

Investigation Methods of Preparation and Aspects of Introduction in Coal Concentrates Chemical Reagents for Addressing the Problem of Coal Raw Materials Freezing Message 2. Prevention of Coal Freezing by Means of Acetates and Silicone Polymer

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## **Abstract**

The freezing of coal in transit is a serious problem for the coal industry. The most promising preventive method is to reduce the pour point of the moisture's active component and reduce the strength of the bonds in the frozen coal. The materials employed should be harmless to the operating staff and the environment, should not cause corrosion of metal components, should not impair coal quality, should not significantly reduce the capacity of the rail car, should not require special storage conditions, and should mix well with coal.

This work is continuing the search for new reagents to prevent the freezing of coal in winter. Attention focuses on the physicochemical characteristics of acetates of alkaline-earth and alkaline metals and silicone polymer, methods of introduction in coal concentrate, and influence these reagents on freezing. The results of studies have shown that the use of organosilicon is a more effective use of acetates and chlorides of metals. The high activity of organosilicon substances is explained by their elemental composition and structure of molecules.

**Keywords:** *Coal freezing; Freezing point; Rare-earth acetates; Degree of freezing; Siloxane skeleton; Silicone polymer.*

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## **1. Introduction**

From November or December on, the wet coal in railroad cars becomes a solid frozen mass. Turnaround times extend, rolling stock is held up at discharge sites, and rail customers complain of lost time. Preventive measures are required to prevent the freezing of the coal to the walls of the railroad cars in cold weather.

The choice of a chemical to prevent the freezing of coal during its transportation in winter should be based on its efficiency and environmental friendliness and should take into account the following aspects: the reagent must be dissolved in the outer moisture of the coal concentrate to form a solution, the concentration of which will ensure the flowability of the coal; preventative means should be inexpensive, affordable and environmentally friendly for service personnel, making their use economically and environmentally sound; must be resistant to changing weather conditions; not to adversely affect technological processes (coking, blast furnace melting) and product quality characteristics.

One way to prevent the freezing of coal concentrates in winter with chemical reagents is to use quicklime [1-2]. The disadvantage of this method is that when using quicklime as a preventive tool, it is necessary to have a carefully closed composition, mechanisms for grinding, dispensing, presentation and mixing; in addition, quicklime is a toxic material that requires reliable ventilation in the process of grinding, careful handling and safety when mixed with coal.

A method of preventing the freezing of coal concentrates in winter, including the use of sodium chloride, calcium, and magnesium (bischofite), has proved to be quite effective [3-5]. Our studies have shown that the introduction of 4-5% bischofite ( $MgCl_2 \cdot 6H_2O$ ) into coal lowers the freezing point to minus 14-15°C [3-5].

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The method of preventing frostbite when using metal chlorides is based on the fact that the interstitial moisture is replaced by a solution with a low eutectic freezing point. The resulting ice is characterized by a defective scaly structure and, as a result, low mechanical strength [1].

But it should be noted that it is advisable to treat with bischofite aqueous solution only coal with low humidity because when processing coal with an aqueous solution of bischofite increases its humidity. The limit on the increase of coal humidity is 10-12%. Within this range, when the temperature drops below minus 15°C, the coal will freeze. At lower air temperatures, deep freezing of coal should be expected.

However, the chlorides are corrosive, and it is difficult to slow the corrosion by inhibitors. In addition, chlorides break down on heating with the liberation of chlorine (by calcium chloride) or hydrogen chloride (by magnesium chloride). These problems do not arise with chemicals that do not contain chlorine, such as acetates, formates, carbamides, and silicone polymer.

## 2. Results and discussions

In the present work, we continue the search for new reagents to prevent the freezing of coal in winter. In laboratory research on the freezing of coal concentrate samples from the coal preparation shop in the coke plant at PAO ArcelorMittal Kryvyi Rig, we also used the acetates of alkaline-earth, and alkaline metals are tested as reagents to prevent freezing of coals.

The positive effect of the use of acetates, formates, and carbamides can be explained by the impact of acetyl radicals on centers of the crystallization in the formation of ice, which ensures that it is loose and weak. In Table 1, we show the results of studies and laboratory data of dependence freezing temperatures of coal from the mass fraction of potassium and sodium acetates added to the coal [5].

Table 1. Dependence of the freezing point of the coal on the added potassium and sodium acetates

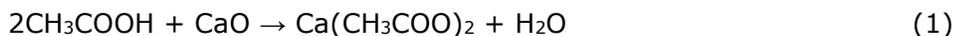
Added acetate, wt %	Freezing point with added potassium acetate, °C	Freezing point with added sodium acetate, °C
1,5	-4,5	-4,3
2,0	-5,0	-5,2
2,5	-6,4	-6,8
3,0	-7,6	-8,0
3,5	-8,6	-8,5
4,8	-9,4	-8,6
5,5	-10,6	-8,7
6,0	-12,3	-8,7

Potassium acetate effectively reduces the freezing point of coal. There is a clear dependence of the salt content on the temperature. In contrast to potassium acetate, sodium acetate reduces the freezing point to -8.5°C at concentrations no greater than 3.0%. With further increase in its concentration, the freezing point of the coal remains unchanged.

