

# Effect of the Mineralogical Composition of Clay on Microwave Sintering of Aluminosilicates

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**Abstract**—This paper presents results of firing of bentonite clay, refractory clay, and metakaolin materials with NaCl additions using convective and microwave heating. Phase structures of microwave-sintered aluminosilicates have been examined and the formation of a nanometer-scale aluminosilicate structure has been demonstrated. The microwave-fired materials have been found to have an increased strength. The mineralogical composition of clay has been shown to influence the microwave sintering behavior of aluminosilicates. Kaolinite and kaolinite-based materials exhibit increased activity in the temperature range 450–550°C during microwave sintering. The role of NaCl as a mineralizing salt has been found out.

**Keywords:** bentonite clay, refractory clay, metakaolin, NaCl, convective heating, microwave firing

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## INTRODUCTION

Sintering is the main step in heat treatment of a wide range of inorganic fired materials, among which aluminosilicate ceramics hold an important place. Sintering produces the final structure of a material, which determines its engineering performance. In addition, the formation of the structure of a material is influenced by parameters of raw materials, specific features of their processing and fabrication of an article, and the heat treatment process. At present, energy efficiency and environmental safety of heating are of special importance in the technology of fired materials. In this respect, microwave heating has obvious advantages over convective heating, which typically involves fuel combustion.

As shown earlier [1–3], the mechanism of high-temperature processes and the final properties of materials are significantly influenced by the heating rate [1–3]. As a result of electric field-assisted flash sintering, one can obtain a material with a microcrystalline structure and good mechanical properties [1–3].

In a number of studies [4–10], microwave energy was used for heat treatment of materials.

In a study of interaction of ceramics with alumina in a microwave field, Binner et al. [4] observed the formation of an intergranular glass phase, good diffusion, homogeneity of the material, lower strain in the materials in comparison with traditional convective heating, and increased strength of the compound. Microwave processing of ceramic materials, kaolin, alu-

mina, and talc [5] was reported to ensure rapid (30 min) heating to temperatures from 1200 to 1400°C and a considerable decrease in reaction time (by three to five times). It was proposed that convective heating should be conducted first, until the maximum dielectric loss tangent of the starting-mixture components would be reached, followed by microwave sintering.

Based on analysis of reports concerned with the use of microwave heating, Bolotov et al. [6] noted not only the increased process rate but also the highest effectiveness of the method in the case of endothermic reactions and the use of electrolytes, for example, salt solutions.

A study of soil hardening by microwave heating [7] showed significant changes in the mineralogical composition and structure of the soil, a considerable increase in its strength, and significant improvement in its water and frost resistance owing to the formation of glass in pores and interphase spaces. Humidity was reported to influence physicommechanical characteristics of heat-strengthened soil.

Clay and diatomite were used as examples to assess the effect of alumina and aluminum sodium chloride modifiers and microwave activation of composites on the sintering process [8, 9]. The results demonstrate a decrease in phase formation temperature, changes in the structure of aluminosilicate materials, the formation of nanometer-scale inclusions during the firing process, and, as a consequence, an increase in the strength of the material.

Tompsett et al. [10] studied microwave synthesis of nanoporous materials. Using a wide range of analytical techniques for characterizing the microstructure of the materials, they assessed distinctions between the crystal structure obtained by microwave synthesis and that obtained by conventional firing. In the case of the crystallization of a mixed oxide ( $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ ), the material was found to have a morphology structured in the form of nanorods made up of connected and scattered particles.

During the convective heating step (800–1000°C), the decomposition of major mineral components of a material on the whole reaches completion and a liquid phase appears [5]. It was found however [8, 9] that microwave processing of raw materials before convective heating influences the formation of the final structure of the material. Transformations in a fine fraction of raw materials during microwave activation influence the entire subsequent process underlying the formation of the structure of the material. Specific features of the final structure of the material are reflected in its engineering performance.

Studies of aluminosilicates demonstrate that, after microwave preactivation of raw materials, convective heating leads to the formation of a nanoscale phase structure in the material [8, 9]. In clay materials, this is favored by the presence of alkali chlorides, which accelerate structural changes in aluminosilicates during the dehydration process and increase the fraction of small crystals during sintering. This leads to an increase in the strength of the material [11–13].

To gain insight into processes that occur during heating and sintering of aluminosilicates, it is especially important to study specific features of the formation of the structure of materials under the effect of an electromagnetic field.

The objectives of this work were to study the firing behavior of aluminosilicates with different mineralogical compositions during convective and microwave heating, determine the phase composition and structure of samples fired in a microwave field, and compare the strength of samples prepared by convective and microwave heating.

