

## Rapid communication

## Arsenic removal from copper–silver ore by roasting in vacuum

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## ABSTRACT

An investigation has been carried out for arsenic removal from a silver–copper ore. The copper ore was roasted in air, in nitrogen atmosphere and in vacuum at high temperature. It was found that arsenic was more easily removed in vacuum at lower temperature with shorter time. By suitably adjusting the main reaction conditions, almost 98.97% arsenic could be removed, while most of the sulfur was particularly retained in the copper ore. It was illustrated that arsenic could be completely removed on anaerobic conditions. After arsenic was removed, the copper ore with higher economic value could be used for feeding to the smelter.

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Tennantite ((CuFe)<sub>12</sub>As<sub>4</sub>S<sub>13</sub>) is the representative of the tetrahedrite-group compounds, the latter is also called fahlerz. Tennantite is a copper arsenosulfide (Cu<sub>12</sub>As<sub>4</sub>S<sub>13</sub>) which is often found in small quantities within chalcopyrite ores but does not present substantial difficulties to the conventional processing route. Being one of the sources of economically value metals (Cu, Zn, Ag, Au and others) sensitive to physical–chemical conditions of ore-formation and having an original crystal structure, these minerals gave rise to numerous experimental and theoretical studies concerning their crystal chemistry [1,2]. There are some shortcomings in wet pretreatment of arsenic removal, such as low arsenic removal ratio, high cost or innocent treatment of arsenic [3]. However, in ores where the arsenic content is relatively high, there are problems with the high content of slag in processing matte, and it is the direct reason of low copper recovery. There are also some problems with direct smelting of the ore due to the expense of sequestering arsenic in to a stable end phase. Most smelters consider arsenic a major penalty element and the price of the concentrate is diminished accordingly, sometimes to the point where the penalty is greater than the value making the ore uneconomically processed.

In wet pretreatment of arsenic removal, the fact that tennantite prevails among the copper bearing minerals combined with the high arsenic content strongly undermine their economic value. For this reason the possibility of the removal of 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 [3–9].

In roasting pretreatment of arsenic removal, the arsenic element could be somewhat removed at higher temperature in air, but the vast majority of the sulfur element could also be removed. For the imperfect removal of arsenic or the majority of the sulfur removal, the concentrate roasted in air could not be well used for feeding to the smelter. However, arsenic could be perfectly removed and most of sulfur satisfactorily be retained at higher temperature in the nitrogen atmosphere, the concentrate could be used for feeding to the smelter [10,11]. D. Villarreal discovered that arsenic was completely removed from copper concentrate and most of the sulfur remains in the concentrate with a vacuum of 10<sup>-2</sup> mm of Hg at a temperature of 1223.15 K [12].

Processing of future copper ores is likely to involve dealing with more complex, fine-grained minerals containing increased levels of toxic and minor elements. In this paper, arsenic was perfectly removed, while most of sulfur was satisfactorily retained at lower temperature in vacuum [13,14].

Copper–silver ore used in this work was from Canada. Mineral is black powder, particle size under 60 mesh. Table 1 shows that the copper–silver ore, containing such elements as copper, silver, lead, gold, has great economic value. Owing to harmful arsenic, it is difficult to use the traditional method of copper pyrometallurgy.

Fig. 4a shows the XRD pattern of the copper–silver ore. The main components in copper–silver ore are tennantite, Iron sulfide, Chalcopyrite, Quartz etal.

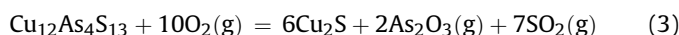
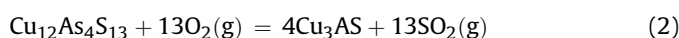
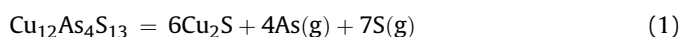
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**Table 1**  
Chemical analysis of copper–silver ore.

Size	Cu%	As%	Fe%	S%	Ag%	Pb%	Au	Zn%
–60 mesh	18.23	7.81	11.35	24.84	0.415	8.51	12 ppm	7.21

In the copper–silver ore, arsenic exists in compound tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ). In fact, tennantite is an unstable substance at high temperature according to [Reactions \(2\) and \(3\)](#) in oxygen presence and [Reaction \(1\)](#) on anaerobic condition. Many other ore bearing arsenic substances react similarly, such as arsenopyrite ( $\text{FeAsS}$ ), ( $\text{Cu}_3\text{AsS}_4$ ). It is known that oxygen pressure is a crucial condition to arsenic removal. The low pressure in vacuum is a good anaerobic condition. This is the basic principle for the separation of arsenic from tennantite. The arsenic vapor and sulfur vapor were taken out in time by flow on vacuum condition. The lower pressure of arsenic vapor and sulfur vapor promotes the reaction of arsenic removal perfectly.



The experiments were carried out on a vacuum tube furnace. The porcelain boat loaded with raw ores was placed at the appropriate position in the furnace, and then heated to the desired temperature which was controlled by a temperature controller connected with thermocouple [15]. The copper–silver ore was heated in the tube furnace, and the complex compound sulfide minerals were decomposed. Decomposition products of the arsenic-bearing minerals contain low boiling point substances, and the volatiles were separated from the solid minerals at differential pressure. The cooled residue in the porcelain boat was taken from the tube furnace and weighed after the experiment was completed.

