

Physics of coal methane: decisive role of iron compounds

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Abstract The role of iron in formation of the coal methane is clarified based on the studies performed on the coal samples taken from different mines in Donetsk coal basin. Using Mössbauer spectroscopy, a correlation is found between the iron content and methane capacity of coal seams. By means of electron paramagnetic resonance, it is found that iron increases the concentration of non-compensated electron spins, i.e. dangled bonds at the carbon atoms. These bonds can be occupied by hydrogen atoms as a prerequisite of methane formation. The two-valence iron is shown to be the most effective in the increase of spin concentration. By using the ion mass spectrometry, the modelling of methane formation is carried out on the mechanical mixture of the iron-free reactor graphite, iron compounds and diluted sulphuric acid as a source of hydrogen atoms. The proposed mechanism is also confirmed by methane formation in the mixture of iron compounds and the coal from the mine where the iron and methane are practically absent.

Keywords Coal · Iron compounds · Methane · Spin concentration · Mössbauer spectroscopy · Electron paramagnetic resonance · Ion mass spectrometry

1 Introduction

In this paper the focus will be on the physical nature of methane formation in the coal. At least for two reasons, this topic is of special significance: (i) the sudden bursts and

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explosions of the methane-air mixture in the mines can be compared with natural calamities, and the knowledge of mechanisms for methane formation can be a prerequisite for elimination of these catastrophic events; (ii) the coal methane properties are close to that of natural gas and it is considered as a promising source of energy.

The following phenomena, biochemical degradation of plant material (e.g. [1, 2]), as well as the mantle gas sorption and occlusion in the pores of coal seams (e.g. [3]), constitute the basis of two popular hypotheses for methane formation. In both cases the methane formation occurred over millions of years.

The abiogenous model suggests the permanent formation of methane in the coal seams (e.g., [4–7]), and the catalytic effect of iron compounds was proposed in [6, 7] as a possible reason for that. For instance, the iron oxide Fe_2O_3 was suggested as being the catalyst [6] for hydrogenation of carbon oxide CO_2 resulting in formation of methane and water. In contrast, the two-valence iron compounds like $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$, FeCO_3 etc. were proposed to be responsible for the catalytic effect in methane formation from the coal [7].

Some indirect evidence of the origin of the methane can be obtained by studying of the location of methane in the coal and it is suggested that the methane is related to the micropores in the coal [8, 9]. However, the available results of measurements of the methane amount in the coal, as obtained using the absorption isotherms, are not consistent with this idea. It is for example difficult to explain why the coals with the smallest total volume of the pores can contain the highest amount of methane [10]. Based on the studies of absorption properties of the coal pieces, it was proposed that a significant methane fraction can be located in “the coal-gas solid solution” [11]. This suggests that methane formation should depend on the coal structure.

According to [12, 13], the coal structure is considered to consist of the nanoclusters with the ordered distribution of carbon atoms (aromatic area) and the “amorphous” bridges between carbon nanoclusters containing hydrocarbon CH_n chains (aliphatic area). Their ratio depends on the carbon content in the coal. At the low carbon content (low metamorphism), the major part of the coal space is occupied by the aliphatic area. With increasing metamorphism, the size of nanoclusters grows, whereas the part of the aliphatic area is reduced.

It follows from the analysis of the radial functions of atomic distribution obtained using x-ray diffraction that short-range atomic order in the carbon nanoclusters is similar to that in graphite [14]. According to measurements of small angle scattering of x-rays [15], the carbon nanoclusters in the coal are distributed periodically with the wave-length of about 2 nm and the distance of 2 nm between their centers remains nearly unchanged with varying metamorphism.

A possible role of atomic interactions in methane formation is so far not clarified. In the EPR studies the aim was to clarify the nature of different paramagnetic centers [16–18] and their relation to the coal structure [19–22] with the main focus of the research on the variations in the systems of paramagnetic centers in the coal due to mechanical, chemical transformations and thermal treatments [17–24].

The authors in Ref. [17] studied how the coal structure changes if the outburst-prone area in the coal seam is approached. They observed a change in the concentration of paramagnetic centers and attributed it to the mechano-chemical degradation of the coal as a result of tectonic forces. According to the authors in reference [21], an effort was made to clarify the contribution of the surface-localized spins to the intensity of the electron spin resonance (ESR) line and its structure. It was found that new localized spin centers (*A*-centers) are created only if the coal contains some organic components attached to the surface. After removing the all organics, no *A*-centres were formed.

