

REDUCTIVE LEACHING PROCESS AND MECHANISMS OF CADMIUM FROM CADMIUM-BEARING ZINC FERRITE USING SULFUR DIOXIDE

Cadmium-bearing zinc ferrite (CBZF) is an unavoidable product in zinc smelting industry during the roasting stage for high cadmium-containing zinc concentrate. In this work, the influences of temperature, initial sulfuric acid concentration and partial pressure of sulfur dioxide on cadmium leaching were investigated. The results showed that an increase of temperature, sulfuric acid concentration and partial pressure of sulfur dioxide significantly enhanced the cadmium leaching efficiency. The maximum leaching efficiency of cadmium reached 99.2% at the temperature of 85°C, the initial sulfuric acid concentration of 80 g/L and the partial pressure of sulfur dioxide of 200 kPa. H^+ played a key role during the reductive decomposition process of CBZF. The probable reaction mechanisms and the diagrammatic sketch were presented.

Keywords: cadmium-bearing zinc ferrite; reductive leaching; mechanisms

1. Introduction

Hunan province in China has the title of 'hometown of non-ferrous metals' and non-ferrous metallurgy and mining are the most important economic industry. As the largest water system in Hunan Province, Xiangjiang River affected the water safety of about 60% of the province's population. Due to the several large zinc smelting companies located in the upper reaches, the whole Xiangjiang River is in a heavy metal pollution area and faces significant risk of cadmium pollution [1]. Cadmium has no independent deposit generally and is always associated with zinc and lead concentrate. If irrelevantly disposed, cadmium from zinc hydrometallurgy can spread into the environment and throw great threat on human health and the ecological system [1,2]. It is generally difficult to enrich heavy metals in the environmental media, so it is necessary to reduce the emission of heavy metals from the source. Zinc smelting is one of the important sources of cadmium pollution. Therefore, cadmium must be beneficiated as the byproduct of zinc production during the production process in case of cadmium pollution. The three-step roasting-leaching- electrowinning process is widely employed currently in zinc hydrometallurgy industry [3-5]. In the roasting process, most the ZnS and CdS in the zinc concentrate were converted into ZnO and CdO. On account of the about 8~10% iron content and the associated cadmium contained in zinc con-

centrate, the unwished byproduct cadmium-bearing zinc ferrite (CBZF, $Cd_xZn_{(1-x)}Fe_2O_4$, $x = 0\sim 1$) inevitably formed which is difficult to be decomposed and restrict the leaching efficiency and recovery of zinc and cadmium in hydrometallurgical processes [6,7].

Just as zinc ferrite, CBZF belongs to the stable spinel-type oxide and is difficult to be dissolved under dilute acid condition [7]. The physical properties of the spinel-type ferrites can be effectively tailored through the cation distribution among the octahedral and tetrahedral sites. During roasting stage, cadmium atoms enter into the lattice structure of zinc ferrite, which leads to the formation of CBZF [8,9]. Selective leaching of zinc from zinc ferrite with hydrochloric acid, synthetic and industrial zinc ferrite leaching in HNO_3 , $HClO_4$ and H_2SO_4 solution and kinetics of zinc and indium extraction from indium-bearing zinc ferrite in H_2SO_4 solution have been investigated [10,11]. However, this traditional hot acid leaching of ferrite required long leaching time and consumed large amounts of acid and energy. In the hot acid leaching process, the temperature was always above 95°C; the initial concentration of sulfuric acid was above 150 g/L; the liquid-solid ratio was above 50:1 and reaction time was more than three hours [10]. Sequentially, ultrasonic leaching, microwave heating and reductive acid leaching had been recently employed to enhance the leaching efficiency of the refractory ores [12-15]. Inorganic sulfur-containing reagents, such as SO_2 , $S_2O_3^{2-}$, $S_2O_4^{2-}$,

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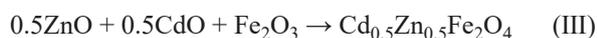
can reduce high-valence oxides of iron to facilitate the leaching of metals in acidic media [16,17]. Consequently, understanding the reductive leaching controlling conditions and mechanisms of CBZF using sulfur dioxide may help recovering cadmium from zinc neutral leaching residue.

