ALUMINIUM COMPLEX IN COAL

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ABSTRACT
On the basis of solid-state aluminium-27 nuclear magnetic resonance measurements a new organo-aluminium complex in coal substance was discovered in the solid extracts obtained both from the Ostrava-Karviná bituminous coal and the North Bohemian Basin brown coal. In the ^{27}Al MAS NMR spectra it was found that the significant chemical shift at 13.6–14.6 ppm corresponds with that obtained for the aluminium hexaphenoxide complex (14.2 ppm). Therefore, organo-aluminium complex with hexa-coordination to oxygen is present in coal substance.

KEYWORDS: aluminium, complex, solid-state NMR, bituminous coal, brown coal, Czech part of the Upper Silesian Basin, North Bohemian Basin

1. INTRODUCTION

As coal is a significant raw material, a deeper knowledge of chemical composition of coal substance is always an important task. Complex compounds with organic ligands are the least researched among coal substance compounds, and our knowledge in this area lacks clarity. During its formation and ageing, coal passed through processes in laboratory practically unfeasible and the unknown complex compounds could be formed within the coal structure. To be able to study complexes in the organic part of coal, it is necessary to take into consideration the concentration of metal elements bound in the coal substance of the coal being considered, the so-far discovered forms of their occurrence, the affinity of these elements to both the inorganic part and organic substance of coal, the ability of the elements in question to form complexes and the possibilities of identifying complex compounds.

An extensive overview of the hitherto discovered forms of the occurrence of elements in coal (Bouška et al., 2000) shows further unspecified complex compounds in the organic part of coal in the case of Be, Cu, Ge, U and W, and there are probably also porphyrine complexes with the central atoms of Ga, Mn, Ni and V. Another work (Straka and Náhunková, 2004) reports phtalocyanine complexes as possible forms of occurrence of Al, Co, Cu, Fe, Ga and V both in bituminous and brown coal.

For the study of coal complexes, it is aluminium within the group of metal elements that seems to be important and whose ability to form organic complexes arises from its electron configuration and sp^3 and sp^{3}d^2 hybridization (exceptionally sp^{3}d hybridization) of valency orbitals providing 4 and 6 σ-

bonds (exceptionally 5 ones). Aluminium belongs to the majority metal elements in coal; it forms the mineral of organic class, mellite, in the coal substance (Bouška et al., 2000; Bouška and Pešek, 1999); it, in general, creates a range of complexes with inorganic ligands and compounds with hydrocarbons (Shriver and Atkins, 1999), tetrahedric complexes with alcoholic, etheric and ketonic ligands (Gažo, 1981), and also Al-phenoxide (CRC Handbook of Chemistry and Physics, Section 4, 1993-1994). Further, the formations of OH-Al-humate complexes and OH-Al-humate-montmorillonite complexes were studied (Violante et al., 1999). It was found that OH-Al-humate complexes formed by different addition sequences of components showed different physicochemical and chemical properties; further, pre-formation of the hydroxyl-Al-humate polymers added to montmorillonite increased an extent of interlayering of humic acid into montmorillonite surfaces at pH 7.0.

In the given context, it is the affinity of the elements to the inorganic and organic part of coal that is important. Based on their affinity, it is possible to divide the elements principally into three groups: elements with a considerable affinity to organic substance, with a considerable affinity to inorganic part, and elements with affinity to both organic and inorganic coal substance. For the study of complexes with organic ligands, only those elements of the first and the third group that also show the capability to form complexes are suitable.

Among others, aluminium is one of the elements with a highly significant affinity to organic substance, whose concentration both in brown and bituminous coals is often relatively quite high (0.5–1 % of Al) (Klika and Kolomazník, 2000) and whose compounds

are identifiable by instrumental methods (X-ray diffraction, X-ray fluorescence spectroscopy together with organic elemental analysis, solid-state aluminium-27 nuclear magnetic resonance spectroscopy, infrared spectroscopy). For the identification of Al-complexes, the magnetic properties of the Al-atom are important, mainly the nuclear spin (I=5/2), the quite high gyro-magnetic ratio (6971.10^4 rad s^{-1} T^{-1}) and relative sensitivity (3.0424 at constant resonant frequency (Spasov and Kamenov, 1981), the nuclear quadrupole moment of 14.03 fm^2, and also the 100% presence of the ^{27}Al isotope in natural aluminium (Spasov and Kamenov, 1981; CRC Handbook of Chemistry and Physics, Section 9, 1993-1994). Thus, one suitable method for the observation of Al-complexes in coal is the solid-state ^{27}Al MAS NMR based on the measurement of chemical shifts in dependence on the chemical environment of the central Al-atom.

