

THE NATURE OF Co IN SYNTHETIC Co-SUBSTITUTED GOETHITES

RAÚL POZAS¹, T. CRISTINA ROJAS¹, MANUEL OCAÑA^{1,*} AND CARLOS J. SERNA²

¹ Instituto de Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, C. Américo Vespucio s/n, 41092 Sevilla, Spain

² Instituto de Ciencia de Materiales de Madrid, CSIC, Campus Universitario de Cantoblanco, 28049 Madrid, Spain

Abstract—The crystallochemical features of Co in Co-substituted goethite solid-solutions prepared by two different procedures have been studied using infrared, X-ray photoelectron and electron energy loss spectroscopies. It was found that the path followed for the synthesis of Co-substituted goethite determines the oxidation state of Co in the goethite structure. Thus, in the solid-solution prepared by precipitation with Na₂CO₃ of an Fe(II) aqueous solution containing Co(II) cations, followed by the aerial oxidation of the precipitate, the Co cations were found to be divalent, whereas trivalent Co was incorporated into the goethite obtained by ageing a solution containing Fe(III) and Co(II) cations precipitated by the addition of KOH. This different behavior is explained by the higher pH of goethite formation in the latter case, which favors the oxidation of the Co(II) cations.

Key Words—Cobalt, EELS, Goethite, IR, Solid-solution, XPS.

INTRODUCTION

Goethite (α -FeOOH) is the most ubiquitous of the Fe oxide minerals in soils and occurs in almost every type of soil environment (Schwertmann and Taylor, 1977). Naturally occurring goethite is unlikely to exist as pure α -FeOOH and usually has incorporations of different foreign elements, such as Al, Cr, Mn and Ni (Kühnel *et al.*, 1975; Norrish, 1975; Schwertmann and Taylor, 1989). The variety of metal cations that has been reported to structurally incorporate (solid-solution) into synthetic goethite is even higher (Al, Cd, Co, Cr, Cu, Ga, Ge, Mn, Ni, Pb, Sc, V and Zn) (Gerth, 1990; Cornell, 1991; Cornell and Schwertmann, 1996). It might be expected that the changes in crystal chemistry and unit-cell size due to the incorporation of these cations in goethite would also lead to a variation in their properties (in crystal size, specific surface area, IR spectra, structural OH content, Mössbauer spectra, thermal and magnetic properties and dissolution) (Murad and Schwertmann, 1983; Schulze and Schwertmann, 1984; Schwertmann, 1984; Gasser *et al.*, 1996) for which several studies have been conducted aiming to investigate the crystallochemical features of such solid-solutions.

The study of synthetic Co-substituted goethite offers additional interest since particles of this material are usually utilized as a precursor for the production of Fe-Co alloys consisting of acicular particles for magnetic recording media (Iwasaki and Yamamura, 2002; Nuñez *et al.*, 2003; Pozas *et al.*, 2004). Most works on the incorporation of Co cations into goethite have been carried out on samples prepared by coprecipitation of

Fe(III) and Co(II) solutions at elevated pH (>11) followed by the ageing of the precipitate at >60°C (Cornell and Giovanoli, 1989; Gerth, 1990; Cornell, 1991; Gasser *et al.*, 1996; Iwasaki and Yamamura, 2002). These studies suggested, mainly on the basis of the observed unit-cell contraction of goethite, that Fe(III) cations are substituted by Co(III) in the octahedral positions of the goethite structure (ionic radius of Co(III) < ionic radius of Fe(III) in high spin configuration) (Shannon, 1976), which must involve the oxidation of Co(II) to Co(III) during the synthesis process. The maximum degree of substitution reported for these Co-goethites was 10 mol.% (Gerth, 1990; Cornell and Schwertmann, 1996; Gasser *et al.*, 1996), which is much lower than that observed for other trivalent ions such as Al(III) (up to 33%) (Schulze, 1984).

