Effect of Microwave Pretreatment on Leaching of Tetrahedrite

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Abstract. In mineral processing, the use of microwave radiation is important especially in pretreatment processes. At present, there is an acceleration of processes as well as an increase in the efficiency of metal recovery. One of the main problems in copper recovery from complex sulphide ores is the removal of impurities such as antimony, arsenic, mercury. In the hydrometallurgical processing scheme, the key step is the leaching. The extraction process can be influenced by the selection of suitable leaching reagents or by suitable pre-treatment of the ore. The article describes the effect of microwave radiation on the leaching Sb, As and Hg of tetrahedrite and tetrahedrite concentrate. The samples were irradiated at the power 900 W for 30 seconds. The leaching of irradiated and non-irradiated samples was realized in an alkaline sodium sulphide. The positive effect of microwave radiation was confirmed by an increase in the recovery of Sb and As already after 15 min of extraction. After microwave leaching of irradiated tetrahedrite samples, the yield of Sb was 43.2 %, in irradiated tetrahedrite concentrate, the yield of Sb was 81.3 %.

1. Introduction

Sulphide ore deposits are an important part of copper ore reserves. Tetrahedrite (Cu₁₂Sb₄S₁₃) is a complex sulphide mineral with fluctuating antimony and copper content. Tetrahedrites show some degree of substitution and usually contain other important metals, such as zinc and silver, associated with toxic elements such as arsenic and mercury [1, 2]. An acceptable technological solution is the leaching of Sb, As and Hg from the flotation tetrahedrite concentrate and subsequent hydrometallurgical processing of the product [3]. Correia et al., 2000 observed leaching kinetics of tetrahedrite in solutions of FeCl₃-NaCl-HCl [1]. The efficiency of leachability is significantly increased by mechanochemical activation [4]. Long-term attention to sulphide concentrate processing was paid at IGT SAS. Alkaline leaching of tetrahedrite concentrate in Na₂S and NaOH by mechanochemical method - by grinding the solid sample in the attritor in the leaching process was used for selective removal of Sb, As and Hg [4, 5]. Sekula et al., 2008 presented the technological process of hydrometallurgical processing of tetrahedrite concentrates from the locality Mária mine (Rožňava, Slovakia) [6]. The research of mechanochemical leaching of various types of sulphide ores was dealt with a team of authors [7-14]. Baláž et al., 1997 described that the mechanochemical activation in the recovery of gold and silver from sulphide ores is the process of mechanical and chemical destruction of minerals to one degree. Mechanochemical leaching of tetrahedrite and other sulphide minerals represents a very efficient process of metal recovery into the leachate [15].
Kušnierová 1995, introduced the formation of new mineral structures such as oxides, sulphates and secondary sulphides after biological-chemical leaching of tetrahedrite [16].

2. Microwave heating
An application of microwave energy in the processing of complex ores and their concentrates is an innovative way. Microwaves represent high-frequency non-ionizing radiation, formed by two oscillating perpendicular fields, electric and magnetic. In the spectrum of electromagnetic radiation, microwaves cover the scale of 300 MHz to 300 GHz in the wavelength range from 1 m to 1 mm in air, resp. vacuum (figure 1).

![Electromagnetic Spectrum](image)

**Figure 1.** Electromagnetic spectrum

In mineral processing was positive effect of microwaves confirmed at modification of physico-chemical properties ores, ore comminution processes and valuables leaching, etc. [17-22]. Amankwaha et al., 2011 studied influence of microwave heating of gold ores for enhanced grindability and cyanide amenability [23]. Microwave pre-treatment achieved a high rate of gold leaching as a result of selective heating of the individual mineral components of the irradiated ore. The formation of microcracks after thermal stress improved the meltability and decrease of compressive strength by 31.2 % of gold ores containing magnetite, hematite, silicates and quartz. Microwave irradiated sample obtained the 97 % gold recovery after 12 hours of leaching, compared to the unirradiated sample, which achieved a yield of 92 % after 24 hours. Cho et al., 2020 dealt with an application microwave-assisted leaching at Au recovery from polymetallic ores [24]. Choi et al., 2017 described that microwave pretreatment of Au-bearing concentrates resulted in total removing of sulphur [25]. Moravvej et al., 2018 dealt with application of microwaves in copper ores processing. They confirmed 2.5 time faster leachability of Cu comparing to classical leaching [26].

