

## **DISSOLUTION KINETICS of CALCINATED MANGANESE ORE in ACETIC ACID SOLUTIONS**

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**Abstract:** In this study, manganese ores supplied from the source in Tavas – Denizli region were firstly calcinated at 700 °C for an hour. The effects of temperature, solid-to-liquid ratio, reaction time, stirring speed, particle size and acid concentration on the dissolution rate of calcinated manganese ore in dilute acetic acid were investigated. It was observed that the dissolution rate increased with the increase in reaction temperature, stirring speed, reaction time and acid concentration, and with the decrease in solid-to-liquid ratio. It was determined that the dissolution process is fitted by pseudo homogeneous first-order reaction model. Activation energy for the reaction was calculated to be 25.51 kJ.mol<sup>-1</sup>.

**Keywords:** *Manganese ore, calcination, dissolution kinetics, acetic acid.*

## **KALSİNE MANGAN CEVHERİNİN ASETİK ASİT ÇÖZELTİLERİNDEKİ ÇÖZÜNME KİNETİĞİ**

**Özet:** Bu çalışmada, Denizli-Tavas yöresinden temin edilen mangan cevheri ilk olarak 700 °C’de bir saat kalsine edildi. Kalsine mangan cevherinin seyreltik asetik asit çözeltileri içindeki çözünme oranı üzerine sıcaklık, katı/sıvı oranı, reaksiyon süresi, karıştırma hızı, tanecik boyutu ve asit konsantrasyonunun etkileri incelendi. Reaksiyon sıcaklığı, karıştırma hızı, reaksiyon süresi ve asit konsantrasyonunun artması ve katı/sıvı oranının azalmasıyla çözünme oranının arttığı gözlenmiştir. Çözünme prosesinin yalancı homojen birinci mertebeden reaksiyon modeline uyduğu ve reaksiyona ait aktivasyon enerjisi 25.51 kJ.mol<sup>-1</sup> olarak hesaplanmıştır.

**Anahtar Kelimeler:** *Mangan cevheri, kalsinasyon, çözünme kinetiği, asetik asit.*

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## 1. INTRODUCTION

Manganese, a less available element in the earth, is an important substance used widely, especially in metallurgy and chemical industries. Approximately 95 % of processed manganese ore is consumed in the battery production, chemical and glass and ceramic industries. For this reason, the processing of manganese ore and the production of manganese metal and its compounds are of vital importance. Manganese sulfate is a manganese compound produced in the largest amount following ferrous-manganese alloys and used as a raw material in the production of some manganese compounds in dye, pharmacy, textile, etc. industries. The processing of manganese ore for the production of manganese compounds is very important from the economical point view [1].

Since the acidity of a lot of inorganic acids used as leaching reagent is generally high, it is expected that their selectivity is not much and the corrosion effect high at the same time, and the controlling pH is more difficult [2]. Extraction of heavy metals by inorganic acids and complexing agent has severe drawbacks. Otherwise, for inorganic acid, fast dissolution abilities may be an advantage. Organic acids have high selectivity although the dissolving abilities of them are weak. Therefore it is advantageous for particularly dissolution of carbeneous compounds. They could be an attractive extracting agent because the extraction can be performed under mildly acidic conditions (pH=3-5), and they are biologically degradable [3]. Additionally, in industrial processes, organic acids can cause a lesser corrosion effect. Even, the corrosion effect can be controlled by adding chemical substances called inhibitors such as benzoic acid and salicylic acid [4].

Abbruzzese investigated the sulfite leaching of an Italian manganese ore to determine the feasibility of extracting manganese by percolation leaching. He found , aqueous SO<sub>2</sub> to be an effective leachant for manganese dissolution owing to the fast dissolution rates and low temperatures [5]. Yartaşı et al. investigated the dissolution kinetics of braunite in sulfuric acid solutions, and calculated the activation energy of the dissolution process to be 40.95 kJ.mol<sup>-1</sup> [6]. By using acetic acid solutions, In the previous study, the dissolution kinetics of calcinated magnesite was investigated by Abalı and it was determined that the dissolution process is controlled by pseudo first-order reaction rate and the activation energy for this dissolution reaction to be 8.78 kJ.mol<sup>-1</sup> [7]. In another study carried out by Rasoni et al., the leaching of manganese dioxide with non-aqueous mixtures (dimethyl sulfoxide-SO<sub>2</sub>) was investigated. They found the optimum conditions to be 50 minutes of reaction time, 650 rpm of stirring speed, pH=8, 0.2 % solid concentration, -35 +44 mesh of particle size and 36 °C of reaction temperature [8].

