Investigation of Leaching Kinetics of Ulexite Waste in Oxalic Acid Solutions

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doi: 10.15255/CABEQ.2013.1860
Original scientific paper
Received: September 9, 2013
Accepted: July 24, 2014

The dissolution of ulexite waste in oxalic acid solutions was studied in a batch reactor after characterization of the waste by X-ray diffraction (XRD) analysis and X-ray fluorescence (XRF) analysis. The dissolution parameters in this study were acid concentration, stirring rate, and reaction temperature. The experimental data were examined using homogeneous and heterogeneous kinetic models, and the dissolution kinetics of the waste was determined to be a first-order reaction control model. The activation energy of ulexite waste in oxalic acid solution was also calculated. It was observed that the dissolution rate increased with increasing reaction temperature, stirring rate and acid concentration. The kinetic model of the dissolution process was determined to be a first-order reaction control model. The activation energy was found to be 41.09 kJ mol⁻¹.

Key words:
ulexite waste, leaching kinetics model, dissolution, boric acid, oxalic acid

Introduction

Boron (B) has both strategic and industrial importance, and is one of the most important elements in the world. In Turkey, it is an economically important resource. Turkey has 72.2% of the world’s boron reserves based on 851 million tons of B₂O₃ content on a total reserve basis. Boron is one of the most important raw materials in industry, but does not exist in a free state in nature; it occurs naturally combined with oxygen and other elements in compounds such as sodium, calcium and magnesium borates. Borate minerals generally occur along with calcite, dolomite, gypsum, realgar, orpiment, anhydrite and sulfur. Boron minerals contain many clay minerals such as montmorillonite, illite, chlorite and hectorite. Boron and its compounds are used in nuclear engineering, in hard and refractory alloys, in the production of heat resistant polymers, and in the glass, ceramics, cosmetics, leather, rubber, paint, textile and agricultural industries. One commercial boron mineral is ulexite, and concentrated ulexite is used, for example, to produce boric acid, sodium perborate and boric acid. Ulexite is a calcium-sodium borate mineral with the chemical formula NaCaB₁₀O₁₆ · 5H₂O, and its content of B₂O₃ is 43%, while colemanite is a calcium borate mineral (theoretically, 50.8% B₂O₃) with a monoclinic crystal structure and a chemical composition of Ca₇B₆O₁₇ · 5H₂O.

Generally, the production of boric acid from ulexite is performed by leaching in mineral or organic acids. During the leaching of ulexite in acid solutions, boric acid, B(OH)₃, forms as a product, and sodium or calcium salts as a by-product. The boric acid remains in the liquid phase, and these insoluble salts are separated by filtration from the pregnant solution containing boric acid. Finally, boric acid is crystallized by cooling. Filtration of calcium salts from pregnant solution has an important role in the production of boric acid, since these salts reduce the quality of the boric acid produced and generate environmental pollution. Bayca reported that boric acid is currently produced in Turkey by the acid leaching process. In this process, colemanite concentrate is leached with a hot sulfuric acid solution, the result being calcium ions. The calcium ions react with sulfate ions, and gypsum forms as a byproduct. To produce high-purity boric acid, gypsum is separated from the reaction solution by filtration.

