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EFFICIENCY OF APPLICATION OF ANTIPYROGENIC MATERIALS FOR COATING COALS AND COKE

Purpose. Selection of the most effective anti-pyrogenic coating for stacks of coal and special coke during open storage to preserve consumer properties.

Methodology. The methods of technological modeling and experimental studies are used.

Findings. Observations of physical changes in stacks covered with various flame retardant materials are conducted through field and laboratory tests over time. Corresponding degrees of preservation of the initial state of the product when using certain coatings are established. The most effective coatings were identified by changes in the technical and particle size parameters of coals and special coke. Monitoring of temperature data in the depth of stacks confirmed a direct relationship between stack volumes and the degree of oxidation processes.

Originality. For the first time, the dependences of the safety of fractions and technical parameters of Shubarkol coal and special coke in stacks on the use of different flame retardants over time have been established. The obtained results on using polymeric materials make it possible to create similar coatings from recycled materials and production wastes.

Practical value. The obtained laboratory results allow us to recommend certain anti-pyrogenic materials for use in production operations on the basis of the Shubarkol and other coal industry enterprises. The development of polymer coatings from recycled coke production will improve the environmental situation in the region.

Keywords: *spontaneous combustion, coal storage, special coke, flame retardant, polymer coatings*

Introduction. Practice has shown that during the storage of coal in a number of deposits in Kazakhstan (Karaganda, Ekibastuz, Shubarkol, Sharynkol, Karazhyrinsk, Maykubensky and others), oxidizing processes occur under certain conditions leading to weathering and, in many cases, spontaneous combustion [1]. This phenomenon causes serious environmental and economic damage to enterprises engaged in coal mining and processing. For more than 60 years, scientists of the world have carried out significant theoretical and experimental studies, which have significantly expanded knowledge in the field of combating oxidative processes in mineral volumes. Factors and processes occurring at the time of coal oxidation are studied in many aspects, and nowadays scientific research is more applied in nature, the desire of researchers is aimed at the invention of effective means of preventing oxidative processes, including spontaneous combustion of coal [2]. However, it should be noted that existing methods for solving the problem of spontaneous combustion of coal either do not give full efficiency, or violate the consumer properties of coal and coke as a product.

The Republic of Kazakhstan has developed state standards [3] and technical regulations [4] for the safe storage of coals of various grades and classes, however, such fundamental recommendations do not always solve storage problems when changing the technological process, therefore, developing enterprises need to develop local control measures and prevent processes of weathering and spontaneous combustion.

So, by the order of one of the enterprises of the Karaganda region, a group of researchers from Karaganda State University studied the factors affecting the spontaneous combustion of special coke when stored in closed containers and the weathering of coal in open areas.

During the study, a number of experimental measurements were carried out to develop further recommendations for the storage of coal and special coke at the facilities of the enterprise in closed and open areas.

In developing the research methodology, the well-known measures to prevent coal oxidation were considered, including methods of heat removal, blocking oxygen access and the use of flame retardant materials to cover stacks of coal and coke [5].

Thus, the article is devoted to the consideration of the effectiveness of the use of various anti-pyrogenic materials to prevent weathering and spontaneous combustion of coal and its processed products in the production conditions of the Shubarkol deposit.

Research methods. When studying the factors affecting the spontaneous combustion of special coke in closed bunkers and the weathering of coal in open areas, laboratory studies of coal and special coke were conducted.

Tracking changes in the initial physicochemical state of stacks coated with various flame retardant materials over time, in our opinion, is the most accurate way to observe the dynamics of the destruction of the structure of coal, its self-heating and identify the most effective flame retardant materials.

To carry out experimental studies on preventing weathering and on the influence of methods and technologies that increase shelf life on the storage safety and lumpiness of raw coal and special coke produced by the KSTU working group, 47 stacks were formed and processed: 3 stacks of 50 tons each, 44 stacks of 12 tons each. Table below reflects only a list of the stacks which, in our opinion, are of interest for review in this article.

Similar coatings were used when laying stacks of special coke made from test coal. Antipyrogens for use were selected based on various scientific studies of domestic and foreign scientists and taking into account the affinity of the climatic conditions of the region.

