THE ALUMINA-SILICATES IN STABILIZATION PROCESSES IN FLUIDIZED-BED ASH

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Presented study of coal fluidized-bed ash solidification was accompanied with specific studies of alumino-silicates residues in ashes. The specific technology of fluid coal burning and its relatively low temperature combustion combines coal burning and decomposition of calcium carbonate added to the fluid layer in the main endeavor to capture all sulfur oxides.
The burning temperature seems be decisive to the behavior of clayed residues and calcium carbonate decomposition in connection for the future solidification of fluidized bed ash. The calcareous substances in combination with alumino-silicate residues form solid bodies where silicates play decisive role of long-term stability and insolubility of obtained solids. The position of aluminum ions in clayed residues of burned coal were studied by MAS-NMR with attention on aluminum ion coordination to oxygen and formation of roentgen amorphous phase of poly-condensed calcium alumina-silicate.

INTRODUCTION

The volume of fluidized-bed ashes increases every day as a result of coal combustion in heating and power plants. The principal aim was to find the technique of fluidized-bed ash (FBA) solidification. The fluid technology of coal burning minimizes air pollution from sulfur oxides and is environmentally-friendly. The technology uses calcite ($CaCO_3$) as an additive to the crushed coal and, during heat exposition, the calcite is decomposed, forming CO_2 gases and lime (CaO). The formed reactive calcium oxide captures sulfur oxides from the burned coal and forms predominantly anhydrite ($CaSO_4$) in the FBA.

The FBA are classified by the ASTM as Class C ashes, i.e. ashes with a high content of calcium components. The high content of the so-called "free CaO" does not allow for the use of FBA in the cement industry. Hydrated calcium oxide in the form of $Ca(OH)_2$ could react in cement with CO_2 and form $CaCO_3$ with its bigger crystals, and the crystal pressure accompanying its occurrence could thus destroy or considerably lower the mechanical properties of the concrete. Moreover, the use of FBA is limited by the content of sulfur oxides, especially when calcium sulfate (anhydrite) is present in a soluble γ-form [1]. Unlike the FBA, the fly ashes from classic boiler combustion do not contain a "free calcium oxide" and are therefore used in many countries as an additive to the Portland cement mixtures.

The stabilization and solidification of FBA were focused on the solids' long-term stability, their insolubility in water and their mechanical properties (compressive and flexural strength) in general. The possible substitution of construction materials by solidified FBA depends on the above-mentioned factors [2]. Stability of the mixtures was proved by measurement of mechanical properties during period of 15 months receiving very similar data of compressive strength. Also the insolubility proved by submerged samples and testing of leaching extracts confirms presence of very small amount of calcium carbonate and calcium sulfates only.

Long-term stability of the tested bars, even submerged in water, opened new aim of study - which components and substances are responsible for mechanical properties? The XRD studies of obtained solids repeated in indicated terms show permanent changes in calcareous substances:

The initially observed and instant formation of primary-formed ettringite (PFE) usually expressed as $6Ca(OH)_2 \cdot Al_2(SO_4)_3 \cdot 26H_2O$ [3, 4] was carefully monitored, because its presence supposed also occurrences of its delayed form (DFE), which is considered to be a significant deleterious component, especially in concretes. The X-ray diffractions at different times after solidification were aimed at the identification of all the crystal phases in the FBA/smectite mixture with a special focus on ettringite (PFE). These studies were motivated by the occurrence of PFE and the possibility of the

potential formation of delayed ettringite (DFE) [5-8]. The destructive role of DFE in cements, mentioned e.g. by Köhler et al. [9], is a menace and should not be neglected in FBA solids either. The appearance of DFE threatens an increase of the specific surface area, efflorescence and the destruction of concrete constructions.

The subsequent tests and studies were orientated on the identification of all phases in the obtained solids with a focus on detecting the participants responsible for long-term stability and insolubility in water. The attention was directed to the chemical analyses and content of the alumino-silicate residues in burned coal because of its major content in the ash.

