

Full Length Research Paper

Analysis of leaching kinetics of tincal in phosphoric acid solutions in high temperatures

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The aim of the study is to propose an alternative process to boric acid generation by researching the dissolution kinetic of tincal in phosphoric acid solutions in high temperature, and to root the procuring of Na_2HPO_4 that is used commonly as byproduct in industry during the process. Reaction temperature, particle size, stirring speed, acid concentration and solid/liquid ratio were selected as parameters of dissolution rate of tincal. The tincal solubility has been found to increase by the temperature, stirring speed and decrease by the particle size and solid/liquid ratio. In the case of acid concentration, the solubility has been found to increase up to 2 M but decrease beyond this concentration. The solubility has been assigned to first order pseudo model. The activation energy has been found to be 46.21 KJ/mol. The solubility of tincal in phosphoric acid solution at high temperature has been defined by the following expression depending on reaction temperature, acid concentration solid/liquid ratio, stirring speed and particle size: $-\ln(1-X) = 1988.D^{-0.78}.C^{0.22}.S/L^{-0.39}.W^{0.99}.e^{5558.4/T}.t$.

Key words: Tincal, phosphoric acid, leaching kinetics, high temperature.

INTRODUCTION

Boron is an element commonly existing in soil, rock and water on earth. Boron exists in high concentrations in the vicinity reposing from Mediterranean and the west regions of the USA to Kazakhstan as well as the boron content of soil which is generally 10 to 20 ppm on average. It is between the range of 0.5 to 9.6 ppm in sea water and 0.01 to 1.5 ppm fresh water. Boron seams in high concentrations and economical dimensions mostly exist in the arid, volcanic regions and the regions whose hydrothermal activity is high of Turkey and the USA as enchaind compounds of boron with oxygen (Woods, 1994).

Boron minerals and boron products have become like a significant substance used in many fields from agriculture to energy, from defence industry to space industry. The specific boron compounds synthesized by using the minerals place a premium on in terms of both economically and usage area rather than the direct consumption of boron minerals.

Those having commercial value within 230 range

natural boron minerals in the nature are especially tincal, kernite, colemanite, inyoite, pandermite, ulexite and probertite (Kirk, 1992)

It can exist in pink, yellow and grey colors on account of some substances in tincal largely existing colorless and transparent in nature. The hardness is 2 to 2.5, the specific gravity is 1.7 and the content of g/cm^3 B_2O_3 is 36.6%. Tincal can easily convert into tincalconite by losing its tincal water.

The solution kinetic of boron minerals in many solvents has been analyzed by using different parameters. Some of the studies conducted about the dissolution kinetic of boron minerals are showed in Table 1. When the usage areas and manufacturing technologies are taken into consideration, boron compounds can be studied under two headings. One of them is boron minerals and commercial borates that are produced in large quantities and have common usage areas, and the other is specific boron products that have special consumption areas and are produced limitedly. One of the significant boron compounds having common usage area is boric acid. Boric acid is a phanocrySTALLINE, scentless and white substance. Its molecular weight is 61.83 g/mol, the content of B_2O_3 is 56.3%, the density is 1.5172 g/cm^3 , the

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Table 1. Summary of dissolution kinetics and activation energy of boron minerals acid or gaseous solutions.

Boron minerals	Leach solutions	Reaction model	Activation energy (kJ/mol)	References
Tincal	Phosphoric acid	First order pseudo homogenous	42.28	(Abali et al., 2007)
Tincal	Oxalic acid	Product layer (ash)diffusion control	35.14	(Abali et al., 2006)
Colemanite	Water saturated with CO ₂	Chemically reaction	57.7	(Gülensoy and Kocakerim 1978)
Colemanite	Potassium hydrogen sulphate solutions	Product plate(cinder) diffusion control	26.34	(Guliyev et al., 2012)
Colemanite	Ammonium sulphate	Chemically reaction	40.46	(Tunç et al., 2006)
Colemanite	Phosphoric acid	Chemically reaction	53.91	(Temur et al., 2000)
Ulexite	Perchloric acid	Avrami	19.12	(Demirkıran and Künkül, 2007)
Ulexite	Borax pentahydrate solutions saturated with CO ₂	Chemically reaction	42.53	(Kuşlu et al., 2010)
Ulexite	Phosphoric acid	Product plate(cinder) diffusion	26.17	(Doğan and Yartaşı, 2009)
Ulexite	Acetic acid	Chemically reaction	55.8	(Ekmekyapar et al., 2008)

heat of formation is 1094.3 KJ/mol and the heat of solution is +22.2 kJ/mol (Smith and McBroom, 1992).

In the process of boric acid generation, notably tincal (borax) and colemanite, some boron minerals are used like kernite, ulexite, probertite, hydroboracite, inderite, datolite and asharite. Two main raw materials are used in the process of boric acid generation in all over the world. In Europe and Turkey, colemanite is used for boric acid generation while in the USA, tincal is used.

Tincal is a readily soluble salt. Its dissolubility increases further in high temperature. The aim of the study is to propose an alternative process to boric acid generation by analysing the dissolution kinetic of tincal in phosphoric acid solutions in high temperature, and to root the procuring of Na₂HPO₄ that is used commonly as byproduct in industry during the process.

MATERIALS AND METHODS

Leaching experiments have been conducted under atmospheric pressure conditions. All reagents used in the

experiments were prepared from analytical grade chemicals (Merck) and distilled water. Tincal ore used in experimental studies has been obtained from Eti General Directorate of Mining Kirka-Boron Operation Directorate. The ore has been water washed and dried several times after being cleaned from apparent impurities. In pursuit of the operation, the ore has been broken with crackers in the laboratory environment then it has been separated into 5 + 8, -8 + 18, -18 + 30, -30 + 40 and -40 + 50 of mesh of sieve fractions by the sieves in standards of American Society for Testing and Materials (ASTM). The result of the chemical analysis of tincal mineral used in the studies is showed in Table 2. Besides X-ray diffraction (XRD) graphic and scanning electron microscope (SEM) picture of tincal sample used in the study are also showed in the Figures 1 and 2.

Experimental procedure

Solution treatments were done in a 250 mL-spherical glass reactor in atmospheric pressure. For mixing process mechanics mixer and in order to keep temperature constant a constant heat water circulator was used. As the studies were held in high heat, the experiments were done by using condensers to restrain substance loss.

Tincal mineral used in the study is a readily soluble salt. Since the experiments were held in high heat, tincal WSE

dissolved more easily. Therefore, in solution process, time was handled in terms of second and the experiment was conducted between the range of 10 and 60 s. The parameters used in solution process are shown in Table 3. Each experiment was repeated twice, and the arithmetic average of the results of the two experiments was used in the kinetic analysis.

In solution processes, 100 ml phosphoric acid solution was put in reactor for each experiment and then the mixing process was started by closing the reactor cap. After the temperature of solution in reactor was reached to the desired value, reaction was launched by putting a certain amount of ore.

At the end of the determined duration, the mixing was finished and then some substances were filtered in G-4 glass crucible by means of squinch in a short time by receiving the substance that is enough to be analyse from reactor.

