HYDROTHERMAL DEGRADATION OF CERAMIC MATERIALS ON THE NATURAL RAW MATERIALS BASE
Part 2: Structural changes

ANDREA PEŠOVÁ, JANA ANDERTOVÁ, ONDREJ GEDEON

Institute of Chemical Technology Prague, Department of Glass and Ceramics
Technicka 5, 16628 Prague, Czech Republic

E-mail: andrea.pesova@vscht.cz

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In this paper is dealt with ageing of ceramics, particularly with structural changes of ceramic materials on the base of natural materials after hydrothermal exposure. Identified structural changes are correlated with physical changes expressed as relative deformation. It is assumed deformation of fired clay-based materials is governed by the rehydroxylation of kaolinite, namely via inner and outer OH-groups, present in clay minerals. Samples from mixtures of clay minerals and calcite and/or dolomite, and from fine kaolinitic clay were prepared. Structural changes during hydrothermal exposures were evaluated by the means of infrared spectroscopy. ^{27}Al MAS nuclear magnetic resonance was also used for confirmation of change of bonds. Correlation between relative deformation and amount of the specific OH bonds in rehydrated samples was confirmed.

INTRODUCTION

Clay raw materials belong among typical natural raw materials. The basic constituents of clay raw materials are so called clay minerals. Their crystal structure, with a few exceptions, consists of the structurally well recognized sheets (therefore the terms sheet silicates or phyllosilicates are used). The crystallographic primitive unit cells are composed of two, three or four sheets. The sheets are formed either by tetrahedrons $[SiO_4]^{4-}$, or by octahedrons, e.g. $[AlO_3(OH)_3]^{6-}$. The interior of tetrahedrons and octahedrons contains smaller metal cations, their apices being occupied by oxygens from which some are connected with protons (as OH). All these fundamental structural elements are arranged to form a hexagonal network in each sheet [1]. Kaolinite is the important representative of clay materials from point of view of ceramic technology. Kaolinite is a dioctahedral 1:1 layer silicate. The crystal chemical formula of this mineral is $Si_2O_5(OH)_4Al_2$ [2].

The thermal reactions of kaolinite have been studied for a very long time. The thermal treatment of kaolinite may be considered as taking place in a series of steps. The first step up to 100 °C contains water desorption. Dehydration depends on the nature of the kaolinite and the degree of disorder of stacking [3]. In the temperature range between 450 - 600°C, the kaolinite dehydroxylates and the product phase is known as metakaolinite:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \rightarrow Al_2O_3{\cdot}2SiO_2 + 2H_2O \quad (1)$$

The kaolinite still retains its layered structure and is able to return into the kaolinite by the uptake of water from atmosphere [4,1]. Bi-dimensional structure of metakaolinite is preserved up to around 950°C where a three-dimensional spinel structure is formed:

$$2(Al_2O_3{\cdot}2SiO_2) \rightarrow 2Al_2O_3{\cdot}3SiO_2 + SiO_2 \quad (2)$$

Further heating above 1100 °C transforms this phase to mullite [3]:

$$3(2Al_2O_3{\cdot}3SiO_2) \rightarrow 2(3Al_2O_3{\cdot}2SiO_2) + 5SiO_2 \quad (3)$$

Moisture (atmospheric water or air moisture) influences service life and suitability of ceramic materials. It causes physical and chemical changes and products expansion [5]. Consequences of this expansion are formation of material defects and destruction. Irreversible moisture expansion can be simply quantified by the relative deformation $\varepsilon = (\Delta l/l)$, where Δl is prolongation of the body after hydrothermal exposure and l is its original length before hydrothermal exposure [5]. Hydrothermal exposure simulates process of long lasting treatment of atmospheric water on ceramic material [6, 7]. The real exposure time is in case of hydrothermal exposure shortened by the increased temperature and higher water vapour pressure, what accelerates the rate of water related processes so that the final influence of simulated exposure is close to the real one.

