Influence of silica-containing additives on physical and mechanical properties of Portland Cement Co Ltd "Karakalpaksement"

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Abstract. The article is devoted to the study of the effect of the Khojakulsandstone deposit of Karakalpakstan on the physical and mechanical properties of Portland cement based on clinker containing unbound calcium sulfate.

1 Introduction

According to scientists [1], when the Earth emerged from the last ice age, the amount of carbon dioxide increased by about 80 parts per million over six thousand years, and from 1979 to 2021, it took only 42 years to increase carbon dioxide emissions by the same amount. In 2019, total greenhouse gas emissions, including changes in land use, reached a new high of 59.1 gigatons of CO_2 equivalent ($GtCO_2e$).

The main reason for the growth of greenhouse gas emissions is that the predominant share in the total volume of emissions, taking into account changes in land use (65%), accounts for carbon dioxide (CO_2) emissions from the use of fossil fuels (from fossil fuel combustion and carbonate processing). In 2019, CO_2 emissions from using fossil fuels reached a record high of 38.0 $GtCO_2$.

As a result of the World Bank analysis [2], the average carbon dioxide emissions per capita for 2018 was 4.24 metric tons. The highest value was 32.42 metric tons (Qatar), and the lowest was 0.03 metric tons (Democratic Republic of Congo). The largest CO_2issuers are China and the United States. These two countries account for over 40% of the world's CO_2 emissions. In the list of 186 countries on the emission of CO, Uzbekistan occupies 83rd place. Among 90 countries on the emission of CO2 in megatons for a year and in % of a share of total emission, our republic is in 37th place, emitting in 2018 108.2 million tons of CO2. In 2020 - 112.1 million tons, that makes 0.3% of the world's emissions [3]. The deteriorating environmental situation around the world, particularly in Uzbekistan, dictates the need to take urgent measures to reduce emissions to ensure a "clean" climate. Within the framework of participation in the 26th session of the Conference of the Parties to the UN Framework Convention on Climate Change in Glasgow, the representative of Uzbekistan A.Abdukhakimov announced the national statement that in the framework of

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the Paris Agreement, Uzbekistan takes an additional commitment to reduce greenhouse gas emissions per unit of GDP by 35% by 2030 to 2010 levels [4]. To achieve this goal, it is planned to develop a National Low-Carbon Development Strategy.

Among the industrial production industries, the leaders in carbon dioxide emissions are known to be the oil and gas and cement industries, as well as thermal power plants that burn solid fuel, which dictates the need to switch to low-carbon "green" technologies. In the production of Portland cement, CO_2 is emitted, resulting in about 5% of the current global, man-made gas emissions. In the cement industry, CO_2 is emitted from the combustion of fuel, as well as from the calcination of limestone in the kiln. Reduction of CO_2 emissions in the industry is possible by improving the kiln's thermal and electrical efficiency, using alternative fuel sources, reducing the proportion of clinker in the composition of cements, and capturing and storing CO_2 in the production of Portland cement [5].In recent years, Uzbekistan has implemented effective, comprehensive measures for developing regions and organizing new industries, including expanding volumes and types of domestic products by stimulating the production of building materials. As a result, over the last four years, there has been a 1.3-fold growth in the production of building materials as one of the rapidly developing industries [6]. Cement production is developing at a new stage in the republic. In 2020, its output was 12.54 million tons; in 2021, Ms 16,4 million tons, which is 31.2% or 3.9 million tons more than in 2020, facilitated by constructing new cement plants [6]. However, the increase in the number of which contributes to an increase in air pollution by carbon dioxide emissions. Hence, a more rational option to increase cement production is its modification by various mineral additives at the clinker grinding stage, providing high profitability of cement production [7-13].

Karakalpaksement" Ltd. has introduced some changes to the traditional technological scheme of Portland cement clinker production consisting of introducing a certain amount of gypsum stone into the raw mix for clinker burning with the following clinker grinding without adding it. The raw mix of such a composition is fired at a relatively lower temperature than a traditional raw mix, as in the clinker composition based on sulfate-containing raw charge during the firing, some amount of calcium$_4$sulfoaluminate $C_4A_3\acute{S}$ can be formed. The products of its hydration are known to ensure the rapid increase of cement strength in the initial periods of hardening which gradually increases, by 28 days ensures its hydraulic activity corresponding to 500 grade and more.

The purpose of research is to save the clinker component of cement, increase the volume of production and reduce the cost of cement, to study the effect of sandstone Karakalpakstan on the physical and mechanical properties of Portland cement, not traditional chemical and mineralogical composition, produced by "Karakalpaksement" Co Ltd.

2 Methods

Chemical compositions of clinker and additives were determined by standard methods of chemical analysis. The phase composition of the components under study was determined using an XRO-6199 diffractometer (Shimadzu, Japan), the hydraulic activity of sandstone was established by the Student's test (t-criterion), and their pozzolanic activity by lime absorption - express method of Chapel. Evaluation of physical and mechanical properties of cements with sandstone was conducted following Russian State Standard GOST 101.78

3 Results and discussion

Clinker of "Karakalpaksement" Co Ltd served as a matrix for obtaining additional cements; the active mineral additives were porphyrite of the Karatau-1 site of the Kekliktau deposit and sandstone of the Khojakul deposit, the chemical compositions of which are shown in Table 1.

