

Experimental Study on the Influence of Surfactants on Ore Surface Wettability

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ABSTRACT: To reveal the evolution law of ore surface wettability under the condition of adding surfactant and chemical reaction, the test experiments of ore surface morphology, roughness, and chemical element distribution were carried out. The results show that the contour of the ore surface morphology was relatively flat in the early stage of leaching and the roughness factor increased slowly, while the contour fluctuated significantly in the late stage of leaching and the roughness factor increased sharply. With the leaching reaction, the roughness factor and spreading coefficient of the ore with a 0.008 mol/L surfactant (sodium dodecyl sulfate) concentration were always higher than those without surfactant and the surfactant enhanced the erosion effect of the solution on the ore surface. During the leaching process, the chemical elements Cu, Al, and K were dissolved on the ore surface, and the content of Cu decreased significantly from 2.01 to 0.86%; the leaching rate of copper was about 57.2%. According to the morphology characteristics of the ore surface during leaching and the distribution law of chemical elements on the ore surface before and after leaching, the leaching process was divided into four stages of “contact–penetration–reaction–disintegration”. The surfactant had the most obvious effect on the ore surface morphology in the two stages of “reaction” and “disintegration”.

1. INTRODUCTION

As an economical, effective, safe, and environmentally friendly mining technology, leaching mining has expanded the recoverable reserves of resources and has a broad application prospect.^{1–3} However, copper resources at home and abroad are scarce, and there are technical problems such as a long leaching period and low leaching rate, which limit the development of this technology to a certain extent. The contact between the ore and solution is a prerequisite for chemical reaction. In the case of a certain chemical reaction ability between the solution and the ore, the contact, wetting, and permeation effects of the solution and the ore determine the leaching rate of the ore. Surfactants can have a great influence on solid–liquid interactions, so it is necessary to study the impact of surfactants on ore wettability and the leaching effect.

Ore surface wettability is an important factor affecting leaching efficiency, and domestic and foreign scholars have conducted a lot of studies on its mechanism.^{4,5} Wei et al.⁶ found that when the surfactant concentration was 0.1%, the contact angle attenuation rate of octyl phenol polyoxyethylene ether was as high as 19°/s. Xiao et al.⁷ showed by contact angle and in situ AFM that the adsorption of dithiocarbonate surfactants on the chalcopyrite surface increased the surface hydrophobicity and roughness. Hong-min et al.⁸ found that the dispersion effect of anionic surfactant sodium dodecyl sulfate on silicon carbide particles was better than that of cationic surfactant cetyltrimethylammonium bromide. Zheng et al.⁹ determined the wettability relationship between coal and surfactants by optical titration and found that the ether group, phenol or aromatic ether carbon, fatty methyl group, and aromatic methyl group in surfactants had a great influence on wettability. AlZaabi et al.¹⁰ showed through relevant experiments that cationic surfactant

cetyltrimethylammonium bromide had significant wettability change potential, and the increase of surfactant concentration did not necessarily lead to better wettability change. Ai et al.^{11–13} found through the column leaching test that the addition of surfactants significantly improved the permeability of the leaching column, and the mining rate increased by about 10%. In addition, “leaching reaction coefficient” and “surface activity coefficient” were introduced. During the leaching process, the surface of ore particles was continuously eroded and deposited, resulting in great changes in surface morphology.^{14,15} Although much has been studied about the leaching reaction process, there are few studies on the solid–liquid contact between solution and ore, especially the leaching mechanism of the surfactant has not been fully explained from the physical and chemical perspectives.

In this paper, using stereology, scanning electron microscopy (SEM), and energy spectrum analysis, the changes in mineral chemical composition, pore and fissure structure, surface morphology, roughness, and other microscopic characteristics were analyzed. The wettability of the ore surface is quantitatively characterized by the spreading coefficient of liquid drops on the ore surface, and the erosion effect and leaching mechanism of ore are revealed, which lay a theoretical foundation for the application of surfactants to enhance ore leaching.

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Table 1. Results of Ore Chemical Composition Analysis

ingredient	Cu	Zn	S	As	Fe ₂ O ₃	MgO	CaO	SiO ₂	Al ₂ O ₃	WO ₃
content (%)	1.26	0.21	0.56	0.16	28.96	1.39	11.48	47.97	7.82	0.19

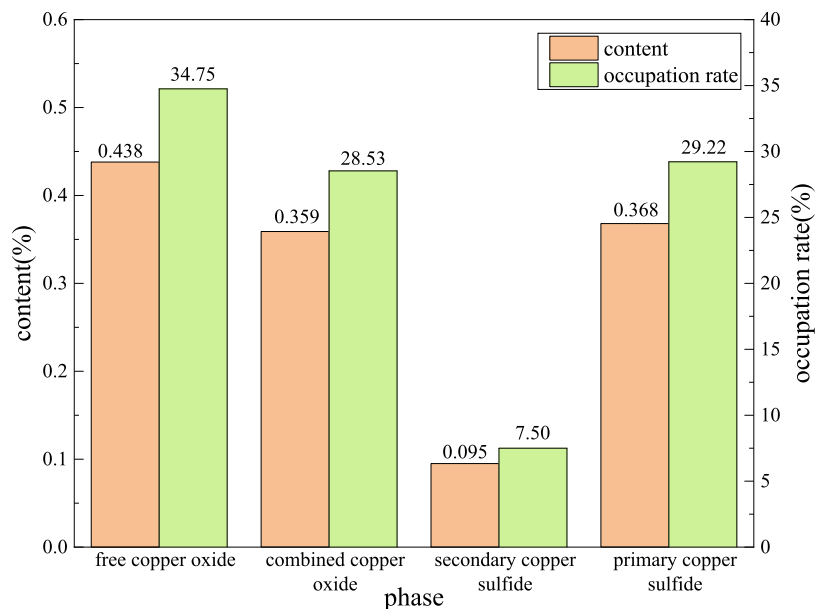


Figure 1. Copper phase analysis results.

2. EXPERIMENT

2.1. Experimental Ore. The ore surface wettability test was carried out by using the raw ore of a copper mine in Yunnan Province. Before the experiment, the surface of the ore was polished with an electric grinding wheel. The chemical composition of the ore was analyzed by X-ray fluorescence spectroscopy (XRF), and the results are shown in Table 1.

As can be seen from Table 1, gangue minerals in the ore are mainly silicates, secondary oxides, and alkaline minerals with a content of more than 40%, which will lead to higher acid consumption value in the leaching process of the ore.

The X-ray diffraction method was used to analyze the copper phase of the ore, as shown in Figure 1.

As can be seen from Figure 1, the copper oxidation rate is high and the copper oxide occupies 63.28%. In addition, copper ore has a high mud content, which is a typical refractory high alkaline oxide copper ore.

2.2. Instruments and Devices. Ultradepth of field stereomicroscopy was used to observe the micromorphology of the ore surface in the experiment. The stereoscopic imaging technology of the stereomicroscope can be used to observe the surface topography of the ore, and the measuring tools in the software of the microscope can be used to obtain the contour curve of the ore surface and the real surface area. FEI Quanta250 scanning electron microscopy (SEM) and energy spectrometry were used to observe the ore surface morphology, energy spectrum rule, and element surface distribution.

2.3. Calculation Method. **2.3.1. Contact Angle.** The wettability of minerals refers to the spreading property of liquid on the ore surface. When the gas–liquid–solid three-phase interface is in equilibrium, the angle between the gas–liquid interface and the solid–liquid interface at any point around the wetting perimeter is called the “equilibrium contact angle”,

referred to as the contact angle (θ), and the equilibrium equation of interfacial tension is obtained¹⁶

$$\sigma_{s-g} = \sigma_{s-l} + \sigma_{l-g} \cdot \cos \theta \quad (1)$$

where σ_{s-g} , σ_{s-l} , and σ_{l-g} are the interfacial tension of solid–gas, solid–liquid, and gas–liquid, respectively, and θ is the contact angle of the ore surface. For the same volume of liquid droplets, the smaller θ indicates that the larger the spread area of liquid droplets on the ore surface, the better the wettability of the ore surface.

