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# KINETICS OF THE DEHYDRATION PROCESS OF ALUMINIUM HYDRATE FORMED IN THE KAOLIN–ALUMINIUM POWDER SYSTEM

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## ABSTRACT

The activation energy of the dehydration process of amorphous aluminium hydrate obtained by aluminium powder hydration ranges from 87 to 100 kJ mol$^{-1}$. Different values of activation energy are the consequence of the degree of order in the metastable structure of amorphous aluminium hydrate. The resistance to the dehydration process increases when the structure is changing to a bayerite formation. The differences in the structure of the amorphous hydrate occur as a result of the variable conditions of hydrate formation.

## INTRODUCTION

The non-isothermally heated kaolin–aluminium powder system, involving numerous changes and complex processes, was investigated. The oxidation and hydration of the aluminium powder are the dominant processes.

The physico-chemical properties of aluminium powder are a function of many factors. The reaction rates of the oxidation and of the hydration processes are high at first and than decrease; they depend on factors such as the level of impurities present, the particle sizes, the temperature, and the duration and intensity of mixing. The oxidation and hydration rates of aluminium are higher if the proportion of impurities is higher.

Aluminium oxidation is a heat-developing process, which increases the temperature of the system ($-1676$ kJ mol$^{-1}$) [1]. Aluminium hydration occurs within the temperature interval 0–100 °C. According to the redox potential–pH diagram for the Al–$H_2O$ system, depending on the concentration of $H^+$ ion at 25 °C, the hydrate groups $Al_2O_3 \cdot 3H_2O$, $Al^{3+}$ ions or $AlO_2^-$ ions can be formed [2]. In the pH range 5–8.5, the hydrate groups are formed.

An amorphous aluminium hydrate is formed by hydration of aluminium powder. Lippens and Boer [3] have studied the structure of amorphous aluminium hydrate. The assumed that the amorphous aluminium hydrate molecule groups are bound by hydrogen bonds of water molecules. The structure is very unstable, and can transform to bayerite with time.

On non-isothermal heating, amorphous aluminium hydrate transforms to bayerite, and then to boehmite and anhydrous aluminium oxide. The investigations of Schwermann et al. [4] have shown that amorphous aluminium hydrate dehydrates at about 280 °C. A flattened endothermic peak is typical of amorphous aluminium hydrate. In the system under investigation, kaolin is present and it also undergoes a process of dehydration. At about 125 °C, the adsorbed water is lost and at about 580 °C dehydroxylation occurs.

The kinetics of the thermal decomposition of $Al_2O_3 \cdot nH_2O$, and especially that of $Al(OH)_3$ and AlOOH, have been studied by a great number of authors [5–9]. To investigate the kinetics of the dehydration of amorphous aluminium hydrate formed during the heating of a mixture of kaolin and aluminium powder, differential thermal analysis at different heating rates was applied. The results obtained were processed using the method recommended by Kissinger [10].

## EXPERIMENTAL

The starting materials in the experimental investigation were Zettlitz kaolin and aluminium powder, whose specific surface area was 1.5 $m^2\ g^{-1}$. The chemical contents of the starting materials are shown in Table 1.

In the experimental phase, three mixtures of kaolin and aluminium powder, in which the aluminium content was 5, 10 and 15 wt.% ($A_5$, $A_{10}$, $A_{15}$) were prepared. They were homogenized in a laboratory ball mill for 4 h. The

TABLE 1

Chemical contents of Zettlitz kaolin and aluminium powder

| | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | Loss on ignition |
|---|---|---|---|---|---|---|---|---|---|
| Zettlitz kaolin | 46.93 | 37.52 | 0.19 | 0.45 | 1.04 | 0.14 | 0.32 | 0.13 | 13.25 |
| | 54.10 | 43.25 | 0.23 | 0.52 | 1.21 | 0.17 | 0.37 | 0.15 | – |
| | Al | Fe | Mn | Cu | Si | Mg | | | |
| Aluminium powder | 95.78 | 0.32 | 0.06 | 0.14 | 0.38 | – | | | |

pH of all three suspensions was 7.5. The suspensions were first dried in a gypsum-cement mould, and then in a drying plant at 60 ° C.

