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Original scientific paper

MULTIPLE INFLUENCE OF SILICA-CONTAINING COMPONENT OF THE CHEMO-BIOGENIC ORIGIN ON THE STRUCTURE AND PROPERTIES OF COMPOSITES ON SILICATE MATRIX

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Abstract: A distinctive feature of the silicate matrix composites unlike silicate autoclaved concrete is that they are made on the basis of the ternary complex activated silicate concrete mixture modified by alkali and mineral additives, and harden at 85 °C and standard atmospheric pressure. Due to the implementation of a complete activation of highly mobile silicate concrete mixture, that is one of the technological features to obtain this type of composites, energy-saving modes of preparation were provided. The composites and products based on them are characterized by low density at high values of strength, water and crack resistance and heat capacity. Now there is clear idea about the functional role and impact on the structure and properties of silica-containing components chemo-biogenic genesis, which were previously used either as active mineral additives or fillers. The comparative analysis of the influence of the tripoli specific surface to the restructuring and silicate matrix properties and porous composites modified of alkali containing additives other additives were carried out. Based on this analysis the mechanism of formation of silicate matrix structure and properties was grounded and proposed. It is shown that the tripoli particles promoted "physical" seal structure of silicate matrix and the formation of capillaries' discontinuous structure, by means of their own micro-porosity.

Keywords: complex activation; silica-containing component; silicate matrix

1 INTRODUCTION

Conservation of the Earth's ecosystem is one of the main mankind tasks. Nowadays, the development strategy of many countries is impossible without environmental technologies or so-called "green" technologies. Their goals are blowout controls, resource-saving, waste management, increasing of productional energy efficiency, etc. The development and adaptation of new resource-saving technologies is one of the most advanced versions for always urgent issue solving of competitive enterprises. The cost of building materials depends on the raw materials they are made of and how energy-consuming their production technology is. Cutting the cost of building materials and construction totally will allow the production of building materials at the site of their using from the local raw materials and with using the non-autoclave [1÷6] and non-fire technologies. Therefore, in order to the conserve the Earth's ecosystem as a planet, optimization is necessary – it is the optimization of the system "man – eco- and energy-saving technologies – composite materials – environmental conditions". This approach will have a beneficial effect on the conservation of the planet's energy and material resources.

As technological methods progress, the possibility of using different types of activation should be noted. This contributes to the reduction of energy costs and allows the control of the structure formation process in such a way as to provide the required and predicted physical and mechanical properties of materials, products, and structures.

The development of new-generation materials is based on complex activated silicate mixtures, which are produced under casted technology with using of modern nanotechnological methods [1÷6].

These materials are characterized by reduced density with sufficiently high strength, high water-, frost-, crack-resistance and heat capacity.

2 NANOTECHNOLOGY RECEPTIONS OF PRODUCING THE COMPLEX ACTIVATED COMPOSITES ON SILICATE MATRIX

One of the research tasks is the identification of general mechanisms of structure and properties formation of the non-autoclaved hardening silicate composites.

Developed by the authors, the complex activation includes the continuous loop of the different types and methods of activation: mechanical, chemical, and thermal [1, 2].

Each type of activation is accompanied by effects which create the conditions for the possibility of subsequent type of activation.

The result of the complex activation is the formation of linear defects, dislocations, and point positions and substitutions. Furthermore, there may be angle change between the bonds and the appearance of dangling bonds, which leads to the formation of free radicals in the crystals with covalent bonds and the amorphization of molecular crystals.

Each type of activation will be caused by the prevalence of any type of deformations of the solid phase structure. The differences will be responsible for the nature and kind of dislocations with allowance for the extent and duration of external and internal influences.

2.1 Mechanical activation

Mechanical effects in the dispersion medium speed mixer activator provide mechanochemical activation of crystalline quartz surface. The term "mechanochemical reaction" was introduced by W. Ostwald in 1891.

Mechanochemical activation is carried out on the special properties of the newly formed surfaces, especially changing the local chemical and phase content of solids, as well as their aggregate state of under the influence of mechanical effects of high intensity [7].

As with nanotechnology reception, the mechanochemical activation reduces the viscosity of 3 or more dispersed systems containing lime [1÷3]. This effect of viscosity reduction was used to compensate the increased water demand of the mixture introducing the composite porous opal-cristobalite rocks and using the activation of the binder together with the fine aggregate.

