



Arsenic leaching from a gold bearing enargite flotation concentrate

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ABSTRACT

The high arsenic content of the flotation concentrate obtained from a gold-bearing enargite ore for pyrometallurgical processing strongly diminishes its market value. An investigation has been carried out for selectively leaching arsenic from enargite–luzonite minerals using alkaline Na_2S solutions. By suitably adjusting the main reaction conditions almost 98% arsenic was leached, as well as part of the gold, particularly with high Na_2S concentrations. Copper was not lost from the solid phase in which the enargite is converted into a new species with the chemical formula $\text{Cu}_{1.5}\text{S}$.

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1. Introduction

The deeper portions of the Serrenti–Furtei gold-bearing deposit in Southern Sardinia (Italy) are host chiefly to sulphide mineralisations composed for the most part of enargite–luzonite and pyrite. Gold and subordinate amounts of tennantite, covellite, chalcopyrite and arsenopyrite are associated with the pyrite (Garbarino et al., 1991; Boi et al., 1996; Fadda et al., 2004).

The gold is refractory to direct cyanidation but potentially economic concentrations of enargite–luzonite are contained in the ores. Thus, the ores have been beneficiated by flotation, recovering the gold and copper in a collective concentrate destined for further processing via pyrometallurgy (Ghiani et al., 2000; Curreli et al., 2005). Commercial application to the ore in question proved fairly efficient, achieving high Cu and Au recoveries in the bulk float. (Di Giovanni et al., 2003).

Unfortunately, the fact that enargite prevails among the copper bearing minerals combined with the high As content of the concentrates strongly undermine their economic value because of the environmental issues associated with pyrometallurgical processing. Thus for the leaner ores direct roasting may well prove uneconomical. For this reason the possibility of removing the arsenic contained in the concentrates prior to roasting has been explored by means of alkaline leaching with a mixture of sodium sulfide and sodium hydroxide (Nadkarni and Kusik, 1988; Achmouchová et al., 1999; Baláž et al., 1999; Baláž et al., 2000; Delfini et al., 2003; Viñals et al., 2003).

In this work, the influence of the most significant process variables has been investigated, namely specific surface area of the solid, temperature, pH and reagent concentration of the leach solution.

2. Methods and materials studied

Tests were conducted on cores removed from exploration boreholes drilled into the deeper part of the mineral deposit. After grinding to below 0.15 mm the product was subjected to flotation with ethyl xanthate after pyrite depression with a mixture of lime and sodium cyanide. As the chemical (Table 1) and diffractometric analyses (Fig. 4) show, the finished product contained high enargite and gold concentrations, making it suitable for the pyrometallurgical production of gold and copper.

To evaluate the influence of solid particle size on leaching results, samples of the untreated concentrate were ground to different degrees of fineness. The specific surface area of the ground products (0.050, 0.020 and 0.010 mm) and of the concentrate itself (~0.150 mm) were then determined using the BET method (Table 2).

Arsenic removal tests were conducted on the flotation concentrate, using alkaline Na_2S solutions, to determine the effect of the following parameters: solid fineness, solution temperature and initial Na_2S and NaOH concentration. All experiments, each lasting 120 min, were carried out on 5 g solid in 0.5 kg leach solution using a 0.75 L Mod. HPM-T Medimex Schlageter & Preuss high pressure laboratory reactor (up to 300×10^5 Pa), provided with a variable speed mechanical stirrer set at 220 rpm and a Medimex C-AE 31 control unit for temperature regulation (up to 300 °C).

The influence of each variable was determined by keeping all the other variables constant. Leaching results were evaluated by means of

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Table 1
Chemical analysis of the flotation concentrate

Assay			
Au [g/10 ³ kg]	Cu [%]	As [%]	Fe [%]
90.25	33.15	12.55	9.16

Table 2
Specific surface area of the flotation concentrate ground to different degrees of fineness (BET method)

D ₁₀₀ [mm]	0.150	0.050	0.020	0.010
Specific surface area [m ² /g]	0.54	1.04	1.75	2.37

chemical determinations on the leach products, diffractometric analysis (XRD) and electron probe micro-analysis (EPMA) of the solid residues.

3. Results and discussion

3.1. Influence of temperature

Tests were conducted on the solid material ground to below 0.020 mm (1.75 m²/g), with initial Na₂S and NaOH dosage of 32.5 g/l (0.42 M) and 100 g/l (2.5 M) respectively.

