

# Ferrites of the $\text{MeFe}_2\text{O}_4$ System (Me – Zn, Cu, Cd) and Their Two Faces

B. S. Boyanov, A. B. Peltekov, K. I. Ivanov

**Abstract**—The ferrites  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  are synthesized in laboratory conditions using ceramic technology. Their homogeneity and structure are proven by X-Ray diffraction analysis and Mössbauer spectroscopy. The synthesized ferrites are subjected to strong acid and high temperature leaching with solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ . The results indicate that the highest degree of leaching of Zn, Cd and Cu from the ferrites is achieved by use of  $\text{HCl}$ .

The charging of five zinc sulfide concentrates was optimized using the criterion of minimal amount of zinc ferrite produced when roasting the concentrates in a fluidized bed. The results obtained are interpreted in terms of the hydrometallurgical zinc production and maximum recovery of zinc, copper and cadmium from initial zinc concentrates after their roasting.

**Keywords**—Hydrometallurgy, inorganic acids, solubility, zinc ferrite.

## I. INTRODUCTION

SOLID-state reactions are carried out between the oxides of zinc and those of other non-ferrous metals (Cd, Cu, etc.) and  $\text{Fe}_2\text{O}_3$  (obtained by oxidation of  $\text{FeS}_2$ ,  $n\text{ZnS}$ ,  $m\text{FeS}$ ,  $\text{CuFeS}_2$ ) during roasting of sulfide zinc concentrates in a fluidized bed furnace (FBF). As a result of these interactions  $\text{ZnFe}_2\text{O}_4$  is obtained, as well as ferrites of Cd, Cu, etc. [1]–[4]. The ferrites of Zn, Cd, Cu and mixed ferrites with NiO, MnO, MgO, CoO, ZnO, BaO, etc. combine the properties of dielectrics, semiconductors, ferro-magnets, catalysts and others. The ferrites are used in an impressive range of applications due to their remarkable properties. However, one big disadvantage of ferrites is that they are undesirably among the end products in many processes in metal manufacturing. The ferrites are very stable and poorly soluble compounds [5]. The remarkable properties of ferrites have been studied in detail, and are used in various fields - engineering, industry, medicine and others [6]. Depending on the technology used to obtain them, as well as their chemical composition, crystal structure, and the presence of impurities, ferrites have a high specific electrical resistance, among many other useful properties [7]. In terms of extractive metallurgy and, in

particular, of the hydrometallurgical production of zinc, however, the obtaining of these ferrites is one of the most unfavorable processes. This reduces the direct leaching of zinc and leads to an increase in production costs and deterioration of the technical and economic parameters of the leaching and all zinc production. In this context, the aim of this study is to synthesize  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  in laboratory conditions, to leach the ferrites with  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ , as well as to determine the influence of conditions of leaching and chemical composition of zinc sulfide concentrates on the degree of leaching of non-ferrous metals.

## II. EXPERIMENTAL

### A. Ceramic Technology

In this study  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  were synthesized using ceramic technology.

### B. XRD Analysis

The X-ray phase analysis of the ferrites and the concentrates was carried out with a “TUR-M62” apparatus (Dresden, Germany), used for the phase identification.

### C. Mössbauer Spectroscopy

Mössbauer spectra (MS) were obtained at 25 °C with a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany).

### D. Chemical Analysis

The chemical analysis of the samples was performed by inductively coupled plasma (ICP-OES) model iCAP 6300 from Thermo Scientific (England).

Weighting analysis was used to determine the degree of metal leaching in the dissolution of  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  in acids according to the difference in mass of the initial ferrite and the residue after leaching.

### E. Web-Based Information System

A Web-based information system for the calculation of the chemical compositions of the charges of concentrates was used. It was built on a modular principle using server programming language PHP.

## III. RESULTS AND DISCUSSION

### A. Synthesis and Leaching

#### 1. Technology

Under laboratory conditions the ferrites  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  were synthesized at 1000°C, using a ceramic technology (Fig. 1). The resulting ferrites are single-phase

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samples and possess properties most similar to the ones obtained during the roasting of zinc sulfide concentrates [8].

