THERMAL CHARACTERIZATION OF KAOLINITIC CLAY

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Abstract. The paper presents thermal analysis studies on a certain type of kaolin which can be used as substitute for cement in mortar recipes prepared with recycled radioactive concrete for the solidification of radioactive waste. For this purpose, there were performed thermal analysis, differential thermal analysis, thermogravimetric analysis, differential scanning calorimetry, as well as the dilatometry of kaolinitic clay to study its behaviour to the progressive heating.

Key words: Thermogravimetry, differential thermal analysis, thermogravimetric analysis, differential scanning calorimetry, dilatometry, kaolinitic clay.

1. INTRODUCTION

The kaolin obtained from natural sources is impure. Thus, it is necessary to transform it from a non-active material into reactive metakaolin (MK) by heating. The process is possible by the calcination which causes water loss and its transformation into meta-kaolinite [1], an aluminium silicate with a disordered structure. The process is known as dehydroxylation and constitute the key on the reactive material obtaining.

Dehydroxylation is a 3-step process, as also predicted Zamzami et al. [2]. In the first step, the physisorbed and the interlayer water are removed by heating (< 200°C) due to its loosely bound as well as mobility. In the second step the strongly bounded water molecules from the first coordination sphere of the interlayer ions is removed at the high temperature (450–500°C). In the third step, the structural hydroxyl groups are condensed and dehydrated between the 500–800°C.

Metakaolinization occurs within the 550–900°C range [3]. The process involves the loss of hydroxyl group, followed by rearrangement of the octahedral layer to tetrahedral shape in the calcined clay [4]. During the thermal decomposition of kaolinite crystal, a partially disordered metakaolin is formed. The new phase metakaolinite does not collapse but rather retains a layered structure.

Kaolin has a 1:1 dioctahedral layered structure [5]. Each layer consists of two sheets, a tetrahedral one in which the silicon atoms are tetrahedrally coordinated by the oxygen atoms and an octahedral sheet, in which the aluminium atoms are coordinated octahedrally to the hydroxyl groups and the apical oxygen divided by...
the silica tetrahedron sheet. Consequently, one part of each layer has the siloxane surface resulted from the bases of the silica tetrahedron, while the other has a surface of hydroxyl groups in the aluminium octahedron. The hydrogen bond between these two surfaces provides significant cohesive energy between the layers that make interleaving difficult in kaolin. Since the kaolinite layer is neutral, the hydrogen bonds AlOHO\textsubscript{Si} are attached to every two unbroken layers [6]. Although tetrahedral sheets have oxide surfaces, there is a formation of an asymmetric octahedral sheet environment that has hydroxyl groups on the intermediate surface. These layers are less bonded by Van der Waals forces along "c axis" direction. The OH groups of the inner surface are located perpendicular to the tetrahedral sheet of the next layer that precedes the creation of the intensive hydrogen bonds. Therefore, kaolinite has been classified as a non-expandable mineral [7].

In this paper, a kaolin powder is thermally characterized for its use as a substitute for cement into the mortar recipes prepared with recycled radioactive concrete in order to solidify radioactive waste. There were performed studies regarding kaolin dehydroxylation for metakaolin obtaining. The process consists in thermal decomposition of kaolinite crystal to a completely disordered metakaolin for which in the new phase, less amorphous, the crystal does not collapse but, rather, retains a layered structure.

2. MATERIALS AND METHODS

A kaolin powder from Bulgaria (Senovo, Vetovo and Ruse region) was used for thermal characterization. The chemical and microstructural characteristics are presented by the authors in reference [8].

The kaolin thermal analysis was performed by two methods:

i) Simultaneous thermal analysis SDTA (TG-DTA-DTG); where: (TG) Thermogravimetry, (DTA) Differential thermal analysis; (TGA) Thermogravimetric analysis;

ii) Differential Scanning Calorimetry (DSC) and Dilatometry (DIL) method using the following devices:

- a thermal analysis device (TG-DTA-DSC-FTIR) STA 409PC with the following process parameters: temperature range: 25–1250°C; heating speed: 10 K/min; aluminium crucible without lid; atmosphere: static air;
- a DSC 204 F1 Phoenix device with the following process parameters: temperature range: 25–600°C; heating speed: 10 K/min; aluminum crucibles with a 3 holes lid; atmosphere: synthetic air (purity 99.999%) with a flow rate of 20 ml/min;
- a dilatometer type DIL 402 PC with the following process parameters: temperature range: 25–1250°C; atmosphere: static air; heating speed: 3°C/min.

