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Mineral Phase Evolution during Oxidation Roasting Pretreatment of Typical Carlin Gold Ore and Effects on Gold Leaching Efficiency

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Abstract: Arsenious and sulphur-bearing micro-disseminated gold ore is a kind of typical refractory Carlin-Type. The gold in Carlin-Type gold ore grains is distributed finely, existing as invisible or submicroscopic gold, encapsulated in arsenopyrite and pyrite. The technical difficulty of treatment Carlin-Type gold ore lies in how to release the fine gold wrapped in pyrite and arsenopyrite. In this study, the oxidation roasting pre-treatment technique was used to treat the Carlin-Type gold ore. This included a two-stage roasting process: the arsenic was removed in the first roasting process, and the sulphur was removed in the second roasting process. The thermodynamic of the roasting process was analyzed, and the mineral phase evolution of the roasting process was investigated by using XRD, SEM and EDS. Finally, the influence of sodium cyanide dosage and leaching time on leaching efficiency was investigated. The results suggest that for the first roasting temperature at 550 °C, and the second roasting at temperature 700 °C with air flow 2.5 L/min, the sodium cyanide dosage is 1.75 kg/t and leaching time is 27 h; a good leaching efficiency is obtained with 83.85%.

Keywords: oxidation roasting pretreatment; Carlin-Type gold deposit arsenopyrite; pyrite; cyanide leaching



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1. Introduction

The natural resources of gold mine are decreased and the high-quality gold ores are gradually depleted. The refractory gold ores have become the main source of gold product. The feature of refractory gold ore is that the gold grain size is extremely fine, and exists in invisible or submicroscopic gold, which is encapsulated in arsenopyrite, sulfide, carbonate or siliceous rock [1–3]. Hence, it is difficult to extract gold from ores using cyanide leaching, even after ultra-fine grinding [4]. In order to render gold amenable to the subsequent cyanide leaching, oxidation pretreatment is considered to be an effective method for treatment of refractory gold ore, and breaks up the sulphide to oxides or sulphates before cyanidation [5–9].

A number of projects have been conducted to improve the extraction of gold from fine-grained refractory gold ores by using oxidation roasting pretreatment [10–12]. Oxidation roasting pretreatment is the most common pretreatment approach to treatment refractory gold ores [13–17]. To achieve good recoveries in subsequent leaching, the majority of the sulfur and organic carbon has to be oxidized to SO₂ and CO₂; the arsenic of ore has to be transformed to the volatile trivalent compound. Some of SO₂ and SO₃ and volatile trivalent compound can be captured with lime or dolomite of ores forms the stable compounds and ends up in the calcine [18].

In this study, the gold in arsenious and sulfur-bearing Carlin-Type gold ore is distributed extremely finely, existing as invisible or submicroscopic gold, encapsulated in

arsenopyrite and pyrite. The technical difficulty of treatment Carlin-Type gold ore lies in how to release the fine gold encapsulated in pyrite and arsenopyrite. In order to achieve a good gold recovery, the thermodynamic analysis was used to verify the feasibility and reliability of the oxidation roasting in this paper. The mineral phase evolution of calcining was investigated by using XRD, SEM and EDS. Finally, a central composite design was used for investigating the operating variables corresponding to the leaching efficiency of gold.

2. Material and Methods

2.1. Raw Materials

An arsenious and sulfur-bearing Carlin-Type gold ore was obtained from Guizhou. The ore sample was prepared by crushing and grinding. Inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima, USA) was used to determine the chemical composition of the sample after dissolution, whereas gold was analyzed with the fire assay method followed by atomic absorption spectroscopy (AAS, WFX-130A, Beijing, China). The main phases were identified via mineral liberation analyzer (MLA 650, FEI Company, Czech Republic), scanning electron microscope (SEM Zeiss Sigma, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford, UK), electron probe scanning and X-ray diffraction (Rigaku SmartLab, Japan).

The main elements of the gold ore are shown in Table 1. It shows that the arsenious and sulfur-bearing Carlin-Type gold ore contains 2.50 g/t of Au, 9.15% of S and 0.79% of As. The SEM-EDS image of arsenious and sulfur-bearing Carlin-Type gold ore is shown in Figure 1. The metal minerals are mainly pyrite and arsenopyrite, and gangue minerals are mainly quartz, sericite, dolomite, calcite, ferrodolomite, kaoline, etc. The occurrence of gold is determined via diagnostic leaching. The occurrence of gold in different phases of Carlin-Type gold ore is shown in Figure 2. The dissemination characteristics and size fraction of main minerals were investigated with a mineral liberation analyzer (MLA). The gold in ore is extremely fine, and exists as invisible or submicroscopic gold, and is encapsulated in pyrite, arsenopyrite and silicate minerals. The particles of pyrite and arsenopyrite are also fine, 76.5% of pyrite have particle size $<300\ \mu\text{m}$, and 83.36% of arsenopyrite have particles size $<38\ \mu\text{m}$. It is interesting that the distribution of gold in pyrite is only 6.08%, and the distribution of gold in arsenopyrite is 93.92%. The large amount of gold in arsenopyrite is the reason it is difficult to treat. The carbon content in the ore is 1.70%. The occurrence of carbon in different phases of Carlin-Type gold ore shows that 93.53% of carbon was presented in inorganic carbon; only 4.41% of carbon was presented in organic carbon and the rest was graphitic carbon. The content of organic and graphitic carbon in the ore was below 1%. Hence, there is almost no preg-robbing organic carbon.

