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Thermal Activation of Kaolin: Effect of Kaolin Mineralogy on the Activation Process †

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Abstract: Kaolin is an industrial mineral used in a wide variety of applications due to its crystalline structure, mineral and elemental composition. After kaolin undergoes heat treatment in a specific temperature range, metakaolin, which exhibits a strong pozzolanic reaction, is formed. This paper examines the effects of different kaolin qualities on the thermal activation process of metakaolin production. The qualities of kaolin depend on the impurities they contain, such as mica, feldspar and quartz. In this study, four different samples of kaolin are investigated. Each sample was heat treated in a lab-scale rotary kiln in order to study the chemical, structural and morphological changes that occurred and their influence on pozzolanic activity. The parameters being considered in the experimental process were the temperature and the duration of the treatment. Thus, the calcination process for each of the four kaolin types was carried out at 600, 650 and 700 °C for 3 h. The occurred changes were monitored using XRD, FTIR and DTA analysis. Additionally, the reactivity of all thermally treated samples was evaluated based on the Chapelle test. The results showed that the fewer the impurities, the easier the transformation of the material to metakaolin. The optimum result was the metakaolin, which originated from the purest quality of kaolin and was comparable to the commercial product. Finally, the pozzolanic activity of the thermally activated samples also depended on the purity of the kaolin.

Keywords: kaolin; metakaolin; thermal activation; pozzolanic activity; mineralogy

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1. Introduction

Kaolinite is a layered silicate mineral with the chemical composition $Al_2Si_2O_5(OH)_4$. It is commonly referred to as "China Clay" because it was first discovered at Kao-Lin, in China. The term kaolin is used to describe a group of relatively common clay minerals dominated by kaolinite and derived primarily from the alteration of alkali feldspar and micas [1]. Kaolin is a white, soft, plastic clay mainly composed of fine-grained plate-like particles [2]. It is a unique industrial mineral, as it is used in a wide variety of applications due to its physical and chemical properties. The most important of these are the production of ceramics and cement, pigments, coating films and filling applications [3].

The controlled calcination process of kaolin at an appropriate temperature and duration transforms the crystalline kaolinite into an amorphous material, which is called metakaolin [4]. Metakaolin is a cementitious material with very high pozzolanic reactivity and has several applications, particularly in the construction industry, which is among its largest users. The main advantage of metakaolin is its capability of improving the mechanical properties and durability of concrete when used as a partial replacement of cement [5]. The reactivity of metakaolin depends on several factors. The most important of them are the clay minerals contained in the raw material, the crystallinity of the raw kaolinite and the thermal activation conditions [6,7].

However, the optimization of calcination conditions regarding the influence of process parameters on the pozzolanic activity of metakaolin is not so easy to achieve. There are a wide variety of kaolin ores, with huge differences in their composition and structure. As a result, there is not only one optimal combination of temperature and time duration for thermal activation [8].

For this research, samples of kaolin of various qualities with different mineralogy characteristics were thermally activated in order to evaluate the influence of the raw material impurities on the obtained metakaolin and its properties.

2. Materials and Methods

2.1. Materials

The examined materials were 4 kaolin minerals of different purities. These materials originated from kaolin deposits in Cornwall, UK. The kaolin which had the highest purity (>95% kaolinite) was called Supreme; there was also medium to high purity kaolin, the Speswhite, and a medium to low quality kaolin, the Polwhite B. Finally, Polwhite E kaolin had the lowest purity (75% kaolinite), and the contained impurities included mica, feldspar and quartz.

2.2. Methods

Thermal activation of the four kaolin samples was carried out in a lab-scale rotary kiln. The duration of the calcination process was 3 h, while the examined temperatures were: 600, 650 and 700 °C. After every thermal treatment, the calcined sample remained in the kiln in order to slowly cool down to room temperature.

2.3. Testing and Analysis Techniques

2.3.1. X-ray Diffraction (XRD)

The mineralogy of both the raw and heat-treated samples was examined using a Bruker D8 Focus diffractometer in the 2θ range 5–70° (step size: 0.02° 2θ). Data analysis was performed by the Profex software.