2.3.2. Spreading Coefficient. Under constant temperature and pressure conditions, when the spreading area is one unit area, the free enthalpy reduction or external work W_s of the system surface is

$$W_s = \sigma_{s-g} - \sigma_{s-l} - \sigma_{l-g} = S \quad (2)$$

where S is the spreading coefficient.

In addition, the drop height method is also used to evaluate the wettability of the ore surface. The principle of this method is to measure the height of liquid droplets forming on the solid surface to obtain the spreading coefficient. The equation is as follows:

$$S = -\frac{1}{2} \rho g \left(\frac{V}{A_0} \right)^2 \quad (3)$$

where A_0 is the spread area of the droplet, m²; ρ is the liquid density, kg/m³; V is the droplet volume, m³; and g is the acceleration of gravity, m/s². The larger the spreading coefficient, the stronger the wetting ability of the liquid on the ore surface.

Equations 1 and 2 can be combined to obtain the expression between the contact angle, spreading coefficient, and interfacial tension

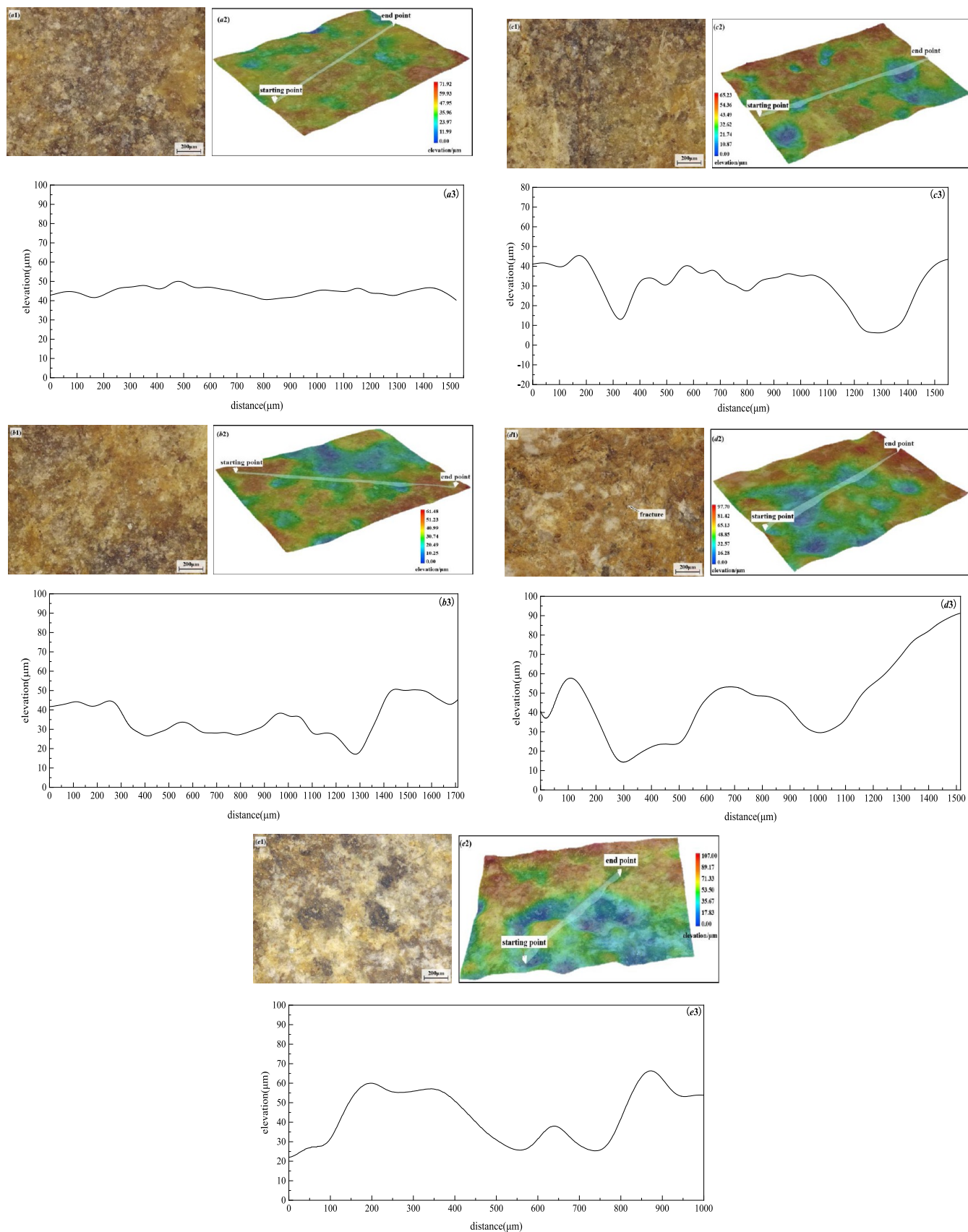


Figure 2. Changes of ore surface morphology and contour with time when the surfactant concentration is 0 mol/L; the concentration of sulfuric acid is 30 g/L: (a) $t = 0$; (b) $t = 48$ h; (c) $t = 96$ h; (d) $t = 144$ h; (e) $t = 192$ h.

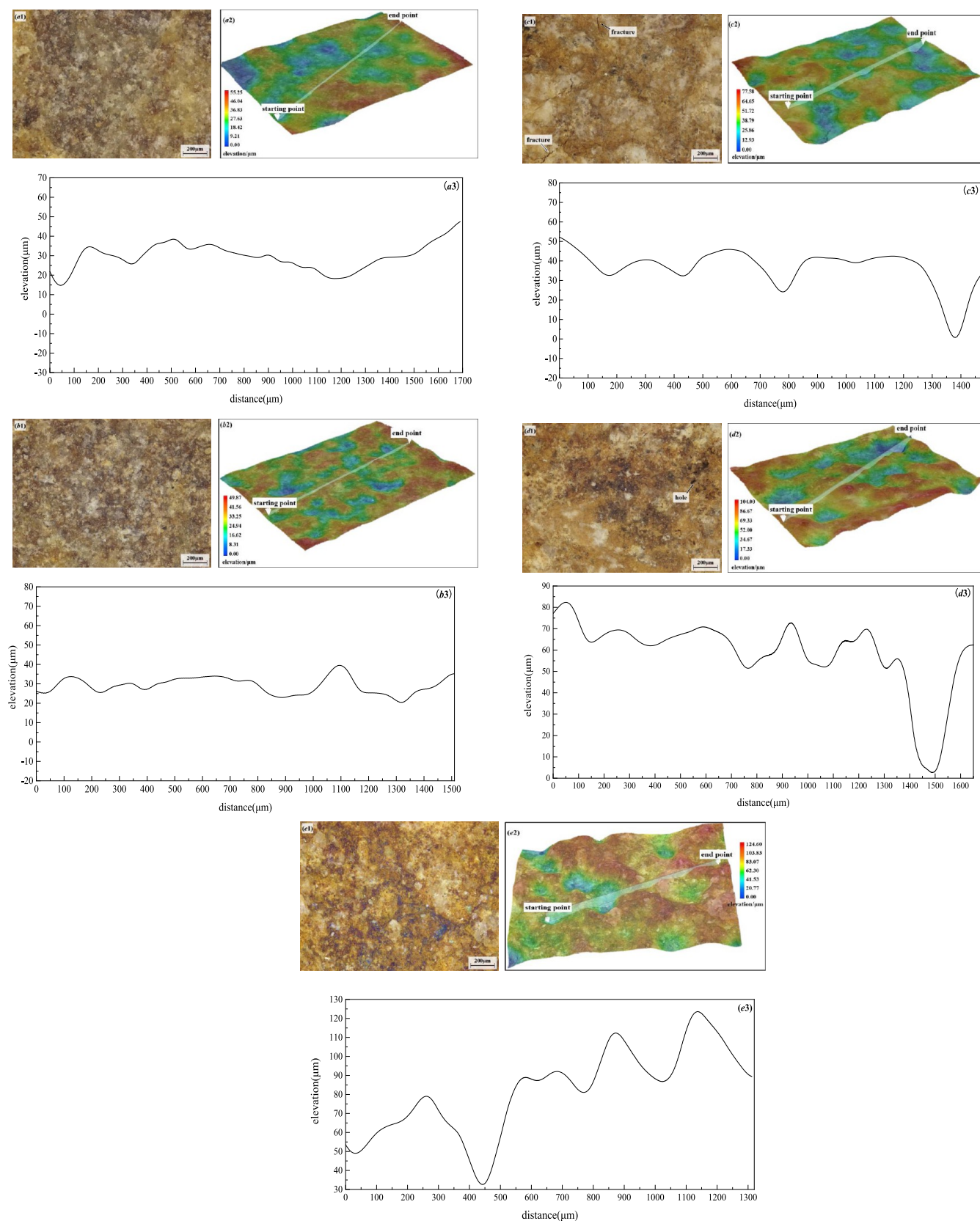


Figure 3. Changes of ore surface morphology and contour with time when the surfactant concentration is 0.008 mol/L; the concentration of sulfuric acid is 30 g/L: (a) $t = 0$; (b) $t = 48$ h; (c) $t = 96$ h; (d) $t = 144$ h; (e) $t = 192$ h.