Because it is impossible to separate and enrich the pure CBZF from the neutral leaching residue, the material used in this study was synthesized using ZnO, CdO and Fe₂O₃ to investigate the reductive leaching behavior of cadmium. The effects of temperature, initial sulfuric acid concentration and partial pressure of sulfur dioxide were studied at the fixed liquid-to-solid of 10:1 and stirring speed of 400 rpm. The raw sample and the leaching residue were also chemically and instrumentally characterized. In addition, the reductive leaching process and the mechanisms of the CBZF using the sulfur dioxide was analyzed, which contributed to determine the optimal technological parameters and to promote the leaching efficiency of cadmium.

2. Materials and methods

2.1. Materials

Synthetic CBZF were prepared by heat-treating mixtures of powdered ZnO, CdO and Fe₂O₃ of analytical grade with certain molar ratio of 0.5:0.5:1 in a muffle furnace. The powder was mixed homogeneously and sintered in crucibles in the furnace for 4h at 960°C in an atmosphere. The crucibles were taken out and the mixtures were immersed and stirred for 1h in a dilute sulfuric acid with the concentration of 80 g/L. The remaining solid samples were washed with deionized water three times. The samples then were transferred into the muffle furnace and heated to 960°C and maintained for 4 h again. Then, the samples were collected for the following experiments. Besides, zinc ferrite and cadmium ferrite were also synthesized for contrast. The chemical reactions can be described as follows:



2.2. Leaching procedure and analysis methods

30g synthesized CBZF samples were adopted to complete the experiments for one time. The leaching experiments were completed in an acid corrosion resistant titanium autoclave equipped with a control device. Specific experimental methods and procedures can be referred to the previously published papers. After the experiments, the samples were collected and chemically or instrumentally analyzed to calculate the leaching rate of cadmium to analyze the leaching mechanisms [7,13]. The X-ray diffraction pattern (XRD), surface morphology (SEM) and

the X-ray photoelectron spectroscopy spectra (XPS) analysis was completed using the Rigaku, TTR- III, SEM, FEI Quanta-200 and ESCALab250Xi, respectively. The operation conditions (Temperature arranged from 70 to 90°C; Initial concentration of sulfuric acid arranged 50 to 90 g/L; Partial pressure of sulfur dioxide arranged from 50 to 250 kPa) were also the same as those in our previous studies [7,13].

3. Results and discussion

3.1. Sample determination

The Cd, Zn and Fe content in the synthesized samples determined by the chemical analysis method were presented in the TABLE 1 and they were 21.1%, 12.3% and 42.3%, respectively, which approximately equaled to the theoretical content of the Cd_{0.5}Zn_{0.5}Fe₂O₄. Fig. 1 presented the X-ray diffraction patterns of Cd_{0.5}Zn_{0.5}Fe₂O₄, CdFe₂O₄ and ZnFe₂O₄ and the diffraction peaks were not overlapped and were not identical. The element contents and XRD analysis indicated that the predominant component was mainly Cd_{0.5}Zn_{0.5}Fe₂O₄. As shown in Fig. 2, the particle size distribution of the synthesized cadmium-bearing zinc ferrites mainly ranged from 8.21 μm to 112.94 μm, and D₅₀ was 46.90 μm. Most of the particles were concentrated near the middle particle size.

TABLE 1

The determined element content of the synthesized sample and theoretical content of Cd_{0.5}Zn_{0.5}Fe₂O₄

Element	Theoretical content/%			Determined content/%
	CdFe ₂ O ₄	ZnFe ₂ O ₄	Cd _{0.5} Zn _{0.5} Fe ₂ O ₄	
Cd	38.9	—	21.1	19.5
Zn	—	27.0	12.3	12.4
Fe	38.9	46.5	42.3	43.9