It has been experimentally proved that the combustion of solid fuel particles begins with the ignition of volatile substances. Those fuels that have the highest volatility yield and contain the largest amount of oxygen and the least amount of carbon in the organic mass have a lower flash point. And, in turn, *Table*

Applied measures to prevent oxidation in stacks of run-of-mine coal of increased coarseness

№ stack	Applied measures Closed-type warehouse	№ stack	Applied measures (open-type warehouse)
1.1.1	Control	1.2.1	Control
1.1.2	No application	1.2.2	No application
1.1.3	Coated Kapts – cement-mineral mixture	1.2.3	Coated Kapts – cement-mineral mixture
1.1.4	With “Teckflex” – polymer coating	1.2.4	With “Teckflex” – polymer coating
1.1.5	Coated with three-layer heat-resistant plastic film (Universal)	1.2.5	Coated with three-layer heat-resistant plastic film (Universal)
1.1.6	Using antipyrogen 3 % urea + 2 % calcium chloride	1.2.6	Using antipyrogen 3 % urea + 2 % calcium chloride
1.1.7	Using antipyrogen 5% lime milk + 4 % calcium chloride	1.2.7	Using antipyrogen 5 % lime milk + 4 % calcium chloride
1.1.8	Using antipyrogen 5 % liquid glass + 1 % surfactant (“Progress”)	1.2.8	Using antipyrogen 5 % liquid glass + 1 % surfactant (“Progress”)
1.1.9	Using antipyrogen 3 % ammonium sulfate + 3 % calcium carbonate	1.2.9	Using antipyrogen 3 % ammonium sulfate + 3 % calcium carbonate
1.1.10	Using anti-pyrogen 10 % inert dust + phenolic water	1.2.10	Using anti-pyrogen 10 % inert dust + phenolic water
		1.2.11	Geof Coated – Organic Mineral Resin
		1.2.12	“EcoFlex” Coated
		1.2.13	With “Teckflex-M” – polymer coating

the yield of volatile substances can be used to indicate the coke carbonization yield, provides a basis for buying and selling to consumers, or to give combustion characteristics [6].

In the course of observing changes in the state of stacks, measurements and analyzes were periodically carried out on such technical characteristics of coal and special coke as humidity, ash and volatile substances, a theoretical calculation of the content of fixed carbon and the calorific value of the product as a relative indicator of the conservation of consumer properties due to the reversibility of coal metamorphism due to exposure oxygen and other environmental factors.

Thus, a change in the content of volatile substances and fixed carbon over time storage of coal and special coke will indicate the presence and speed of the oxidation process of the product, and a comparison of the analysis results of stack samples coated with various materials demonstrate the effectiveness of one or another flame retardant.

The yield of volatile substances, moisture, and ash of special coke was determined using an Eltra Thermostep thermogravimetric analyzer. Sample preparation is carried out as usual, crushed to a fraction of 0.25 mm according to ASTM D7582-15.

Tracking changes in the fractional state of coal over time is also considered an objective indicator of coal weathering during long-term storage in open areas, since the change can be interpreted as a process of destructive processes due to coal weathering. The analyzed coal belongs to the long-flame type of coal and according to the fractional composition is ranked as ordinary, thus conducting a sieve analysis of piles will objectively demonstrate the effectiveness of a particular coating [7].

Along with particle size analysis in the field, the temperature of the stacks was taken, assuming that the intensity of the oxidation processes can be tracked by the temperature difference under the same external conditions.

Temperature control was carried out using a thermometer or thermocouple. A vertical control metal pipe with a diameter of 50 mm was installed in the stack, the lower ends of which were closed tightly and sharpened, and the upper ends were closed with a wooden cork attached to the end of the pipe. A thermometer (thermocouples) was suspended from a cork on a cord, which descended into the pipe. Pipes in the stack were installed at a distance of 1/4 of the height of the stack.

The effectiveness of the use of various means to reduce the decomposition of coal is evaluated by determining the coal coarseness in the processed stacks in comparison with a “control” stack (with no cover). The same principle is used to estimate efficiency by the class of 0–6 mm.

Results. Granulometric analysis. The relevance of the sieve analysis is also justified by commercial demand, as according to the manufacturer coal of a fraction from 0 to 6 mm is not commercially attractive to consumers of municipal coal, and therefore an analytical review of the data was aimed at assessing the growth of this fractional group.