The DTA of the mixtures was performed on a MOM Derivatographer (Budapest). The heating rates were 1.25, 2.5, 5 and 10 ° C min$^{-1}$. The sample mass was always 687.5 mg, so that the heating throughout the entire body can be considered uniform.

The change of mass during heating was evaluated by thermogravimetry (TG) using a Du Pont Thermal Analyser, Model 1090, Wilmington, at a heating rate of 10 ° C min$^{-1}$.

Diffractometry was performed using a Philips powder diffractometer, model PW 1051. In the course of the preparation of $A_{10}$ and $A_{15}$ in the ball mill, the temperature rose to around 65 ° C. This increase in the temperature of the suspension can bring about the transformation of amorphous aluminium hydrate. To determine the influence of temperature on this transformation, samples heated in an electric furnace to 210 ° C were analysed by diffractometry. The samples were kept at the maximum temperature for 2 h, and then rapidly removed from the furnace.

## RESULTS AND DISCUSSION

All the mixtures were investigated by DTA at different heating rates. Figure 1 shows the DTA curves of kaolin and of the mixtures, and Fig. 2

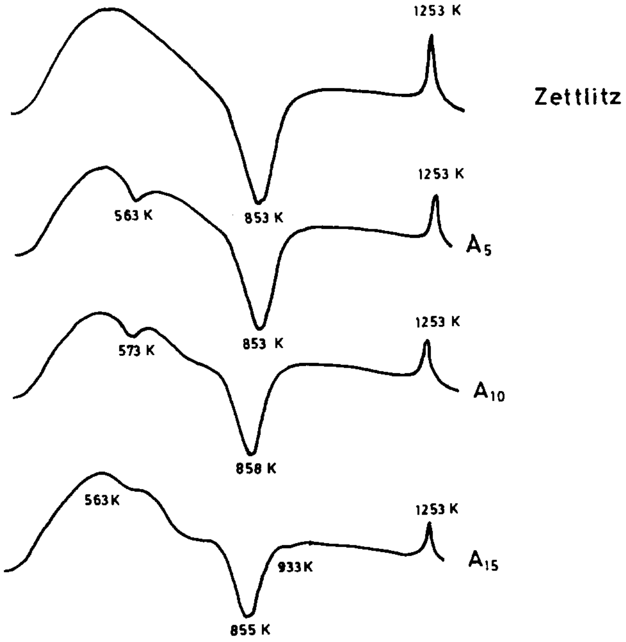

Fig. 1. DTA curves of kaolin and samples at 10 ° C min$^{-1}$.

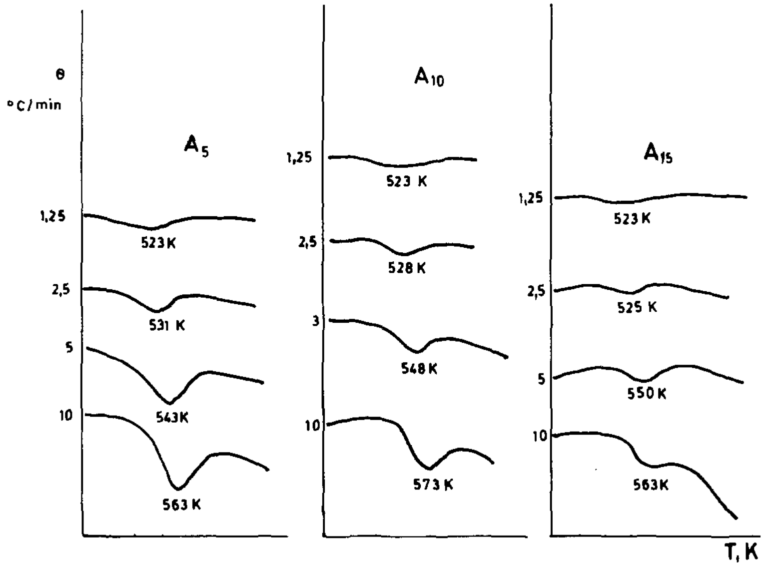

Fig. 2. DTA curves of samples showing the endothermic effect at different rates.

