SURFACE AREA CHANGE OF KAOLIN CAUSING ANNEALING

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Abstract
In case of this study of washed kaolin (WK) from the locality Sedlec (CZ) water begins to release before the temperature attains 400 °C and the dehydroxylation process finishes at 750 °C. The specific surface area of washed kaolin (19 - 19.5 $m^2.g^{-1}$) starts to decrease at annealing from 200 to 450 °C. In the temperature range of 550 to 750 °C when the dehydroxylation conversion degree achieves the value of 0.4 to 0.9 the specific surface area stagnates at 16 – 17.5 $m^2.g^{-1}$. A marked decrease in the value of the specific surface area was observed at a temperature of 950 °C. Thermal activated "kaolin", converted from 80 -90 % to metakaolin , shows little decrease of specific area at the temperature of 550 °C for time 60 - 90 min. up to 650 °C but shorter time (30 min.). Specific surface area and reactivity are very difficult for geopolymeric binders.

Keywords: minerals, kaolinite, dehydroxylation, metastable phases, surface area

1 Introduction
Structure changes of solid substances occur at chemical decomposition and phase transformations. The transformation can be very fast or slow. It is well known, that the reactivity of materials is very sensitive to its structural disordering. If gas is formed at the decomposition sudden release of gas may cause permanent or temporary expansion and increase of specific surface area of material. For example, an important growth of specific surface area occurs at thermal decomposition of carbonates of $MgCO_3$, $MgCa(CO_3)_2$ and $FeCO_3$. Maximum value of surface area is detected at 0.8 (i.e. 80 %) conversion of $MeCO_3$ to MeO [1,2]. Similarly, vulcanized hydrated glasses and hydrated minerals with disordered structure expanse at sudden heating-up. If the bond water in the structure releases the surface and/or the porosity increases (e.g. vermiculite. perlite) [3].

Kaolinite is a clay mineral belonging to layered aluminosilicate minerals of the kaolin group. The kaolin mainly consists of high-defected kaolinite with some impurities of feldspar and quartz. The particles of kaolinite are very fine, less than 2 μm. Basic kaolinite particle is a hexagonal platelet formed from a tetrahedral sheet $[Si_2O_5]^{2-}$ linked through oxygen atoms to an octahedral sheet of alumina $[Al_2(OH)_4]^{2+}$. These 2 sheets form layers. ¾ of the hydroxyl (-OH) groups are bond on top and ¼ in octahedral sheets [4,5]. The kaolinite ($Al_2Si_2O_5(OH)_4$) contains 39.5 wt.% Al_2O_3, 46.5 SiO_2 and 13,96 wt.% H_2O.

The kaolin is hydroscopic. As kaolinite is heated to 300 °C the physically adsorbed water desorbs. Heating to higher temperature causes the release of –OH groups from kaolinite and

transformation it into "metakaolin". The properties of mineral irreversibly change with loss of the structurally bound water.

$$2\ Al_2Si_2O_5(OH)_4 \rightarrow 400 - 650\ °C \rightarrow 2\ Al_2Si_2O_7 + 4\ H_2O(g)\ \text{(endothermic process)} \qquad (1)$$
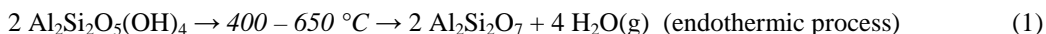
The initial dehydroxylation temperature depends on the structural arrangement (i.e. chemical bond, structure parameters of lattice) and lattice defects. The more mineral structure defects, the lower the dehydroxylation temperature [4-11]. Heating up to 950 °C and above converts metakaolin to a defect aluminium-silicon spinel, $Si_3Al_4O_{12}$ and the structure shrinks by about 20 % [4,6,7]. Transformation of metakaolin to spinel is exothermic process.

