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ISOMORPHIC SUBSTITUTION IN ATTAPULGITE AND ITS INFLUENCE ON THE DEHYDRATION PROCESS

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ABSTRACT

The influence of isomorphic substitution in an octahedral sheet of attapulgite on its dehydration process has been examined by thermal analysis. The loss of the water coordinated to the edge octahedral cations occurs in two stages. The same percentage of water is not lost in each of these stages: the percentage loss depends on the chemical nature of the substituents at the octahedral sites of the attapulgite structure. Based on a TG/DTG examination of a series of attapulgite samples and their chemical analyses, it was deduced that the higher the Mg^{2+} (M^{2+}) content of these sites, the greater the water loss in the first stage.

INTRODUCTION

Attapulgite is a fibrous clay mineral, a crystalline hydrated magnesium silicate, which possesses microchannels oriented longitudinally with the fibres. The chemical composition of this clay mineral varies within certain limits according to its origin. The main variation is that an Al^{3+} cation can replace Mg^{2+} in the octahedral sheet. In this way, depending on the degree of isomorphic substitution, its ideal formula would be: $Si_8(Mg_{5-3x}Al_{2x})O_{20}$-$(OH)_2(OH_2)_4 \cdot nH_2O$.

This formula shows that attapulgite contains three forms of water in its structure: (i) zeolitic within the channels; (ii) coordinated to the edge octahedral cations; and (iii) hydroxyl groups at the centre of the ribbons. (They appear in the formula in the reverse order.)

The dehydration of attapulgite has been studied extensively [1–7]. Most researchers consider that, on heating, the four H_2O molecules bound to the octahedral cations are evolved in two stages. During the first stage, two of these molecules are lost. In the second stage, as the temperature increases, the remaining two molecules of coordinated H_2O are lost and the dehydroxylation of the material takes place. According to the literature cited above, this dehydration process does not depend on the degree of isomorphic substitution.

The loss of the first half of the coordinated water causes a partial collapse or folding of the attapulgite structure. This folding closes the mouths of the microchannels which run parallel to the length of the fibre axes. At this stage the structure can easily be rehydrated by exposure to water vapour. After the second stage, once the remaining coordinated water and the hydroxyl groups have been removed, attapulgite cannot be rehydrated.

In this paper, we attempt to show that there is a connection between the water loss at each of the two stages described above and the chemical composition of the octahedral sheet. To this end, we examine the results obtained, from a series of samples from different sources as well as those from a set of samples collected from the literature.

EXPERIMENTAL

Starting materials

The starting materials were four Spanish attapulgites (A-1, A-2, A-3, A-5) and one Cuban attapulgite (A-4), which were analysed by González [8] giving the following results for the structural formulae:

Sample A-1

$(Si_{7.13}Al_{0.87})_T(Mg_{1.08}Al_{1.63}Fe_{0.92}Ti_{0.19})_O(Mg_{0.09}Ca_{0.03}K_{0.04}Na_{0.01})_{CC}$

Sample A-2

$(Si_{7.91}Al_{0.09})_T(Mg_{1.69}Al_{1.62}Fe_{0.48})_O(Mg_{0.10}Ca_{0.003}K_{0.01}Na_{0.18})_{CC}$

Sample A-3

$(Si_{7.95}Al_{0.05})_T(Mg_{1.79}Al_{1.45}Fe_{0.39})_O(Mg_{0.19}Ca_{0.21}K_{0.06}Na_{0.10})_{CC}$

Sample A-4

$(Si_{7.90}Al_{0.10})_T(Mg_{2.83}Al_{0.83}Fe_{0.51})_O(Mg_{0.08}K_{0.05}Na_{0.21})_{CC}$

Sample A-5

$(Si_{7.25}Al_{0.75})_T(Mg_{3.18}Al_{0.90}Fe_{0.41}Ti_{0.05})_O(Mg_{0.08}Ca_{0.03}K_{0.01}Na_{0.01})_{CC}$

T are cations in tetrahedral sites, O are cations in octahedral sites, and CC are exchangeable cations.

Apparatus and methods

The thermal analyses were performed on a Perkin–Elmer TGS-2 connected to a 7/4 temperature controller system and a 3600 data station. The heating rate was 10 °C min^{-1}, under a dynamic flow of dry nitrogen of 100 ml min^{-1}.

RESULTS AND DISCUSSION

Thermograms (TG/DTG) for the four samples of Spanish attapulgites and one Cuban attapulgite are shown in Fig. 1. Three stages can be observed