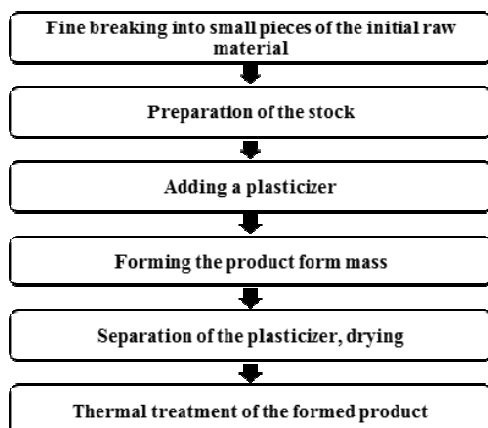


Fig. 1 Ceramic technology for synthesis of ferrites

## 2.XRD Analysis

The complete process of the solid-state reactions between initial oxides (ZnO, CdO and CuO) and  $\text{Fe}_2\text{O}_3$  to obtain ferrites was checked by XRD analysis. The resulting XRD patterns are presented in Fig. 2.

Zinc ferrite crystallizes in a cubic structure, and the calculated parameter ( $a$ ) of the crystal lattice on the basis of the analysis is 8.442 Å. XRD analysis indicates the formation of a spinel structure of  $\text{CdFe}_2\text{O}_4$ . Intense diffraction peaks characterizing single-phase ferrite in cubic structure are present in the XRD patterns. The calculated lattice parameter ( $a$ ) for  $\text{CdFe}_2\text{O}_4$  is 8.690 Å. Observed intense diffraction lines of  $\text{CuFe}_2\text{O}_4$  are typical of a single-phase sample. The calculated lattice parameters ( $a$  and  $c$ ) for the  $\text{CuFe}_2\text{O}_4$  sample are respectively 8.370 Å and 8.490 Å. Established X-ray diffraction patterns and parameters of the crystal lattice of ferrites are very similar to the parameters presented by other authors [9]–[16].

The results from the X-ray phase analysis show that in the studied zinc concentrates there are six phases typical for all concentrates studied up to now:  $\beta$ -ZnS (a main phase),  $n\text{Zn}\cdot m\text{FeS}$ ,  $\text{FeS}_2$ ,  $\text{CuFeS}_2$ ,  $\text{SiO}_2$  ( $\alpha$ -quartz), and PbS [1].

## 3.Mössbauer Spectroscopy

The single phase of the obtained ferrites is proved by Mössbauer spectroscopy. The Mössbauer spectra obtained are shown in Fig. 3, and the calculated Mössbauer parameters - in Table I.

TABLE I  
MÖSSBAUER PARAMETERS OF SYNTHESIZED FERRITES

| Phase                     | Components   | IS, mm/s | QS, mm/s | $H_{\text{eff}}$ , T | FWHM, mm/s | G, % |
|---------------------------|--|----------|----------|----------------------|------------|------|
| $\text{ZnFe}_2\text{O}_4$ | Db - $\text{Fe}^{3+}_{\text{octa}}$ - $\text{ZnFe}_2\text{O}_4$                                  | 0.34     | 0.36     |                      | 0.33       |      |
| $\text{CdFe}_2\text{O}_4$ | Db - $\text{Fe}^{3+}_{\text{octa}}$ - $\text{CdFe}_2\text{O}_4$                                  | 0.37     | 0.78     |                      | 0.36       |      |
| $\text{CuFe}_2\text{O}_4$ | Sx1- $\text{Fe}^{3+}_{\text{octa}}$  | 0.36     | -0.14    | 51.5                 | 0.54       | 49   |
|                           | $\text{CuFe}_2\text{O}_4$ -o Sx2- $\text{Fe}^{3+}_{\text{tetra}}$ - $\text{CuFe}_2\text{O}_4$ -t | 0.26     | -0.01    | 48.7                 | 0.51       | 51   |

