

## THE SOLUBILITY OF MILAS BAUXITE ORE IN SULPHURIC ACID

Mustafa GULFEN, Ali Osman AYDIN

**Abstract** - The effects of calcination conditions, sulphuric acid concentrations and dissolving temperature and period as parameters to the solubility of the bauxite ore from Gobekdagı reserves in Mugla-Milas region were investigated. The bauxite samples were calcined in different periods at different temperatures. Then the solubility of the calcined bauxite samples in sulphuric acid solution was examined. Dissolving activation energy ( $E_a$ ) was calculated using the optimum kinetics equation and the results obtained from the solubility studies examined dissolving temperatures and periods

**Key words** - Bauxite, calcination, solubility, sulphuric acid, kinetics

### I. INTRODUCTION

It is known that aluminium occurrence is 8% in nature. In other words, it has the most occurrence as metal. Therefore there are a lot of aluminium minerals and mines. Metallic aluminium is produced from pure  $Al_2O_3$  electrochemically[1,2]. Bauxite ore, an aluminium ore, is used to produce pure  $Al_2O_3$  industrially by Bayer Method. In general bauxite ore has higher aluminium content than the other ones. Bauxite ore is preferred in producing pure  $Al_2O_3$  by Bayer Method since the basic process depends on high aluminium and low silica contents in aluminium ores. As aluminium metal and aluminium compounds are used widely, aluminium demand is increasing[3]. On the other hand  $Al_2O_3$  production by acidic methods is also being investigated to use bauxite ore with low aluminium and high silica contents, and the other aluminium ores[4]. In this work, the solubility of Milas bauxite ore in sulphuric acid solution was investigated.

Bauxite ores may include aluminium minerals such as  $Al_2O_3 \cdot 3H_2O$  (gibbsite),  $Al_2O_3 \cdot H_2O$  (boehmite) and  $Al_2O_3 \cdot H_2O$  (diaspore). These minerals depend on bauxite ore's origin. Boehmite and diaspore are similar as chemical compounds but different in crystalline forms as  $\delta-Al_2O_3 \cdot H_2O$  (orthorhombic) and  $\alpha-Al_2O_3 \cdot H_2O$  (hexagonal), respectively. While two mole  $H_2O$  in gibbsite are dehydrated when it is calcined at 603-623 K but third mole  $H_2O$  in gibbsite and one mole  $H_2O$  in boehmite and diaspore are dehydrated when they are calcined at 803 K and over temperatures[5,6]. Therefore the effect of calcination conditions to the solubility of the bauxite ore was investigated in calcined bauxite in different period at different temperatures.

It is known that dissolving any ore in a solution or liquid solvent is heterogeneous reaction. These type reactions occur different steps that is limit film diffusion, interface chemical reaction and product phase diffusion. The one of the steps may limit the dissolving process. So this step represents the rate of the process and kinetics calculations can be done using the related equation. Example equations for the steps are shown following where  $\alpha$  is dissolving ratio;  $k$  is rate constant ;  $t$  is dissolving period[8].

$$\begin{aligned}y_1 &= 1-(1-\alpha)^{1/3} = kt \quad (\text{limit film diffusion}) \\y_2 &= 1-(1-\alpha)^{1/3} = kt \quad (\text{interface chemical reaction}) \\y_3 &= [1-(1-\alpha)^{1/3}]^2 = kt \quad (\text{product phase diffusion})\end{aligned}$$

The solubility values depending on temperatures and period are evaluated in calculating rate constant ( $k$ ) using a kinetics equation and activation energy using Arrhenius Equation ( $k=Ze^{-E_a/RT}$ ) so that the results can be compared with any other dissolving process or whether the process is productive. The kinetics equations of limit film diffusion and interface chemical reaction steps are similar. However they are different in activation energy values. If  $E_a$  value is lower than 20-23 kJ/mole, the rate depends on limit film diffusion. Otherwise the rate depends on interface chemical reaction[8].