2.3.2. Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR measurements were performed on a Perkin Elmer Spectrum 100 spectrometer using a ZnSe ATR crystal. All the samples were measured within the wave range of 4000–650 cm^{-1}.

2.3.3. Thermal Analysis (TG-DTA/DSC)

DTA analysis was applied in order to investigate the thermal behavior of the samples. For the measurements, a Labsys TG-DTA/DSC by Setaram was used. The samples were heated in the range between 20 °C and 900 °C with a heating rate of 20 °C in a He atmosphere and using a platinum (Pt) crucible.

2.3.4. Chapelle Test—Reactivity

The pozzolanic activity of the samples was assessed using the modified Chapelle test according to the NF P18-513 standard [9]. This test allows the quantification of fixed $Ca(OH)_2$, which is consumed by 1 g of metakaolin sample when mixed with 2 g of CaO. The suspension was boiled at 90 °C for 16 h under continuous stirring, and after that, was cooled to room temperature. Finally, an amount of the solution was filtered and then titrated using HCl in order to define the consumed $Ca(OH)_2$ [10].

3. Results and Discussion

In the XRD results show the effect of kaolin mineralogy in the formation of metakaolin. Kaolin E and kaolin B (Figures 1 and 2) seemed to have the lowest purity, as they contained quantities of mica minerals (Biotite, Phlogopite, Muscovite), feldspar minerals (Albite, Microcline) and Quartz. All these minerals seemed to delay the complete transformation

of the sample. Even at the highest temperature of 700 °C, some of their significant peaks still remained in the diagrams. For *Speswhite* and *Supreme* kaolin (Figures 3 and 4), the impurities were significantly decreased after the calcination process, giving better results concerning the obtained metakaolin.

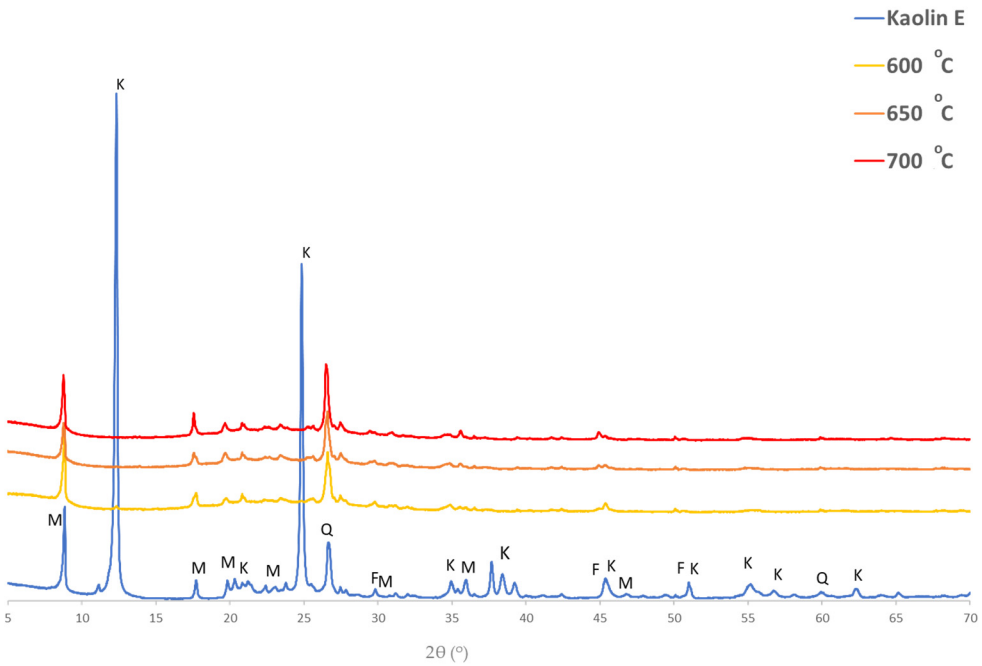

Figure 1. XRD patterns for Kaolin E and its calcined products in 600, 650 and 700 °C (K: Kaolinite M: Mica minerals F: Feldspar minerals Q: Quartz).

