

CLAY MINERAL RESEARCH AT THE INSTITUTE FOR SILICATE CHEMISTRY, ZAGREB

by

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ABSTRACT

Part of the research on the structure, synthesis, and properties of clay minerals in Yugoslavia is reviewed with particular reference to the following problems: (a) attempts to synthesize halloysite from solutions under normal conditions; (b) structure and properties of synthetic montmorillonites; (c) dehydroxylation of kaolin minerals under nonequilibrium conditions; (d) structural properties of metakaolin as shown by adsorption of colloidal gold; and (e) free silica in bentonites.

INTRODUCTION

Clay mineral research in Yugoslavia was intensified after World War II, when fast-growing industries required investigation of clays for application to the ceramic industry, petroleum industry and others. Clay mineral research has been done in the Geological Institute in Belgrade, Building Research Station in Ljubljana, Petroleum Institute in Zagreb, and Institute for Silicate Chemistry in Zagreb. Applied research has been done in some of the industrial laboratories. Some of the original investigations done in the Institute of Silicate Chemistry, Zagreb, are summarized briefly in this report.

ATTEMPTS TO SYNTHESIZE HALLOYSITE FROM SOLUTIONS UNDER NORMAL CONDITIONS

Starting from the work of Schwarz and Brenner (1923), using dilute solutions of aluminum salts (aluminum chloride, sodium aluminate) and sodium silicate and seeding these solutions at normal temperature with 1–5 percent of natural halloysite, Karšulin and Stubičan (1951, 1953) obtained crystalline precipitates having morphology similar to halloysite. Precipitation takes place in two steps; DTA curves of the precipitates (treated with sodium carbonate) show endothermic maxima at 130°C and 550°C. Electron microscopic investigation showed not only the large tubular halloysite seeds but also many much smaller tubular crystals that formed synthetically. The general mechanism of formation of clays from dilute solutions was discussed.

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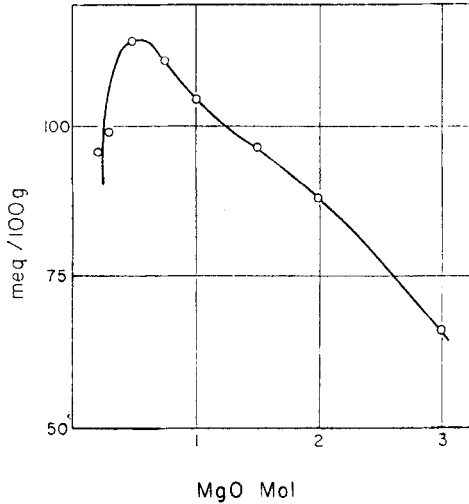


FIGURE 1.—Base exchange capacity of synthetic specimens as a function of amount of MgO in the hydrothermal system.

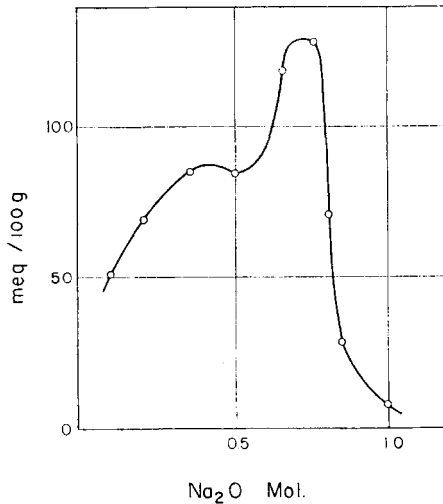


FIGURE 2.—Base exchange capacity of synthetic specimens as a function of amount of Na₂O in the hydrothermal system.