The influence of temperature is shown in Fig. 1. Arsenic removal >50% is achieved only at temperatures >85 °C. At higher temperatures, efficiency improves significantly, in a practically linear fashion up to 92.5% at 105 °C. At temperatures over 105°, the amount of soluble arsenic continues to increase though less markedly. Throughout the tests, the autoclave pressure was around 200 kPa at 85 °C and 250 kPa at 115 °C.

3.2. Influence of solid specific surface area

Tests were conducted at 115 °C again using 32.5 g/l (0.42 M) Na₂S and 100 g/l (2.5 M) NaOH. The influence of specific surface area is shown in Table 3. Clearly, arsenic solubilisation increases with decreasing grain size because of the greater surface area exposed.

3.3. Influence of NaOH concentration

Tests were performed at 115 °C on the solid ground to below 0.020 mm (1.75 m²/g), using two different concentrations of Na₂S leachant. In each of the two series of tests the NaOH concentration was varied, holding the Na₂S concentration constant. The results in Fig. 2

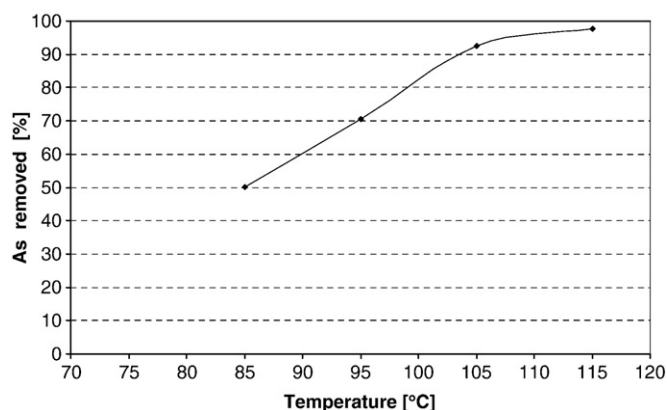


Fig. 1. Influence of temperature on arsenic removal efficiency. Fineness and specific surface area of the solid 0.020 mm and 1.75 m²/g; solids concentration 10 g/kg; Na₂S 0.42 M; NaOH 2.5 M; leach time 120 min.

Table 3
Results of leaching vs specific surface area of solid

Specific surface area [m ² /g]	0.54	1.04	1.75
As solubilised [%]	52.4	77.5	97.7

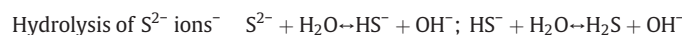
Temperature 115 °C; solids concentration 10 g/kg; Na₂S 0.42 M; NaOH 2.5 M; leach time 120 min.

indicate that arsenic leaching efficiency increases with the amount of NaOH for both Na₂S concentrations in the leach solution. Comparable leaching results can be obtained using different combinations of Na₂S–NaOH. In this case, the combination containing smaller quantities of the more expensive Na₂S is preferable in principle.

3.4. Influence of Na₂S concentration

Tests were performed under the most favourable temperature and fineness conditions found for arsenic solubilisation, namely 115 °C and specific surface area of 1.75 m²/g. Two series of tests were conducted at two different NaOH concentrations, varying the quantity of Na₂S. The results in Fig. 3 show As solubilization to increase with increasing concentrations of Na₂S in solution.

The results obtained by varying the combination of Na₂S and NaOH in the leach solution can be explained by the following reactions (Baláž et al. 1999; Achmovičová et al., 1999; Delfini et al., 2003).



As the pH is increased, the fraction of hydrolysing S²⁻ ions gradually decreases, resulting in increased availability of S²⁻ ions and other polysulfide aqueous species that can complex and solubilize arsenic. Thus a strongly basic medium with high NaOH concentration is required to minimise consumption of the more expensive Na₂S.

Experimental results show favorable conditions for As leaching to be: fineness and specific surface area of the solid 0.020 mm and 1.75 m²/g; temperature 115 °C and initial overall concentration of leachants in the 160–200 g/l range with not less than 9.75 g/l Na₂S (0.125 M) and 150 g/l NaOH (3.75 M).

