



SOLID PHASE SULPHATIZING OF ZINC FERRITE SPINEL WITH IRON SULPHATES AS AN ENVIRONMENTAL FRIENDLY WAY FOR RECOVERING ZINC

Anurag Saini^[a], László Kótai^[a], István E. Sajó^[a], Imre Miklós Szilágyi^[b], Károly Lázár^[c], Zoltán May^[a], Péter Fazekas^[a], István Gács^[a], Vinita Sharma^[d] and Kalyan K. Banerji^[e]

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The scarcely reactive zinc ferrite can be decomposed in solid phase to water-soluble ZnSO₄ and water-insoluble Fe₂O₃ polymorphs by excess of solid iron(II or III) sulphates at 650°C in 4 h. Since SO₃ forms in situ from the Fe₂(SO₄)₃ as well as anhydrous Fe₂(SO₄)₃ forms in the thermal oxidation of iron(II) sulphate, therefore the gaseous SO₃ is the active sulphatization agent in the reaction of the hydrated iron(II and III) sulphates and the zinc ferrite. The sulphatization process were monitored by XRD, TG/DTA-MS, Mössbauer, Raman and IR-spectroscopy and the changes in reaction's heat and Gibbs energy are reported. The Fe₂O₃ polymorphs formed is worth processing into iron(III) sulphate by sulphuric acid. Since the Fe₂(SO₄)₃ formed in this way can be recycled to the sulphatization process, the only reagent consumed is the sulphuric acid. Therefore, these selective sulphatization reactions can be taken as "iron salts mediated" decompositions of zinc ferrite into ZnSO₄ and Fe₂O₃ by sulphuric acid.

* Corresponding Authors

Fax: +36-23-376-456

E-Mail: kotail@chemres.hu

- [a] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1025, Pusztaszeri u. 59-67, Budapest, Hungary; Permanent address: Department of Materials Science and Engineering, Indian Institute of Technology, 208 016 Kalyanpur, Kanpur, India
- [b] Department of Chemistry, University of Helsinki, Helsinki, P.O. Box 55, FI-00014, Finland; Permanent address: Research Group of Technical Analytical Chemistry of the Hungarian Academy of Sciences, Department of Inorganic and Analytical Chemistry, University of Technology and Economics, H-1111, Szent Gellért tér 4, Budapest, Hungary
- [c] Nuclear Analysis Department, Centre for Energy Research, Hungarian Academy of Sciences H-1525, P.O.B. 49, Budapest, Hungary
- [d] J. N. V. University, Department of Chemistry, 342 005, Jodhpur, Rajasthan, India
- [e] National Law University India, Faculty of Science, 342 005 Boranada, Jodhpur, Rajasthan, India

1. Introduction

The scarcely reactive spinel type zinc ferrite, ZnFe₂O₄, is one of the most common wastes from the thermal treatment of various zinc and iron containing industrial wastes¹. Its recycling into the blast furnace technologies is not possible because the elementary zinc formed during its reduction destroys the wall of the blast furnace². Removal of its zinc content, however, is a complicated process due to its low reactivity toward most of the chemicals even under very strict conditions³⁻⁸.

One of the possible reactions is the sulphatization with hot sulphuric acid (100-300°C)^{5,6}. Since concentrated sulphuric acid forms a basic iron sulphate layer on the surface of the ferrite grains which prevents it from the further

dissolution, therefore diluted (15 -60 %) sulphuric acid is generally used in these reactions. But dilute H₂SO₄ is very corrosive and the main disadvantage is that both zinc and iron content of ZnFe₂O₄ are transformed into the appropriate sulphate, and the iron content of the solution can be separated only as slightly soluble Na[Fe₃(SO₄)₂(OH)₆], which cannot be used in blast furnace technologies due to its sodium and sulphur content. In order to avoid these problems, sulphatization with gaseous reactants, e.g with SO₂ or SO₃ have been developed^{7,8}. ZnFe₂O₄ can be sulphatized by SO₂ gas, especially in the presence of air or oxygen at 500-600 °C with formation of ZnSO₄ and ZnO.2ZnSO₄ and the maximal conversion is roughly 54 % even in the presence of Fe₂O₃ which catalyses the SO₃ formation.

