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Materials Science

Technological Basis of Modification of Clay Shale of the River Duruji into the Energy Efficient Porous Aggregate Claydite for Cementconcrete

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(Presented by Academy Member Tamaz Shilakadze)

The mudflows periodically developed in Duruji gorge-bed accumulate clay shale sediments near the city of Kvareli, which create the risk of ecological catastrophes. To prevent this, it is necessary to remove the accumulated clay shale from the Duruji riverbed and process it into a useful product claydite, lightweight and porous low heat conducting aggregate for cementconcrete, which will also contribute to the development of energy efficient construction in Georgia. In order to process the sedimentary clay shale into claydite, the technological basis of its modification into a porous material was studied and a relevant knowledge base has been created. *© 2021 Bull. Georg. Natl. Acad. Sci.*

Dehydration, swelling, grain size analysis, strength, heat conduction, environmental conditions, prevention

Among the challenges of the 21th century the ecology of environment and the energy efficiency of buildings are of great importance. In developed countries, the increase of energy efficiency in the construction sector is ensured by the widespread use of inorganic natural and artificial porous materials for aggregates in cement concrete and wares. From these materials, artificial porous materials are preferred, because on their basis it is possible to obtain the cement concrete and ware of desired performance properties (thermal conductivity, mechanical strength, etc.) for example, claydite cementconcrete, where the aggregate claydite is porous material distinguished by its properties, obtained by thermal modification of various natural raw materials [1-3].

The aim of the research is elaboration of technology of the clay shale modification to claydite to prevent the ecological risk of city Kvareli to be covered by clay shale sediments accumulated in valley-bed of river Duruji and problems of low energy efficiency of buildings and structures in Georgia.

The objectives of the research are: modification of the sedimentary clay shale into claydite; determination of the optimal conditions for swelling and transition to porous material (temperature interval of swelling, duration, fractionation); investigation of the characteristic properties of the obtained porous material; evaluation of the process of clay shale transforming into porous material; defining the perspective of targeted use of the obtained claydite.

Scientific novelty: Study of sedimentary clay shale and porous material obtained from it by thermal modification – the claydite by thermal, X-ray and petrographic analysis methods;

Determining the impact of grain size on the properties (bulk density, water absorption, compressive strength etc.) of sedimentary clay shale and porous product (claydite) and optimum parameters of the swelling process, evaluation of the structure arrangement of porous material.

Materials and Methods

Sedimentary clay shale is disintegrated rock of sedimentary-metamorphic origin, which accumulates in the Duruji riverbed during the mudflow. Physically, it consists of a gray irregularly shaped flat pieces, up to 50mm in size. Chemical analysis of the mean sample composition of the clay shale under investigation is presented in Table 1.

Table 1. Chemical composition of clay shale. Mass %

LOI	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	Mn_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
4.6	60.6	0.9	17.5	3.5	3.7	0.6	1.5	2.4	0.3	2.2	2.2

The study of sedimentary clay shale and porous material claydite obtained by thermal processing from it was carried out using technical analysis, structural arrangement, recommended to study the characteristic properties of inorganic porous materials, and methods of investigation of material physical-mechanical properties.

The study used mechanical shredding of materials (jaw crushing, metal and porcelain grinder, porcelain mill) and fractionation (0.5 to 20 mm) by sieve analysis; X-ray and thermal (DTA) analysis methods, standard testing of lightweight cement concrete samples obtained by swelling in electric kilns.

Petrographic evaluation of sedimentary clay shale showed that it is a rock of complex mineralogical composition in which coexist: quartz and plagioclase, layered magnesium-iron hydroaluminosilicates (clorites), (Ca-Na), feldspar. The rock contains clay and iron-bearing minerals (hercynite -$FeAl_2O_4$, magnesioferrite – $MgFe_2O_4$ and/or maghemite - γ-Fe_2O_3), individual crystals of orthoclase and constituents of organic nature. The complex phase composition of the sedimentary clay shale and the radical modification of its structure were fully reflected in the studies performed by thermal analysis and X-ray method, the results of which are presented in Fig. 1 and Fig. 2.

