Acid dissolution of soil kaolinite were carried out in two series of experiments. The first series involved dissolution of kaolinite in HCl with 3 levels (1N, 2N and 3N) of acid strength at 60°C. The aim of this experiment was to study the effects of acid strength and temperature on the dissolution rate of kaolinite. The dissolution reactions were not carried to completion. The second series was conducted at a higher temperature (80°C) but with only 1 level (2N HCl) of acid strength was applied and the dissolution reactions were carried to completion. The second series of the experiment was designed to evaluate the congruency of Fe, Al and Si release from kaolinite.

Fe and Al released from kaolinite which are expressed as Fe, Al (dissolved/total) during the first series of experiment increased slightly with time. It was approximately linear initially (T<sub>1/2</sub> region) and became more curvy with progressive dissolution. Dissolution rate constant (k) also increased significantly as the acid strength increased from 1N, 2N and 3N HCl. The increasing value of k is about one-half and it is about two folds as acid strength increased from 1N to 2N and from 2N to 3N HCl respectively. The increase of temperature, however, had a more astounding effect on the dissolution rate. The dissolution temperature change from 60°C to 80°C resulted in the dissolution rate being lifted 4.5 and 3 folds for Fe and Al respectively. The dissolution data within the limited initial linear-region (T<sub>1/2</sub>) of the first series of the experiment appeared to have fitted well to the cuba root law. However, it inadequately described the dissolution data of the second series where the dissolution reactions were conducted to completion. Per complete dissolution reactions, dissolution kinetics is best described with the modified first order of the Kishin's equation. Regression analysis shows that there is no significant relation between (k) and the properties of kaolinite analysed in this experiment.

In contrast with the standard Georgia kaolinite, it has been found that for soil kaolinite the release of Fe, Al and Si occur at identical rate. Therefore, the dissolution is congruent which indicates that Fe, Al and Si in kaolinite under the present study are distributed uniformly within the crystal grains.

* Department of Soil Science & Plant Nutrition, University Western Australia, Nedlands, Australia
** Faculty of Agriculture, Macquarie University, Sydney, Australia
The occurrence of cations as impurities in kaolinite has been reported by several authors, i.e. iron (Deer and Howie, 1972; Herbillon et al., 1976; Mendolia and others, 1979; Psut et al., 1963; St Pierre et al., 1992; Babanovski et al., 1994; Mallonee et al., 1994), titan oxides (Dolcer et al., 1970; Weaver, 1976; Roepasny, 1976; Singh, 1971; Peacoy, 1952), vanadium (Gohring et al., 1993; Milikin and Tummanu, 1992), chromium (Mackinovic and others, 1981; Singh and Gilkes, 1991; Mace et al., 1992), molybdenum and tungsten (Milikin and Tummanu, 1993). These cations may be occurred in kaolinite as part of its structure or as separate phases. Usually both types of contamination "structural" and "non structural" ions are coexist (Babamovski et al., 1993).

The said dissolution technique has been used to interpret the release mechanism of cations included in natural iron oxides (Singh and Gilkes, 1991).

The curve iron raw 1 (COO)^2 = at where a and is the weight of solid at times t and t=0, and is m constant. The plot of the curve root of the undissolved element against time should yield a straight line with a slope (-m) if the dissolution process follows this law. This equation successfully described dissolu-
Dissolution kinetics of kaolinite

The first series was aimed to study the effect of acid strength on dissolution of kaolinite. This experiment was carried out at two temperatures (60°C and 100°C) with three levels of acid strength: 1 M, 2 M, and 3 M HCl.

The dissolution rate was calculated using the following equation:

\[ \frac{dC}{dt} = k(1 - C) \]

where \( C \) is the fraction of kaolinite dissolved at time \( t \), \( k \) is the rate constant, and \( C_0 \) is the initial concentration of kaolinite.

\[ \ln\left(\frac{1}{1 - C(t)}\right) = \ln k + C(t) \]

A plot of \( \ln(1/(1-C)) \) against time results in a straight line from which \( k \) and \( C(t) \) can be calculated.

Materials and Methods

Soil kaolinite used in this experiment was concentrated from clay fraction with the removal of iron oxides in buffer dihydrogen-dihydroxy-bicarbonate solution. This procedure has been described in detail elsewhere (Sridhar, 1997). Two series of experiments were conducted.