Table 1. The main elements of the Carlin-Type gold ore.

Element	Content (%)	Mineral	Content (%)
Au (g/t)	2.50	Pyrite	22.93
Ag (g/t)	0.82	Arsenopyrite	1.27
S	9.15	Sericite	32.00
As	0.79	Quartz	25.09
Fe	9.55	Dolomite	5.95
Mg	1.75	Calcite	2.68
Ca	3.9	Ferrodolomite	3.06
Ti	1.5	Kaoline	2.53
K	2.46	Chlorite	1.51
Na	0.03	Rutile	1.33
P	0.33	Others	1.65
C	1.70		
Al	3.12		
SiO ₂	40.74		

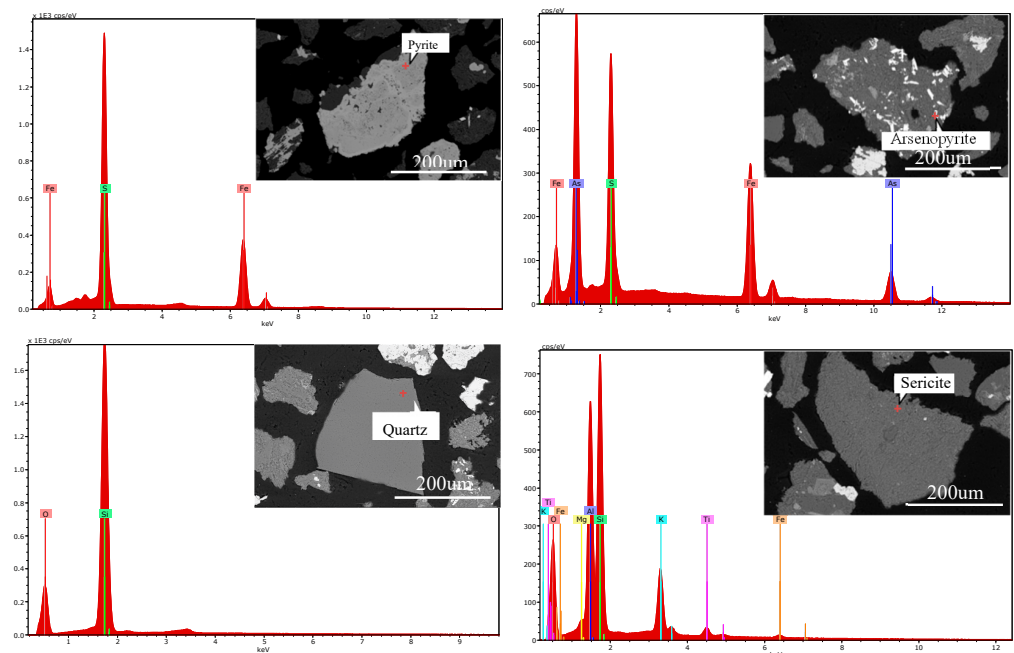


Figure 1. The SEM-EDS images of arsenious and sulfur-bearing Carlin-Type gold ore.

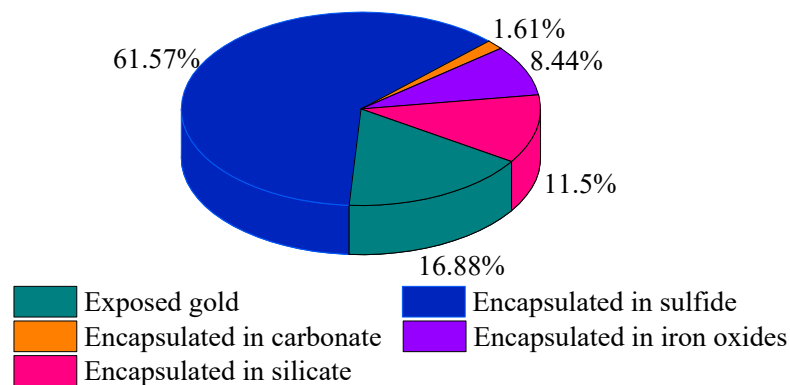


Figure 2. The occurrence of gold in different phases of Carlin-Type gold ore.

2.2. Roasting and Cyanide Leaching

The ground ore, with 85% passing size of 74 μm , was dried. Air oxidation roasting experiments were carried out in controlled atmosphere chamber furnace (static furnace). A 20 g sample was weighed and placed in a quartz crucible; a desired air flow was set which was controlled by adjusting the flowmeter. The sample was heated to a predetermined temperature with a temperature increase speed of 20 $^{\circ}\text{C}/\text{min}$. When the desired temperature was reached, the temperature was maintained for a certain time. Subsequently, the calcine was cooled to room temperature and gold was leached under the following conditions: the calcine was ground to 92.23% passing size of 38 μm , concentration of slurry 25%, pH of leaching solution 11–12 and leaching temperature 25 $^{\circ}\text{C}$. After the leaching test, the slurry was filtrated via a vacuum filtration device. The residue was dried and the gold content was analyzed via the fire assay method followed by atomic absorption spectroscopy.

