

## ФИЗИКО-ХИМИЧЕСКОЕ ИЗУЧЕНИЕ КАОЛИНА МЕСТОРОЖДЕНИЯ ЖУРАВЛИНЫЙ ЛОГ (РОССИЯ). ЧАСТЬ 2

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*Изучены спектры ядерного магнитного резонанса с вращением под магическим углом (ЯМР ВМУ) обогащенного каолина месторождения Журавлиный Лог (Челябинская область, Россия) и продуктов его нагревания. В исходном каолине сильный сигнал  $^{29}\text{Si}$  наблюдался при  $-91,2$  ppm, который соответствовал характерному резонансу слоистой силикатной структуры, не содержащей Al тетраэдров ( $Q^3(0Al)$ ). После нагревания до  $800$  °C центр сигнала Si смещался к  $-102,9$  ppm. Пик становился шире, частично асимметричным, что могло указывать на разупорядоченную слоистую структуру метакаолина ( $Q^3$ ). При  $900$  °C центр спектральной линии находился при  $-106,8$  ppm ( $Q^4$  Si), что соответствовало присутствию аморфного кремния или кристобалита. Спектр  $^{27}\text{Al}$  ЯМР исходного каолинита состоял из единственной острой линии с центром при  $1,3$  ppm, отнесенной к  $Al^{VI}$ . Тепловая обработка выше  $500$  °C приводила к частичному разрушению слоистой структуры; появлялись две новые линии при  $58,1-60,2$  и  $29,0-32,9$  ppm, которые соответствовали атомам  $Al^{IV}$  и  $Al^V$  соответственно. Интенсивность сигнала  $Al^{IV}$  быстро возрастала. Исходный каолин имел остроугольные частицы псевдогексагональной формы, которые указывали на высокую упорядоченность структуры минерала. С повышением температуры обработки ( $800-1200$  °C) чешуйки становились более округленными, а при  $1000-1200$  °C наблюдалась их агломерация. По данным дилатометрической кривой каолина, в интервалах  $500-650$  °C и  $630-880$  °C наблюдалась небольшая усадка, отнесенная к дегидроксилированию каолинита и структурной перестройке метакаолинита соответственно с последующим переходом в Si-Al шпинель выше  $900$  °C.*

**Ключевые слова:** каолин, каолинит, Журавлиный Лог, метакаолинит, ядерный магнитный резонанс, дилатометрия, морфология

## THE PHYSICOCHEMICAL INVESTIGATION OF THE ZHURAVLINY LOG KAOLIN. PART 2

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*MAS NMR spectra of concentrated kaolin of the Zhuravliny Log deposit (Chelyabinsky district, Russia) and its heated products were studied. In a raw concentrated kaolin, a sharp absorption of  $^{29}\text{Si}$  NMR was observed at  $-91.2$  ppm, which corresponded to the characteristic signal of layered structure in silicates with no Al tetrahedra ( $Q^3(0Al)$ ). In the heated at  $800$  °C samples, the center of the Si resonance shifted to  $-102.9$  ppm. The peak became broader and partially asymmetric that might ascribe the disordered layered structure of metakaolin ( $Q^3$  state). At  $900$  °C the spectral line center was at  $-106.8$  ppm ( $Q^4$  Si) related to the presence of amorphous  $\text{SiO}_2$  or cristo-*

*balite. The  $^{27}\text{Al}$  NMR spectrum of a raw kaolinite consisted of only a single sharp resonance centered at 1.3 ppm which was assigned to  $\text{Al}^{\text{VI}}$ . Heat treatment at a temperature above 500 °C led to the partial destruction of the layered structure. Two new lines appeared at 58.1–60.2 and 29.0–32.9 ppm which were attributed to both Al atoms in tetrahedral and penta-coordinated positions, respectively. The signal intensity of  $\text{Al}^{\text{IV}}$  peak increased rapidly. The raw kaolinite had particles with angular edges of pseudo-hexagonal form which suggested a well-ordered mineral. The burning temperature increasing (800–1200 °C), flakes got the more rounded boundaries. At 1000–1200 °C flakes were agglomerated. According to the dilatometry curve for kaolin, in 500–650 °C and 630–880 °C intervals there was a small shrinkage which was related to dehydroxylation of kaolinite and structural reorganization of metakaolinite, respectively, with the subsequent transformation into the Si-Al spinel phase above 900 °C.*