Sieve analysis and particle size distribution were carried out according to GOST 2093-82 [8]. A sample amount taken for analysis depends on the desired fraction size and ranged from several kilograms to 150 kilograms of analyzed coal. The error in determining the yield of size classes was 2.7 %.

The analysis was performed on site in the immediate vicinity of the stacks being tested. And fractions to be tested are 0–3, 3–6, 6–13, 13–25, 25–50, 50–100 and 100–300 mm.

Despite various fractions estimated during test performance changes in the fractional compositions of 0–6 and 50–300 mm are considered as indicative for the research, since a decrease in the content of fineness of 50–300 mm and an increase in the number of particles of size 0–6 mm have a clear expression of oxidative processes. Changes in particles within sizes from 6 to 300 mm are not so detrimental to the production and sale of the product; however, monitoring the trend and slowing down the destructive processes in this range will make it possible to predict trends in the deterioration of coal quality.

As shown in the diagrams (Figs. 1–4), according to the criterion for the growth of the fractional composition 0–6 mm, 1.1.3, 1.1.4, 1.1.5, 1.2.3, 1.2.4, 1.2.5 were the most promising for a further assessment of the application , similarly, positive dynamics is tracked on the same stacks, but for sieves in sizes from 50–300 mm, namely, a smaller degree of destruction of large particles is observed.

Comparison of the absolute difference in the fractional state of each stack with the value of the weathered coal fraction from the control stack (highlighted in yellow) indicates the performance grade of anti-pyrogen. This approach allows us to identify the most effective anti-pyrogenic mixtures and coatings.

From overview of above diagrams, the following flame retardants demonstrated technical effectiveness: Kapts coating – cement-mineral mixture, Teckflex – polymer coating, three-layer heat-resistant polyethylene film coating (Universal), flame retardant (5 % water glass + 1 % surfactant (Prog-

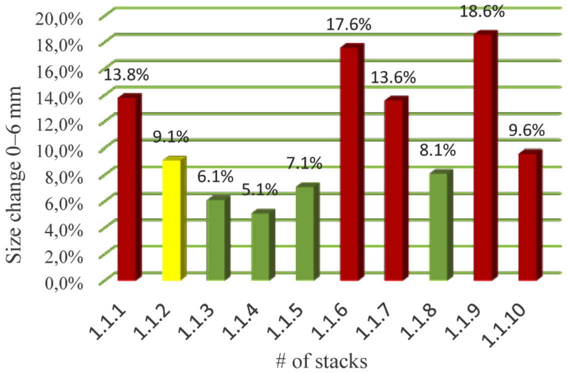

Fig. 1. Changes over time. Closed-type warehouse. Run-of-mine coal increased size. Fraction 0–6 mm

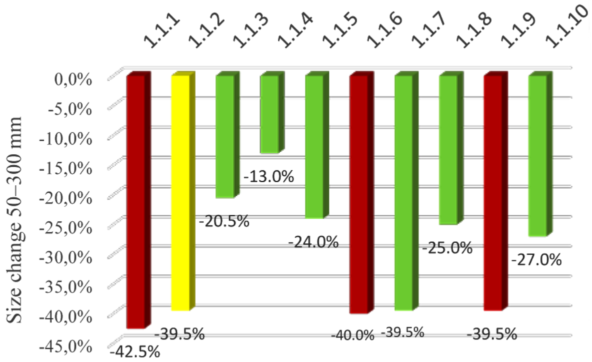

Fig. 2. Changes over time. Closed-type warehouse. Run-of-mine coal increased size. Fraction 50–300 mm

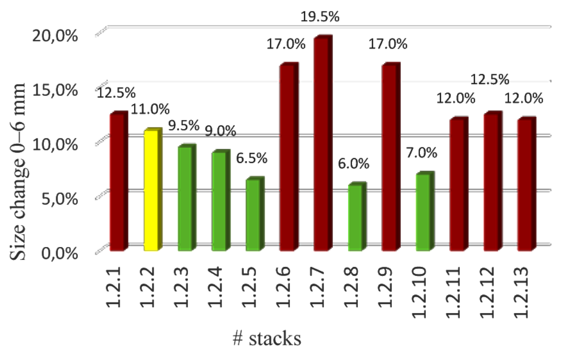

Fig. 3. Changes over time. Open-type warehouse. Run-of-mine coal increased size. Fraction 0–6 mm

