

# Atmospheric oxygen-rich direct leaching behavior of zinc sulphide concentrate

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Received 17 October 2012; accepted 14 October 2013

**Abstract:** The leaching behavior of main metallic sulphides in zinc concentrate under atmospheric oxygen-rich direct leaching conditions was studied through mineralogical analysis. The results show that the sulphides dissolve obviously except pyrite. Based on the relationship between elemental sulfur and the residual sulphides in the leaching residue, the dissolution of sphalerite, chalcopyrite, covellite and galena is assumed to follow the indirect oxidation reactions, where the acidic dissolution takes place firstly and then the released H<sub>2</sub>S transfers from the mineral surface into bulk solution and is further oxidized into elemental sulfur. The interface chemical reaction is further supposed as the controlling step in the leaching of these sulphides. The direct electrochemical oxidation reactions are assumed to contribute to the dissolution of pyrrhotite, which is controlled by the diffusion through elemental sulfur layer.

**Key words:** zinc sulphide concentrate; atmospheric direct leaching; oxygen-rich leaching; leaching behavior; mineralogy

## 1 Introduction

The roasting–leaching–electrowinning (RLE) process is the primary route for zinc production and responsible for more than 85% of zinc in the world [1]. Fugitive SO<sub>2</sub> in the roasting causes air pollution, which is a great challenge to the RLE process [2]. In the 1980s, the innovative process of zinc pressure leach (ZPL) was industrialized, in which zinc sulphide concentrate is directly leached and the sulphidic sulfur is oxidized to elemental form rather than to SO<sub>2</sub>, so that the pollution of SO<sub>2</sub> is completely avoided. The ZPL process offers an attractive alternative to roasting in the expansion plans of existing zinc plants, or in the design of new facilities. Although the ZPL process makes the zinc industries more competitive, it needs high-cost autoclave and thereby its application is limited.

In the 1990s, the atmospheric direct leaching (ADL) process of zinc sulphide concentrate was developed [3,4]. Actually, the ADL process is operated under oxygen-rich conditions, which is similar to low-temperature pressure leaching know-how [5–7]. The ADL process has been practiced at an industrial scale [8,9]. In 2008, Zhuzhou

Smelter Group, the leading Chinese zinc producer, integrated the ADL process with the existing production plant to increase zinc production capacity by 100000 t/a [10]. Compared with the ZPL process, the ADL process employs less harsh conditions and meanwhile proceeds much slower leaching kinetics. It requires 10–20 h to achieve zinc extraction more than 95% [3,9]. The ADL process is still in development to promote the leaching rate of zinc sulphide concentrate.

The acidic dissolution and the subsequent oxidation of H<sub>2</sub>S are assumed as main reactions during the ADL process of sphalerite [11]. The slowing-down of the leaching rate of sphalerite with the increase of retention time is mostly regarded as the result of the encapsulation of elemental sulfur to the unreacted ore [12]. The rate-controlling step of leaching reaction is further suggested as the diffusion of dissolved Zn<sup>2+</sup> from sphalerite to bulk solution or H<sub>3</sub>O<sup>+</sup> from bulk solution to the unreacted ore through a polysulfide layer on the mineral surface [13]. But JAN et al [14] suggested that the rate-controlling step appears to be the oxidation of H<sub>2</sub>S which is not a homogeneous reaction in solution but a heterogeneous process occurring on the surface of sphalerite. Actually, most of the researches on the

leaching of sphalerite in sulfuric acid solution rely on the numerical analysis of kinetic data [15–20]. Besides the numerical analysis, the mineralogical analysis, such as chemical and structural description of mineral surface, is a very powerful assisting method [21]. BUCKLEY et al [22] applied the surface analysis methods in the oxidative leaching of sphalerite to support the conclusions that a surface layer of a metal-deficient sulphide forms with the dissolution of zinc in which sulfur partially presents in the elemental form and this altered surface layer protects sphalerite from further leaching. The mineralogical analysis has also already been used in further study of sulfur behavior in leaching [23–25].