Many others studies about the dissolution of manganese minerals have been carried out in several different conditions. the dissolutions of manganese ores for the production of manganese compounds were investigated in different mineral acidic solutions [9,10] and under the CO<sub>2</sub> pressure [11,12].

As indicated above, in the previous studies, generally, mineral acids, and pressure of some gases were used for dissolution of manganese ore but in this study, the dissolution kinetics of manganese ore (rhodochrosite) calcinated at 700 °C was investigated in organic acid under atmospheric pressure. The effects of temperature, solid-to-liquid ratio, reaction time, stirring speed, particle size and acetic acid concentration on the dissolution rate of calcinated manganese ore were determined

## 2. MATERIALS and METHODS

The manganese ore, rhodochrosite, used in the present study was supplied from the source in Denizli-Tavas region in western of Turkey. The visible impurities were removed by hand, and the ore was ground and then sieved using ASTM standard sieves, giving 3 fractions of -1700+1400, -4255 +250 and -150  $\mu\text{m}$ . Each fraction of ore was calcinated in the range of 500-800  $^{\circ}\text{C}$  in the Carbolite furnace (Fig.1-2). X-ray analysis showed that the original ore contains manganese carbonate (Fig.3). The calcinated ore was analyzed by gravimetric and volumetric methods [13]. It was determined that the calcinated manganese ore contains MnO 89 %.

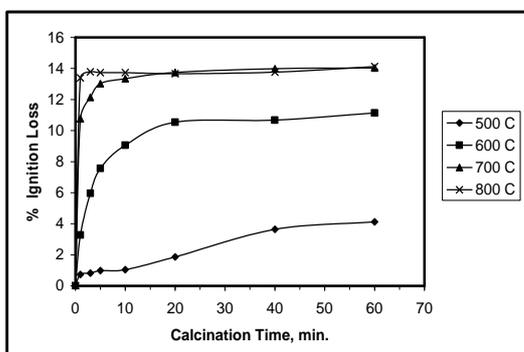


Fig. 1. Ignition loss of rhodochrosite for the range of 500-800  $^{\circ}\text{C}$ .

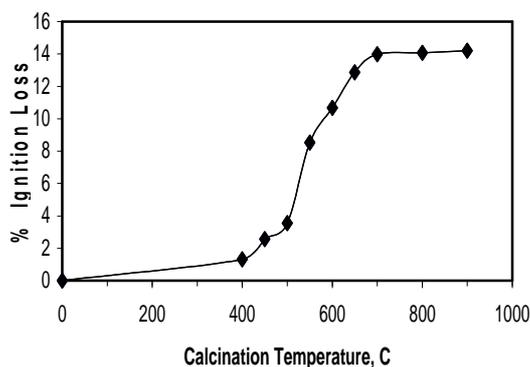


Fig. 2. Ignition loss of rhodochrosite for the range of 400-900  $^{\circ}\text{C}$  at the 40 min.

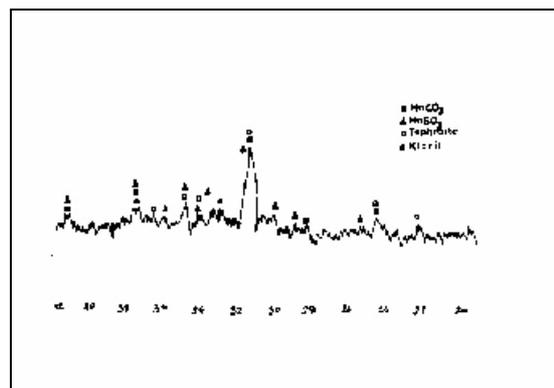


Fig 3. X-ray diffractogram of manganese mineral

The dissolution process was carried out in a 250 mL 3-necked round-bottomed glass reactor at atmospheric pressure. A mechanical stirrer was used to stir the reactor contents, and a thermostat was employed to maintain the reaction medium at a given temperature. To prevent loss of the reactants and products by evaporation, a cooler was attached to the reactor. The particle characteristics and the experimental conditions are summarized here. In the dissolutions experiments 100 mL of  $\text{CH}_3\text{COOH}$  solution was first put into the reactor, and after it reached the desired temperature, a given amount of the ore sample was added to the solution while the stirring was started. At the end of the chosen reaction time, the stirring was stopped, and all of the reactor contents were then filtered off. The amount of  $\text{Mn}^{++}$  content of the filtrate was determined by gravimetric and volumetric methods [13]. The parameters and the ranges used in the experiments are given in Table 1.