**Key words:** kaolin, kaolinite, Zhuravliny Log, metakaolinite, MAS NMR, dilatometry, morphology

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## INTRODUCTION

Earlier [1], there were studied chemical and dispersion characteristics of the Zhuravliny Log kaolin, its dehydroxylation, and phase formation by thermal, X-ray analysis, and infrared spectroscopy. It was of interest to find out whether pentacoordinated aluminum  $\text{Al}^{\text{V}}$  is present during the thermal transformations of kaolin. Al and Si in different forms stay accompanied by oxygen atoms but their coordination number and therefore coordination polyhedrons may change. First, it concerns aluminum ions. There are two points of view. Authors [2, 3] discussed the possibilities of only two  $^{27}\text{Al}$  signals corresponding to  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$ . The most part of researchers [4-11] reported three  $^{27}\text{Al}$  resonances for tetrahedral ( $\text{Al}^{\text{IV}}$ ), penta-coordinated ( $\text{Al}^{\text{V}}$ ) and octahedral ( $\text{Al}^{\text{VI}}$ ) coordination.

The magic angle spinning nuclear magnetic resonance (MAS-NMR) techniques for  $^{27}\text{Al}$  is an effective method of coordination and local structure study as differently coordinated Al atoms have different chemical shifts. It is known that  $^{27}\text{Al}$  shift differences among  $\text{AlO}_6$  (octahedral ion, O-positions) at 0–20 ppm and  $\text{AlO}_4$  (tetrahedral ion, T-positions) at 50–80 ppm, and  $\text{AlO}_5$  (penta-coordinated species, P-positions) at 20–50 ppm [6, 7]. L. Andrini et al. [10] found by XANES (X-ray Absorption Near Edge Structure) not only IV, V, and VI coordination, but also III coordination for one of investigated kaolin. Al had octahedral coordination in kaolinite, and  $\text{Al}^{\text{III}}$ ,  $\text{Al}^{\text{V}}$ ,  $\text{Al}^{\text{VI}}$  coordination were identified for metakaolin. Finally,  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$  were found in the spinel type aluminosilicate

and mullite. This knowledge will help to understand the relationship between kaolin structure and its acid-activation reactivity [12-15].

The practical use of any kaolin demands some information on volume and crystal morphology changes during the heating. So, the aim of this study was to determine a distribution Al atoms between differently coordinated positions using MAS NMR spectroscopy and to characterize the dilatometric behaviour and morphology of the Zhuravliny Log kaolin. The knowledge of zeta potential that is necessary to value the kaolin application possibility in a casting slipping was characterized earlier [12-16].

## MATERIALS AND EXPERIMENTS

The mineral composition of a raw kaolin of the Zhuravliny Log deposit (Chelyabinsky region, Russia) and oxide content of a concentrated samples were described earlier [1].

$^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR spectra were obtained by magic angle spinning ( $54^\circ 44'$ ) using a BRUKER AVANCE 400 spectrometer operating at 104.23 MHz for  $^{27}\text{Al}$  and 79.46 MHz for  $^{29}\text{Si}$ . Rotation frequencies of 10 and 12 kHz were used for the  $^{27}\text{Al}$  (400 accumulations) and  $^{29}\text{Si}$  (1800 accumulations) MAS spectra, respectively.  $^{27}\text{Al}$  and  $^{29}\text{Si}$  chemical shifts were determined using 1 M  $\text{Al}(\text{NO}_3)_3$  solution and 10%  $(\text{CH}_3)_4\text{Si}$  solution, relatively, as the external references having chemical shift at 0 ppm [3].

The particle morphology of the kaolin sample was analyzed using the micrographs (SEM) obtained by a scanning electron microscope Tescan VEGA 3 SBH.

The thermal irreversible changes of samples were determined by the dilatometer measurements for pre-dried compacted samples from room temperature up to 1050 °C at a heating rate of 10 °C min<sup>-1</sup> in air atmosphere using Netzsch Dil402 PC.

## RESULTS

Fig. 1 shows <sup>29</sup>Si MAS NMR spectra of a raw concentrated kaolin and its heated products. In the first sample, a sharp absorption of <sup>29</sup>Si NMR was observed at -91.2 ppm with full-width-at-half-maximum (FWHM) of ~4 ppm, which corresponded to the characteristic signal of layered structure in silicates [3],

i.e., was also characteristic of layered silicates with no Al tetrahedra (*Q*<sup>3</sup>(0Al)) [4, 5]. It might indicate that Si was linked via oxygens to three other Si atoms in a three-dimensional network of SiO<sub>4</sub> tetrahedra [2]. In heated at 800 °C samples, the center of the Si resonance shifted to -102.9 ppm. The tetrahedral sheets began to change at that, the peak became broader and simultaneously partially asymmetric. FWHM increased to ~19 ppm, so, this peak might ascribe the disordered layered structure of metakaolin. Its shift might be caused by changes of bond-length, bond-angle, etc. Si in metakaolinite was dominantly present in *Q*<sup>3</sup> state [5].