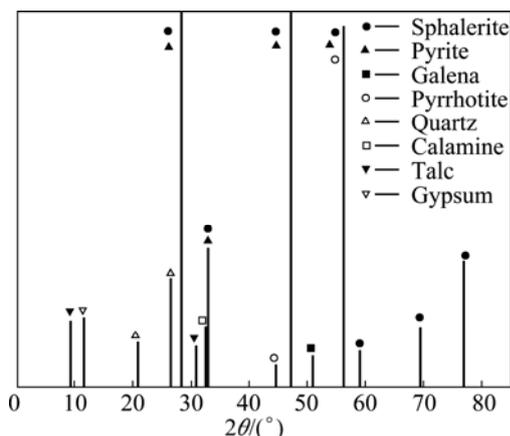
We have ever combined the kinetic analysis with the mineralogical analysis in the study of low-temperature pressure leaching of sphalerite [26]. The assumption is proposed that the interface chemical reaction is the rate-controlling step for zinc extraction on the basis of calculation of apparent active energy, which is further proved by the observed microstructure of leaching residue. In this work, the mineralogical analysis on main sulphides, such as sphalerite, pyrite, pyrrhotite, chalcopyrite, covellite and galena in zinc concentrate under the ADL conditions is developed and the microstructure of the residual sulphides as well as elemental sulfur in the leaching residue is focused on the leaching behavior.

## 2 Experimental

The chemical composition of zinc sulphide concentrate is listed in Table 1. The X-ray diffraction (XRD) pattern is presented in Fig. 1. As shown in Fig. 1,

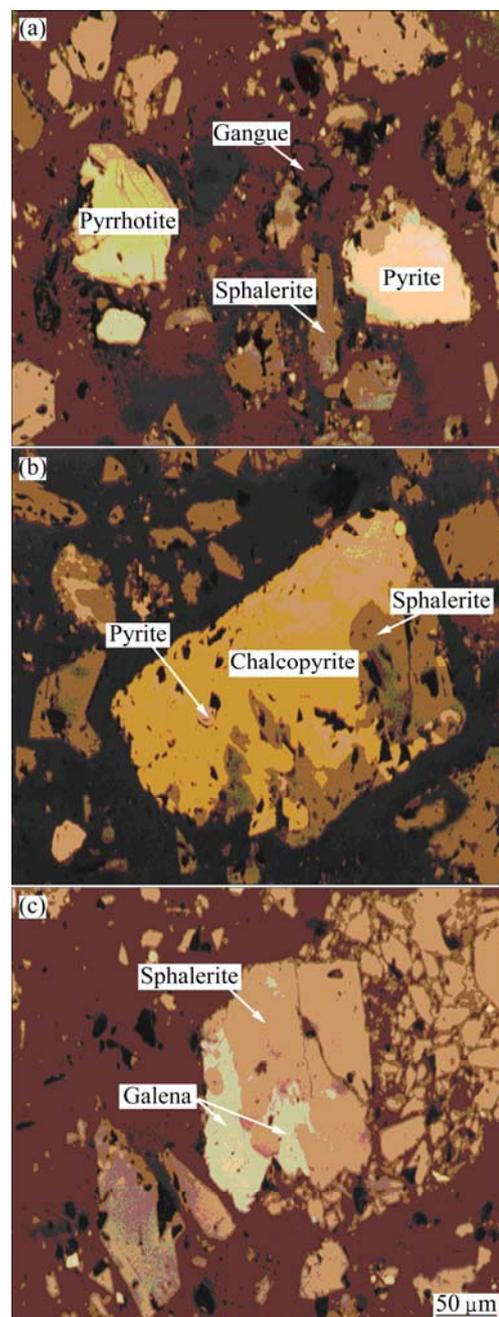
**Table 1** Chemical composition of zinc sulphide concentrate (mass fraction, %)

Zn	Fe	Pb	S	Si	Cu	Others
46.83	7.62	2.41	28.08	1.96	0.32	12.78



**Fig. 1** XRD pattern of zinc sulphide concentrate

sphalerite is the most important sulphide in the concentrate. In addition to sphalerite, the concentrate contains other sulphides, such as pyrite, pyrrhotite and galena. A small quantity of chalcopyrite and covellite are further observed through optical microscope. The microstructures of the sulphides are given in Fig. 2. As shown in Fig. 2, pyrite and pyrrhotite mostly present in single and free form, while chalcopyrite and galena mostly adhere to sphalerite and form a large intergrowth. Moreover, the concentrate contains smithsonite, quartz, talc and gypsum. Quartz and talc are the original gangue minerals, while gypsum is introduced in the flotation process.



