Dissolution Kinetics of an Oxidized Copper Ore in Ammonium Chloride Solution

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The dissolution kinetics of malachite ore in ammonium chloride solutions has been investigated with respect to the effects of ammonium chloride concentration, particle size, solid/liquid ratio, stirring speed, and reaction temperature. It was determined that the dissolution rate increased with increasing ammonium chloride concentration, stirring speed, and reaction temperature. However, increasing particle diameter and solid to liquid ratio decreased the dissolution rate. Examination of data by heterogeneous model suggested that the dissolution rate is controlled by mixture kinetics. The following mathematical model was proposed to represent the reaction kinetics.

$$1 - 2(1 - x)^{1/3} + (1 - x)^{2/3} = 1 \cdot 10^{-5} \, (c)^{2.10} \cdot (d_p)^{-1.96} \cdot (\rho_{S/L})^{-0.64} \cdot (n)^{1.78} \cdot e^{(-8500/T)} \cdot t$$

The activation energy for the dissolution reaction was calculated as 71 kJ mol^{-1}.

Where x is the reacted fraction of the solid, c is the ammonium chloride concentration, d_p is the particle diameter, $\rho_{S/L}$ is the solid to liquid ratio, n is the stirring speed, E is the activation energy, T is the reaction temperature and t is the reaction time.

Key words:
Malachite, dissolution kinetics, ammonium chloride

Introduction

Among the copper oxide ores, malachite is the most common. Hydrometallurgical methods are used to obtain metallic values from low- grade ores because pyrometallurgical methods are not feasible. Therefore, investigations in this subject have been focused on the extraction of oxidized copper ores.[1–3]

The lixiviant used for copper leaching is generally sulfuric acid. However, other metals in ore matrix cause excess acid consumption. In addition, some impurities, particularly iron, dissolved in the leaching solution when sulfuric acid is used, cause some problems in further processing of the leaching solution.[4] For these reasons, ammonium chloride solution has been chosen as lixiviant in this research.

The leaching kinetics of oxidized copper ores have been studied, using different lixiviants. Leaching kinetics of azurite and malachite in EDTA solutions, has been investigated.[5] The determination of the optimum leaching conditions of malachite and the dissolution kinetics of malachite in sulfuric acid solutions, have been studied.[6,7] Furthermore, chlorine, ammonium carbonate, ammonia, sulphur dioxide, ammonium sulfate solution are used as the lixiviant for leaching of malachite.[1–3,8–12] Ammonium chloride solutions are employed as lixiviant for leaching of different copper minerals.[13,14]

The use of ammonium chloride solution has some advantages. One of the important characteristics of leaching in ammonium chloride solution is that pH 6.2 is almost constant during the leaching. In addition, ammonium chloride provides the chloride ion, and the ammonium ion gives rise to the protons required for the dissolution reaction of malachite. Ammonia produced by ammonium ions forms stable complexes with metal ions such as Cu^{+2}, Cu^+, Zn^{+2} and this leads to an increase in dissolution rate of minerals.[3,13] As ammonium chloride is a mild lixiviant, a high purity solution is obtained and Fe^{+3} ions are precipitated into $Fe(OH)_3$ during leaching of the mineral, due to the solution the medium has an adequate high pH value.[1]

In general, precipitation, direct electrowinning and solvent extraction-electrowinning methods have been used to recover copper from leach solutions.

Although, several precipitation methods are applied, cementation is the most common. In this method, any metal more active than copper could, potentially, be used as a precipitation agent. The process of solvent extraction can be stated briefly, the copper is selectively extracted from the leach solution by chelating Cu^{2+} with an organic solvent, and then the solvent is stripped from the chelat by sulfuric acid to give a solution to be amenable to electrowinning.[11] This system produces a very pure product.

According to the authors' knowledge, the dissolution kinetics of malachite in ammonium chloride

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solutions has not been investigated. Therefore, the objective of this research was to investigate the leaching kinetics of malachite in ammonium chloride solutions. In this context, the effect of ammonium chloride concentration, particle diameter, solid to liquid ratio, stirring speed, and reaction temperature on the leaching rate, were studied.

