Univ. Coll. Ann. Rev.
Vol 17 (1992).

EVALUATION OF LOCAL CLAY AS DEHYDRATION CATALYST

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Abstract

As long as Egypt is rich with natural clays, they can be used as cheap dehydration local catalyst instead of imported synthetic catalysts. Sample from Wadi El Hai Helwan was studied for this purpose in the raw and activated forms. Activation include either thermal activation by calcination of the clay in stream of dry air at different temperatures or chemical one by treatment with different concentration of sulphuric acid solution. Dehydration activity of the prepared clay catalyst was studied using absolute ethyl alcohol. The optimum condition of activation were found by treating Helwan raw clay with 20 % sulphuric acid solution at 104 °C and acid solution: clay ratio 1.5:1 by weight, then calcined at 500 °C. The activation energy of this reaction over Halwan clay was estimated and equal to 17.5 Kcal/mole.

1. Introduction:

In Egypt ethylene was imported for the production of PVC which is the basic material in petrochemical industry. This is accompanied by many difficulties such as hard currency needed, increasing prices every year, shipment and transport problems of ethylene from a_broad. This amount of needed ethylene can be produced in Egypt cheaply from the dehydration of annual surplus of ethyl alcohol produced from local cane sugar industry. In the same time Egypt is very rich with natural clays which are used as dehydration catalysts instead of imported alumina and alumino_silicate catalyst.

Many natural clays were studied as catalysts e.g., Fayoum clay gave maximum conversion of ethylene of ≃ 100 mol % after activated for 6 hour in 10 % H_2SO_4 at 104 °C and acid: clay ratio 1.5 : 1 and after washing and drying it calcined at 500 °C for hour hours. The reaction was made at 400 °C and space velocity 0.5[1]. Many other clays were studied as dehydration catalyst e.g. Sultanov Yu. M.[2] can co-workers and Khanlar bentonite (mainly montmorillonite with 8 % carbonate of particle size < 0.001 mm treated by 30 % by weight sulphuric acid. The obtained catalyst was used for isoamyl alcohol dehydration. The amylene yield was 86 % at 425 °C and 95 % at 450 °C for 20 minutes of contact.

Radev R.H.[3] and co-workers studied Dimitrovograd clay after activation by HCl and showed that this catalyst had good properties in the dehydration of ethyl alcohol and very pure ethylene was obtained at 400 °C and space velocity 1.0 hr^{-1}.

Akemova[4] studied 16 sample of volga area clays for dehydration of EtOH, PrOH and BuOH. Botirov S.A. *et al.*[5] studied the activity of natural and activated Guliab bentonite for dehydration of BuOH and Me_3COH and found that the activated bentonite gave 10 - 15 higher yield than the natural.

In this work we try to continue the study of local clays by new sample of clay from Helwan region to evaluate its activity towards dehydration of ethyl alcohol.

2. Experimental:

The clay sample from Wadi El Hai Helwan clays, was grounded and sieved to mesh size less than 100 mesh and then subjected to activation either physically, chemically, or physico-chemically.

Physical activation was carried out by subjecting the raw clay samples to calcination in the presence of dry air at temperatures 400, 450 and 500 °C for 4 hr. Chemical activation was carried out by refluxing the fine samples with different concentrations of sulphuric acid solutions (10, 20 and 30 % acid solutions) for 6 hr. at 104 °C, washing until free from sulphate ions dried and pelleted with the aid of 5 % by weight of starch.

Catalyst Activity Testing

The dehydration of ethyl alcohol was carried out at different temperatures in the range of 30 - 420 °C using flow system under atmospheric pressure. Gas products were analysed by gas chromatography using Perkin Elmer chromatograph model Sigma 3B and column packed with 15 % silicon oil on chromosorb W.

From the gas chromatographic analysis data, it was found that the gaseous product was mainly ethylene.

In order to get a general picture of the changes that occurred as a result of treatment, the treated materials have been studied by different techniques such as differential thermal analysis, thermal gravimetric analysis, x-rays and surface area measurements. Acidity was also studied.

Results and Discussion

Differential thermal analysis was carried out by using thermal analysis apparatus STA 40 g Netzesch firm for DTA and TGA.