**Fig. 2** Micrographs of pyrite and pyrrhotite (a), pyrite and chalcopyrite (b) and galena (c) in zinc sulphide concentrate

The ADL process of zinc sulphide concentrate is simulated in a 2.0 L titanium lining autoclave. The leaching agent is composed of spent electrolyte (50 g/L  $Zn^{2+}$  and 180 g/L  $H_2SO_4$ ). The leaching experiments are carried out under such conditions as follows: the concentrate particle size of 44  $\mu m$  (95%), the temperature of 373 K, the liquid to solid ratio of 5 mL/g, the oxygen partial pressure of 0.3 MPa, the leaching time of 5 h, the agitation speed of 800 r/min. The leaching solution as well as the leaching residue is sampled and further analyzed respectively. Based on the analysis of leaching residue, the extraction of zinc is achieved as 94.65%.

The mineralogical analysis on leaching residue is performed by a Rigaku D/MAX-10 X-ray diffractometer, HITACHI S-3500N scanning electron microscope combined with INCA Oxford energy dispersive spectroscope.

### 3 Results and discussion

The XRD pattern of the leaching residue is given in Fig. 3. As can be seen, a large amount of elemental sulfur and a few of lead sulphate and  $CaSO_4 \cdot 0.5H_2O$  exist in the leaching residue. Elemental sulfur is the oxidation product of sulphidic sulfur. Lead sulphate and  $CaSO_4 \cdot 0.5H_2O$  are respectively produced from the leaching of galena and the dehydration of gypsum in leaching. In comparison of Fig. 1 and Fig. 3, it can be seen that pyrrhotite, smithsonite and talc also dissolve obviously. However, quartz and pyrite are insoluble and thus enriched in the leaching residue.

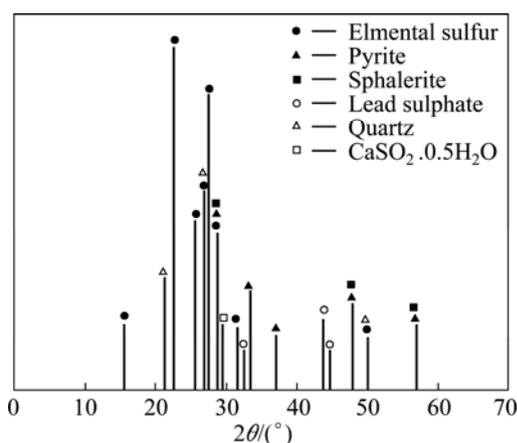


Fig. 3 XRD pattern of leaching residue

The microstructure of the leaching residue is presented in Fig. 4. As shown in Fig. 4, only a few of sulphides, such as pyrite and sphalerite, exist in the leaching residue. The residual sphalerite is independent to each other and its boundary is corroded seriously. Elemental sulfur exists in the form of compact spherulite,

which is separated from the residual sphalerite. Moreover, the particle size of elemental sulfur is obviously larger than that of residual sphalerite. So it can be assumed that elemental sulfur could be generated not on the mineral surface but in bulk solution. Once the solid nucleus of elemental sulfur forms in bulk solution, it becomes the target where continuous oxidation of sulphidic sulfur takes place. Thereby, the elemental sulfur particles become bigger and bigger.

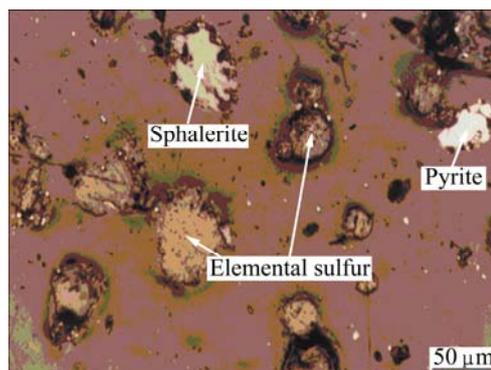


Fig. 4 Micrograph of leaching residue

#### 3.1 Sphalerite

Under the ADL conditions, the leaching reaction of sphalerite may be simplified as follows:

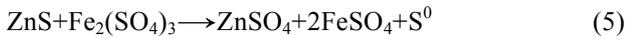


In fact, the dissolution of sphalerite follows two possible ways, namely, the indirect oxidation and the direct oxidation. According to the former way, the acidic dissolution of sphalerite takes place firstly and then the released  $H_2S$  transfers from the mineral surface into bulk solution and is further oxidized into elemental sulfur by dissolved oxygen or ferric iron [27]. Under the temperature lower than 423 K, the oxidization of  $H_2S$  is mainly through the reaction with oxygen [28]. No matter how the oxidization of  $H_2S$  is going on, elemental sulfur rarely forms on the mineral surface once it is produced. Thereby, the elemental sulfur particles are always separated from the residual sphalerite. The indirect oxidation reactions of sphalerite can be given as follows:



According to the latter way, sphalerite is directly oxidized by ferric iron in solution or by a coupling electropositive mineral through galvanic cell reaction [29]. Because the leaching temperature is lower than the melting point of elemental sulfur, elemental sulfur appears in solid state and hardly moves freely away from the mineral surface once it is produced. Thus, there must be a significant encapsulation of elemental sulfur to the

residual mineral. The electrochemical oxidation reactions of sphalerite in leaching are shown as follows:

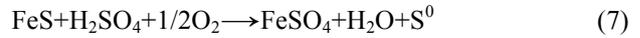


The appearance of the residual sphalerite and elemental sulfur in the leaching residue is presented in Fig. 5. It can also be seen that the sphalerite surface is rarely contaminated by elemental sulfur and the residual sphalerite mostly separates from the elemental sulfur particles. Because the diffusion through the compact elemental sulfur layer does not exist in leaching, the dissolution of sphalerite can be supposed as the indirect oxidation reactions. Furthermore, we have successfully applied shrinking core model to the description of the ADL process of sphalerite and the apparent activation energy of  $(44.28 \pm 4.28)$  kJ/mol is achieved on the basis of numerical analysis, which proves that the interface chemical reaction is the controlling step.

### 3.2 Pyrite and pyrrhotite

The microstructure of pyrite and the backscattered electron image of pyrrhotite in the leaching residue are respectively presented in Figs. 6 and 7. As shown in Fig. 6, the boundary of pyrite is very smooth and no corrosion takes place. Thus, it can be concluded that pyrite hardly dissolves under the ADL conditions. But the zigzag contour of the residual pyrrhotite is obvious in

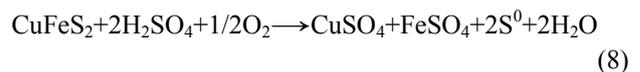
Fig. 7, which proves the occurring of the dissolution of pyrrhotite. The dissolution of pyrrhotite has also two possibilities, indirect and direct oxidation. The overall reaction for the leaching of pyrrhotite can be given as follows:



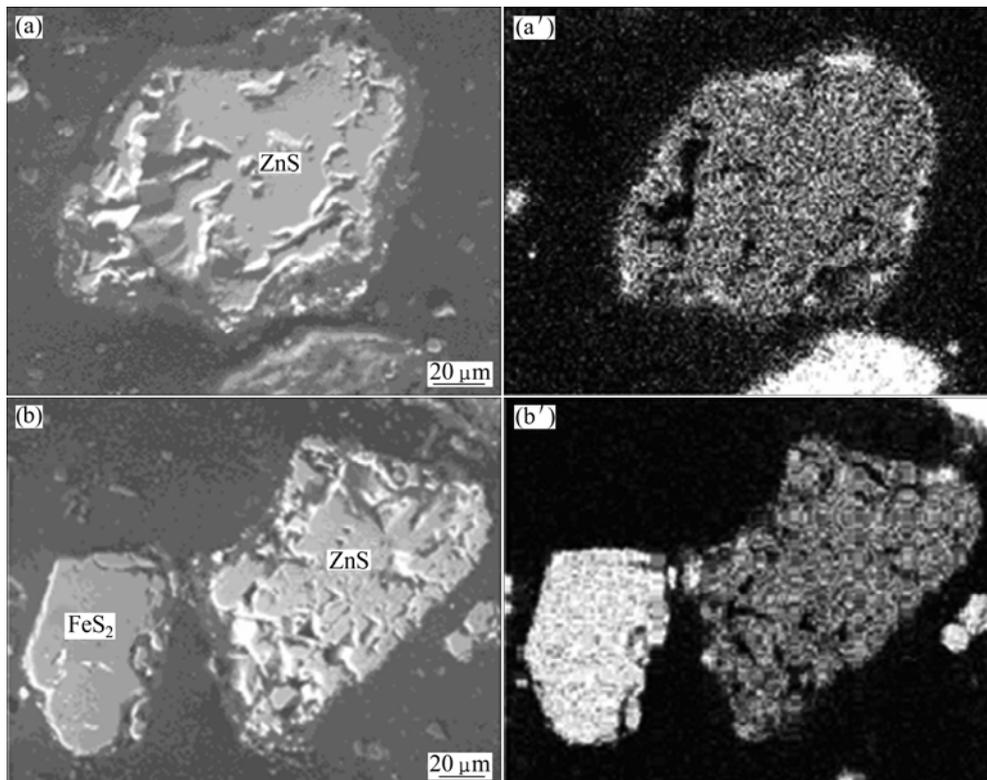
As shown in Fig. 7, there is an obvious elemental sulfur layer around the residual pyrrhotite. It is further proved that the encapsulation of elemental sulfur to the residual pyrrhotite is quite common in the leaching residue through the microscopy observation. Therefore, it is supposed that the dissolution of pyrrhotite should follow the direct electrochemical oxidation reaction. The diffusion through the layer of elemental sulfur may be the controlling step in the leaching of pyrrhotite.