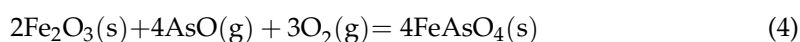
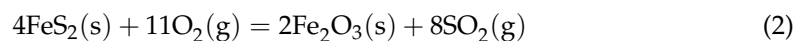
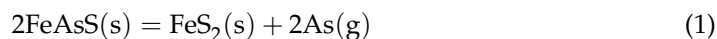
3. Results and Discussion

3.1. The Oxidation Roasting Pretreatment

3.1.1. The Thermodynamics Fundamental of Roasting

The oxidation roasting of arsenious and sulfur-bearing Carlin-Type gold ore is a complex chemical reaction process. The arsenopyrite and pyrite in the gold ore is oxidized

to iron oxides, arsenic oxides, sulfur oxides, sulfate and arsenate in the oxidation roasting process so that the finely disseminated gold particles can be dissolved via cyanide during leaching. The main equilibrium reaction can be expressed as follows:



To understand the phase evolution of arsenopyrite and pyrite of gold ore in the roasting process, a thermodynamic model was calculated by using the Equilibrium Composition module of HSC Chemistry 6.0. The amount of O_2 (g) and N_2 (g) in the calculation was normalized to be 1.0 mol and 3.71 mol, respectively. The equilibrium amounts of species and temperature for the reaction of FeAsS and O_2 , and FeS_2 and O_2 at different content of O_2 are shown in Figures 3 and 4, respectively. It can be seen from Figures 3 and 4 that the content of oxygen is an important factor for affecting FeAsS and FeS_2 oxidation roasting. At temperature 200–600 °C, the As_2O_3 is easily formed at lower amounts of oxygen, and the FeAsS is decomposed to FeS_2 , As_2O_3 , SO_2 and iron oxide is lower. When the amount of oxygen is increased, the main compositions are changed to FeAsO_4 , SO_3 and SO_2 . Compared to FeAsS , FeS_2 is easily oxidized to SO_2 , Fe_3O_4 and Fe_2O_3 at lower amounts of oxygen. When the amount of oxygen is increased, the FeS_2 is oxidized to SO_2 , SO_3 and Fe_2O_3 . From the analysis, the arsenic and sulfur can be removed by using control roasting conditions, e.g., amount of oxygen and roasting temperature.

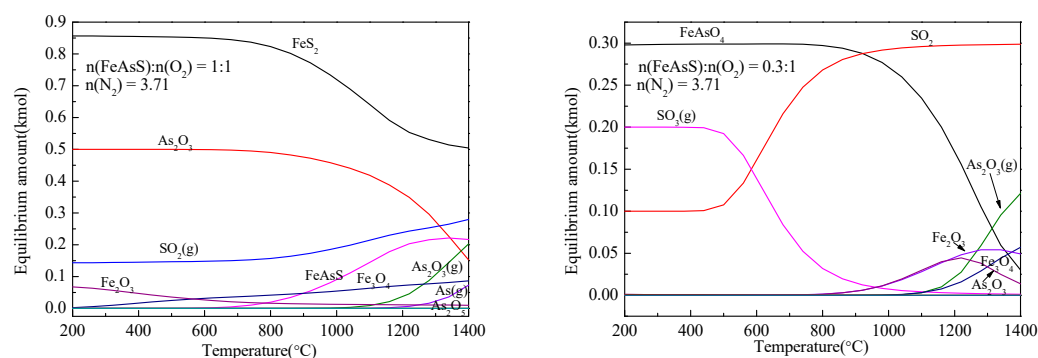


Figure 3. Equilibrium amounts of species as a function of temperature for reaction of FeAsS and O_2 .

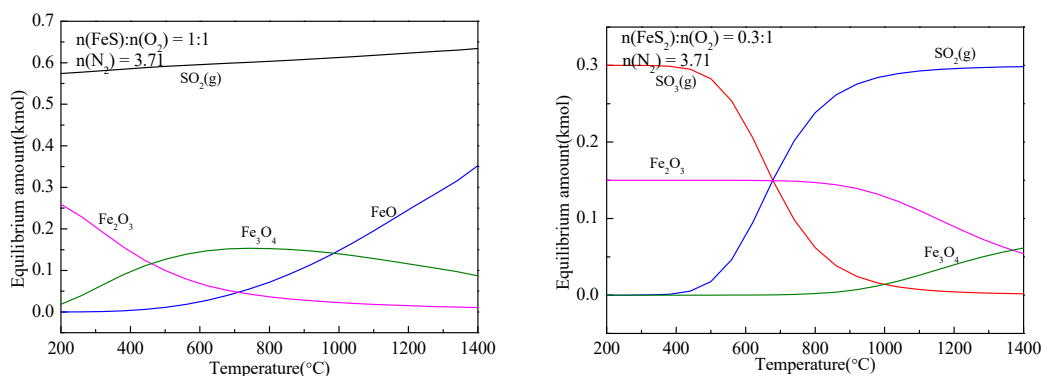


Figure 4. Equilibrium amounts of species as a function of temperature for reaction of FeS_2 and O_2 .