The aim of this work is to describe the new complex of aluminium discovered in the organic substance of selected bituminous and brown coals and their fractions through analysis of the solid phases of leaches and the solid residues after leaching. The leaches and residues were obtained by long-term leaching of coals and their separates using 2-methoxy-ethanol in some experiments while carbon tetra-chloride in the others.

2. EXPERIMENTAL

For the research of Al-complexes, the following leaches and residues were used: firstly, the leaches and residues from the bituminous coal from the Czech part of the Upper Silesian Basin (Ostrava-Karviná Mining District, the Dukla mine); further, the leaches and residues from fractions (separates) of this coal. Secondly, the leaches and residues from the brown coal from the North Bohemian Basin (North Bohemian Brown Coal Mining District, the CSA opencast mine); further, the leaches and residues from low-ash fraction of this coal (<1.25 g .cm^{-3}) were used.

The coal fractions were obtained by applying a sink-float method on the native coals in the organic liquids (xylene-carbon tetrachloride mixtures) of varying densities (Zubková, 2003). As result, the fractions with apparent densities of <1.27 g.cm^{-3}, in the range of 1.27–1.50 g.cm^{-3} and >1.50 g.cm^{-3} in the case of bituminous coal, and the fraction <1.25 g.cm^{-3} in the case of brown coal were separated. Ash and aluminium contents of coals and coal fractions in question are summarized in Table 1.

Both the original bituminous coal and the obtained fractions were further leached. In each case 60–70 g of coal or coal fraction was mixed with 140–150 ml 2-methoxyethanol and then it was leached in sealed flasks at a room temperature for a period of 20 months. Then, liquid phase was separated; subsequently, 2-methoxyethanol having evaporated, the obtained solid phase of leach was analyzed by the solid-state ^{27}Al MAS NMR method. Also solid residue after leaching was analyzed by this method.

The brown coal was being leached in the mentioned way both in 2-methoxyethanol and in carbon tetrachloride. In a similar way, a low-ash fraction of the brown coal with the apparent density <1.25 g.cm^{-3} was leached. The solvents having evaporated, the obtained solid phases of leaches were analyzed again using the solid-state ^{27}Al MAS NMR method. Solid residues after leaching were analyzed by this method, too.

The efficiency of the leaching was tested on the CSA coal. The solid phases of leaches contained more than 1.5 wt.-% of Al_2O_3 and very little of SiO_2, while the solid residues after leaching contained 2–3 wt.-% of Al_2O_3 and 2–6 wt.-% of SiO_2 (confirmed by the XRF method). Thus, the leaching efficiency was considered appropriate.

For the interpretation of spectra of the obtained solid phases of leaches and solid residues after leaching, the spectra from following comparative Al compounds were acquired: Al-phtalocyanine chloride (Fig. 1), Al-phenoxide (Fig. 2), further, α-Al_2O_3 (Fig. 3) and the mixture of Al-hexaphenoxide complex with Al-phtalocyanine chloride (Al standard mixture) (Fig. 4), declared by the producer as aluminium-tetraphenoxy-phtalocynine chloride (all Sigma Aldrich).

Table 1 Ash and aluminium contents in the investigated coal samples.