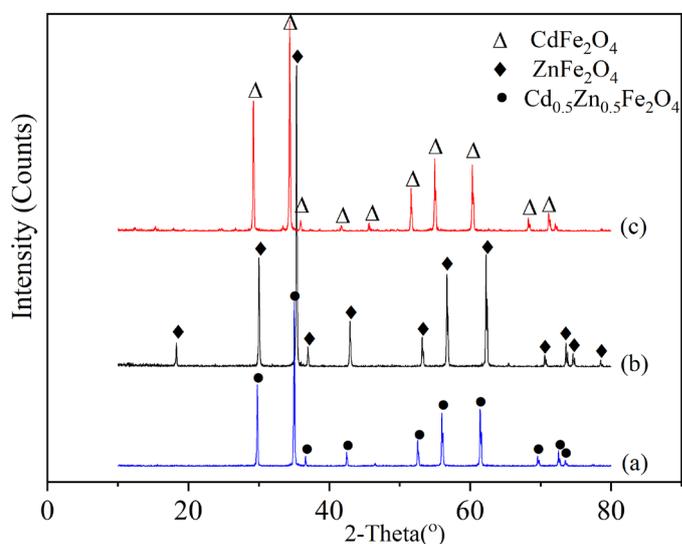


Fig. 1. XRD diffraction pattern of Cd_{0.5}Zn_{0.5}Fe₂O₄, ZnFe₂O₄ and CdFe₂O₄

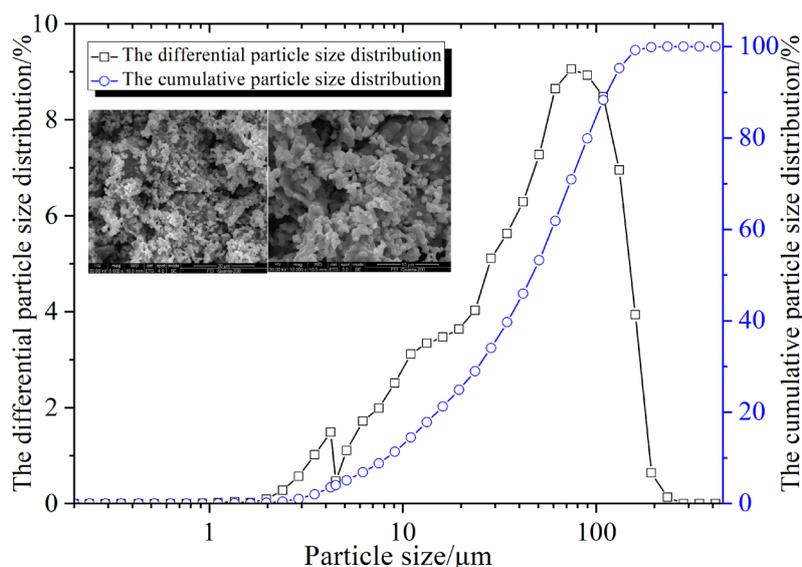


Fig. 2. Particle size distribution of cadmium-bearing zinc ferrite

3.2. Leaching process

3.2.1. Effect of sulfur dioxide on cadmium leaching

In this study, three different reaction systems were adopted to preliminarily value the influence of sulfur dioxide on the decomposition efficiency of the CBZF. The experiments were conducted at the temperature of 85°C, partial pressure of sulfur dioxide of 200 kPa and initial concentration of sulfuric acid of 80 g/L. As shown in Fig. 2, when only SO₂ or H₂SO₄ was used in the leaching system, cadmium leaching efficiency only reached 23.1% and 54.7% after reaction, respectively. However, cadmium leaching efficiency reached 99.47% in the mixed SO₂-H₂SO₄ system after 105 min's reaction when other conditions were kept constant. This indicated that the reductive leaching of cadmium from CBZF using sulfur dioxide needed certain acidity. Researchers have given some explanations of the reductive decomposition of Fe (III)-containing compound by sulfur dioxide [17-18]. It was suggested that the reductive leaching can be attributed to acid attack of the surface defects of the compound, which helped the oxidation-reduction reaction between sulfur dioxide and Fe (III)-containing compound. The rate of reductive acid dissolution of iron oxide was controlled by originally present on the surface of the compound. The effect of the number of defects was not presented directly. Nevertheless, the formation rate of Fe(II) in the solution was proportional to $[H^+]^{0.5}$ and $[HSO_3^-]^{0.5}$ [17,19].

3.2.2. Effect of temperature

Higher temperature devotes to violent molecular motion and more probability of molecular collision; the reaction proceeds faster and the rate increases in a certain time. Accordingly, the effects of the leaching temperature ranged from 70°C to 90°C were assessed when the other parameters were kept constant at

an initial sulfuric acid concentration of 80 g/L, partial pressure of sulfur dioxide of 200 KPa. The significant effects of the temperature on cadmium leaching efficiency were presented in Fig. 4. As Fig. 4 showed, cadmium leaching efficiency reached 99.2% after 90 minutes' reaction at 85°C. Besides, an increase of temperature to 90°C contributed little to the cadmium leaching efficiency when other reaction parameters were constant. The traditional leaching temperature of high temperature and high acid process is generally above 95°C, the initial acidity is more than 150 g/L, the liquid-solid ratio is more than 50:1, and the leaching reaction time is more than 3 h. Compared with the traditional leaching process, the adopted initial sulfuric concentration, liquid/solid ratio and reaction time in the reductive leaching using sulfur dioxide as reducing agent were sharply reduced compared [14,15].

