

Application of Mechanochemical Activation Followed by Thermal Treatment for Utilization of Pyrite Concentrates

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Abstract

The possibilities to utilize pyrite concentrates from Chelopech Region (Bulgaria) were investigated using mechanochemical and thermal methods to obtain soluble iron-containing compounds and to extract useful microelements from the polymetallic ore. Mechanochemical activation was carried out in a planetary mill for 10 h; the resulting solid-phase samples were heated under isothermal conditions at 573 K for 4 h. To estimate mechano and thermochemical effects, Mössbauer spectroscopy, X-ray phase analysis and thermal methods of analysis in the oxidative gas medium were used. It was proved by means of physicochemical methods that phase transformation of pyrite to FeSO₄ and a decrease in its ignition temperature by 120 K are possible after triboactivation of pyrite samples.

INTRODUCTION

It is known that mechanochemical activation is a suitable method for processing solid-phase substances because its application causes the formation of structural defects, active surface states, etc. [1]. As a result, excited and energy-unstable states arise; during the relaxation of the accumulated mechanical energy they promote phase transformations, chemical reactions and irreversible transformations [2]. The joint application of mechanochemical and thermal methods allows one to avoid the disadvantages of chemical methods bringing about the formation of solid-phase and gaseous wastes. Pyrite is a waste product of this kind, too. On the one hand, accumulation of pyrite concentrates causes ecological problems; on the other hand, this material is a source of sulphur and microelements. This defines the necessity to develop up-to-date and waste-free technologies of processing pyrite wastes to obtain pigments, catalysts, magnetic materials, etc. [6, 7].

In the present work we investigated the possibility to utilize pyrite concentrates (Chelopech Region, Bulgaria) by means of mechanochemical activation followed by thermal treatment. In order to estimate mechanochemical effects, we used spectroscopic methods (X-ray phase analysis, Mössbauer spectroscopy) and thermal methods of analysis.

EXPERIMENTAL

Mechanochemical activation was carried out in Fritch-Pulverizette-7 planetary mill with milling bodies made of steel 12 mm in diameter in the air. The mass ratio of milling bodies to the sample was 9 : 1, time of mechanochemical activation was 10 h.

The samples were investigated using electromechanical spectrometer Wissel (Wissenschaftliche Elektronik, GMBH, Germany) operating in the regime of constant acceleration. The resulting spectra (above 10⁶ pulses per channel) were treated with the least squares.

The experimental curves were approximated with Lorentz function. The major parameters of hyperfine interaction were determined: IS – isomeric shift (with respect to α -Fe), QS – quadrupole splitting, FWHM – line width, A – the area of the spectrum of partial component. The error of parameter measurement together with the error of calibration was ± 0.02 mm/s.

The X-ray phase diffraction patterns were obtained with TUR-M62 instrument with the computer-controlled goniometer HZG-4 (CoK α radiation). The resulting spectra were compared with the JCPDS database [8]. Mean crystallite size was determined according to Scherer equation approximating the diffraction line with the Lorentz function.

Isothermal heating of the samples of non-treated and mechanically activated pyrite was carried out at a temperature of 573 K for 4 h. Experiments on TG, DTG and DTA were carried out with the thermal unit Stanton Redcroft (England) within temperature range 20–1400 K at the heating rate of 10 K/min in the gas medium (air). Sample mass was (10 ± 0.3) mg.

Sample composition, mass concentration: pyrite – S 41.87, Fe 37.63, SiO $_2$ 10.58; FeSO $_4 \cdot$ H $_2$ O – S 55.93, Fe 34.57, crystal water 9.50. A model mixture with the 1 : 1 mass ratio of components (a reference) was prepared from pyrite and ferrous sulphate.

