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Development of the Composition of Energy-Saving Raw Materials for Sintering Cement Clinker

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Abstract: *This article describes scientific research on the creation of highly efficient mineralizers based on iron dross of a rolling mill during the firing of cement clinker in order to reduce the sintering temperature. So, in modern conditions, there are acute problems of energy saving and the production of high-quality, high-strength cements, the authors propose an innovative method and scientific justification for the solution problems in the workplace. New ideas and results of experimental developments, technological regulations and practical experiments in this direction are proposed. The authors made an attempt to implement the idea by using the local iron dross of the Tashkent Metallurgical Plant as a ferrite additive during clinker firing. The joint venture Tashkent Metallurgical Plant is a super modern enterprise of New Uzbekistan, with an annual capacity of 500 thousand tons of cold-rolled steel with galvanized and polymer coating.*

Keywords: *Portland cement, sintering, cement clinker, structure formation, charge, energy saving, cement clinker minerals, mineralizers, sintering temperature, iron dross, cinders, ferrites.*

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1. Introduction

An analysis of the global construction market, in particular the production of binders and cement, its implementation, shows that the use of resource and energy-saving, innovative technologies is a requirement of today and the future.

“In terms of implementing the decisions of the Development Strategy of Uzbekistan for 2020 ... 2025 [1], a concept has been developed for the development of new capacities through the development and modernization of the cement industry and the construction of new plants in a number of regions. In recent years, the cement industry has become a direct reflection of large-scale plans for urbanization: the implementations of infrastructure projects, as well as industrial and residential construction in the republic, have led to such a tangible increase in the consumption of this material that the industrial sector has only to increase its capacity and production potential. In terms of speed, availability and environmental friendliness, cement remains an alternative material that meets modern construction requirements. The main goal of the cement industry for the real future is to achieve the production of 20.2 million tons of cement by 2026 [2, 7, 8].

The most important direction in the development of the cement industry is the introduction of resource and energy-saving technologies. One of the most common ways to reduce the temperature and intensify the firing processes is the use of mineralizers - various substances that accelerate the formation of clinker minerals. The use of mineralizers during firing makes it possible to increase the reactivity of the cement raw mixture, which improves the conditions for the formation of minerals that make up the clinker, primarily dicalcium and tricalcium silicates [6].

The relevance of the study lies in the fact that this paper proposes the idea of using ferrite-containing compounds in the firing of traditional cement clinker. The proposed scientific and practical idea will help solve economic problems; for this purpose, industrial waste from the Tashkent Metallurgical Plant is proposed. The idea involves the use of a secondary product of steel sheet - mill iron dross [3, 4, 6].

JV "Kyzylkumcement" is the leader of the cement market of Uzbekistan with a share of 36.8%. The second place was taken by Almalyk Mining and Metallurgical Plant JSC and Akhangarantsment JSC with a share of 22.6% and 21.9% respectively.

The following places were occupied by OJSC Kuvasoycement with a share of 6.2% and OJSC Bekabadcement with a share of 4.8%. The share of other cement industry vendors is about 7.6%. The volume of products put up for auction by these enterprises is 92.4% of the total volume sold on the cement exchange [6].

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Today, the country has become a huge construction site that requires a radical improvement in production, including the production of economical, energy-efficient types of cement. Decree No. PQ 4335 of May 25, 2019 “On additional measures for the accelerated development of the building materials industry” provides for a doubling of cement production volumes [2]. In addition, in accordance with the Decree of the President of the Republic of Uzbekistan on measures to implement the investment project "Construction of the Tashkent Metallurgical Plant" dated April 7, 2017 for the Tashkent Metallurgical Plant in 2020.

The production of steel sheets by rolling is carried out in a 4-stage technological process. At the first stage, a sheet is rolled under pressure from a finished steel casting in a molten state, during which a burnt layer (iron dross) is formed on the surface of the molten steel sheet under the action of atmospheric oxygen, which is exposed to steel, and this layer is chemically resistant, but brittle, therefore, it is cleaned from the metal surface by chemical and mechanical treatment [5].

At the next stage of metalworking, metal scale is removed in the cold rolling process. This secondary product accumulates during the production process and 48...50% of ferrite compounds were found in its composition, Table. 1. This led us to the idea of using iron storm (dross) as a ferrite additive in the firing of cement clinker.

It is known that limestone and aluminosilicate clay are used as raw materials for cement clinker. Iron oxide III (Fe_2O_3), silicon oxide II (SiO_2) and alumina (Al_2O_3), which are important oxides in the formation of clinker minerals, play an important role in the formation of clinker minerals. When firing cement clinker, the composition of the charge is always planned, and corrective additives are actively used to regulate the composition of raw materials [9, 10, 11].

