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IMPACT OF THE USE OF COMBUSTIBLE TECHNOGENIC WASTE ON PHYSICAL AND CHEMICAL PROCESSES OF CEMENT PRODUCTION AND PROPERTIES

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Abstract.

The Russia's cement industry is the largest fuel consumer. As known, the natural fuel can not be restored, therefore, its replacement with the waste is relevant now; it also solves the environmental issues, since a cement kiln is the most environmentally friendly unit for waste disposal, including the waste hazardous to humans and environment.

Since the majority of Russian factories use the wet method, it is the most expedient way to introduce the technogenic waste as a combustible additive into the slurry, because this method does not require the use of any additional equipment. The work considers the impact of combustible technogenic waste on the physical and chemical processes of cement production, namely the processes of burning the feedstock mixture, grinding of clinker, cement quality, and work of the process equipment. It has been established that the addition of combustible waste can increase the dust removal from a kiln, reduce the sulphate sublimation temperature complicating the production process of sulphoferrite and commercial clinkers, intensify grinding of clinker at a specific particle size of combustible waste. With the introduction of 5-10% of combustible waste in the feedstock mixture, the strength of cement stone reaches the strength of the top-quality commercial cement stone.

Key words: Technogenic waste, combustible additives, adhesive and cohesive properties, sublimation of sulphates, grinding intensifier, strength of cement stone.

Introduction. Using energy-efficient technogenic waste in the cement production is a very urgent task, because it allows replacing a part of the natural fuel with alternative one in combination with simultaneous disposal of environmentally hazardous secondary materials [1-3]. The technogenic waste to replace a part of the fuel can be introduced both through a burner and in the feedstock mixture as a combustible additive. Based on the fact that the secondary materials often exist in different aggregate states (liquid or solid), have different size, their introduction through a burner is difficult because it requires constant modernization for a particular type of waste. The introduction of waste containing a combustible component in the feedstock mixture is the most appropriate method; it does not require any additional equipment. However, the introduction of combustible additives in the feedstock mixture can lead to a change in the kiln operation, composition of kiln charge, intensity of grinding processes and processing properties of the finished cement. So, studying the impact of various combustible additives on physical and chemical processes of cement production and properties is relevant.

Main part. Introduction of combustible additives to feedstock mixture in the preparation of cement may have an impact both on its processing properties, and the physical and chemical processes occurring in various units.

The cement rotary kiln's operation is often complicated by the phenomenon of dust formation [4]. Since the wet cement production process dominates in Russia, trouble-free operation of a kiln depends on the optimization of heat transfer devices, which are the main source of dust [5]. Therefore, in the production of wet cement it is very important to study the impact of combustible additives on the adhesive-cohesive properties of the slurry, which determines the dust formation and heat transfer efficiency in the zone of chain system. The slurry drying process can be divided into two stages: from the initial to the critical moisture content when the amount of the slurry, which has passed in chains, reaches a maximum, and from the critical moisture content to a moisture when material sheds from the chains. The longer the chains are coated with the material, better heat transfer is in a kiln, since the material is in the hot exhaust gas stream, and the more dust carried by the gas stream is captured in the zone of chain system [6]. Therefore, the section - up to the critical moisture content - can be considered as a dust collection zone where the slurry collects dust fraction due to its excessive moisture. The second section where the slurry loses slowly its mobility and plasticity may be regarded as a dust formation zone. The flow of gases moving in a rotary kiln lifts individual particles from the surface of the material. The larger particles from the lifted ones are deposited along the kiln length, and the remaining are carried away by gases. Lignin, which introduction into the slurry in an amount of 6% will reduce the fuel consumption by 35 kg per ton of clinker, is used as a fuel-containing additive. The effect of lignin on the change in the adhesive-cohesive properties was studied on the chalk-based Krichevsk slurry and limestone-based Novotroitsk slurry. Introduction of lignin in the Novotroitsk slurry changed the nature of the slurry drying curve and increased the slurry weight on chains from 0.32 to 0.39 kg/kg and the amount of critical moisture content from 30 to 32% (Figure 1). As a result, the moisture content range of dust deposition decreased, and the intensity of material shedding from the chains reduced significantly. Lignin introduced to the Krichevsk slurry led to the fact that the nature of the curve changed more significantly, the critical moisture content increased from 28 to 37% resulting to a considerable reduction of the dust deposition zone and expansion of the dust formation zone.

