Thermal removal of arsenic from copper concentrates: Three-dimensional isothermal predominance diagrams for the Cu-As-S-O system

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HIGHLIGHTS

- Quaternary Cu-As-S-O system studied.
- Volatilization of arsenic analyzed.
- A variety of reaction products discussed.
- Total pressure plane (0.25 atm) superimposed.
- Three-dimensional predominance volume diagram (PVD) constructed.

GRAPHICAL ABSTRACT
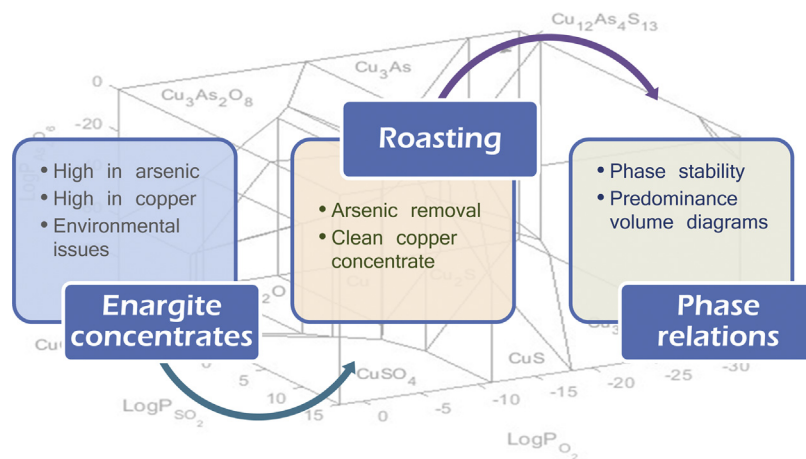
ARTICLE INFO

ABSTRACT

The three-dimensional predominance volume diagrams (PVDs) for the system Cu-As-S-O were constructed at 900 K using $P_{As_4O_6(g)}$, $P_{O_2(g)}$, and $P_{SO_2(g)}$ as independent coordinates. The constant total pressure surface was used to identify the equilibrium phases that are stable at 0.25 atm total pressure. The isobaric surface superimposed on the predominance diagram provides useful insights into the roasting of complex copper sulfosalts such as enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$). There are nine interior invariant points each with four associated condensed phases at 900 K. The expanded diagrams showing the stability volumes of each individual phase are presented. According to the PVD for the Cu-As-S-O system, the transformation of enargite to copper sulfate follows the $Cu_3AsS_4 \rightarrow CuS \rightarrow CuSO_4$ or $Cu_3AsS_4 \rightarrow Cu_2S \rightarrow CuS \rightarrow CuSO_4$ sequence when the pressure of As_4O_6 (g) is extremely low. At high As_4O_6 (g) pressures however, enargite can directly transform to copper sulfate.

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1. Introduction

The desired products of the oxidative roasting of sulfide minerals depend on the subsequent processing strategy; i.e. high temperature carbothermic reduction as for the roasting of galena

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Table 1
Freedom, variance, and geometry in a four-component PVD at constant temperature with a gas phase present.

Number of boundaries invoked	Number of condensed phases	F	Variance	Shape	Line segments
0	1	3	Trivariant	Volume	–
	2	2	Bivariant	Plane	–
	3	1	Univariant	Line	–
	4	0	Invariant	Point	4
1	1	2	Bivariant	Plane	–
	2	1	Univariant	Line	–
	3	0	Invariant	Point	4
2	1	1	Univariant	Line	–
	2	0	Invariant	Point	4
3	1	0	Invariant	Point	3

and sphalerite or leaching followed by electrolytic reduction as is commonly done with copper sulfides. The products of the roasting process at thermodynamic equilibrium are determined by the consideration of the roasting reactions. The authors have previously reviewed and described the practice of using two-dimensional predominance area diagrams (PADs) [1] and roaster diagrams [2]. In these analyses the composition of the gaseous phase plays a determining role in phase transformations given the heterogeneous nature of the roasting reactions.