RESULTS AND DISCUSSION

The diffraction patterns of the samples under investigation are shown in Fig. 1, *a–d*. It was established that the component prevailing in the initial sample of pyrite concentrate after floatation (see Fig. 1, *a*, sample A) is FeS $_2$ (PDF 42-1340); a small amount of SiO $_2$ (PDF 83-0539) and trace amount of FeSO $_4$ (PDF 73-1057) were also observed. Insignificant deviations in the interplanar spacing *d* after thermal treating at 573 K for 4 h (see Fig. 1, *b*, sample B) provide evidence of the conservation of composition and structure of pyrite. After mechanochemical treatment for 10 h, two effects are observed in the diffraction patterns (see Fig. 1, *c*, sample C): a clear presence of FeSO $_4$, FeSO $_4 \cdot$ H $_2$ O (PDF 45-1365) and a decrease in the mean size of

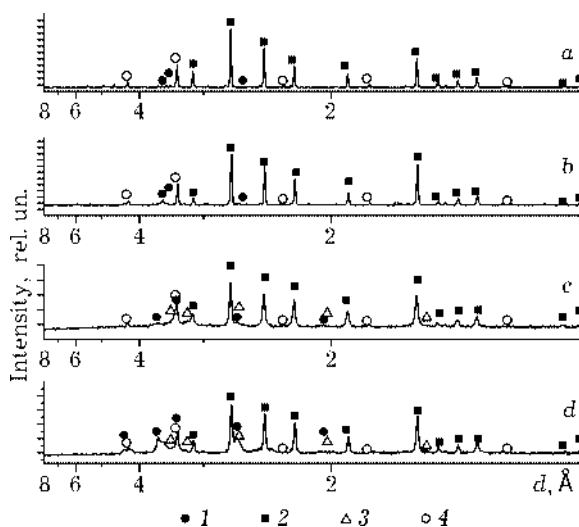


Fig. 1. X-ray diffraction patterns. Here and in Fig. 2: *a* – Fe $_2$ S (sample A); *b* – the same after heating at 573 K for 4 h (sample B); *c* – FeS $_2$ after mechanochemical treatment for 10 h (sample C); *d* – the same after heating at 573 K for 4 h (sample D); 1 – FeSO $_4$, 2 – FeS $_2$, 3 – FeSO $_4 \cdot$ H $_2$ O, 4 – SiO $_2$.

pyrite crystallites (Table 1) accompanied by the accumulation of structural defects.

In agreement with the latter statement, an increase in parameter *a* and the volume of elementary cell *V* is observed: from $a = 5.419$ Å and $V = 159.1$ Å 3 for the initial sample to $a = 5.423$ Å, $V = 159.4$ Å 3 for the mechanically activated one. A combination of mechanical and thermal treatment (see Fig. 1, *d*, sample D) leads to a substantial increase in the intensities of diffraction lines of ferrous sulphate (FeSO $_4$ and FeSO $_4 \cdot$ H $_2$ O) with the conservation of the mean crystallite size. Analysis of the spectra (see Fig. 1, *b* and *d*, samples B and D) suggests that mechanochemical treatment promotes thermal dissociation of pyrite.

The results of Mössbauer spectroscopic investigation are shown in Fig. 2, *a–d*, and in Table 2. The spectrum of sample A (see Fig. 2, *a*) consists of two components which are inten-

TABLE 1

Mean crystallite size of pyrite phase FeS $_2$, nm

| <i>hkl</i> | Sample | | | |
|------------|--------|----|----|----|
| | A | B | C | D |
| 200 | 54 | 45 | 30 | 27 |
| 210 | 51 | 48 | 27 | 32 |
| 211 | 48 | 46 | 28 | 33 |

