Isothermal Coal-Based Reduction Kinetics of Fayalite in Copper Slag

Lin Zhang, Yu Zhu, Wanzhong Yin, Bao Guo, Feng Rao, and Jiangang Ku*

ABSTRACT: The coal-based reduction of fayalite was characterized using thermogravimetric (TG) and differential TG methods with reduction temperatures from 1123 to 1273 K. The results of fayalite isothermal reduction indicate that the reduction process is divided two stages. The corresponding apparent activation energy \( E \) was gained using the isoconversional and model-fitting methods. At the first stage, the effect of temperature on the reduction degree was not clear, and the phase boundary chemical reaction was the controlling step, with an apparent activation energy \( E \) value of 175.32–202.37 kJ mol\(^{-1}\). At the second stage, when the temperature was more than 1123 K, the conversion degree and the reaction rate increased nonlinearly with increasing temperature, and two-dimensional diffusion, three-dimensional diffusion, one-dimensional diffusion, and phase boundary-controlled reaction were the controlling stages, with an apparent activation energy \( E \) ranging from 194.81 to 248.96 kJ mol\(^{-1}\). For the whole reduction process, the average activation energy \( E \) and pre-exponential factor \( A \) were 185.07–225.67 kJ mol\(^{-1}\) and 0.796–0.797 min\(^{-1}\), respectively.

INTRODUCTION

Flash smelting and converter smelting have been used in the copper industry for a number of years as a relatively advanced, most widely available technology for refining metallic copper from the copper ore.\(^1\) The main phases and compositions of the copper ore are chalcopyrite (CuFeS\(_2\)), chalcocite (Cu\(_2\)S), covellite (CuS), quartz (SiO\(_2\)), and pyrite (FeS\(_2\)).\(^2\) However, nearly all of the impurity metals enter the slag phase, under the action of oxygen-rich blowing, because the affinity of copper to oxygen is less than that of impurity metals. Therefore, a metal-rich fayalite is discharged as a byproduct with copper slag in the process of the matte smelting and refining of copper.\(^3,4\) Production of 1 ton of metallic copper generates approximately 2.2–3.0 tons of slag.

It is estimated that 19–26.7 million tons of copper slag is discharged into the environment annually in China. Generally, the compositions and contents of copper slag vary in the range of Fe\(_2\)O\(_3\) 35–65%, SiO\(_2\) 20–45%, CaO 0.2–15%, MgO 0.5–12%, and so forth.\(^5\) Clearly, million tons of iron resources exist in the annually generated slag. However, only a little part of slag is used in construction materials, paving materials, and so forth.\(^6,7\) Recent research found that copper slag contains Cu in the form of sulfides, which can be recycled mainly by flotation,\(^8–10\) and Fe mainly in the form of fayalite, which can be difficult to recycle using conventional mineral processing methods. Compared to the natural raw ore, most secondary raw materials are of a higher grade\(^11\) but have a complicated structure and chemical phases, which seriously restrict the recycling efficiency of metals.

At present, the comprehensive use of resources, such as the coal-based reduction of copper slag, has become a topic of significant interest. The effects of reduction conditions such as reduction temperature, reduction time, and C/O ratio on the reduction and magnetic separation were investigated in detail, and metallic iron containing more than 90% Fe was obtained under optimal conditions.\(^12–15\) Although studying the effectiveness factors of the reduction process is very important, the kinetics of metal grain growth is more significant in prompting comprehensive utilization of iron. Three-dimensional (3D) diffusion model of the Jander equation\(^16\) and reaction geometry model,\(^17\) gas–liquid reaction theory and double membrane theory,\(^18\) and equilibrium model based on Gibbs free energy minimum principle\(^19\) usually can be used to describe the iron grain growth during the gas-based and oil-based reduction process, respectively. In the process of coal-based reduction, three models, that is, Hillert dynamics,\(^20\) integral method,\(^21\) and kinetic phenomenological theory,\(^22\) often describe the kinetics of the grain growth process. However, the formation and characterization of metallic iron grains during the copper slag reduction remain unclear, which are imperative for understanding and optimizing the coal-based reduction process.
Furthermore, we might introduce a suitable model to describe the whole reduction process. In this paper, as the main phase of the copper slag, fayalite would be considered. First, the granularity and composition of raw fayalite after magnetic separation were characterized by laser particle size analysis and X-ray diffraction (XRD). Second, the coal-based reduction process was identified by thermogravimetric analysis (TGA). Then, to illustrate the kinetics and mechanism of the coal-based reduction of fayalite, a relatively reasonable model was established via the isothermal thermal analysis kinetic method at 1123−1273 K.

