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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

Influence of Acid Activation on the Adsorptive Properties of Keskin Clay

by

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lit by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

Influence of Acid Activation on the Adsorptive Properties of Keskin Clay

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ABSTRACT

The activation of clay from Keskin/Ankara was carried out with sulphuric acid by the "dry process" at various acid dosages. The nitrogen surface areas were determined after outgassing the products in vacuum at 160°C for 2 hours. Therefore, the change of surface area with the acid dosage by the activation has been obtained. It was observed that the surface area increases with increasing acid percentage of acid and clay mixture up to 30% and then decreases rapidly to lower values. Maximum surface area was found to be 262 m^2/g upon activation with 30% sulphuric acid.

INTRODUCTION

Clay minerals are used extensively as bleaching agents for mineral and vegetable oils, as adsorbents, as catalyst supports and, as cracking catalysts in petroleum industry. Clay minerals are porous materials. Therefore, their physical properties, such as surface area, porosity and, pore-size distribution are very important as well as their chemical composition. Change in the pore structure of clays, i.e. changes in the surface, can be produced by external factors, such as heat and chemical agents or by the adsorption process itself[1,2].

The activation of clay minerals with hot acids leads to a sharp increase in their adsorptive, bleaching and catalytic powers[3,4,5]. Therefore, many studies on the acid activation of clays have been carried out and, various theories have been put forward regarding the mechanism of the acid-clay reactions. This problem has not yet been solved exactly and further studies are required.

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In this study, the effect of sulphuric acid activation on surface area and limited adsorption volume of Keskin Clay has been estimated. In a previous work, chemical analysis, DTA and the adsorptive properties of the unactivated Keskin Clay were obtained[6].

EXPERIMENTAL

The clay was dried at 105 °C and ground to pass a 200 mesh sieve. Samples were prepared as 10, 20, 30, 40 and 50 percent sulphuric acid in a mixture of the acid and the clay. The activation were carried out by the "dry process" at 105 °C for 12 hours. Then, the samples were washed at room temperature until the washing were free from sulfate ion. The activated clays were dried and ground to pass a 200 mesh sieve. The powder samples were outgassed at 160 °C and 10^{-4} torr. The physical adsorption of nitrogen on activated clay samples were measured by using a pyrex adsorption apparatus[7] at the liquid nitrogen temperature. The apparatus operates at a low pressure which can be varied from very close to zero up to about the liquefaction pressure (p_o) of nitrogen. After adsorption was completed, desorption was carried out. The obtained data for adsorption and desorption were gas volumes at various pressures (p) in the adsorption cell. The observed nitrogen volumes (v) adsorbed on per gram clay samples were corrected to cm^3 at 0 °C and 1 atm. (STP).

RESULTS

The adsorbed nitrogen volumes at STP for per gram clay samples were plotted versus relative equilibrium pressure (p/p_o) as shown in Fig.1. The specific surface area (A) of samples were determined by B.E.T. method[8]. The limited adsorption volumes (V_p) were taken as the liquid volume of nitrogen at the relative pressure $p/p_o = 1$ and —196 °C. Also, the mean pore radius ($\bar{r}$) have been calculated with the equation $\bar{r} = 2V_p/A$. These results are given in Table 1.

Table 1. Adsorptive properties of acid activated Keskin clay.

Acid %	V_p [cm^3/g]	A [m^2/g]	$\bar{r}$ [Å]
0	0.140	61	46
10	0.232	113	41
20	0.294	192	31
30	0.356	262	27
40	0.433	157	55
50	0.495	131	76

