percentage of the main elements for the ore types No. 1 and No. 2, as results from the microprobe analyses.

Element	Ore type No. 1	Ore type No. 2
Cu %	≈ 39	≈ 41
Sb %	21-23	13-14
Zn %	≈ 4.9	≈ 6.8
As %	≈ 5	≈ 11
Hg %	≈ 5	≈ 1.6
Ag %	≈ 0.2	≈ 0.1

The flotation tests were carried out on a representative sample considering the real situation that will appear during the exploitation; such sample is constituted for about 30 % from ore type No. 1 (associated with the Carboniferous flyschoid), the left over 70 % is ore type No. 2 (associated with the Devonic limestone).

Table VII reports the size composition and grades of the material used for the flotation tests. For this material d_{80} equals 188 μ.

Table VII Size composition and grades of the flotation feed.

		Cu	Sb	Ag
Size Range μm	wt %	%	%	%
+ 188	20.0	3.8	1.8	410
- 188 + 150	6.0	3.3	1.8	213
- 150 + 125	16.0	4.4	2.2	175
- 125 + 105	11.7	4.3	2.4	111
- 105 + 75	9.7	5.2	3.0	139
- 75	36.6	4.8	2.8	126
Feed(calc.)	100.0	4.4	2.4	195
Feed(anal.)		4.3	2.3	193

A great number of laboratory tests were carried out with the purpose of establishing the best reagents modulation.

Concerning the choice of flotation collector the available literature has been considered [5]. A number of tests has been carried out with different collectors: the best results have been obtained using K-isopropylxanthate. A more detailed study for the comparison of the results obtained with K-isopropylxanthate and Aerofloat 75 showed a better selectivity for the first one, in contrast with results obtained by Surges [5]. This fact is probably due to the different characteristics of the ores.

Concerning the dispersing and frothing agents the following selection was made:

- dispersant: sodium silicate;
- frother: M.I.B. (Methyl isobutyl carbinol).

For the selection of the best operating conditions the following variables were considered:

a) conditioning time;

b) pulp density;

c) collector quantity.

A twelve-levels factorial design was realized. The optimizing variable was the copper recovery. Two levels (5 and 7 min) were considered for the conditioning time, two levels for pulp density (1.32 and 1.4 $g \cdot cm^{-3}$) and three levels for the collector quantity (150, 200 and 250 $g \cdot ton^{-1}$).

The variance analysis has permitted the determination of the best reagents modulation:

a) conditioning time:	5 min
b) pulp density:	1.32 $g \cdot cm^{-3}$
c) collector quantity:	200 $g \cdot ton^{-1}$

Using a Wedag flotation cell (3.5 l of capacity) a flotation experiment was carried out on a 800 g sample of tetrahedrite under the following optimum operating conditions:

Pulp density:	1.32 $g \cdot cm^{-3}$
Collector:	K-isopropilxanthate, 200 $g \cdot ton^{-1}$
Conditioning time:	3 + 5 min
Frother:	M.I.B., 150 $g \cdot ton^{-1}$
Dispersant:	sodium silicate, 1500 $g \cdot ton^{-1}$
Impeller speed:	1500 $rev \cdot min^{-1}$
Ph:	9.7
Flotation time:	15 min

The results are presented in Table VIII.

Table VIII Results of a batch flotation test.

	wt %	Cu		Sb		Ag	
		%	dist %	%	dist %	g/ton	dist %
Concentrate	27.14	15.50	98.8	8.10	98.7	690	98.5
Tailing	72.86	0.07	1.2	0.04	1.3	4	1.5
Feed(calc.)	100.00	4.26	100.0	2.23	100.0	190	100.0

A flotation circuit with rougher and cleaner sections were simulated; the results are reported in Table IX.

Table IX Results of the simulated flotation circuit.

	wt %	Cu		Sb		Ag	
		%	dist %	%	dist %	g/ton	dist %
Concentrate	15.60	26.40	95.5	14.40	95.7	1178	95.2
Tailing	84.40	0.23	4.5	0.12	4.3	11	4.8
Feed(calc.)	100.00	4.31	100.0	2.35	100.0	193	100.0

The yield, copper and silver recovery curves versus flotation time, obtained with the best operating conditions, are reported in Figs. 1, 2 and 3.

