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STABILITY FIELDS OF HYDRATION STATES OF AN HALLOYSITE

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ABSTRACT

A detailed knowledge of the *P-T* diagram of an hydrated halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) at pressures to 30,000 psi (2070 bars) and at temperatures to 200°C has been obtained. A statistical analysis of a parameter which indicates the degree of hydration of the mineral as a function of the pressure, temperature, and time of duration of hydrothermal treatments in this *P-T* range has been carried out. It is shown that at least 79% of the variations in this parameter are accounted for by variations in the temperature of treatment while the pressure and time (above 3 days) have no significant effect on this parameter. It is concluded from this analysis that dehydration of this halloysite takes place via a series of hydration states and over a range of temperatures rather than through a phase transformation at a single temperature. Each of the hydration states is stable over a significant period of time.

INTRODUCTION

A study of the hydrothermal dehydration of an hydrated halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) to the fully dehydrated form of the mineral $Al_2Si_2O_5(OH)_4$) has provided a detailed knowledge of the *P-T* diagram for this mineral at pressures $\leq$ 30,000 psi (2070 bars) and at temperatures below 200°C.

This study arose out of an investigation which was designed to resolve a conflict in the literature over the relationship between the most hydrated and least hydrated forms of halloysite. Many workers (*e.g.*, Hendricks, 1938; Alexander *et al.*, 1943; Brindley and Goodyear, 1948) have regarded these two forms as separate mineral phases. MacEwan (1947), on the other hand, concluded that they are two forms of a single substance rather than entirely separate substances. By means of the analysis of X-ray diffraction line profiles of halloysites at various stages of their dehydration at room temperature it was concluded that halloysites may show a variation in their average interlayer water content throughout the whole range from zero to two H_2O molecules per $Al_2Si_2O_5(OH)_4$ unit cell (Churchman, 1970). Thus the mineral may occur in partially hydrated forms as well as in a fully hydrated and a fully dehydrated form.

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The relative stabilities of the partially hydrated forms of halloysite were determined in this present study by means of the analysis of results of the dehydration of an halloysite under hydrothermal conditions for varying lengths of time. The possibility of the existence of phase boundaries was examined.

Roy and Osborn (1954) also studied the hydrothermal dehydration of an hydrated halloysite. The aim of their study, viz. the determination of the stability fields of (1) an halloysite which contained interlayer water and (2) a dehydrated halloysite, was different from those of the present study.

EXPERIMENTAL

Apparatus

The hydrothermal treatment of the samples was carried out in stellite pressure vessels which were heated in an electric furnace. Hydrostatic pressure was generated by a hydraulic pump. The temperature of each vessel was measured by a chromel-alumel thermocouple which had one end inserted in the pressure vessel close to the samples. The temperatures were controlled to ±5°C by Ether Transitrol regulators while the pressures were controlled to ±500 psi (±40 bars).

Material

The halloysite was obtained from the same deposit as that studied by Hughes (1966). The deposit occurs near Te Puke, New Zealand. The material was in a lightly ground aggregate form and was stored in the form of a paste with water. No perceptible changes occurred in the shape of the 001 peak profile of the sample after it has been stored under water at atmospheric pressure for three years. It is concluded that the mineral has long term stability under these conditions. Thus, samples of the mineral were immersed under water in order to prevent the occurrence of further dehydration (see below).

Procedure

Samples were contained in annealed silver tubes which had been closed at each end by pinching. The temperature regulators were set to 40°C below the appropriate run temperatures to avoid overshooting during the heating period. Following a run, the pressure vessel containing the sample was quenched to room temperature with an air blower and the pressure in the vessel was released only when this temperature was reached.

Examination of products

The products were examined by X-ray diffraction. Samples were spread with water on a glass slide and Ni filtered CuKα radiation was used. Traces from the starting material and products in the 001 basal peak region (from 5° to 14°2θ) were obtained while the samples were still wet.