Since the decomposition of zinc ferrite in SO₂ or in Ar-SO₂ gas mixture without oxygen source could scarcely be observed, the active ingredient in the sulphatization is essentially the gaseous SO₃. Sulphatization of zinc compounds with ammonium sulphate around its thermal decomposition temperature showed that the in-situ generated SO₃ reacting with the mixture of ZnO and Fe₂O₃ converts ZnO selectively into ZnSO₄. However, the zinc ferrite is completely transformed into a mixture of ZnSO₄ and Fe₂(SO₄)₃^{4,9}.

The partial pressure of SO₃ above the Fe₂(SO₄)₃ is higher than that above the ZnSO₄,¹⁰ thus there is a chance to initiate a selective sulphatization of ZnFe₂O₄ with SO₃ produced in situ from Fe₂(SO₄)₃ to form water-soluble ZnSO₄ and a water-insoluble iron-compound (Fe₂O₃) which is suitable as raw material for blast furnace.

In order to clarify the mechanism of this sulphatization reaction, we studied the reaction of zinc ferrite with hydrated iron(II) and iron(III) sulphates at various temperatures.

2. Experimental Section

The wet hot-dip galvanising sludge obtained directly from Dunaferr Co. (Dunaujváros, Hungary) was dried at 200 °C for 2 h to remove its physically sorbed water content. The zinc was mainly found in the form of basic zinc(II) chloride, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. The sample was divided into three parts, and they were heated up to 500, 750 and 1000 °C, respectively. XRD analysis of these samples showed that the crystallinity increased with increasing temperature. We have attempted leaching of ZnO from the heat treated samples with treatment with diluted (1:1, v/v) HCl, however, the sample prepared at 500 °C contained highly defectuous ferrite compounds and almost completely dissolved in the aq. HCl. Therefore, an ammoniacal leaching process¹¹ was selected to remove ZnO from ZnFe_2O_4 . The ZnO could only be removed from the sample prepared at 500 °C in 96 h, the other two samples prepared at higher temperature contained less reactive sintered ZnO particles, thus for complete removal of the ZnO a 2 h treatment with 10 % of acetic acid was consecutively used. The ZnO free samples were heated again at 500, 750 and 1000 °C for 2 h. Zinc ferrite samples (0.5 g in each) were mixed with the sulphatizing agent in an agate mortar (1 equivalent of iron(II) sulphate heptahydrate, 1/3 equivalent of iron(III) sulphate nonahydrate), and the mixtures were kept at 500 °C for 4 h. The Fe_2O_3 and ZnSO_4 appeared only in the most reactive spinel containing sample prepared at 500 °C, but the conversion has not been complete. The samples prepared at 750 and 1000 °C did not react with these sulphates at 500 °C. Therefore, the next series of experiments were performed with the samples prepared at higher temperatures, even at 600 °C. In this case, the sample prepared at 750 °C showed the presence of Fe_2O_3 (hematite).

Based on these experiences, all the further experiments were done with the less reactive zinc ferrite samples prepared at 1000 °C, and the sulphatizing temperature was selected to be 650 °C based on the relative thermal stability ranges of zinc and iron sulfates. The less reactive zinc ferrite prepared at 1000 °C was mixed thoroughly in an agate mortar with iron(II) sulphate heptahydrate, iron(III) sulphate nonahydrate or $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at 1:2, 1:5 and 1:12.5 molar ratios and heated at 650 °C for 4 h. The mixture formed was subjected to XRD analysis and Mössbauer investigations.

X-ray powder diffraction measurements were performed by means of a Philips PW-1050 Bragg-Brentano parafocusing goniometer, equipped with a secondary beam graphite monochromator and proportional counter; scans were recorded in step mode by using CuK_α radiation at 40 kV and 35 mA tube power. Evaluation of the diffraction patterns have been obtained by full profile fitting techniques.

Raman spectra were measured by a Nicolet 950 FT-Raman spectrometer equipped with a Nd:YAG laser (1064 nm line) for excitation in the 4000-100 cm^{-1} region of Raman shifts in a diffuse reflection mode. IR spectra were recorded in diffuse reflection mode at room temperature in KBr (instrument: Nicolet 205 FT-IR). These vibrational spectroscopic methods were only used for monitoring of sulphate band intensity decreasing and checking the perfectness of sulphate recovering from the end-products.

