**TEMPERATURE EFFECT ON INTERCALATION OF KAOLINITE**

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**ABSTRACT**

Intercalation of small molecules (such as urea, formamide, DMSO) in the interlayer space of kaolinite is a process of fundamental and technological importance [1]. Although intercalation has been investigated since the ‘60s, its rate and extent are affected by the properties of kaolinite in a manner that is not yet fully understood [2 and references therein]. The amount of non-reactive kaolinite in otherwise pure samples was found to be larger than previously estimated [3]. Elevated temperatures (60-80 °C) are commonly employed to accelerate intercalation, but their effect on the intercalation capacity is controversial and rarely addressed in the literature.

The present work presents the first systematic study of the intercalation capacity of kaolinite as a function of temperature. FT-near infrared spectroscopy (NIR) was used to record *in situ* the kinetics of intercalation in four kaolinites (CMS reference KGa-1b, KGa-2, Hywite from Imerys and Keokuk) with excess of liquid N-methylformamide (NMF). The sealed slurries were measured over long time periods (up to 1 week) in the 5-150 °C range. The amplitude of the 2nd derivative 2vNH mode of the intercalating NMF molecules normalised by the corresponding intensity of the 2v inner OH mode of kaolinite was employed as a temperature-independent indicator of the degree of reaction.

In all kaolinites investigated, it was found that the reaction was accelerated upon increasing temperature, as expected, but the final NMF uptake was decreased significantly and, in most cases, vanished above ~100 °C. These unexpected findings were confirmed by independent thermogravimetric analysis (TGA) of the final intercalation products. Stepwise decrease of temperature resulted in the stepwise increase of intercalated NMF. However, increasing the temperature of pre-intercalated systems did not cause deintercalation, indicating that the successfully intercalated NMF molecules were no longer in equilibrium with the surrounding fluid.

The possible origins of this unusual behavior are discussed. Temperature is assumed to affect the adsorption of NMF on the edges of the crystallites, which is a prerequisite for intercalation.

**KEYWORDS:** kaolinite, intercalation, N-methylformamide (NMF), temperature, Near-infrared spectroscopy (NIR)

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