STRUCTURE AND PROPERTIES OF SYNTHETIC MONTMORILLONITES

Using synthetic montmorillonites, Karšulin and Stubičan (1954) proved experimentally the relation between isomorphic substitution and base exchange capacity, and also discovered factors that influence the distribution of alumina ions in the two coordinations. An attempt was made to interpret dehydration curves obtained by a thermobalance. Montmorillonites

were synthesized in the systems $MgO-Al_2O_3-SiO_2-H_2O$ and $Na_2O-Al_2O_3-SiO_2-H_2O$ at $312^\circ C$ and 100 atm. The crystallinity of the synthetic montmorillonites was determined by x-ray diffraction and electron microscopy. The synthetic specimens were analyzed and their structural formulas calculated. Experimentally determined base exchange capacity was correlated with amount of isomorphic substitution. With increasing amounts of mag-

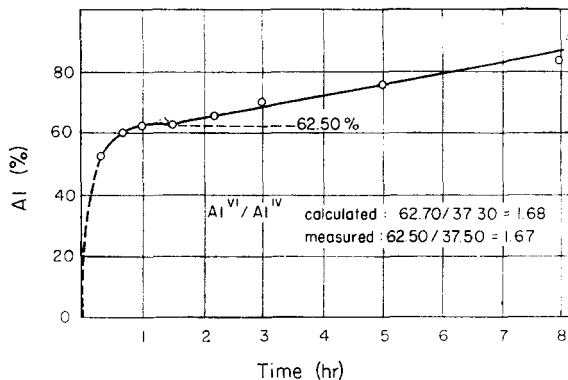


FIGURE 3.—Dissolution curve of aluminum in a synthetic Mg-montmorillonite.

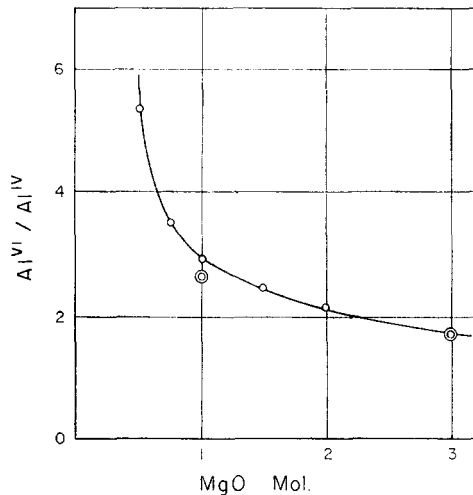


FIGURE 4.—The ratio Al^{VI}/Al^{IV} as a function of amount of MgO in the hydrothermal system, as calculated by the method of Ross and Hendricks. Double circles represent experimental values obtained by the dissolution method.

nesium oxide in the hydrothermal system, the base exchange capacities of synthetic specimens increase to about 0.5 mol MgO. In the increasing part of the curve (Fig. 1) a mixture of kaolinite and montmorillonite is present. From the maximum only montmorillonites with different exchange capacities are formed. In the system $Na_2O-Al_2O_3-SiO_2-H_2O$ (Fig. 2) the region of

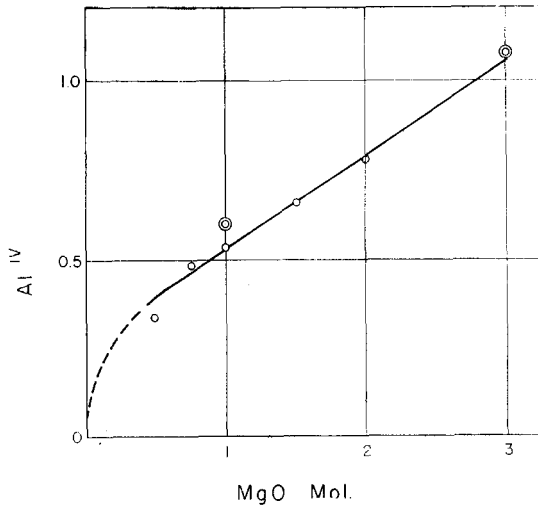


FIGURE 5.—Amount of Al^{IV} in synthetic montmorillonites as a function of MgO in the hydrothermal system, as calculated by the method of Ross and Hendricks. Double circles represent experimental values obtained by dissolution method.