Differential thermal behaviour are represented in fig. (1) which indicate that in all cases an endothermic peak at 120 - 130 which represent the escape of adsorbed water and accompanied with loss of weight which represent surface water adsorption capacity of the clay according to Zulfugarov *et al.*[5]. Another endothermic peak at 320 - 390 °C was also detected in all cases which indicate the existance of gibbsite (free alumina). The peaks obtained at 500 - 550 °C was accompanied by loss of weight (TGA line) represent lattice destruction and the escape of structural water. An exothermic peak at 884 °C was detected for 10 % acid treated clay, but the kaolinite exothermic peak is hardly detected for raw, 20 % and 30 % acid treated clay.

Table (1)

Sample Condition	*Entothermal Peak °C*	*Corresponding Weight Loss*
Helwan raw	148	47.9 %
	538	4.45%
10 % acid treated	130	25.2 %
Acid : clay ratio		
(1.5:1)	540	5.76%
20 % acid treated	122	31.25%
	530	3.94%
30 % acid treated	128	19.57%
	520	6.90%

sample were obtained using a Philips model PW 1050 x-ray diffractometer at λ = 1.54 A° - A Cu K_α target with a nickel filter was used.

From x-ray diffraction patterns, (Fig. 2), the characteristic spacing d(A°) and the relative intensities I/I_o for the examined samples indicated that the raw clay contain kaolinite which is in accordance with DTA analysis, and contain also montmorillonite.

Increasing the acid solution concentration the x-ray diffraction patterns show that the structure of the clay is not affected. However, the intensities of some lines decrease as a result of the lower cation density.

The surface area S_{BET} was calculated using the conventional Brunauer-Emmett-Teller (BET) equation[6]. This surface area value was compared with the area obtained by the V_l-t method[7].

Fig. (3,4) show the adsorption-desorption isotherms of the raw clay and the 20 % acid treated. Curve (a) represents the amount of nitrogen expressed in c.c./g of the adsorbent, versus the relative vapour pressure of adsorbate P/P^o. The curve appeared with hysteresis loop and with rounded knee which belongs to type IV isotherm of Brunauer's classification[8]. Figure (b) represents the linear plot for nitrogen adsorption according to BET equation. The specific surface area estimated by the BET plot was equal to 190 m^2/g and 229 m^2/g for the raw and 20 % acid treated clay respectively.

Acidity of catalyst is an important factor for acid catalyzed reactions such as cracking, isomerization and dehydration. The results in table (2) show that the raw clay posses the lowest acidity.

The acidity increase with increase of acid concentration.

Table (2) Acidity of Helwan clay samples meq/100 gm.

Activation Condition	*Acidity*
Raw	78.72
10 % acid	82.00
20 % acid	91.84
30 % acid	101.68

<u>Effect of Calcination Temperature</u>

The raw clay samples of Wadi El Hai Helwan were sieved to 100 mesh size then made in pelleted form, dried and calcined at three different temperature, 400, 450, 500 °C, each sample was tested for dehydration of ethanol at 300 °C.

Since ethylene production is the aim of this work thus the conversion of ethyl alcohol with respect to ethylene was calculated as follow:

$$\text{Ethanol conversion to ethylene} = \frac{\text{moles ethylene}}{\text{moles ethanol}} \times 100$$

Result are given in fig. (5) from which it is seen that acid activated sample activate at 500 °C is the most active one.

Effect of Acid Concentration on Activity

Samples from the raw sieved clay activated with acid solutions of different concentrations 10, 20, 30 % using acid: clay ratio 1.5:1. Fig. (6) shows that 20 % acid activated clay is most active towards dehydration of ethanol. The higher concentration of acid destroy the clay structure while 20 % acid is quite enough to extract undesirable amounts of iron and alkali metals and leach minimum amount of Al_2O_3. Such small leaching of Al_2O_3 leads to the unbalance of electrical charges in the clay lattice and formation of acid protons responsible for its high catalytic activity.

Kinetic Treatment of Experimental Data

The energy of activation of dehydration reaction over Helwan clay was graphically determined by using Arhenius equation:

$$K = Ae^{\frac{-E}{RT}}$$

Result are in fig. (7) from which the calculated activation energy equal 17.5 Kcal/mole over all the samples, which indicate that the reaction takes place on the same type of active centers regardless of their numbers.

