

INVESTIGATION ON THE THERMAL PROPERTIES OF $\text{Fe}_2\text{O}(\text{SO}_4)_2$ Part I

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Abstract

The data on the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ upon various regimes of heating and gaseous environment prove the formation of intermediate products of the types $\text{Fe}_2\text{O}(\text{SO}_4)_2$ and FeOHSO_4 , their stability and amount being determined mainly by temperature and oxygen-reduction potential.

This communication aims at presenting results on the synthesis and characterization of $\text{Fe}_2\text{O}(\text{SO}_4)_2$. The synthesis was carried out using a laboratory thermal equipment operating under isothermal conditions in the temperature range 713–813 K in a gaseous environment either poor in oxygen or containing 100% oxygen. The experimental conditions under which $\text{Fe}_2\text{O}(\text{SO}_4)_2$ is stable are established. The effect of three basic parameters on the synthesis of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ is clarified: the oxygen partial pressure, the ratio $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$ and the temperature and the mode of heating. Mössbauer spectroscopy and X-ray diffraction data for $\text{Fe}_2\text{O}(\text{SO}_4)_2$ are presented.

Keywords: $\text{Fe}_2\text{O}(\text{SO}_4)_2$, Mössbauer spectroscopy, TG, thermal decomposition, X-ray diffraction

Introduction

The data on the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in various gaseous environments and upon differing regimes of heating [1–4] prove the formation of intermediate products of the type of FeOHSO_4 and of $\text{Fe}_2\text{O}(\text{SO}_4)_2$. There are different suggestions published concerning both the type of the intermediate compounds formed during the decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and the temperature regions of their formation and decomposition [4–7].

In a previous study [8] we have proved that the formation of the intermediate products FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ is determined by temperature and the ratio between the partial pressures of water vapors and oxygen in the reactor and the values of this ratio result in the formation of different amounts of intermediate products. The synthesis of either FeOHSO_4 or $\text{Fe}_2\text{O}(\text{SO}_4)_2$ requires strictly defined experimental conditions with re-

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spect to temperature, partial pressures of H_2O and O_2 as well their supply to and out of the reactor.

This study continues our preceding investigations and aims at presenting results on a possible formation of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ via decomposition of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ under isothermal conditions and controlled gaseous environment.

Method of investigation

For the purpose of this study $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ was used as a starting material and was previously dried at 353 K and a pressure of $0.6\cdot 10^{-5}$ Pa to be dehydrated into $\text{FeSO}_4\cdot\text{H}_2\text{O}$. The obtained monohydrate contains 55.93% SO_4^{2-} ; 34.57% Fe and 9.5% H_2O . Figures 1a, 3a and 5c and Table 1 present data on X-ray diffraction, Mössbauer spectroscopy and electron microscopy data for the obtained $\text{FeSO}_4\cdot\text{H}_2\text{O}$ studied later experimentally.

Table 1 Mössbauer spectroscopy data for $\text{FeSO}_4\cdot\text{H}_2\text{O}$

Compound	Parameters		Content of $\text{Fe}^{n+}/\%$	Phase identified by	
	$\delta_{\text{is}}/\text{mm s}^{-1}$	$\Delta E_{\text{Q}}/\text{mm s}^{-1}$		Mössbauer spectroscopy	X-ray diffraction
$\text{FeSO}_4\cdot\text{H}_2\text{O}$	1.20	2.73	100.0	$\text{FeSO}_4\cdot\text{H}_2\text{O}$	$\text{FeSO}_4\cdot\text{H}_2\text{O}$

The process of thermal decomposition of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ upon isothermal heating is studied in a laboratory equipment (Fig. 2) consisting of an electrical resistant furnace, 4, equipped by thermal-controlling circuit (8, 9, 10). The gases used (either a mixture of $5.0\cdot 10^{-3}$ $\text{O}_2\%$ +Ar or pure O_2) were supplied at a rate of $5.6\cdot 10^{-6}$ $\text{m}^3 \text{s}^{-1}$. Prior the supply to the reactor the gas was dried by P_2O_5 . After the necessary temperature had been established and the system flowed the sample was put in the quartz reactor (6). The sample mass was 1.0 g and the duration of the experiments 30 min.