Infrared (IR) spectroscopy has a long and successful history as an analytical technique and is used extensively in various applications [8, 9]. Infrared spectroscopy is widely used to determine and investigate the structure of mineral phases [10]. IR spectrum can serve as a fingerprint for mineral identification, but it can also provide unique information about mineral structure, e.g. determination of the family of minerals to which the specimen belongs, the degree of regularity within the structure, the nature of isomorphic substituents, distinction of molecular water from constitutional hydroxyl, and the presence of crystalline and/or non-crystalline impurities [11]. IR can be performed using a large variety of experimental geometry. Powdered materials can be studied by diffuse reflectance [12] or attenuated total reflectance to investigate the interface between solids and aqueous solutions [13]. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) is widely used in the analysis of solids and powders and generally requires little sample preparation. Its use is limited somewhat by interference effects created by particle size and incident IR wavelengths, which may appear toward the low-frequency region, normally below 1200 cm^{-1} for clays. To minimize such effects, the clay is mixed with KBr to obtain good DRIFT spectra in the 1200-400 cm^{-1} region [14].

High-resolution ^{27}Al nuclear magnetic resonance (NMR) has proved to be useful for determining of the coordination numbers of aluminium in various Al-O compounds [15]. This technique seems particularly valuable for studying the structure of the intermediate phases formed by heating kaolinite what is of fundamental importance in the production of clay-based ceramics [16]. Previous works on the synthesis of kaolinite minerals from different materials [17] suggested that in order to understand the processes involved, it may be important to monitor the amounts of 4- and 6-coordinated Al.

In part I physical changes of the (hydrothermally) exposed materials were evaluated [5]. Results have shown a strong dependence of the found irreversible deformation on the content of kaolinite and hydrothermal exposure conditions. However, understanding of moisture expansion unnecessarily needs study of chemical (structural) changes. In this paper structural changes and a correlation between physical and structural changes are studied. To our best knowledge, nobody has tried to correlate physical changes (measured as relative deformation) and structural changes expressed through AlOH structure units.

EXPERIMENTAL

Raw materials used for the experiment were natural clay raw materials, calcite and dolomite from Czech Republic. Raw materials were characterized with analytical methods results of which are reported in [5].

At first, model mixtures from clay raw materials and from calcite and dolomite were prepared. The first group of mixtures contained calcite in the range from 0 wt. % to 20 wt. % in the batch; marked C0 – C20 according to the calcite content. The second group of mixtures, marked D0 – D20, contained from 0 wt. % to 20 wt. % of dolomite in the batch. Finally, fine kaolinitic clay raw material signed K without addition of calcite or dolomite was used.

Samples were formed by a laboratory pressing machine and were fired in a laboratory furnace under time variable high temperature treatment. Five different firing regimes were chosen. A base regime was the commercial "fast-firing" used in industry. The whole temperature treatment can be divided into the following parts. Part A is a slow heating up to temperature 800 °C while the following part B is heating to up temperature 1150 °C with a different rate. Next part C is holding at maximal temperature 1150 °C for 15 minutes. Then a controlled cooling down to room temperature is followed. Modification of the described temperature regime consists in time prolongation of the particular parts. Firing regime F1 was the base regime; F2, F3, and F4 regimes correspond to the time prolongation (5 times) of the A, B, and C parts, respectively. F5 firing regime represents a regime where all of the referred parts were 5 times prolonged.

The firing was followed by hydrothermal exposure in autoclave under the variable conditions of temperature and exposure time. The following regimes were used. A1 - exposure lasts 2 hours at the temperature 80°C, A2 - exposure lasts 2 hours at the temperature 160°C, A3 - exposure lasts 20 hours at the temperature 80°C, and A4 - exposure last 20 hours at the temperature 160°C ([5] describing details).

For diffuse reflectance infrared spectroscopy (DRIFT) analysis of earthenware shards, two methods were used. One group of samples was measured with methods of internal standard and the mixture of KBr : sample : KSCN (internal standard) in ratio of 90 : 9 : 1 (mass fractions) was used. The second group of samples was measured in powder state without mixing with KBr. The samples were homogenized in an agate mortar. Before DRIFT analysis, the sample was dried in an evacuated dessicator with an activated silica gel for complete moisture removal from the analyzed mixture. DRIFT spectra were measured immediately after opening of the dessicator. The spectra were measured using a Nicolet 7600 spectrometer (Thermo Nicolet Instruments Co., Madison, USA) with a DTGS detector, KBr beamsplitter, equipped with a Spectra Tech cuvette (so-called Central Focus Version). Measurement parameters: spectrum accumulation 128 scans, resolution 4 cm^{-1}, Happ-Genzel apodization. Spectra were transferred to Kubelka-Munk units (MK) corresponding to absorbance units in the transmittance mode. For spectral manipulation, OMNIC Software Version 7.3 was used.

