THERMAL INVESTIGATION OF ACID-ACTIVATED CLAY MINERALS

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ABSTRACT

Samples of the clay mineral from the Çanakkale reserve in Turkey were activated with sulphuric acid under three different sets of conditions. DTA and TG curves of both natural and activated samples were then obtained and compared with one other.

INTRODUCTION

The montmorillonite-type clay minerals are composed of units, each consisting of two silica tetrahedral sheets with a central alumina octahedral sheet. A number of metal ions in the octahedral layer are removed from the clay lattice by leaching with an inorganic acid at elevated temperatures: this process is known as activation. The activated clays are employed as cracking catalysts in the petroleum industry and as bleaching agents for edible oils [1–3]. Several investigations have been carried out into the acid activation of clays, and various theories have been proposed for the reaction between inorganic acids and clay minerals [4–7]. The mechanism of activation of clay minerals with acids has not yet been completely solved: more insight into this problem would be very useful in adsorption and catalysis studies.

In the present work the clay mineral from the Çanakkale reserve in Turkey has been activated with sulphuric acid by means of a dry process [7,8]. The changes in structure of the mineral as a result of acid dissolution have been studied using DTA and TG measurements in order to throw more light on the activation mechanism.

EXPERIMENTAL

As mentioned above, samples of the clay mineral from the Çanakkale reserve were activated with concentrated sulphuric acid under three different sets of conditions. The first sample (C1) was prepared at an acid/clay ratio

(ml g^{-1}) of 0.2 and a temperature of 150°C, the second (C2) at an acid/clay ratio of 0.5 at 150°C, and the third (C3) at an acid/clay ratio of 0.2 at 300°C. The products were mixed with water while hot, then filtered and washed to a pH of 3.2. The filtrates were dried overnight at 110°C, ground to a diameter of < 50 μm and stored in a desiccator.

Thermal analyses were performed using a Netzch DTA and TG simultaneous instrument at a heating rate of 10°C min^{-1} and a paper speed of 120 mm h^{-1}, using kaoline heated to 1200°C as an inert material. The sample mass was kept constant at 130.00 mg and the range investigated was from ambient temperature to 1000°C.

RESULTS AND DISCUSSION

The clay mineral from the Çanakkale reserve in Turkey can be defined as a mixed-layer illite–montmorillonite according to its X-ray diffraction (XRD) traces (Fig. 1) and chemical composition (Table 1).

In a layered clay mineral such as montmorillonite, the loss of sorbed water from the interlayer space is called dehydration and the loss of hydroxyl groups from the octahedral sheet of the clay lattice is referred to as dehydroxylation [9].

Çanakkale clay gave one endothermic peak due to dehydration at 105°C and the event was complete at about 175°C (Fig. 2). In the montmorillonites the amount of water in the interlayer space varies with the sizes and charges of the exchangeable cations [10]. With increasing size and decreasing cation charge, the hydration energy of the cation decreases and the amount of adsorbed water between layers decreases. The ionic diameters of Na$^+$, K$^+$ and Ca^{2+} are 2.00, 2.60 and 2.00 Å, respectively [11]. From chemical analysis of this sample (Table 1), it may be seen that the amount of Na$_2$O and K$_2$O together (4.88% in total) is greater than the amount of CaO (2.75%). This results in the dehydration peak area of Çanakkale clay being small. The weight loss corresponding to this peak is 1.923% (Table 2). In addition, since the bonding energy between adsorbed water and Na$^+$ and K$^+$ ions is low, the peak maximum appears at 105°C [12].

The exothermic peak at 300°C is due to the combustion of organic materials and reaction is complete at about 450°C. The weight loss involved is 0.846% (Table 2).