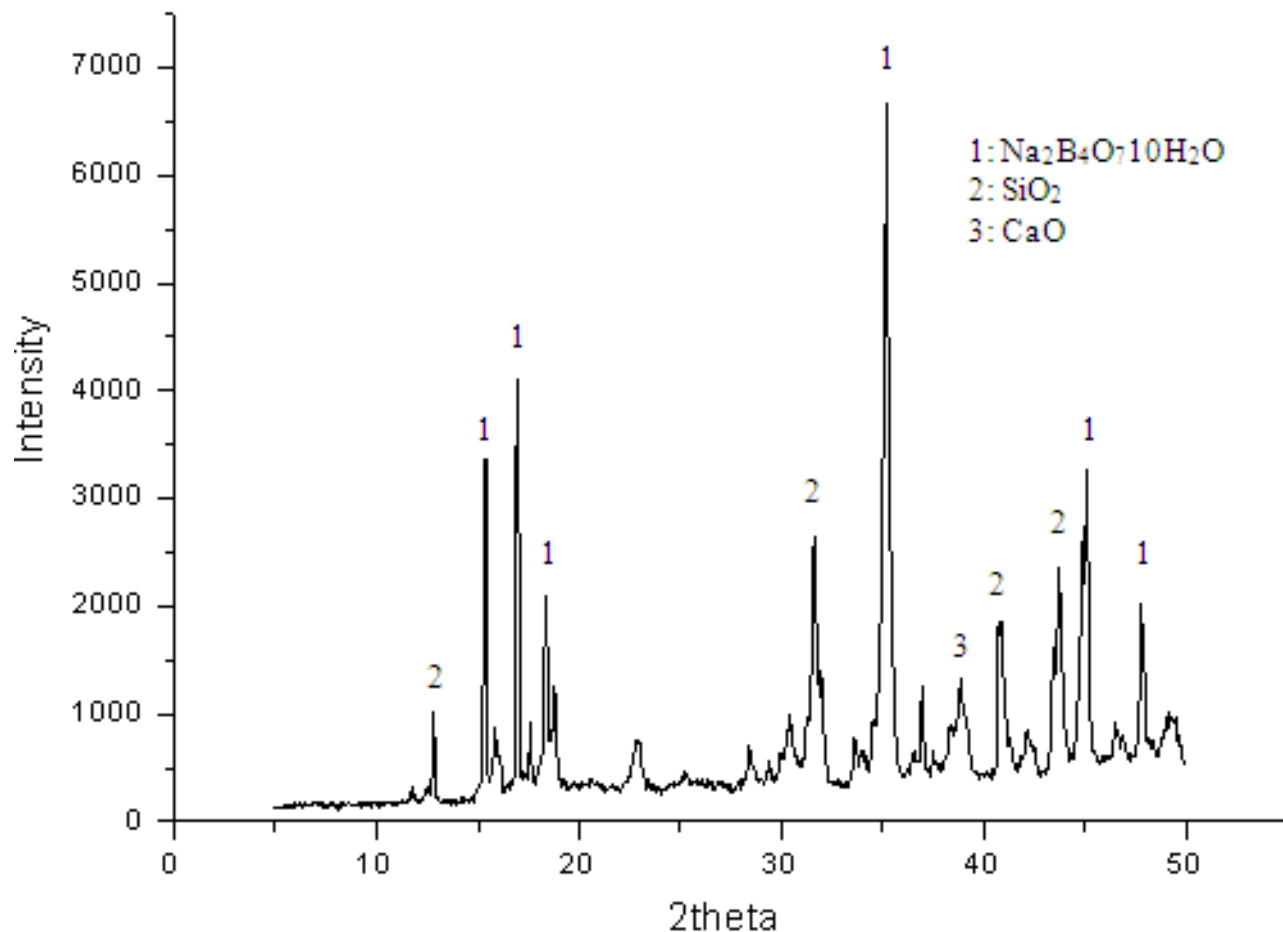
In the study, B₂O₃ determination was done by using potentiometric method. Boric acid is a low acid. The separately set up of boric acid is a crucial process. Thus, boric acid is determined with titration by solving boric acid into a strong acid after adding a polyalcohol into a boric acid solution (Scott, 1963).

The conversion quantity was found by transferring the dissolving H₃BO₃ quantity at the end of the reaction into B₂O₃ quantity.

The conversion fraction of the ore in terms of B₂O₃ is as

Table 2. Chemical analysis of tincal ore used in this study.

Component	Composition (%)
B ₂ O ₃	36.2
Na ₂ O	15.6
SiO ₂	1
CaO	0.8
H ₂ O	46.1
Other	0.3

**Figure 1.** XRD diffractogram of tincal minerals used in this study.**Table 3.** Parameters and their ranges used in the experiments.

Parameter	Value
Particle size (mesh)	-5 + 8 [*] , -8+18, -18 + 30, -30 + 40, -40 + 50
Concentration of phosphoric acid (M)	0.25, 0.5, 1 [*] , 2, 3, 5, 7
Solid/liquid ratio (g/mL)	1/100, 2/100, 4/100 [*] , 6/100, 8/100, 10/100, 12/100
Stirring speed (rpm)	50, 100, 200 [*] , 300, 400, 600, 800, 900
Reaction temperature (°C)	60 [*] , 65, 70, 75, 80, 85, 90, 95

*The constant values used when the effect of other parameters was investigated.

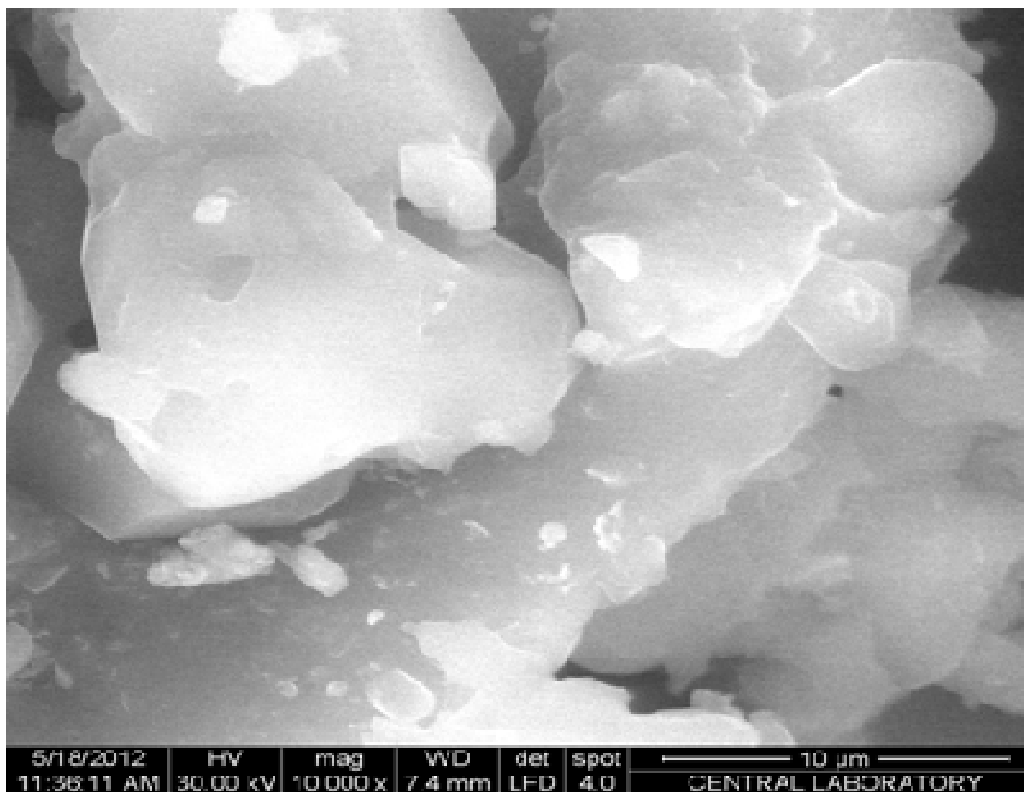
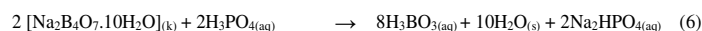
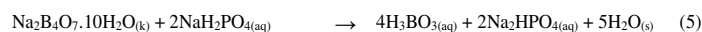
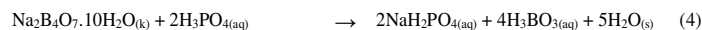
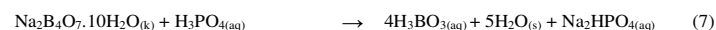


Figure 2. SEM photograph of tincal minerals used in this study.

It is regarded as the dissolvability of tincal in phosphoric acid solutions originates according to the following equations.



The total reaction is as follows:



Effect of parameters

Temperature, acid concentration, particle size, solid/liquid ratio, stirring speed as the parameters that influences dissolution ratio of tincal in phosphoric acid solutions were selected and the effect of these parameters on dissolution ratio was analysed.

Effect of reaction temperature

The effect of temperature on dissolution ratio of tincal has been analyzed at 60, 65, 70, 75, 80, 85, 90 and 95 °C.