Conclusion

It may be concluded that:

(1) Optimum calcination temperature is reached at 500 °C.

(2) The clay activated by 20 % acid concentration solution is the most active clay towards dehydration of ethanol.

(3) Energy of activation studied by Arhenius relation for dehydration reaction in presence of this clay equal to 17.9 Kcal/mole in all cases of activation.

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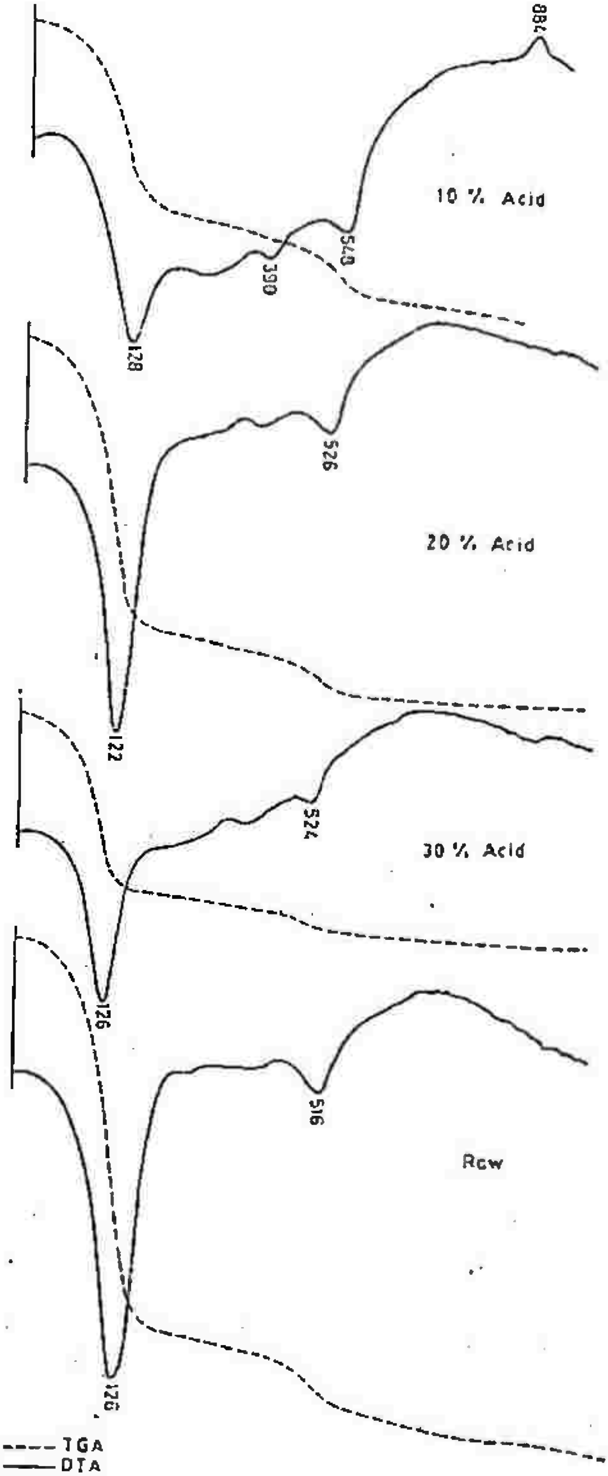

Fig. 1 : Differential thermal analysis profiles of 10% . 20% . 30% and raw Wadi El-Hai Helwan clay

