

## **MODIFICATION OF THE ADSORPTIVE PROPERTIES OF A BETONITIC CLAY**

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### **ABSTRACT**

The technological characteristics of a bentonite supplied from Kütahya region were determined by chemical analysis, differential thermal analysis, particle size analysis and x-ray diffraction techniques. The bentonite containing calcium montmorillonite and illite as clay minerals and also  $\alpha$ -cristobalite, a non clay mineral was treated thermally between 100°C-1300°C. The changes in the adsorptive properties, such as the specific surface area and specific pore volume, under the effect of thermal treatment temperature, which are determined by the adsorption and desorption of nitrogen at 77K, were discussed. The bentonite was activated by the "wet process" with sulfuric acid at various acid ratios from 10% to 70% in acid and clay mixture. The dependency of adsorptive properties of the bentonite on the acid ratio by the activation procedure was discussed

### **INTRODUCTION**

Natural homogeneous mixtures that contain one or few of the clay minerals such as kaolinite, montmorillonite, illite, chlorite, sepiolite and attapulgite and that also contain one or a few of the non-clay minerals such as  $\alpha$ -cristobalite, amphibole, feldspar, calcite, magnesite, dolomite, gibbsite, alunite, and corundum are generally called as "clay" (Grim 1968 and 1988). Depending upon the mineral content and the chemical composition the color of the clay may be at various shades of white, pink, gray, green, yellow, blue and brown.

It has been understood from x-ray diffraction (Brindley and Brown 1980) that all clay minerals which are hydrated aluminium and magnesium silicates are formed by the packing of the silica tetrahedrons (T) and alumina (or magnesia) octahedrons (O) in the form of a chain.

Although the layers of the kaolinite which is the basic mineral of the kaolin clay is formed of TO layers, the layers of the bentonite clay is formed of TOT layers. Considering the chemical analysis and the mineralogical formation the chemical formula of the montmorillonite mineral has been determined as  $\text{Si}_8 (\text{Al}_{3,31} \text{Mg}_{0,66}) \text{O}_{20} (\text{OH})_4 \text{M}^+_{0,66} n\text{H}_2\text{O}$  (Clarke 1989). Although the  $\text{Si}^{4+}$  ions in the formula are at the centers of the tetrahedrons the  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions are at the centers of the octahedrons. Although 2/3 of the octahedron centers is full in the montmorillonite mineral that contains only  $\text{Al}^{3+}$ , all of the octahedron centers are full in the montmorillonite mineral which contains only  $\text{Mg}^{2+}$ . The excess of negative charge that occurs by the exchange of some of the aluminium ions by the magnesium ions is balanced by the  $\text{M}^+$  cations that are hydrated by water, and the electroneutrality is preserved in the mineral.

Instead of  $\text{Al}^{3+}$  other ions of lower oxidation states such as,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^+$  can enter into the centers of the octahedrons. Although  $\text{Si}^{4+}$  of a higher oxidation state can not enter into the place of  $\text{Al}^{3+}$  in the alumina layer, ions like  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}$  of a lower oxidation state can enter into the place of  $\text{Si}^{4+}$  in the silica layer, and cause an excess of negative charge. This excess is also balanced by cations such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  symbolized generally as  $\text{M}^{n+}$ .

The ions which provide electroneutrality by insertion between the layers are called "exchangeable cations" as they are capable of exchanging places by all organic and inorganic cations. The equivalent molar mass number of the exchangeable cations found in 1000 grams of montmorillonite and other clay minerals or clays that contain these minerals is defined as the "cation exchange capacity CEC" (Adams and Evans 1979).

Besides montmorillonite, clay minerals such as hektorite, bidellite, nontronite and saponite derived from montmorillonite by isomorphic ion exchange, are generally called "smectite". Depending upon the amount of water that enters in between, the layer thickness of smectites varies between  $d(100)=9.20 - 21.40 \text{ \AA}$ . While the  $\text{Na}^+$  ion that is found as an

exchangeable cation between the layers causes the swelling of the montmorillonite mineral to a great extent as it attracts a lot of water, the  $\text{Ca}^{2+}$  ions attracts water less and causes a little swelling of the mineral (Parker et al. 1980, Pennino et al. 1981). For this reason the sodium montmorillonites (Ca-M) that swell by water and give suspensions with infinite lifetime are called swelling montmorillonites, and the calcium montmorillonites (Ca-M) that swell a little and give suspensions with a short lifetime are called non-swelling montmorillonites.

These two montmorillonites can be converted reversibly to each other by ion exchange. While the original layer thickness for the Na-M is around  $d(001)=12 \text{ \AA}$  it is  $d(001)=15 \text{ \AA}$  for the Ca-M. Because of this difference it can be easily seen from xray diffraction patterns whether the mineral in the clay is Na-M or Ca-M.