| Coal/fraction	Apparent density (g.cm^{-3})	Al (wt.-%)	Ash (dry basis) (wt.-%)
Dukla	-	0.91	10.20
fractions	-1.27	1.05	-
	1.27–1.33	1.19	2.39
	1.33–1.40	1.26	8.54
	1.40–1.50	1.56	17.64
	+1.50	3.68	35.39
CSA	-	1.02	17.42
fraction	-1.25	0.81	3.65
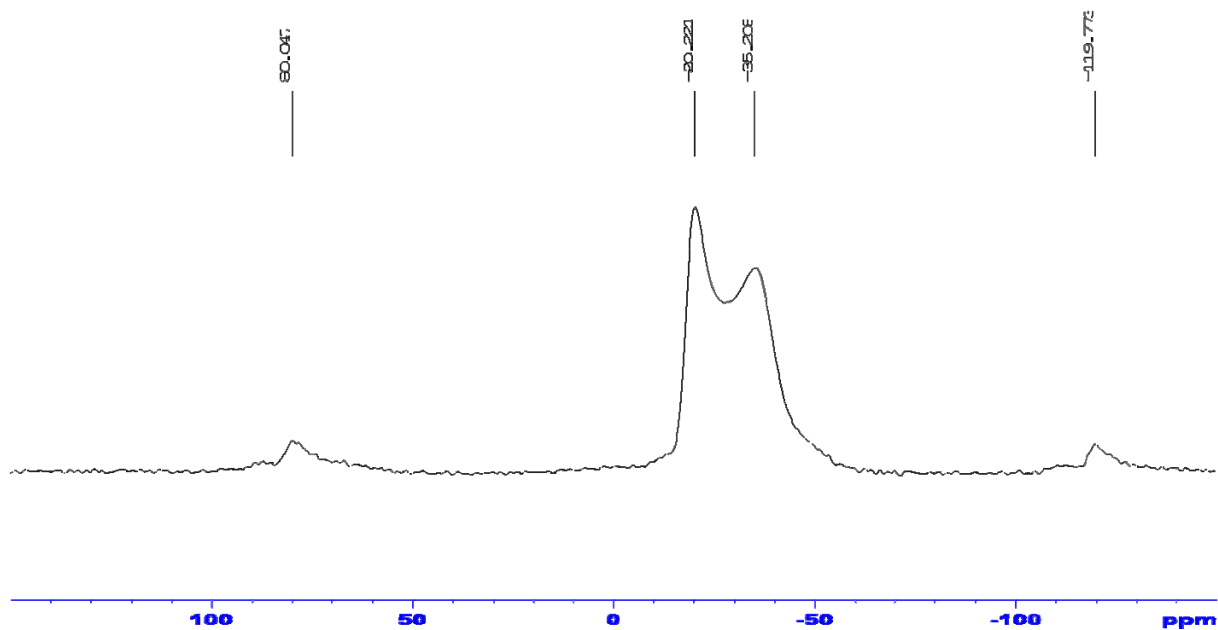
Fig. 1 ²⁷Al MAS NMR spectrum of Al-phtalocyanine chloride. Signals at -20.2 a -35.2 ppm belong to Al tetra-coordinated with the pyrrole nitrogen and the Al–Cl bond.
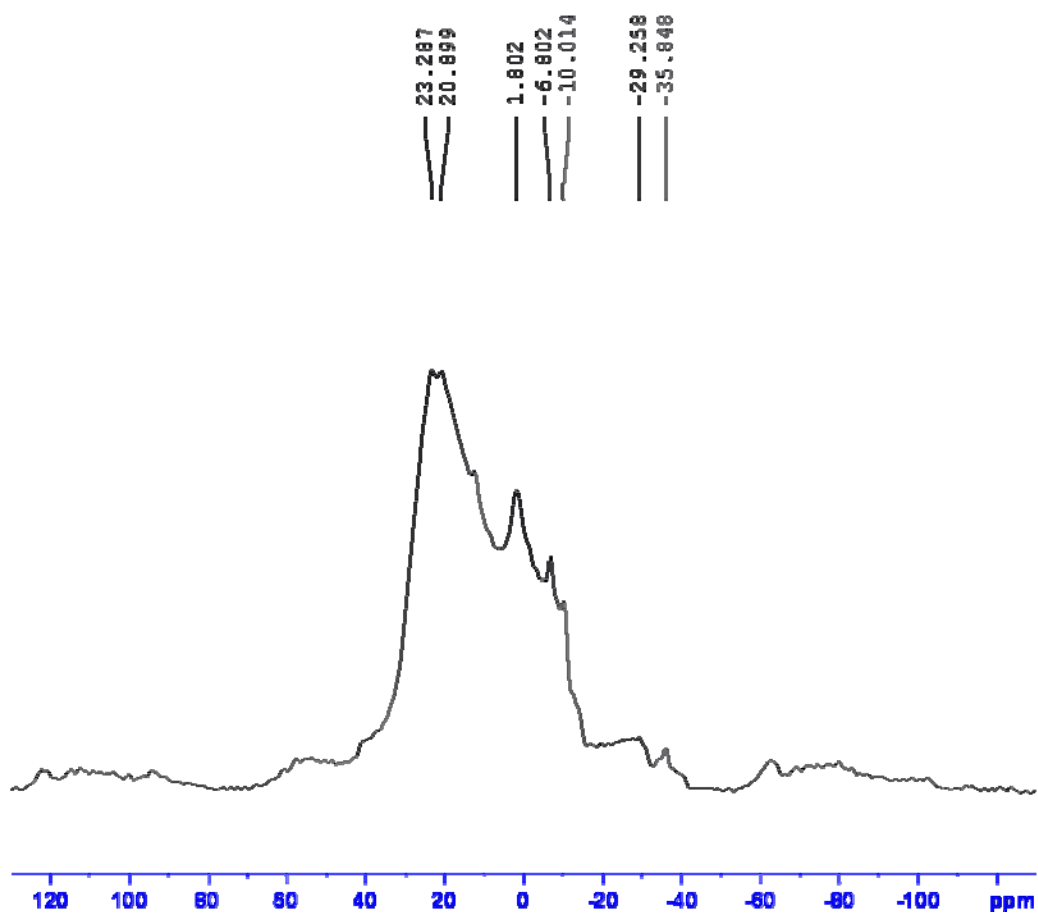
Fig. 2 ²⁷Al MAS NMR spectrum of Al-phenoxide. The double signal at 23.3/20.9 ppm corresponds to Al bonded with 3 atoms of oxygen.