2.2 Thermal activation

Used as a binder, quicklime promotes the "inner activation" of dispersed system under an elevated temperature T= 40÷60°C. The formation of multiple point contacts in the dislocation fields appears and the conditions for the hydration hardening unrelated in hydrous calcium lime are created.

External thermal activation occurs in conditions of thermal-moisture treatment. In such conditions at T=85 °C contradiction is canceled, which relates to the increasing the quartz solubility and decreasing lime solubility with increasing its dissolution [8, 9]. In addition, the increase of pH system causes to create favorable conditions for longevity growths GSK during the operational phase when $11.5 \leq pH \leq 12.5$.

2.3 Chemical activation

According to E. Avvakumov's works [10], with the presence of water in the inorganic solid-phase system the "method of soft mechanochemical synthesis" is developed. Hydroxides are used as the starting components to obtain composite oxides from the simple oxide. One of these is characterized by acidic, the other one is characterized by basic properties. By means of the neutralization reaction the intensification of the processes takes place. In addition, in such system the conditions for the hydrothermal processes are created.

The acid activation occurs by introducing the amorphous-crystalline silica, alkaline activation – the introduction of increased amounts of lime; it raises pH. The replacement of ground quartz sand in the binder by opal-cristobalite rocks increases frost and water resistance of the silicate matrix while reducing its density matrix to 20÷25%.

Moreover, the presence of opal-cristobalite rock in the dispersion causes formation of nanoscale in the GSK pores of these rocks; in this case, they are "nanoreactor". Its walls restrict the growth of neoplasm [11]. Also, the presence of particles of porous rocks with different dispersion binder allows adjusting the speed and reaction kinetics of hydration [3].

The use of quicklime determines the possibility of using high modulus liquid glass as one of the alkali additions, so the temperature rise on the forming stage allows regulating rapid setting of such mixture.

Alkali and alkali-containing additives increase the thermodynamic instability of systems by shifting the equilibrium caused by the formation of additional defects on the surface of silica-containing components. Alkali-containing additives are capable for aeration of mixtures under certain conditions [12].

In this work, the low-temperature aeration of concrete during introduction of the activation to the mixture for the silicate matrix by liquid glass additives $Na_2O \cdot nSiO_2 + mH_2O$ and sodium hydroxide NaOH is provided.

3 EXPERIMENTAL

In this study, one of the objectives is to identify local laws of formation of structure and properties of the aerated complex activated composites on the silicate matrix of thermal-moisture hardening to establish and use in practice the most effective and cost-effective methods of nanotechnology in the production process.

The forming of informative base for the optimization of technological decisions is provided using the methods of the experimentally-statistical modeling. The multifactor experiment was carried out with the use of the mathematical theory of planning of the experiment [13÷15]. Two comparable complexes of six-factor experimentally-statistical models are calculated. ES models by type (1) describe the dependence "mixture-properties" and "mixture-structure". It allows studying the dependence "content-structure-properties".

To analyze the possibilities of the regulation of the structure and properties of the aerated composites on the silicate matrix six factorial field experiments according to the 24-point plan, such as "triangles on the cube" by type "mixture-technology-quality", were carried out [13÷15]. In the plan, three mixed factors and three independent of the content vary simultaneously. With three mixed factors the surface area of tripoli as the component of lime-silica binder at levels was fixed: υ_1 – S_{sp1}=400 m^2/kg, υ_2 – S_{sp2}=500 m^2/kg, υ_3 – S_{sp3}=600 m^2/kg. With three independent factors in the experiments the content of alkali-containing additives was varied: x_4 – NaOH – (0.5÷1)%, x_5 –$Na_2O \cdot nSiO_2 + mH_2O$ – (1÷5)% and gypsum additives x_6 – $CaSO_4 \cdot 2H_2O$ – (2÷4)%.

The data on the properties and characteristics of the structure of full-scale experiments carried out in each of the 24 points of the plan were the basis for the ES models' calculations.

According to the experiment results, ES model is calculated, which allowed to estimate the effect of alkali-containing additives and the specific surface area of tripoli on the properties and characteristics of the structure of aerated composites on silicate matrix.

