

## **SOLID STATE INTERACTIONS IN THE SYSTEMS CaO(CaCO<sub>3</sub>)-Fe<sub>2</sub>O<sub>3</sub> and CuFe<sub>2</sub>O<sub>4</sub>-CaO**

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### **Abstract**

*The solid state interactions in the systems CaO(CaCO<sub>3</sub>)-Fe<sub>2</sub>O<sub>3</sub> and CuFe<sub>2</sub>O<sub>4</sub>-CaO have been studied using X-ray diffraction analysis. The influence of the temperature on the ferrite formation process has been investigated in the range of 900-1200 °C and duration up to 360 min. It has been shown that a mixture of ferrites forms at 1000 °C and interaction of 240 min. The exchange reactions in the systems CuFe<sub>2</sub>O<sub>4</sub>-CaO and Cu<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>-CaO have been studied, too. It has been established that Ca<sup>2+</sup> ions exchange Cu<sup>2+</sup> and Zn<sup>2+</sup> partially and the solubility of copper and zinc in a 7 % sulfuric acid solution increases 10-15 times.*

*Keywords:* Calcium ferrites; CaO-Fe<sub>2</sub>O<sub>3</sub>; CaCO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>; CuFe<sub>2</sub>O<sub>4</sub>-CaO; Interactions

### **1. Introduction**

On the basis of the solid state reactions many new compounds are formed having different technical significance and are mainly used as constructing materials. An important place among them take the ferrites which are compounds of Fe<sub>2</sub>O<sub>3</sub> with the oxides of other metals and possess unique magnetic, electrical and semi-conductor properties [1-3].

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The basic solid state reaction in the manufacturing of cast iron, Pb, Zn, Cu and others are connected with the interactions of the oxides of iron, calcium and silicon that have not been investigated thoroughly enough [4]. Both theoretical and practical investigations have been devoted to ferrite production [5-10], but the role of CaO has not been defined clearly enough and the data are contradictory. With regard to this the more detailed investigation of ferrite production in the process of thermal treatment of different double and triple systems in which CaO and CaCO<sub>3</sub> take part is of considerable interest.

It is known that in the system CaO-Fe<sub>2</sub>O<sub>3</sub> there are three types of calcium ferrites (Fig.1): 2CaO.Fe<sub>2</sub>O<sub>3</sub> /C<sub>2</sub>F/; CaO.Fe<sub>2</sub>O<sub>3</sub> /CF/ and CaO.2Fe<sub>2</sub>O<sub>3</sub> /CF<sub>2</sub>/ [11-13]. Above 1100 °C the interaction between CaO and Fe<sub>2</sub>O<sub>3</sub> takes place almost completely, forming a mixture of ferrites [14,15]. There are data for the forming of the phase CaFe<sub>12</sub>O<sub>19</sub>, but this is an unstable phase [16].

The kinetics of the process between CaO and Fe<sub>2</sub>O<sub>3</sub> is described with the diffusion equations of Jander and Ginstling, but in certain limits. The processes are best described with the general equation of Kolmogorov-Erofeev [15]. As a first product in the interaction between the two oxides appears the dicalcium ferrite whose temperature of forming is lower (400 °C) compared to the one of the monocalcium ferrite (500 °C) [15]. There are data that contradict these facts, however. It has been found that the dicalcium ferrite forms at a higher temperature than the monocalcium ferrite [17]. Other authors point that in the system CaCO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> after thermal treating and quick cooling a mixture is formed that consists of various types of ferrites – 50 % CF<sub>2</sub>, 20 % CF, 5-8 % C<sub>2</sub>F and Fe<sub>2</sub>O<sub>3</sub> [18]. It has also been established that the content of the products depends on the molar proportion of the initial oxides. The ferrite formation is based on the chemical reaction at the boundary between the phases and the oxide diffusion in the new phase. It has been shown that the coefficient of diffusion D for Fe<sup>3+</sup> and Ca<sup>2+</sup> in CF is respectively 3.2 and 30 cm<sup>2</sup>/s at an activating energy E<sub>a</sub> = 300.96 and 359.48 kJ/mol, which is evidence for preferred diffusion of Ca<sup>2+</sup> over the iron ions. Data have also been presented for the thermodynamic parameters of the ferrites CF and C<sub>2</sub>F [19]. On the basis of the experimental results the change of ΔH, ΔS and ΔG with the temperature has been calculated.

