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Investigation Methods of Preparation and Aspects of Introduction in Coal Concentrates Chemical Reagents for Addressing the Problem of Coal Raw Materials Freezing Message 1. Prevention of Coal Freezing by the Chlorides of Alkaline-Earth and Alkaline Metals

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Abstract

In the cold season, irregular coal supplies to coke plants are aggravated by the need to heat the coal cars. The thawing of rail cars in garages (enclosures) is the least efficient and most expensive approach. Treatment of the coal concentrates with chemical additives reliably prevents freezing in winter during transit from suppliers to consumers. With a view to finding new reagents for preventing the freezing of coal in winter, the lime and the chlorides of alkaline-earth and alkaline metals are studied. Attention focuses on their physicochemical characteristics, methods of preparation and of introduction in coal concentrate, and their influence on freezing.

Keywords*: Coal freezing; Freezing point; Chlorides of alkaline-earth and alkaline metals; Granulometric composition of coal, Effectiveness of mixing.*

1. Introduction

Among the problems encountered by coke plants in the cold season is freezing of the coal concentrates on transportation, which hinders their discharge from the rail cars. The individual coal particles freeze together and also bond with the floor and walls of the car.

This is not a new problem. It has traditionally been addressed by heating the cars with coal in special garages (enclosures), which consume considerable quantities of energy. It is much less expensive (by several orders of magnitude) to prevent freezing than to heat the frozen coal.

Protection against freezing depends on the analysis of the responsible factors and study of the heat and mass transfer and the rate of freezing of coal on transportation. At present, we may identify two basic approaches to addressing the problem [1-2]:

1) prevention of freezing;
2) restoration of the frozen coal's friability before or during discharge.

Methods of the first type include drying of the coal, mixing of wet and dry coal, refreezing of the coal, and the application of hydrophobic protective coatings to the coal and the walls of the rail cars.

Methods of the second type include heating of the cars with frozen coal in special garages (enclosures) and mechanical action by drilling, vibration, and agitation machines.

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.

2. Results and discussions

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 using the lime, the chlorides of alkaline-earth and alkaline metals are tested as reagents to prevent freezing of coals.

It is found that CaO may expediently be used to prevent freezing if its activity is no less than 85–88%, and the ambient temperature is not below – (15–16)°C [3]. At lower temperatures, freezing is not prevented by unslaked lime, even in quantities of 3–6% of the mass of coal. Unslaked lime only serves an auxiliary function; it may be used as a mechanical layer between the coal layers.

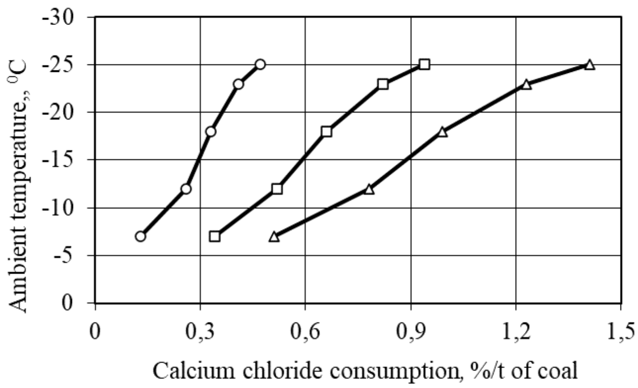

Fig. 1. Calcium chloride consumption to prevent the freezing of coal with 3% (1), 6% (2), and 9% (3) moisture content

We now turn to solutions of calcium chloride and magnesium chloride [3-4]. For coal of moisture content up to 12%, the optimal addition of $CaCl_2$ solution is 1.5– 2.0%/t of coal. About 30% of the solution should be mixed with the lower layers of the coal, which freeze more severely; the remainder should be distributed uniformly through the rest of the coal. In Fig. 1, we show laboratory data for calcium chloride.

The use of calcium chloride is not advised if the coal will subsequently be subjected to high-temperature treatment. Above 900°C, the calcium chloride added to the coal begins to break down, with the liberation of chlorine.This process is especially vigorous in the presence of oxides of silicon and aluminum, which act as catalysts. The presence of free chlorine and hot coke may lead to the formation of toxic dioxin. Other problems with calcium chloride are its high cost and corrosive properties.

These concerns do not apply to magnesium chloride, the main component of natural bischofite. It is mined, for example, in the Poltavsk and Chernigovsk deposits in Ukraine. This solution is safe and has medicinal properties. In contrast to calcium chloride, it is not corrosive; in fact, it can slow corrosion rates. In laboratory tests, the quantity of magnesium chloride added is 1–5% of the coal mass. The moisture content of the coal concentrate employed (≤3 mm class) is 12%. Table 1 presents the experimental results.

