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NMR Study of Aluminium Coordination in Clays

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Abstract. This work is aimed at monitoring of Al ions coordination in clays and clay minerals by the nuclear magnetic resonance (NMR) spectroscopy. Knowledge of the clays structure is important for their use as raw materials in engineering practice. For further processing (e.g., preparation of geopolymers), the 5- and 4-fold coordination of oxygen around aluminium atoms is crucial, and therefore it is necessary to transform the original 6-fold coordinations of the Al ions by proper thermal treatment. The ^{27}Al isotope is suitable for NMR investigations as the spectral parameters (chemical shift and quadrupole interactions) are very sensitive to the surrounding (coordination, chemical bonding) of the resonating nuclei. NMR of ^{29}Si yields complementing information on structure. Magic angle spinning (MAS) technique was applied to measure spectra of selected clay samples.

Introduction

One of the most widespread materials which could be found in any corner of the world is clay. The large variety of the clays composition is the consequence of weathering of generally feldspars and micas under conditions of thermal, pressure and specifically humidity treatment. The explanation of the feldspars transformation is usually presented by the following equation (under time, water, pressure and temperature) [*Deer and Zussman*, 2001]:

$$\mathrm{Na_2O \cdot Al_2O_3 \cdot 6\ SiO_2 \rightarrow Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O + Na_2O + 4\ SiO_2} \qquad (1)$$

The main representative of clay is mineral kaolinite contained in rock kaolin which is used in engineering practice (geopolymers) [*Singh et al.*, 2005]. Structure of kaolinite clay is composed of tetrahedral silicate and octahedral aluminium layer which are connected with hydrogen bond. The original 6-fold coordination of oxygen around aluminium atoms depends on thermal and chemical treatment and can be changed to 5- or 4-fold coordination that are required for processing. NMR method is very sensitive to the ^{27}Al and ^{29}Si atoms surroundings (i.e., coordination) and their changes. Isotopes ^{27}Al and ^{29}Si were used for our NMR studies of selected clays, the parameters of nuclei are listed in Table 1.

Table 1. Nuclear properties.

Nucleus	Spin I	Gyromagnetic ratio $\gamma/2\pi$ (MHz/T)	Quadrupolar moment Q (barn)	Natural abundance (%)
^{27}Al	5/2	11.10	0.15	100.0
^{29}Si	1/2	−8.47	0.00	4.7

NMR of ^{27}Al

The most significant interactions affecting the nuclear spin system besides Zeeman interaction in external magnetic field are chemical shielding (chemical shift), dipole–dipole interaction and electric quadrupole interaction.

Hamiltonian operators of these interactions are described by relations [*Duer et al.*, 2002]:

$$\hat{H}_Z + \hat{H}_\sigma = -\gamma\hbar\hat{\boldsymbol{I}} \cdot (1 - \hat{\boldsymbol{\sigma}}) \cdot \boldsymbol{B_0}, \qquad (2)$$

where $\hat{H}_Z$ and $\hat{H}_\sigma$ denote Hamiltonians of Zeeman interaction and chemical shielding, γ is gyromagnetic ratio specific for each nucleus, $\hbar$ is reduced Planck constant, $\boldsymbol{B_0}$ is applied magnetic field, $\hat{\boldsymbol{I}}$ is (reduced) nuclear spin operator and $\hat{\boldsymbol{\sigma}}$ is second-rank chemical shielding tensor operator;

$$\hat{H}_{d-d} = -\frac{\mu_0}{4\pi}\gamma_I\gamma_S\hbar^2\left[\frac{\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{S}}}{r^3} - 3\frac{(\hat{\boldsymbol{I}}\cdot\hat{\mathrm{r}})(\hat{\boldsymbol{S}}\cdot\hat{\mathrm{r}})}{r^5}\right] \tag{3}$$

describes dipole–dipole interaction between spins I and S. The permeability of vacuum is μ_0, $\gamma_{I,S}$ are gyromagnetic ratios of nuclei with spins I and S, $\boldsymbol{r}$ is radius vector between spins I, S and $\hat{\boldsymbol{I}}$, $\hat{\boldsymbol{S}}$ are nuclear spin operators. Hamiltonian of electric quadrupolar interaction is described by formula

$$\hat{H}_Q = \frac{e\,Q}{6I(2I-1)\hbar}\hat{\boldsymbol{I}}\cdot e\boldsymbol{q}\cdot\hat{\boldsymbol{I}} \tag{4}$$

where $e\boldsymbol{q}$ is a tensor of electric field gradient (EFG) at nucleus (a symmetric second rank tensor), $\hat{\boldsymbol{I}}$ is nuclear spin operator, Q is nuclear quadrupolar moment and e is electron charge. The total spin Hamiltonian is a sum of all contributions ($\hat{H} = \hat{H_Z} + \hat{H}_\sigma + \hat{H}_{d-d} + \hat{H}_Q$).