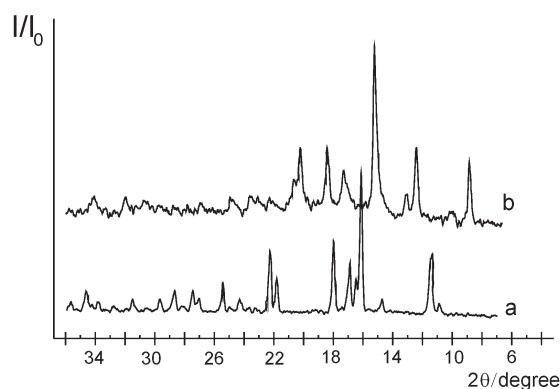


Fig. 1 X-ray diffraction patterns of: a – the starting material $\text{FeSO}_4\cdot\text{H}_2\text{O}$; b – $\text{Fe}_2\text{O}(\text{SO}_4)_2$ obtained upon heating at 813 K

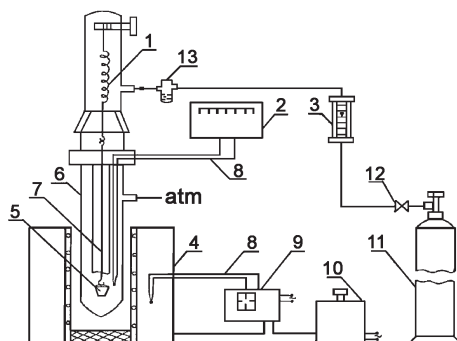


Fig. 2 Experimental setup : 1 – spiral thermal balance; 2 – recording device; 3 – rotameter; 4 – electric heating furnace; 5 – crucible; 6 – reactor; 7 – platinum filament; 8 – thermocouples; 9 – thermoregulator; 10 – V-converter; 11 – gas mixture container; 12 – valves; 13 – drier

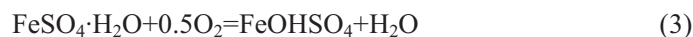
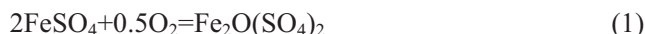
The value of P_{O_2} in the mixture with argon was measured in a laboratory equipment operating with a solid-electrolyte sensor, its principle has been described elsewhere [10]. It was found that the content of O_2 in the mixture is $5.0 \cdot 10^{-3} \text{ O}_2\% + \text{Ar}$.

X-ray diffraction analyses were carried out using a Philips apparatus and FeK_α radiation, while Mössbauer spectral analyses by a Mössbauer spectrometer under the constant acceleration of a radioactivity source (^{57}Co in Pd). The rate scale is calibrated with respect to $\alpha\text{-Fe}$.

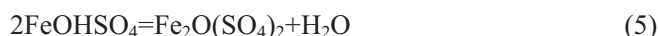
Electron microscopy pictures were taken with a Philips EM 400 instrument at 60 kV in the electron magnification range 11 700–33 000.

Results

The conditions for two series of experiments were specified on the basis of our previous results [8, 9], namely buffering by a mixture of $5.0 \cdot 10^{-3} \text{ O}_2\% + \text{Ar}$ and by pure oxygen. Thus, we performed experiments under conditions, where by varying the content of O_2 in the buffering gas one can control the maximum yield of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ resulting as final products of the following reactions:



The drier P_2O_5 , put on the reactor input, assures that $P_{\text{H}_2\text{O}}$ would be confined and determined only by the proceeding of the dehydration reactions (2) and (3) as well as by the following reactions:



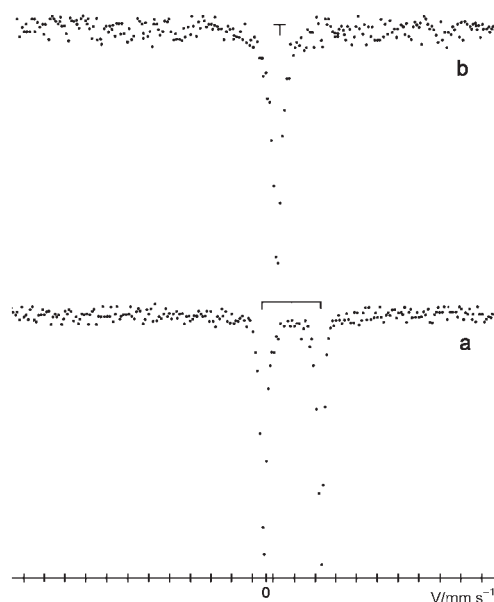


Fig. 3 Mössbauer spectra of: a – the starting material $\text{FeSO}_4 \cdot \text{H}_2\text{O}$; b – $\text{Fe}_2\text{O}(\text{SO}_4)_2$ synthesized upon isothermal heating at 813 K in oxygen