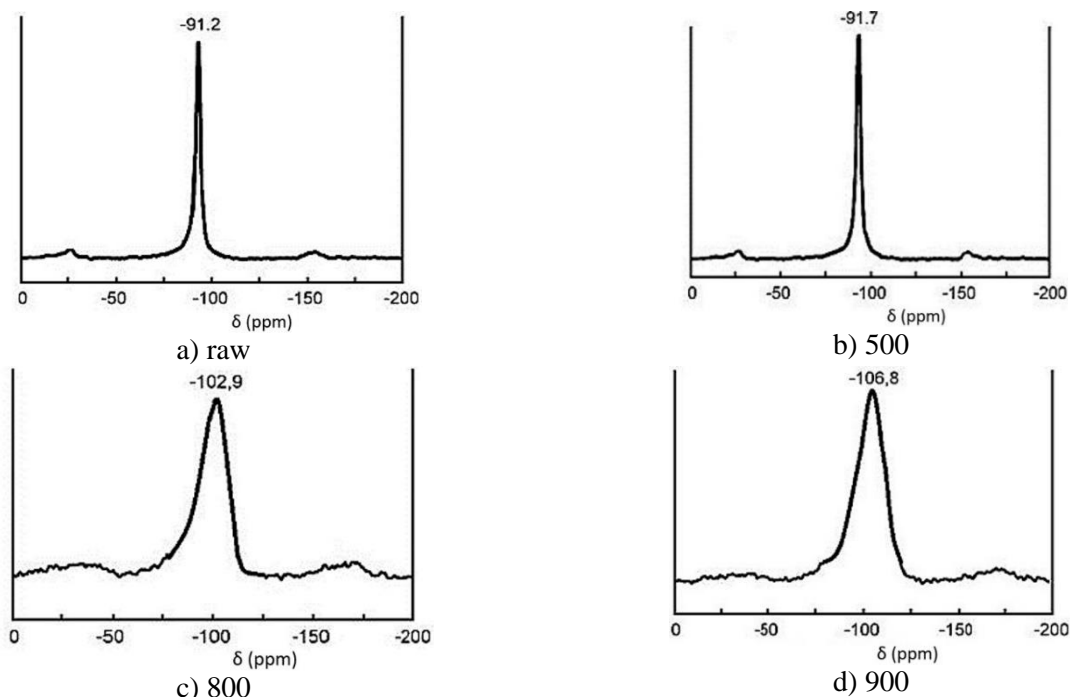


Fig. 1. <sup>29</sup>Si NMR-spectra of a raw concentrated kaolin (a) and its burned products at various temperatures, °C: 500 (b), 800 (c), 900 (d)  
Рис. 1. Спектры ЯМР <sup>29</sup>Si сырого концентрированного (a) и термообработанного при различных температурах каолина, °C: 500 (b), 800 (c), 900 (d)

With temperature growth a greater amount of amorphous SiO<sub>2</sub> began to emerge. At 900 °C the spectral line center was at -106.8 ppm that was characteristic of the *Q*<sup>4</sup> Si environments [11] related to the presence of amorphous SiO<sub>2</sub> or cristobalite (Si surrounded by four Si – Si(OSi)<sub>4</sub>).

As shown in Fig. 2, MAS NMR spectra of the <sup>27</sup>Al chemical shifts are significantly different at various temperatures.

NMR <sup>27</sup>Al spectra of samples of a raw concentrated kaolin and kaolin after heat treatment showed changes in the coordination of aluminum atoms in the structures. The <sup>27</sup>Al NMR spectrum of a raw kaolinite (a) consisted of only a single sharp resonance centered at 1.3 ppm which could be assigned to hexacoordinated

Al atoms (Al<sup>VI</sup>) in AlO<sub>6</sub> structure. This kind of spectrum was consistent with data on the natural kaolin structure, according to which aluminum is in an octahedral layer of silicate. Heat treatment at a temperature above 500 °C led to the partial destruction of the layered structure, the intensity of this line decreases, and in the spectrum (Fig. 1, c) two new lines appeared at 58.1-60.2 and 29.0-32.9 ppm which were attributed to both Al atoms in T- and P-positions, respectively. The peaks were rather well-resolved. Metakaolin contained approximately equal amounts of tetrahedral (Al<sup>IV</sup>), octahedral (Al<sup>VI</sup>) and penta-coordinated Al (Al<sup>V</sup>).