Mössbauer spectra were obtained at 77 and 300 K in the constant acceleration mode (instrument: KFKI standard spectrometer equipped with a $^{57}\text{Co}/\text{Rh}$ source).

Thermal studies were performed on a SDT 2960 TA Instruments TG/DTA instrument coupled with a Balzers Thermostat GSD 200 mass spectrometer in air or He flow (130 ml/min) at 10 °C/min heating rate using open platinum crucible. Each studied sample weighed ca. 10 mg.

3. Results and Discussion

3.1. Preparation of zinc ferrite

Zinc ferrite samples were prepared from a sludge consisting of $\gamma\text{-FeOOH}$, $\varepsilon\text{-Zn}(\text{OH})_2$ and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ^{1a} by heating it at 500, 750 and 1000 °C for 5 h. These samples contained ZnFe_2O_4 and ZnO, which were identified by XRD and leached with 25% NH_4OH . Since the sintered ZnO particles formed at higher temperatures could not be completely dissolved in the ammonia solution, an aqueous acetic acid leaching after the ammoniacal treatment was also used that led to pure ZnFe_2O_4 . The samples prepared in this way were heat treated again at their preparation temperatures, namely at 500, 750 or 1000 °C for 2 h.

3.2. TG-MS studies on the zinc ferrite + hydrated iron(II) and iron(III) sulphate mixtures

In order to determine the optimal temperature ranges for isothermal sulphatization reactions of zinc ferrite with stoichiometric amounts of iron(II) and iron(III) sulphates, TG-MS studies were performed on the mixtures of $\text{ZnFe}_2\text{O}_4:\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnFe}_2\text{O}_4:\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ mixtures. Since the oxidation processes have key role in the sulphatization process performed with iron(II) sulphate, the iron(II) sulphate heptahydrate – zinc ferrite mixture was studied in inert (He) and oxidative atmosphere (air) as well. The TG-MS curves can be seen on Fig. 1 and 2.

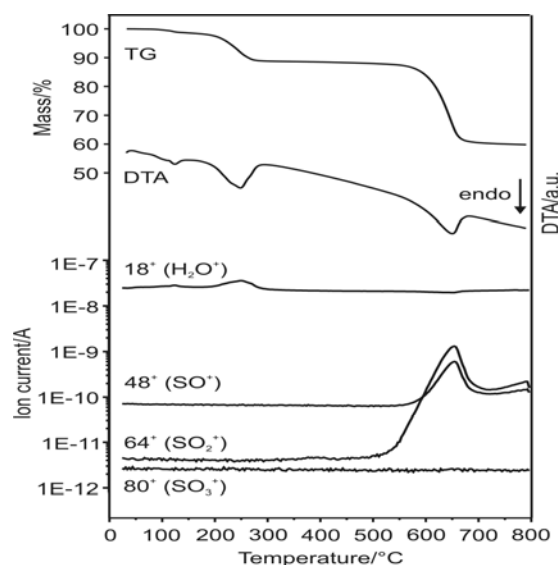


Figure 1. TG/DTA-MS monitoring of the reaction between zinc ferrite and iron(III) sulphate nonahydrate in air

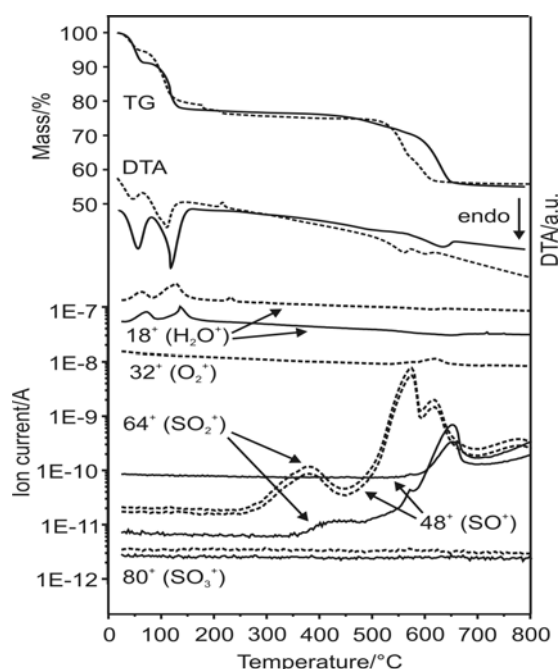


Figure 2. TG/DTA-MS monitoring of the reaction between zinc ferrite and iron(II)sulphate heptahydrate in air (dashed) and under helium (solid).