In previous works, we have reported that Co-substituted goethite particles can also be obtained by precipitation with Na₂CO₃ of Fe(II) aqueous solutions containing Co(II) followed by oxidation by air bubbling of the precipitate (Nuñez *et al.*, 2003; Pozas *et al.*, 2004). Here, the unit-cell parameters of the resulting goethite samples were found to increase in comparison with undoped goethite, which seems to indicate that Co cations were incorporated into the goethite structure in a divalent state since the radius of this ion (low-spin configuration) in octahedral position (0.74 Å) is higher than that corresponding to Fe(III) (0.65 Å) (Shannon, 1976).

The aim of this work is to determine the Co chemical state in the Co-substituted goethites obtained as described above from both Fe(II) and Fe(III) solutions. For this purpose, we have first studied the crystallochemical features of the Co-substituted goethite samples using X-ray photoelectron spectroscopy (XPS), which is known to be sensitive to the Co oxidation state (Jiménez

* E-mail address of corresponding author:

mjurado@icmse.csic.es

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et al., 1998). Since this technique is more appropriate for surface analysis, the samples were also studied by electron energy loss spectroscopy (EELS) conducted on individual goethite particles (Leapman *et al.*, 1982). The unit-cell parameters of samples were also measured in order to confirm the formation of Co-goethite solid-solution in the samples.

EXPERIMENTAL

Sample preparation

The Co-substituted goethite particles were synthesized using two different procedures. The first (Pozas *et al.*, 2004) involved precipitation of a 0.6 mol dm^{-3} aqueous solution of Fe(II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Aldrich, 99%) containing Co(II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich 98%) (Co/(Fe+Co) atomic ratio = 10%), by the addition of a 0.9 mol dm^{-3} sodium carbonate (Na_2CO_3 , Aldrich 99.5%) solution, which resulted in a pH, after precipitation, of 9.0. The suspension precipitated was then oxidized at constant temperature (40°C) for 6 h by bubbling air at a constant flow rate ($2 \text{ dm}^3 \text{ min}^{-1}$). It should be noted that the selected Co(II) content corresponds to the maximum amount that could be added to goethite without the appearance of secondary phases (Pozas *et al.*, 2004). A pure goethite sample was also obtained by this procedure (Pozas *et al.*, 2002) for comparison purposes. The samples obtained in the absence and in the presence of Co by this method were named as G_{FeII} and Co- G_{FeII} , respectively.

The second procedure (Gasser *et al.*, 1996) consisted of the precipitation of a 1 mol dm^{-3} Fe(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich 99.99%) aqueous solution containing Co(II) nitrate (Co/(Fe+Co) atomic ratio = 22.5%) by the addition of a 5 mol dm^{-3} potassium hydroxide (KOH, Fluka = 85%) solution, after which a pH value of 12.5 was noted. The suspension obtained was further aged at 63°C for 15 days. After this treatment, the remaining X-ray amorphous materials were removed from the sample by a 2 h treatment with 3 mol dm^{-3} sulfuric acid (H_2SO_4 , Aldrich 98%) at 50°C . According to Gasser *et al.* (1996), the amount of Co selected here gave the maximum incorporation of Co into goethite without appearing in other crystalline phases after washing. The sample obtained by this method was named Co- G_{FeIII} .

Once the reactions were complete, all precipitates were centrifuged and washed several times with deionized water for purification. Finally, the powdered solids were collected by filtration and dried at 50°C before analysis.

Characterization techniques

Transmission electron microscopy (TEM, Philips 200 CM) was used to examine the size and morphology of the particles. Phase identification was carried out by

X-ray diffraction (XRD) in a Siemens D501 apparatus using $\text{CuK}\alpha$ radiation and a diffracted-beam graphite monochromator. Unit-cell parameters of the samples were determined by a least-squares fit of the XRD data using Si as the internal reference standard. The infrared (IR) spectra of the powders diluted in KBr were recorded in a Nicolet 510 FTIR spectrometer. The quantitative composition of the samples, in terms of the Co/(Co+Fe) atomic ratio, was determined by X-ray fluorescence (XRF, Siemens SRS 3000). To gain additional information on the particles' composition, the samples were also analyzed by energy dispersive X-ray analysis (EDX, Philips DX4), installed in the TEM microscope.

