

The influence of alkali concentration and temperature on chemical activation of halloysite

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The influence of alkali activation on clay minerals is not thoroughly investigated, particularly in terms of its impact on adsorption possibilities of clay minerals. One of the studied applications of base treated clay minerals was to control sustained drug release (Wang et al. 2013). Based on the recent studies, the base treatment can cause changes in structure, texture, and morphology of clay minerals. These changes are related to partial dissolution of layered structure and subsequent release of Si and Al to the solution (White et al. 2012, Yuan et al. 2015). This modification can be especially promising in case of halloysite, which is a clay mineral revealing unique nanoscale tubular morphology. Previous studies indicate that selective dissolution of halloysite's aluminosilicate layers can lead to opening of the tubes interior (lumen) (Wang et al. 2013). This type of structural alteration can influence utilization possibilities of halloysite. Therefore, the aim of this work is to investigate the influence of alkali concentration and reaction temperature on the halloysite structure.

The halloysite used in the studies came from Polish deposit located in Dunino, near Legnica (SW Poland) which is constantly exploited. The base activation was carried out using sodium hydroxide (NaOH). Firstly, the effect of NaOH concentration on activation efficiency was investigated. The experiments were carried out for the concentration range from 0.01 to 5.0 mol/L at room temperature. Additionally, for the 1.0 mol/L concentration the experiments were performed at temperatures of 50°C, 60°C, 70°C, 80°C and 90°C.

The suspensions consisting of 2 g of halloysite and 50 mL of appropriate solution were mixed for 24 h using magnetic stirrer. Subsequently, the samples were washed with water and dried at 60°C. The prepared materials were characterized using XRD and FTIR methods.

The IR results revealed that the concentrations of NaOH below 5 mol/L at room temperature did not cause significant changes in spectra of the tested samples. However, the results of experiments carried out in the temperature range from 60°C to 90°C showed that the temperature of the suspension can significantly affect the alkali activation. Based on the IR spectra the reaction at 50°C did not alter the structure of halloysite, in contrast to 60°C, 70°C, 80°C and 90°C temperatures. The changes of relative intensities of the bands associated with inner surface hydroxyls were observed in the 3700–3600 cm^{-1} region. These results suggest a gradual removal of inner surface hydroxyls, with the temperature increase. The results also indicated a gradual increase of intensity and broadening of the band with the maximum at 3430 cm^{-1} and 1647 cm^{-1} which were attributed to H–O–H stretching and bending vibrations of adsorbed water, respectively. It can be also observed that base treatment at higher temperature also caused structural changes within the aluminosilicate framework of halloysite. The frequency shift and broadening of bands assigned to Si–O–Si stretching (1033 cm^{-1} , 1008 cm^{-1}) and bending (540 cm^{-1}) vibrations were observed. The perturbations and/or removal of Al–O–H was confirmed by the decrease of bands intensity assigned to

bending vibrations at 936 cm^{-1} and 914 cm^{-1} . The higher temperatures resulted in an appearance of new bands at 1470 cm^{-1} and 1400 cm^{-1} associated with carbonates. These bands become more evident with the increase in temperature. The XRD results indicated the formation of additional crystalline phases: sodium aluminum silicate, hydrated sodium carbonates and sodium aluminum carbonate silicate. The presence of carbonates in the samples was confirmed also by FTIR spectra. It was suspected that the presence of carbonate may be related to uptake of atmospheric CO_2 and its reaction with NaOH in accordance with earlier reports by Slaty et al. (2013) and Aldabsheh et al. (2015).

The results of this work suggest that different variations of the activation conditions should be examined, to find the optimal temperature for alkaline treatment that leads to an increase in the

lumen diameter of halloysite, but does not affect the mineral morphology.

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