Dissolution behavior and dissolution mechanism of palygorskite in HCl solution^{*}

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Abstract The 1 moV L, 3 moV L and 5 moV L HCl solutions were employed to leach two palygorskites with different trioctahedral contents in their crystal structure for different period of time. The results of the dissolution experiments show that the dissolution process could be divided into three steps, and that this dissolution behavior can be attributed to its higher M g^{2+} content, and is restricted by the extraction behavior of Si⁴⁺. The preferential extraction for M g^{2+} promotes the extraction behavior of Si⁴⁺ from Si-O framework. Because the Si⁴⁺ in the form of amorphous SiO₂ is adsorbed onto the surface of palygorskite fibre, the reaction between palygorskite and acid is obstructed. With the elapsing of time or the increasing of the acid concentration, the amorphous SiO₂ flocculates, and then the channels of chemical reaction are reopened. The ratio value of M $g^{2+}/$ (Fe³⁺+ Al³⁺) in leaching solution tends to a fixed value showing that the acid attack on the palygorskite with a low er trioctahedral content. The differential behavior for two palygorskites is discussed.

Keywords: palygorskite, acid leaching dissolution mechanism, Anhui, Mingguang, Guanshan.

Palygorskite is a kind of phyllosilicate with a fibrous morphology. Its crystal structure is built up of amphibole-like ribbons of 2 :1 layer modules, but the neighbouring ribbons are mutually linked by inversion of Si-O tetrahedrons at the corner of the ribbons. This kind of linkage results in the interior channels of 0.37 nm \times 0.64 nm in cross-section^[1]. The external surface and the inner surface of this mineral have an efficient adsorption capacity. It is usually used as adsorbents, desiccants, decoloring agents. In order to increase the specific surface, attapulgite clay whose main mineral component is palygorskite is always activated by means of acid leaching $[2^{-8}]$. The concentration of the acid is commonly controlled at about $2 \mod L^{[4,5]}$. The properties and structures may be modified for the surface of fibre and channels of activated palygorskite. The acid treatments not only increase the specific surface area of palygorskite but also increase its potential function in industrial applications. This kind of practical demand also promotes the study of acid leaching mechanism of palygorskite. Many papers have been published since the 1980s. Because of the difference in the focus of the attention, the manner, acid concentration, leaching time, and compositions of palygorskite adopted by authors, there are various opinions on the acid leaching mecha-

nism. For example, Gonzalez et al.^[9] considered that acid leaching is spread all over the structural channels of palygorskite. Corma et al.^[8] made a conclusion that acid leaching was processed from surface to inner of the structure and fitted for a reacting-shell model. Corma et al.^[2] also carried out a short-time leaching experiment; they thought that the composition of the octahedral sheet had little effect on acid leaching. On the basis of above-mentioned results, we studied two palygorskites purified in distilled water and with different dioctahedral and trioctahedral occupancy ratios. Treated by the acid at different concentrations, and using the inductively coupled plasma quantometer (ICP-AES) the concentration of the extracted octahedral cations in leaching solution was measured. The process of extraction of cations, the changes of crystal structure, and the mechanism of acid leaching were investigated.

1 Descriptions of the samples

Two palygorskite samples were collected in Guanshan attapulgite deposits in Mingguang, Anhui Province, China. One is gray in color, and the other is pink. Their mineralogical and compositional characters have been presented in Ref. [9]. According to EPMA and Fe₂O₃/FeO ratio from wet chemical anal-

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ysis results, the structural formulae can be written as:

 $(M g_{1.96}A l_{1.01}Fe^{3+} 0.42 \square) (Si_{7.50}A l_{0.50})$ $(Ca_{0.02}K_{0.07}N a_{0.02}) O_{20}(OH)_2 (OH_2)_4 ° nH_2O$ for gray palygorskite,

and

Gray

Pink

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 $(M g_{2.93} A l_{0.54} F e^{3+}_{0.23} \Box) (Si_{7.63} A l_{0.37})$ $(Ca_{0.002} K_{0.07} N a_{0.01}) O_{20} (OH)_2 (OH_2)_4 ° n H_2 O$ for pink palygorskite.

The R^{2+}/R^{3+} ratios of octahedral layer are 1.4 for gray palygorskite and 3.8 for pink one. The Fe²⁺, Ti⁴⁺ and Mn²⁺ are omitted in the formulae due to their very low contents.

