Akagenéite (β–FeOOH) precipitation in inland acid sulfate soils of south-western New South Wales

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Iron sulfide minerals are one of the end products of sulfate reduction process occurring naturally in lakes, rivers and oceans. Pyrite, greigite, pyrrohtite, chalcopyrite and mackinawite are commonly found iron sulfide minerals in natural environment (Fanning, 2002). These minerals are thermodynamically stable under reducing conditions, however, upon exposure to air these minerals get oxidized and release copious amounts of sulfuric acid into the surrounding environment. Ferrous sulfate produced by the weathering of iron sulfide minerals can get oxidized to ferric sulfate and upon hydrolysis leads to the formation of various secondary iron oxides depending on the factors such as pH, sulfate activity and the presence or absence of base cations (Bigham, 2002; Bigham, 2000). The most commonly occurring iron oxide phases in acidic, sulfate–rich environments are ferrihydrite ($Fe_5HO_8.H_2O$), jarosite $[K,H_3O,Na]Fe_3(SO_4)_2(OH)_6$, schwertmannite $[Fe_8O_8(OH)_6SO_4.nH_2O]$, lepidocrocite (γ–FeOOH) and goethite (α–FeOOH) (Bigham, 1996). At low pH (< 3), high sulfate ion concentrations (> 3000 mg/L) and constant bacterial activity, jarosite will precipitate in the presence of required cations (Bigham and Nordstrom, 2000). Schwertmannite is the dominant mineral forming at relatively higher pH (3–4) and lower sulfate concentrations (1000–3000 mg/L). Schwertmannite formation also requires bacterially mediated rapid oxidation of Fe^{2+} (Bigham, 1994; Regenspurg, 2004). Slightly acidic to near neutral pH values are favourable for ferrihydrite and goethite precipitation. The precipitation of these mineral phases have been identified in many acidic sulfate–rich environments including coastal and inland acid sulfate soils (ASS), acid rock drainage and acid mine drainage sites. In comparison to the commonly reported secondary iron minerals such as goethite, hematite and lepidocrocite in soils; akaganéite has often been reported to form as a corrosion product of Fe in chloride rich aquatic environments. Akaganéite is relatively rare in the soil environment. Fitzpatrick et al. (2008) have reported the presence of akaganéite in drains of wheatbelt region of Western Australia. The secondary iron minerals mentioned above serve as potential sinks of trace metals because of their great reactive surface area and high affinity for trace metals in the acidic environments.

The objective of the present study was to determine the mineralogy of the precipitates formed in the oxidized surface horizon of an ASS. The study site is an inland ASS, Bottle Bend Lagoon, in the south–west of New South Wales, Australia. In 2002, previously inundated lagoon transformed into an active ASS with extreme saline acidic conditions (pH < 3, EC = 30 dS/m) upon separation from the

Murray River following low riverine flows (McCarthy, 2006). Another acidification event occurred at the site in 2009 when the lagoon dried again and resulted in even more extreme levels of salinity and acidity (pH ~ 2, EC = 216 dS/m).

Soil samples were collected from the oxidized surface layer (0–5 cm depth) of the partially dried lagoon in February 2009, and were characterized mineralogically by random powder X-ray diffraction (GBC MMA: CoKα radiation, λ= 1.7890 Å, operating conditions of 35 kV and 28.5 mA). Transmission electron microscopy (TEM), scanning transmission electron microscopy combined with energy dispersive X-ray spectroscopy (STEM-EDS) and scanning electron microscopy (SEM) in conjunction with XRD were used to determine the mineralogy and chemical composition of the mineral phases present in the samples. For TEM and STEM-EDS, the samples were sonified in E–pure water and then the specimens were prepared by putting a drop of the suspension on carbon-coated copper grid. Transmission electron micrographs were recorded on Phillips CM 12 operating at 120 kV. Scanning transmission electron microscopy and energy dispersive X-ray spectroscopy were performed using JEM-2200 FS operated at 200 kV.