The forms and types of aluminous phases are absent in all of the studied X-ray diffraction patterns. The discrepancy between the aluminum oxide content identified by the chemical analyses of the FBA and the X-ray diffraction - absence of aluminous crystal phases should be explained. The solids could contain the specific roentgen amorphous alumino-silicate substance. For the identification of such a premise the clayed residue and especially the aluminum coordination to oxygen was studied by ^{27}Al MAS NMR in solid state. The aluminum coordination level reflects the temperature of coal burning in fluid boilers (reaching 820°C only) [10].

EXPERIMENTAL

Materials

All of the solidifying experiments dealt with fluidized-bed ash from the Ledvice Coal-Fired Power Plant in the Czech Republic. This power plant uses brown coal from the North Bohemian Coal Basin. Table 1 presents an average chemical analysis of the fluidized-bed ash used in all experiments. The alumina and silica oxides were complemented by iron, titanium and alkali/alkali earth oxides (Na_2O, K_2O, CaO and MgO). The content of SiO_2 and Al_2O_3 oxides in the ash confirms the presence of dehydrated clay minerals in the coal from the North Bohemian Coal Basin [11].

A guideline was provided by previous experiments with the solidification of waste materials [12] based on the hydration of thermally treated alumina-silicates in alkali aqueous solutions. The experiments and tests which used only finely milled FBA in admixture with water to prepare a workable material do not comply with the requirements for the stability of construction

materials. The obtained solids have decomposed in water, and compressive strength was very low, maximum of 7 MPa.

When looking for a complementary material improving the quality of the solids, natural smectite was chosen, using experience of Martemjanovic [13]. The smectite use was justified by its particles size, which fills the gaps between the milled grains of ash. With the decreasing porosity of the system and probably also the high ion-exchange capacity, the mechanical properties of the obtained solids improve (compressive and flexural strengths are the most important properties for the eventual construction use). The natural smectite was from North Bohemia, extracted by Keramost, a.s., Most, Czech Republic, and its chemical analysis is also shown in Table 1.

The final composition in studied mixtures used 10 wt.% of natural smectite resulting of a preliminary testing series using before an addition from 5 to 20 wt.% of smectite to the milled FBA. The resulting 10 wt.% of natural smectite addition yields the best mechanical properties e.g. compressive strength reaching average value of 15 MPa in 18 months old samples [2]. The mentioned paper presented measurement of oscillating compressive strength from 15-16 MPa (180 days old) when the testing bars were left at ambient laboratory conditions.

The present paper describes experiments, conducted under ambient laboratory conditions, with chosen 90/10 proportion of FBA/smectite (in wt.%) and we do not suppose specific chemical reactions between FBA substances and small amount of smectite filler.

Calculated content of calcium carbonates (calcite) in smectite is about 11 wt.%, but the admixture of smecite and FBA was 10 wt.% only. The presence of calcite in FBA is in fresh ash limited by presence of the non-decomposed calcite originally added to the crushed coal (7-8 wt.%). The Table 1 determinates high content of alumina and silica representing more than 50 wt.% of the mass and especially the aluminum content and coordination is discussed later.

Testing bars
and samples preparation

The FBA were milled together with smectite (with a chosen proportion of 90/10 in weight percent) for 60 minutes in a vibrant-mill MTA KUTESZ, Type 2014

Table 1. Chemical analyses of the FBA from the Ledvice Power Plant and used smectite (wt.%).

Oxides/sources	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	CaO	MgO	K$_2$O	Na$_2$O	SO$_3$	L.O.I
Ledvice FBA	35.99	22.55	5.05	1.87	18.9[a]	0.63	0.75	0.19	10.28	3.21[b]
Smectite	45.90	13.09	11.08	2.43	6.44	5.67	0.82	0.23	-	15.33

a - "free CaO" 12.6 wt.%
b - L.O.I. is characterized by a loss of OH- groups from portlandite and CO$_2$ from calcite. The unburned carbon content is below 0.2 wt.%.

(Hungary), reaching a final finesse of 1200 $m^2.kg^{-1}$. The water addition was 45 ml to 100 g of FBA/smectite mixture, hence yielding a workable paste, using food processing mixer with planetary stirrer (5-8 minutes).