As the firing temperature increased, the ratio of intensities of these peaks changed. Part of the aluminum came out of its O-positions in the lattice and went

into T-positions. The reduction of the 29.0-32.9 ppm signal under further heating might indicate that penta-coordinated Al nuclei ( $Al^V$ ) were generated as an intermediate stage of transformation between  $Al^{VI}$  and  $Al^{IV}$ . Al-atoms in metakaolin might be in unsaturated and distorted state. The signal intensity of the 58.1-60.2 ppm

$Al^{IV}$  peak increased rapidly. The  $Al^{VI}$  peak apparently weakened, i.e., the  $AlO_4(OH)_2$  sheet of kaolinite collapsed and was reordered.

Fig. 3 shows SEM images of particles morphology for a raw concentrated kaolin and powders burned at 800, 1000, and 1200 °C, respectively.

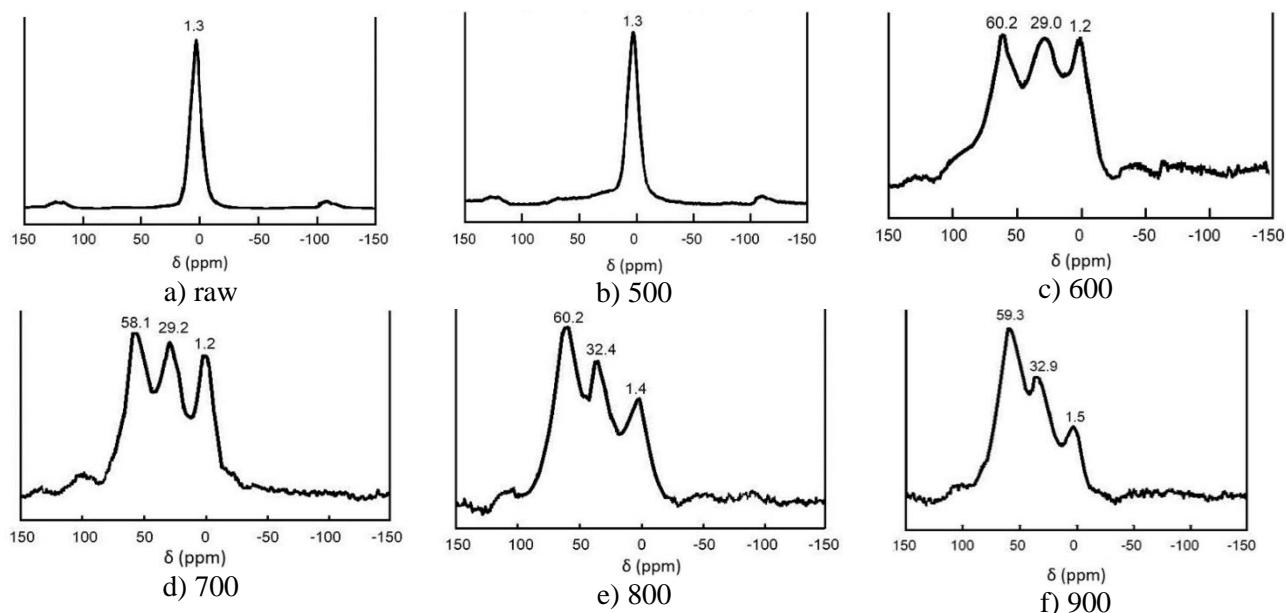


Fig. 2.  $^{27}Al$  NMR-spectra of a raw concentrated kaolin (a) and its burned products at various temperatures, °C: 500 (b), 600 (c), 700 (d), 800 (e), 900 (f)

Рис. 2. Спектры ЯМР  $^{27}Al$  сырого концентрированного (a) и термообработанного при различных температурах каолина, °C: 500 (b), 600 (c), 700 (d), 800 (e), 900 (f)