3.1.2. Effect of Roasting Condition on Removal Efficiency of As and S, and Leaching Efficiency of Gold

The gold of refractory gold ore is encapsulated in arsenopyrite and sulfide. The content of gold in pyrite is only 6.08%, and the distribution of gold in arsenopyrite is 93.92%; it is necessary to remove As and S from the sulfide refractory gold ore using the air oxidation roasting for releasing the fine gold encapsulated in pyrite and arsenopyrite. Figure 5 shows effects of the temperature (a) and air flow rate (b) on the removal efficiency of As and S, and leaching efficiency of gold in single stage roasting. It can be seen from Figure 5a (air flow rate 2.5 L/min, roasting 1 h) that the removal efficiency of As is less than 30%, and decreases on increasing the roasting temperature; the removal efficiency of S increases on increasing the roasting temperature. The leaching efficiency of gold is less than 80%, and increases on increasing the roasting temperature from 500 °C to 700 °C. The effects of air flow rate on the removal efficiency of As and S, and leaching efficiency of gold are shown in Figure 5b (roasting temperature 700 °C, roasting 1 h), which shows that the removal efficiency of As decreases on increasing the airflow rate; however, the removal efficiency of S shows the opposite trend. The leaching efficiency of gold decreases on increasing the air flow rate. It also can be seen that the removal of As has an important effect on leaching of gold.

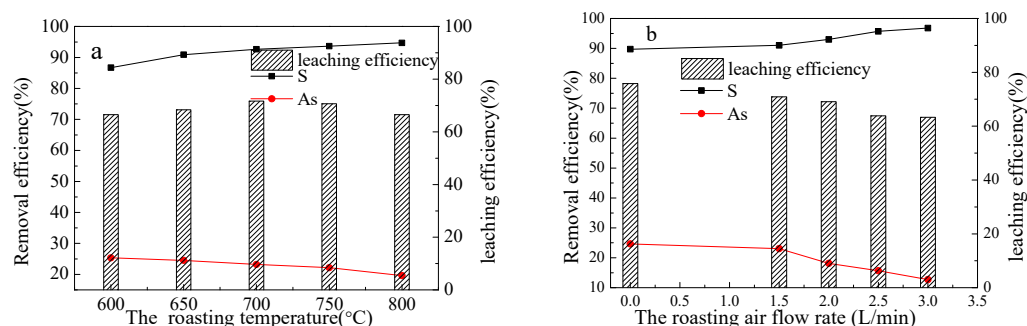


Figure 5. Effects of the temperature (a) and air flow rate (b) on the removal efficiency of As and S, and leaching efficiency of gold in single stage roasting.

In order to obtain the best removal efficiency of As and S, and leaching efficiency of gold, a series of two stage roasting experiments was used to investigate the effect of roasting condition on removal efficiency of As and S, and leaching efficiency of gold, which investigated the first roasting temperature, the second roasting temperature and the second roasting air flow. The effects of roasting condition on removal efficiency of As and S, and leaching efficiency of gold are shown in Figure 6. The effects of first roasting temperature on the removal efficiency of As and S are shown in Figure 6a (the sample was roasted in air (air flow 0 L/min) at different temperatures (450–600 °C) for 1 h). It can be seen from Figure 6a that the optimum removal efficiency of As is 46.91% at temperature 550 °C with only 38.41% S removal. To further remove S from the first stage roasting calcine (obtained at temperature 550 °C, air flow rate 0 L/min, roasting time 1 h), the higher temperature (600 °C–800 °C) and higher air flow rate (1.5 L/min–3.0 L/min) were used to roast the first stage roasting calcine. It can be seen from Figure 6b that the removal efficiency of S increased on increasing temperature, the leaching efficiency also increased on increasing the second stage roasting temperature below 750 °C. The leaching efficiency of gold decreased when the temperature exceeded 750 °C; this is because the sample was sintered under over roasting conditions and as a result the gold was not accessible to cyanide. The effects of the air flow on the removal efficiency of S, and leaching efficiency of gold in second stage roasting are shown in Figure 6c. It can be seen that the removal efficiency of S increases on increasing of air flow; the leaching efficiency of gold also increases with air flow. Above all, the As and S can be removed by controlling the operating parameters and condition of roasting process, which can give a good leaching efficiency of gold.