The effect of microwave pretreatment on leaching and magnetic separation of tetrahedrite and tetrahedrite concentrate was also tested [3, 27]. Seflek et al., 2018 microwavely irradiated Au-bearing ore before leaching in NaCN. They confirmed the decrease of work index in comminution process and higher Au leachability [28]. Leaching of blended cooper slag in microwave oven dealt with Turan et al., 2017 [29].

3. Materials and methods
The samples of tetrahedrite and flotating tetrahedrite concentrate from an area of Rožňava with granularity below 0.2 mm were used in this study. The chemical composition of the studied samples is in Table 1.
Table 1. Chemical composition of tetrahedrite samples

| Sample                  | Cu   | Sb   | As   | Hg   | Fe   |
|-------------------------|------|------|------|------|------|
| Tetrahedrite            | 2.85 | 7.69 | 2.17 | 0.73 | 6.42 |
| Tetrahedrite concentrate| 27.36| 15.93| 1.02 | 0.71 | 14.58|

The microwave pretreatment of samples before of leaching was realized in microwave oven Panasonic with maximum power 900 W and frequency 2.45 GHz. Tetrahedrite samples were irradiated for 30 seconds in closed vessels in nitrogen atmosphere. The chemical compositions of samples were evaluated by atomic absorption method. The leaching experiments were aimed to obtain Sb together with As and Hg, with Cu concentration in the form of solid phase being separated by filtration. Conventional leaching of non-irradiated and microwave irradiated of tetrahedrite and tetrahedrite concentrate were realized. 10g of sample was leached with 200 ml of Na$_2$S solution at the temperature 90 °C under permanent agitation. Concentration of Na$_2$S was 300 g.l$^{-1}$. Leaching of tetrahedrite samples was realized during 15 minutes. The leaching laboratory tests of irradiated samples in microwave oven were realized, too. The condition of microwave leaching were: samples were leached in glass quartz banks in laboratory microwave oven Whirpool, providing cooling of samples at power 300 W. The stirring of the suspension was ensured by means of a magnetic stirrer in lower part of microwave oven. The temperature of the suspensions was controlled by an optical fibre of firm Nortech Fibronic.

4. Results and discussions

Utilization of microwave energy in tetrahedrite processing was evaluated by comparison the yields of Sb, As and Hg after leaching of irradiated and non-irradiated samples in Na$_2$S at 90 °C. During the short exposure of microwave irradiation to samples of tetrahedrite and flotation tetrahedrite concentrate new phases have not yet been formed, no significant substantial differences in composition change were found. On the contrary, the microwave radiation caused a selective heating for individual mineral components of the heterogeneous ores. The different degree of microwave heating causes the stress and thermal dilatation and followed faulting of heated materials. After microwave heating was observed increase of magnetic susceptibility of tetrahedrite samples. The result was better leachability of the monitored elements. The leaching kinetics of Sb, As and Hg depending on the leaching time and temperature were performed. A significant effect of microwaves was observed in As leaching (figure 2).
After 15 min conventional leaching of tetrahedrite irradiated sample was confirmed the recovery of As 29.3 % in comparison to non-irradiated sample. By microwave leaching was the recovery of As 31.8 %. No significant difference was found during Hg leaching due to radiation (figure 3). The highest recovery of Sb 43.2 % was observed after microwave leaching (figure 4).

The effect of microwave energy on the leaching of the flotation tetrahedrite concentrate was also observed. A significant result was evident at the yield of Sb (figure 5). After conventional leaching of tetrahedrite concentrate was achieved the recovery of Sb 70.1 %. The recovery of Sb after microwave pretreatment increased to 77.3 %. Followed leaching in microwave field was obtained the recovery 81.3 %.
5. Conclusions
Copper concentrates obtained by flotation processes from sulphidic tetrahedrite ores contain impurities such as antimony, arsenic and mercury, which reduce the value of the concentrations of the useful components. One of the ways to eliminate unwanted metals, before to obtain rare metals, is microwave pretreatment of polycomponent ores and their concentrate before their subsequent leaching. The application of microwave energy (30 s microwave irradiation) in the pretreatment of tetrahedrite, a 2.4-multifold increase of As and 1.2-multifold increase of Sb were achieved after 15 min of leaching. The main aim of the use of microwave radiation is not only to shorten the leaching time, but also the decrease the amount of leaching agents from an environmental aspect.

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