Serious environmental and health problems occur when significant amounts of boron waste rocks or fines, formed in operations at the end of mining activities, are discharged to landfill. From the aspect of living habitats, ecosystems, and the natural environment, as well as from an economic aspect, boron waste should be evaluated and the boron in the waste should be recovered. Physically and physicochemically beneficial methods such as flotation, magnetic separation, and thermal processing have been used to recover boron from boron waste.
such as tincal, colemanite and ulexite. Although the content of B$_2$O$_3$ in pure ulexite can reach a level of 41–43 %, waste ulexite contains 21.83 % B$_2$O$_3$.\textsuperscript{7,20–23} Mineral acids are generally used as lixiviants in hydrometallurgy. The important factors taken into consideration for the selection of an acid are as follows: 1) The acid should be easily and economically recoverable for reuse; 2) The selected lixiviant for dissolution should be cheap; and 3) After the process, the products must be collectable separately.\textsuperscript{8} However, such acid processes are uneconomical because excess acid is consumed during leaching. Moreover, with inorganic acid, the dissolution is very severe, and undesired impurities can pass into the leaching media. When weaker acid or alkaline solutions are used in the leaching process, the corrosive effect is reduced.\textsuperscript{24,25} Organic acids provide mildly acidic conditions (pH = 3–5), and therefore, organic acids such lactic acid, citric acid and gluconic acid can be attractive leaching agents. They are also easily biodegradable.\textsuperscript{26} Although organic acids are not highly effective in dissolving ores or minerals, they have a less corrosive effect than inorganic acids. Besides, it has been found that organic acids used at high temperatures decompose in a shorter time. In the light of these advantages, the use of organic acids is widespread in industrial processes.\textsuperscript{24,25}

There are many studies reported in the literature involving the dissolution kinetics of ulexite in various solutions. These studies are summarized in Table 1.

The aim of this study was to investigate the dissolution of ulexite waste in oxalic acid solutions and to determine the effects of various experimental parameters on the kinetics of reaction. No study was found in the literature that used ulexite waste. Therefore, the present study can have an important environmental effect, and can also assess the value of the ulexite waste provided from tailing dams in the area of Balikesir-Bigadic.

### Materials and methods

The ulexite waste used in this study was provided from Bigadic in the province of Balikesir, Turkey. The waste was dried under atmospheric conditions. The characterization of the waste by XRD (Rigaku D/Max-2200/PC) and XRF analysis was carried out on a Shimadzu apparatus with Cu Kα radiation.

The flowsheet of dissolution experimental methods is given in Fig. 1 The detailed experimental setup is available in Bayca.\textsuperscript{17} The dissolution experiment was conducted under atmospheric conditions in a 500 mL three-necked glass reactor, with a mechanical stirrer with a digital display to agitate the solution and a water bath to heat it. A programmable refrigerated bath circulator was used to keep the reaction medium at a constant temperature, and a spiral condenser was fitted to prevent loss of solution by evaporation. The temperature of the solution in the reactor was measured with a portable digital

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### Table 1 – Dissolution of ulexite kinetic models and activation energies

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reagents</th>
<th>Kinetic models</th>
<th>Activation energies, kJ mol$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ulexite</td>
<td>Borax pentahydrate solutions saturated with CO$_2$</td>
<td>Surface chemical reaction control</td>
<td>42.50</td>
<td>Kuslu et al.\textsuperscript{4}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Oxalic acid</td>
<td>Product layer diffusion control</td>
<td>24.00</td>
<td>Abali et al.\textsuperscript{7}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Citric acid</td>
<td>Chemical reaction control</td>
<td>39.40</td>
<td>Ekmekyapar et al.\textsuperscript{13}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Phosphoric acid</td>
<td>Product layer diffusion control</td>
<td>26.17</td>
<td>Dogan and Yartas\textsuperscript{15}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Ammonium nitrate</td>
<td>Chemical reaction control</td>
<td>58.20</td>
<td>Demirkiran\textsuperscript{25}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Water saturated SO$_2$</td>
<td>–</td>
<td>59.00</td>
<td>Alkan and Kocakerim\textsuperscript{28}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Ammonia solutions saturated with CO$_2$</td>
<td>First order reaction control</td>
<td>55.00</td>
<td>Kunkul et al.\textsuperscript{29}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>EDTA</td>
<td>Chemical reaction control</td>
<td>35.95</td>
<td>Alkan et al.\textsuperscript{30}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Sulfuric acid</td>
<td>Avrami model</td>
<td>-</td>
<td>Tunc et al.\textsuperscript{31}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>CO$_2$</td>
<td>Product layer diffusion control</td>
<td>20.50</td>
<td>Copur et al.\textsuperscript{32}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Oxalic acid</td>
<td>Product layer diffusion control</td>
<td>30.13</td>
<td>Alkan et al.\textsuperscript{33}</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Perchloric acid</td>
<td>Avrami model control</td>
<td>19.12</td>
<td>Demirkiran and Kunkul\textsuperscript{34}</td>
</tr>
</tbody>
</table>
temperature controller with a probe, and was found to range between 0 and 150 ± 0.1 °C. Waste was weighed to 0.1 mg using an analytical balance. A digital chronometer was used to measure the retention time. The oxalic acid, D-mannitol, sodium hydroxide, methyl red, and phenolphthalein reagents were obtained from Merck. The parameters selected in this study are given in Table 2.

