Study on preparation and properties of zinc ferrite product by leaching from zinc calcine

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Abstract: In this paper, zinc ferrite was prepared from zinc calcine by sulfuric acid leaching, and its properties were studied by the methods of XRD, XRF and SEM/EDS. The results show that sulfuric acid leaching of zinc ferrite from zinc calcine is mainly affected by the initial concentration of sulfuric acid and leaching temperature. If the initial concentration of sulfuric acid and leaching temperature are too low, the soluble oxides in zinc calcine can not be completely dissolved. The prepared zinc ferrite was not suitable for application for too many impurities. However, the higher initial concentration of sulfuric acid and leaching temperature are, the lower recovery of zinc ferrite is. The suitable conditions for preparation of zinc ferrite from zinc calcine by sulfuric acid leaching are liquid-solid ratio 7:1, stirring speed 400rpm, sulfuric acid concentration 160g/L, leaching temperature 85°C, leaching time 120min. The particle size of zinc ferrite is fine, most of them is between 2~5μm. The impurity content of zinc ferrite is less. Zinc ferrite particles are composed of spherical and irregular shape, and they are agglomerate and encase each other.

1. Introduction
Zinc ferrite is a complex metal oxide with a spinel structure, high hardness and stable chemical property. Zinc ferrite is in great demand at home and abroad, and has a broad application prospect. It is mainly used in the fields of gas desulfurization, catalytic oxidative dehydrogenation of olefins and magnetic materials and so on[1]. A series of ZnFe₂O₄ desulfurizers were prepared by coprecipitation method with Xu et al., Feng et al. and Cao et al. It is found that the desulfurizers have high desulfurization efficiency and stable regeneration performance[2,3]. The effect of the addition of CsₓH₃₋ₓPW₁₂O₄₀ on oxidative dehydrogenation of N-butene by ZnFe₂O₄ catalyze was investigated, and a series of spinel ferrites were prepared by Co-precipitation method with adding different divalent metals (Mg, Ni, Co and Cu) into ZnFe₂O₄. In the catalytic tests, the surface acid content of ZnFe₂O₄ catalyst was the highest, and its catalytic effect on oxidative dehydrogenation of butene was the best. Zinc ferrite shows superparamagnetism at room temperature and is an ideal microwave absorbing material in high frequency band[4]. At present, the preparation methods of zinc ferrite are coprecipitation method, sol-gel method, hydrothermal synthesis method and high temperature roasting method and so on[5-8]. They have different advantages and disadvantages. The preparation of zinc ferrite products has become the key to restrict the development of zinc ferrite industry. In zinc
metallurgy, zinc ferrite can not be avoided after roasting sphalerite at high temperature. In the process of zinc hydrometallurgy, zinc ferrite can not dissolve in dilute acid, but remains in the leaching residue. Therefore, based on the recovery and utilization of metallurgical wastes and the wide application prospect of zinc ferrite, this paper simulates the process of zinc hydrometallurgy, the preparation of zinc ferrite from zinc calcine by sulfuric acid leaching and its properties were studied.

2. Preparation of Zinc ferrite product

The sample zinc calcine is obtained from a smelter in Guangxi. The XRD analysis of zinc calcine shows that it contains zinc ferrite. The structure and properties of zinc ferrite are stable. It does not dissolve in water, alkali and dilute acid at normal temperature, but only in hot acid, after the soluble matter in the zinc calcine is dissolved by sulfuric acid of a certain concentration, zinc ferrite remains in the leach residue. Therefore, the enrichment of zinc ferrite can be achieved initially. That is to say, zinc ferrite was prepared from zinc calcine by sulfuric acid leaching.

The XRD pattern of leaching residue under different initial concentrations of sulfuric acid is shown in Fig. 1. It can be seen from Fig. 1, the diffraction peak intensity of ZnFe₂O₄ decreases with the increase of the initial concentration of sulfuric acid at the same leaching temperature. When the concentration of sulfuric acid is 120g/L~160g/L, the diffraction peak intensity of ZnFe₂O₄ is relatively strong. When the concentration of sulfuric acid is more than 200g/L, the diffraction peak of ZnFe₂O₄ begins to weaken, which means that zinc ferrite begins to dissolve when the concentration of sulfuric acid is too high.

![Fig.1 XRD patterns of leaching slag of different initial concentrations of sulfuric acid](image)

The XRD pattern of leached slag under different leaching temperatures is shown in Fig. 2. It can be seen from Fig. 2 that the diffraction peaks of Fe₂O₃ and ZnSiO₄ disappear and the diffraction peaks of ZnFe₂O₄ weaken when the leaching temperature increases. It indicates that zinc ferrite begins to dissolve with the increase of leaching temperature. It can be concluded that zinc ferrite will dissolve in the too high leaching temperature and too high concentration of sulfuric acid. It will affect the purity of zinc ferrite in the too low leaching temperature and too low concentration of sulfuric acid. Therefore, it is suitable to prepare zinc ferrite in liquid-solid ratio 7:1, stirring speed 400rpm, leaching temperature 75°C~85°C, sulfuric acid concentration 120g/L~160g/L, leaching time 60min~180min.
3. Study on the properties of zinc ferrite product

Aimed at zinc ferrite prepared under the conditions of liquid-solid ratio 7:1, stirring speed 400rpm, sulfuric acid concentration 160g/l, leaching temperature 85°C and leaching time 120min, its properties such as chemical composition, mineral composition and particle morphology were studied by the methods of XRD, XRF and SEM/EDS.

