

## STUDY OF SOLID STATE INTERACTIONS IN THE SYSTEMS $ZnFe_2O_4 - CaO$ , $ZnFe_2O_4 - MgO$ AND ZINC CAKE WITH CaO AND MgO

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### Abstract

The solid state interactions of CaO and MgO with synthetic and industrial  $ZnFe_2O_4$  (in zinc cake) have been studied using chemical, XRD analysis and Mössbauer spectroscopy. The exchange reactions in the systems  $ZnFe_2O_4 - CaO$  and  $ZnFe_2O_4 - MgO$  have been investigated in the range of 850–1200 °C and duration up to 180 min. It has been established that  $Ca^{2+}$  and  $Mg^{2+}$  ions exchange  $Zn^{2+}$  in ferrite partially and the solubility of zinc in a 7% sulfuric acid solution increases. The possibilities for utilization of the obtained results in zinc hydrometallurgy have been discussed.

Keywords:  $ZnFe_2O_4$ , Zn cake, CaO, MgO, XRD analysis, Mössbauer spectroscopy, leaching

### 1. Introduction

Natural zinc ores are polymetallic and their resulting zinc concentrates, except Zn, contain various impurities such as Fe, Pb, Cu, Cd,  $SiO_2$ , CaO, MgO, etc. [1-4]. When roasting zinc concentrates ZnO and  $Fe_2O_3$  are obtained from the oxidation of ZnS,  $FeS_2$  and  $mZnS.nFeS$ . These oxides are in close contact and zinc ferrite ( $ZnFe_2O_4$ ) forms as a result of the solid state reaction between them [5-8]. According to the studies of H. G. El-Shobaky and N. R. E. Radwana [9-11] the interaction of ZnO and  $Fe_2O_3$  occurs at temperatures starting at 600 °C and increases to 900 °C with the formation of crystalline  $ZnFe_2O_4$ .

This process is a major reason for the decrease in direct leaching of zinc from zinc calcine due to the insolubility of  $ZnFe_2O_4$  in diluted  $H_2SO_4$  confirmed by M. R. C. Ismael, M. Loan et al. [12, 13]. This creates an important technological problem in hydrometallurgical plants [14], and thus requires the development of various methods for dilution or reduction of zinc ferrite. Although the hydrometallurgical method is essential for the production of zinc [15], one of the pyrometallurgical methods used is the Waeltz-process which is a reductive thermal treatment of zinc cakes, semi-finished products, zinc oxide ores, etc. [16,17].

Research conducted by M. R. C. Ismael, G. Ye et al. [18,19] shows that the addition of raw materials or intermediate products containing CaO to the Waeltz charge improves the performance of the Waeltz-process, as the total degree of leaching of zinc

increases. It is known that ions of calcium and magnesium can compete with and displace zinc ions from oxide mixtures, leading to reduced obtaining of zinc ferrite [20].

From the data presented in the literature it is not sufficiently clear what the influence of various factors (temperature, time, ratio of oxides, etc.) is on the exchange reactions between  $ZnFe_2O_4 - CaO$  (MgO). This creates problems in assessing the effectiveness of the treatment of certain materials with a high content of CaO and MgO, including semi-finished products from non-ferrous metallurgy. In this context, the aim of this study is a more detailed investigation of interactions in the  $ZnFe_2O_4 - CaO$  and  $ZnFe_2O_4 - MgO$  systems (zinc cake – CaO or MgO), and the discussion of the obtained results in terms of their application in zinc hydrometallurgy.

### 2. Experimental

Zinc ferrite used in the study was obtained in laboratory conditions by ceramic technology [21].

For its synthesis ZnO (p.a.) and  $Fe_2O_3$  (p.a.) of the company MERCK, Germany are used. A mixture of equalmol ratios of starting oxides ZnO and  $Fe_2O_3$  is prepared and mixed for 180 min in an alcohol medium using ball mill to obtain a homogeneous mass. After drying at 120 °C the samples are heated in a muffle furnace for 10 h at 1000 °C. The resulting solid mass is crushed and sieved through a 0.2 mm sieve. In this way pure  $ZnFe_2O_4$  is obtained, which is proved by X-ray diffraction analysis (XRD) and Mössbauer

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spectroscopy (MS) [22]. The zinc ferrite crystallizes in cubic symmetry and the calculated parameter of the crystal lattice based on XRD analysis is 8.442 Å, which is much closer to the data presented by A. Z. Juhasz, et al. [23-25].

The chemical composition of the used zinc cake is (in mass %): Zn-20.1; Pb-7.77; Cd-0.7; FeO-27.25; CaO-3.3; MgO-0.82; SiO<sub>2</sub>-7.5; Al<sub>2</sub>O<sub>3</sub>-1.75; Stot.-4.76; Sso4-4.6; Ss-0.16; Cl-0.22; F-0.052; As-0.23; Se-23 g/t; Te-36 g/t; Ge-17 g/t; Sb-290 g/t.

Zinc cake was characterized using XRD analysis (Figure 1). It is a relatively crystal sample whose X-ray pattern includes lines of ZnFe<sub>2</sub>O<sub>4</sub>, PbSO<sub>4</sub>, ZnSO<sub>4</sub>.xH<sub>2</sub>O and SiO<sub>2</sub>. Diffraction peaks belonging to the main phase in the zinc cake (ZnFe<sub>2</sub>O<sub>4</sub>) are (in Å): 4.862; 2.975; 2.536; 2.429; 2.105; 1.719; 1.621; 1.488; 1.333; 1.284. Designated phase composition of the crystalline phases based on XRD analysis is as follows (in mass %): ZnFe<sub>2</sub>O<sub>4</sub> – 58.7; ZnSO<sub>4</sub>.xH<sub>2</sub>O – 14.8; PbSO<sub>4</sub> – 7.7; SiO<sub>2</sub> – 6.3; CaSO<sub>4</sub> – 6.1, other – 6.4.