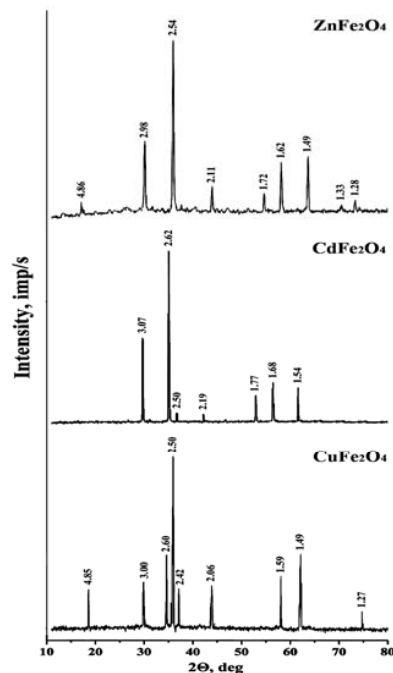


Fig. 2 X-ray diffraction patterns of studied  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$

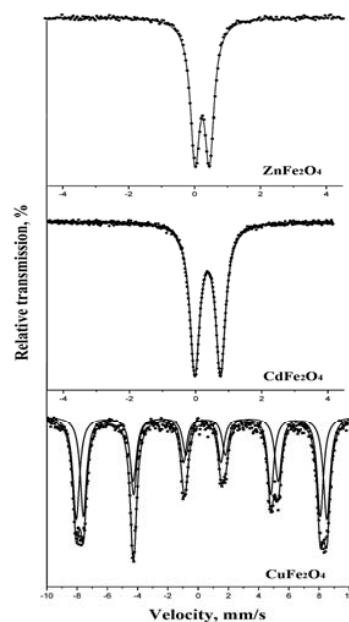


Fig. 3 Mössbauer spectra of studied  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$

The experimental Mössbauer spectrum of  $\text{ZnFe}_2\text{O}_4$  is a quadrupole doublet. Mathematical processing gives parameters characteristic of  $\text{ZnFe}_2\text{O}_4$ . The iron ions are in the third degree of oxidation and octahedrally coordinated. The quadrupole splitting of  $\text{ZnFe}_2\text{O}_4$  is 0.36 mm/s [17].

The Mössbauer spectrum of  $\text{CdFe}_2\text{O}_4$  represents a quadrupole doublet and has parameters characteristic of

$\text{CdFe}_2\text{O}_4$ . They are close to those presented in the literature [18]–[20].

The formation of  $\text{CuFe}_2\text{O}_4$  is substantial at  $650^\circ\text{C}$  and very intensive at  $750^\circ\text{C}$ . In the solid phase interaction between  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$  the most significant influence on the reaction is time. Raising the temperature up to  $1000^\circ\text{C}$  also strongly influences the rate of ferrite formation [21].

The Mossbauer spectrum of  $\text{CuFe}_2\text{O}_4$  represents a sextet containing  $\text{Fe}^{3+}$  (octa) and  $\text{Fe}^{3+}$  (tetra) with an inverse distribution of ions.  $\text{CuFe}_2\text{O}_4$  is a ferrimagnetic spinel.

#### 4. Leaching of Ferrites

##### Leaching of $\text{ZnFe}_2\text{O}_4$

Fig. 4 shows the degree of leaching of zinc ferrite according to the temperature (25, 55, 75, 85 and  $95^\circ\text{C}$ ), with 7, 10 and 15 vol. % solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$  for a time of 30 and 60 min. These conditions were selected based on the industrial technology of zinc calcine leaching.

From the results it is clear that the higher the temperature and the longer the time of treatment, the better the degree of zinc leaching is.

In all leaching conditions up to a temperature of  $55^\circ\text{C}$  the degree of zinc recovery is less than 20%. Raising the temperature above this value significantly affects the extraction process. There is complete dissolution of ferrite at  $95^\circ\text{C}$  with the use of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ .

