FORMATION OF ZEOLITE TYPE A FROM HALLOYSITE AND ALLOPHANE

by

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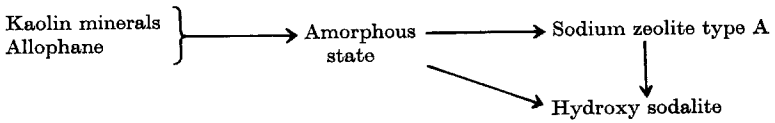
EXTENDED ABSTRACT

IT IS well known that kaolinite and halloysite change into hydroxy sodalite by treatment with sodium hydroxide. It is also known that sodium zeolite type A can be formed from kaolinite, after it has been heat-treated into metakaolin, or ground into non-crystalline material. From such facts it is presumable that the probability of formation of zeolite type A from a kaolin mineral is closely related to the crystallinity of the original mineral. From such a consideration, in the present experiments allophane and some kaolin minerals with different degrees of crystallinity were used as starting materials. Starting samples were Mesa Alta kaolinite, Kibushi-clay, Wagon Wheel Gap halloysite, Ina-kaolin, and Iijima allophane. Of these starting samples, Mesa Alta kaolinite is a species with the highest degree of crystallinity among the kaolin minerals, and Kibushi-clay has a lower degree of crystallinity similar to fire-clay. Ina-kaolin is a halloysite with the lowest degree of crystallinity of all the kaolin minerals, and it belongs to the allophane–halloysite series. Iijima allophane is the most typical soil-allophane found in Japan.

To examine the effect of crystallinity on the structural change of kaolin minerals by treatment with sodium hydroxide, the following experiments were made. For each run, 50 g of a starting sample were added to 250 ml of 4N NaOH aq solution, and treated for 3 hr at the boiling point under agitation. From the X-ray diffraction results, it is found that kaolinite and halloysite change to hydroxy sodalite during this treatment, and that sodium zeolite type A can be recognized in the products from poorly crystallized halloysite and allophane.

Next, to investigate the mechanism of the formation of zeolite type A from Ina-kaolin by treatment with NaOH in further detail, the correlation between the zeolite content of the product and the treatment time in the process of NaOH treatment was obtained. In this experiment, the amount of NaOH used was the conversion value corresponding to 110 mol% of Na_2O required for the formation of zeolite type A. And the quantitative analysis of the zeolite content was measured by the X-ray diffraction method with fluorite as the internal standard. From these results, it is found (1) that the zeolite content of the product generally increases with the progress of treatment at a certain temperature, but after reaching a certain point of the treatment time the apparent zeolite content decreases, and (2) that zeolite type A with a 100% purity is obtained by reaction for 16–24 hr at 70°C. In this reaction, an induction period is observable, and the length of this period depends on the treatment temperature. This induction period corresponds to the following two phenomena, that is, (1) kaolin mineral reacts to NaOH, and consequently the original kaolin structure is broken and becomes amorphous and (2) the nucleus of zeolite type A forms in this amorphous state.

The structural changes of kaolin minerals and allophane into zeolite type A by treatment with sodium hydroxide may take the following process:



The formation of sodium zeolite type A from kaolin minerals should depend on the concentration of sodium hydroxide, treatment temperature, time of treatment, etc. However, the transformation toward the sodium zeolite type A takes place more readily the lower the crystallinity of the kaolin mineral. It is possible to produce sodium zeolite type A directly from natural kaolin minerals having a low crystallinity, without employing any pretreatment.