

Dehydration of the washed potassium acetate complex of halloysite

(Received 26 February 1973)

INTRODUCTION

MANY alkali metal salts of short chain fatty acids have a strong affinity towards the formation of interlayer complexes with kaolin minerals (Weiss *et al.*, 1963). The complexes of kaolin minerals with potassium acetate, KOAc, in particular have been the subject of much investigation; e.g., Wada (1959, 1961, 1965); Deeds *et al.* (1966); Wiewiora and Brindley (1969).

One of the observations made in these studies is that the removal of intercalated KOAc by washing results in different products for the different kaolin minerals. Halloysites have the spacing of the fully hydrated form (10.1 Å) restored when intercalated KOAc is removed in this way, regardless of whether they had been intercalated with the salt while in this form (Wada, 1961). Nacrite also forms a water complex as a result of the washing of its KOAc complex (Wada, 1965; Deeds *et al.*, 1966). The nacrite hydrate formed in this way has a basal spacing of 8.4 Å. Kaolinite and dickite do not form water complexes following intercalation with KOAc and the subsequent removal of the salt by washing, although it has been observed that the original structural order of kaolinite may not be preserved by these treatments (Wiewiora and Brindley, 1969).

This report concerns a part of an investigation of the relationship between the different hydration states of halloysite (Churchman *et al.*, 1972). The behavior on drying of halloysite-water complexes which were formed by washing various intercalation complexes of the mineral were compared with the drying behavior of naturally hydrated halloysite.

METHODS

The halloysite was obtained from Te Puke, New Zealand, A *ca.* 1-2 µm fraction, obtained by sedimentation procedures and X-ray pure, was used in these experiments. This sample was predominantly in the hydrated form.

The KOAc complex was prepared by soaking 2 g of the sample in 200 ml of 6.5 M KOAc at *ca.* 20°C for 3 days. There were sharp X-ray diffraction peaks for a 14.0 Å spacing (001) and for a 3.49 Å spacing (004). By way of comparison, the cesium chloride and the hydrazine complexes were also prepared. The former was obtained by soaking 1-2 g of the sample in 50 ml of a saturated CsCl solution at *ca.* 20°C for 3 days. There were prominent X-ray diffraction peaks for spacings of 10.5 Å (001), 5.28 Å (002) and 3.55 Å (003). The halloysite-hydrazine complex was prepared by soaking 1-2 g of the sample in 100 ml of hydrazine hydrate at *ca.* 20°C for 3 days. There were prominent X-ray diffraction peaks for a 10.4 Å spacing (001) and for a 3.45 Å spacing (003). No halloysite basal reflections were seen in X-ray traces of any of these complexes.

The hydration of each complex was achieved by washing the solid, which was held in retentive filter paper,

with distilled water. Complete removal of the intercalated compound was indicated when X-ray diffraction charts for the residue showed no trace of the complex 001 peaks. The hydrated samples were sedimented on glass slides for study with the X-ray diffractometer. Repeated oscillation of the goniometer over the basal peak region resulted in diffraction charts which indicated the changes taking place during the initial stages of drying. Further dehydration was observed in samples that had been dried in an oven at various temperatures and for different times. Air drying procedures were carried out on the same day, so that similar drying conditions prevailed in each case.

RESULTS AND DISCUSSION

Figure 1, Traces Ia, b and IIa, b, c show a comparison between the basal peak regions of the X-ray traces for the naturally hydrated halloysite and the washed KOAc complex during the initial stages of drying (at room temperature). Two traces of the 001 peaks only, for naturally hydrated mineral oven dried to give samples with interlayer water contents roughly similar to the 3-h air dried washed acetate complex (Fig. 1, Trace IIc), are also shown (Fig. 1, Traces Ic and d). Traces obtained from the washed CsCl and washed hydrazine complexes during the drying process showed peak shapes similar to those obtained during drying of the naturally hydrated material.

The shapes of peaks for the naturally hydrated, washed CsCl, and washed hydrazine complexes on drying show those features which are characteristic of the 001 peak profiles for partially hydrated halloysites (Churchman *et al.*, 1972). These profiles have a significant intensity above background over the entire 001 peak region, with maxima either absent or appearing within only two

