

DEHYDRATION OF FULLY HYDRATED HALLOYSITE FROM LAWRENCE COUNTY, INDIANA¹

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ABSTRACT

The changes occurring in fully hydrated halloysite during dehydration have been studied by X-ray diffraction at relative humidities that ranged from 0 to 100 percent. From the results of this study it has been concluded that: (1) layers dehydrate randomly, but instantaneously; (2) the diffraction from an individual crystallite is governed by the ratio of hydrated to dehydrated layers present; and (3) halloysite dehydrated to any degree shows no detectable rehydration when exposed to 100 percent relative humidity for 2 months.

INTRODUCTION

This paper is a report of an investigation of the dehydration of fully hydrated halloysite from a halloysite deposit in Lawrence County, Indiana. The most recent comprehensive study of the dehydration of hydrated halloysite in relation to relative humidity was done by Brindley and Goodyear (1948), using film techniques and relative humidities from 0 to 30 percent. The present study extends the range of relative humidities to 100 percent, and direct recording techniques were used.

Samples of fully hydrated halloysite were obtained from Gardner Mine Ridge in Lawrence County, Ind. These samples came from approximately the same location as Bedford halloysite samples 12a and 12b of the American Petroleum Institute Research Project 49 (1949). Halloysite in the mine at Gardner Ridge has three chief modes of occurrence: (1) massive white halloysite, (2) massive brown halloysite, and (3) nodular white or blue halloysite. The massive varieties are commonly associated with allophane, gibbsite, iron oxides, and crandallite. The white nodular material, which is vitreous, fully hydrated, and relatively dense and breaks with conchoidal fracture, was chosen for this study because it is the purest material available.

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PROCEDURE

Immediately upon removal from the wall of the mine the samples studied were placed in bottles that were filled with distilled water. The walls of the mine are wet constantly, and the relative humidity in the mine is about 90–93 percent as measured with a wet bulb thermometer.

The samples were ground under water, and sedimented slides were prepared by pipetting a suspension of the ground halloysite onto a glass slide. The slides were dried in desiccator jars containing various concentrations of sulfuric acid so that drying could take place at relative humidities that ranged from 0 to 100 percent. After coming to equilibrium at a particular relative humidity, the slide was removed from the desiccator and immediately placed in a General Electric X-ray sample holder, which was then covered quickly and completely with an inverted beaker. The X-rays (CuK_α radiation) entered the beaker through a slot that was covered with mylar; moist air entering through another slot in the beaker was constantly passed over the slide. A slide dried at a relative humidity of 100 percent and subjected to this procedure gave the same X-ray trace when left in the beaker for an extended period of time. Thus while the sample was being X-rayed, the relative humidity surrounding the slide was essentially 100 percent. Slides originally dried at humidities below 100 percent showed no detectable rehydration after having been kept at a relative humidity of 100 percent for at least 2 months. A few drops of ammonium hydroxide gave a much better suspension of halloysite than pure distilled water. Slides made with and without ammonium hydroxide gave the same X-ray trace, however. Therefore the X-ray traces shown in Fig. 1 were made from slides that came from suspensions which contained a few drops of ammonium hydroxide.

RESULTS

Fig. 1 shows the X-ray traces of halloysite preparations that were dried at various relative humidities (100, 90, 60, 50, 40, 30, 20, and 0 percent). At 100 percent relative humidity, an intense and sharp peak (001) appears at $8.8^\circ 2\theta$ (10.1 Å). As the relative humidity decreases, this peak gradually diminishes and broadens on the high-angle side, and the band that extends from 10.1 Å to 7.2 Å ($12.3^\circ 2\theta$) gradually increases. At about 30 percent relative humidity, broad peaks are found at 10.1 Å and 7.2 Å, and a broad band is present between these two peaks. Below 30 percent relative humidity the intensity and sharpness of the 7.2 Å peak increases, and the intensity of the broad band between 7.2 Å and 10.1 Å diminishes. The 10.1 Å peak disappears in relative humidities of less than 20 percent,

The 003 peak at about $27^\circ 2\theta$ also shifts as the relative humidity decreases. As the relative humidity lessens this peak gradually moves to about $24^\circ 2\theta$, where it is the 002 peak.

