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Adsorption kinetics of silicic acid on akaganeite

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ABSTRACT

As part of a series of studies on the interaction between ferric ions and silicic acid in the hydrosphere, the adsorption of silicic acid on akaganeite was investigated kinetically at various pH values. The adsorption of silicic acid increased with increasing pH over an initial pH range of 4–11.5. In the kinetic experiment, the Cl^- was released from akaganeite much faster than silicic acid was adsorbed. From this result, we concluded that chloride ions bound on the surface of akaganeite are released and Fe–OH or $Fe–O^-$ sites are formed, which then acts as an adsorption site for silicic acid. The uptake mechanism of silicic acid by akaganeite is significantly different from that by schwertmannite, despite the presence of the same tunnel structure.

1. Introduction

Chloride-rich environments, such as mines, oceans, groundwater, hot brines, and acidic soils, often contain akaganeite, a common iron oxyhydroxide that is often represented as β-FeOOH whose chemical formula can also be written as $(FeO_{0.833}(OH)_{1.167}Cl_{0.167})$ [1–5]. In contrast to other iron oxyhydroxides, such as goethite (α-FeOOH) or lepidocrocite (γ-FeOOH), akaganeite contains channels in which Cl^- ions are stabilized by hydrogen bonding [6]. A structural model of akaganeite is shown in Fig. 1[5]. The unit cell consists of 8 $FeO_3(OH)_3$ octahedra forming a double ring structure, and there is one cavity with a diameter of 0.5 nm (where it is normally possible for Cl^- to incorporate). Bigham et al. described that akaganeite is isostructural to the mineral shcwertmannite $(Fe_8O_8(OH)_{8-2x}(SO_4)_x$ $(1 \leqslant X \leqslant 1.75))$, which is a poorly crystalline Fe(III) oxyhydroxy sulfate mineral that is commonly found at pH levels between 2.5 and 4.5 in acid mine drainages where the SO_4^{2-} concentration is high [7–9].

Akaganeite has recently been the subject of several investigations about the effect of foreign cations (Ti^{4+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Al^{3+}, etc.) on its formation [10–12]. Ishikawa et al. also studied the influence of anions such as SO_4^{2-}, HPO_4^{2-}, NO_3^-, and SiO_3^{2-} on the formation of akaganeite [13]. They showed that the crystallinity of akaganeite was appreciably reduced by adding SO_4^{2-} or HPO_4^{2-}, improved by adding SiO_3^{2-}, and only slightly influenced by NO_3^-. Moreover, trace metals such as uranium (VI) [14] and cadmium [15] are known to have an especially high affinity for akaganeite, and the uptake behavior of the toxic anions, arsenite [16], chromate [17], and bromate [18] has been thoroughly investigated from the perspective of environmental chemistry.

Silicon is the second most abundant element in the earth's crust after oxygen. When rocks undergo chemical weathering, silicon is released into natural waters as silicic acid $(Si(OH)_4)$. Silicic acid is therefore ubiquitous in rivers, lakes and ground and spring waters. Research on the circulation of silicon as silicic acid on the earth's surface has extensively documented the uptake behavior of silicic acid by iron(III) minerals, such as amorphous iron(III) hydrous oxide $(Fe_2O_3{\cdot}nH_2O)$, goethite (FeOOH), hematite $(\alpha\text{-}Fe_2O_3)$, and magnetite (Fe_3O_4) [19–22]. Harder demonstrated the possibility of forming quartz by coprecipitating silicic acid with amorphous iron(III) hydroxide at low temperatures [19], and Yokoyama et al. made a detailed examination of the polymerization of silicic acid adsorbed on amorphous iron(III) hydroxide by gel chromatography [20] and trimethylsilylation–gas chromatography [23]. To our knowledge, no study on the adsorption of silicic acid on akaganeite has been conducted.

The adsorption behavior of silicic acid on synthesized akaganeite was examined in this study. This investigation may provide new and valuable information on the interaction between ferric ions and silicic acid in the hydrosphere and advance the field of geochemistry by improving the understanding the behavior of silicic acid on the surface of the earth.

2. Experimental

2.1. Synthesis of akaganeite

Akaganeite was synthesized according to methods developed by Schwermann and Cornell [2]. A volume of 2 dm^3 of $FeCl_3{\cdot}6H_2O$

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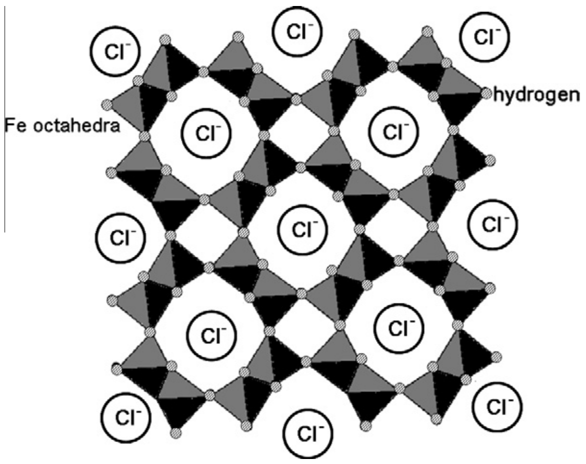

Fig. 1. A structural model of akaganeite.

solution (0.1 M, M = mol dm^{-3}) was maintained at 70 °C for 48 h. The suspension was filtered with a 0.45 μm membrane filter, and the resulting precipitate was air-dried. The precipitate was identified by powder X-ray diffraction (XRD), and its specific surface area was measured by the BET method. To determine the chemical composition, a portion of the precipitate was dissolved with nitric acid. The concentration of Fe was then measured by atomic absorption spectrometry (AAS), and the concentration of chloride ion was measured by titration (Mohr method).

