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Oxidative Activity of Heated Coal Affected by Antypirogens

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Abstract. The effect of antypirogens on chemical activity of heated coal is studied. It is proved that ammonium sulfate, calcium phosphate, calcium chloride, calcium nitrate and acid fluoride are the most effective antypirogens.

1. Introduction

A great amount of wastes damaging natural environment is one of the most serious problems of coal mining industry hampering its further development. Pollution of air, water, changing soil composition cause degradation of flora and fauna in the area affected by mining, threaten people's health and life. Mine fires lead to a sharp increase of hazardous and harmful effects [1]. Fires reduce coal mining efficiency, deteriorate quality of the produced coal, damage the environment, can cause explosions of inflammable gas and dust, require money for fire suppression.

Spontaneous combustion of coal and coal-bearing rocks occurs when a substance is oxidized with air oxygen and generates heat that raises the rock temperature with radiation heat loss. When the temperature rises the oxidation process accelerates and after some time coal or coal-bearing rocks combust [2]. The research in coal spontaneous combustion discovered that the probability of endogenous underground fire in mines is characterized by such factors as oxidation activity of coal (liability to spontaneous combustion), liability of a coal bed to spontaneous combustion, fire safety in mines.

Oxidation activity of coal is its natural property generated by its origin and genesis conditions. It is determined by the speed of oxidizing reaction of coal.

Research in coal oxidation, experience of spontaneous fire suppression and prevention show that spontaneous fire hazard can be mitigated by means of treatment of coal with different agents.

Antipyrogens are substances which can reduce sorption activity of coal and slow down spontaneous fires. Many organic and non-organic substances possess antipyrogeneous properties. Antipyrogens applied in mining industry should meet the following requirements: they should be nontoxic, cheap, abundant, have great mechanical, chemical or complex effect on coal if added to water or clay pulp in small quantities.

Mechanically active antypirogens are substances which form protective films on the coal surface and prevent air from leaking. They include talc, carbonate of lime, cretaceous and others. Most filming agents are organic compounds: caoutchouc, polyvinylchloride, resins, nondrying oil and others. Gaseous filming agents are carbon dioxide, nitrogen, hydrogen sulfide and others.

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Chemically active antypirogens include substances which:

- react with coal in the adsorption layer (hydrogen peroxide, potassium permanganate, potassium chromate);

- educe gases in decomposition (calcium bicarbonate, ammonium carbonate);

- break down generating new chemically active substances (magnesium chloride, calcium chloride, ammonium phosphate, ammonium chloride).

Antypirogens having a combined (mechanical and chemical) effect on coal can be presented by water suspension of calcium hydrate.

For prevention and suppression of fires in coal mines the following substances can be used: calcium chloride, ammonium phosphate, ammonium chloride, potassium permanganate, ammonium nitrate, aluminium sulphate, calcium hydrate, formaldehyde resin, polyacrylimide, rock dust, grind of open-hearth and blast-furnace slag, nonutilizable sand and water from tailing storage facility of aluminum plants, wastes from alkali-works and others.

Research in antypirogens were first initiated and carried out under the direction of academician A.A. Sochinsky.

A great contribution to the research in antypirogen of low temperature coal oxidation was made in the Institute of Anthracides [4, 5]. Water solutions of non-organic compounds were tested. Experiment findings determine a positive effect of ammonium sulphate, ammonium carbonate, ammonium chloride, sodium chloride, calcium chloride, magnesium chloride and prove that these substances can be used as antypirogens.

Antypirogens were tested for effectiveness in prevention of coal self-combustion in many mines of Kuzbass. But due to different methods used for estimating the affect of different substances on coal chemical activity the obtained results were contradictory.

As an example, experiments by V.S. Veselovsky determine that suspensions of calcium hydrate are mostly nonreactive to coal but sometimes can be oxidation catalysts [6]. At the same time A.I. Khrisanfova and V.M. Mayevskaya prove that these suspensions are the most effective of available and cheap antypirogens [7].

2. Results and discussion

Problems of choosing an antypirogen are exacerbated by the fact that the same chemical substances can be either positive or negative catalysts of the oxidation depending on coal composition and properties and a theoretical basis for the choice of antypirogens has not been worked out so far because their effect on coal has not been revealed.

In order to improve prevention of spontaneous fires in coal mines the effect of antypirogens on the chemical activity of heated coal has been researched. Chemical activity of coal was determined with the help of the method developed by Institute of Mining named after A.A. Skochinsky. It is applied for evaluating chemical activity of coals and their liability to spontaneous combustion, it determines the influence of different factors (temperature, humidity, antypirogens) on kinetics of oxidation, evaluates the speed of oxidation when calculating the thermal balance and studies the probability of spontaneous combustion.

Coal test samples weighing 100 gr each were treated by 3 % water solutions of antypirogens:

- sodium oxalate;
- calcium oxide;
- calcium chloride:
- calcium phosphate;
- calcium dihydrogen orthophosphate;
- ammonium sulphate;
- calcium acetate;
- wetting reagent for coal dust "Elfor-M";
- foaming agent PO-6 "Elfor";
- liquid glass;

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- calcium nitrate;
- calcium oxalate;
- melting slag;
- clay;
- acid fluoride.