## EXPERIMENTAL

We studied bentonite from Nurlat (60% montmorillonite, 5% mica), with the following concentrations of basic oxides (wt %):  $\text{SiO}_2$ , 56.4;  $\text{Al}_2\text{O}_3$ , 20.0;  $\text{Fe}_2\text{O}_3$ , 8.1;  $\text{CaO} + \text{MgO}$ , 4.4;  $\text{K}_2\text{O} + \text{Na}_2\text{O}$ , 2.0; refractory clay from the Nizhnevskoe occurrence (60.0% kaolinite, 5.0% mica), with the following concentrations of basic oxides (wt %):  $\text{SiO}_2$ , 58.0;  $\text{Al}_2\text{O}_3$ , 30.2;  $\text{Fe}_2\text{O}_3$ , 4.3;  $\text{CaO} + \text{MgO}$ , 1.2;  $\text{K}_2\text{O} + \text{Na}_2\text{O}$ , 0.9; and VMK-47 metakaolin (92% amorphous kaolin, 3%

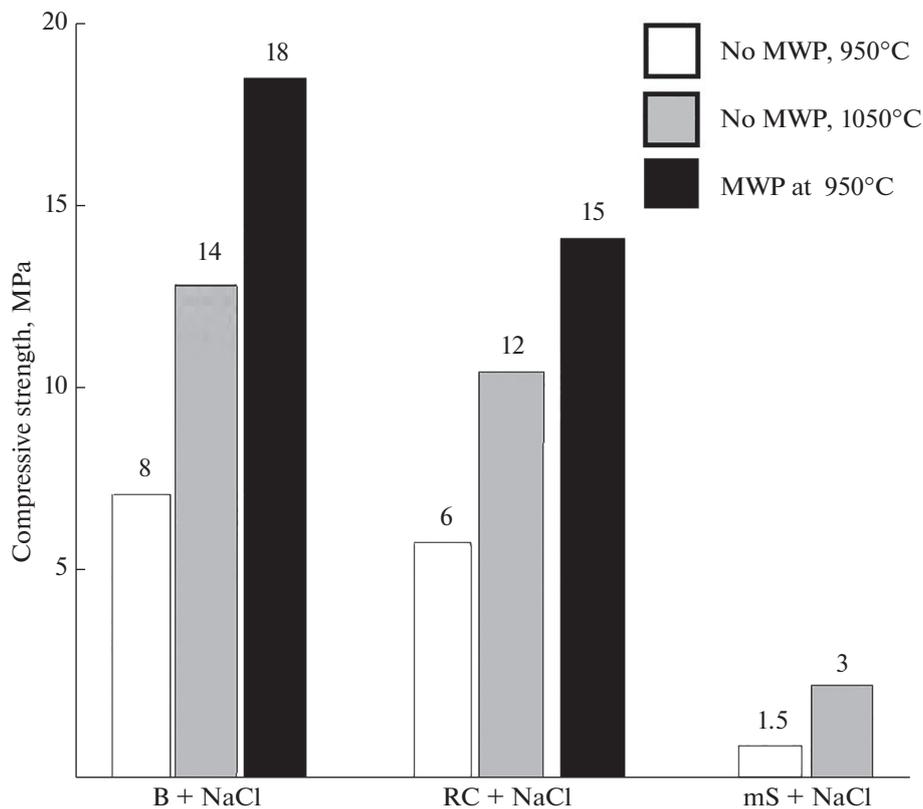
mica). The mineralizer used was NaCl (Russian Federation State Standard GOST 51574-2000).

The samples were heat-treated in a PVK-1,4-17 muffle furnace and Samsung M 1711 NR microwave oven at an output microwave power of 800 W at a working frequency of 2.45 GHz. Its operation was accompanied by a strong magnetic field generated by the 50 Hz (industrial frequency) current flowing in the power supply system of the oven. To prevent heat losses, a muffle from mullite–silica plates was mounted in the chamber of the furnace, and samples for firing were placed in it. The temperature was monitored with a thermocouple with coating protected from radiation. The junction of the thermocouple was located next to the samples. After the samples were placed in the muffle furnace or microwave oven, the highest heating rate was maintained, for 4–4.5 h in the muffle furnace and for 30 min in the microwave oven. The samples were heated to 950 and 1050°C and held at the highest temperature for 30 min in the muffle furnace and 5 min in the microwave oven.

