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## Research features of opening of refractory arsenopyrite concentrates by using low-temperature roasting

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**Abstract.** The article describes an alternative pre-treatment method of refractory arsenopyrite concentrates using low temperature roasting. The process consists of carrying out oxidative roasting in the temperature range of 200–400 °C – relatively low for traditional process. The calculation results of the equilibrium composition of roasting products are presented on the example of a flotation gold-bearing concentrate of the Uderey's deposit in the HSC Chemistry 6 program. The main concentrate minerals containing gold are pyrite (FeS<sub>2</sub>) and arsenopyrite (FeAsS). In addition, the concentrate of the Uderey's deposit is characterized by the presence of antimony in the form of Sb<sub>2</sub>S<sub>3</sub>. During the calculations of the equilibrium composition, the optimal conditions for low-temperature roasting were selected. It was found that under these conditions, the dissociation of higher sulfides occurs, arsenic goes into the form of trisulfide (As<sub>2</sub>S<sub>3</sub>) and some of the iron goes into the form of sulfate (FeSO<sub>4</sub>). All this suggests that the process of low-temperature roasting allows to open the refractory concentrate and get a cinder, the further processing of which will not cause special problems: the non-volatile form of arsenic trisulfide will not cause complications when cleaning exhaust gases, and iron sulfate will simplify further leaching processes.

### 1. Introduction

The main reason for the refractoriness of arsenopyrite concentrates is the thin dissemination of gold in the main host minerals – arsenopyrite (FeAsS) and pyrite (FeS<sub>2</sub>). In such minerals the gold is contained in a submicroscopic form, which does not allow extracting it without opening before. It is proved that, the refractoriness of gold associated with sulfides is the presence of not only native gold nanoparticles, but also solid solution, colloidal particles, and surface gold. The presence of pre-robbing carbon in the composition of ores and concentrates also leads to the manifestation of refractory gold [1–3].

The main objective of the pretreatment in such refractory materials is the oxidation of gold-containing minerals in order to destroy their crystal lattice and release gold particles. The most common methods are autoclave and bacterial oxidation, operations of thermal decomposition, hydrometallurgical opening with preliminary fine grinding [4–6]. However, these methods entail high costs for consumables, such as bacterial strains, leaching reagents, and others. Another quite effective way is smelting [7]. Its advantage is that, when the particles of the concentrate are melted, the release of gold particles occurs by itself and there is no need for pre-treatment. But this method also has its drawbacks: a significant proportion of arsenic and sulfur may be contained in the exhaust gases, which can also be expensive to clean.



Oxidative roasting is one of the most economical methods for pretreating refractory gold-bearing concentrates. However, to achieve the desired recovery, roasting is often operated in two or even three stages. Since single-stage roasting provides significant savings in both capital investment and operating costs, most other studies, by scientists through over the world, focus on optimizing conditions for single-stage roasting, which can provide gold recovery comparable to two-stage roasting processes [8–9].

In turn, the low-temperature roasting method make it possible for us not only to convert arsenic to the trisulfide form, but also to convert some of the iron to the sulfate form, which will significantly reduce operating cost when cleaning exhaust gases and at further stages of leaching of the calcined product.

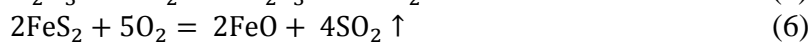
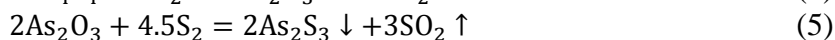
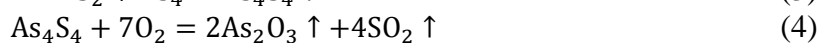
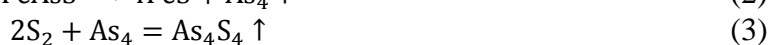
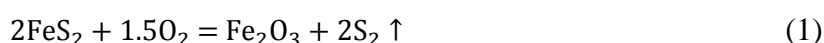
## 2. Low temperature roasting

Roasting is called low temperature, since it's carried out at low temperatures relative to traditional oxidative roasting: in the range of 200–400 °C. At these temperatures, the reactions do not proceed as intensively as during traditional roasting (500–700 °C) [10], however, this avoids the melting of concentrate particles, a typical problem of roasting processes.

The main goal of roasting is the dissociation of higher concentrate sulfides (FeAsS and FeS<sub>2</sub>) and the conversion of arsenic to non-volatile As<sub>2</sub>S<sub>3</sub>. Since arsenic in this form does not get into the exhaust gases and will not cause additional problems of cleaning them. The same can be said about further processing of the cinder - arsenic trisulfide can be easily eliminated by leaching with sulfuric or nitric acid [11].