RESULTS

The 001-peak region in diffraction charts from the products of the runs at high temperatures and pressures showed reflections for spacings of *ca.* 10 Å and/or *ca.* 7 Å with varying degrees of prominence and with a spread of intensity throughout this region appearing in many of the charts. The peak profiles were of a similar shape to those which were obtained during the study of the dehydration at room temperature (Churchman, 1970). The shapes of the profiles obtained in the room temperature dehydration were compared with the shapes of basal peak profiles which were given by the fully hydrated form and the fully dehydrated form of the mineral. This comparison showed that the profiles could not be obtained from a sum of two peaks, each characteristic of a single form of halloysite. Nevertheless, it was shown in this study that the intensities of the reflections at low angles decrease relative to those of the high angle reflections as dehydration proceeds. This observation was used as a basis for the description of the charts of products of the runs (see later).

In contrast, the diffraction chart obtained from the starting material showed a sharp peak for a spacing of 10.1 Å. There was virtually no significant spread of intensity on the high angle side of this peak. An insignificant amount of loss of interlayer water from this starting material is indicated by this observation. The starting material appears to be almost entirely composed of a single form of halloysite with a unique basal spacing.

Description of Results

Maxima occur within only two narrow angular ranges in all of the profiles. Some of the profiles have a maximum at *ca.* 9°2θ, while others have their maximum at *ca.* 12°2θ. Profile maximum intensities may thus be described as either I(9°), the intensity of a peak near 9°2θ, or I(12°), the intensity of a peak near 12°2θ. These intensity values must be corrected for factors which vary between different treatments if the results of the different treatments are to be compared. The amount of material in the X-ray beam is a variable factor of this kind. These corrections are made by dividing the peak heights by the appropriate value of I(20.1°), the height of the (0.2.11) peak at 20.1°2θ. It had been observed that the relative intensities of peaks in X-ray diffraction charts were the same when well characterized samples of this particular halloysite (*e.g.*, fully dehydrated samples) were in the form of either specimens sedimented on to glass slides or loose powders (Churchman, 1970). Thus it is seen that no preferred orientation of this particular halloysite sample takes place on sedimentation. It may be concluded that the intensity of the standard (0.2.11) peak is insensitive to possible variations in mounting the different samples. The intensity of this peak is also insensitive to changes in the interlayer water content (Brindley and Robinson, 1948). Corrected peak intensities, which are comparable, one with another, are thus given by

$$H = \frac{I(9°)}{I(20.1°)}$$

and

$$D = \frac{I(12°)}{I(20.1°)}$$

The method of obtaining these quantities is shown in Figure 1 by reference to charts from two partially hydrated halloysite samples.

While it has been shown (Churchman, 1970) that the basal peaks from halloysites with interlayer water contents intermediate between the fully hydrated and fully dehydrated forms may not be regarded as single entities with unique layer spacings, each particular value of H or D is characteristic of a sample with a particular interlayer water content.

The results of runs are expressed in terms of the value of either H or D in Table 1.

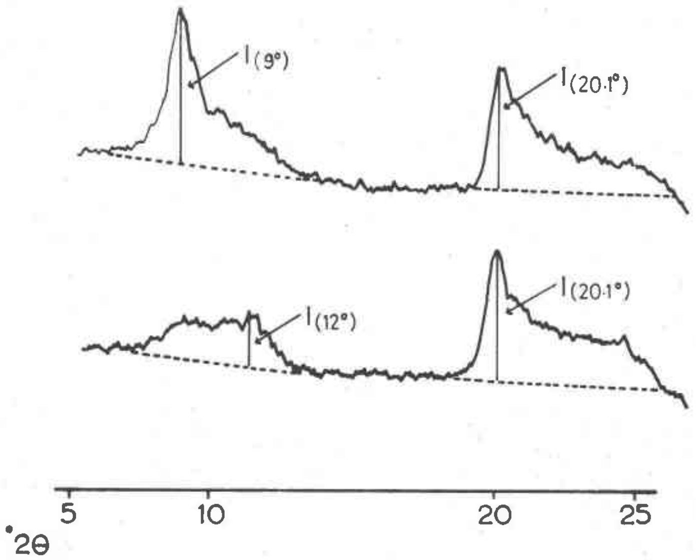

Fig. 1. Method of obtaining intensity values from diffraction charts.

