THERMAL RESISTANCE OF FOAMED FLUIDIZED BED ASHES

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ABSTRACT
The thermal resistance is one of the important behaviors of the construction and thermal insulating materials. This study describes foamed material made from fluidized bed ash (FBA) in combination with natural smectite having a filler function. The foaming effect was insured by addition of metallic aluminum to the FBA/smectite mixture. Highly calcareous FBA containing calcium oxide creates during slaking processes an alkali reaction and with aluminum develops foaming agent - hydrogen. Study of thermal resistance was a part of experiments directed on heat insulating materials and article presents test results of this life gardening material. Specific attention was focused on differences between the results of chemical analyses and the crystal phases identified by X-ray diffractions. The paper presents hypothesis of chained alumina-silicates acting as bonding agent confirmed by infra-red spectroscopy and assuring together with calcium sulfates high thermal resistance even under condition of direct flame attack.

KEYWORDS: thermal resistance, fluidized bed ash, XRD, calcium components, FTIR

INTRODUCTION

The aim of the presented work was to find possibility to use solidified bodies made from fluidized bed ash as insulating material. The fluidized bed ash (FBA) is specified by exceptional high content of calcium components excluding this type of ash (ASTM classification C-ashes) from the use in cement industry. Relatively low temperature of coal combustion (820 °C) does not form the calcium-silicates or calcium-aluminates and practically all calcite addition to the burning coal has the only objective – to capture the coal sulfur (sulfur oxides). The formatted anhydrite [$CaSO_4$] is dominant calcium containing phase in fluidized bed ashes, but also some small rests of original calcite [$CaCO_3$], portlandite [$Ca(OH)_2$] and in fresh ash also lime [CaO] could be found, these calcareous matters are complemented by quartz [SiO_2]. The chemical analyses identify also an important content of aluminum and silicon oxides in these ashes. The supposed alumina-silicates are dewatered residues of clayed minerals in coal (Thomas, 2002).

The stabilization and solidification of the fluidized bed ash at ambient temperature and pressure was described by Perna et al. (2007). The use of 10 wt. % of smectite does not change anything in self solidification processes of FBA and the addition of smectite was chosen according to the experiments and experience of Martemjanovic (2001) as filler between milled ash grains. Secondary effect of smectite addition is in better ash/smectite mixture workability.

This study is focused on thermal resistance of FBA/smectite mixtures and specifically on their foamed variation. The previously obtained results of FBA solids (Perná et al., 2007), their long term stability and insolubility in water, lead to the conclusion that formatted components of solidified bodies should resist the high temperatures contrary to the cement's common calcium-silicates.

The hardening processes of ordinary cements products form a calcium-silicate-hydrate; so-called C-S-H gels. These gels are considered as a binding agent and agent responsible for strength of concrete mixtures. The gel means highly hydrated structure and therefore is difficult to call the ordinary concrete as thermal resistant material. Usually over 300 °C the concrete losts its stability, the surface cracks and the mass structure starts to disintegrate (Arioz, 2007).

For this reason the thermal resistant materials are usually prepared from different type of binding agent (Hammell et al., 2000; Leiva et al., 2008; Giancaspro et al., 2009). In case of ashes the thermal and thermal resistance could be approximated from the combustion temperatures of different materials. The solids made form ashes or ash mixtures are known (Leiva et al., 2008, 2009; Vilches et al., 2005) and reflect the ash origin.

Thermal resistance of any material is a function of density (total porosity) and also by thermal conductivity of the components. The porous material has generally lower thermal conductivity and pores in the inorganic materials usually improve thermal properties (e.g. ceramics, glass, etc.).

The solids made from FBA/smectite mixture, due to the preparation from watered system, are porous and their density could be lowered by foaming in objective to ameliorate the thermal and thermal resistance. Foamed FBA/smectite solids with increased porosity lowered in the mean time its thermal conductivity.

METHODS

The XRD investigation of the crystallography phases was held by Phillips Source Data, path 0.050°, angle range 4.7024–62.9784 [° 2 Th.], Cu-lamp to identify the type of mineralogical composition.