$$2\ Al_2Si_2O_7 \rightarrow Si_3Al_4O_{12} + SiO_2 \qquad (2)$$

The dehydroxylation process of clay minerals is explained by more theories [6-8,12]. The theory that orderliness of structure on short distance exists in metakaolin predominates over the theory that the structure of metakaolin is amorphous. Review works [4-7] present that the disappearance of high-order X-ray reflection indicates multiple defects in the structure that are a result of interruption of metastable bonds. After the release of water the disturbed stability is partially restored by rearrangement of oxygen and vacancies. The sheets partially dislocate when heated but the sheet structures still exist. The 2/3 of the hydroxyl groups situated on top of the octahedral sheet probably leave the structure more easily, it means at lower temperatures (420 – 600 °C) than the other -OH groups (1/3) in the octahedral sheet. These later ones probably leave the structure partially at a higher temperature [7,13]. Survey articles [6,7] state that loss of structurally bound water causes decrease of specific density of the material, increase of porosity by about 5 % and the specific surface area increases by about 5 m^2g^{-1}.

Metakaolin has a defected structure and that increases its reactivity and, accordingly, such thermally activated clays are suitable for preparation of geopolymers [13-17]. The activity of kaolin increases with the increase of temperature but decreases abruptly in the temperature region of "spinel" formation. The calcination at the temperature of 550 to 750 °C is preferred for the preparation of activated kaolin. Chemical a surface reactivity of metakaolin characterizes the adsorption capacity/cation exchange capacity (CEC) and specific surface area (S_{BET}) [16-19]. Kaolin raw materials have very different these parameters therefore they depend on genesis minerals (structure clay minerals) and impurities. Kaolin raw materials with high content of kaolinite (80 - 95 wt %) have surface area 9 - 45 $m^2.g^{-1}$. Several studies point to gradual decrease of surface area with increase temperature and time of calcinations [5,16,17] others on increasing of surface [6,7] .

The work verifies the changes of specific surface area of washed natural kaolin-Sedlec depending on dehydroxylation at annealing. Transformation of kaolinite to metakaolinite was observed by TG-analysis, FTIR-emission spectroscopy and X-ray diffraction analysis.

2   Materials and experimental methods

Changes of specific surface area of kaolin due to its annealing at different temperatures were tested on washed natural kaolin from the locality of Sedlec (CZ). The chemical composition of kaolin is shown in **Table 1.** The kaolin was characterized by thermal analysis (Derivatograph MOM D 1500Q) and investigated by SEM-EDS analysis (JEOL JSM-7000 F), by X-ray diffraction (Mikrometa II with Cu Kα radiation). The infrared spectra of the samples were measured by FTIR spectrometer FTLA2000 instrument (ABB, resolution 4 cm^{-1}) by Attenuated Total Reflectance (ATR) measurements with diamond window.

Before annealing the kaolin was dried at 110 °C to a constant weight and kept in desiccator. The kaolin samples have been annealed in static regime in a laboratory furnace (LM 212.11) in a temperature range of 200 to 950 °C for 5 to 120 min. The conversion of kaolinite to metakaolin was evaluated from weight loss in relation to the weight of the sample annealed at a temperature of 950 °C for 120 min..

The surface area of kaolin was measured by nitrogen gas adsorption analyzer (Quantochrome-NOVA-1000; software NovaWin Version 10.01) not later then 24 h after annealing. Before measuring the annealed samples (0,25 – 0,45 g) have been dried at a temperature of 120 °C for 2 h. and after that degasified in vacuum at 120 °C for 2 h. The started sample of kaolin (WK) was degasified for 20 h. The specific surface area (S_A) was determined by BET method from the corresponding nitrogen adsorption isotherm ($p/p_o = 0.05 – 0.30$) and pore size distribution in the micro-, mezzo- and macopore diameter range were calculated using the HK (Horvath-Kawazoe) and BJH (Barrett-Joyner-Halenda) theory.

3   Result and discussion

The chemical composition and weight loss by annealing of dried kaolin (WK) in **Table 1** indicates ≈ 93 % of kaolinite in the sample. The weight loss of kaolin evaluated from the record of TG-analysis corresponds with the results (**Fig.1, Table 2**). Intensive endothermic effect in the DTA-records that is a result of decomposition of the kaolinite to metakaolin can be seen in the temperature range from 500 to 650 °C. No exothermic effects are observed on the DTA record in the temperature range from 950 to 1000 °C.

