

# OXIDIZING MODIFICATION OF SHUNGITES

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## Introduction

Although shungites (carbon-rich rocks of Karelia, Russia) are a subject of scientific interest for more than the century, they are still poorly studied in comparison with other natural carbonaceous species. Unique structure and properties of shungite carbon (ShC) didn't allow us to ascribe it to any of the known carbon materials. Due to a high adsorption and catalytic activity as well as mechanical and thermal stability shungites were regarded as a promising material for a wide range of industrial application [1]. Opposite to some carbonaceous materials ShC is characterized by essential quantity of oxygen containing surface groups even in the original state.

An effective coal oxidation couldn't be reached at ambient conditions. But in the case of using oxygen-ozone mixture an intensive interaction of ozone with coal resulted in coal gasification to carbon oxides and formation of different carbon-oxygen containing complexes. Since oxidative treatment enables to perform intrinsic modification of properties of carbon materials accompanying with changes in structural, chemical and adsorption characteristics it could be used for their activation.

In this paper, we present data on modification of physical chemical properties of shungites by ozone treatment and oxygen, and argon plasma discharge.

## Experimental

Shungite samples under study were taken from different deposits. They distinguished in carbon content (98, 60, 32 wt.%). Shungite samples taken from Shunga deposit contain 96-98 wt% of carbon (ShI), 60 wt.% of carbon (ShII); samples from Maksovo deposit contain 90 wt.% of carbon (MI) and samples from Zazhogino deposit 32 wt.% of carbon (ShIII). Two series with different particles size were investigated: fine powders less than 50 µm and grains of 3-6 mm in size.

Oxidation of shungite samples by ozone was carried out at flow rate 5-12 l/hour and 20-60 °C. Ozone was synthesized under barrier electrical discharge from oxygen (high purity). Ozone content in the mixture was 2-5 vol.%.

Low temperature plasma treatment of shungites was carried out at pressure of gases near 1 mm Hg. Plasma treatment conditions were 1.5 kV and 310 mA for oxygen plasma and 200 mA for argon plasma, respectively.

Surface area of the samples was determined by BET method before and after modification. Concentration of oxygen containing groups (OG) was measured by titration method and analysing of FTIR-spectra for both pristine and modified shungite powders.

FTIR–spectra were registered by Bruker EQUINOX 55/S spectrometer on pills with KBr (1:100).

## Results and Discussion

Kinetics of ozonation was studied on shungites in comparison with activated and brown coals. Obtained differential curve of ozone absorption and carbon (IV) oxide formation for shungite samples are presented in Fig.1.

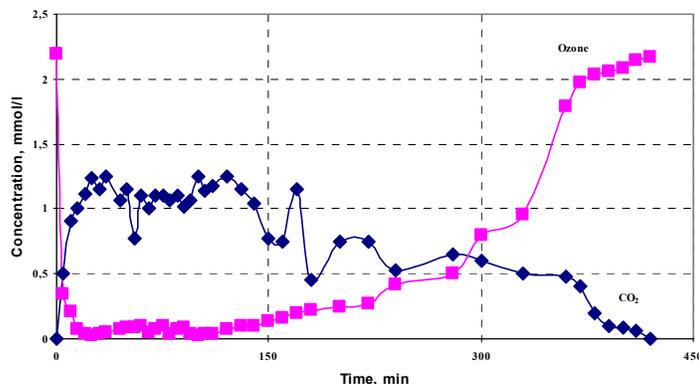


Figure 1. Differential kinetic curves of ShI (fine powder) ozonation, 20°C, flow rate 5 l/h, ozone concentration 5vol. %

Unusual formation regime, namely, chaotic oscillation of reaction rate of CO<sub>2</sub> formation from carbonyls, which were created on ShC surface during ozonation, was established. Carbon (II) oxide was not found among the reaction products in contrast with coal oxidation. Ratio between the absorbed ozone and formed CO<sub>2</sub> was equal to 2:1 for all shungites with carbon content more than 90 wt.%. It corresponds to the reaction:

$$2\text{O}_3 + \text{C} = \text{CO}_2 + 2\text{O}_2$$

The process reaches rapidly a stationary regime of ozone consumption. During this period ozone content in output gases is close to 0. Amplitude of oscillation of reaction rate depends on particle size and contact time. An attenuation of oscillations takes place when reaction comes to the end. Since the oscillations of a similar type haven't been observed for oxidation of other carbonaceous materials (activated coals, graphite, diamonds and carbon fibres) the control experiments were carried out for some coals (brown coal and activated coal AG-3) at the same conditions. But the oscillation regime was not observed either.

ShC was supposed to catalyse oxidation of CO to CO<sub>2</sub> as in the case of CO oxidation on Pd-zeolite catalysts. We assume that kinetics of auto-oscillation of reaction rate could be stipulated by periodic oxidation and reduction of surface active sites of ShC. According to [3] oscillations of chaotic character often arise due to intra-diffusion inhibition. It could be one of the most probable reasons of the displayed effect taking into account ShC structural characteristic features.

Integral kinetic curves show the total quantity of absorbed ozone and created CO<sub>2</sub> for ShI (Fig.2). ShC quantity which didn't react with ozone varied from 15 to 20 mass. %

depending on experimental conditions (temperature, ozone concentration) and shungite type. Loss of activity is probably caused by saturation of ShC surface with OG, playing a role of steric barrier for further ozone penetration.

