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Contribution of components from volume defect in natural pyrite and quartz to solution chemistry of flotation pulp

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Abstract: The volume defects in pure pyrite and quartz from a classical Cu–Pb–Zn–Fe sulfide deposit were investigated. The results indicate that a large number of volume defects exist in natural pyrite and quartz. The volume defects assume a variety of shapes, including long strips, oval shapes and irregular shapes, with sizes ranging from a few microns to dozens of microns. These volume defects are rich in metallogenic elements as a result of the capture of metallogenic and mineralizing fluid during the defect-forming process. The volume defects are fractured during the grinding process, and their chemical components are released into the solution, as confirmed by the abundant presence of various metal and non-metal components in the cleaning water and EDS results. Under the experimental conditions of 10 g pyrite or quartz with grinding fineness of $d_{90}=37 \,\mu\text{m}$, which was cleaned in 40 mL of pure deionised water under an inert atmosphere, the total average concentrations of Cu, Pb, Zn, Fe, Ca, Mg and Cl⁻ in the aqueous solution are 32.09×10^{-7} , 16.51×10^{-7} , 19.45×10^{-7} , 516.52×10^{-7} , 129.50×10^{-7} , 35.30×10^{-7} and 433.80×10^{-7} mol/L, respectively, for pyrite and 19.20×10^{-7} , 8.88×10^{-7} , $8.2.71 \times 10^{-7}$, 16.21×10^{-7} , 4.28×10^{-7} and 731.26×10^{-7} mol/L, respectively. For quartz. These values are significantly greater than those from the experimental non-oxidative dissolution of the pyrite or quartz, respectively. Therefore, the metallogenic fluid in volume defects of mineral crystal is concluded to represent the dominant contribution to the solution chemistry of sulfide flotation pulp. The present investigation will help to deeply understand the flotation theory of sulfide minerals.

Key words: pyrite; quartz; volume defect; metallogenic fluid; component release

1 Introduction

Froth flotation is a widely used method for the beneficiation or separation of complex sulfide minerals in industry. However, the flotation practice shows that the floatability of sulfides from various deposits and even from different diggings in one deposit is very different. which often leads to unsatisfactory effectiveness of separation of the complex sulfides by flotation. In order to solve this problem, many experimental studies on the flotation performance of sulfide minerals have been performed using various analytic and testing technologies in the past several decades. It has been well known that most of the sulfides are semiconducting minerals with narrow band gap and their flotation process closely involves electrochemical

reactions. In the process of sulfide flotation, it has been well proved that oxygen accepts electrons on the sulfide surface on which the cathodic reaction occurs, while xanthate (X^-) loses electrons on the sulfide surface on which the anodic reaction occurs. The above processes can be summarized by the following redox reactions:

- Anodic reaction for pyrite: $2X^{-} \rightarrow X_{2} + 2e$ (1)
- Anodic reaction for galena: $2X^{+}PbS \rightarrow PbX_{2}+S$ (2) Cathodic reaction: $O_{2}+2H_{2}O+4e \rightarrow 4OH^{-}$ (3)
- Californic reaction: $O_2 + 2\Pi_2 O + 4e \rightarrow 4O\Pi$ (3)

From Reactions (1)–(3), the rest potential of sulfide electrode predominantly affects the electrochemical reaction on sulfide surface [1-5].

As we know, perfect mineral crystal does not exist in nature. Even under absolute zero condition, the crystal defect is also impossible to be avoided. During the ore-forming, the lattice defect of sulfide always results from the loss of its anions or cations, causing