The choice of the isothermal regime of heating in the temperature range 690–970 K [8, 9] provokes a higher yield of reactions (1)–(5).

The data presented in Table 2 and Fig. 4a illustrate the change in the content of solid products formed as a result of the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in gaseous environment of $5.0 \cdot 10^{-3} \text{ O}_2\% + \text{Ar}$ upon isothermal heating. The main phase identified by Mössbauer spectroscopy as a doublet of isomeric shift of δ_{is} and quadruple splitting of ΔE_Q is FeSO_4 . The X-ray diffraction patterns of the same samples indicate the presence of FeSO_4 combined with other crystal hydrates such as $\text{FeSO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. As the water-free FeSO_4 absorbs strongly water vapors when exposed to air, the indication on the X-ray patterns for the presence of these crystal hydrates can be explained through secondary re-hydration in the course of the sample preparation rather than as due to intermediate products formed during the hydration processes in the reactor. In the temperature range 713–778 K the amount of FeSO_4 preserves relatively high (Fig. 4a), 77–90%, these values being specified on the basis of the distribution of the content of Fe^{2+} between the iron-containing phases in the solid products from the thermal decomposition. Later on this specification will be used for presenting the content of iron in all phases in the final solid products. Only at temperatures higher than 788 K a reduction to 26% is detected at 813 K. One can suppose that at this temperature a direct decomposition of FeSO_4 to $\alpha\text{-Fe}_2\text{O}_3$ starts due to its thermal stability limits being reached:

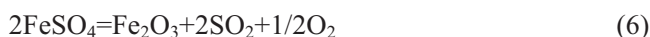


Table 2 Mössbauer spectroscopy data for the solid products from the thermal decomposition of FeSO₄·H₂O in 5.0·10⁻³ O₂%+Ar and upon isothermal heating

Temperature/K	Parameters			Content of Fe ⁿ⁺ / %	Phase identified by	
	δ _{is} / mm s ⁻¹	ΔE _Q / mm s ⁻¹	ΔH _{eff} / kOe		Mössbauer spectroscopy	X-ray diffraction
693	1.22	2.94	–	77.00	FeSO ₄	FeSO ₄ ·H ₂ O, FeSO ₄ ,
	0.40	1.44	–	17.00	FeOHSO ₄	FeOHSO ₄ ,
	0.44	–	–	6.00	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
713	1.25	2.90	–	90.00	FeSO ₄	FeSO ₄ ,
	0.44	1.44	–	6.00	FeOHSO ₄	FeOHSO ₄ ,
	0.55	–	–	4.00	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
733	1.18	2.88	–	91.40	FeSO ₄	FeSO ₄ ·3H ₂ O,
	0.50	–	–	8.60	Fe ₂ O(SO ₄) ₂	FeSO ₄ , Fe ₂ O(SO ₄) ₂
753	1.21	2.88	–	87.60	FeSO ₄	FeSO ₄ ·7H ₂ O,
	0.40	–	–	12.40	Fe ₂ O(SO ₄) ₂	FeSO ₄ ·H ₂ O, FeSO ₄ ,
763	1.25	2.95	–	80.60	FeSO ₄	FeSO ₄ ·H ₂ O, FeSO ₄ ,
	0.48	–	–	19.60	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
768	1.30	2.84	–	78.80	FeSO ₄	FeSO ₄ ·H ₂ O, FeSO ₄ ,
	0.44	–	–	16.70	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ , Fe ₂ O ₃ ,
	0.325	0.00	508.9	4.50	α-Fe ₂ O ₃	FeOHSO ₄
778	1.25	2.78	–	77.30	FeSO ₄	FeSO ₄ ·H ₂ O,
	0.55	–	–	6.80	Fe ₂ O(SO ₄) ₂	FeSO ₄ , Fe ₂ O(SO ₄) ₂ ,
	0.325	0.22	–	15.90	α-Fe ₂ O ₃	Fe ₂ O ₃
788	1.30	2.89	–	61.20	FeSO ₄	FeSO ₄ ·3H ₂ O,
	0.51	–	–	30.90	Fe ₂ O(SO ₄) ₂	FeSO ₄ , Fe ₂ O(SO ₄) ₂ ,
	0.325	0.00	508.9	7.90	α-Fe ₂ O ₃	Fe ₂ O ₃
800	1.30	2.90	–	60.00	FeSO ₄	FeSO ₄ ,
	0.475	–	–	26.20	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ ,
	0.325	0.00	508.9	13.80	α-Fe ₂ O ₃	Fe ₂ O ₃
813	1.30	2.90	–	26.60	FeSO ₄	FeSO ₄ ,
	0.475	–	–	37.00	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ ,
	0.325	0.00	508.9	37.00	α-Fe ₂ O ₃	Fe ₂ O ₃

