Structure and reactivity of synthetic Co-substituted goethites

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ABSTRACT

A set of synthetic goethites were prepared from Fe3+- and Co2+-nitrate solutions in alkaline media with a Co/(Co + Fe) ratio ($x_{Co}$) up to 10 mol%. The structural characterization of the resultant solid phases was carried out by X-ray diffraction (XRD). XRD analyses showed that in preparations with $x_{Co}$ <10 mol%, Co-substituted goethite was the only crystalline phase present. Atomic and cell parameters for the samples synthesized were obtained by the Rietveld refinement of the XRD data, and showed that the unit cell in the goethite-like phase is contracted as a function of $x_{Co}$. Little deviation from the Vegard rule was observed for all unit-cell parameters. Cobalt substitution produces an increase in the surface area of the goethite, as well as an increment in the dehydroxylation temperature. The acid dissolution of all Co-goethites showed an increase in dissolution rate with the Co content, and a congruent behavior was observed. The activation energy for dissolution was obtained two samples. A modified first-order Kabai equation best describes the dissolution data.

Keywords: Co-goethite, isomorphous substitution, Rietveld refinement, acid dissolution

INTRODUCTION

Goethite is the most common Fe oxide present in soils (Cornell and Schwertmann 1996). Goethite has isostructural equivalents in which cations, other than Fe, occupy the interstices of the oxygen framework. Most of these oxide-hydroxides exist as pure minerals although they are rarer than goethite. The existence of these structural compounds suggests the likelihood of isomorphous substitution for Fe3+ by other cations. Naturally occurring goethite is unlikely to exist in pure form, and different foreign elements such as Al, Mn, Cr, and Ni may be present in its structure (Kühnel et al. 1975; Norrish 1975; Schwertmann and Taylor 1989). Isomorphous replacement of Fe in the goethite structure by other cations can be readily achieved in synthetic goethites.

The incorporation of foreign ions alters the properties of goethite such as its cell parameters, structural OH content, thermal and magnetic properties, and dissolution behavior (Murad and Schwertmann 1983; Schwertmann 1984; Gasser et al. 1996; Pozas et al. 2004). Among the foreign cations, Co is attractive because of its significance for plant and animal nutrition (Alloway 1990). Besides, Co-substituted goethite has been used as precursor for the production of Co-Fe metallic particles (Iwasaki and Yamamura 2002; Nuñez et al. 2003).

Different aspects of Co-substituted goethite obtained in alkaline media have been studied by other authors (Cornell and Giovanoli 1989; Gerth 1990; Cornell 1991; Gasser et al. 1996; Iwasaki and Yamamura 2002). Recent studies of Co-goethites obtained from aerial oxidation of both Fe2+ and Co3+ solutions were carried out by Pozas et al. (2002, 2004).

The aim of this work was to obtain Co-substituted goethite by co-precipitation of Fe3+ and Co2+ solutions in alkaline media by the same pathway described for the synthesis of Mn-substituted goethite (Sileo et al. 2001). Then, the morphology, thermal, and acid dissolution behavior of these samples was studied as a function of Co content in the goethite structure. The unit-cell parameters and atomic distances were calculated by the Rietveld refinement method (Rietveld 1969).

EXPERIMENTAL METHODS

Materials

The α-FeOOH particles were prepared from mixed ferrihydrites containing different molar ratios ($x_{Fe}$) that varied in the 0–10 mol% percent range. Ferrihydrites were precipitated by adding 2 mol/dm3 NaOH solution to different Fe3+ and Co2+ nitrate solutions; final ratio Me/OH– in all preparations was 0.076. Initial Fe + Co concentration was 0.53 mol/dm3 in all samples. The resultant precipitates were washed twice with doubly distilled water and centrifuged. After this treatment, the samples were held at 60 °C for 15 days in closed polyethylene flasks containing 0.3 mol/dm3 NaOH. Initial values of (Co)/(Co + Fe) × 100 mole ratios ($x_{Co}$) were 0, 3, 5, 7, and 10 mol% (samples were named G0, G3, G5, G7, and G10, respectively). After the aging period, the samples were centrifuged, dried at 40 °C, and the amorphous materials were extracted with 0.4 mol/dm3 HCl at room temperature (Cornell and Giovanoli 1989). The crystalline solids were washed with doubly distilled water until the conductivity of the filtrated solution was similar to that of doubly distilled water. The final samples were dried at 40 °C and gently crashed. All chemicals used were reagent grade.

Characterization

The Fe and Co contents were determined by atomic absorption spectrometry (AAS) in a GBC, Model B-932 spectrometer. Chemical analyses were made in duplicate by dissolving the samples in concentrated HCl and diluting to an adequate concentration with water. Diffraction patterns were recorded using a Siemens D5000 diffractometer in a Bragg-Brentano geometry equipped with CuKα radiation and a graphite monochromator. Data were collected in the 18.500° ≤ 2θ ≤ 132.000° range; the scanning step was 0.025°. Divergence, scattered, and receiving radiation slits were 1°, 1°, and 0.2 mm, respectively. The step width assured a minimum of about 12 intensity points for the narrower peaks. Generator settings were fixed at...