Table 1. Freezing temperature of coal treated with bischofite

Added bischofite, %	Calculated freezing temperature of bischofite solution, °C	Freezing temperature of coal treated with bischofite, °C
1,0	-7,3	-4
2,0	-11,6	-8
3,0	-14,6	-10
4,0	-16,3	-16
5,0	-19,3	-18

We see that adding 4–5% bischofite ($MgCl_2 \cdot 6H_2O$) reduces the freezing temperature of the coal particles to –16–18 °C. Since the air temperature in Ukraine rarely reaches –20°C in winter, adding 2.5–3% bischofite to coal transported within the country is best; the effectiveness of mixing must be no less than 96–98%. As shown by experiments, adding bischofite to coal does not change the packing density of the coal and raises the basicity index by only 0.5%. In this approach, the moisture between the coal pieces is replaced by a solution with a low eutectic freezing point. The ice formed is characterized by a defective flake structure and, consequently, is fragile.

Another benefit of magnesium chloride over calcium chloride is that its decomposition at high temperatures does not release chlorine

$$MgCl_2 \cdot 6H_2O \xrightarrow{20\text{–}60\,^\circ C} MgCl_2 \cdot 4H_2O \xrightarrow{90\,^\circ C} MgCl_2 \cdot 2H_2O \xrightarrow{119{,}5\,^\circ C} MgCl_2 \cdot H_2O \xrightarrow{505^\circ C} MgO + 2HCl$$

Research shows that coal with low moisture content (no more than 11–12%) may expediently be treated with an aqueous solution of bischofite since such treatment will raise the coal's moisture content.

A comparison of protective additives shows that sodium chloride is active to –10°C, calcium chloride to –10–16 °C, and magnesium chloride to –16–18°C.

We propose a system of rotor type for the final mixing of the coal batch with any protective additive. The mixer (Figs. 2 and 3) is mounted above a conveyer belt so that its rotors fit within the cross-sections formed by the ribbed conveyer belt, with a gap between the plane of the belt and the rotor blades.

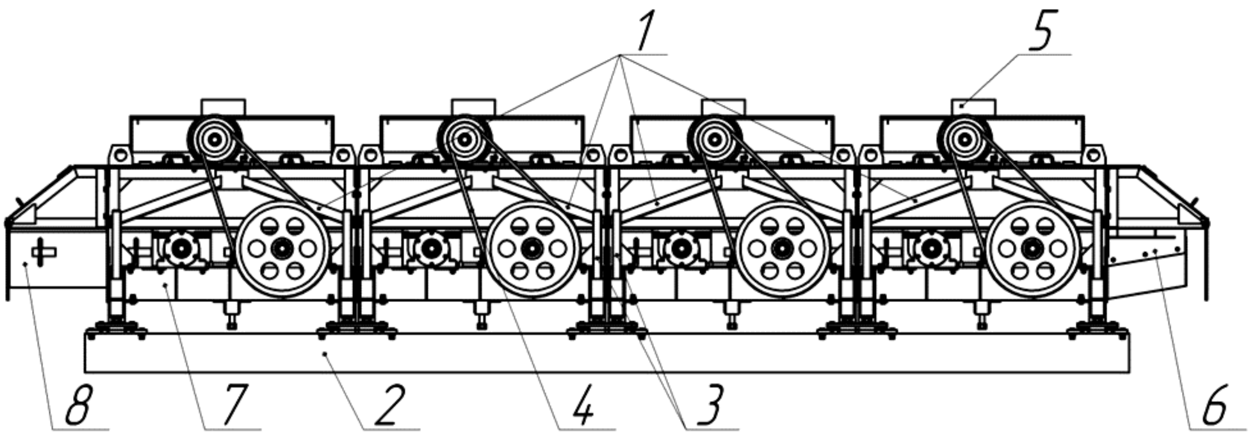

Fig. 2. Four section rotary mixer: (1) mixer section; (2) support; (3) adjustable screws; (4) V-belt transmission; (5) electric motor;
(6, 8) shielded input and output sections; (7) seal