To remove ZnSO<sub>4</sub>.xH<sub>2</sub>O and possibly small amounts of ZnO in the cake, it is pre-extracted with a 7% sulfuric acid solution for 60 min and then repeatedly washed with warm water. Thus ZnFe<sub>2</sub>O<sub>4</sub> remains a major phase of zinc in the cake.

The interactions in the ZnFe<sub>2</sub>O<sub>4</sub> – CaO and ZnFe<sub>2</sub>O<sub>4</sub> – MgO (zinc cake - CaO and zinc cake - MgO) systems were studied by thermal treatment of samples in a tube furnace in air atmosphere. The main factors affecting the interaction (temperature and duration of treatment) vary in the range 850-1200 °C and 15-120 min. Before thermal treatment ZnFe<sub>2</sub>O<sub>4</sub> mixes with CaO and MgO at ratios ZnFe<sub>2</sub>O<sub>4</sub> - CaO

(MgO) = 1:1 and 1:2 [26].

The used CaO and MgO are of technical purity. The behavior of CaO when heated up to 1000 °C was examined by DTA and TGA analysis. The DTA curve obtained shows that the initial CaO undergoes two endothermic processes in the temperature ranges of 450-530 °C and 650-820 °C. According to data from our studies and from researches conducted by B. K. Shahraki et al. [27] both processes are accompanied by a reduction in the mass of the sample. The first process is due to the dissociation of Ca(OH)<sub>2</sub>, and the second – to the dissociation of CaCO<sub>3</sub>. Increasing the purity of CaO was accomplished by heating the required amount of CaO in a muffle furnace at 900 °C. The obtained DTA curve of the calcined sample shows that Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> are fully dissociated and passed into CaO.

The mixtures of zinc cake (in which zinc is mainly in the form of zinc ferrite) with CaO and MgO were obtained similarly. The mass of each sample is 5 g and ceramic crucibles are used for the thermal treatment. After thermal treatment the samples were analyzed for free ZnO by chemical analysis and subjected to XRD analysis and Mössbauer spectroscopy.

The obtained ferrites according their composition and structure are also suitable as catalysts for hydrogen production.

The X-ray diffraction analysis was carried out with an apparatus "TUR-M62" (Dresden, Germany) equipped with a computer-controlled HZG-4 goniometer with Co-K<sub>α</sub> radiation and Bragg-Brentano geometry. Data base (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used for the phase

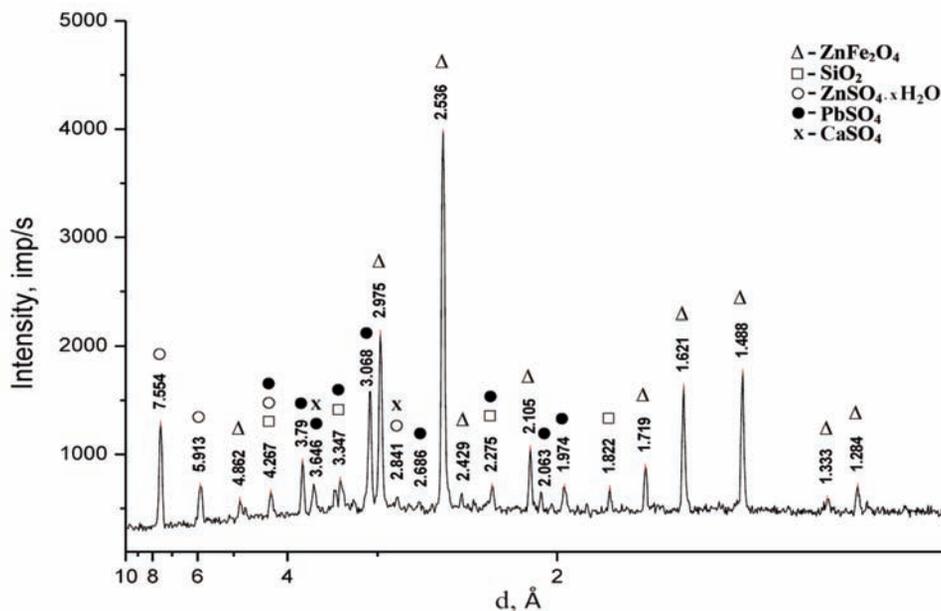


Figure 1. X-Ray pattern of zinc cake

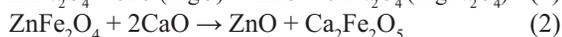
identification.

Mössbauer spectra (MS) were obtained at room temperature (RT) with a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working at a constant acceleration mode. A  $^{57}\text{Co}/\text{Cr}$  (activity  $\cong 45$  mCi) source and an  $\alpha\text{-Fe}$  foil standard were used. The experimentally obtained spectra were treated using the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field ( $H_{\text{eff}}$ ) as well as the line widths (FWHM) and the relative weight (G) of the partial components of the spectra were determined.