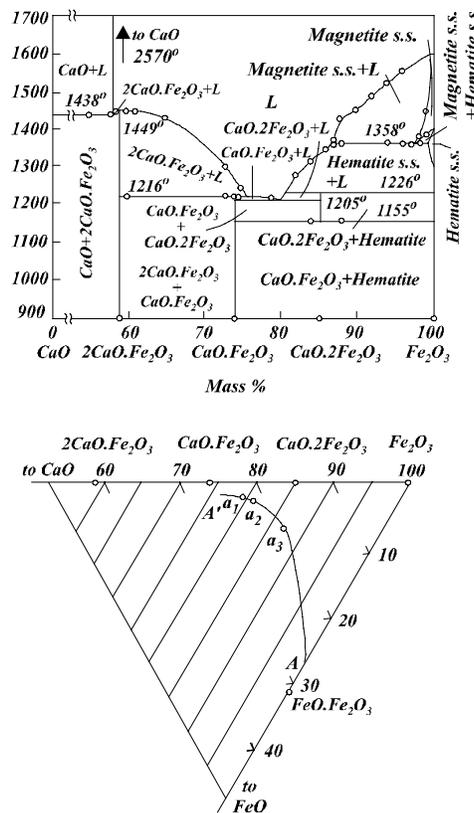
In hydrometallurgy of zinc and copper the ferrite formation is a primary reason for the decrease of the direct leaching of these metals due to the

insolubility of their ferrites in dilute solutions of  $\text{H}_2\text{SO}_4$  [20,21].

For the rational processing and utilizing of zinc, copper, cadmium and other metals of the zinc and copper-zinc concentrates it is necessary to know the solid state interactions which account for the undesirable formation of ferrites.

In connection with this the goal of the current investigation is to study the solid state interactions in the  $\text{CaO}(\text{CaCO}_3)\text{-Fe}_2\text{O}_3$  and  $\text{CuFe}_2\text{O}_4\text{-CaO}$  systems and to determine the role and the place of ferrite formation in them for the hydrometallurgy of zinc and copper and the pyrometallurgy of cast iron, copper and lead.

Fig.1. Diagram of the phase equilibrium of the  $\text{CaO-Fe}_2\text{O}_3$  system in air atmosphere



## 2. Experimental

Various methods for the obtaining of calcium ferrites are known [22,23], but in this particular case ceramic technology has been chosen. In this way the conditions of ferrite formation are modeled to be closest to the real ones in industrial conditions at the obtaining of different metals. As initial materials CaO, CaCO<sub>3</sub>, CuO, ZnO,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with purity p.a. of Merck company, Germany have been used. The ferrites have been obtained at a temperature of 900-1200 °C and duration of the thermal treatment up to 360 min.

X-ray diffraction analysis is carried out with a TUR-M62 apparatus (Dresden, Germany) using CoK<sub>a</sub> radiation and an iron target.

DTA and TGA (a Q Derivatograph, Hungary) are carried out under the following conditions: sensitivity of DTA, 0.5 mV; DTG, 1 mV; TG, 100 mg; heating rate, 10° min<sup>-1</sup>; sample mass 50-100 mg. A platinum crucible was used. All the studies were performed in air medium.

## 3. Results and discussion

The influence of the factors temperature and duration of the interaction on the content of the obtained products has been studied.

The carrying out of the solid state interactions with the participation of CaO in the hydrometallurgy of zinc is limited in the temperature interval 900-1000 °C. This temperature is considerably higher at the waeltzing of the zinc cake and the obtaining of cast iron and lead. This gave grounds to select such a temperature interval of study – 900-1200 °C so as the obtained results could be used and interpreted in terms of the production of these metals. The upper value of the temperature is also limited by the possibility to obtain a melt according to the diagram of the phase equilibrium of the CaO-Fe<sub>2</sub>O<sub>3</sub> system in air atmosphere [11]. The influence of the duration on the process of ferrite formation in this system at 900 °C is presented in Fig.2. Investigations with different durations have been made and the figure presents X-ray diagrams of the initial mixture and ones obtained after 60 and 360 min interaction.