The obtained mixtures were poured into steel molds (No. 100606-33) of standard dimensions 40×40×160 mm, and a slight mold vibration eliminated the air bubbles. The molds were covered with plastic sheets to retard surface-water evaporation. The standard molded bars were left under ambient laboratory conditions for 12 hours. The remolded bars were subsequently stored under laboratory conditions for 7, 28, 180 days and the last one was checked after 15 months. The samples for X-ray diffraction were prepared from crushed and milled bar rests.

Analyses

The XRD examination of the crystallography phases was performed by Phillips Source Data with a path of 0.050° and an angle range of 4.7-62.9° (2θ), using a Cu tube to identify the type of mineralogical composition. The step size was 0.017° (2θ) and the counting time 10 s.

The ^{27}Al MAS NMR spectra in solid state were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer equipped with a double-resonance 4-mm probe head. These spectra were acquired at 130.287 MHz, the spinning frequency was $\omega_r/2\pi =$ = 13 kHz, tip angle was 20° (1 μs pulse length) with a recycle delay of 2 s, and the spectra were referenced to Al $(NO_3)_3$ (0.0 ppm).

The chemical analyses were performed by an XRF analyzer (Spectro IQ, Kleve, Germany). The target material was palladium, where the target angle was 90° from the central ray and the focal spot was a 1 mm^2 square. The maximum anode dissipation was 50 Watts

with 10 cfm of forced air cooling. The tested samples were prepared by the fusing method with lithium tetraborate and lithium metaborate in a 2:1 ratio [14]. All the results were automatically recalculated to the oxides form.

Microstructural investigation was realized by microscope NIKON Optiphot S100 equipped by digital camera JENOPTIK (Germany) and evaluated by Laboratory Imaging system of image analysis NIS-elements AR2.0.

RESULTS AND DISCUSSION

In all our samples of the FBA, besides the dominant anhydrite and minor content of quartz was identified complementing portlandite $(Ca(OH)_2)$ and remaining non-decomposed calcite $(CaCO_3)$, see Figure 1. The XRD analysis of FBA identifies neither the "glass" phases nor the calcium-silicates due to the low temperature of combustion used by the fluid technology. As mentioned before the XRD analysis do not indentify clayed residues and we could pretend the presence of its dehydrated form. Table 1 shows more than 50 wt. % of this residue and than the influence of alumino-silicates in solid form must be pronounced.

The patterns in Figure 2 show the X-ray diffractions of a solidified FBA/smectite sample aged 28 days and a 15-month-old sample prepared from fragments of solidified bars allowing a comparison. The 28-day pattern (upper line) exhibited predominantly peaks of ettringite (E) and quartz (Q), followed by a small amount of anhydrite (A), calcite (C), muscovite (M) (K Al_2 $(Si_3Al)O_{10}$ $(OH,F)_2$) and magnetite (Ma) $(Fe^{2+} Fe^{3+}_2O_4)$ as minor phases. The Figure 2 depicts once again the absence of aluminous components with the exception of small amount of muscovite. The founding of rather
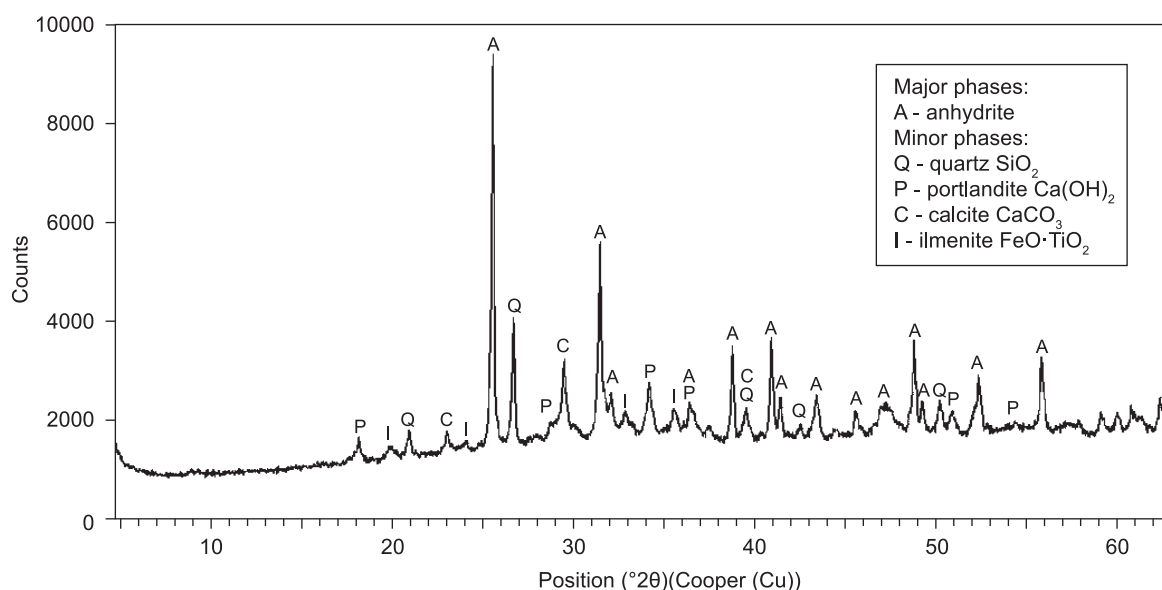