The mineral particles less than 2 microns in size were separated from the attapulgite clay by sedimentation and centrifuging in distilled water. No quartz diffractions were found in the XRD patterns of the mineral particles (Fig. 1), and no montmorillonites in the form of floccule or flake were found by means of TEM.



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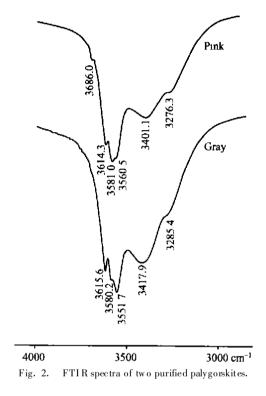
The infrared absorption spectra of the purified samples were recorded on a Nexus 870 Fourier Transform Infrared Spectrometer (FTIR) in Modern Analysis Center of Nanjing University. The KBr pressed-disc was used to prepare FTIR samples. As can be seen in Fig. 2, the absorption bands for these two palygorskites are at 3615 cm^{-1} (vAl2 \square OH), 3580 cm^{-1}

$$(\nu(Al, Fe)_2 \Box OH), \quad 3417 \, \mathrm{cm}^{-1} \quad (\nu \mathrm{Si} - \mathrm{O} - \mathrm{Si}),$$

H

3240 cm⁻¹ (ν Si^{-O}Al). The latter two bands "shift because of ν OH vibrations of the hygroscopic

water. By comparison two vibrations of 3686 and 3560 cm^{-1} appear in the spectrum of the pink one. These two vibrations were assigned to $\nu \text{Mg3OH}^{[10,11]}$, and $\nu (\text{Fe}^{3+}, \text{Mg}) \square \text{OH}$, respectively. As mentioned above there are about 68% tri-octahedral component in gray palygorskite and 82% component in the pink one. That is, the νMg3OH and $\nu (\text{Fe}^{3+}, \text{Mg}) \square \text{OH}$ vibrations appear in the FTIR spectrum of the pink one, probably resulting from the higher trioctahedral components.



2 Leaching experiments and results

The two palygorskites mentioned above were leached in HCl solution in batch reactors at room temperature. The solutions of 1, 3, and 5 mol/L HCl were employed to leach two palygorskites, and the solid/liquid ratio was 3 g/300 mL for each experiment. The leaching time was controlled at 0.25, 0.5, 1, 1.5, 2, 3, 4, 5, 6, and 7 h, respectively. The equal amounts of suspension were extracted from the batch reactors at predetermined time and then centrifuged in a high speed centrifuger. The liquid was analyzed by means of ICP-AES. The ICP-AES testing was carried out by Modern Analysis Center in Nanjing University. Fig. 3 is plotted based on the analysis results. In the figure, the leachates were denoted by "g" or "p" followed by a number, where "g" and "p" represent gray palygorskite and pink shing House. All rights reserved. http://www.cnki.net

one, respectively. The following number is the concentration of the HCl solution, for example, "1" means 1 mol/L HCl solution, etc.

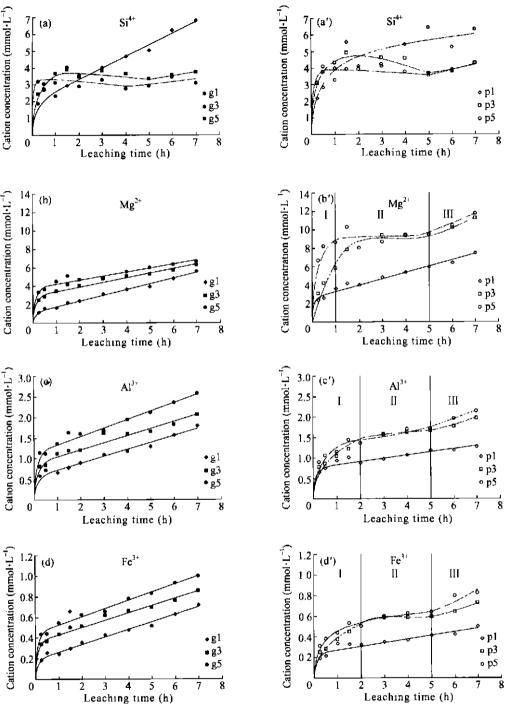


Fig. 3. Pbts of cation concentrations in leachate versus leaching time for two palygorskites dissolved by 1, 3, and $5 \mod L$ HCl. (a), (b), (c), and (d): gray palygorskite (a'), (b'), (c'), and (d'): pink palygorskite.