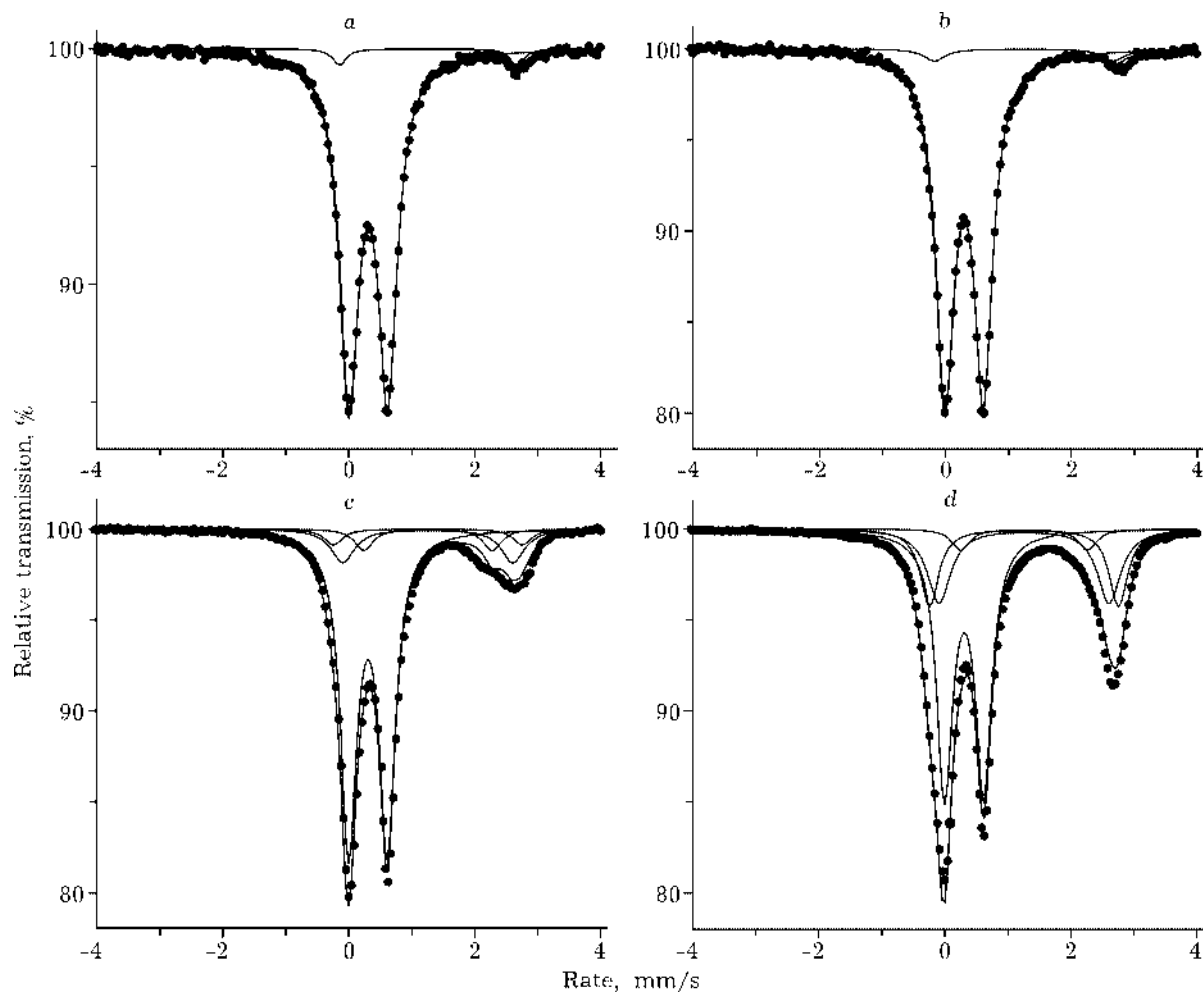


Fig. 2. Mössbauer spectra. For designations, see Fig. 1.

sive lines related to the present of low-spin ions Fe^{2+} , characteristic of FeS_2 , and the lines of low intensity related to the high-spin Fe^{2+} close to FeSO_4 [9]. These components are conserved in the pyrite concentrate also after its heating at 573 K (see Fig. 2, b). The spectrum of sample B (see Fig. 2, c) is a superposition of total lines; their mathematical processing allows one to distinguish four components (see Table 2). It follows from the analysis of the parameters of these spectra that they correspond to compounds FeS_2 [7, 9], FeSO_4 [9–11], $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ [10, 12] and Fe^{2+} ions. The chemical nature of the compound corresponding to the latter component of the spectrum is unclear. These ions may have been formed on pyrite surface after its treatment with sulphuric acid as a result of oxidation in the air medium with increased humidity [13]. After additional mathematical processing,