Figure 1. The XDR diffraction pattern of fresh FBA from the Ledvice Power Plant.
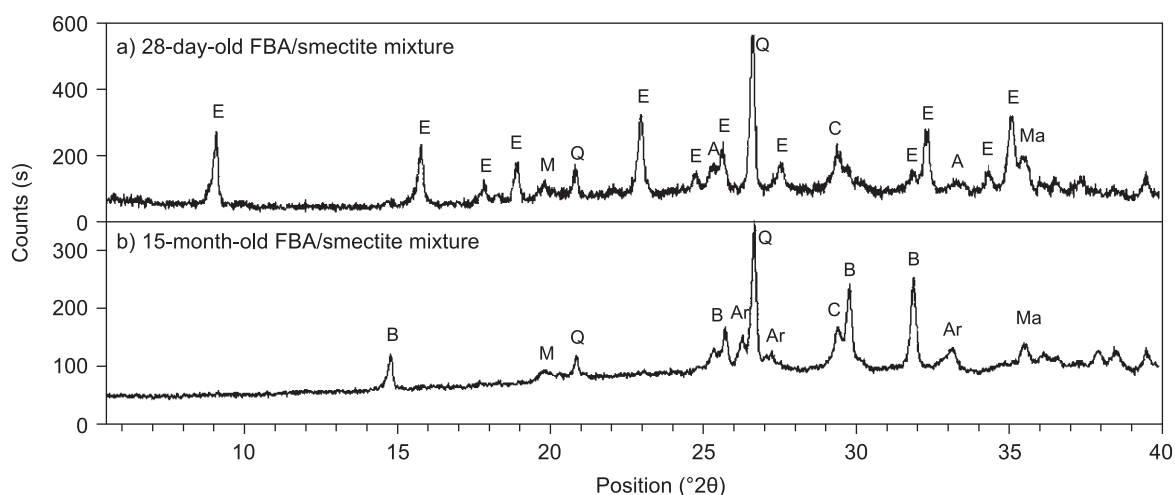
Figure 2. The comparative X-ray diffraction patterns of the FBA/smectite solidified bodies.
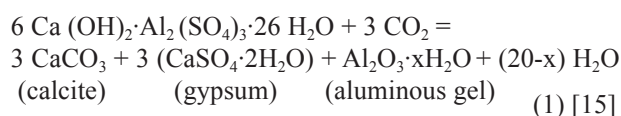
high amount of clay mineral residues in FBA detected by chemical analyses do not correspond to the identified crystal phases by XRD analyses.