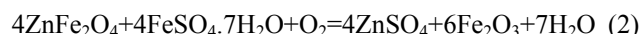
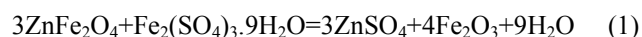
The iron(III) sulphate nonahydrate-zinc ferrite mixture shows two endothermic dewatering steps in the ranges of 100-150 °C and 200-300 °C with losing of one and eight water molecules (1,27 % and 9,80 % mass losses, respectively) from the hydrated iron(III) sulphate. The decomposition of anhydrous sulphate and the consecutive reaction of the formed SO_3 with zinc ferrite take place between 550-700 °C. The decomposition of the anhydrous iron(III) sulphate is endothermic. The SO_3 formed during the decomposition of anhydrous SO_3 either completely reacts with ZnFe_2O_4 or decompose into fragments in the gas phase during the measurement conditions (only SO_2^+ and SO^+ can be observed at $m/z=64$ and 48, the signal of SO_3^+ at $m/z=80$ could not be detected at all).

The iron(II) sulphate heptahydrate loses its water in helium in two main steps between 50-70 or 70-150 °C with elimination of 2.5 and 4.5 moles of water, respectively (8.85 % and 13.59 % mass losses in the two consecutive steps). In air, however, the iron(II) centers of the $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ intermediate are oxidized with formation of $\text{Fe}(\text{OH})\text{SO}_4$ and 0.5 mol of H_2O (a small exothermic peak appears in the DTA curve), and the 0.5 mole of water is eliminated with formation of $\text{Fe}_2\text{O}(\text{SO}_4)_2$. The water elimination steps in air are observed between 50-60 (5.15 %), 60-150 (15.17%) and 180-230 °C (1.1%), which means evolution of 1.5, 4.5 and 1 mol (0.5 +0.5) of water. Small amount of SO_2 could be detected in helium atmosphere between 350 and 550 °C and the main decomposition step occurred between 550 and 700 °C. The SO_2 and its fragmentation products were observed at lower temperature in air but the main decomposition step consists of two overlapping processes due to the stepwise decomposition character of $\text{Fe}_2(\text{SO}_4)_3$ into Fe_2O_3 .

3.3 Sulphatization of zinc ferrite with iron(II) and iron(III) sulphates

Isothermal heat treatment of the solid mixture of the stoichiometric amounts of hydrated iron(II)-sulphate (1:1 molar ratio) or hydrated iron(III)- sulphates (3:1 molar ratio) in air were monitored at 500, 750 and 1000 °C for 4 h. The XRD of the residues showed the same diffraction patterns, which indicated that the same chemical reactions took place, thus only the less reactive zinc ferrite samples prepared at 1000 °C were used in further experiments. The optimal reaction temperature was found to be 650 °C in air for the reactions and large excess (iron sulphate/zinc ferrite ≥ 12.5 molar ratio) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ were required to complete the zinc ferrite decomposition with 4 h reaction time. Similar experiments with aluminium sulphate, which has much less SO_3 tension at the sulphatization temperature, proved to be ineffective for the decomposition of zinc ferrite.

The XRD (Figs. 3 and 4) and Mössbauer investigations (Figs. 5 and 6, Table 1) unambiguously show that the only iron containing end products of the reactions are the Fe_2O_3 polymorphs, mainly hematite, $\alpha\text{-Fe}_2\text{O}_3$, thus the reactions can be expressed with the following equations:



The reactions are completed at 650 °C. Since the sulphur distribution is uniform across the iron(II) and iron(III) sulphate samples during their complete decomposition, and the chemical form of sulphur on the surface was proved to be adsorbed SO_3 ¹², the reactions (1) and (2) are probably SO_3 mediated gas-solid phase interactions as observed in sulphatization of red mud with iron(II) and iron(III) sulphates¹³. Therefore the conditions for in-situ generation of SO_3 and the mechanism of SO_3 formation from these iron sulphate compounds are important factors in order to determine the optimal conditions for zinc ferrite decomposition and for the preparation of zinc-free iron containing blast furnace raw materials.