As shown in Fig. 3, a and a' give the trends of Si⁴⁺ concentration in leachate versus leaching time in different concentrations of HCl solution of two paly-gorskites, respectively. As 1 mol/L HCl solution was used, the Si⁴⁺ concentration increased gradually. However at 3 and 5 mol/L HCl, at the beginning of ?1994-2018 China Academic Journal Electronic Put

the leaching, namely within 0.5 h, the Si⁴⁺ concentration increased along with increasing of the acid concentration, and from 0.5 to 5 h, the concentration of Si⁴⁺ decreased and it was less than that in 1 mol/L at the same dissolution time. After 5 h, the Si⁴⁺ concentration is crescent. The concentration of Si⁴⁺ in mg House. All rights reserved.

3 mol/L HCl is higher than 5 mol/L. In a word, the trends of Si⁴⁺ concentration in leachate versus leaching time could be divided into 3 steps. The Si⁴⁺ concentration versus time increases sharply at the beginning. The Si⁴⁺ concentration slightly decreases in the second step, and the decreasing slope much bigger in 5 mol/L than in 3 mol/L. The pink palygorskite in 1 mol/L also presents this step in which the curve is going up mildly. The third step is a gradually increasing step. The slope is much smaller than the first step.

Fig. 3(b), (c), (d), (b'), (c'), and (d') give the extracted trends of octahedral cation Mg^{2+} , Al³⁺, Fe³⁺ in different concentrations of HCl solution of two palygorskites, respectively. As can be seen in the figures, the dissolution curves are different for two palygorskites. For gray palygorskite, the concentrations of octahedral cations are increasing with the increase of leaching time and the concentration of HCl solution. However, the same leaching trend was only seen in 1 mol/L HCl solutions for pink palygorskite. It is obvious that three steps can be considered for the pink one. The first step extends to 2 h. If the same concentration HCl solution is used, the cation concentration is increasing along with the elapsing of dissolution time, and the concentration of leached cations is much higher than in gray palygorskite at the same dissolution time. If the dissolution time is fixed and the higher HCl solution is used, the more octahedral cations can be extracted. The concentrations of leached cations were almost kept unchanged with the increase of HCl solution and elapsing of dissolution time for the second step. Like the extraction of Si⁴⁺, the extraction octahedral cations are gently increasing with the time elapsing for the third step, and this step starts after 5 h.

3 Discussions

3.1 Dissolution of Mg^{2+} , Al^{3+} , Fe^{3+}

It can be seen from Fig. 4 that the M $g^{2+}/(Al^{3+}+Fe^{3+})$ ratio increases gradually along with time elapsing at the beginning, and is steady at a constant value. The ratio value is 2 for gray palygorskite and >4 for pink palygorskite. They are bigger than the M $g^{2+}/(Al^{3+}+Fe^{3+})$ ratio 1.4 for gray palygorskite and 3.8 for pink palygorskite of their unit formulae. M any researchers^[2~5,7,8] concluded that the M g^{2+} is more easily leached because it is at the edge of the octahedral ribbons. However, Heller-Kallai et al.^[12] and Augsburger et al.^[13] proved that the Fe³⁺ is also at the edge of the octahedral ribbons by the Mössbauer spectra. Thus, it seems to us that it is difficult to explain why much more Mg²⁺ cations were leached from the crystal than Al³⁺ and Fe³⁺. Corma et al.^[2] considered that the Mg²⁺ is easier for extracting than Al³⁺ and Fe³⁺. He et al.^[14] researched the acid activating of montmorillonite, and found that Mg²⁺ was preferentially leached. That is the Mg²⁺/(Al³⁺ + Fe³⁺) ratio values in leachate for two palygorskites are higher than those in unit formulae, proving that Mg²⁺ is preferentially leached.

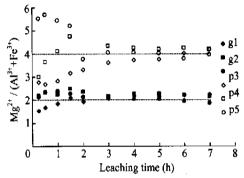


Fig. 4. Plot of $M\,g^{2+\!/}\,(Al^{3+}\!+Fe^{3+})$ versus leaching time for two palygorskites in HCl solution.