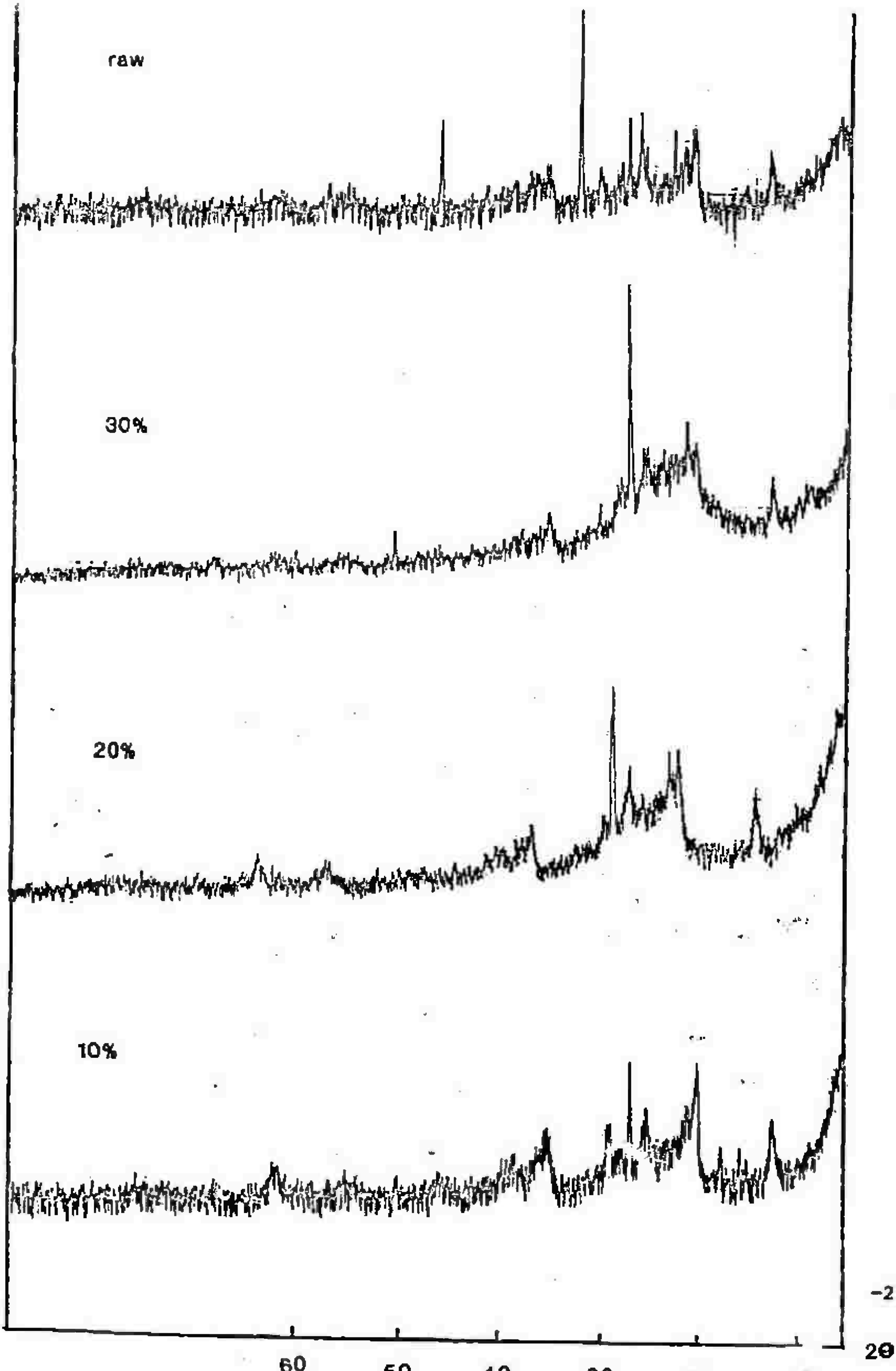

Fig. (2) X-ray diffraction patterns for catalyst samples