The computation experiment has shown that the factor which has the greatest influence on the properties is the specific surface area of tripoli. Due to the synergistic action of alkali additives and liquid glass, taken in optimal ratios for each property and given S_{sp} of tripoli, the aeration of the mixture is achieved. This lowers the density and high values of the properties: compressive strength R_b (MPa), bending strength R_{btb} (MPa), water resistance (coefficient of softening) k_s, crack resistance (critical coefficient of stress intensity) k_{Ic} (MPa·m$^{-0.5}$), heat conductivity (coefficient of heat conductivity) λ (Wt/m·K), frost resistance F (cycles). The introduction of additives of alkali and liquid glass increases the volume of the mixture to 1.2÷1.4 times. The density of the composite varies from 1300 to 1500 kg/m^3, which is 17÷23% lower than the density of the matrix material and 25÷30% lower than the density of autoclaved silicate brick.

4 RESULTS AND DISCUSSION

According to the experimental results, the experimental-statistical (ES) models were calculated. By ES models the optimal values of quality criteria and compositions of mixtures have been installed. Compressive strength R_b varies from 12 to 18.5 MPa, i.e. 1.5 times, and it is in the range of changing of the matrix material strength. Maximum strength is greater than 18 MPa and is obtained for compositions which contain 5% of liquid glass, 0.5% of alkali, and 4% of gypsum, S_{sp}=400 m^2/kg of Tripoli. The same strength of the silicate matrix is obtained on tripoli with S_{sp} = 500 m^2/kg.

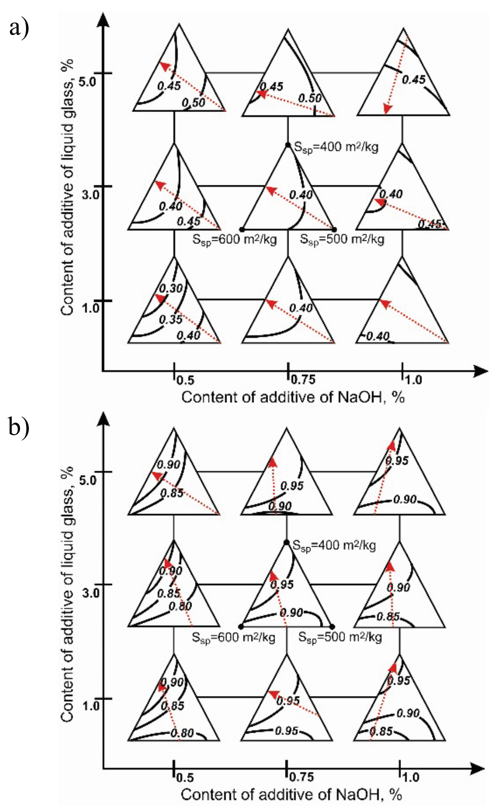

Figure 1 The influence of additives NaOH and liquid glass on coefficient of heat conductivity λ (a) and softening coefficient k_s (b) and for a fixed value additive of gypsum 4%

According to the ES model (1), the coefficient of heat conductivity λ of aerated composites under the influence of all six factors varies 1.9 times, from 0.28 to 0.54 Wt/m·K. The minimum value of the heat conductivity coefficient λ = 0.28 Wt/m·K is obtained on the contents which contain 0.5% NaOH and 1% liquid glass, a mixture of tripoli particles with a specific surface S_{sp}=400 and S_{sp}=600 m^2/kg in equal ratio and gypsum additive 4% (Fig. 1a).

Softening coefficient is varied by k_s 0.81÷1. The values k_s≥0.95 were obtained with the content 0.75% NaOH and 5% liquid glass on specific surface of tripoli S_{sp}=400 m^2/kg and the gypsum additive content of 4% (Fig. 1b).

Frost resistance of aerated materials is 25÷30 cycles that lay within the changes in frost resistance of matrix material – F25-50. The maximum value of the frost resistance of aerated composites was obtained on S_{sp}=400 m^2/kg, and the content of additives gypsum is 4%. The similar values of frost resistance of silicate matrix were obtained in the mixture of tripoli particles S_{sp}=400 and S_{sp}=600 m^2/kg in equal proportions and gypsum content 2.5%.