Material and methods

The malachite ore used in this study was obtained from Ovacik, Tunceli, Turkey. The material was grinded and sieved to obtain different fractions of particle diameter. The chemical composition and X-ray diffractogram of malachite ores used, are given in Table 1 and Figure 1. It is seen that the sample contains malachite, quartz and smithsonite (Fig 1). The experiments were carried out in a 500 mL spherical glass reactor equipped with a mechanical stirrer, reaction temperature control unit and a cooler to avoid loss of solution by evaporation. Ammonium chloride solution (350 mL) was placed in the glass reactor. The reactor was adjusted to the
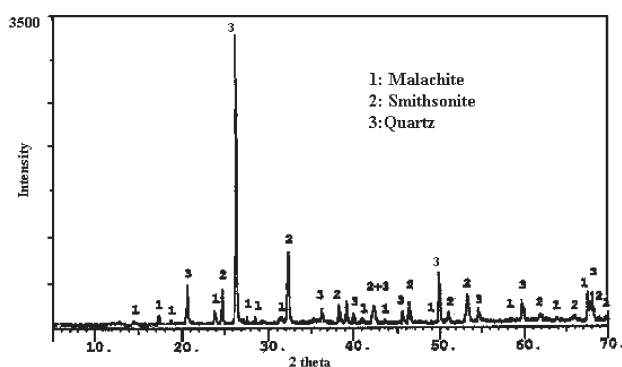

F i g . 1 – *X-ray diffractogram of the malachite ore*

T a b l e 1 – *Chemical analysis of malachite ore used in the study*

Component	$w/\%$
SiO_2	50.41
CuO	10.55
Fe_2O_3	8.43
Al_2O_3	1.81
ZnO	15.23
CaO	0.31
Na_2O	0.29
K_2O	0.06
MgO	0.07
Heating loss	12.40
Other oxides	0.44

desired temperature and stirring speed. The solid sample was added to the solution in reactor. At the end of experiment, the contents of the vessel were filtered and the amount of Cu^{+2} in the solution was determined.[15] In the experiments regarding the effect of particle diameter, the amount of copper in the leach solution was calculated by considering copper contents in each sieved fraction of malachite ore. Each experiment was repeated twice and the average of results was used in kinetic modeling. Ammonium chloride concentration, particle diameter, solid to liquid ratio, stirring speed and reaction temperature, were employed as experimental variables, which may affect the dissolution rate. The values of experimental variables are given in Table 2.

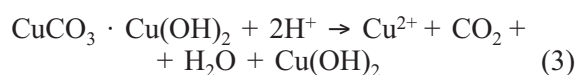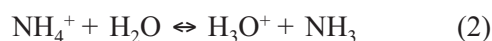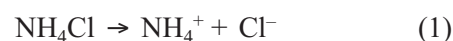T a b l e 2 – *The quantities and their range used in the experiments*

Quantities	Values
Concentration of NH_4Cl, kmol m^{-3}	1, 2, 3, 4*, 5
Particle diameter, mm	0.150–0.125, 0.125–0.106, 0.106–0.075, 0.075–0.063*, 0.063–0.053
Solid to liquid ratio, g g^{-1}	0.5/350, 1/350, 2/350*, 4/350, 8/350
Stirring speed, s^{-1}	1.67, 3.33, 5.00*, 8.33
Temperature, K	293, 303*, 313, 323

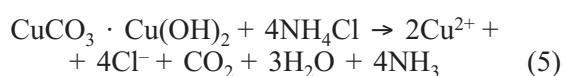* The values used when the effect of the other quantities was investigated

## Results and discussion

Dissolution reactions

The copper in the ore is in the form of $CuCO_3 \cdot Cu(OH)_2$. The reactions for malachite ores in ammonium chloride solution can be written as follows:
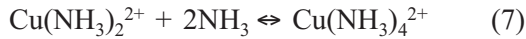
$$NH_4Cl \rightarrow NH_4^+ + Cl^- \qquad (1)$$

$$NH_4^+ + H_2O \leftrightarrow H_3O^+ + NH_3 \qquad (2)$$

$$CuCO_3 \cdot Cu(OH)_2 + 2H^+ \rightarrow Cu^{2+} + CO_2 + \\ + H_2O + Cu(OH)_2 \qquad (3)$$

$$Cu(OH)_2 + 2H^+ \rightarrow Cu^{2+} + 2H_2O \qquad (4)$$

The net equation of the dissolution is

$$CuCO_3 \cdot Cu(OH)_2 + 4NH_4Cl \rightarrow 2Cu^{2+} + \\ + 4Cl^- + CO_2 + 3H_2O + 4NH_3 \qquad (5)$$