$$\cos \theta = \frac{S}{\sigma_{l-g}} + 1 \quad (4)$$

2.3.3. Roughness. The chemical reaction between the solution and the ore causes erosion of the ore surface, changes the surface morphology and roughness of the ore, and affects the

wettability of the ore surface. The roughness factor is used to characterize the roughness of the ore surface, the equation is as follows

$$r = \frac{A}{a} \quad (5)$$

where r is the coarseness factor; A is the real surface area of the ore surface; and a is the apparent area of the ore surface.

2.3.4. Flatness. When the surface topography of ore is analyzed, the concept of variance is used to measure the fluctuation degree of ore surface elevation. Variance reflects the deviation of a set of data from the mean value and is a characteristic quantity that reflects the overall fluctuation size of a set of data. The greater the elevation variance of the ore surface, the greater the flatness and the rougher the ore surface. Elevation variance is calculated as follows:

$$s^2 = \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n} \quad (6)$$

where s^2 is the variance; x_i is the elevation of any point on the ore surface; \bar{x} is the mean of the total elevation; and n is the total number of cases.

2.4. Experimental Scheme. The leaching agent used in the experiment is the sulfuric acid solution; its mass concentration is 30 g/L, and the chemical reaction between sulfuric acid and copper-bearing minerals in the ore is used to convert copper from solid phase to liquid phase into the solution. Studies by relevant scholars have shown that the use of dilute sulfuric acid as a leaching agent had a good leaching effect on most copper-combined minerals.^{17–19} According to the previous experimental results,^{20,21} the surfactant sodium dodecyl sulfate was selected as the leaching aid, and the surfactant concentrations were 0 and 0.008 mol/L, respectively.

3. RESULTS AND DISCUSSION

3.1. Ore Surface Wettability Changes with Leaching Time.

To investigate the influence of chemical reaction on the ore surface wettability during leaching, the ore was soaked in the leaching solution with or without surfactants for 0, 48, 96, 144, and 192 h, respectively, and the ore surface morphology was observed regularly. By comparing the surface morphology of ore during leaching, the variations of roughness and wettability of the ore surface with leaching time were analyzed.

3.1.1. Ore Surface Morphology Evolution. The surface morphology of the two groups (leaching solution and leaching solution with surfactant solution) of ores was observed by stereomicroscope, and the contrast analysis was made by stereo imaging technology. Meanwhile, representative contour curves of the ore surface were drawn to quantitatively characterize the degree of concavity on the ore surface, and the results are shown in Figures 2 and 3.

Compared with Figures 2a3 and 3a3, it can be seen that before the leaching reaction, the ore surface is relatively flat, the contour is gentle, there is no obvious fluctuation, and the elevation difference between the highest point and the lowest point is about 10–30 μm . At the late stage of leaching, the characteristic contour curve shows that the ore surface becomes uneven with a height difference of 90 μm between the highest and lowest points in Figure 3e3.

With the leaching reaction, the surface of the ore was obviously eroded by the solution, the surface became rough and uneven, and cracks and holes appeared (Figure 3c1,d1). It can

be seen from the figure that some white quartz particles are embedded on the ore surface. When other minerals dissolve, the dissolution rate of quartz particles in sulfuric acid is much slower than that of copper minerals or similar substances, which is an important reason for the uneven surface of the ore.

The variance of the ore surface elevation before and after leaching can be calculated from eq 6, as shown in Figure 4.

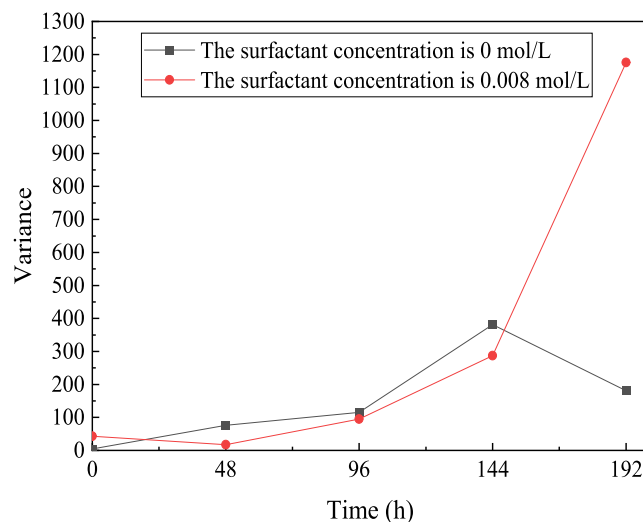


Figure 4. Variance of different surfactant concentrations.

As can be seen from Figure 4, the variance between 0 and 144 h without adding surfactant and adding surfactant concentration of 0.008 mol/L is close, but the variance of 0.008 mol/L surfactant concentration in the late leaching period (after 144 h) shows a rapidly rising trend. The variance of the surfactant concentration of 0.008 mol/L at 192 h is about 6.4 times that of the variance without the addition of the surfactant. When the concentration of surfactant in the solution is 0.008 mol/L, the roughness of the ore surface after leaching is greater, indicating that the addition of surfactant strengthens the erosion of acid.

3.1.2. Ore Surface Roughness Change. In Figures 2 and 3, the size of the ore is 1500 $\mu\text{m} \times 1237.8 \mu\text{m}$, which is the apparent area of the ore surface. The real area of the ore surface at each time was measured by a stereomicroscope, and the coarseness factor was calculated according to eq 5, as shown in Table 2.

It can be seen from the changing trend of the curve in Figure 5 that with the progress of the leaching reaction, the coarseness factor increases, indicating that the ore surface becomes more and more rough. This is consistent with the observations in Figures 2 and 3. From the perspective of the curve growth rate, in the early stage of leaching (0–48 h), the roughness factor increases slowly, and chemical reactions occur between the solution and the mineral. However, due to the density of the ore surface,²² the penetration of the solution on the ore surface is not sufficient. At the later stage of the experiment (after 144 h), the roughness factor increases sharply, the ore surface has dissolved and disintegrated, and the solution has fully reacted in the cracks on the ore surface. Comparing the effect of the two groups of solutions on the ore in Figure 5, it can be seen that the roughness factor of the ore added with surfactant is larger, which is about 1.8% larger than that of the ore without surfactant, indicating that the surfactant enhances the erosion effect of the solution on the ore surface. There are two main assumptions for this:

Table 2. Calculation Results of Ore Surface Roughness Factor

time (h)	the surfactant concentration is 0 mol/L			the surfactant concentration is 0.008 mol/L		
	A (μm^2)	a (μm^2)	r	A (μm^2)	a (μm^2)	r
0	2056629	1856700	1.1077	2056644	1856700	1.1077
48	2058319	1856700	1.1086	2061881	1856700	1.1105
96	2067996	1856700	1.1138	2073795	1856700	1.1169
144	2082686	1856700	1.1217	2121233	1856700	1.1425
192	2161233	1856700	1.1640	2191233	1856700	1.1802

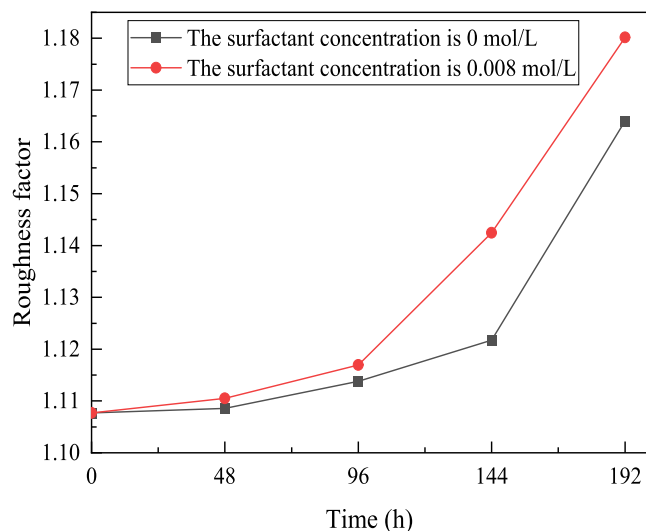


Figure 5. Curve of ore surface roughness factor with time.