The subsequent studies (bottom line) by X-ray diffraction analyses showed a lowering and later the disappearance of the peaks of ettringite and its substitution by bassanite ($CaSO_4.1/2\ H_2O$) and aragonite ($CaCO_3$). The final crystallographic state after 15 months of the solidification is depicted on the bottom line. The identified phases are: dominant bassanite (B), followed by quartz (Q), aragonite (Ar) and a minor content of calcite (C). The next phases are magnetite (Ma) and muscovite (M), not entering into the changes of the calcium-containing phases and certainly having no effect on the spontaneous decomposition of ettringite.
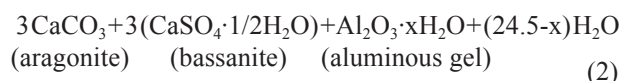
The comparative diffraction patterns resolve the problem of aluminum ion content and coordination only partially (Table 1 presents alumina) by its participation in ettringite. Its amount corresponds to the hexa-coordinated aluminum ions only and could not explain the quantity of alumina detected by chemical analysis.

A rather high content of SO_3^{2-} anion in FBA (Table 1) is present in the form of soluble γ-$CaSO_4$ [1]. The content of soluble anhydrite (see the situation after 28 days) decreases and primary-formed ettringite grows. The answer to its later gradual decomposition could be found in the lowered pH surrounding and gradual carbonation. Calcite, a product of carbonation (Figure 2), replaces the lime and portlandite, but its small quantity does not progressively affect the processes of setting and hardening.

The paper by Nishikawa et al. [15] offers the equation (Equation (1)) of carbonation studied on artificially prepared samples of ettringite. In solid bodies, we have detected some differences (Equation (2)) - instead of gypsum ($CaSO_4.2H_2O$), the presented XRD pattern (Figure 2) shows bassanite ($CaSO_4·1/2\ H_2O$) and calcium carbonate in the form of aragonite ($CaCO_3$).

$6\ Ca\ (OH)_2·Al_2\ (SO_4)_3·26\ H_2O + 3\ CO_2 =$
$3\ CaCO_3 + 3\ (CaSO_4·2H_2O) + Al_2O_3·xH_2O + (20-x)\ H_2O$
(calcite) (gypsum) (aluminous gel)

(1) [15]

Variation for solid FBA/smectite bodies:

$3\ CaCO_3+3(CaSO_4·1/2H_2O)+Al_2O_3·xH_2O+(24.5-x)H_2O$
(aragonite) (bassanite) (aluminous gel)

(2)

The X-ray reflections of quartz, calcite, muscovite and magnetite did not change in either pattern, but the other components changed considerably. The DFE did not appear, and the most important outcome was a spontaneous decomposition of the PFE. In agreement with the results of Zhou and Glasser [16] and Grounds et al. [17], we have confirmed the assumption that the carbonation of ettringite occurs not only on artificially prepared samples but is possible also in solid materials. The content of calcite in both X-ray patterns is a result of the lime and portlandite carbonation and also reflects the remnants of the non-decomposed calcite additive to the burned coal (the amount of calcite in smectite is not considered due to its minimal content in mixture). The amount of the reactive forms of calcareous components (CaO, $Ca(OH)_2$) originally present in ash was lowered after their transformation to calcium carbonate. The leaching liquid originally having pH in the range of 10.5-11.0 changed after solidification to almost neutral values, i.e. from 7.2 to 7.5. According to the paper by Myneni et al. [18] confirming the stability of ettringite over pH 10.5 only, the ettringite decomposition is explicable even when occurring in solidified, stable bodies.