TABLE 1. Results of Hydrothermal Treatments of an Hydrated Halloysite

Pressure (p.s.i.) [bars]	Temp. (°C)	Time (days)	Intensity function		W**	Pressure (p.s.i.) [bars]	Temp. (°C)	Time (days)	Intensity function		W**
			H*	D					H*	D	
3,000	50	5	>2.0		≥1	10,000	80	6	2.6		1.1
[210]						[690]					
"	60	5	2.5		1.1	"	80	7	2.3		1.0
"	60	12	2.1		0.9	"	80	11	2.5		1.1
"	90	6	2.0		0.9	"	100	6		0.5	-0.3
"	90	8	2.5		1.1	"	130	24		0.4	-0.3
"	90	17	1.2		0.5	"	160	6		0.8	-0.5
"	100	6	1.1		0.5	"	160	7		0.8	-0.5
"	100	7	0.9		0.4	"	190	3		1.0	-0.6
"	100	8	0.4		0.2	"	220	3		1.5	-0.9
"	100	9	0.5		0.2	15,000	100	6	1.4		0.6
"	120	22	0.5		0.2	[1030]					
"	140	6		0.6	-0.4	"	110	6	1.0		0.4
"	150	6		1.6	-1.0	"	120	26		0.8	-0.5
5,000	70	6	>2.5		>1	"	160	4		1.1	-0.7
[340]						"	160	7		1.3	-0.8
"	70	7	>2.0		≥1	"	160	9		1.2	-0.8
"	70	7	>2.2		≥1	"	190	3		0.9	-0.6
"	90	6	1.1		0.5	"	210	3		1.6	-1.0
"	90	6	0.8		0.3	"	250	3		1.6	-1.0
"	90	7	1.2		0.5	30,000	80	6	>2.0		≥1
"	100	7	1.3		0.6	"[2070]	100	30	2.0		0.9
"	130	4		0.3	-0.2	"	100	36	1.3		0.6
"	140	6		0.4	-0.3	"	110	28	1.6		0.7
"	140	7		0.7	-0.4	"	120	6	1.1		0.5
"	140	7		0.5	-0.3	"	120	26	0.5		0.2
7,000	80	6	1.6		0.7	"	140	5		0.5	-0.3
[480]						"	150	7		0.6	-0.4
"	110	22	0.8		0.3	"	180	6		1.0	-0.6
"	120	7		0.8	-0.5	"	190	6		1.1	-0.7
"	140	6		0.8	-0.3						
"	140	7		0.9	-0.4						
"	140	7		1.5	-0.3						

$\underline{H} = 2.3$

$\underline{D} = 1.6$

*In the table, H is given in the form "H > x" when the intensity of the peak at ca. 9°2θ was greater than the full scale deflection of the chart at the rate meter settings used.

**W is the parameter which indicates the degree of hydration of the sample.

Analysis of Results

A parameter W which expresses the degree of hydration of the samples is defined. When $\underline{H}$ is the value of the corrected peak height H for the hydrated starting material and $\underline{D}$ is the value of the corrected peak height D for the most dehydrated sample,

$$W = H/\underline{H} \text{ if profile maximum is at } ca.\ 9°2\theta$$

$$\text{or, } W = D/\underline{D} \text{ if profile maximum is at } ca.\ 12°2\theta$$

Since the maximum is not found at positions between *ca.* 9° and *ca.* 12°2θ, W is defined for all profiles in this way.