3.1 Elemental analysis

The contents of zinc and iron in the samples were determined by chemical analysis. The results showed that the contents of zinc and iron are 19.36% and 37.09%, respectively. The multi-element semiquantitative analysis of the sample were obtained by X-fluorescence analysis, and the results are shown in Table 1. It can be seen from Table 1, the chemical element composition of the sample is complex, the main chemical element are Zn, Fe and O, in addition to containing Si, Pb, Cu, S, Mn, Al, Ca, Sb and other elements.

| Element  | Fe₂O₃ | Zn  | SiO₂  | Pb  | Cu  | SO₃ | Mn  |
|----------|-------|-----|-------|-----|-----|-----|-----|
| Content/%| 58.1  | 23.7| 4.4   | 3.6 | 2.6 | 2.0 | 1.5 |

| Element  | Al₂O₃ | CaO | Sb   | Sn  | Cd  | As  | Na₂O|
|----------|-------|-----|------|-----|-----|-----|-----|
| Content/%| 1.2   | 0.7 | 0.5  | 0.5 | 0.3 | 0.3 | 0.2 |

| Element  | In    | Ti   | Bi   | I   | P₂O₅| Zr  | MgO |
|----------|-------|------|------|-----|-----|-----|-----|
| Content/%| 0.1   | 0.09 | 0.04 | 0.03| 0.02| 0.01| 0.01|

3.2 Phase analysis

In order to find out the mineral composition of zinc ferrite products, the phases of zinc and iron in zinc ferrite products were quantitative analysis. The results are shown in Table 2 and Table 3. From Table 2, zinc in zinc ferrite products mainly exists in the form of insoluble zinc. The insoluble zinc accounts for 91.94% of the total zinc in the product, while the zinc in the oxidation and sulfide phases is only 8.06%. As can be seen from Table 3, iron in zinc ferrite products mainly exists in the form of limonite, hematite, magnetite and pyrrhotite. The iron content in hematite and limonite is 79.06% of the total iron content in the product, and the iron content is 18.58% in magnetite and pyrrhotite.
Table 2 The analysis results of zinc phase in zinc ferrite products

| Zinc phases                | Zinc content/% | Zinc distribution/% |
|----------------------------|----------------|---------------------|
| Insoluble zinc             | 17.84          | 91.94               |
| Zinc in oxidation phase    | 0.89           | 4.56                |
| Zinc in zinc sulfide       | 0.68           | 3.50                |
| Total                      | 19.41          | 100.00              |

Table 3 The analysis results of iron phase in zinc ferrite products

| Iron phases                           | Iron content/% | Iron distribution/% |
|---------------------------------------|----------------|--------------------|
| Iron in limonite and hematite          | 29.08          | 79.06              |
| Iron in magnetite and pyrrhotite       | 7.02           | 18.58              |
| Iron in siderite                       | 0.22           | 0.58               |
| Iron in ferric silicate                | 0.29           | 0.77               |
| Iron in pyrite                         | 0.17           | 1.01               |
| Total                                  | 37.78          | 100.00             |

3.3 XRD analysis

The XRD pattern of zinc ferrite product is shown in Fig. 3. According to the XRD quantitative analysis of zinc ferrite product, zinc ferrite products contain 83% zinc ferrite, 5% quartz, 2% hematite, 9% anglesite and 1% arcanite.

3.4 SEM/EDS analysis

The SEM results are shown in Fig. 4, and the EDS results are shown in Table 4. It can be seen from Fig. 4, the particle sizes are fine, most of which are between 2~5μm. The product of zinc ferrite is composed of spherical and irregular shape, and the particles are agglomerate and envelop each other. It can be seen from Table 4 that the product of zinc ferrite is mainly composed of zinc, iron and oxygen, in addition, it also contains Cu, Pb, Al, Mn, S and so on. The results show that the percentages
of Zn, Fe and O in Spectrogram 1, Spectrogram 2 and Spectrogram 3 are in good agreement with those of corresponding elements in ZnFe₂O₄. The results show that most of the sample are zinc ferrite, which contains a small amount of anglesite and other impurities.

![Fig.4 Scanning electron microscope images of zinc ferrite products](image)

Table 4 Element composition of zinc ferrite products

| Spectrogram | Element | Pb | Al | Mn | S |
|-------------|---------|----|----|----|---|
| 1           | Content/% | 1.68 | 1.40 | 1.25 |   |
| 2           | Content/% | 2.81 | 1.82 | 0.91 | 0.57 |
| 3           | Content/% | 1.56 | 1.67 | 0.82 | 0.39 |

4. Conclusions

(1) The sulfuric acid leaching of zinc ferrite from zinc calcine is mainly affected by the initial concentration of sulfuric acid and leaching temperature. If the initial concentration of sulfuric acid and leaching temperature are too low, the soluble oxides in zinc calcine can not be completely dissolved. The prepared zinc ferrite was not suitable for application for too many impurities. However, the higher initial concentration of sulfuric acid and leaching temperature are, the lower recovery of zinc ferrite is.

(2) The suitable conditions for preparation of zinc ferrite from zinc calcine by sulfuric acid leaching are liquid-solid ratio 7:1, stirring speed 400rpm, sulfuric acid concentration 160g/L, leaching temperature 85°C, leaching time 120min. Under aboved conditions, the prepared zinc ferrite products contain 83% zinc ferrite, 5% quartz, 2% hematite, 9% anglesite and 1% arcanite.
(3) The product of zinc ferrite mainly consists of zinc, iron and oxygen, in addition, it also contains Cu, Pb, Al, Mn, S and so on. The particle size of zinc ferrite is fine, most of them is between 2~5μm. The impurity content of zinc ferrite is less. Zinc ferrite particles are composed of spherical and irregular shape, and they are agglomerate and encase each other.

Acknowledgements
The authors would like to acknowledge the financial support received from National Natural Science Foundation of China (No. 51774099, No. 51364003).

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