3.2.3. Effect of initial sulfuric acid concentration

The initial sulfuric acid concentration affected the cadmium reductive leaching efficiency greatly as Fig. 3 presented in section 3.2.1. Fig. 5 presented the effects of an increase in sulfuric acid concentration from 50 g/L to 90 g/L at the temperature of 85°C and the partial pressure of sulfur dioxide 200 KPa. The increase in initial acid concentration was found to improve the reductive leaching efficiency of cadmium. The maximum recovery in excess of 99% can be achieved at the acid concentration of 80 g/L. However, it should be noted that when the acid concentration was higher than 80 g/L, the increase of cadmium leaching efficiency was not significant. Obviously, the initial sulfuric acid concentration in the reductive leaching process using sulfur dioxide is about half of the traditional hot acid leaching used for the decomposition of ferrites [10]. Obviously, the introduction of sulfur dioxide into the reaction system contributed to the oxidation-reduction reaction between S(IV) and Fe(III) in the synthesized CBZF, which promoted the leaching efficiency of cadmium [14-19].

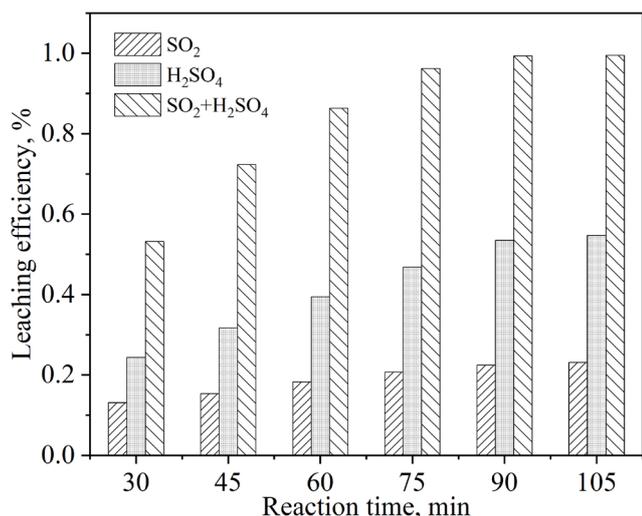


Fig. 3. Cadmium leaching efficiency in SO₂, H₂SO₄ and SO₂ + H₂SO₄ system

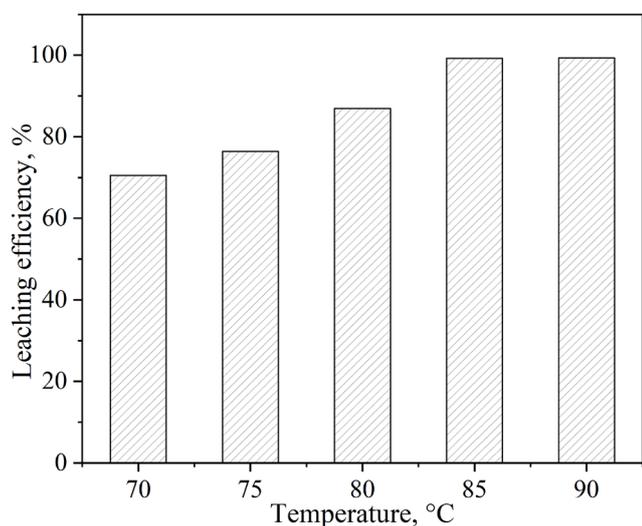


Fig. 4. Effect of temperature on cadmium leaching efficiency (sulfuric acid concentration: 80 g/L; partial pressure of sulfur dioxide: 200 KPa)

