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M. Gharabaghi[a]; B. Rezai[a]; M. Irannajad[a]; M. Noaparast[b]
[a] Department of Mining & Metallurgical Engineering, Amirkabir University of Technology, Tehran, Iran [b] School of Mining, Faculty of Engineering, University of Techran, Tehran, Iran

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Tailings Management and Leaching Kinetics in Iron Removal from Kaolin Washing Plants Tailings

M. Gharabaghi,[1] B. Rezai,[1] M. Irannajad,[1] and M. Noaparast[2]
[1]*Department of Mining & Metallurgical Engineering, Amirkabir University of Technology, Tehran, Iran*
[2]*School of Mining, Faculty of Engineering, University of Techran, Tehran, Iran*

A study has been made of the leaching process to remove iron oxides from quartz presented in kaolin washing plant tailings. The tailings mineralogical constituents were quartz, clay minerals, hematite, and calcite. The leaching rate of Fe_2O_3 increased with increasing acid concentration, temperature, reaction time, and decreasing pulp solid percent. Shrinking core first-order kinetics model was presented to analyse the data. The activation energy was 23.51 kJ/mol and process was reaction-controlled process ($1-(1-\alpha)^{1/3} = 46.52e^{-23.51/RT}t$). Using this method, the Fe_2O_3 amount decreased to 0.03% with a recovery of 89.06%. The results showed that the leaching approach was the best method for the management of these tailings.

Keywords iron oxides; leaching kinetics; mine waste management; silica; sulphuric acid

INTRODUCTION

Mining activities are known to be a major source of contamination. Movement of contaminants in and near mining sites is a complex function of the geology, hydrology, geochemistry, pedology, meteorology, microbiology, and mining and mineral processing history (1).

Large and medium scale mining activities were intensively developed in several regions of Iran resulting in significant environmental damage from tailings and few scientific studies have evaluated tailings related contamination problems. Recycling or reusing mining tailings for other industry is a good approach for minimizing these problems. Beneficiations of old tailings have become more important in recent years due to the shortage of high quality ore reserves. This situation naturally brings about the processing of tailing to produce marketable product.

Zonoz kaolin mine has 40 Mt ore reserves and the samples were taken from its tailings dam contained high amounts of silica (about 90%) and quartz amount in the samples was about 82.5% (2). These tailings can be used as raw material for the glass making industry but the major problem was iron impurity which confines this application.

The presence of metal, especially iron in many industrial minerals such as quartz sands, kaolin, and talc can prevent their use by industry. Iron content can limit the application area of quartz sand. The lower the iron content, the greater the area of application. The sand with iron content lower than .0035% is suitable for float glass manufacture (3).

Considerable efforts have been directed towards the removal of iron contaminants by physical and chemical means (4–5). Typically, physical and chemical methods such as gravity and magnetic separation, attrition, flotation, and acid or alkaline leaching are used to remove iron from quartz sands (5–8). However, physical separation techniques are generally less effective for iron removal than chemical leaching. HGMS (high gravity magnetic separation) or blending processes are also employed in the beneficiation of industrial minerals. Depending on the type, form, and size of iron minerals, a combination of these techniques are to be employed to remove the maximum quantity of iron mineral impurities.

Acidic reductive leaching is one of the best known and most widely employed chemical processes for beneficiating minerals of industrial interest. Conventional acidic leaching with sodium dithionite ($Na_2S_2O_4$), employed to leach industrial minerals used in the production of ceramics, glassware, paper, etc., does not always allow products of high quality to be obtained (9). Other effective technique is based on the use of H_2SO_4, HCl, HNO_3 or organic acids for iron removal (5).