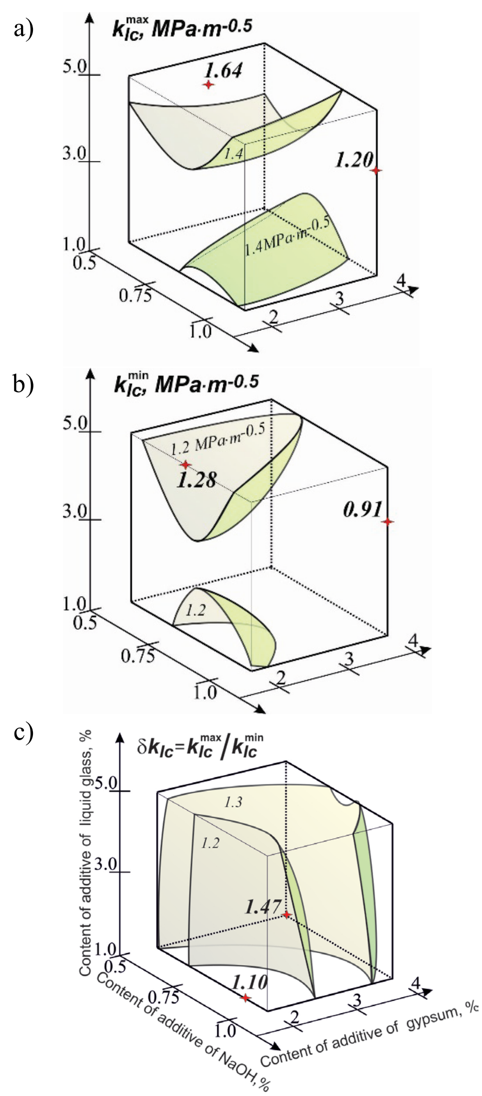

Figure 2 The changing the maximum (a) and minimum (b) values k_{Ic} under the influence of content and technological factors, taking into account the values of S_{sp} of tripoli determining the maximum and minimum values k_{Ic} respectively. Relative change ratio $\delta k_{Ic} = k_{Ic}^{max}/k_{Ic}^{min}$ (c) due to changes of S_{sp} of tripoli

The critical coefficient of stress intensity k_{Ic} under the influence of all factors varies by 1.8 times, from 0.91 to 1.64 MPa·m$^{-0.5}$ (Fig. 2, b). According to the ES models, taking into account the quantities of S_{sp} tripoli, which provide maximum and minimum values k_{Ic}, the ratio $\delta k_{Ic} = k_{Ic}^{max}/k_{Ic}^{min}$=1.1÷1.47 time was calculated (Fig. 2c).

The maximum values of the critical stress intensity factor k_{Ic}=1.64 MPa·m$^{-0.5}$ of aerated composites are equal to k_{Ic} of matrix material and the minimum value k_{Ic} = 0.91 MPa·m$^{-0.5}$ of aerated composites is twice the k_{Ic} of the matrix material [5]. In this case, the maximum and minimum values k_{Ic} for porous composite and the matrix material were obtained at the different values of tripoli S_{sp}. Thus, maximum k_{Ic} for aerated composites was obtained on S_{sp}=600 m^2/kg, and for the matrix material, on the mixture S_{sp}=400 and S_{sp}=600 m^2/kg with an equal ratio. It may be associated with different particles density in the volume and cramped conditions of aerated composites.

The visualization of ranges of property changes under the influence alkali-containing additives and the specific surface area of tripoli is shown in Fig. 3.

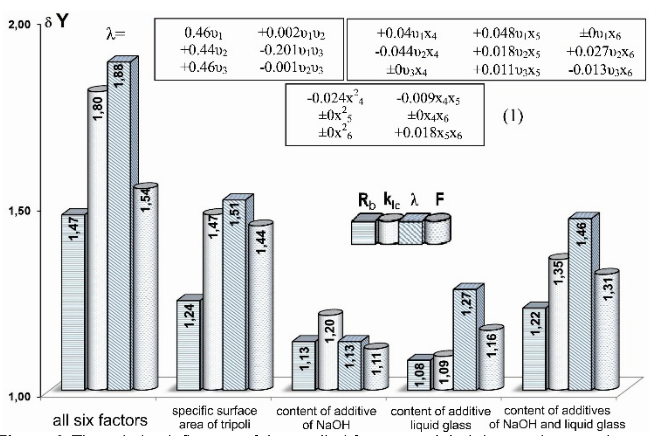

Figure 3 The relative influence of the studied factors and their interactions on the change of properties