The Zeeman interaction H_Z causes splitting of the spin system into $2I+1$ equidistant energy levels which are shifted due to the chemical shift Hamiltonian H_σ. The resonance frequency is proportional to this splitting and NMR spectrum of magnetically equivalent sites in single crystal consists of one line for each inequivalent position in the structure.

In clays and in magnetic fields usually applied in NMR experiments, magnetic interaction $H_Z + H_\sigma$ is much stronger than the electric quadrupolar interaction described by the Hamiltonian H_Q and perturbation theory can be used to calculate stationary states and energies of the total Hamiltonian of the spin system. The result of the first order of the perturbation theory is that the $2I+1$ energy levels become non-equidistant and $2I$ spectral lines appear in the spectrum of magnetically equivalent sites in single crystal. The resonance frequencies of an isotope with non-integer spin number correspond to the central transition (between the levels of magnetic quantum numbers $-1/2$ and $+1/2$, the energy difference being the same as in unperturbed system) and satellite transitions (between the other levels). The second order of the perturbation theory of the quadrupolar Hamiltonian gives also a correction of the frequency of the central transition [*Fitzgerald and Paul*, 1999].

As a result of the chemical shielding anisotropy and the electric field gradient, the resonance frequencies depend on the orientation of the crystal with respect to the external static magnetic field. In a powder sample, a distribution of orientations needs to be considered, the spectral lines get broader and have a typical powder patterns lineshape [*MacKenzie and Smith*, 2002]. The width of ^{27}Al NMR spectra in clays can be significant mainly due to the quadrupolar interaction and may be of the order of magnitude of MHz.

The chemical shielding of ^{27}Al depends strongly on the coordination of the aluminium atom. The chemical shifts are typically 0–5 ppm for 6-fold coordination and 50–60 ppm for 4-fold coordination (referenced to the resonance frequency of Al in $\mathrm{Al(NO_3)_3}$ dissolved in water as 0 ppm) [*Kinsey et al.*, 1985; *Lambert et al.*, 1989; *MacKenzie*, 2004]. Spectral lines are further broadened due to the distribution of parameters depending on the surroundings of the resonating nucleus, such as the chemical shift and EFG tensors.

NMR of ^{29}Si

^{29}Si nucleus has spin number of 1/2 and zero quadrupolar moment, therefore only magnetic interaction affects resonance frequency. However, the low abundance of the isotope ^{29}Si and its long spin-lattice relaxation times are disadvantages in comparison with ^{27}Al NMR spectroscopy, therefore this nucleus is used less often and rather as a complementary method.

MAS NMR

Static spectra of powder samples have often broad and overlapping spectral lines and low intensities because of the effects of anisotropy of the chemical shift, dipole–dipole and quadrupolar interaction. Magic angle spinning technique (MAS) is used to partially average these interactions and narrows spectral lines. The sample is spun in a rotor under magic angle (54° 44') to the external field [*Duer et al.*, 2002; *Massiot et al.*, 1994]. The anisotropies of quadrupolar interaction are not usually fully averaged using frequency of spinning of the order of magnitude of 10^1 kHz which can be achieved by current technology [*Frydman and Harwood*, 1995]. If the frequency of rotation is lower than the width of the static spectrum, spinning sidebands occur in the spectrum. The envelope of MAS spectrum corresponds to shape of the static spectrum and the distance between two spinning sidebands is equal to the frequency of rotation.

The MAS ^{27}Al NMR spectroscopy focuses mainly on central transitions, the main transition resonating frequency depends on chemical shift and quadrupole interaction.

Experimental

Samples

We have tested two series of samples.

1st series: Slate clay is thermally transformed, usually fired in rotary kilns on temperatures slightly below 1200 °C and under the melting temperature. The exact temperature depends on clay quality and kaolinitic clays are usually used. The chosen sample identified as L05 was industrially supplied by České lupkov zvody, Nové Strašecí. The material L05 is a byproduct of the slate clay fabrication recollected on the cleaning filters of the rotary kiln. The main advantage of this material is in a very small particle sizes which are smaller than 10 μm.