The samples were kept in tightly closed containers, measurements were taken at fixed intervals (each 12 hours) under the temperature of 70 °C. After each measument the container was aired, then sealed again and placed into the same conditions.

As a result it has been found out that sodium oxalate, calcium dihydrogen orthophosphate, foaming agent PO-6 "Elfor", liquid glass, calcium oxalate and melting slag do not have any positive effect on coal. Suspensions of clay and calcium oxide had been reducing chemical activity of coal for 48 hours but then the speed of oxygen sorption increased intensively. Evidently it happens because clay and calcium oxide do not solve in water and after drying down they become more brittle and drop off. While in suspension these substances encapsulate coal pores. But as soon as they run dry coal pores peel off and become penetrable for air.

Solutions of calcium phosphate and ammonium sulfate have given good results. The speed of sorption of oxygen by coal did not exceed 0.15 cm³/(gr-hour) during the experimental period. Fig. 1 shows correlation of chemical activity of the coal treated by calcium phosphate and ammonium sulfate solutions with untreated coal.

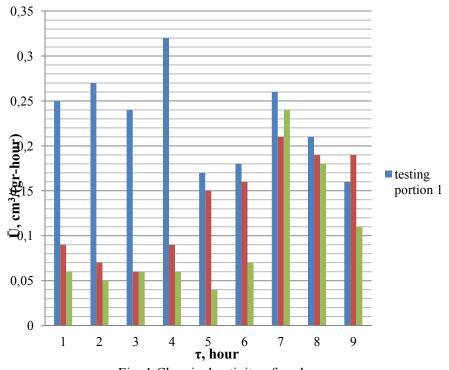


Fig. 1 Chemical activity of coals: testing portion 1 – untreated coal, testing portion 5 – coal treated by calcium phosphate, testing portion 7 – coal treated by ammonium sulfate

Ammonium sulfate is a colorless transparent salty-tasting crystalline substance. It is classified as ammonium salt of sulfuric acid. Ammonium sulfate is one of the most widely spread mineral fertilizers used in agriculture. It is applied for all agricultural crops (from potatoes to citruses) on black and grey soils. This fertilizer has a very valuable quality – low liability to migration because ammonium kation is absorbed by soil and thus protected from fluviraption. That is why it is

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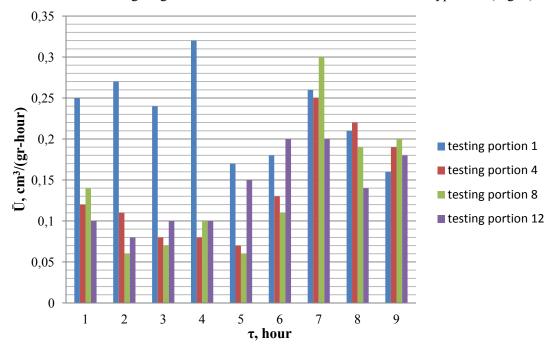
recommended to apply ammonium sulfate with irrigation on light soils where the loss of nitrogen from a fertilizer is possible due to migration. Ammonium nitrogen of ammonium sulfate is assimilated by plants. Sulfur is needed to feed all crops as it is found in some important amino acids synthesized by plants.

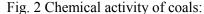
Ammonium sulfate is also used in viscose fiber production. In biochemistry, reprecipitation by ammonium sulfate is a common method of protein purification. In food industry, it is certified as food additive E517.

Ammonium sulfate is also applied for water chlorination with ammonation. It is introduced into the water a few seconds before chlorine and fixes the chlorine to form chloramines. It reduces chlorinated organics which is bad for human health, cuts down chlorine consumption, lowers water pipe corrosion.

In fire suppression ammonium sulfate is used as an antypurine. In mining it serves a gelling material for protective treatment of the mined-out space being introduced into the explosive to reduce flammability and prevent spontaneous combustion.

The research has also proved that water solutions of calcium acetate, calcium chloride, calcium nitrate, acid fluoride and wetting reagent for coal dust "Elfor-M" can be used as antypurines (Fig. 2).





testing portion 1 – untreated coal, testing portion 4 – coal treated by calcium chloride, testing portion 8 – coal treated by calcium acetate, testing portion 12 – coal treated by calcium nitrate The resulting regularities can determine the periodicity of antypurine supply for fire suppression at rock disposal dumps. Thus ammonium sulfate and calcium phosphate are enough to introduce as often as once a week if there are no fire areas, while water solutions of calcium chloride, calcium nitrate, acid fluoride are introduced every 3–5 days.

3. Conclusions

1. Coal is a complex high-molecular compound. There is no general opinion about coal structure as well as about the origin of self-heating and self-combustion of coal.

2. The research proved that ammonium sulfate, calcium phosphate, calcium chloride, calcium nitrate and acid fluoride are the most effective antypirogens.

3. Water solutions can be applied to treat coal rock immediately prior to loading them into trucks.

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