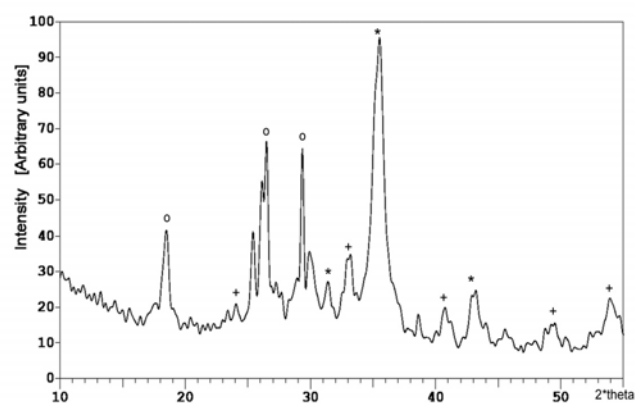
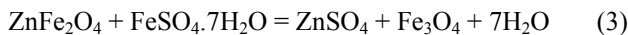


Figure 3. XRD of the $\text{ZnFe}_2\text{O}_4:\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1:1) mixture after heat treatment at 600 °C for 4 h.

+ $\text{Fe}_2(\text{SO}_4)_3$, * Fe_2O_3 (hematite), o $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$

The formal solid-solid phase “metal-exchange” reaction between the zinc ferrite and hydrated iron(II) sulphate would result in the formation of magnetite as in reaction (3). The reaction (3) is associated with the enthalpy change, $\Delta H = 400.3$ kJ/mol and the Gibbs free energy change, $\Delta G = -183.3$ kJ/mol (all enthalpy and free enthalpy values were calculated with Factsage program package with using the database of this program)



However, the only iron containing reaction product is the hematite, $\alpha\text{-Fe}_2\text{O}_3$. The reaction heat and Gibbs energy change for the reaction given by Eq. (2) are 228.9 kJ/mol and -267.2 kJ/mol respectively, thus thermodynamically the reaction (2) is more favourable than the reaction (3).

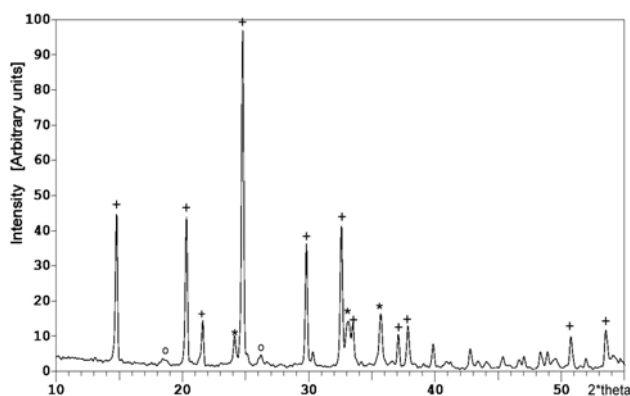
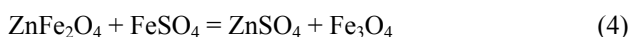


Figure 4. XRD of the $\text{ZnFe}_2\text{O}_4:\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (3:1) mixture after heat treatment at 600°C for 4 h.

+ - Fe_2O_3 (hematite), * - ZnFe_2O_4 (franklinite), o - ZnSO_4

Furthermore, these reactions are strongly endothermic and take place at high temperature therefore hydrated forms of iron sulphates cannot exist. The formal reaction of the water-free iron(II) sulphate, FeSO_4 can be written as:



The reaction (4) has positive reaction heat and Gibbs free energy values, $\Delta H = 16.1$ kJ/mol and $\Delta G = 11.3$ kJ/mol, respectively. The reaction (5), in which Fe_2O_3 is formed has negative reaction enthalpy, $\Delta H = -105.8$ kJ/mol, and Gibbs energy, $\Delta G = -72.3$ kJ/mol.