Table 1   Chemical analysis of washed kaolin-Sedlec

Chemical composition	
Oxides	[wt. %]
SiO_2	46,44
Al_2O_3	36,57
Fe_2O_3	1,26
CaO	0,67
MgO	0,46
Na_2O	-
K_2O	-
ratio Al : Si [mol]	1 : 2,15
Weight loss	13,1
Rational calculation of clay composition	≈ 93 wt % kaolinite and ≈ 3 wt % quartz

Table 2   Weight loss of kaolin during TG analysis

Temperature [°C]	Weight loss of kaolin [wt. %]	Relative loss of structurally bound water in kaolin [-]
105	- 0.3	0
200	- 0.7	0.031
350	- 0.9	0.046
450	- 1.5	0.092
550	- 2.8	0.192
650	- 10.6	0.79
750	- 12.0	0.9
1000	- 13.3	1

The theoretic ratio of Si : Al : O atoms is 1: 1: 9 in kaolinite and 1: 1: 7 in metakaolin. The ratios of Si : Al : O measured by EDS analysis are 1: 1: 8 (±0,2) in the dried kaolin and 1: 1: 6,5 (±0,4) in the kaolin annealed at a temperature of 500 °C for 2 h. The change of oxygen content corresponds with the loss of structurally bound water. The laminar character of kaolinite can be seen in **Fig.2.**

X-ray analysis records of kaolin annealed at temperatures of 350, 450, 550, 650 and 950 °C for 30 min. are shown in **Fig.3** and FTIR-spectra in **Fig.4.**
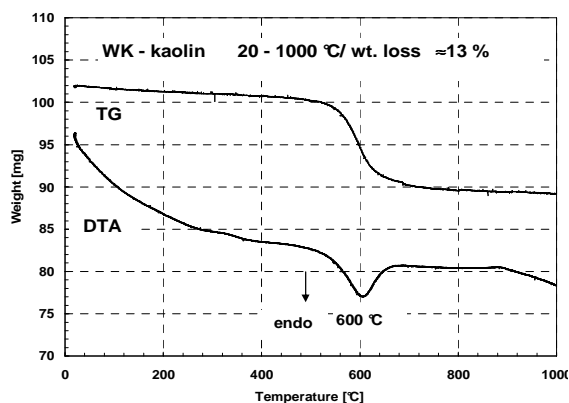
Fig.1 Records of thermal analysis TG and DTA of kaolin (heating rate of 10 °C/min.)
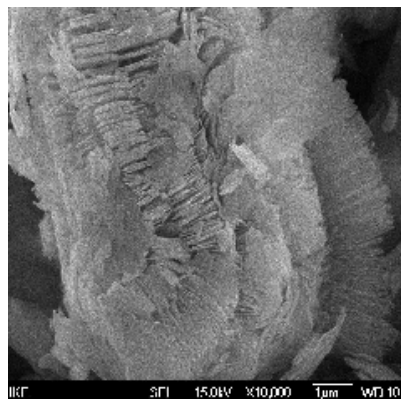

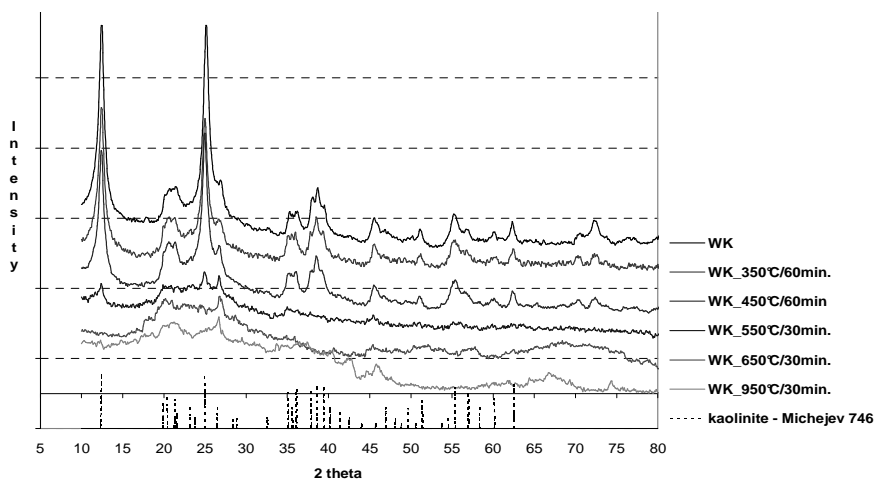**Fig.2** Aggregation of kaolinite particles