Gypsum, quartz, halite, akaganeite, kaolinite and illite were identified as the major phases in the original samples. X-ray diffraction analysis of surface precipitates revealed the abundance of halite and gypsum in the surface precipitates. A sequential washing procedure was followed to dissolve halite and gypsum from the samples (sequential washings with E-pure water, 0.01 M HCl and 0.01 M EDTA). The X-ray diffraction patterns of the original and washed samples showed the presence of akaganéite as a single iron oxide phase as the oxidation product of iron sulfides. The XRD patterns of a representative sample before and after washing are shown in Figure 1.

The TEM images of the untreated and washed samples (Fig. 2) also indicated the presence of akaganéite, as the only iron oxide. The length of the akaganéite particles was variable with particles ranging from 50–500 nm. Most of the particles were spindle shaped with some particles also showing a cigar–shaped morphology. The bright field STEM imaging of the original and washed samples was done to determine the chemical composition of the akaganéite particles identified in the XRD patterns and TEM images of the samples. The STEM–EDS imaging confirmed the results from XRD and TEM for the presence of akaganéite. The energy dispersive spectroscopic analyses of the samples showed the presence of with Fe, O and Cl in the crystal structure.

The results from the present study showed that akaganéite was the major iron oxides in the surface horizon of an inland acid sulfate soil and the mineral was stable under the prevailing conditions i.e. highly saline and acidic. The results provide an insight to understand the conditions favourable for the formation and stability of akaganéite in the soil environment and the consequences of the presence of the mineral on soil properties.
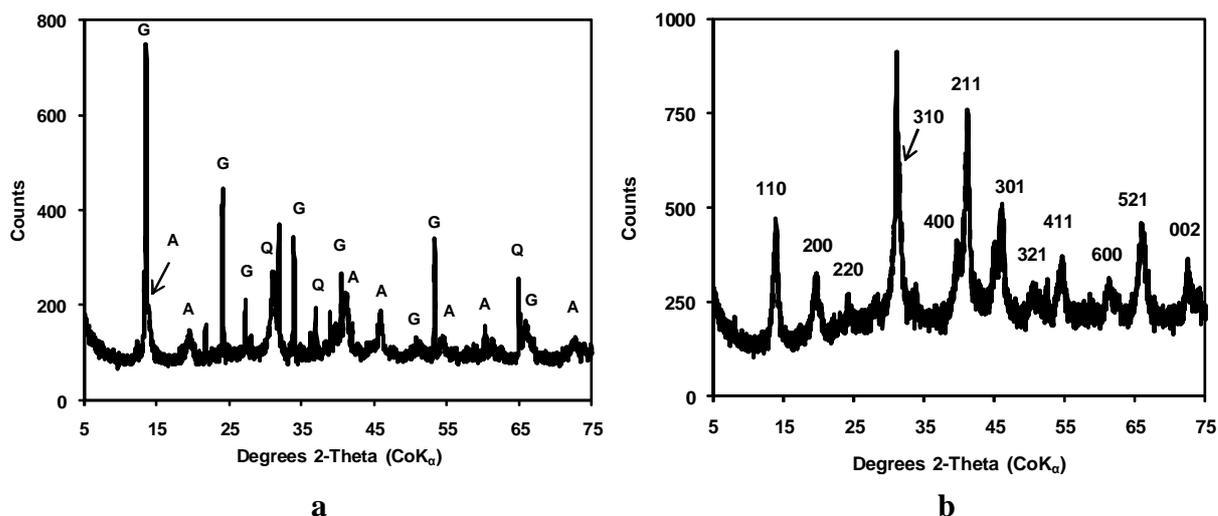
Fig. 1. Random powder XRD patterns of (a) untreated surface precipitate from an inland acid sulfate soil. A = akaganeite, G = gypsum and Q = quartz (b) surface precipitates after removal of halite and gypsum showing all hkl diffraction peaks of akaganéite.