In the experiments, particle size was kept constant as -5 + 8 mesh of sieve, solid/liquid ratio as 4/100 g/mL, stirring speed as 200 rpm and 1 M H_3PO_4 acid concentration. According to the results obtained, as the temperature of reaction increases, dissolution rate increases as it is seen from the Figure 3.

Effect of concentration of phosphoric acid

The effect of acid concentration on dissolution rate of tincal was researched in the concentration of 0.25, 0.5, 1, 2, 3, 5 and 7 M. In the experiments, particle size was kept fixed as -5 + 8 mesh of sieve, temperature as 60 °C, solid/liquid ratio as 4/100 g/mL, stirring speed as 200 rpm.

In the experiment of acid concentration, dissolution ratio showed increase from 0.25 to 2 M in direct proportion to acid concentration, and after 2 M, it showed decrease in inversely proportion to the increasing acid concentration (Figures 4 and 5).

It is regarded as the increasing acid concentration and dissolution ratio decrease on the values on the concentration of 2 M. XRD graphic and SEM picture of the solid remained as a result of the concentration of 5 M (Figure 6 and 7). By taking the change that forms on the surface of tincal mineral into consideration, it can be

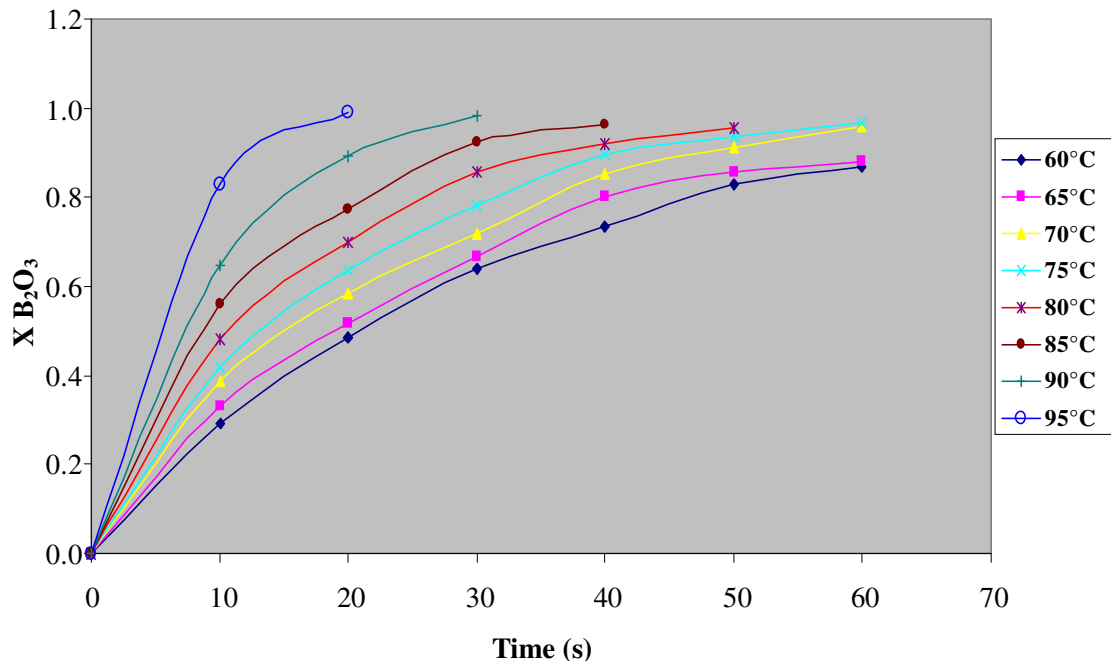


Figure 3. Effect of reaction temperature on dissolution rate of tincal.

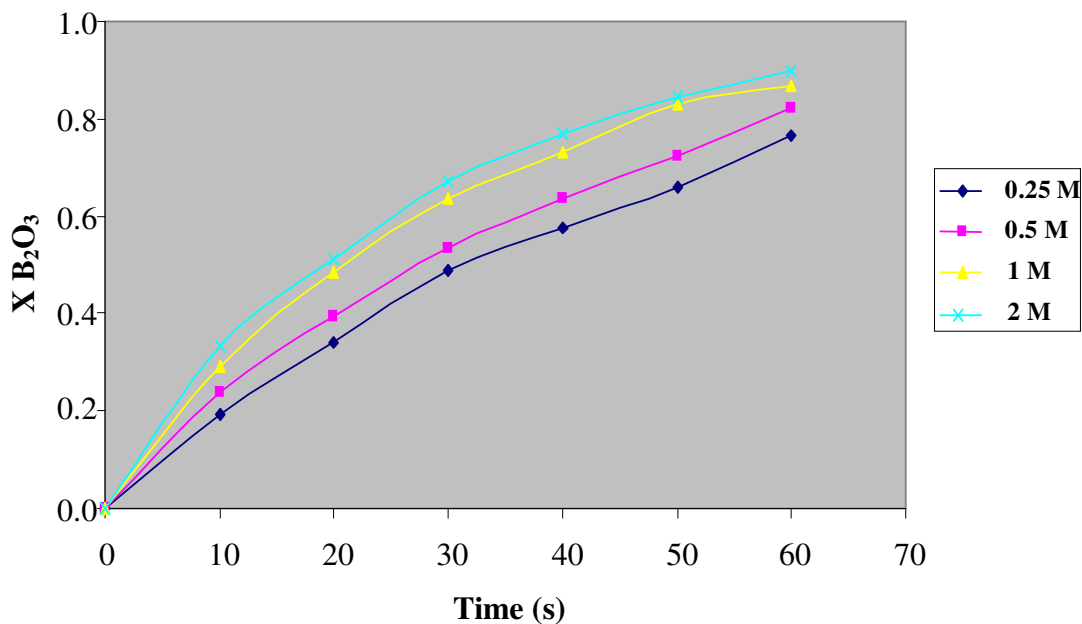


Figure 4. Effect of concentration of phosphoric acid on dissolution ratio of tincal (0.25 to 2 M).

remarked that a film layer forms on the surface of mineral there by boric acid reaches saturation quickly, and it prevents solution.

Effect of tincal particle size

The effect of particle size on the dissolution ratio of tincal

ore in phosphoric acid solutions were studied in the fractions of -5 + 8, -8 + 18, -18 + 30, -30 + 40, -40 + 50 mesh of sieve. In the experiments, heat was kept fixed as 60°C, acid concentration as 1 M, solid/liquid ratio as 4/100 g/mL and stirring speed as 200 rpm. In Figure 8, the effect of particle size on dissolution ratio is showed. Dissolution rate increases with the decrement of particle size.

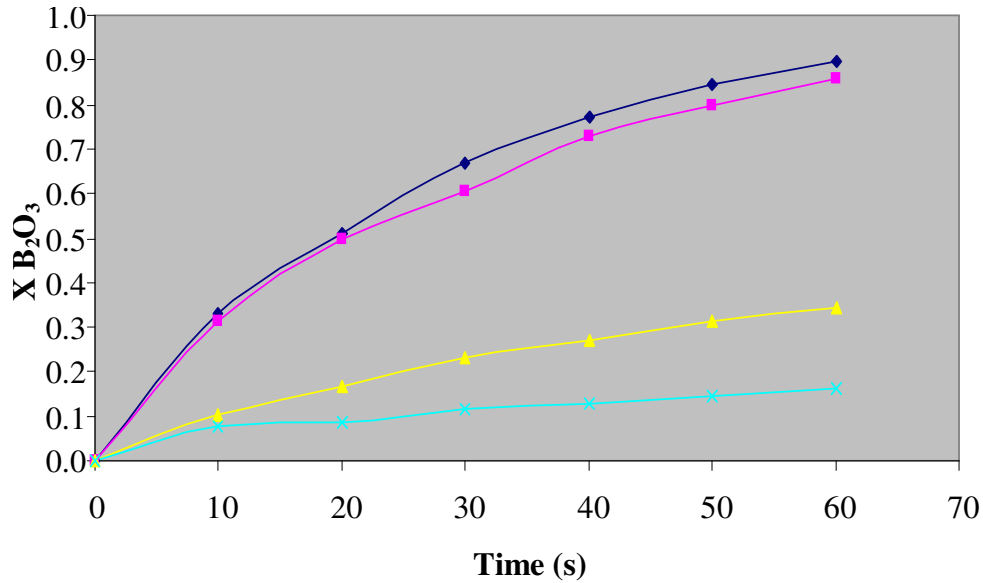


Figure 5. Effect of concentration of phosphoric acid on dissolution ratio of tincal (2 to 7 M).

