Study on thermal decomposition and arsenic removal of a silver bearing copper ore

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ABSTRACT

By thermodynamic calculation and analysis, a hypothesis is suggested and provided that tennantite gets easily converted to Cu_3As which exists in slag in the traditional pyrometallurgy process. Due to the formation of Cu_3As, the economic value of high-arsenic silver bearing copper ore is greatly reduced, and the copper recovery ratio declines. Arsenic in the silver bearing copper ore is a punitive element in a trade. It is verified that arsenic could be removed from tennantite and most of sulfur is retained satisfactorily at low oxygen pressure. Investigation has been carried out for arsenic removal from a silver bearing copper ore. The copper ore was roasted in nitrogen atmosphere (>99%) at temperatures ranging from 923.15 K to1123.15 K. By suitably adjusting the main reaction conditions, nearly 98% arsenic was removed at 1053.15 K for 3 h in nitrogen atmosphere, while most of the sulfur was particularly retained in the copper ore. After the arsenic removal, the arsenic content was reduced from 7.81% to 0.13% and the copper ore could be used for feeding the smelter. Compared with the traditional method of arsenic removal from copper ore by roasting in oxygen, our proposed method of arsenic removal in nitrogen atmosphere at temperature of 1053.15 K is more effective.

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1. Introduction

Arsenic impurities occur commonly in copper ores where the most important minerals of arsenic are orpiment (As_2S_3), realgar (As_2S_2), arsenopyrite (FeAsS) and complex sulfide minerals including proustite (Ag_3AsS_3), enargite (Cu_3AsS_4), tennantite (($Cu,Fe)_{12}As_4S_{13}$) (Pierfranco et al., 2008; Smith, 1986; Filippou et al., 2007; Graham et al., 2012). Many studies have focused on the separation of ores containing arsenic (tetrahedrite, enargite, proutite, tennantite) from other copper/iron sulfides such as covellite (CuS), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu_5FeS_4) and Pyrite (FeS_2) by selective flotation to obtain concentrate with arsenic content below 0.5 wt% for feeding the smelters (Malhotra and Harris, 1999; Hangone et al., 2005; Senior et al., 2006; Fornasiero et al., 2001). However, arsenic commonly exists in (copper, silver) bearing minerals, such as proustite (Ag_3AsS_3), enargite (Cu_3AsS_4), and tennantite (($Cu,Fe)_{12}AsS_{13}$). The arsenic content in these minerals depends, to a great extent, on the chemical structures. Many treatment options have been suggested by researchers to remove arsenic from (copper, silver) bearing ores or concentrates. Leaching of tennantite(($CuFe)_{12}As_4S_{13}$) and other materials containing arsenic in media such as alkaline, sulfide, chloride, ammoniacal solutions has been conducted at different temperatures and different pressures, with or without bacteria (bio-leaching) (Himawan et al., 2012; Padilla et al., 2005; William et al., 2010; Canales et al., 2002).

Many studies have considered arsenic removal from copper concentrates by roasting. In the treatment of Gortdrum copper mine in the Republic of Ireland, Stuart and Down (1973) discovered that lower oxygen content during the roasting process would reduce the content of mercury and arsenic in the ore. Roasting was also used to reduce the arsenic content of copper concentrates at the El Indio mine, Chile. In the post roasting step, oxygen was expected to oxidize the elements of arsenic and sulfide to arsenic trioxide and sulfur oxide. Approximately 60% of the concentrates were treated in this way (Smith, 1986; Malhotra and Harris, 1999).

It is considered that the method of arsenic removal by roasting the ores in nitrogen atmosphere can solve the problems of environment pollution and obtain good economic and social benefit, such as simple technological flow sheet, reduced environmental pollution, and no consumption of acid, alkaline, sulfide and kinds of auxiliary materials. High grade of arsenic bearing products containing >40% arsenic could be obtained and used as the raw material for the production of arsenic with great economical value.

The arsenic removal of high-arsenic copper-bearing gold concentrate (3.93 wt% As) in fluidized bed roaster was studied by Yun et al. (2008), and arsenic and sulfur content of the calcine were respectively 0.62 wt% and 2.86 wt%. 86.0% of arsenic was removed and most of sulfur (87.1%) was retained. The arsenic remove from the tennantite concentrate (3.73 wt% As) in nitrogen at 973.15 K was studied by Bruckard et al. (2010), and the calcine was low in arsenic (0.41% As) and rich in copper and sulfur. The percentage of arsenic removed is 91.2% and the percentage of sulfur retained is 80.1%.

