ELABORATION OF OPTIMAL MODE FOR HEAT TREATMENT OF SHALES FOR OBTAINING METAKAOLIN

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Production of metakaolin to increase the properties of cement and mortar has been studied from ordinary multicomponent mineral clays and shales as cheap raw materials. Alluvium clay shales formed as a result of mudflows were used as starting material and the optimal mode of its heat treatment has been elaborated to obtain the maximal amount of metakaolin. The pozzolanic properties of the heat-treated clay shales were monitored with making and testing various types of cement.

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INTRODUCTION

Portland cement concrete products and reinforced concrete structures are considered as the most widely used building materials of the modern construction industry. The main advantages of Portland cement based concrete the reliability and durability, the resistance towards aggressive environments, the high physical and mechanical properties and the possibility of regulating key characteristics. Despite many remarkable features and accessibility of raw material components, the global problem is that concrete belongs to energy- and material-consuming construction materials. Herewith, the most expensive and energy intensive component of the concrete is cement, more precisely, its basis - clinker. In order to improve the construction and technical characteristics of types of cement and give them specific properties such as sulfate resistance, water resistance, durability, etc., a variety of pozzolan admixtures have been added, which additives effectively reduce the consumption of the clinker part of the cement, reduce fuel consumption.[1,2]

A variety of materials containing silicon dioxide like geopolymers can be used as pozzolanic admixtures in cement production[3–6] and other processes in the production of fertilizers, detergents, special glasses, ion exchangers and catalysts.[7–10] In recent years, metakaolin as an active pozzolanic admixture to Portland cement has become very popular worldwide.[11,12] Metakaolin creates an opportunity to increase the density, water resistance and strength of cement (due to its high specific surface area – up to 13000 cm^2/g), and using it decreases the consumption of clinker. Metakaolin is obtained by heat treatment of kaolin clays, but the kaolin clay deposits availability is highly limited.

Therefore, studies have been carried out to obtain metakaolin from ordinary multicomponent mineral clays and shales.[13,14]

EXPERIMENTAL PART

The thermal studies have been performed on a MOM Q-1500D derivatograph (Hungary), with 10 ^{0}C min heating rate, in the air atmosphere, and with alumina standard.

The X-ray phase analyzes were carried out using a Dron 1.5 diffractometer ("Burevestnik", St. Petersburg, Russia), with a Cu-anode and a graphite monochromator, intensity - 500 imp/sec, time constant - 5 s, U = 35 kV, I = 20 mA. λ = 1,54778 Å.

RESULTS AND DISCUSSIONS

Clay shales formed as a result of the accumulation of rocks collapsed due to mudflow stream to obtain metakaolin were removed from the bed and banks of the river Duruji. The phase analysis (XRD showed that the shales were the mixtures of hydromica, muscovite, biotite, pyrite, limonite, quartz, augite, sericite, calcite, plagioclase, orthoclase, chlorite. The chemical composition of shales is presented in Table 1.

The differential thermal analysis shows an endothermic effect between 100 and 150 °C corresponds to the removal of the physically or crystallization water. It is 4 % weight loss in the temperature range of 440–680 °C due to loss of constitutional water, while at 560–650 °C temperature an exothermic effect shows the burning out of organic inclusions and oxidizing of iron(II) content. In the temperature range of 680–730°C there is noted an endothermic effect, which is the result of the destruction of the crystalline lattice and proceeding of active amorphization.

Table 1. Chemical composition of shales, wt.%.

L.O.I.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	P_2O_5	MnO	CaO	MgO	SO_3	Na_2O	K_2O
0.40	59.95	1.02	17.30	5.80	1.30	0.26	0.21	1.53	2.43	0.30	2.20	2.20

Based on the abovementioned results, the temperature range for the treatment of raw materials was selected to be between 600 and 800 °C. According to this, the temperature treatment of shales was performed at 600, 700 and 800 °C for 2 and 3 h.

X-ray phase analysis showed phase transformations of clay shales due to decomposition of components during the heat treatment (Figure 1). The diffractogram of natural shale (No.1) shows the presence of quartz (d=4.250, 3.340, 2.454, 2.285, 2.238, 2.128, 2.000, 1.985, and 1.817 Å), clay mineral chlorite (d=14.14, 7.08, 4.73, 3.54, 2.88, and 2.383 Å), mica (d=9.96, 4.96, 2.564, and 2.000 Å), and Ca–Na feldspar (d=4.03, 3.78, 3.67, 3.20, 2.954, 3.000, 2.930, and 2.395 Å). On diffractograms of samples heat-treated at 600 °C for 2 and 3 h (No.2 and 3, respectively), the amount of chlorite and mica decreases and an amorphous X-ray phase appears – the X-ray curve acquires a convex shape. On the diffractograms of samples heat-treated at 700 °C (2 and 3 h, No.4 and 5, respectively) the clay minerals completely disappear, the amount of mica is further reduced, and the amount of the amorphous phase is growing. The diffractograms of products formed at 800 °in 2 or 3 h (No. 6. and 7, respectively) are identical to diffractograms No.4 and 5, respectively. The decomposition of clay into amorphous pozzolanic oxides contain SiO_2, Al_2O_3, and Fe_2O_3, which are able to bind calcium hydroxide to form insoluble calcium hydrosilicates, starts at 600 °C and this process is completed by raising the temperature to 800 °C.