**RESULTS AND DISCUSSION**

**TG and Reduction Degree Curves.** Reduction degree curves and mass loss TG as a function of time at different reduction temperatures are shown in Figure 1. The reduction degree and mass loss increased sharply with increasing temperature. When the fayalite is reduced at relatively low temperatures (~1123−1173 K), the reduction degree is strongly affected by the reduction temperature; the maximum degree of fayalite was 0.0816, 0.1935, 0.5566, and 0.9936 at 1123, 1173, 1223, and 1273 K, respectively. These experimental results indicate that when the temperature is less than 1173 K, the activation energy provided is inadequate to bring about a significant reduction; therefore, obvious reduction starts at 1223 K and above.

**Determination of Mode Function G(α). ln−ln Analysis Method.** The whole reaction process is divided into two stages on the basis of eqs 10 and 11 and the TG experimental data, and the range of corresponding reduction is shown in Table 1. The fitting data obtained at different temperatures are shown in Figure 2. The gained intercepts n ln k and slopes n are shown in Table 2. At the first stage, the slopes n are 0.98, 0.87, 0.83, and 0.77. These values are between 0.77 and 0.98, which accurately match (0.9933 ≤ R^2 ≤ 0.9991) the values of F_1(α) in Table 3. Therefore, the first stage can be described as the mode function F_1(α). At the second stage, the slopes n are 0.58, 0.37, 0.79, and 1.39, which better match (0.9467 ≤ R^2 ≤ 0.9997) the values of D_2(α), D_3(α), D_4(α), and R_2(α), respectively (Table 3). In the case of 1123 K, the second reduction stage is expressed by the following equation:

![Figure 1](https://pubs.acs.org/doi/abs/10.1021/acsomega.9b04497)

![Figure 2](https://pubs.acs.org/doi/abs/10.1021/acsomega.9b04497)

**Table 1. Reduction Degree Range of Different Stages with Different Reduction Temperatures**

| T/K  | 1123 K | 1173 K | 1223 K | 1273 K |
|------|--------|--------|--------|--------|
| first stage | 0.0000−0.0248 | 0.0000−0.0687 | 0.0000−0.1331 | 0.0000−0.3324 |
| second stage | 0.0248−0.0816 | 0.0687−0.1935 | 0.1331−0.5566 | 0.3324−0.9936 |

Figure 1. (a) Mass loss and (b) reduction degree as a function of time at different temperatures.

Figure 2. Avrami transformation plots of ln[−ln(1−α)] vs ln t at different temperatures. The reduction temperatures were (a) 1123, (b) 1173, (c) 1223, and (d) 1273 K, respectively.
mode function \(D_2(\alpha)\), thus, a two-dimensional (2D) diffusion process is proposed, described by the kinetic equation \(G(\alpha) = (1 - \alpha)\ln(1 - \alpha) + \alpha\). For the temperatures of 1173–1273 K, the second reduction stage is expressed by mode functions \(D_3(\alpha)\) and \(D_4(\alpha)\), respectively. In this case, a process from tridimensional particle shape Jander equation to one-dimensional (1D) diffusion is proposed, described by the kinetic equation \(G(\alpha) = \frac{1}{2}(1 - (1 - \alpha)^3)^3\) and \(G(\alpha) = \alpha^2\). For a temperature of 1273 K, the second stage is expressed by the mode function \(R_2(\alpha)\); in this case, a phase boundary-controlled reaction process is proposed, described by the kinetic equation \(R_3(\alpha) = 1 - (1 - \alpha)^{1/3}\).