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The purpose of this paper is to explore a method to treat the silver bearing copper ore with high arsenic content (7.81% As) for feeding the smelter and to verify that the process route is thermodynamically feasible. The feasibility of the process route is proved by our experiments. Tennantite was decomposed in inert atmosphere at 1123.15 K; the residue is low in arsenic (0.13 wt%) and rich in sulfur (26 wt%) and copper (23 wt%), and the percentage of arsenic removed is 98.6% and the percentage of sulfur retained is 84%. Low-arsenic and high sulfur bearing copper concentrate is sought after for copper smelter and the economical value is promoted.

2. Thermodynamic calculation and analysis

Tennantite is easily decomposed at high temperature and low oxygen pressure to arsenic vapor, sulfur vapor, and copper sulfide. In the presence of oxygen, Cu_3As is a more stable product compared to Cu_2S from reaction 1 to reaction 6. Cu_3As will be formed in the slag if tennantite is fed to the smelter either by itself or with other copper bearing minerals to get matte. From Table 1, it can be seen that arsenic is difficult to be removed, which can be verified by the thermodynamic calculation. It is known that the oxygen pressure is a crucial factor to the removal of both arsenic and sulfur. At low oxygen pressure, the removal of arsenic can be promoted while the removal of sulfur can be prevented. Our experiments were carried out in nitrogen atmosphere (>99%) so that low oxygen pressure can be guaranteed.

1. $Cu_{12}As_4S_{13} = 6\,Cu_2S + 4\,As(g) + 7\,S(g)$ (no available thermodynamic data for $Cu_{12}As_4S_{13}$);

2. $Cu_{12}As_4S_{13} + 13O_2(g) = 4Cu_3As + 13SO_2(g)$ (no available thermodynamic data for $Cu_{12}As_4S_{13}$); Reaction3 = Reaction2-Reaction1;

3. $4Cu_3As + 13SO_2(g) = 6Cu_2S + 4As(g) + 13O_2(g) + 7S(g)$
$\Delta_rG_m = 1185.311$ kJ/mol(T = 993.15 K);
Reaction4 = Reaction2-Reaction1;

4. $4\,Cu_3As + 13SO_2(g) = 6Cu_2S + 4As(g) + 13O_2(g) + 7S(g)$
$\Delta_rG_m = 1160.154$ kJ/mol (T = 1053.15 K);

5. $Cu_{12}As_4S_{13} + 10O_2(g) = 6Cu_2S + 2As_2O_3(g) + 7SO_2$ (no available thermodynamic data for $Cu_{12}As_4S_{13}$)
Reaction6 = Reaction2-Reaction5;

6. $Cu_3As + 6SO_2(g) = 6Cu_2S + 2As_2O_3(g) + 3O_2(g)$
$\Delta_rG_m = 132.395$ kJ/mol (T = 993.15 K) ($As_2O_3(g)$(no available thermodynamic data at T > 1000 K).

(*The above thermodynamic data are from database of HSC Chemistry).

From the phase stability diagram of As-O-S in Fig. 1, Table 2 and reactions (7)–(12), it can be seen that the system is in the equilibrium zone of arsenic trioxide - arsenic - sulfur vapor. Table 2 shows that the linear relation (arsenic trioxide - sulfur dioxide) is:

$$Y + 18.229 = K * (X + 17.223), \qquad (1)$$

where K is $(300 + 18.229)/(221.495 + 17.223)$, Y is $Logp_{sulfur}$, X is $Logp_{arsenic}$, if $X > -14.2, Y > X$. In fact, the partial pressure of system is in the interval of $X = [-14.2, 0]$, even X and Y are closer to zero, and $X \approx Y$ as the pressure of sulfur is close to the pressure of arsenic. The system is in the equilibrium zone of arsenic trioxide - arsenic - sulfur vapor when the pressure of oxygen is 0.01 bar as shown in Table 2 and Fig. 1. As the partial pressure of oxygen in our practical process is <0.01 bar, the system should be in the equilibrium zone of arsenic trioxide-arsenic-sulfur vapor.
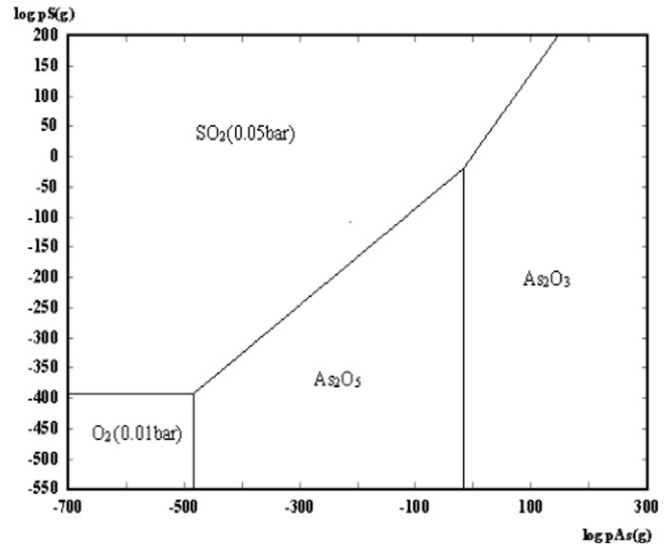

Fig. 1. Phase stability diagram of O-As-S at 1053.15 K.

With nitrogen flow and the formation of arsenic trioxide, the decomposition reaction of tennantite completes easily. And the partial pressures of arsenic vapor and sulfur vapor above the surface of solid raw ore are reduced in the nitrogen flow. The arsenic vapor above the surface of solid raw ore is also reduced with the formation of arsenic trioxide. This is the basic principle for the separation of arsenic from tennantite (Denis, 2012; Fiona and Zhang, 2013; James et al., 2003).

7. $5/3\,As_2O_3 = 4/3As(g) + As_2O_5$	$\Delta_rG_m = 463.253$ kJ/mol;
8. $2/3\,As_2O_3 = 4/3\,As(g) + O_2(0.01$ bar$)$	$\Delta_rG_m = 7999.541$ kJ/mol;
9. $2/3\,As_2O_3 + S(g) = 4/3\,As(g) + SO_2(0.05$ bar$)$	$\Delta_rG_m = 94.262$ kJ/mol;
10. $2/5As_2O_5 = 4/5\,As(g) + O_2(0.01$ bar$)$	$\Delta_rG_m = 7814.293$ kJ/mol;
11. $2/5\,As_2O_5 + S(g) = 4/5As(g) + SO_2(0.05$ bar$)$	$\Delta_rG_m = -91.093$KJ;
12. $O_2(0.01$ bar$) + S(g) = SO_2(0.05$ bar$)$	$\Delta_rG_m = -7905.289$ kJ/mol.

3. Experimental

3.1. Materials

Silver bearing copper ore used in this work was from Canada. Table 3 shows the chemical composition of the ore (wt%). The main elements were: 7.81% As, 18.23% Cu, 24.84% S. The ore was in the form of black powder with particle size under 60 mesh. Fig. 2 shows the XRD pattern of the ore. From Table 4, the main components in the ore are tennantite, iron sulfide, Zinc sulfide chalcopyrite, and quartz et al.

3.2. Chemical analysis of products

The silver bearing copper ore and the products generated in the roasting process were assayed for suit of elements by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a standard method. The elements included arsenic, copper, Iron, silver, lead, gold, and zinc.

Table 1
Effect of temperature on arsenic removal and sulfur removal in air.

Temperature (K)	Arsenic removal (%)	Sulfur removal (%)
973.15	35.6	36
1053.15	68.8	56.6
1323.15	72.1	71.5

Table 2
The equilibrium zone of arsenic trioxide-arsenic-sulfur vapor at T = 1053.15 K and p_{O2} = 0.01 bar (1 bar = $1.0 * 10^5$ pa).

	Log pAs (g)	Log pS (g)	Log pAs (g)	Log pS (g)
As_2O_5-SO_2 (0.05 bar)	−17.223	−18.292	−484.207	−391.878
As_2O_3-As_2O_5	−17.223	−550	−17.223	−18.292
As_2O_3-SO_2 (0.05 bar)	221.495	300	−17.223	−18.292
As_2O_5-O_2 (0.01 bar)	−484.207	−550	−484.207	−391.878
O_2(0.01bar)-SO_2 (0.05 bar)	−700	−391.878	−484.207	−391.878