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## II. MATERIAL AND METHODS

Firstly the bauxite ore from Gobekdagi bauxite reserves in Mugla-Milas region was ground and analysed chemically. Secondly this powder bauxite sample was calcined for 1, 2, 3 and 4-hour periods at 473, 573, 673, 773, 873, 973, 1073 and 1273 K temperatures so that the effect of calcination conditions to the solubility can be investigated. Next the calcined bauxite samples were dissolved in 2 M H<sub>2</sub>SO<sub>4</sub> solutions for one-hour period at room temperature. After the effect of calcination conditions was determined, the acid concentration was investigated for 2, 4, 6, 8 and 10 M. In the investigation experiments of dissolving temperature and period, the solubility studies were done for 1, 2, 3 and 4-hour periods at 323, 353, 373, 393 and 403 K temperatures. Finally the rate constant for different temperatures and the activation energy were calculated from the obtained results.

## III. RESULTS AND DISCUSSION

The chemical analysis of the original bauxite from Mugla-Milas is given in Table-1. The ore includes 53.87% Al<sub>2</sub>O<sub>3</sub> and 24.73% Fe<sub>2</sub>O<sub>3</sub> components and it has 10.89% calcination loss at 1273 K.

Table-1. The chemical analysis of the original bauxite

Components	%
SiO <sub>2</sub>	5.19
Fe <sub>2</sub> O <sub>3</sub>	24.73
Al <sub>2</sub> O <sub>3</sub>	53.87
TiO <sub>2</sub>	2.98
CaO	1.43
Calcination loss	10.89
Others	0.91

The effect of calcination temperature and period to the solubility of the bauxite was investigated using 100 mL 2 M H<sub>2</sub>SO<sub>4</sub> solution and 1 g calcined bauxite at room temperature and the results are shown in Figure-1.