Table 2 – Parameters studied in the oxalic acid leaching tests

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temperature, K</td>
<td>298 313 323 333 343</td>
</tr>
<tr>
<td>Stirring speed, rpm</td>
<td>200 500  700</td>
</tr>
<tr>
<td>Acid concentration, g L⁻¹</td>
<td>40 80 100</td>
</tr>
</tbody>
</table>

In the dissolution experiments, 100 mL of pure water was put into the reactor and the contents of the reactor heated to the desired temperature. Oxalic acid in solid form was added to the reactor. Subsequently, a selected amount of the waste was added to the solution, and the mixture was stirred at given rates. At the end of each experiment, the stirring was stopped, and the content filtered through blue paper in a funnel. The boron oxide content of the filtrate was analyzed by the Koklu et al.³⁵ volumetric method with mannitol.

Results and discussion

The characterization of the waste by XRD is given in Fig. 2. The chemical analysis results of XRF of the waste are shown in Table 3. Parameters were chosen that were expected to affect the dissolution rate of ulexite waste in oxalic acid solutions. These were reaction temperature, acid concentration, stirring rate, and solid-to-liquid ratio. In the

XRD analysis of ulexite waste containing 21.83 % B₂O₃, the major minerals observed were ulexite, colemanite, dolomite, calcite and quartz. It was calculated from the results of XRD and chemical analysis that ulexite waste contained approximately 27.58 % ulexite, 15.00 % colemanite, and 5.05 % meyerhoffite as boron minerals.

The same parameters were selected as control variables to investigate the effect of these parameters on the dissolution process of ulexite waste. During the experiments, the effect of one parameter at a time was studied while keeping the values of the other parameters constant. Each experiment was carried out three times. These experiments were repeated with a maximum deviation of approximately ± 2 % in terms of the fractional conversion.

The dissolution rate is given as a percentage:

Dissolution rate = \frac{\text{Dissolved amount of } \text{B}_2\text{O}_3}{\text{Total of } \text{B}_2\text{O}_3 \text{ in the sample}} \times 100 \%
The data obtained were plotted in the form of time versus fractional conversion. The arithmetic average of the results was used to determine a kinetic reaction model and calculate the activation energy of ulexite waste.

The effect of reaction temperature on dissolution rate was studied at an acid concentration of 40 g L\(^{-1}\), a stirring speed of 500 rpm, and a solid-to-liquid ratio of 1 %. Fig. 3 shows boron oxide extraction as a function of reaction temperature in the range of 25 – 70 °C. Dissolution rate was lowest at a temperature of 25 °C and a time of 60–120 minutes. Between 5 and 30 minutes, the dissolution rate rose as temperatures were increased to 50 °C, but with an increase from 60 to 70 °C, the dissolution rate was observed to rise only very slowly. Between 60 and 120 minutes, the dissolution rate rose as the temperature was increased to 40 °C, but with an increase in temperature from 40 to 70 °C, no increase was observed in the dissolution rate. Optimum boron extraction was obtained at 70 °C.