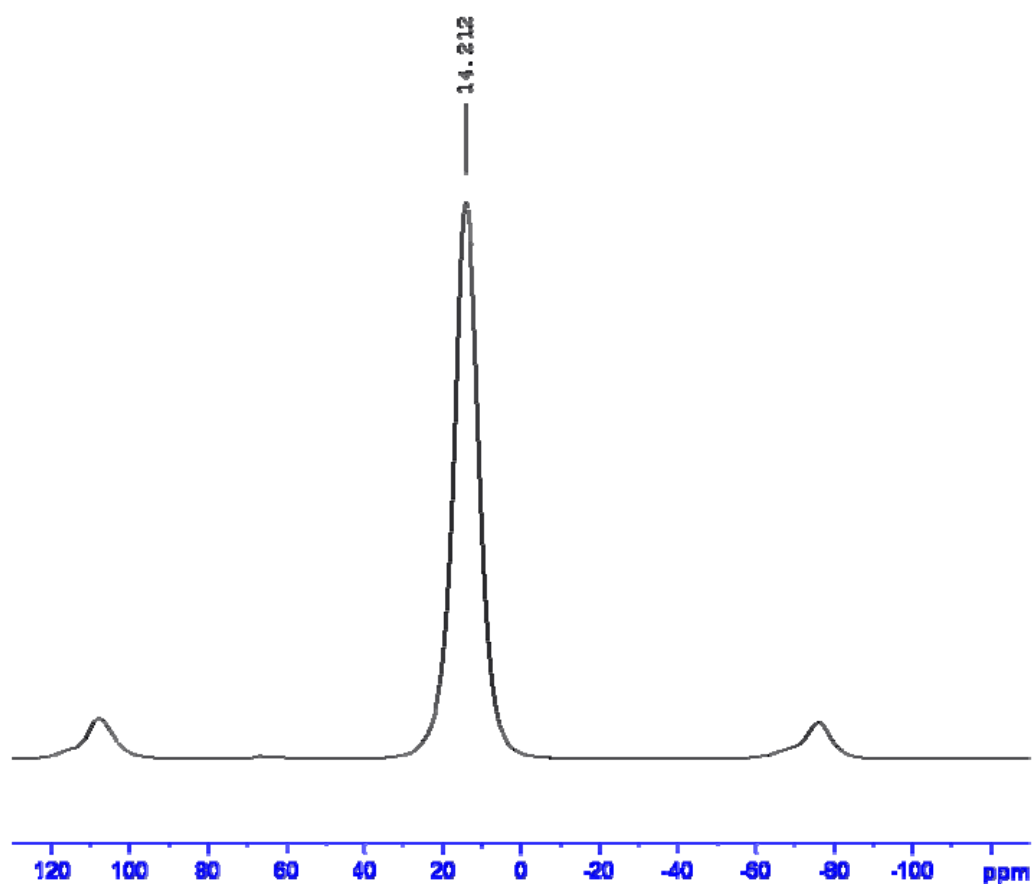
Fig. 3 ^{27}Al MAS NMR spectrum of α-Al$_2$O$_3$. Signal at 14.2 ppm corresponds to Al hexa-coordinated with oxygen in octahedral arrangement.
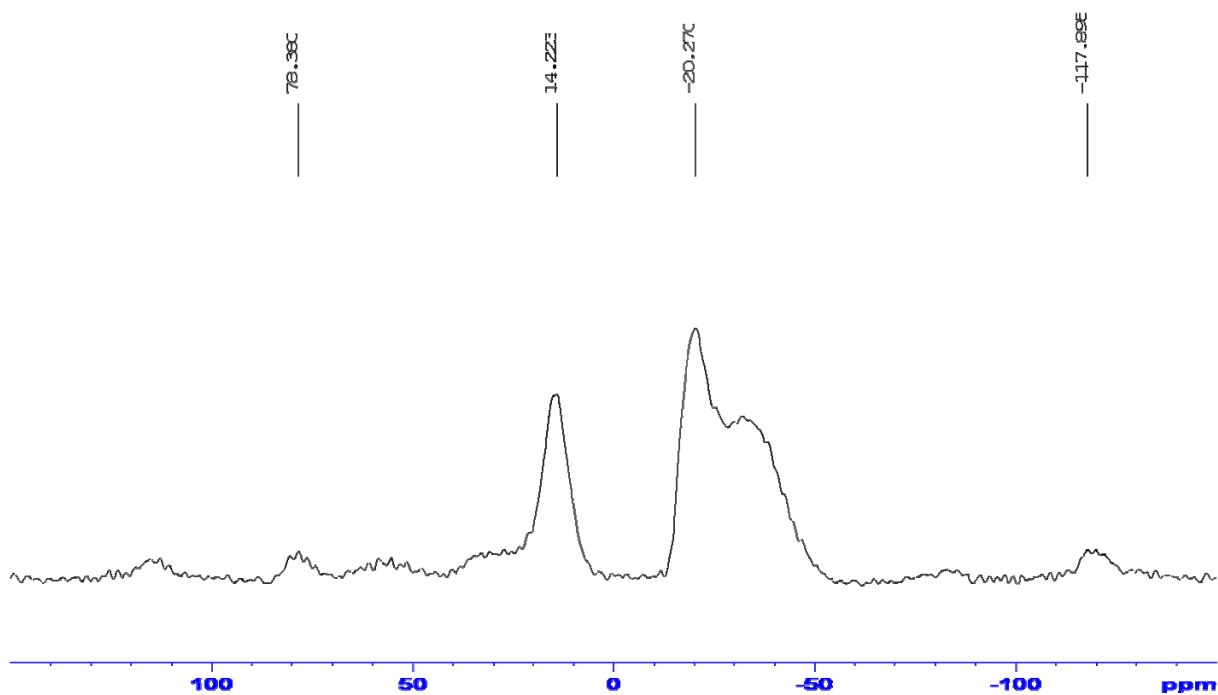
Fig. 4 ^{27}Al MAS NMR spectrum of the mixture of Al-hexaphenoxide complex with Al-phtalocyanine chloride. Signal at 14.2 ppm corresponds to Al hexa-coordinated with oxygen. Signals at -20.2 a -35.2 ppm belong to Al tetra-coordinated with nitrogen and Al–Cl bond in the phtalocyanine chloride structure (see Fig. 1).