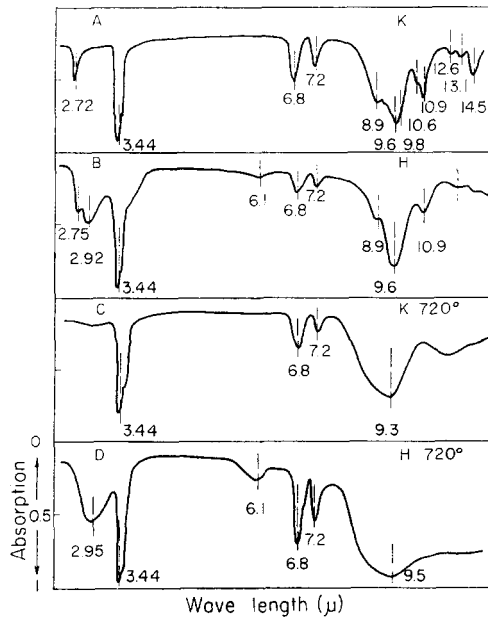


FIGURE 6.—Infrared spectra in Nujol. *A*, a well crystallized kaolinite; *B*, a halloysite; *C*, a well crystallized kaolinite heated to 720°C; *D* a halloysite heated to 720°C.

formation of beidellites is very narrow under specific conditions of temperature and pressure. With low concentration of sodium oxide, kaolinite is also formed. Beidellites as single phases with different exchange capacities are formed only between 0.2 and 0.5 mol Na₂O. Above 0.5 mol Na₂O, zeolites are formed.

The same authors showed [by determining the amounts of aluminum ions in octahedral and tetrahedral coordination by the dissolution method of Brindley and Youell (1951)] that the structure of two synthetic Mg-montmorillonites was the same as the Hofmann-Wilm-Endell-Marshall-Hendricks structure of montmorillonite. The agreement between calculated and experi-

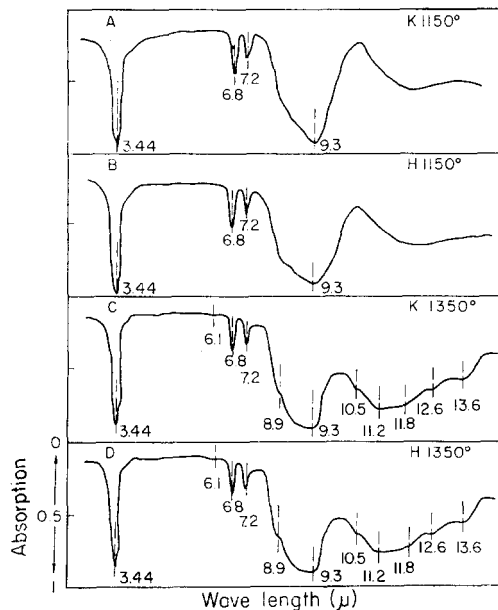


FIGURE 7.—Infrared spectra in Nujol. *A* and *C*, well crystallized kaolinite heated to 1150°C and 1350°C respectively for 3 hr. *B* and *D*, a halloysite heated to 1150°C and 1350°C, respectively for 3 hr.

mental values (Fig. 3) was good. With increasing amounts of MgO in the hydrothermal system, the ratio of Al^{VI}/Al^{IV} decreases (Fig. 4) and more aluminum ions are found in tetrahedral coordination (Fig. 5).

DEHYDROXYLATION OF KAOLIN MINERALS UNDER NONEQUILIBRIUM CONDITIONS

The heating products of kaolin minerals were studied by Stubičan and Günthard (1957) and Stubičan (1959) by infrared spectroscopy in order to secure additional data on the mechanism of dehydroxylation. The samples studied were (a) various size fractions of a well ordered kaolinite, (b) a poorly crystallized kaolinite showing random displacement of layers by multiples of $b_0/3$, and (c) a halloysite. The specimens were heated (at a rate of 10°/min)

in the differential thermal apparatus or in small Pyrex tubes that were sealed immediately after heating. Using well crystallized kaolinite (Fig. 6) absorption bands at 2.75μ (free hydroxyl groups) and 10.9μ disappear at the temperature at which the endothermic reaction is completed. In halloysite