These reagents are less corrosive and are characterized by lower environmental impact. Metal acetates are safe for most surfaces, including concrete, metal, and wood. They are non-toxic and biodegradable under the action of bacteria. Alkaline-earth metals, in contrast to alkaline metals, are present in fluxes and improve the blast-furnace process. Their addition in the salt form to coal does not impair its technological properties.

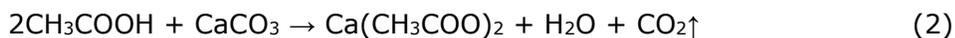
Therefore, we now focus on the use of calcium and magnesium acetates to prevent the freezing of coal [5]. Calcium and magnesium acetates were added to the coal raw materials in various ways:

- 1) the acetates are mixed with the coal of 12% moisture content in quantities of 1.5, 2.0, 3.0, 4.5, 5.5, and 6.0 wt %
- 2) method of producing calcium and magnesium acetates within the coal mass. To that end, the coal is preliminarily mixed with calcium or magnesium oxide. Then the equivalent quantity of 60% acetic acid is carefully added to the mixture obtained in accordance with the reaction



Since water is liberated by reaction with 60% acetic acid, we need to calculate the effect on the overall moisture content of the coal. It follows from the calculation that, even with 6.0% salt, the moisture content of the coal is increased by no more than 0.6%.

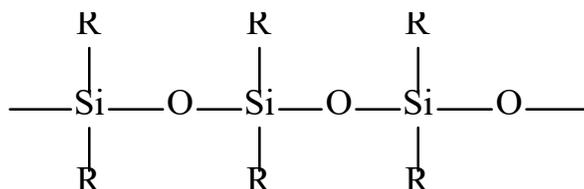
3) method of producing calcium and magnesium acetates based on the reaction of the carbonates of these metals with acetic acid by the reaction:



In contrast to the previous method, carbon dioxide is formed in this case. In the case of careful mixing with acetic acid, the freezing point of the coal remains precisely the same. However, if mixing is minimized so that the gas formed is largely retained within the coal, the freezing point falls. In this case, a weighed sample of coal is divided into five 100-g portions. Each portion is carefully mixed with calcium or magnesium carbonate and then built up in layers within a vessel. Each layer is combined with the calculated quantity of acid without mixing. Comparison of results indicates that treatment with 5.0% salt by the third proposed method reduces the freezing point of the coal from  $-14.7^\circ\text{C}$  and not at  $-13.5^\circ\text{C}$  (1 and 2 methods) [5].

The search for the most effective chemical preventive agent to prevent the freezing of coal concentrates in winter at very low temperatures (below minus  $15^\circ\text{C}$ ) during transportation from the supplier (coal processing plants) to coke plants showed that these requirements are satisfied when using silicone polymer.

Molecules of organosilicon compounds combine in part the structure of polymeric inorganic and organic molecules. The basis of their molecules is the siloxane skeleton - a chain of alternating atoms of silicon and oxygen. Other silicon bonds are compensated by organic radicals or groups of atoms [6].



where R – H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, and etc.

The peculiarity of the structure is associated with the unusual properties of these polymers, which combine the stability of these compounds to the action of low temperatures. Organosilicone liquid polymers can be obtained with a freezing temperature of minus  $130^\circ\text{C}$  or even lower.

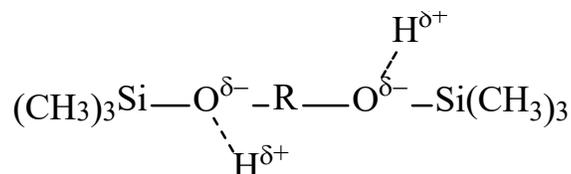
A valuable property of silicone liquids is the weak dependence of their viscosity on temperature. Thus, as the temperature decreases, the viscosity of the organosilicon compounds increases to a lesser extent than for petroleum oils. This makes it easier to apply to the surface of a metal wagon and mix with coal [6].

For polysiloxanes, low freezing temperatures and chemical inertness to metals are typical. The flammability of organosilicon liquids is much lower than that of organic compounds. The final combustion products are carbon dioxide, water, and silica as fine powder. Polysiloxane fluids do not irritate the skin and eyes.

Thus, the most valuable technical properties of organosilicon liquids are determined by their physical and chemical properties: low pour point (minus 70 to minus  $140^\circ\text{C}$ ), low viscosity dependence on temperature (multiplicity of viscosity change is 5-10 times in the interval temperature temps from  $-50$  to  $+50^\circ\text{C}$ ) [6].

Emulsions of silicone polymers are stable structures of the type «oil in water». Due to the fact that it is practically more convenient to use aqueous emulsions of silicone liquids instead of their solutions in organic solvents, the industry produces 30-70% silicone emulsions. These emulsions are easily diluted with water and used in 5-10% concentration. In commercial form, the emulsions are a white mass of creamy consistency.