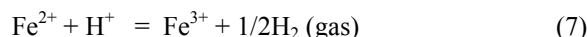


This unambiguously shows that the hydration degree of the iron(II) sulphate is only one among the essential factors, which plays role in the Fe_2O_3 formation and in preventing the magnetite formation. In inert atmosphere the decomposition reaction of freeze-dried iron (II) sulphate¹⁴ can be written as

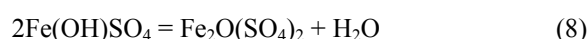


The stepwise dehydration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, leads to $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ¹⁵ and the solid-state ^1H NMR of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ showed the presence of two different kind of protons in 1:1 ratio, thus the formula could be written as $\text{Fe}(\text{OH})\text{SO}_4(\text{H})$ ¹⁶.

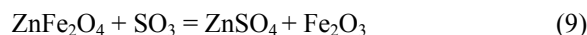
Since the OH group is located in the first coordination sphere, and the other proton is located at the sulphate oxygen and therefore acts as a strong acidic centre with the redox equilibrium.



In the absence of oxygen, the reaction (7) is shifted to left because increasing the partial pressure of the hydrogen terminates the oxidation of the iron(II) centres, however, in the presence of oxygen the elementary hydrogen is, probably, catalytically oxidized to water and the equilibrium shifts completely to the right. The consideration of this reaction is therefore an indication that the hydrated iron(II) sulphate is not converted to the anhydrous iron(II) sulphate. $\text{Fe}(\text{OH})\text{SO}_4$ is formed as intermediate that loses a water molecule and gets converted to the detected $\text{Fe}_2\text{O}(\text{SO}_4)_2$ intermediate^{15,17}.



The decomposition products of $\text{Fe}_2\text{O}(\text{SO}_4)_2$, as studied in detail in, are Fe_2O_3 and $\text{Fe}_2(\text{SO}_4)_3$, and these compounds were identified in the 1:5 $\text{ZnFe}_2\text{O}_4:\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ mixture after heating at 600°C for 4 h (Table 1) which is in conformity with XRD (Fig. 3) as well TG-MS results (Fig. 1). Since the intermediate $\text{Fe}_2\text{O}(\text{SO}_4)_2$ formed in the reaction (8) decomposes directly into anhydrous iron(III) sulphate, and the same compound is produced from the hydrated iron(III) sulphates¹⁸, the sulphatization of zinc ferrite can be performed in a similar way by the SO_3 generated along with Fe_2O_3 from the decomposition of anhydrous $\text{Fe}_2(\text{SO}_4)_3$. The reaction of zinc ferrite with SO_3 is expressed by Eq. (9).



The reaction (9) is thermodynamically more favourable ($\Delta H = -223.7$ kJ/mol, $\Delta G = -119.5$ kJ/mol) than the “direct” solid-solid phase interaction between the solid anhydrous iron(II) sulphate and zinc ferrite (reaction 4). The formation of $\text{Fe}_2(\text{SO}_4)_3$ intermediate in the reaction of ZnFe_2O_4 with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is confirmed by XRD and Mössbauer results (Fig. 3, Fig. 5, Table 1). The assignment of the singlet without quadruple splitting at $\text{IS} = 0.45$ was ambiguous, because this peak was assigned to $\text{Fe}_2\text{O}(\text{SO}_4)_2$ ¹⁹. However, Zboril et al. assigned this peak to $\text{Fe}_2(\text{SO}_4)_3$ ²⁰ and determined a QS value for the compound $\text{Fe}_2\text{O}(\text{SO}_4)_2$.

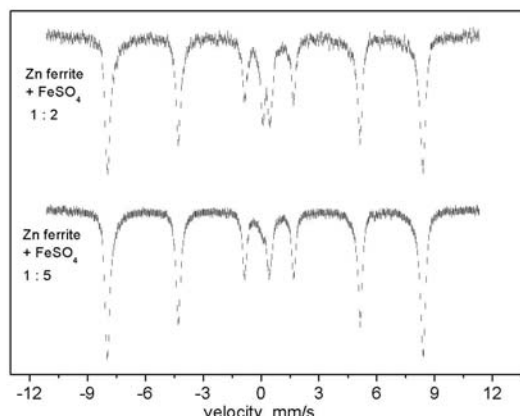


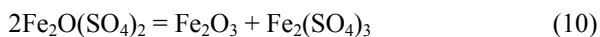
Figure 5. Mössbauer spectrum of the reaction product formed in the reaction of ZnFe_2O_4 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in air at 600°C for 4 h.