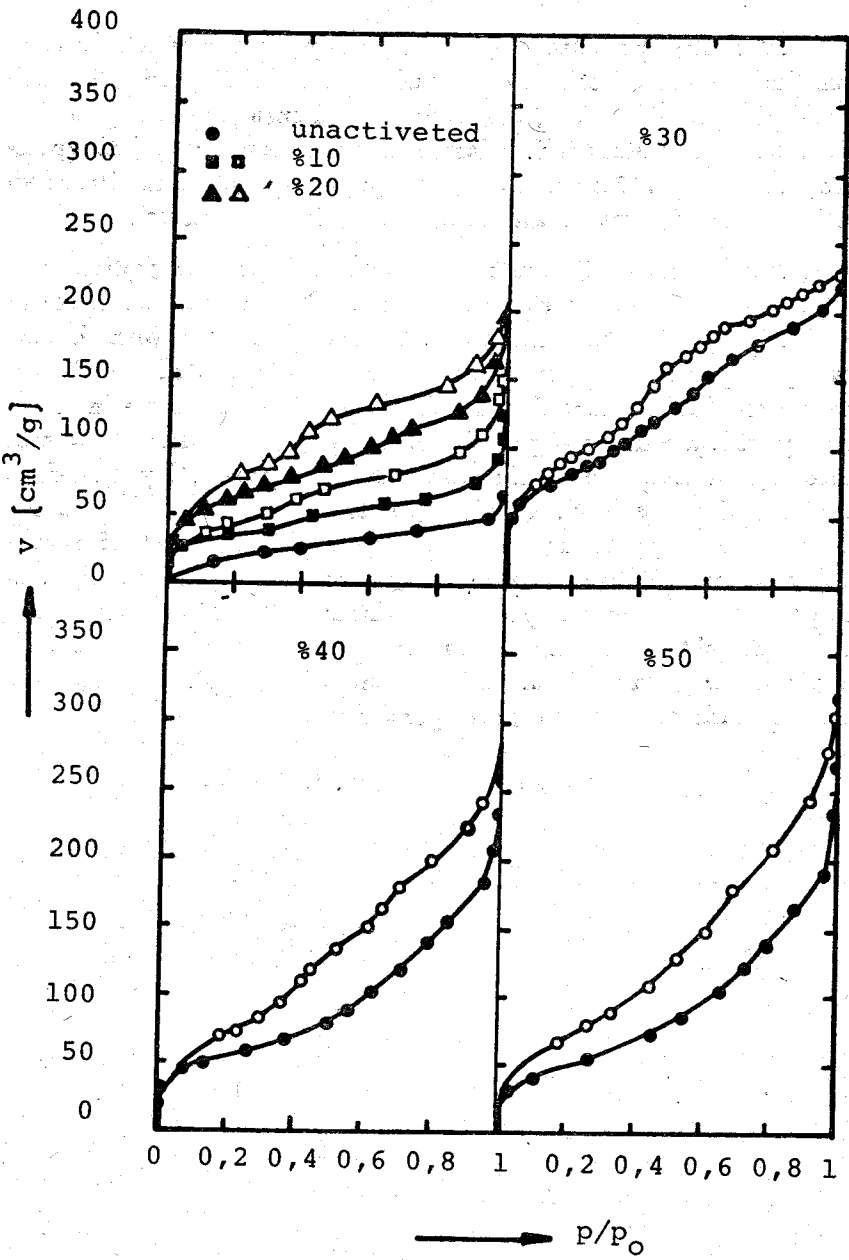

Fig.1. Adsorption and desorption isotherms of nitrogen at —196°C of acid activated Montmorillonite with the various percentages.
(● ■ ▲ adsorption, ○ □ Δ desorption)

The effective pore radius ($\bar{r}$) in clay samples have been calculated from the desorption isotherms using adjusted Kelvin equation[9] at various relative pressures. Also, the micropore volumes (V) of samples were taken as liquid volumes of the adsorbed nitrogen at various relative pressure and —196 °C. The calculated micropore volumes as function of effective pore radius are shown in Fig.2. at various acid percentages.

Change of the specific surface area and the limited adsorption volume of Keskin clay with the acid activation are given in Fig.3. As it can be seen from curves, the surface area of the clay increases with the increasing sulphuric acid percentage up to a maximum, then decreases sharply to a lower value; also, the limited adsorption volume increases linearly with the increasing sulphuric acid percentage. Increasing acid percentage in the acid-clay mixture creates small pore in clay; therefore, first the surface area of the clay increases to a maximum, then combination of these small pore to produce larger pore decreases the surface area of clay to smaller values. That means, activation by sulphuric acid changes pore volume as well as pore size distribution in the clay. As seen in Fig.4., the acid activation changes the mean micropore radius of clay; first it reaches to a minimum value around 30 % sulphuric acid, then increases with the increasing acid percentage.