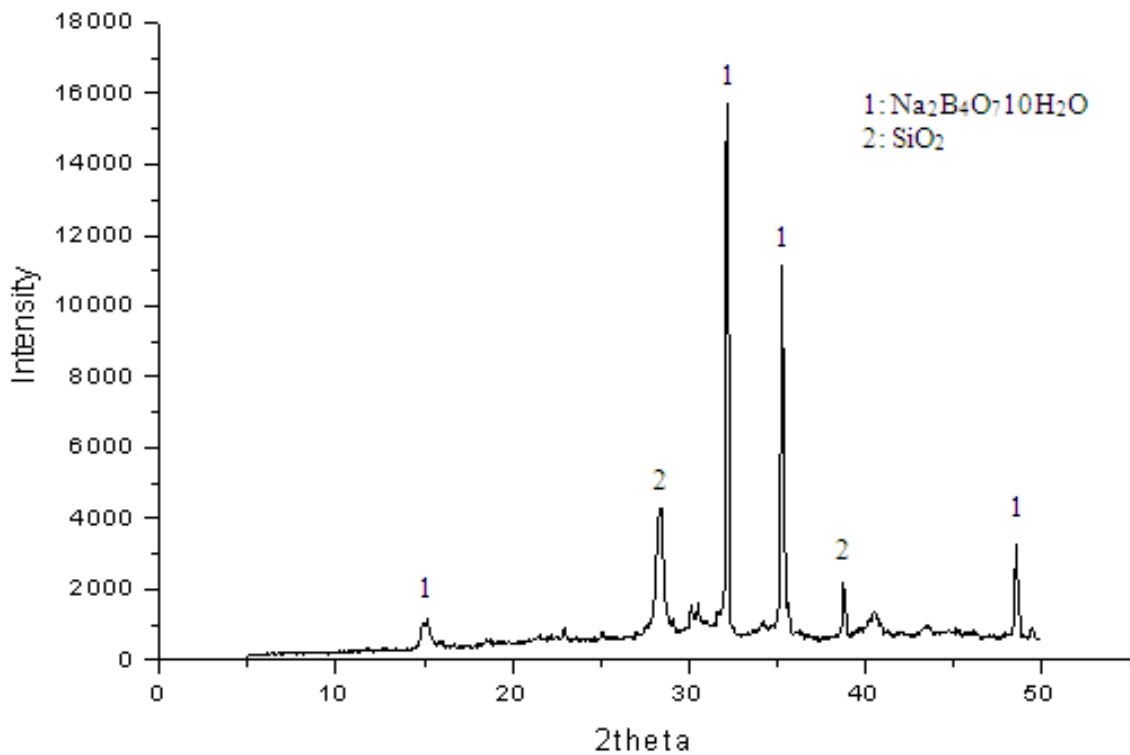


Figure 6. XRD diffractogram of remained as a result of the concentration of 5 M.

Effect of solid/liquid ratio

The effect of solid/liquid ratio on the dissolution rate of tincal ore in phosphoric acid solutions were studied in the

values of 1/100, 2/100, 4/100, 6/100, 8/100, 10/100 and 12/100 g/mL. In the experiments, particle size was kept fixed as -5 + 8 mesh of sieve, reaction heat as 60°C, acid concentration as 1 M and stirring speed as 200 rpm. As

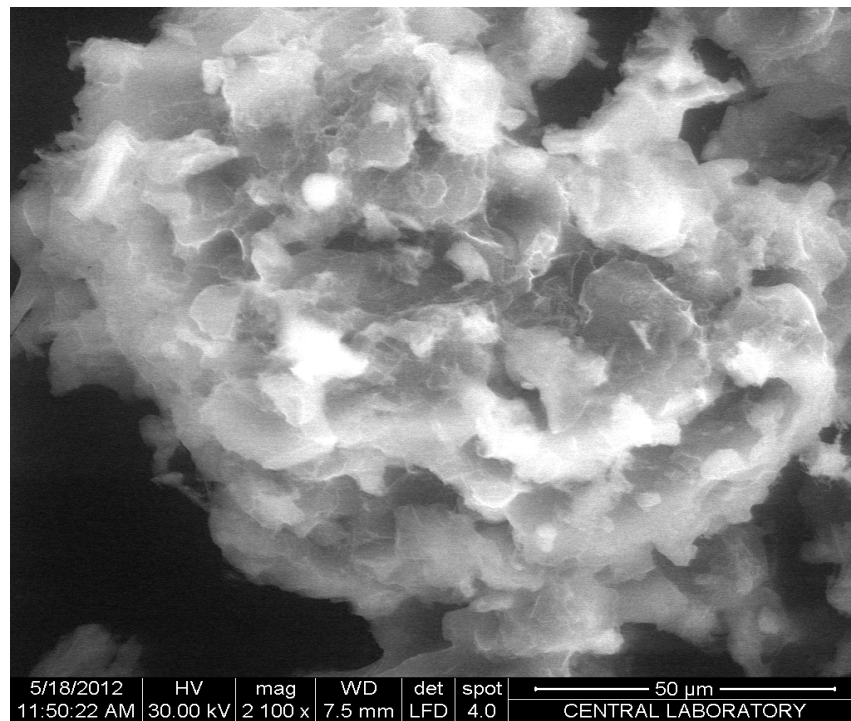


Figure 7. SEM photograph of remained as a result of the concentration of 5 M.

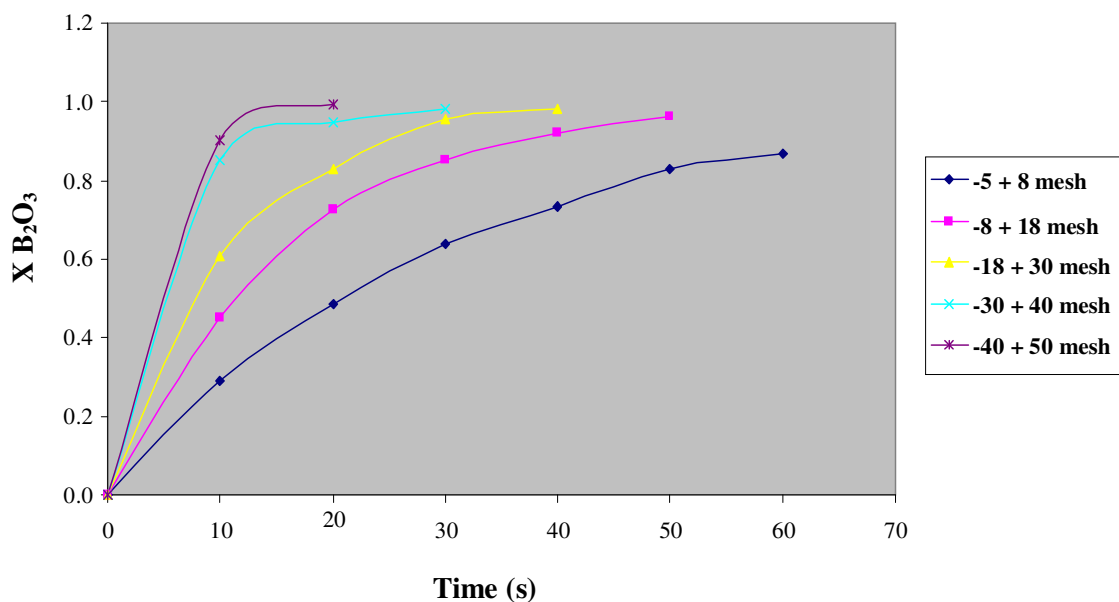


Figure 8. Effect of particle size on dissolution ratio of tincal.

shown in Figure 9, as solid/liquid ratio increases, dissolution rate decreases.

