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### FORMATION OF A PORE-FORMING GAS SOURCE BY WETTING NATURAL ALUMINUM-SILICATE WITH NaOH SOLUTION

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The characteristic features of heat-activated pore-formation of zeolite-containing rocks (ZR) and opoka in alkali compositions were examined. It was determined that the low-temperature pore-forming gas phase in the systems opoka + NaOH and ZR + NaOH is water vapor that formed during dehydration of hydrated sodium silicates. In the mix ZR + NaOH the second, higher-temperature source of water vapor was found to be hydrated silicate surfaces of amorphized post-zeolite components.

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**Key words:** zeolite-containing rocks, opoka, thermally activated pore formation, melting, heat-insulation materials.

A well-known raw material for obtaining foamed materials is siliceous rock (trepels, opokas) and natural glass (perlite) [1 – 4]. The most effective flux in the technologies used to manufacture heat-insulating materials from natural raw material without first obtaining quenched cullet is sodium hydroxide. In a number of cases, when manufacturing heat-insulating building materials from aluminum silicate raw materials not containing a source of pore-forming gas such a source forms when the sodium hydroxide interacts together with the rock components [2 – 4]. The technological processes and temperature regimes for manufacturing foam materials are largely associated with the temperature range of gas release, which is determined by the nature of the source of gas. The source of pore-forming gas in aluminum silicate rock as can be different. However, it is often characterized by analogy to another, similar raw material or on the basis of assumptions concerning the probabilistic interaction processes occurring between rock components and alkaline solutions. Such assumptions or analogies lead to erroneous ideas about the thermally activated pore-formation processes occurring in aluminum silicate compositions.

According to the data [2 – 4] the source of pore-forming gas in compositions based on siliceous rock is the hydrated

surface of silicate particles, which is formed when comminuted or mechanically activated rock is wetted with a NaOH solution.

At present porous building materials are fabricated using zeolite-containing rocks (ZR) as aluminum silicate raw material. On the basis of their size the ZR resources in Russia and abroad can be categorized as abundant and regarded as local raw materials. In Russia the reserves of volcanogenic-sedimentary zeolite-containing rock are estimated as more than  $3 \times 10^9$  tons. Natural zeolites are framework aluminum-silicates whose composition represented by the empirical formula  $M_{2/n} \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ , where  $x \geq 2$ ,  $n$  is the valence of the cation [5]. The zeolite frameworks contain channels and communicating cavities which have cations and water molecules capable of reversible degradation and ion exchange without damage to the structure. It is these features that determined the unique properties of minerals of this class — the molecular-sieve separation effect, high ion-exchange, sorption and catalytic capacity. When natural zeolites are used as sorbents, catalysts and molecular sieves they must meet high specifications with regard to the content of zeolite in nature, they must be highly zeolitized. Rocks with zeolite content  $> 80\%$  are rarely encountered. Usually, the content of the zeolite mineral in rock fluctuates within the range 20 – 50%. The most likely user of ZR with average and low zeolite content is the construction industry in the manufacture of ceramic and, especially, heat-insulation materials.