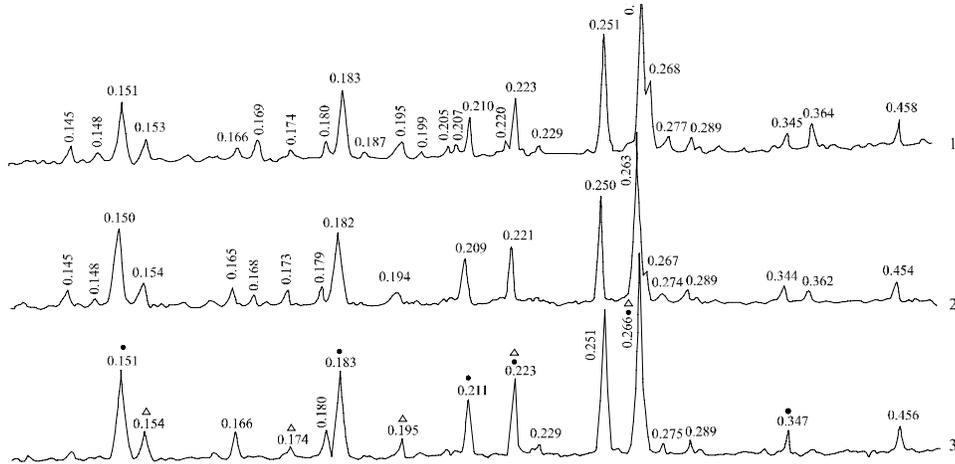


Fig.2. X-ray diagrams of the  $\text{CaO}-\text{Fe}_2\text{O}_3$  system: 1 – initial oxide mixture; 2 – thermal treated at  $900\text{ }^\circ\text{C}$ , 60 min.; 3 -  $900\text{ }^\circ\text{C}$ , 360 min.;  
 • –  $\text{CaFe}_2\text{O}_4$ ;  $\Delta$  -  $\text{Ca}_2\text{Fe}_2\text{O}_5$

The results show that the process of ferrite formation has started at  $900\text{ }^\circ\text{C}$  and is clearly visible even at 15 min of interaction. When the time of reaction is increased to 60 min the diffraction maximums that belong to the calcium ferrites are clearly visible and are comparable to those of the unreacted  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ .

With the increasing of the duration of the interaction to 360 min the quantity of the two calcium ferrites increases, but in the final product of the heating unreacted initial oxides still remain.

The best interpretation of the X-ray diagrams is made using the diffraction maximums between 0.143 and 0.155 nm. At these values of  $d$  the separate lines belonging to  $\text{CaO}$ ,  $\text{CaFe}_2\text{O}_4$  and  $\text{Ca}_2\text{Fe}_2\text{O}_5$  are visible. This allows close inspection of the process of interaction between the initial oxides and the obtaining and increasing in quantity of the calcium ferrites.

When the temperature of the solid state reactions increases up to 1000, 1100 and  $1200\text{ }^\circ\text{C}$  the process of ferrite formation increases. It is established that at time of interaction of 15 min and at  $1000\text{ }^\circ\text{C}$  the content of the obtained product is very close to that obtained at  $900\text{ }^\circ\text{C}$  for 360 min.

At 1000 °C the duration of interaction is also a significant factor influencing the content of the final product. The obtained X-ray diagrams clearly show that when time is increased from 15 to 60 min a certain decrease of the intensity of the lines of the initial oxides takes place, most significantly at 240 min. Despite that, the presence of a small diffraction maximum at  $d=0.1446$  nm reveals that the process of complete interaction of the initial oxides has not finished.

The increasing of the temperature of the solid state reaction to 1100 and 1200 °C leads to the complete consumption of the initial oxides. Comparison of the X-ray diagrams shows a very small difference in the content of the end products of the interaction. The absence of the CaO and  $Fe_2O_3$  lines at 1100 °C confirms the results displayed in [14] for the sum degree of transformation in the studied system. The data show that a mixture of the two calcium ferrites forms in the end products. The size of the maximums of the X-ray diagrams does not change significantly which is evidence for the relative stability of the quantity proportions between  $CaFe_2O_4$  and  $Ca_2Fe_2O_5$ . However, we can maintain that the products obtained at 1100 and 1200 °C differ by their content, which is evident from the existence of a diffraction maximum at  $d = 0.288$  nm (1100 °C) that cannot be observed at 1200 °C.