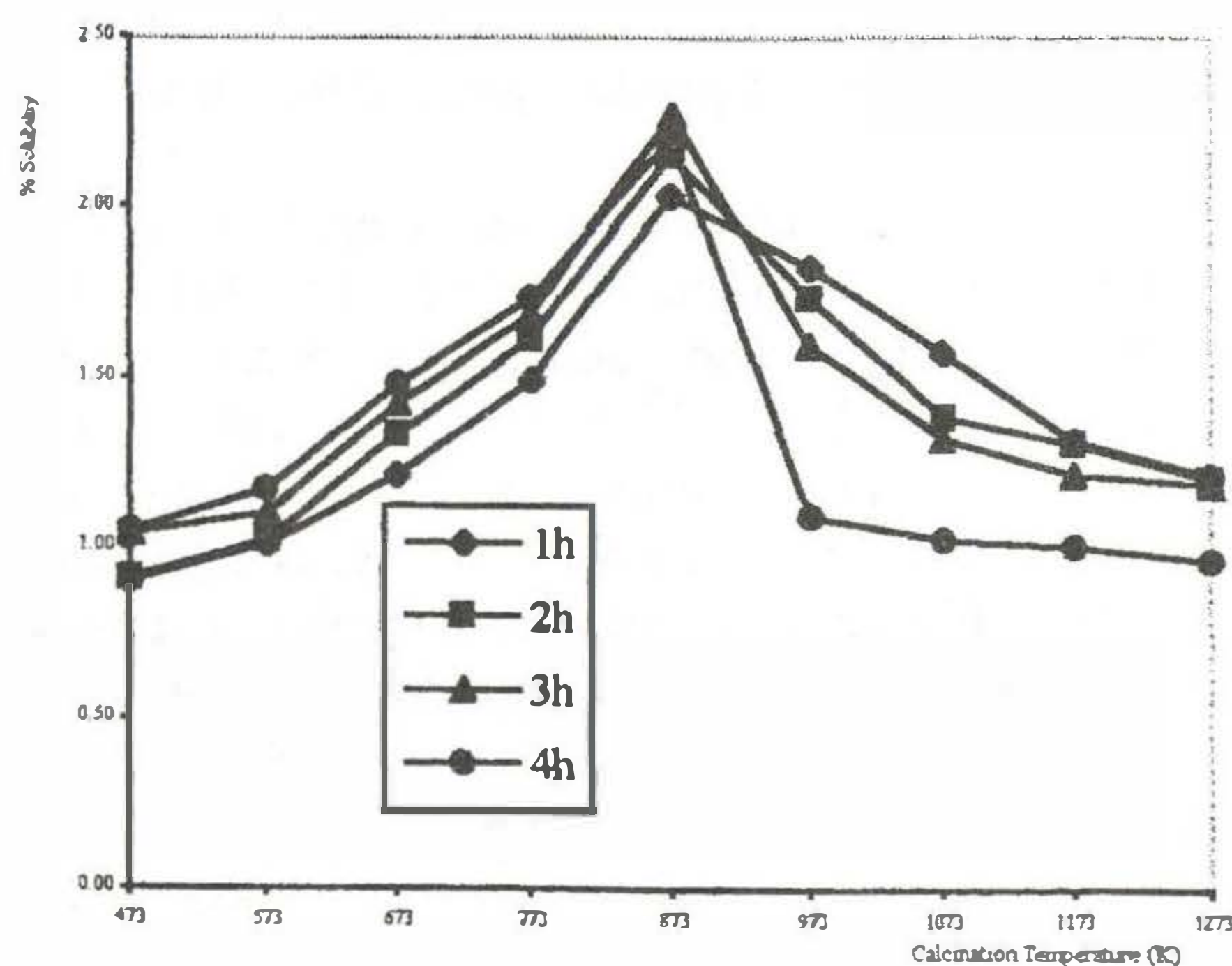


Figure-1. The effect of solubility related to calcination temperature

As it can be seen in Figure-1, the bauxite sample for three-hour period at 873 K temperature has the maximum solubility in 2 M H<sub>2</sub>SO<sub>4</sub> solution. In addition while the solubility is increasing up to 873 K but it is decreasing above 823 K. This increase is due to releasing H<sub>2</sub>O from the ore during the calcination.

However the decrease can be explained that releasing H<sub>2</sub>O decreases and the change of crystalline structure occurs in the ore from  $\delta$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. When the bauxite including Al<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O mineral is calcined at 803-823 K temperatures, 90% of the crystallized water can be removed approximately. That is bigger surface area and more decomposed minerals. Moreover hard dissolving ferrous compounds form at 1173 K and over temperatures. Therefore the bauxite sample calcined at 873 K was more dissolved than the other ones[9,10].

After determining calcination conditions the acid concentration effect was investigated using different H<sub>2</sub>SO<sub>4</sub> concentrations (2, 4, 6, 8 and 10 M) for 1, 2, 3 and 4-hour periods. The results are given in Figure-2.