This investigation is focused on the application of the sulphuric acid to process samples taken from Zonoz kaolin washing plant tailings which is located in mountainous and wet areas in northwest of Iran. This region has a large amount of rainfall that facilitates the transfer of metals (10). The geochemistry properties of minerals, weather conditions, and the type of geological structure in the tailings dam increase the metals pollution and their

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Address correspondence to M. Gharabaghi, Department of Mining & Metallurgical Engineering, Amirkabir University of Technology, Hafez St., Tehran, Iran. Tel.: +98 21 64542900; Fax: +98 21 66405846. E-mail: m.gharabaghi@gmail.com

TABLE 1
The chemical analysis of the head sample

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	TiO_2	L.O.I
Amount (%)	90.76	1.53	0.32	3.31	0.04	0.25	0.01	3.72

environmental impacts (11). Therefore, it is necessary to mitigate these negative effects and preventing severe environmental impacts. In this study, leaching with sulphuric acid was applied to remove as much Iron (III) from samples as possible to achieve an acceptable Fe_2O_3 level and also introduce a good method for tailings management. The objectives of this study were to investigate the main factors involved in the leaching such as reaction time, acid concentration, pulp solid percent, and temperature, and also to determine what mechanism controls the rate of dissolution of iron impurities and which kinetics model can be applied. Using this method, it is possible to reuse these tailings as new material for glass making industries.

EXPERIMENTAL

Materials

The samples were taken from tailings of kaolin washing plant used in this investigation. Complete physical, chemical and mineralogical characterisation was carried out before performing the leaching tests. The chemical analysis of representative samples is presented in Table 1. The samples contain non-desirable iron as shown in the Table 1. X-ray diffraction (XRD) analysis indicated that the mineralogical constituents were quartz, kaolinite, calcite and small quantity of hematite (Fig. 1). The particle size analysis showed that the sample size was −210 micron.

Methods

The −0.210 + 0.032 mm fraction was used in a 500 ml glass batch reactor and agitated with a stirrer at 500 rpm. Previous experiments results had shown that further increases of the stirring speed had no effect on the iron impurity dissolution rate. Experiments were carried out with varied acid concentration, pulp density, reaction times, and process temperatures. The reaction was stopped by placing the reactor in an ice bath at the end of each reaction and then leach slurry and solid phase were separated by filtration and the remaining solid dried at 110°C in an electrical oven, before weighing and analysis. Then the products were analysis for Fe_2O_3 content. After leaching, for each experiment the % Fe_2O_3 removal was calculated as follows:

$$\%\ Fe_2O_3\ \text{removal} = \left[\frac{f - c}{f}\right] \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Effect of Reaction Time

In the leaching system, the following reaction takes place (Eq. (2)). Figure 2 presents the results obtained from this reaction under different reaction times at 25°C using 15 (kg/t) sulphuric acid and 50% solid percent. With the increasing of the reaction time, the Fe_2O_3 removal

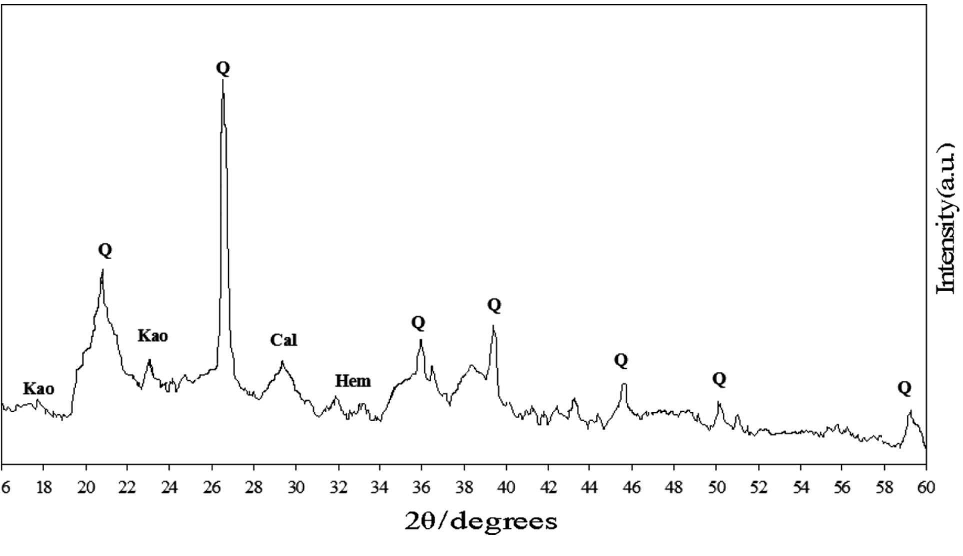

FIG. 1. X ray diffraction pattern (XRD) of head sample. (Kao = Kaolinite, Q = quartz, Cal = Calcite, Hem = Hematite).