At temperature 813 K in the environment poor in oxygen, the content of both Fe₂O(SO₄)₂ and α-Fe₂O₃ is the highest (about 37%). The Mössbauer spectrum of Fe₂O(SO₄)₂ in all the samples studied reveals a single line of isomeric shift 0.44–0.51 mm⁻¹. The X-ray diffraction data also prove the presence of Fe₂O(SO₄)₂, the most characteristic peaks corresponding to inter-atomic distances *d*, Å=6.07; 4.37; 3.62; 3.02; 2.76, in a good accordance with our preceding data on the thermal decomposition of FeSO₄·H₂O upon dynamic heating in air [8]. The Mössbauer spectrum of α-Fe₂O₃ consists of a single sextet with δ_{is}=0.325 mm s⁻¹, ΔE_Q=0 mm s⁻¹ and effective magnetic moment ΔH_{eff}=508.8 kOe characterizing α-Fe₂O₃ as the only magnetic-active compound among the solid products of the decomposition of FeSO₄·H₂O.

It is worth noting that small amounts of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ were detected in the products even at 693 K, whereas the formation of $\alpha\text{-Fe}_2\text{O}_3$ begins at 768 K.

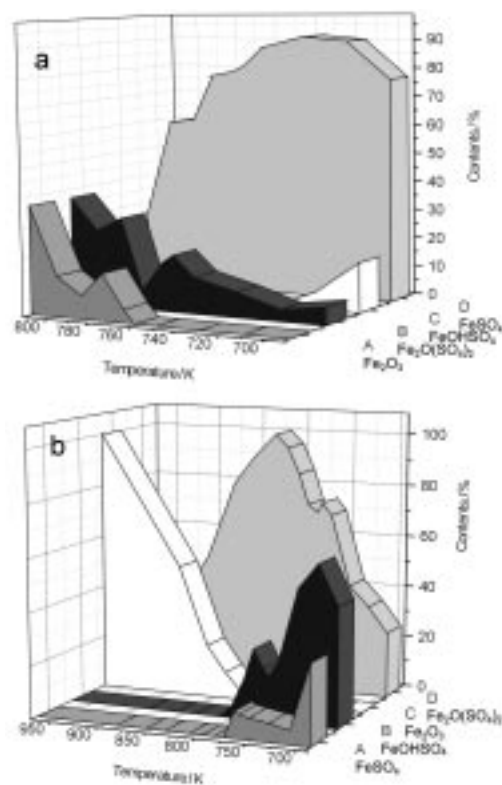


Fig. 4 Distribution of the content of Fe in the solid products of the decomposition of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ in: a – environment poor in oxygen; b – in oxygen

FeOHSO_4 is formed in an amount smaller than that of $\text{Fe}_2\text{O}(\text{SO}_4)_2$, being 17% in the solid product from the decomposition of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ at 713 K and its Mössbauer spectrum also is a doublet, but characterized with $\delta_{\text{is}}=0.44 \text{ mm s}^{-1}$ and $\Delta E_{\text{Q}}=1.44 \text{ mm s}^{-1}$.