The studied sample L05 was compared with the same material (L05) but treated in laboratory kiln at 750 °C, labeled in Table 2 as L05 750. The third sample L05 750 served as a matrix material for geopolymer reaction. The Table 2 presents this material under the name of L05 750 react.

2nd series: The second tested material was slate clay from the Zbůch deposit (West Bohemia region, Czech Republic). There are a huge amount of dumps of the extracted, layered material, remaining after coal mining. This specific material contained a proportion of coal which has been slowly burning over the last 50 years. The coal burning was sufficient for the thermal activation of the slate clay, which naturally changed the aluminum-ions coordination.

The naturally activated slate clay samples from the Zbůch, West Bohemia region were measured. In this large deposit area (800×600 m), samples were taken from three different parts of the heaped slate clay (L_1, L_2 and L_3). The sampling points were distanced by more than 300 m, and the selected points also differed in the color of the material from light to dark red. Differences in color (L_{wh}, L_{bl}, L_{dr}) mean collection of samples from different layers of the heaped clay, e.g., black with dominant part of the unburned carbon.

The list of the studied samples is given in Table 2.

Table 2. Studied samples.

Sample notation	Origin	Treatment	Notes (sample characterization)
L05	Kaolin from Kamenná Panna deposit	Industrial	Supplied by ČLUZ Nové Strašecí
L05 750	Kaolin from Kamenná Panna deposit	Following laboratory treatment	Secondary laboratory treatment at 750° C
L05 750 react	Kaolin from Kamenná Panna deposit	Geopolymer reaction	Reaction with aqueous alkali solution
L_1, L_2, L_3, L_{wh}, L_{bl}, L_{dr}	Zbůch deposit	none	See “Samples”

NMR

Measurements were performed on spectrometer Bruker Avance 500 (magnetic field 11.7 T) at ambient temperature. ^{27}Al resonance is 130.3 MHz and ^{29}Si is 99.3 MHz in this field. Standard for magic angle adjustment was KBr. Samples were inserted in 4 mm rotors, frequency of rotation was 14 kHz. The Free Induction Decay (FID) signal after one pulse was detected. The typical settings used for ^{27}Al spectra were: pulse with the length of 2 μs and with the tipping angle $\pi/12$ [*Massiot et al.*, 1990], number of scans 1600, delay between scans 5 s.

Acquisition parameters for ^{29}Si: $\pi/2$ pulse with the length of 2 μs, dwell time 5 μs, time domain 4096 points, number of scans 10240, delay between scans 5 s, digital quadrature detection mode of acquisition. The time domain signal was transformed to frequency domain by Fast Fourier Transform (FFT). Phase and baseline corrections were applied either by our purpose-made software or Bruker Topspin packet. Resulting ^{27}Al spectra are given in Figures 1 and 2, ^{29}Si spectra in Figure 1.

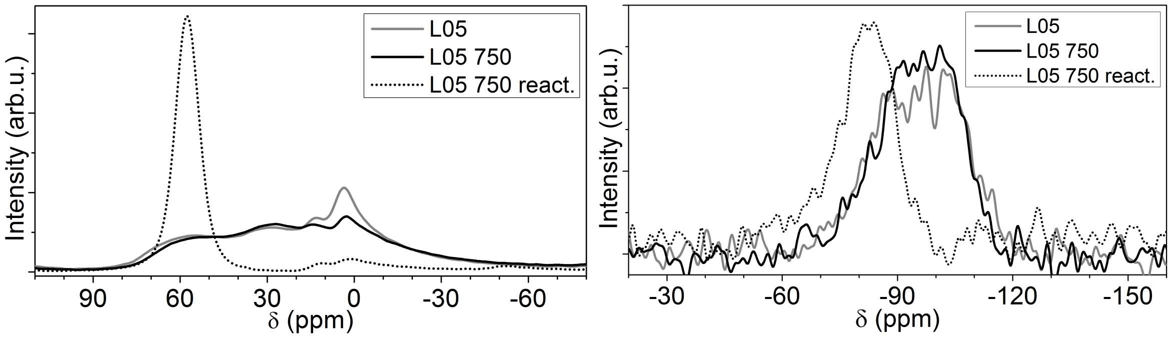

Figure 1. Spectra of sample series No. 1: ^{27}Al MAS NMR (left) and ^{29}Si MAS NMR (right).