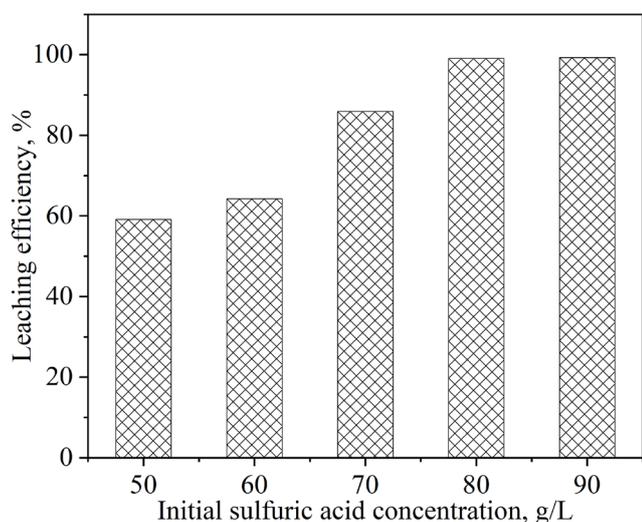


Fig. 5. Effect of initial sulfuric acid concentration on cadmium leaching efficiency (Temperature: 85°C; partial pressure of sulfur dioxide: 200 KPa)

3.2.4. Effect of partial pressure of sulfur dioxide

Introducing of sulfur dioxide into the reaction system provided a reductive circumstance and Fe(III) in the samples could be reduced to Fe(II), which helped to dissolve iron into the solution. The gaseous sulfur dioxide with purity of more than 99% was adopted in the experiments. The partial pressure is one of the impulse of chemical reaction and can inevitably affected the leaching efficiency. Rakesh Kumar studied the reductive leaching of refractory iron-containing minerals using sulfur dioxide and the “power law model” was used to describe the leaching behavior of iron [20].

$$r_i \propto \prod_j [X_j]^{m_j} \quad (4)$$

Where r_i means rate of leaching reaction; $[X_j]$ means the concentration of S-bearing species, namely SO₂ (aq.) and HSO₃⁻. However, the solubility of SO₂ is affected by the partial pressure. The effect of the partial pressure of sulfur dioxide on cadmium leaching efficiency was presented in Fig. 6. After 90 min’s reaction, the cadmium leaching efficiency reached 82.47% at the partial pressure of 150 kPa and 99.12% at 200 kPa, which implied that the decomposition of CBZF was approximately complete. When the partial pressure was enhanced to 250 kPa, the leaching only increased to 99.43%.

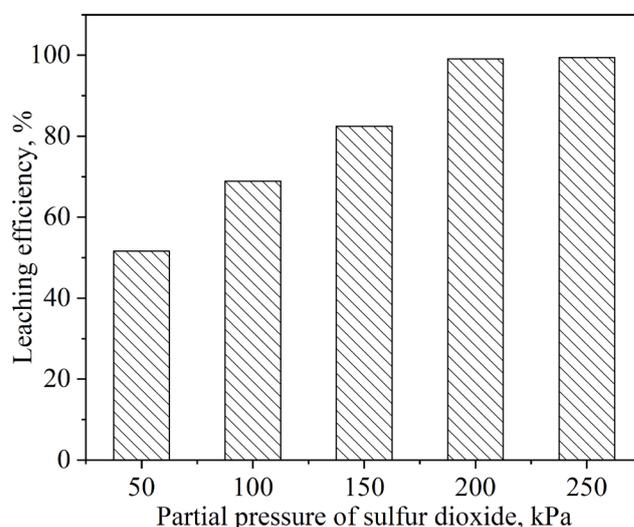


Fig. 6. Effect of partial pressure of sulfur dioxide on cadmium leaching efficiency (Temperature: 90°C; sulfuric acid concentration: 80 g/L)

3.3. Mechanism analysis

3.3.1. FT-IR and XRD analysis

The FT-IR spectra of the prepared sample Cd_{0.5}Zn_{0.5}Fe₂O₄ samples and the intermediate products (Temperature: 85°C; sulfuric acid concentration: 80 g/L; partial pressure of sulfur dioxide: 200 KPa) were shown in Fig. 7. The spectra were