The characterization of fluidized bed ash was studied by chemical analyses realized by XRF method of fused pearl (Broton, 1997). The chemical analyses were performed by an XRF analyzer (Spectro IQ, Kleve, Germany, where the target material is palladium, target angle 90° from the central ray and the focal spot a 1 mm x 1 mm square, the maximum Anode Dissipation 50 Watts with 10 cfm forced air cooling).

The infrared spectra were measured using the Nicolet 7600 (Thermo Nicolet Instruments Co., Madison, USA) spectrometer with a DTGS detector and a KBr beam splitter. The measurement parameters were the following: the number of spectra accumulation was 128, resolution 2 cm^{-1}, the transmission method was performed by means of KBr tablets and the apodization was Happ-Genzel. The spectra were evaluated by the Nicolet OMNIC software, version 7.3.

The solid-state NMR spectrum was measured using a Bruker Avance 500 WB/US NMR spectrometer (Karlsruhe, Germany, 2003) in 4-mm double-resonance probeheads at magic angle spinning (MAS) $\omega_r/2\pi = 13$ kHz. The ^{29}Si MAS-NMR spectrum was acquired at 99.37; using a tip angle of 90° (4 μs pulse length) with a recycle delay of 7 s. The spectrum was referenced to M8Q8 (-109.8 ppm).

The thermal resistance test was acquired according to the international norm EU 1364-1 of thermal resistance control in the Czech Centre of Thermal resistance Authority at Veselí nad Lužnicí (South Bohemia region) by authorized person AO 216. The sample plate was built into the wall of testing kiln. Used testing kiln is a 1 m^3 chamber made from refractory bricks. One wall, on opposite side of mounted burner, has 3 – 5 openings, where tested plates were fixed. Each tested plate was equipped by two pairs of thermocouples on its "cold" side. The kiln burner operates with an open flame orientated directly contra located plate (called "hot" side). The register of the temperature course begins immediately when the fire test starts. The tested material is considered as a fire resistant in different time laps (15, 30, 45 or 60 minutes) registering the temperature on "cold" side, until does not exceed 120 °C, considered by mentioned EU norm as a critical temperature.

SAMPLE PREPARATION

Fluidized bed ashes were from North Bohemia and North Moravia Coal Basin. Both ashes were used for laboratory experiments, comparing chemical analyses and mineralogical composition (presented below). Previous tests defined the best results of compressive strength resistance when mixing the FBA (90 wt. %) with 10 wt. % of natural smectite from Keramost Most A.S., company at North Bohemia (Perna et al., 2007).

The components (ash and smectite) were together milled for 60 minutes in a vibrant-mill MTA KUTESZ, Type 2014 (Hungary) reaching the final finesse 1200 $m^2.kg^{-1}$. The 100g of milled FBA and smectite needs from 40 - 45 ml of water to make the mixture workable. The mortar-like consistency of mixture was additionally mixed with 0.2 wt. % of powdered metallic alumina (foaming agent) just before filling the standard plate mold. The setting and hardening occurs in 12 hours (room temperature 23 °C and current humidity of 65 %). Remolded sample plate in dimensions 200 x 200 x 35 mm was left in laboratory condition for next 7 days and after that dried to the constant weight on 105 °C in laboratory drier.