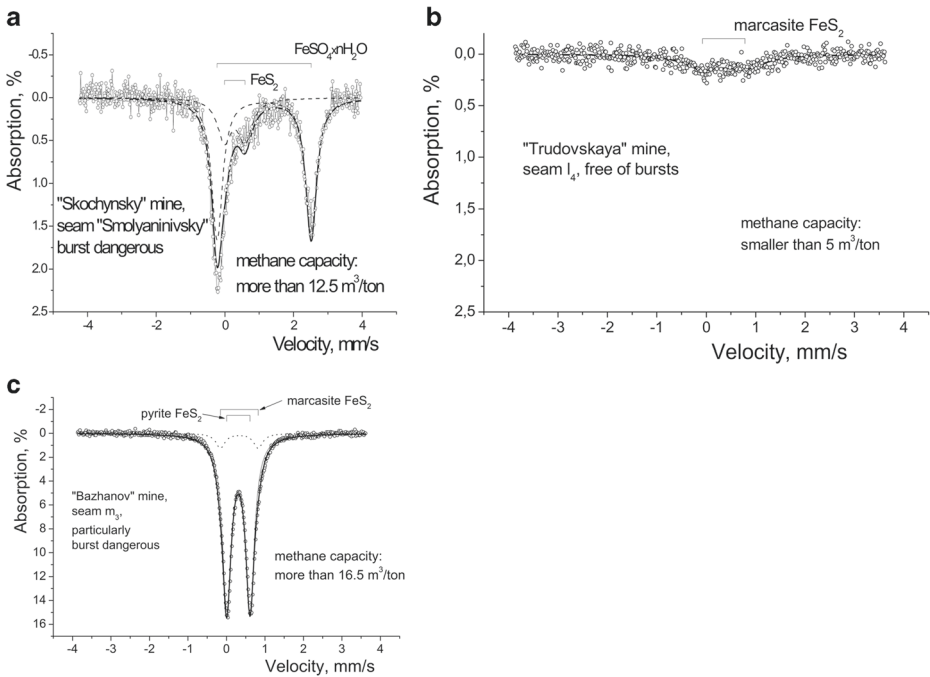


Fig. 1 Mössbauer spectra of the coal taken from the mines of the Donetsk basin: **a** “Skochynsky” mine, seam “Smolyaninivsky”; **b**, “Trudovskaya” mine, seam I₄; **c** “Bazhanov” mine, seam m₃. The area under the peaks is proportional to the iron content in the coal

A systematic *in situ* EPR study of the effects of minerals and iron on the formation of free radicals during the coal pyrolysis was carried out in [23]. It was shown that the addition of pyrite to the raw coal causes an enhancement in the radical yield in presence of other inherent minerals. In other words, this result suggests that the metallic iron can play a catalytic role in the formation of free radicals.

Based on the ideas of the catalytic effect of three- [6] or two-valence [7] iron compounds on methane formation, the aim of the present study is to use Mössbauer spectroscopy and EPR in order to clarify the effect of the iron valence in the iron compounds on the inter-atomic bonds C-C between carbon atoms and C-H between carbon and hydrogen atoms in the coal and carry out a modelling of methane formation using a mixture of iron compounds and pure graphitic which does not contain any iron and methane.

2 Experimental

The coal samples were ground into the grains of less than 1 mm in size and a fraction of 450 mg in weight of coal was subjected to Mössbauer studies. The EPR was measured using blocks of 4x4x4 mm³ in size or the powder.

Mössbauer spectra were recorded in a transmission mode. A WISSEL Mössbauer spectrometer and a ⁵⁷Co gamma ray source in a Cr matrix with an activity of 100 mCi were used for the measurements. This equipment was characterized by the line-width of 0.22 mm/s for the 14 keV gamma rays.