When comparing the effects of different acids the following conclusions can be made:

1. The solubility of  $\text{ZnFe}_2\text{O}_4$  in  $\text{HNO}_3$  is significantly lower, regardless of the conditions of leaching.
2. The zinc ferrite is dissolved better in solutions of  $\text{HCl}$ , compared to solutions of  $\text{H}_2\text{SO}_4$ , but when using the 7% solutions of both acids, no big difference is observed.
3. With regards to increasing the acid concentration, the degree of leaching of  $\text{ZnFe}_2\text{O}_4$  increases more significantly when using solutions of  $\text{HCl}$ . Almost complete dissolution of ferrite with  $\text{HCl}$  is obtained at a temperature of  $75^\circ\text{C}$ , 15%  $\text{HCl}$  solution and leaching time 60 min. In order to achieve the same result using  $\text{H}_2\text{SO}_4$ , with the same leaching time and solution concentration, the temperature must be raised to  $95^\circ\text{C}$ .
4. The results correspond with those obtained by several authors on high-temperature and high-concentration leaching - zinc is recovered by  $\text{H}_2\text{SO}_4$  in hydrometallurgical production, while iron is removed through the formation of jarosite, goethite or hematite [22]–[24].
5. Although there are various difficulties that must be overcome in the electrolysis of  $\text{ZnCl}_2$  (release of  $\text{Cl}_2$ , equipment corrosion, etc.), research in these guidelines continues [25], [26].

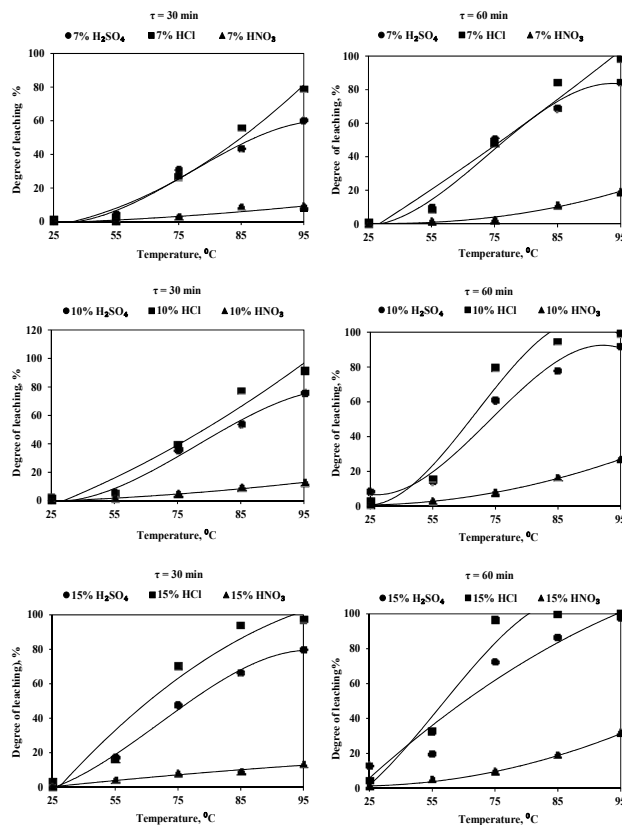


Fig. 4 Influence of temperature on the leaching of  $\text{ZnFe}_2\text{O}_4$  using 7, 10 and 15% acids concentration for a time of 30 and 60 min

##### Leaching of $\text{CdFe}_2\text{O}_4$

Data in Fig. 5 show the degree of leaching of  $\text{CdFe}_2\text{O}_4$  as a function of temperature, acids concentration (7, 10 and 15 vol.% solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ ) and process duration (30 and 60 min). From the results it is clear that increasing both the temperature and the time of treatment leads to an increase in the degree of leaching of cadmium. Regardless of the experimental conditions, the degree of recovery of  $\text{CdFe}_2\text{O}_4$  at  $25^\circ\text{C}$  is below 20%. Increasing the temperature significantly affects the extraction process. At  $75^\circ\text{C}$ , using  $\text{HCl}$ , complete dissolution of the ferrite is achieved. When using  $\text{H}_2\text{SO}_4$ , total recovery was achieved at  $95^\circ\text{C}$ .

