Analysis and visualization of enargite and tennantite roasting using Cu-As-S-O system predominance volume diagrams

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ABSTRACT

The roasting of enargite (Cu_3AsS_4) in the temperature range 673 K (400 °C) to 900 K (673 °C) has been considered in the light of three-dimensional predominance volume diagrams (PVDs). Condensed phases considered were Cu, Cu_3As, Cu_2O, Cu_2S, CuO, CuS, $CuSO_4$, $CuO \cdot CuSO_4$, Cu_3AsO_4, $Cu_3As_2O_8$, Cu_3AsS_4, $Cu_6As_4S_9$, and $Cu_{12}As_4S_{13}$. Gases considered were As_4, As_4O_6, AsS, As_4S_4, O_2, S_2, SO_2, and SO_3. There are four line segments associated with each of the nine invariant points while each corner has three. The PVD at 900 K shows the gas composition during vacuum decomposition of tennantite with selected O_2 infiltration. Calculations show that increasing the O/Tennantite reacted ratio in the system leads to the formation of $Cu_3As_2O_8$ at 900 K and $CuSO_4$ at 673 K. Roasting experiments at 673 K showed that enargite transformed into tennantite ($Cu_{12}As_4S_{13}$) in the absence of oxygen; whereas, in the presence of oxygen it transformed into $CuSO_4$ and $CuO \cdot CuSO_4$. Enargite does not appear to transform directly into $CuSO_4$, but follows a path that includes Cu_2S or CuS. Sulfate formation is favored over oxide at lower roasting temperatures.

1. Introduction

There is significant interest in developing processes for sequestering arsenic, antimony, and bismuth, as copper concentrates free of these heavy elements are exhausted. The presence of these heavy elements imposes additional costs arising from the need to safely remove and ensconce them. This paper focuses on the behavior of arsenic, which is present in copper concentrates as enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$). Both oxidative and neutral roasting are employed to remove arsenic [1], but it and its compounds readily vaporize as oxides and sulfides to form a fume. Therefore, roasting requires extensive dust control to prevent environmental harm; however, the cost of such control processes is often offset by gold and other precious metal values in arsenic-rich sulfide concentrates [2–5].

Oxidative roasting to remove arsenic as As_4O_6 gas is associated with copper arsenate ($Cu_3As_2O_8$) formation, which requires subsequent removal by leaching. This was common practice before the need for stringent arsenic capture was recognized. The cost of dust control stimulates consideration of alternative processing methods such as neutral or vacuum processing of enargite and tennantite. In this case arsenic is removed as As_4S_4 gas with S_2 gas to form CuS, although, as it will be shown in this work, $Cu_3As_2O_8$ and $CuSO_4$ are also potential products.

This paper offers insights and visualization tools useful to continued consideration and understanding of both oxidative and neutral (or vacuum) avenues. Experimental work is presented to characterize low-temperature oxidative roasting of enargite to copper sulfate. Also presented is a theoretical analysis of vacuum roasting and the role of unavoidable fugitive oxygen. Both processes are described using 3D predominance volume diagrams (PVDs), which offer valuable visualizations not possible via previously-available 2D predominance area diagrams (PADs) [6–8].

2. Previous roasting literature

In the absence of oxygen, the system reduces to a ternary Cu-As-S system, which can be represented by a predominance area diagram (PAD) at a fixed temperature, as shown in Fig. 1. Adding oxygen to this ternary system adds another dimension to the predominance area diagram (PAD), making it into a predominance volume diagram (PVD) described by Howard [10].

In the presence of oxygen, enargite forms predominantly As_4O_6 and SO_2 gases, while under neutral or vacuum conditions As_4S_4 and S_2 gases predominate.

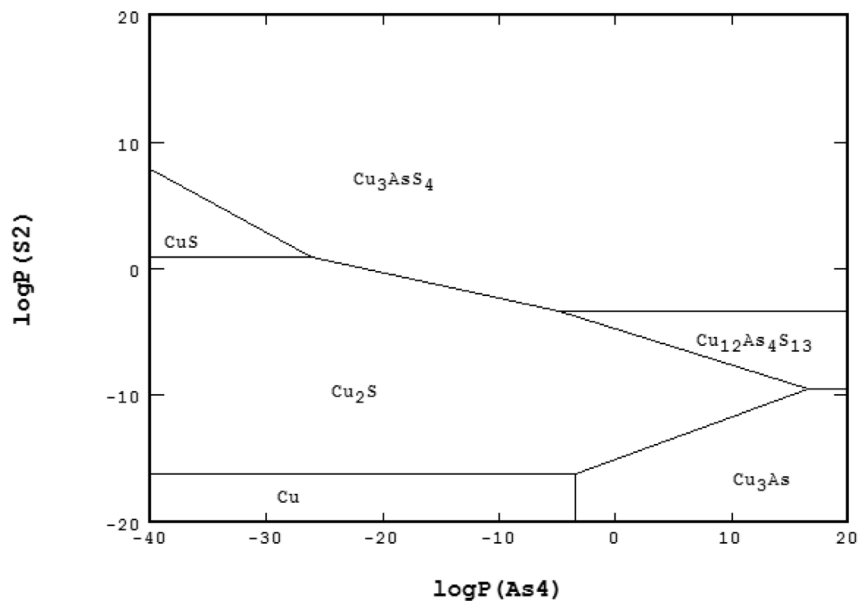Villarroel [11] removed ~99% of the arsenic from a copper