Effect of stirring speed

The effect of stirring speed on the dissolution ratio of

tincal ore in phosphoric acid solutions were studied at a rate of 50, 100, 200, 300, 400, 600, 800 and 900 rpm. In the experiments, particle size was determined as -5 + 8 mesh of sieve, solid/liquid ratio as 4/100 g/mL, reaction heat as 60°C and acid concentration as 1 M. According to experimental data, as shown in Figure 10, while stirring speed increases, dissolution rate increases.

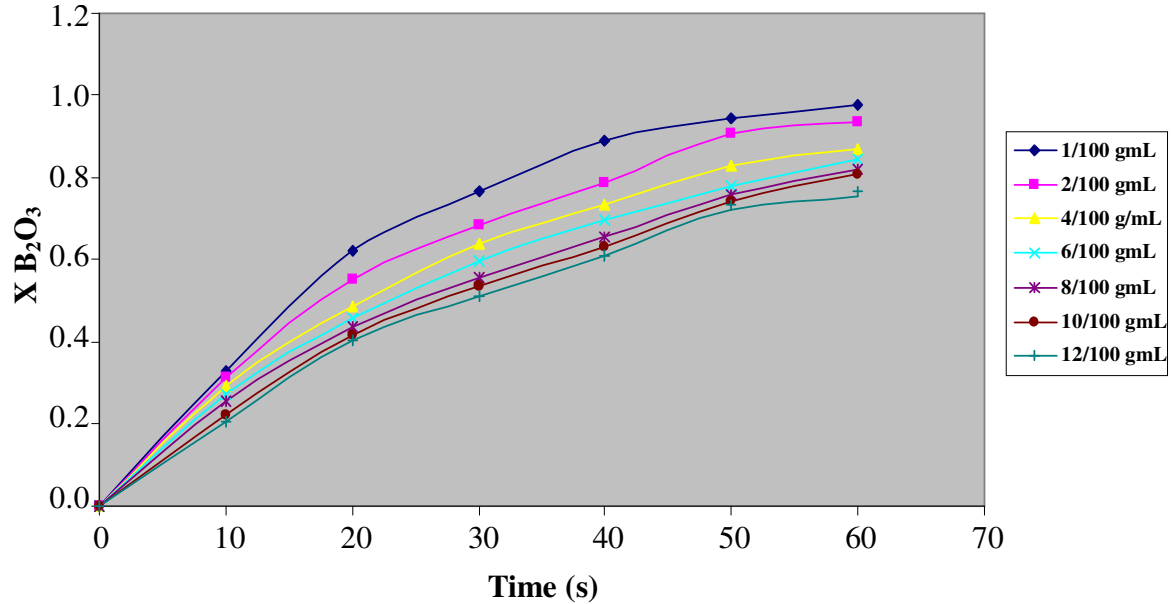


Figure 9. Effect of solid/liquid ratio on dissolution rate of tincal.

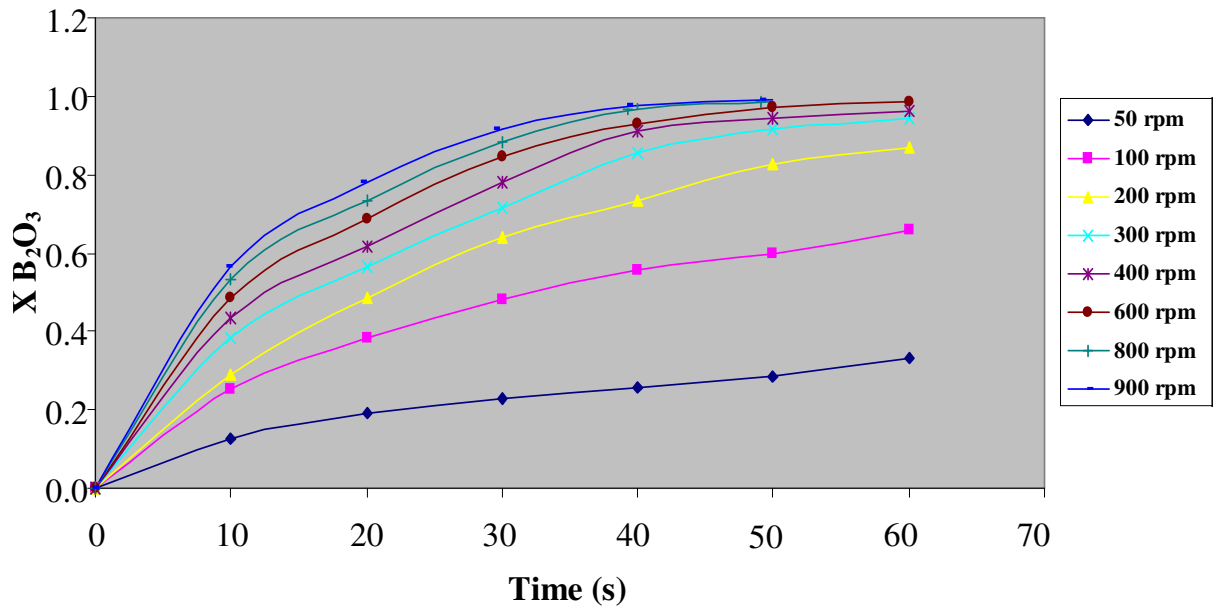


Figure 10. Effect of stirring speed on dissolution ratio of tincal.

Kinetics analysis

The reaction systems are divided into two classes as homogeneous and heterogeneous.

Homogeneous reactions

Those are the reacting substances and the reactions whose reaction products comprise of just one phase. The

phase can be solid, liquid or gas. It is studied in the form of catalytical and non-catalytical reactions.

Heterogeneous reactions

Least two phases are needed for forming of reaction. There are parameters effecting the rate of reaction like the contact styles of phases, interface areas, temperature and pressure, the shape of reactor, the diffusion

Table 4. Integrated rate equations for various shapes of particles, shrinking-core model and other models.

Particle and sphere	Rate controlling step	Rate equation	
	The film diffusion control	$t / \tau = X_B$	$\tau = \frac{\rho_B R}{3bK_g C_{Ag}}$
Constant size particles	Diffusion control through the ash or product layer	$t/\tau = 1 - 3(1-X_B)^{2/3} + 2(1-X_B)$	$\tau = \frac{\rho_B R^2}{6bDeC_{Ag}}$
	Surface chemical reaction	$t/\tau = 1 - (1 - X_B)^{1/3}$	$\tau = \frac{\rho_B R}{bk'' C_{Ag}}$
Shrinking sphere		$t/\tau = 1 - (1 - X_B)^{2/3}$ (small particle)	$\tau = \frac{\rho_B R o^2}{2bDC_{Ag}}$
	The film diffusion control	$t/\tau = 1 - (1 - X_B)^{1/2}$ (large particle)	$\tau = (\text{const})R^{3/2}$ C_{Ag}
	Surface chemical reaction	$t/\tau = 1 - (1 - X_B)^{1/3}$	$\tau = \frac{\rho_B R o}{bk'' C_{Ag}}$
	First-order pseudo- homogeneous model	$-\ln(1 - X_A) = k.t$	

characteristics of fluidal phase. They are analyzed as catalytical and non-catalytical reactions.

In solid-liquid reactions including more than one phase the process of putting the desired and undesired substance into the solution by dissolving is called leaching.

Leach process is a process of selectively dissolving the whole or a part of ore with a suitable dissolver reactive. Leach event can be thought as the dissolution of solid as a result of the reaction between solid and liquid dissolver. In leaching processes the rate of reaction demonstrates the alteration of the amount of the products reacting or forming in the wake of reaction in time. The ratio of reaction generally decreases in time in the process of leaching. It is regarded as situation stems from the decrement of surface on it and the reaction occurs as the reaction progresses, the reduction of the dissolver concentration or a new layer formation on solid surface. In leach processes, dissolution ratio directly depends on the activation energy. While the amplitude of activation energy demonstrates that dissolution is difficult, the meanness of it indicates that it is easy.