RESULT AND DISCUSSION

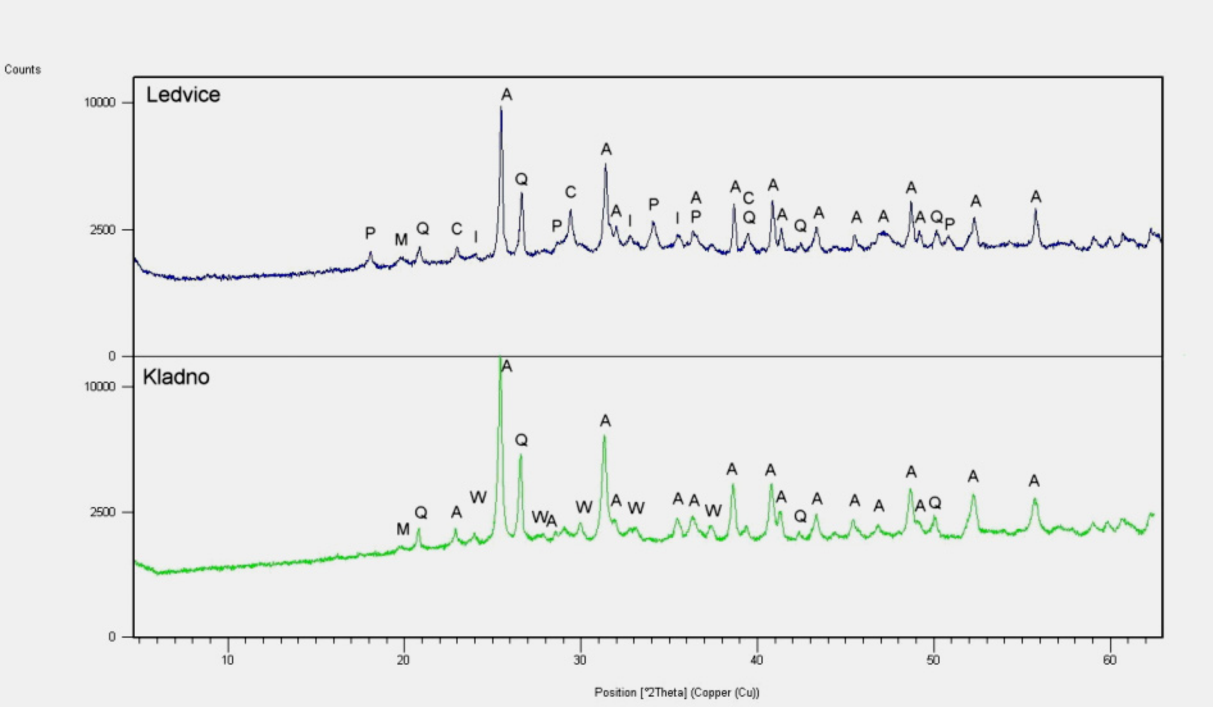
Used sources of FBA (Ledvice and Kladno Power Stations) were, as mentioned above, from different coal deposits – North Bohemian and North Moravian Coal Basin (brown and bituminous coal, respectively). The chemical compositions of used ashes and smectite are presented in Table 1.

Table 1 Chemical analyses of FBA from the Ledvice, Kladno Power Plant and used smectite.

Materials/oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3	L.O.I
Ledvice FBA	43.85	22.40	4.10	1.70	17.9[a]	0.75	0.71	0.28	2.90	4.47[b]
Kladno FBA	47.30	16.10	4.54	1.16	22.62[a]	0.92	0.96	0.18	3.60	6.12[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. % and 14.75 wt. %, respectively

[b]/ L.O.I. exhibits the loss of OH^- groups and CO_2 from portlandite and calcite respectively. The unburned carbon content is less than 0.2 wt. %.



Legend:
P – portlandite, M – mica, C – calcite, Q- quartz, A- anhydrite, I – ilmenite, W- wollastonite

Fig. 1 Comparative XRD patterns of Ledvice and Kladno FBA.

The Figure 1 depicts comparative XRD patterns of ashes from Ledvice and Kladno Power Stations and shows very similar mineralogical composition.

The patterns have distinguishing XRD courses only in minorities' reflections: ilmenite [$FeTiO_3$] in Ledvice power plant ash is not present in Kladno, but on this pattern the traces of wollastonite [$CaSiO_3$] could be identified. In both XRD patterns, could be seen dominate amount of anhydrite and quartz.

The identification of all components by X-ray diffraction analyses, identifying crystal phases, should correspond with the results of chemical analyses. On presented XRD patterns could not be identified the presence of calcium-silicates or calcium-aluminates but chemici analysis detected more than 55 wt. % of alumina and silica (see Table 1). Important is a content of alumina and its form, or form of dehydrated alumina-silicates as resulting residues of thermally treated clay in burned coal. The presented analyses proved the similarity of both tested ashes in chemical and mineralogical composition. For next experiments the FBA from Kladno source was chosen by reason of better availability of this material.