### 3. Results and Discussion

#### 3.1. Chemical analysis

The obtained ZnO according to the following exchange reactions can be quantified through a chemical analysis after products leaching:



In this case, as a quantitative measure of the degree of interaction between zinc ferrite and oxides is accepted the degree of leaching ( $\eta$ ) of zinc in the 7% solution of sulfuric acid.

$$\eta = (G_{\text{Zn}} / G_{\text{Zn}}^0) \cdot 100 \text{ (\%)},$$

where:

$G_{\text{Zn}}$  – mass of zinc passed into the solution determined by chemical analysis, g

$G_{\text{Zn}}^0$  – mass of zinc in the initial sample, g

Only 0.3% of zinc can be leached from the initial zinc ferrite into the solution of sulfuric acid. The increase of this quantity after solid state interaction indicates that new amounts of free zinc oxide are obtained in the studied systems.

The results of the influence of temperature and the ratio of ferrite and oxides in the  $\text{ZnFe}_2\text{O}_4 - \text{CaO}$  and  $\text{ZnFe}_2\text{O}_4 - \text{MgO}$  systems on the degree of extraction of zinc in 7%  $\text{H}_2\text{SO}_4$  solution are presented in Figs. 2

and 3.

Better results are obtained at a ratio of  $\text{ZnFe}_2\text{O}_4 - \text{CaO} = 1:2$ , and varying effects of temperature are observed. At 850 °C, the difference in the amount of free zinc oxide is considerably less than at 1200 °C for another ratio of ferrite and calcium oxide. Increasing the temperature has a positive effect on enhancing the solubility of zinc in a 7% sulfuric acid solution in all ratios of zinc ferrite and calcium oxide.

It is apparent in the  $\text{ZnFe}_2\text{O}_4 - \text{MgO}$  system that raising the temperature and increasing the quantity of the magnesium oxide has a favorable effect on the amount of soluble zinc in a 7% sulfuric acid solution. This indicates that  $\text{MgFe}_2\text{O}_4$  has been obtained in the studied system. Investigations made by G. A. El-Shobaky and A. A. Mostafa [10] also show that increasing the temperature up to 1100 °C is conducive to the formation of  $\text{MgFe}_2\text{O}_4$ .

In the temperature range of 850 – 1000 °C, the influence of the higher content of MgO is negligible. Above 1000 °C there is a measurable increase in the rate of recovery of zinc as the amount of MgO in the system is increased.

From the results presented it is obvious that the degree of substitution of ZnO in zinc ferrite with CaO and MgO can reach 50-80% depending on the conditions of thermal treatment.

The influence of the duration of the thermal treatment as well as of the temperature (Figs. 4 and 5) clearly shows that both factors are beneficial in increasing the degree of zinc leaching.

Of particular interest in terms of the application of the Waeltz-process is the interaction between  $\text{ZnFe}_2\text{O}_4$  contained in zinc cake with added specific quantities of CaO and MgO. The amount of cakes obtained in zinc production rises sharply (due to high content of iron in zinc concentrates) and they usually contain 15 to 30% Zn and about 25% Fe. This requires their processing, both for economic reasons and because of environmental requirements [28, 29], due to the possibility that the charge for Waeltz-processing may incorporate various intermediate products as well as

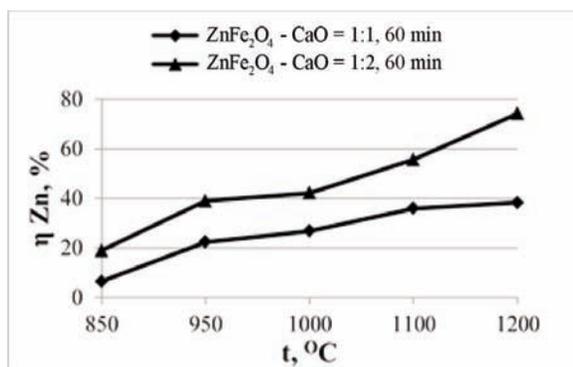


Figure 2. Influence of temperature and ratio  $\text{ZnFe}_2\text{O}_4 - \text{CaO}$  on the degree of leaching of zinc ( $\tau=60$  min)

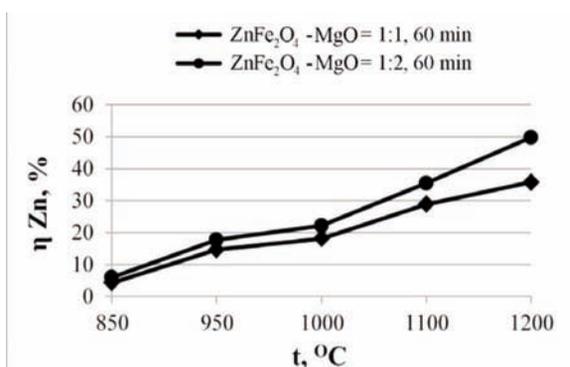


Figure 3. Influence of temperature and ratio  $\text{ZnFe}_2\text{O}_4 - \text{MgO}$  on the degree of leaching of zinc ( $\tau=60$  min)

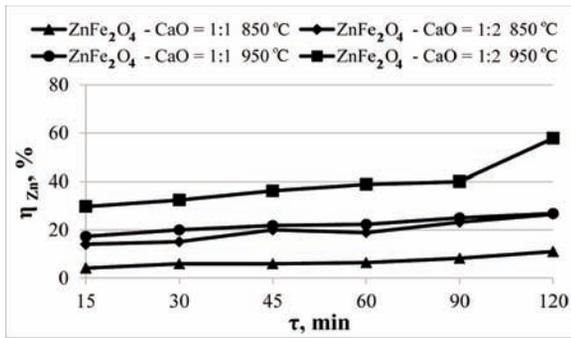


Figure 4. Relationship between the degree of zinc leaching and the time at different temperatures of heating in the system  $\text{ZnFe}_2\text{O}_4 - \text{CaO}$ , 1:1 and 1:2