### 3.3 Chalcopyrite and covellite

The overall leaching reactions for chalcopyrite and covellite can be respectively given as follows:



It can be seen that chalcopyrite and covellite do not enrich in the leaching residue even though the productivity ratio of the residue is less than 50% after the leaching. It is possibly due to the great dissolution of copper sulphides.



**Fig. 5** Backscattered electron images of sphalerite (a) and sphalerite and pyrite (b) in leaching residue and corresponding elemental surface distribution of S (a', b')

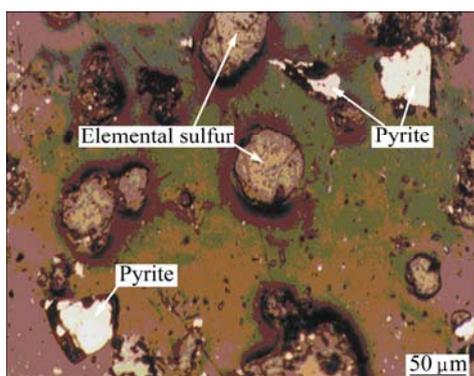


Fig. 6 Micrograph of pyrite in leaching residue

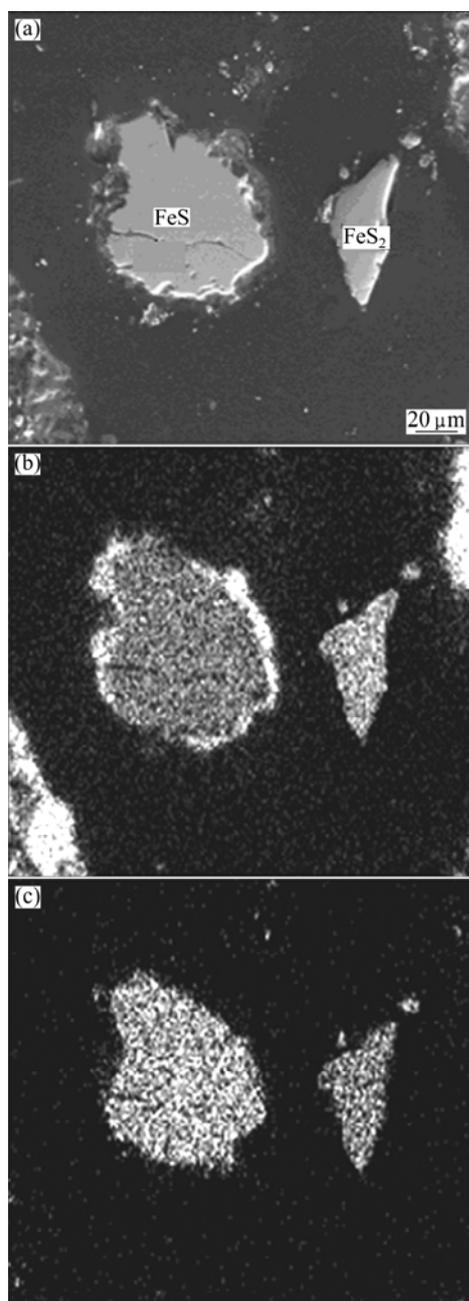


Fig. 7 Backscattered electron images of pyrrhotite and pyrite (a) in leaching residue and elemental surface distribution of S (b) and Fe (c)