Thus, the changed conditions of structure formation by introducing alkali-containing additives promoting aerated composites, predetermine the introduction of tripoli with a specific surface area. This may be connected, in this case, with the formation of the matrix structure in "straitened circumstances" of interporous partitions. For obtaining optimal compositions of porous composites, introducing alkali-containing additives they condition the necessity of changes S_{sp} of tripoli and adjustment of the content of gypsum additives compared with the optimal composition of the silicate matrix at constant quantitative content of other components for the mixture and the conditions of their hardening.

This change of the properties is associated with the change of structural parameters of porous composites under the influence of alkali-containing additives and S_{sp} of tripoli.

To analyze the impact of the structure characteristics on the properties the ES models of change of total, open and closed porosity and parameters of capillary porosity were calculated. The content of closed pores can be increased by reducing the content of open pores 1.7 times.

The total porosity can be increased to 30%. The average size of the capillaries d_k is changed in 4.3 times; the coefficient of distribution uniformity according to their size α_k in 2.3 times.

In the next phase of research using the computational experiments [14, 15] according to ES models, the comparative analysis of property changes and the structure characteristics of the silicate matrix and aerated composites based on the isoparametric conditions at the constant total porosity P_{tot}=const=40% was carried out.

It was found that at the constant total porosity P_{tot}=const=40% the aerated composites are characterized by k_{Ic}=1.2÷1.35 MPa·m$^{-0.5}$, that is 1.5÷1.7 times higher and the coefficient of heat conductivity is 1.8÷2.8 times lower than at the matrix material; the softening coefficient is k_s≥0.95 (Fig. 4a).

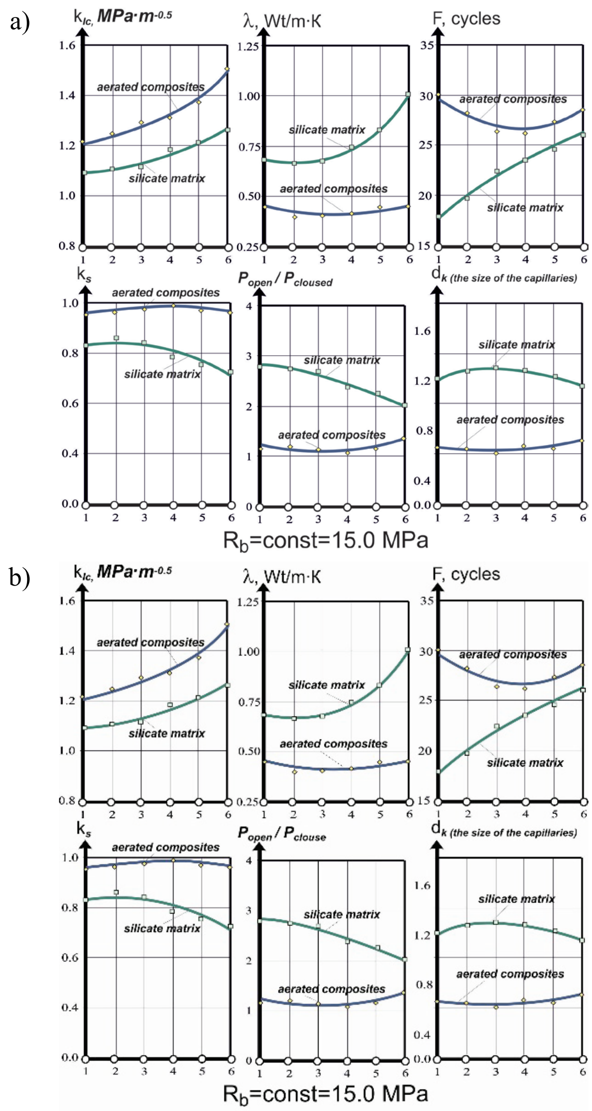

Figure 4 The comparative analysis of the changes in the properties and characteristics of the structure of the silicate matrix and of aerated composites based on isoparametric conditions: (a) P_{tot}=const=40% and (b) R_b=const=15.0 MPa

This improvement relates to the change of the structure parameters. Thus, at the aerated composites comparing with the silicate matrix the ratio of the open and closed pores is reduced 3.5 times; the average size of the capillaries relative d_k from 1.2 to 0.35 is reduced more than 3 times.