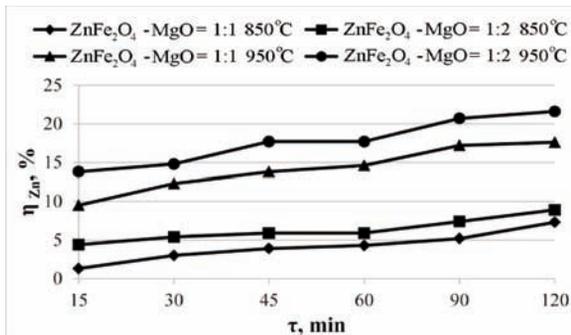


Figure 5. Relationship between the degree of zinc leaching and the time at different temperatures of heating in the system  $\text{ZnFe}_2\text{O}_4 - \text{MgO}$ , 1:1 and 1:2

waste materials containing zinc and also containing oxides and carbonates of calcium and magnesium.

The results of the experiments with industrial zinc cake in which zinc is mainly formed as  $\text{ZnFe}_2\text{O}_4$  are presented in Figs. 6 and 7. It is apparent that as the temperature is raised from 900 to 1200 °C the amount of zinc soluble in 7% sulfuric acid solution is steadily increasing.

Increasing the amount of CaO and MgO in the mixtures with zinc cake also has a positive impact. With the change of the ratios of  $\text{ZnFe}_2\text{O}_4 - \text{CaO}$  and  $\text{ZnFe}_2\text{O}_4 - \text{MgO}$  from 1:1 to 1:2 the degree of zinc leaching is boosted too. However, in this case, the quantitative effect of increasing of calcium and magnesium oxides is not as strong as in the synthetic systems (Figs. 2 and 3).

The results obtained show that CaO (MgO) under the experimental conditions lead to displacement of ZnO from  $\text{ZnFe}_2\text{O}_4$  within 40-70 %. These values are smaller compared with those obtained for mixtures  $\text{ZnFe}_2\text{O}_4 - \text{CaO}$  and  $\text{ZnFe}_2\text{O}_4 - \text{MgO}$ , which can be explained by the presence of impurity components in the zinc cake. They reduce the contact surface between the ferrite and oxides that is a major factor in the course of solid state reactions. It is also clear that the influence of temperature on the degree of implementation of exchange reactions is greater

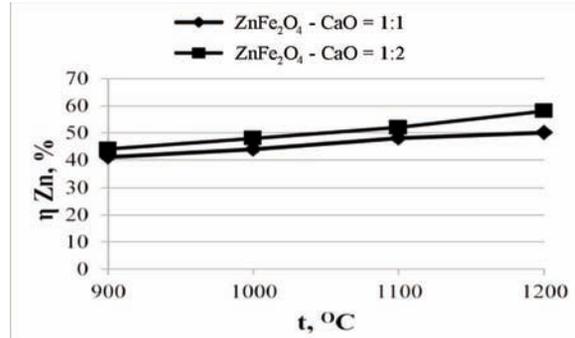


Figure 6. Relationship between the degree of zinc leaching and the temperature and the ratio of  $\text{ZnFe}_2\text{O}_4$  in cake and CaO ( $t=30$  min)

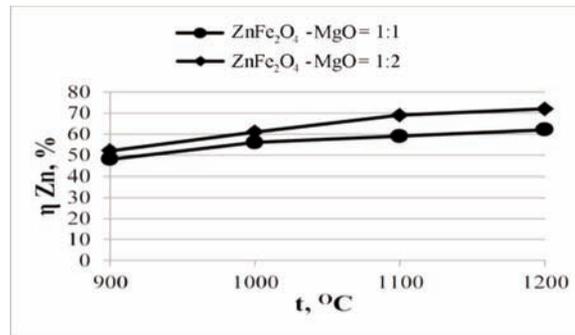


Figure 7. Relationship between the degree of zinc leaching and the temperature and the ratio of  $\text{ZnFe}_2\text{O}_4$  in cake and MgO ( $t=30$  min)

compared to the increase of the thermal treatment duration and the increase of the amounts of CaO and MgO.

### 3.2. X-ray diffraction analysis

The results of XRD analysis of samples from the system  $\text{ZnFe}_2\text{O}_4 - \text{CaO}$ , calcined under different conditions (Figure 8) show that the exchanged reactions occur in varying degrees depending on experimental conditions. Through the obtained results the course of the substitution reaction between  $\text{ZnFe}_2\text{O}_4$  and CaO can be followed.

The lines of  $\text{ZnFe}_2\text{O}_4$  [22] are mainly observed in the X-ray pattern of the sample presented in Figure 8a. The temperature of thermal treatment is relatively low (900 °C) and the time (30 min) is insufficient for a significant interaction between the ferrite and oxide. Confirmation that this reaction has commenced anyway is the observed peak with  $d = 2.468 \text{ \AA}$  which corresponds to the most intense line of the obtained ZnO.