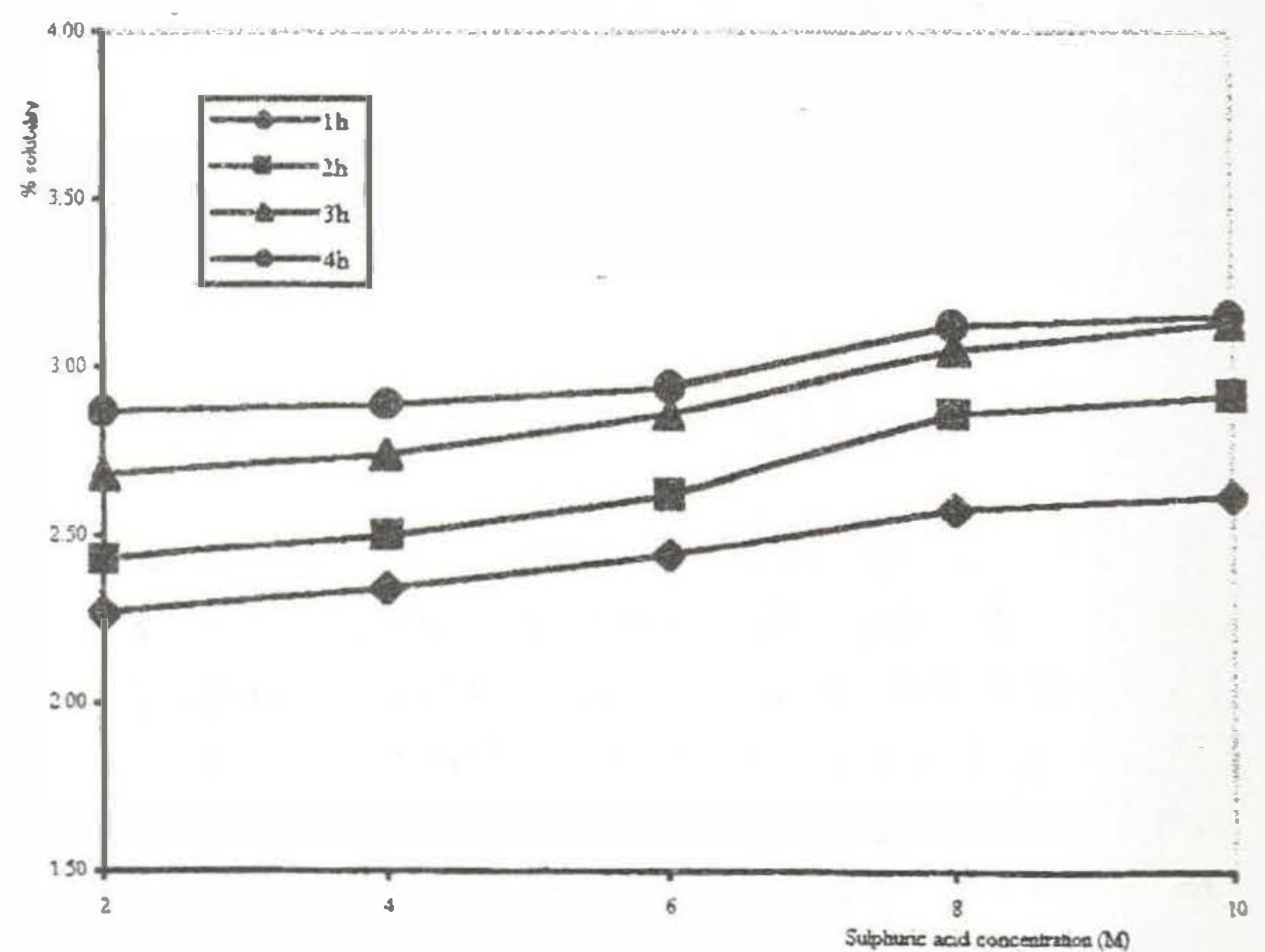


Figure-2. Solubility-acid concentration change

As a result of acid concentration determining studies, the optimum concentration was chosen as 8 M. Although it was seen steadily increase from 2 to 10 M there was a little sharp increase from 6 to 8 M. In addition it was seen that the solubility increased for long periods. According to this results, 8 M acid concentration was determined for the later studies. In the studies investigated the effect of dissolving temperature and period to the solubility of the bauxite, the ore calcined for 3 hours at 823 K and 8 M H<sub>2</sub>SO<sub>4</sub> solution which had been determined were used. The solubility is given in Figure-3.