The endothermic peaks in the 500–750°C region are associated with dehydroxylation reactions. In this region one small peak at about 570°C and two other peaks at 670 and 725°C have been observed. It is known [3] that illite mineral gives one endothermic peak between 550 and 580°C. In the illite, replacement of Si^{4+} by Al^{3+} in the tetrahedral positions lowers the decomposition temperature to this value [12]. As mentioned above, Çanakkale clay is a mixed-layer illite–montmorillonite, so it gives an endo-
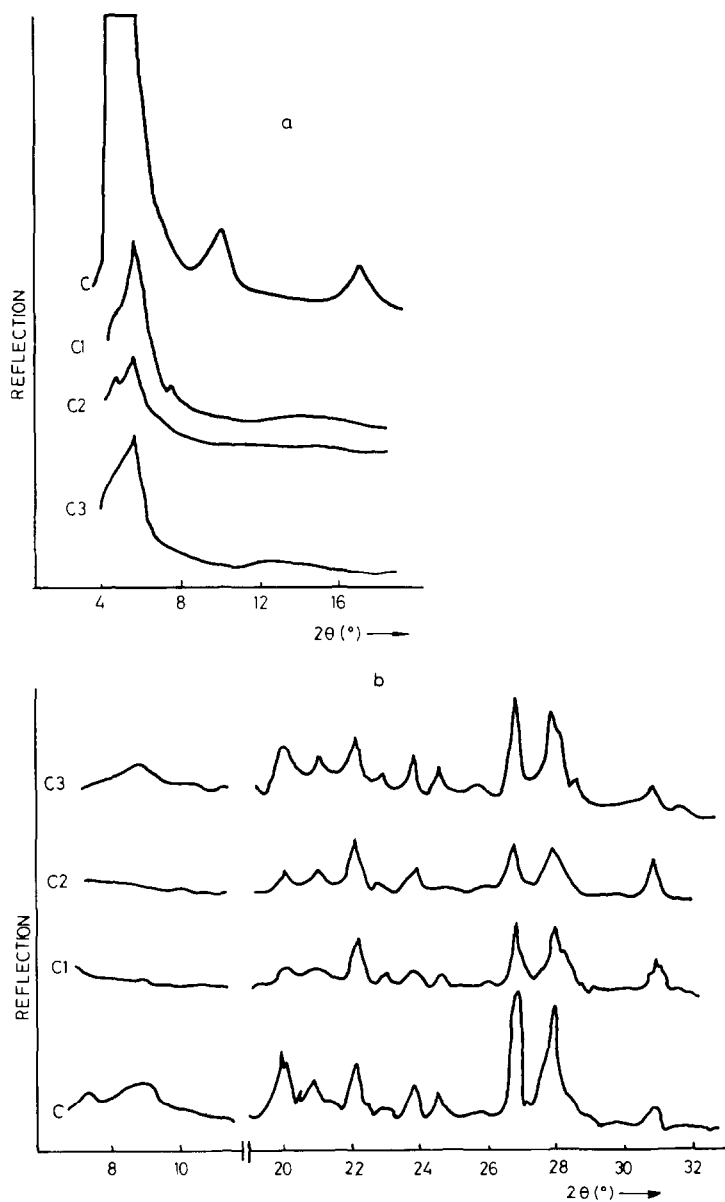
Fig. 1. X-ray diffraction results for natural and acid-activated Çanakkale clays: (a) after treatment in glycerol, (b) powder.

thermic peak at 570°C which is due to its illite component. On the other hand, the appearance of two peaks at 670 and 725°C shows that the positions of the hydroxyl ions in octahedral packing are different from one

TABLE 1

Chemical composition of natural and acid-activated Çanakkale clays

Oxide	% by weight			
	Natural	C1	C2	C3
SiO_2	59.75	71.33	81.75	72.00
Al_2O_3	16.95	14.50	8.50	14.20
Fe_2O_3	5.60	2.35	0.76	2.10
MgO	1.83	0.81	0.19	0.82
CaO	2.75	2.15	1.95	1.90
Na_2O	3.20	2.50	1.90	3.10
K_2O	1.68	0.50	0.71	1.68
Ignation	6.97	4.64	3.75	2.50

other, i.e. the mineral layers are not identical. The substitutions of the larger diameter Mg^{2+} and Fe^{3+} ions for Al^{3+} in the octahedral sheet increase the distance between hydroxyl groups and this affects the energy necessary for the release of hydroxyl ion, so that dual endothermic peaks appear for the main dehydroxylation reaction [12,13].