2. Materials and control methods

The investigated iron dross contains iron oxide III (Fe_2O_3) - 48.38% and silicon oxide II (SiO_2) - 6.02%, which are necessary when firing cement clinker. The main clinker minerals in silicon oxide

(SiO_2) in the scale are actively involved in the formation of tricalcium silicate (alit)-3CaO*SiO_2 and bimetallic silicate (belite)-2CaO*SiO_2. Iron III oxide (Fe_2O_3) is an important oxide in the formation of four-calcium aluminoferrite (cellite) - 4CaO*Al_2O_3*Fe_2O_3. In addition, iron oxide (Fe_2O_3) acts as an alloying agent during alit crystallization during clinker firing, which increases the activity of cements. It can be seen that the addition of iron III (Fe_2O_3) to the clinker increases the activity of cement, its resistance to mineralized salts, and reduces the maturation temperature of Portland cement clinker.

The production of Portland cement includes two main technological limits - the production of clinker and the grinding of clinker together with gypsum and other additives. In the cost of Portland cement, up to 70 ... 80% is the cost of clinker. Its production mainly uses fuel, the cost of which is more than 20% of the total cost of cement. At the same time, approximately 40% of the total electricity consumed is spent on cement grinding.

The features of cement production are high capital intensity, due to the saturation of complex equipment, materials and energy intensity, the need for solutions aimed at increasing production efficiency [12].

The disadvantage of cement production is that, along with the useful properties of this material, many negative properties appear, namely the need for a guaranteed temperature in the clinker firing process. To reduce the sintering temperature, a corrective iron component is usually added to the composition of the raw mixture; however, in the conditions of the republic, such a component is scarce.

The objective of the proposed technology is to expand the raw material base, recycling production waste and reducing the temperature of clinker formation reactions and the energy intensity of Portland cement clinker production.

The problem to be solved is achieved by the fact that the raw mixture for clinker roasting contains limestone, aluminosilicate components and, as a ferruginous component, contains the scale of the steel sheet rolling production of the Tashkent Metallurgical Plant (TMZ) or the cinder of the Almalyk Mining and Metallurgical Plant (AMMP) in the following ratio of components, table. 1.

According to the grain composition, TMZ iron scale is a finely dispersed substance (more than 92% passes through a sieve with an opening of 0.08 mm) and does not require additional grinding before use. Table 1 shows the chemical composition of the constituent components of the raw mixture and the iron scale of the rolling production of steel sheet, fig.1.

Table 1. Chemical composition of raw materials

Components	SiO_2	Al_2O_3	*FeO*	Fe_2O_3	*CaO*	*MgO*	SO_3	*RFP*	*Other*	*Sum*
Carbonate raw material - limestone of the Navoi (Kermena II) deposit	8,73	1,04	0.00	1,01	48,76	1,23	0	35,51	3,72	100
Aluminous raw materials-clay shale of the Navoi deposit	45,52	13,53	0.00	5,6	14,37	3,69	0,00	15,56	1,64	100
Iron dross of Tashkent Metallurgical Plant	6,02	0	42.09	48,38	0.4	2,36	0,12	0,92	0.63	100
Cinder (slag) of the Almalyk Mining and Metallurgical Plant	35,11	5,23	2.73	49,76	4,10	2,40	0,49	0,18	000	100

The studies were carried out within the framework of the analytical control of the "Testing Laboratory and Technical Supervision Department" of JV "KIZILKUMCEMENT". Based on the results of the analysis in table 1, the following results were obtained.

The new property is that the scale is removed from the surface of the sheet steel by forced cleaning and is a waste product. However, iron scale contains a large amount of ferrites oxides (Table 1), which is a high quality corrective component for cement clinker sintering. **The cause-and-effect relationship** between the set of essential features and the technical result obtained is that components and technical means imported from other countries are not required to obtain a raw mixture. Ferrous scale in the form of a finely ground free-flowing fraction allows it to be used as part of the raw mix for cement clinker sintering. The proposed ferruginous scale has a sufficiently high carbonizing effect, as a catalyst reduces the sintering temperature by 150-170 ° C, therefore, it is an effective national and environmentally friendly remedy.