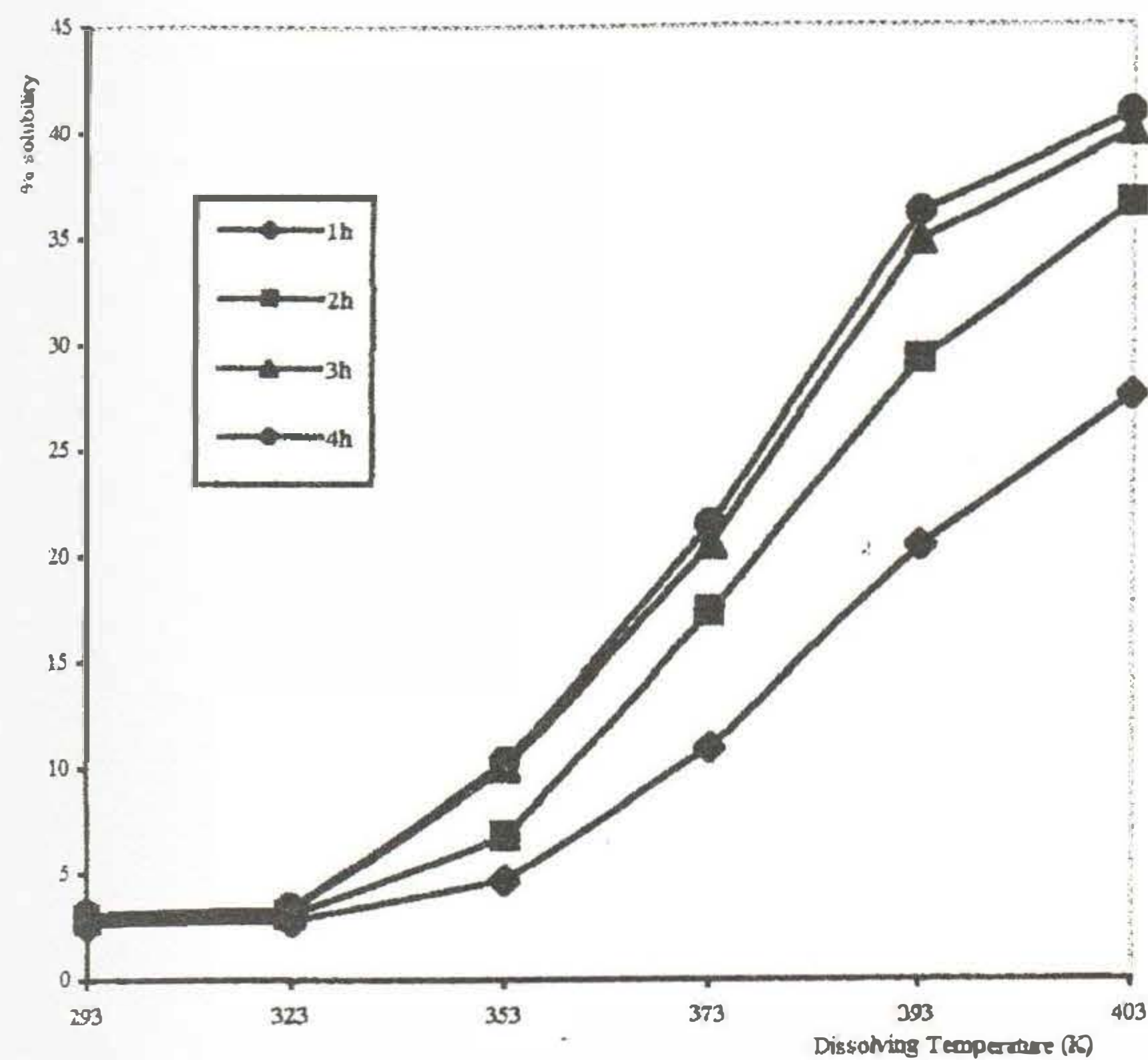


Figure-3. Effect of dissolving temperature and period to the solubility

It was found that the solubility increased in high temperatures and long periods. Because of under atmospheric pressure the studies could be done up to 403 K in which the boiling point. Temperature was so effective that the solubility at 403 K was much higher than that at 293-323 K temperatures. On the other hand considering dissolving period, the solubility for 3 and 4-hour periods were approximately same, but not same for 1, 2 and 3-hour periods. So the conditions for the optimum solubility can be given as 3-hour period at 403 K temperature, the boiling point of the mixture. Moreover if Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> components are wanted to examine in dissolving, their solubilities for 3 hours at different temperatures are shown in Table-2. When Fe<sub>2</sub>O<sub>3</sub> was dissolved as 87.90% for 3-hour period at 403 K, Al<sub>2</sub>O<sub>3</sub> was 21.27% at the same time. So because the dissolving process for Al<sub>2</sub>O<sub>3</sub> was uncompleted under atmospheric pressure the process should be applicable under pressure that is high temperature.

Table-2. The solubility of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>

Components	Solubility values (%) depending on temperature					
	293 K	323 K	353 K	373 K	393 K	403 K
Fe <sub>2</sub> O <sub>3</sub>	2.57	6.54	18.59	46.88	81.40	87.90
Al <sub>2</sub> O <sub>3</sub>	1.83	2.00	5.53	7.86	15.52	21.27

For kinetics evaluation, the solubility values as percent were converted to α values which are relative solubility, and they are shown in Table-3.

Table-3. The relative solubility values of the calcined bauxite

Period	Relative solubility values (α) depending on temperature					
	293 K	323 K	353 K	373 K	393 K	403 K
1 h	0.0258	0.0282	0.0470	0.1094	0.2050	0.2758
2 h	0.0286	0.0304	0.0678	0.1736	0.2930	0.3661
3 h	0.0305	0.0328	0.1007	0.2056	0.3486	0.3999
4 h	0.0312	0.0335	0.1028	0.2153	0.3620	0.4081

$y_3 = [1-(1-\alpha)^{1/3}]^2 = kt$  equation, called Jander Equation and represented product phase diffusion was determined comparing with regression coefficients ( $r^2$ ) of different kinetics equations. The equation represented product phase diffusion had the highest  $r^2$  values for y-t graphs among different equations ( $r^2 = 0.9460$  for 353 K; 0.9684 for 373 K; 0.9713 for 393 K; 0.9158 for 403 K). The rate constants (k) were calculated from  $[1-(1-\alpha)^{1/3}]^2 - t$  graphs (Figure-4). They were found as  $3.55 \cdot 10^{-4}$ ;  $1.61 \cdot 10^{-3}$ ;  $5.11 \cdot 10^{-3}$  and  $6.54 \cdot 10^{-3}$  1/hour for 353, 373, 393 and 403 K, respectively.