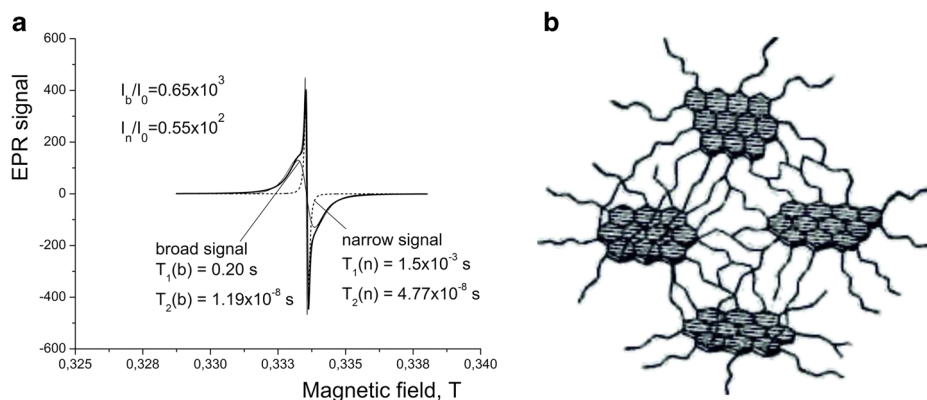


Fig. 2 **a** EPR signal of the coal from Skochynsky mine. I_0 is the intensity of the signal from the reference sample obtained at the same experimental conditions; **b** Two areas in the coal structure: graphite-like carbon nanoclusters ('aromatic' area) and long one-dimensional molecules of CH_n type ('aliphatic' area)

The EPR measurements were carried out using a spectrometer of electron paramagnetic resonance at the frequency of 9.3 GHz and microwave power $P = 10$ dB for measurements of the iron compounds or 15 dB for the coals. The modulated field was used with the amplitude of $H_m = 2 \cdot 10^{-4}$ T. Before obtaining the integral intensities of spectral lines, spectra were reduced to the same experimental conditions: power, coefficient of amplification etc. A piece of the diphenyl-picryl-hydrazil with the spin number of 1.7×10^{14} was used as a reference sample.

The recorded EPR spectrum was presented by 3000 experimental points obtained at the same experimental conditions, namely, microwave power, amplification coefficient and modulation field amplitude. The line shape of the spectrum and slowly decaying wings indicate to existence of two signals with different resonance fields, H_{res} , line widths, ΔH , and signal amplitudes, A . The fitting of the calculated sum of two derivatives of the Lorentz functions with varying H_{res} , ΔH , and A to the experimental data was done.

The pure graphite used in the nuclear reactors and not containing any iron admixtures and two compounds, pyrite FeS_2 with the three-valence iron ions and siderite $FeCO_3$ with the two-valence iron ions were used for modelling. To dope the samples with hydrogen, this mixture was held for 24 hours in the 5 % H_2SO_4 water solution.

The gas extraction from the coal was analyzed using the ion mass spectrometer manufactured by G.V. Kurdyumov Institute for Metal Physics. It is characterized by the range of the mass analysis of 1 to 200 atomic mass units, M , and the mass resolution not worse than 1 M . A controlling program allowed one to measure simultaneously the extraction of 6 chosen isotopes in any mass range. In this study the temperature dependence of extracted H_2 , O_2 , H_2O , CO , CO_2 , CH_4 was measured.

3 Results and discussion

3.1 Iron compounds in the coal

Preliminarily, the chemical analysis of the coal was carried out using the ion mass spectrometry. It was found that the iron is the main metallic element in the coal, whereas the content

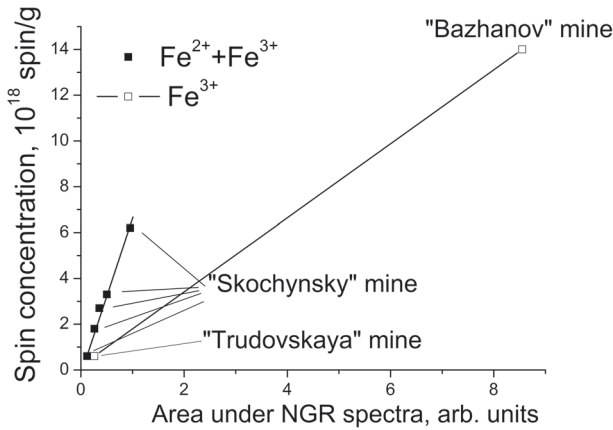


Fig. 3 Concentration of non-compensated electron spins as function of iron content in the coal estimated on the area under Mössbauer spectra. The coal samples were taken out within the area of methane burst and far from it in “Skochynsky” mine, where the two-valence iron prevails, and from “Trudovskaya” and “Bazhanov” mines with the three-valence iron