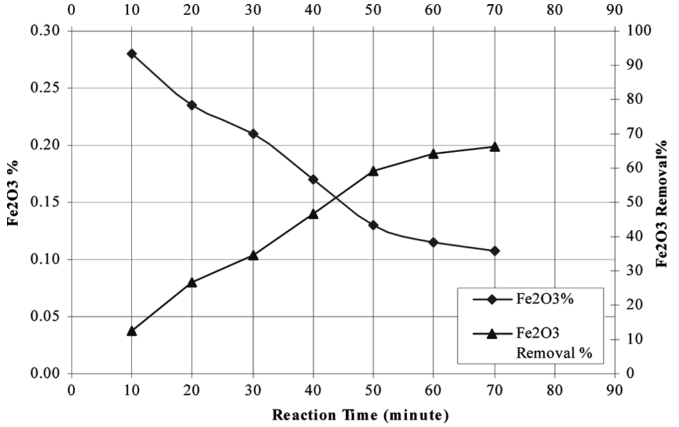

FIG. 2. Effect of reaction time on Fe_2O_3 contents (15 (kg/t) CA; 50% w/w ore; 25°C).

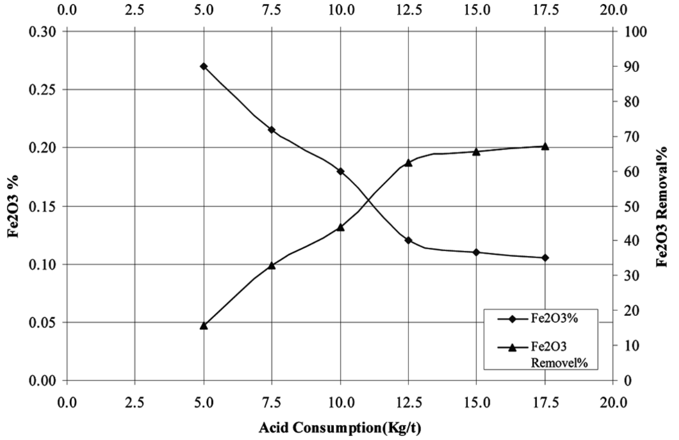

FIG. 3. Effect of acid concentration on Fe_2O_3 contents (25°C; 50 minutes; 50% w/w ore).

increases along with the corresponding decrease in Fe_2O_3 percent. It is known that the rate of Fe_2O_3 dissolution is governed by the rate of diffusion of sulphuric acid, formation of solid product at the surface of the hematite, and the chemical reaction rate at the surface of the particles.

$$Fe_2O_3 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 3H_2O \qquad (2)$$

The time required for Fe_2O_3 dissolution depends on the particle size and the nature of the adherent materials existing in the samples. After 50 minute, the reaction was observed to reach equilibrium or caused the formation of a solid product at the surface of hematite which prevented further leaching of the Fe_2O_3 as shown in Fig. 2. Another important factor that prevented further dissolution is the precipitation of clay minerals and other insoluble silicates which are present in the leaching system on the hematite. Therefore 50 minute was selected as optimum leaching time and extended leaching times (>50 minute) was found to have no significant effects on Fe_2O_3 percent.

Effect of Acid Concentration

For the selective leaching of the iron impurities both the nature of the acid and its concentration are significant factors. To study acid concentration effects on leaching performance, a number of experiments were carried out. The effects of acid concentration were investigated at a dissolution time of 50 minute and a temperature of 25°C. As observed from the experimental results given in Fig. 3, the Fe_2O_3 content decreased by increasing the acid concentration up to 12.5 (kg/t), and then remained almost constant.

Decreasing Fe_2O_3 contents as acid concentration increases to 12.5 (kg/t), is due to the acid concentration effect on increasing the H^+ activity, that result in further dissolution of iron impurities. As shown in Fig. 3, any increase in the acid concentration more than 12.5 (kg/t) had no significant effects on the leaching rate of Fe_2O_3. The major factor influenced results were type and characterization of the rock and optimum acid concentration regarding to the obtained results, was 12.5 (kg/t).