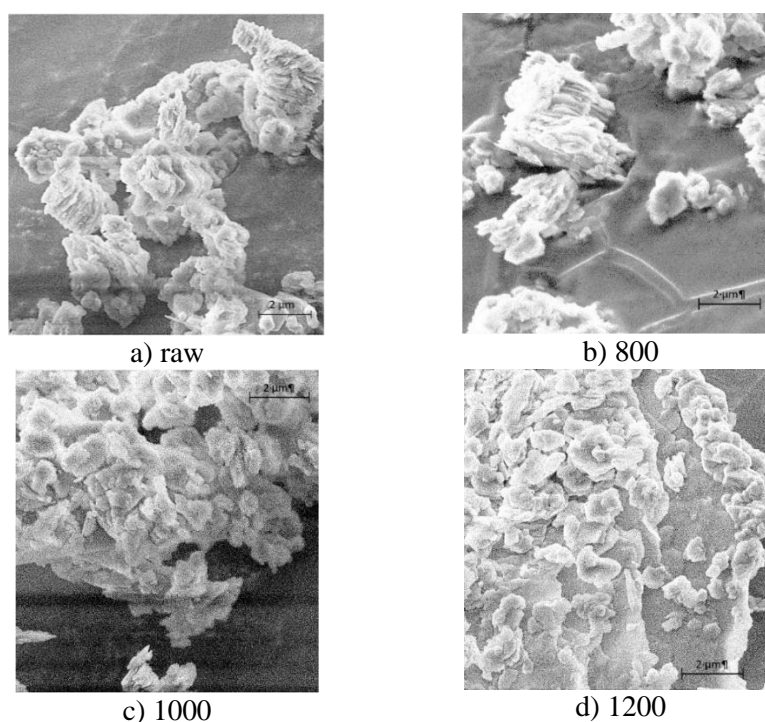


Fig. 3. SEM images of a raw concentrated kaolin (a) and its burned products at various temperatures, °C: 800 (b), 1000 (c), 1200 (d)  
Рис. 3. СЭМ-изображения сырого концентрированного (a) и термообработанного при различных температурах каолина, °C: 800 (b), 1000 (c), 1200 (d)

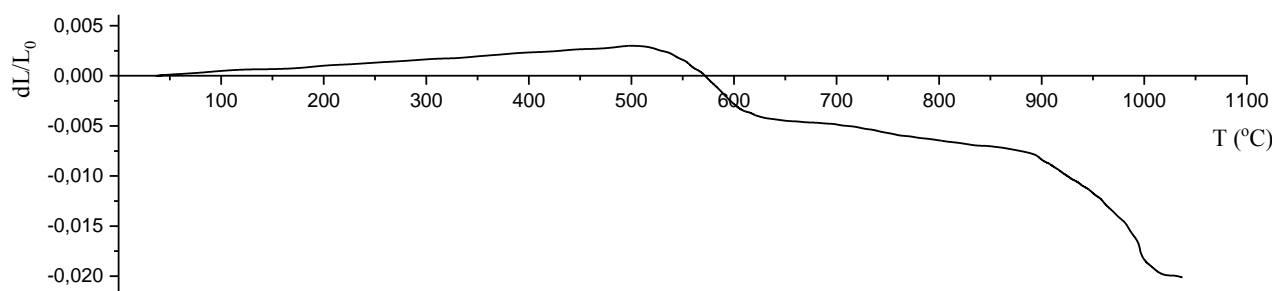


Fig. 4. Dilatometry curve for a raw concentrated kaolin  
Рис. 4. Дилатометрическая кривая сырого концентрированного каолина

The raw kaolinite showed particles with angular edges which suggested a well-ordered mineral. Most of initial particles were lamellar of pseudo-hexagonal form. The morphology did not exhibit significant differences as it was noted earlier [17-19]. Particles burned at 800 °C were also flaky with slight changes. The burning temperature increasing (800-1200 °C), flakes got the more rounded boundaries. At 1000-1200 °C, flakes were stacked one by one to form agglomerates.

The dilatometer measurements (Fig. 4) showed a sequence of linear changes for a raw concentrated kaolin sample.

A slight regular expansion was observed from room temperature up to 500 °C. Between 500 °C and 650 °C, kaolin showed a small contraction which was related to dehydroxylation of kaolinite and its transformation into metakaolinite. No expansion at about 570-580 °C which could indicate  $\alpha \leftrightarrow \beta$ -quartz inversion was observed because of a small quantity of the free quartz. A very slight shrinkage between 630 and 880 °C was believed to be caused by structural reorganization of metakaolinite with the subsequent transformation into the Si-Al spinel phase in the interval above 900 °C. A considerable contraction might also indicate the start of the sintering [13-20].

#### CONCLUSION

Si and Al atoms' coordination was studied by MAS NMR method. Transitions  $Al^{VI}$  (in a raw kaolinite up to 500 °C)  $\rightarrow Al^{VI} + Al^V + Al^{IV}$  (600–900 °C) with an essential dominance of  $Al^{IV}$  at 900 °C were noticed. Si atoms' environment was not practically changed under such conditions ( $Si^{IV}$ ), but layered structure ( $Q^3$ ) became amorphous ( $Q^4$ ). The morphology of kaolin's grains was described. The linear size changes of a sample under heating up to 1050 °C were analyzed. The shrinkage was related to kaolinite  $\rightarrow$  metakaolinite transition and to the subsequent formation of Si-Al spinel phase.

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*The authors declare the absence a conflict of interest warranting disclosure in this article.*

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