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vacancy defect. In addition, the extraneous ions such as Pb, Cu, Se, Zn, Au and Ag ions, substitute for lattice sites or occupy interstitial void of sulfide crystal. In recent years, some researchers have proposed that the lattice defects in the sulfide crystal change the electrochemical properties of the mineral and impact the electrochemical processes, which vary floatability of sulfide from different areas during flotation [6]. SUN et al [7] reported that the lattice substitution of Cu and Fe ions in sphalerite resulted in increasing the surface free-electrons and the electro-chemical activity of sphalerite. In the study of the density functional theory (DFT), LI et al [8] found that vacancy defects significantly influenced the covalence and electrochemical properties of pyrite and adversely affected pyrite flotation. In a series of experiments, CHEN et al [9-11] studied the effect of lattice substitution on electronic structures and flotation behaviors of sphalerite, and the results showed that the lattice substitution of Mn, Fe, Ni, Cu, Sn and Pb ions in sphalerite benefited the adsorption of O₂ and xanthate. CHEN et al [12] reported that the lattice substitution of Sb and Mn ions led to the over-oxidation of galena, which is unfavorable for the flotation of galena. In a series of experiments, it is demonstrated that the presence of Co, As and Ni ions in pyrite results in the semiconductor type conversion of pyrite and influences the oxidation of the pyrite surface under moist-air conditions [13-15]. These studies provide valuable background and methods for understanding the correlation between lattice defects and flotation behavior of sulfides. However, some import science issues remain unresolved. In fact, during the ore-forming, beside the above-mentioned lattice defects (point defects), the natural mineral crystal also contains many volume defects formed through growing and extending the point defects to three-dimensional defects. So far, there has been little discussion on the correlation between the volume defects and the floatability of sulfides.

The geochemistry knowledge represents that mass metallogenic fluid has been trapped and closed in volume defects of minerals of hydrothermal ore deposits which often precipitate as sulfides in abundance from hot metal-rich fluid passing through small porous or fractured rocks [16]. This implies that the metallogenic fluid in volume defects may contain active metal ions due to their ability of carrying metal metallogenic ions during ore formation. Once the ores are crushed and ground during the mineral liberation processing, the volume defects in the minerals are deteriorated and their chemical components are released into the flotation pulp, which significantly influence the solution chemistry of the flotation pulp and the surface properties of sulfide minerals, as well as the flotation performance of metal-sulfide minerals. However, there are few reports about the characterization of volume defects in mineral crystal. Hence, in this work, the characterization of volume defects formed in pyrite and its closely associated quartz was investigated, and the concentrations of various components released from the volume defects were determined. The results would be helpful for the understanding of flotation solution chemistry.

2 Experimental

2.1 Description of deposit and material

The material used in the present investigation was from a Cu–Pb–Zn–Fe sulfide deposit at Dapingzhang in the Lancangjiang River zone of Southwest Yunnan Province in China. This deposit is an important representative of a large volcanogenic hydrothermal sedimentary deposit and occurs as polymetallic massive sulfide mineralization mainly containing pyrite, sphalerite, galena, chalcopyrite and tetrahedrite– tennantite metal mineral. The gangue is mainly composed of quartz and small amounts of calcite and barite [17].

Twelve representative bulk-rock samples were chosen for the metallogenic fluid-release tests. The samples were crushed into +0.5-1 mm particles, and the high-purity pyrite and quartz crystals liberated from the sulfides were hand-picked under a microscope. The chemical analysis of the materials showed that the pyrite contained 44.06% Fe and 54.57% S, and the quartz contained 98.35% SiO₂. An X-ray diffraction (D/Max 2200, Rigaku, Japan) analysis of the pyrite and quartz demonstrated that their high purity with no apparent impurities.

2.2 IUM characterization of volume defect

Pure pyrite or quartz bulk was cut into thin slices with a thickness of 1 mm, and the slices were doubly polished. The morphology of volume defect was observed through an infrared-ultraviolet microscope (IUM, BX51, USA). The information obtained from the microscope observation was converted into a data signal using infrared electronic induction, and the data signal was subsequently treated using computer software to produce an output picture.

2.3 HRXMT characterization of volume defect

High resolution X-ray micro tomography (HRXMT) with cone-beam and micro-computed tomography (CT) system was introduced to investigate granular pyrite. Cone-beam X-ray micro-tomography [18,19] offers a unique imaging capability which can produce three-dimensional images of the internal structure of samples

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