The problem for such roasting is the search for optimal conditions to achieve the desired result. The main parameters affecting the efficiency of the process: temperature and the amount of oxygen. Even though temperature range is from 200 to 400 °C, the reactions proceed not so intensively, their speed can be compensated by the amount of air blast supplied. However, there is a risk of dramatic increase of the roasting temperature due to exothermic sulfur oxidation reactions. Therefore, when conducting low temperature roasting happened, it is necessary to constantly monitor the temperature and volume of oxygen supplied [12].

Below are the main reactions that occur during the low-temperature roasting, also the values of the Gibbs energy and the logarithms of the equilibrium constants calculated for the temperature range 200–450 °C (tables 1, 2) [13].



**Table 1.** Calculations of changes in Gibbs energy, kJ/mol, for reactions 1–8.

T, °C	Number of reaction, ΔG, kJ/mol							
	1	2	3	4	5	6	7	8
200	-284.546	-127.284	-258.215	-1755.855	-680.344	-1367.174	-108.743	-174.482
250	-291.197	-133.336	-241.730	-1747.596	-646.841	-1365.746	-99.278	-164.970
300	-297.898	-139.543	-225.364	-1739.152	-613.655	-1364.294	-89.824	-155.520
350	-304.653	-145.903	-209.105	-1730.553	-584.665	-1362.833	-80.388	-146.132
400	-311.465	-152.243	-192.945	-1721.820	-557.587	-1361.375	-70.973	-136.807
450	-318.337	-158.438	-176.877	-1712.970	-531.220	-1359.923	-61.582	-127.541

**Table 2.** Calculations of the logarithms of equilibrium constants, for reactions 1–8.

T, °C	Number of reactions, $\ln K_p$							
	1	2	3	4	5	6	7	8
200	31.416	14.053	28.509	193.859	75.115	150.946	12.006	19.264
250	29.077	13.314	24.138	174.506	64.590	136.376	9.913	16.473
300	27.152	12.718	20.540	158.513	55.931	124.347	8.187	14.175
350	25.539	12.231	17.529	145.073	49.013	114.247	6.739	12.250
400	24.171	11.815	14.973	133.620	43.271	105.648	5.508	10.617
450	22.996	11.445	12.777	123.742	38.374	98.238	4.449	9.213

According to the results of calculating the values of the Gibbs energy change and the logarithms of the reaction equilibrium constants from tables 1 and 2, we can conclude that the thermodynamic probability of reactions 1–8 under the considered conditions of low-temperature firing is high.

To determine the desired parameters of the low-temperature roasting process, the equilibrium composition of the process products was calculated under certain conditions of temperature and blast volume. The calculations were made of using the gold-bearing concentrate of the Uderrey's deposit as an example in the HSC Chemistry 6 program.

### 3. The calculation of the equilibrium composition

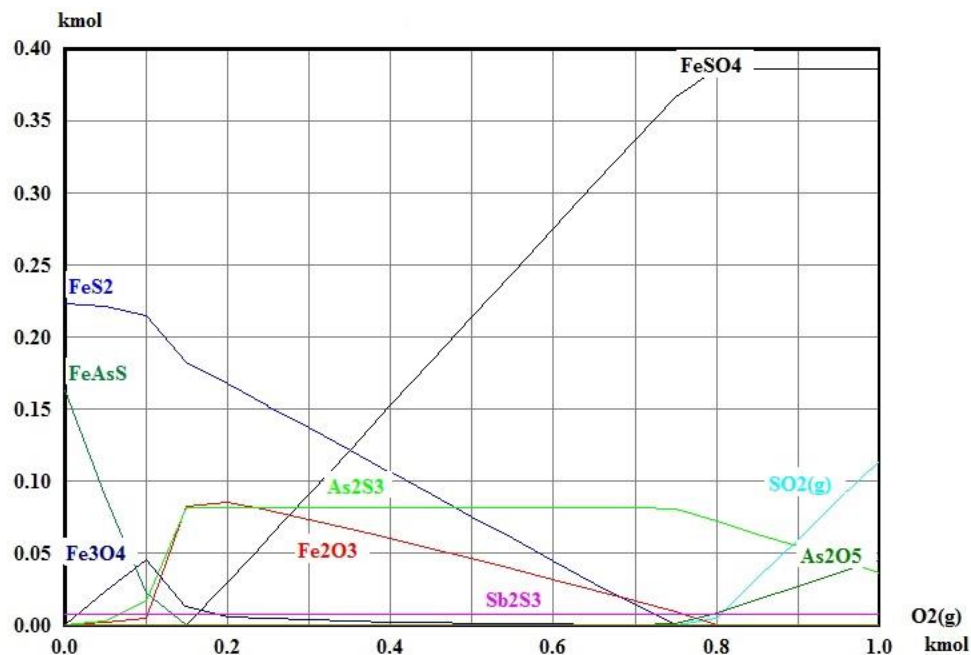
To determine the optimal roasting parameters, the 'Equilibrium compositions' module of the HSC Chemistry 6 application software package was used. The module is designed to calculate the equilibrium compositions of the contacting phases involved in technological processes. In our case, only two phases are considered: solid and gaseous. The solid phase consists of the initial concentrate and cinder formed during the process. The gaseous phase is represented by air blast and the resulting furnace gases, consisting mainly of sulfur dioxide ( $\text{SO}_2$ ) [14].