The conclusions that can be drawn on the basis of the effects of different acids are:

1. Using  $\text{HNO}_3$  to dissolve  $\text{CdFe}_2\text{O}_4$  shows no significant results. However, even such results are more satisfactory than those obtained by the dissolution of  $\text{ZnFe}_2\text{O}_4$  in the same conditions. The maximum degree of leaching with  $\text{HNO}_3$  is about 70%.
2. The solubility of  $\text{CdFe}_2\text{O}_4$  responds well to the use of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ . The best results from leaching are achieved using  $\text{HCl}$ . Even at  $95^\circ\text{C}$  and 7% concentration of  $\text{HCl}$ , after 30 min a complete dissolution of ferrite is achieved. The same result using  $\text{H}_2\text{SO}_4$  is only achieved when the time is increased to 60 min.

- With the increase of acid concentration, the degree of  $\text{CdFe}_2\text{O}_4$  leaching considerably increases at lower temperatures (75 °C and 85 °C).
- In order to achieve complete dissolution of the ferrite at a lower temperature using  $\text{H}_2\text{SO}_4$ , it is necessary to increase acid concentration to 15%, with an extraction time of 60 min.
- On the basis of the results obtained it can be concluded that  $\text{CdFe}_2\text{O}_4$  is more unstable than  $\text{ZnFe}_2\text{O}_4$ .

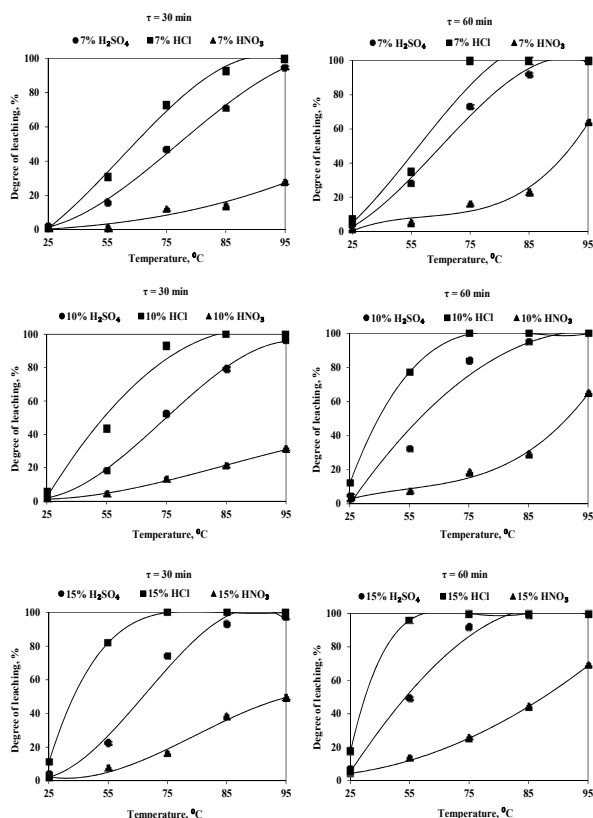


Fig. 5 Influence of temperature on the leaching of  $\text{CdFe}_2\text{O}_4$  using 7, 10 and 15% acids concentration for a time of 30 and 60 min

#### Leaching of $\text{CuFe}_2\text{O}_4$

Fig. 6 presents the degree of leaching of  $\text{CuFe}_2\text{O}_4$  depending on the temperature when using different solution concentrations of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$  for a time of 30 and 60 min. From the results it is clear that with increasing temperature and longer time of treatment, the degree of leaching of the copper from the ferrite increases, but regardless of the conditions of the experiment, total dissolution of ferrite is achieved in only one case.

In all experiments of leaching with 7 and 10% solutions of the three acids to a temperature of 55 °C the degree of copper leaching is less than 40%. When the concentration is increased to 15%, the degree of copper leaching is between 60-80%. Raising the temperature above 55 °C has a measurable impact on the extraction process.