Effect of Pulp Solid Percent

Figure 4 presents the leaching results using different solid values. The amount of iron impurity decreased with decreasing pulp solid percent and at the higher solid percent, the Fe_2O_3 percent increases with the corresponding reduction in Fe_2O_3 removal.

The improvement of leaching results in low solid percent might be attributed to the fact of the amount of reagent to each particle increases with decreasing solid amounts in the leaching process. Therefore in the diluted pulp it was

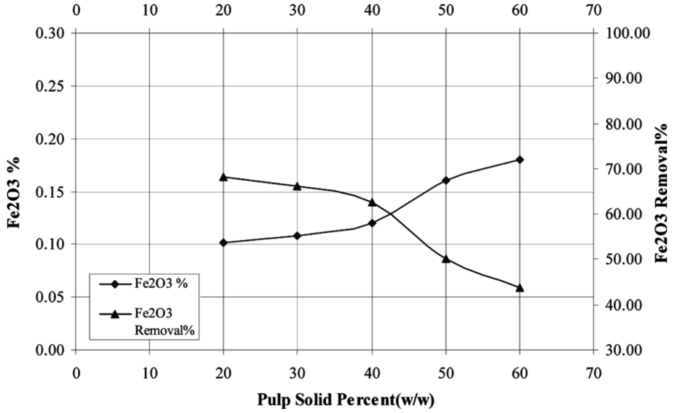

FIG. 4. Effect of pulp density (% solids) on Fe_2O_3 contents (25°C; 50 minutes; 12.5 (kg/t) CA).

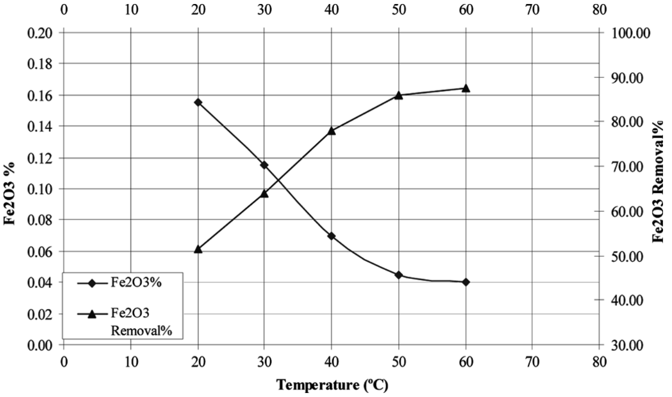

FIG. 5. Effect of temperature on Fe_2O_3 contents (50 minutes; 12.5 (kg/t) CA; 40% w/w ore).

expected to achieve an increase in the dissolution rate. Although with decreasing pulp solid percents it is possible to improve the leaching performance, but it has a limitation because of the process economy. Considering the process performance and economy, the results indicate 40% as the optimum percent solids.

Effect of Temperature

To examine the effect of reaction temperature on the leaching process a number of experiments were carried out in the range 20–60°C for a reaction time of 50 minutes in 12.5 (kg/t) sulphuric acid. It is observed in Fig. 5, that by the increasing of temperature, the Fe_2O_3 content was decreased from 20 to 50°C and then, it remains almost constant.

Increasing Fe_2O_3 removal by increase in temperature is attributed to the fact of higher temperatures which improve reaction rate and reactant diffusion. After about 50°C the leaching rate of iron impurity remains almost constant. Regarding to results shown in Fig. 5, the optimum temperatures was 50°C.

Final Optimum Experiment

By optimization of the leaching parameters summarised in Table 2, the final test was performed. The results showed that with employing these optimum factors, it was possible to reduce iron content to marketable level with 89.06% iron removal.

KINETIC ANALYSIS

In heterogeneous reactions of solid-liquid, the soluble reactants diffuse across the interface and/or through the porous solid layer. Afterwards, chemical reactions occur. In a fluid-solid reaction system, the reaction rate is controlled either by the diffusion of the reactant through the solution boundary layer, or through a solid product layer, or by rate of the chemical reaction at the surface of the core of unreacted particles. The rate of the process would be controlled by the slowest of these sequential steps. The shrinking core model considers that the leaching process is controlled by these steps. In the absence of an ash/product layer around the unreacted core during the reaction, there would be only two controlling steps, fluid film diffusion or chemical reaction control. The simplified equations of the shrinking core model when either diffusion or the surface chemical reactions are the slowest step can be expressed as follows, respectively (5,12):

$$\left[1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}}\right] = \frac{2M_B D C_A}{\rho_B a r_0^2} t = k_d t \qquad (3)$$

$$\left[1 - (1-\alpha)^{\frac{1}{3}}\right] = \frac{k M_B C_A}{\rho_B a r_0} t = k_r t \qquad (4)$$