When the interaction temperature is increased the degree of the process of replacement of ZnO by CaO in  $\text{ZnFe}_2\text{O}_4$  changes significantly. This is evident from the X-ray pattern of sample b (Figure 8b) – its most intense peak of ZnO has increased considerably. Similar results are presented in a study by S. K.

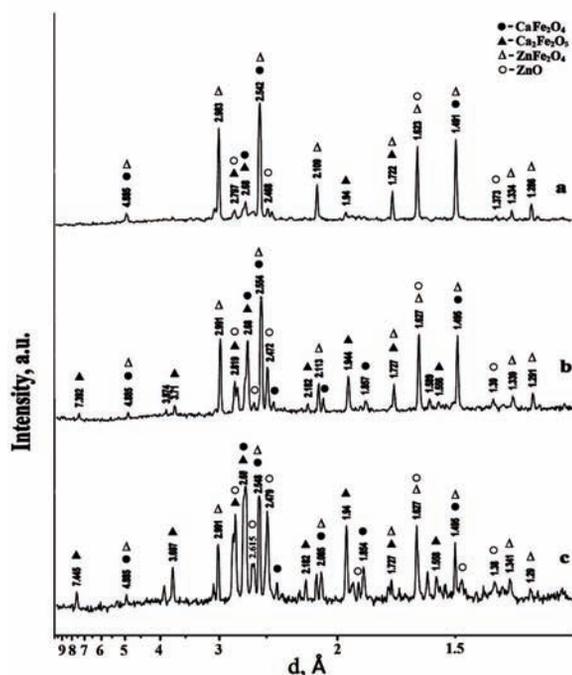


Figure 8. X-ray patterns of the samples from the  $ZnFe_2O_4$  –  $CaO$  system: **a** - 900 °C, 30 min, 1:1; **b** - 1200 °C, 30 min, 1:1; **c** - 1200 °C, 30 min, 1:2

Pardeshi and R. Y. Pawar [30].

From the obtained X-ray patterns and their analysis it can be concluded that the interaction between  $ZnFe_2O_4$  and  $CaO$  forms a mixture of calcium ferrites. The lines of both monocalcium ( $CaFe_2O_4$ ), and dicalcium ferrite ( $Ca_2Fe_2O_5$ ) are present in the X-ray patterns and their obtaining is probably according to reactions (1) and (2). The appearance of new diffraction peaks (2.68 Å; 1.944 Å; 1.857 Å etc.) can be attributed to the calcium ferrites being obtained –  $CaFe_2O_4$  and  $Ca_2Fe_2O_5$  [24].

In sample c (Figure 8c), where the amount of  $CaO$  is increased, a great flow of replacement reactions are observed, as evidenced by intense lines of calcium ferrites ( $d = 2.68$  Å) and the resulting  $ZnO$  ( $d = 2.479$  Å) from the exchange interaction.

In our study the obtaining of  $Ca_2Fe_2O_5$  through the exchange reaction method corresponds to research conducted by G. Ye, E. Burstrom and others [31]. The acquiring of  $Ca_2Fe_2O_5$ , however, is not favorable in terms of the fact that it includes 2 moles  $CaO$  that displace only 1 mole  $ZnO$  from  $ZnFe_2O_4$ . In this case, in order to obtain a high degree of substitution reaction, a considerable excess of  $CaO$  should be utilized.

Similar results are observed when using  $MgO$  to exchange  $ZnO$  from  $ZnFe_2O_4$ . In this instance, the lines of  $ZnFe_2O_4$  ( $MgFe_2O_4$ ) and  $ZnO$  can be seen in the ferrite.

The results obtained (Fig.9) for of the interaction between  $ZnFe_2O_4$  in the zinc cake and  $CaO$  ( $MgO$ ) confirm the above conclusion for the complexity of the processes involved. The observed lines obtained for  $Ca_2Fe_2O_5$ ,  $CaFe_2O_4$  and  $MgFe_2O_4$  are less pronounced. The lines of the obtained  $ZnO$  at the X-rays patterns are not so clearly manifested as in the pure systems. In our opinion, the probable explanation of this fact is the fault of the impurity components, mainly  $SiO_2$ .

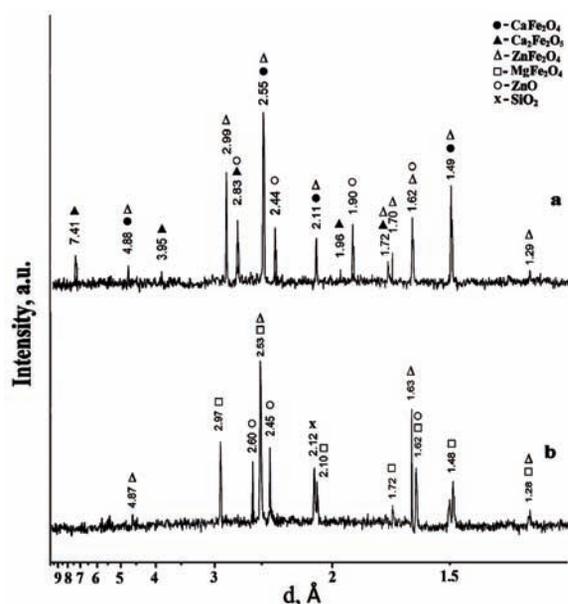


Figure 9. X-ray patterns of the samples from zinc cake –  $CaO$  mixture (**a**); zinc cake –  $MgO$  mixture (**b**); (1200 °C, 60 min,  $ZnFe_2O_4$  –  $CaO$  ( $MgO$ ) = 1:2)

The zinc ferrite is a main phase in the zinc cake. When the zinc content is about 20-25% (in the Waelz process the requirement is the zinc content to be above 22%) the zinc ferrite amount is 73-92% of the total mass of the cake. The presence of  $PbSO_4$  is a few percent (3-8%) which at the temperature of the Waelz process (1100-1300 °C) dissociates and the resulting  $PbO$  is partially reduced and passes into gas phase.