**Málek Method.** We, in the Málek method, replaced the parameters in eq 12 with each of the 10 mechanism functions and tested the experimental data. Through a comparison of the experimental \((\alpha - \gamma(\alpha))\) curves with theoretical ones, the most suitable \(f(\alpha)\) was identified when the experimental \((\alpha - \gamma(\alpha))\) values all matched with the theoretical line. Standard kinetic curves and fitting curves for fayalite samples at different reduction temperatures are shown in Figure 3. The experimental data accurately fit the value of \(F_1\) at the first stage, so the reaction follows the \(F_1(\alpha)\) model. An instantaneous nucleation and unidimensional growth (bimolecular decay law) process described by the kinetic equation \(G(\alpha) = -\ln(1 - \alpha)\) is proposed. When the temperature is 1173 K, the second stage is expressed by the mode function \(D_3(\alpha)\), described by the kinetic equation \(G(\alpha) = \frac{1}{2}(1 - (1 - \alpha)^3)^3\). When the temperature is 1223 K, the second stage is described by the mode function \(D_4(\alpha)\) expressed by the kinetic equation \(G(\alpha) = \alpha^2\). When the temperature is 1273 K, the second stage is described by the mode function \(A_3(\alpha)\), expressed by the kinetic equation \(G(\alpha) = 1 - (1 - \alpha)^{1/2}\). Therefore, the second stage is a 2D diffusion, 3D diffusion, 1D diffusion, and phase boundary-controlled reaction process at the different reduction temperatures. The mechanisms controlling the fayalite reaction process are identical as determined by the two methods. The Málek method provides another evident reaction mechanism for the whole reduction process of fayalite, compared to the In−ln analysis method.

**Apparent Activation Energy.** *Isoconversional Method.* According to eq 13, the linear fitting of \(\ln(k(T))\) versus \(1/T\) is shown in Figure 5, whose slopes are the corresponding reaction rates \(k(T)\) of various temperatures at various reduction stages. The reaction rates \(k(T)\) for various temperatures at various reduction stages are shown in Table 5. According to eq 14, linear fitting of \(\ln(k(T))\) versus \(1/T\) is shown in Figure 6, which yields a straight line because that reduction degree \((\alpha)\) is a constant. From the slope of the line, we can calculate the apparent activation energy \(E\) values of the reaction reduction process at various reduction stages. The apparent activation energy \(E\) values of the first and second stages are 194.81 and 248.96 kJ mol\(^{-1}\), respectively. For the whole reduction process, the average apparent activation energy \(E\) value is 221.88 kJ mol\(^{-1}\), which is lower than the apparent activation energy \(E\) values gained by the isoconversional method.

On the basis of the apparent activation energy \(E\) values, the \(k(T)\), and eq 14, the pre-exponential factor \(A\) was gained by the isoconversional method and the model-fitting method (Table 6). It can be seen that when the temperature ranges from 1123 to 1273 K, at the first stage, the values of pre-exponential factor \(A\) increase sharply with increasing temperature. The average values

| Table 2. Data Fitting Values for Different Temperatures Determined by the In−ln Analysis Method |
| --- |
| reduction stage | T/K | slope/\(n\) | intercept/ln \(k\) | \(R^2\) |
| first stage | 1123 | 0.98 | −8.26 | 0.9991 |
| | 1173 | 0.87 | −6.23 | 0.9966 |
| | 1223 | 0.83 | −5.60 | 0.9947 |
| | 1273 | 0.77 | −5.60 | 0.9933 |
| second stage | 1123 | 0.58 | −6.44 | 0.9997 |
| | 1173 | 0.59 | −4.12 | 0.9967 |
| | 1223 | 0.79 | −5.64 | 0.9941 |
| | 1273 | 1.39 | −7.74 | 0.9467 |

| Figure 3. Standard kinetic curves and fitting curves for samples at various temperatures. |

| Table 3. Model Function \(G(\alpha)\) of Different Stages at Different Temperatures |
| --- |
| reduction stage | mode function | 1123 | 1173 | 1223 | 1273 |
| first stage | \(G(\alpha)\) | −\ln(1 - \alpha) | −\ln(1 - \alpha) | −\ln(1 - \alpha) | −\ln(1 - \alpha) |
| second stage | \(G(\alpha)\) | \((1 - \alpha)\ln(1 - \alpha) + \alpha\) | \([1 - (1 - \alpha)^{1/3}]^3\) | \(\alpha^2\) | \(1 - (1 - \alpha)^{1/2}\) |
of $A$ obtained by the isoconversional method and model-fitting method are 1.054 and 1.055, respectively. At the second stage, the values of pre-exponential factor $A$ increase slightly with increasing temperature, and the average values of pre-exponential factor $A$ were 0.538 and 0.539, respectively. Therefore, for the whole reduction process, the values of the pre-exponential factor $A$ gained by the isoconversional method and the model fitting method are 0.796 and 0.797, respectively.