The active components of the clays chosen for this study are montmorillonite (metastable homopolar layered crystal structure) and metakaolinite, an amorphous structure resulting from kaolinite (heteropolar layered crystal structure) decomposition during heating in the temperature range 500–600°C. To compare the reactivity of a dehydrated aluminosilicate to that of clays in a microwave field, metakaolin was used.

Given the role of mineralizers in the sintering of aluminosilicates [9, 11–13], NaCl-modified materials were prepared. To this end, preprepared starting-mixture components, ground and passed through a sieve with a nominal aperture size of 1 mm, were homogenized in a ball mill for 0.5 h. The samples were moistened with a rocksalt solution in distilled water to form plastic mass, which was used to prepare samples 30 × 30 × 60 mm in dimensions. Each sample was cut into two parts 30 × 30 × 30 mm in dimensions, which were dried to constant weight. Some of the samples were fired in the muffle furnace, and some, in the microwave oven.

The materials thus prepared were characterized using equipment at the Tomsk Shared Materials Characterization Facilities Center, Tomsk Regional Shared Research Facilities Center, Scientific Management, Tomsk State University. The phase composition of the samples was determined by X-ray diffraction on a Shimadzu XRD 6000 diffractometer with  $\text{CuK}\alpha$  radiation (PDF 4+ database, POWDERCELL 2.4 profile analysis program). The samples were characterized by thermal analysis using a TG–DTA/DC simultaneous analysis system (in combination with a QMS 403 C quadrupole mass spectrometer). Fracture surfaces



**Fig. 1.** Compressive strength of samples prepared from plastic masses based on bentonite (B), refractory clay (RC), and microsilica ( $\mu$ S) (MWP = microwave processing).

were examined using a focused ion beam/scanning electron microscope system (Quanta 200 3D).

## RESULTS AND DISCUSSION

The strength test results for our samples are presented in Fig. 1. It is seen that the strength of the samples prepared from NaCl-modified clay materials and fired in the microwave oven exceeds that of the samples fired in the muffle furnace. The metakaolin-based samples had the lowest strength, and those fired in the microwave oven had large surface cracks, so they were not tested in strength.

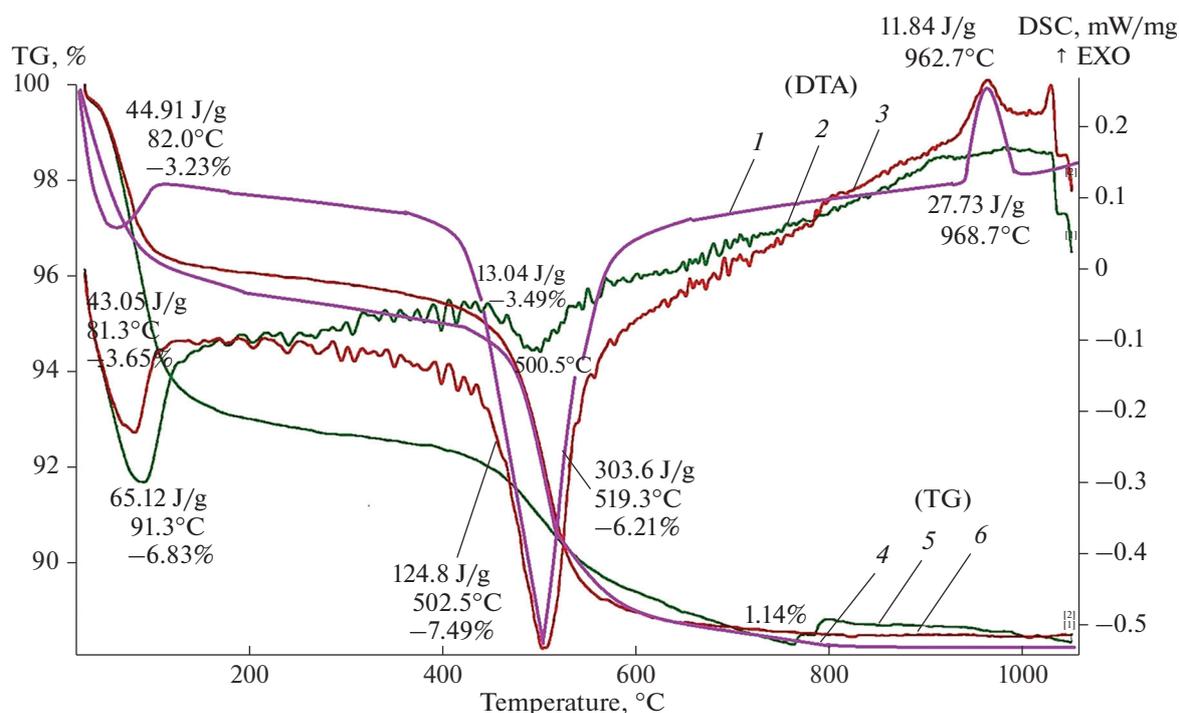
To understand the role of the salt mineralizer in sintering, we tested NaCl-free compositions as model systems. The bentonite clay-based samples did not fracture during firing. The kaolin clay-based samples (refractory clay from the Nizhnevskoe occurrence and metakaolin) fractured on heating. In the microwave oven, they exploded when the temperature reached 450–500°C.