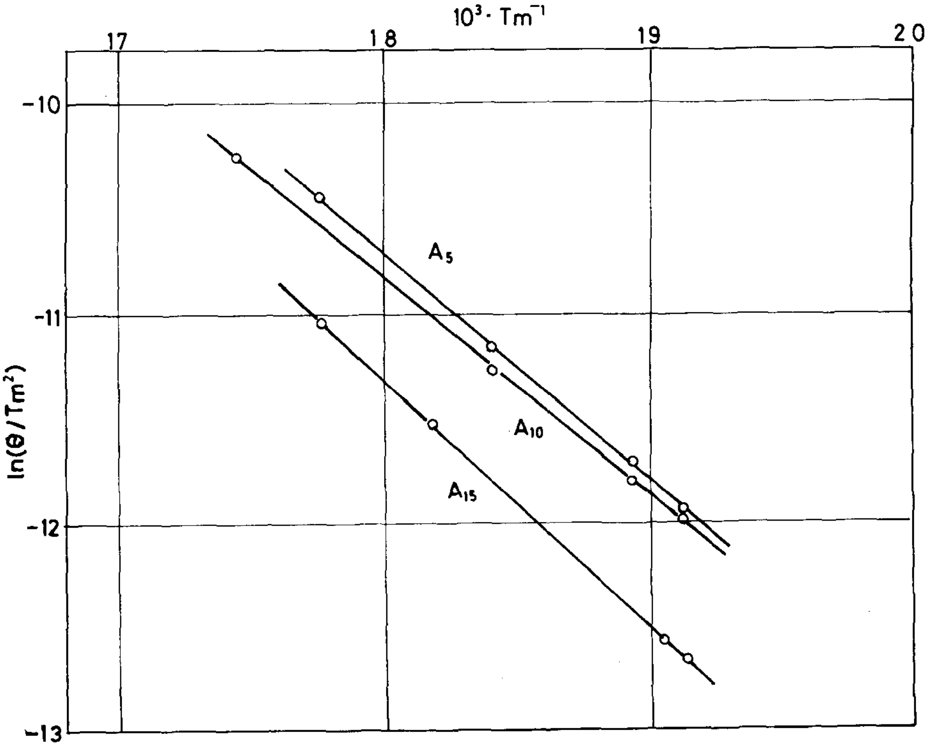

Fig. 3. ln $\theta = f(1/T)$ dependency of $A_5$, $A_{10}$, and $A_{15}$.

gives the endothermic peaks of amorphous aluminium hydrate dehydration at different heating rates. The obtained results were then used to calculate the kinetic parameters of the aluminium hydrate dehydration.

By plotting the graph of dependencies, according to Kissinger's equation $\ln \theta/T_m^2 = C - E/RT_m$, where $\theta$, $T_m$, $C$, $E$ and $R$ denote the heating rate, peak temperature, integrating constant, activation energy and gas constant, respectively, a straight line is obtained, see Fig. 3.