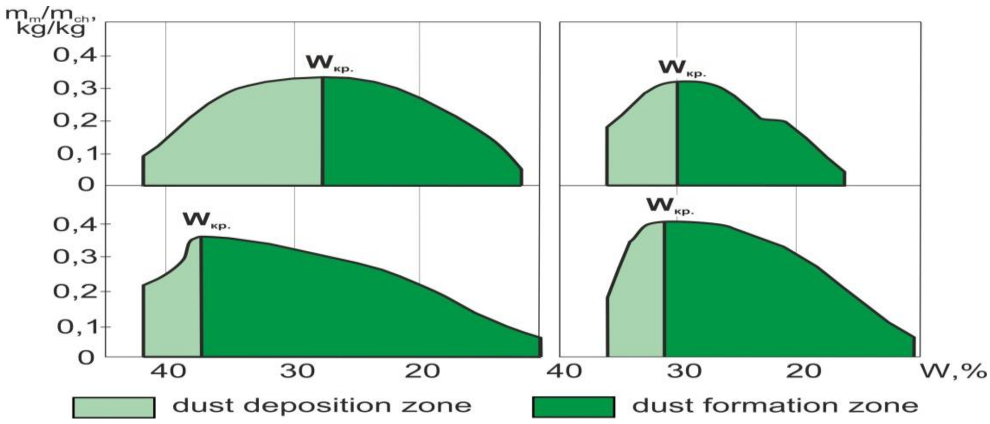

Figure 1. Special features of lignin influence on changing the specific mass of slurry on the chains during drying: 1 - without additive, 2 - with lignin; left - Krichesvsk slurry, right – Novotroitsk slurry

Hence, the introduction of lignin in the slurry leads to change in the nature of the slurry drying curve, namely, a range of the moisture content difference is reduced to the critical one, and such range of the moisture content difference increases after the critical one. In Krichevsk slurry with the introduced lignin, the difference in moisture content amounts to 5 and 27%, while in Novotroitsk slurry - 4% and 22%, respectively.

Regardless of the component composition of raw slurry (chalk or limestone), lignin increases the specific mass of the material on the chains, intensifies the mass exchange, shifts the critical moisture content towards increase in the slurry moisture content, thereby reducing the dust collection zone and increasing the dust formation zone.

Thus, when introducing a combustible additive to the slurry studying its adhesion-cohesion properties is needed to determine the possibility of dust formation in the drying zone. Change in the nature of the slurry behavior on the chains during the drying process is possible thanks to a changed structure of the chain systems.

Another important indicator of the kiln operation is a degree of alkali sulphate circulation therein, which leads to the formation of sulphate rings. In addition, the constantly developing industry requires production of new types of cement with special properties. One of the most promising is shrinkage-compensated cement produced with the addition of sulphoferrite clinker. The sulphoferrite clinker is synthesized from chalk, ferritic and sulphate components, often waste, so that during burning its main phase - calcium sulphoferrit – is formed [7-9].

As is known, the introduction of combustible additives in the feedstock mixture can cause reducing atmosphere in a kiln, which can affect the sulphate sublimation onset temperature. In the case of the production of sulphoferrite clinker, the early sublimation of sulphate phase will lead not only to violation of the kiln operation, but also to faulty production as clinker will not contain calcium sulphoferrit, which is the main phase. It is therefore necessary to study the process of sulphate oxide sublimation from the sulphoferrite clinker in the presence of a combastible additive.

The difference between the temperatures of onset of sulphate decomposition and volatilization of decomposition products in the mixture prepared for producing sulphoferrite clinker was determined using an integrated thermal analysis by creating different gas atmospheres: neutral, oxidizing and reducing.