Prepared and dried FBA/smectite foamed plate from Kladno source was tested in the mentioned laboratory at Veselí nad Lužnicí (South Bohemia region). Presented Figure 2 shows course of temperatures registered by the thermocouples fixed on "cold" side of tested plate. The increasing line is a course of "cold" side temperature of FBA foamed plate. We could observe the long temperature flat plateau between 70 to 90 °C in time laps exceeding 115 minutes. The temperature limit of 120 °C on the "cold" side (flat line in Figure 2) is reached after 2 hours of heat exposition when estimated temperature of the open burner flame was 1150 °C.

The foamed FBA/smectite mixture has shown excellent result of thermal resistance. The inner (hot) side even changed in color does not collapse by effect of high temperature. In this connection was very important that the plate installed in the kiln wall have had no shrinkage after two hours of heat exposition.

The Figure 3 presents the cross section of the foamed FBA/smectite plate after thermal resistance test. Material on a "cold" side has different color than the "hot" (flame exposed) side. The color changes from grayish to light pinkish.

The samples prepared from the "cold" and "hot" plate sides were later studied by X-ray diffraction and the mineralogical compositions are presented in Figure 4.

Dominant phases on a "cold" side are anhydrite (A), quartz (Q), calcite (C) and bassanite – $CaSO_4.1/2H_2O$ (B), hematite - Fe_2O_3 (H) and magnetite – Fe_3O_4 (Ma) was identified as minor phases. The analysis of material from "hot" side showed as major phases anhydrite (A) and gehlenite (G) and as minor phases quartz (Q), hematite (H) and ferrosilite – ($Mg_{0.318}Fe_{0.666}Ca_{0.016}$) SiO_3 (F).

Newly formed gehlenite [$Ca_2Al(Al,Si)O_7$] occurs resolving partially the problem of aluminum content, which was not identified on X-ray diffraction on "cold" side. The content of anhydrite confirms its resistance against high temperatures. Similar reflection pictured in Figure 5 supports the fact, that decomposition of calcium sulfate is observed above

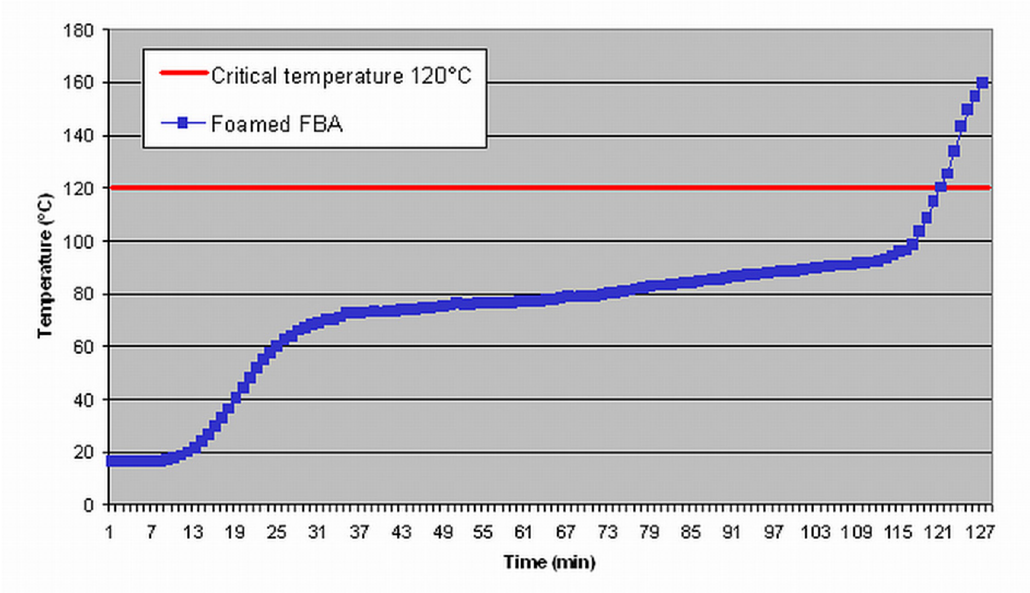


Fig. 2 Course of rising temperature registered on "cold" sides.