CONCLUSIONS

The 10.1 Å peak probably is due to crystallites of halloysite that have all their interlayer positions completely filled with water. The broad band between 7.2 Å and 10.1 Å is probably caused by crystallites that contain

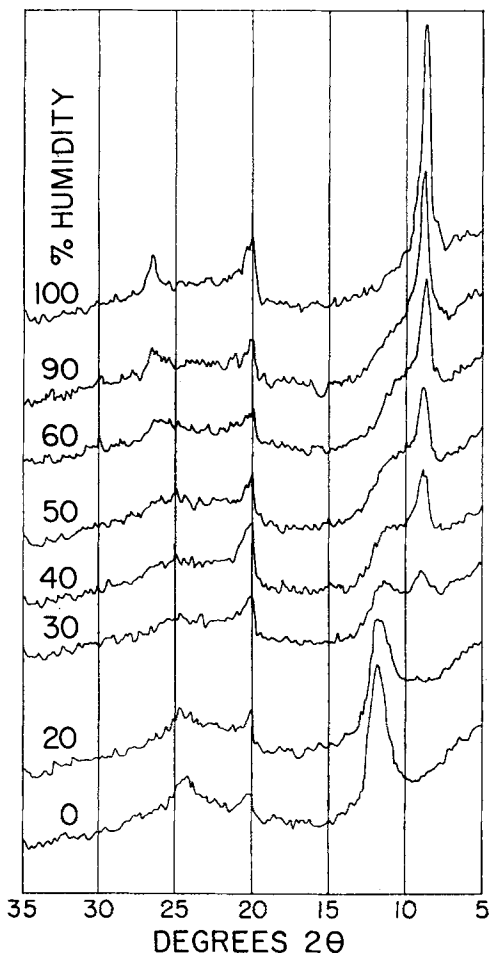


FIGURE 1.—Smoothed X-ray spectrometer traces of halloysite at various stages of dehydration. $\text{Cu } K_{\alpha}$ radiation.

both completely hydrated interlayer positions and interlayer positions that have little or no water. The ratio of filled to unfilled interlayer positions in any crystallite determines where the greatest intensity of the broad band will be. For example, at 90 percent relative humidity the greatest intensity of the band is just below 10.1 Å; this indicates that the ratio of filled to

unfilled interlayer positions is high. At 20 percent relative humidity the greatest intensity of the band is just above 7.2 Å; this indicates that the ratio of filled to unfilled interlayer positions is low. The peak at 7.2 Å is due to crystallites that have little or no water in any of their interlayer positions.

X-ray traces that do not contain peaks at either 7.2 Å or 10.1 Å have been obtained, but they contain only a broad band between these two positions. We have not been able to obtain these traces at known relative humidities, but by comparison with the traces in Fig. 1 the relative humidity probably is about 30 percent. The difficulty in obtaining a trace that has only a broad band between 7.2 Å and 10.1 Å possibly means that most partially dehydrated halloysite samples possess some crystallites that have all their interlayer positions completely filled with water or possess some crystallites that have little or no water in their interlayer positions. The unchanging position of the 001 peak during dehydration to a relative humidity of 30 percent and the lack of elasticity of the silicate layers suggest that all the water in any one interlayer position comes off instantaneously and not gradually. In a crystallite, however, all the interlayer positions do not lose their water at the same time; this is shown by the gradual shift in X-ray bands.

REFERENCES

- American Petroleum Institute (1949) *Reference Clay Minerals*: Research Project 49, New York.
- Brindley, G. W. and Goodyear, J. (1948) X-ray studies of halloysite and metahalloysite, II. The transition of halloysite to metahalloysite in relation to relative humidity: *Min. Mag.*, v. 28, pp. 407-422.