another explanation becomes possible: the spectral component with parameters $\text{IS} = 1.16 \text{ mm/s}$ and $\text{QS} = 1.70 \text{ mm/s}$ is likely to be due to the presence of ferrous carbonate (Fe^{2+}) from the dolomite group [14, 15], which can be formed during carbonization of ferrous ions during mechanochemical treatment and subsequent exposure to the air. The last spectrum of sample D (see Fig. 2, d) proves that almost half of pyrite undergoes phase transformations during the joint mechanochemical treatment.

The formation of ferrous sulphates (II) as a result of high-energy mechanochemical treatment of pyrite was proved also in previous investigations [6, 12]. Transformation degree depends on the time of treatment and exposure to the air environment (with ferrous sulphate (II) already formed); as this time increases, the content of the latter increases, too.

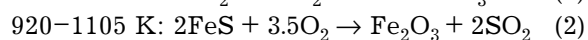
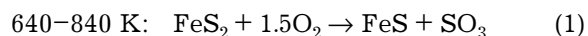
TABLE 2

The parameters of Mössbauer spectra of pyrite samples

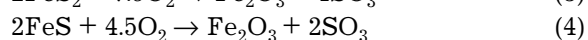
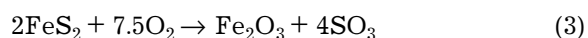
| Sample | Components | IS, mm/s | QS, mm/s | FWHM, mm/s | A, % |
|--|--------------------------------------|----------|----------|------------|------|
| Initial (sample A) | FeS ₂ | 0.31 | 0.61 | 0.37 | 97 |
| | FeSO ₄ | 1.26 | 2.82 | 0.27 | 3 |
| After heating (sample B) | FeS ₂ | 0.31 | 0.61 | 0.37 | 96 |
| | FeSO ₄ | 1.26 | 2.85 | 0.44 | 4 |
| After mechanochemical treatment (sample C) | FeS ₂ | 0.31 | 0.61 | 0.31 | 78 |
| | FeSO ₄ · H ₂ O | 1.26 | 2.70 | 0.45 | 12 |
| | FeSO ₄ | 1.26 | 3.00 | 0.35 | 4 |
| | Fe ²⁺ | 1.26 | 2.04 | 0.35 | 6 |
| The same and heating (sample D) | FeS ₂ | 0.31 | 0.62 | 0.31 | 54 |
| | FeSO ₄ · H ₂ O | 1.26 | 2.70 | 0.45 | 23 |
| | FeSO ₄ | 1.26 | 3.00 | 0.35 | 18 |
| | Fe ²⁺ | 1.26 | 2.01 | 0.35 | 5 |

These data, along with the results obtained previously, indicate that mechanochemical activation of pyrite leads to a decrease in temperatures of phase transformations and in the temperature of thermal dissociation [16, 17].

The results of thermal analysis of the investigated samples of pyrite and a mechanical mixture of FeS₂ and FeSO₄ · H₂O at the mass ratio of 1 : 1 are shown in Fig. 3, *a-e* and in Table 3. It follows from the analysis of TD and DTA data that thermal dissociation of pyrite proceeds within two temperature ranges: 640–840 and 920–1105 K. At first, the first sulphur atom evolves from the pyrite structure, then the resulting pyrrhotines are oxidized to α-Fe₂O₃. The mechanism of this process corresponds to the model presented in [5, 7]:



The process of primary evolution of sulphur from pyrite is accompanied by intense exothermal effects within temperature range 720–730 K. Lower (14.1 %) mass loss (ΔG) in comparison with those theoretically possible for this stage (see Fig. 3, *a*, Table 3) is an evidence that in addition to reactions (1) and (2) other processes connected with the oxidation of FeS₂ and FeS can proceed in the low-temperature region according to the schemes:



The obtained thermal effects of the data on ΔG are the evidence of almost complete oxidation of FeS₂ to α-Fe₂O₃ within the temperature range investigated, in the oxidative gaseous environment.