### Table 4. Activation Energy Values Obtained by the Isoconversional Method

| reduction stage | $A$ | slope | $E/(kJ \cdot mol^{-1})$ | $R^2$ |
|-----------------|-----|-------|------------------------|-------|
| first stage     | 0.05| -21,088| 175.32                | 0.9795|
|                 | 0.10| -27,595| 229.42                | 0.9979|
| average         |     | -24,341| 202.37                |        |
| second stage    | 0.15| -20,863| 173.45                | 0.9988|
|                 | 0.20| -28,646| 238.16                |        |
|                 | 0.30| -34,874| 289.94                |        |
|                 | 0.40| -29,892| 248.52                |        |
|                 | 0.55| -35,808| 297.71                |        |
| average         |     | -30,016| 249.55                |        |
| all stage       | average |     | 225.96                |        |

### Table 5. Reaction Rates $k(T)$ for Different Temperatures at Different Reduction Stages

| reduction stage | $T/K$ | $k(T)/10^{-3}$ | $R^2$ |
|-----------------|-------|---------------|-------|
| first stage     | 1123  | 0.187         | 0.9896|
|                 | 1173  | 0.602         | 0.9693|
|                 | 1223  | 1.060         | 0.9819|
|                 | 1273  | 2.290         | 0.9903|
| second stage    | 1123  | 0.0704        | 0.9937|
|                 | 1173  | 0.1120        | 0.9866|
|                 | 1223  | 0.5530        | 0.9994|
|                 | 1273  | 1.3800        | 0.9909|

### CONCLUSIONS

Based on the results of our study, the following conclusions can be drawn.

1. The reduction process of fayalite was divided into two different steps, and the corresponding apparent activation energy was gained using a model-fitting method and the isoconversional method.
2. At the first stage (0.00 ≤ $\alpha$ ≤ 0.33), the reduction process follows the $F_1$ model, and an instantaneous nucleation and unidimensional growth process is proposed, described by.

![](image1.png)

Figure 4. Linear fitting of data (a) ln(dα/dt) vs 1/T and (b) $E$ vs $\alpha$.

![](image2.png)

Figure 5. Fitting curves of $G(\alpha)$ vs $t$ for different temperatures at different reduction stages.
the kinetic equation \[ G(\alpha) = -\ln(1 - \alpha). \]

At the second stage (0.33 ≤ \( \alpha \) ≤ 0.98), the reduction process is controlled by 2D diffusion, 3D diffusion, 1D diffusion, and phase boundary-controlled reaction as the reduction temperature is increased from 1123 to 1273 K. The function model of coal-based reduction reactions matches the \( D_2(\alpha) \), \( D_3(\alpha) \), \( D_1(\alpha) \), and \( A_2(\alpha) \) models, respectively.

The equations are
\[
G(\alpha) = (1 - \alpha)\ln(1 - \alpha) + \alpha \\
G(\alpha) = [1 - (1 - \alpha)^{1/3}]^2 \\
G(\alpha) = \alpha^2 \\
G(\alpha) = 1 - (1 - \alpha)^{1/2}
\]

respectively.

(3) For the whole fayalite reduction process, the average apparent activation energy \( E \) value is 221.88–225.96 kJ⋅mol\(^{-1}\) and the average pre-exponential factor \( A \) value is 0.796–0.797 min\(^{-1}\), respectively.

The research method of the study can be applied to the reduction process of different kinds of smelting slag and difficult-to-float oxide ore. The research results can control the particle size of metal particles and can be applied to the fields of magnetic particle size control and metallurgical raw material preparation.

## EXPERIMENTAL SECTION

### Materials

We obtained fayalite powder, using magnetic separation, from the copper slag provided by Zijin Copper Co., Ltd. (Fujian Province, China). The fayalite sample is subjected to particle size distribution analysis that was performed by a laser particle size analyzer (Malvern Mastersizer 2000). The analysis results indicate that more than 90% of the fayalite particles have a granularity less than 74 μm (Figure 7a). The chemical composition and material composition are shown in Table 7 and Figure 7a, respectively. The XRD pattern shows that fayalite

\[
(\text{Fe}_2\text{SiO}_4)
\]

is the dominant mineral in the copper slag and magnetite (\( \text{Fe}_3\text{O}_4 \)) and quartz (\( \text{SiO}_2 \)) are minor components.

### Reduction Mechanism

The Gibbs free energy as a function of temperature was calculated using the HSC Chemistry 7.0 software. As shown in Figure 8, the Gibbs free energy values of eqs 1 and 2 become increasingly negative with increasing temperature, while the values of eq 3 become increasingly positive with increasing temperature. In Figure 8, the evidence can be obtained easily; eq 1 is the predominant reaction, eq 2 cannot continue the reaction normally in a high temperature, and the reaction in eq 3 cannot continue during the given reduction temperature range, which resulted from the lack of CO in the initial stage of reaction and higher Gibbs free energy with the increasing temperature.