Evaluation curves DTA, DTG and TG obtained by thermal analysis revealed one strong (maximum 105°C) and several weak (170-570°C) endo effects caused by hydration water evaporation, which indicates the partial/complete separation of the bound water by the hydroaluminosilicate compounds contained in the rock. Numerous endo effects are accompanied by small weight losses reflected on the TG curve. According to the DTA curve, the study material undergoes a significant transformation in the temperature range of 570-730°C, where the continuous transformation of the exo effect (maximum 660°C) into an endo effect (maximum 670°C) is observed. At the same interval, the maximum weight loss and indistinct reflex on the DGT curve were observed on the TG curve.

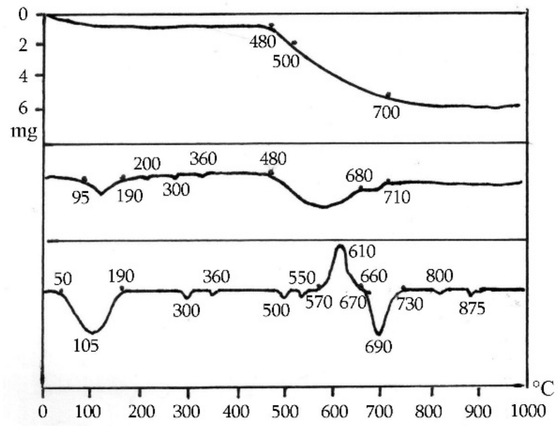

Fig. 1. Thermal analysis of clay shale.

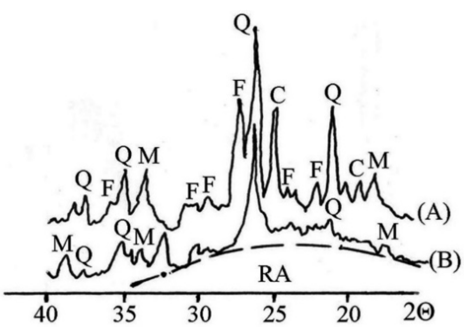

Fig. 2. Fragment of diffractogram of Initial (A) and 1000°C processed clay shale (B).

Thermal analysis data can be explained by the running in parallel processes of different nature in the temperature range 570-730°C, in particular, oxidation-reduction of iron oxide FeO – containing compounds with air oxygen or organic matter in the material is expected, as well as their conversion at the expense of bond water molecules released by hydromica/clayey minerals. The intensity of dehydration is strong, and therefore increasing weight losses are observed on the TG-curve. The possible transformation of iron-containing compounds is indicated by a change in the surface color of the shale grains, starting at 600°C, when by visual assessment the gray color changes to a yellowish-brown color. X-ray analysis showed that high-temperature processing of shale significantly alters the mineralogical and phase composition of the study material. There is a reduction in the number of phases and the formation of a new X-ray amorphous phase, in particular, the decomposition of feldspars (F), chlorites (C), micaceous (M) minerals and transition to the glassy state. The glassy (amorphous) component, in turn, is a necessary condition for converting shale into a pyroplastic state and conducting the swelling process. Additional binocular (computer-assisted) microscopic examination (magnification 30x) confirmed the presence of numerous pores of different sizes in the swelled shale, whose connection partition is the vitreous phase.

Predisposition to the swelling of sedimentary clay shale was determined by studying the swelling coefficient $K\alpha$) for materials of three fractions (δ_1=1-2; δ_2=3-5; δ_3=5-10mm) which was carried out at a temperature interval of 800-1250°C, at a temperature step of 50°C.

It was found that the growth tendency of $K\alpha$ is high for δ_1 fraction material (curve 3), which is almost 2.5 times higher than that of δ_3 fraction material. It should be noted that the maximum intensity of swelling is observed in the temperature range of about 1050-1200°C (Fig.3).

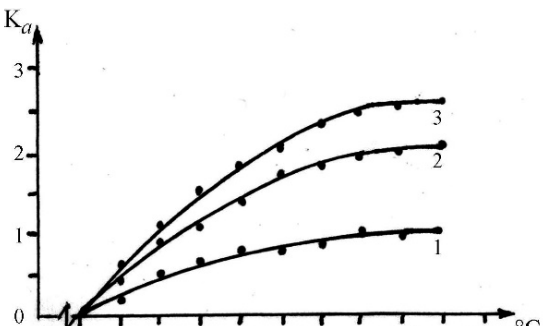

Fig. 3. Influence of heat treatment temperature on the value of swelling coefficient on the value of swelling coefficient.