A similar comparative analysis of property changes and structure characteristics of the silicate matrix and aerated composites based on isoparametric conditions was carried out at R_b=const =15.0 MPa.

Under these conditions, the levels of the properties and their variation intervals vary: λ is decreased 1.5÷2 times, k_s=1.0, k_{Ic}=1.1÷1.45 MPa·m$^{-0.5}$, it confirms the ambiguous influence P_{tot} on R_b. R_b is determined not only by the total porosity, but also a variety of other characteristics of the structure.

The optimization problem was to obtain the aerated composites on the silicate matrix, whose physico-mechanical properties were above the properties of the silicate matrix.

The isoparametric analysis while retaining R_b=const=15 MPa and P_{tot}=const=40% showed that the ranges of other properties and structure parameters are significantly reduced: $\delta\lambda$=20%, δR_{btb}=18%, δk_s=6%, δk_{Ic}=7%, δP_{tot} – 10%, $\delta \alpha_k$ – 5% with aerated composites simultaneously with two properties of specified level (R_b and P_{tot}) (Tab. 1).

Table 1 The changing of the properties and structure parameters of aerated composites in isoparametric conditions P_{tot}=const=40% and R_b=const=15.0 MPa

	Main properties and structure parameters of aerated composites	Specific surface area of tripoli S_{sp} (m²/kg)		
		S_{sp}=400	S_{sp}=500	S_{sp}=600
1	Compressive strength R_b (MPa)	constant 15 MPa		
2	Total porosity P_{tot} (%)	constant 40 %		
3	Bending strength R_{btb} (MPa)	2.45	2.75	2.98
4	Coefficient of softening k_s	1.00	0.94	0.94
5	Critical coefficient of stress intensity k_{Ic} (MPa·m$^{-0.5}$)	1.31	1.28	1.37
6	Coefficient of heat conductivity λ (Wt/m·K)	0.42	0.43	0.43
7	Frost resistance F (cycles)	28	27	29
8	Ration open and closed porosity P_{open}/P_{close}	1.47	1.24	1.48
9	Average size of the capillaries α_k	0.55	0.53	0.56
10	Coefficient of uniformity of distribution of capillaries size d_k	0.58	0.72	0.60

Changes of $\delta\lambda$, δR_{btb}, δk_s, δk_{Ic} are associated with the presence of a mixture of different specific surface of tripoli, which confirms its significant influence on the formation of the structure as a silicate matrix with aerated composites based on it. It allows regulating the properties and structure characteristics of the materials at the constant compressive strength and porosity by varying the specific surface of tripoli.

5 CONCLUSIONS

The mechanism of formation structure and properties of complex activated lime-silica mixture, modified by the filler in the form of tripoli on quicklime was proposed.

It is shown that the particles of tripoli contribute to seal structure of silicate matrix and the formation of discontinuous structure of capillaries, including its own microporosity. Furthermore, due to the high sorption capacity, the tripoli pores can be the matrix from ultrafine size hydrosilicates whose properties differ from the properties of the calcium hydrosilicates formed in the mixture free space. It contributes to obtaining the aerated composites with high physical and mechanical properties.

Thus, the structure modification of the silicate matrix by using quicklime, alkali-containing additives, and tripoli predetermined specific surface area, allows adjusting the levels of the properties and structure parameters of the aerated composites on silicate matrix in a wide range.

According to the results of optimization the recommended contents are those which allow to get aerated composites on the silicate matrix given grades of strength, heat conductivity and frost resistance: compressive strength R_b – 10 MPa, 12.5 MPa, density ρ=1300÷1400 kg/m^3, frost resistance F25, heat conductivity λ=0.30÷0.40 Wt/m·K, critical coefficient of stress intensity k_{Ic}≥1 MPa·m$^{-0.5}$, coefficient of softening k_s≥0.9.

Note: This research was presented at the International Conference MATRIB 2017 (29 June - 2 July 2017, Vela Luka, Croatia).

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