Figure 3 summarized all changes in the calcium-containing phases registered by X-ray diffraction analyses over 15 months (450 days). The sketch compares FBA composition, its hydrated forms and also final state of the stabilized solids. The alumina-silicates in the sketch reflect the situation confirmed by the MAS NMR analyses of the ^{27}Al ions (Figure 4).
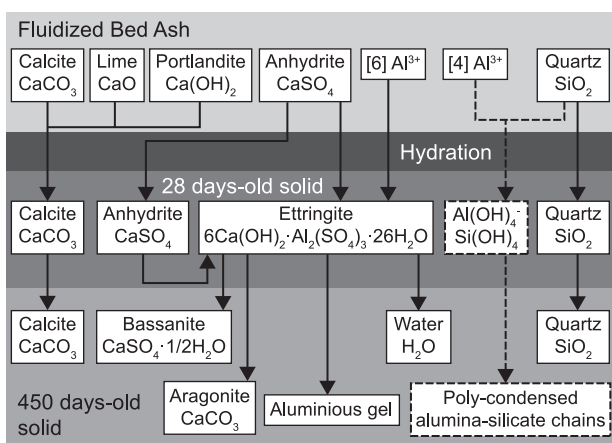
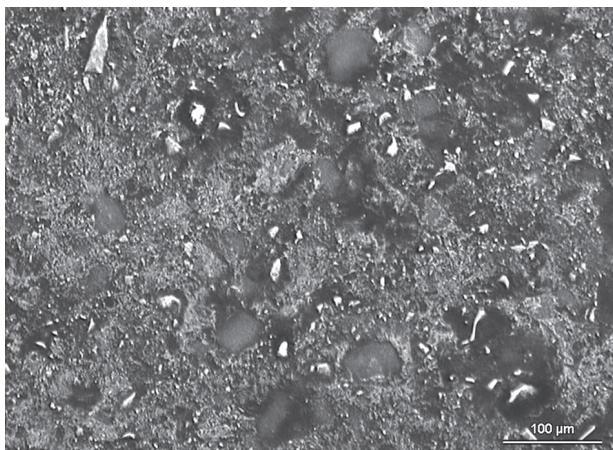Figure 3. The sketch of all phase changes in FBA/smectite solids.

Figure 4. Microstructure of FBA/smectite polished surface solid (180 days old).

The solids prepared from the FBA/smectite mixtures do not exhibit, even over time, the tendency to the formation of the DFE (see the 15-month X-ray diffraction pattern) but show the slow and spontaneous decomposition of primary-formed ettringite. Neither the PFE nor DFE present therefore any serious threat to FBA/smectite material stability. The determination of the ettringite content and the possibility for the formation of PFE and also for its delayed form DFE are generally limited by these two factors:

- a high or dominant content of soluble anhydrite,
- the aluminum ions being in hexa-coordination.

The measurement of the compressive strength [2] on the prepared standard bars made from FBA/smectite mixtures showed values of 15-18 MPa after 180 days. The stability and compressive strength data aged for 180 days are not affected by cracks on the sample surfaces or edges. Observation of microstructure of 180-day-old sample didn't present visible fissures in the structure how is demonstrated on Figure 4.

Stability of solids should concern other reason responsible for mechanical properties than the above-mentioned constant changes in the calcium containing phases. The difference between the alumina content (the chemical analysis shows 22.55 wt.% in FBA) and the aluminous phases (ettringite and mica) identified in the X-ray diffraction patterns of solids formed from aluminum could be accounted through the ^{27}Al MAS NMR analysis.