Concentrate of the Uderrey's deposit was taken as a starting material for calculations. Gold-bearing ores of this deposit, in addition to the main components in the form of pyrite and arsenopyrite, are characterized by the presence of antimony in the ore. The rational composition per 100 kg of this concentrate is shown in table 3.

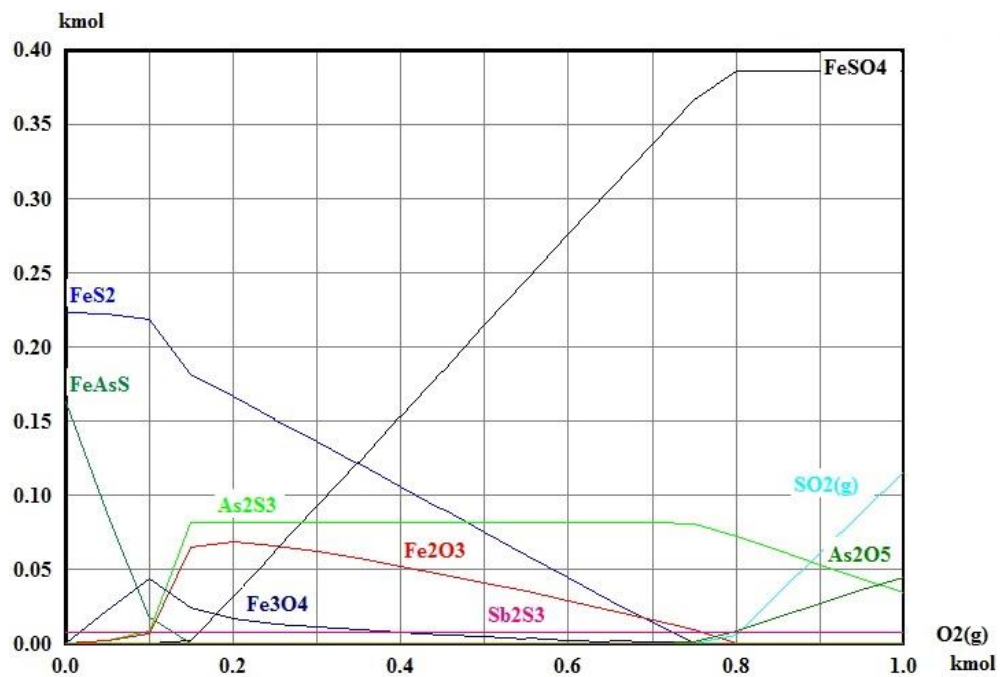
**Table 3.** The rational composition of the concentrate of the Uderrey's deposit.

	Fe	Cu	S	Sb	As	Si	Al	O	Other	Total
$\text{FeS}_2$	9.3	–	10.7	–	–	–	–	–	–	20.0
$\text{FeAsS}$	12.4	–	7.1	–	16.6	–	–	–	–	36.0
$\text{Sb}_2\text{S}_3$	–	–	1.7	4.3	–	–	–	–	–	6.0
$\text{SiO}_2$	–	–	–	–	–	7.5	–	8.5	–	16.0
$\text{Al}_2\text{O}_3$	–	–	–	–	–	–	10.6	9.4	–	20.0
Other	–	–	–	–	–	–	–	–	2.0	2.0
Total	21.7	0.0	19.4	4.3	16.6	7.5	10.6	17.9	2.0	100.0