The copper ion forms following amine complexes with ammonia

$$Cu^{2+} + 2NH_3 \leftrightarrow Cu(NH_3)_2^{2+} \qquad (6)$$

$$Cu(NH_3)_2^{2+} + 2NH_3 \leftrightarrow Cu(NH_3)_4^{2+} \qquad (7)$$
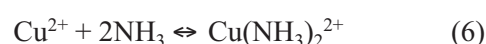
It is reported that $Cu(NH_3)_2^{2+}$ formed during the reaction is a intermediate and that, at the end, the complex of $Cu(NH_3)_4^{2+}$ is produced.[2,3]

At the end of each experiment, it was determined that no iron ions in the leach solution were present. In hydrometallurgical processing of copper, a leach solution containing no iron ions is an important advantage from an electrochemical viewpoint, as the iron ions cause additional energy consumption. Furthermore, the possibility of zinc recovery from the leach solution obtained in this study seems a significant result.

In this study, the leaching of copper from malachite ore has occurred selectively, and gang minerals consumed no reagent, therefore, most of the impurities were eliminated.

Effect of parameters

The dissolution rate of malachite was determined as a function of time by changing the ammonium chloride concentration, particle size, solid to liquid ratio, stirring speed and reaction temperature. The effect of one parameter was examined while the other parameters were kept constant. The results obtained were plotted as time versus reacted fraction, described as *x*, which is the ratio of amount of Cu in the solution to the amount of Cu in original malachite ore.

The effect of ammonium chloride concentration on the dissolution rate was examined at 1, 2, 3, 4 and 5 kmol m^{-3} concentrations while the particle diameter of 0.075–0.063 mm, solid to liquid ratio of $\rho_{S/L} = 2/350$, stirring speed of $n = 5$ s^{-1}, and the reaction temperature of 30 °C were kept constant. The results plotted in Figure 2 show that the dissolution rate increases with increase in the ammonium chloride concentration.
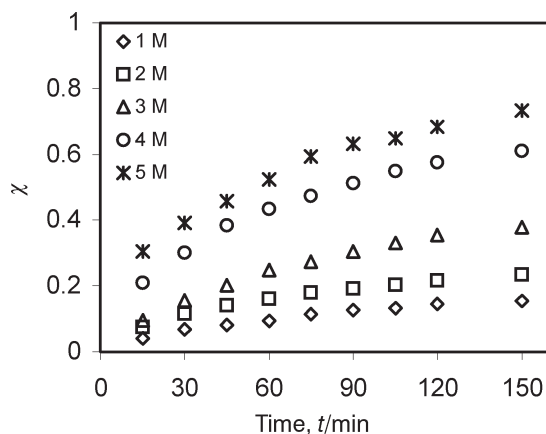
The effect of particle dimension on the dissolution rate was determined by using 0.150–0.125, 0.125–0.106, 0.106–0.075, 0.075–0.063 and 0.063–0.053 mm fractions while ammonium chloride concentration, stirring speed, solid to liquid ratio and the reaction temperature were kept constant at $c = 4$ kmol m^{-3}, $n = 5$ s^{-1}, $\rho = 2/350$, and $T = 30$ °C, respectively. Figure 3 shows that as the particle diameter decreases the dissolution rate increases due to increased surface area.
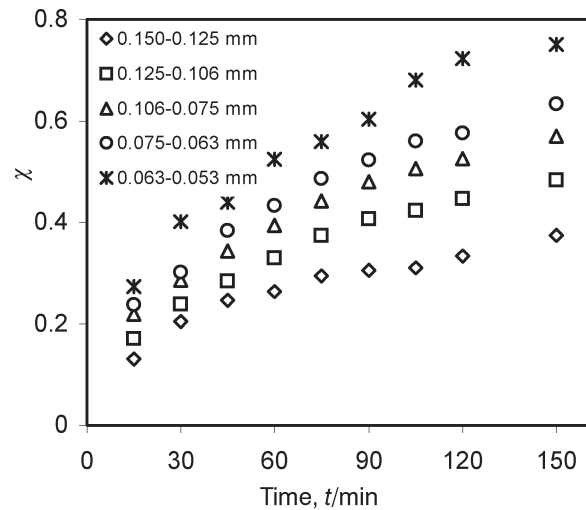

F i g . 3 – *The effect of particle diameter on the dissolution rate*

The effect of solid to liquid ratio was investigated by carrying out experiments at $\rho_{S/L} = 0.5/350$, 1/350, 4/350 and 8/350 values. Ammonium chloride concentration, particle diameter, stirring speed and the reaction temperature were kept constant at $c_{NH_4Cl} = 4$ kmol m^{-3}, $d_p = 0.075$–0.063 mm, $n = 5$ s^{-1} and $T = 30$ °C, respectively. As seen in Figure 4, the dissolution rate decreases as solid to liquid ratio increases.