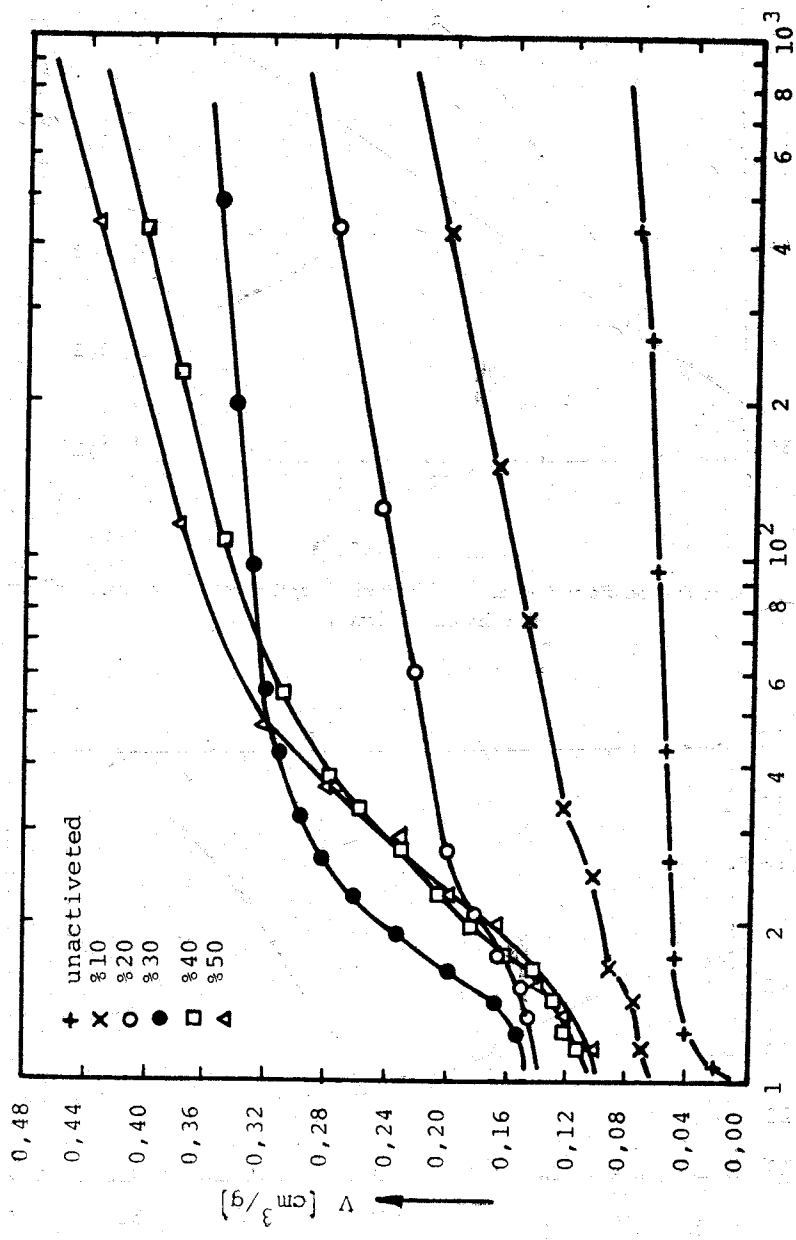

Fig.2. Calculated micropore volume as function of effective pore radius.