- (1) The surfactant changes the physical properties of the solution. Surfactants reduce the surface tension and viscosity of the solution, improve the wettability of the ore surface, enhance the permeability of the solution in the cracks on the ore surface, which is conducive to a larger contact area between the solution and the ore, and is also conducive to the solute migration of the reaction products, and increase the leaching reaction rate.
- (2) Surfactant molecules are adsorbed on the ore surface.^{23,24} Sodium dodecyl sulfate is an anionic surfactant, which is

adsorbed on the ore surface to increase the adsorption force between the ore and H^+ and strengthen the chemical reaction.

3.1.3. Ore Surface Wettability Analysis. The change in ore surface roughness will change its wettability. With the progress of the leaching reaction, the roughness of the ore surface increases, resulting in a change of the spreading coefficient and contact angle. The change of spreading coefficient with time is calculated according to eq 3. According to Figures 5 and 6, it can be seen that the spreading coefficient increases with an increase in ore surface roughness. When the concentration of surfactant is 0.008 mol/L, the surface spreading coefficient of the ore is larger, indicating that the wettability of the ore group is better than that without the addition of surfactant. The change of the contact angle with the leaching time was calculated by applying eq 4 according to the results in Figure 6, and the results are shown in Figure 7 (The interfacial tension of the solution with surfactant is 40, and the interfacial tension of the solution without surfactant is 78).

It can be seen from Figures 6 and 7 that the ore surface wettability is enhanced with the leaching reaction. Ore leaching is a wettable system; for this kind of system, reducing the surface tension of the solution and increasing the roughness of the solid surface are conducive to wetting. The most obvious effect of the addition of surfactant on the solution is to reduce the surface tension, and the greater the concentration of surfactant, the smaller the surface tension of the solution; the addition of surfactant will improve the wettability of the ore. The chemical erosion of the solution on the ore surface increases the roughness and wettability of the ore, and the higher the

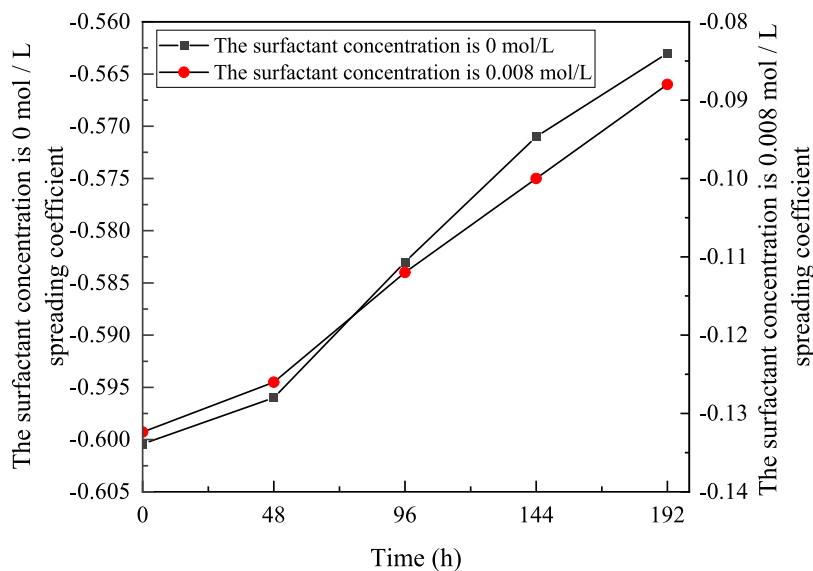


Figure 6. Changes of the ore surface spreading coefficient with leaching time.

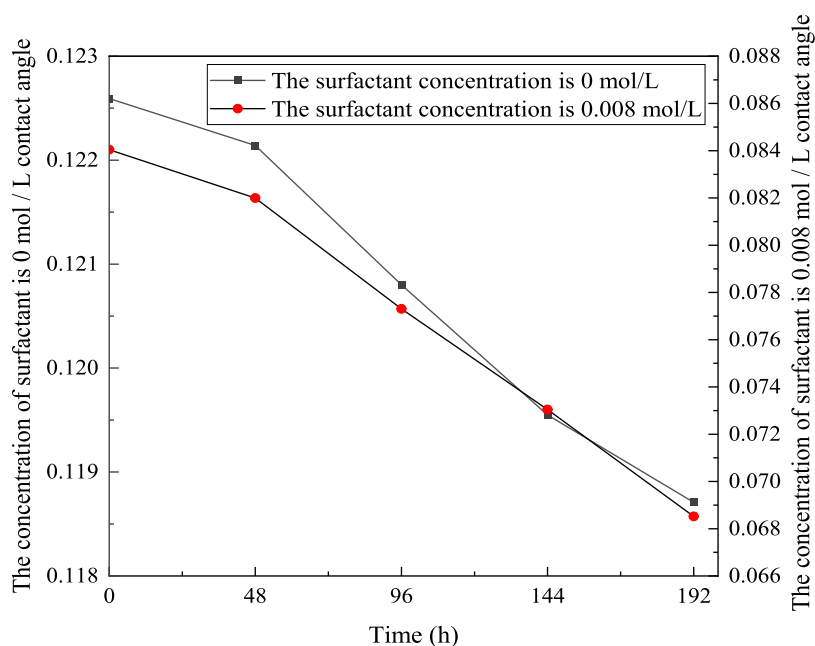


Figure 7. Change of the ore surface contact angle with leaching time.

concentration of sulfuric acid and surfactant, the greater the coarsening degree. Therefore, increasing the concentration of sulfuric acid and the amount of surfactant will be beneficial to ore leaching.

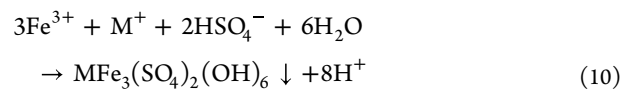
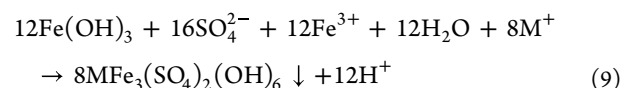
3.2. Evolution of Ore Morphology and Wettability under Leaching. **3.2.1. Variation of Element Distribution on Ore Surface.** Electron microscope scanning and energy-dispersive X-ray spectroscopy (EDS) energy spectrum analysis were conducted on the ore surface before and after leaching. The ore surface morphology, energy spectrum rule, and element surface distribution are shown in Figures 8 and 9. By comparison of Figures 8a and 9a, it can be seen that the surface morphology of ores changes greatly before and after leaching. The ore surface is relatively flat before leaching, but the leaching reaction causes serious erosion on the ore surface, and many holes and cracks appear. At the same time, the distribution of elements on the ore surface is very different before and after leaching.

Before leaching, the ore particle surface is composed of a dense block structure; after leaching, the ore surface structure is loose, pores are increased, and the specific surface area of the ore is increased. Leaching makes the pore crack expand and deepen, which is conducive to the solution entering the ore, and the chemical reaction continues.