Values of W for the results of all of the runs are also given in Table 1.

The effect of variations in the temperature, pressure, and time of duration of hydrothermal treatments of the mineral upon the value of this parameter W and therefore upon the degree of hydration of the halloysite was investigated by means of a multiple regression. Table 2 gives correlation coefficients for multiple linear correlations of the parameter W with one or more of the variables temperature, pressure or time.

DISCUSSION

Linear correlations between W, the parameter which is related to the degree of hydration of the mineral and all independent variables when taken either separately, two at a time, or all together was carried out by computer. The best correlations of each number of independent variables, which are shown in Table 2, lead to the following conclusions:

(a) Temperature variations account for 79 percent of the variation in W.
(b) Neither of the other two variables has a significant effect on the correlation.

It was observed that the correlation between W and time, which gave a regression coefficient, R, of 0.227 could be significant at an approximately 10 percent level. Nevertheless, the multiple correlation of W with time and temperature gave a value for $100R^2$ which was greater than that for the single correlation of W with temperature by only 0.08. The single correlation between W and pressure gave a value of -0.12 for R. Pressure also has an insignificant effect on the degree of hydration of a product of this type of treatment.

The parameter indicating the degree of hydration of halloysite which is used in the correlations is only an empirical one and has no theoretical basis. Consequently, a correlation coefficient of exactly 1.0 may

TABLE 2. Correlation Coefficients for the Highest Degree of Correlation for Each Number of Independent Variables

Dependent variable	Independent variables	$100R^2$
W	T	79
W	T, P	81
W	T, P, t	81

Where T = Temperature
P = Pressure
t = Time of duration of runs

not be expected. Experimental errors also have an influence on this coefficient, however, and it is found that, using the estimated errors of ± 10 percent in values of both H and D, a maximum value for $100R^2$ of 87 may be calculated for the linear correlation of W and temperature.

This correlation strongly suggests that, within the range of pressures which were studied (from 3,000 to 30,000 psi or 210 to 2070 bars) and for times of treatment of from 4 to 36 days, a particular form of halloysite with a unique interlayer water content results from a treatment at a particular temperature.

It is seen from Table 1 that there is a discontinuity between $+0.2$ and -0.2 in the values of W which are obtained from the products of the runs. This discontinuity arises from the definition of W. This is illustrated by reference to the lower chart in Figure 1. The basal peak region in this chart shows only a slight maximum (at *ca.* $12°2\theta$) and can almost be seen as a broad band of constant intensity over the whole spacing range. W for this chart is -0.2. Charts from the halloysite at a stage of dehydration just prior to that giving rise to this particular chart show only a slight maximum at *ca.* $9°2\theta$ and give a W value of $+0.2$. When it is considered that W values are subject to errors of ± 20 percent, it is seen from Table 1 that there are no other discontinuities between $+1.0$ and -1.0 in values of W for the products of runs.

It is concluded that the hydrothermal dehydration studies revealed no sharp boundary between a fully hydrated halloysite and a fully dehydrated halloysite. Roy and Osborn (1954) determined the position of a boundary of this type. Nevertheless, it is noted that these workers had assumed that only two stable forms of halloysite were possible and that a product giving any reflections above background at the low angle end of the basal spacing region was an hydrated halloysite (or an endellite, according to the nomenclature used by these workers). On the other hand, they noted that several of their runs produced a form of halloysite with a basal spacing of 7.4 Å, which could be reduced to one of 7.17 Å on further heating. They noted that halloysites which had been dehydrated by mild treatments by other workers had exhibited this larger spacing (*e.g.*, Brindley and Goodyear, 1948) and claimed that a form of the mineral with this spacing had a "unique stability". Nonetheless, Roy and Osborn did not consider that this observation precluded the possibility of the existence of a phase boundary between the two end members of the dehydration series.