Table 2 Ash content and elemental organic analysis of the solid phases of leaches from both bituminous (Dukla) and brown coal (CSA) used (wt.-%).

Solid phase of leach	Ash (db)	C	H	N	S	O
from the Dukla coal	0.5	82.4	7.0	1.1	0.6	8.4
from the CSA coal	1.2	80.4	7.9	0.9	2.6	7.4

Table 3 ^{27}Al MAS NMR analyses of solid phases of leaches (shortly leaches) and solid residues after leaching from the Dukla and the CSA coals and their fractions. 2-MOE means 2-methoxyethanol.

Initial coal/fraction	Analyzed sample	ppm	Al-coordination
the Dukla coal	leach (2-MOE)	14.6	6
	solid residue after 2-MOE leaching	3.6	6
fraction (-1.27)	leach (2-MOE)	no signals	
fraction (1.27–1.33)	leach (2-MOE)	14.5	6
fraction (1.27–1.33)	solid residue after 2-moe leaching	3.6	6
fraction (1.33–1.40)	leach (2-MOE)	no signals	
fraction (1.40–1.50)	leach (2-MOE)	no signals	
fraction (+1.50)	leach (2-MOE)	no signals	
the CSA coal	leach (2-MOE)	14.6	6
the CSA coal	solid residue after 2-MOE leaching	3.4	6
fraction (-1.25)	leach (2-MOE)	no signals	
	solid residue after 2-MOE leaching	3.1	6
		13.9	6
the CSA coal	leach (CCl$_4$)	3.5	6
		13.6	6
	solid residue after CCl$_4$ leaching	3.5	6

For the organic elemental analyses, the Flash 1112 EA analyzer (Thermo Finnigan, Rodano) was used; for the analyses of Al and SiO$_2$ the XRF spectrometer EDS Spectro X-Lab (SPECTRO Analytical Instruments, Kleve) was used. The ^{27}Al MAS NMR spectra were obtained using the Bruker Avance 500 spectrometer (Bruker, Rheinstetten), with Al(NO$_3$)$_3$.6 H$_2$O serving as the NMR standard. For the XRD analyses of the solid residues after leaching, the Philips X´Pert PW 1113 was used, namely for the halloysite prove.