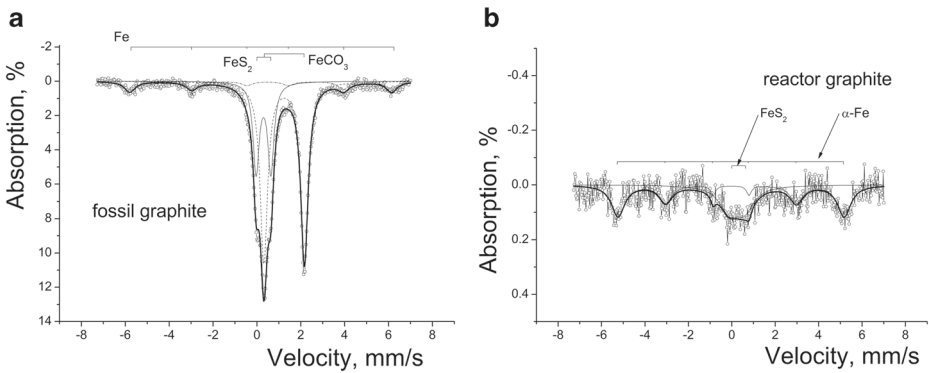


Fig. 4 Mössbauer spectra of iron contained in the fossil (a) and reactor (b) graphites

of other metallic impurities is negligible. Thereafter, the coal of 15 mines in the Donetsk coal basin characterized by different methane capacity was tested on the presence of iron compounds using Mössbauer spectroscopy. As example, Mössbauer spectra of coal samples from three mines of Donetsk basin are presented in Fig. 1. The iron content can be qualitatively estimated on the area under spectra. Some correlation between the coal methane capacity and fraction of iron was derived from these data. The coal of “Skochynsky” mine, notoriously known by frequent methane bursts, contains a remarkable fraction of the sulphate $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ with two-valence iron and a small part of the pyrite Fe_2S where the iron is considered to be the three-valence one (Fig. 1a). A minor methane capacity of the coal in “Trudovskaya” mine corresponds to the negligible amount of the pyrite (Fig. 1b). “Bazhanov” mine containing a lot of methane is extra burst dangerous and is characterized by a giant amount of pyrite present (compare spectra intensities in Fig. 1c and a).

Based on repeated measurements, it was concluded that two-valence iron in the sulphate FeSO_4 , siderite FeCO_3 etc. is more effective in methane formation in comparison with the

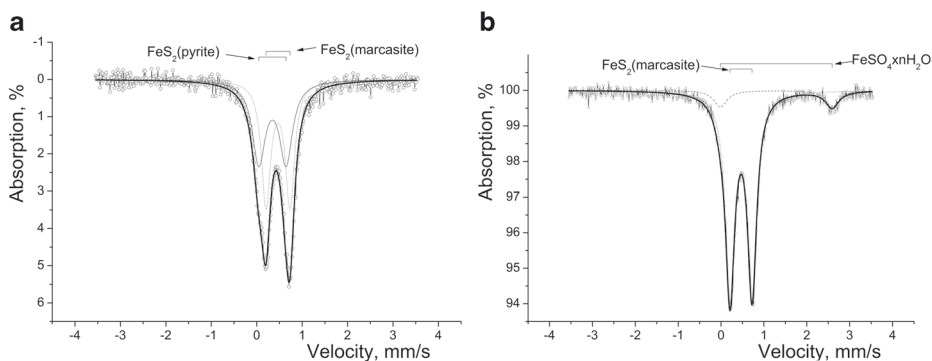


Fig. 5 **a** Mössbauer spectrum of iron in the mixture of reactor graphite and pyrite FeS_2 after holding for 24 hours in the 5 % water solution of H_2SO_4 . A partial transformation of pyrite into marcasite occurs; **b** Mössbauer spectrum of iron in the mixture of reactor graphite and siderite FeCO_3 after holding for 24 hours in the 5 % water solution of H_2SO_4 . A full transformation of siderite into the mixture of marcasite and iron sulphate occurs