During thermal decomposition, the Çanakkale clay mineral shows a third endothermic peak at $855°C$ (Fig. 2). At this temperature, the observation of a small weight loss of the order of 0.115% (Table 2) is a sign that the loss of hydroxyl groups has continued above $750°C$. As mentioned above, the distance between hydroxyl ions affects the strength of bonding of OH and hence the energy necessary for its release. Since the rate of reaction of the hydroxyl groups depends upon the distance between the reacting groups, once near-neighbours have reacted a number of isolated groups are likely to remain. These latter would require a greater activation energy and hence react at a higher temperature [14]. Thus, dehydroxylation continues beyond the main endothermic peak. But the weight loss at $855°C$ (0.115%) is small
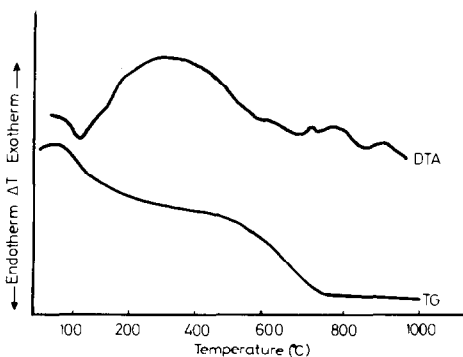

Fig. 2. DTA and TG curves for natural Çanakkale clay.

TABLE 2

DTA and TG results for natural and activated clays

Sample	Peak range (°C)	Peak temperature (°C)	Reaction	Weight loss (%)
Natural	30–175	105	Endothermic	1.923
	175–450	300	Exothermic	0.846
		570	Endothermic	
	450–745	670	Endothermic	3.577
		725	Endothermic	
	745–900	855	Endothermic	0.115
C1	30–180	105	Endothermic	1.846
		220	Endothermic	
	180–475	320	Exothermic	0.538
	475–690	515	Endothermic	1.577
		655	Endothermic	
	690–930	890	Endothermic	0.385
C2	30–175	105	Endothermic	2.654
	175–455	220	Endothermic	
		260	Exothermic	0.769
	455–675	510	Endothermic	1.385
		650	Endothermic	
	675–930	890	Endothermic	0.808
C3	30–130	105	Endothermic	2.769
	130–450	145	Endothermic	0.885
	450–715	515	Endothermic	1.692
		655	Endothermic	
	715–930	890	Endothermic	1.000

in comparison with the size of this peak. The ordered montmorillonite which lost the lattice hydroxyl groups, essentially during the main endothermic reaction, changes into a disordered, amorphous material at about 800–900 °C; this causes an entropy increase and the corresponding absorption of a certain amount of heat [15,16]. For this reason, the size of the third endothermic peak is large compared to the weight loss at this temperature.

DTA and TG curves for the acid-activated Çanakkale montmorillonite are shown in Figs. 3 and 4. It may be observed that the position of the peak at 105°C does not change, but that the amount of adsorbed water is approximately twice as great as in the natural sample (Table 2). The extent of the deformation of mineral structure due to acid and heat effects cannot readily be assessed with the aid of this peak, since the size of the peak is not sensitive to the mineralogical composition of the sample [17].