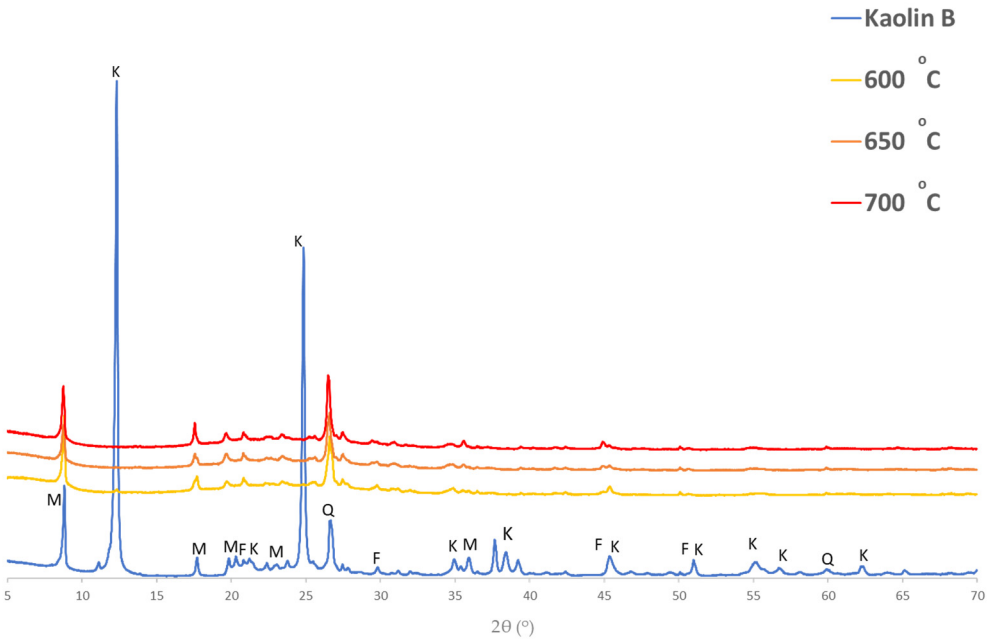

Figure 2. XRD patterns for Kaolin B and its calcined products in 600, 650 and 700 °C (K: Kaolinite M: Mica minerals F: Feldspar minerals Q: Quartz).

