Extraction of Amorphous Iron Oxides by EDTA from a Mixture of Akaganéite (β -FeOOH) and Amorphous Iron Oxides

O. K. BORGGAARD

Royal Veterinary and Agricultural University,
Chemistry Department, Thorvaldsensvej 40,
DK-1871 Copenhagen V, Denmark

Iron oxides are important constituents of catalysts and soils. Their effect depends on their surface area or crystallinity,¹⁻³ making the amorphous and poorly crystalline iron oxides the relatively most important. Prolonged extraction (>3 months at 20 °C) with EDTA (ethylenediamine-*N,N,N',N'*-tetraacetic acid) can selectively remove these amorphous and poorly crystalline iron oxides from soil^{4,5} and mixtures of amorphous and crystalline iron oxides.^{6,7} These crystalline iron oxides did not include akaganéite (β -FeOOH). However, the short-term interaction between akaganéite and EDTA, investigated recently,⁸ showed that negligible amounts of iron were dissolved in the pH range 2.5 to 7.5 but above pH 7.5 considerable dissolution of iron was found, i.e. up to nearly 1 % Fe dissolved after 11 days at 22 °C. Longer times are, however, required to reach equilibrium.⁸ Therefore, prolonged extractions of a mixture of amorphous iron oxides and akaganéite with various EDTA solutions were carried out. The results of this investigation are reported in this paper.

Akaganéite was prepared by heating a solution made to contain 0.2 M FeCl₃ in 0.01 M HCl for 24 h at 90–100 °C. After centrifugation the precipitate was washed once with water, twice with ethanol and once with acetone and dried at 65 °C. Chloride was determined by potentiometric titration after dissolution in 20 % H₂SO₄ in a closed vessel at 100 °C.⁹ The iron content was 57.7 %, determined by permanganate titration. The zero point of charge was 7.2, determined by the salt-addition technique.¹⁰ The specific surface was 31 m² g⁻¹, determined by applying the BET equation to N₂ adsorption after outgassing 20 h at 60 °C and 1 mPa and 44 m² g⁻¹, determined by water adsorption at 19 % relative humidity.¹¹

Amorphous iron oxides were prepared as described elsewhere⁷ by mixing Fe(NO₃)₃ and NaOH solutions (OH/Fe 3.0, pH ~7). The product contained 53.1 % Fe. A 1+1 mixture of akaganéite and amorphous iron oxides was prepared for the extraction experiments.

EDTA solutions were prepared as described previously⁴ by dissolving Titriplex II (Merck) and ammonium acetate in NH₃ and adding more NH₃ until the desired pH was obtained. The amounts of ammonium acetate were adjusted to give an ionic strength of 1.0 in the extractants.

The iron oxide mixture was weighed into PE bottles and the desired volume of EDTA was added. The bottles were closed by screw caps and shaken at room temperature (20 °C) in an end-over-end shaker for periods of from a few days to several months. The pHs of the 0.1 M or 0.2 M EDTA solutions were 4.0 to 9.9 and the solid-solution ratios were 1:2000 or 1:1000. Dissolved iron was measured by atomic absorption spectrophotometry.

Samples of akaganéite, before and after extraction for 180 days with 0.1 M EDTA at pH 9.9, were examined by X-ray diffraction using Fe-filtered Co-K α radiation.

X-Ray diffraction showed the presence of 5–10 % of poorly crystalline hematite in the akaganéite. The X-ray spectra before and after extraction of the akaganéite for 180 days with 0.1 M EDTA at pH 9.9 showed no appreciable difference in the number and positions of lines, i.e. the hematite impurity was not dissolved.