Fig.3 X-ray diffraction record of heated kaolin up to 950 °C

The records clearly show the influence of increase in annealing temperature on the structure decomposition and vanishing of hydroxyl bands. As is shown in the X-ray records the kaolinite structure significantly transforms up to 450 °C. But on the FTIR records only minor differences can be seen in the intensity of wavenumber signal between the initial and the annealed sample at this temperature. However, removal of the structurally bound water from the kaolin a temperature of 550 °C is evident. That agrees with the structural changes detected by X-ray analysis; the structure is disintegrated at 550 °C. No intense reflections on X-ray diffraction records were observed which would confirm any new crystalline phase created at a temperature of 950 °C.

The water molecules in kaolin are detected by the presence of the H-O-H bending mode at $\approx$ 1630 cm^{-1}. Bands at 3695, 3675, 3654 and 3620 cm^{-1} characterize the hydroxyl bands in kaolin.

The weak signal at the wavenumber of $\approx$ 1630 cm^{-1} was apparent only at dried sample of kaolin. The bands at wavenumber of 3620 – 3630 cm^{-1} are due to the –O-H groups bond into octahedral

sheets, that constitutes ¼ of –OH groups in mineral, and bands of 3690 - 3698 cm^{-1} belonging to the –O-H groups bond on face of octahedral sheets, those constitute ¾ -OH [4]. A proof of dehydroxylation is the gradual loss of signal of 3695 – 3620 cm^{-1} and 914 and 935 cm^{-1} which occurs at temperatures of 450 – 550 °C. With increasing of annealing temperature decrease of intensity of bands at wavenumber range of 1150 – 752 cm^{-1} becomes evident. Modification of structure at heating is observed as well by changes in the Si-O from plane stretch at 1109 cm^{-1} and the decrease in the intensity of the 540 – 550 cm^{-1}. Wavenumber of $\approx$ 792 cm^{-1} characterizes –OH translation in kaolin lattice [13].

3698 cm^{-1}	- signal due to the O-H stretching vibration; bands of O-H vibration ;
3650 - 3620 cm^{-1}	- signal due to the O-H stretching vibration; bands of internal O-H vibration;
1630 cm^{-1}	- H-O-H bending mode, vibration of molecular water in the clay;
1115 - 1005 cm^{-1}	- adsorption valence vibration of Si-O; SiO - stretch;
935 cm^{-1}	- bands of external vibration of O-H; (Al-OH)
914 cm^{-1}	- deformation bands of internal vibration of O-H; (AlOH)
792 cm^{-1}	- OH translation in kaolin lattice;
752 and 677-650 cm^{-1}	- OH translation;
538 - 470 cm^{-1}	- Al-O deformation vibration, Si-O-Al and Si-O-Si in octaeder and thetraeder nets;
457 - 400	- Si-O bending vibration, amorphous SiO$_2$;