By applying the least-squares method, the slopes and the intercepts for the best straight lines can be obtained. The activation energy of all three mixtures was calculated: $E_5 = 91$, $E_{10} = 87$ and $E_{15} = 100$ kJ mol$^{-1}$. The average activation energy is 93 kJ mol$^{-1}$. The calculated activation energy

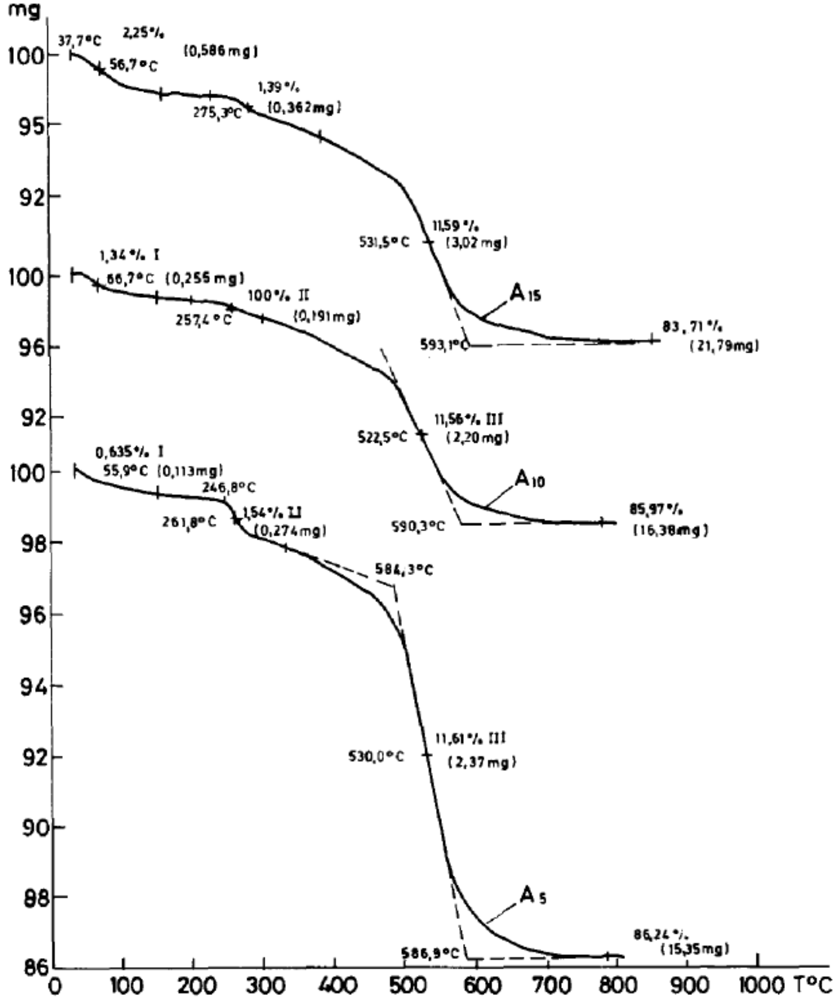

Fig. 4. Thermogravimetry of $A_5$, $A_{10}$ and $A_{15}$ mixtures.

value of amorphous aluminium hydrate dehydration is lower than that of a pure $Al(OH)_3$ which is 116 kJ $mol^{-1}$ [6]. This difference is a result of different resistances to the processes which originate from different degrees of order in the metastable structures of amorphous aluminium hydrate.

The TG curves of $A_5$, $A_{10}$ and $A_{15}$ (Fig. 4) show that the loss of mass caused by the dehydration of amorphous aluminium hydrate is not functionally dependent on the content of aluminium powder in the mixtures. If it is assumed that $Al_2O_3 \cdot 3H_2O$ is formed, it can be calculated that $A_5$, $A_{10}$ and $A_{15}$ contain 30.8, 10.0 and 9.3 wt.% amorphous aluminium hydrate, respectively.