To determine the onset of SO_3 volatilization in a neutral environment, the thermogram surveying was carried out in argon, to set the temperature corresponding to the onset of sulphate sublimation in an oxidizing atmosphere - in the air. The reducing environment was created artificially by introducing in the feedstock mixture of 2% petroleum coke, which burning resulted in a change of atmosphere from oxidizing to reducing. The survey was carried out in the air in sealed platinum crucibles. So, in the neutral environment the sublimation began at 1050ºC, in the reducing environment - at 1200°C, in the oxidizing environment - at 1300°C.

In the laboratory kiln, where the oxidizing environment was predominant, but there was the local reducing environment through the use of a combustible additive, the sublimation also started at 1300°C, but its rate significantly increased compared to the oxidizing environment (Figure 2).

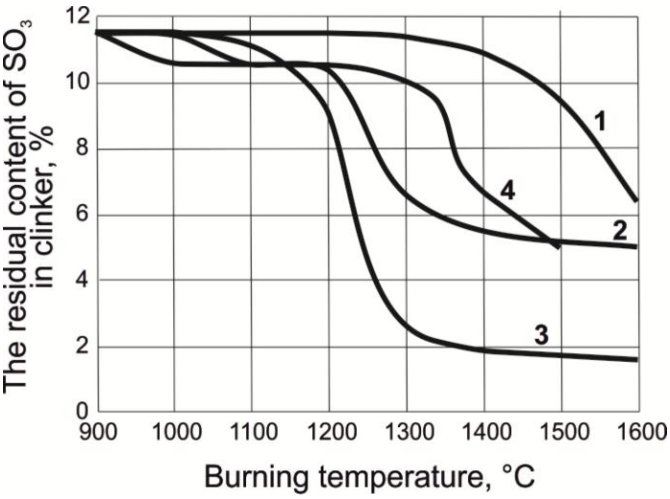

Figure 2. Relationship between SO_3 sublimation onset temperature and gas environment: 1 – oxidizing, 2 – reducing, 3 – neutral, 4 – local reducing

Thus, in the production of sulphoferrite clinker, as well as commercial clinker in the presence of a combustible additive it is necessary to control the kiln atmosphere so that the SO_3 sublimation process, namely, the sublimation onset and rate could be controlled. Using combustible technogenic waste in the cement production has a favorable effect not only on the consumption of primary fuel, but also on the power consumption of a cement mill, since it allows obtaining easier to grind clinkers [5]. The use of petroleum coke in this capacity should also enhance the grindability. In addition, petroleum coke consists of carbon, so it can be used as an intensifier of clinker grinding. The impact of carbonaceous materials on the intensification of clinker grinding is not new, but the impact of the additives' fractional composition on the process has not been studied previously. The impact of petroleum coke on the grinding kinetics of Portland cement clinker was studied on the clinker produced in Belgorod Cement Plant, JSC, which chemical composition is shown in Table 1. Free CaO content amounted to 0.47% in the clinker.

Table 1: Chemical composition of the clinker produced in Belgorod Cement Plant, JSC, %.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2
21.55	5.48	4.33	66.74	0.54	0.24	0.56	0.27	0.52

The clinker grinding kinetics was studied in a 1 liter laboratory mill. The mass of ball load in the mill was 1.2 kg. To study the processes taking place in the mill, the stability of the initial granulometric material is very important. Therefore, to the end that the material loaded to the mill has a uniform particle size distribution, the clinker was ground and classified before obtaining the following fractions: -1.25+0.315 mm – 65% and -0.315+0 mm – 35%. After obtaining the fractional composition required for grinding, 6 test charges were selected by quartering; 5% natural gypsum of fraction -0.63 mm was added to them. During grinding the material was sampled every 10 minutes, necessary measurements were carried out, and then they were returned back to the mill; afterwards grinding continued. The efficiency of petroleum coke as an intensifier of grinding strongly depends on the particle size distribution. Thus, when using a 0.08 mm fraction, grinding of cement slows down in the presence of an additive. To exceed the grinding rate of an additive-free cement, the concentration of small-sized petroleum coke had to be increased from 0.5-1% to 1.5% (Figure 3). Moreover, in the process of cement grinding to obtain the small size, the change (induction period) in the specific surface area of cement stopped in achieving Ssp. ~ 250 m^2/kg. For a relatively large size of -0,2+0,08 mm, such induction period was not observed, the cement grinding rate remained virtually unchanged and was the same for the additive's concentration of 0.5-1.5%.