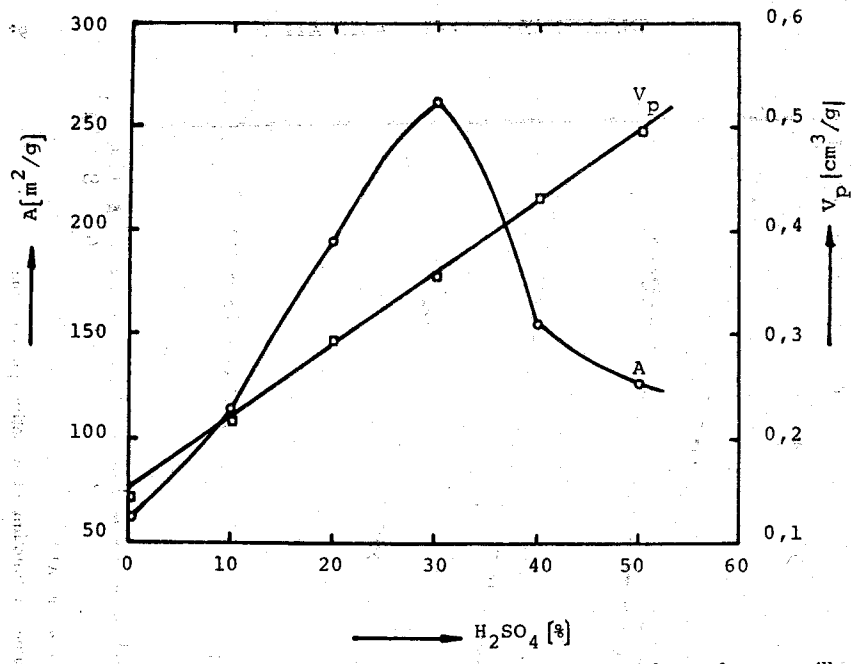

Fig.3. Changes of the specific surface area and limited adsorption volume of montmorillonite with the acid activation.

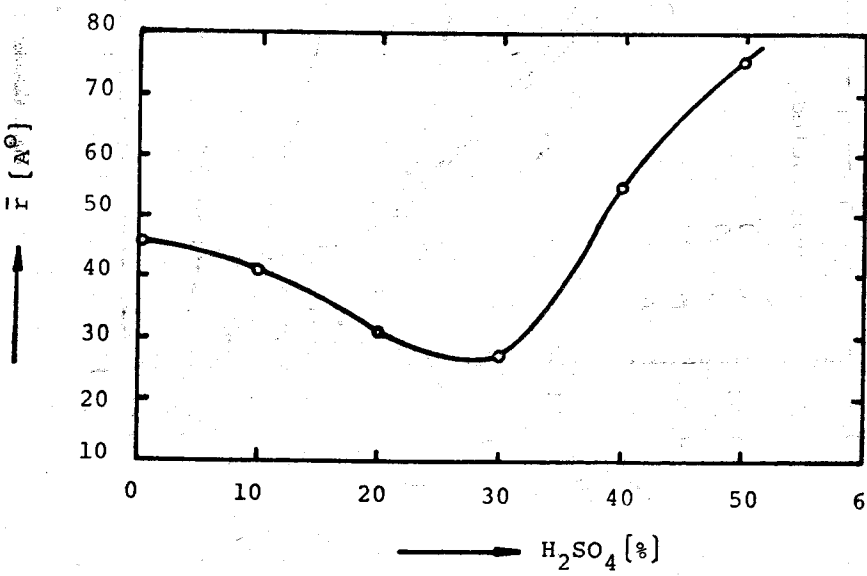

Fig.4. Changes of the mean micropore radius of montmorillonite with the acid activation.

ÖZET

Keskin/Ankara bölgesinden alınan kil, sülfürik asit ile farklı oranlarda karıştırılarak "kuru yöntem" ile aktiflenmiştir. Aktivasyondan sonra vakumda ve 160°C da 2 saat süre ile ısıtılan ürünlerin azot gazı adsorpsiyonu ile yüzey alanları tayin edilmiştir. Yüzey alanının % 30 asit oranına dek arttığı, sonra da küçük değerlere hızla düştüğü gözlenmiştir. Asit oranı % 30 iken yapılan aktivasyonda 262 m^2/g değerindeki en büyük yüzey alanı bulunmuştur.

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