Data in Table 3 and in Fig. 4b present the change in the content of solid phases from the thermal decomposition of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ upon isothermal heating in pure oxygen. Figure 4b illustrates a totally different phase distribution in the temperature range 693–973 K obtained in an environment poor in oxygen (Fig. 4a). The main phase for this experimental series is $\text{Fe}_2\text{O}(\text{SO}_4)_2$. Even at 693 K, 25% of the decomposition's solid product is in the form of $\text{Fe}_2\text{O}(\text{SO}_4)_2$, and the yield of its production increases with increasing gradually the temperature, reaching 100% at 813 K (Fig. 3b). The Mössbauer spectroscopy and X-ray diffraction data for this phase point to a subsequent decomposition of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ to $\alpha\text{-Fe}_2\text{O}_3$ at temperatures between 888 and 973 K according to the reaction

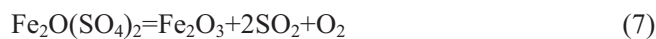


Figure 4b shows that at small temperature deviations from 813 K (e.g. 800 and 838 K), besides the main product Fe₂O(SO₄)₂, FeOHSO₄ (at 800 K) and α-Fe₂O₃ (at 838 K) are present in the solid phase.

Table 3 Mössbauer spectroscopy data for the solid products of the thermal decomposition of FeSO₄·H₂O upon isothermal heating in oxygen atmosphere

Temperature/K	Parameters			Content of Fe ⁿ⁺ / %	Phase identified by	
	δ _{is} / mm s ⁻¹	ΔE _Q / mm s ⁻¹	ΔH _{eff} / kOe		Mössbauer spectroscopy	X-ray diffraction
693	1.33	2.94	–	30.00	FeSO ₄	FeSO ₄ ·H ₂ O,
	0.44	1.23	–	45.00	FeOHSO ₄	FeOHSO ₄ ,
	0.50	–	–	25.00	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ , FeSO ₄
713	1.18	2.88	–	5.20	FeSO ₄	FeSO ₄ ,
	0.33	1.50	–	60.10	FeOHSO ₄	FeOHSO ₄ ,
	0.37	–	–	34.70	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
733	1.15	2.88	–	91.40	FeSO ₄	FeSO ₄ ,
	0.42	1.45	–	50.60	FeOHSO ₄	FeOHSO ₄ ,
	0.44	–	–	8.60	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
753	1.47	2.88	–	8.10	FeSO ₄	FeSO ₄ ,
	0.34	1.46	–	22.30	FeOHSO ₄	FeOHSO ₄ ,
	0.44	–	–	69.60	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
763	1.25	2.84	–	8.90	FeSO ₄	FeSO ₄ ,
	0.44	1.48	–	17.00	FeOHSO ₄	FeOHSO ₄ ,
	0.44	–	–	74.10	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
768	1.20	2.78	–	9.85	FeSO ₄	FeSO ₄ ,
	0.48	1.55	–	19.72	FeOHSO ₄	FeOHSO ₄ ,
	0.50	–	–	70.42	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
778	0.44	1.55	–	26.70	FeOHSO ₄	FeOHSO ₄ ,
	0.50	–	–	73.30	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
788	0.50	1.47	–	15.00	FeOHSO ₄	Fe ₂ O(SO ₄) ₂
	0.55	–	–	85.00	Fe ₂ O(SO ₄) ₂	
800	0.40	1.40	–	5.00	FeOHSO ₄	Fe ₂ O(SO ₄) ₂
	0.475	–	–	95.00	Fe ₂ O(SO ₄) ₂	
813	0.475	–	–	100.0	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂
838	0.50	–	–	90.00	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ ,
	0.35	0.30	508.8	10.00	α-Fe ₂ O ₃	α-Fe ₂ O ₃
858	0.50	–	–	80.00	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ ,
	0.35	0.28	508.8	20.00	α-Fe ₂ O ₃	α-Fe ₂ O ₃
888	0.55	–	–	50.00	Fe ₂ O(SO ₄) ₂	Fe ₂ O(SO ₄) ₂ ,
	0.35	0.25	505.8	50.00	α-Fe ₂ O ₃	α-Fe ₂ O ₃
973	0.35	0.00	508.8	100.0	α-Fe ₂ O ₃	α-Fe ₂ O ₃

The second in amount phase, obtained upon treating of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in pure oxygen, is FeOHSO_4 , its amount varying from 25% at 693 K to 60.10% at 713 K. The temperature range of the existence of the latter is wider in pure oxygen (up to 800 K) than in environment of low oxygen concentration (up to 733 K).