The small endothermic peaks of samples C1, C2 and C3 below 250°C are due to the dehydration of calcium sulphate produced during the sulphuric acid treatment because the clay is associated with a little calcite [18].
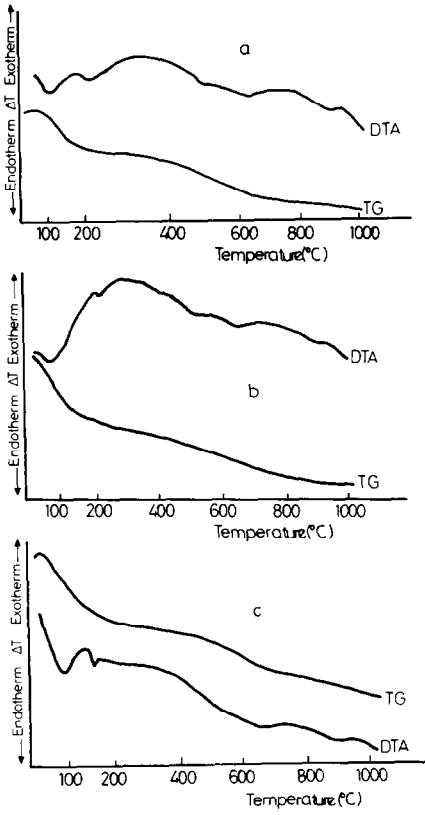
Fig. 3. DTA and TG curves for acid-activated Çanakkale clay samples: (a) C1; (b) C2; (c) C3.
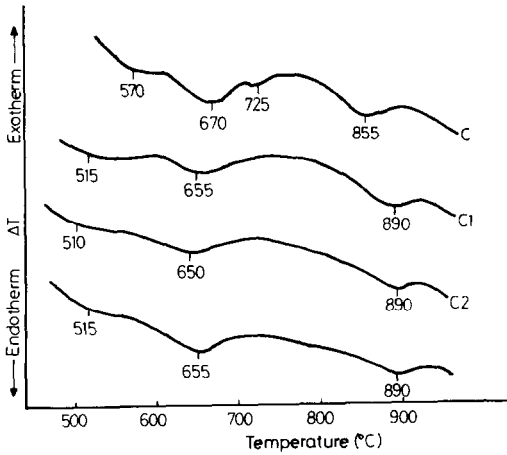

Fig. 4. Dehydroxylation peaks for acid-activated clays.

The size of the exothermic peak, which is due to the combustion of organic materials, decreases gradually with increasing amount of acid. When the sample was activated at the combustion temperature of organic residuals (300°C (C3)), the exothermic peak disappeared completely.

For C1 and C3, which were activated at the same acid/clay ratio, 0.2, in the dehydroxylation region the peak temperatures shifted from 570 to 515°C and from 670 to 655°C, respectively, the peak areas decreased and the peak at 725°C disappeared completely. Under the influence of the acid, the mineral has started to lose its individual properties (in other words the amount of montmorillonite decreases) and this causes the observed peak size reduction and lowering of peak temperature [19,20]. The percentages of metal oxides removed for samples C1 and C3 are approximately the same, at 27.11 and 29.90%, respectively (Table 1), but the weight loss of 1.692% for sample C3 corresponding to the dehydroxylation region is greater than the 1.577% recorded for C1. This shows that the proportion of montmorillonite mineral in C3 which remained unaffected by the acid is approximately 11.5% greater than that of C1. Sample C3 was activated at 300°C, by which stage the dehydration of interlayer water was complete; for this reason the acid was unable to penetrate the interlayer space and was effective only at the edges and in the units near to the surface of the mineral.

In sample C2, which was activated at a higher acid/clay ratio than C1, the dehydroxylation peak temperatures were shifted to 510 and 650°C: peak sizes decreased more than than those of C1. During activation, breaks in the layers can result from the effects of acid, heat and mixing. The hydroxyl groups near to the broken edges are more weakly bound than those within the lattice [21], so that after activation, dehydroxylation commences at a lower temperature than in the unactivated natural sample. The peak size reduction is the result of an increased proportion of metal ions leached from the octahedral layer.

In activated samples, the peak at 725°C was not observed: this indicates that one kind of hydroxyl group has disappeared during the activation process. It is assumed that this peak may be attributed to hydroxyl groups shared between Mg^{2+} and Fe^{3+} ions and between these ions and Al^{3+} [17]. The disappearence of this peak after acid activation indicates that acid treatment is accompanied by preferential breakdown of the Mg^{2+}- and/or Fe^{3+}-containing octahedra.