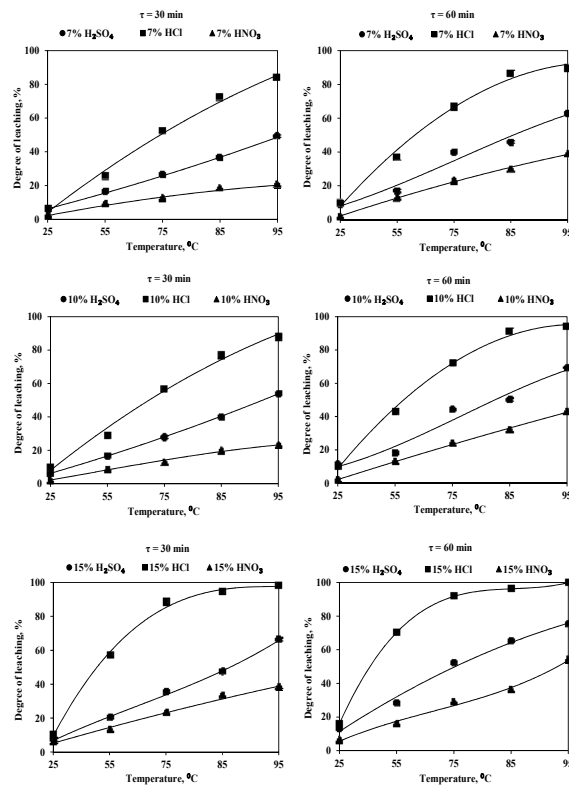


Fig. 6 Influence of temperature on the leaching of  $\text{CuFe}_2\text{O}_4$  using 7, 10 and 15% acids concentration for a time of 30 and 60 min

When comparing the effects of different acids the following conclusions can be drawn:

- The effect of  $\text{HNO}_3$  on the leaching process is weak, irrespective of the conditions of the experiment.
- The copper ferrite is better dissolved in solutions of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ . More significant leaching is achieved by using  $\text{HCl}$ . When raising the temperature and increasing the time of extraction, the use of  $\text{HCl}$  provides about 20% more recovery of  $\text{CuFe}_2\text{O}_4$  than the use of  $\text{H}_2\text{SO}_4$ .
- Complete dissolution of ferrite is achieved with the use of  $\text{HCl}$ , at an elevated temperature of 95 °C and an increased acid concentration of 15% for a period of 60 min. Under the same conditions, the maximum degree of leaching of ferrite with the use of  $\text{H}_2\text{SO}_4$  is about 80%.
- On the basis of the results obtained it can be concluded that  $\text{CuFe}_2\text{O}_4$  is more stable than  $\text{ZnFe}_2\text{O}_4$  and  $\text{CdFe}_2\text{O}_4$ .

#### B. Industrial Study

##### 1. Chemical Analysis of the Zinc Concentrates With Different Iron Content

The content of Zn and Fe is an important characteristic of zinc sulfide concentrates used in zinc production. Eighteen concentrates processed at KCM - SA, Plovdiv (Bulgaria) were tested in connection with the ferrite formation and implementation of the process of roasting in fluidized bed furnace (Fig. 7).

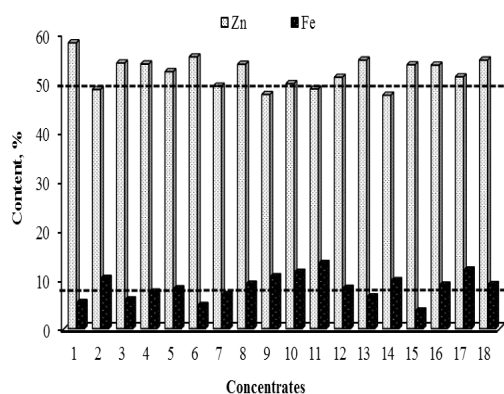


Fig. 7 Content of Zn and Fe in the studied concentrates

The data presented in Fig. 7 show that 12 concentrates meet the requirement for zinc content greater than 50%. At the same time 10 of the concentrates have iron content above the upper limit of 8% (Fig.8). This is the reason that a significant amount of  $ZnFe_2O_4$  is obtained, adversely affecting the leaching of zinc [27].