Another element of the smectite group that is derived from montmorillonite by isomorphic ion exchange or whose basic mineral is montmorillonite is called "bentonite". Those that have the basic mineral Na-M are called sodium bentonite (Ca-B), and those that have the basic mineral Ca-M are called calcium bentonite (Ca-B). While the suspensions of Na-B that swell a lot with water have a long lifetime, the suspensions of Ca-B that swell a little with water have a short lifetime (Low and Margheim 1979). The second clay mineral that is found in Bentonite is generally illite.

Depending upon the properties of the smectite group mineral that the bentonite contains besides the swelling and non-swelling bentonites, bentonite varieties such as the intermediate bentonite (Ca-B + Ca-B), meta bentonite (smektite+illite) and washer soil (smectite + attapulgit) are encountered in the nature. Names such as volcanic clay, soap clay, mineral soap, bleaching clay, bleaching soil, adsorptive soil and adsorptive clay are also used instead of bentonite.

## MATERIAL AND PROCEDURE

The Kütahya Bentonite supplied by Eczacıbaşı Endüstriyel Hammaddeler Sanayi ve Ticaret A.Ş. (ESAN) has been chosen as the

material. This bentonite of which the chemical analysis, the particle magnitude distribution, the differential thermal analysis and the x-ray diffraction has been performed, has been used for thermal treatment and acid activation.

### **Thermal Process**

Powder samples of 200 g. taken from the original bentonite have been thermally treated by keeping the samples during 2 hours at 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200 and 1300°C respectively (Sarikaya et al. 1987). 13 different samples obtained as a result of thermal treatment in a temperature controlled oven, have been labeled as K100, K200, K1300 respectively.

### **Acid Activation**

In activations carried by the wet procedure 98 %  $H_2SO_4$  (MERCK) has been used. 400 cm<sup>3</sup> of sulfuric acid solution has been added on 200 g. samples such that the mass percentage of the acid in the mixture was 10, 20, 30, 40, 50, 60, and 70 respectively. The mixtures in the form of suspension have been activated by sulfuric acid and by keeping the mixture in a tumbling water bath at 97°C during 6 hours (Sarikaya et al 1982). Every activated sample has been filtered under vacuo and the filtrate has been washed with distilled water until it did not contain any  $SO_4^{2-}$  ion (Sarikaya et al. 1989). The samples dried during 24 hours at 105°C in an oven were labeled as K10, K20,..., K70 and the original bentonite submitted to the same procedure without acid addition was labeled as K00 so that a total of 8 different sample has been prepared.

### **The Adsorption and Desorption of Nitrogen**

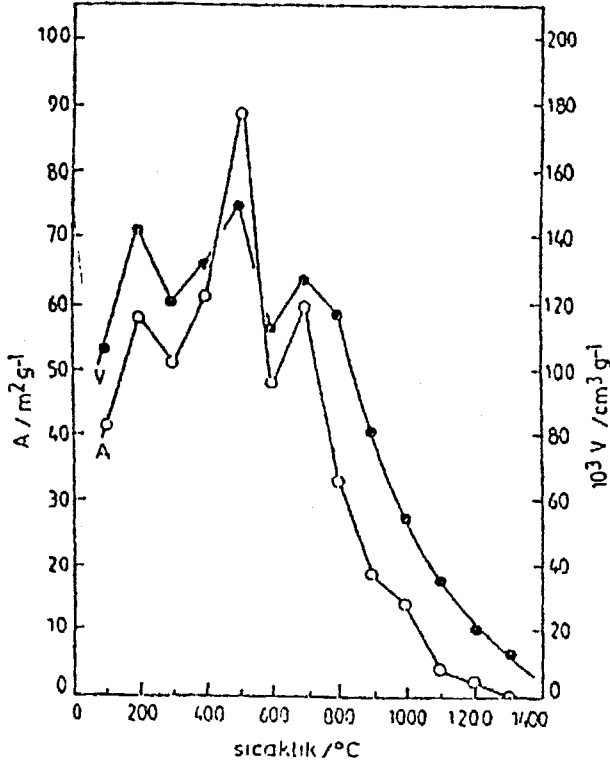
The adsorption and desorption of nitrogen at 77 K on a total of 20 samples, which were treated thermally and by acid activation, has been measured by a volumetric adsorption instrument (Sarikaya and Aybar 1978) that was built being connected to a high vacuum system. Before the adsorption experiment the water and the adsorbed  $N_2$  (g) on the samples that were heated under vacuum at 100°C during 4 hours have been eliminated.