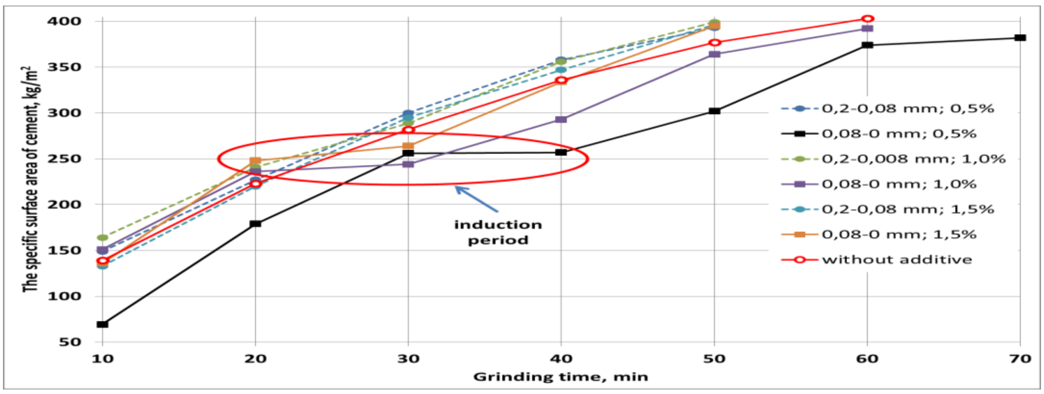

Figure 3. Impact of particle size distribution of petroleum coke and its concentration on the grinding kinetics of clinker produced in Belgorod Cement Plant, JSC.

Such difference in behavior of ground clinker in the presence of petroleum coke can be explained by the fact that under the similar size of a combustible additive and clinker particles the additive is crushed by harder and larger clinker particles during grinding. In this case, the clinker particles are coated with a layer of petroleum coke with the subsequent increase gin the grinding rate.

Therefore, the impact of the petroleum coke's fractional composition on Portland cement clinker grinding efficiency was established. When grinding the clinker particles of fractional composition: -1.25+0.315 mm – 65% and -0.315+0 mm – 35%, an increased grinding rate is observed when introducing an 0.5-1.5% additive of -0.2 + 0.08 mm fraction. Using an additive of -0.08 + 0 mm fraction in an amount of less than 1.0% leads to slower cement grinding rate. When petroleum coke of -0.08+0 mm fraction is used as a grinding intensifier, the increase in the specific surface of cement is stopped at the studied concentrations in achieving 250 m^2/kg.

Apart from impact of combustible waste on the physical and chemical processes in the cement production, the introduction of technogenic materials in the feedstock mixture can also affect the quality of the finished product.

To study the effect of various technogenic waste containing a combustible component on the cement properties, the work examined agricultural, paper waste, waste of oil and wood processing.

All studied waste was introduced in an amount of 5 and 10% to the Belgorod Cement Plant slurry, which chemical composition is presented in Table 2.

Table 2: Chemical composition of the raw slurry of Belgorod Cement Plant, JSC.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	Percentage of other impurities
14.03	3.49	2.84	43.17	0.42	0.09	0.5	0.16	0.25	35.13

The agricultural waste in Russia is an almost unclaimed resource today. Only 10% of the total volume of straw is used. At the same time, the mass of accumulation of cereal and cereal crop straw is 80-100 million tons in Russia for a year. The straw is usually burned or plowed in the ground, but it has a high calorific value of 16 MJ/kg [10, 11].

The introduction of 5 and 10% of straw in the feedstock mixture had no effect on the clinker burning rate, because all clinkers had a close content of free CaO not exceeding 2%.