To follow the processes occurring in the samples during heating, The NaCl-containing bentonite and refractory clay-based materials were characterized by simultaneous thermal analysis (differential thermal

analysis (DTA) + thermogravimetry (TG)). The results are presented in the form of a joint plot in Fig. 2.

It is seen that the bentonite clay-based material has a broad low-energy endothermic peak with a gradual weight loss above 450°C, due to the breakdown of the crystal lattice of the clay minerals and salt inclusions and the onset of glass phase formation, without active chemical interaction and, as a consequence, without disintegration of the samples.

The refractory clay-based material has a large endothermic peak in the same temperature range, accompanied by absorption of a considerable amount of energy and a large weight loss. The process is associated with the breakdown of the crystal lattices of the kaolinite, hydromica, and salts; the conversion of kaolinite into metakaolin; and the onset of the formation of high-temperature phases, which ends with a sharp exothermic peak at 962.7°C. In the unmodified refractory clay, these processes occur at higher temperatures (519.3 and 968.7°C) than in the modified clay (502.5 and 962.7°C) and are accompanied by absorption of considerably more energy (303.6 against 124.8 J/g). This probably led to disintegration of the NaCl-free refractory clay and metakaolin samples. The modified refractory clay samples remained intact,



**Fig. 2.** Thermal analysis ((1–3) DTA and (4–6) TG) results for the samples based on (1, 4) refractory clay, (2, 5) bentonite clay + NaCl, and (3, 6) refractory clay + NaCl.

but the metakaolin samples were found to have large cracks and chips. The strength of the metakaolin samples fired in the muffle furnace is an order of magnitude lower than that of the refractory clay samples (Fig. 1). This may be due to the reactivity of NaCl in the presence of H<sub>2</sub>O vapor, which is released as a result of the decomposition of kaolinite crystals in the refractory clay and activates interphase chemical processes, while metakaolin is free of water [14].

Turning to a model proposed by Anenkov and Ivashutenko [15] for interpreting the sintering behavior and modification of ceramics in a high-frequency electromagnetic field, we can explain the sintering behavior of the clay-based materials in the presence of NaCl as a mineralizing salt. The moistening of the aluminosilicate material with a NaCl solution, which concentrates in intergranular spaces, is accompanied by energy release (due to high dielectric losses) and by the formation of a liquid phase [14]. Thermal diffusion ensures rapid sintering of the entire material [15]. The presence of NaCl stimulates the formation of a liquid phase and interphase interactions. This prevents disintegration of the refractory clay samples and ensures effective sintering of the material. In the case of the metakaolin sample, no effective sintering was detected, most likely because of the absence of water of crystallization, which was released during the heat treatment of kaolinite as a result of the breakdown of its crystal structure in the temperature range 450–

600°C [16] and which was necessary for the formation of new phases in the presence of NaCl [14].

Such processes should occur in the bentonite clay samples as well. Since transformations in bentonite clay proceed less actively at higher temperatures, because the homopolar layered montmorillonite is less active than the heteropolar kaolinite, the bentonite clay samples remain intact during rapid heating.

X-ray diffraction characterization of the microwave-sintered samples indicated the presence of a nanometer-scale phase structure of the material (Table 1), which accounts for the high strength of the samples fired in the microwave oven. The bentonite clay-based material was found to contain up to 40% glass phase, responsible for its increased strength.

The microstructure of the fired samples was examined on an electron microscope (Fig. 3). The bentonite clay-based material is seen to contain flaky Al<sub>2</sub>SiO<sub>5</sub> aluminosilicate particles evenly distributed throughout the sample. In the refractory clay, the aluminosilicate is present in the form of small inclusions.