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**Table 6. Arrhenius Parameter (A) in the Two Stages at Different Temperatures**

| method                      | first stage |                    |                    |                   | second stage |                    |                    |                   |
|-----------------------------|-------------|-------------------|-------------------|-------------------|--------------|-------------------|-------------------|-------------------|
|                             | 1173        | 1223              | 1273              | 1323              | average      | 1173              | 1223              | 1273              | 1323              | average         |
| isoconversional method      | 0.190       | 0.614             | 1.080             | 2.332             | 1.054        | 0.072             | 0.114             | 0.556             | 1.412             | 0.538           |
| model-fitting method        | 0.191       | 0.615             | 1.081             | 2.334             | 1.055        | 0.072             | 0.115             | 0.557             | 1.413             | 0.539           |

**Table 7. Chemical Composition of Fayalite**

| TFe  | MFe | SiO\(_2\) | Al\(_2\)O\(_3\) | CaO | S  | P  |
|------|-----|----------|----------------|-----|----|----|
| 43.80 | 1.76 | 29.875    | 2.988          | 2.118 | 0.147 | 0.102 |
The reduction degree, in the isothermal reduction process, is described as follows

\[ \alpha = \frac{w_{\text{ini}} - w}{w_{\text{ini}} - w_{\text{end}}} \]  

where \( \alpha \) is the reduction degree and \( w_{\text{ini}}, w, w_{\text{end}} \) indicate the initial mass, the mass at time \( t \), and the final mass of the sample, respectively. Generally, the method for the solid-state process can be expressed by a complex differential kinetic equation:\(^\text{23,24}\)

\[ \frac{d\alpha}{dt} = k(T)f(\alpha) \]  

where \( t \) represents the time, \( k(T) \) indicates the temperature-dependent rate constant, and \( f(\alpha) \) is a function that expresses the reaction model.

Combining eqs 5 and 6 results in the following description

\[ \frac{dt}{d\alpha} = A \exp\left( -\frac{E}{RT} \right) \]  

where \( G(\alpha) \) is the integral form of the reaction model (Table 8), \( T \) is the absolute temperature (K), \( R \) is the gas constant (J·mol\(^{-1}\)·K\(^{-1}\)), \( t \) is the time (min), \( A \) is the pre-exponential factor (min\(^{-1}\)), and \( E \) is the apparent activation energy (kJ·mol\(^{-1}\)).

**Determination of the Reaction Model.** ln–ln Analysis Method. The Avrami–Erofeev model often applies to analyze phase transformation kinetics, especially in isothermal kinetics analysis.\(^\text{25,27,28}\) The model can be defined as

\[ 1 - \alpha = \exp(-kt^n) \]  

where \( k \) indicates the reaction rate constant and \( n \) represents the Avrami exponent, which depends on the growth mechanism and geometry of the powder. The value of \( n \) provides information about the reduction mechanism related to the reaction process; the \( n \) values of each model are given in Table 8.

From eq 9, we can obtain the calculated equation of \( n \).

\[ \ln[\ln(1 - \alpha)] = n \ln t + \ln k \]  

where \( \ln[\ln(1 - \alpha)] \) is plotted versus \( \ln t \). Eqs 10 and 11 are generally used to evaluate practical data. The slope and intercept of the resulting straight line are \( n \) and \( \ln k \), respectively. The index \( n \) is a criterion for distinguishing the model-fitting function. The algebraic expressions for \( G(\alpha) \) used to describe the solid-state reactions are summarized in Table 8.

**Málek Method.** The Málek method describes that the \( f(\alpha) \) function is proportional to the \( y(\alpha) \) functions, which can usually be derived from a simple calculation of the TG data. With \( \alpha = 0.5 \) as a reference point, in isothermal conditions, the function can be defined as\(^\text{29,30}\)

\[ y(\alpha) = \left( \frac{T}{T_{0.5}} \right)^2 \times \frac{d\alpha/\alpha}{(d\alpha/\alpha)_{0.5}} = \frac{f'(\alpha)g(\alpha)}{f(0.5)g(\alpha)} \]  