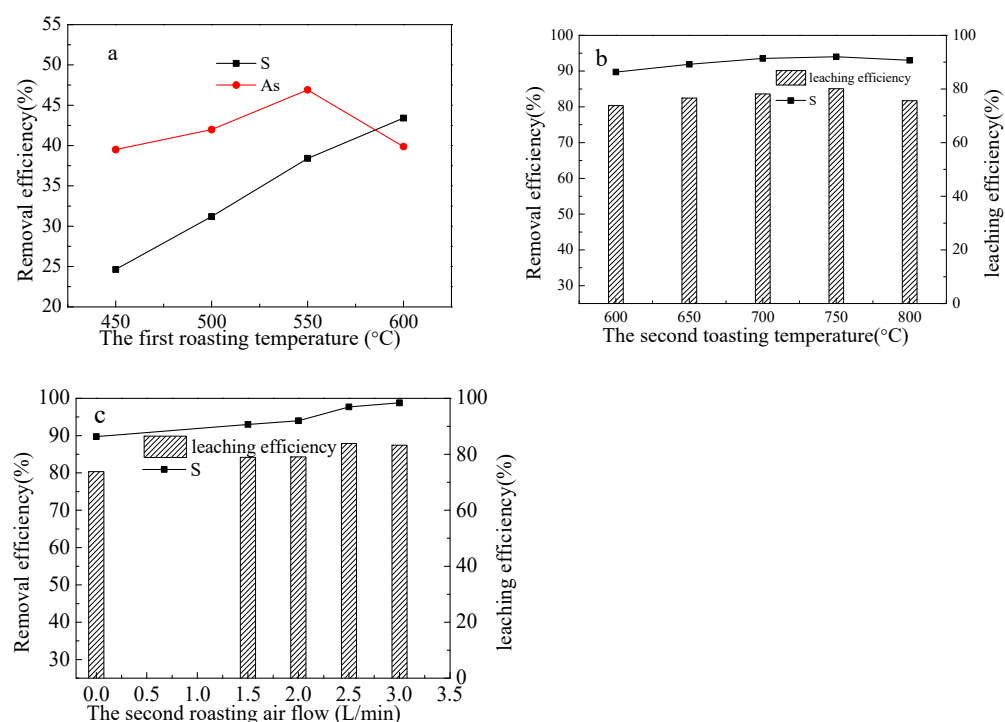


Figure 6. Effects of the first roasting temperature (a), the second roasting temperature (b) and air flow rate of second stage roasting (c) on the removal efficiency of As and S, and leaching efficiency of gold in the two stage roasting.

3.2. Mineral Phase Evolution of Carlin-Type Gold Ore

The arsenic was removed in the first roasting process at a temperature of 550 °C, and the sulfur was removed in the second roasting process at 700 °C with air flow 2.5 L/min. The mineral composition and microstructure of calcine was determined via X-ray diffraction, the electron probe microanalysis technique (EPMA) and SEM. The X-ray diffraction pattern of arsenious and sulfur-bearing refractory gold ore and calcine are shown in Figure 7. It can be seen from Figure 7 that the main components of calcine were quartz and hematite. Comparing with raw material, the diffraction peak of pyrite and arsenopyrite disappeared completely in calcine and is replaced by the hematite peak. This indicates that the pyrite and arsenopyrite were almost completely oxidized to hematite in calcine.

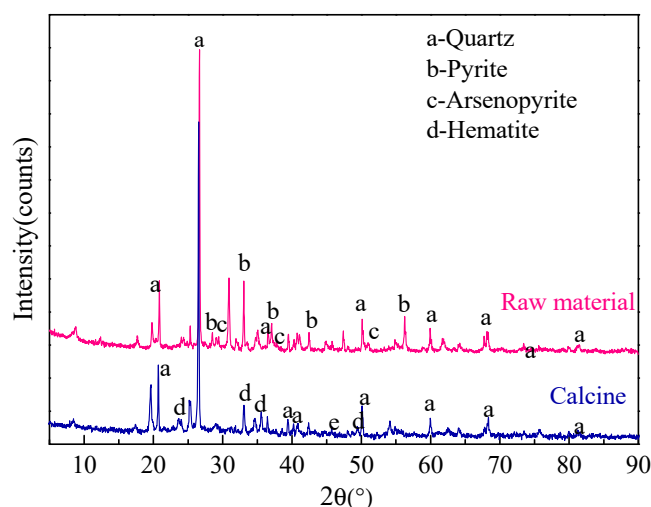


Figure 7. X-ray diffraction pattern of arsenious and sulfur-bearing refractory gold ore and calcine.

The surface micro structure and elemental composition of raw ores and hematite in calcine were observed via map analyses with the electron probe microanalysis technique (EPMA). The electron probe microanalysis of hematite in calcine is shown in Figures 8 and 9. It can be seen from Figures 8 and 9 that the pyrite contains some arsenic in raw ore. The gold in ore is extremely fine, and exists as invisible or submicroscopic gold, which does not reveal the presence of any discrete grains of gold. In these gold ores, gold is chemically bound within the arsenopyrite in a non-metallic form, owing to its suitable atomic spacing and crystal chemistry with respect to gold (Swash, 1988). As shown in Figures 8 and 9, comparing with raw ore, most arsenic and sulfur was removed in roasting process, and hematite was the main product of the calcine. The microstructure of hematite is shown in Figure 10. It can be seen from Figure 10 that the hematite possesses a porous structure resulting from the escape of the arsenic or sulphur atoms from the sulphide grains. Those micro-pores could provide a diffusion channel for CN^- , which is conducive to improving the leaching efficiency of gold.