3.5. Gold solubilisation

Analysis of the leach residue indicated a small reduction in the quantity of gold originally contained in the concentrate. Further work

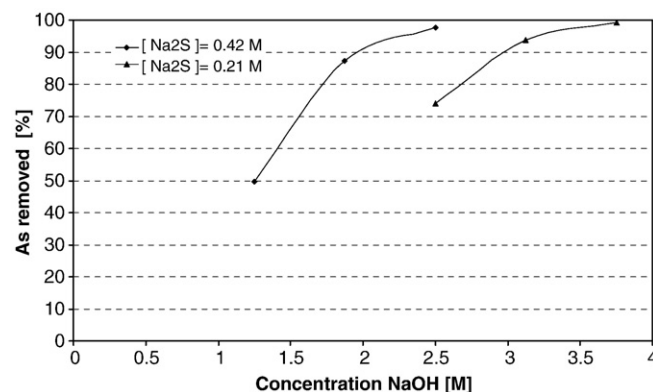


Fig. 2. Influence of NaOH concentration on arsenic removal efficiency. Na₂S = 0.21 M and 0.42 M. Other conditions as Fig. 1.

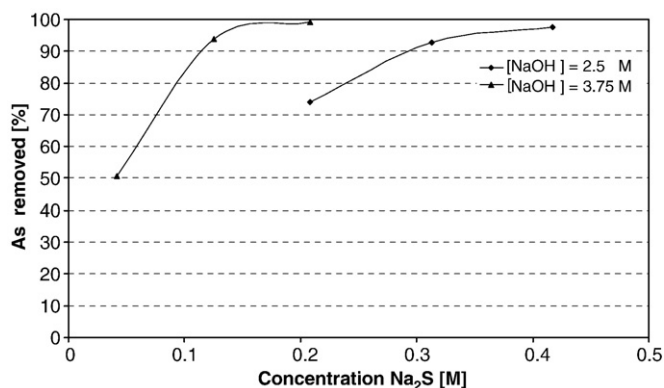
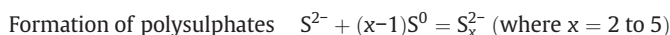
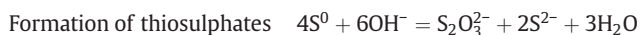
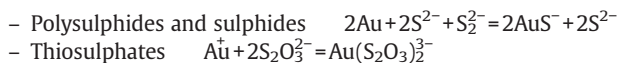


Fig. 3. Influence of Na_2S concentration on arsenic removal efficiency. NaOH 2.5 M and 3.75 M. Other conditions as Fig. 1.

is currently underway to quantify the gold leached and to determine factors that affect the amount of gold leached. This will be the subject of a future paper. Gold dissolution may be attributed to the action of the thiosulphates and polysulphides formed in the basic conditions through reaction between OH^- and sulphide ions with the free sulphur released during enargite leaching. The following reactions are proposed (Aylmore and Muir, 2001; Jeffrey and Anderson, 2003; Anderson, 2003; Senanayake 2004; Anderson and Twidwell, 2008).



Gold solubilisation:

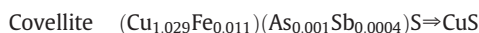
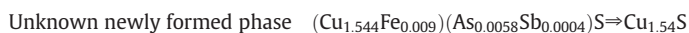
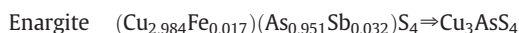


3.6. Characterisation of leach residues

To identify the chemical–mineralogical changes brought about by leaching, the flotation concentrate and solid leach residue were analysed by means of XRD and EPMA and observed under the optical microscope. Diffractometric determinations (Fig. 4) and minero-petrographic

analysis of the flotation concentrate (Fig. 5A and B) and the leach residue (Fig. 5C, D, E, F, G, H) showed the formation of a new product which did not match any compound in the JCPDS index. This product is presumably the result of decomposition of the enargite phase – also detected in the analyses. In particular, observation of polished sections of the leach residues revealed a microporous structure of the new solid phase often enclosing a nucleus of un-transformed enargite. Quartz, pyrite and covellite on the other hand remain intact.

For the crystal chemical characterisation of the new mineral phase, the leach residue was analysed by means of EPMA using an ARL SEMQ microprobe. The analyses were performed at different points of the polished sections, corresponding to the mineral phases of interest, in order to quantify S, As, St, Cu and Fe contents. By so doing it was possible to determine the average Cu, Fe, As, Sb and S assay of the enargite (Cu_3AsS_4), the newly formed mineral species and the covellite (CuS). The results provided the following average crystal chemical formula for each phase:



The results of electron microanalysis are also schematically shown in the triangular phase diagram in Fig. 6.