In the natural copper, zinc, lead sulfide concentrates and other raw materials  $CaCO_3$  is essentially present. It dissociates in the process of their oxidized roasting. According to the DTA and TGA of the initial  $CaCO_3$  from the TG curve this process obviously starts at 620 °C and is thoroughly complete at 805 °C. The calculated total decrease of sample mass is quite close to the theoretical value (44 %).

In this connection the  $CaCO_3$ - $Fe_2O_3$  system has been studied, in which almost the same processes as in the  $CaO$ - $Fe_2O_3$  system take place. The peculiarity in this case is the necessity for dissociation of  $CaCO_3$  to CaO and a following solid state interaction with  $Fe_2O_3$ . The expectations that the ferrite formation will take place at a lower speed have not been confirmed completely. Comparison of the X-ray diagrams of the  $CaCO_3$ - $Fe_2O_3$  system with the ones of  $CaO$ - $Fe_2O_3$  for samples thermally treated at 900 °C reveals a similar picture. Again as a result of the solid state interaction a mixture of a mono- and a dicalcium ferrite is formed. Comparing the intensities of their

two separate lines shows that the proportion between the two ferrites remains constant. Following the most powerful line of  $\text{Fe}_2\text{O}_3$  ( $d = 0.268$  nm) in the initial mixture and of the obtained X-ray diagrams of the samples, heated with different durations, a decrease of its intensity is observed. This decrease, however, is smaller (at the same conditions of thermal treatment) compared to the one of the  $\text{CaO}-\text{Fe}_2\text{O}_3$  system. A possible explanation of this fact should be sought in the necessity for the dissociation of the initial  $\text{CaCO}_3$  and the diffusion of the released  $\text{CO}_2$  through the volume of the forming ferrites and the unreacted initial mixture.

The X-ray data display that there is no full interaction between  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  at a temperature of  $900$  °C and duration up to  $360$  min.

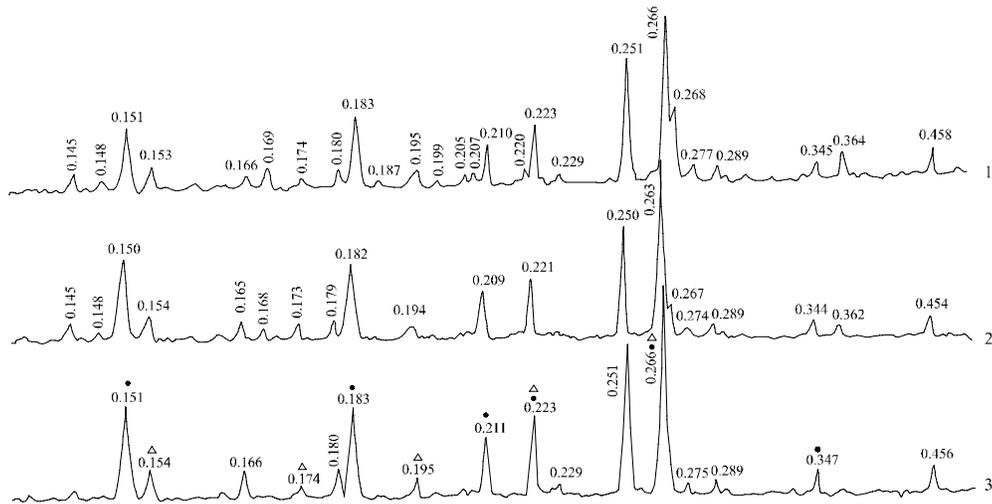


Fig3. X-ray diagrams of samples of the  $\text{CaCO}_3-\text{Fe}_2\text{O}_3$  system thermal treated at  $1000$  °C: 1 – 15 min; 2 - 60 min; 3 - 360 min;  
● –  $\text{CaFe}_2\text{O}_4$ ; Δ -  $\text{Ca}_2\text{Fe}_2\text{O}_5$

When the temperature is increased to  $1000$  °C the solid state interactions in the double system take place more completely (Fig.3). The comparative evaluation of the obtained X-ray diagrams at this temperature for the systems  $\text{CaCO}_3-\text{Fe}_2\text{O}_3$  and  $\text{CaO}-\text{Fe}_2\text{O}_3$  shows very small differences. With the increase of the duration of thermal treatment the intensity of the  $\text{Fe}_2\text{O}_3$  lines constantly decreases. At the same time the diffraction maximums of the new coming

phases become more intense and more clearly expressed. At 1000 °C and 360 min of thermal treatment there is no complete interaction of the initial components, which is evidenced by the weak line of Fe<sub>2</sub>O<sub>3</sub>.