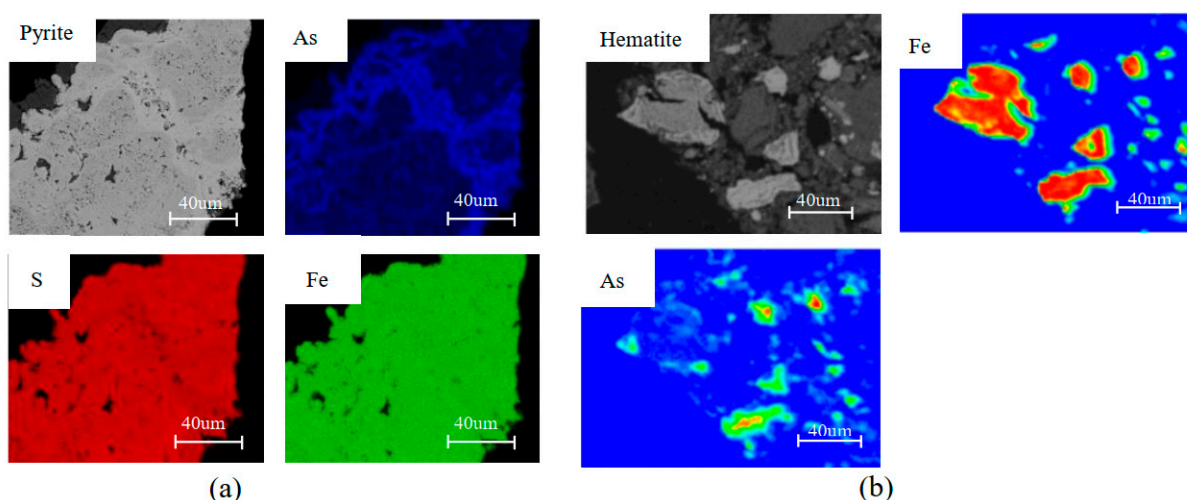


Figure 8. The electron probe microanalysis of pyrite (a) and hematite in calcine (b).

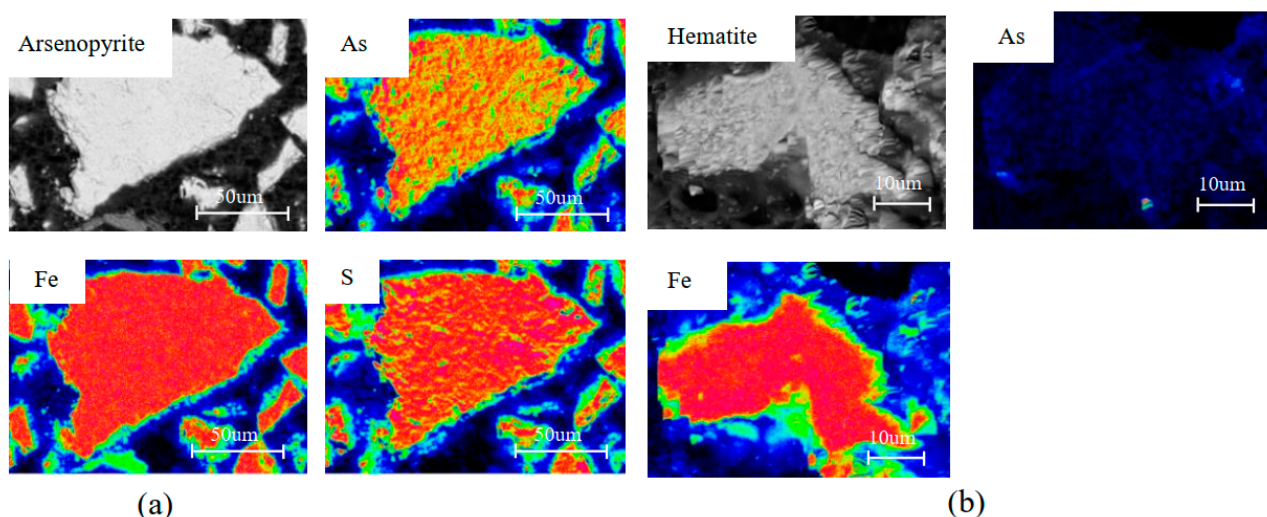


Figure 9. The electron probe microanalysis of arsenopyrite (a) and hematite in calcine (b).

The mineral phase evolution during roasting is followed by a change in the occurrence state of gold. The change in the occurrence state of gold directly affects the gold leaching efficiency. The occurrence of gold is determined via diagnostic leaching. The occurrence of gold in different phases of the arsenious and sulfur-bearing Carlin-Type gold ore and

the calcine is shown in Figure 11. It can be seen from Figure 11 that only 16.88% of gold is exposed in raw ore, with up to 61.6% of the gold encapsulated in sulfides. After roasting, the calcine contains up to 56.4% exposed gold, iron oxide-encapsulated gold up to 31.50% and sulfide-encapsulated gold almost reduced to 0 %. This will facilitate the subsequent gold leaching process.