The XPS spectra were obtained in a VG Escalab 220 apparatus using the $\text{MgK}\alpha$ excitation source. Calibration of the binding energy scale of the spectra was done at the C1s peak of the surface carbon contamination taken at 284.6 eV .

To analyze the samples by EELS, commercial Co(II) oxide (CoO, Aldrich 99.9%) and synthetic Co(III) oxyhydroxide (CoOOH) obtained by the method described by Mcardell *et al.* (1998) were used as reference compounds for divalent and trivalent oxidation states of Co, respectively. The energy resolution of the EELS spectra, measured at the zero-loss peak of the coupled microscope/spectrometer system was $\sim 1.2 \text{ eV}$. The spectra were corrected for dark current and channel-to-channel gain variation. A low-loss spectrum was also recorded with each edge in the same illuminated area and using the same experimental conditions. After the subtraction of the background with a standard powder-law function, the spectra were deconvoluted for plural scattering with the Fourier-ratio method. All these treatments were performed within the EL/P program (Gatan). To calibrate the energy we used as internal standard the $\text{L}_{2,3}$ edges of Fe, which was added to the reference compounds as goethite particles. In all cases, the Fe- L_2 edge appeared at 709 eV .

RESULTS AND DISCUSSION

Acicular particles of 130 nm length and axial ratio 5 were obtained when starting from the Fe(II) solution (sample Co- G_{FeII}), whereas the particle size and axial ratio were greater (700 nm long and axial ratio of 10) for the sample obtained from the Fe(III) salt (sample Co- G_{FeIII}) (Figure 1). According to XRD, both samples consisted of single-phase goethite (Figure 2). It should be noted that the relative intensity of the peaks corresponding to the $hk0$ reflections were higher for sample Co- G_{FeIII} , which is probably due to the higher preferential orientation on the plane of the sample holder induced in this sample, as consequence of its greater axial ratio (Figure 1). The Co content (Co/(Fe+Co) mole ratio) measured by XRF was similar (10%) to the raw value for sample Co- G_{FeII} (Table 1), suggesting the complete incorporation of Co in the goethite particles.

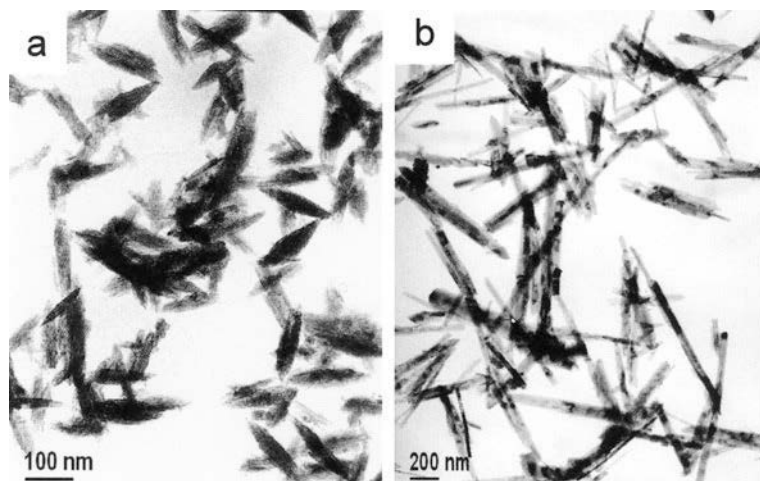


Figure 1. TEM images of the Co-goethite samples synthesized from Fe(II) and Co(II) salts (sample Co-G_{FeII}) (a) and from Fe(III) and Co(II) salts (sample Co-G_{FeIII}) (b).

However, in the case of sample Co-G_{FeIII}, the amount of Co cations detected by XRF was less (12%) than the raw value (22.5%), as a consequence of the release of amorphous phases during the washing procedure. Chemical analysis carried out for both samples by EDX also showed the presence of Co in each single particle in a proportion similar to that of the overall solids, indicating good chemical homogeneity at the particle level.