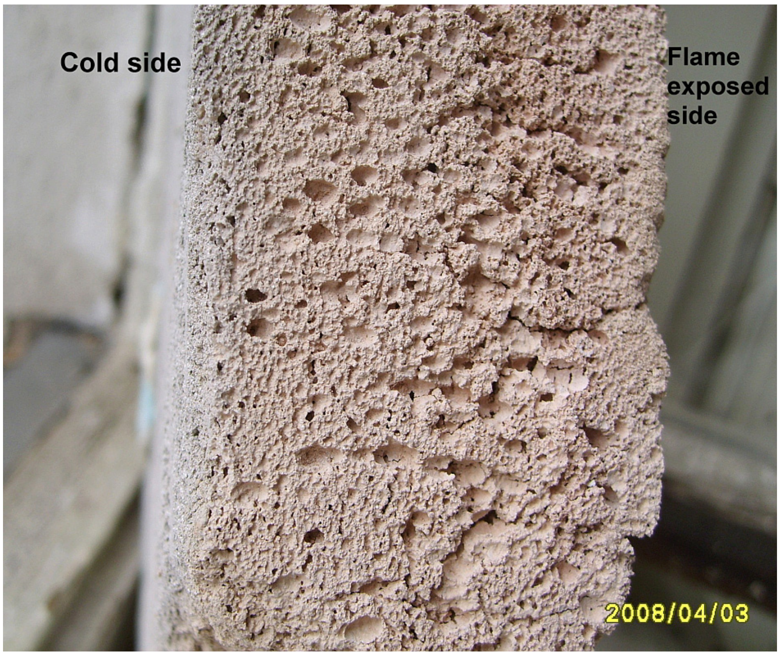


Fig. 3 Cross section of foamed FBA/smectite after thermal resistance test.

the temperature of 1200 °C. The position of quartz is changing according to its participation in gehlenite (Figure 4). The content of iron is now found in its oxidized form as hematite and in ferrosilite, confirmed also by the change of color presented in Figure 3.

From the presented Figure 4 there is no direct proof of alumina-silicate formation, but this could be expected because of:

1. Clay content in the coal (Thomas, 2002; Spears, 2000; Bouška, 1981; Sýkorová et al., 1997) could be estimated on theoretical base, rating Al_2O_3: SiO_2, as in kaolinite (1: 2 in molar quantities), from 35 to 48 wt. % in the mass.
2. The limited temperature of coal burning (820 °C) has a decisive influence on components in FBA (http://www.thyssenkrupp-xervonenergy.com/, 2009). In the mean time should be explained difference between findings obtained by chemical analyses and identification of components by XRD analyses. Especially low combustion