The Figure 5 presents the ppm position of the ^{27}Al ions in the FBA milled sample and shows a significant shift from the obvious position of [6] Al^{3+} (close to "0", found at 4.25 ppm) to the thermally excited state of the [4] Al^{3+} position (59.25 ppm) [10].
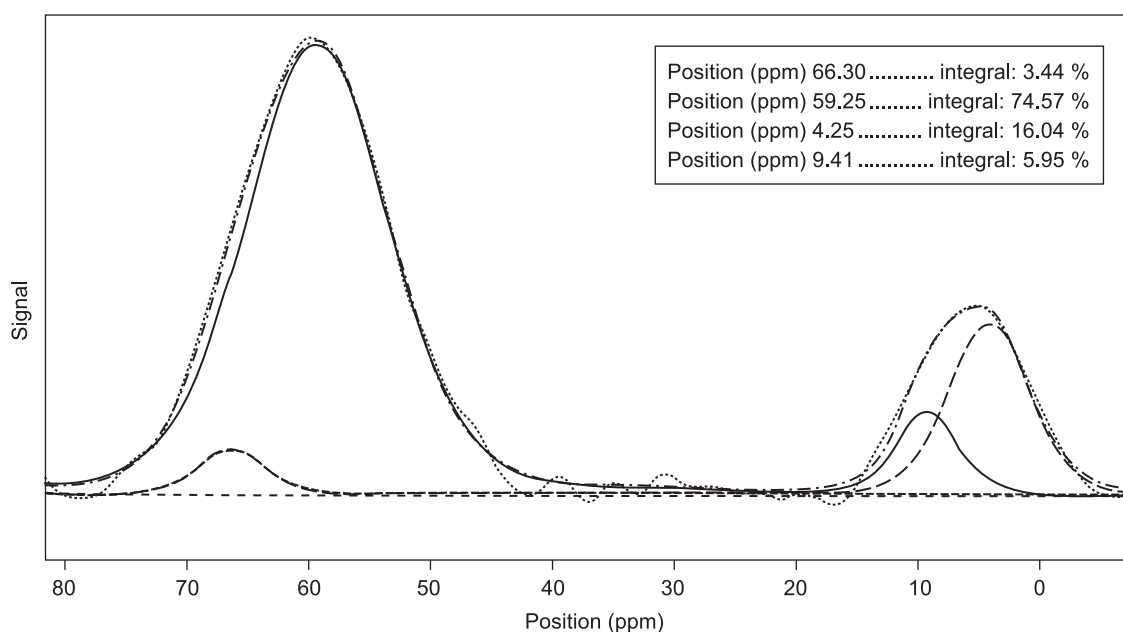

Figure 5. The 27Al MAS NMR of the Ledvice FBA.

We can confirm that the available aluminum ions for the formation of ettringite are limited by the content of [6] Al^{3+} ions only. In the studied FBA, approx. 21-22 wt.% of them is in natural hexa-coordination (see the positions at 4.25 and 9.41 ppm).

The aluminum ions coordination to the oxygen is changed considerably from natural octahedrons in clays and after thermally treatment is identified its tetra-coordination (position 59.25 ppm - more than 74 wt.%). The temperature of coal burning (820°C) does not reach the formation of spinel and mullite and according to the Sanz et al. [10], the changes depicted on ^{27}Al MAS-NMR pattern (Figure 5) show tetra-coordination of aluminum ions. The theory and practice of geopolymer technology in general [19-22] confirm that thermally treated clays, under the temperature of spinel, mullite formation (both participants, Al and Si, are in four-fold coordination) are able to be hydrated in alkaline surroundings.

The alkalis balance the negative charge of aluminum ion in tetra-coordination and both main participants form partial chaining or complete netting - generally amorphous form of alumino-silicates [19-22].

CONCLUSION

Daily increasing amount of FBA presents a serious environmental problem consuming more and more land for deposit areas. This paper presents possibility of FBA solidification based on chemical and crystallographic analyses. The used combustion technology and burning coal temperature determinates basic chemical components. Among others soluble form of anhydrite (γ-$CaSO_4$) was found. The anhydrite solubility in water converts to the instant ettringite occurrence, but PFE does not pose a serious threat because PFE decomposes spontaneously and gradually over time because of carbonation and the decreasing pH level. Over 15 months were observed permanent changes in the calcium-containing phases detected by X-ray diffractions and all these changes had any effects on mechanical properties. The compressive strength and insolubility in water as major requirement for construction material were studied on base of the alumina-silicate coal remnants. The identification of their state and coordination level explains discrepancy between the phases on X-ray diffraction and chemical analyses in terms of the aluminum content. The ^{27}Al MAS NMR analyses in solid state and their results show that the majority of the aluminum ions are in tetra-coordination, which conditions their possible hydration in aqueous alkali surrounding. Formation of hydrated monomers of aluminum tetrahedrons together with hydrated silicon chains both participants. Formed shorter or longer alumina-silicate chains are responsible for the good mechanical properties, long-term stability and insolubility of the FBA/smectite solids in water. The knowledge that a FBA/smectite solid prepared from an aqueous mixture is not affected by either of the deleterious forms of ettringite is important and with confirmed long-term stability and practically stabile compressive strength, this material could be used as alternative construction material.

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