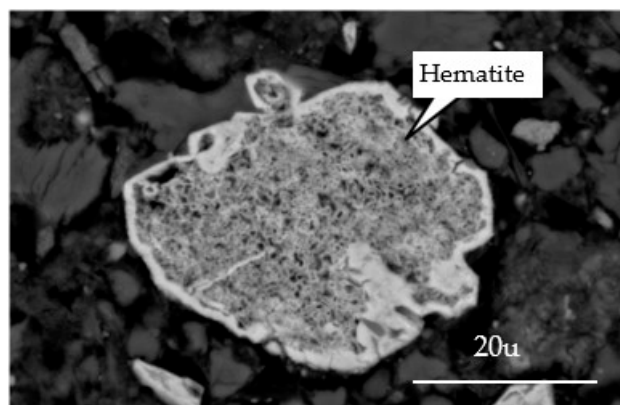


Figure 10. The microstructure of hematite in calcine.

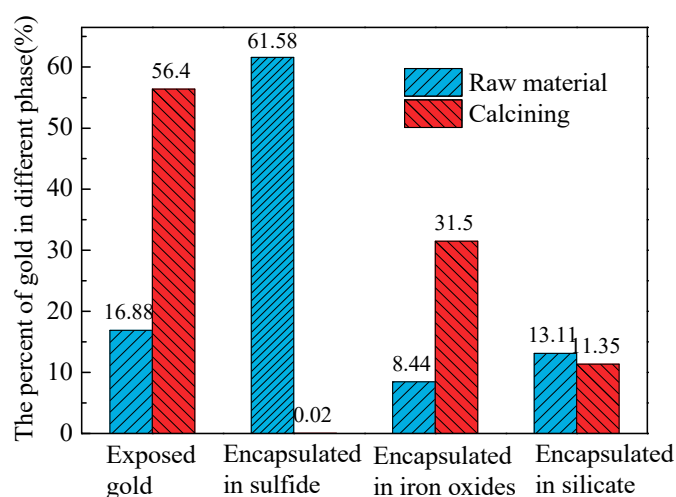


Figure 11. The occurrence of gold in different phases of Carlin-Type gold ore and calcine.

3.3. The Effects on Gold Leaching Efficiency

As mentioned above, the arsenic was removed in the first stage roasting process at temperature 550 °C, air flow rate 0 L/min and roasting time 1 h. The sulfur was removed in the second roasting process at 700 °C, air flow 2.5 L/min with roasting time 1 h. Hence, the calcine was prepared at the above conditions, and the influence of sodium cyanide dosage and leaching time on leaching efficiency was investigated. Figure 12a shows the leaching efficiency of gold at different sodium cyanide dosages with a constant leaching time of 24 h. It can be seen from Figure 12a that the leaching efficiency of gold increases with increasing sodium cyanide dosage. When the sodium cyanide dosage is more than 1.75 kg/t, the leaching efficiency of gold does not significantly increase. Figure 12b shows the leaching efficiency of gold at different leaching times with a constant sodium cyanide dosage of 1.75 kg/t. It can be seen from Figure 12a that the leaching efficiency of gold increases with increasing leaching time. When leaching time is more than 27 h, the leaching efficiency of gold does not significantly increase. Based on the above analysis, the results suggest that for the first roasting temperature at 550 °C, and the second roasting at temperature 700 °C with air flow 2.5 L/min, the sodium cyanide dosage is 1.75 kg/t and leaching time is 27 h; a good leaching efficiency is obtained with 83.85%.

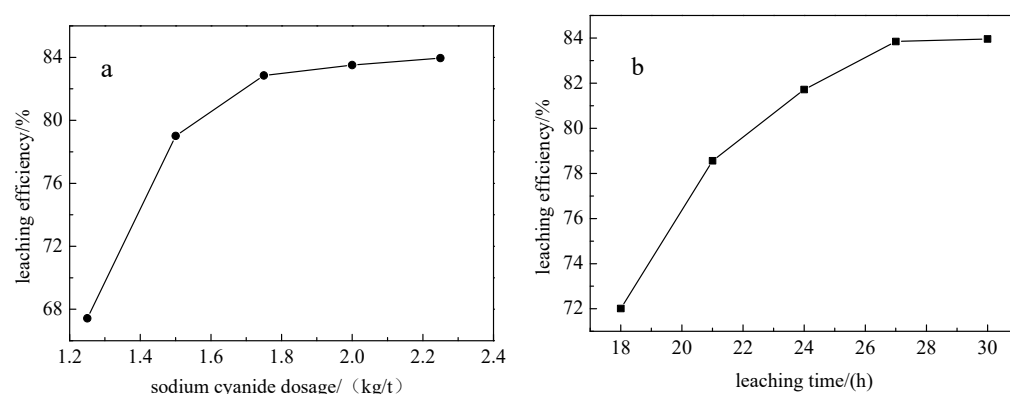


Figure 12. The effect of sodium cyanide dosage (a) and leaching time (b) on the leaching efficiency.

4. Conclusions

This study investigated the two stage oxidation roasting technique, which was used to treat the arsenious and sulfur-bearing Carlin-Type gold ore with the purpose of improving leaching efficiency of gold. In the roasting process, the arsenic was removed in the first roasting, and the sulfur was removed in second roasting. The thermodynamic of the roasting process was analyzed, and the mineral phase evolution of calcining was investigated by using XRD, SEM and EDS. After roasting, the pyrite and arsenopyrite were almost completely oxidized to hematite. The exposed gold is up to 56.40%, iron oxide-encapsulated gold is up to 31.50% and sulfide-encapsulated gold is reduced almost to 0%. The porous structure of the hematite facilitates the subsequent gold leaching process. Finally, a small scale (20 g) batch test with first roasting temperature at 550 °C for 1 h without air flow, and second roasting at temperature 700 °C for 1 h with air flow 2.5 L/min, followed by 27 h cyanidation with 1.75 kg/t cyanide addition gave 83.5% gold extraction.