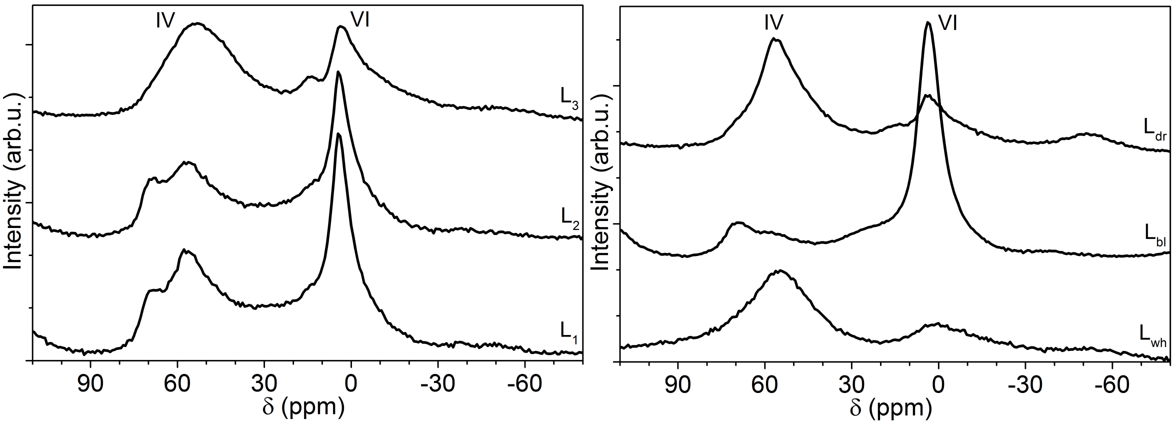

Figure 2. ^{27}Al MAS NMR spectra of sample series No. 2.

Analysis of spectra

Sample series 1

The view of figure of ^{27}Al MAS NMR spectra (see Figure 1) gives directly the qualitative information on the presence of different coordination of aluminium. It is clearly seen that sample L05 contains all investigated coordinations and that the sample L05 750 has a higher content of 4- and 5-fold coordination. The 4-fold coordination dominates in sample L05 750 react, i.e., after geopolymer reaction. Also ^{29}Si MAS NMR spectra (Figure 1) indicate significant differences between L05, L05 750 and L05 750 react.

A quantitative analysis of ^{27}Al MAS NMR spectra of clays is difficult because of complicated phase and baseline correction for such a broad spectral shapes, broadened in comparison with homogeneous crystallites by distribution of spectral parameters, and also because of overlap of spectral lines belonging to the different coordinations. We processed the spectra uniformly to find out actual differences between the samples.

The quantitative analysis of ^{27}Al spectra of sample series 1 was performed as a decomposition into six simple lines (Lorentzians raised to fitted power, the line positions and power in the fit were common for all three spectra). As an example, the decomposition of spectrum for L05 750 sample is shown in Figure 3. Calculated relative areas of deconvolution lines for these sample are given in Table 3.

Sample series 2

The 4- and 6-fold coordinations predominate in comparison with 5-fold coordination as show ^{27}Al MAS NMR spectra in Figure 2. A quantitative analysis for this sample series was performed by two ways. In the first case the spectra of all samples were processed by Singular Value Decomposition (SVD) method. Using SVD method, four simple spectral components were constructed and then their relative contributions to the spectra were found. Two of these components were assigned to aluminium in tetrahedral coordination, the other two to octahedral sites. The results suggested that the basic profiles of spectra were captured but not the details. The obtained relative amounts of the 4-fold and 6-fold coordinations are shown in Table 4.

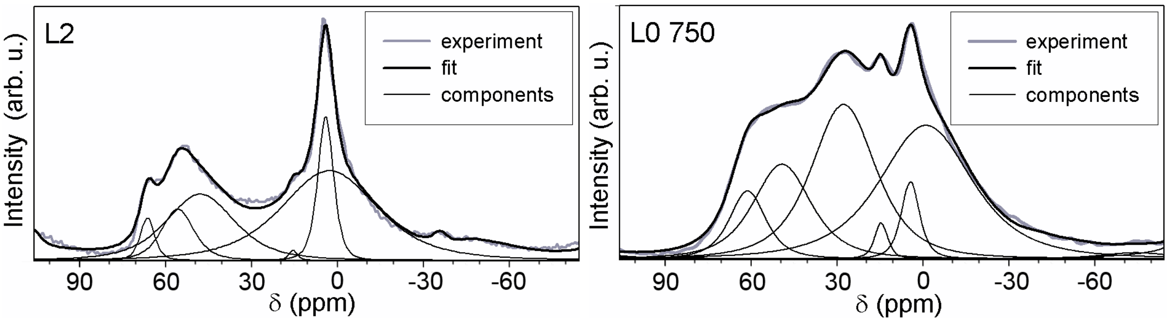

Figure 3. Deconvolution of ^{27}Al MAS NMR spectra of samples L_2 (left) and L05 750 (right).