- (1) During the leaching process, some chemical elements (such as Cu, Al, K, etc.) on the surface of the ore are dissolved and leave the leaching system with the seepage of the solution. The content of Cu is reduced, and the mass fraction of Cu on the ore surface is 2.01% before leaching, and the distribution is very uneven. After leaching, the Cu content decreased to 0.86%, and the distribution was uniform.
- (2) Some other chemical elements (such as Ca, Fe, S, etc.) dissolve into the solution from the ore surface and interior, forming a precipitate attached to the surface of the particles, and the content of these elements increases. The leaching reaction changes the distribution of Ca elements on the ore surface from uniform to concentrated, indicating that Ca reprecipitates and crystallizes on

the ore surface after dissolution. As can be seen from the following equation, the Ca element is mainly converted into CaSO_4 ; in addition, $\text{Fe}(\text{OH})_3$ gel and pyrite vanadium precipitates are also produced.^{25,26}

- (3) After leaching, the Si distribution on the ore surface is relatively concentrated. As can be seen from Figure 9a, the region where the Si element belongs forms a “bulge” on the ore surface, and the content of Fe and Al elements in the bulge is very low. Because the Si element in the ore mainly exists in the form of SiO_2 , it dissolves very slowly under acidic conditions. When other minerals are dissolved, the SiO_2 morphology changes little, so it is higher than the surrounding part. This is the reason for the increase of ore surface roughness caused by leaching.



where M is K^+ , Na^+ , NH_4^+ or H_3O^+ .

3.2.2. Process of Ore Surface Erosion during Leaching. During the leaching process, a series of complex physical and chemical interactions occur between copper ore and acid solution, resulting in dissolution and disintegration on the surface and inside the ore. There are many kinds of chemical reactions, such as dissolution reaction, adsorption–desorption reaction, redox reaction, etc., between the solution and the useful minerals of the ore, and the ions involved in these reactions all move in the form of convection and diffusion. According to the analysis results of ore surface morphology, wettability energy, element distribution, and other changes in the leaching process, the leaching process is divided into four

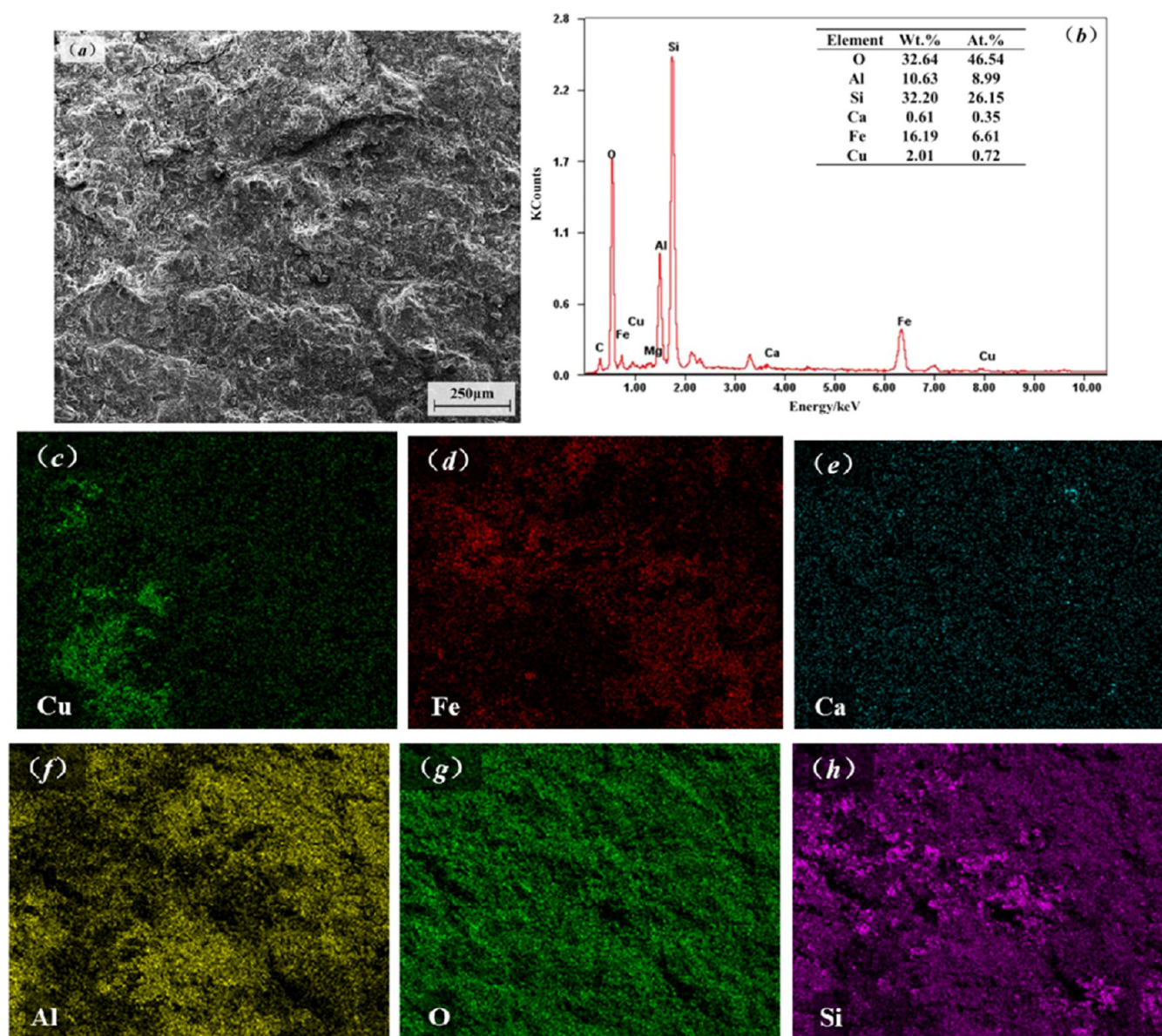


Figure 8. Surface morphology (a) and element distribution (b) of ore before leaching (c: Cu; d: Fe; e: Ca; f: Al; g: O; h: Si).

stages of “contact, penetration, reaction and disintegration” according to the degree of ore erosion, as shown in Figure 10.

- (1) Contact stage. The chemical reaction between ore and solution starts from the solid–liquid contact, which is affected by the roughness of the ore surface, the surface tension of the solution, and the intensity of the chemical reaction. The greater the roughness of the ore surface and the lower the surface tension of the solution, the more favorable the wetting effect. Increasing the concentration of sulfuric acid to strengthen the degree of the chemical reaction is also conducive to solid–liquid contact. The distribution of the surfactant on the surface of the solution is shown in Figure 10a1, with the hydrophilic group of the surfactant in the liquid and the hydrophobic group pointing toward the air. In the meantime, the surfactant will be adsorbed on the ore surface, the hydrophilic group points to the liquid, and the hydrophobic group is adsorbed on the ore surface.
- (2) Penetration stage. The ore surface is hydrophilic and chemically reacts with the solution, so the solution will produce a spreading motion after contact with the ore surface, and the solution will penetrate the pore cracks. Furthermore, the surfactant also enters the pore crack with the solution and adsorbs on the inner surface of the ore, as shown in Figure 10b1. At this stage, the solution has been in full contact with the ore, and chemical reactions begin. Secondary cracks appear on the ore surface due to swelling and chemical reactions, as shown in Figure 10b2.
- (3) Reaction stage. The chemical reaction between the solution and the ore does not start from this stage, but it is more thorough and complete in this stage. A series of chemical reactions in eqs 11–24 occurred between the ore and the solution. With the extension of the reaction time, the ore continues to dissolve, and the free reaction products are formed, which will have convection and diffusion movement due to the existence of liquid flow and concentration gradient. The primary pores and