Table 1. Parameters and range employed in experiments

Parameters	Selected Parameter Values
Acid Concentration, M	0.3 ; 0.5 ; 3.0 ; 5.0
Solid-to-Liquid Ratio, g/mL	0.5/100 ; 1/100 ; 2/100
Stirring Speed, $\text{min}^{-1}$	300 ; 700 ; 1050
Reaction Temperature, $^{\circ}\text{C}$	20 ; 40 ; 60 ; 70
Particle Size, mesh	-1700+1400; -425+250; -150

### 3. RESULTS and DISCUSSION

#### 3.1. Calcination

Due to the solubility of manganese ore in organic acid is very limited, the calcination process was applied at high temperature. In order to investigate the effect of calcination temperature on the weight loss, the crushed ore was calcinated at 500-800 °C. The results are given in Figure 1. As can be seen from Figure 1, the weight loss is increased with calcinated temperature

#### 3.2. Dissolution Parameters

##### 3.2.1. The effect of reaction temperature

Experiments on the effect of temperature were carried out in the temperature range of 20-70 °C, maintaining the solid-to-liquid ratio at 0.5/100 (w/v); stirring speed at 700 min<sup>-1</sup>, the average particle size at -425+250 µm., and acid concentration at 5.0 M. As seen from the experimental results given in Fig. 4, the dissolution rate increases regularly as the temperature increases.

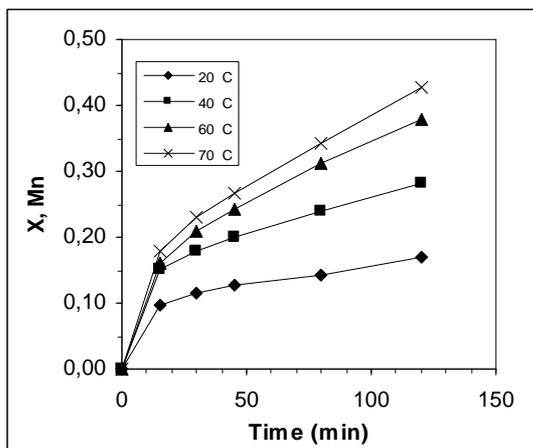


Fig 4. Effect of temperature on the dissolution process in the range of 20-70 °C

##### 3.2.2. The effect of solid-to-liquid ratio

The effect of the solid-to-liquid ratio on the dissolution process was studied using the ratios in the range of 0,5/100 to 10/100 (w/v). For these experiments the value of the other parameters maintained constant during the reaction, were: leaching temperature 50 °C, acid concentration 5 M, the average particle size at -425+250 µm. and stirring speed 700 min<sup>-1</sup>. Fig. 5 shows the experimental results. The dissolution rate decreased substantially with increasing solid-to-liquid ratio. This can be attributed to the decrease in the fluid reactant per unit weight of solid.

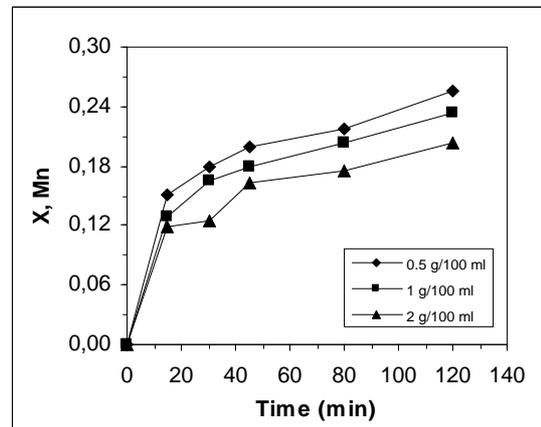


Fig 5. Effect of solid-to-liquid ratio on the dissolution process

##### 3.2.3. The effect of acid concentration

The effect of acid concentration on the dissolution process was studied using the values in the range of 0.3 – 5.0 M. For these experiments the value of the other parameters maintained constant during the reaction were: leaching temperature 50 °C, stirring speed 700 min<sup>-1</sup>, the average particle size at -425+250 µm. and solid-to-liquid ratio of 0.5/100 (w/v). The results obtained by these experiments are shown in Figure 6. Dissolution rate was increased by increasing the acid concentration.