Leach event is regarded as a heterogeneous process. Leach reactions happen in an environment consisting of

of a heterogeneous phase, a liquid reactive or reactive mixture and a solid. One of the effective factor in determining leach conditions is the size and the form of particle which will be dissolved. During the leaching in low solid/liquid ratio of a system consisting of fairly small particle sized-solid, the environment can be regarded as homogeneous. In explaining leach kinetic of this system, homogeneous reaction models can be utilized. However, generally such a modelling is not accepted as enough to explain the reactions happening in leach environment. Therefore, when kinetic definition of leach processes is done, heterogeneous phase models are used (Levenspiel, 2012).

The experimental data obtained in this study was analyzed by using heterogeneous and homogeneous reaction models (Table 4). When R^2 values belonging to all the parameters were examined, it was seen that the highest value belongs to first order pseudo homogeneous reaction model. It was determined that only the values belonging to first order pseudo homogeneous reaction model are in between 0.9900 to 0.9999 for all parameters when R^2 values of all parameters used in kinetic examinations are analyzed whereas the others are quite lower than these values. For example, R^2 values obtained

Table 5. R² values at different temperatures.

Kinetic models and equations	R ² values	Temperatures (°C)						
		60	65	70	75	80	85	90
Film diffusion control A ₁ = X	R ²	0.9500	0.9323	0.9195	0.9010	0.9003	0.9240	0.9088
Diffusion control through the ash or product layer A ₂ = 1-3(1 - X) ^{2/3} + 2(1 - X)	R ²	0.9883	0.9689	0.9709	0.9451	0.9387	0.9482	0.9311
Surface chemical reaction control A ₃ = 1 - (1 - X) ^{1/3}	R ²	0.9500	0.9323	0.9195	0.9010	0.9003	0.9240	0.9088
Film diffusion control A ₄ = 1 - (1 - X) ^{2/3}	R ²	0.8377	0.8167	0.7925	0.7343	0.7530	0.7976	0.8160
Film diffusion control A ₅ = t/τ = 1 - (1 - X) ^{1/2}	R ²	0.9500	0.9250	0.9414	0.9010	0.9003	0.9240	0.9334
First order pseudo homogeneous A ₆ = -ln(1 - X)	R ²	0.9974	0.9924	0.9978	0.9962	0.9978	0.9916	0.9928

in experimental data belonging to temperature parameters can be seen in Table 5.

When the obtained R² values were studied, it was found that the dissolution kinetic of tincal in phosphoric acid solutions in high heat complies with first order pseudo homogeneous reaction model.

$$-\ln(1-X) = k \cdot t \quad (8)$$

$$K = k_0 \cdot W^a \cdot C^b \cdot S/L^c \cdot W^d \cdot e^{-E/RT} \quad (9)$$

The obtained rate expression depending upon acid concentration, heat, solid/liquid ratio, stirring speed and particle size parameters belonging to the dissolution of tincal in phosphoric acid solutions in high heat can be procured as a result of mathematical processes comprising of several steps.

Dependence on particle size

By benefiting from the results belonging to the experiments conducted with -5 + 8, -8 + 18, -18 + 30, -30 + 40 and -40 + 50 mesh of sieve particle size having an effect on the rate of transformation, the values of -ln(l-X) against t were displayed in graphic in Figure 11. By displaying the values of lnk existing here against lnD in graphic, a exponential was found for particle size.

$$k = k_1 \cdot D^{-0.7775} \quad (10)$$

Dependence on acid concentration

The effect of acid concentration upon the rate of

transformation has been examined in the concentration of 0.25, 0.5, 1, 2, 3, 5 and 7 M. The rate of transformation indicates an increase in the range of this concentration between 0.25 to 2 M, and after 2 M it indicates a decrease. According to the results obtained in experimental processes, -ln(l-X) values against t have been displayed in graphic in Figure 12. Then, by displaying the found lnk₁ values against lnC values in graphic, b exponential value was found for acid concentration.

As the dissolvability in the concentrations after 2 M decreases by increasing acid concentration, it is not suitable to work in more concentrated concentration than 2 M in this study. Both the substance and time loss are the point in question. Thus, for the ratio expression to be formed, by taking into consideration 0.25 to 2 M concentrations, velocity equality equation will be written according to acid concentrations lower than 2 M.

In the wake of the process held, it has been found as

$$k_1 = k_2 \cdot D^{-0.7775} \cdot C_A^{0.2162}$$

Dependence on solid/liquid ratio

By benefiting from the results belonging to the experiments conducted with solid/liquid ratio of 1/100, 2/100, 4/100, 6/100, 8/100, 10/100 and 12/100 g/mL having an effect on the rate of transformation, the values of -ln(l-X) against t were displayed in graphic in Figure 13. By the lnk₂ values found later a c exponential value for solid/liquid were found by displaying in graphic against lnS/L. It was found as

$$k = k_3 \cdot D^{-0.7775} \cdot C^{0.2162} \cdot S/L^{-0.3893}$$

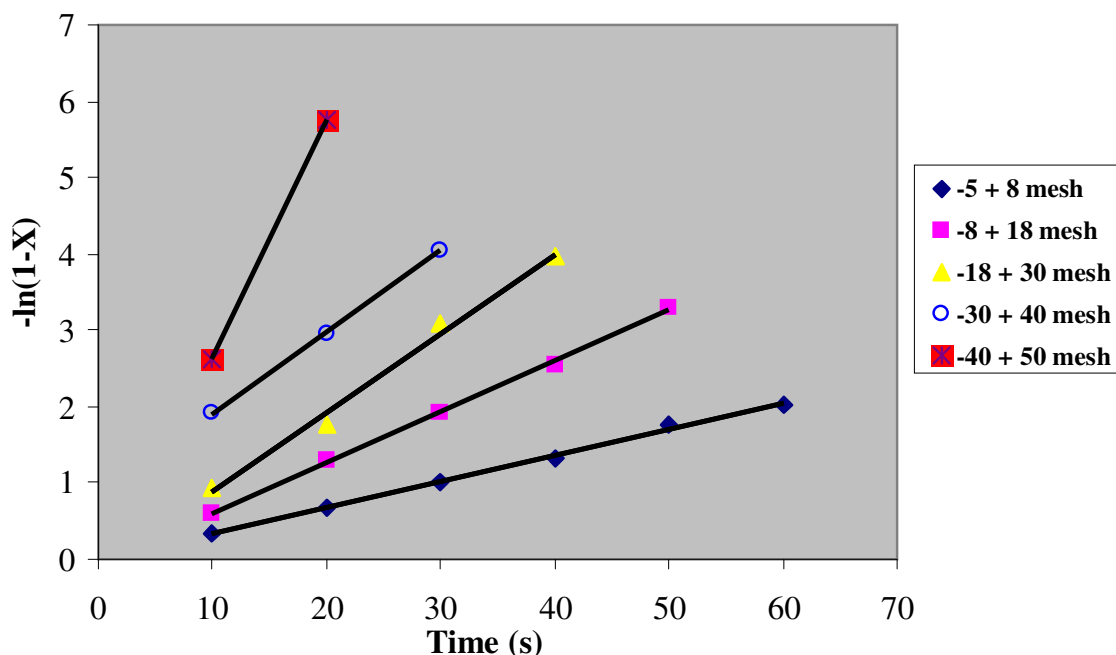


Figure 11. Graph of $-\ln(1-X)$ versus time for particle size.