As can be observed from the triangular phase diagram, after leaching the crystal chemical formula of enargite changes from Cu_3AsS_4 to $\text{Cu}_{1.54}\text{S}$, a newly formed product with a micro-porous structure that usually encloses a nucleus of un-transformed enargite. Note that the covellite (CuS) maintains its position in the diagram, indicating that the leach process has not altered its crystal chemical formula.

Further leaching tests on pure enargite crystals from the same ore body confirmed the newly formed product to be unequivocally attributable to the transformation of enargite and not of the other species contained in the flotation concentrate. Analysis of the diffractograms for pure enargite (Fig. 7) and the leach product of the flotation concentrate (Fig. 8) allowed the signals of the transformed enargite phase to be distinguished from enargite and the other mineral phases of the flotation concentrate.

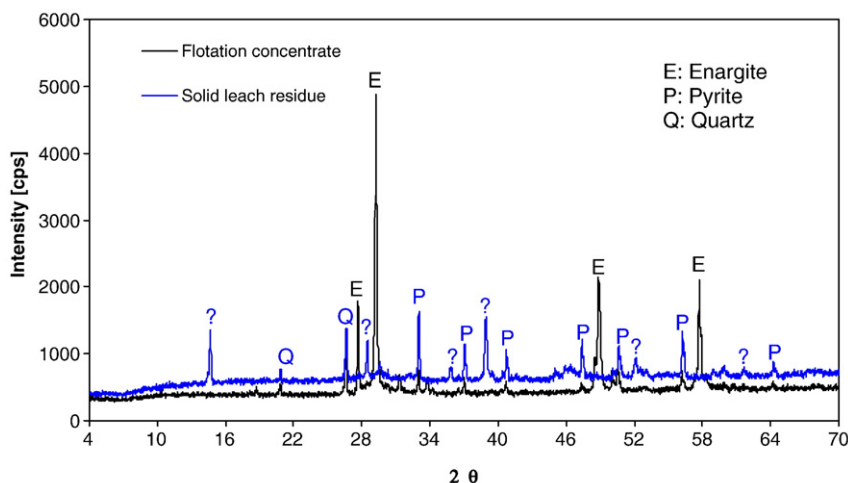


Fig. 4. XRD analysis of flotation concentrate (specific surface area $0.54 \text{ m}^2/\text{g}$) and solid leach residue (leach conditions as Fig. 1).