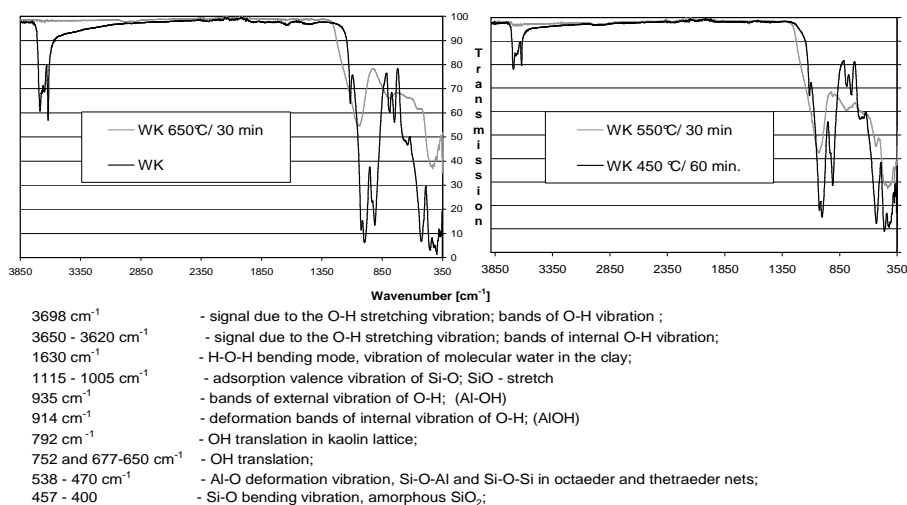**Fig.4** FTIR spectra of washed kaolin and annealed kaolin up to 650 °C [4,17,20,21].

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The specific surface areas (S_A) of kaolinite are listed in relation to the temperature/duration of annealing and the conversion degree of dehydroxylation in **Table 3** and $S_A=f(\alpha_{dehyd.})$ is described in **Fig. 5.** The **s**pecific surface area of dried kaolin was $\approx$ 19.2 m^2.g^{-1}. Narrow hysteresis loop on sorption isotherm of all kaolin samples points to negligible porosity. Distribution of micropores (pores with diameters not exceeding 2 nm), mezopores (ϕ 2-50 nm) and macropores (exceeds ϕ 50 nm) calculated form desorption isotherms are shown in **Table 4**.

The loss by annealing of kaolin-Sedlec was 13.1 $\pm$ 0.2 wt.%. Even though the kaolin sample has been dried before annealing for a long time, only a little weight loss was observed in the range of temperature of 200 to 350 °C. The 0.4 wt.% of loss by annealing to the total loss of water (13.1 wt.%) corresponds to 0.03 conversion (3 %) of dehydroxylation.

As can be seen in **Table 3;** the weight losses practically did not show much different values according to the time of annealing if annealing was carried out at a temperature of 350 °C. In this case water is escaping from the intermediate sheets and from the defective crystal structure. The weight loss is accompanied by decrease of specific surface of kaolin by about 2 $m^2.g^{-1}$, i.e. by about -7 to -8 %.

The records of FTIR and X-ray diffraction analysis (**Fig. 3, 4**) show escape of structurally bound water from the annealed sample and disintegration of kaolin structure at a temperature of 550 °C. The conversion of kaolinite to metakaolinite increases with temperature and time of exposure. In the temperature interval of 400 - 800 °C the value of the specific surface area of metakaolin is approximately 16 – 17.5 $m^2.g^{-1}$.

Table 3 Development of specific surface area (S_A) by dehydroxylation of kaolin (locality of Sedlec) to metakaolin