The measurement of the specific BET surface area of the kaolin powder was performed using the AUTOSORB-1C device.
3. RESULTS AND DISCUSSION

In the Figure 1 are presented DTA, TG and DTG curves obtained from the simultaneous thermal analysis of the kaolin powder. The thermal parameters of these processes are presented in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Process</th>
<th>( \Delta T / \text{(°C)} )</th>
<th>%( \Delta m/% )</th>
<th>( T_{\text{min}}(\text{DTG})/ \text{(°C)} )</th>
<th>Peak DTA/(°C)</th>
<th>( \Delta H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal of the absorbed water from the surface pores</td>
<td>25–210</td>
<td>0.78</td>
<td>61.9</td>
<td>70.3</td>
<td>endotherm</td>
</tr>
<tr>
<td>Kaolin dehydroxylation with metakaolin formation</td>
<td>210–945</td>
<td>11.86</td>
<td>537.1</td>
<td>537.4</td>
<td>endotherm</td>
</tr>
<tr>
<td>Crystallization of alumina and silicic acid</td>
<td>945–1050</td>
<td>–</td>
<td>–</td>
<td>990.9</td>
<td>exotherm</td>
</tr>
<tr>
<td>Formation of mullite and cristobalite</td>
<td>1100</td>
<td>–</td>
<td>–</td>
<td>1240</td>
<td>exotherm</td>
</tr>
</tbody>
</table>

\( \Delta T = \text{process temperature range; } \% \Delta m = \text{mass loss; } T_{\text{min}}(\text{DTG}) = \text{Minimum DTG corresponding temperature; peak DTA= temperature corresponding to the minimum/ maximum DTA; } \Delta H = \text{thermal effect.} \)

3.1. DIFFERENTIAL THERMAL ANALYSIS (DTA)

The DTA curve highlights the presence of an endothermic peak (70.3°C), in 25–210°C range, due to removal of the absorbed water from the surface pores as well as an endothermic peak (537.4°C) in 530–590°C range due to the mineral dehydroxylation. Wilson [9] and Shvarzman et al. [10] showed that this peak is associated with a mass loss of 13.76% for pure kaolinite. For the analyzed kaolin, this reaction is associated with a mass loss of 11.86 wt%.

\[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3\text{2SiO}_2 \text{ (amorphous metakaolinite)} + \text{H}_2\text{O} \]

According to the DTA analysis, the initial temperature range for kaolinite dehydroxylation is 450–700°C.

Zamzami [2] showed that a clarity of endothermic and exothermic peaks can reflect a well crystallized nature of kaolinite minerals, who was already confirmed by the X-ray diffraction. It has been observed that the positioning of this endothermic peak is dependent on the amount of clay minerals. Over the time, different classifications of kaolinite types have been proposed based on the temperature value, symmetry, width as well as the thermal peak intensity.


Liétard [12] introduced the slope ratio (SR) representing the ratio between the maximum slope of the descending branch of the dehydroxylation peak in the
DTA curve and the slope of the ascending branch of this peak. The slope ratio is a measure of the density of surface defects. When SR = 1, the peak is symmetrical and the kaolinite has not surface defects. The ratio value increases with the number of defects in kaolinite. When SR = 2 kaolinite has a high density of surface defects. Bich [11] showed that a higher degree of dehydroxylation corresponds to an increased amount of surface defect in the remaining kaolinite.

For the analysed kaolin sample (see Fig. 2), SR is equal to 1.22 ($S_{sp} = 15.96 \text{ m}^2/\text{g}$). It means that the material does not have many surface defects.

Fig. 1 – Simultaneous thermal analysis (SDTA) of kaolin powder: DTA, TG and DTG curves.

Fig. 2 – DTA curve slope ratio “corrected” determination.
3.2. THERMOGRAVIMETRIC ANALYSIS (TG)

For thermogravimetric analysis, the calculated kaolinite content in the sample was 98 wt.%, (see Fig. 1) which corresponds to the main phase observed by XRD (94.43%). The following reaction occurs when kaolinite is heated:

\[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O} \]

kaoliniti         metakaolin

The hydroxylation water is removed around 455°C, which corresponds to the theoretical mass loss for pure kaolin of 13.95 wt.%. The TG results show that the main mass loss is between 400–700°C, which actually corresponds to the clay minerals destruction. The mass loss measured in the raw kaolin, of 11.86 wt.%, is not much below the theoretical value. The difference can be attributed to the presence of quartz in kaolin as an impurity.