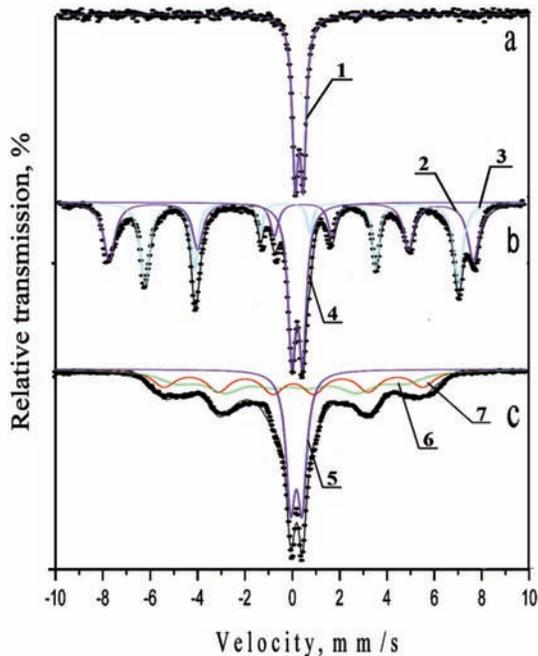
There are always small amounts of  $CaO$  and  $MgO$  in the zinc cake, which is favorable for the flow of the processes of reduction of zinc ferrite.

The presence of significant quantities of  $SiO_2$  would block and combine  $CaO$  and  $MgO$  as silicates. In this case, the  $SiO_2$  content is 7.5%, thereby reducing the effect of exchange reactions 1 and 2.

### 3.3. Mössbauer study

In order to fully clarify the reactions occurring in the studied systems some of the samples obtained by heating were investigated using Mössbauer spectroscopy.

The Mössbauer spectrum of the initial mixture of  $\text{ZnFe}_2\text{O}_4$  and  $\text{CaO}$  is a doublet (Fig. 10a). There is only one phase of iron –  $\text{ZnFe}_2\text{O}_4$ , displaying the typical parameters of hyperfine interactions (Table 1): isomer shift (IS) to the  $\alpha\text{-Fe}$  is  $0.34 \pm 0.01$  mm/s and quadrupole splitting (QS) is  $0.36 \pm 0.02$  mm/s, both of which come close to data presented by H. Ehrhardt and others [32]. No residual lines of the  $\text{Fe}_2\text{O}_3$  sextet are seen, which also confirms the full course of the



**Figure 10.** Mössbauer spectra: **a** -  $\text{ZnFe}_2\text{O}_4$  -  $\text{CaO}$ , 1:2, initial mixture; **b** -  $\text{ZnFe}_2\text{O}_4$  -  $\text{CaO}$ , 1:2, 1h, 1200 °C; **c** -  $\text{ZnFe}_2\text{O}_4$  -  $\text{MgO}$ , 1:2, 1h, 1200 °C 1 -  $\text{ZnFe}_2\text{O}_4$ ; 2, 3 -  $\text{CaFe}_2\text{O}_5$ ; 4 -  $\text{CaFe}_2\text{O}_4$ ; 5 -  $(\text{Mg}, \text{Zn})\text{Fe}_2\text{O}_4$ ; 6, 7 -  $(\text{Mg}, \text{Zn})\text{Fe}_2\text{O}_4$

solid state reaction between the initial  $\text{ZnO}$  and  $\text{Fe}_2\text{O}_3$  during the synthesis of  $\text{ZnFe}_2\text{O}_4$ .

The Mössbauer spectrum of sample  $\text{ZnFe}_2\text{O}_4$  -  $\text{CaO}$  (1:2, 1h, 1200 °C) includes both a doublet and a sextet part (Figure 10b). The doublet (Db) has high-spin parameters of iron ions in the third degree of oxidation which differ from those of zinc ferrite in the initial mixture - more quadrupole splitting and line width.

This component can be associated with the obtaining of both  $\text{ZnFe}_2\text{O}_4$  and  $\text{CaFe}_2\text{O}_4$ . D. Hirabayashi et al. [33] have shown the possibility of jointly producing two types of calcium ferrite -  $\text{CaFe}_2\text{O}_4$  and  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , respectively having doublet and sextet Mössbauer spectrums.

Referenced data for the quadrupole splitting of the doublet associated with  $\text{CaFe}_2\text{O}_4$  are close to the data for the sample obtained in our investigation. On the other hand, the line width of the doublet component is greater than that determined for the zinc ferrite in the initial mixture. Therefore, it can be assumed that the resulting quadrupole doublet we obtained is a superposition of the spectra of residual zinc ferrite and synthesized calcium ferrite ( $\text{CaFe}_2\text{O}_4$ ). Both sextet components having parameters of iron ions in the third degree of oxidation in tetrahedral (Sx2) and octahedral (Sx1) coordination are associated with calcium ferrite of type  $\text{Ca}_2\text{Fe}_2\text{O}_5$ .