At 1100 °C and duration 240 min there is an almost complete consumption of the initial CaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, and a mixture of the two ferrites is formed. The presence of very weakly expressed lines of Fe<sub>2</sub>O<sub>3</sub> reveals that the process of ferrite formation has not finished completely. The attempt to obtain a complete interaction between the initial components by increasing the temperature to 1200 °C led to the melt obtaining.

The X-ray diagrams of the two systems display that in the end products of the solid state reactions the phases CaFe<sub>2</sub>O<sub>4</sub> and Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> are observed. At 1200 °C in the CaO-Fe<sub>2</sub>O<sub>3</sub> system the processes of interaction between the initial oxides are completely finished.

It is known that in the solid state reactions of certain ferrites with CaO a free metal oxide is formed according to the equation [9]:

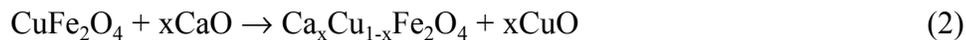


This interaction can play an important role in the carrying out of high-thermal processes such as waelzing, reducing melting of lead agglomerate, roasting of zinc concentrates and others. It is essential for the hydrometallurgy of the zinc to destroy the zinc ferrite during the reduction of the zinc cake in the waeltz furnace. The presence of CaO and MgO as well as the possibility that they can be additionally supplemented with other semi-products create better conditions for a more complete utilization of the zinc-containing materials.

In terms of clarifying certain processes taking place in a solid phase during waelzing, it is interesting to examine the possibility for an exchange interaction between a copper and a copper-zinc ferrite with CaO. These investigations are also significant for the complex and profound processing of copper-zinc sulfide concentrates, at the roasting of which are formed mixed copper-zinc ferrites with changeable composition.

Two types of ferrite are used - CuFe<sub>2</sub>O<sub>4</sub> and Cu<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>. Mixtures with equals mols between the ferrites and CaO are prepared, ground in a ball mill

and heated in corundum crucibles at 1000 °C with a duration of 60 min. The obtained products are leached with a 7 % solution of H<sub>2</sub>SO<sub>4</sub> at room temperature for 60 min. After filtering the Cu and Zn content in the filtrate is determined. Due to the insolubility of the ferrites, the quantity of the derived Cu and Zn appears as an indicator for the exchange reactions:



On the basis of the content of the copper and zinc in the ferrites and in the solution their degree of leaching is calculated.

The obtained results show that the initial CuFe<sub>2</sub>O<sub>4</sub> and Cu<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> are components that are slightly soluble in a 7 % solution of H<sub>2</sub>SO<sub>4</sub>. In the samples after heating of the ferrites with CaO, however, a significant solubility of the metals Cu and Zn is observed. The copper solubility increases almost 10 times and the zinc one – about 15 times. This is most probably due to the forming of free copper and zinc oxides as a result of the solid state interaction, which are compounds easily soluble in weak solutions of sulfuric acid.

#### 4. Conclusions

1. The solid state interactions in the CaO-Fe<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> systems have been investigated using X-ray diffraction analysis in the temperature interval 900-1200 °C and duration up to 360 min.

2. The conditions of complete interaction between the initial components have been determined. It has been shown that in the studied systems at these conditions a mixture of the ferrites CaFe<sub>2</sub>O<sub>4</sub> and Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> in a different quantity proportion forms.

3. The possibility of exchange reactions in the systems CuFe<sub>2</sub>O<sub>4</sub> + CaO and Cu<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> + CaO has been examined. It has been established that Ca<sup>2+</sup> partially displace Cu<sup>2+</sup> and Zn<sup>2+</sup> from the ferrites increasing the solubility of copper and zinc in a 7% solution of H<sub>2</sub>SO<sub>4</sub>.

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