That the $Mg^{2+}/(Al^{3+}+Fe^{3+})$ values in the leachates of 3 and 5 mol/L HCl solutions are bigger than 2 and 4 for two palygorskites respectively shows that Mg^{2+} was preferentially leached. According to the theory of ionic polarization and bond-strengths^[15], Mg^{2+} could be easily extracted into acid solution from the crystal. As the three cations composed octahedral coordination with oxygen, the strength of the ionic linkage is influenced by the ability of ionic polarization. The radius of Al^{3+} , Fe^{3+} and Mg^{2+} is 0.0535, 0.055, 0.072 nm, respectively, so the order of the ability of ionic polarization is Al^{3+} $Fe^{3+} > Mg^{2+}$, and the strength of the ionic linkage is Al - O > Fe - O > Mg - O. In addition, according to the theory of electrostatic bond $^{[15]}S = Z/n$ (S, strength of electrostatic bond; Z, charge numbers; n, coordinate numbers), the S of Al^{3+} , Fe^{3+} and Mg^{2+} is 0.5, 0.5, and 0.33. According to the capability of ionic polarization and strength of electrostatic bond for these three cations, the Mg-O bond is most easily broken by H⁺, then Fe-O bond, and at last the Al-O bond. Corma et al.^[8] calculated the activation energies of these three cations of Spanish palygorskites, and concluded that the activation energy of Al^{3+} is greater than that of Fe^{3+} , and that of Fe^{3+} is greater than Mg²⁺ AllIt, was in agreement with the abovementioned results. In other words, in these cations the Mg^{2^+} was most easily extracted into acid solution. Myriam et al.^[7] found that sepiolite is more easily collapsed by acid attack than palygorskite and attributed it to the higher content of Mg^{2^+} in sepiolite. The leaching result of two palygorskites with different amounts of Mg^{2^+} shows that the higher content of Mg^{2^+} is much easier subjected to erosion by HCl solution at the same concentration.

3.2 Dissolution of Si⁴⁺

It is well known that the H4SiO4 is the first product during the dissolution of silicates in acid solution^{16^{-19}}. The experimental results explained that the Si⁴⁺ concentration increased gradually with time elapsing, and the leached cation concentration in lower concentrations of acid can exceed the higher concentration. It seemed that the size of the H4SiO4 colloid is varying, and the colloids suspend when the dissolution is in the low state, namely the low concentration of acid or shorter leaching time. It can be tested by ICP-AES. Schott et al.^[20] detected the amorphous silica by SEM at the surface of chain silicates which had been dissolved in acid. He et al.^[14] also tested that there was amorphous silica by MAS NMR in acid activation experiment of montmorillonite. Hence, the slowly elevating step of Mg^{2+} and Si^{4+} may show that the amorphous silica is adsorbed onto the surface of the palygorskite, and the extraction of the cations is temporarily obstructed. As a consequence, the leaching process of the minerals is hindered. If the dissolution develops to a high level (high concentration of HCl solution and much longer leaching time), along with the size increasing of the silica particulates, or increasing of the acid concentration, the silica particulates flocculate, and precipitate. Thus the \hat{Si}^{4+} concentration decreases in the leachate.

3.3 Conditionality of leached Si^{4+} and Mg^{2+}

Fig. 3 (b) and (b') reveal that the leached Mg^{2+} concentration of pink palygorskite at 0.5 h leaching is much higher than the concentration of gray palygorskite at 7 h in 5 mol/L HCl solution. Fig. 3(a) and (a') show that the leached Si⁴⁺ concentration of pink palygorskite is higher than that of gray palygorskite in the same concentration of HCl solution. Consequently, the leaching rate of pink palygorskite. In other words, higher content of Mg^{2+} in pink palygorskite in a higher dissolution rate.

when it is attacked by the HCl solution. Due to its fast dissolution rate, the collapse of octahedral layer accelerates the extraction of Si^{4+} , and makes the shift point between the first step and the second step appear earlier than gray palygorskite (0.5 h for pink palygorskite, and 1 h for gray palygorskite). After this point, the Mg²⁺ concentration in leachate goes up more slowly. After 5 h, the Mg²⁺ and Si⁴⁺ concentration increase gradually with the time elapsing according to Fig. 3. It resulted from the fact that after the silica was flocculated and precipitated, the structural channels of the palygorskite were reopened, so that Mg²⁺ was re-extracted from the crystals.