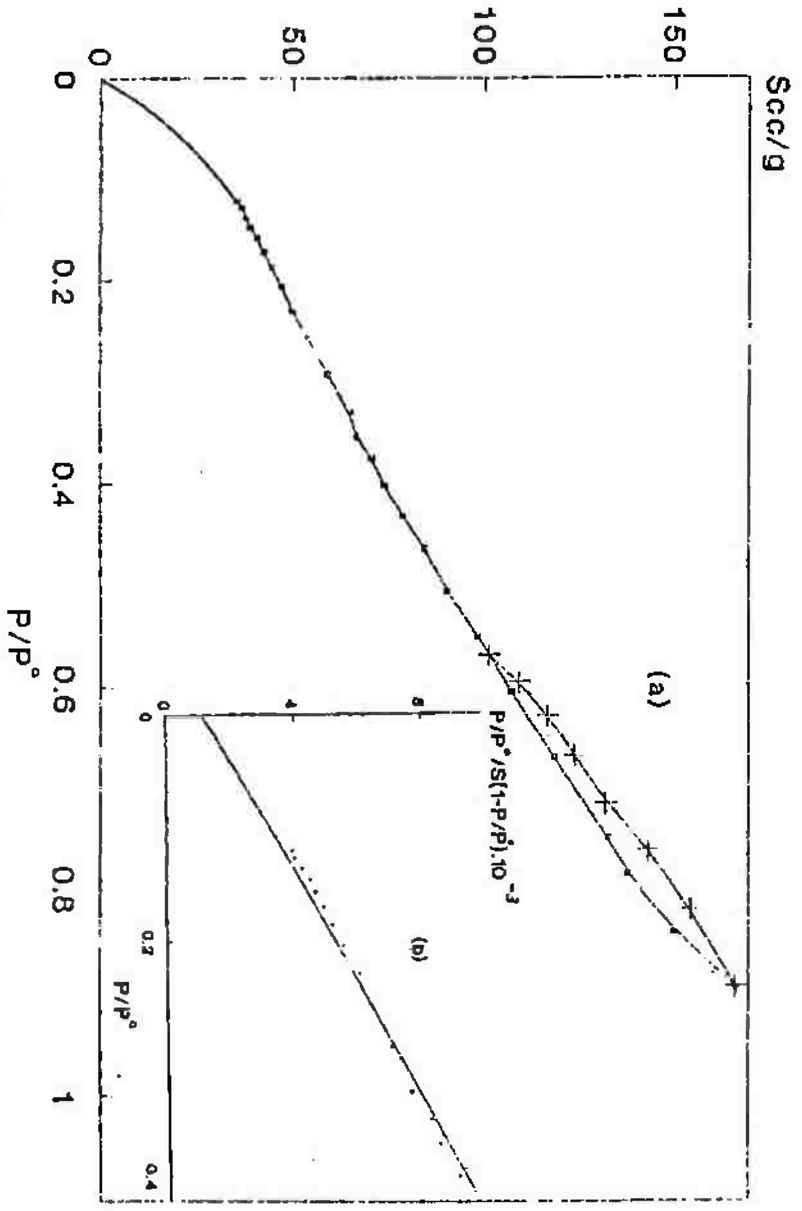

Fig. (3) Surface characteristics for raw clay
a) adsorption-desorption isotherm b) BET plot

