

SHORT NOTES

Formation of Faujasite-Like Zeolite From Halloysite

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It was previously reported that type *A* zeolite was formed from halloysite of extremely low crystallinity and from allophane by using sodium hydroxide under normal pressure without any pretreatment (Takahashi and Nishimura, 1967). In the present experiment, the structural change of halloysite into faujasite-like zeolite by treatment with sodium hydroxide solution was studied and the process of the structural change was investigated.

Ina-kaolin (Komagane, Nagano), a halloysite of extremely low crystallinity, was used as a starting material and commercial water glass was added to the sample to increase the silica-alumina mole ratio. The mixture was heat-treated with sodium hydroxide solutions of differing sodium content under normal pressure.

The relations between the concentration of NaOH solution and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ mole ratio for the formation of faujasite from halloysite when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio was equal to 5, the treatment temperature was 90°C, and treatment time 32 hr are shown in Fig. 1.

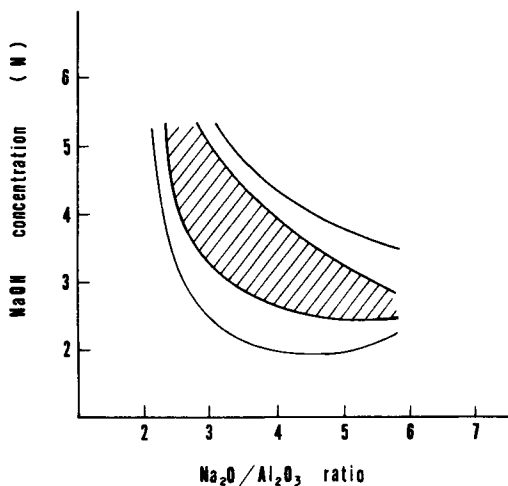


Fig. 1. The range of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ mole ratio and the concentration of NaOH solution for the formation of faujasite-like zeolite.

By heat-treating with sodium hydroxide solution, the mixtures of halloysite and water glass change into faujasite-like zeolite or type *P* zeolite related to the harmotomephillipsite group, which has chemical composition resembling that of faujasite but is structurally different. The structures of the products varied with the quantities of Na_2O and the concentration of the solution. Within

the hatched area of the figure, the principal product was faujasite; in the areas between the outer curves, a small amount of type *P* zeolite was formed together with faujasite; and outside the outer curves, type *P* zeolite only was recognized. Faujasite formed when the Na_2O content was more than three times the Al_2O_3 content in the original mixture.

To investigate the effect of treatment temperature, the mixture having $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 4$, and 3 N NaOH solution was heat-treated at different temperatures. Under these experimental conditions the relations between the zeolite content of the products and treatment times are shown in Fig. 2. The zeolite content of the products was determined by X-ray diffraction using anatase as an internal standard. When the mixture was heat-

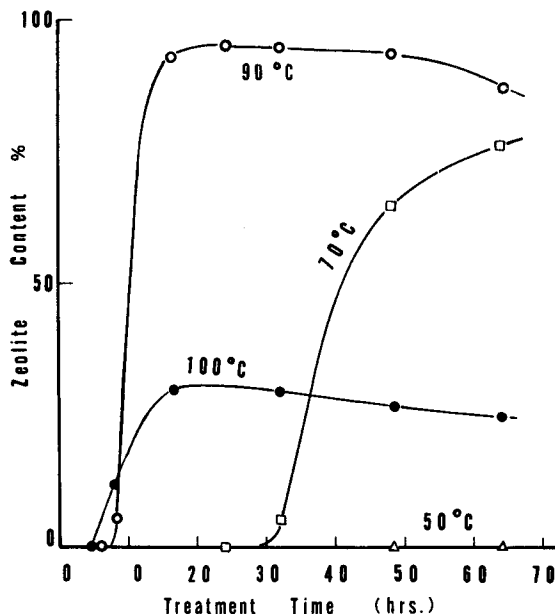


Fig. 2. Relations between the content of faujasite-like zeolite and treatment time at different temperatures.