Infrared spectroscopy is widely used to study changes of hydroxyl groups in clay minerals. Clay minerals in kaoline contain more types of hydroxyl groups (see Figure 1 and Table 1): the outer hydroxyl groups (also called inner surface hydroxyls), and the inner hydroxyl groups. These hydroxyl groups were designated by Frost and van der Gaast [15] OuOH and InOH, respectively. The OuOH groups are situated in an outer, unshared plane, whereas the InOH groups are located in the plane shared with the apical oxygen atoms of the tetrahedral sheet. Several distinct bands referring to OH vibration are observed in the infrared spectrum of kaolinite, namely at 3745, 3720, 3690, 3670, 3650, and 3620 cm^{-1} [18-22]. The frequency bands at 3745 a 3720 cm^{-1} are attributed to Si-OH groups. Bands at 3690, 3670, 3650 a 3620 cm^{-1} belongs to Al-OH groups, among which bands at 3690, 3670, 3650 cm^{-1} are assigned to OH stretching modes of the outer hydroxyl groups (OuOH) [22]. The band at 3620 cm^{-1} is assigned to the stretching mode of an inner hydroxyl group (InOH) [23-27] (see Table 1). The band at around 3200 cm^{-1} is normally associated with water, which is coordinated to a metal ion. Bands at around 3570 cm^{-1} are associated with bound water and bands around 3590 cm^{-1} with interlamellar water [28-32].

^{27}Al MAS NMR spectra were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer equipped with double-resonance 4-mm probehead. Spectra were acquired at 130,287 MHz; spinning frequency was $\omega_r/2\pi$=11 kHz; 20° pulse width was 1 ms; recycle delay 2 s; and the spectra were referenced to $Al(NO_3)_3$ (0.0 ppm).

Table 1. Positions of hydroxyl groups or water in kaolinite.

Kind of OH groups or water	Band positions (cm^{-1})
Si–OH	3745, 3720
Al–OH (OuOH, outer)	3690, 3670, 3650
Al–OH (InOH, inner)	3620
interlamellar water	3590
water	3200-3570

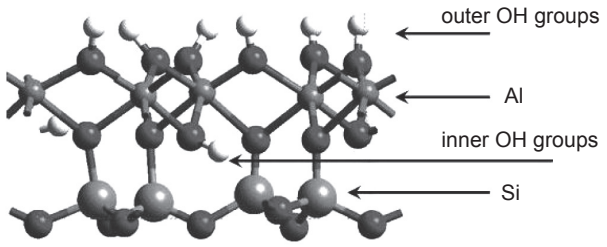

Figure 1. Scheme of kaolinite structure showing the stacking of two layers. Two kinds of OH groups can be distinguished. The outer OH groups are located at the top of the dioctahedral sheet. And inner OH groups are located inside the layer, between the dioctahedral and tetrahedral sheets.

RESULTS

DRIFT spectra of samples from mixtures C0 and C15 (firing regime F1) before and after hydrothermal exposure A2 are shown in Figure 2. Concerning sample C15, hydrothermal exposure in autoclave obviously increased band intensities of both outer OH groups and inner OH groups. Especially remarkable increases of intensities can be seen at 3690 cm^{-1} (OuOH), 3620 cm^{-1} (InOH), and 3540 cm^{-1} (water). (Peaks at 2990 to 3010 cm^{-1}, attributed to C-H vibrations, visible for some samples, come from impurities of matrix.) In case of C0 sample the differences between exposed and unexposed samples seems to be very small, but for the quantitative arguing they need to be related to the intensity of a standard. In opposition to the previous sample, a pronounced new peak attributed to interlamellar water (3590 cm^{-1}) is observed after the exposure. Interestingly, well visible peak at 3540 cm^{-1} (water) nearly disappeared due to the exposure.