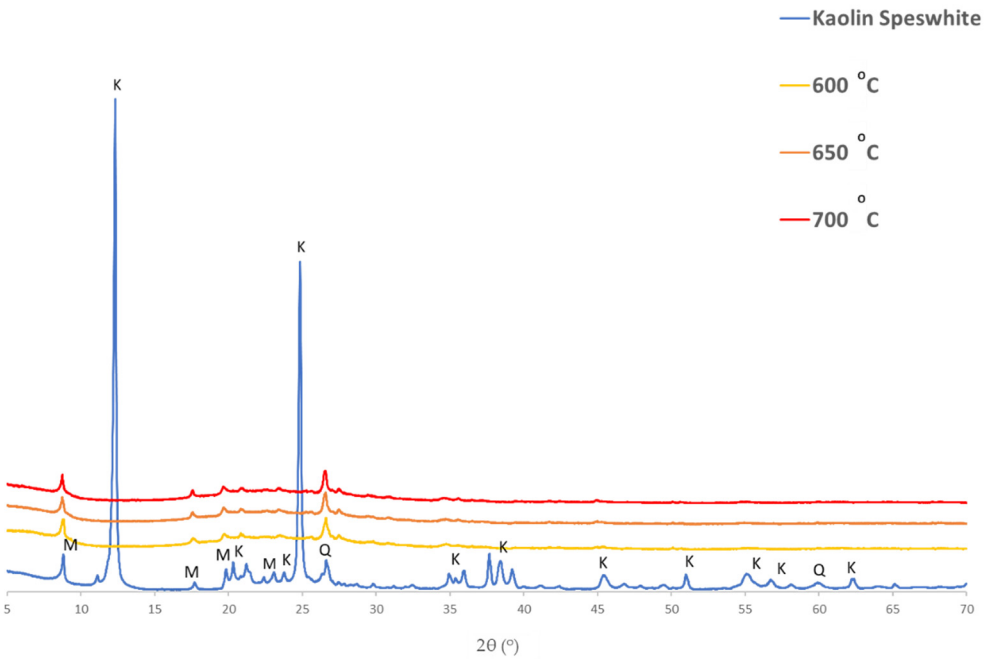

Figure 3. XRD patterns for Kaolin Speswhite and its calcined products in 600, 650 and 700 °C (K: Kaolinite M: Mica minerals Q: Quartz).

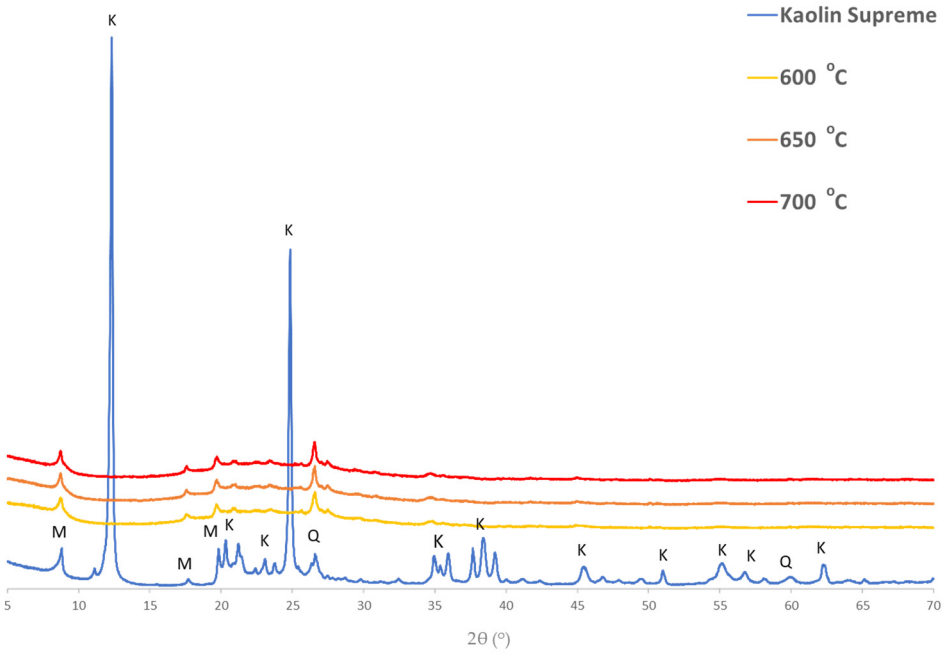

Figure 4. XRD patterns for Kaolin Supreme and its calcined products in 600, 650 and 700 °C (K: Kaolinite M: Mica minerals Q: Quartz).

According to the displayed curves from FTIR, there was a significant difference between the raw kaolins and the calcined samples.

At all temperatures, there was a noticeable reduction in the appearance of the kaolinite bands and in their intensity, probably because of the transformation occurrence. The curves corresponding to the calcined samples were quite similarly independent of the calcination temperature, but they still had some low intensity bands, probably due to the impurities' existence (Figures 5–7). Finally, as can be clearly observed, the *Supreme* kaolin (Figure 8) appeared to have the desired curves even from 600 °C.