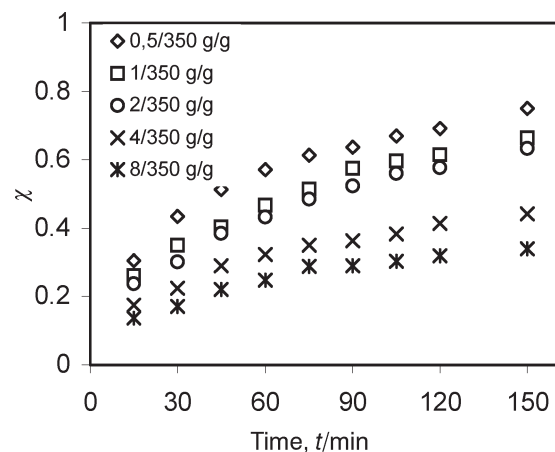F i g . 2 – *The effect of ammonium chloride concentration on the dissolution rate*

F i g . 4 – *The effect of solid to liquid ratio on the dissolution rate*

Tests were carried out at stirring speed of n = 1.67, 3.33, 5 and 8.33 s^{-1} to observe the effect of stirring speed on the dissolution rate. At these experiments, ammonium chloride concentration, particle size, solid to liquid ratio and the reaction temperature were fixed at c = 4 kmol m^{-3}, d_p = 0.075–0.063 mm, $\rho_{S/L}$ = 2/350 and T = 30 °C, respectively. The increase in stirring speed leads to increases in the dissolution rate (Figure 5).
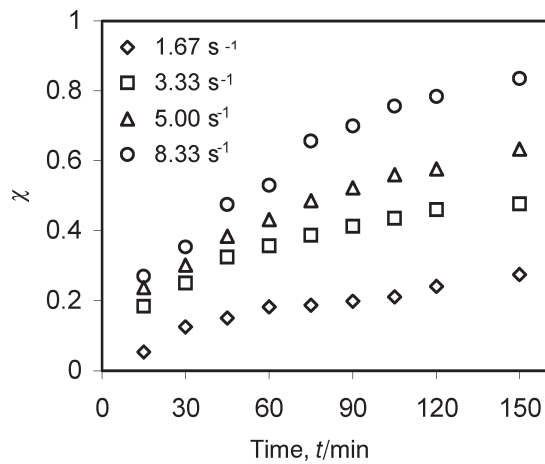

F i g . 5 – *The effect of stirring speed on the dissolution rate*

The effect of the reaction temperature on the dissolution rate was also studied. The reaction were tested at 20, 30, 40 and 50 °C while ammonium chloride concentration, particle diameter, solid to liquid ratio and the stirring speed were set at c = 4 kmol m^{-3}, d_p = 0.075–0.063 mm, ρ = 2/350 and n = 5 s^{-1}, respectively. Figure 6 shows that higher dissolution rates were obtained as the reaction temperature increased.
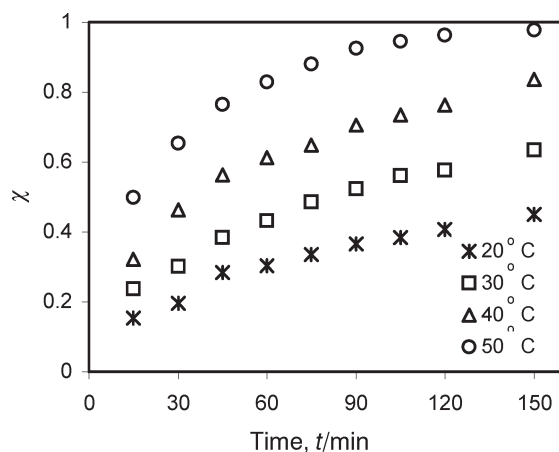

F i g . 6 – *The effect of reaction temperature on the dissolution rate*

Kinetic analysis

It has been assumed that the solid particles have spherical shape and do not change their dimensions during reaction. In addition, they contain reactive material uniformly embedded in an inert matrix.[1]

By considering that insoluble gangue minerals covering the unreacted malachite surface form an ash layer, the unreacted-core model can be chosen for kinetics calculations.