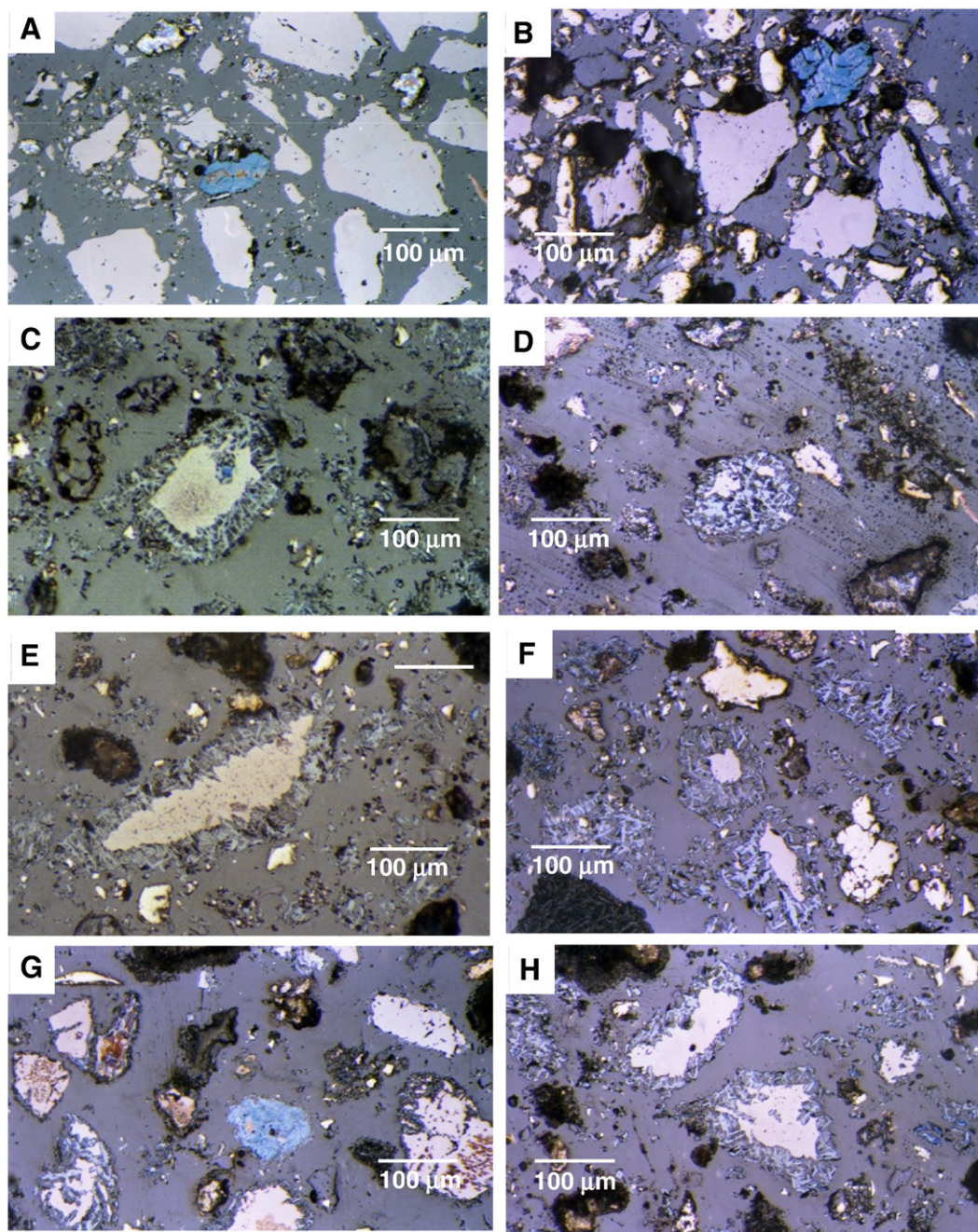


Fig. 5. Optical micrographs; 20×. A, B: flotation concentrate, specific surface area 0.54 m²/g. C, D, E, F, G, H: solid leach residue from conditions in Fig. 1.

The average crystal chemical formulae of the solid residue determined by means of electron microanalysis on the unattacked enargite and on the transformed phase confirm the conversion of enargite into a copper sulphide having stoichiometry $\approx \text{Cu}_{1.5}\text{S}$



There is practically complete solubilisation of arsenic and partial solubilisation of sulphur, while the copper is concentrated almost entirely in the solid residue.

4. Conclusions

Leaching a gold and enargite concentrate obtained by bulk flotation with basic Na_2S solutions is an effectual means of removing arsenic prior to pyrometallurgical processing. Leaching selectively solubilises the arsenic and some gold but does not affect the copper which transforms almost entirely in the leach residue as a new species having the chemical formula $\approx \text{Cu}_{1.5}\text{S}$. Process efficiency improves with increasing specific surface area of the concentrate at temperatures of over 100 °C. The concentrations of Na_2S and NaOH , as well as sulphur content in the enargite, influence the leaching process. In fact they are responsible for the S^{2-} , HS^- , OH^- , S_x^{2-} and polythionates in the solution whose equilibrium governs arsenic and gold solubilisation. The gold is partly solubilised in the form of various anionic Au–S complexes, which is the subject of further studies. Gold and arsenic

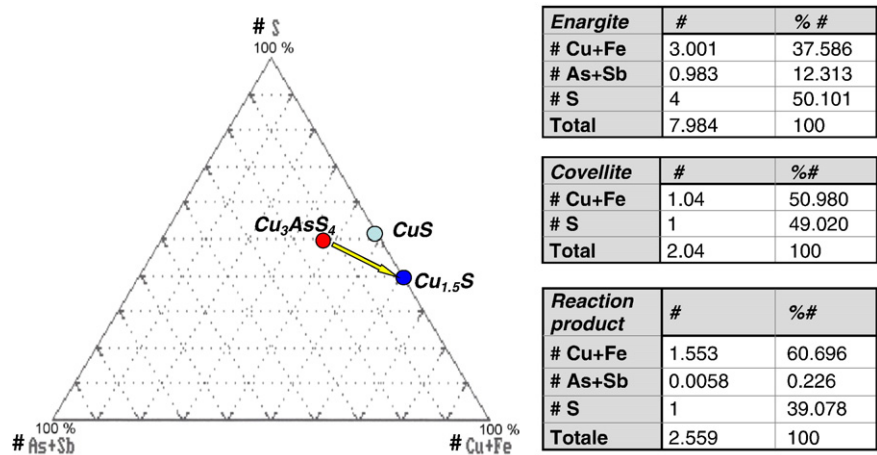


Fig. 6. Triangular diagram of formula numbers of solid phases analysed with electron microprobe.