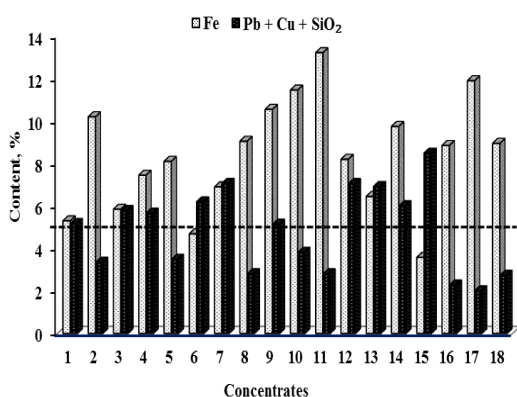


Fig. 8 Content of Fe and the sum of Pb, Cu and  $SiO_2$  in the studied concentrates

The increased content of Fe, Pb, Cu and  $SiO_2$  (Fig. 8) causes another adverse effect – coarsening of the calcine particles. This leads to deterioration of the oxidation process and the hydrodynamics in the FBF, as well as to an increase in the quantity of ferrites obtained.

The obtained data (Fig. 8) show that in 8 concentrates the sum of Pb, Cu and  $SiO_2$  exceeds the limit value of 5.5%. This makes it especially dangerous to conduct the oxidation process in FBF.

The chemical composition of five zinc sulfide concentrates with different iron content is presented in Table II. Their origin is from Bulgaria (1), Macedonia (2), Turkey (3), Greece (4) and Serbia (5).

The chemical composition of the zinc concentrates shows that they do not fully meet the requirements for the content of the main components [28]. For this reason, these concentrates, in practice, are not suitable for independent processing. Part of the impurity components will pass in the calcine, and then in the solution after the leaching. The high content of iron

(concentrates 3, 4 and 5) is particularly unfavorable, leading to increased ferrite formation.

TABLE II  
CHEMICAL ANALYSIS OF ZINC CONCENTRATES

| Components | Concentrates /% |       |       |       |       |
|------------|-----------------|-------|-------|-------|-------|
|            | 1               | 2     | 3     | 4     | 5     |
| Zn         | 49.30           | 50.22 | 46.45 | 50.37 | 47.16 |
| Stot       | 30.00           | 32.30 | 32.50 | 33.50 | 32.85 |
| Cu         | 1.96            | 0.53  | 2.06  | 0.21  | 1.52  |
| Cd         | 0.29            | 0.26  | 0.23  | 0.30  | 0.36  |
| Pb         | 2.85            | 2.77  | 2.65  | 1.06  | 0.85  |
| Fe         | 6.90            | 6.90  | 9.75  | 10.85 | 13.15 |
| $SiO_2$    | 2.25            | 4.55  | 3.30  | 0.95  | 2.20  |

## 2. Mössbauer Spectroscopy of the Zinc Concentrates

For a more detailed study of the distribution of the iron between the individual phases ( $FeS_2$ ,  $CuFeS_2$ ,  $nZnS.mFeS$ ) in zinc concentrates, particularly useful information can be provided by Mössbauer spectroscopy.

The experimental Mössbauer spectra of studied concentrates are shown in Fig. 9.

All Mössbauer spectra contain quadrupole doublets, and concentrates 1 and 4 contain sextet components too. In all 5 concentrates data indicate the presence of a mixed zinc-iron sulfide corresponding to the marmatite phase. Based on these results, it can be claimed that almost the entire amount of iron (as  $Fe_2O_3$ ) in the oxidizing roasting of zinc concentrates may react with zinc (as  $ZnO$ ) to obtain  $ZnFe_2O_4$ . As a result of this solid state interaction, the degree of direct leaching of zinc will decrease and the quantity of the resulting zinc cake will increase. This incurs additional costs for further processing of the cake using Waelz processing or hydrometallurgical methods [29].