Determination of strength values of the cement obtained from the clinker burnt in the presence of a combustible additive showed that during the initial period of cement hardening (2 days) the control cement had the highest hydraulic activity. By the 7th day of hardening, the highest strength of the clinker samples with 10% addition was 74 MPa. By the 28th day of hardening, the strength of the additive-free clinker samples reached 90 MPa. The samples with 10% addition revealed the highest strength. Addition of 5% straw has almost no effect on the strength (Table 3).

It is evident from the obtained data that when introducing straw in the slurry in an amount of 10% the cement has the highest strength compared with the cement produced from the additive-free clinker and clinker with 5% additive.

The calculation found that replacement of a part of process fuel with the straw would save from 1.5 to 3.1% of gas fuel.

The waxed paper packaging consists of several alternating layers of polyethylene (about 25%) and cardboard (75%), so it is quite difficult to process, and the consumption of products in this packaging is widespread, so it becomes waste in large quantities. The calorific value of the studied waste is 28 MJ/kg [11].

The completion of reactions of the clinker minerals formation was judged on the content of free calcium oxide in the burnt clinkers during the burning process. In all clinkers the synthesis of clinker minerals can be considered complete, since the content of free CaO does not exceed 2%.

As seen from Table 3, the highest strength is detected in the samples with a 10% addition both in the initial period of hardening and in the age of 28 days. Addition of waste in an amount of 5% has almost no effect on the strength properties.

The calculation found that replacement of a part of process fuel with the paper waste would save from 2 to 6% of gas fuel.

Husks are waste of oil processing; they are formed by separation of sunflower kernels in an amount of about 14% of the total number of seeds at oil pressing plants. The sunflower husk briquettes and pellets can also be a great alternative to such expensive, non-renewable and environmentally harmful types of fuel as coal and gas; moreover, they are cheaper than wood pellets. To produce briquettes the husk is crushed and pressed into pellets. The final moisture content of the finished product amounts to 8-12%, and the raw material is compacted by 5-10 times. This is convenient for storage and transportation. At a partial replacement of the process fuel, the husk can be also used in a non-compacted form. The fuel produced from sunflower husks has undeniable advantages: such fuel is twice cheaper than coal; the fuel is environmentally friendly; husk has a very low ash content - up to 3%; the calorific value of husk amounts to 22 MJ/kg, whereas that of the gas – up to 37 MJ/kg.

During the initial period of hardening, the cement based on the clinker synthesized with the addition of 5% waste oil had the greatest strength. By 28 days of hardening, the cement stone's strength characteristics become equal. The oil waste input in the slurry does not adversely affect the quality of clinker, and the quantity of a combustible additive is limited only by the excess air needed for its combustion. Addition of up to 3% of husk of the feedstock mixture mass to the slurry would save 2.14% of process fuel (Table 3).

The waste of wood processing industry (WPI) has an allowed calorific value of 15-20 MJ/kg or 3500-4500 kcal/kg [12-13].

Introduction of WPI waste in the feedstock mixture as a combustible additive has shown that during the initial period of hardening the highest hydraulic activity has the cement based on the clinker synthesized with adding 10% of WPI waste.

By 28 days of hardening, the strength of the cement stone produced from clinker with the addition of 10% of WPI exceeded the strength of additive-free cement (Table 3).

In terms of fuel saving, the offered process operation of input of up to 10% of WPI waste of the feedstock mixture as a combustible additive can save up to 3.1% of natural gas, which makes a partial replacement of process fuel with an alternative one rather effective.

Table 3: Impact of introduction of combustible waste in the feedstock mixture on cement quality.

Waste containing a combustible component	Amount of additive introduced to the slurry, %	Compressive strength, MPa, number of days		
		2	7	28
Cement produced from additive-free clinker		44	69	89
Straw	5	38	63	88
	10	41	74	90
Waxed paper packaging	5	42	63	81
	10	54	69	108
Husks - waste of oil processing	5	48	63	100
	10	43	63	87
Waste of wood processing	5	40	77	88
	10	45	79	96

Thus, the introduction of all studied combustible waste in the feedstock mixture had a positive impact on the cement stone strength. Furthermore, the cost of waste disposal is much lower than the cost of waste disposal in the special plants that require significant capital and operating costs [14].