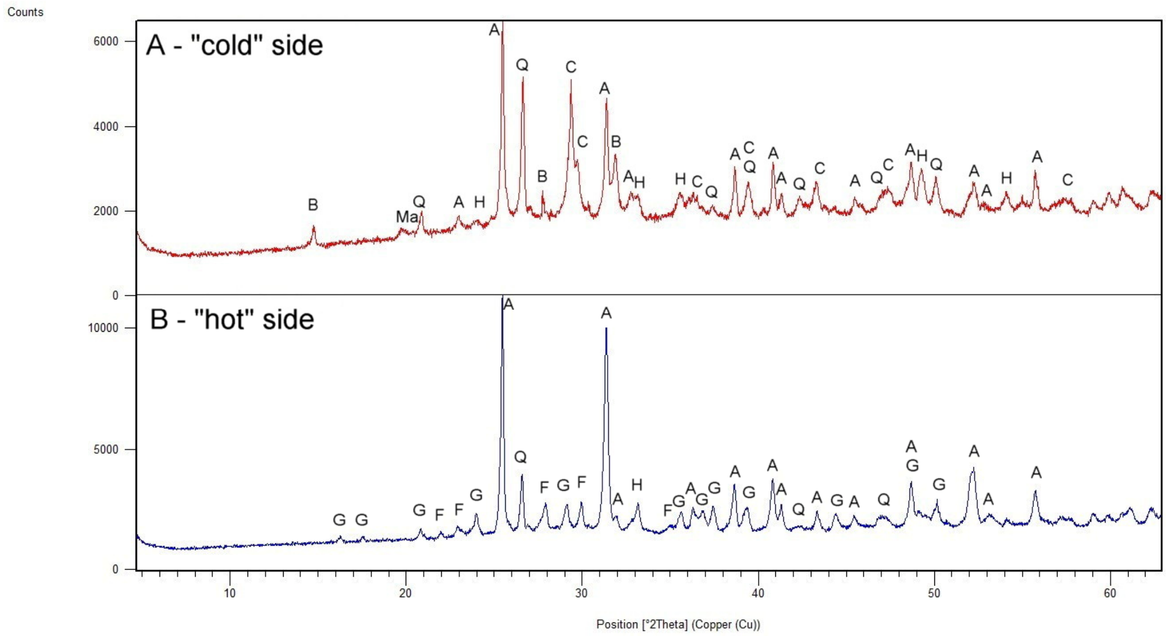


Fig. 4 The comparative XRD patterns of tested sample form "cold" (A) and "hot" (B) sides.

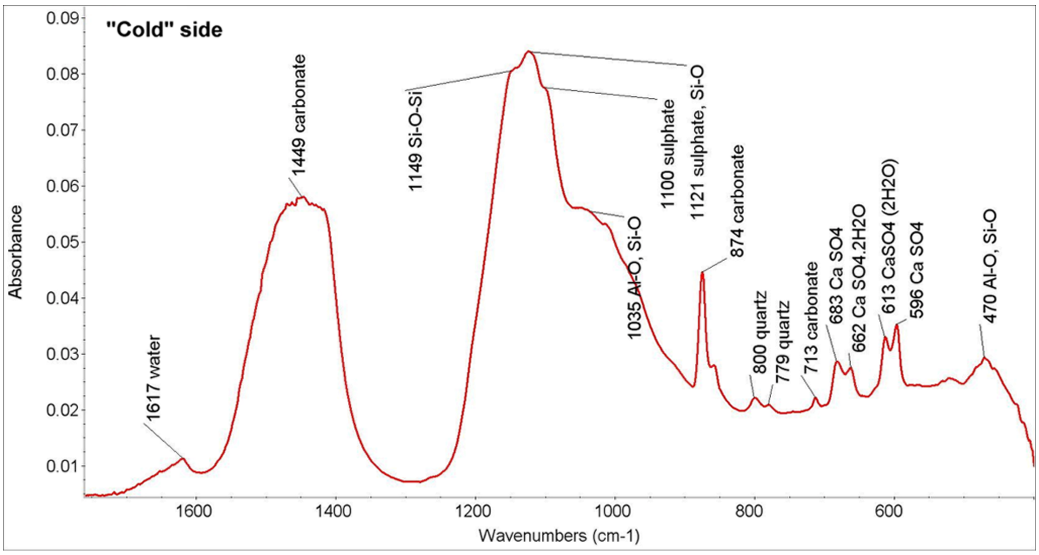


Fig. 5 The infrared analysis of material from "cold" side (temperature of slightly above 120 °C after two hours).

temperature of FBA could be considered as a temperature of clay dehydration and its "activation" - temperature of transformation in Al^{3+} coordination (Sanz et al., 1988). The alumina and silica treated by the same temperature result in generally amorphous clay residues. This state and form is invisible on XRD patterns. This resembles the situation of thermally "activated" clay in alkali aqueous surroundings when mixed with water.

3. In case of FBA, the alkali surrounding is ensured by soluble anhydrite [γ-$CaSO_4$] (Bezou et al., 1995). The clay residues create in aqueous condition poly-condensed formations and this fact leads to the hypothesis of alumina-silicate chaining (Sanz et al., 1988; Barbosa and MacKenzie, 2003).

For verification of this hypothesis the infrared spectroscopy was used and the results are presented in Figures 5 and 6.