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**Table 8. Nine Algebraic Expressions for \( G(\alpha) \) Used To Describe Solid-State Reaction Mechanisms**\(^\text{27,31}\)

| function | \( G(\alpha) \) | \text{n} | mechanism |
|---------|--------------------|-------|----------|
| \( D_1(\alpha) \) | \( a^2 = kt \) | 0.62 | 1D diffusion |
| \( D_2(\alpha) \) | \((1 - \alpha)\ln(1 - \alpha) + \alpha = kt \) | 0.57 | 2D diffusion (bidimensional particle shape) |
| \( D_3(\alpha) \) | \( [1 - (1 - \alpha)^{1/3}]^3 = kt \) | 0.54 | 3D diffusion (trimidimensional particle shape Jander equation) |
| \( D_4(\alpha) \) | \((1 - 2/3\alpha) - (1 - \alpha)^{1/3} = kt \) | 0.57 | 3D diffusion (trimidimensional particle shape Ginstling–Brounstein equation) |
| \( F_1(\alpha) \) | \( -\ln(1 - \alpha) = kt \) | 1 | bimolecular decay law (instantaneous nucleation and unidimensional growth) |
| \( R_1(\alpha) \) | \( 1 - (1 - \alpha)^{1/2} = kt \) | 1.11 | phase boundary-controlled reaction (contracting area, e.g., bidimensional shape) |
| \( R_2(\alpha) \) | \( 1 - (1 - \alpha)^{1/3} = kt \) | 1.07 | phase boundary-controlled reaction (contracting volume, e.g., trimidimensional shape) |
| \( A(\alpha) \) | \([\ln(1 - \alpha)]^{1/2} = kt \) | 2 | random instant nucleation and 2D growth of nuclei (Avrami–Erofeev equation) |
| \( A_1(\alpha) \) | \([\ln(1 - \alpha)]^{1/3} = kt \) | 3 | random instant nucleation and 3D growth of nuclei (Avrami–Erofeev equation) |
According to the Málek method, we substituted the parameters in eq 12 with each of the nine mechanism functions shown in Table 8 and tested the experimental data. The most suitable \( f(\alpha) \) was identified when the experimental \((a, y(\alpha))\) values fell on the theoretical line, through a comparison of the experimental \(\alpha-y(\alpha)\) curves with theoretical ones.

**Determination of the Apparent Activation Energy** \(E\).
The kinetic method is expected to lead to the derivation of an appropriate kinetic description of the process in the light of the apparent activation energy. In this research, the apparent activation energy \(E\) values were gained by a model functional method and by an isoconversional method from experimental data. The isoconversional method relates to a number of experiments which are carried out at different temperatures. According to eq 5, the following equation can be obtained

\[
E = -R \frac{d\left(\ln \frac{da}{dt}\right)}{dT}
\]  
(13)

According to eqs 5 and 6, the logarithmic function of the Arrhenius equation is described as

\[
\ln k(T) = -\frac{E}{RT} + \ln A
\]  
(14)

where a linear fitting of \(\ln k(T)\) versus \(T^{-1}\) should result in a straight line whose slope and intercept can usually calculate the pre-exponential factor \(A\) and the apparent activation energy \(E\), respectively.

**AUTHOR INFORMATION**

**Corresponding Author**

Jiangang Ku — College of Zijin Mining, Fuzhou University, Fuzhou 350116, Fujian, PR China; Fuzhou University-Zijin Mining Group Joint Research Center for Comprehensive Utilization of Mineral Resources, Fuzhou 350116, PR China; orcid.org/0000-0003-3035-4320; Phone: +86 0591 22865210; Email: kkkc222@163.com; Fax: +86 0591 22865211

**Authors**

Lin Zhang — College of Zijin Mining, Fuzhou University, Fuzhou 350116, Fujian, PR China; orcid.org/0000-0002-6183-0476

Yu Zhu — College of Zijin Mining, Fuzhou University, Fuzhou 350116, Fujian, PR China

Wanzhong Yin — College of Zijin Mining, Fuzhou University, Fuzhou 350116, Fujian, PR China; Fuzhou University-Zijin Mining Group Joint Research Center for Comprehensive Utilization of Mineral Resources, Fuzhou 350116, PR China; School of Resources & Civil Engineering Northeastern University, Shenyang, Liaoning 110004, PR China

Bao Guo — College of Zijin Mining, Fuzhou University, Fuzhou 350116, Fujian, PR China

Feng Rao — College of Zijin Mining, Fuzhou University, Fuzhou 350116, Fujian, PR China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b04497

**Notes**

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