

Correlation between thermal behavior of clays and their chemical and mineralogical composition: a review

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Abstract. Clay's abundance has been widely used as industrial raw materials, especially ceramic and tile industries. Utilization of these minerals needs a thermal process for producing ceramic products. Two studies conducted by Septawander et al. and Chin C et al., showed the relationship between thermal behavior of clays and their chemical and mineralogical composition. Clays are characterized by XRD analysis and thermal analysis, ranging from 1100°C to 1200°C room temperature. Specimen of raw materials of clay which is used for the thermal treatment is taken from different geological conditions and formation. In raw material, Quartz is almost present in all samples. Halloysite, montmorillonite, and feldspar are present in Tanjung Morawa raw clay. KC and MC similar kaolinite and illite are present in the samples. The research illustrates the interrelationships of clay minerals and chemical composition with their heat behavior. As the temperature of combustion increases, the sample reduces a significant weight. The minerals which have undergone a transformation phase became mullite, cristobalite or illite and quartz. Under SEM analysis, the microstructures of the samples showed irregularity in shape; changes occurred due the increase of heat.

1. Introduction

Clay is a material which is a product of in-situ alteration, e.g. by means of weathering, hydrothermal action or alternatively, stored as a sediment during an erosional cycle or in-situ product which evolved into authigenic clay deposit. It is a natural, earthy, fine-grained material that develops plasticity when mixed with a limited amount of water [1]. Clay is generally used as a raw material to manufacture tiles or ceramics. Thermal reaction is needed in the production process because of the effect on the vitrification and sintering reaction. Both reactions determine the quality of the desired ceramic products. Natural clay deposits are associated with other minerals; these minerals are pollutant materials that could affect the manufacture of certain types of ceramic body [2]. Members of clay minerals groups are kaolinite, montmorillonite, smectite, illite, halloysite, etc. The modification of the clay minerals may improve thermal properties of clay mineral-based form. Different modification methods are suitable for different clay mineral materials due to the diverse physical properties and crystal structure [3].

Clay minerals are essentially hydrous aluminum silicates with magnesium or iron substituting as a whole or as a part of the aluminum in some minerals, and in some of them, alkalis or alkaline earth are also present as essential constituents [1]. Thermal analysis is one way to study fired clay transformation from the raw material, which is then heated at a temperature above 1000°C. It provides valuable information such as the dihydroxylation process which includes transformation phases of metakaolin, spinel to mullite at certain temperatures [4, 5]. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is commonly formed in fired clay through firing process at above 1150°C.



The study to determine a correlation of mineralogy of clays and their chemical composition and thermal behavior in certain temperature is widely practiced; two of which will be discussed in this paper. The first study was conducted by Septawander et al. [6] to clays originating from Tanjung Morawa (Indonesia) and the second study, Chin C [7] used clays originating from Ipoh and Romping (Malaysia). The research was based on the difference of geological conditions and formations. It determines the relationship between mineralogy and chemical composition and their thermal behavior of clays when fired at 1000°C to 1200°C and its possibility when they are used for ceramic industry. Both use the same characterization method, i.e. x-ray diffraction to analyze the clay mineral composition before and after the firing process, chemical analysis to identify the chemical composition and thermal analysis (TGA/thermogravimetry analysis and DTA/differential thermal analysis). Septawander performed a chemical analysis using atomic absorption spectrophotometry (AAS) and Atterberg to support the analysis. Chin C L performed chemical analysis with multi-dispersive X-ray fluorescence method and additional detailed analysis, such as grain size distribution analysis, dilatometry analysis, and microstructure analysis of clay morphology before and after burning by means of field emission scanning electron microscope (FESEM Zeiss, Supra TM 350 VP). The morphology of the fired samples was examined by using SEM (Hitachi TM3000).

Septawander used samples that passed the ASTM 80 mesh/177 µm sieve and the size of mold sample was 15x2.5x1.5 cm. The sample preparation was described in detailed by Chin C; it increased the assurance of data accuracy. In a dry condition, clays were crushed to small pieces and the sample was collected by means of coning and quartering. Then the sample was watered with a sprayer until it reached the value of moisture content of about 6% [8]. Samples had to pass 35 mesh/500 µm sieve, molded into button of 50 mm in diameter with pressing pressure of 27 MPa and dried overnight before they were fired in a muffle furnace (Nabertherm N60 / 14) with firing temperature of 1000°C, 1100°C and 1200°C respectively, according to the common practice by tile manufacturers.

2. Discussion

Worral [9] explained that kaolinite released water on the surface at firing temperature of 105°C. Kaolinite would decompose at a temperature of 450°C and release its hydroxyl group (-OH) as water and turn into metakaolin (reaction 1). At higher temperatures, metakaolin reacted and transformed into crystalline compounds, finally free silica (cristobalite) and mullite became the end products. Chemical reaction in thermal process are formulated in the reactions (1,2,3,4).