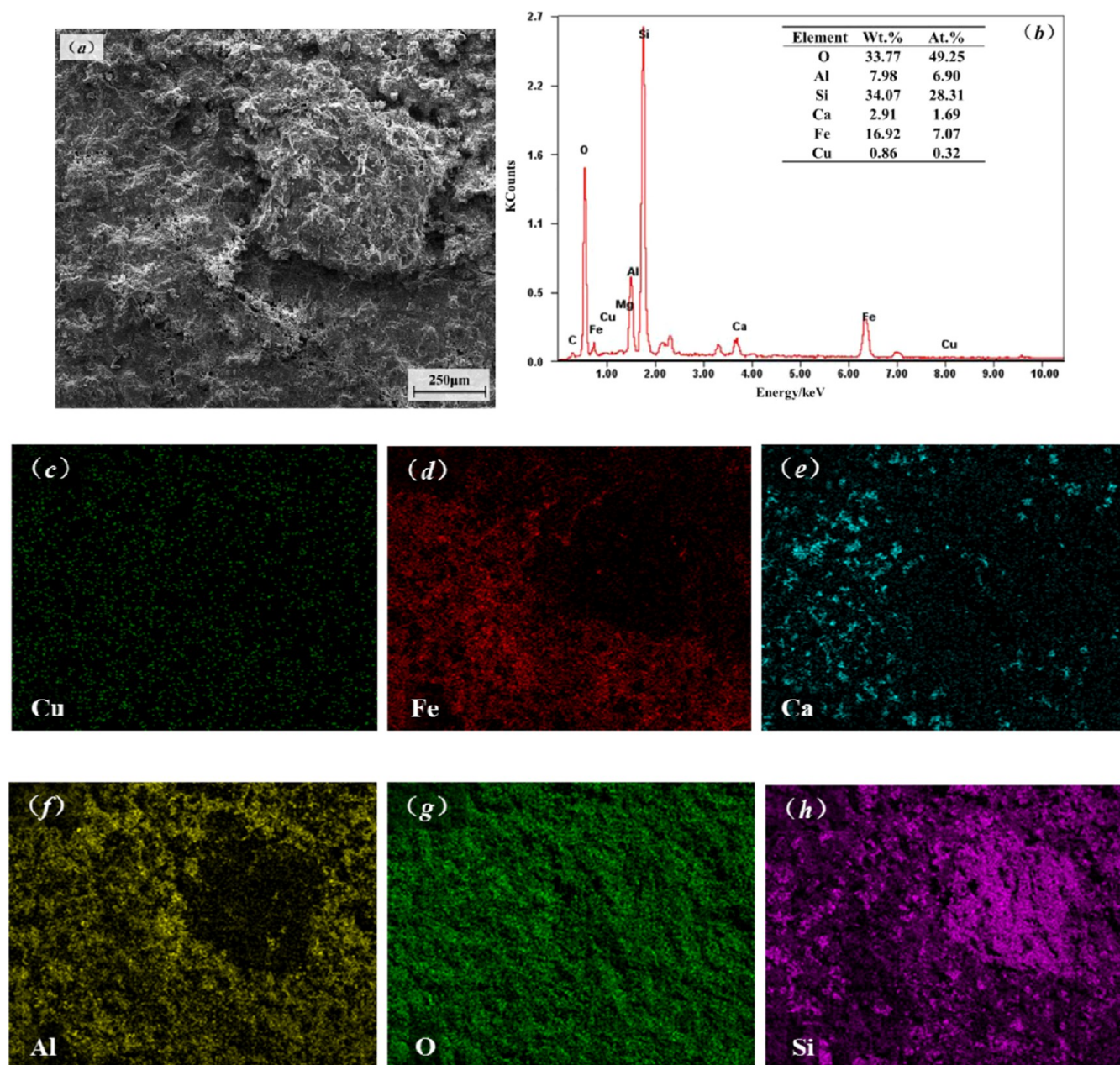
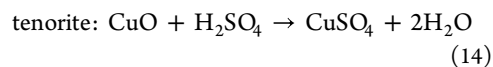
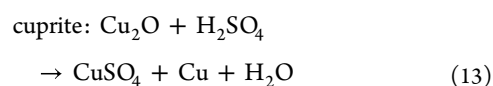
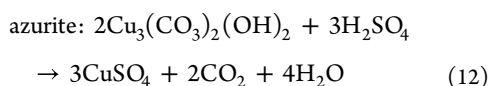
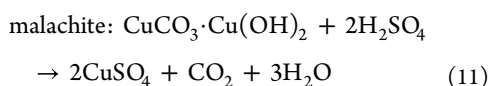


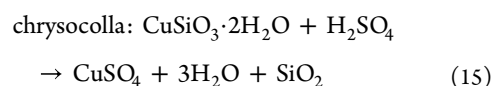
Figure 9. Surface morphology (a) and element distribution (b) of ore after leaching (c: Cu; d: Fe; e: Ca; f: Al; g: O; h: Si).

fissures on the ore surface develop into caves and holes with the reaction, while the secondary fissures continue to expand. After the ore surface is eroded, some solution pits are formed, and surfactants are adsorbed on these new surfaces, which continue to promote wetting and chemical reactions. In this stage, the corrosion traces on the ore surface are obvious, as shown in Figure 10c2.

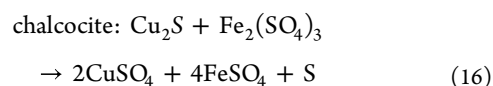
(a) Free copper oxide



(b) Combined copper oxide



(c) Secondary copper sulfide



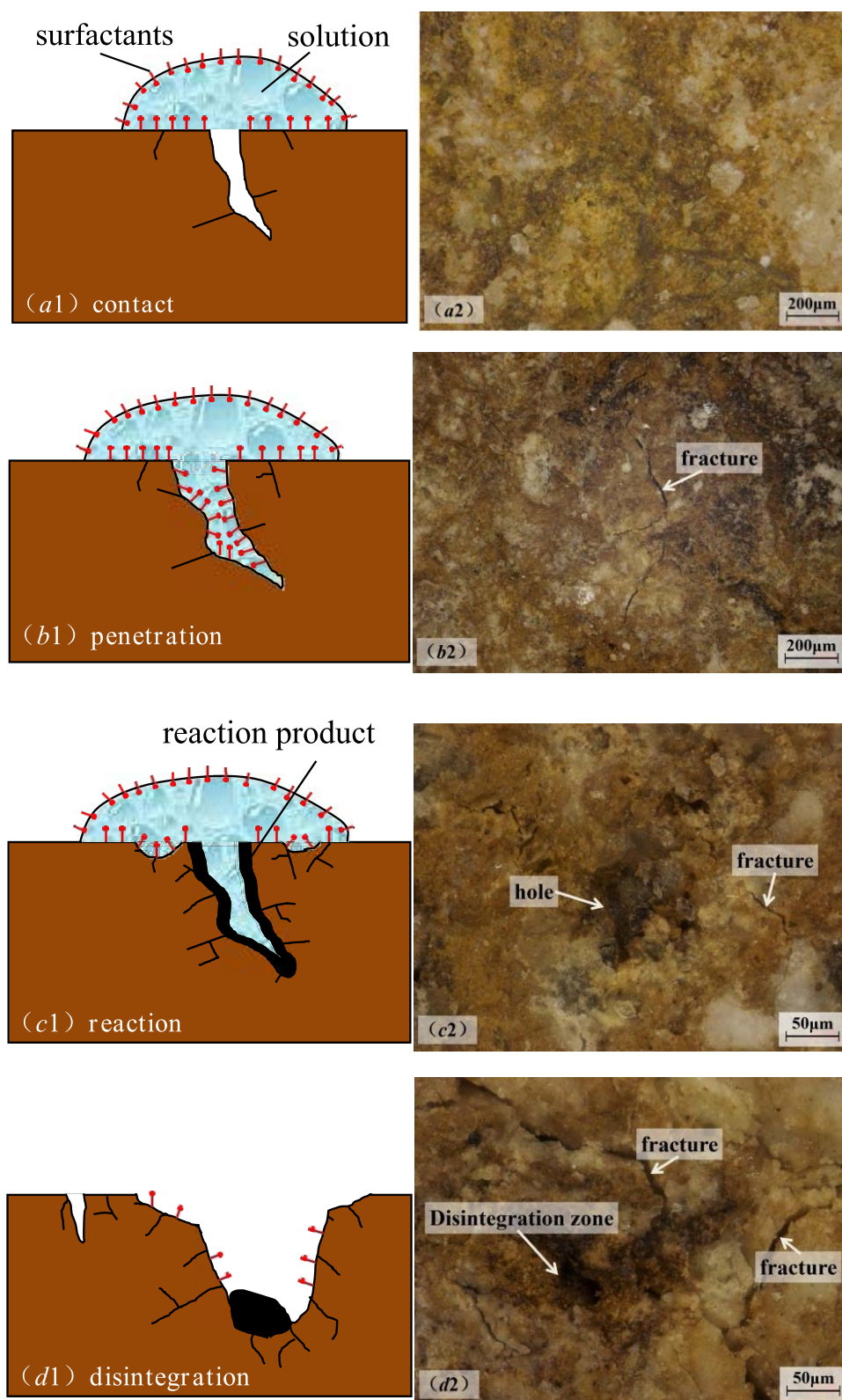
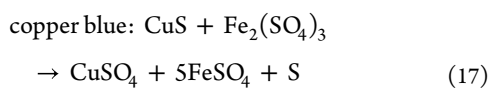
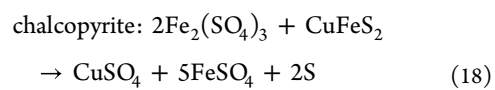