The problem of the phase status of the different forms of halloysite may be seen as an instance of the general problem of the phase identities of mixed layer clays which is discussed by Zen (1962). Zen contends that the number of phases in a mixed layer clay could be obtained by observing the behavior of a number of "thermodynamically meaningful parameters" during certain experiments performed on the system. Neither of the methods which he proposes for this purpose, viz. (1) the observation of the results of equilibrations of the clay with a third solution phase, and (2) the observation of the nature of phase separation during titrations with alkali metal cations, is useful for determining the phase status of any particular hydration state of halloysite. Furthermore, while partially hydrated forms of halloysite have been shown to be stable over significant periods of time, the possibility that these forms do not represent an equilibrium state must also be considered. Such a possibility is suggested by Chukrov and Zvyagin's (1966) conclusion that hydrated halloysites undergo a spontaneous loss of water in nature. On the other hand, Hughes and Foster (1970) pointed out that laboratory dehydrations of halloysite which are extremely fast by comparison with the natural process are not accompanied by the increase in crystalline order which takes place in nature. This reordering is responsible for the free energy lowering which enables the natural dehydration to take place. It is conceivable that such an increase in order could take place in a laboratory treatment, *e.g.*, a hydrothermal treatment, which was carried out for a longer period of time, however. Thus, any line of demarcation between different forms of halloysite may be only a kinetic boundary and the dehydrated form may be the only stable phase among the series of hydration states.

Finally, it is noted that a number of hydrothermal treatments which were carried out at higher pressures than 30,000 psi (2070 bars) also produced hydration states of halloysite with average interlayer water contents of between 0 and 2 molecules of H_2O per $Al_2Si_2O_5(OH)_4$ unit. These higher pressure runs were performed under the following conditions:

at 45,000 psi (3100 bars) and 130°C for 8 days
at 45,000 psi (3100 bars) and 140°C for 7 days
at 45,000 psi (3100 bars) and 145°C for 7 days
at 60,000 psi (4140 bars) and 130°C for 7 days
at 60,000 psi (4140 bars) and 135°C for 7 days
at 60,000 psi (4140 bars) and 150°C for 7 days
at 60,000 psi (4140 bars) and 160°C for 7 days.

Values for $I(20.1°)$ and therefore values for the corrected peak intensities H and D were not obtained for the products of these runs but the samples were positively identified as partially hydrated forms of the mineral by virtue of the fact that the intensities at the maxima at either 9° or 12°2θ were less than two times the intensities of the reflections at either 12° or 9°2θ respectively in the same profiles. The observation of this feature of the profile shapes is sufficient for the identification of halloysite samples as partially hydrated forms of the mineral, although not all partially hydrated halloysites give rise to this type of profile. It is noted from observations of the profiles of samples treated at lower pressures that this feature of the profile shapes is associated with W values of between $+0.5$ and -0.5 (Churchman, 1970). Values of W within this range would be expected to result from runs at these temperatures at the lower pressures (see Table 1). It is likely, then, that the results of this present investigation apply as well to pressures above 30,000 psi (2070 bars) as to those in the 3,000 to 30,000 psi (210 to 2070 bars) range.

CONCLUSIONS

The effect of the pressure, temperature, and time of duration of a hydrothermal treatment upon the degree of hydration of an hydrated halloysite has been determined for the range of pressures between 3,000 and 30,000 psi (210 and 2070 bars) for temperatures below 200°C and for durations of runs of between 3 and 37 days. It is shown that the temperature of the treatment determines the nature of the product, while time and pressure (within the ranges of values which were studied) have no significant effect on the result. It is concluded, therefore, that a particular form of halloysite with a specific average interlayer water content will persist under constant temperature hydrothermal conditions for significant periods of time.

The dehydration of a sample of halloysite does not proceed via a single transformation between phases but rather through the formation of a continuous series of hydration states of the mineral with the loss of successive increments of water. The irreversibility of the dehydration process implies that the fully dehydrated form is the only stable phase in the halloysite dehydration series.

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