The backscattered electron images of chalcopyrite and covellite in the leaching residue are shown in Fig. 8 and Fig. 9 respectively. The obvious zigzag contour of the residual chalcopyrite is observed, which proves the dissolution of chalcopyrite. A large amount of penetrative fissure appears in the covellite particles, which shows that the dissolution of covellite is much more serious than that of chalcopyrite.

As far as the dissolution of covellite is concerned, elemental sulfur should exist in the inner fissures if covellite was directly oxidized through in-situ electrochemical oxidation. But there is no adherence of elemental sulfur to the residual covellite, as shown in Fig. 9. Chalcopyrite is rarely contaminated by elemental sulfur too. Therefore, it is supposed that the dissolution of both chalcopyrite and covellite should follow the indirect oxidation reactions, which is similar to that of sphalerite.

### 3.4 Galena

The backscattered electron image of galena in the leaching residue is given in Fig. 10. As shown in Fig. 10, lead sulfate forms around the residual galena. It is due to the fact that lead sulfate can neither dissolve nor further transfer into bulk solution freely because of its low solubility once it forms in situ. Moreover, no elemental sulfur layer forms around the residual galena. So it is supposed that the dissolution of galena should follow the indirect oxidation reactions, which is similar to that of sphalerite or copper sulphides. The overall reaction for the leaching of galena is as follows:



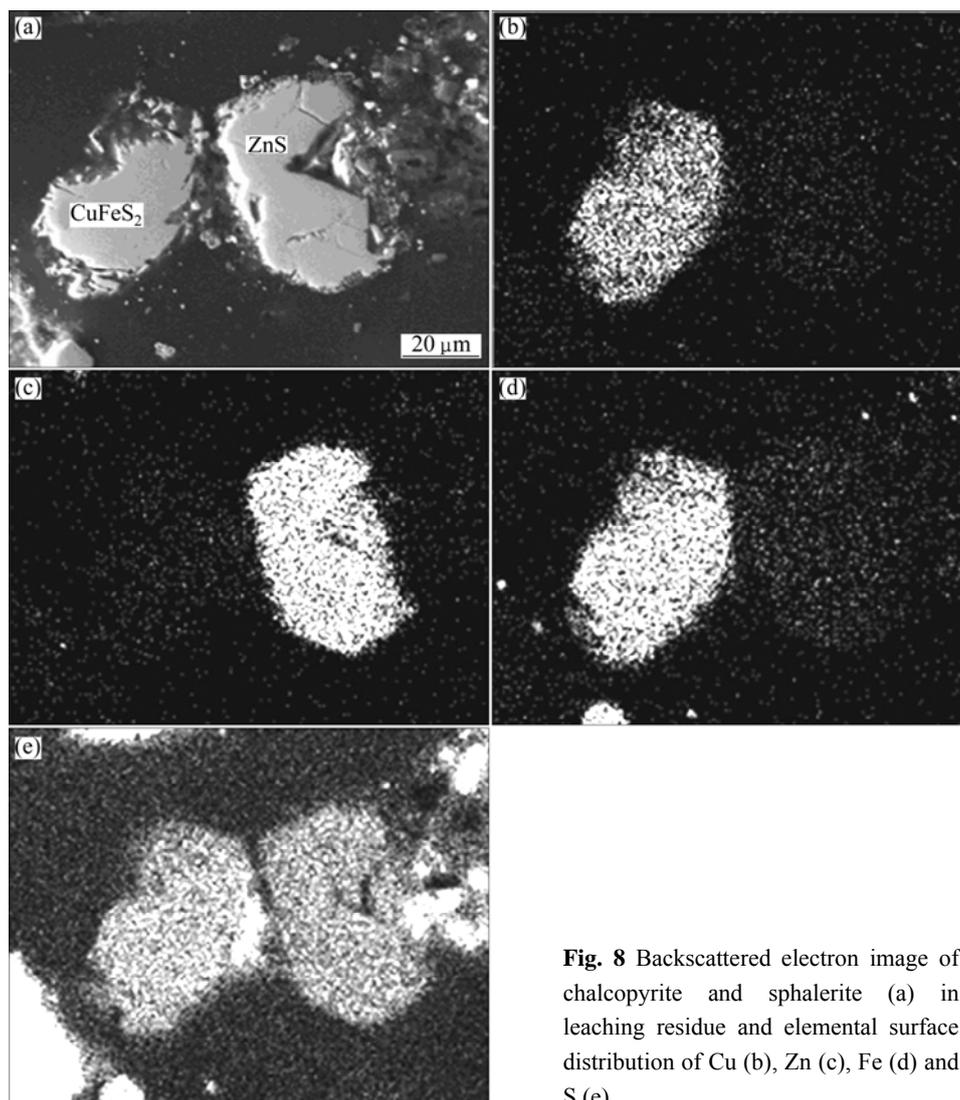
Because the sulfur particles are rarely observed near the residual galena in leaching residue, another possibility for the dissolution of galena is proposed as follows:



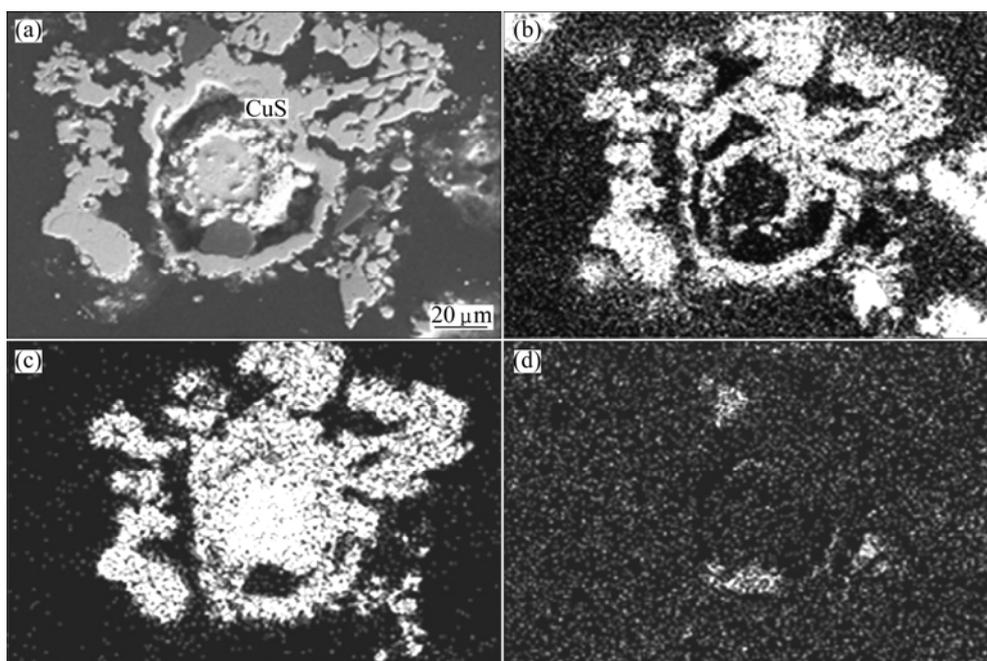
## 4 Conclusions

1) Most of the metallic sulphides in zinc concentrate except pyrite dissolve obviously under the atmospheric oxygen-rich direct leaching conditions. Moreover, smithsonite and talc also dissolve obviously while quartz is insoluble and thus enriched in the leaching residue.