To determine the effects of stirring rate on boron oxide extractions, dissolution experiments were performed within a stirring rate range of 200–700 rpm, and at a temperature of 70 °C, an acid concentration of 40 g L\(^{-1}\), and a solid-to-liquid ratio of 1 %. The results in Fig. 4 show that the dissolution rate generally increased with an increase in acid concentration. Lowest dissolution rate between 5 and 30 minutes was obtained with an acid concentration of 40 g L\(^{-1}\). Maximum dissolution according to the percentage of B\(_2\)O\(_3\), was obtained at an acid concentration of 100 g L\(^{-1}\). This can be explained by the increase in solution concentration causing an increase in H\(^+\) ions. This causes dissolution to increase. Mobility of H\(^+\) ions decreases and saturation rapidly occurs, and a film layer is formed around the particles. As a result of the formation of this film layer, the dissolution rate decreases. Thus, the preferred optimum acid concentration is 40 g L\(^{-1}\). Dissolution rate increased at acid concentrations between 40 and 80 g L\(^{-1}\). Dissolution rate declined between 5 and 30 minutes at an acid concentration of 100 g L\(^{-1}\), but...
increased slowly between 60 and 120 minutes at the same acid concentration.

The rate of reaction is explained in terms of heterogeneous and homogeneous reaction models in a fluid-solid reaction system. The reaction is thought to take place on the outer surface of the unreacted particle. In heterogeneous reactions, the unreacted core of the particle shrinks with increasing conversion, and the layer of solid product thickens. The homogeneous reaction mechanism is visualized as a liquid reactant diffusing the particle and reacting throughout the particle at all times of the dissolving process. As a result, solid particles dissolve very well.\(^\text{15}\)

The non-catalytic reactions between solid and liquid have two ideal models:

- a) Progressive conversion,
- b) Unreacted shrinking-core models.\(^\text{37,38}\)

Shrinking-core consists of three models:

- a) Film diffusion,
- b) Surface chemical reaction,
- c) Diffusion through the ash or product layer.

The rate of the process is controlled by the slowest of these sequential steps, which occur in succession during the reaction.\(^\text{37,38}\) Integrated rate equations and kinetic models for the heterogeneous and homogeneous reaction are listed in Table 4.

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|}
\hline
Models & Equations & \(k\) Values \\
\hline
Film diffusion control (sphere particle) & \(kt = X\) & \(k = \frac{3bk_f C}{\rho R}\) \\
Film diffusion control (small particle) & \(kt = 1 - (1 - X)^{2/3}\) & \(k = \frac{2bk_f C}{\rho R^2}\) \\
Chemical reaction control (sphere particle) & \(kt = 1 - (1 - X)^{1/3}\) & \(k = \frac{bk_f C}{\rho R}\) \\
Chemical reaction control (cylinder particle) & \(kt = 1 - (1 - X)^{1/2}\) & \(k = \frac{bk_f C}{\rho R}\) \\
Ash layer Diffusion control (sphere particle) & \(kt = 1 - 3(1 - X)^{2/3} + 2(1 - X)\) & \(k = \frac{6bD_f C}{\rho R^2}\) \\
Ash layer Diffusion control (cylinder particle) & \(kt = X + (1 - X)\ln(1 - X)\) & \(k = \frac{4bD_f C}{\rho R^2}\) \\
Ash layer Diffusion control (plate particle) & \(kt = X^2\) & \(k = \frac{2bD_f C}{\rho L^2}\) \\
First-order reactions control & \(kt = -\ln(1 - X)\) & \\
Second-order reaction control & \(kt = X(1 - X)^{-1}\) & \\
\hline
\end{tabular}
\caption{Integrated rate equations and kinetic models for the heterogeneous and homogeneous reaction.}\(^\text{17}\)
\end{table}