In sample  $\text{ZnFe}_2\text{O}_4$  -  $\text{MgO}$  (1:2, 1h, 1200 °C) - Figure 10c, the experimentally obtained spectrum is complicated due to relaxation phenomena - strongly overlapping lines that differ significantly from the theoretical Lorentz shape, violation of 3:2:1 ratio of 6 (1): 5 (2): 4 (3) line in the sextet. The widths of the lines are several times larger than that of the standard, as they include relaxation sub-sextets with different discrete values of the parameters.

The values of the effective internal magnetic field determined for both sextet components are

**Table 1.** Hyperfine parameters of the studied samples

Samples	Components	IS, mm/s $\pm 0.01$	QS, mm/s $\pm 0.02$	$H_{\text{eff}}$ , T	FWHM, mm/s	G, %
$\text{ZnFe}_2\text{O}_4$ - $\text{CaO}$ 1:2, Initial mixture	Db - $\text{Fe}^{3+}_{\text{octa}}$ - $\text{ZnFe}_2\text{O}_4$	0.35	0.34	-	0.3	100
$\text{ZnFe}_2\text{O}_4$ - $\text{CaO}$ 1:2, 1 h, 1200 °C	Sx1 - $\text{Fe}^{3+}_{\text{octa}}$ - $\text{Ca}_2\text{Fe}_2\text{O}_5$	0.35	-0.25	48.7	0.53	36
	Sx2 - $\text{Fe}^{3+}_{\text{tetra}}$ - $\text{Ca}_2\text{Fe}_2\text{O}_5$	0.19	0.35	41.9	0.35	36
	Db - $\text{Fe}^{3+}_{\text{octa}}$ - $\text{CaFe}_2\text{O}_4$ , $\text{ZnFe}_2\text{O}_4$	0.35	0.47	-	0.4	28
$\text{ZnFe}_2\text{O}_4$ - $\text{MgO}$ 1:2, 1 h, 1200 °C	Sx1 - $\text{Fe}^{3+}_{\text{octa}}$ - $(\text{Mg}, \text{Zn})\text{Fe}_2\text{O}_4$	0.21	0	34.2	1.15	33
	Sx2 - $\text{Fe}^{3+}_{\text{tetra}}$ - $(\text{Mg}, \text{Zn})\text{Fe}_2\text{O}_4$	0.11	0	30.2	1.91	38
	Db - $\text{Fe}^{3+}_{\text{octa}}$ - $(\text{Mg}, \text{Zn})\text{Fe}_2\text{O}_4$ , $\text{ZnFe}_2\text{O}_4$	0.34	0.49	-	0.47	29

significantly smaller than those for pure magnesium ferrite, which are also established by T. K. Pathak, N. H. Vasoya et al. [34]. This can be explained by the formation of mixed magnesium-zinc ferrites, in which strong relaxation phenomena are manifested.

The doublet component has parameters of iron in the third degree of oxidation and quadrupole splitting similar to that of zinc ferrite. It may therefore be associated with the presence of unreacted initial zinc ferrite. Such values were also obtained by H. Ehrhardt, S. J. Campbell et al. [35] for zinc ferrite with different inversion than that of the standard pure zinc ferrite. Because of that the doublet component can be also attributed to a zinc ferrite with modified inversion, due to the involvement of magnesium ions in its crystal lattice.

Based on the interpretation of the sextet and doublet components it can be concluded that mixed magnesium-zinc ferrites have been obtained with varying degrees of substitution, but the presence of residual zinc ferrite cannot be excluded either.

The performed investigations show the possibility to improve the indicators of the reduction processes involving  $ZnFe_2O_4$ , CaO and MgO in processed cakes and other semi-finished products due to substitution reactions between ferrite and oxides. This gives rise to claims that the raw material base for the Waelz-process is being expanded, leading to economic benefits, as well as more environmental-friendly solutions and sustainable development.

#### 4. Conclusions

1. It was established that CaO and MgO substitute ZnO from synthetic  $ZnFe_2O_4$  and zinc ferrite included in zinc cake – residue from zinc hydrometallurgy.

2. The amount of the obtained free ZnO increases with the increasing of temperature, duration and amount of used CaO and MgO. The most favorable results were obtained with a ratio of  $ZnFe_2O_4$  - CaO = 1:2,  $t = 1200\text{ }^\circ\text{C}$  and duration of 60 min, where the maximum amount of extracted free ZnO is 74.1%. Under the same conditions and ratio using MgO the obtained free ZnO is 49.7%.

3. On the basis of XRD analysis and Mössbauer spectroscopy it can be concluded that both  $CaFe_2O_4$  and  $Ca_2Fe_2O_5$  form as a result of the solid state interactions in the  $ZnFe_2O_4$ -CaO system.

4. Mixed zinc-magnesium ferrites are obtained in the exchange reaction between MgO and  $ZnFe_2O_4$  which is confirmed by Mössbauer spectroscopy.

5. The results obtained give grounds to argue that the use of CaO and MgO (or intermediate products containing them) in the Waelz-process can lead to a more complete and more rapid reduction of zinc ferrite with a corresponding improvement of technical and economic parameters of the process.