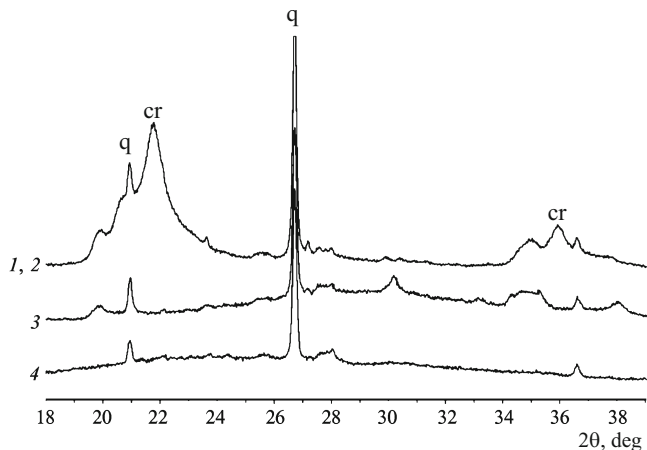
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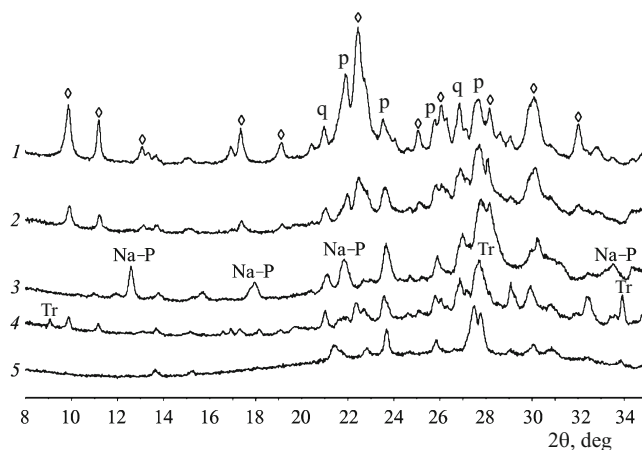
**Fig. 1.** Powder diffraction profiles: 1) opoka; 2) opoka + NaOH, mix unheated and heated at 50°C; 3) opoka + NaOH, mix heated at 90°C; 4) porous material obtained at 800°C; q) quartz; cr) cristobalite.

It is known that some natural zeolites are capable of thermally activated pore formation at their natural melting temperature (1100–1200°C). Nature and the mechanism of high-temperature pore formation in natural zeolites are studied and presented in a number of works [6–9]. The pore formation process in the range 700–900°C in compositions based on ZR was not studied in detail, and it is impossible to optimize the technological processes and temperature regimes for making porous construction materials without a clear understanding of the transformations occurring in zeolite-containing compositions.

In the present work we study the intensity of pore formation and thermally activated physical-chemical processes occurring in the interior volume of comminuted clinoptilolite rock, wetted with a NaOH solution, from the Kholinskoe deposit. For comparison similar studies were done with opoka, whose chemical composition is very similar but whose mineralogical composition is different.

## METHODS OF STUDY AND ROCK CHARACTERISTICS

X-ray fluorescence was used for chemical analysis of rock (VRA-20R x-ray Analyzer) and powder x-ray diffractometry for phase analysis of the initial raw material and intermediate products (Thermo Scientific ARL-X'tra diffracto-



**Fig. 2.** Powder diffraction profiles: 1) ZR from the Kholinskoe deposit; 2) ZR + NaOH, mix unheated and heated at 50°C; 3) ZR + NaOH, mix heated at 90°C; 4) quenched glass corresponding to curve 2, after contact with atmospheric air for 2 days; 5) porous material obtained at 800°C; ◇) clinoptilolite; q) quartz; p) plagioclase; Na-P) zeolite with idealized composition of the unit cell  $[\text{Na}_x\text{Al}_x\text{Si}_{16-x}\text{O}_{32}] \cdot 4\text{H}_2\text{O}$ ; Tr) trona  $(\text{Na}_3[\text{CO}_3][\text{HCO}_3] \cdot 2\text{H}_2\text{O})$ .

meter,  $\text{CuK}\alpha$  radiation, regime 40 kV, 40 mA) using the PDF-4 database and scanning electron microscopy (Phillips XL30-FEG). The chemical composition of the experimental rocks is presented in Table 1.