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Fig. 1. Predominance area diagram for the system Cu-As-S at 673 K (constructed using STABCAL$^{®}$ software [9]).

concentrate at 950 °C under a vacuum of 10^{-2} Torr in 1 h. Padilla et al. [12] reported kinetic data from 575 °C to 700 °C for thin layers of ~63-μm enargite concentrate in a nitrogen atmosphere and under vacuum. They concluded the process occurred in two first order sequential reactions

$$Cu_3AsS_4 = Cu_{12}As_4S_{13} + 1.5S_2(g) \tag{1}$$

$$Cu_{12}As_4S_{13} = 6Cu_2S + As_4S_4(g) + 1.5S_2(g) \tag{2}$$
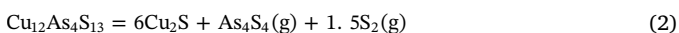
with activation energies of 125 kJ/mol and 236 kJ/mol.

Hu and Qiu [13] removed essentially all the arsenic from a sulfide residue (~34% arsenic) by vacuum evaporation at 0.11–1.01 Torr, followed by a three-step distillation at 180 °C. Yin, Lu, and Xiao [14] removed arsenic at 973–1323 K from a tennantite ore (~7.8% arsenic) by roasting in air, nitrogen, and in a vacuum at 1023 K for 1 h. The nitrogen and vacuum (2.25 Torr) each effectively removed most of the arsenic, while oxidative roasting in air prevented the removal of approximately 30% of the arsenic. Lin and Qiu [15] reported similar results.

Padilla et al. [12], Winkel et al. [16], and Villarroel [11] investigated the roasting or synthesizing of enargite in laboratory-scale experiments in either nitrogen atmosphere or in a vacuum. Padilla et al. [12] measured rate constants for reactions (1) and (2) in flowing nitrogen and found that the first reaction is somewhat faster than the second, and that for the conditions of their work, mass transfer was not rate-controlling. In the investigation by Winkel et al. [16] a vacuum was employed at 1173 K (900 °C) that removed 99% of the arsenic from small samples of enargite.

3. Cu-As-S-O system

The PVD for the Cu-As-S-O system at 900 K was published by Safarzadeh and Howard [17,18]. The three independent gases selected to define the phase space were O_2, SO_2, and As_4O_6, which are sources of As, S, and O. All other gaseous species composed of As, S, and O in the gas phase are fixed once these three gases are fixed. There are no Cu-bearing gases known in the Cu-As-S-O system. All of the condensed phases within the PVD contain copper. Condensed phases such as As_2O_5 which do not contain Cu do not appear on the PVD [16]. The formation reactions, by definition, are from Cu (s), SO_2 (g), O_2 (g), and As_4 (g). The use of SO_2 rather than the conventional most stable form of S avoids having to deal with the many phase changes of S.

Fig. 2 shows the six PADs that bound the three-dimensional isothermal PVD in the Cu-As-S-O system at 673 K. These PADs were constructed at a constant value of one of the three independent gases (O_2, SO_2, and As_4O_6). The other two variable independent gases were then used as the axis and the ordinate of each PAD. Ideal gas behavior was assumed, even though in some cases regions of the diagram reach very high or low pressures. Such extension was done to show the PVD geometry.

Fig. 3a shows the complete PVD for the Cu-As-S-O system at 673 K. Fig. 3b shows the expanded view of Fig. 3a for easier visualization of each phase. If the boundaries are extended to such extent that no additional phase intersections occur (i.e. only unbounded phases exist with further extension of boundaries), there are 9 invariant points as shown in Table 1. These 9 invariant points are independent of the coordinate (independent) gases selected.

Fig. 3a shows that the theoretical transformation of enargite to copper sulfate at very low pressures of $As_4O_{6(g)}$ should follow the roasting path $Cu_3AsS_4 \to CuS$ or $Cu_2S \to CuSO_4$, but at high pressures of $As_4O_{6(g)}$ it could be either $Cu_3AsS_4 \to Cu_{12}As_4S_{13} \to CuSO_4$ or $Cu_3AsS_4 \to Cu_{12}As_4S_{13} \to CuS$ or $Cu_2S \to CuSO_4$, depending upon the prevailing gas pressures. These roasting paths assume a straight line path on the PVD and adherence to sequential thermodynamic equilibrium. A curved path at very low SO_2 pressures would include the oxide phases, but this will be shown to be impossible because of the position of the isobaric surface described in the next section. After enargite undergoes the initial reaction, the actual roasting path may conform to a 0.25 atm total pressure isobaric surface.

4. Isobaric surface

The following criterion was used to determine the total pressure surface

$$P_T = \sum_{i=1}^{M} p_i \tag{3}$$

where

p_i = the partial pressure of gas species i
M = the number of gas species in system (8) excluding nitrogen

The total pressure considered for the Cu-As-S-O system was