

**FERRITE FORMATION IN THE MeO – Fe₂O₃ (Me - Zn, Cd, Cu) SYSTEMS
AND ITS IMPACT FOR THE ZINC HYDROMETALLURGY**

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Abstract

Study on the solid state interactions between MeO (Me - Zn, Cd, Cu) and α -Fe₂O₃ is very important for metallurgy as well as for the preparation of magnetic materials and new catalysts. Zinc, copper and cadmium ferrites are obtained by the conventional ceramic technology. Chemical, DTA and TG analyses, Mössbauer spectroscopy and X-ray phase analysis have been used in the study of intermediate and final products of solid state interactions. The kinetics of formation of MeFe₂O₄ is investigated by different kinetics equations and the activation energy values are obtained.

The ferrite formation process in the system ZnO - α -Fe₂O₃ and the effectiveness of zinc extraction during the hydrometallurgical treatment of the zinc calcine and the fuming of zinc containing slags are discussed.

Key words: ferrites, zinc, copper, cadmium, kinetics, zinc concentrate, Mössbauer spectroscopy, X-ray phase analysis

1. INTRODUCTION

The ferrite formation process in the system ZnO - α -Fe₂O₃ influences the effectiveness of zinc extraction during the hydrometallurgical treatment of the calcine and the oxides from zinc containing slags fuming. The study of the solid state interaction between ZnO and α -Fe₂O₃ is relevant to metallurgy [1 - 18] as well as to the preparation of magnetic materials [19 - 32].

On the basis of the considerable experimental data concerning the interaction of ZnO and α -Fe₂O₃, those between pure oxides as well as during an oxidation roasting of sphalerite, marmatite and zinc concentrates [2,7,9,14,15,17,18,31,], the following general conclusions may be drawn:

The quantity of ZnFe₂O₄ being formed depends little on the temperature and the duration of roasting. It depends mainly on the content and the phase of iron in the concentrate [1].

The presence of CaO, CuO, PbO, Al₂O₃ in the charge formation materials, also affects the ferrite formation process [4,6,7,10,12,22,25,30,33,34]. The magnetic permeability of ZnFe₂O₄ is increased with 1.02 - 1.08 H/m, at temperature of obtaining 950 - 1150 °C. The degree of inversion of the ferrite being obtained is $\delta \sim 0.1$.

The degree of ferrite formation is affected by: temperature, duration, the ratio ZnO:Fe₂O₃, the quantity of air during the process in a fluidized bed, the content of SO₂ in the gas phase, the size of the particles, the method of contacting, the "pre-history" of the oxides etc. [1]. The difference between the degree of ferrite formation in a fluidized bed and the one in a stationary bed is inconsiderable.

The kinetics of formation of ZnFe₂O₄ is investigated employed a comparatively small number of kinetics equations. The activation energy values obtained differ essentially. The investigations were

carried out mainly with samples prepared by the ceramic method and the obtained results may not be used for explaining the processes proceeding in metallurgy.

Contradictory results regarding the influence of the temperature upon the ferrite formation and various values of the activation energy were obtained during the investigations. Moreover the point concerning the zinc solubility changing with the raising of the temperature of ZnFe_2O_4 preparation, as well as the effect of the admixture oxides on the ferrite formation were not explained to a sufficient degree. A small number of kinetic equations for investigation of the kinetics of ferrite formation were used and complete mathematical treatment of the experimental data was not employed.

The aim of the present work is to continue the investigations [1,30-33] on the interaction between MeO (Me – Zn, Cd, Cu) and $\alpha\text{-Fe}_2\text{O}_3$, and the experimental data obtained to be worked up using various kinetic equations; to calculate the activation energy of the reaction for the temperature ranges 600 – 750 °C and 800 – 1000 °C.

2. EXPERIMENTAL

Zinc, copper and cadmium ferrites are obtained by the conventional ceramic technology. Chemical, DTA and TG analyses, Mössbauer spectroscopy and X-ray phase analysis have been used in the study of intermediate and final products of solid state interactions.