The limits of input into the composition of the raw mixture of ferruginous scale are due to the content of iron oxides in it, which is characterized by a high carbonizing ability. With the usual heat consumption for burning Portland cement clinker in the range of 3000 kcal/kg, the maximum allowable level of iron dross input into the raw mixture, taking into account losses during ignition, is 4.5%. The lower limit of scale input is determined based on the effect of increasing the reactivity of the raw mixture (see table 2). The limits of fluctuations of the remaining ingredients of the raw mixture are determined by calculation based on the given values of the modular characteristics of the raw mixture - the silicate module (1.7-3.5) and the saturation coefficient (0.88-0.92). As can be seen, the addition of iron scale as a corrective component to the composition of the raw mix significantly intensifies the firing process of Portland cement clinker. The completion of the firing process, characterized by the value of CaO free 2%, occurs at a temperature of 1450 ^{o}C, which corresponds to the firing temperature of conventional Portland cement clinker and confirms the achievement of the task of reducing the energy intensity of Portland cement clinker production. The increased reactivity of the raw mixture and the decrease in the clinker firing temperature due to this provide an effect in reducing heat consumption, estimated according to the data of the carried out heat engineering calculations by the value of 800-1200 kcal/kg of clinker.

According to Table 2, briquettes were prepared from the obtained raw meal in the form of cylinders with a height of 2.0 and a diameter of 4 cm. The briquettes were fired in a cryptal furnace (to create a reducing firing medium) to a temperature of 1250 ^{o}C and an isothermal holding time of 20 minutes. The obtained clinker samples were cooled with a temperature gradient of 500 deg/min. The control of the completeness of the clinker formation processes was carried out by the analytical method by the amount of free calcium oxide CaO in the samples fired at different temperatures. The results of calculating the chemical composition of the raw mixture and clinker, tables 2 and 3. The results of determining free CaO and cement activity during natural hardening are shown in table 3. The charge is made up of pre-dried and ground components to the same fineness. From the obtained raw meal, similarly to the first example, briquettes were made and a comparative analysis was made. The results of the determination of free CaO and the activity of the clinker are shown in table.3.

Table 2. The results of calculating the chemical composition of the raw mix for clinker burning

Components	SiO_2	Al_2O_3	*FeO*	Fe_2O_3	*CaO*	*MgO*	SO_3	*RFP*	*Other*	*Sum*
Carbonate raw material - limestone 83.03 wt.%	7,25	0,86	0.00	0,84	40,49	1,02	0	29,48	3,09	83,03
Aluminous raw materials-shale 18.83	7,21	2,14	0.00	0,89	2,27	0,58	0,00	2,48	0,26	15,83

wt.%										
Iron dross of the Tashkent Metallurgical Plant	0,07	0,00	0,45	0,55	0,00	0,03	0,02	0,01	0,01	1,14
Composition of raw meal, wt.%	14,53	3,00	0,45	2,28	42,76	1,63	0,02	31,97	3,36	100
Clinker composition, wt.%	21,34	4,41	2,44	3,35	62,86	2,40	0,00	-	3,20	100

As can be seen from the table, the proposed technology is simple, cheap, reliable, and iron scale or cinders are very effective corrective components that reduce material costs through waste disposal.

The firing of clinker according to this method is technically and economically most feasible in cases where the raw materials are characterized by low moisture content, as well as relative uniformity in chemical composition and physical structure, which makes it possible to save a significant amount of energy.

Figure 1. External view of the iron dross of the Tashkent Metallurgical Plant and the copper-smelting cinder of the Almalyk Mining and Metallurgical Plant

Table 3. Comparative analysis of finished clinker

Compo-nents	Charge composition					Free lime content CaO	Compressive strength, MPa, after	
	Waste of neutralization of rolling production	Iron dross of the Tashkent Metallurgical Plant	Iron dross of the Tashkent Metallurgical Plant	Alum-nous raw materials - shale	Carbonate raw material - limestone		3 days	28 days
analogue	1	-	-	20	rest	2,8	23	40
analogue	7	-	-	18		1,65	24	39
1	-	1,1	-	15		0,76	28	46
2	-	1,65	-	15,5		0,66	32	50
3	-	2,2	-	16,0		0,32	36	52
4	-	-	1,3	15		0,80	28	45
5	-	-	1,95	15,5		0,70	30	47
6	-	-	2,6	16		0,45	33	44

Grinding of raw materials and finished clinker in mills can be carried out at a raw material moisture content of not more than 1%. In nature, there are practically no raw materials with such humidity, therefore, at all stages of the technological chain, the drying process precedes, while the drying of the components is carried out by hot gases exhausted from the main kiln. It is desirable to combine the drying process with the grinding of raw materials. Grinding is carried out to a residue on the sieve of 6-10% on a sieve № 008.

With an increase in the number of glandular components, it is overused;

With a decrease in the amount of ferruginous components, the quality decreases, more temperature is required for the clinker formation process;

Iron scale and cinders are local secondary waste, the disposal of which provides a significant economic benefit;

Due to high-quality roasting, the grinding capacity of clinker improves, which increases its strength characteristics at 28 days of age by 44-52 MPa.