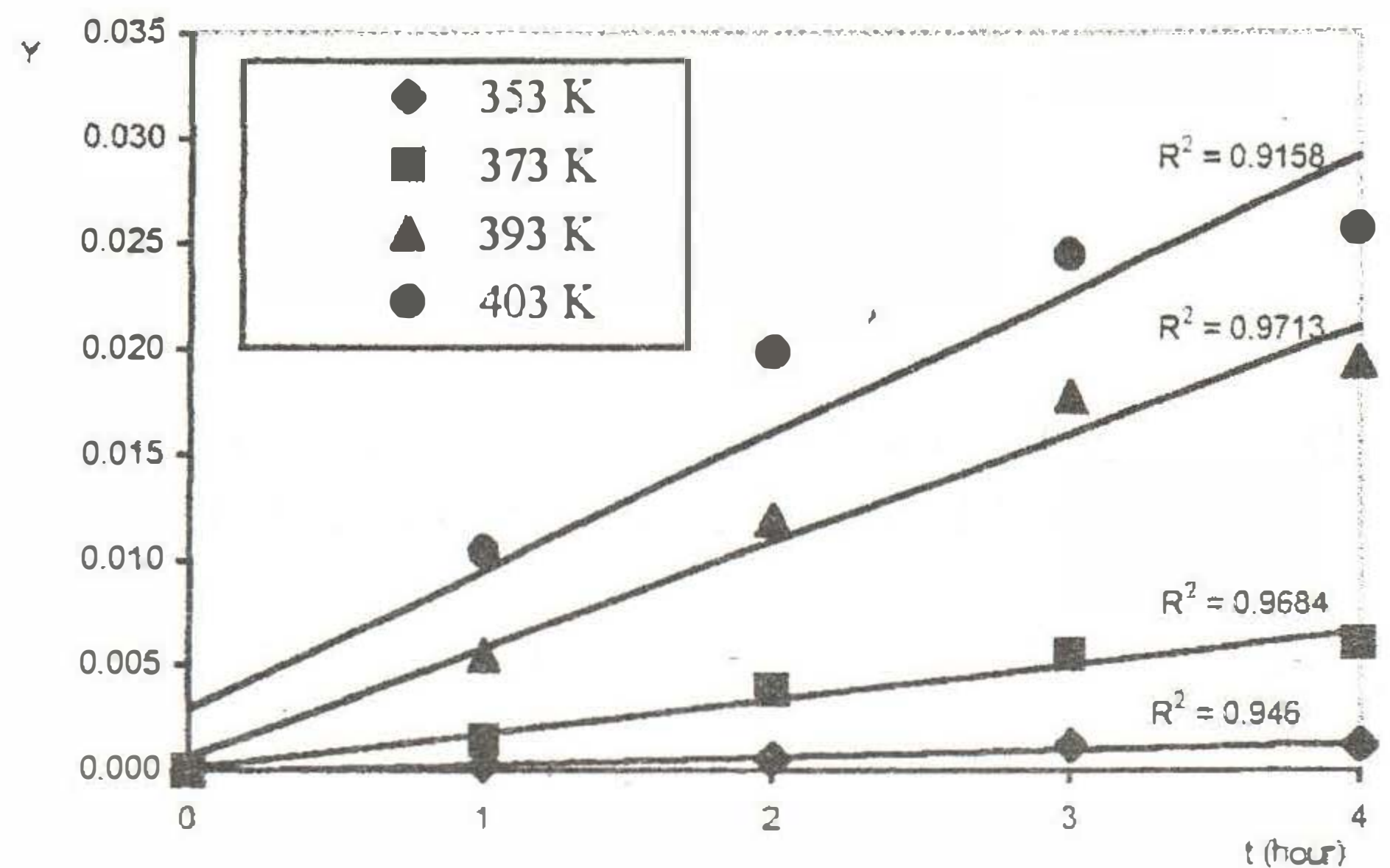


Figure-4.  $Y = [1-(1-\alpha)^{1/3}]^2 - t$  graphs for the different temperatures