It was expected that an increase in aluminium content in the mixture would result in an increase in amorphous aluminium hydrate: the results obtained show that this is not so. The reason for the fall in amorphous aluminium hydrate content derives from the instability of the conditions prevailing during the preparation of the mixtures. In fact, the increase of

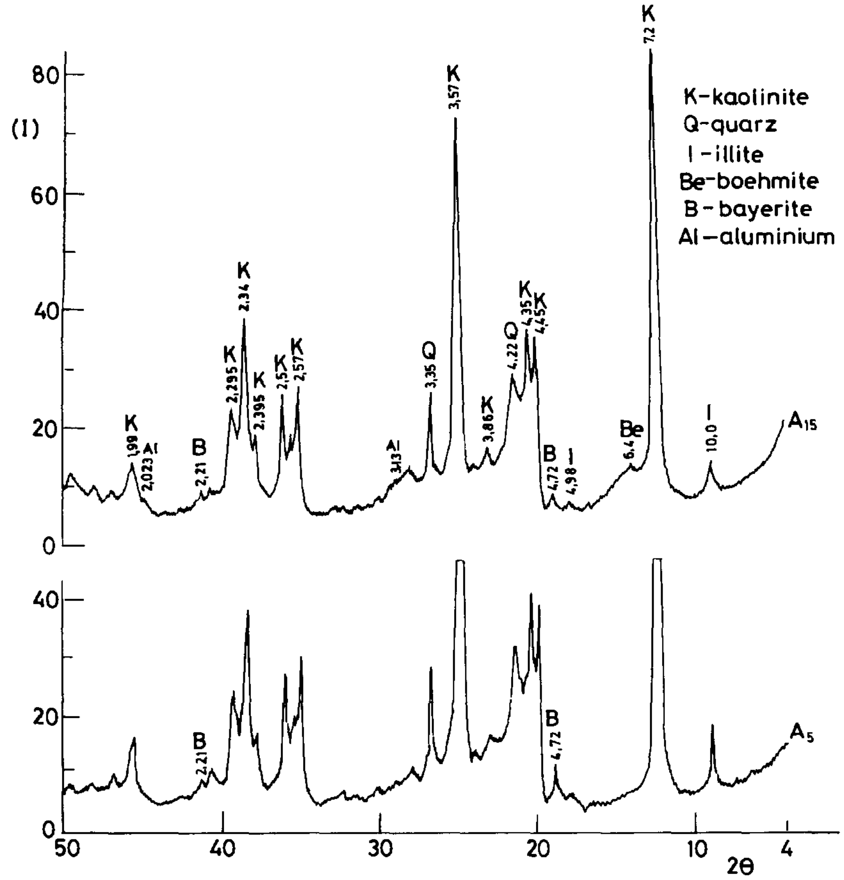

Fig. 5. Diffractometry of $A_5$ and $A_{15}$ heated at 210 °C for 2 h.

aluminium in $A_{10}$ and $A_{15}$ led to an increase in the heat developed in the exothermic reaction. This increase in the temperature of the system contributed to the faster transformation of amorphous aluminium hydrate into bayerite and boehmite.

Diffractometry of $A_5$ and $A_{15}$ samples heated at 210 °C confirmed that an increase in the aluminium content accompanied by a temperature increase, caused a faster distortion of the metastable structure of amorphous aluminium hydrate. From the diffractograph in Fig. 5, it can be seen that the bayerite formation took place in both mixtures. In $A_{15}$, where the portion of aluminium was greater, the beginning of boehmite formation, at $d = 0.64$ nm, can be seen.

The evaluation of activation energy, DTG and diffractometry revealed that the conditions under which the mixtures are prepared can significantly influence the kinetics of the dehydration process of the amorphous aluminium hydrate obtained from aluminium powder.

## CONCLUSION

The activation energy of amorphous aluminium hydrate obtained by aluminium powder hydration was determined. The different values for the activation energy of amorphous aluminium hydrate, ranging from 87 to 100 kJ $mol^{-1}$, indicate the existence of different resistances to the dehydration process. The different degrees of order of the metastable structure are the main cause of the different values of activation energy. The effects of the properties of the aluminium powder and of the water vapour resistance in the water layer on the activation energy, should not be neglected in fundamental research. High activation energy values are obtained if the aluminium hydrate approaches the bayerite structure.

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