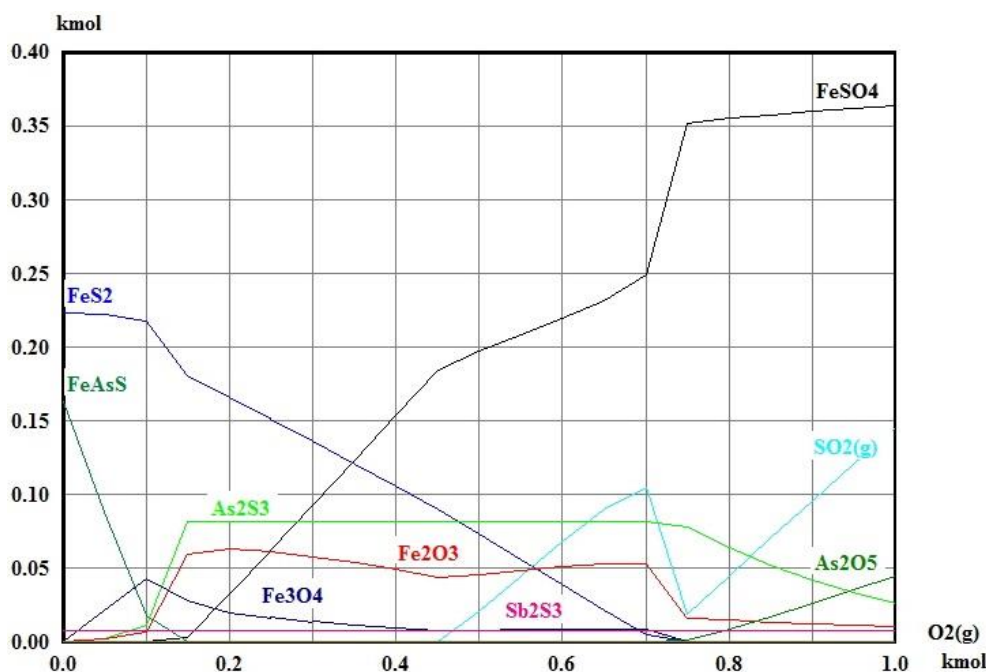
Calculations of the equilibrium composition were carrying out at various temperatures and the amount of oxygen per 100 kg of concentrate. The calculation results at various temperatures are shown in the form of diagrams in Figures 1–3.



**Figure 1.** The equilibrium composition of the products of low-temperature roasting at 200 °C.



**Figure 2.** The equilibrium composition of the products of low-temperature roasting at 350 °C.



**Figure 3.** The equilibrium composition of the products of low-temperature roasting at 350 °C.

As shown in Figures 1–3, the most optimal flow rate is 0.6–0.7 kmol of oxygen per 100 kg of concentrate, since the maximum amount of arsenic in the form of trisulfide is maintain in this range. Also, with such an amount of oxygen, the maximum possible amount of iron sulfate is formed. With a further increase in such amount of oxygen, the formation of volatile arsenic pentoxide ( $\text{As}_2\text{O}_5$ ) occurs, which contradicts the purpose of this roasting – to convert all arsenic to non-volatile form and leave it in the cinder. The calculation results at temperatures of 250 and 300 °C are comparable with the results of calculations at temperatures of 200 and 350 °C. The best result can be achieved at high temperatures of this roasting (Figure 2 and 3), since at temperatures of 350–400 °C oxidation reactions will proceed faster than at 200–300 °C, which will reduce operating cost.

As shown in Figure 3 at a temperature of 400 °C, the  $\text{SO}_2$  curve begins to change and the sulfur content in the exhaust gases increases markedly with increasing oxygen, which indicates an increase in the intensity of exothermic sulfur oxidation reactions. In this case, there is a risk of allowing the melting of the cinder particles and thereby only complicate the further extraction of gold. So we can conclude that at temperatures more than 400 °C roasting is not advisable.

All figures show that the amount of  $\text{Sb}_2\text{S}_3$  is presented in a straight line and does not change during the reaction. This means that antimony, known for its volatility and toxicity, will not affect the results of the roasting process in these conditions.

#### 4. Conclusions

Calculations of the equilibrium composition were carried out in order to find the suitable conditions for carrying out roasting. Roasting under such conditions is intended to produce a cinder containing arsenic in the form of trisulfide, which is confirmed in Figures 1–3. Based on the calculation results, it can be concluded that the most optimal conditions for low-temperature roasting are temperatures in the range 350–400 °C and approximately 0.6–0.7 kmol of oxygen per 100 kg of concentrate.

In addition, Figures 1–3 show that even at 0.7 kmol  $\text{O}_2$ , complete dissociation of pyrite does not occur. This suggests that the opening did not occur completely and some of the gold will remain in a closed state and will be difficult to extract. However, the degree of opening of pyrite at a level of 90 % indicates a high degree of efficiency of low-temperature roasting as a pre-treatment of the concentrate.

It is also worth noting that the degree of opening of arsenopyrite is about 100%. Since the main goal of low-temperature roasting was to convert all arsenic to trisulfide, the goal can be achieved.

At this stage of analytical research, is a positive calculation result and the optimal parameters for roasting are selected, which is the basis for continuing research in this direction. In the future, it is planned to carry out calculations with the raw materials of other gold deposits, as well as conduct experiments to confirm analytical calculations.

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