In order to confirm the formation of a solid-solution of Co in goethite, we measured the unit-cell parameters for both Co-substituted samples (Co-G_{FeII} and Co-

G_{FeIII}), which were compared with those for undoped goethite (sample G_{FeII}). A clear decrease in these unit-cell parameters was observed for sample Co-G_{FeIII} in comparison with pure goethite (sample G_{FeII}) (Table 1), suggesting, in agreement with previous works, (Cornell and Giovanoli, 1989; Gerth, 1990; Gasser *et al.*, 1996) that Co cations are incorporated in the goethite particles in a trivalent state, since the ionic radii for these Co(III) cations in high-spin configuration (0.525 Å) is lower than that of high-spin Fe(III) (0.65 Å) (Shannon, 1976). It should be noted that octahedral Co(II) and Co(III) cations are found in most oxide structures in low-spin and high-spin configurations, respectively, whereas Fe cations are always in the high-spin configuration (Burns, 1976; Cornell and Giovanoli, 1989; Gerth, 1990; Jiménez Mateos *et al.*, 1990). Moreover, it was observed that although only the *c* parameter followed Vegard's law (Gasser *et al.*, 1996), the decrease of the unit-cell volume detected (Table 1) obeyed Retgers' rule (Retgers, 1889). This behavior seems to suggest that most Co(III) cations were incorporated into the goethite structure. Obviously, these findings indicate that an oxidation process from Co(II) to Co(III) occurred during synthesis.

On the contrary, an increase of the unit-cell parameters *b* and *c* when compared with those of undoped goethite was observed for sample Co-G_{FeII} (Table 1), which would be in agreement with the formation of a solid-solution between Co(II) and goethite since the ionic radii for low-spin Co(II) in octahedral position (0.74 Å) is greater than for high-spin Fe(III) (0.65 Å) (Shannon, 1976). It should be noted that the value of the unit-cell parameter *a* remained unchanged with respect to that of pure goethite. However, it is well known that it is affected by structural defects (Schulze, 1984; Schulze and Schwertmann, 1984; Gasser *et al.*, 1996) which, in this case, should

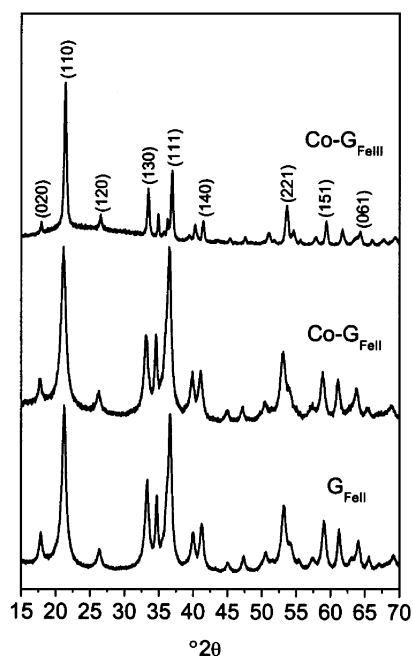


Figure 2. XRD patterns of samples G_{FeII}, Co-G_{FeII} and Co-G_{FeIII}.

Table 1. Composition, unit-cell parameters (a , b , c) and unit-cell volume (V) for the goethite samples.