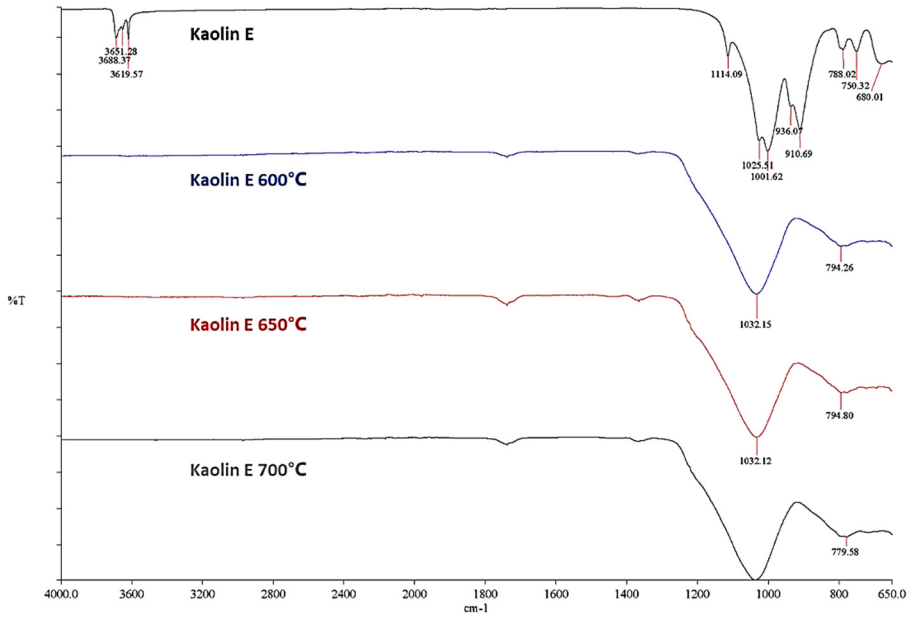

Figure 5. FTIR spectra of Kaolin E and its calcined products at 600, 650 and 700 °C.

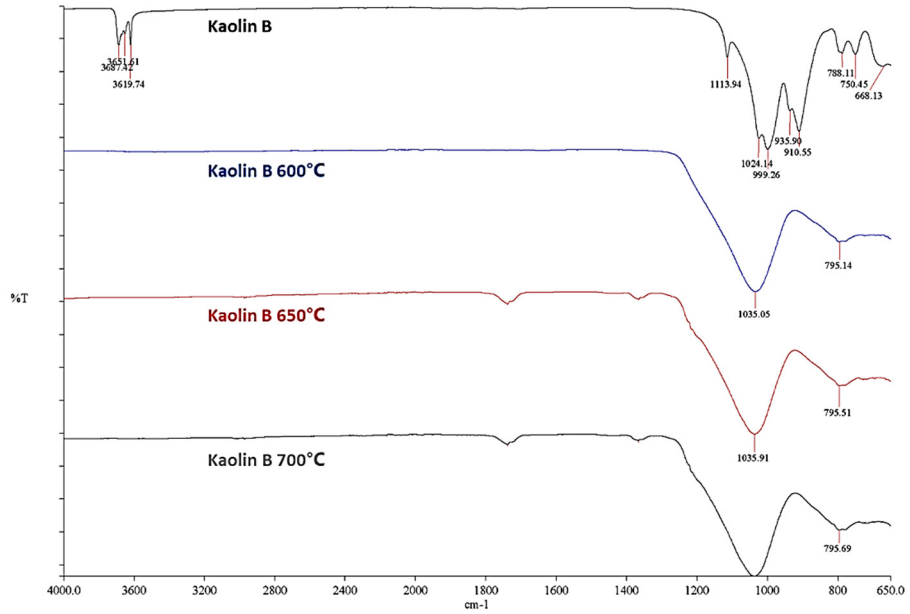

Figure 6. FTIR spectra of Kaolin B and its calcined products at 600, 650 and 700 °C.