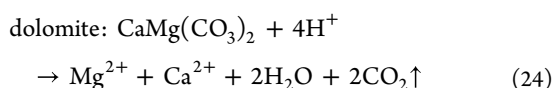
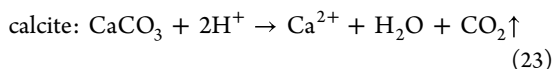
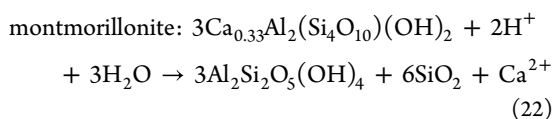
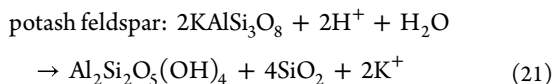
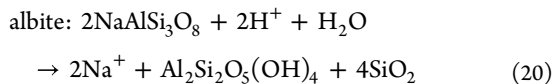
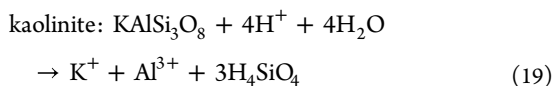
Figure 10. Dissolution process of ore surface under leaching.



(d) Primary sulfide ore



(e) Gangue mineral



- (4) Disintegration stage. At this stage, the ore surface has undergone great changes. With the progress of the reaction and the swelling of the ore surface, the pores continue to expand and eventually form a disintegration zone. The cracks around them continue to expand, and the width of the cracks increases compared with the previous stage. Some of the precipitation and crystallization generated by the chemical reaction are consolidated on the ore surface. The formation of a new surface with the solution continues to occur in phase (a) of the action, and so does the cycle.

The above four stages are not completely independent, especially because the chemical reaction runs through each stage, and there is no clear time limit for each stage. When the solution is in contact with the ore surface, a chemical reaction will occur and at the same time spread and permeate the ore surface. In the chemical reaction stage, the solution continues to permeate the secondary fissure. When the chemical reaction is relatively complete, the dissolution zone disintegrates, and a new ore surface is formed. The solution and the new surface continue to contact and react, and they have a series of physical and chemical effects.

The leaching process changes the surface morphology of the ore and results in a change in the surface roughness of the ore. The change of the ore surface roughness factor over time in Figure 5 corresponds to four stages of pore evolution (a)–(d), as shown in Figure 11. In Figure 11, stages (a) and (b) belong to the early stage of leaching. Although chemical reactions have begun, the ore surface morphology changes are not obvious due to the short time, so the ore surface roughness factor increases little. In the (c) stage, the surface corrosion of the ore is obvious, the pore cracks expand into holes, and secondary cracks appear; therefore, the surface roughness of the ore increases. When the reaction proceeded to stage (d), the pore disintegrated, the ore morphology changed greatly, and the roughness factor increased sharply at this stage.

3.2.3. Analysis of Ore Morphology Change during Leaching. The chemical reaction between ore and solution is a process of energy balance in which the cohesion energy of ore decreases continuously and finally reaches the lowest energy

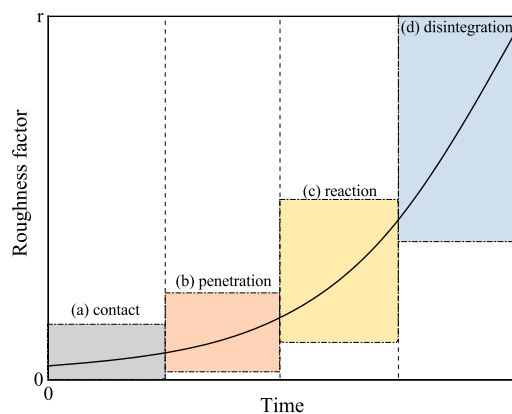


Figure 11. Change of the ore surface roughness factor in the leaching process.

state. Under the action of external energy (chemical reaction, gravity, etc.), the ore adjusts to an equilibrium state that is compatible with the surrounding environment through various changes. The absorption of active chemical components on the mineral surface will lead to a decrease in the solid surface energy. When a critical value is reached, the lattice energy of the mineral is destroyed and released. There are tiny pore cracks between the grains in the ore. Due to the above effects, the chemical bonds at the crack tip are destroyed, resulting in a new surface energy zone, and the microporous cracks will also expand into the interior of the ore.²⁷ The leaching reaction not only destroys the grain itself but also destroys the intergrain connection of the ore.

There are many defects distributed on the surface of minerals, and there is excess stress energy at some of the defect sites; therefore, the solid–liquid interaction will preferentially occur at the defect sites. In the process of etching, the defects on the ore surface continue to expand and eventually form a disintegration zone. From the perspective of surface reaction dynamics, the energy change involved in the expansion of surface defects is shown in eq 25.^{28,29}

$$dG^* = \frac{\Delta G_b}{V_m} \cdot 2\pi r \cdot dr + \kappa 2\pi \cdot dr + \frac{\mu b^2}{4\pi r K} \cdot dr \quad (25)$$

where dG^* is the change of free energy per unit depth, ΔG is the change of reaction free energy caused by the change of concentration, V_m is the molar volume of the mineral, r is the radius of the ore surface defect, K is the characteristic value of the ore surface defect morphology type, μ is the main shear modulus, b is the Burger vector, and κ is the average metrological coefficient.

Take VanDerhoek's expression of stress energy distribution density and integrate it with eq 25 to obtain the expression of free energy change

$$G^* = -\frac{\pi \Delta G_b}{V_m} r^2 + 2\pi \kappa r - \frac{\mu b^2}{8\pi K} \ln \left[1 + \left(\frac{r}{r_0} \right)^2 \right] \quad (26)$$

where r_0 is the initial defect radius of the ore surface.

Equation 26 shows that the radius of the erosion pit on the ore surface is related to the reaction conditions and the free energy at the defect decreases with the increase of the defect radius. This indicates that the leaching reaction takes place first at the activation site during the initial phase of solid–liquid contact. With the progress of the leaching reaction, the radius of the

surface defect increases, the residual stress energy at the defect weakens, and the leaching reaction loses its advantage.

There is a chemical imbalance between different minerals, resulting in irreversible reaction kinetics between ore and sulfuric acid, which changes the physical state and microstructure of the ore, weakens the connection between minerals, destroys the lattice structure, and reduces the strength of the ore. The degree of ore strength reduction depends on the shape characteristics of ore pore fracture, seepage field, temperature field, mineral composition, ore hydrophilicity, and concentration of leaching agent.

4. CONCLUSIONS

- (1) By observing the change of ore surface morphology during leaching, it was found that with the leaching reaction, the roughness factor of ore with 0.008 mol/L surfactant concentration increased from 1.1077 to 1.1802, and was always greater than that without surfactant addition. The spreading coefficient has the same changing trend, and the contact angle of the ore surface is negatively correlated with the leaching time. The contact angle of the ore surface with 0.008 mol/L surfactants added at 192 h is 0.58 times that of the ore without surfactants added, indicating that the erosion effect of the solution on the ore is strengthened by surfactants.
- (2) There are obvious differences in the distribution of elements on the ore surface before and after leaching. The mass fraction of Cu on the ore surface is 2.01% before leaching, the Cu content decreases to 0.86% after leaching, and the copper leaching rate is about 57.2%. The Ca element on the ore surface changes from uniform distribution to concentrated distribution during the leaching reaction. Because the dissolution rate of SiO₂ in sulfuric acid is much slower than that of copper minerals or other substances, when other minerals are dissolved, a bulge forms on the surface of the ore in the area where Si belongs.
- (3) The ore leaching is divided into four stages “contact–penetration–reaction–disintegration”. The four leaching stages exist at the same time and are repeated, and chemical reactions run through the whole process. In the two stages of “reaction” and “disintegration”, the roughness factor increases sharply, and the ore surface topography changes the most.

