


# Tennantite and Enargite Rejection in the Copper Flotation—A Mini-Review

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## Abstract

With the development of arsenic removal technologies, biological method and sulfide method have been applied in industrial fields, other methods have also been applied in arsenic-containing copper flotation, including coagulation process, ion exchange method, direct precipitation method and so on. In the paper, a short review on the progress of arsenic removal technologies of copper flotation during the last decade is presented, and the importance and the trend of arsenic removal are discussed. The existing and possible strategies of improving copper recovery in porphyry copper ores and rejection of penalty elements such as Tennantite and Enargite in copper flotation concentrates are also presented.

## Keywords

Tennantite, Enargite, Mineralogy Analysis, Characterization

## 1. Background

In copper ores, other valuable minerals such as gold occur in trace proportions (0.5 - 2 g/t) [1]. Optimizing their flotation recovery leads to significant increase in value to the operation. In the flotation of copper ores, the flowsheet is designed to produce a bulk flotation concentrate of chalcopyrite and gold. The concentrate is later smelted to obtain copper and gold separately. Most copper flotation plants, however, are optimized for copper recovery in terms of collector selection for surface hydrophobiation, under the assumption that gold will behave in a similar manner [2]. The process does not usually result in optimum

recovery of gold due to the difference in mineralogy, morphology and surface chemistry between copper minerals and gold-bearing particles [3]. Consequently, gold recovery in copper ores always lags copper recovery by 10% - 15% [1].

A great amount of work has been published and further research is continuously being undertaken to improve copper recovery and grade in copper flotation circuits [4]. Furthermore, naturally occurring elements such as Tennantite and Enargite often occur in copper ores as minor or accessory elements. High levels of these elements above acceptable limits, (e.g., 500 ppm) in the copper concentrates are undesirable as it leads to financial penalties imposed by smelters [2]. In this literature review, mineralogical shortcomings and factors relative to optimizing copper recovery and minimizing department of penalty elements (Tennantite and Enargite) in copper sulphides flotation are discussed.

## 2. Introduction

In some copper flotation circuits, Arsenic department in the concentrate is undesirable as it often leads to hefty smelter penalties [1] [2] [3]. Moreover, the copper concentrate with containing higher than 0.5% as usually cause the rejection from concentrate recipient country's Customs [4]. In copper ores, Arsenic occurs mainly in the minerals Tetrahedrite (Tennantite) and Enargite, which often contain economic levels of copper. These Sulphosalts of copper and Arsenic usually occur with copper minerals such as Chalcopyrite, Bornite and Chalcocite that possess similar surface chemistry and flotation behaviour, making selectivity difficult. The recovery of Tennantite or Enargite into the concentrate is generally the main source of Arsenic accumulation, although minerals like Arsenopyrite (FeAsS) and Realgar (Sb<sub>2</sub>As<sub>3</sub>) are known to contribute to some extent [5] [6]. Roasting of the copper concentrate prior to smelting is a proven technique to remove Arsenic, a method which utilizes the volatility of Arsenic at low temperatures (300°C). This method, although economical, is limited by environmental concerns. Leaching, on the other hand, is safer environmentally. However, disposal of the Arsenic containing raffinate further presents a challenge [7]. Moreover, roasting or leaching is capital intensive. Recent research has been focused on selectively rejecting Arsenic bearing minerals at the froth flotation stage. This review narrowly reviews the selective flotation of Arsenic bearing minerals, mainly Tennantite and Enargite.

## 3. Mineralogy Analysis

### 3.1. Tennantite Mineralogy

Tennantite belongs to the tetrahedrite group of minerals, with the most varied chemistry of any sulphide. The general chemical formula is given in Equation (1), with sites available for uni-, di- and trivalent cations.



Arsenic (and antimony) is the M<sup>3+</sup> element, and M<sup>+</sup> is copper [8]. The typical

formula of Tennantite is  $\text{Cu}_{10}\text{Zn}_2\text{As}_4\text{S}_{13}$ . Tellurium ( $\text{Te}^{4+}$ ) and selenium are the only elements known to replace Arsenic (antimony) to form the mineral Goldfieldite,  $\text{Cu}_{10}\text{Te}_4\text{S}_{13}$ . The natural conditions (temperature, pressure and redox potential) under which Tellurium/Selenium replaces Arsenic/Antimony in Tennantite are important in order to exploit such phenomena for selective Arsenic removal.

Tetrahedrite minerals are known to associate and co-exist with a much wider range of base metal sulphides (Chalcopyrite, Galena and Sphalerite) as well as gold tellurides [9]. Tetrahedrite minerals are found in hydrothermal sulphide deposits globally, as precipitates from acidic and saline mineralising fluids at a temperature range between 200°C and 400°C. It is expected that Tennantite forms at temperatures less than 300°C.