Flotation kinetics

A number of kinetic tests were performed under different operating conditions. Figure 2 represents the copper recovery versus the flotation time for one of the tests. The kinetic order n and the kinetic constant k were determined by a fitting procedure using the following equation [10]:

$$(1 - R)^{1-n} = 1 + k\ t\ (n - 1)\ C_o^{n-1}$$

where:

R copper recovery;

C_o initial concentration of particles with identical flotation properties.

Using Marquardt's algorithm [11] and minimizing the differences between experimental and theoretical copper recoveries the following results have been obtained:

kinetic order: 1.65;
kinetic constant: 1.11 min^{-1}.

These values are useful for the project of a flotation plant that treat the same mineral.

CONCLUSIONS

1) The valuable mineral is constituted, with a large prevalence, by tetrahedrite and the associated minerals are present in very small amount;

2) the tetrahedrite composition shows some variations for the different ore types; however, within an ore type the variation is limited;

3) the tetrahedrite can be easily liberated at a comminution size suitable for flotation;

4) For the optimization of flotation process a 2·2·3 levels factorial design was used; the variables considered were conditioning time, pulp density and collector quantity;

5) A kinetic study performed under the best operating conditions showed that for the granulometric composition of the ore considered the order of the kinetic equation is 1.65 and the kinetic constant equals 1.11;

6) The results of the tests performed with the best operating conditions are very good: from a feed with 4.31 [%] Cu, 2.35 [%] Sb and 193 [g/ton] Ag it is obtained a concentrate with 26.40 [%] Cu, 14.40 [%] Sb and 1178 [g/ton] Ag and with a metal recovery of 95.5 [%] for copper, 95.7 [%] for antimony and 95.2 [%] for silver.

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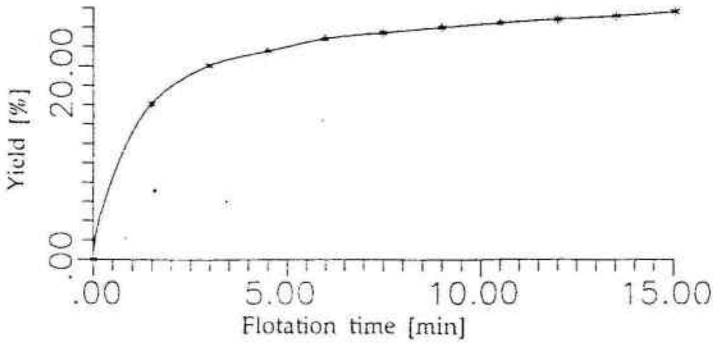

Fig. 1 Tetrahedrite yield versus flotation time.

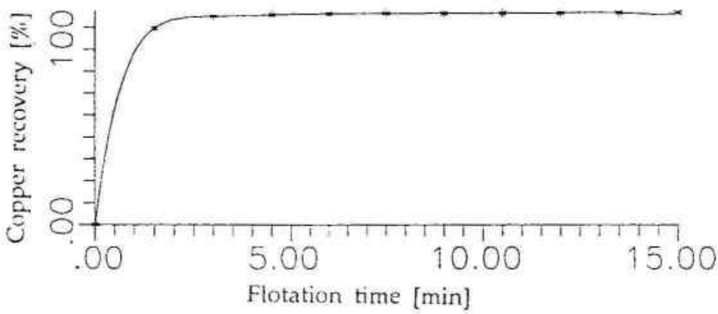

Fig. 2 Copper recovery versus flotation time.

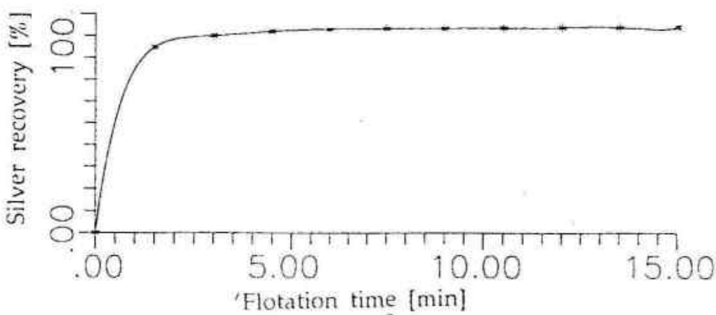

Fig. 3 Silver recovery versus flotation time.