4. Results and Discussion

The proposed compositions of raw mixes relate to compositions for the production of Portland cement clinker. Effect reduced temperature of clinker formation reactions, power consumption of Portland cement clinker production and disposal of industrial waste. The raw mix for clinker roasting contains limestone, aluminosilicate components and, as a corrective and activating component, contains TMZ ferruginous scale or AMMP cinders in the following ratio of components, wt. %:

1. Aluminosilicate component 15-16; iron scale TMZ 1.1-2.2; limestone component - the rest, 3 tabs.
2. Aluminosilicate component 15-16; cinder AMMP 1.3-2.6; limestone component - the rest, 3 tabs.

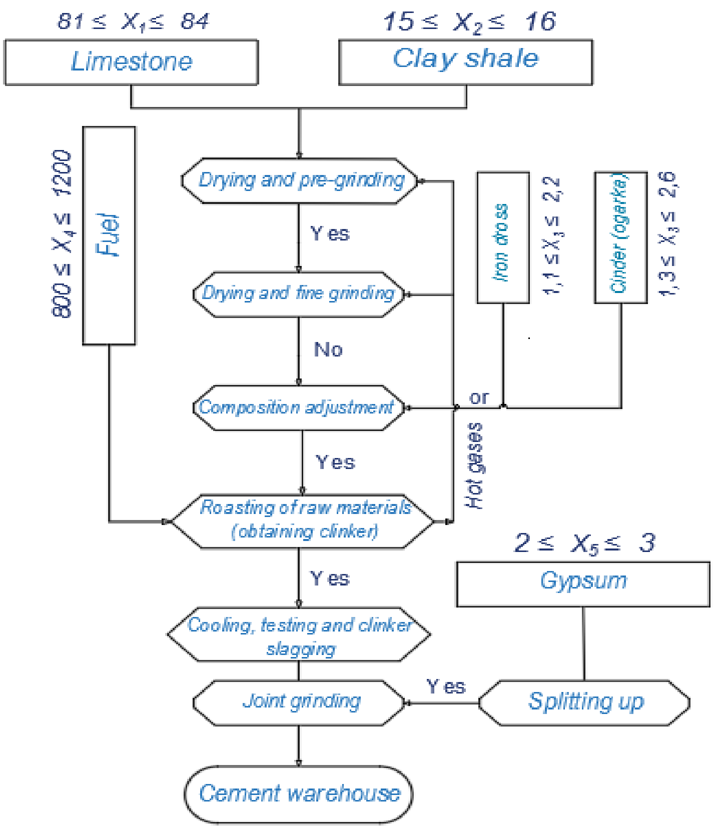

Figure 2. Technological scheme for the production of energy-efficient cement

The efficiency of the utility model was 100%, compared with the deficient waste of neutralization of rolling production, while the firing temperature is reduced by 150-170 ° C, therefore, it is an effective national and environmentally friendly remedy and the clinker activity increases after 28 days of hardening to 44-52 MPa .

5. Conclusion

The most important direction in the development of the cement industry is the introduction of resource- and energy-saving technologies. One of the most common ways to reduce the firing temperature of cement clinker and intensify the firing process is to activate the formation of clinker minerals in exchange for mineralizers. Many people suggest using ferrite and emir oxides as such mineralizers. The use of mineralizers in the clinker firing process makes it possible to increase the reactivity of the cement-raw mixture, which improves the ability to form minerals that make up the clinker, primarily dicalcium and tricalcium silicates.

Mineralizers are substances added to the raw material of Portland cement clinker in an amount of 1-3% by weight of the charge, regardless of the phase state, not included in the final composition of the synthesized substance, but only with the presence in the composition, physically or chemically affect and activate the clinker sintering process. The reasons for the activation of the clinker burning process by mineralizers are: the formation of a solution at a level below the temperature of traditional clinker burning; promoting the formation of intermediates; deformation of the crystal lattices of the constituent components. Reducing the energy intensity of cement production is one of the issues that attract the constant attention of researchers and practitioners. The most energy-intensive process in the production of Portland cement is the firing of clinker. The improvement of this process and the optimization of energy consumption will form the basis for various studies exploring the possibilities of firing clinker at temperatures well below 1400°C.

Based on our research, the idea was proposed to reduce the sintering temperature of cement clinker by using iron dross of the Tashkent Metallurgical Plant as mineralizers. To this end, the use of iron storm (dross) as common mineralizers in our country changes the mineralogical composition of the clinker, which leads to an increase in the content of tricalcium silicate. Such additives increase the activity of Portland cement clinker and reduce the temperature of clinker formation by 100-150°C. At present, research has important scientific and practical implications for a significant reduction in the clinker firing temperature.

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