Table 1. Mössbauer data of the mixtures formed in the reactions of ZnFe₂O₄ with excess iron(II) and iron(III) sulphates at 600 °C for 4 h*

Sulphatizing material	Component	IS	QS	MHF	FWHM	RI
2-fold excess of FeSO ₄ .7H ₂ O	α-Fe ₂ O ₃	0.35	0.20	507	0.29	65
	ε-Fe ₂ O ₃	0.37	-	481	0.53	15
	ZnFe ₂ O ₄	0.31	0.39	-	0.31	19
5-fold excess of FeSO ₄ .7H ₂ O	α-Fe ₂ O ₃	0.35	0.21	508	0.29	76
	ε-Fe ₂ O ₃	0.35	-	483	0.58	12
	ZnFe ₂ O ₄	0.30	0.44	-	0.41	5
	Fe ₂ (SO ₄) ₃	0.45	-	-	0.30	6
2-fold excess of Fe ₂ (SO ₄) ₃ .9H ₂ O	α-Fe ₂ O ₃	0.35	0.20	508	0.26	24
	ε-Fe ₂ O ₃	0.30	-	487	0.65	30
	ZnFe ₂ O ₄	0.33	0.63	-	0.41	14
	Fe ₂ (SO ₄) ₃	0.45	-	-	0.30	31
5-fold excess of Fe ₂ (SO ₄) ₃ .9H ₂ O	α-Fe ₂ O ₃	0.35	0.20	508	0.26	20
	ε-Fe ₂ O ₃	0.31	-	486	0.65	17
	ZnFe ₂ O ₄	0.34	0.69	-	0.41	22
	Fe ₂ (SO ₄) ₃	0.45	-	-	0.30	41

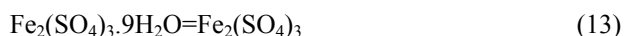
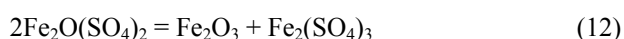
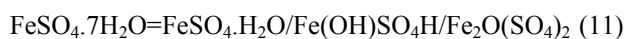
*IS-isomer shift, mm/S; QS-quadruple splitting, mm/s; FWHM-full width of half-maximum, mm/s; RI-relative spectral area, %, MHF-mean hyperfine field, Tesla.

Our XRD studies, however, confirmed the presence of anhydrous Fe₂(SO₄)₃, which could be formed as decomposition intermediate of Fe₂O(SO₄)₂²¹.



The hydrated iron(III) sulphate loses water molecules to form Fe₂(SO₄)₃ which decomposes in air between 500 and 600 °C with the formation of Fe₂O₃ and SO₃¹⁸. The SO₃ evolution contributes to the formation of ZnSO₄ (Eqn. 9) and slows down its dissociation into ZnO.2ZnSO₄⁴.

The sulphatization temperatures with FeSO₄.7H₂O and Fe₂(SO₄)₃ compounds are the same and located in the range of the decomposition of Fe₂O(SO₄)₂ intermediate^{15,18}. The similarities between the results of sulphatization reactions of both iron sulphates indicate that the same SO₃ mediated reaction takes place. The formation of SO₃ from these two iron sulphates during the same conditions can be explained easily with taking into consideration the formation of Fe₂(SO₄)₃ both in the dehydration of Fe₂(SO₄)₃.9H₂O and in the aerial oxidation of FeSO₄.7H₂O.



All iron(II) and iron(III) sulphate hydrates give the same decomposition intermediate in air, Fe₂(SO₄)₃.

The X-ray microanalysis of the thermal decomposition process of iron(II) and iron(III) sulphates unambiguously showed that the S/Fe ratio vs. temperature relationship is practically the same.