The obtained kinetic data on interactions in the systems under study are processed by means of kinetic equations based on certain models of interactions in solid state. In this series of experiments, the isothermal curves are processed by using the following kinetic equations:

1. Jander's equation:

$$F_1 = (1 - \sqrt[3]{1 - \alpha})^2 = k_1 \cdot \tau$$

2. Ginstling-Brounshtein-equation:

$$F_2 = 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = k_2 \cdot \tau$$

3. Carter equation:

$$F_3 = \frac{z}{z-1} - (1 - \alpha)^{\frac{2}{3}} - \frac{[1 + \alpha(z-1)]^{\frac{2}{3}}}{z-1} = k_3 \cdot \tau$$

where z is the volume ratio of final reacted sphere to initial reacting sphere (1,98 for $\text{ZnFe}_2\text{O}_4\text{:}\alpha\text{-Fe}_2\text{O}_3$).

4. Dunwald-Wagner equation:

$$F_4 = \ln \frac{6}{\pi^2(1-\alpha)} = k_4 \cdot \tau$$

5. Tamman equation:

$$F_5 = 1 - \sqrt[3]{1-\alpha} = k_5 \cdot \ln \tau$$

6. Kröger-Ziegler equation:

$$F_6 = (1 - \sqrt[3]{(1-\alpha)^2}) = k_6 \cdot \ln \tau$$

7. Ginstling-Brounshtein-Hulbert equation:

$$F_7 = 1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = k_7 \cdot \ln \tau$$

8. Carter-Valensi-Hulbert equation:

$$F_8 = \frac{z}{z-1} - (1-\alpha)^{\frac{2}{3}} - \frac{[1 + \alpha(z-1)]^{\frac{2}{3}}}{z-1} = k_8 \cdot \ln \tau$$

9. Kolmogorov-Erofeev equation:

$$\alpha = 1 - \exp.(-k \cdot \tau^n)$$

k – apparent rate constant, n – kinetic parameter.

3. RESULTS AND DISCUSSION

The kinetics of ferrite formation in the MeO – Fe₂O₃ systems in the temperature range of 650-950 °C has been studied. Mössbauer spectra of samples prepared under various time and temperature conditions have been obtained.

The results obtained indicate that the increase of temperature from 650 to 850 °C has a considerable effect on the degree of ferrite formation. At 650 °C the yield of CdFe₂O₄ is insignificant. At 950 °C, after 15 min of interaction, the degree of ferrite formation α reaches the value of 0,985. On increasing

the temperature of heating, the effect of time decreases. It is considerable at 750 °C and is of almost no consequence at 950 °C.

The obtained Mössbauer spectra were processed by means of a personal computer programme, and the values of the following hyperfine interactions were determined: isomer shift (IS), quadrupole splitting (QS) and intrinsic magnetic field (H_{eff}) for $\alpha\text{-Fe}_2\text{O}_3$ and CuFe_2O_4 . The summarized data for the three ferrites are presented in Table 1.

At room temperature, the Mössbauer spectra of $\alpha\text{-Fe}_2\text{O}_3$ and the cubic CuFe_2O_4 are sextets, and those of ZnFe_2O_4 and CdFe_2O_4 are doublets. All ferrites were obtained by quenching into water down from 1000 °C.

The obtained kinetic data on interactions in the systems under study are processed by means of kinetic equations based on certain models of interactions in solid state [4]. In this series of experiments, the isothermal curves are processed by using the kinetic equations of: Jander (F_1); Ginstling-Brounshtein (F_2); Dunvald-Wagner (F_3); Tamman (F_4); Kröger-Ziegler (F_5); Ginstling-Brounshtein-Hulbert (F_6) and Kolmogorov-Erofeev (F_7). The processing procedure is described in details in [31]. The results of kinetic curve linearization by the first six equations for the $\text{CdO-Fe}_2\text{O}_3$ system are presented on Fig. 1. The calculated kinetic parameters of ferrite formation in the studied three systems are summarized in Table 2.

Table 1. Hyperfine interactions in ferrites and $\alpha\text{-Fe}_2\text{O}_3$

Compound	IS, mm/s ($\pm 0,01$)	QS, mm/s ($\pm 0,01$)	H_{eff} ($\pm 1,0$)
ZnFe_2O_4	0.34	0.32	0
CuFe_2O_4 (cubic)	0.35	0.11	471
CdFe_2O_4	0.36	0.79	0
$\alpha\text{-Fe}_2\text{O}_3$	0.44	-0.25	516