According to the data in Table 1, SO_3 content in clinker is quite high, so we determined its mineralogical composition by X-ray diffraction analysis. According to Figure 1, apart from the main minerals$_3$ CS with d/n = (0.302; 0.295; 0.276; 0.274; 0.260; 0.218; 0.175...) nm; $_2$CS with d/n = (0.276; 0.274; 0.260; 0.218; 0.198...) nm; $_3$CA with d/n = (0.270; 0.218; 0.157; 0.138...) nm; $_4$CAF with d/n = (0.716; 0.276; 0.263; 0.204; 0.192...) nm. The clinker of KarakalpaksementLtd. also contains a small amount of $C_4A_3\acute{S}$, the diffraction reflections of which are identified at d/n = (0.376; 0.263 and 0.243) nm. An Anhydrite line of considerable intensity was also detected at d/n= (0.348; 0.295; 0.204; 0.162....) nm.

Table 1. Chemical compositions of source materials of Karakalpakstan

Material name	Oxide content, mass %								
	P.p.p.	SiO_2	$A1_2O_3$	Fe_2O_3	CaO	MgO	SO_3	Pr.	∑
PC clinker	0.31	18.03	6.22	3.94	58.93	1.98	5.55	5.04	100
Sandstone	2.54	76.72	8.20	4.78	0.83	1.40	0.24	5.30	100
Gypsum Stone	At 400°C 19.10	1.52	0.13	0.14	33.04	0.20	43.46	2.41	100

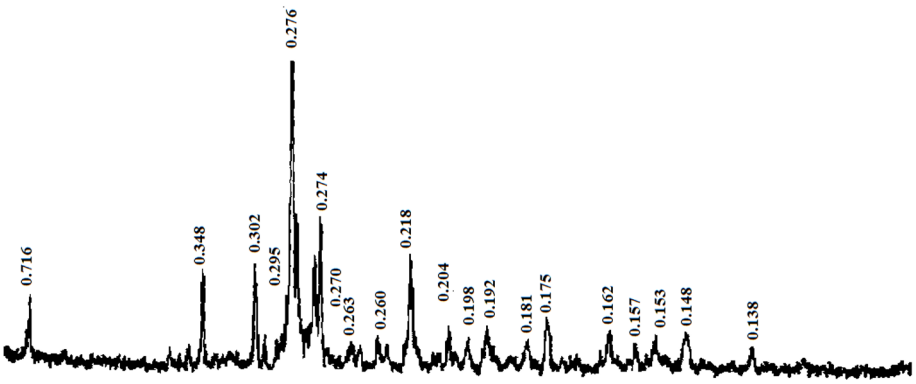


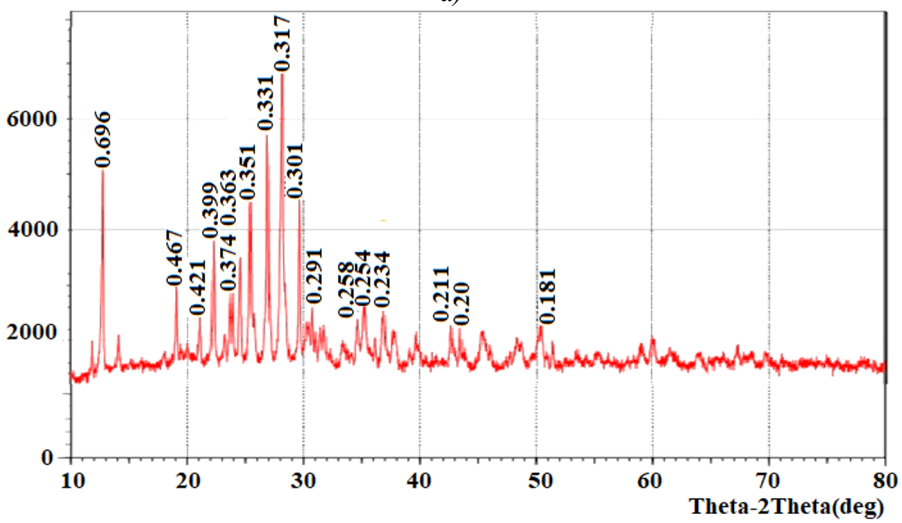
Fig. 1. Diffractogram of clinker of IP LLC "Karakalpaksement"

The sandstone of the Khojakul deposit belongs to the polymictic varieties of sandstones, and it is a sedimentary rock consisting mainly of quartz grains (d/n = 0.421; 0.331; 0.211; 0.200; 0.181) nm, which content is 76.72% (Table 1), cemented by plagioclases in the form of various feldspar forms, including albitas (d/n=0.399; 0.363; 0.351; 0.317; 0.291; 0.258; 0.254) nm (Figure 3). The hydraulic activity of sandstone by the Student's criterion was ≥29,15.07, allowing us to refer to the group of mineral additives of average activity and use it to produce additive cements. The CaO uptake activity of the sandstone for 30 days was 24.78 mg/l. Its hydraulic activity, also determined by the method of the degree of saturation of the liquid phase with lime, showed that the content of CaO in the liquid in which the samples were with sandstone was 6.84%, and the total alkalinity of the solution -53.6 mekv/l [14].