Maximum yields of FeOHSO_4 were observed in the low-temperature range (up to 733 K in oxygen), while those of the oxysulphate at higher temperatures (778–858 K). FeSO_4 and $\alpha\text{-Fe}_2\text{O}_3$ are the phases formed next in amount, that of the former being low even at about 713, whereas the latter was detected at 838 K, its amount being increased with raising temperature due to desulphurization of various sulphates.

Discussion

Thermodynamic analysis of the system Fe–S–O at 500 K [8, 9] shows the possibility for simultaneous existence of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$, the equilibrium between them is determined by the values of $P_{\text{H}_2\text{O}}$ in reaction (5). Below the equilibrium value of $P_{\text{H}_2\text{O}}$ FeOHSO_4 is more stable, while above it $\text{Fe}_2\text{O}(\text{SO}_4)_2$. As the equilibrium between FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ can be reached at very low oxygen partial pressures ($>1 \cdot 10^{-23}$ Pa), the formation of FeOHSO_4 and/or $\text{Fe}_2\text{O}(\text{SO}_4)_2$ depends only on the $P_{\text{H}_2\text{O}}$.

With respect to the effect of temperature, the obtained experimental results correspond to those based on the thermodynamic analysis. In order to obtain FeOHSO_4 and/or $\text{Fe}_2\text{O}(\text{SO}_4)_2$ not containing other sulphates or oxides values of $P_{\text{H}_2\text{O}}$ and P_{O_2} higher than the equilibrium ones are required. It was found that in order to decompose $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in an oxygen-poor atmosphere at temperatures 693–753 K, the ratio $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$ determined by the dehydration processes, is not sufficient for oxidation of Fe^{2+} to Fe^{3+} present in FeOHSO_4 only. At the same time, these values of the ratio cannot assure the oxidation of Fe^{2+} to Fe^{3+} present in $\text{Fe}_2\text{O}(\text{SO}_4)_2$ only, too. That is why, in an oxygen-poor environment the water-free FeSO_4 is the main phase from the decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (6), while FeOHSO_4 (17.0% from the Fe^{3+} at $T=693$ K) and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ (19.4% from the Fe^{3+} at $T=763$ K) are products of its oxidation. This is in accordance with the results reported by Gallagher *et al.* [2]. To improve the conditions for the oxidation Fe^{2+} to Fe^{3+} in FeOHSO_4 , one should keep the temperature below 753 K and the ratio $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$ far above the equilibrium value. The increase of temperature above 813 K does not accelerate the oxidation processes, rather initiates the thermal decomposition of the already formed sulphates to $\alpha\text{-Fe}_2\text{O}_3$.

Another is the distribution of the solid phases obtained in oxygen (Fig. 4b), where the oxidation of Fe^{2+} in the water-free FeSO_4 into Fe^{3+} present in FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ is to a great extent over depending on temperature, a fact confirmed by the Mössbauer spectroscopy and X-ray diffraction data (Fig. 4b and Table 3). The reaction yields of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ in this case are higher than of those in oxygen-poor environment, e.g. the content of FeOHSO_4 reaches 60.10% in the solid product from the decomposition at 713 K. In the temperature range 693–733 K its content is determined by the partial pressure of the water vapors and by the dehydration processes taking place and this the reason why the hydroxysulphate is the main

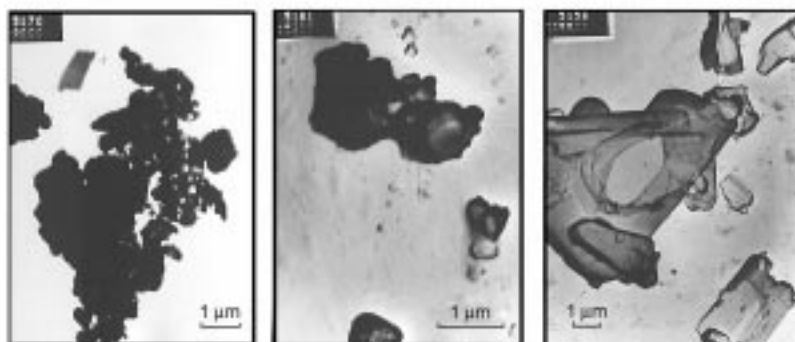


Fig. 5 Scanning electron microscopy pictures of: a – $\alpha\text{-Fe}_2\text{O}_3$; b – $\text{Fe}_2\text{O}(\text{SO}_4)_2$; c – $\text{FeSO}_4\cdot\text{H}_2\text{O}$

phase in the solid products from the decomposition of FeOHSO_4 in this temperature range.