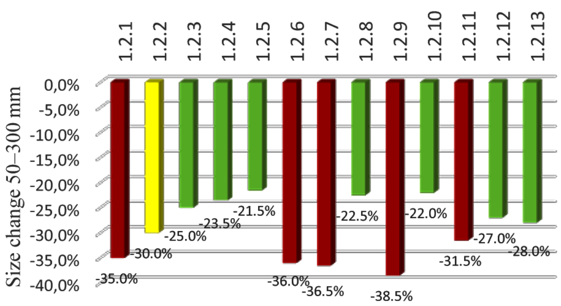

Fig. 4. Changes over time. Open-type warehouse. Run-of-mine coal increased size. Fraction 50–300 mm

ress), flame retardant (10 % inert dust + phenolic water.) The listed flame retardants and coatings were shown to be effective in closed and open warehouse types applying to different classes of coals.

Based on the values of the sieve analysis, the greatest positive effect among the materials listed above is observed for the Teckflex polymer coating and three-layer polyethylene film.

Technical analysis. The analysis was carried out in the laboratory of methane energy of the mining and metallurgical complex of KSTU with 10 parallel measurement repetitions per sample. The result of averaged data on coal and special coke is given below (Figs. 5–7).

Analytical work was carried out in accordance with the standards ST RK ISO 17246-2009 and ASTM D7582-15. Test results precision is evaluated within 2–3 %, which was also taken into account when comparing similar results. Due to the fact that the analysis was carried out 10 times with each sample, a difference of 3 % was taken as incomparable and ne-

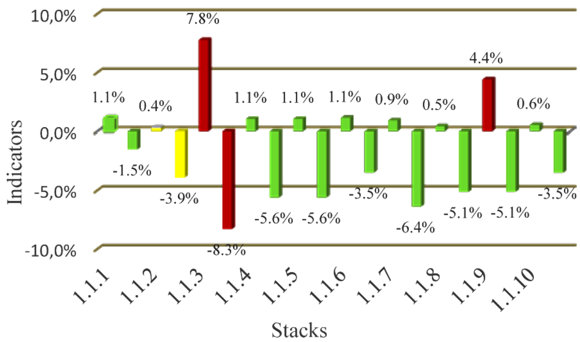

Fig. 5. Run-of-mine coal increased size. Closed-type warehouse. Change in fixed carbon levels (lower half-plane) and ash content (upper half-plane)

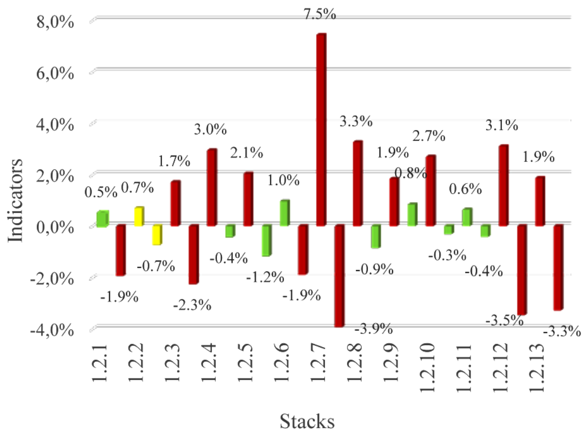

Fig. 6. Run-of-mine coal increased size. Open-type warehouse. Change in fixed carbon levels (lower half-plane) and ash content (upper half-plane)