Acknowledgements

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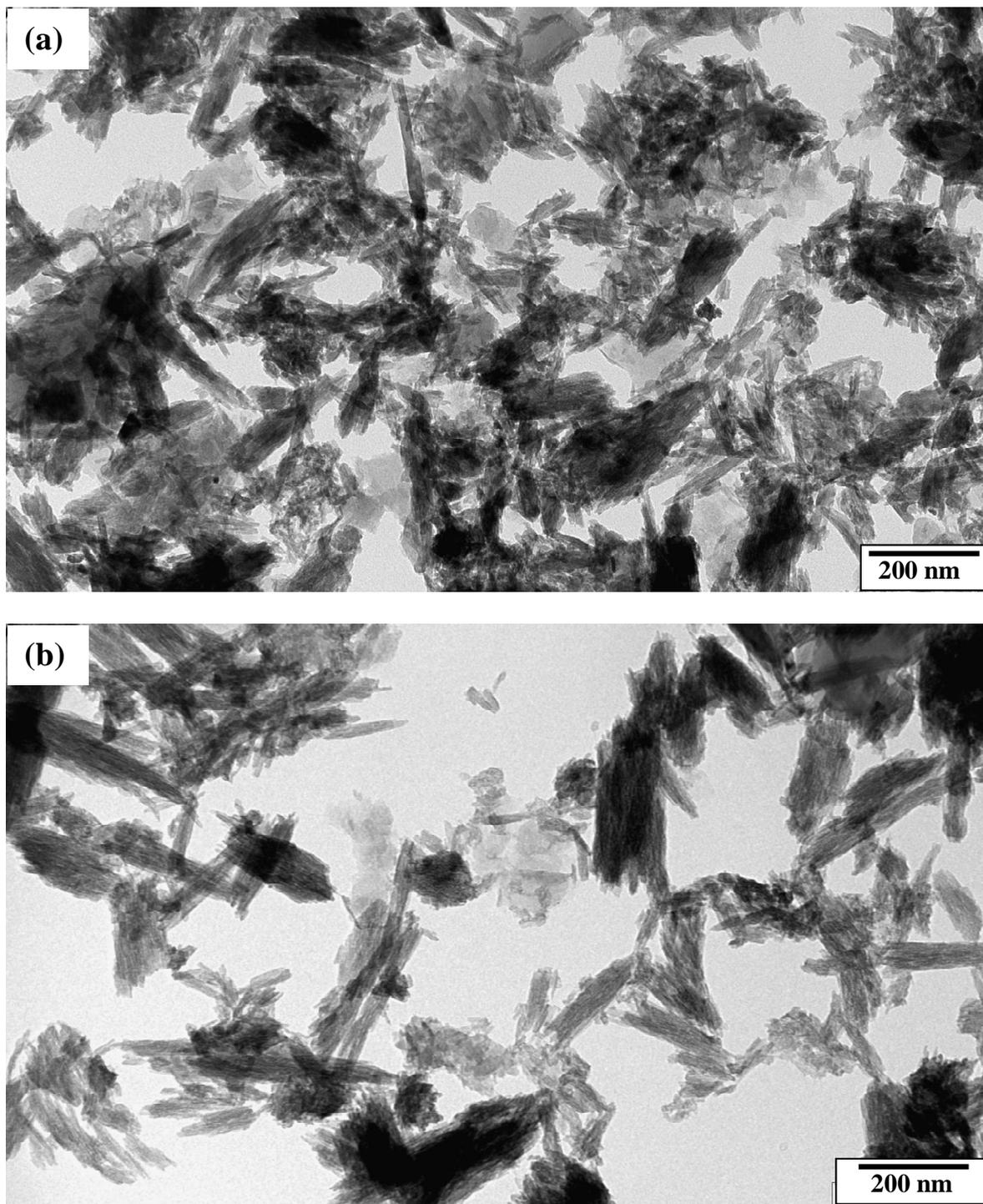
Fig. 2. Transmission electron microscopic images of (a) untreated surface precipitates and (b) precipitates after removal of halite and gypsum showing spindle shaped akaganéite particles.