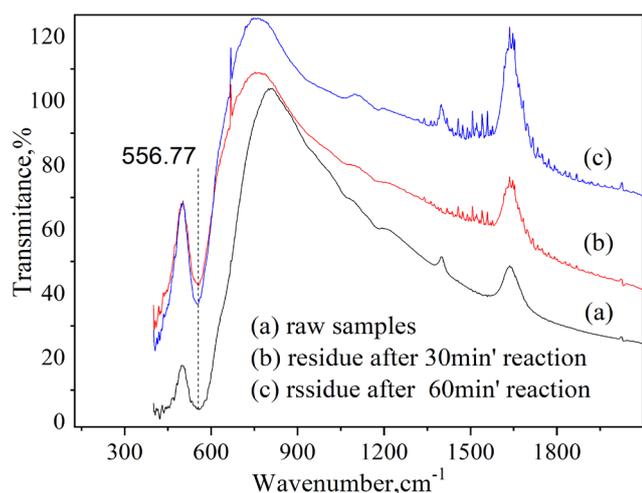


Fig. 7. FT-IR spectra analysis for the raw synthesized $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and the intermediate samples

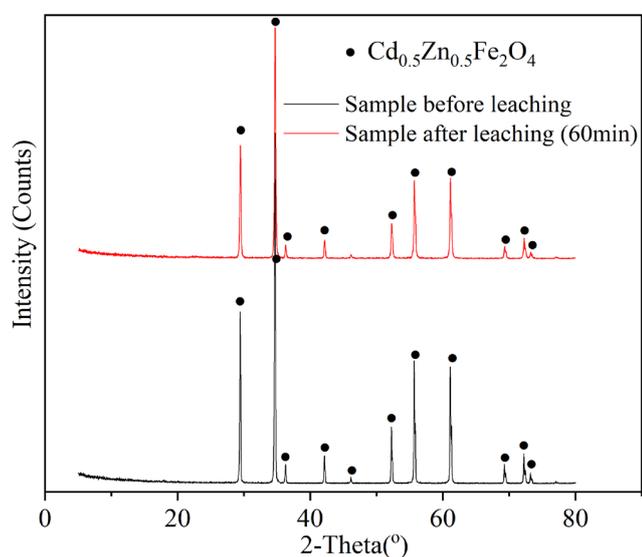


Fig. 8. XRD diffraction pattern of the precursor before and after leaching

recorded in the range from 400 cm^{-1} to 2100 cm^{-1} . In the standardized positive-going spinel type structure, A^{2+} always occupies tetrahedral sites and B^{3+} occupies octahedral sites. But in the reversed spinel type structure, $1/2\text{B}^{3+}$ occupies octahedral sites; A^{2+} and the other $1/2\text{B}^{3+}$ occupies tetrahedral sites. The general expression for the two spinel type structure are $[\text{A}^{2+}][\text{B}^{3+}\text{B}^{3+}]\text{O}_4$ and $[\text{B}^{3+}][\text{A}^{2+}\text{B}^{3+}]\text{O}_4$, respectively [21,22]. The band appeared at $350\text{ cm}^{-1}(\nu_2)$ was attributed to the stretching vibration of $\text{Fe}^{3+}\text{-O}^{2-}$ in the octahedral complexes and $500\text{-}600\text{ cm}^{-1}(\nu_1)$ to the bending vibrations in tetrahedral complexes. In the present spectra for the samples, band ν_1 appears at 556.77 cm^{-1} for the samples and intermediate products, which showed that the synthetic $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples possess reversed spinel type structure [23-28]. The intermediate products had similar structure with the synthesized $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples according to the XRD analysis in Fig. 8. As shown in Fig. 9, the morphology presented partial dissolution and a decrease of agglomeration degree compared with the raw synthesized CBZF sample.

3.3.2. XPS characterization and analysis

The O1s spectra of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples and the leaching intermediate products are showed in Fig. 10. According to XPS analysis software, it was easily found that in the O1s spectra, both the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples and the intermediate products had the identical peak at 529.9 eV , which could be attributed to the Fe-O in the cadmium-bearing zinc ferrite. Simultaneously, O1s peak was split into two obvious peaks in the intermediate cadmium-extracted samples, indicating that another kind of oxygen existing situation different to the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples appeared. The new peak appeared at 531.5 eV , which could be ascribed to the newly-generated hydroxyl groups of oxygen [24-25]. This also demonstrated that in the reductive ex-