The amount of OH-groups present in the body was quantified by means of IR spectroscopy, using internal standard KSCN. Band intensities of the stretching vibration of OH groups at 3620 cm^{-1} (InOH) and 3690 cm^{-1} (OuOH) were normalized to the band intensity of KSCN at 2800 cm^{-1}. Differences in the normalized intensities of hydroxyl groups after the hydrothermal exposures determined this way for both 3690 cm^{-1} (outer OH groups) and 3620 cm^{-1} bands (inner OH groups) are presented in Figure 3. While inner hydroxyl groups show a strong linear dependence on e, outer hydroxyl groups (at least those at 3690 cm^{-1}) don't correlate with values of the relative deformation of the studied samples. The linear fit shows even for no deformation, i.e. no exposure or in other words after firing, some amount of InOH groups is present

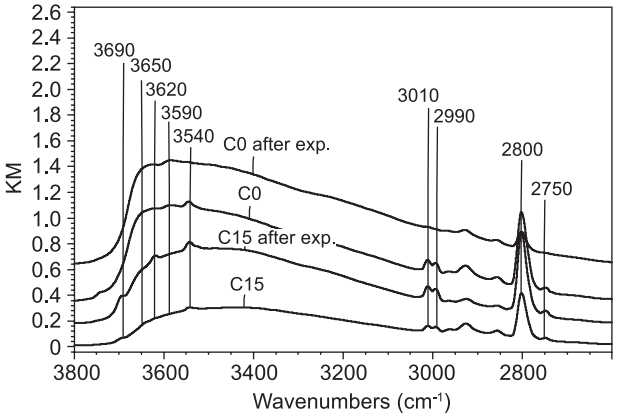

Figure 2. DRIFT spectra of samples from mixtures C15 and C0 before and after hydrothermal exposure A2. Samples were fired under the condition of the firing regime F1. The wavenumbers of the prominent peaks are indicated. Spectra are shifted for a better visualization.

As experiments performed for C*x*, D*y*, samples showed apparent influence of kaolinite on the relative deformation the next study was focused just to the fine kaolinitic clay K. This was fired under condition of firing regime F5 and exposed to the three different regimes of the hydrothermal exposure (A1, A2, and A4). The following denomination is used: KF5 is kaolinitic clay K calcinated with firing regime F5; KF5A1 is kaolinitic clay K calcinated with firing regime F5 and hydrothermally exposed to A1, etc. In Figure 4 DRIFT spectra of kaolinitic clay K within the frequency range 3800-2600 cm^{-1} are presented. It is evident bands attributed to both hydroxyl groups and water increased in their intensity with increasing time and/or temperature of the hydrothermal exposure. However, different bands changed differently. Bands at 3745 a 3720 cm^{-1} (attributed to Si-OH groups) do not seem to depend on the exposure. In addition, the well recognizable peak at 3745 cm^{-1} is continuously broadening so that it nearly disappearing for A4 exposure. Bands at 3690, 3650 and 3620 cm^{-1}, belonging to Al–OH groups, as well as band at 3590 cm^{-1}, belonging to interlamellar water showed a systematic increase with the time and/or temperature increase during the hydrothermal exposures. Similar trend can be seen for bands between 3570-3200 cm^{-1}, belonging to water. Here, a peak at around 3500 cm^{-1} and a peak at 3590 cm^{-1} were formed by the hydrothermal exposures.

Band intensities of the stretching vibration of OH-groups at 3745 cm^{-1} (Si-OH), 3650 cm^{-1} (Al-OH), and interlamellar water at 3590 cm^{-1} were normalized to the band intensity at 1300 cm^{-1}. In Figure 5 is presented an abundances of Si-OH and Al-OH groups (OuOH) as well as interlamellar water in dependence on values of relative deformation of calcinated and hydrotermally exposed clay K. While relative abundances of Si–OH groups are not changed, i.e. the hydrothermal exposure doesn't affect silicon bonding bands intensities of Al–OH groups as well as that corresponding to interlamellar water show significant dependences on hydrothermal exposure conditions. It should be noticed that intensities of Al–OH group at 3690 cm^{-1} shows a similar course as in Figure 3, i.e. a sudden decrease of intensity can be observed for a high relative deformation (A4 exposure) and intensities of Al-OH group at 3670 cm^{-1} follow the presented intensities at 3650 cm^{-1}.