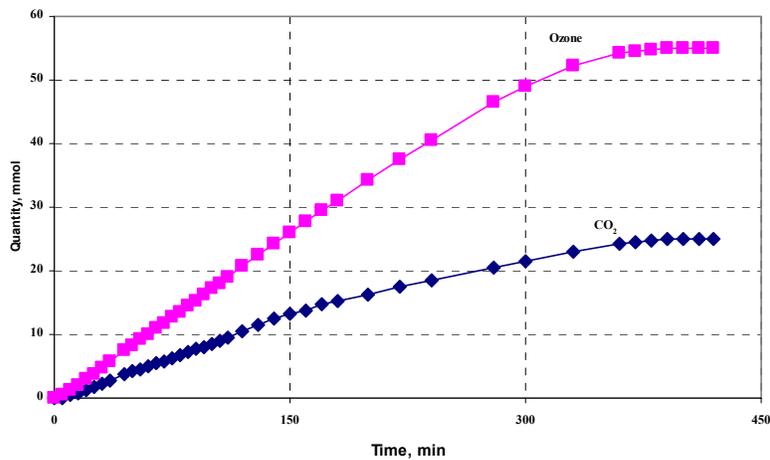


Figure 2. Integral kinetic curve of ShI (fine powder) ozonation, 20°C, flow rate 5 l/h, ozone concentration 5 vol.%

Effective constants of the process rate which were calculated according to Frost equation (the first order reaction) at 20°C were  $0.1 \cdot 10^{-3} \text{ mol}/(\text{s} \cdot \text{cm}^3)$  and  $5.5 \cdot 10^{-3} \text{ mol}/\text{s} \cdot \text{cm}^3$  for MI and ShI, respectively. Thus ozone affinity is higher for shungite with higher carbon content (ShI) in spite of a value of surface area of MI is 20 times as much as the value of ShI (307 and  $14.9 \text{ m}^2/\text{g}$ , respectively). Activation energy of the reaction is  $32.6 \pm 2.0 \text{ kJ/mol}$ .

Concentrations of OG for pristine and oxidized shungites are presented in Table. Total OG content increased to 16% after two hours of ozone treatment. At the same time concentration of carboxyl groups decreased four times that probably connected with their oxidation to  $\text{CO}_2$ . The total content of OG after ozonation for ShI and ShIII shungites was  $0,005 \text{ mmol}/\text{m}^2$  that was close to the values for activated carbon obtained earlier ( $0,008 \text{ mmol}/\text{m}^2$ ) [4]. The content of OG for ShII is 10 times as much.

Comparing FTIR spectra special attention was paid to the band at  $1090 \text{ cm}^{-1}$ , which is correlated with vibrations of different -C-O- bonds (ethers, peroxides, epoxy-groups). The intensity of this band increases after ozonation. We suppose the formation of functional groups containing a large amount of the “non functional oxygen” which is difficult to determine by analytical methods.

Plasma treatment is a way for cleaning of ShC surface. Intensity of almost all bands correspondent to OG decreased significantly in FTIR spectra for samples after plasma the treatment. Treatment of shungites by oxygen and argon plasma leads to decrease in weight up to 30 % and 40 %, respectively. Since decrease in OG was obtained after plasma treatment the main process was connected with gaseous products formation. Surface area for ShI after oxygen and argon plasma treatment was equal to 10,7 and  $7,2 \text{ m}^2/\text{g}$ , respectively. Ozonation leads to the increase in surface area of shungites: for

ShI it increased from 14.9 to 19,6 m<sup>2</sup>/g and from 22.9 up to 28,4 m<sup>2</sup>/g for ShIII after 2 hours of ozonation.

Special features of ShC structure are favorable for creation of essential quantity of unstable peroxide compounds similar to cyclic trioxides [5]. Further ozonation resulted in degradation of trioxides to form of carbonyl groups in the excited state and generation of singlet oxygen. The latter is known as a strong oxidizer together with trioxides. The excited carbonyl groups when pulling off results in CO formation which is completely oxidized to CO<sub>2</sub>.

Table

Concentration of oxygen containing groups on shungites

Samples of shungite	NaHCO <sub>3</sub> carboxyl groups		Na <sub>2</sub> CO <sub>3</sub> -NaHCO <sub>3</sub> lactone groups		NaOH – Na <sub>2</sub> CO <sub>3</sub> phenolic groups		Σ OG	
	mmol/g	mmol/m <sup>2</sup>	mmol/g	mmol/m <sup>2</sup>	mmol/g	mmol/m <sup>2</sup>	mmol/g	mmol/m <sup>2</sup>
ShI/ShII/ShIII pristine	0,022/ 0,084/ 0,059	0,0015/ 0.0140/ 0.0026	0,023/ -/ 0,018	0,0015/ -/ 0,0006	0,043/ 0.041/ 0,022	0,0029/ 0,0070/ 0,0007	0,088/ 0,125/ 0,099	0,0053/ 0,0210/ 0,0043
ShI/ShII/ShIII after ozonation for 2 hours	0,005/ 0.180/ 0,085	0,0003/ 0.0300/ 0,0032-	0,035/ 0.017/ 0,003	0,0018/ 0,0030/ 0,0001-	0,067/ 0.108/ 0,047	0,0034/ 0.0200/ 0,0018	0,102/ 0,305/ 0,135	0,0052/ 0,0530/ 0,0051

## Conclusions

Ozonation of shungites results in the increase of oxygen containing groups concentration on the surface. Chaotic oscillation of reaction rate of CO<sub>2</sub> formation from carbonyls, which were created on ShC surface during oxidation, was established. In contrast to coals, carbon(II) oxide was not found among the products of the reaction.

Specific structure of shungite carbon was responsible for formation of large quantity of unstable compounds of peroxide type. Treatment with oxygen and argon plasma leads to cleaning of shungite surface and decreasing of oxygen containing groups concentration.

## Acknowledgements

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