The effect of heat treatment duration on the swelling coefficient was determined for the fixed temperature of samples (1100°C) for the variable duration (5-30min) delays (Fig.4). According to the results of the experiment, an increase in $K\alpha$ values is particularly effective during thermal processing for 10-15 min, but a further small increase in Kα values is observed with a delay of up to 25 min.

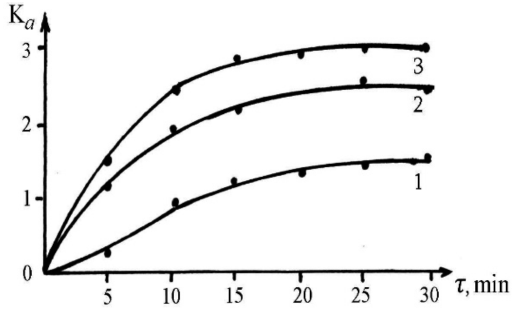

Fig. 4. Influence of heat treatment duration on the value of swelling coefficient.

Examining the influence of temperature and heat treatment duration on the value of *Ka*, it was found that the optimal parameters for the swelling of clay shales with a fraction of more than 5 mm are: temperature (1150-1200)±25°C and delay time 10-15 minutes.

Testing of claydite physical-mechanical properties showed that: the claydite obtained from clay shale by thermal treatment at 1200±25°C during 10-12 minutes has the following features (by fraction): bulk density – 350-500kg/m^3; compression strength – 2.5-15.0MPa; low hygroscopicity (0.5%), moderate water absorption (12-15%); high water resistance (the softening coefficient is greater than 0.7) and low thermal conductivity (1.01.9kJ/m.grad). The effect of swelled shale granulometry on the basic properties is shown in Table 2. It was determined by studying the structure of claydite obtained from clay shale: Its structure is cellular; Porosity 10 times higher than the porosity of natural rock; True porosity reaches 80% and up to 70% of them come in closed and up to 10% in open porosity.For testing the claydite as lightweight concrete aggregate the gravel: 5-10 mm, sand: 0-5 mm, cement CEM 32.5 A/P were selected. A parallel study was conducted with natural porous

Table 2. Influence of grain fractionation on the properties of swelled shale

Grain sizes, mm	Bulk Density t/m^3	Sorption Ability, %	Water Absorption, %	Compression Strength, MPa	Softening Coefficient
> 20	0.35	0.2	8	2.4	0.70
10-20	0.40	0.3	10	2.8	0.71
5-10	0.45	0.4	22	4.9	0.79
3-5	0.47	0.5	35	11.4	0.88
2-3	0.48	0.7	41	13.0	0.90
1-2	0.50	0.9	47	15.4	0.96
mean	0.45	0.5	27.1	8.3	0.82

Table 3. Composition of 1 m^3 mixtures composed of swelled clay shale (C) and natural pumice (P)

Marking of Mixtures	Weight Proportions of the Components of the Mixture and their Species, g				Cement CEM 32.5 A/P	Water ml (g)
	Natural Pumice		Swelled Clay Material			
	Sand	Gravel	Sand	Gravel		
P - I	900	-	-	-	300	300
P - II	450	450	-	-	300	300
P - III	680	220	-	-	300	270
C - IV	-	-	900	-	300	300
C - V	-	-	450	450	300	280
C - VI	-	-	680	220	300	280

material – pumice. Concrete mixtures were composed on the basis of claydite, pumice (see Table 3).

Test cubes made of concrete were tested for strength, water absorption and densities were determined (see Table 4).

Table 4. Test results of concrete obtained from swelled shale (C) and natural pumice (P)

Sample N	Values of Properties		
	Density, g/cm^3	Water Absorption, %	Compression Strength, kg/cm^2
P- I	1.53	19.5	138.7
P - II	1.49	20.1	132.6
P - III	1.45	20.8	130.4
C- IV	1.36	21.6	127.3
C - V	1.26	23.4	122.5
C - VI	1.08	25.2	118.2

Results

The sedimentary clay shale raw material accumulated in the river Duruji gorge-bed by heating at temperature of 1100-1200°C is transformed into a closed porous light aggregate (200-600kg/m^3) – claydite. Cement concretes containing the claydite obtained from clay shale are lighter than cement concretes containing pumice and practically identical in terms of strength. The obtained claydite has all the necessary qualitative characteristics, so its use is advisable for the manufacture of light energy-efficient cement concretes, wares, monolithic energy-efficient buildings. The technology is patented in Georgia [4].

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