| Thermal treatment [°C/min]	α -Conversion of kaolin to metakaolin	S_A (± 0.4) [$m^2.g^{-1}$]	Change of S_A at annealing [%]
Non-annealed, dried at 120 °C to constant weight	0	19.2	0.0
200 °C/ 60 min	0.005 (± 10%)	19.7	+ 2.6
350°C/ 60 min	0.03 (± 5%)	17.7	- 7.8
350°C/ 120 min.	0.04 (± 5%)	17.6	- 8.3
450°C/ 60 min	0.28 (± 5%)	16.7	- 12.8
450 °C/ 120 min	0.38 (± 3%)	16.0	- 16.7
550°C/ 30 min	0.73 (± 3%)	17.1	- 10.9
550°C/ 60 min	0.86 (± 3%)	17.9	- 6..8
550°C/ 120 min	0.89 (± 2%)	17.8	- 7.3
650°C/ 13 min	0.68 (± 3%)	16.8	- 12.5
650°C/ 30 min	0.91 (± 2%)	17.9	- 6.8
650°C/ 120 min	0.95 (± 2%)	16.9	- 12.0
750°C/ 10 min	0.84 (± 4%)	16.5	- 14.0
750°C/ 15 min	0.92 (± 3%)	16.8	- 12.5
750°C/ 30 min	0.98 (± 1%)	16.8	- 12.5
850°C/ 15 min.	0.96	16.4	- 14.6
950°C/ 15 min	0.98	9.7	- 49.2
950°C/ 30 min	0.99 (± 0.5%)	10.2	- 47.6
950°C/ 120 min	1 (± 0.5%)	9.3	- 51.5
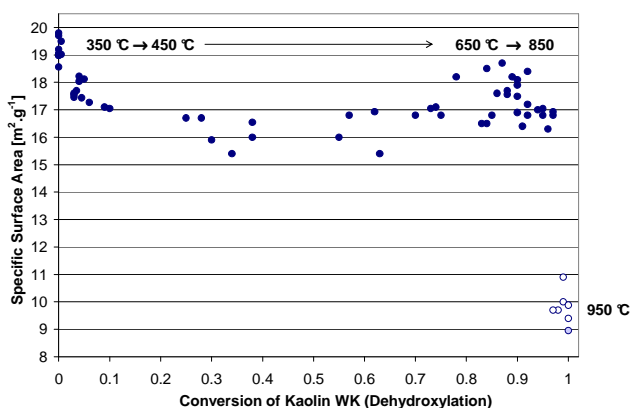
Fig.5 Change of surface area with conversion of kaolin WK

Kaoline raw material (WK) creates agglomerates (**Fig. 2**) which keep together after calcinations, too. The porosity of kaolin is negligible as show the results in **Table 4**. The pore volume decreased more above the temperature of 650 °C. The increase of temperature up to 950 °C involves abrupt decreases of the surface area by as much as ≈ 50 % of the initial value.

Table 4 Evaluation of micro- and mezoporosity dried kaolin at 200 °C /1200 min. and calcined kaolin at 550, 650, 950 °C /120 min. by HK and BJH methods

Samples [°C/min]	External Surface $[m^2.g^{-1}]$	BJH_D Cumulative Pore Volume $[cc.g^{-1}]$	BJH_D ϕ Pore Mode $DV(d)$ [nm]	HK method Cumulative Volume $[cc.g^{-1}]$	HK method ϕ Pore Mode $DV(d)$ [nm]
WK 120 °C/ 1200 min	19.7	0.148	3.70	0.0122	0.43
WK 550°C / 120 min	17.8	0.141	3.71	0.0121	0.43
WK 650 °C / 120 min	16.9	0.115	3.63	0.0110	0.43
WK 950°C / 120 min	9.3	0.071	4.07	0.0056	0.43

V- volume.

4   Conclusion

The specific surface area of the studied natural washed kaolin was 19 $m^2.g^{-1}$. The weight loss by annealing of kaolin was $13,1 \pm 0,2$ wt.%.

Dehydroxylation of the kaolinite started certainly as early as in temperature intervals 350 – 450 °C but the release of water was very slow. Rapid conversion to metakaolin occurs at temperatures above 550 °C. The metakaolin showed lower structural arrangement than kaolinite in all temperature ranges of 450 – 950 °C.

A decrease of specific surface area of more than 10 % was observed with the natural dried kaolin (WK) and annealed kaolin at a temperature of 350 °C. The surface area of annealed kaolin ranges to about 16 -17 $m^2.g^{-1}$ in the temperature interval of 350 to 750 °C. Pore volume decreased with surface area.

A significant decrease of specific surface of annealed kaolin up to half of the initial value was detected at a temperature of 950 °C. The new spinel phase formation was not detectable by X-ray diffraction at this temperature.

Acknowledgements

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