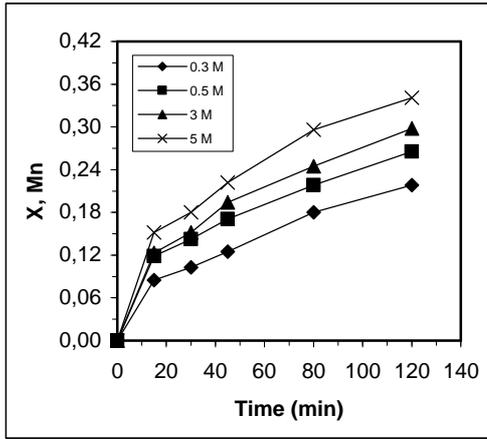


Fig. 6. Effect of acid concentration on the dissolution process

### 3.2.4. The effect of stirring speed

The effect of stirring speed on the dissolution process was investigated in the range of 300-1050  $\text{min}^{-1}$ , with a temperature of 50  $^{\circ}\text{C}$ , solid-to-liquid ratio of 0.5/100 (w/v), average particle size of  $-425+250 \mu\text{m}$ . and acid concentration of 5 M. Increasing in stirring speed causes a decrease in the thickness of the film layer; therefore, the dissolution rate increases (Fig.7).

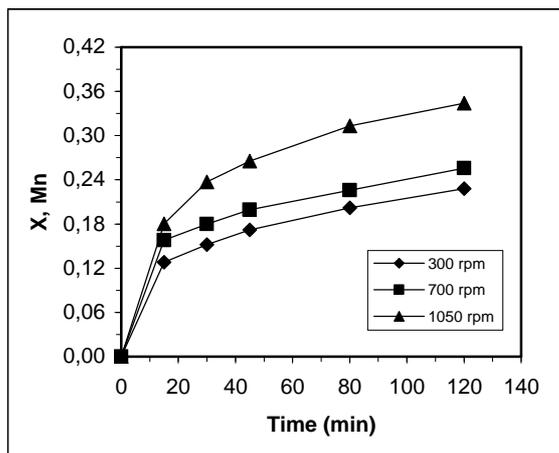


Fig. 7. Effect of stirring speed on the dissolution process

### 3.2.5. The effect of particle size

The effect of particle size on the dissolution rate was investigated using three different particle size fractions in the range of  $(-1700+1400) - (-150) \mu\text{m}$  and keeping other parameters constant: temperature at 50 $^{\circ}\text{C}$ , solid-to-liquid ratio at 0.5/100 (w/v), acid concentration at 5 M and stirring speed at 700  $\text{min}^{-1}$ . The dissolution rate increases with decreasing particle size (Fig.8). This behavior can be explained by the increase in the solid surface area in contact with fluid with decreasing particle size.

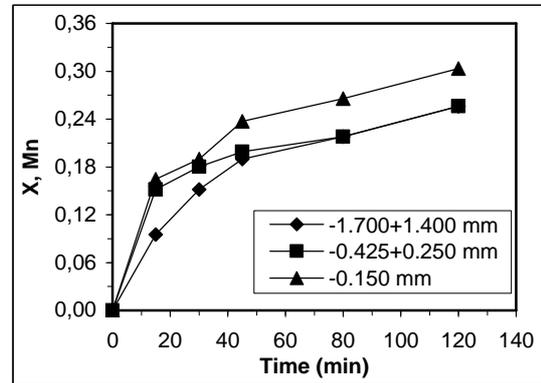


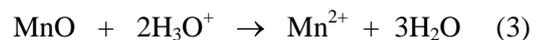
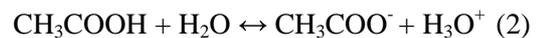
Fig. 8. Effect of particle size on dissolution process

## 3. 3. Dissolution Reactions and Kinetics

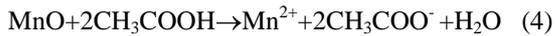
The manganese mineral was firstly calcinated for an hour at 700  $^{\circ}\text{C}$  according to the following reaction,



The MnO obtained from the calcination process was dissolved in acetic acid solutions with different concentrations. The dissolution reaction can be written as;



The overall reaction for manganese can be written as;



Nowadays, fluid-solid heterogeneous reaction systems have applications and importance in chemical and metallurgical processes. A successful reactor design for these processes depends essentially on kinetic data. The reactions occurring in the fluid-solid system generally have the following steps;

1. Diffusion of fluid reactant through the fluid layer to the surface of the solid.
2. Reaction of the fluid reactant and solid on the surface of the solid.
3. Diffusion of the products through the film layer to the bulk fluid.