treated at 50°C, no crystalline substance was recognized although the original structure of halloysite was destroyed. At 70°C small amounts of faujasite-like zeolite were recognized after 32 hr, and the content of faujasite increased with increasing treatment time. At 90°C faujasite formed rapidly. The content of faujasite amounted to 95 per cent but decreased after 48 hr owing to a change of

faujasite to hydroxy-sodalite. At 100°C faujasite formed more rapidly than at 90°C, but the apparent zeolite content did not increase so much because type *P* zeolite formed together with faujasite at the higher temperature.

The samples treated with sodium hydroxide change into faujasite or type *P* zeolite after passing through an amorphous state, and faujasite finally changes into hydroxy-sodalite while type *P* zeolite is stable under normal

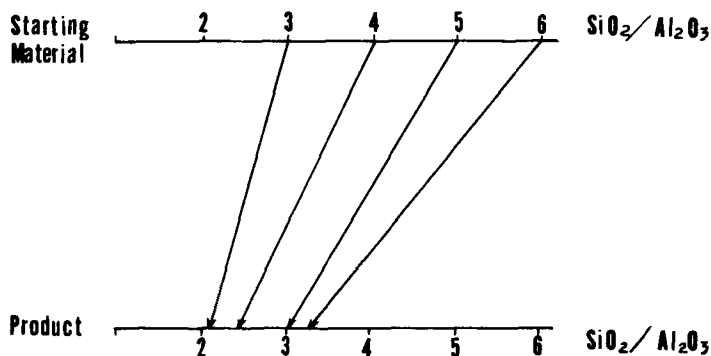
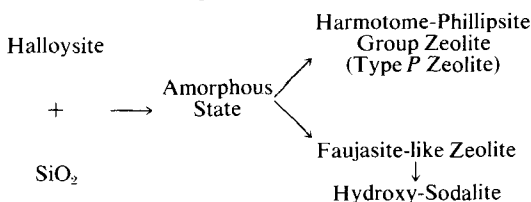


Fig. 3. Relations between the silica-alumina mole ratio of the starting materials and the products.

It is known that the silica-alumina mole ratio of faujasite-like zeolite ranges from 2.4 to 6.0, and the unit cell dimensions decrease with increasing silica-alumina mole ratio. The relations between the silica-alumina mole ratio of the products determined by precise measurement of unit cell dimensions and that of the starting material are shown in Fig. 3. As shown in this figure, faujasite-like zeolite at different silica-alumina mole ratios can be obtained from starting materials of differing silica-alumina ratios.

From these experiments, it appears that the structural change of halloysite mixed with water glass might have resulted from the sequence shown below:



pressure. The formation of either faujasite or type *P* zeolite from halloysite depends upon the treatment temperature, the amount of Na₂O, and the concentration of sodium hydroxide solution. For the formation of faujasite, the concentration of sodium hydroxide must be low when the sample is treated with a large amount of Na₂O, or the concentration of sodium hydroxide must be high when the sample is treated with a smaller amount of Na₂O.

REFERENCE

Takahashi, Hiroshi, and Nishimura, Yoichi (1967) Formation of zeolite type *A* from halloysite and allophane (abstr.): *Clays and Clay Minerals* **15**, 185-186.

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Clay Alteration Associated With Mineralization in the Michigan Copper District

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INTRODUCTION

Chlorite and vermiculite occur in close association with native copper ore in the Keweenaw County, Michigan, copper district. The main clay phases include (1) chlorite in "skull" replacements of conglomerate pebbles, (2) chlorite-montmorillonite in red clay fault gouge, and (3) mica and chlorite in red brown fault gouge.

GEOLOGIC SETTING

The Keweenaw, Michigan, Copper District, (see location map, Fig. 1) is unique in North America in that native copper is the dominant ore mineral. Some native silver and copper sulfides and arsenides are present, but these are of minor importance.

Mineralization is found chiefly in a number of amygdala-