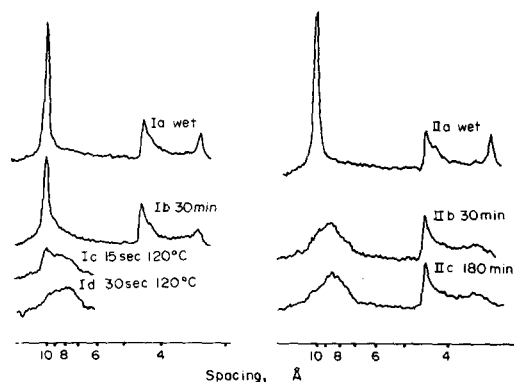


Fig. 1. X-ray diffraction charts for a naturally hydrated halloysite (series I, on left) and for the washed KOAc complex of this halloysite (series II, on right) at various stages of dehydration. Times shown are for air drying unless the temperature is specified.

narrow ranges at either ends of this region; i.e. at spacings of between 9.4 and 10.1 Å and between 7.2 and 7.9 Å. There are no diffraction maxima appearing between these two extreme ranges of spacings in the typical halloysite 001 peak profiles.

A different behavior on drying is shown by the washed KOAc complex of halloysite. The interlayer water in this form of halloysite was seen to be more labile than that in the naturally hydrated mineral. The observation of most interest, however, was that the 001 peak region, while relatively broad, tended to show only one maximum. The position of this maximum shifted continuously from a spacing of 10.1 Å for the wet sample (Fig. 1, Trace IIa) to a spacing of 8.4 Å for a sample which had been air dried for 3-hr (Fig. 1, Trace IIc). The peak for the washed KOAc complex was shifted to a diffraction angle representing a 7.6 Å spacing when a sample of this washed complex was over dried at 85° for only 5 sec.

It has been shown (Churchman *et al.*, 1972) that the 001 peak profile shapes for partially dehydrated halloysites which have been derived by drying the naturally hydrated mineral can be closely reproduced throughout the range of possible interlayer water contents by profiles calculated for a partially segregated interstratification of the hydrated and dehydrated layers (with 10.1 and 7.2 Å spacings respectively). It was concluded that the loss of halloysite interlayer water takes place through an interstratification in which there is a partial segregation of the two layer types. In the case of the washed KOAc complex, however, the shapes of the 001 peaks from partially hydrated samples are more similar to those for randomly interstratified stacking sequences of layers than they are to those for stacking sequences in which the two types of layers are segregated to a significant extent. Calculations show that the completely random mixing of the two layer types leads to X-ray patterns which each have a single 001 peak maximum. The spacing represented by the maximum decreases continuously from 10.1 to 7.2 Å as the proportion of dehydrated layers increases; i.e. as drying occurs.

Wada (1965) noted that a washed KOAc complex of halloysite which was dried at 50°C gave diffuse basal reflections, with a maximum covering the range of spacings between 7.6 and 8.4 Å. It was observed earlier that the hydrated form of nacrite which was formed by washing the KOAc complex of this mineral gave sharp reflections corresponding to several orders of a spacing of 8.4 Å (Wada, 1965; Deeds *et al.*, 1966). These workers proposed that this hydrate has a regular structure, with a unique configuration of the water molecules. The washed halloysite-KOAc complex resulting from the drying process in this present study showed only a broad second or third order basal reflection at spacings between 3.5 and 3.6 Å (Fig. 1, Trace IIc) together with the 8.4 Å 001 maximum. Since this broad lower angle spacing does not represent an integral higher order of the 8.4 Å spacing, it may be deduced that this observation does not represent the formation of a hydrate which is analogous to the reported nacrite hydrate.

CONCLUSIONS

Thus, it appears that the intercalation and removal of KOAc changes the nature of interaction between neighboring clay layers, which allows both the easier removal of the interlayer water and the occurrence of a more random interstratification of layers in the partially dehydrated samples than is the case when either CsCl or hydrazine are intercalated and then removed. There is a decrease in the attractive forces binding the aluminosilicate layers together. The fact that halloysites undergo an excessively large expansion in the *c*-axis direction on intercalation with KOAc is considered to be the cause of the distinctive behavior of the washed KOAc complex.

It was noted earlier that KOAc will form intercalation complexes not only with hydrated halloysite but also with 7 Å kaolin minerals, including dehydrated halloysites. The formation of the acetate complex of dehydrated halloysite and the removal of the salt by washing, to form a water complex with a 10.1 Å spacing, has suggested the possibility of the indirect rehydration of a dehydrated halloysite. The weakening of interactions between the layers as a result of the intercalation of KOAc precludes the possibility that the dehydration may be perfectly reversed, however. A fully hydrated halloysite which is identical to the original fully hydrated mineral cannot be recovered by washing the potassium acetate complex of the dehydrated form of the mineral.

Acknowledgements—This work was supported by a Fellowship from the New Zealand Pottery and Ceramics Research Association for one of the authors (G.J.C.).

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