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Professor C.A. provided the idea and framework of the article. S.W. and C.L. performed the experimental data collection. The first draft was written by C.A., and S.W. and T.L. made the subsequent revisions. All of the authors reviewed the final version of the paper.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Tian, Z.; Li, H.; Wei, Q.; et al. Effects of redox potential on chalcopryrite leaching: An overview. *Miner. Eng.* **2021**, *172* (1), No. 107135.
- (2) Wang, L.; Yin, S.; Deng, B.; Wu, A. Copper sulfides leaching assisted by acidic seawater-based media: ionic strength and mechanism. *Miner. Eng.* **2022**, *175* (1), No. 107286.
- (3) Beiza, L.; Quezada, V.; Melo, E.; et al. Electrochemical Behaviour of Chalcopryrite in Chloride Solutions. *Metals* **2019**, *9* (1), 1–12.
- (4) Eick, J. I.; Siqueira, L. P.; Eduardo, D. W.; et al. Influence of surfactants addition on the properties of calcium hypochlorite solutions. *J. Appl. Oral Sci.* **2019**, *27*, 1–9.
- (5) Shabani, M. A.; Irannajad, M.; Meshkini, M.; et al. Investigations on bioleaching of copper and zinc oxide ores. *Trans. Indian Inst. Met.* **2019**, *72* (3), 609–611.
- (6) Wei, J.; Jiang, W.; Si, L.; et al. Experimental study of wetting effect of surfactant based on dynamic wetting process and impedance response of coal. *Environ. Sci. Pollut. Res.* **2023**, *30* (2), 4278–4292.
- (7) Xiao, J.; Yao, C.; Wu, Y.; et al. Adsorption and flotation mechanism of a ketoxime-dithiocarbonate surfactant to chalcopryrite. *J. Central South Univ.* **2022**, *29* (12), 3847–3857.
- (8) Hong-min, K.; Yuan-yuan, M.; Reddy, R. G. Influence of particle size and surfactants on uniformity and quantity of silicon carbide particles in electrodeposited nickel-silicon carbide coatings. *J. Central South Univ.* **2021**, *28* (6), 1627–1636.
- (9) Zheng, L.; Liu, Z.; Li, D.; et al. Micromechanism analysis of surfactant wetting of coal based on ¹³C NMR experiments. *ACS Omega* **2021**, *6* (2), 1378–1390.
- (10) AlZaabi, A.; Arif, M.; Ali, M.; et al. Impact of carbonate mineral heterogeneity on wettability alteration potential of surfactants. *Fuel* **2023**, *342*, No. 127819.
- (11) Ai, C.-M.; Sun, P.-P.; Yin, S.-H.; Chen, X.; Zhong, J.-L. Influence of surfactant on the permeability at different positions of a leaching column. *PLoS One* **2022**, *17* (9), 1–20.
- (12) Ai, C.-m.; Wu, A.-x.; Wang, Y.-m.; Hou, C.-l. Optimization and mechanism of surfactant accelerating leaching test. *J. Central South Univ.* **2016**, *23* (5), 1032–1039.
- (13) AI, C.-m.; Sun, P.-p.; Wu, A.-x.; et al. Accelerating leaching of copper ore with surfactant and the analysis of reaction kinetics. *Int. J. Miner., Metall. Mater.* **2019**, *26* (3), 274–281.
- (14) Hashemzadeh, M.; Liu, W. The response of sulfur chemical state to different leaching conditions in chloride leaching of chalcocite. *Hydrometallurgy* **2020**, *192*, No. 105245, DOI: [10.1016/j.hydro-met.2020.105245](https://doi.org/10.1016/j.hydro-met.2020.105245).
- (15) Wu, A.; Yao, G.; Wang, Y. Evolution of micropore fractures on the surface of ore particles during leaching. *J. Central South Univ.* **2012**, *43* (4), 1462–1468.
- (16) Ai, C.; Sun, P.; Wu, A.; Chen, X.; Liu, C. Liquid spreading behavior and surface wettability of copper ore under controlled sulfuric acid solution and surfactants. *J. Central South Univ.* **2022**, *29* (2), 433–442.

- (17) Zhang, R.; Mao, Y.; Liu, C.; Ni, W. Synergistic catalytic effect of chloride ion and ammonium ion on the leaching of chalcopyrite in sulfuric acid solution. *Miner. Eng.* **2022**, *185*, No. 107686.
- (18) Hossain, S. M.; Yahaya, A. N. A.; Yacob, S. L.; et al. Selective recovery of Copper from waste mobile phone printed circuit boards using Sulphuric acid leaching. *Mater. Today: Proc.* **2018**, *5* (10), 21698–21702.
- (19) Atesoglu, G.; Atilgan, S. Effect of Roasting Temperature on the Leaching of Chalcopyrite Concentrate in Sulphuric Acid. *Min., Metall., Explor.* **2022**, *39* (5), 2199–2208.
- (20) Aixiang, W.; Chunming, A.; Yiming, W.; et al. Influence of surfactant on heap leaching permeability of copper ore. *J. Central South Univ.* **2014**, *45* (3), 895–901.
- (21) Aixiang, W.; Chunming, A.; Yiming, W.; et al. Surfactant accelerating leaching of copper ores. *J. Univ. Sci. Technol.* **2013**, *35* (6), 709–713.
- (22) Hashemzadeh, M.; Liu, W. Analysis of iron and copper speciation and activities in chloride leaching solutions of high ionic strength. *Hydrometallurgy* **2020**, *192*, No. 105262, DOI: [10.1016/j.hydro-met.2020.105262](https://doi.org/10.1016/j.hydro-met.2020.105262).
- (23) Qun, Z.; Botao, Q.; Banghao, Z.; et al. Effects of surfactant adsorption on the surface functional group contents and polymerization properties of coal dust. *Process Saf. Environ. Prot.* **2023**, *173*, 693–701.
- (24) Kaur, R.; Mehta, S. K. Self aggregating metal surfactant complexes: Precursors for nanostructures. *Coord. Chem. Rev.* **2014**, *262*, 37–54.
- (25) Qian, L.; Jun, L.; Rui, X.; et al. Synergistic enhancement effect of Ag^+ and organic ligands on the bioleaching of arsenic-bearing gold concentrate. *Hydrometallurgy* **2021**, *240*, No. 105723, DOI: [10.1016/j.hydromet.2021.105723](https://doi.org/10.1016/j.hydromet.2021.105723).
- (26) Kaksonen, H. A.; Lakaniemi, A.; Tuovinen, H. O. Acid and ferric sulfate bioleaching of uranium ores: A review. *J. Cleaner Prod.* **2020**, *264*, No. 121586, DOI: [10.1016/j.jclepro.2020.121586](https://doi.org/10.1016/j.jclepro.2020.121586).
- (27) Xueming, Z.; Shaohui, Z. Enhanced copper extraction in the chalcopyrite bioleaching system assisted by microbial fuel cells and catalyzed by silver-bearing ores. *J. Environ. Chem. Eng.* **2022**, *10* (6), No. 108827.
- (28) Bunin, Z. I.; Khabarova, A. I. Study of the Effect of Dielectric-Barrier Discharge on the Surface Morphology and Physical-Chemical Properties of Pyrrhotite and Chalcopyrite. *J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech.* **2022**, *16* (2), 281–284.
- (29) Jie, S.; Wenxiang, Z.; Pei, Y.; et al. Effect of Corrosive Medium and Surface Defect-Energy on Corrosion Behavior of Rolled ZK61M Alloy. *Materials* **2022**, *15* (12), 1–17.