Change of bond character (coordination) in samples before and after the hydrothermal exposure was studied by ^{27}Al MAS NMR. Measurements were carried on samples of kaolinitic clay K before and after hydrothermal exposures A1, A2, and A4. It was evaluated the ratio between the peaks corresponding to 4-coordinated Al

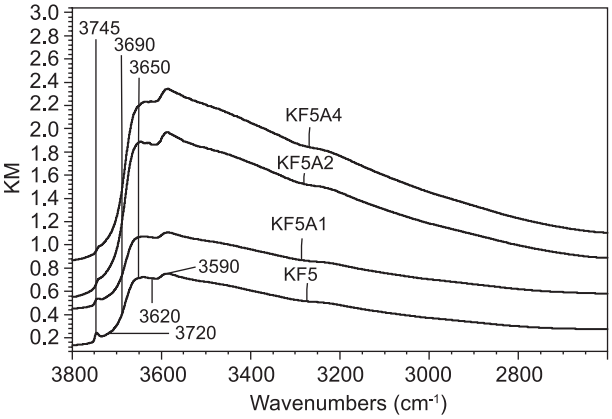

Figure 4. DRIFT spectra of calcinated and hydrotermal exposed clay K within the frequency range 3800-2600 cm^{-1}. Samples were fired under the condition of the firing regime F5 and were exposed to the three different regimes of the hydrothermal exposure (A1, A2, A4) as indicated by tags. Spectra are shifted for better visualization.

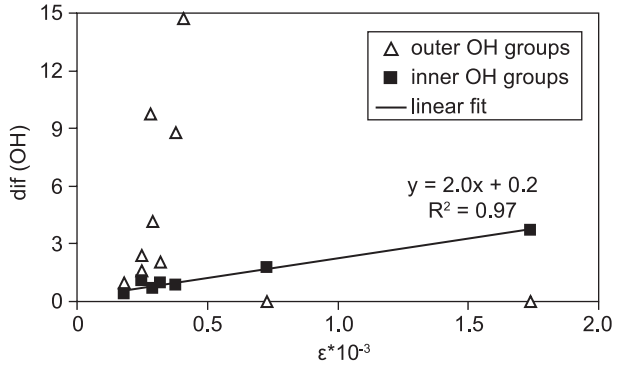

Figure 3. Correlation between relative deformation and the differences in the normalized intensities of hydroxyl groups for some samples C0-C15 and D0-D15 for A2 hydrothermal exposure. Samples were fired in conditions of firing regime F1. Notice a strong correlation between inner OH groups and relative deformation. Outer OH groups are represented by intensity at 3690 cm^{-1}.

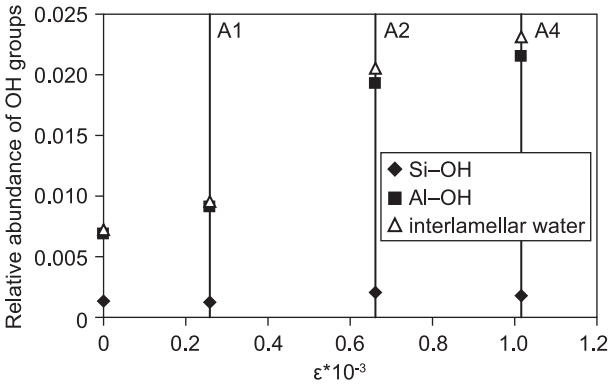

Figure 5. Abundances of Si–OH and Al–OH groups of calcinated and hydrothermally exposed clay K. Samples located on y-axis are before the hydrothermal exposure and the tags denote hydrothermal exposures A1, A2, and A4, respectively. Samples were fired under the condition of the firing regime F5.

and 6-coordinated Al. Relevant changes were found only between spectra of samples KF5 and KF5A4, i.e. only the longlasting hydrothermal exposure leads to change in coordination of some Al atoms (the octahedral ones transform to the tetrahedral ones). It is in accordance with concept, that OH groups could change octahedral coordination of Al to the tetrahedral one. By contrast, spectra of samples KF5A1 and KF5A2 didn't show significant changes in comparison with KF5.