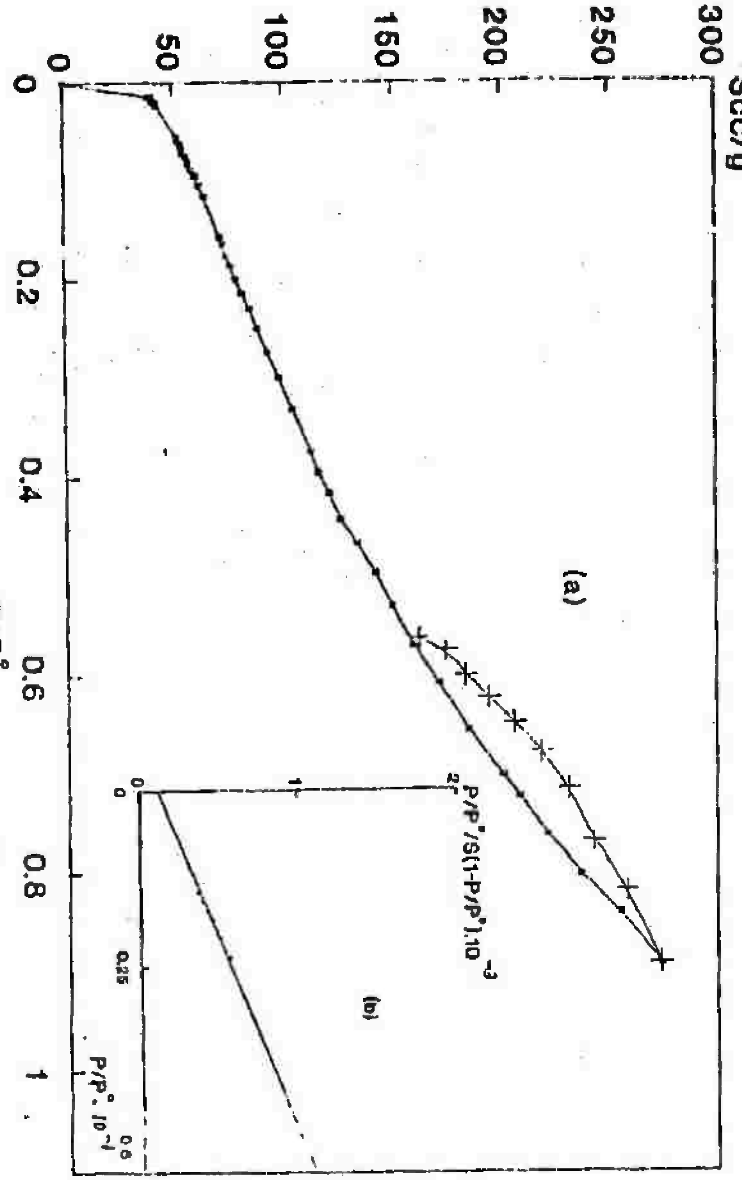

Fig. (4) Surface characteristics for 20% acid treated
a) adsorption-desorption isotherm b) BET plot