Let us consider a solid particle B immersed in a fluid A, and reacting as:

$$A_{(fluid)} + b\, B_{(solid)} \rightarrow products$$

If the fluid A diffuses from r_0 to r_c and react at r_c, the reaction rate of the particle is controlled by diffusion through ash layer. By pseudo steady-state assumption, the material balance of component A can be written on the particle between r_0 and r_c for a spherical particle.[16]

$$D\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dc}{dr}\right)=0 \qquad (8)$$

By solving Eqn. 8 and by making equal the rate of reaction to the diffusion rate, the time required for the particle to reduce the unreacted core from r_0 to r_c is obtained as follows:[16,17]

$$t=\frac{c_B}{b\,D\,c_0}\left[\frac{r_c^3}{3r_0}-\frac{r_c^2}{2}+\frac{r_0^2}{6}\right] \qquad (9)$$

Eqn. 9 can be written in terms of reacted fraction of the solid (x)

$$1-3(1-x)^{2/3}+2(1-x)=\frac{6bDc_0}{c_B r_0^2}t \qquad (10)$$

If the reaction rate is controlled by chemical reaction, the integrated rate equation is expressed by following equation.[17,18]

$$1-(1-x)^{1/3}=\frac{b\,k_d\,c_0}{c_B r_0}t \qquad (11)$$

These models have been applied to fluid-solid reactions systems.[1–5,7,14,19–21] The results of this study were evaluated according to eqs. 10 and 11 that are theoretical models, and $1 - 3(1 - x)^{2/3} + 2(1 - x)$ versus t plots corresponding to ash layer diffusion model gave straight lines. However, since the dissolution rate was sensitive to temperature (Figure 6), it has been considered that the rate of the process can be controlled by mixture kinetics. Therefore, alternative mixture kinetics models were tested and, it was found that following equation could suitably

good represent the kinetics of the dissolution process.

$$1 - 2(1 - x)^{1/3} + (1 - x)^{2/3} = k\,t \qquad (12)$$

where k is the apparent rate constant.

As an example in Figure 7, at different temperature, the plots gave straight lines passing through the origin whose slopes are equal to k. In this case, the ash layer is $Cu(OH)_2$ formed as an intermediate product and $Fe(OH)_3$ formed from iron in the ore; that they cover surface of the particles and this product layer causes the reduction of the diffusion rate. $Fe(OH)_3$ and $Cu(OH)_2$ which blocked the surface of the malachite ore can be broken by increasing the stirring speed. Consequently, the rate of diffusion to surface of the malachite particle can be increased.
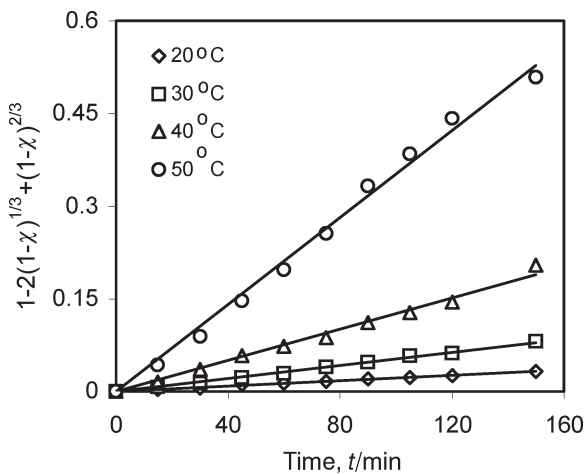

F i g . 7 – *Plots of $1 - 2(1 - x)^{1/3} + (1 - x)^{2/3}$ versus t for different temperatures*

On the other hand, the experimental variables of this study such as temperature, particle size, ammonium chloride concentration, stirring speed and solid to liquid ratio, affect reaction kinetics. To determine the effect of these parameters on the kinetics model, the following semi-empirical model was established.

$$1 - 2(1-x)^{1/3} + (1-x)^{2/3} = k_0 c^a d_p^b \rho_{S/L}^c n^d e^{-E/RT} t \quad (13)$$

The values of the constants k_0, a, b, c and d were estimated as $1 \cdot 10^{-5}$, 2.10, –1.96, –0.64 and 1.78, respectively.