3.4. Industrial significance of the zinc ferrite sulphation with iron(II) and iron(III) sulphates

One of the main advantages of the solid phase sulphatization of zinc ferrite with iron sulphates with the sulphuric acid leaching is that the solid zinc sulphate is

formed and sulphuric acid is not present in the aqueous leachate solution. The only insoluble iron compound formed is Fe₂O₃, which can be removed by simple filtration. The residual water soluble Fe₂(SO₄)₃ can be easily separated by hydrolysis at 185-200°C with precipitation of Fe₂O₃ without Fe(OH)SO₄ formation²². In the presence of sulphuric acid and in the absence of zinc sulphate, however, the main product would be Fe(OH)SO₄^{22,23}. Since the iron contents of the starting materials (ZnFe₂O₄ and iron sulphates) are completely transformed into Fe₂O₃ polymorphs, these polymorphs can be recycled to regenerate iron sulphate or can be used as raw material for blast furnace technologies. In order to regenerate the sulphatization agent, the Fe₂O₃ polymorphs are treated with dilute sulphuric acid at 60 °C to form iron(III) sulphate. Depending on the concentrations, Fe₂(SO₄)₃.6H₂O, Fe₂(SO₄)₃.7H₂O and Fe₂(SO₄)₃.8H₂O can be crystallized out²⁴.

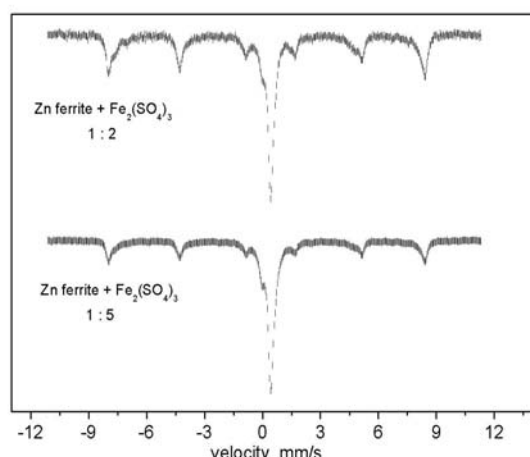
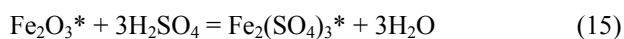
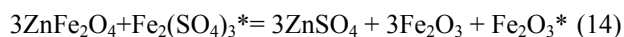


Figure 6. Mössbauer spectrum of the reaction product formed in the reaction of ZnFe_2O_4 and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ in air at 600°C for 4 h

Both $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ transform into Fe_2O_3 in their reaction with zinc ferrite, and dissolution of Fe_2O_3 in H_2SO_4 gives iron(III) sulphate compound for which molar sulphatization activity, defined as the number of evolved SO_3 moles per mole of iron(III) sulphate, is 1.5 compared to the value of 1 for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Formally, the sulphate content of the iron sulphates is completely transformed into zinc sulphate, and the Fe_2O_3 formed from the iron sulphates can be recycled into iron(III) sulphate with sulphuric acid, therefore the only reagent consumed is the sulphuric acid.

Iron sulphates act as a “selective form of sulphuric acid” to decompose zinc ferrite into ZnSO_4 and Fe_2O_3



where Fe_2O_3^* means the iron(III) oxide polymorphs formed from iron sulphates.

4. Conclusions

The scarcely reactive zinc ferrite can completely be decomposed by solid iron(II) or iron(III) sulphates at 650°C for 4 h into water-soluble ZnSO_4 and water-insoluble Fe_2O_3 polymorphs. The in situ formation of SO_3 during thermal decomposition of iron(III) sulphate or the thermal oxidation of iron(II) sulphate proved to be the active sulphatization agent. The intermediate, $\text{Fe}_2(\text{SO}_4)_3$, was formed in the decomposition of hydrated iron(III) sulphate as well, thus both iron sulphate compounds give practically the same characteristics of the zinc ferrite sulphatization process. The sulphatization equivalent of iron(III) sulphate is, however, 1.5 times the sulphatization equivalence of iron(II) sulphate. The Fe_2O_3 formed from these compounds can be used to regenerate iron(III) sulphate which is used in the sulphatization process, thus the only reagent used in the sulphatization process is the sulphuric acid. Therefore, the selective sulphatization is an “iron salts mediated” decomposition of zinc ferrite into

ZnSO_4 and Fe_2O_3 by sulphuric acid. This new method is the only known process for transformation of zinc ferrite into sodium-, sulphur- and zinc-free iron raw material for blast furnace technologies in a solvent free simple solid state reaction, including a simple regeneration possibility of the used solid reagents with using the cheapest chemical – sulphuric acid.

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