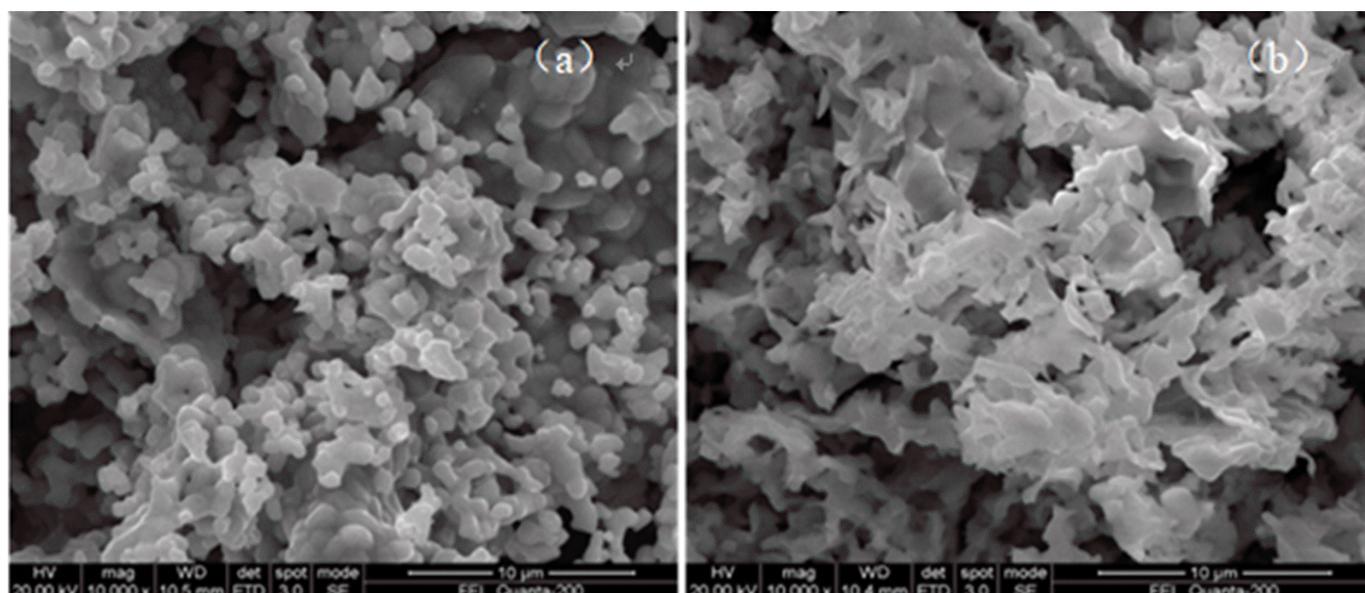


Fig. 9. (a) SEM micrograph of the raw $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and (b) sample treated for leaching 30 minutes

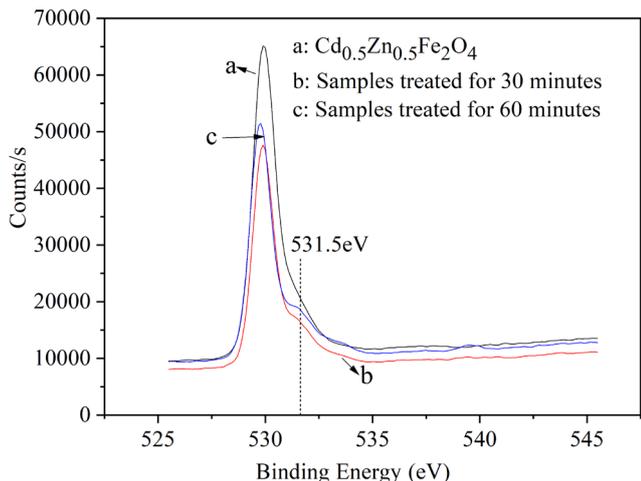
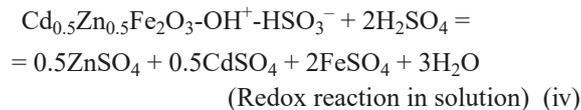
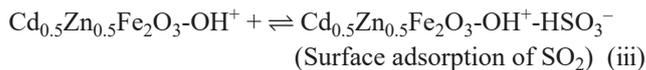
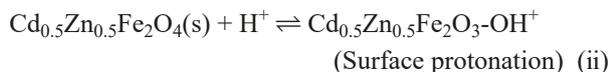