## RESULTS AND DISCUSSION

### The Variation of the Specific Surface Area and the Specific Pore Volume by the Thermal Treatment Temperature

It has been observed that the forms of the adsorption and desorption isotherms of nitrogen at 77 K determined by samples submitted to thermal treatment at different temperatures resembled to a great extent to those given for the original bentonite. The adsorption and desorption isotherms that resemble in form to each other and which are observed to be of the 2nd sort depending upon the Brunauer classification show quantitative differences depending upon the treatment temperature.

The specific surface area has been calculated by the help of the BET line drawn from the adsorption isotherm for the original bentonite and other bentonites, the specific pore volume has been calculated from the desorption isotherm. The variation of the calculated specific surface area and the specific pore volume by the thermal treatment temperature is given in Figure 1. From this figure, it can be observed that the specific surface area and the specific pore volume show a zig-zag variation until the thermal treatment temperature reaches 700°C, at higher temperatures there is an abrupt fall. This parallel variation shows that the specific surface area stems from the walls of the micro and meso pores. As the temperature increases from 700°C to 1300°C the crystal structure of the clay minerals such as montmorillonite and illite in the bentonite, rapidly collapses. Parallel to this collapse as the empty spaces between the layers have been destroyed the specific pore volume and consequently the specific surface area drops rapidly. As the temperature increases upto 1300°C as all the micro and meso pores are destroyed by sinterization the specific pore volume and the specific surface area approach to zero. In the original bentonite the specific surface area which is  $43 \text{ m}^2\text{g}^{-1}$  increases more than 100% and reaches its maximum which is  $90 \text{ m}^2\text{g}^{-1}$  as a result of the thermal treatment applied during 2 hours at 500°C. The adsorptive properties that decrease as the TOT layers which do not have anything else than exchangeable cations at 600°C increase a little because of the elimination of hydroxyl groups bound to the crystal. For a



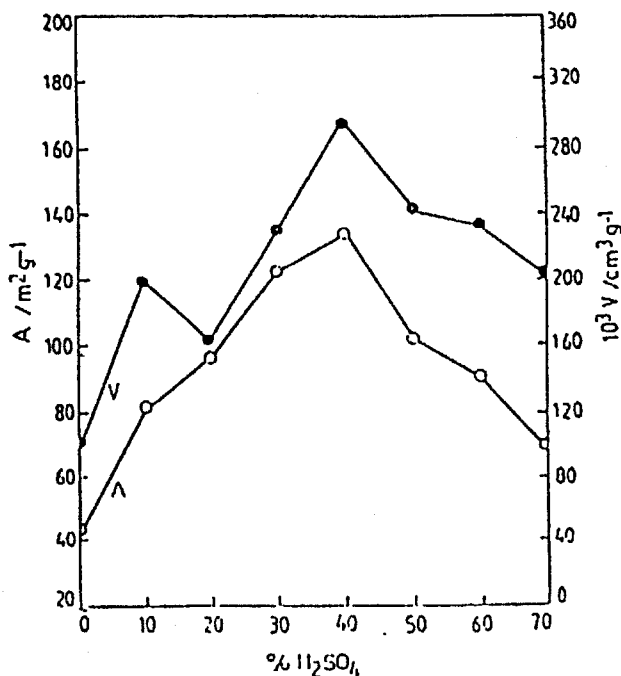
**Figure 1.** The variation of the specific surface area and the specific pore volume of the Kütahya Bentonite by the thermal treatment temperature.

complete explanation of this observed zig-zag variation detailed crystallographic studies are needed.

### The Variation of the Specific Surface Area and the Specific Pore Volume by Acid Activation

The adsorption and desorption isotherms of nitrogen at 77 K on the bentonite samples activated by sulfuric acid at different ratios resemble in form to those of the original bentonite and bentonite that was submitted to thermal treatment. It has been observed that these isotherms show that the adsorptive capacity varies to a great extent by the acid activation, and they belong to the 2nd type depending upon the Brunauer classification.

**Figure 2.** The variation of the specific surface area and the specific pore volume of the



Kütahya Bentonite by the percentage of the acid in the activation.