3. RESULTS AND DISCUSSION

The selected coals and their fractions had good prerequisites for the observation of Al-complexes (and the accompanying Al-silicates), because they contained sufficient amounts of Al (Table 1). The obtained solid phases of leaches from coals had very low ash contents and acceptable contents of organic nitrogen and oxygen (Table 2), which was important considering the fact that the complexes in question contain Al–N and Al–O bonds. Further, high contents of hydrogen were found. These findings mean that the ligands in supposed Al-complex can be considered as organic ones. The carbon content was similar at the bituminous Dukla coal and the brown CSA coal. Because coalification of coals in question was quite different, this fact can mean that the supposed Al-complex is similar or the same both in bituminous and brown coal.

We proceeded from the assumption that the affinity of aluminium to the organic substance of the bituminous coal examined by the OEA method (Klika and Kolomazník, 2000) is relatively high – about 76 % –, further, the affinity to the brown coal substance can be comparable. Since the aluminium contents in the solid phases of leaches was sufficient – about 1 wt.-% –, the ^{27}Al MAS NMR spectra obtained were used as a source of the data to enable a structural outline of the organo-aluminium complex of coal.

Al-coordination in coal samples was the first to be examined. The ^{27}Al MAS NMR spectra were evaluated, both from the solid phases of leaches from the bituminous coal and its fractions and from the solid phases of leaches from the brown coal and its low-ash fraction, and also the spectra of the solid residues after leaching. The overview of the results is shown in Table 3.

Table 3 ^{27}Al MAS NMR analyses of solid phases of leaches (shortly leaches) and solid residues after leaching from the Dukla and the CSA coals and their fractions. 2-MOE means 2-methoxyethanol.

Initial coal/fraction	Analyzed sample	ppm	Al-coordination
the Dukla coal	leach (2-MOE)	14.6	6
	solid residue after 2-MOE leaching	3.6	6
fraction (-1.27)	leach (2-MOE)	no signals	
fraction (1.27–1.33)	leach (2-MOE)	14.5	6
fraction (1.27–1.33)	solid residue after 2-MOE leaching	3.6	6
fraction (1.33–1.40)	leach (2-MOE)	no signals	
fraction (1.40–1.50)	leach (2-MOE)	no signals	
fraction (+1.50)	leach (2-MOE)	no signals	
the CSA coal	leach (2-MOE)	14.6	6
the CSA coal	solid residue after 2-MOE leaching	3.4	6
fraction (-1.25)	leach (2-MOE)	no signals	
	solid residue after 2-MOE leaching	3.1	6
		13.9	6
the CSA coal	leach (CCl$_4$)	3.5	6
		13.6	6
	solid residue after CCl$_4$ leaching	3.5	6

In the spectra of the solid phases of leaches from the Dukla bituminous coal and its fraction 1.27–1.33 g.cm^{-3} (quantitatively the main fraction), significant signals were found at 14.6 (with the Dukla coal) and 14.5 ppm (with the mentioned fraction – Fig. 5) (Table 3) corresponding to the signal of the Al standard mixture at 14.2 ppm (Fig. 4). This standard mixture, however, showed in addition to the signal at 14.2 ppm also two signals – at -20.2 and -35.2 ppm. In comparison with the Al-phtalocyanine chloride standard (Fig. 1) it is obvious that last-mentioned negative signals are reached by Al tetra-coordinated with nitrogen and by the Al–Cl bond in the Al-phtalocyanine chloride structure, while the signal at 14.2 ppm is reached by Al hexa-coordinated with oxygen, because the interval 20 to -20 ppm is typical for this type of aluminium bond, as it is also clearly demonstrated in Fig. 3 (spectrum of α-Al$_2$O$_3$ represents Al hexa-coordinated with oxygen (Gažo, 1981) at 14.2 ppm). Considering the organic character of the solid phase of leach and the tendency of Al to form organic complexes (Shriver and Atkins, 1999), it is also possible to attribute this signal to Al hexa-coordinated with phenoxide oxygen (Fig. 4). Further, we may suppose the occurrence of Al-hexaphenoxide complex based on the high content of phenolic structures in the coal (Zubková, 2003; Straka, 2003). Regarding the difference between the spectra of the solid phase of leach from the Dukla coal main fraction (Fig. 5) and the Al-phtalocyanine chloride standard

(Fig. 1), it may be said that the Al-phtalocyanine complex was not present in the coal substance. Also Al-phenoxide was not present in the coal substance, as it follows from comparison of spectra in Fig. 2 and Fig. 5.