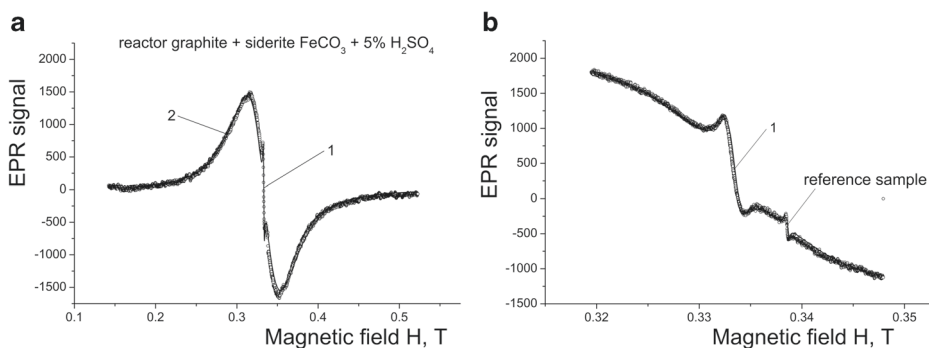


Fig. 6 EPR spectrum of the products formed after holding the mixture of the reactor graphite and siderite FeCO_3 in the 5 % water solution of H_2SO_4 for 24 hours: **a** the total spectrum where signal 1 belongs to graphite and signal 2 comes from the transformed iron compounds (pyrite + $\text{FeSO}_4 \times n\text{H}_2\text{O}$), **b** a local part of the spectrum with signal 1 and the reference sample

three-valence iron in the pyrite or marcasite FeS_2 . Taking into account the scattering in the iron distribution along the coal seams, further measurements were concentrated on the coal taken in the vicinity of the methane burst area in the “Skochynsky” and “Bazhanov” mines.

3.2 Spin concentration

Searching for a reason of the correlation between methane capacity of the coal and the iron content, the electron paramagnetic resonance was used in order to estimate the fraction of non-compensated electron spins in the coal. As example, the EPR signal of the coal from the burst zone in Skochynsky mine is presented in Fig. 2a. It consists of two components, broad and narrow lines, which correspond to the non-compensated electron spins within two areas in the coal structure: the carbon nanoclusters (‘aromatic’ area) and long one-dimensional hydrocarbon molecules of CH_n type (‘aliphatic’ area), as schematically shown in Fig. 2b.

Table 1 Parameters of EPR spectra and spin concentrations for the reactor graphite, pyrite FeS₂ and siderite FeCO₃

Material	Mass, g	Signal	I/I ₀ , a. u.	N, 10 ²⁰ spin/g
Graphite	0.025	1	2.7·10 ²	0.11
FeS ₂	0.101	1	5.9·10 ⁵	59
		2	1.65·10 ⁵	16.5
		3	5.1	5.1·10 ⁻⁴
FeCO ₃	0.112	1	1·10 ⁶	89.3
		2	7.2·10 ⁴	6.4
		3	86	7.7·10 ⁻³

Table 2 Parameters of EPR spectra and spin concentrations for the mixtures of reactor graphite with the iron compounds and 5 % water solution of H₂SO₄

Material	m, g	Signal	I/I ₀ , a. u.	N, 10 ²⁰ spin/g
C+FeS ₂ +H ₂ SO ₄	0.01	1	1.9·10 ²	0.19
		2	4.8·10 ⁴	48
C+FeCO ₃ +H ₂ SO ₄	0.01	1	2.6·10 ²	0.26
		2	5.3·10 ⁵	530

The identification of these EPR signal components was made through determining the times of spin-lattice relaxation T₁ and spin-spin relaxation T₂ (see about details [24]). The product (T₁·T₂)^{1/2} was determined from the signal saturation with increasing microwave power. The spin-spin relaxation T₂ was obtained from the signal broadening: T₂ = 1.176·(γ · ΔH)⁻¹, where γ is the gyromagnetic ratio and ΔH is the line-width from peak-to-peak. According to [24], the broad signal comes from the graphite-like carbon nanoclusters, whereas the narrow signal corresponds to the hydrocarbon molecules.