Table 3. Percentage of coordinations in the sample series No. 2 obtained by SVD method and direct decomposition (DIRECT), see text.

	SVD		DIRECT	
	Al^{VI}(%)	Al^{IV}(%)	Al^{VI}(%)	Al^{IV}(%)
L_1	71	29	62	38
L_2	71	29	62	38
L_3	59	41	46	54
L_{wh}	58	42	—	—
L_{bl}	88	11	—	—
L_{dr}	45	54	—	—

Table 4. Relative areas and amount of coordination in percent for sample series No. 1.

		L05	L05 750	L05 750 react
	σ (ppm)	Rel. area (%)	Rel. area (%)	Rel. area (%)
Line 1	−4.5	31	38	9
Line 2	3.2	14	4	2
Line 3	14.0	2	2	0
Line 4	28.0	32	31	0
Line 5	51.0	11	17	89
Line 6	63.0	11	8	0
1+2+3	Al^{VI}(%)	47	45	11
5+6	Al^{IV}(%)	21	25	89
4	Al^{V} (%)	32	31	0

For samples L_1, L_2 and L_3 was made direct decomposition into Lorentz curve lines besides the SVD analysis. The decomposition of L_2 sample is shown in Figure 3. The numerical results were obtained from integration and percentage distribution of each coordinations for all sample series is in Table 4.

Conclusions

NMR spectra show structural differences between measured samples. The influence of laboratory thermal and chemical treatment/geopolymer reaction is seen on the sample series 1, where the amount of 4-fold coordination of Al rises. This conclusion is confirmed by changes in ^{29}Si NMR spectra. The similarities and differences in sample series 2, naturally activated by coal burning, are pronounced in ^{27}Al spectral shapes.

For quantitative analysis two methods were used. The results validate the conclusions from qualitative analysis of spectra. The SVD methods seems to be suitable for investigation of larger set of samples for comparison of basic differences. The DIRECT method is appropriate for comparison within smaller set of similar or closely related samples.

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References

W. A. Deer, J. Zussman, R. A. Howie: Framework Silicates: Feldspars, ROCK FORMING MINERALS, Volume 4A, Geological Society, 2001, ISBN 1862390819, 9781862390812.

M. J. Duer, et al.: Solid-State NMR Spectroscopy, Principles and Applications, Blackwell Science, UK, 2002.

J. J. Fitzgerald, S. M. de Paul: Solid State NMR Spectroscopy of Inorganic Materials: An Overview, in Solid State NMR Spectroscopy of Inorganic Materials, ACS Symposium series, Washigton, p. 2–133, 1999, ISBN 0-8412-3602-X.

L. Frydman, J.S. Harwood: Isotropic Spectra of Half-Integer Quadrupolar Spins from Bidimensional Magic-Angle Spinning NMR, J. Am. Chem. Soc., Volume 117, p. 5367–5368, 1995.

R. A. Kinsey, et al.: High resolution aluminium-27 and silicon-29 nuclear magnetic resonance spectroscopic study of layer silicates, including clay minerals, Am. Mineral., Volume 70, p. 537–548, 1985.

J. F. Lambert, et al.: Revisiting Kaolinite Dehydroxylation: A ^{29}Si and ^{27}Al MAS NNR Study, J. Am. Chem. Soc., Volume 111, p. 3517–3522, 1989.

K. J. D. MacKenzie: Solid State multinuclear NMR: a versatile tool for studying the reactivity of solid systems, Solid State Ionics 172, p. 383–388, 2004.

K. J. D. MacKenzie, M. E. Smith: Multinuclear Solid State NMR of Inorganic Materials, Pergamon, Chapter 2, 2002, ISBN 0-08-043787-7.

D. Massiot, B. Cote, F. Taulelle, J.P. Coatures: ^{27}Al MAS NMR of Crystalline and Amorphous Materials, in Application of NMR Spetroscopy to Cement Sciences, Gordon and Breach Science Publishers, p. 153–169, 1994, ISBN 2-88124-965-5.

D. Massiot, et al.: A quantitative Study of ^{27}Al MAS NMR in Crystalline YAG, J. Magn. Res., Volume 90, p. 231–242, 1990.

P. S. Singh, M. Trigg, I. Burgar, T. Bastow: Geopolymer formation processes at room temperature studied by ^{29}Si and ^{27}Al MAS-NMR, Materials Science and Engineering A, Volume 396, p. 392402, 2005.