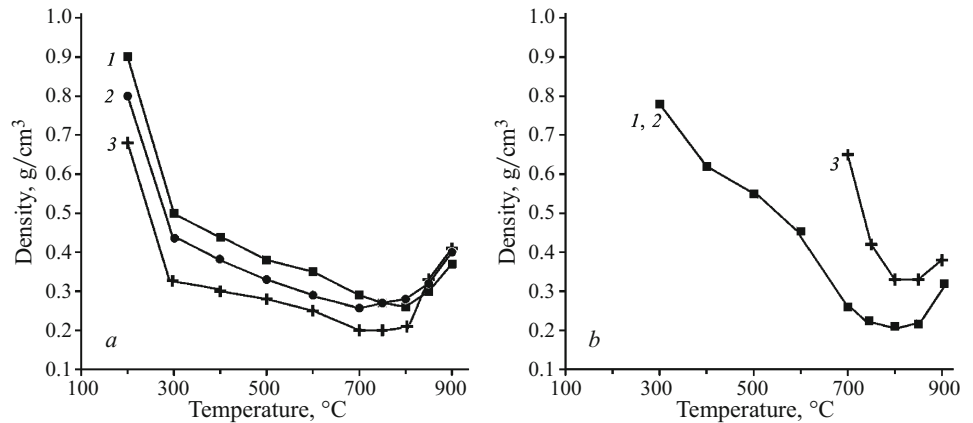
It is well known that opoka is comprised predominantly of amorphous silica. Powder x-ray diffractometry data show that the main crystalline phases of opoka are quartz and cristobalite (Fig. 1, curve 1). The mineral composition of ZR contains (in decreasing amount): zeolite (clinoptilolite)  $\gg$  plagioclase  $>$  quartz (Fig. 2, curve 1).

To investigate the intensity of the pore formation and physical-chemical processes in alkali compositions opoka and ZR were comminuted in a vibrating mill. The powder was wetted with a water solution of NaOH to a plastic state with the following ratio in the dry state (wt.%): rock — 81; NaOH — 19. The plastic mix was divided into three parts. A 4–5 mm in diameter cullet was formed directly from one part (experiment I), the second part of the mix was kept at 50°C (experiment II) and the third at 90°C (experiment III) for 10 h for each value of the temperature. The mix was kept from drying while it was heated. Quenched glass was made from the heated mix. The quenched cullet was dried at 100°C in air to an air-dry state, after which it was fired and its density determined. The dried cullet was heat-treated in the in-

**TABLE 1.** Chemical Composition of Rocks

Substance	Content, wt.%										
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	MnO	MgO	CaO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$	other
Zeolite rock	69.24	12.72	0.13	1.17	0.06	0.26	2.51	1.53	4.58	0.02	7.74
Opoka	81.07	7.63	0.43	3.87	0.036	1.08	0.69	0.23	1.66	0.08	3.59

**Fig. 3.** Density variation of opoka (*a*) and zeolite-containing rock (*b*) versus firing temperature. The cullet was made as follows: 1 (■) immediately after wetting the powder with a NaOH solution; 2 (●) after heating moist mix at 50°C; 3 (+) after heating moist mix at 90°C. The soaking time when heating the mix was 10 h.



terval 200 – 900°C in steps 100°C to 700°C, and at a higher temperature in steps 50°C with 10-min soaking at each temperature.

## RESULTS AND DISCUSSION

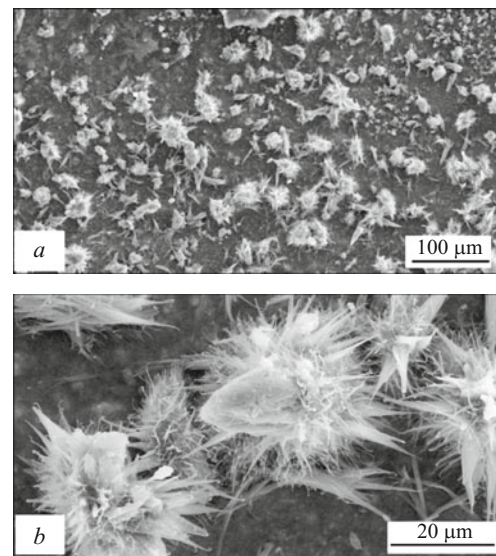
For the opoka composition (Fig. 3*a*) with and without pre-heating at 50 and 90°C the powder formation process remains same as the intensity of the process increases with increasing heating temperature of the moist mix. Pore formation in quenched cullet starts at 200°C and increases sharply at 300°C. As the firing temperature increases the density of the cullet gradually decreases to 800°C and starts to increase at higher temperatures.