In addition, two models, the first-order pseudo reaction and the second-order pseudo reaction in the homogeneous reactions, were analyzed to determine kinetics models of the dissolution of ulexite waste in oxalic acid solutions. The kinetic analysis was performed by taking into consideration the heterogeneous and homogeneous reaction models. The application of these models to the experimental data helped to find the model of the dissolution process. The validity of the experimental data in the integrated rate equations was tested by statistical and graphical methods. The rate equations used to evaluate the experimental data are given in Table 5. Variations in all the reaction models were plotted against time \((t)\). At the end of the kinetic analyses, all of the plots showed nonlinear variation with time, while plots of the first-order pseudo equation against time showed linear variation and gave straight lines. The straight lines showed that ulexite waste dissolved adequately in oxalic acid.\(^\text{12}\) Because ulexite waste was taken from a tailing pond in Bigadic, Balikesir, the particle size was not considered as a variable and was kept constant in this study. Calcium and sodium oxalates precipitated during the reaction. Therefore, the reaction model could be envisioned as film diffusion, diffusion control through the ash or product layer, or the chemical surface reaction model. However, the reaction model was not film diffusion or diffusion control through the ash or product layer, since the stirring rate had no effect on the dissolution process. If the rate is very sensitive to temperature variation, the rate-controlling step is the surface chemical model.\(^\text{15}\) However, the results indicated that the variation of \(1 - (1 - X)^{1/3}\) versus time \((t)\) had low linearity and the regression coefficient \(R^2\) was smaller than 0.9999. Briefly, the dissolution did not fit the heterogeneous reaction models.\(^\text{4}\)

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|}
\hline
Parameters & Values & Regression coefficient, \(R^2\) & \(k\) \(\text{min}^{-1}\) \\
\hline
Temperatures, K & 298 & 0.9973 & 0.0048 \\
& 313 & 0.9897 & 0.0175 \\
& 323 & 0.9934 & 0.0292 \\
& 333 & 0.9927 & 0.0356 \\
& 343 & 0.9988 & 0.0430 \\
Stirring speed, rpm & 200 & 0.9976 & 0.00020 \\
& 500 & 0.9861 & 0.00009 \\
& 700 & 0.9846 & 0.00009 \\
Acid concentration, g L\(^{-1}\) & 4 & 0.9919 & 0.0215 \\
& 80 & 0.9951 & 0.0201 \\
& 100 & 0.9949 & 0.0439 \\
\hline
\end{tabular}
\caption{Values of regression coefficients (\(R^2\)) and \(k\) values of first-order reaction control.}\(^\text{15}\)
\end{table}
The rate equations and regression coefficients are listed in Table 5. The variation of $-\ln(1-X)$ with time ($t$) was plotted for reaction temperature. The analyses showed that the data fitted the first-order reaction control. The $R^2$ value was close to 1 and the plots of $-\ln (1-X)$ versus time ($t$) had high linearity. The linearity showed that ulexite waste dissolved in the oxalic acid solutions and the most appropriate model was the first-order pseudo reaction. In addition, the variation of the first-order pseudo reaction model versus the selected optimum values of temperature, stirring rate, acid concentration, and solid-to-liquid ratio in this study was plotted, and the correlations between these were investigated. High correlation was observed and the regression coefficients were determined for each parameter, as shown in Figs. 6, 7 and 8. It was proved using these figures that the main kinetic model of the dissolution process of ulexite waste was the first-order pseudo reaction model. The plots of $-\ln(1-X)$ versus time ($t$) for each temperature value was used to calculate the activation energy related to the dissolving of ulexite.

The Arrhenius plots of $\ln k$ versus $1/T$ were drawn as shown in Fig. 9. From the slope in Fig. 9, the activation energy was found to be 41.09 kJ mol$^{-1}$. It has been reported that the activation energy of a chemical surface controlled reaction is in excess of 40 kJ mol$^{-1}$, and low activation energy confirms that the dissolusion rate may be product layer (ash layer) diffusion. The activation energy of ulexite waste is close to 40 kJ mol$^{-1}$ and is in accordance with the chemical surface model. Briefly, the results showed that the kinetic models do not fit the chemical model or the heterogeneous reaction model. In this study, the activation energy of the dissolution process of ulexite waste in oxalic acid solutions was found to be 41.09 kJ mol$^{-1}$.
of ulexite waste in oxalic acid solutions was found to be 41.09 kJ mol\(^{-1}\). Alkan \textit{et al.} found the activation energy of the dissolution of ulexite in oxalic acid solution to be 30.13 kJ mol\(^{-1}\).\(^{33}\)