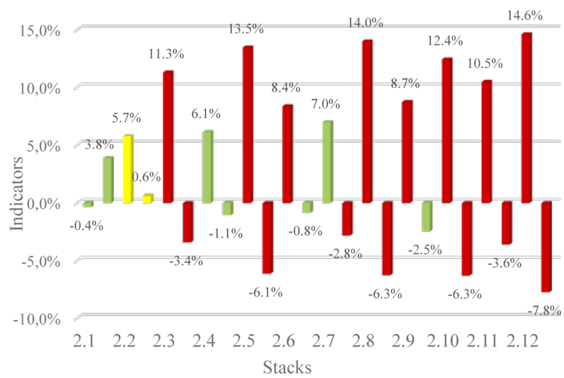

Fig. 7. Run-of-mine coal with high content of fine particles. Open-type warehouse. Change in fixed carbon levels (lower half-plane) and ash content (upper half-plane)

glected in case of comparison with control stacks. Overview diagrams are shown in Figs. 5–7 (the yellow fill is applied to the control stacks of the same volume as the test ones; the red fill is applied to the stacks showing a negative effect relative to the control; the green fill is applied to the stacks showing the positive dynamics relative to the control stack).

A significant increase in ash content is observed in all open warehouses, when the components of the technical analysis in closed warehouses remained almost unchanged, with the exception of the stack covered with a cement-mineral mixture. Despite the positive result demonstrated in the sieve analysis, it can be concluded that the mixture is not a rational solution, especially in seasons with a high probability of rainfall.

Similar analyzes were carried out on stacks of special coke with slightly different criteria for evaluating the effectiveness of anti-pyrogenic materials [9].

The data obtained from a technical analysis of control stacks of the special coke confirms a decrease in the calorific value with time, which indicates the ongoing processes of oxidation. In turn, the difference in calorific value decreases with increasing coarseness of the special coke fractions, which also confirms the stability of large particles to the weathering of coal.

Since calorie count was considered according to the method proposed by R. A. Sukhanov and G. P. Sidorova [10], it was necessary to objectively take into account all the physicochemical parameters, including humidity and ash content, which is difficult with the open-type storage of coal and coke used at the customer's production site.

Among the anti-pyrogenic materials, stacks coated with Techflex-polymer coating and three-layer film resulted with the highest caloric values. However, stacks 1.1.1, 2.1 (control stack of coal with fine particles) and 3.1 (control stack of power-generating coal) also showed a significant increase in volatile compounds. We believe this is due to the nature and composition of the coating polymer, since with the stable caloric values, the detected volatile substances cannot be of coal origin. In general, in their series, stacks showed a high carbon content.

Temperature control. In most cases, oxidative processes are exothermic reactions and externally, these processes can be fixed and controlled by monitoring changes in the temperature of the studied medium. These actions can be carried out both with a conventional thermometer and with more automated sensors such as a thermal imager and thermocouples with electronic displays (Figs. 8–9).

During the monitoring period from October 2017 to April 2018, critical temperatures were not recorded on the stacks studied; however, a maximum difference of 10 °C was observed in the stack of the control 50 ton stack in December 2017, which leads to the conclusion that the volume of stacks studied (12 tons) cannot be perceived objectively to track the heat of

Fig. 9. Temperature measurement of a stack of polymer coated – "Techflex-M"

exothermic reactions of coal oxidation, since growth and changes of 1–2 °C cannot be interpreted within the measurement error. As well as technical and sieve analyzes demonstrate the objectivity of choosing the size of the stacks to interpret the effectiveness of a particular stack, while reproducing typical storage in the domestic conditions.

However, according to the diagram (Fig. 10), during the research period, a significant difference is observed in the reading of temperatures between stacks of open and closed storages, which reaches max 10 °C. These data allow us to conclude that open storage stacks are exposed to oxygen more, although they do not reach critical temperatures even at control stacks.

Conclusions. Thus, in the case of prevention of weathering of coals and self-heating of special coke at the production sites of the Shubarkol deposit, the highest efficiency was demonstrated by antipyrogenic materials of polymer origin.

Polymer coatings or polyethylene films made it possible to preserve the integrity and energy value of products without increasing ash content due to the absence of inorganic impurities in their composition. However, the economics of applying a polymer coating is not an example of rationality and requires studying the application or developing cheaper analogues as technology for processing secondary raw materials or by-products of coal coking. For example, Phenolic water resulting from coking on Shubarkol coal is a real environmental problem that must be neutralized in any case could be applied as a raw material for the synthesis of polymers at the production site.