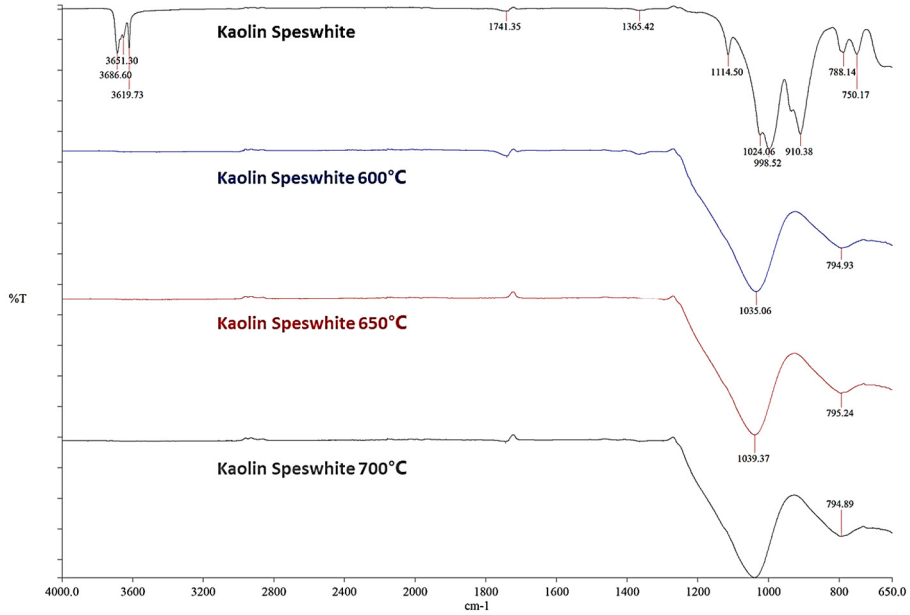

Figure 7. FTIR spectra of Kaolin Speswhite and its calcined products at 600, 650 and 700 °C.

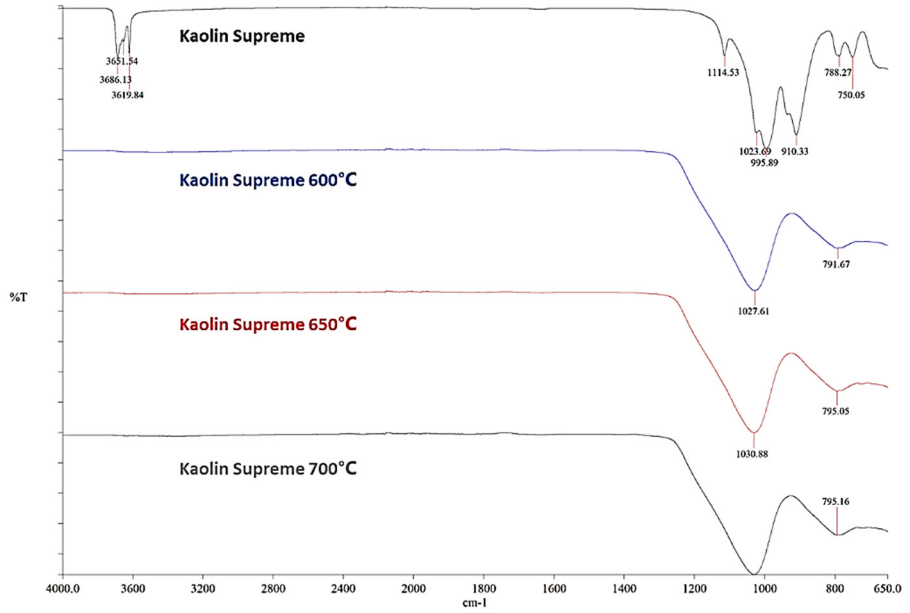

Figure 8. FTIR spectra of Kaolin Supreme and its calcined products at 600, 650 and 700 °C.

Figure 9 presents the DTA curves of the raw materials. First of all, the release of the absorbed water occurred for temperatures below 100 °C. Within the temperature range of 450–700 °C, for all the kaolin qualities, there was a characteristic endothermic peak (560–580 °C) which revealed that the dihydroxylation of kaolinite was achieved. All the received DTA curves did not seem to have huge differences between them. The slope of the DTA curve corresponded to the dehydroxylation process. These curves were generally sharper (greater absolute value of slope) for the well-crystallized materials [6]. Finally, the kaolinite transformation of the *Supreme* and *Speswhite* kaolin seemed to be completed at lower temperatures (~640 °C) than the other two qualities (~700 °C).