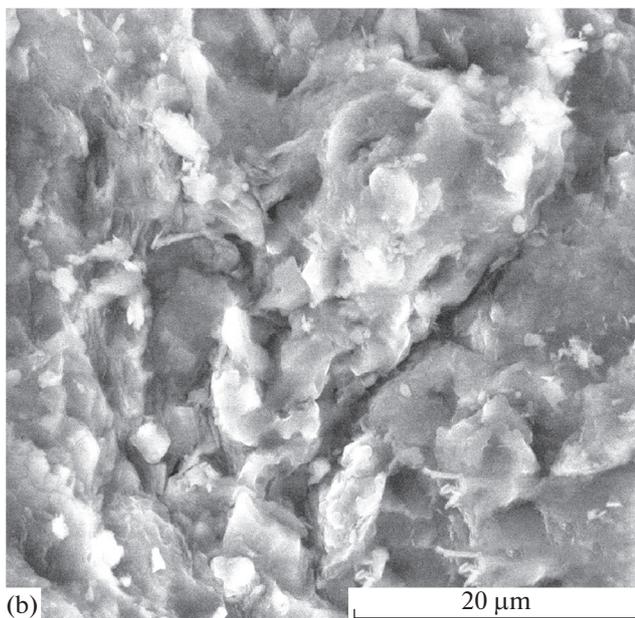
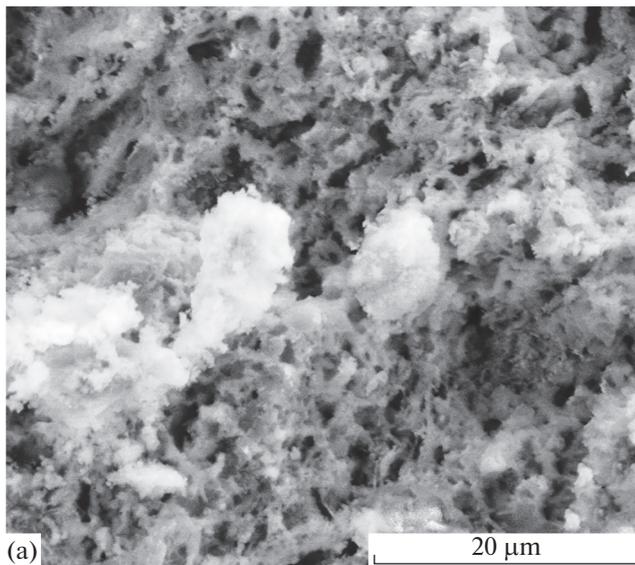
## CONCLUSIONS

The present results demonstrate the following:

aluminosilicates from natural clays with various mineralogical compositions can be sintered in a microwave field;

**Table 1.** Phase composition of the samples fired in the microwave oven

Composition	Phases identified	Weight percent	Crystallite size, nm
Bentonite clay + NaCl	SiO <sub>2</sub>	1.6	>100
	NaAlSi <sub>3</sub> O <sub>8</sub>	22.6	35.53
	Na <sub>7.5</sub> (Al <sub>7.2</sub> Si <sub>8.8</sub> O <sub>32</sub> )	37.4	30.33
	Al <sub>2</sub> SiO <sub>5</sub>	38.5	22.40
	Trace levels of NaAlO <sub>2</sub> , MgSiO <sub>3</sub> , and Na <sub>2</sub> SiO <sub>3</sub>		
Refractory clay + NaCl	Al <sub>2</sub> O <sub>3</sub>	19.5	6.39
	SiO <sub>2</sub>	63.4	63.28
	Al <sub>2</sub> SiO <sub>5</sub>	17.1	3.63



**Fig. 3.** Structure of fracture surfaces of the microwave-sintered samples (a) based on bentonite clay and NaCl and (b) based on refractory clay and NaCl.

in the case of both convective and microwave heating, the sintering process depends on the mineralogical composition of the material;

the sintering process is influenced by the presence of a component (the polar salt NaCl in this study) that activates interphase interactions in the starting mixture;

the presence of NaCl in refractory clay lowers the temperature of its phase transition during sintering and reduces its energy;

the presence of NaCl during microwave sintering leads to the formation of a nanometer-scale crystalline phase structure of the material;

microwave sintering of bentonite clay in the presence of NaCl leads to the formation of a sodium aluminosilicate glass phase together with a nanometer-scale crystalline phase; and

the strength of the samples prepared using microwave heating considerably exceeds that of the samples obtained using convective heating.

Investigation of sintering and processes related to fundamental aspects of the formation of the structure of materials in a microwave field is necessary for the development of energy-saving and environmentally friendly technology for the fabrication of fired materials. Research in this direction will allow one to obtain materials with improved performance and utilize widespread and often low-grade clay raw materials for the fabrication of high-strength ceramics.

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