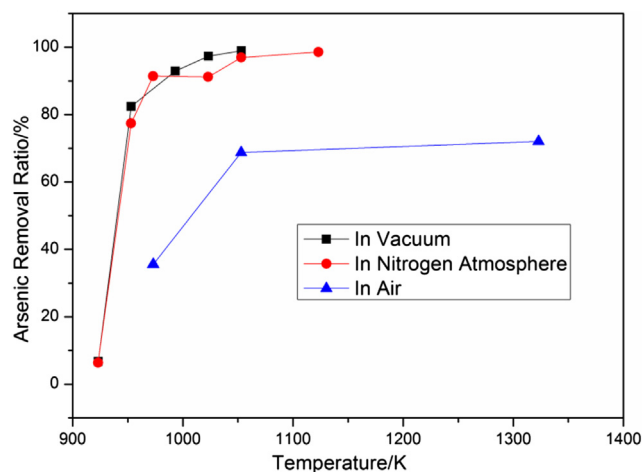
Initial evaluation of arsenic removal was respectively performed using copper–silver ore with arsenic content of 7.81% for 3 h in air at temperatures ranging from 973.15 K to 1323.25 K, in the nitrogen flow at temperatures ranging from 923.15 K to 1123.15 K, in vacuum at temperatures ranging from 923.15 K to 1073.15 K.

The effect of temperature on arsenic removal in air, in nitrogen flow and in vacuum was showed in [Fig. 1](#) when other conditions were kept constant. It can be seen that the arsenic removal ratio from copper–silver ore increases obviously in nitrogen atmosphere and in vacuum but changes relatively little in air with the increase of temperature.

As temperature increases from 973.15 K to 1323.15 K, the arsenic removal ratio increases from 35.6% to 72.1% in air. It is obviously that the removal of arsenic is not ideal in air. [Reactions \(2\) and \(3\)](#) occur in air with the increase of temperature. The arsenic removal is very difficult according to [Reaction 2](#) as the arsenic-bearing product ( $\text{Cu}_3\text{As}$ ) is a very stable compound even though at higher temperature.

It can be seen that the arsenic removal ratio increases with temperature in [Fig. 1](#). It increases from 6.40% to 98.59% in nitrogen atmosphere ranging from 923.15 K to 1123.15 K. It can be inferred that the major reaction is [Reaction \(1\)](#) in the temperature range.

It is obviously that the temperature of arsenic removal was lower compared to that in nitrogen atmosphere. At the same temperature, the arsenic removal was easier in vacuum compared to that in nitrogen atmosphere. As the temperature increases from 923.15 K to 1073.15 K, the arsenic removal ratio increases rapidly from 6.79% to 98.98%. Even the arsenic removal ratio in vacuum at



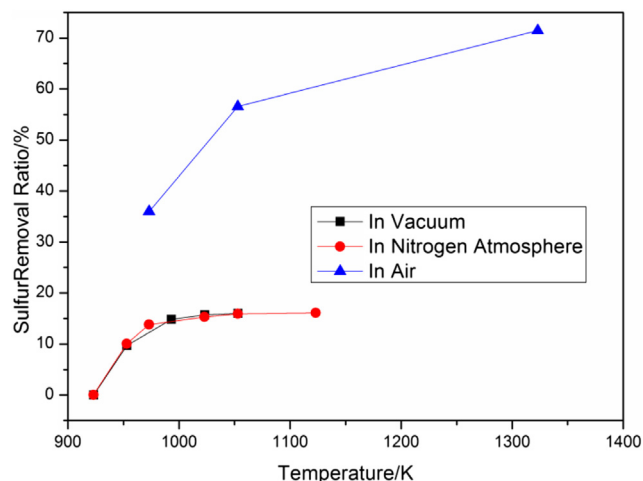
**Fig. 1.** Effect of temperature on arsenic removal in air, in nitrogen and in vacuum.

1023.15 K is close to that in the nitrogen atmosphere at 1123.15 K. Therefore, the energy consumption in vacuum is less than that in nitrogen atmosphere.

[Fig. 2](#) shows that the sulfur removal ratio increases rapidly with the increase of temperature in air. But the sulfur removal ratio is almost constant in nitrogen atmosphere or in vacuum with the pressure of 300 Pa, when the temperature exceeds 973.15 K. It is clear that the sulfur removal ratio for the copper–silver ore in air is quite high. It can be concluded that it is the oxygen content in the system that promotes the sulfur removal. The sulfur was seldom removed in nitrogen atmosphere or in vacuum.

[Figs. 1 and 2](#) also illustrates that temperature is an important factor for arsenic removal and oxygen pressure is indispensable for arsenic removal and sulfur retainment below 1323.15 K. [Figs. 1 and 2](#) also verifies that anaerobic system is a decisive condition for arsenic and sulfur retainment and arsenic is more easily removed in vacuum.

The experiments were conducted by holding the roasting time from 0.5 h to 4 h in nitrogen atmosphere and in vacuum with the pressure of 300 Pa at 1023.15 K. The relationship between the removal ratio of arsenic and sulfur and roasting time is summarized in [Fig. 3](#). Experiments showed that the longer the roasting time, the higher the copper–silver ore in nitrogen atmosphere, but, after the



**Fig. 2.** Effect of temperature on sulfur removal in air, in nitrogen and in vacuum.

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