Results and Discussion

Effect of acid strengths

The first series of experiments was aimed to study the effects of acid strength and temperature on the dissolution rate of Fe and Al from soil kaolinite. Three levels of acid strength were used: 1 M, 2 M, and 3 M HCl.
HCl. The release of Fe and Al during the dissolution reaction at 60°C and 3 levels of acid strength were expressed as Fe, Al (dissolved/total) and are shown in Figure 1. The curves for all 3 levels of acid strength indicate that the release of Fe and Al during the dissolution increased with time. It was approximately linear initially (~50% of dissolution = T1/2) and became curvy with progressive dissolution. The decrease in dissolution rate may have occurred in response to a reduction in total surface area of the samples with the extent of dissolution (Lim-Nunez and Gilkes, 1987). Coneill et al. (1973) working on dissoluted complexes ability of the acid involved. The occurrence of continues smooth dissolution-time curves may indicate the all kaolinite samples in the present study are homogenous.

In all samples, the relative amount Fe and Al released at higher acid strength is always higher than in a lower acid strength. This suggests that dissolution rate is related to the acid concentration. Similar findings had been reported (Gismondo et al., 1970; Coneill et al., 1976; Sidhu, 1978; Konrad et al., 1986). The values of Fe (dissolved) and Al (dissolved) between soil kaolinite are solution of iron oxide found that the dissolution rate increased by 50% as the acid strength increase from 0.1N to 0.5N HCl. At high C1 concentration, the curve started to level off. They suggested that the dissolution rate is related to the complexing ability of this anion. Therefore the decrease of the dissolution rate at higher acid strength (7N HCl) may be related to the narrow and these values are much higher than the values for Georgia kaolinites. This exhibits that the release of Fe and Al in soil kaolinite is much faster than in Georgia kaolinite.

Dissolution kinetic has often been described using cube-root law (Gismondo et al., 1970; Coneill et al., 1977; Sidhu et al., 1981; Lim-Nunez and Gilkes, 1987)
or Kabai's equation (Kabai, 1973; Schwerdtmann and Latham, 1986; Singh and Gilkes, 1992; Rumm and Gilkes, 1995). For comparison and evaluation purposes, the dissolution data of Fe and Al under different dissolution temperature and acid strength at the initial nearly linear region (T_e) were fitted into the cube-root law and Kabai's equation. The rate of dissolution (α) were obtained from the slope of linear relationship of dissolved-time curves of Fe and Al. It appears that the dissolution data of Fe and Al in this region (T_e) fitted well into the cube-root law (Figure 2) as well as to Kabai's equation (Figure 3). The regression parameters of dissolved Fe and Al following cube-root law and Kabai's equation are presented in Table 1. As seen in Table 1, the dissolution rate constant (α) of Fe and Al following cube-root law increased strongly with the increase in acid strength. For soil kaolinite, the magnitude of α (Aα) was about 1.5 for both Fe and Al as the acid strength increase from 1N to 2N HCl. The value of Aα doubled when the acid strength increased from 1N to 2N HCl. Similar finding had been reported by Singer (1977) working on Australian polygorskite.

**Figure 2.** Dissolution rate of Fe and Al in 2N HCl, 80°C following cube-root law

**Figure 3.** Dissolution rate of Fe and Al in 2N HCl, 80°C following Kabai's equation
Table 1. Dissolution parameters at initial linear region \( (T_{0}) \) of Fe and Al following cube-root law

<table>
<thead>
<tr>
<th>Acid Strength</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta n )</td>
<td>( \Delta a )</td>
</tr>
<tr>
<td>Sulfuric 96%</td>
<td>-0.022</td>
<td>1.00</td>
</tr>
<tr>
<td>Sulfuric 70%</td>
<td>-0.022</td>
<td>1.00</td>
</tr>
<tr>
<td>Coke 70%</td>
<td>-0.047</td>
<td>2.55</td>
</tr>
<tr>
<td>Coke 88%</td>
<td>-0.001</td>
<td>1.00</td>
</tr>
<tr>
<td>Coke 89%</td>
<td>-0.001</td>
<td>1.00</td>
</tr>
<tr>
<td>Coke 90%</td>
<td>-0.001</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\( \alpha \) - dissolution rate (slope of regression line)
\( \Delta n \) - magnitude of \( \alpha \)
\( \Delta a \) - constant (intercept of regression line)
\( R^2 \) - regression coefficient

Effect of temperature

The increase in temperature, however, had a more astounding effect on the dissolution rate. The dissolution temperature change from 60 °C to 80 °C resulted in the dissolution rate being lifted 4.5 and 3 folds for Fe and Al respectively (Figure 4).

![Figure 4. Effect of temperature on dissolution of Fe and Al](image-url)
Congruency of dissolution of Fe, Al, and Si

The second series of experiment was aimed to investigate the congruency of dissolution of iron, aluminium and silicon in 2N HCl at 80°C. If Fe, Al and Si are released at an identical rate, then it is reasonable to assume that the metals are uniformly distributed throughout the kaolinite crystals. Conversely, if Fe, Al and Si show quite different patterns of dissolution, then it is unlikely that these metals are present in a single mineral of uniform composition.