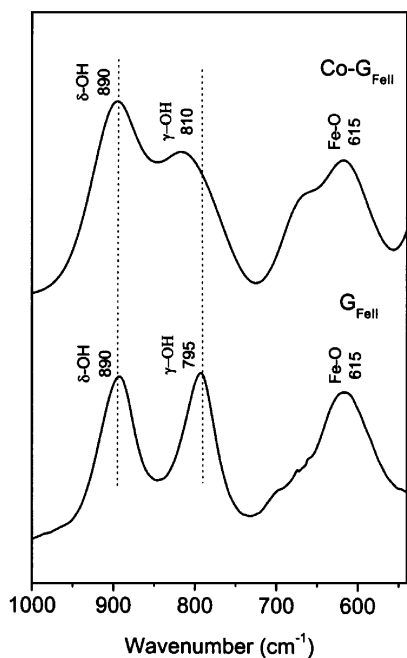
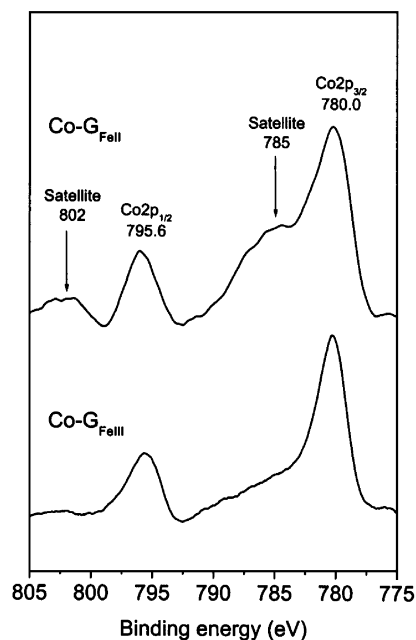
Sample	Co/(Fe+Co) (% mole)	a (nm)	b (nm)	c (nm)	V (nm ³)
Goethite	0	0.4622 (4)	0.9956 (4)	0.3028 (1)	0.1393 (3)
Co-G _{FeII}	10	0.4616 (2)	0.9986 (3)	0.3034 (1)	0.1399 (1)
Co-G _{FeIII}	12	0.4573 (2)	0.9922 (3)	0.3008 (1)	0.1365 (2)

mainly come from the required charge compensation due to the different valence of Co(II) and Fe(III). Finally, since this substitution is not isomorphous, Vegard's and Retgers' rules cannot be applied in this case to gain information on the extent of the Co(II) incorporation into the goethite structure. Nevertheless, the amount of Co(II) in solid-solution in our case might be less than the total Co content ($\text{Co}/(\text{Fe}+\text{Co}) = 0.1$) since it has been reported that the degree of Fe(III) substitution is usually less for the divalent cations ($M(\text{II})/M(\text{II})+\text{Fe}(\text{III}) \leq 0.07$) than for the trivalent ones ($M(\text{III})/M(\text{III})+\text{Fe}(\text{III}) \geq 0.1$) (Cornell and Schwertmann, 1996).

The difference in the Co chemical state suggested above seems to be supported by the IR spectrum of the samples. Thus, in the case of sample Co-G_{FeIII}, an increase in the $\delta\text{-OH}/\gamma\text{-OH}$ band splitting was detected with respect to goethite (data not shown), as was previously observed for goethites substituted with trivalent cations, including Co(III) (Gasser *et al.*, 1996) and Al(III) (Schulze and Schwertmann, 1984, 1987), suggesting the isomorphous substitution of Fe(III) by Co(III). In contrast, in the case of sample Co-G_{FeII}, broader bands along with a decrease of the $\delta\text{-OH}/\gamma\text{-OH}$

band splitting was detected in comparison with undoped goethite (Figure 3). These features have previously been attributed to an increase of the amount of structural defects in goethite (Schulze and Schwertmann, 1984), which evidently occurs in this case since, as mentioned above, the substitution of Fe(III) by Co(II) cations in the goethite structure, would require a charge compensation that may involve either the generation of O^{2-} vacancies or the presence of an excess of OH^- anions. Although it has not been confirmed experimentally, the latter mechanism has usually been assumed to be more likely in the substitution of Fe(III) by divalent cations (Cornell and Schwertmann, 1996).

This finding was supported by the XPS spectra for Co-G_{FeII} and Co-G_{FeIII} samples. Thus, the Co2*p* XPS spectrum for sample Co-G_{FeII} presented two strong satellites located at the high binding energy side (785 and 802 eV) of the broad main peaks due to Co2*p*_{3/2} and Co2*p*_{1/2} (780.0 and 795.6 eV, respectively) (Figure 4), which indicates the presence of Co with a divalent oxidation state at least in the outer particle layers (Jiménez *et al.*, 1998). The absence of both satellites for sample Co-G_{FeIII} (Figure 4) provides further evidence

Figure 3. IR spectra of samples G_{FeII} and Co-G_{FeII}.Figure 4. Co2*p* XPS spectra for samples Co-G_{FeII} and Co-G_{FeIII}.