The reactivity of heat-treated clay shales towards lime is primarily due to the fact that at 600–800°C the main component of clay – inert kaolinite $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ – is dehydrated and turns into the active kaolinite anhydride – metakaolin ($Al_2O_3{\cdot}2SiO_2$), in its amorphized form as a result of the removal of water. Addition of metakaolin into cement compositions promotes the formation of new hydrated phases. The active silica reacts with lime to form calcium hydrosilicates, the active alumina forms a stable hydroaluminates and hydrogarnets. As a result of the reaction of Ca^{2+} and Al^{3+} ions with an amorphous silica content of metakaolin, new compounds are created, including the strong mineral stratlingite C_2ASH_8.[15,16]

X-ray phase analysis cannot be used to determine the amount of metakaolin due to its amorphous nature, but it is possible to determine the amount of active SiO_2 (Table 2) and the kinetics of its growth by the method of chemical analysis.[17]

According to Table 2, the maximum amount of active SiO_2 is formed in the temperature range of 700–800 °C. In this case, the exposure time is also essential; 2 h can be considered as optimal because with 3 h exposure, the sintering of the formed metakaolin occurs and it becomes less reactive. Thus, the optimal temperature treatment of clay shales was found to be 700-800°C with an exposure time of 2 h.

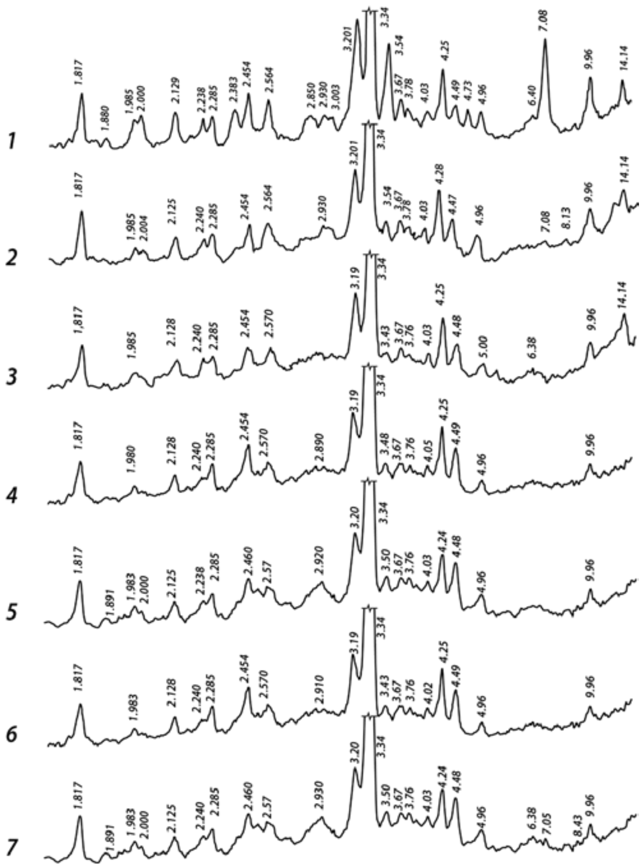

Figure 1. Diffraction patterns of shales: No.1 – natural (untreated shale), No.2 – heat-treated at 600 °C, 2 h exposure, No.3 – heat-treated at 600 °C, 3 h exposure, No.4 – heat-treated at 700 °C, 2 h exposure, No.5 – heat-treated at 700 °C, 3 h exposure, No.6 – heat-treated at 800 °C, 2 h exposure, and No.7 – heat-treated at 800 °C, 3 h exposure.

Table 2. Kinetics of growth of active SiO_2 with increasing temperature and exposure time.

No.	Treatment temperature, °C	Exposure, h	Amount of active SiO_2, wt.%
1	Untreated	–	10.21
2	600	2	16.88
3	600	3	20.64
4	700	2	26.77
5	700	3	21.00
6	800	2	26.93
7	800	3	19.56

To determine the pozzolanic properties of heat-treated clay shales, cement samples were made according to the ASTM C 311–05 standard. The test results are shown in Table 3.

Table 3. Physical-mechanical properties of cement samples.

Cement composition, wt. %	Compression strength, MPa		Strength activity index, %	
	7th day	28th day	7th day	28th day
Clinker – 95 Gypsum – 5	28.5	35.6	–	–
Clinker – 85 Shale* – 10 Gypsum –5	31.2	37.9	109.5	106.5
Clinker – 75 Shale* – 20 Gypsum-–5	24.1	31.5	84.6	88.5

* Shale was processed at 800 °C with an exposure time of 2 h.

According to ASTM C 618–05 the value of the “strength activity index” must obtain at least 75 % of the control mixture after 7 or 28 days.

CONCLUSION

The optimal mode of heat treatment of clay shales is heating at 800°C with an exposure time of 2 h. Shales processed in this way contain a certain amount of metakaolin and can be used as an active pozzolanic admixture to Portland cement.

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