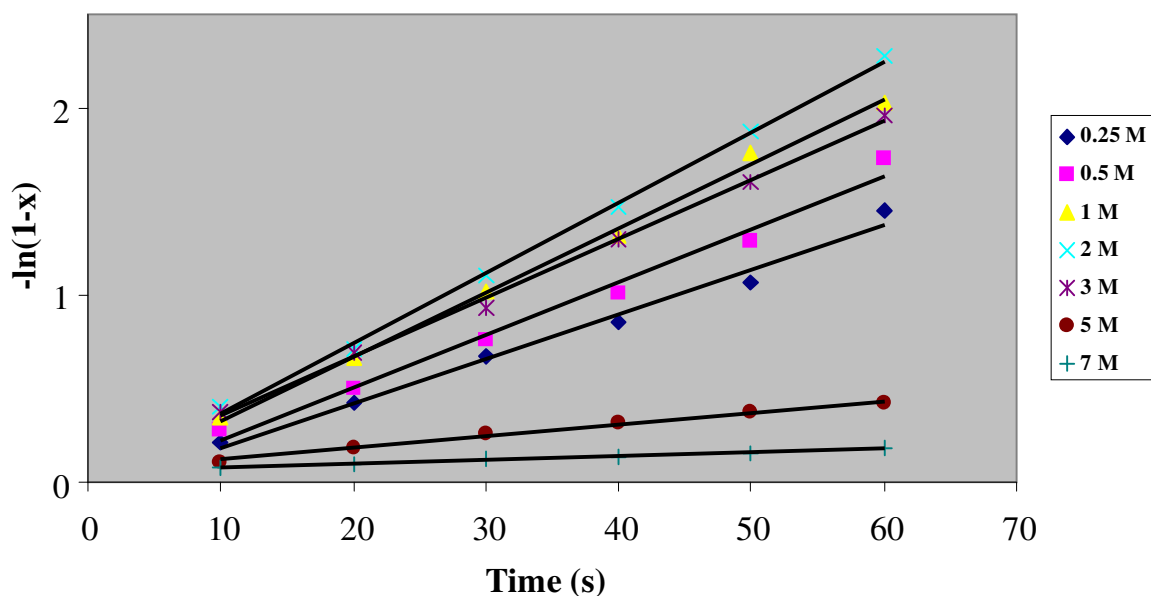


Figure 12. Graph of $-\ln(1-X)$ versus acid concentration.

Dependence on stirring speed

The effect of stirring speed on the rate of transformation was studied at a rate of 50, 100, 200, 400, 600, 800 and 900 rpm. According to the results obtained from stirring speed, the graphic of $-\ln(1-X)$ against t in Figure 14 that is shown below was drawn. Then for the mixing rate from Figure 14, an exponential value was found for $\ln W$ values

against $\ln k_3$ obtained from this graphic. It was determined as $k_3 = k_4 \cdot D^{-0.7775} \cdot C^{0.2162} \cdot S/L^{-0.3893} \cdot W^{0.9901}$.

Dependence on reaction temperature

While the effect of the reaction temperature upon the rate of transformation is examined tests about 60, 65, 70, 75,

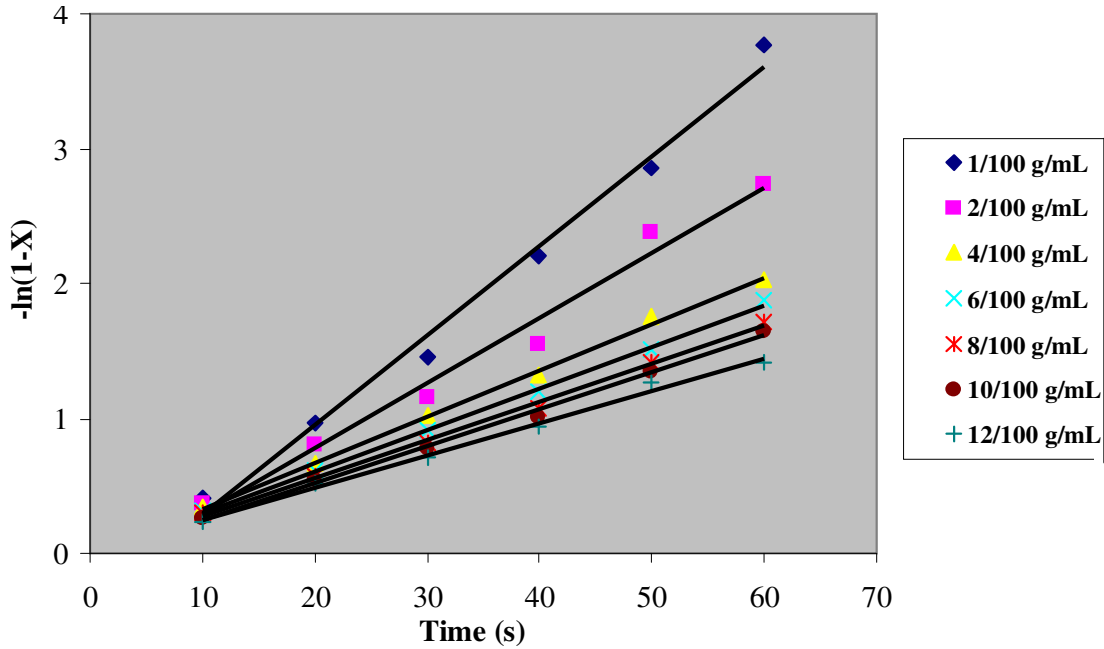


Figure 13. Graph of $-\ln(1 - X)$ versus solid/liquid ratio.

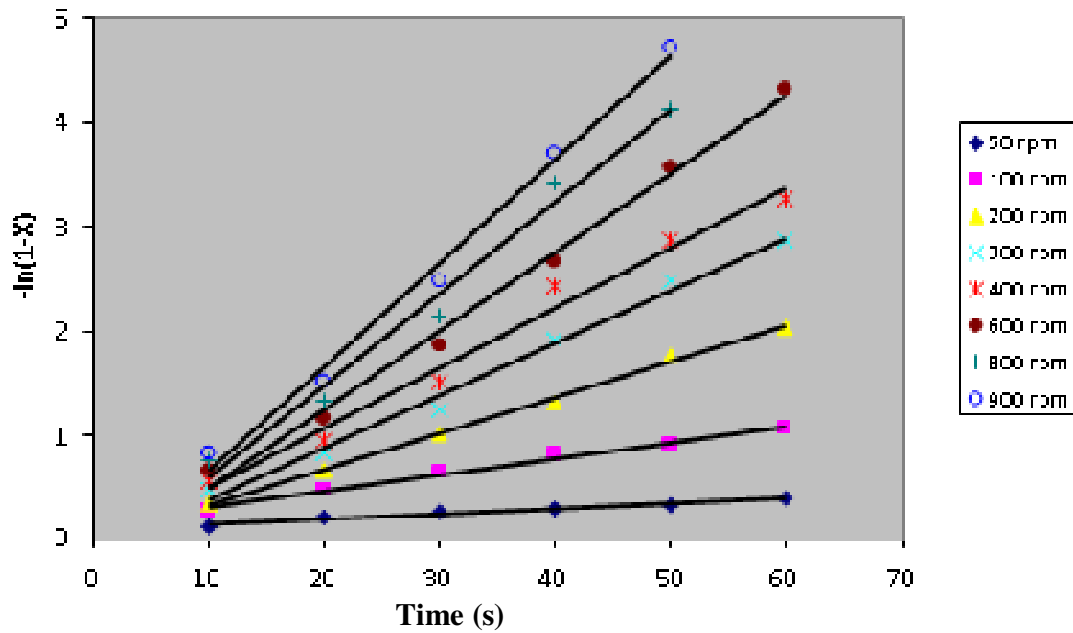


Figure 14. Graph of $-\ln(1 - X)$ versus stirring speed.