The concentration of non-compensated electron spins as a function of the iron content in the coal is presented in Fig. 3. The occurrence of non-compensated spins suggests the existence of dangled bonds at the carbon atoms in their nanoclusters or free radicals in the CH_n molecules. It is seen that their amount increases with increasing content of iron and the two-valence iron is more effective in comparison with the three-valence one. It is natural that these dangled bonds can be occupied by hydrogen atoms of which content in the mine coal is immense. Such a process is a prerequisite for methane formation.

3.3 Modelling of methane formation

For this purpose, the reactor graphite and two- or three-valence iron compounds, namely siderite FeCO₃ and pyrite FeS₂, respectively, were chosen. Mössbauer spectra of the fossil and reactor graphite are presented in Fig. 4. In comparison with the fossil graphite, the reactor one contains a negligible amount of iron and is quite appropriate for such modelling.

The mixture of graphite and iron compounds was held for 24 hours in the 5 % solution of H₂SO₄ in the distilled water. Mössbauer spectra of iron in these mixtures are given in Fig. 5. Some transformations proceed during holding this mixture in the diluted acid solution. Pyrite is partly transformed to marcasite with a different quadrupole value, whereas siderite completely disappears, transforming into the three-valence marcasite and a small fraction of iron-sulphate.

The change in spin concentration was measured using EPR. The EPR signal of the mixture of graphite + siderite + 5 % H₂SO₄ is presented in Fig. 6. The narrow signal 1 belongs

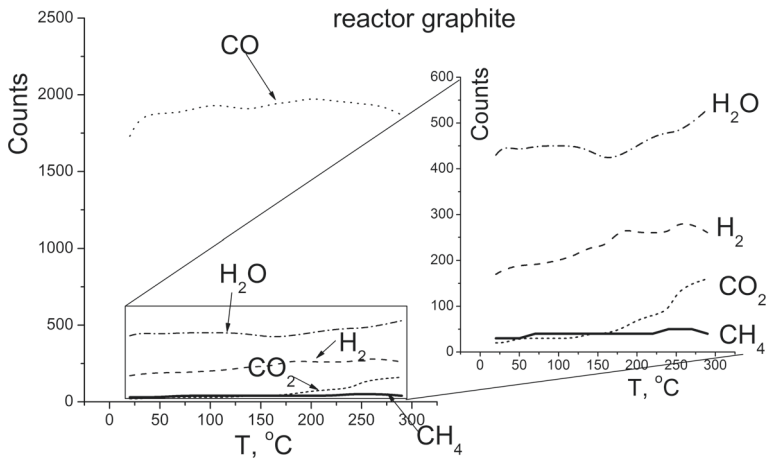


Fig. 7 Gas extraction from the reactor graphite during heating. The amount of degassed methane does not exceed 50 atomic mass units (a.m.u.)

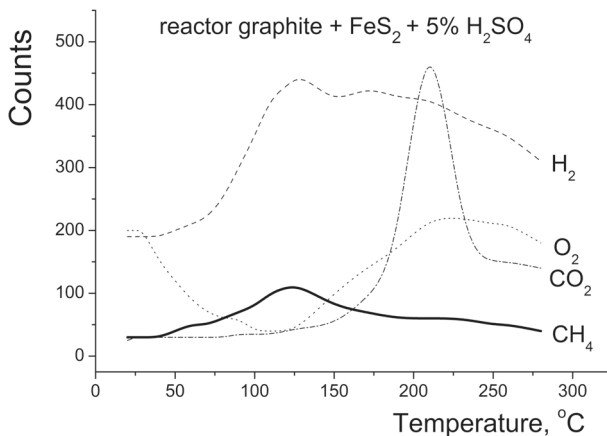


Fig. 8 Gas extraction from the mixture of reactor graphite + FeS_2 + 5 % H_2SO_4 water solution during heating. The maximum of methane degassing (about 120 a.m.u.) occurs at about 150 °C. The hydrogen degassing follows that of methane

to the graphite and signal 2 comes from the iron compounds. In accordance with Fig. 5b, signal 2 comes from the mixture of marcasite + $\text{FeSO}_4 \times n\text{H}_2\text{O}$ transformed from siderite.