### 3.2. Enargite Mineralogy

Enargite,  $\text{Cu}_3\text{AsS}_4$  forms at higher temperatures (300°C - 400°C), mainly in high sulphidation gold-vein deposits [10]. The lower temperature dimorphous form of Enargite is luzonite,  $\text{Cu}_3\text{SbS}_4$ . Enargite replaces Pyrite and Bornite in porphyry copper deposits. For example, in the Andean copper deposits, Chalcopyrite and Pyrite are the main minerals with trace amounts of Tennantite and Enargite. In the El Indio deposit, Tennantite and Enargite occur as the major minerals with trace amounts of Arsenopyrite, Chalcopyrite and Tetrahedrite. It was found that Chalcopyrite and gold were mainly associated with Enargite. Other copper deposits that contain significant amounts of Tennantite and Enargite are Cananea (Mexico), Chiprovtsi (Bulgaria), and Tampakan (Philippines). A more recent work identified a substantial amount of Tennantite (with Chalcopyrite and Bornite as the major copper minerals) in a copper ore at Northparkes (Australia). Detailed information on various copper deposits together with the nature of the occurrence of copper-Arsenic bearing minerals can be found in the paper of “A review of copper-arsenic mineral removal from copper concentrates” by Xu *et al.*, 2001 [11].

## 4. Flotation Behaviour of Arsenic Bearing Minerals

Tennantite and Enargite are reportedly floatable in a wide pH range, from pH 5 to 12, quite similar to other major copper minerals such as Chalcopyrite [12]. The two main factors promoting Arsenic recovery into copper concentrates are poor liberation between the primary copper minerals (*i.e.* Chalcopyrite, Bornite, Chalcocite, etc.) and the copper-Arsenic bearing minerals (*i.e.* Tennantite, Enargite, Tetrahedrite, etc.), and the similar chemical composition between them. The poor liberation of copper-Arsenic minerals makes selectivity difficult during copper sulphide flotation. Consequently, fine regrinding is required to liberate these minerals to enable differential flotation of the copper-Arsenic and the primary copper minerals. Recently two research both incorporated regrinding into a copper flotation circuit to effect liberation of Tennantite and Tetrahedrite from

Chalcopyrite [13] [14] [15]. Although, this approach achieved significant improvement in copper recovery, there were still some challenges (e.g. hydrodynamic effect, low particle-bubble collision) in floating Chalcopyrite at the fine grind size (~20  $\mu\text{m}$ ). Lower Chalcopyrite recovery was obtained due to excessive regrinding, which produced more fines of poor collision efficiency. However, a thorough mineralogical characterisation is required to establish the optimal liberation size (that is, the grind size to liberate the copper-Arsenic minerals).

Even after liberation, due to the similar chemical composition between the copper-Arsenic bearing minerals and the primary copper minerals, the former exhibit similar flotation behaviour, thereby reporting to the copper concentrate. Therefore, in order to minimise Arsenic recovery, different researchers have come out with various mechanisms of rejecting significant Arsenic from copper concentrates before getting to the smelter. Some of these techniques are magnetic separation; roasting; regrinding and controlled-potential flotation. Chemical depression strategies (Lime, Cyanide, sulphides, aeration, etc.) were also employed to reject copper-Arsenic bearing mineral. Flowsheet modifications have also shown significant improvements in Arsenic rejection in copper ores at Neves-Corvo, Tampakan and Northparkes. Nevertheless, potential controlled flotation (using pulp potential as the major factor to achieve differential flotation) has been the most widely used approach for differential flotation of Enargite or Tetrahedrite from Chalcopyrite, Bornite or Chalcocite. At both laboratory and industrial scale, pulp potential is controlled by either chemical addition or externally applied potential. The chemical potential control involves the use of hydrogen peroxide and sodium hypochlorite as pulp oxidants while sodium sulphide and sodium dithionite are often used as reductants. Controlling Eh by applying external potential is not as effective as chemical adjustment. Pulp potential is also controlled by flotation gases such as oxygen and nitrogen and has been extensively discussed.

## 5. Conclusions

Challenges associated with rejection of penalty trace elements (e.g. F, As) in copper flotation have been discussed. The major limiting factors are the inherent low grade, the finely sized mineralisation and mostly the lack of complete and accurate mineralogical/surface/morphological characterization. Each copper deposit presents unique mineralogical characteristics, hence one method employed in one copper concentrator differs from another. However, a sound mineralogical analysis using a combination of QEMSCAN (and/or MLA), QXRD and bulk chemical analysis is vital and is the first step to address any metallurgical challenge.

Moreover, comprehensive mineralogical and liberation characterisation of the ore, together with surface and pulp chemistry analysis, is a key step to maximise penalty fluorine/arsenic rejection. Speciation of the fluorine/arsenic bearing phases, mode of occurrence, liberation, and size distribution are important fac-

tors. Development of a sound mineralogical profile during start-up and throughout the operation is critically important. This is because process mineralogy, pulp/solution chemistry and hydrodynamic conditions all govern the deportment of the different minerals.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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