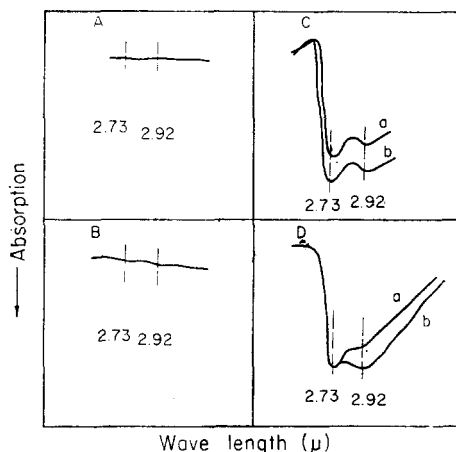


FIGURE 8.—Absorption in the range of hydroxyl groups. *A*, a well crystallized kaolinite heated to 680°C , particles larger than 0.6μ , Nujol; *B*, a well crystallized kaolinite heated to 680°C , particles smaller than 0.15μ , Nujol; *C*, hydrothermal kaolinite heated to 680°C (*b*) and 720°C (*a*), Nujol; *D*, a halloysite heated to 680°C (*b*) and 720°C (*a*), hexachlorbutadiene. Rate of heating $10^{\circ}/\text{min}$.

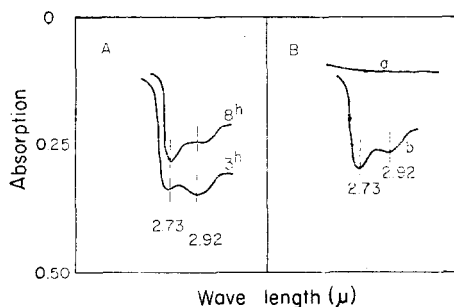


FIGURE 9.—Absorption in the range of hydroxyl groups. *A*, a hydrothermal kaolinite heated at 650°C for 3 and 8 hr, respectively; *B*, a hydrothermal kaolinite (*a*) and a halloysite (*b*) heated to 750°C for 10 min.

heated between 640° and 800°C a large band at 2.95μ and a band at 6.1μ were present. All specimens show strong absorption in the region of 9.5μ .

At 1350°C (Fig. 7) with kaolinite as well as with halloysite the infrared spectra show many broad bands even after cristobalite is dissolved in hydrofluoric acid. These spectra are not typical of mullite or sillimanite. The residual hydroxyl groups are present at 680°C or 720°C only in poorly crystallized kaolinite and halloysite and not in well crystallized kaolinite, regardless of particle size (Fig. 8).

Even after longer heating (3 hr, 8 hr) at 640°C, the disordered kaolin minerals show free hydroxyl groups and adsorbed water molecules (Fig. 9). The differences in dehydroxylation of kaolin minerals probably are connected with different phases formed during heating. With disordered kaolin minerals, the Si—O network collapses during dehydroxylation, and formation of γ -Al₂O₃ is much more probable. In dehydroxylation of disordered kaolin minerals small nuclei of γ -Al₂O₃ hydrogen spinel probably are formed. Karšulin (1956) grew γ -Al₂O₃ nuclei by adding 5 percent NaCl to halloysite and heating at 650°C.

ADSORPTION OF COLLOIDAL GOLD BY METAKAOLIN

The product of dehydroxylation of even well-crystallized kaolinite seems to have only relict order within the Si—O layer (Roy, Roy and Francis, 1955). So far it has not been possible to determine either the structure of dehydroxylated gibbsite layers in metakaolin or the relation between these layers and the Si—O hexagonal network. Stubičan and Wrischer (unpublished results) tried to obtain more information by adsorbing colloidal gold on the dehydroxylated platelets of well-crystallized kaolinite. The negatively charged colloidal gold is adsorbed only on the edges of untreated kaolinite (Fig. 10) as shown by Thiessen (1942), and Méring, Mathieu-Sicaud and Perrin-Bonnet (1953). According to the latter authors, this adsorption proceeds by intervention of exchangeable cations. A completely different picture was obtained with specimens heated over 600°C. Dehydroxylated platelets adsorb gold also on (001) faces, indicating a strong charge deficiency of the metakaolinite phase resulting from broken bonds and structural defects.