The results of theoretical treatment of the obtained EPR spectra are presented in Tables 1 and 2. One can conclude that the mixing of graphite and iron compounds in presence of the water solution of H_2SO_4 enhances the paramagnetic signals and increases the concentration of non-compensated spins in the graphite by two times in the mixture with FeS_2 and three times in the mixture with FeCO_3 . This result confirms that the effect of iron compounds in the coal amounts to an increase in the number of dangled bonds on the carbon atoms.

Ion mass spectrometry was used to identify the methane precipitated from the graphite during its heating. The corresponding data are presented in Figs. 7 to 9.

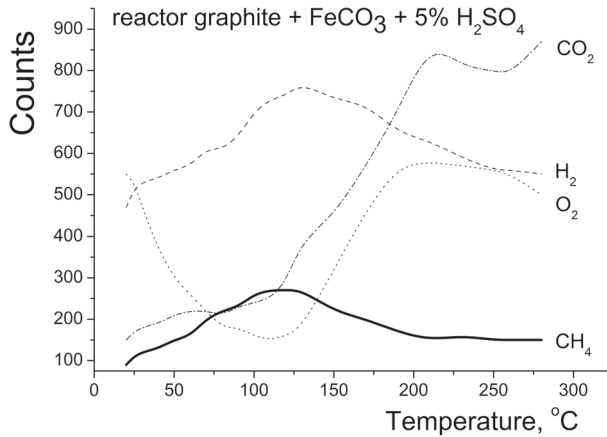


Fig. 9 Gas extraction from the mixture of reactor graphite + FeCO_3 + 5 % H_2SO_4 water solution during heating. The maximum of methane degassing (about 270 a.m.u.) occurs at about 140 °C. The hydrogen degassing follows that of methane

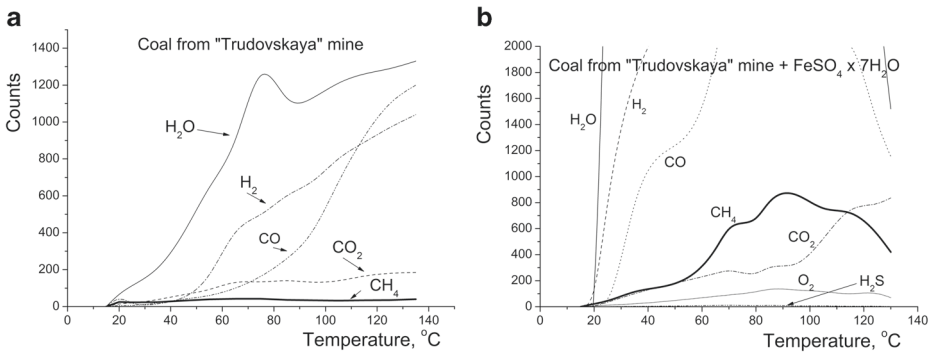


Fig. 10 a Gas extraction from the coal of the mine “Trudovskaya” which does not contain the iron; **b** the same from its mixture with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

It follows from Fig. 7 that methane degassing from the pure reactor graphite is negligible. The ion mass analysis of the mixture of the reactor graphite with the iron compounds and the sulphur acid allows one to compare the effect of the three-valence pyrite and the two-valence siderite on methane formation. The results presented in Figs. 8 and 9 show that siderite is by two times more effective as a catalyst for methane formation. It is remarkable that the temperature behaviour of methane and hydrogen degassing is similar with the maximum of their output at about 100 °C. The heating to higher temperatures intensifies the extraction of the oxygen and carbon oxide.

The same measurements were carried out with the coal of “Trudovskaya” mine where, as shown above, the iron content is negligible and methane capacity is small (see Fig. 1b). It is seen from Fig. 10 that no methane degassing occurs during the heating of this coal, whereas a remarkable amount of methane is obtained from the mixture of this coal with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

4 Conclusions

1. A correlation is found between the methane capacity of the coal seams and the fraction of iron compounds in the coal.
2. A mechanism of the effect of iron on the methane formation in the coal includes the increase in the concentration of non-compensated electron spins, i.e. dangled bonds on the carbon atoms. In this relation, the two-valence iron is more effective in comparison to the three-valence one.
3. The validation of this mechanism for methane formation is carried out using the mixture of the pure iron-free graphite with the iron compounds and diluted sulphur acid as a source of hydrogen. The proposed mechanism is also confirmed using in this modelling the coal from the mine instead of graphite.

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