The slowest of these sequenced steps is the rate-determining step. Because the products are not solid, as seen in reactions 4, there is not ash film resistance. Heterogeneous reactions can be classified into two groups, fluid-fluid reactions and fluid-solid reactions. For fluid-solid reactions, two models are suggested,

- Shrinking particle model
- Homogeneous reaction model

It was considered that the reaction occurs as [14,15].



and shrinking – core model was examined for the reaction, but it was determined statistically that the reaction did not fit this model. The kinetics was also tested using pseudo homogeneous reaction models, and it seems that the reactions rate does fit a pseudo

homogeneous first-order reaction model in the following form

$$-\ln(1-X) = kt \quad (6)$$

To observe the effect of the reaction temperature on the dissolution rate, the values of  $-\ln(1-X)$  versus time were plotted at different temperatures, as shown in Figure 9. From the slope of the straight lines, the rate constants for each temperature were calculated and then k values were derived. These values are given in Table 2.

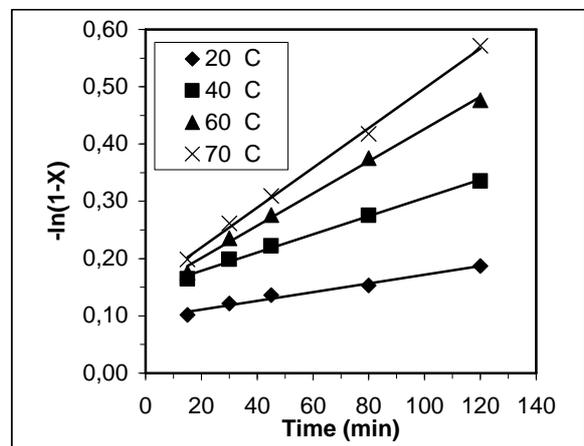


Fig. 9. Plot of  $t/t^*$  versus  $t$  for the temperature range of 20-70 °C

Table 2. Values of k for different temperatures

T, K	293	313	333	343
k, $\text{cm}^{-1}$	$0.76 \cdot 10^{-3}$	$1.59 \cdot 10^{-3}$	$2.81 \cdot 10^{-3}$	$3.48 \cdot 10^{-3}$

After calculating the rate constant, the values of  $\ln k$  versus  $1/T$  were plotted to find the activation energy and the Arrhenius constant, according to the Arrhenius equation in the following form

$$k = A \cdot e^{-E_a/RT} \quad (7)$$

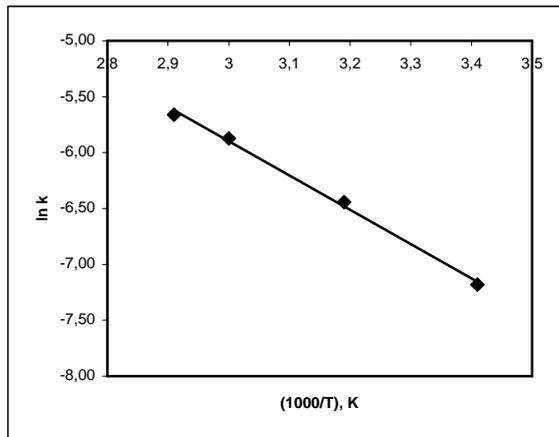


Fig. 10. Arrhenius plot for the temperature range of 20-70 °C.

From the straight lines in Fig. 10, the following values were calculated:

$$E_a = 25.51 \text{ kJ.mol}^{-1} \quad (\text{for } 20\text{-}70 \text{ } ^\circ\text{C})$$

$$A = 45.4 \times 10^{-2} \text{ cm.s}^{-1} \quad (\text{for } 20\text{-}70 \text{ } ^\circ\text{C})$$

#### 4. CONCLUSIONS

The optimum calcinated temperatures was found out as 700 °C. The dissolution of calcinated rhodochrosite in acetic acid was investigated, with the parameters having the ranges: temperature 20-70 °C; solid-to-liquid ratio 0.5-2 g solid/100 mL liquid; stirring speed 300-1050 min<sup>-1</sup>; average particle size (-1700+1400) – (-150) μm and acid concentration 0.3–5.0 M. It was observed that the dissolution of calcinated rhodochrosite increased with increasing reaction temperature, stirring speed, reaction time and acid concentration and with decreasing particle size and solid-to-liquid ratio. The kinetic analysis provided that the dissolution process is controlled by pseudo first-order reaction and the activation energy for the reaction was calculated to be 25.51 kJ.mol<sup>-1</sup>. Finally, it can be concluded that the manganese acetate can be produced by dissolution of calcinated manganese mineral with acetic acid.

#### Nomenclature

A	: Arrhenius constant (kJ.mol <sup>-1</sup> )
aq	: aqueous
b	: a coefficient in Eq.(5)
E <sub>a</sub>	: Activation energy (kJ.mol <sup>-1</sup> )
k	: rate constant in Eq.(6)
t	: time (min.)
t*	: time for complete conversion (min.)
T	: temperature (K)
s	: solid
X	: conversion fraction

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