Inserting the estimated values into Eqn.13 it is obtained the following kinetics model.

$$\begin{aligned} 1 - 2(1 - x)^{1/3} + (1 - x)^{2/3} = \\ = 1\cdot 10^{-5} c^{2.10} d_p^{-1.96} \rho_{S/L}^{-0.64} n^{1.78} e^{-8500/RT} t \end{aligned} \qquad (14)$$

In order to determine the activation energy of the dissolution reaction; $\ln k$ versus $1/T$ was plotted. The slope of this line in Figure 8 gives the E/R value and intercept is k_0. From E/R, activation energy E was calculated as 71 kJ mol^{-1}. Figure 9 shows the agreement between the experimental conversion values and the values predicted from model.
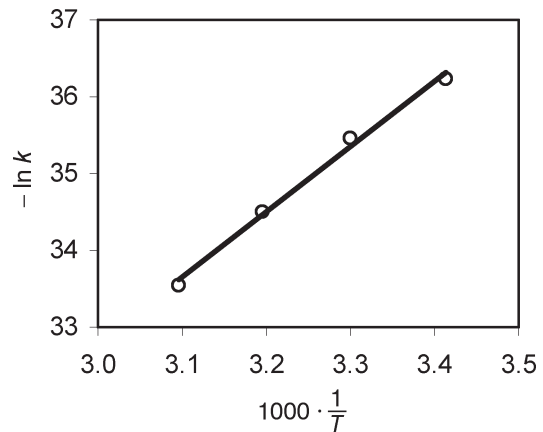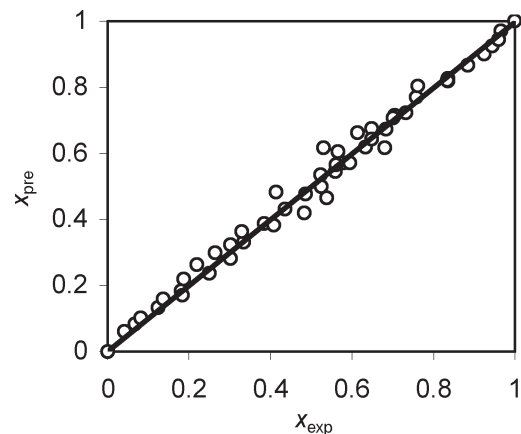

F i g . 8 – *Arrhenius plot*

F i g . 9 – *The plot of experimental conversion values versus calculated values from the model*

Conclusions

In the present study in which the dissolution kinetics of malachite in ammonium chloride solutions was studied, it was found that the reaction rate increases with increase in ammonium chloride concentration, reaction temperature, stirring speed, with decrease in particle size and solid to liquid ratio.

An unreacted shrinking core model can be used to describe the dissolution kinetics of malachite ore in ammonium chloride solutions. The dissolution process was found to be controlled by mixture kinetics. Dissolution rate can be expressed by Eqn. 14 which is a semi-empirical mathematical model representing the process properly.

The following advantages of the ammonium chloride leach system for malachite can be proposed:

1. Ammonium chloride is a convenient leaching agent for selective leaching of the copper from the malachite ore.

2. This process usually produces a very pure solution since the mild operating conditions are available.

3. The reactants are consumed at a minimum level by this system.

4. The resultant solution is entirely free of iron.

ACKNOWLEDGEMENT

Nomenclature

x – fractional conversion of malachite

c_{NH_4Cl} – ammonium chloride concentration, kmol m^{-3}

d_p – particle diameter, m

$\rho_{S/L}$ – solid to liquid ratio, g g^{-1}

n – stirring speed, s^{-1}

T – temperature (K)

k_0, a, b, c and d are the constants in Eqn.13

t – reaction time, s

r – Position in the particle, m

r_c – position of the reaction front inside the particle, m

r_0 – initial outside radius of the particle, m

c_0 – concentration of fluid outside the particle, mol m^{-3}

c_B – apparent concentration of the solid reactant, mol m^{-3}

k – apparent reaction rate coefficient, s^{-1}

k_d – mass trasfer coefficient, m s^{-1}

D – diffusion coefficient of fluid in the ash layer inside the particle, m^2 s^{-1}

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