As has been explained above, the specific surface area, for each sample has been calculated by the help of the BET line drawn from the adsorption isotherm and the specific pore volume has been calculated from the desorption isotherm. The variation of the calculated specific surface area and specific pore volume by the sulfuric acid percentage in the activation is given in Figure 2. It can be observed from this figure that the specific surface area and the specific pore volume shows a parallel variation to the acid ratio in the activation. This situation verifies the thought that the surface area originates only from the walls of the micro and meso pores. The contribution of the walls of the macropores is so small that it lies within the limits of experimental error. As the acid percentage in the activation increases i.e. as the activation progresses, because of the micro and meso pores that appear at the empty spaces left by Al<sup>3+</sup>, Fe<sup>3+</sup> and Mg<sup>2+</sup> that are eliminated from the crystal structure of the clay minerals in the bentonite, the specific pore volume increases

rapidly and because of the walls of those pores the specific surface area increases rapidly. The specific surface area of the original bentonite which is  $43 \text{ m}^2\text{g}^{-1}$  increases more than 300 % and reaches  $134 \text{ m}^2\text{g}^{-1}$  during the activation, by taking the sulfuric acid ratio as 40 %. If the acid ratio in the activation increases more, because of the destruction of the walls between the micro and meso pores and because of the regional collapses in the crystal structure the specific pore volume and the specific surface area decrease. The bentonitic properties of samples obtained from activations in which the acid percentage is high, disappear to a great extent.

## CONCLUSION

It has been determined that the Kütahya Bentonite which has a white shade contains a great amount of calcium montmorillonite mineral which is well crystallised. It seems possible that an approximately pure calcium montmorillonite mineral can be separated from the Kütahya Bentonite by the precipitation of the cristobalite, which it contains as a (non-clay) mineral, from the suspension.

It has been concluded that the Kütahya Bentonite is a good quality raw material for ceramics, because the particle sizes of 80% of the particles of the Kaolinite mineral are smaller than  $2 \mu\text{m}$ , and as the thermal treatment temperature increase up to  $1300^\circ\text{C}$ , it has been observed that the pore volume and the surface area approaches to zero and this indicates that the sinterisation is good. The fact that no fracture has been observed during the maturation of a cylindrical sample at  $1250^\circ\text{C}$  verifies this conclusion. Because of its highly plastical properties observed during the experiments it has been understood that the Kütahya Bentonite can also be used as a bonding agent.

As the specific surface area of the Kütahya Bentonite increases by acid activation it seems possible that it can be used in the bleaching process during the oil raffination, but this point requires further investigation.



**REFERENCES**

- [ 1 ] ADAMS, J.M. and EVANS, S., Determination of cation exchange capacity (layer charge) of small quantities of clay minerals by nephelometry. *Clays and Clay Minerals*. 27: 137-139 (1979).
- [ 2 ] BRINDLEY, G.W. and BROWN, G., eds., *Crystal Structure of Clay Minerals and Their X-Ray Identification*. Mineralogical Soc., London (1980).
- [ 3 ] CLARKE, G., ed., *Industrial Clays: A Special Review*. Industrial Minerals, London (1989).
- [ 4 ] GRIM, R.E., *Clay Mineralogy*. 2 nd ed., McGraw-Hill, New York (1968).
- [ 5 ] GRIM, R.E., The history of the development of clay mineralogy. *Clays and Clay Minerals* 36: 97-101 (1988).
- [ 6 ] LAW, P.H. and MORGHEIM, J.F., The swelling of clay: I. Basic concepts and empirical equations. *Soil Sci. Soc. Am. J.* 43: 473-480 (1979).
- [ 7 ] PARKER, J.C., ZELAZNY, L.W., and AMOS, D.F., Swelling components of compacted Ca-montmorillonite. *Clays and Clay Minerals* 28:1 35-141 (1980).
- [ 8 ] PENNINO, U.D., NAZZEGA, E., VALERI, S., ALIETTI, A., BRIGATTI, M.F., and POPPI, L., Interlayer Water and swelling properties of monoionic montmorillonites. *J. Colloid Interface Sci.* 84: 301-309 (1981).
- [ 9 ] SARIKAYA, Y. and AYBAR, S., The adsorption of  $NH_3$ ,  $NO$  and  $CO_2$  gases on the 5A molecular sieve. *Communications, Fac. Sci. Uni. Ank.* 24B/5:33-39<sup>2</sup> (1978).
- [10] SARIKAYA, Y., CEYLAN, H., ÇORAPÇIOĞLU, Ö. ve BOZDOĞAN, İ., Kuru yöntem ile sülfürik asit aktivasyonunun bazı killerinin ağartma gücü üzerine etkisi, *Doğa Temel Bilim* 6: 123-124 (1982).
- [11] SARIKAYA, Y., ULUSOY, H. and BOZDOĞAN, İ., Magnezit ve dolamitli bir kilin adsorplama özellikleri üzerine ısı aktivasyonunun etkisi. III Ulusal Kil Sempozyumu, Bildiriler: 161-167 (eds. A.G. Türkmenoğlu ve O. Akıman) METU Geological Engineering Department, Ankara (1987).
- [12] Sarıkaya, Y., Ceylan, H. and BOZDOĞAN, İ., Asit aktivasyonunun bir bentonit kilinin adsorplama özelliklerine etkisi. *Doğa TU Kim. D.* 13: 94-109 (1989).