Goethite was also synthesized according to the method described by Schwermann and Cornell [2]. The resulting precipitate was identified by XRD. The XRD pattern of the precipitate was in good agreement with the literature [2]. The BET surface area of the synthetic precipitate was 39.23 m^2 g^{-1}.

2.2. Effect of initial pH on the adsorption of silicic acid on akaganeite

All adsorption experiments were performed at 25 °C. To investigate the effect of pH on adsorption, 0.76 g of the synthetic akaganeite was added to 250 cm^3 of 1 mM ortho-silicic acid solutions with various pH values, and the suspended solutions were magnetically stirred for 24 h. At appropriate intervals, an aliquot of the suspended solution was taken and filtered with a 0.2 μm membrane filter. The concentration of silicic acid in the filtrate was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the concentration of chloride was determined by titration (Mohr method). For comparison, the adsorption of silicic acid on goethite at various pH values was also performed. In the adsorption experiments, a quantity of goethite with the same specific surface area as the akaganeite was used.

2.3. Adsorption kinetics of silicic acid on akaganeite and goethite

A sample of 3.04 g of the synthetic akaganeite was added to 1000 cm^3 of 1 mM ortho-silicic acid solution with a pH of 11.5, and the suspended solution was magnetically stirred for 30 min. Every minute, an aliquot of the suspended solution was taken and filtered with a 0.2 μm membrane filter. Silicic acid and chloride ion concentrations in the filtrates were measured using the methods described above. The change in pH over time was also measured using a glass electrode attached to a pH meter (Horiba pH METER F-52). For comparison, the adsorption experiment of silicic acid on goethite was also performed at pH 9. In the experiment, a quantity of goethite with the same specific surface area as the akaganeite was used.

3. Results and discussion

3.1. Characterization of synthetic precipitates

Fig. 2 shows the powder X-ray diffractogram of the synthetic precipitate (akaganeite). The precipitate showed good crystallinity. All characteristic peaks were attributable to akaganeite. The precipitate is referred to as “s-akaganeite” (synthetic akaganeite) throughout this paper. The BET surface area of the s-akaganeite was 88.61 m^2 g^{-1}.

For the other synthetic precipitate (goethite), several clear reflection peaks were observed. All the peaks were attributable to goethite.

3.2. pH dependence of silicic acid adsorption and the release of chloride ions

Fig. 3a shows the amount of silicic acid adsorbed on s-akaganeite and the amount of chloride ion released as a function of the pH. From pH 4 to pH 10, the amount of silicic acid adsorbed on the s-akaganeite was approximately 0.05 mmol g^{-1}, while above pH 10, the adsorbed amount increased abruptly and reached 0.2 mmol g^{-1} at pH 11.5. Fig. 3b shows the amount of silicic acid adsorbed on goethite as a function of the pH. The adsorption behavior of silicic acid differs considerably from that on goethite. The amount of adsorbed silicic acid increased with increasing pH up to a maximum 0.08 mmol g^{-1} at approximately pH 8–9 and then decreased as the pH value increased further. These data suggest that silicic acid is more able to adsorb on akaganeite than goethite. This difference in adsorption behavior may be attributable to the structural difference between the two adsorbents, as described below.

When silicic acid adsorbed on goethite, the species released were only H^+ and OH^-, which are potential-determining ions on the surface. Conversely, as shown in Fig. 3a, chloride ions were released when silicic acid adsorbed on akaganeite. This difference is thought to be a result of different mechanisms of silicic acid adsorption on akaganeite and goethite.

3.3. Kinetic analysis of adsorption of the silicic acid on akaganeite

To monitor the adsorption reaction mechanism in detail, changes in the pH and the concentrations of silicic acid and chloride ions were measured frequently throughout the reaction. The adsorption reaction was initiated at pH 11.5. Fig. 4 shows the variations of silicic acid, Cl^- and OH^- concentrations with time. When s-akaganeite was immersed in the sodium silicate solution, the pH decreased from 11.5 to approximately 9 within 1800 s, suggesting that silicic acid and OH^- ions are simultaneously adsorbed on the

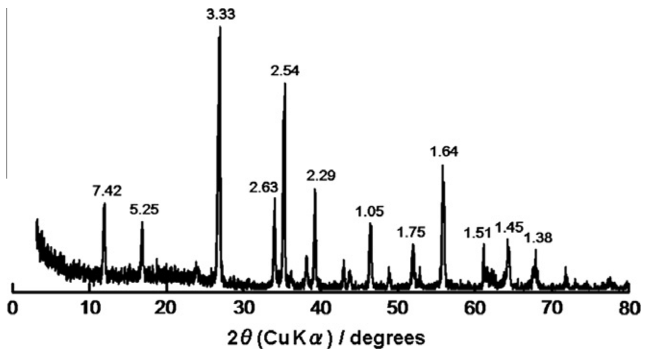

Fig. 2. X-ray diffraction pattern of the synthetic precipitate (numbers in the pattern: *d*-values).