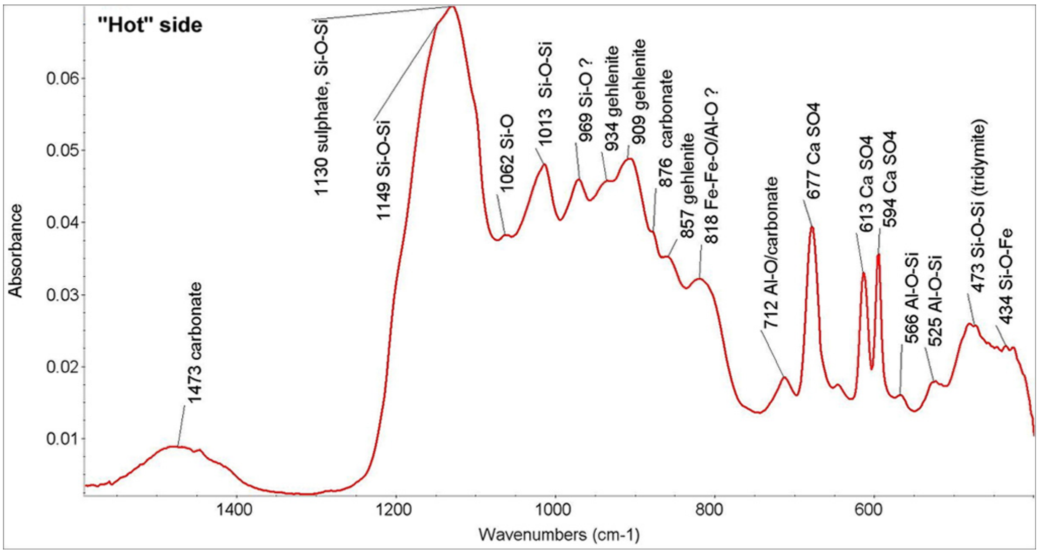


Fig. 6 The infrared analysis of material from "hot" side (temperature of 1150 °C).

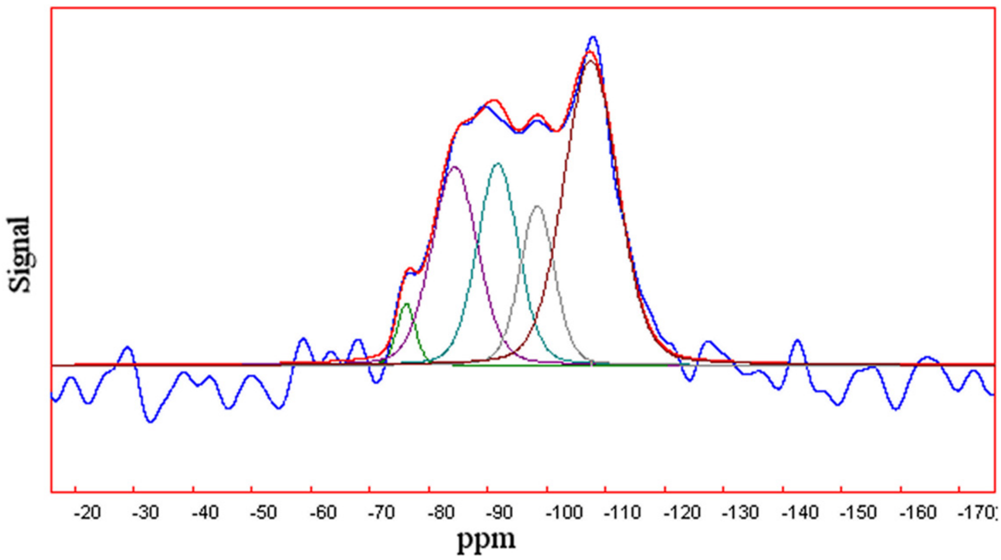


Fig. 7 The ^{29}Si MAS NMR in solid state of FBA/smectite mixture from Kladno source.