The third endothermic peak shifted from 855 to 890°C, but its size did not change. However, the weight loss rose from 0.115 to 0.385% in C1, to 0.808% in C2 and to 1.000% in C3: in other words, the increases in weight loss of samples C1, C2 and C3 were 3, 8 and 10 times greater than that of the natural mineral, respectively. It seems that the number of cavities in the lattice gradually increases, depending upon the amount of acid present and the temperature of activation. Therefore, during thermal analysis the heat easily penetrates into the inner parts of the lattice via these cavities and the

rate of dehydroxylation increases. The increase in peak temperature to 890°C may be due to the presence of illite-type layers, since it is known [22] that the third endothermic peak of pure illite mineral occurs at about 890°C. Acid dissolution of illite mineral is very difficult, when it is encountered as a mixed-layer mineral with montmorillonite, illite solubility increases slightly but not significantly [23]. During activation, montmorillonite-type layers of sample start to decompose; on the other hand, illite-type layers are relatively protected against acid attack. For this reason the third endothermic peak appears at 890°C.

The present results will in future work be combined with XRD data, IR spectra and surface acidity experiments to explore further the probable mechanism of activation of montmorillonite minerals [8].

REFERENCES

1   A. Grenall, Ind. Eng. Chem., 41(7) (1949) 1485.
2   T.K. Mag, J. Am. Oil Chem. Soc., 50(1) (1973) 251.
3   L.L. Richardson, J. Am. Oil Chem. Soc., 55(7) (1978) 777.
4   F.D. Ovcharenko, Yu.I. Tarasevich, F.A. Belik, I.I. Martsin and V.L. Vasilenko, Kolloidn. Zh., 35(3) (1973) 467.
5   G.A. Mills, J. Holmes and B. Cornelius, J. Phys. Colloid Chem., 54 (1950) 1170.
6   A.C. Mathews, S.B. Weed and N.T. Coleman, Clays Clay Miner., 395 (1955) 403.
7   R.D. Heyding, R. Ironside, A.R. Norris and R.Y. Prysiaznink, Can. J. Chem., 38 (1960) 1003.
8   N. Sarier, Ph.D. Thesis, Izmir, 1986.
9   J.C. Keattch and D. Dollimore, An Introduction to Thermogravimetry, Heyden, London, 1975, pp. 126–127.
10 R.W. Mooney, A.G. Keenan and L.A. Wood, J. Am. Chem. Soc., 74 (1952) 1367.
11 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, NY, 1960.
12 P. Murray and J. Whate, Trans. Brit. Ceram. Soc., 54 (1955) 137.
13 R.E. Grim, Clay Mineralogy, McGraw-Hill, New York, 1968.
14 P.F. Kerr, J.L. Klup and P.K. Hamilton, Am. Pet. Inst. Project 49, Columbia University, New York, 1949.
15 J.W. Earley, B.B. Osthaus and I.H. Milne, Am. Mineral., 38 (1953) 707.
16 W.F. Bradley and R.E. Grim, Am. Mineral., 36 (1951) 187.
17 R. Greene-Kelly, The Montmorillonite Minerals, in R.C. Mackenzie (Ed.), The Differential Thermal Investigation of Clays, Mineralogical Society, London, 1966, pp. 140–164.
18 M.K.H. Siddiqui, Therm. Anal., 3 (1971) 649.
19 F.H. Norton, J. Am. Ceram. Soc., 22 (1936) 54.
20 M. Kruger and W. Smykatz-Kloss, Thermochim. Acta, 83 (1985) 107.
21 P. Murray and J. White, Trans. Br. Ceram. Soc., 48 (1949) 187.
22 W.F. Cole and J.S. Hosking, in R.C. Mackenzie (Ed.), The Differential Thermal Investigation of Clays, Mineralogical Society, London, 1966, pp. 248–274.
23 J.A. Pask and B. Davies, U.S. Bur. Mines Tech. Pap., 664 (1945) 56.