In order to obtain complete dissolution, the reactions were carried out up to 192 h. When the concentration of dissolved Fe, Al and Si in solution were calculated as percentage of the initial Fe, Al and Si contents, the release of Fe, Al and Si during this series of experiment exhibit a smooth and nearly superimposed curves. Plotting the proportion of dissolved Fe/Al, Fe/Si and Al/Si of all data points gave a single line with slope -1 (Figure 5). This indicates that Fe and Al and Si were uniformly distributed within the crystal of soil kaolinite and that dissolution temperatures. Singh and Gilkes (1992) reported that the mixture of goethite and hematite could be described both by the cube root law and Kabai's equation. Gastache et al (1960) who worked with well crystallized, homogeneous kaolinite from South Africa found that the dissolution of Al and Si in 0.1 N HCl at 104°C followed
the cube root equation. For comparison the dissolution data of Af from Gastache et al. (1960) were fitted to cube root as well as to the Kabal's equations.

Under present study it appears that the cube root law did not adequately describe the complete dissolution (second series of experiment) data of Fe, Al and Si. In contrast, the dissolution data can be described with one straight line by the modified first order of Kabal's equation (Kabal, 1977). For comparison, the dissolution data of Al of Gastache et al. (1960) also fitted into the first order of Kabal's equation. The dissolution rate constant (a) of Al of soil kaolinite is higher than those of Gastache's kaolinite.

Table 2. Correlation coefficients between dissolution parameters (a) of Fe derived from Kabal's equation and some properties of kaolinite

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Correlation Coefficient (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-600</td>
<td>0.18 M20% 0.13</td>
</tr>
<tr>
<td>C-600 (2), nm</td>
<td>0.05 SiO2% 0.20</td>
</tr>
<tr>
<td>C-600 (3), mm</td>
<td>0.31 FeO% 0.03</td>
</tr>
<tr>
<td>AI203%, %</td>
<td>0.35 CaO% 0.51</td>
</tr>
<tr>
<td>M2 index</td>
<td>0.23 N2O% 0.14</td>
</tr>
<tr>
<td>CEC mg mg/L</td>
<td>-0.62 KCl% 0.01</td>
</tr>
<tr>
<td>AI203%, mg/L</td>
<td>0.16 H2O% 0.60</td>
</tr>
<tr>
<td>X-ray diff</td>
<td>0.24 P2O5% 0.25</td>
</tr>
<tr>
<td>LOI gc</td>
<td>0.21 SO3% 0.07</td>
</tr>
</tbody>
</table>

Dissolution constants and some properties of soil kaolinite

Dissolution of mineral may greatly be affected by surface morphology i.e. composition, structure, topography, thickness and surface area (Kitch, 1994). The relationship between dissolution parameters as derived from Kabal's equation and some properties of soil kaolinite is presented in Table 2. It has been expected that the dissolution rate constant (a) is related to the crystal size as it is an indirect measure of surface area. However, it appears that the value of a is not related to any of the kaolinite properties measured. In this study, the surface area has been estimated from XRD line broadening. The value of a is positive but not significantly related to the crystal size of kaolinite measured from XRD line broadening. The reason for this might be, as indicated by Schwertmann and Latham (1980), that the surface area calculated from XRD line broadening may not reflect the true surface.

CONCLUSIONS

The release of Fe and Al during the dissolution reaction at 60°C and 3 level of acid strength, expressed as Fe, Al (dissolved/total), increased strongly with time. It was approximately linear initially (~ 50% of dissolution + T), and became more curved with progressive dissolution. The decrease in dissolution rate probably occurred in response to a reduction in total
The dissolution rate constant (α) of kaolinite samples dissolved in HCl increased significantly as the acid strength increased from 1N 2N and 3N HCl. The increase of the value of α is about one-half and two-fold as acid strength increase from 1N to 2N and from 2N to 3N HCl respectively. In contrast with standard Georgia kaolinite, it has been found that for soil kaolinite the release of Fe, Al and Si occurred at identical rate and the dissolution is congruent. This indicates that Fe, Al and Si in soil kaolinite were distributed uniformly within the crystal grains.

Dissolution kinetics of samples containing a mixture of kaolinite and bauxite in 2N HCl at dissolution temperature of 89°C as obtain from the second series of experiment is better described by the modified first order Kabai's equation than by the cubic-root law. Data from present studies conform to one straight line following the Kabai's equation. Regression analysis shows that dissolution rate constant (α) of complete dissolution reaction does not significantly relate to any properties of soil kaolinite measured in this study.

REFERENCES


Cornell, R. M., Posner, A.M. and Quick, J. P. 1976. Kinetic and mechanistic of the acid dissolution of goethite (a-

Dissolution Kinetics of Kaolinite 41


Lim-Nunez, B. and Gilkes, R. J. 1987. Acid dissolution of synthetic metal con-