Fig. 1 gives the amounts of iron dissolved from the mixture of akaganéite and amorphous iron

Fig. 1. Amount of iron extracted from a 1+1 mixture of akaganéite and amorphous iron oxides by various EDTA solutions plotted against extraction time at 20 °C. The dashed line corresponds to the amount of extractable iron assuming only added amorphous iron oxides are dissolved.

oxides as a function of extraction time at various pH values, EDTA concentrations and solid-solution ratios. After 20 days, an amount of iron corresponding to that in amorphous iron oxides was dissolved by all extractants. During the dissolution of the amorphous fraction the pH of the extractant seemed of minor importance but the further developments were pH dependent. At pH 4 only negligible amounts of iron were extracted between 20 days and 101 days. A difference may, however, be seen between the amount of iron extracted after 20–101 days at pH 4 and the iron content of added amorphous iron oxides. This difference, corresponding to $0.32 \text{ (mmol Fe) g}^{-1}$ akaganéite, is undoubtedly due to a small content of amorphous iron oxides in the akaganéite, because this fraction was extracted along with the added amorphous iron oxides. At pH 8.4–9.9 extracted iron continued to increase up to approximately 80 days. Between 80 days and 155 days no further iron was released. This surplus amounted to $1.18 \text{ (mmol Fe) g}^{-1}$ akaganéite and corresponds to the dissolution of approximately 11 % akaganéite.

The results of this long-term interaction between akaganéite and EDTA are consistent with those of the short-term investigation,⁸ showing that only weakly alkaline EDTA solutions but not weakly acidic or neutral EDTA solutions affect akaganéite. The results reported previously^{6,7} for a number of other iron oxides, showing only negligible attack on the crystalline iron oxides when mixtures of amorphous and crystalline iron oxides were treated with EDTA, agree with the results for the interaction between akaganéite and EDTA at pH 4. The further increase in extracted iron between 20 days and 80 days with weakly alkaline EDTA solutions resembles that obtained when soils or selected minerals were extracted with EDTA^{4,5,7} and was attributed to the dissolution of poorly crystalline iron oxides. This explanation does not apply to akaganéite, because no increase was observed between 20 days and 101 days at pH 4.

The resistance towards dissolution of akaganéite at pH ≤ 7.5 was considered⁸ due to adsorption of EDTA onto the oxide, which inhibits dissolution. Even though this explanation may apply to akaganéite, it does not hold for amorphous iron oxides, which are shown (Fig. 1) to be dissolved with similar rates at pH 4 and pH 9.9. Furthermore, adsorption of anions by ligand exchange onto crystalline iron oxides does not necessarily inhibit their dissolution, e.g. it was shown^{6,7,12} that several crystalline iron oxides dissolved in oxalate solution at pH 3, although oxalate is specifically adsorbed at least by goethite.¹³

Alternatively, the special structure of akaganéite may be responsible for the discrepancy between the akaganéite results and those of the other iron oxides, including the different susceptibility of akaganéite below and above pH ~ 7.5 . The micro-structure of this oxide is based on the hollandite unit cell, which has a small central tunnel. These units are considered packed into bundles forming large square tunnels, approximately 3 by 3 nm wide,¹⁴ although the existence of these large tunnels has been doubted.^{15,16} The small tunnels are occupied – at least during formation – by chloride ions and the large tunnels by water.¹⁴ Chloride ions seem essential for the structure and stability of akaganéite.^{9,16} Thus, the stability was claimed to be markedly reduced when the chloride content was reduced.⁹ In the present investigation, the chloride content of akaganéite was 4.3 %, close to the 4.6 % expected for one chloride ion per unit cell.¹⁶ The chloride content was reduced to 1.7 % after extraction with 0.1 M EDTA for 180 days at pH 9.9, whereas extraction with 0.2 M EDTA for 80 days at pH 4.0 only reduced the content to 3.8 %. The greater reduction at pH 9.9 may be attributed to the higher hydroxyl concentration if it is assumed that the chloride ions are exchanged by hydroxyl ions. The reduction of the chloride content by extraction in alkaline solution may then increase the susceptibility of the oxide towards EDTA resulting in the observed surplus of $1.18 \text{ (mmol Fe) g}^{-1}$ akaganéite being extracted between 20 days and 80 days.

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