This seems perspective to apply three-layer polyethylene film in various forms which appears as an effective coating and packaging material in transportation and storage of coal and its derivatives. The production of so-called bugs for transporta-

Fig. 8. Temperature measurement of a stack coated with a three-layer film

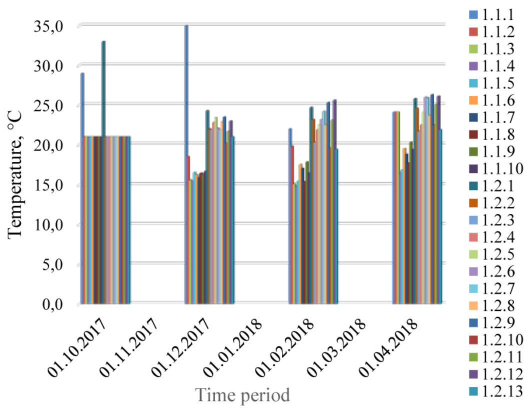

Fig. 10. Temperature difference between stacks from open and closed storages for the entire study period

tion, storage of coal and products will ensure both product safety and mobility when using certain volumes.

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Ефективність використання антипірогенних матеріалів для покриття вугілля та спецкоксу

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Мета. Підбір найбільш ефективного антипірогенного покриття для штабелів вугілля та спецкоксу при відкритому зберіганні для збереження споживчих властивостей.

Методика. Використані методи технологічного моделювання та експериментальних досліджень.

Результати. Проведені спостереження фізичних змін штабелів із плином часу, покритих різними антипірогенними матеріалами, шляхом проведення польових і лабораторних випробувань. Установлені відповідні міри збереження первинного стану продукту при використанні певних покриттів. За зміною технічних, гранулометричних параметрів вугілля та спецкоксу виявлені найбільш ефективні покриття. Моніторинг температурних даних у глибині штабелів підтвердив пряму залежність обсягів штабелів і ступеня окислювальних процесів.

Наукова новизна. Уперше встановлені залежності збереження фракцій і технічних параметрів Шубаркольського вугілля та спецкоксу у штабелях від застосування різних антипірогенів із плином часу. Отримані результати з використання полімерних матеріалів дають можливість створення схожих покриттів із вторинної сировини та відходів виробництва.

Практична значимість. Отримані результати лабораторних досліджень дозволяють рекомендувати певні антипірогенні матеріали для використання у виробничих операціях на базі Шубаркольського та інших підприємств вугільної галузі. Розробка полімерних покриттів із вторинної сировини коксового виробництва поліпшить екологічну ситуацію в регіоні.

Ключові слова: *самозаймання, зберігання вугілля, спецкокс, антипіроген, полімерні покриття*

Эффективность применения антипирогенных материалов для покрытия углей и спецкокса

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Цель. Подбор наиболее эффективного антипирогенного покрытия для штабелей углей и спецкокса при открытом хранении для сохранения потребительских свойств.

Методика. Использованы методы технологического моделирования и экспериментальных исследований.

Результаты. Проведены наблюдения физических изменений штабелей с течением времени, покрытых различными антипирогенными материалами, путем проведения полевых и лабораторных испытаний. Установлены соответствующие степени сохранности первичного состояния продукта при использовании определенных покрытий. По изменениям технических, гранулометрических параметров углей и спецкокса выявлены наиболее эффективные покрытия. Мониторинг температурных данных в глубине штабелей подтвердил прямую зависимость объемов штабелей и степени окислительных процессов.

Научная новизна. Впервые установлены зависимости сохранности фракций и технических параметров Шубаркольского угля и спецкокса в штабелях от применения разных антипирогенов с течением времени. Полученные результаты по использованию полимерных материалов дают возможность создания похожих покрытий из вторичного сырья и отходов производства.

Практическая значимость. Полученные результаты лабораторных исследований позволяют рекомендовать определенные антипирогенные материалы для использования в производственных операциях на базе Шубаркольского и иных предприятий угольной отрасли. Разработка полимерных покрытий из вторичного сырья коксового производства улучшит экологическую ситуацию в регионе.

Ключевые слова: *самовозгорание, хранение углей, спецкокс, антипироген, полимерные покрытия*

Recommended for publication by T. K. Isabek, Doctor of Technical Sciences. The manuscript was submitted 21.10.18.