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#### References

- [1] B. S. Boyanov, M. P. Sandalski and K. I. Ivanov, World Academy of Science, Engineering and Technology, 73 (2011) 420-427.
- [2] S. Nikolov, B. Boyanov, N. Moldovanska and R. Dimitrov, Thermochemica Acta, 380 (2001) 37-41.
- [3] P. Djordjevic, N. Mitevska, I. Mihajlovic, D. Nikolic, D. Manasijevic and Z. Zivkovic, J. Min. Metall. Sect. B-Metall., 48 (1) (2012) 143-151.
- [4] M. Sokić, B. Marković, V. Matković, D. Živković, N. Štrbac, J. Stojanović, J. Min. Metall. Sect. B-Metall. 48 (2) B (2012) 185-195.
- [5] A. Blonska-Tabero, M. Bosacka, G. Dabrowska, E. Filipek, M. Piz, I. Rychlowska-Himmel, P. Tabero and E. Tomaszewicz, Journal of Mining and Metallurgy, B 44 (2008) 19-26.
- [6] T. T. Chen and J. E. Dutrizac, Journal of Metallurgy, 56 (2004) 46-51.
- [7] J. W. Graydon, and D. W. Kirk, Metallurgical transactions B, Process metallurgy, 19 (1988) 777-785.
- [8] S. A. Degterov, E. Jak, P. C. Hayes and A. D. Pelton, Metallurgical and Materials Transactions B, 32 B (2001) 643-657.
- [9] H. G. El-Shobaky, Thermochemica Acta, 343 (2000) 145-150.
- [10] G. A. El-Shobaky and A. A. Mostafa, Thermochemica Acta, 408 (2003) 75-84.
- [11] N. R. E. Radwana, H. G. El-Shobakyb, Thermochemica Acta, 360 (2000) 147-156.
- [12] M. R. C. Ismael and J. M. R. Carvalho, Minerals Engineering, 16 (2003) 31-39.
- [13] M. Loan, O. M. G. Newman, R. N. G. Cooper, J. B. Farrow and G. M. Parkinson, Hydrometallurgy, 81 (2006) 104-112.
- [14] B. S. Boyanov, Journal of Mining and Metallurgy, 41 B (2005) 67-77.
- [15] F. Habashi, Journal of Mining and Metallurgy, B 45 (2009) 1-13.
- [16] J. E. Clay and G. P. Schoonraad, Journal of the South African Institute of Mining and Metallurgy, 1976, 11-14.
- [17] S. I. Evdokimov and A. M. Pan'shin, Russian Journal of Non-Ferrous Metals, 50, 2 (2009) 81-88.
- [18] M. R. C. Ismael and J. M. R. Carvalho, Minerals Engineering, 16 (2003) 31-39.
- [19] G. Ye and E. Burstrom, Global Symposium on Recycling, Waste Treatment and Clean Technology, Madrid, Spain, September 26 – 29, 2005, 2103-2111.
- [20] D. Hirabayashi, T. Yoshikawa, K. Mochizuki, Y. Kojima, K. Suzuki, Y. Sakai, K. Ohshita and Y. Watanabe, Hyperfine Interact, 167 (2006) 809-813.
- [21] H. G. El-Shobaky and N. R. E. Radwan, Thermochemica Acta, 398 (2003) 223-231.
- [22] A. B. Peltekov and B. Boyanov, University of Plovdiv

- “Paisii Hilendarski”, Scientific papers, 38, 5 (2011) 177-190.
- [23] A. Z. Juhasz, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 141 (1998) 449-462.
- [24] V. V. Boldyrev, S. V. Pavlov and E. L. Goldberg, Int. J. Miner. Process, 44-45 (1996) 181-185.
- [25] A. M. Gismelseed, K. A. Mohammed, N. M. Widatallah, A. D. Al-Rawas, M. E. Elzain and A. A. Yousif, Journal of Physics: Conference Series, 217 (2010) 012138.
- [26] G. A. El-Shobaky, G. A. Fagal, A. Abd El-Aal and A. M. Ghozza, Thermochemica Acta, 256 (1995) 429-411.
- [27] B. K. Shahraki, B. Mehrabi, K. Gholizadeh and M. Mahammadinasab, Journal of Mining and Metallurgy, B 47 (2011) 89-97.
- [28] P. Lessidrenski, I. Gruev, A. Apostolov, S. Stoyanova and E. Bekrieva, Proceedings of the 4<sup>th</sup> International Conference ZINC 2006, Plovdiv, Bulgaria, 11-12 September, 2006, 213-216.
- [29] A.F.S. Schoukenst, F. Shawt, and E.C. Chemaly, Journal of The South African Institute of Mining and Metallurgy, 93, 1 (1993) 1-7.
- [30] S. K. Pardeshi and R. Y. Pawar, Materials Research Bulletin, 45 (2010) 609-615.
- [31] G. Ye, E. Burstrom, M. Maccagni, L. Bianco and H. Stripple, Sohn International Symposium; Advanced Processing of Metals and Materials Volume 6: New, Improved and Existing Technologies: Aqueous and Electrochemical Processing, 6 (2006) 397-411.
- [32] H. Ehrhardt, S. J. Campbell and M. Hofman, Journal of Alloys and Compounds, 339 (2002) 255.
- [33] D. Hirabayashi, T. Yoshikawa, K. Mochizuki, Y. Kojima, K. Suzuki, Y. Sakai, K. Ohshita, and Y. Watanabe, Hyperfine Interact, 167 (2006) 809-813.
- [34] T. K. Pathak, N. H. Vasoya, V. K. Lakhani, and K. B. Modi, Ceramics International, 36 (2010) 275-281.
- [35] H. Ehrhardt, S.J. Campbell and M. Hofman, Scripta Materialia, 48 (2003) 1141-1146.