Infrared analyses confirmed the results acquired by XRD method. The analysis of "cold" side (Figure 5) depicts quartz (779 and 800 cm^{-1}) and small water content (1617 cm^{-1}). The "hot" side analysis (Figure 6) demonstrates a gehlenite formation (857, 909 and 934 cm^{-1}) and the Si-O-Fe and Fe-Fe-O bonds which could correspond to magnetite or ferrosilite. Both graphs showed the presence of carbonates (712-713, 874, 876, 1473 and 1449 cm^{-1}) and sulphates (594-596, 613, 662, 677, 683, 1100, 1121 and 1130 cm^{-1}). The samples from both sides contain also Si-O, Si-O-Si, Al-O and Al-O-Si bonds which are codified by many authors (Sanz et al., 1988; Singh et al., 2005; Palomo and Fernández-Jiménez, 2007) as the bonds corresponding to the alumina-silicate chaining.

For identification of silicon the ^{29}Si MAS NMR in solid state was used and the Figure 7 demonstrates a deconvulated spectrum of Kladno FBA/smectite mixture.

The spectrum in Figure 7 confirmed that silicon is present in two forms. The first one, at position -107.44 ppm, indicates 40.66 % of silicon ions in crystalline phases of silica (quartz). The second form of silicon is created by polymerized Si tetrahedra. The most important sinals are at positions -91.68 ppm and -98.36 ppm. The Kladno FBA/smectite mixture has 13.6 wt. % (at -98.36 ppm) of Si^{4+} ions in coordination Q_4(1-2Al) and 20.41 wt. % (at -91.68 ppm) in coordination Q_4 (3-4Al) and these coordinations mean that Si^{4+} ion is surrounded through oxygen ions by 1-2 and 3-4 four-fold coordinated Al^{3+} ions, respectively (Sanz et al., 1988; Singh et al., 2005; Palomo and Fernández-Jiménez, 2007). The absence of significant amounts of C-S-H gels is evidenced in presented spectrum of Kladno FBA/smectite mixture (Figure 7) in which only the broad signal indicating formation of amorphous alumina-silicate species is detected. The ^{29}Si MAS NMR signals of monomeric silica tetrahedra in C-S-H gels are usually located at ca -70 ppm (Andersen et al., 2003; 2004).

The analyses of FTIR and ^{29}Si MAS NMR confirmed the presence of poly-condensed chains created by silicon and aluminum ions. The negative charges of two four coordinated aluminum ions, connected by oxygen with silicon, are balanced by calcium ion. The formation of long branched clusters of alumina-silicates is limited by aluminum tetrahedrons occurrence (Hanzlíček et al., 2007). According to the results of chemical analyses the amorphous form of alumina-silicates creates significant component of the mass. The alumina-silicate chains are spread among calcium containing phases and together with anhydrite are decisive compacting phenomena, especially on “cold” side of tested plate.

However is known that slowly evaporated aqueous systems leave micro/nano-porous structure which results in resistance to the thermal shock, the structure of foamed FBA/smecite combines this phenomenon with open porous mass demonstrating high thermal resistance. The porous system compensated the calcite decomposition, eventually changes in bassanite dewatering. The most important is a fact that during the test were no observed changes in volume – no shrinkage or volume expansion. The tested plate stayed firm producing no gases during or after the exposition to the direct flame.

CONCLUSION

Thermal resistance of foamed FBA/smectite mixture presents a combination of components behavior. Each participant plays its specific role – major content of XRD amorphous alumina-silicates are in form of poly-condensed chains distributed in calcareous surroundings formed by thermally stabile anhydrite (both resist until 1200°C). Poly-condensed alumina-silicates and anhydrite are responsible for physical stability of shape even attacked by direct flame. The attention focused on difference between crystal phase’s identification and chemical analyses result were explained and confirmed by amorphous part of alumina-silicates.

The porous structure is responsible for dilatation between hot and cold side and ensures space for outbound decomposed gases from carbonates and other formatted calcium containing substances as bassanite.

The “hot” side of the tested plate shows the formation of gehlenite - product of high temperature transformation of alumina-silicates in contact with calcium. The gehlenite is an obvious product of high furnaces slag, but could not be denominated as binding agent of the mass. The stability of rectangular form without shrinkage or visible surfaces cracks during the exposition against open flame confirms that products made from foamed FBA/smectite mixture could be one of the best life guarding materials.

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