The data on the TG and DTA dependencies of thermal decomposition of sample B are shown in Fig. 3, *b* and in Table 3. Preliminary isothermal heating of the floatation sample of pyrite at 573 K was carried out in order to investigate its possible transformation to Fe²⁺/Fe³⁺ sulphates during the subsequent high-temperature treatment in the oxidative medium. The data obtained by means of thermal analysis (see Fig. 3, *b*) and spectroscopy (see Fig. 2, Table 2) are the evidence of approximately the same phase and thermal changes as those observed in non-treated sample. It is likely that thermal treatment of pyrite (sample C) causes stabilization of the internal strain and a decrease in the degree of structural defects. As a result, the reactivity of the sample decreases; this is confirmed by insignificant rise of temperature ranges and a change in mass loss. The analysis of spectroscopic data confirms the results of thermal analysis, too. Therefore, it may be concluded that the Fe²⁺/Fe³⁺ sulphates are absent in the solid-phase products during thermal heating (samples A and B). This conclusion corresponds to the results of investigations carried out in [6, 7].

Thermal decomposition of a mixture of FeS₂ and FeSO₄ · H₂O (sample E) was investigated in

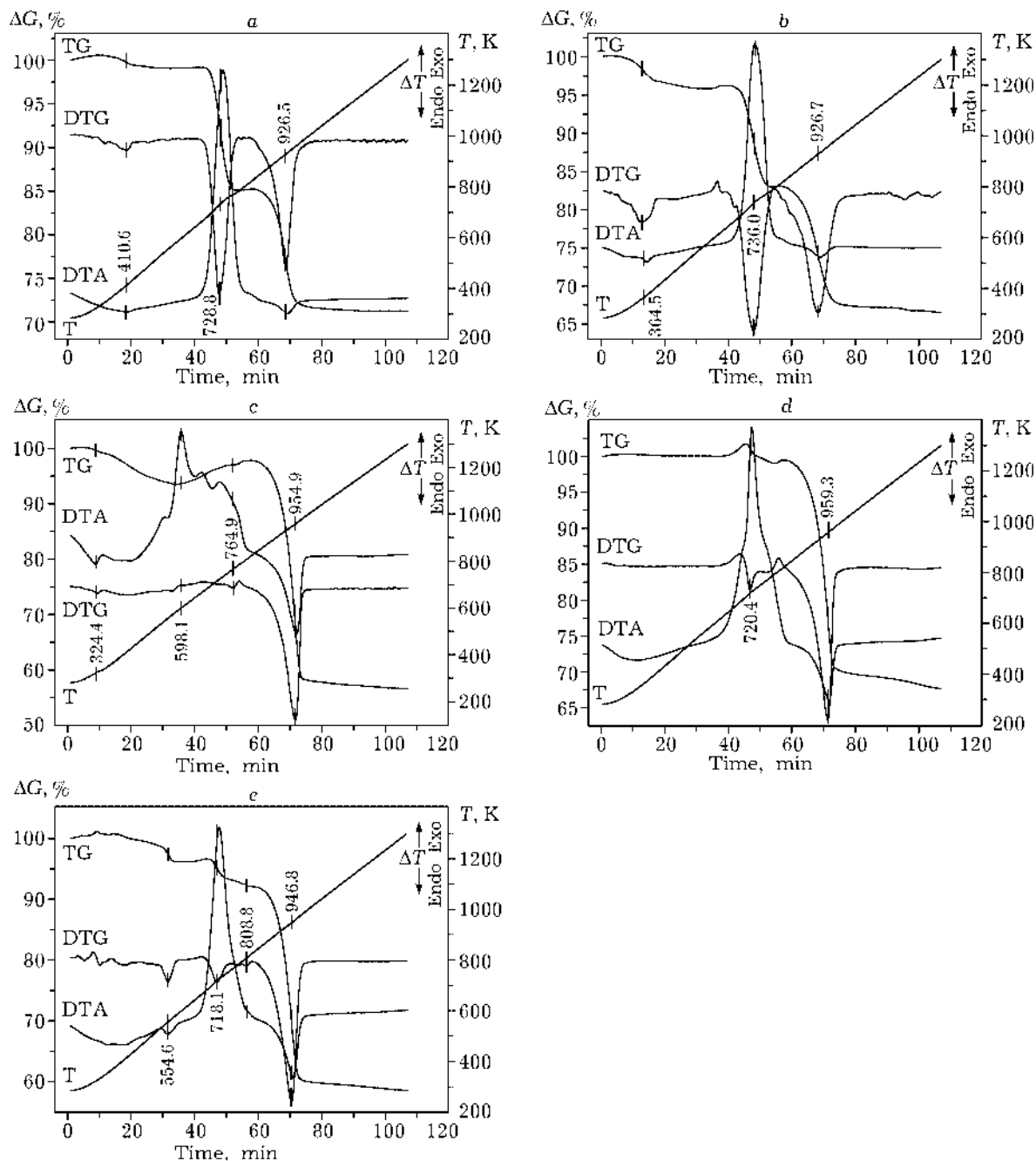


Fig. 3. TG, DTA and DTG dependencies for pyrite samples: *a* – initial FeS_2 ; *b* – the sample heated at 573 K under isothermal conditions; *c* – mechanically activated for 10 h; *d* – the same after heating at 573 K under isothermal conditions; *e* – a mechanical mixture of FeS_2 and $FeSO_4 \cdot H_2O$.

order to establish thermal effects under experimental conditions and to compare them with the data for activated samples. It follows from the results (see Fig. 3, *e*, Table 3) that the presence of $FeSO_4 \cdot H_2O$ promotes decomposition of pyrite. Lowering of thermal intervals (by 10–20 K) in which thermochemical reactions (1) and (2) occur was established. Changes in the oxygen balance of the system