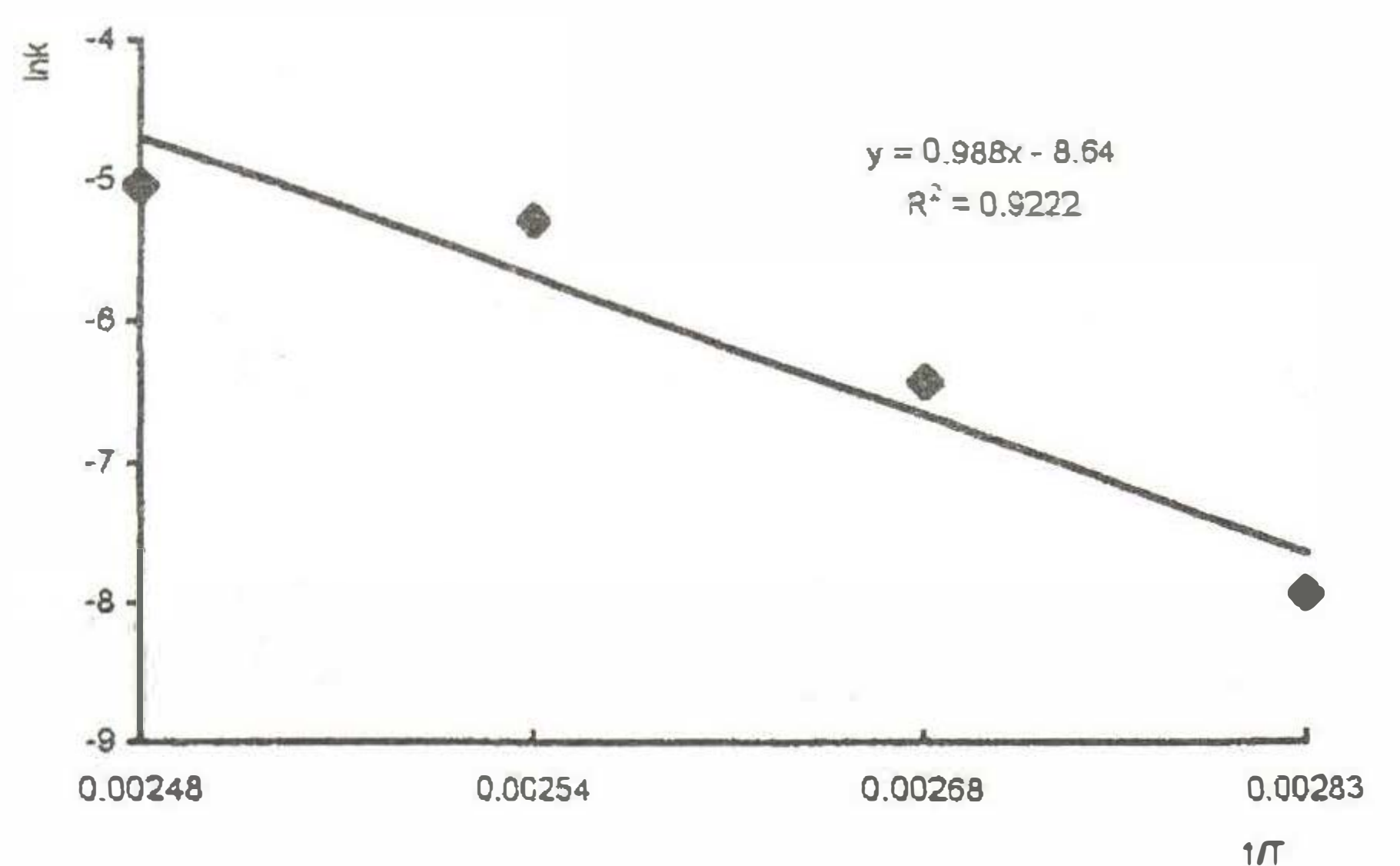


Figure-5.  $\ln k - 1/T$  graph

Finally the activation energy (E<sub>a</sub>) was calculated from  $\ln k - 1/T$  graph derived from Arrhenius Equation (Figure-5). It was found that the activation energy was 71.46 kJ/mole. It was concluded that this value was high. Therefore a catalyst must be used to low activation energy in the process. In addition the process may be applicable for ferrous bauxite and considered as pre-study for later studies.

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