The solid phases of leaches from the fractions of 1.33–1.40, 1.40–1.50 and more than 1.50 g.cm^{-3} did not show any signal. That means that organic complex of aluminium was concentrated chiefly in the medium density fraction of 1.27–1.33 g.cm^{-3}. Probably, the organo-aluminium complex in the coal is more likely to be present in vitrinites, which have a medium density; in this connection it is significant that in the solid phase of leach from a fraction with a density lower than 1.27 g.cm^{-3}, no signals were registered (Table 3).

In the solid residue after leaching both of the considered coal and its fraction 1.27–1.33 g.cm^{-3}, we have identified halloysite, which was proved both by the spectrum of the coal leach itself and the fraction mentioned. These spectra reached a signal at 3.6 ppm corresponding to the signal at 3.4 ppm in the comparative aluminosilicate, which was dominantly halloysite (proved by the XRD method).

Similar results have been obtained in the solid phase of leach from the brown coal CSA (Fig. 6). In the 2-methoxyethanol leach of the coal itself, we have detected a strong signal at 14.6 ppm (Table 3) corresponding again to the signal at 14.2 ppm in the Al standard mixture (Fig. 4) and thus also the
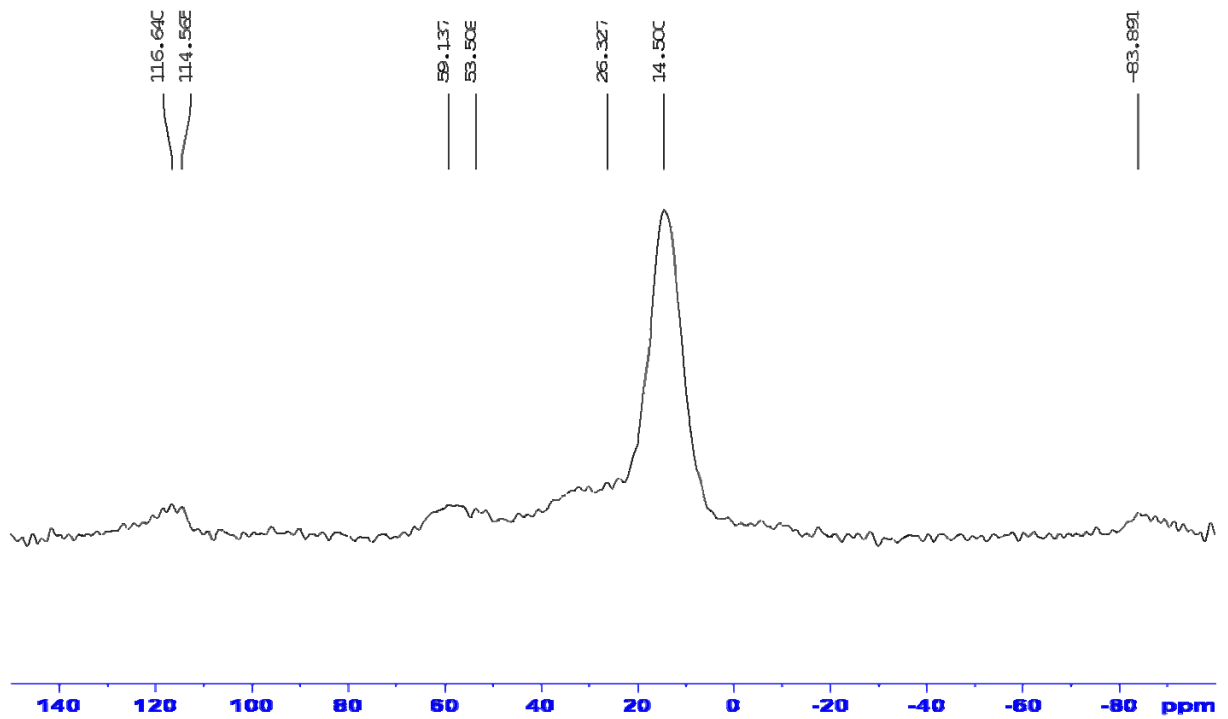
Fig. 5 ^{27}Al MAS NMR spectrum of solid phase of leach from the fraction 1.27–1.33 g.cm^{-3} of the Dukla bituminous coal. Signal at 14.5 ppm corresponds to Al hexa-coordinated with oxygen.
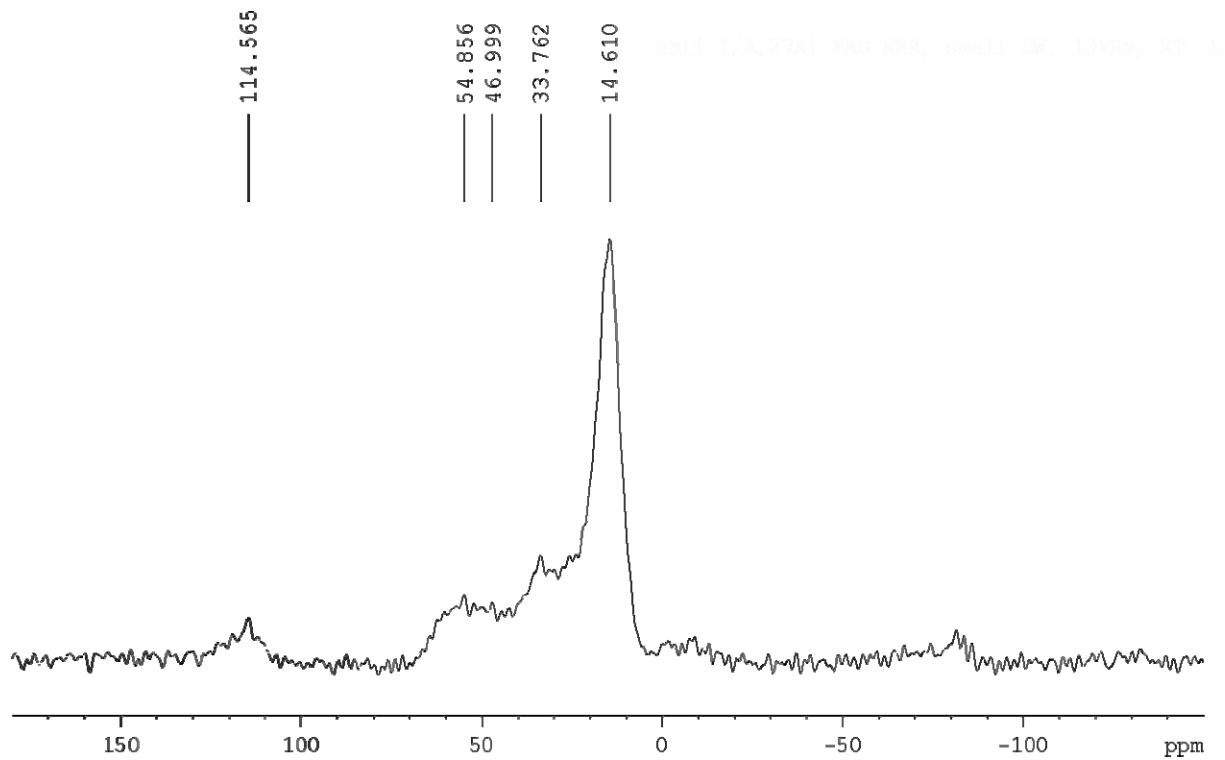
Fig. 6 ^{27}Al MAS NMR spectrum of solid phase of leach from the CSA brown coal. Signal at 14.6 ppm corresponds to Al hexa-coordinated with oxygen.