Molecules of organosilicon compounds contain an oxygen atom, so the electron density at oxygen atoms is localized. As a result, the reagents can specifically interact with the sorption-active centers of the coal surface bearing a positive charge (protonated hydrogen atoms of phenolic, carboxyl groups in macromolecules of organic mass of coal) according to the scheme:



where R – alkyl radical.

Molecules of oxygen-containing organosilicon compounds also contain hydrocarbon radicals that can interact with the apolar centers of the coal surface due to Van der Waals intermolecular forces. Therefore, when adsorbed on the coal surface, molecules of organosilicon exhibit both specific (hydrogen bonds) and universal nonspecific intermolecular forces of interaction with positive parts of the coal surface. This determines their high adsorption on the coal surface.

If the solution or emulsion is mixed with coal, these atoms or groups are reacted with the organic mass of the coal and water hydrate. Organosilicon bonds - Si - O - Si - O -, which provide physical and chemical interaction with coal, facing the surface, and organogenic groups framing the silicon atom, are directed in the opposite direction - outwards.. The orientation of organosilicon bonds and hydrocarbon radicals, when applied to the surface, can be schematically represented in Fig.1.

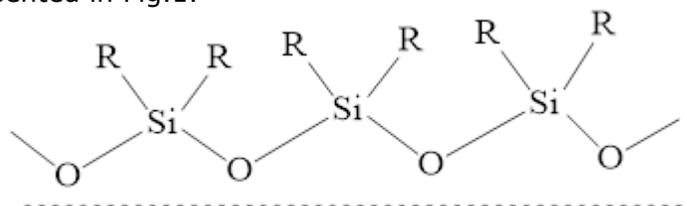


Fig. 1. Orientation of organosilicon bonds and hydrocarbon radicals on the coal surface

Organosilicon compounds, when applied to a coal surface, react with water approximately molecule to molecule. The films of organosilicon compounds are very thin. The thickness of the film, which is calculated by the material flow and film weight, assuming that its density is equal to one, is  $0.1 \cdot 10^{-6}$ - $2.5 \cdot 10^{-5}$ . The film on the surface is invisible, does not wear away when rubbed, does not wash off with water, is stable over a wide temperature range (from -200 to +300°C). Polymeric silicones on the surface of coal, even in small quantities, provide a great water repellent effect.

For the experiment, a sample of coal weighing 500 g was taken, the moisture content of the coal was 12%, the size class was 0-3 mm. The coals were carefully treated with an emulsion. Next, the processed coal was loaded into a metal tank with a diameter of 50 mm, height 50 mm, without bottom and cover. This metal container was placed in the freezer and kept at a predetermined temperature for 24 hours. Then the tank was turned over, and the coal that was poured was weighed. The degree of freezing was thus determined. The study used an organosilicon fluid GKZh-94, which is a colorless, slightly yellow liquid. Density – 0.996-1.003 g/cm<sup>3</sup>; freezing temperature -50°C; pH not less than 6. In water, it is insoluble but well forms an emulsion, corrosion inactive, does not emit harmful vapors and gases, weatherproof.

The organosilicon additive was used as 5 and 10% aqueous emulsions. The emulsion was thoroughly stirred with charcoal for 3-5 minutes. The amount of emulsion was changed from 4 to 40 g per 1 kg of coal. The concentration of the emulsion was 5 and 10%. The results of the experiment are shown in Table 2.

Table 2. The degree of freezing of the treated coal GCZh-94 emulsion at minus 15°C

Quantity of GCZh-94, g/kg	Mass of spilled coal, g	Variation of mass, g	Degree of freezing, %
5 % emulsion			
4	150	350	70
8	170	330	66
12	190	310	62
16	220	280	56
20	260	240	48
24	290	210	42
28	310	190	38
32	390	110	22
36	450	50	10
40	490	10	2
10 % emulsion			
4	200	300	60
8	220	280	56
12	250	250	50
16	270	230	46
20	290	210	42
24	360	140	28
28	400	100	20
32	420	80	16
36	480	20	4
40	500	0	0

Studies have also been conducted to identify consumption rates of known and claimed prophylactic agents to prevent freezing of coal with a moisture content of 12% (Table 3).

Table 3. Dependence of the freezing point of the coal with a moisture content of 12% added of prophylactic agents

Freezing point of sample, °C	Added of prophylactic agents, wt %			
	CaCl <sub>2</sub>	MgCl <sub>2</sub>	CH <sub>3</sub> COOK	10 % GCZh -94
-15	5.0	4.6	4.0	3.6

The analysis of these tables shows that the organosilicon emulsions reduce the freezing point well, and when compared with salts, it can be seen that the consumption of the organosilicon emulsion in comparison with the consumption of calcium chloride, magnesium, and potassium acetate is lower.

### 3. Conclusions

Thus, the proposed method not only prevents the concentration of coal concentrates in winter during their transportation from the manufacturer to the coke plant but also reduces the cost of coke by reducing the cost of defrosting (in greenhouses) and unloading coal to prevent the corrosion of cars and equipment of coal-preparation shops of coke-chemical plants. Organosilicon compounds are less toxic. The use of organosilicon is more effective than the use of acetates and chlorides of metals. The high activity of organosilicon substances is explained by their elemental composition and structure of molecules.

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