Fig. 10. XPS O1s spectra of Cd_{0.5}Zn_{0.5}Fe₂O₄, samples treated for 30 and 60 minutes at 90°C

traction process of cadmium, the assault of protons from H₂SO₄ on cadmium and zinc sites resulted in the displacement of Cd in Cd-O and Zn-O by H⁺ and H-O bonds formed subsequently [26,27]. The surface adsorption and electrochemical theories for the oxide dissolution can be used to propose the chemical equation for iron dissolution in acid solution. Under the role of pressure and agitation, the gaseous sulfur dioxide dissolved in the reaction system and the surface protonation took place on the interface of the solid-liquid reaction, which was presented in the equation (ii). Meanwhile, the formatted HSO₃⁻ was adsorbed on the surface as equation (iii) showed. Correspondingly, the newly formed solid intermediate reacted with the sulfuric acid as the equation (iv) presented. The probable reaction diagrammatic sketch was shown in Fig. 11 and the proposed reaction paths were as follows:



4. Conclusion

Cadmium-bearing zinc ferrite (CBZF) was synthesized and chemically and instrumentally determined. The particle size distribution of the sample mainly ranged from 8.21 μm to 112.94 μm, and D50 was 46.90 μm. Simultaneously, the process and mechanisms of the reductive leaching of cadmium from CBZF using sulfur dioxide as reductant was studied. In addition, the effects of temperature, sulfuric acid concentration and partial pressure of sulfur dioxide on the leaching efficiency were assessed. The cadmium leaching efficiency reached 99.2% under the optimum conditions of leaching temperature 85°C, the initial sulfuric acid concentration of 80 g/L and the partial pressure of sulfur dioxide of 200 kPa. Compared with the traditional hot acid leaching, the temperature, initial concentration of sulfuric acid, liquid-solid ratio and reaction time were all dramatically reduced, which can be attributed to the introduction of sulfur dioxide. In the reductive leaching process, acidity affected the cadmium leaching efficiency greatly. The surface protonation and adsorption contributed to the electrochemical reaction. H⁺ played a key role during the reductive decomposition process of CBZF, which implied that the acid in the reaction system could promote the oxidation-reduction reaction.

Acknowledgements

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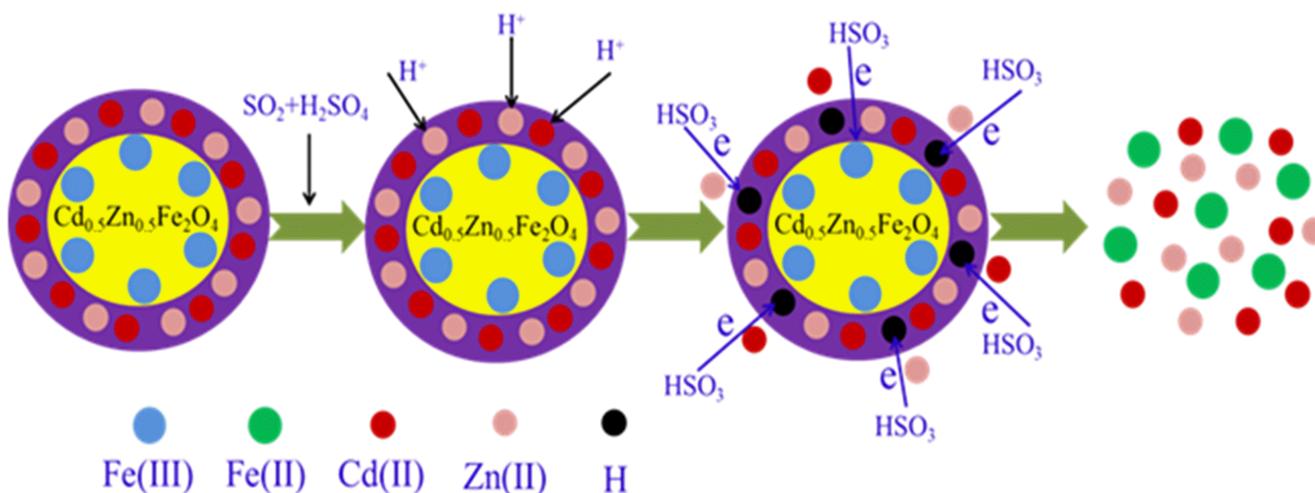


Fig. 11. The reaction diagrammatic sketch of reductive leaching of cadmium

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