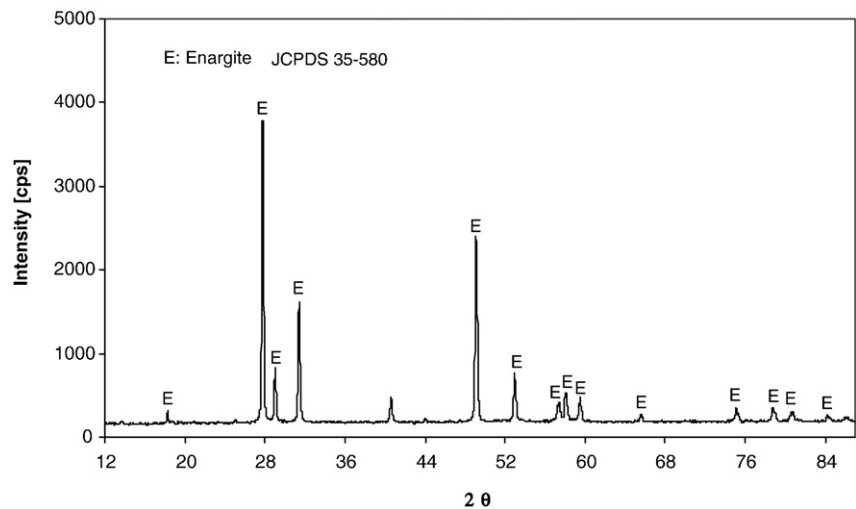


Fig. 7. XRD analysis of enargite crystals. Specific surface area 1.75 m²/g (–0.045 mm).

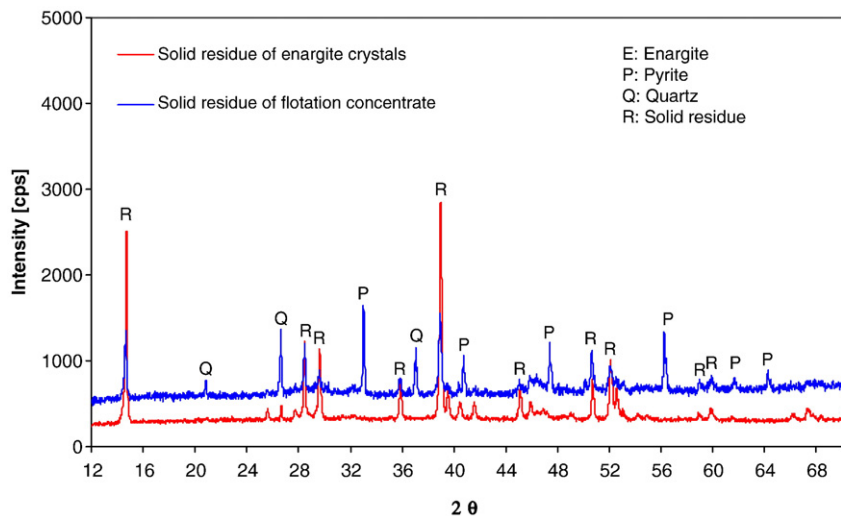


Fig. 8. XRD analysis of solid residues of the enargite crystals (specific surface area 1.75 m²/g, temperature 115 °C, solids concentration 10 g/kg, Na₂S 0.42 M, NaOH 2.5 M, leach time 120 min) and flotation concentrate.

would need to be recovered from the solution by standard techniques used in plant practice that are currently under investigation.