80, 85, 90 and 95°C temperature were obtained. By benefiting from the results belonging to these results, $-\ln(1-X)$ values against t were displayed in graphic in Figure 15. From the slope of line obtained from graphic apparent ratio constant for each reaction heat (k) was accounted. Then from $\ln k_4$ against temperature graphic Figure 16 activation constant and energy were

accounted. As the dissolution is very fast in 95°C it was not used in kinetic accounts.

$$k_4 = k_0 \cdot e^{-E/RT} \tag{11}$$

$$-\ln(1-X) = 1988 \cdot D^{-0.78} \cdot C^{0.22} \cdot S/L^{-0.39} \cdot W^{0.99} \cdot e^{5558.4/T} \cdot t \tag{12}$$

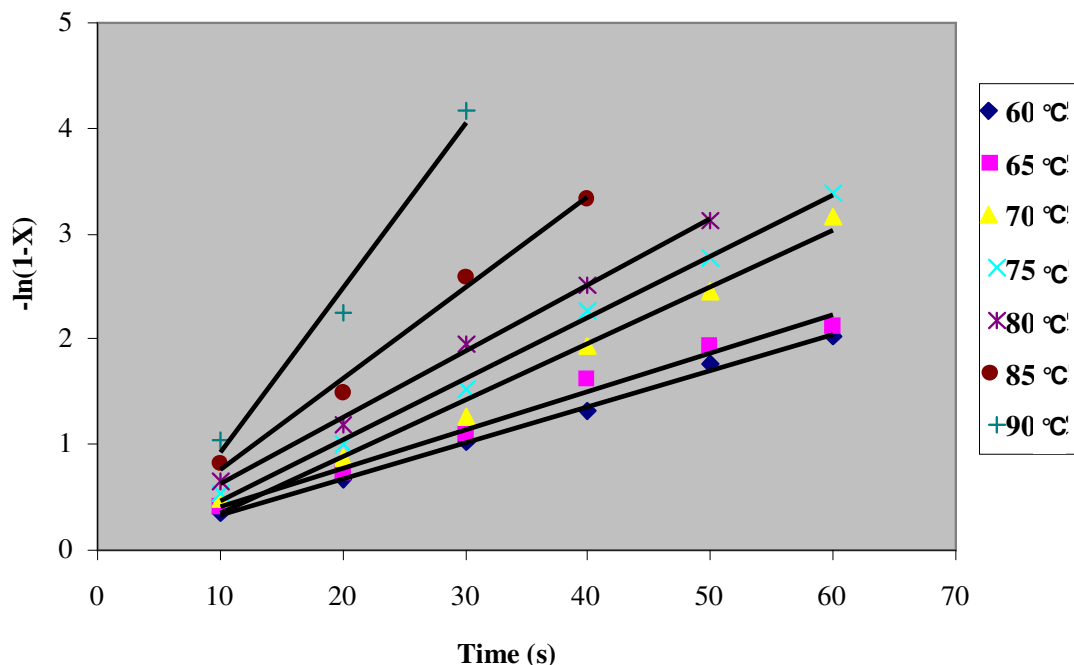


Figure 15. Graph of $-\ln(1 - X)$ versus reaction temperature.

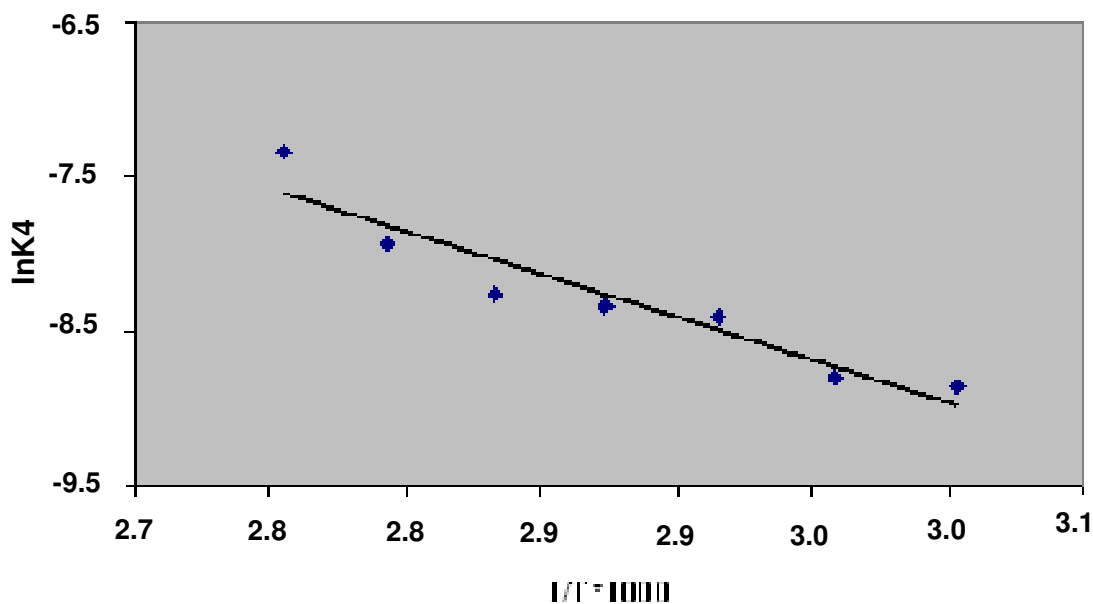


Figure 16. Arrhenius plot.

The graphic including all theoretic and experimental results in which all the data was used is shown in Figure 17.

Conclusion

Tincal has been examined by taking into consideration the acid concentration in phosphoric acid solutions in high

heat, mixing rate, particle size, solid/liquid rate and temperature parameters. It has been determined that the rate of solution increases by increasing temperature and mixing rate while it decreases by increasing of solid/liquid rate and particle size. As for acid concentration studies have been held in concentrations between 0.25 to 7 M. It has been found that the dissolution decreases by increasing acid concentration after 2 M. This condition is

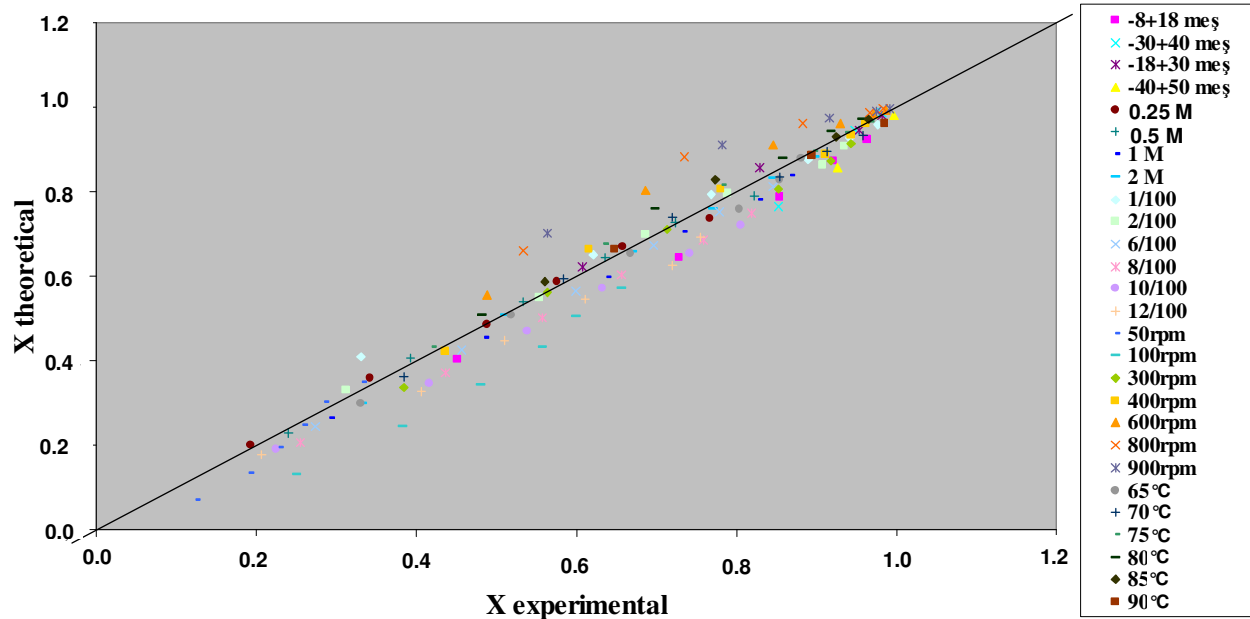


Figure 17. Experimental transformed values versus theoretical conversion values from expression in equation (12).

thought to occur due to a film layer appearing on ore surface. Rate equality obtained as a result of experimental studies has been formed according to 0.25 to 2 M concentration range. It is not suitable to use acid concentration over 2 M in this study. In the study conducted, the dissolution kinetic of tincal in phosphoric acid solutions in high heat has been examined by using graphical and statistical method. At the end of the study by determining that the solution complies with first order pseudo homogeneous reaction model, it has been found that the activation energy is 46.21 kJ/mol.

The mathematical form of the model depending on the chosen parameters was found as follows:

$$-\ln(1-X) = 1988 \cdot D^{-0.78} \cdot C^{0.22} \cdot S/L^{-0.39} \cdot W^{0.99} \cdot e^{5558.4/T} \cdot t$$

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