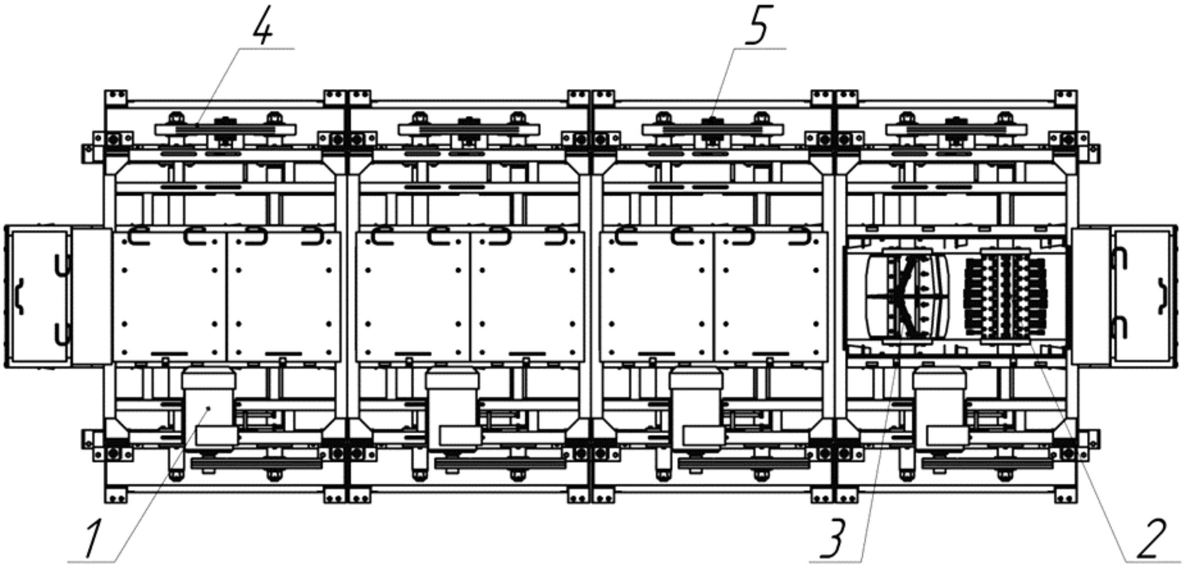

Fig. 3. Four section rotary mixer (top view): (*1*) electric motor; (*2*) cable rotor; (*3*) blade rotor; (*4*) V-belt transmission; (*5*) tension roller

As the coal batch moves over the belt, it is acted on by the rotor blades and mixed with the protective additives. The characteristics of the SR-2-520×1.0 mixer are as follows:

Width of the conveyer belt, mm	1000
Number of sections	2
Rotor diameter, mm	520
Rotor speed, rpm	250
Length of rollers in horizontal support, mm	410
Conveyer slope, deg	0
Rated power, kW	15
Power of a single electric motor, kW	7.5
Number of motors	2

The rotors (Figs. 4 and 5) are responsible for the mixing. Each section of the mixer contains two types of rotors: one with regular blades and one with cable elements. The rotors turn in the same direction as the coal batch moves through the mixer. This mixer is effective in terms of batch characteristics such as the packing density, granulometric composition, and petrographic data, as indicated by the gain in coke quality despite declining coal quality and irregular coal supplies [1]. In addition, when this mixer is employed, the treatment of coal with protective additives prevents the freezing of the coal on transportation over any distance at negative temperatures.

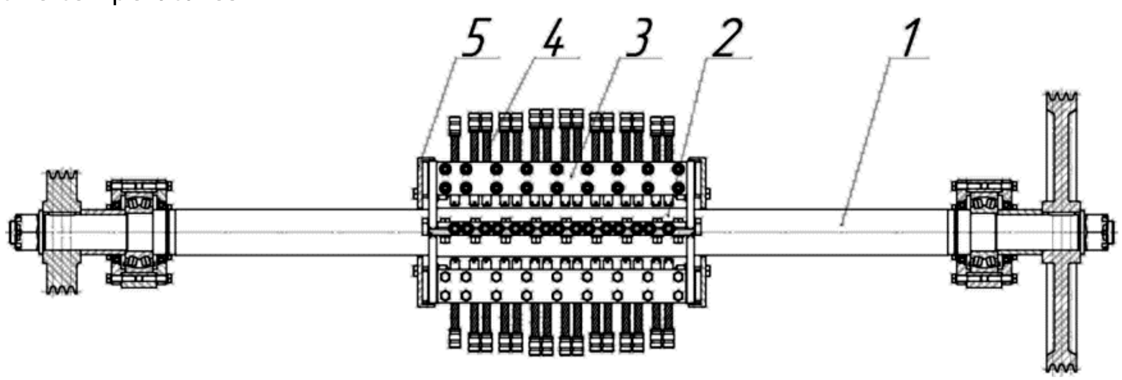

Fig. 4. Cable rotor of mixer: (*1*) shaft; (*2*) drum; (*3*) removable blades; (*4*) cable elements; (*5*) lock