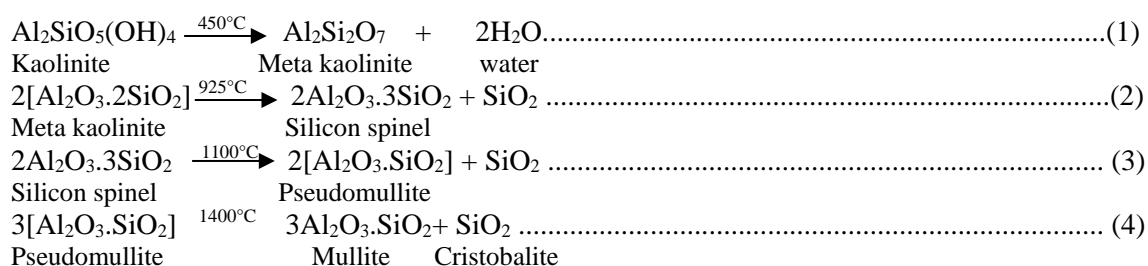


Table 1 presents the mineralogy of raw material and fired clays under XRD characterization. Chin C performed XRD pattern in one figure, making it easy to compare. Quartz is almost present in raw clays. Halloysite, montmorillonite, and feldspar are present in Tanjung Morawa raw clay. KC and MC, similar to kaolinite and illite, present in the samples. The intensity of the XRD peak shows considerable mineral presence. Intensities of mullite peaks noticeably increased and became dominant at firing temperature of 1200°C. All clays show the presence of mullite phase at firing temperature of 1100°C.

Table 2 presents the chemical composition of all clays. Chemical composition of clay was able to provide valuable information that can directly provide prediction of possible minerals present in the clays. The alkali oxides are excellent flux; these ions will reduce the melting point of the system and usually react with silica in a gradual manner at a temperature of 1100°C to form a viscous liquid that

fills the pores of Si-O. After the cooling process, they became solidified form of glass. This process led to the formation of complex glass (vitrification) and strengthened the clay after the combustion process [9].

Table 1. Mineralogy of raw clays and fired clays.

Location	raw material	Heated at temperature \geq 1000°C
Tanjung Morawa [6]	feldspar, halloysite, montmorillonite, mica, quartz	mullite, cristobalite a-quartz
KC [7]	quartz, kaolinite, illite	mullite, quartz, illite
MC [7]	quartz, kaolinite, illite	mullite, quartz, illite

Table 2. Chemical composition (in wt%) in raw clay.

Raw Clay	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Loss of ignition
Tanjung Morawa [6]	60,51	21,51	1,26	0,13	1,64	1,07	1,09	1,28	11,49
KC [7]	63,21	24,77	0,56	0,95	0	0,46	0,05	4,62	5,43
MC [7]	68,14	20,58	0,93	1,11	0	0,66	0,06	3,63	5,03

Based on TGA, DTA, and dilatometry conducted in Chin C L research, the thermal behavior of the clays was determined by the presence of quartz, illite, and kaolinite. Expansion was observed in both samples from the temperature of 200°C to 950°C. At this temperature the thermal expansion and contraction were more sensitive to kaolinite–illite interactions [10,11]. Resizing that happened very quickly could lead to crack during the firing process if the process of heating or cooling was done quickly through the temperature inversion [4]. The presence of other minerals at certain temperatures slightly inhibited kaolinite contractions, such as high-concentration illite minerals inhibited at temperatures of 550°C to 900°C, whereas quartz inhibited kaolinite contractions at 550°C to 650°C.

TGA curve of both KC and MC clays showed small weight loss that was attributed to the removal of absorbed water under the temperature of 300°C. Endothermic reaction peak showed in DTA curve at about 500°C to 550°C. The endothermic peak was the indication of dehydroxylation process of formation of metakaolin from kaolinite [12]. TGA curve showed changes in weight with respect to quartz and illite, at about temperature of 920°C and 980°C. The formation of mullite was detected at firing temperature of 1100°C and above; there was no significant weight loss or thermal reaction.

All the microstructures of the specimens showed irregularity in shape under SEM analysis. The differences of surface morphology of the clays are obviously related to their mineralogy. The K₂O content acted as an effective flux in improving densification process by vitreous phase [13] at certain firing temperature. At firing temperature of 1100°C, morphology of MC clay showed better densification than KC clay. It is obvious that the mineralogy of the clays affects the densification under firing condition. The present of alkali earth improve fluxing power of tile's body formulation, and also reduce vitrification temperature in the production of tiles.

3. Conclusions

Correlation of thermal behavior with mineralogy and chemical composition of clays has been studied by Septawander et al and Chin C et al. The research illustrates the interrelationships of clay minerals and chemical composition with their heat behavior, the weight loss gradually increases as the temperature of combustion increases. The mineralogical composition of clay is the determining factor in obtaining fired properties of ceramic product. The presence of different major minerals has been used to different applications in developing body formulation of ceramic products. At firing temperatures of 1100°C and 1200°C, the minerals undergo transformation phase to become mullite, cristobalite or illite and quartz as major components of clay. The growth of mullite increases with increasing of firing temperatures. K₂O compound in clays improves fluxing power and reduces vitrification temperature of ceramic tile body.

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