The pore-formation process for the alkali composition made from ZR is more complex (Fig. 3*b*). Pore formation to 600°C for mix without and with pre-heating at 50°C, similarly to this process for opoka mix, starts at low temperature (300°C) with cullet density decreasing gradually as the firing temperature increases. As the temperature increases to 750°C, the intensity of pore formation of ZR mix increases sharply. The cullet density starts to increase only at firing temperature above 850°C. The densities of fired cullet made from mix pre-heated mix at 50°C are close to the densities obtained without heating.

A large difference in the character of pore formation is observed after ZR mix is heated at 90°C. Pore formation in quenched cullet in this case starts only at 700°C, i.e., at the formation temperature of low-melting eutectics. At higher temperatures, pore formation proceeds as in unheated mix.

One other difference is observed between thermally activated processes in quenched cullet made from opoka and natural zeolite. After being kept in air for more than one day dry cullet made from ZR, corresponding to the experiments I and II (Fig. 3*b*, curves 1 and 2, respectively), breakup into fragments. After opoka granules are kept standing similarly a thermally activated pore-formation process occurs, as usual, without loss of integrity.

The x-ray diffraction (see Figs. 1 and 2) and electron-microscopic (Fig. 4) studies of the initial raw material and



**Fig. 4.** SEM image of a dry cullet chip with the composition ZR + NaOH after being kept in air for 2 days (the wetted mix was not heated).

cullet made it possible to determine the reason for the differences in the thermally activated processes in alkaline mixes made from opoka and ZR.

Low-temperature pore formation (before the mix transitions into a pyroplastic state, i.e. before melt appears in it) is characteristic for liquid glass, which is comprised of hydrated alkali silicates with the chemical composition  $R_2O \cdot mSiO_2 \cdot nH_2O$ . The capability of liquid glass to form a well-developed porous system at low temperature is the basis for the method used to obtain porous materials with powders of inorganic raw material as filler [10]. Such a porous material is unstable with respect to water and is characterized by low mechanical strength. It acquires water resistance and mechanical strength when heated to the melting temperature of the filler.

The possibility of hydrated alkali silicates being formed at room temperature in a moist opoka + NaOH mix is related

with the high chemical activity of amorphous silica, the major mineral component of this rock. The x-ray diffraction pattern corresponding to the initial state of opoka remains unchanged after it is wetted with a NaOH solution and the mix is heated at 50°C (see Fig. 1, curves 1, 2). After each moist alkali mix is heated at 90°C the cristobalite reflections (see Fig. 1, curve 3) in the diffraction pattern vanish completely. Thus, as the heating temperature increases the formation of hydrated alkali silicates accelerates in such a composition, as a result of which the concentration of the source of the gas phase increases and pore formation at low temperatures to melting increases.

Considerable amorphization of clinoptilolite is observed after ZR powder is wetted with an alkaline solution at room temperature (see Fig. 2, curve 2). Colloidal hydrated sodium silicate probably forms in this composition as a result of the interaction of highly reactive silica, freed during the amorphization of clinoptilolite, with the dissolved sodium hydroxide. Quartz and plagioclase remained practically unchanged.

Rapid solidification of the plastic mix was observed at 50°C when the alkaline mix made from ZR was heated. It is known that under alkaline conditions zeolites are characterized by pozzolanic (binding) activity that increases with moderate heating [8]. In solid mix the formation of hydrated sodium silicates stops, so that the concentration of the source of pore-forming gas does not increase and, therefore, the intensity of pore formation in mix pre-heated at 50°C does not change.