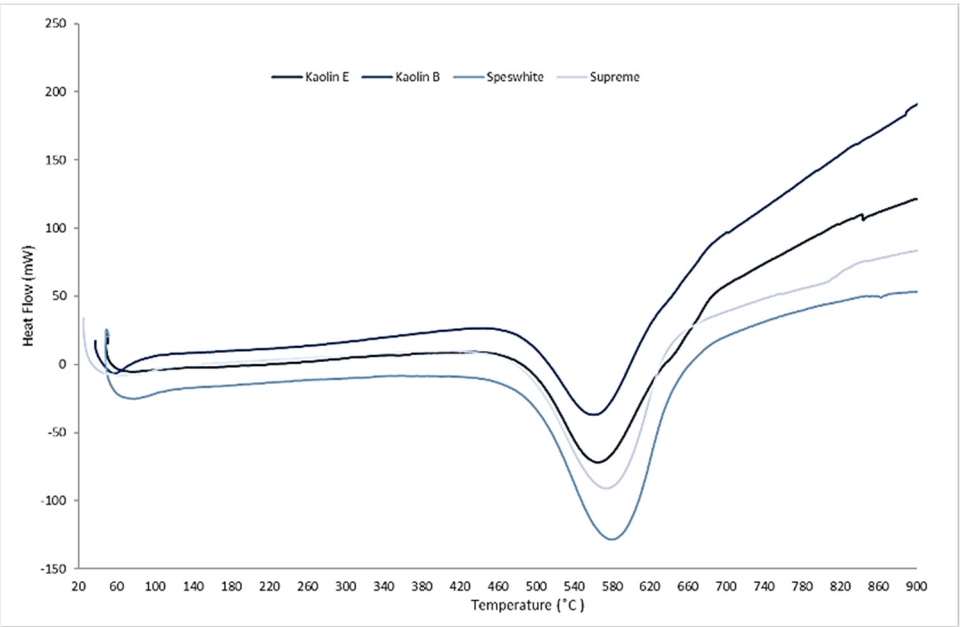

Figure 9. DTA curves of raw materials.

Finally, Table 1 presents the reactivity results (Chapelle test) of the calcined samples. Considering that the reactivity of commercial metakaolin is 1880 mg $CaOH_2$, the nearest value to this corresponded to the purest kaolin, *Supreme*. All the other values were far lower than the *Supreme* kaolin, although the purer qualities tended to have higher reactivity values.

Table 1. Chapelle test results for the raw materials and the calcined samples.

Kaolin Quality	600 °C	650 °C	700 °C
		mg of $CaOH_2$	
Kaolin E	1421	1522	1576
Kaolin B	1492	1542	1602
Speswhite	1567	1607	1676
Supreme	1724	1767	1782

Concerning the temperature effect, it can be noticed that for the purest qualities, the transformation began even at 600 °C. As the impurities increased, the transformation required temperatures of at least 650 °C or higher.

4. Conclusions

The conclusions obtained from this research can be summarized as follows:

1. The conditions of the thermal activation are built upon the mineralogical characteristics of the raw material. Specifically, samples with less impurities need calcination at lower temperatures in order to be activated.
2. The XRD and FTIR results showed that for all the kaolin qualities, the transformation to metakaolin started even at 600 °C, which is the lowest temperature that was investigated.
3. Particularly in the low purity calcined samples, only the impurities seemed to be present at higher temperatures.
4. The DTA curves revealed that the two purer qualities (*Supreme* and *Speswhite*) had a better crystallinity than the other samples.

5. As shown by Chapelle test results, the pozzolanic activity of thermally activated kaolins depended on the contained impurities.
6. The purer qualities tended to form metakaolin with a higher reactivity.
7. The purest kaolin (*Supreme*) appeared to have the optimum results. *Supreme* had the best thermal behavior and the obtained metakaolin had the highest pozzolanic activity in comparison to the other three kaolin qualities.
8. Finally, it seems that the purer the kaolin, the easier its thermal activation.

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Conflicts of Interest: The authors declare no conflict of interest.

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