Summary. The introduction of combustible additives in the feedstock mixture during burning of clinker in order to increase the energy efficiency of production leads to changes in the physical and chemical processes during the cement production. The combustible additives can affect the adhesion-cohesion properties of the slurry during its drying, sulphate sublimation as a result of changed gas environment in a kiln and clinker grinding process. Therefore, when using a particular additive an integrated study of all processes is needed in its presence.

In introducing up to 5-10% of combustible additives, the cement stone's strength does not usually yield or even exceed the strength of the cement stone based the commercial clinker.

Conclusions.

1. Introducing a combustible additive in the raw slurry results in changed adhesive-cohesive properties of such slurry and hence changed nature of the slurry drying curve in the chain system zone. Regardless of the raw slurry's component composition, lignin shifts the critical moisture content towards an increase in the moisture content of slurry, thereby reducing the dust collection zone and increasing the dust formation zone.

2. Combustible additives creating a local reducing atmosphere in a kiln lead to lower sulphate sublimation onset temperature and sublimation acceleration, which can cause the formation of sulphate rings in a kiln. Should the sulphoferrite clinker be produced, which is an additive in the preparation of expanding cements, the early sublimation of sulphate entails faulty production.

3. The impact of petroleum coke on intensification of the clinker grinding process depends on the fractional composition of coke. The larger particles of coke in size of -0.2+0.08 mm introduced in the clinker of fractional composition -1.25+0.315 mm - 65% and -0.315+0 mm - 35% result in intensification of grinding, and the particles of coke in size of -0.08+0 mm introduced in the clinker, on the contrary, slow the grinding process down.

4. Using a variety of combustible technogenic waste as combustible additives in an amount of 5-10% allows producing cement that is not inferior to the strength characteristics of the commercial one and saves up to 3% of the primary fuel.

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References

1. Gubareva V.V, Rakitchenko K.S., 2005. Reduction of fuel consumption in the cement production. Bulletin of BSTU named after V.G. Shukhov, Issue 10, pp. 65-67.
2. Tongbo S., 2012. The use of industrial waste in Chinese cement industry. ALITinform, Issue 6, pp. 6-15.
3. Zharko V.I., Guz V.A., Vysotskiy E.V., 2010. Use of waste in the cement industry of Russia. Cement and its Application, Issue 6, pp. 60-62.
4. Klassen V.K., 1994. Burning of cement clinker, 323 p.
5. Klassen V.K., Borisov I.N., Manuilov V.E., 2008. Technogenic materials in the cement industry, 125 p.
6. Timashev V.V., Sulimenko L.M., Albats B.S., 1978. Agglomeration of powdered silicate materials, 136 p.
7. Osokin A.P., Krivoborodov Yu.R. and Dyukova N.F., 1990. Sulphoferrite cements. Proceedings of 9th ICCC, Volume 3, pp. 256-261.
8. Osokin A.P., Krivoborodov Yu.R., Potapova E.N., 1993. The modified Portland cement, Moscow, 328 p.
9. Dr. Roppelt T., Dr. Dienemann W., Prof. Dr. Klaska R., Lethand I., Sievert Th., 2006. Use of alternative raw materials for cement clinker production. Cement International, Issue 1, pp. 54-63.
10. Alternative fuel. Processing of agricultural wastes. http://www.ipa-don.ru/offers/projects/altt.
11. Fuel briquettes. Pellets. Alternative fuel. http://press-briket.blogspot.ru/2008/10/blog-post.html.
12. Golovkov S.I., Koperin I.F., Naidenov V.I., 1987. The use of wood waste for power production, 224 p.
13. Ravich M.B., 1977. Fuel efficiency, 344 p.
14. Bushihin V., 2006. The current state and prospects of development of the cement industry in Russia, report on the III Scientific Conference “Modern Cement Plant”.