Table 2. Values of k_0 and E_a obtained by different equations

Interaction	Temperature range, °C	Equation	k_0	E_a , kJ/mol
$\text{ZnO}+\text{Fe}_2\text{O}_3 \rightarrow \text{ZnFe}_2\text{O}_4$	600 – 750	F_1	$1,47 \times 10^3$	284
	600 – 750	F_2	$6,45 \times 10^2$	278
	800 - 1000	F_6	$3,16 \times 10^3$	112
$\text{CuO}+\text{Fe}_2\text{O}_3 \rightarrow \text{CuFe}_2\text{O}_4$	850 - 1000	F_4	$6,40 \times 10^3$	117
$\text{CdO}+\text{Fe}_2\text{O}_3 \rightarrow \text{CdFe}_2\text{O}_4$	750 – 950	F_4	$1,41 \times 10^5$	55
	750 - 950	F_6	$9,48 \times 10^3$	68

Notable is the great difference in the activation energy values, E_a , for CdFe_2O_4 as compared to those for ZnFe_2O_4 and CuFe_2O_4 . Comparison of kinetic data of the three systems shows that more complete interaction between CdO and Fe_2O_3 occurs at lower temperatures, which leads to lower E_a values.

This explains observed reduced solubility of cadmium at the leaching of zinc calcine in certain periods of the work of zinc production plant in KCM S.A., Plovdiv, Bulgaria. The main ferrite (ZnFe_2O_4), which is obtained during the roasting of zinc concentrates may include also some amounts of Cu, Cd, Mg, Mn and others.

At room temperature, the Mössbauer spectrum of zinc calcine has one doublet. Its Mössbauer parameters are: IS – 0.34 mm/s; QS – 0.36 mm/s. They are similar to the obtained for a pure ZnFe_2O_4 (Table.1).

Differences, which are observed in the solubility of zinc from calcine, obtained under different conditions of roasting, can be explained as use of the terms, introduced by us: "primary" ZnFe_2O_4 , obtained by the oxidation of marmatite and "secondary" ZnFe_2O_4 , formed as a result of solid phase interaction of ZnO (from oxidation of $\beta\text{-ZnS}$) and Fe_2O_3 (from oxidation of FeS_2). The conditions of roasting and their variety affect mainly on the obtaining of the "secondary" ZnFe_2O_4 , as in the same time, they are less essential factor in the forming of "primary" ZnFe_2O_4 .

A typical example of the obtaining of a significant amount of "primary" zinc ferrite is the roasting of zinc concentrate of Serbia, with following chemical composition (in mass %): Zn - 47.16; S - 32.85; Cu - 1.52; Cd - 0.36; Co - 0.01; Ni - 0.006; Al_2O_3 - 0.35; Pb - 0.85; Fe – 13.55; SiO_2 - 2.2; As - 0.007; Sb – 0.001; CaO - 0.45; MgO - 0.09 .

It is evident that the content of iron is very high. For the practice of oxidative roasting and the ability to obtain "primary" or "secondary" zinc ferrite is of importance how is distributed iron between the three main phases - ZnS, FeS_2 and CuFeS_2 . For this purpose, a study is conducted with the help of X-ray phase analysis and Mössbauer spectroscopy (Figs. 1 and 2).