With increasing temperature to 813 K the dehydration of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ proceeds faster and, accordingly, $P_{\text{H}_2\text{O}}$ maximizes rapidly as well and then decreases due to the dehydration processes is over. These conditions are more suitable for the oxidation of Fe^{2+} into Fe^{3+} to proceed with the formation of $\text{Fe}_2\text{O}(\text{SO}_4)_2$, not of FeOHSO_4 . Under such conditions the reaction yield of FeOHSO_4 decreases, while that of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ strongly increases, reaching 100% at 813 K (Fig. 3b, Table 3).

The thermal decomposition of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ upon isothermal heating leads also to changes in the morphology of the materials studied which are illustrated in Fig. 5, where scanning electron microscopy pictures of the starting, an intermediate and the final phases formed during the process of decomposition are presented. It is obvious that temperature and the gaseous environment determine – to a great extent – the size, shape and homogeneity of the grains and crystallites building the formed products.

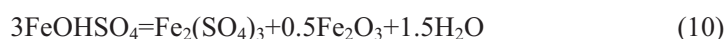
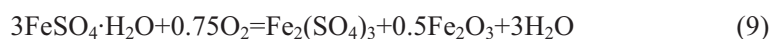
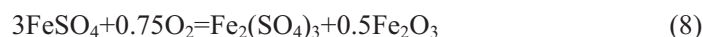
Table 4 X-ray diffraction data for $\text{Fe}_2\text{O}(\text{SO}_4)_2$ measured with FeK_α radiation

I/I_0	$D/\text{Å}$	I/I_0	$D/\text{Å}$
33.30	6.05	9.10	2.52
3.03	5.31	9.50	2.45
40.60	4.37	9.50	2.40
12.12	4.14	8.50	2.27
100.00	3.62	9.60	1.88
24.24	3.19	12.10	1.82
40.00	3.02	10.90	1.72
37.50	2.76	10.90	1.62
20.60	2.70	13.30	1.58

The results obtained prove that at high values of P_{O_2} the oxidation of Fe^{2+} to Fe^{3+} may be accomplished completely with the formation of $\text{Fe}_2\text{O}(\text{SO}_4)_2$. One can accept that isothermal heating at 813 K in oxygen provides most appropriate conditions for the production of pure $\text{Fe}_2\text{O}(\text{SO}_4)_2$. The Mössbauer spectrum (Fig. 3b) and the X-ray diffraction pattern (Fig. 1) can be considered as typical of this compound. Figure 1b and Table 4 present the characteristic inter-planar spacings (in Å) and peak intensities.

At temperatures higher than 813 K $\text{Fe}_2\text{O}(\text{SO}_4)_2$ decomposes forming $\alpha\text{-Fe}_2\text{O}_3$ which at 973 K becomes the main phase of the decomposition product.

As it has already been mentioned, in both gaseous environments $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ form at different temperatures. This is especially characteristic of the oxygen-rich environment, where $\text{Fe}_2\text{O}(\text{SO}_4)_2$ was detected in the solid decomposition product at 693 K, while $\alpha\text{-Fe}_2\text{O}_3$ at 768 K. One can suppose that $\text{Fe}_2\text{O}(\text{SO}_4)_2$ instead of $\text{Fe}_2(\text{SO}_4)_3$ is formed in the system according to the reactions



It is evident from (8)–(10) that in the framework of such a mechanism sulphur is always bound into the solid phase and there is no emission of sulphur oxides from the system, which would prove the contribution of these reactions. The balance with respect to Fe could be realized only if $\alpha\text{-Fe}_2\text{O}_3$ were also formed in the solid phase. The simultaneous production of $\text{Fe}_2(\text{SO}_4)_3$ and $\alpha\text{-Fe}_2\text{O}_3$ at the same temperature in oxygen-rich environment would also be an indication for the reactions (8)–(10) to be responsible for the formation of $\text{Fe}_2(\text{SO}_4)_3$. Therefore, our results undoubtedly reject this mechanism and, thus, the possibility to obtain $\text{Fe}_2(\text{SO}_4)_3$ instead of $\text{Fe}_2\text{O}(\text{SO}_4)_2$.