When preparing charges for the preparation of Portland cement with sandstone additive, due to the presence of the clinker, gypsum stone was not introduced. The substantial

composition of a batch containing Karakalpakstan sandstone as an additive and the physical and mechanical properties of Portland cement containing 10-25% sandstone are shown in Table 2. It was found that sandstone shortens the setting time of Portland cement, with both the beginning and the end of the setting being accelerated compared with the matrix Portland cement indicators. However, these results are within the requirements of GOST 10178 for the setting times of Portland cement (Table 2).

a)



b)

Fig. 2. Sandstone (a) and its radiograph (b)

It was noted that with an increasing amount of additives, the strength values of additive cements decrease smoothly: their decrease at additive content of 10-20% by 28 days of hardening is from 11.5-51.0 MPa (figure 3). However, taking into account the high strength of additive-free cement IE LLC "Karakalpaksement", which is fast hardening and high

strength (grade 500), its "dilution" to increase the output and reduce the cost of production, replacing up to 20; clinker component with obtaining cement grade 400, is a profitable way of providing the developing construction industry of the Republic of Karakalpakstan with sufficient amount of cheap cement.

Table 2. Physical and mechanical properties of cement based on clinker of "Karakalpakcement" Co Ltd with sandstone additive (samples-cubes 2x2 cm composition 1:0)

№	Component ratio, mass %		V/C	Setting time, h-min.	
	Clinker	Addendum		Beginning	End
1	100	-	2.40	4:00	5:35
6	90	10		3:10	4:15
7	85	15		4:15	5:30
8	80	20		3:50	5:30
9	75	25		4:25	6:00

Cotinuation table № 2.

№	Strength at compression, MPa, in (day):			
	1	3	7	28
1	39.5	44.1	45.0	55.0
6	26.2	37.0	39.0	41.0
7	29.1	34.1	36.0	40.0
8	26.2	28.5	35.8	42.5
9	25.4	28.0	36.0	38.0

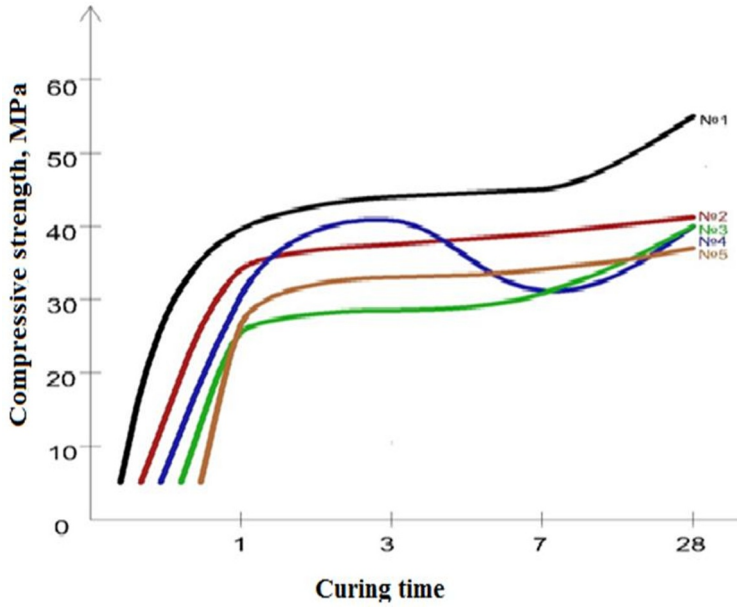


Fig. 3. Kinetics of Portland cement strength gain depending on the content of sandstone additive: 1-PC-D0; 2-PC-D10; 3-PC-D15; 4-PC-D20; 5-PC-D25.

It should be noted that the results of determining the strength values of augmented cements with sandstone on small samples-cubes, 1:0 composition, do not evaluate the true hydraulic activity of cements, so we determined their strength on standard prisms 4x4h16 cm size

composition 1:3, made following Russian State Standard GOST 310.4-81. It is established that 28-days term hardening strength of samples in bending was 5,8 MPa, and in compression was 40,5 MPa, which corresponds to the brand of cement PC400-D20 GOST 10178 [16].

4 Conclusions

According to the value of the Student's criterion and the absorption capacity of lime, the conclusion about the suitability of the sandstone of the Khojakul deposit of Karakalpakstan for use as an active mineral additive in cement was made. By replacing 20% of clinker "Karakalpaksement" Co Ltd local sandstone, it is possible to obtain general building cements grade PC400-D20, and at the expense of saving 20% of clinker to produce additional products, to increase the output of Portland cement additive by 24% and reduce its cost. At the same time, by reducing the content of alite in cement and increasing the content of aluminosilicate components with sufficiently high absorption capacity, the resistance of cement stone against mineral-aggressive environments increases, which is important for the construction of buildings and structures in the Republic of Karakalpakstan, where soil and subsurface waters are characterized by a high level of their mineralization.

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