Oxalic acid has two acidity constants, \(K_1 = 5.6 \cdot 10^{-2}\) (pK\(_{a1} = 1.27\) ) and \(K_2 = 5.42 \cdot 10^{-5}\) (pK\(_{a2} = 4.28\) ). In view of pK\(_{a1}\) (1.27), oxalic acid is a strong acid. Pure oxalic acid crystallizes with two moles of water.\(^{39,40}\)

Oxalic acid in an aqueous medium decomposes during the dissolution process according to reaction 1:

\[
\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}_{(aq)} \rightarrow \text{C}_2\text{H}_2\text{O}_4^{(aq)} + 2\text{H}_2\text{O} \quad (1)
\]

Oxalic acid in an aqueous medium ionizes during the dissolution process according to reaction 2:

\[
\text{C}_2\text{H}_2\text{O}_4^{(aq)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{C}_2\text{O}_4^{2-}^{(aq)} + 2\text{H}_3\text{O}^+_{(aq)} \quad (2)
\]

When the ulexite waste is added to the oxalic acid solution, the reaction taking place in the solution can be written as follows (reaction 3):

\[
\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}_{(s)} +
+3(\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O})_{(aq)} \rightarrow 2\text{Na}^+_{(aq)} + 2\text{CaC}_2\text{O}_4_{(s)} + (3)
+\text{C}_2\text{O}_4^{2-}^{(aq)} + 10\text{B(OH)}_3^{(aq)} + 10\text{H}_2\text{O}
\]

The reaction between ulexite and oxalic acid results in boric acid and sodium oxalate in the liquid phase. In the solid phase, calcium oxalate, quartz and others are observed.

\section*{Conclusions}

The mineral content of ulexite waste was calculated to be 27.58 \% ulexite, 15.00 \% colemanite and 5.05 \% meyerhoffite as boron minerals. Impurities constituted about 52.37 \% of the waste. After investigation of the kinetics of the solid-liquid reaction between ulexite waste and oxalic acid solutions in a mechanical agitation system and the effect of different parameters (temperature, acid concentration, stirring rate and solid-to-liquid ratio) on the dissolution process of ulexite waste, the following conclusions were reached. The dissolution rate of ulexite waste increased with increasing temperature and stirring rate. Stirring rate had very little effect on dissolution rate in a dissolution time of 120 minutes. The dissolution rate was highly dependent on the temperature. Thus, oxalic acid solutions can be appropriate as a leachant for ulexite waste.

The kinetic model of the dissolution process was determined to be a first-order reaction control model. The activation energy was found to be 41.09 kJ mol\(^{-1}\). The activation energy of ulexite waste was higher than the activation energy of pure ulexite.

The reaction between ulexite waste and oxalic acid resulted in boric acid, sodium oxalate, calcium oxalate and impurities. The boric acid and sodium oxalate formed passed into the liquid phase, while the calcium oxalate, magnesium oxalate and quartz remained in the solid phase. As the liquid phase cooled, white pure boric acid crystals were precipitated. Pure boric acid crystals were obtained by the reaction of ulexite waste in oxalic acid. Thus, pure boric acid crystals can be produced using ulexite waste, and this can benefit the environment and the economy. The leaching kinetics of this laboratory-scale study was determined by the mathematical models. The findings of this study can be very useful for designing reactors on an industrial scale.

\section*{ACKNOWLEDGMENTS}

The authors would like to thank Eti Maden Works General Management Turkiye for the XRD, XRF and particle size analysis.

\section*{List of symbols}

\begin{itemize}
  \item \(k\) – Reaction rate constant, \(\text{min}^{-1}\)
  \item \(X\) – Dissolution rate or fractional conversion
  \item \(t\) – Reaction time, \(\text{min}\)
  \item \(T\) – Temperature, \(\text{K}\)
  \item \(E\) – Activation energy, kJ mol\(^{-1}\)
  \item \(R\) – Universal gas constant, J mol\(^{-1}\) K\(^{-1}\)
  \item \(k_w\) – Frequency or pre-exponential factor, \(\text{min}^{-1}\)
\end{itemize}

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