The comparison between our experimental data contributes to clarify the contradictions concerning the decomposition mechanism of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ published so far [2, 4–7]. The majority of authors have proposed a general mechanism for this process not accounting for the specific experimental conditions. Our results make it possible to state that the mechanism of this process correlates strictly with the combined effect of temperature, $P_{\text{H}_2\text{O}}$ and P_{O_2} . So, in a nearly inert atmosphere, where P_{O_2} is low, dehydration of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ becomes stable phase at temperatures between 650 and 750 K, while at temperatures higher than 750 K desulphurization of FeSO_4 to $\alpha\text{-Fe}_2\text{O}_3$, SO_2 and O_2 takes place.

In an environment rich in oxygen, $\text{Fe}_2\text{O}(\text{SO}_4)_2$ forms at 813 K, which at temperatures higher than 813 decomposes to $\alpha\text{-Fe}_2\text{O}_3$, SO_2 and O_2 .

In all other cases, when oxygen or water vapors are present in the reactor, conditions for the formation of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ exist at various temperatures. This fact explains the published differences in the pathways presenting the stages in the dehydration of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ via partial oxidation of Fe^{2+} to Fe^{3+} and a multi-step mechanism of desulphurization of formed sulphates.

The results obtained in characterizing $\text{Fe}_2\text{O}(\text{SO}_4)_2$ prove that in its structural, chemical and morphological properties $\text{Fe}_2\text{O}(\text{SO}_4)_2$ is quite similar to $\text{Fe}_2(\text{SO}_4)_3$. This

similarity provokes discussions [6] about the formation of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ or the identification of this compound as $\text{Fe}_2(\text{SO}_4)_3$.

Conclusions

The results presented prove that the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ results in the formation of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ independently of the gaseous environment. It is possible to produce a mixture of iron sulphates, FeSO_4 , FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ in varying proportions depending on temperature, and the values of $P_{\text{H}_2\text{O}}$, P_{O_2} and the ratio $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$.

By controlling the mode of heating and the ratio $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$, one can govern the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in order to produce a desired final product. At 813 K, high P_{O_2} and low $P_{\text{H}_2\text{O}}$, dehydration resulting in a complete oxidation of Fe^{2+} to Fe^{3+} and the formation of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ can be performed.

References

- 1 S. Mahapatra, T. P. Prasad, K. K. Rao and R. Nayak, *Thermochim. Acta*, 161 (1990) 279.
- 2 P. K. Gallagher, D. W. Johnson and F. Schrey, *J. Amer. Ceram. Soc.*, 53 (1970) 666.
- 3 S. Music, A. Vertes, G. W. Simmons, I. Czako-Nagy and H. Leidheiser, *Radiochem. Radioanal. Letters*, 45 (1981) 315.
- 4 M. S. R. Swamy and T. P. Prasad, *J. Thermal Anal.*, 16 (1979) 471.
- 5 E. Margulis, L. Shokarev, L. Savcheva, I. Kopilov and L. Beisekeeva, *J. Neorgan. Chemistry (in Russian)*, 16 (1971) 734.
- 6 K. Skeff Neto and V. K. Garg, *J. Inorg. Nucl. Chem.*, 37 (1975) 2287.
- 7 A. Bristoti, J. I. Kunrath and P. J. Viccaro, *J. Inorg. Nucl. Chem.*, 37 (1975) 1149.
- 8 Y. Pelovski, V. Petkova and S. Nikolov, *Thermochim. Acta*, 274 (1996) 273.
- 9 Y. Pelovski and V. Petkova, *J. Thermal Anal.*, 48 (1997) 1227.
- 10 Y. Pelovski, V. Petkova, I. Gruncharov, B. Pacewska and J. Pysiak, *Thermochim. Acta*, 205 (1992) 283.