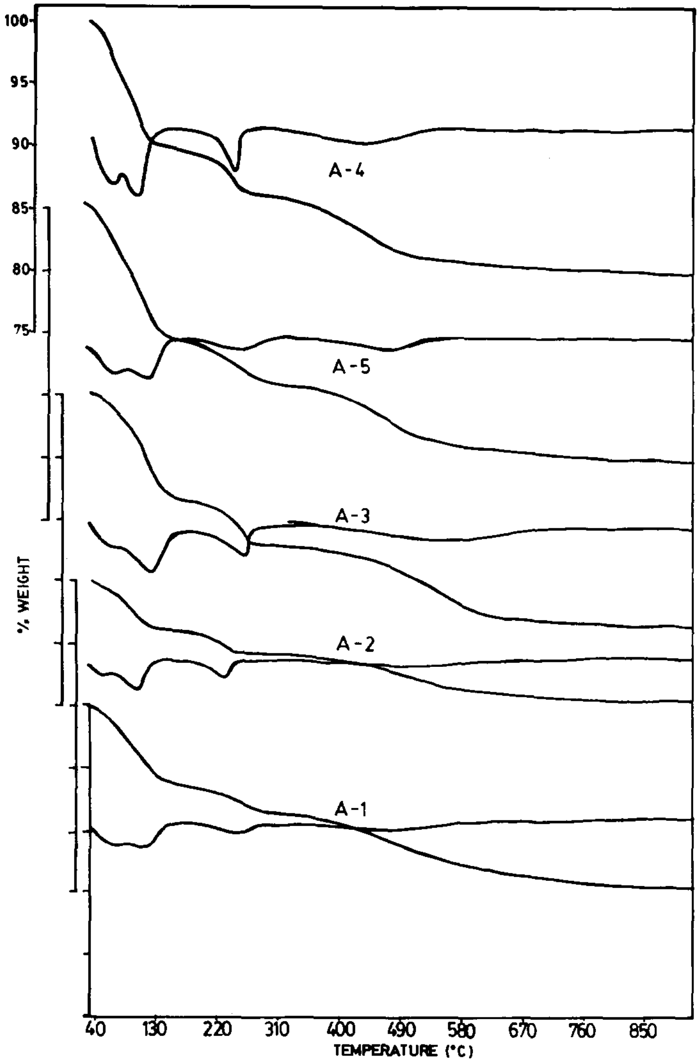

Fig. 1. TG/DTG curves of attapulgites from different sources (under N_2 atmosphere).

TABLE 1

Observed water losses

Temperature range (° C)	Weight loss (%)				
	A-1	A-2	A-3	A-4	A-5
25– 85	2.69	1.64	2.69	4.95	5.58
85–180	3.90	2.59	6.09	5.44	5.47
180–350	2.22	1.76	3.72	4.14	4.33
350–650	4.38	3.11	5.83	4.93	4.96

in each of the curves. The first stage, between 35 and 180 ° C, corresponds to the loss of surface-adsorbed water and zeolitic water within the channels. These two processes can be clearly distinguished in the DTG: the first extends up to 85 ° C and the zeolitic water loss occurs between 85 and 180 ° C. The next two stages, 180–350 and 350–650 ° C, correspond respectively to the loss of the first and second water molecules coordinated to the octahedral sheet. In the third stage, the hydroxylation also takes place.

The percentage weight losses corresponding to the three stages are shown in Table 1.

Table 2 shows the ion content ratios, Al^{3+}/Mg^{2+} and M^{3+}/M^{2+}(M^{3+}, $M^{2+} \equiv$ all trivalent and divalent cations), corresponding to the cations of the octahedral sheet, together with the weight-loss ratios, 3rd step/2nd step.

If we consider Bradley's structure for attapulgite [9] and the interpretation given above, the theoretical weight-loss ratio would be 1.50. The deviations of the experimental data from this value, in our opinion, may be attributed to the different percentages of Mg^{2+} or M^{2+} in the octahedral sheet. Thus, the lower the $Mg^{2+}(M^{2+})$ content in the octahedral sheet, the higher the value of the ratio between the weight losses in the 3rd and 2nd steps.

This correlation between chemical composition and loss of mass has also been found in other attapulgite samples: the experimental data taken from the literature [3] are shown in Table 3. From these data it can be deduced that the correlation described above is also valid. However, these data cannot be inserted in Table 2 because the dehydration depends not only on the temperature but also on other experimental conditions, such as heating

TABLE 2

Ion content ratios in the octahedral sheet and weight-loss ratios, 3rd step/2nd step

Samples	A-1	A-2	A-3	A-4	A-5
Al^{3+}/Mg^{2+}	1.51	0.96	0.81	0.29	0.28
M^{3+}/M^{2+}	2.36	1.24	1.03	0.47	0.41
3rd step/2nd step	1.97	1.77	1.57	1.19	1.15

TABLE 3

Ion content ratios in the octahedral sheet and weight-loss ratios, 3rd step/2nd step [3]

Samples	Algeria	France	Morocco	U.S.A.
Al^{3+}/Mg^{2+}	1.82	1.57	0.66	0.37
3rd step/2nd step	2.30	1.63	1.55	1.17

rate, time of heating, atmosphere conditions and its flow rate, etc., so that the data of the two series are not comparable.

Therefore, we believe, that the loss of the coordinated water in each of these two stages depends on the chemical composition of the octahedral sheet. Thus, the higher the Mg^{2+} content, the greater the percentage weight loss in the 2nd step. This is due to the greater number of water molecules coordinated to the Mg^{2+} cations, whose bonds are weaker than the H_2O–Al^{3+} bonds, considering the higher charge and smaller radius of the Al^{3+} cation.

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