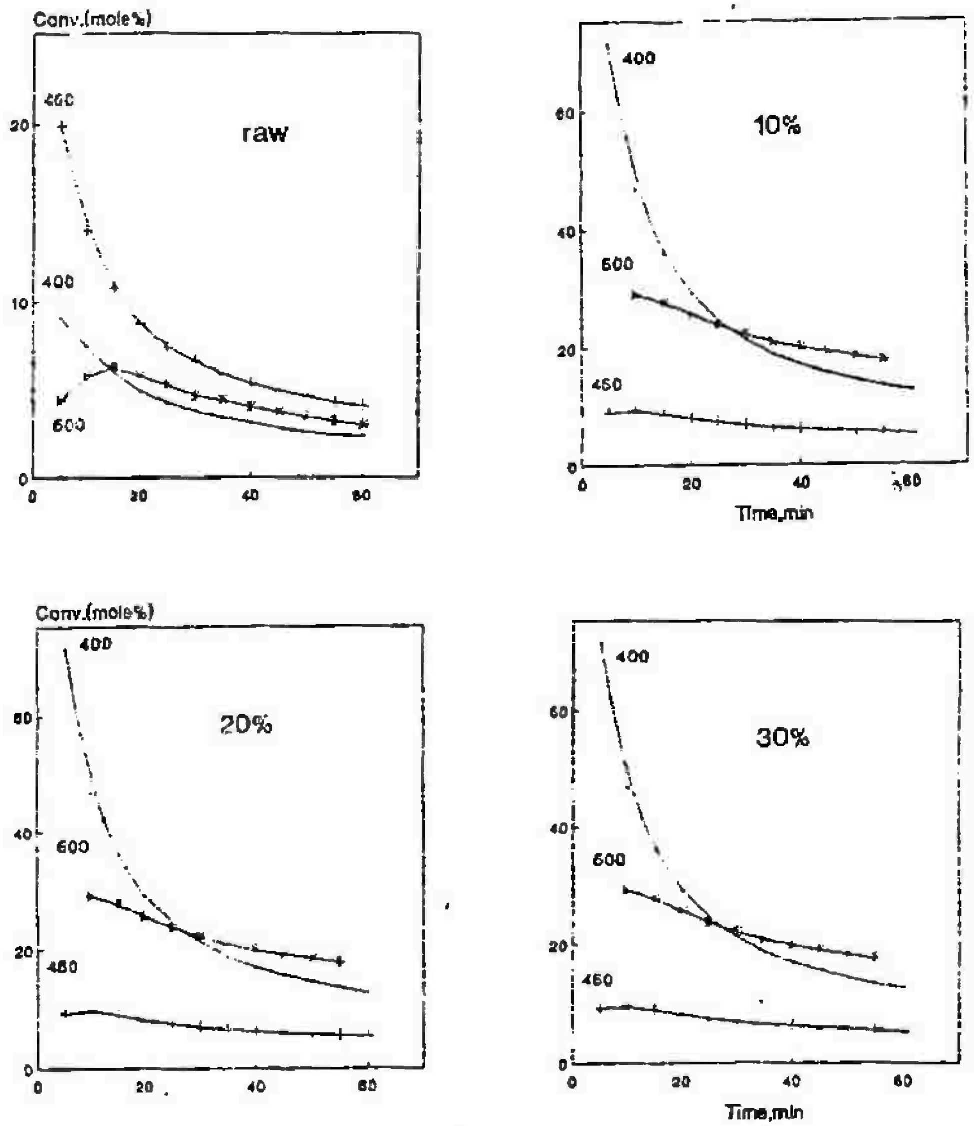

Fig. (5) Effect of calcination temperature

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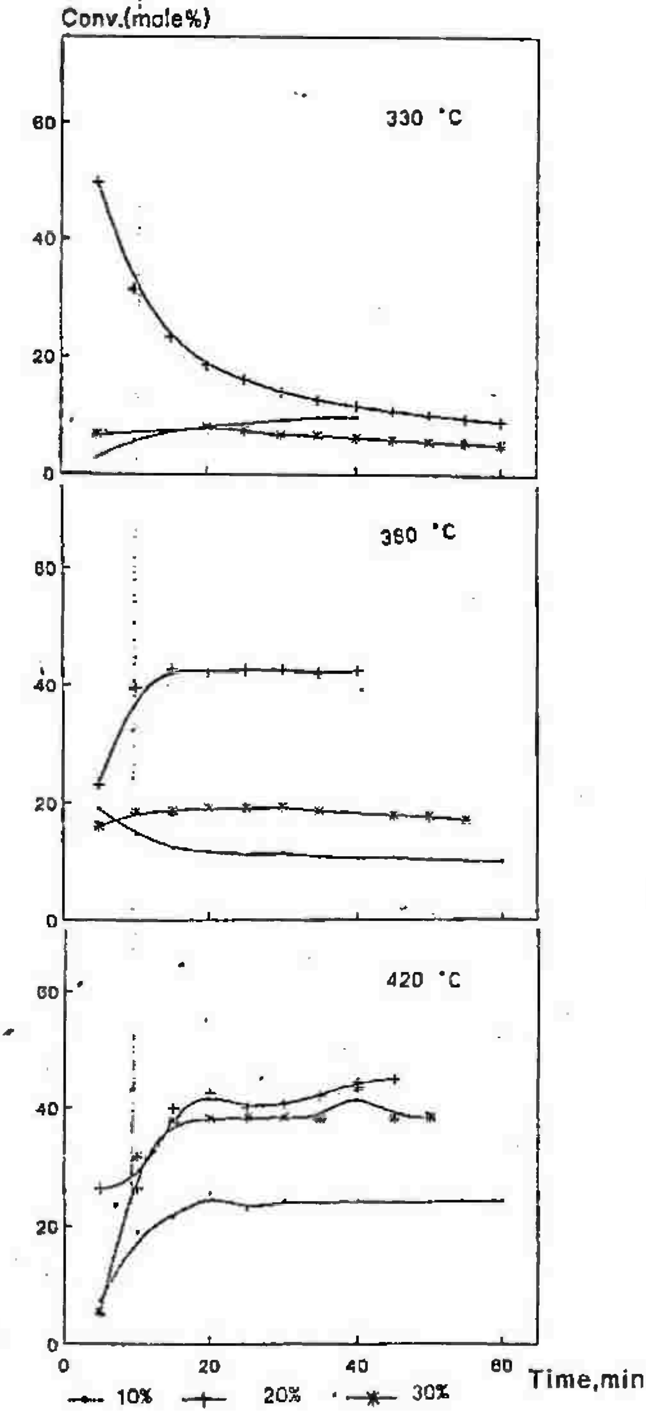

Fig. (6) Effect of acid concentration on activity at different reaction temperatures.