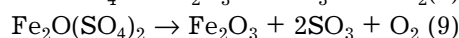
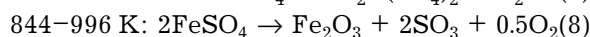
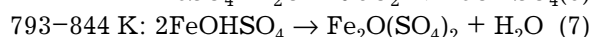
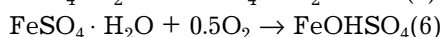
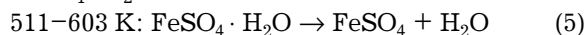
lead to incompleteness of reaction (1) (only 3.8%), while the reactions of direct oxidation of FeS_2 to $\alpha-Fe_2O_3$ accelerate (reaction (3)). The stage of complete oxidation in the high-temperature region coincides with thermal decomposition of $FeSO_4$. The recorded mass loss (41.5%) is close to the theoretical value (43.1%) for the joint decomposition of FeS_2 and $FeSO_4 \cdot H_2O$ in the oxidative gaseous

TABLE 3

The data on temperature in inflection point T_i and mass loss ΔG during thermal treatment of the activated and thermally treated FeS_2 samples

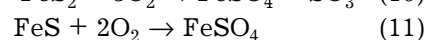
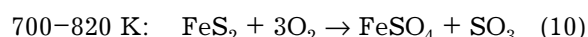
| No. | Sample A | | Sample B | | Sample C | | Sample D | | Sample E | |
|-----|---------------|-------------------|---------------|-------------------|---------------|-------------------|---------------|-------------------|---------------|-------------------|
| | T_i , K | ΔG , % | T_i , K | ΔG , % | T_i , K | ΔG , % | T_i , K | ΔG , % | T_i , K | ΔG , % |
| 1 | 410.6 | 0.6 | 364.5 | 3.1 | – | – | 324.4 | 1.1 | – | – |
| 2 | – | – | – | – | 554.6 | 3.8 | – | – | – | – |
| 3 | 728.8 | 14.1 | 736.0 | 13.2 | 718. | 13.8 (+0.4+3.4) | 598.1 | +0.5 | 720.4 | 2.7 (+1.8+0.9) |
| | exo | | exo | | exo | | exo | | exo | |
| 4 | – | – | – | – | 808.8 | 0.7 | 764.9 | +3.4 | – | – |
| 5 | 926.5 | 13.4 | 926.7 | 15.6 | – | – | – | – | – | – |
| 6 | | | | | 946.8 | 31.9 | 954.9 | 39.6 | 959.3 | 30.2 (+0.4+29.9) |
| | Total: 30.5 % | | Total: 33.5 % | | Total: 45.4 % | | Total: 32.2 % | | Total: 41.5 % | |