3.3. DERIVED THERMOGRAVIMETRIC ANALYSIS (DTG)

The DTG curve shows that the dehydroxylation reaction takes place starting at about 380°C and reaches a maximum at 537.1°C confirming the results previously obtained by the Gabor et al. [13], Foldvari [4] and Tironi et al. [14]. From the DTG curve can be observed the kaolinite conversion to metakaolinite in the range 450–650°C. The peak area is proportional to the kaolinite content of the raw kaolin sample. The obtained curves indicate that on the gradual heating of the kaolin sample the following processes occurs successively:

– removal of the absorbed water from the surface pores;
– dehydroxylation of kaolin with metakaolin formation:
  \[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 (\text{metakaolin}) + 2 \text{H}_2\text{O} \];
– crystallization of alumina and silicic acid:
  \[ 2\text{Al}_2\text{Si}_2\text{O}_7 \rightarrow \text{Si}_3\text{Al}_4\text{O}_{12} + \text{SiO}_2 \];
– formation of mulite and cristobalite.

Reactions:

– **530–590°C**: endothermic, dehydroxylation:
  \[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow (\text{Al}_2\text{O}_32\text{SiO}_2) (\text{amorphous metakaolinite}) + 2(\text{H}_2\text{O}); \]
– **900–1000°C**: exothermic, transformation into crystalline phase:
  \[ \text{Al}_2\text{O}_32\text{SiO}_2 \rightarrow 2\text{Al}_2\text{O}_33\text{SiO}_2 + \text{SiO}_2\text{H}_2\text{O} \text{amorpha} + \gamma \text{Al}_2\text{O}_3 \text{(primary Mullite or pseudo-mullite: Si-Al spinel with composition similar with Mullite composition)}. \]

The presence of impurities on the particle surface reduces or enlarge 990.9°C exothermic peak.

3.4. DSC ANALYSIS

Figure 3 shows the DSC curve obtained from the kaolin powder analysis. Removal of the absorbed water from the surface pores and kaolin dehydroxylation follows by the metakaolin formation occurs successively in 25–600°C range:
\[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 = \text{Al}_2\text{Si}_2\text{O}_7 \text{ (metakaolin)} + 2 \text{ H}_2\text{O} \]

The thermal parameters of these processes are presented in Table 2. It is noticed that the parameters highlighted by DSC analysis are in good agreement with those obtained by SDTA.

**Table 2**

<table>
<thead>
<tr>
<th>Process</th>
<th>(\Delta T ) (^{\circ}\text{C})</th>
<th>Peak DTA/(°C)</th>
<th>(\Delta H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal of the absorbed water from the surface pores</td>
<td>25–125</td>
<td>64.8; 72.0</td>
<td>endotherm</td>
</tr>
<tr>
<td>Kaolin dehydroxylation with metakaolin formation</td>
<td>300</td>
<td>531.2</td>
<td>endotherm</td>
</tr>
</tbody>
</table>

\(\Delta T\) = temperature range where processes occur; peak DTA = temperature corresponding to the minimum DTA; \(\Delta H\) = thermal effect.

![Fig. 3 – DSC curve obtained on DSC analysis of kaolin powder.](image)

### 3.5. DILATOMETRIC TEST

Figure 4 emphasizes the thermogram of the analyzed kaolin sample. The results indicate that there is a temperature difference between the value recorded by the thermocouple and the real one in the sample due to the high thermal inertia of the test support. This explains the differences between the temperatures in the TG/DTG/DTA and DIL curves.

The initial contraction, from room temperature to \(~70\)°C is due to the settlement of the sample in powder form. A suddenly dilation observed at 540°C, followed by
a suddenly return, is an artifact due to the water vapor elimination in kaolin dehydration process which push the piston of the test support.

![Graph showing thermal characterization of kaolinitic clay](image)

Fig. 4 – Curve dL/L0 depending on the temperature for kaolin sample.

The contractions observed at 818°C and 1164°C respectively are due to the phase transformations of kaolin.

### 4. CONCLUSIONS

Kaolin dehydroxylation for metakaolin producing is a thermal decomposition of kaolinite crystal to a completely disordered metakaolin for which in the new phase less amorphous the crystal does not collapse but, rather, retains a layered structure.

The kaolin analysed is medium crystallized showing a small amounts of surface defects and a specific BET surface of 15.96 m²/g. The degree of crystallinity is correlated with BET specific surface which range between 8 and 27 m²/g. Thus, a well crystallized kaolin corresponds to a small specific surface and a weakly crystallized one corresponds to a large specific area.

DTA analysis for the kaolin sample indicate that the material does not have many surface defects.

The TG analysis suggests that the main mass loss of 11.86 wt.% in the raw kaolin is not so much below the theoretical value and difference can be due to the quartz presence in the kaolin.

DTG analysis revealed the kaolinite conversion to meta-kaolinite. The peak area is proportional to the kaolinite content of the raw kaolin sample.
The processes parameters revealed by DSC analysis are in good agreement with those obtained by SDTA.

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REFERENCES