If the diffusion through the product layer controls the leaching rate, the relation between the left side of Eq. (3) and time must be linear. Equation (4) reveals that if the surface reaction controls the rate, there must be a linear relation between the left side of equation and time, and the slope of this line is rate constant, k_r. The rate constants values, k_d and k_r calculated from Eqs. (3) and (4), respectively, for each temperature are given in Table 3. These results propose that the dissolution rate of iron impurities is controlled by surface chemical reactions. The dissolution of iron impurity at various reaction temperatures is presented in the Fig. 6. The application of surface chemical reactions kinetic model $(1-(1-\alpha)^{1/3})$ using a specific size range of particles and the acid concentration under known solid percent for different temperatures is shown in Fig. 7. Using the Arrhenius equation, $k_r = k_0 e^{-Ea/RT}$, a plot of $\ln k_r$ versus 1/T is a straight line with a slope of $-E_a/RT$ and an intercept of $\ln k_0$. This equation was plotted as $\ln k$ versus (1/T) for each reaction temperature and it is

TABLE 2
Most suitable conditions for leaching

Time (minute)	Acid concentration (kg/t)	Solid percent (%)	Temperature (C)	Fe_2O_3 (%)	Fe_2O_3 removal (%)
50	12.5	40	50	0.03	89.06

TABLE 3
The k_r, k_d and correlation coefficients values for different temperatures

Temperature (°C)	Rate constants (minute^{-1})		Correlation coefficient (R^2)	
	k_r	k_d	k_r	k_d
20	0.00282	0.0005	0.989	0.939
30	0.00412	0.0010	0.981	0.957
40	0.00608	0.0019	0.989	0.932
50	0.00781	0.0028	0.9934	0.966
60	0.00864	0.0033	0.998	0.968

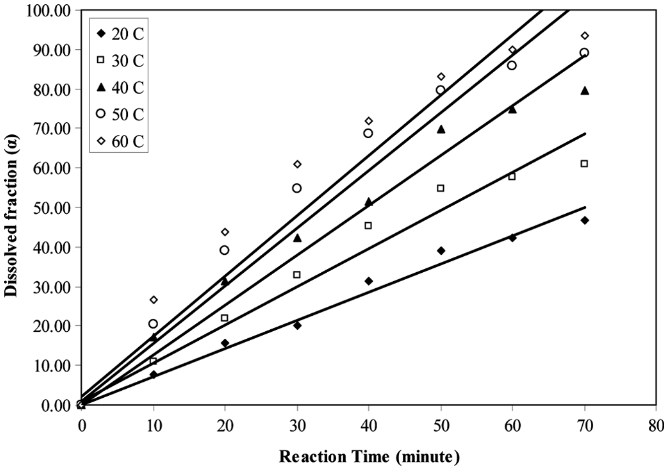

FIG. 6. Effect of leaching time on the dissolved fraction for various temperatures. (12.5 (kg/t) CA; 40% (w/w) ore; stirrer speed: 500 rpm; 50 minutes; particle size: −0.210 + 0.32 mm.)

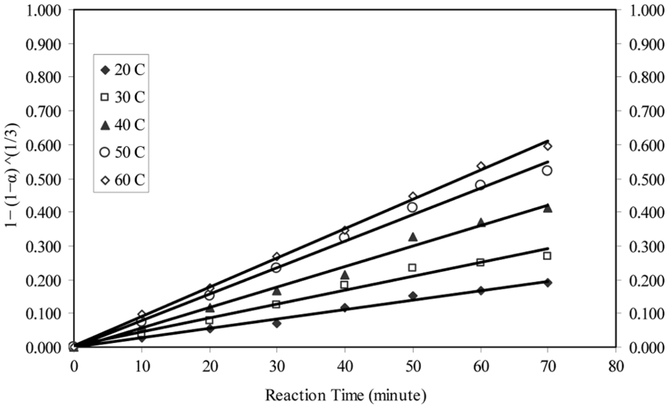

FIG. 7. Plot of $1-(1-\alpha)^{1/3}$ versus t for different temperatures.