presence of Al-hexaphenoxide complex was considered. In the solid residue after leaching the signal at 3.4 ppm was detected corresponding to halloysite. On the other hand, no signal was found in the 2-methoxyethanol solid phase of leach of the fraction of -1.25 g cm^{-3}, while the solid residue after leaching had two signals – at 13.9 and 3.1 ppm (Table 3), from which it arises that the organo-aluminium complex and halloysite were concentrated in the solid residue this time. This means that the analysed fraction contained only little of the organo-aluminium complex, and not before raising the concentration by removing a part of the organic substance by leaching was it possible for the Al-signal to appear in the spectrum. It may be concluded again that the organo-aluminium complex is concentrated rather in the coal fractions with a medium density.

In the carbon tetrachloride solid phase of leach of the CSA coal, we have found two signals – at 13.6 and 3.5 ppm (Table 3). This means that in the leach both the organo-aluminium complex of the given structure and halloysite were concentrated. In the solid residue after leaching of the coal in question a halloysite was identified, because the spectra exhibited signal at 3.5 ppm (Table 3).

4. CONCLUSION

On the basis of solid-state ^{27}Al MAS NMR measurements the new organo-aluminium complex in coal substance was discovered. For experiments, the solid phases of leaches and the solid residues after leaching were used. The samples were obtained by long-term leaching both from the Ostrava-Karviná bituminous coal and its fractions and the North Bohemian Basin brown coal and its low-ash fraction. For leaching 2-methoxyethanol and carbon tetrachloride were used. It was found that the significant chemical shift at 13.6–14.6 ppm corresponds with that obtained for the aluminium hexaphenoxide complex as the Al signal at 14.2 ppm is typical for hexa-coordination of aluminium. Therefore, organo-aluminium complex with hexa-coordination of Al to oxygen is present in coal substance. This organo-aluminium complex is concentrated rather in the coal fractions with a medium density.

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