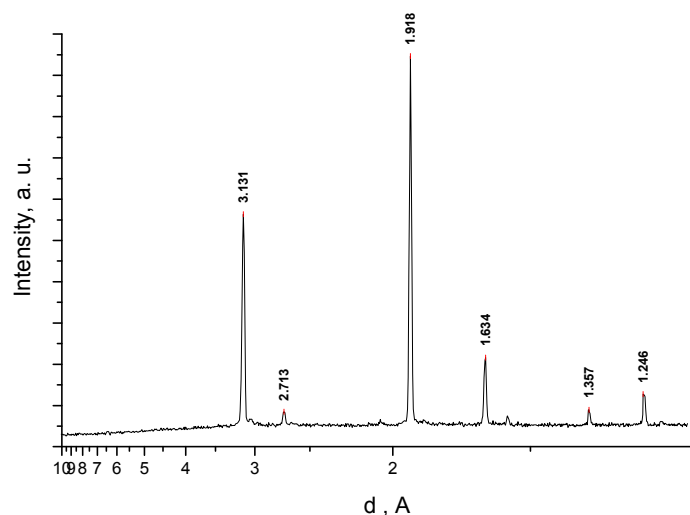


Fig.1. X-ray diffraction pattern of zinc sulfide concentrate

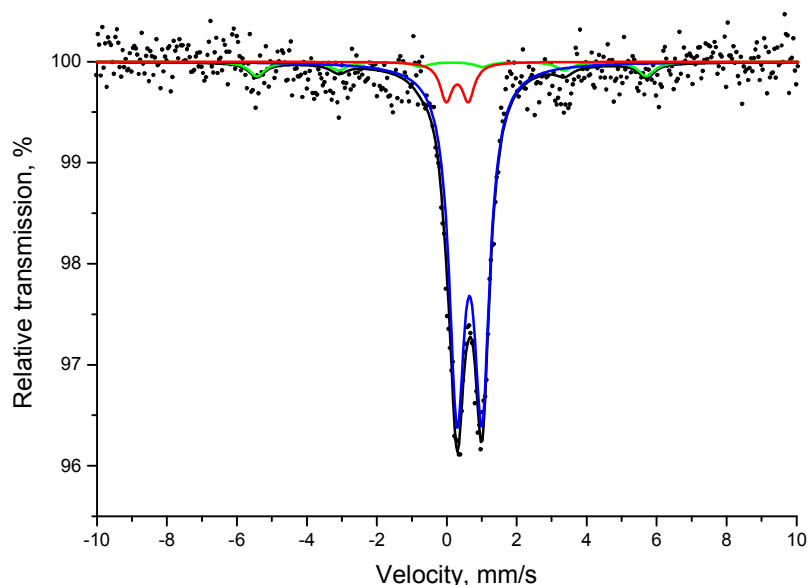


Fig.2. Mössbauer spectrum pattern of zinc sulfide concentrate

The studied concentrate represents a sample with a high crystallinity and has a major phase sphalerite β -ZnS, $a = 0.5421$ nm, showing content of structural iron. Additional phases PbS, CuFeS₂ and FeS₂ are identified.

According to chemical composition (13.15 % Fe) and the presence only of traces of CuFeS₂, FeS₂ and PbS can be concluded that the most iron ions are structurally included in sphalerite.

In Mössbauer spectrum two doublet components are observed with superfine parameters $IS = 0.62$ mm/s and $QS = 0.2$ mm/s and $IS = 0.30$ mm/s and $QS = 0.62$ mm/s and third component sextet. The first superfine parameters are typical respectively for a mineral zinc concentrate with significant quantity of iron ions, included in the structure of sphalerite. The structural iron in sphalerite do not form a separate phase, but they isomorphously replace part of tetrahedronic coordinated zinc ions in the structure of sphalerite.

The second doublet belongs to the pyritic phase.

The calculated superfine parameters of sextet component are $IS = 0.21$ mm/s, $QS = 0$ mm/s and $H_{\text{eff}} = 34.627$ T. They are typical for the presence of chalcopyrite phase CuFeS₂.

The defined content of iron-containing phases according to the Mössbauer analysis is CuFeS₂ – 3.49 % and FeS₂ – 2.25 %. The rest iron is included in crystalline structure of ZnS, and the calculated formula is: Zn_{0.80}Fe_{0.20}S. The content of the mixed zinc-iron sulfide is 88.48 %.

The results obtained for the content of iron-containing phases may with confidence to claim that almost the whole quantity of iron in oxidative roasting of the concentrates will forms with zinc the phase ZnFe₂O₄. This is especially adversely by the classical two-step scheme of leaching of zinc calcine - about 12 % of zinc from the concentrate will remain insoluble and will pass in the zinc cake. This will lead to a low level of direct extraction and increasing the quantity of the obtained cake. The latest requires additional costs for its processing by Waelts-process or modern hydrometallurgical methods - jarosite, hematite or goethite - for extraction of zinc remained in cake.

CONCLUSIONS

1. Mössbauer spectroscopy in combination with X-ray diffraction analysis were used to study solid state interactions in the systems: MeO - Fe₂O₃ (Me – Zn, Cd, Cu).
2. The obtained kinetic data on interactions in the systems under study are processed by means of kinetic equations based on certain models of interactions in solid state. In this series of experiments, the isothermal curves are processed by using the kinetic equations of: Jander; Ginstling-Brounshtein Dunvald-Wagner; Tamman; Kröger-Ziegler; Ginstling-Brounshtein-Hulbert and Kolmogorov-Erofeev.
3. The calculated values of kinetic parameters k_0 and E_a obtained by different equations are presented.
4. The obtained results have been used to explain some processes taking place at roasting of zinc concentrates in fluidized bed and during the leaching of the obtained zinc calcine.

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