environment. Along with thermal effects accompanying the stages of oxidative dissociation of FeS_2 and decomposition of FeSO_4 to $\alpha\text{-Fe}_2\text{O}_3$ [10], mass loss was observed also at a temperature of 554 (3.8 %) and 808 K (0.7 %). The latter ones are due to specific thermochemical reactions connected with FeSO_4 : incomplete oxidation of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ to FeOHSO_4 under the effect of water vapour evolved during dehydration of the last hydrated molecule (554 K) and subsequent transformation of FeOHSO_4 to $\text{Fe}_2\text{O}(\text{SO}_4)$. The mechanism of thermal decomposition of a mixture of FeS_2 and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in the oxidative gaseous environment is described by reactions (1)–(4) and thermal transformations specific for $\text{FeSO}_4 \cdot \text{H}_2\text{O}$:



The TG, DTG and DTA dependencies for mechanically activated samples (see Fig. 3, c, d, Table 3) show that the character of thermal decomposition processes is similar to that for the non-activated mixture. For instance, the TG and DTA data for sample C (see Fig. 3, c, Table 3) provide evidence of a decrease in pyrite ignition temperature by 120 K, while reactions (1) and (2) proceed without any loss of the sample mass. It is interesting that an increase in the mass of sample C starting at 680 K proceeds till the temperature of 820 K. Corresponding mass loss of sample C for the

stage of thermal decomposition of FeSO_4 (820–990 K) is 39.6 %, which is higher than that for sample E by 7.7 %. Mass loss for sample D within the same temperature region is 30.2 %, which corresponds to the data for sample E. These results are likely to be explained by thermochemical transformations of FeS_2 to form FeSO_4 (reactions (9) and (10)) in parallel to reactions (1)–(4):



An increase in sample mass is due to the contribution from all the oxidative reactions in the system at these temperatures.

The new data allow us to assume that the amount of FeSO_4 obtained during mechanochemical activation (see Fig. 2, c, Table 2) increases as a result of thermal decomposition of sample C. The data on mass loss serve as a confirmation of the assumed course of thermal reactions.

The data obtained for sample D only insignificantly differ from those for sample C: temperature of pyrite ignition increases to 628 K, while mass loss remains almost the same (30.2 %). This is due to restructuring of the solid phase during isothermal treatment at 573 K and due to the appearance of energetically more stable state, which results in a decrease in the reactivity of the sample. Subsequent thermal analysis established a small (0.4 %) increase in the sample mass within temperature range up to 820 K. This is an evidence that an increase in the amount of ferrous sulphate is insignificant, and desulphuring stage (825–

990 K) involves only decomposition of FeSO_4 obtained during mechanochemical activation. The data obtained on the mass loss (30.2 %) (see Fig. 3, d) confirm that the mass ratio of pyrite to FeSO_4 in the system is approximately the same as that in sample E, that is, 1 : 1.

Therefore, we may state that an increase in the degree of phase transformation of FeS_2 into FeSO_4 with a decrease in the emission of sulphur oxides into the environment can be achieved by choosing the conditions of mechanochemical and thermochemical treatment of pyrite concentrates in the oxidative gaseous medium.

CONCLUSIONS

The results obtained in the complex investigation of pyrite concentrates prove the possibility to apply mechanochemical and thermal methods for utilization of pyrite concentrates. Separate application of thermal and mechanochemical methods results in partial decrease in the reactivity (in the case when thermal method is used) or to insufficient transformations of FeS_2 into useful products of utilization (mechanochemical method). The joint application of these methods allows one to unite the positive results and to increase in the amount of useful components in the final products.

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