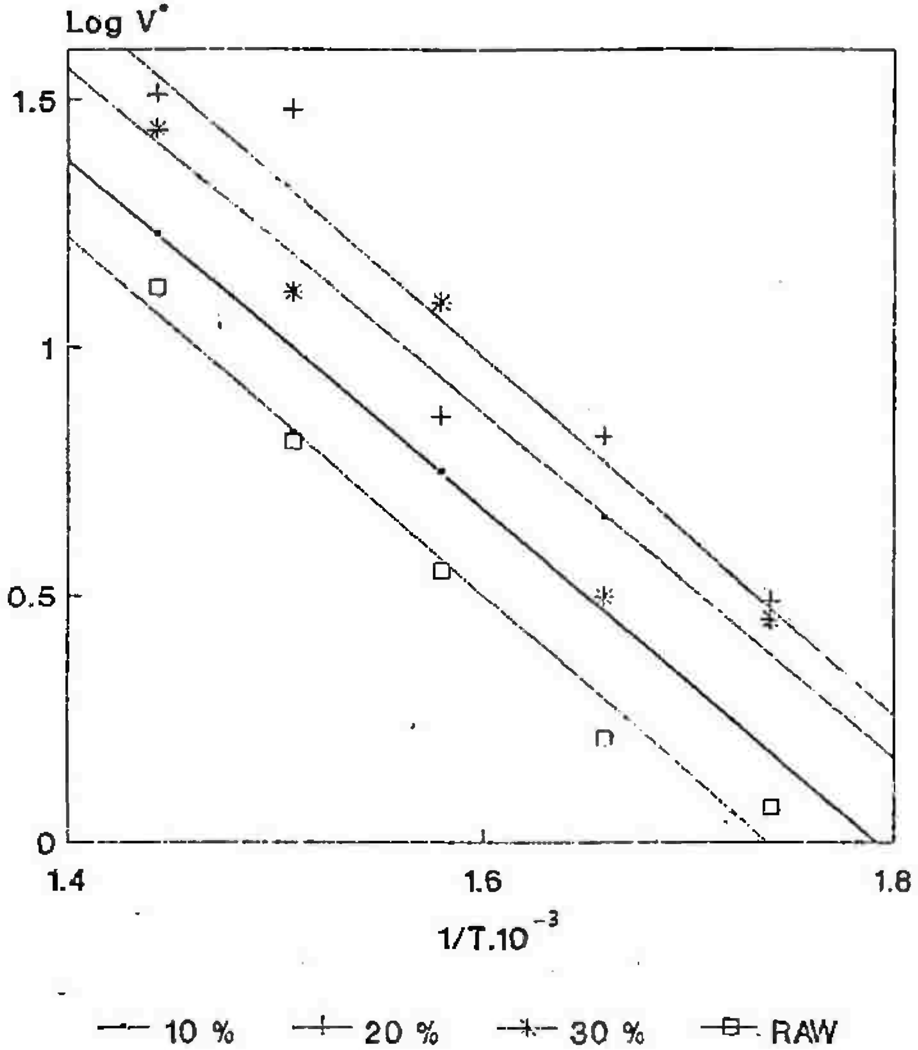

Fig.(7) Arrhenius plot

Univ. Coll. Ann. Rev.
Vol 17 (1992).

بسم الله الرحمن الرحيم

الملخص العربى
تقييم الطمى المحلى كعامل حفاز فى عمليات
انتزاع المـــاء

تعتبر مصر من الدول الغنية بالطمى الطبيعى الذى يمكن استعماله كعامل حفاز محلى فى عمليات انتزاع الماء بدلا من العوامل الحفازة المصنعة و المستوردة .

و لقد تم لهذا الغرض دراسة عينات من وادى هاى بحلوان فى صورتيها الخام و المنشطة .
ولقد تم التنشيط اما بطريقة حرارية عن طريق المعالجة الحرارية للطمى فى وجود تيار من الهـــواء الجاف عند درجات حراره مختلفة أو بطريقة كيمياشية عن طريق المعالجة بمحاليل مختلفة التراكيـز من حمض الكبريتيك .

و لقد تم قياس النشاط الحفزى للطمى بواسطة تفاعل تحول الايثانول .

و لقد تم التوصل الى نتائج اهمها أن :

1 - الطمى المنشط بواسطة ٢٠٪ من محلول حامض الكبريتيك يعتبر هو من انشط انواع الطمى تجاه تفاعل انتزاع الماء من الكحـول .

٢ - تم حساب قيمة طاقة النشاطية من معادلة ارهينوس و وجداتها تساوى ٩ر١٧ كيلو كالورى .