Author Contributions: Investigation, Writing—original draft, Data curation, Visualization, Writing—review and editing, L.M. and L.W., Conceptualization, Methodology, L.M. and X.L., Resources, Validation, Funding acquisition, L.M. and L.W., Investigation, Data, J.Q., Review, L.M. and J.Q. All authors have read and agreed to the published version of the manuscript.

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References

1. Cline, J.S. Timing of gold and arsenic sulfide mineral deposition at the Getchell Carlin-type gold deposit, north-central Nevada. *Econ. Geol.* **2001**, *96*, 75–89. [\[CrossRef\]](#)
2. Rui-Zhong, H.; Wen-Chao, S.; Xian-Wu, B.; Guang-Zhi, T.; Hofstra, A.H. Geology and geochemistry of Carlin-type gold deposits in China. *Miner. Depos.* **2002**, *37*, 378–392. [\[CrossRef\]](#)
3. Su, W.; Xia, B.; Zhang, H.; Zhang, X.; Hu, R. Visible gold in arsenian pyrite at the Shuiyindong Carlin-type gold deposit, Guizhou, China: Implications for the environment and processes of ore formation. *Ore Geol. Rev.* **2008**, *33*, 667–679. [\[CrossRef\]](#)
4. Corrans, I.J.; Angove, J.E. Ultra fine milling for the recovery of refractory gold. *Miner. Eng.* **1991**, *4*, 763–776. [\[CrossRef\]](#)
5. Komnitsas, C.; Pooley, F.D. Mineralogical characteristics and treatment of refractory gold ores. *Miner. Eng.* **1989**, *2*, 449–457. [\[CrossRef\]](#)
6. Piervandi, Z. Pretreatment of refractory gold minerals by ozonation before the cyanidation process: A review. *J. Environ. Chem. Eng.* **2023**, *11*, 109013. [\[CrossRef\]](#)
7. Li, J.; Yang, H.; Zhao, R.; Tong, L.; Chen, Q. Mineralogical characteristics and recovery process optimization analysis of a refractory gold ore with gold particles mainly encapsulated in pyrite and Arsenopyrite. *Geochemistry* **2023**, *83*, 125941. [\[CrossRef\]](#)
8. Majumdar, S.; Singh, S.; Sahoo, P.R. Characterization of organic matter and its implications for pyrite hosted refractory gold mineralization along the South Purulia Shear Zone, eastern India. *Ore Geol. Rev.* **2020**, *124*, 103584. [\[CrossRef\]](#)
9. Qin, H.; Guo, X.; Tian, Q.; Yu, D.; Zhang, L. Recovery of gold from sulfide refractory gold ore: Oxidation roasting pretreatment and gold extraction. *Miner. Eng.* **2021**, *164*, 106822. [\[CrossRef\]](#)

10. Amankwah, R.K.; Pickles, C.A. Microwave roasting of a carbonaceous sulphidic gold concentrate. *Miner. Eng.* **2009**, *22*, 1095–1101. [[CrossRef](#)]
11. Fraser, K.S.; Walton, R.H.; Wells, J.A. Processing of refractory gold ores. *Miner. Eng.* **1991**, *4*, 1029–1041. [[CrossRef](#)]
12. Nanthakumar, B.; Pickles, C.A.; Kelebek, S. Microwave pretreatment of a double refractory gold ore. *Miner. Eng.* **2007**, *20*, 1109–1119. [[CrossRef](#)]
13. Swash, P.M. A mineralogical investigation of refractory gold ores and their beneficiation with special reference to arsenical ores. *J. South Afr. Inst. Min. Metall.* **1988**, *88*, 173–180.
14. Arriagada, F.J.; Osseo-Asare, K.A. Gold extraction from refractory ores: Roasting behaviour of pyrite & arsenopyrite in Precious Metals. In *Min Extn & Processing*; Kudryk, V., Liang, W.W., Eds.; Metallurgical Society of AIME: Englewood, CO, USA, 1984; pp. 367–385.
15. Marsden, J.; House, I. Oxidative Pre-treatment. In *Chemistry of Gold Extraction*; SME: Chandler, AZ, USA, 2006; Chapter 5; pp. 147–231.
16. Fernández, R.R.; Collins, A.; Marczak, E. Gold recovery from high arsenic containing ores at Newmont's roasters. *Miner. Metall. Process.* **2010**, *27*, 60–64. [[CrossRef](#)]
17. Hammerschmidt, J.; Güntner, J.; Kerstiens, B.; Charitos, A. Roasting of gold ore in the circulating fluidized-bed technology. *Dev. Miner. Process.* **2005**, *15*, 433–453.
18. Thomas, K.G.; Cole, A.P. Roasting developments—especially oxygenated roasting. In *Gold Ore Processing*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 373–392.

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