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References

- Achmovičová, M., Balaž, P., Bastl, Z., Sánchez, M., 1999. Characterization of the solid residue of enargite Cu_3AsS_4 after alkaline leaching. *Physicochemical Problems of Mineral Processing* 33, 7–14.
- Anderson, C.G., Twidwell, L.G., 2008. The alkaline sulfide hydrometallurgical separation, recovery and fixation of tin, arsenic, antimony, mercury and gold. *International Symposium on Lead and Zinc Processing, Lead & Zinc 2008*, Durban, South Africa, February 25–February 29, 2008. The Southern African Institute of Mining and Metallurgy (SAIMM), pp. 121–132.
- Anderson, C.G., 2003. Alkaline sulfide recovery of gold utilizing nitrogen species catalyzed pressure leaching. In: Young, C.A., et al. (Ed.), *Hydrometallurgy 2003 – Fifth International Conference*, vol. 1. TMS, Warrendale, pp. 75–87. and references therein.
- Aylmore, M.G., Muir, D.M., 2001. Thiosulfate leaching of gold – a review. *Minerals Engineering* 14 (2), 135–174.
- Baláz, P., Achmovičová, M., Sánchez, M., Kammel, R., 1999. Attrition grinding and leaching of enargite concentrate. *Metall* 53, 53–56.
- Baláz, P., Achmovičová, M., Bastl, Z., Ohtani, T., Sánchez, M., 2000. Influence of mechanical activation on the alkaline leaching of enargite concentrate. *Hydrometallurgy* 54, 205–216.
- Boi, M., Dessi, R., Fiori, M., Garbarino, C., Grillo, S.M., Humphries, B., Marcello, A., Morris, J., Pilurzu, S., Pretti, S., Tore, G., 1996. Le potenzialità aurifere della Sardegna. *Atti del Convegno “Nuove realtà minerarie in Sardegna” Ente Minerario Sardo. Associazione Mineraria Italiana, Iglesias*, pp. 81–113.
- Curreli, L., Ghiani, M., Surracco, M., Orrù, G., 2005. Beneficiation of a gold bearing enargite ore by flotation and As leaching with Na-hypochlorite. *Minerals Engineering* 18, 849–854.
- Delfini, M., Ferrini, M., Manni, A., Massacci, P., Piga, L., 2003. Arsenic leaching by Na_2S to decontaminate tailings coming from colemanite processing. *Minerals Engineering* 16 (1), 45–50.
- Di Giovanni, S., Ghiani, M., Peretti, R., Serci, A., Zonedda, G., Zucca, A., 2003. Beneficiation of gold bearing ores associated with the Tertiary volcanism in south Sardinia (Italy). In: Lorenzen, L., Bradshaw, D.J. (Eds.), *Proceedings of the XXII International Mineral Processing Congress, Cape Town, South Africa, September 29–October 3, 2003*. The Southern African Institute of Mining and Metallurgy (SAIMM), pp. 493–500.
- Fadda, S., Fiori, M., Grillo, S.M., Matzuzzi, C., 2004. Vertical zoning of mineralization in some drill-holes of the M. S. Miali sector at the Furtei epithermal gold deposit, Sardinia, Italy. *Interim IAGOD Conference, Vladivostok, Russia*, pp. 423–426.
- Garbarino, C., Grillo, S.M., Marcello, A., Pretti, S., Uras, I., Fiori, M., 1991. First data on epithermal occurrences in Sardinia, Italy. In: Ladeira, E.A. (Ed.), *Brazil Gold '91*. Balkema, Rotterdam, pp. 143–150.
- Ghiani, M., Serci, A., Peretti, R., Zucca, A., 2000. Beneficiation of gold sulphide ores from south Sardinia, Italy. In: Ozbayoglu, G., Hosten, C., Atalay, M.U., Hicyilmaz, C., Arol, A.I. (Eds.), *Mineral Processing on the Verge of the 21st Century*. Balkema, Rotterdam, pp. 305–308.
- Jeffrey, M.I., Anderson, C.G., 2003. A fundamental study of the alkaline sulfide leaching of gold. *The European Journal of Mineral Processing & Environmental Protection* 3 (3), 336–343.
- Nadkarni, R.M., Kusik, C., 1988. Hydrometallurgical removal of arsenic from copper concentrates. In: Reddy, R.G., et al. (Ed.), *Arsenic Metallurgy, Fundamentals and Applications*. TMS, Warrendale, pp. 263–286.
- Senanayake, G., 2004. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. *Minerals Engineering* 17, 785–801.
- Viñals, J., Roca, A., Hernandez, M.C., Benavente, O., 2003. Topochemical transformation of enargite into copper oxide by hypochlorite leaching. *Hydrometallurgy* 68, 183–193.