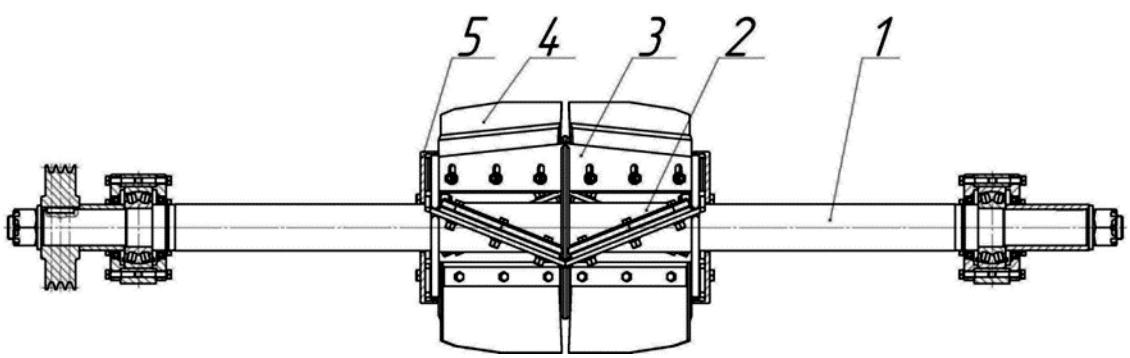

Fig. 5. Blade rotor of mixer: (*1*) shaft; (*2*) drum; (*3*) removable blades; (*4*) flexible blade elements; (*5*) lock

The chloride consumption depends on the coal's size class, as is clear from the dependence of the degree of freezing on the moisture content (Table 2).

With the increase in size class, as we see in Table 2, the chloride consumption falls. Thus, the calcium chloride consumption declines from 9.2 to 5.3 g/kg of coal at −5°C, from 15.3 to 8.4 g/kg at −10°C, and from 18.3 to 12.3 g/kg at −15°C. Analogous results are obtained for magnesium chloride. Its consumption declines from 6.2 to 3.8 g/kg of coal at −5°C, from 10.5 to 5.5 g/kg of coal at −10°C, and from 15.6 to10.8 g/kg of coal at −15°C.

Table 2. Consumption of calcium chloride and magnesium chloride to prevent freezing

Size class, mm	Chloride consumption, g/kg of coal					
	$CaCl_2$	$MgCl_2$	$CaCl_2$	$MgCl_2$	$CaCl_2$	$MgCl_2$
	at -5°C		at -10°C		at -15°C	
0-3	9.2	6.2	15.3	10.5	18.3	15.6
3-7	7.4	5.4	10.7	8.6	14.2	13.5
7-15	5.3	3.8	8.4	5.5	12.3	10.8

Note also that the consumption of calcium chloride practically doubles with the decrease in temperature from −5 to −15°C for all size classes: from 9.2 to 18.3 g/kg for the ≤3 mm class; from 7.4 to 14.2 g/kg for the 3–7 mm class; and from 5.3 to 12.3 g/kg for the 7–15 mm class. In the same conditions, the consumption of magnesium chloride increases from 6.2 to 15.6 g/kg for the ≤3 mm class; from 5.4 to 13.5 g/kg for the 3–7 mm class; and from 2.3 to 10.8 g/kg for the 7–15 mm class. The magnesium chloride consumption is less than calcium chloride consumption [4].

As is evident from Table 3, treating only the ≤3 mm class increases chloride consumption. Therefore, to prevent freezing, careful mixing of all the coal with reagent is expedient, without division into size classes.

Table 3. Consumption of magnesium chloride in treating the ≤3 mm class [4]

Content of ≤3 mm class, %	$MgCl_2$ consumption, g/kg of coal		
	at -5°C	at -10°C	at -15°C
50	8.2	11.4	16.8
70	12.4	17.4	21.6
80	16.2	22.1	26.6
90	18.7	26.5	30.5

3. Conclusions

The treatment of coal concentrates with protective additives may reliably prevent freezing on transportation from suppliers to consumers in winter. The coal may easily be discharged from the rail cars, without large energy expenditures to heat the cars in special garages (enclosures). The increase in coal cost due to its treatment with protective additives by the supplier is more than compensated by the savings at the consumer, where no heating is required. Also, the coal does not need to be crushed by heavy-duty machines, which usually results in an excessive reduction in piece size and increase in the leanness of the batch, especially in the case of valuable coal ranks, and sharply impairs coke quality.

In laboratory experiments, the optimal additions of calcium chloride and magnesium chloride for the treatment of coal mixtures are determined as a function of the content of the ≤3 mm class. Note, however, that the effectiveness of treatment with protective additives depends critically on the effective mixing of the coal and additives (at least 96–98%).

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