In metal-sulfur-oxygen (M-S-O) ternary systems, it is relatively convenient to determine the products of roasting by considering the equilibrium relations. However, the addition of a volatile component such as arsenic significantly complicates the phase relations. In the four-component Cu-As-S-O system, the predominance diagram becomes a predominance volume diagram (PVD). The six faces of this diagram were presented elsewhere [1]. In this paper, the interior of the three-dimensional predominance diagram for the Cu-As-S-O system at 900 K is presented. This quaternary system is relevant to the roasting of high-arsenic copper concentrates, namely enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$) described by Safarzadeh and Howard [1]. The diagram facilitates visualization of the roasting path of copper sulfosalts (enargite and tennantite). The construction of PVDs has been described in a separate paper [3]. These diagrams determine the location of each stable component under isothermal roasting conditions and provide insights into other common arsenic-bearing quaternary systems that are significant for non-ferrous extractive metallurgists. These include, but are not limited to, Co-As-S-O, Ni-As-S-O [3], and Fe-As-S-O systems. Furthermore, there is an economic incentive for the processing of these arsenic-bearing sulfide concentrates since precious metals appear to be associated with arsenic-rich phases in the sulfide deposits [4–7]. It should be noted that there have been few attempts to render the quaternary systems in three-dimensional form, but these have been the diagrams representing the projections of the volumes on xy, xz, and yz planes. For example, such a diagram was reported by Chakraborti and Lynch for the Fe-As-S-O system using the pressures of O_2, S_2, and As_4 gases as coordinates [8].

2. Gibbs Phase Rule

The degrees of freedom in a chemical system are determined by the Gibbs Phase Rule
as follows [3]:

$$F = \begin{pmatrix} number\ of \\ components \end{pmatrix} - \begin{pmatrix} number\ of \\ independent\ reactions \\ among\ the\ components \end{pmatrix} - \begin{pmatrix} number\ of\ independent \\ restricting\ equations \\ including\ B\ boundaries \end{pmatrix} - \begin{pmatrix} number\ of \\ phases\ present \end{pmatrix} + 2 \quad (1)$$

For the M-As-S-O system at a fixed temperature,

$$F = (M, As, S, O)_4 - (none)_0 - (T = fixed)_1 - (number\ of\ boundaries\ invoked)_B - P + 2 = 5 - P - B \quad (2a)$$
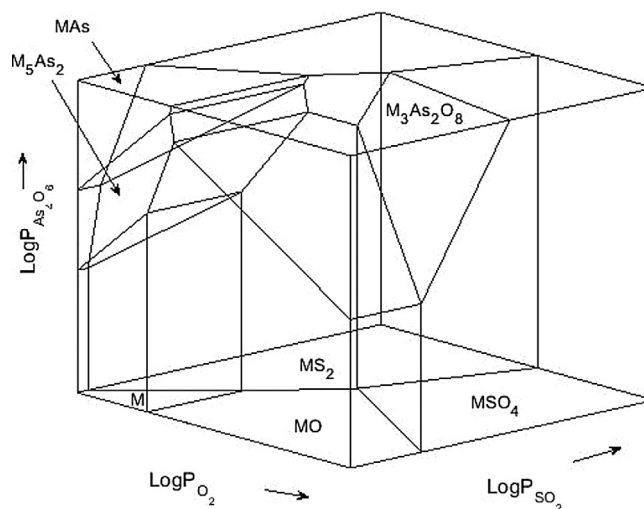

Fig. 1. The hypothetical PVD for the M-As-S-O system at constant temperature.

where subscripts denote the value of each quantity.

If a gas phase is always assumed present, then

$$F = 4 - P_{Cond} - B \quad (2b)$$

where P_{Cond} is the number of condensed phases present.

Table 1 shows the relationships between boundaries, condensed phases, freedom, and geometrical shapes within the PVD. Fig. 1 shows a hypothetical (M-As-S-O) PVD. Each invariant point has four associated line segments except for the corner points, which have three.

3. Cu-As-S-O system

To construct the PVD diagram for the Cu-As-S-O system, three independent gases must be selected that satisfy the following conditions:

1) They provide sources of As, S, and O
2) They are independent (i.e. none of the gases can be formed from the other two)

In this work the independent gases selected were O_2, SO_2, and As_4O_6. Because these three gases are sources of As, S, and O, all other gaseous species composed of As, S, and O present in the system can be produced from them. These gases include As_4, S_2, SO_3, AsS, and As_2S_3. If significant gas species involved Cu, the reaction to form it would necessarily include the prevailing condensed Cu-containing phase; however, there are no such gases known in the Cu-As-S-O system. Copper is necessarily present in every condensed phase within the PVD. Condensed phases not containing Cu such as As_2O_5 and As_2O_3 are discussed later.

The thermodynamic data for the species considered in this study are same as presented elsewhere [1]. The formation reaction for all species is from Cu (s), SO_2 (g), O_2 (g), and As_4 (g), which are commonly used for this system. This selection is arbitrary and has no effect on the resulting PVD. It is mentioned here so that comparisons of the values used in this study may be made with the other