Before the alkaline mix made from ZR was preheated at 50°C it was additionally wetted with water to a paste-like state in order to forewarn against rapid solidification. After such a mix was heated for 10 h at 90°C complete amorphization of clinoptilolite and formation of Na-P zeolite (see Fig. 2, curve 3) with ideal unit-cell composition  $[\text{Na}_x\text{Al}_x\text{Si}_{16-x}\cdot\text{O}_{32}] \cdot 14\text{H}_2\text{O}$  and  $\text{Si}/\text{Al} = 1.1 - 2.5$  are observed [5]. Since pore-formation in this state starts only at 700°C, it can be supposed that the hydrated sodium silicate formed at room temperature in zeolite mix was the component for crystallization at 90°C of zeolite Na-P which is stable under these conditions. The appearance of melt in such a composition at 700°C leads to blockage in the micropores of surface hydroxyl groups (Si-OH) remaining after dehydration of Na-P zeolite amorphized by this temperature and a post-clinoptilolitic amorphous component. Starting at 700°C the polycondensation of such hydroxyl groups with the release of water vapor in micropores is accompanied by the formation of a porous macrostructure. The change of the nature and, probably, concentration of the gas source shifts pore formation to higher temperatures.

The experimental results show that the formation of a porous microstructure in alkaline mix based on ZR with no pre-heating of the mix is due to two gas sources: first — hydrated silicon sodium, which promotes low-temperature pore formation starting at 300°C and second — hydrated silicate

surfaces of amorphized zeolites, which promote continuation of the pore-forming process and maintain the porous microstructure with no shrinkage to 850°C. At higher temperature the foam settles as a result of a decrease of the melt viscosity. In compositions made from opoka, because the second, higher-temperature gas source is absent the foam settles at a temperature above 800°C.

When dry quenched cullet with the composition ZR + NaOH (experiments I and II) are kept standing in air a carbonate compound — trona  $\text{Na}_3[\text{CO}_3][\text{HCO}_3] \cdot 2\text{H}_2\text{O}$  — is recorded in the x-ray diffraction pictures (see Fig. 2, curve 4). It is known that alkali in an unbound state possesses sorption ability. It is possible that a film distribution of the alkali over the zeolite particles accelerates its carbonatization. Trona manifests in electronic pictures as micron-length needle-like formations protruding from very small pores in a dense zeolite-containing matrix (see Fig. 4). Such a surface microstructure of dried cullet chips is typical for the crystallization of salts through micropores. Trona formation in quenched cullet from the mix ZR + NaOH explains their decomposition on fragments during firing. The formation of trona and intense gas release during heating of dense cullet leads to its decomposition into fragments.

A feature common to all porous materials obtained at 800°C from opoka and ZR is their glass-enamel nature. In the x-ray diffraction patterns of quenched cullet fired at this temperature the reflections due to quartz for the opoka composition and plagioclase for the ZR composition remain unchanged (see Figs. 1 and 2). More complete vitrification of the porous material requires either higher temperature, which is impossible because the foam is unstable, or longer soaking than 10 min.

## CONCLUSIONS

1. The low-temperature pore-forming gas phase in the system opoka + NaOH and ZR + NaOH is water vapor, formed during dehydration of hydrated sodium silicates. In the ZR + NaOH mix the second phase, a higher-temperature source of water vapor, is the hydrated silicate surface of amorphized post-zeolite components. Water vapor formed during polycondensation of silanol hydroxyl groups participates in pore formation starting at 700°C, i.e., after glass melt appears, which seals the water vapor in the micropores.

2. Heating of the alkaline opoka mix at 50 – 90°C increases the concentration of hydrated sodium silicates and intensifies pore-formation in the mix.

3. Wetted ZR + NaOH mix should not be heated. At 50°C the mix solidifies and hydrated sodium silicates no longer form. At 90°C hydrated sodium silicates in alkaline mix participate in the crystallization of a new phase — Na-P zeolite, as a result of which pore-formation becomes less intense.

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