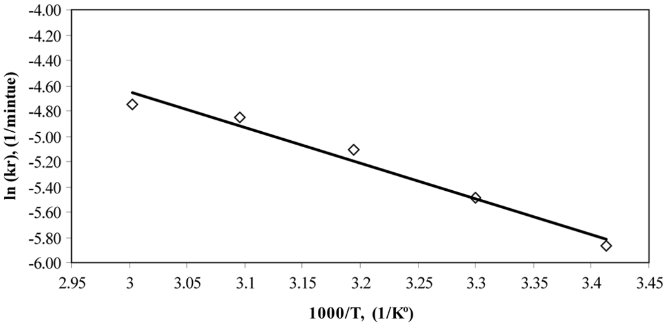

FIG. 8. Arrhenius plot for the selective dissolution of iron impurities.

shown in Fig. 8. Using the Arrhenius equation, the following values were calculated:

$$E_a = 23.51\,\mathrm{kJ/mol} \quad k_0 = 46.52\,\mathrm{s}^{-1}$$

This value of activation energy clearly suggests the chemical reaction control for the process (5,13,14). The value of the obtained activation energy in the leaching process reveals that the dissolution of iron impurity from tailings in sulphuric acid is controlled by chemical change. After the evaluation of activation energy and the preexponential factor, the kinetic model for the leaching process (Eq. (5)) can be expressed as:

$$1-(1-\alpha)^{1/3} = 46.52\,e^{-23.51/RT}t \qquad (5)$$

Depending on the parameter conditions and the type and nature of the solid materials and leaching reagent, different reaction mechanisms have been suggested. However, most of the studies have concluded that the overall rate of dissolution is controlled by chemical reactions that supported the results of the present study (5,14,15). Therefore, kinetic analysis for the rate impurities leaching shows that the diffusion-controlled mechanism is not the main mechanism in the dissolution process.

CONCLUSIONS

In the present study, Zonoz kaolin washing plant tailings management was performed using agitating leaching method. These tailings have metals and can be a major source of contamination in this region. Sulphuric acid was used to decrease the Fe_2O_3 contents in the which contained about 90.76% SiO_2 and 0.32% Fe_2O_3. This treatment upgraded the samples to produce marketable silica concentrates and it was the best method for tailings recycling. Depending on the leaching conditions, the results indicated that the leaching rate of iron impurities increased with increasing the reaction time, acid concentration and temperature, and decreasing pulp solid percent. According to the results analysis, the parameters values for the optimum selective leaching rate were equal to 50 minutes of reaction time, acid concentration 12.5 (kg/t), temperature 50°C and 40% solid. In the selective leaching of iron impurity in the determined optimum conditions, it was found that the Fe_2O_3 content can be reduced to 0.03 with Fe_2O_3 removal of 89.06%.

The dissolution process was found to be controlled by the shrinking core model for the reaction-controlled process. The value of the activation energy was found to be 23.51 kJ/mol, which agrees with a chemically controlled reaction.

The experimental results indicate that using the agitating leaching approach, it is possible to produce marketable silica concentrate and this method is the best approach for Zonoz kaolin washing plant tailings management.

NOTATION

c	% Fe_2O_3 in concentrate,
f	% Fe_2O_3 in feed sample,
C_A	acid concentration (%, w/w),
α	fraction reacted,
k	kinetic constant, ($\mathrm{m\,min^{-1}}$)
M_B	molecular weight of the solid, (g/mol)
ρ_B	molar density of solid, $\left(\frac{\text{moles B}}{\text{m}^3\text{ solid}}\right)$
a	the stoichiometric coefficient of the reagent in the leaching reaction,
r_0	the initial radius of the solid particle, (m)
t	the reaction time, (s)
T	the temperature, Kelvin
D	the diffusion coefficient in the porous product layer, $\left(\frac{\text{m}^2}{\text{s}}\right)$
k_d and k_r	rate constants, which are calculated from Eqs. (3) and (4), respectively.

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