The conditionality of Mg^{2+} and Si^{4+} gives the three steps to dissolution curves as the palygorskite is leached by the HCl solution, but the model is not obvious in gray palygorskite. It could be suggested that pink palygorskite has a very high Mg^{2+} content, and it has a sharp slope in the much earlier dissolution process, so the point between two steps can be clearly shown when their extraction to HCl solution slows down.

3.4 Leaching mechanism of Mg^{2+} , Al^{3+} , Fe^{3+}

As can be seen in Fig. 4, the ${\rm Mg}^{2+}/\,({\rm Al}^{3+}\,+\,$ Fe³⁺) ratio increases steadily with leaching time and then reaches a constant value in leached solution of 1 mol/L HCl. However as it leached by 3 and 5 mol/L HCl, the $Mg^{2+}/(Al^{3+}+Fe^{3+})$ ratio becomes a bigger value, and then decreases to a constant value of 2 for gray palygorskite, and > 4 for pink palygorskite. The different dissolution among different concentration of HCl solution indicates that the concentration has influenced the extraction rate of Mg^{2+} . Based upon this fact, it is believed that at the earlier stage of dissolution by 1 mol/L HCl, the extraction of the cations is controlled by diffusion mechanism, i. e. the cations diffuse from the crystal surface to the solution, and the H⁺ from solution to the surface. Initially, not only the octahedral cations, but also the tetrahedral cations with Al³⁺ in tetrahedron site are exposed on the surface of the crystal. Therefore, the $Mg^{2+}/(Al^{3+}+Fe^{3+})$ ratio is lower. The chemical reaction gradually becomes a leading factor along with the developing of the dissolution. The preferential leaching of Mg^{2+} results in the gradual increase of Mg^{2+} concentration. The penetration of the H^{+} from solution to the inner structural channels of the crystal makes the leaching throughout the channels, and the $Mg^{2+}/(Al^{3+}+Fe^{3+})$ ratio reaches a constant value.

The leaching behavior in higher concentration of 3 and 5 mol/L HCl shows that the chemical reaction appears easier. Because of the diffusion superposed on the chemical reaction, much more Mg²⁺ is leached, especially for pink palygorskite. The Mg²⁺/(Al³⁺ + Fe³⁺) value does not keep steady until the H⁺ diffuses into all structural channels.

4 Conclusions

(1) The structural formulae of two Guanshan palygorskites from Anhui Province showed that their crystal structures had different contents of trioctahedral occupation. The contents of trioctahedral occupation are 82% for pink palygorskite and 68% for grav palygorskite. Thus the former had the absorption band at 3686 cm⁻¹ for its FTIR spectrum. The S_{BET} of these two palygorskites are $214 \text{ m}^2 \circ \text{g}^{-1}$ for the pink one and $182 \text{ m}^2 \text{ sg}^{-1}$ for the gray one, respectively. They have the same dissolution behavior in 1 mol/L HCl solution. The concentration of M g^{2+} increased gradually along with the dissolution time. Nevertheless, three steps had to be considered for the leaching of Mg^{2+} , Al^{3+} , and Fe^{3+} in overall reaction in 3 and 5 mol/L HCl leachates, i.e., fast extracting step, extracting step, and reextracting step.

(2) That the leached concentrations of cation for pink palygorskite versus leaching time are obviously divided into three steps can be attributed to the higher Mg^{2+} content. The preferential selectivity of Mg^{2+} and the lowest activation energy in HCl solution lead to the faster erosion of pink palygorskite. After a sharply leaching of cations, amorphous silica hindered the diffusion of H⁺ from solution to channels of crystal structure, and the dissolution curve is turned to a gentle slope. Due to the flocculation of the amorphous silica, the micro-channels in the crystal structure are reopened, and the dissolution is promoted.

(3) As two palygorskites are dissolved by the HCl solution, the $Mg^{2+}/(Al^{3+} + Fe^{3+})$ ratio may reach a constant value. The values are related to the original chemical composition of palygorskite, and reach the value from a lower value to 2 for gray palygorskite and 4 for pink palygorskite in lower acid concentration, for example, 1 mol/L. It is believed that the H⁺ has been penetrated throughout the structural channels of the crystal, reacted with crystal, and reached a chemical equilibrium. The higher the concentration of acid is employed, the shorter time it takes to reach a constant value.

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