DISCUSSION

From the strictly thermodynamic point of view, firing of clay raw materials up to 1150 °C should leave stabile waterless phases in the fired body. If kaolinite were fired (sample K), only mullite and SiO_2 should be found in the fired body (see reaction 3). Nevertheless, such conclusion is incorrect as the firing must be taken as a set of kinetic processes and the amounts of final products in reactions (1-3) depend on the particular firing regime. Hence, even if no traces of kaolinite or metakaolinite are found in XRD spectra of the fired bodies it does not mean that small crystals, unresolved with XRD, are not preserved in the fired body. Such view is also supported by IR spectra of the fired samples which prove existence of OH-groups, which frequencies correspond to those found for kalolinite (see Figures 2 and 4). As show previous results [2] metakaoline is able to rehydroxylate to kaolinite and this reaction is accompanied with a volume change. Hence, our experiments were focused to kaolinite bands located in IR spectra and to their correlations to relative deformations of samples exposed to various hydrothermal treatments.

Kaolinite structure enables to recognize at least two different types of OH-groups bound to Al, inner ones and outer ones. Because outer OH bounds are not in structurally equivalent positions three different stretching frequencies are found in IR spectra. DRIFT spectra of samples prepared from mixtures of clay raw material with calcite and/or dolomite before and after hydrothermal exposures have shown inner and outer OH groups (corresponding to 3690 cm^{-1}) are related to the relative deformation in a very different manner (Figure 3). While OuOH show no straightforward relation to the deformation, InOH yield a surprisingly strong linear correlation with the relative deformation of the fired and successive hydrothermally treated bodies. The linear fit confirms the idea that even in the unexposed body some firmly bound InOH groups are found. It can be interpreted that either some kaolinite was preserved in the fired body or the transformation from metakaolinite to kaolinite took place very fast just in normal atmosphere. On the other hand results presented in Figure 3 indicate OuOH do not play a significant or at least simply related role in connection with aging.

Detail analyses of sample K exposed to various hydrothermal exposures showed, not surprisingly, Si-OH groups are not related with the found deformations. In addition, the groups seem to be nearly unaffected by the exposures.

Abundances of Al–OH groups (outer OH groups at 3650 cm^{-1}) and of interlamellar water in dependence on relative deformation are shown in Figure 5. Relative abundances of Si-OH groups do not change with the hydrothermal exposure; it means Si-bonds are fully saturated after the firing and further hydrothermal exposure is not able to change the bond character of Si. By contrast bands intensities of Al–OH groups at 3650 cm^{-1} and of interlamellar water follow the same increasing course in dependence on relative deformation. As expected, longer time or higher temperature exposures lead to the higher relative deformations. However, bands corresponding to the different stretching frequencies of Al-OH behave in the different manner. While hydroxyles groups at 3690 cm^{-1} is not monotone function of deformation intensities of hydroxyles groups at 3650 cm^{-1} (and also at 3670 cm^{-1}) increase with an increasing *e*. Hence, it seems that at first kaolinite is predominantly hydroxylated via Al-OH corresponding to 3690 cm^{-1} but longer times and or higher temperatures causes that these OH groups are hopping to the more favourable sites corresponding to Al-OH at 3650cm^{-1} and 3670 cm^{-1}. ^{27}Al MAS NMR has shown the situation can be even more complicated. While exposures A1, and A2 do not change Al coordination exposure A4 leads to the transformation from Al^{VI} to Al^{IV}. Although the quantitative estimation of the number of transformed Al is relatively small (6%) it can further increase with the prolonged times of the exposure.

CONCLUSION

The aging of ceramics based on clay was shown to depend mainly on the presence of kaolinite. Intensity of bands corresponding to different OH groups and water were identified in the fired bodies by means of infrared spectroscopy. Hydrothermal exposures differing in times and temperatures were used to simulate aging. Intensity of band at 3620 cm^{-1}, corresponding to inner OH-groups, was found to be linearly related with relative deformation. On the other hand, the outer OH groups do not behave equivalently. While the number of Al-OH groups corresponding to the vibrations at 3650 cm^{-1} and 3670 cm^{-1} increase with relative deformations the number of Al-OH groups corresponding to the vibration at 3650 cm^{-1} does not reveal any simple relation to the deformations. In addition, the exposure at the highest temperature and the longest time used is accompanied with change of coordination around Al.

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