## 3. Web-Based Information System

A Web-based information system, described in detail in [30], [31] was used to calculate charges of zinc sulfide concentrates. In this specific case, concentrates 1- Bulgaria and 2- Macedonia were chosen as main optimal concentrates according to the algorithm used [30]. Only concentrates (local or imported) that can provide the largest amounts available over the longest periods of time are chosen to be main optimal concentrates. It is not necessary that they have the best content for roasting in FBF.

The number of calculated charges from zinc concentrates that satisfy the claimed requirements [32] is only 3. The recipes are sorted by an optimizing criterion of minimum content of zinc ferrite (maximum zinc, soluble in 7%  $H_2SO_4$ ) as a percentage. The resulting charges contain zinc dissolved in 7% sulfuric acid solution, in the range from 90.35 to 90.69%, and zinc ferrite in the range from 8.31 to 8.65%. In the best recipe, according to the chosen criterion, the zinc, soluble in 7%  $H_2SO_4$ , is 90.69% of the total zinc in it. This high percentage indicates that the degree of leaching of the zinc calcine can be expected to be high. The results obtained for the percentage of zinc as ferrite are very close to those obtained in industrial roasting of a charge of zinc concentrates.

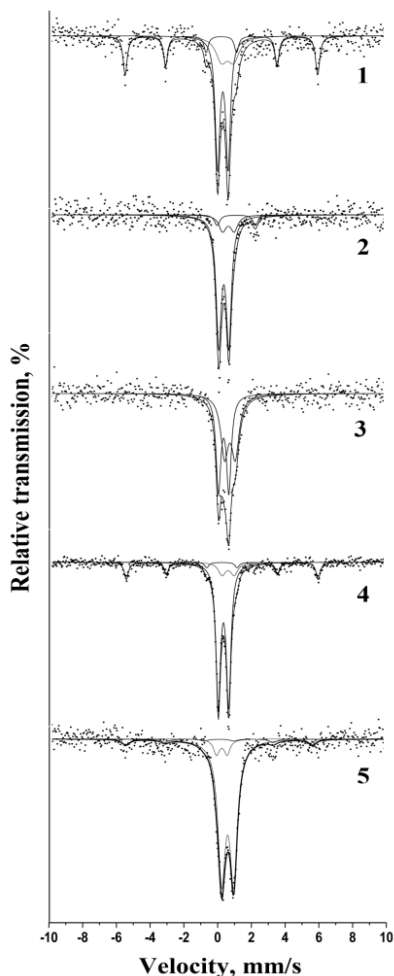


Fig. 9 Mössbauer spectra of the studied concentrates

#### IV. CONCLUSION

The ferrites  $ZnFe_2O_4$ ,  $CdFe_2O_4$  and  $CuFe_2O_4$  are synthesized using ceramic technology. The completion of solid-state reactions between initial oxides ( $ZnO$ ,  $CdO$  and  $CuO$ ) and  $Fe_2O_3$  to obtain ferrites has been checked and proven by XRD analysis and Mössbauer spectroscopy.

The dissolution of ferrites with solutions of  $H_2SO_4$ ,  $HCl$  and  $HNO_3$  has shown that the highest degree of leaching of  $Zn$ ,  $Cd$  and  $Cu$  from them is achieved with the use of  $HCl$ . At temperatures above  $85^\circ C$  and 60 min of leaching the three non-ferrous metals pass into the solution completely. The resulting values for the degree of leaching of metals using  $H_2SO_4$  are lower, but still remain significantly higher for all of the experimental conditions, compared to the values obtained using  $HNO_3$ .

Five zinc sulfide concentrates are characterized by chemical analysis for iron content and by Mössbauer spectroscopy for iron-containing phases. This is done to optimize the charging by the criterion of minimal amount of zinc ferrite obtained at roasting the concentrates in a fluidized bed.

#### ACKNOWLEDGMENT

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