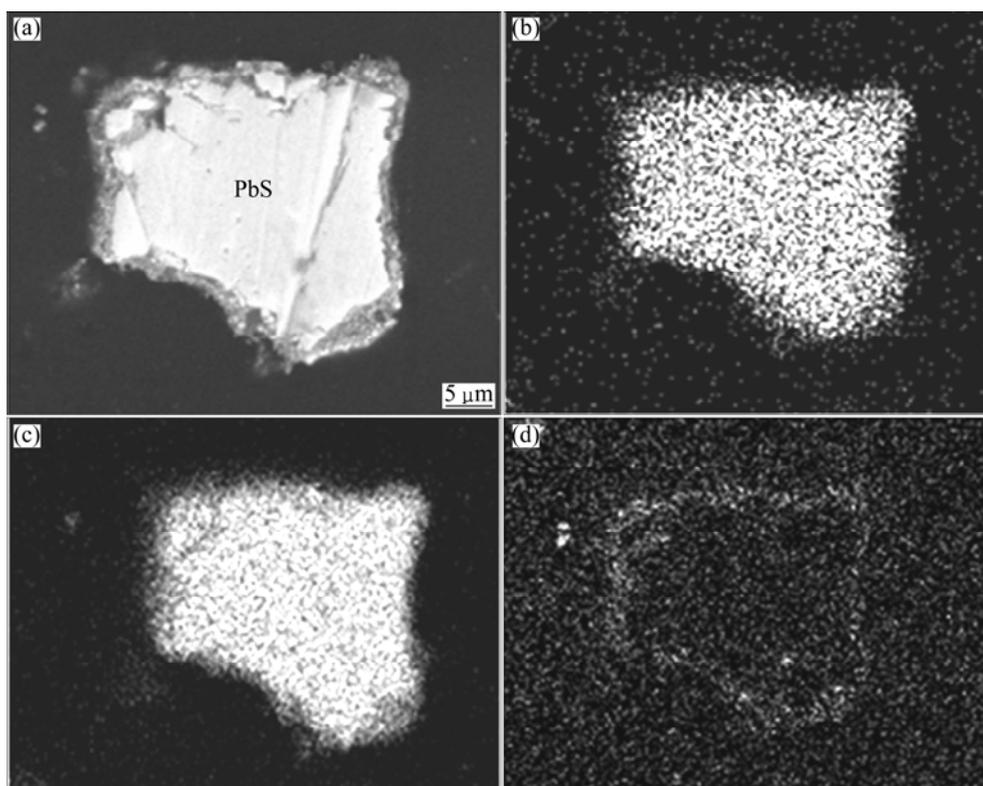
2) There are no coatings of elemental sulfur around the residual sphalerite, chalcopyrite, covellite and galena in the leaching residue, which shows that the dissolution of these sulphides may follow the indirect oxidation reactions. The acidic dissolution takes place firstly and then the released  $\text{H}_2\text{S}$  transfers from the mineral surface



**Fig. 8** Backscattered electron image of chalcopyrite and sphalerite (a) in leaching residue and elemental surface distribution of Cu (b), Zn (c), Fe (d) and S (e)



**Fig. 9** Backscattered electron image of covellite (a) in leaching residue and elemental surface distribution of S (b), Cu (c) and O (d)



**Fig. 10** Backscattered electron image of galena (a) in leaching residue and elemental surface distribution of Pb (b), S (c) and O (d)

into bulk solution and is further oxidized to elemental sulfur. The sulfur particles can grow up in the bulk solution. The dissolution of pyrrhotite is assumed to follow the direct electrochemical oxidation reactions because of the obvious coating of elemental sulfur on the mineral surface.

3) The leaching of sphalerite, chalcopyrite, covellite and galena may be controlled by the interface chemical reaction, while that of pyrrhotite controlled by the diffusion through sulfur layer.

### Acknowledgement

The author, Dr. Zhi-feng XU, is grateful to the support from the 4th Young Scientists Cultivating Project of Jiangxi Province, China.

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## 硫化锌精矿常压富氧直接浸出行为

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**摘要:** 借助工艺矿物学分析对常压富氧直接浸出条件下锌精矿中主要硫化物的浸出行为进行研究。结果表明, 除黄铁矿外, 其他硫化矿均会明显溶解。基于对浸出渣中单质硫与反应残余硫化物之间关系的分析, 认为闪锌矿、黄铜矿、铜蓝、方铅矿的溶出可能遵循间接氧化方式, 即硫化物首先酸溶, 生成的 H<sub>2</sub>S 脱离矿物表面并迁移至溶液本体中进而氧化成单质硫。上述硫化矿的浸出过程可能受界面化学反应控制。对于磁黄铁矿的溶出, 直接电化学氧化可能起主导作用, 其浸出过程可能受产物层单质硫的扩散控制。

**关键词:** 硫化锌精矿; 常压直接浸出; 富氧浸出; 浸出行为; 工艺矿物学

(Edited by Xiang-qun LI)