FREE SILICA IN SOME BENTONITES

Several Yugoslav deposits of bentonite have been investigated intensively by the Petroleum Institute in Zagreb, and the Research Laboratories of the Factory of Active Clays in Kutina and Yugoslavia has been shown to have some of the richest deposits of naturally active bentonite in Europe. Basic research has been undertaken at the Institute of Silicate Chemistry in Zagreb: Stubičan, Lisenko and Wrischer (1956) and Stubičan, Težak and Wrischer (1957) investigated the crystal form and distribution of free silica in bentonites, the solubility of free silica in dilute solutions of sodium hydroxide, the morphology of montmorillonite crystals as a function of the crystal form of free silica present, and the possible influence of very finely dispersed free silica on the viscosity of bentonite suspensions. The investigated bentonites contain free silica in the form of quartz, strongly disordered low-cristobalite, and possibly amorphous silica. The range of particle size of free silica in bentonite is broad and the authors observed, in electron micrographs, particles smaller than 80–100 Å in diameter. Some of the free silica is attached to the edges of montmorillonite crystals. Those bentonites that

do not contain appreciable amounts of cristobalite have fairly large, well developed, highly elongated crystals of montmorillonite, as compared with bentonites that contain larger amounts of cristobalite. The latter are generally more impure and their suspensions in water are less viscous.

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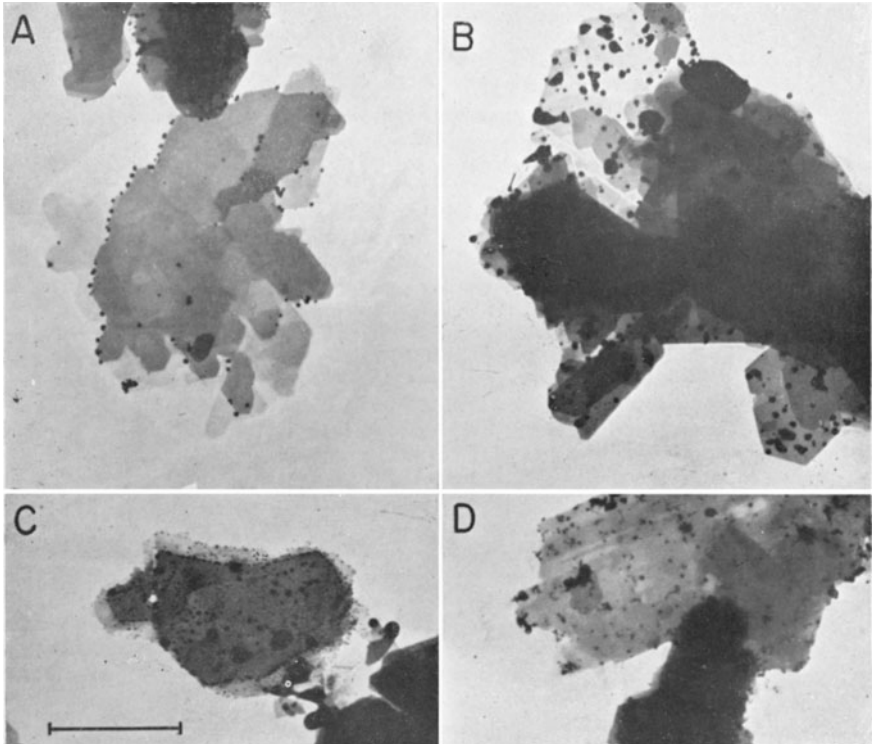


FIGURE 10.—Electron micrographs. *A*, gold adsorbed on untreated kaolinite; *B*, *C*, *D*, gold adsorbed on kaolinite heated at 680°, 800°, and 950°C.

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