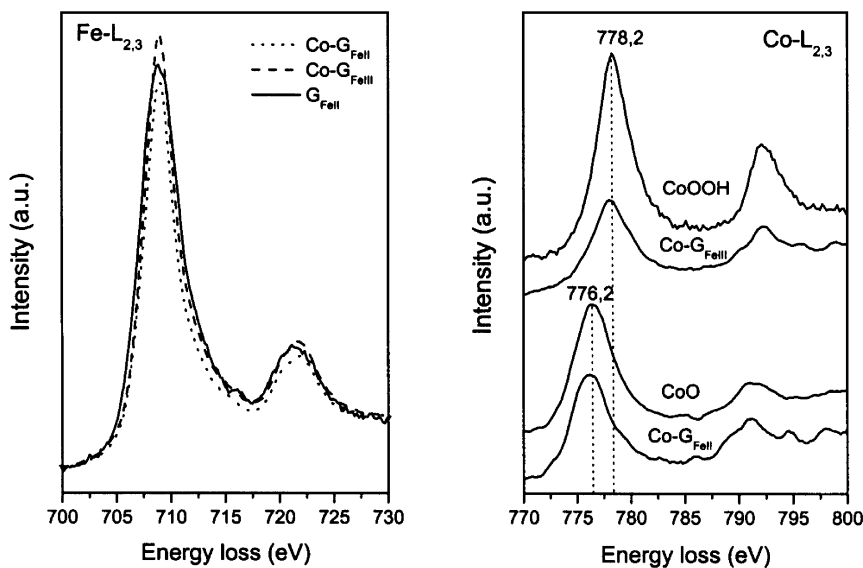


Figure 5. EELS spectra for samples G_{FeIII} , $Co-G_{FeII}$ and $Co-G_{FeIII}$ at the $Fe-L_{2,3}$ (left) and the $Co-L_{2,3}$ (right) edges and for the reference compounds. The edges are normalized to the jump.

that Co cations are trivalent in this case, as previously suggested (Cornell and Giovanoli, 1989; Gerth, 1990; Gasser *et al.*, 1996).

It should be noted that XPS is a surface analysis technique. The unambiguous determination of the Co oxidation state in goethite requires further characterization of the samples by using a bulk technique, *e.g.* EELS (Figure 5). We have restricted our attention to the $L_{2,3}$ edges of the EELS spectrum, in which an incident electron of well defined energy excited a $2p_{1/2}$ or $2p_{2/3}$ core electron to empty bound states or to continuous ones. These L_2 and L_3 transitions include sharp and intense peaks known as 'white lines' due to transitions of these core electron to empty $3d$ states. It is well known that the interpretation of the near edge structure of the $L_{2,3}$ edges of the transition metals and their compounds is not simple. The different characteristic parameters of

the spectra such as peak energy, absolute intensity of the white-line (normalized to the continuum after the edge), or the L_3/L_2 area ratios, depend on chemical composition, structure, formation of alloys, crystal field, particle size, or magnetic moment (Pearson *et al.*, 1988; Pease *et al.*, 2001; Falqui *et al.*, 2003). However, in spite of the difficulty of this analysis, it is clear that these $L_{2,3}$ edges are sensitive to the oxidation state and to the electronic structure around the absorbed atoms (Leapman *et al.*, 1982).

The $Fe L_{2,3}$ spectra for samples $Co-G_{FeII}$ and $Co-G_{FeIII}$, and for the undoped goethite sample (sample G_{FeII}), normalized to the continuum spectrum after the edge, are shown in Figure 5 (left). The differences observed in the intensity of the $Fe L_{2,3}$ resonances could be attributed to changes in the electronic structure (the density of states and relative occupation of the $3d$ bands) of the $Fe(III)$ cations. This effect can probably be associated with the variation of the unit-cell dimensions of goethite as a consequence of the formation of a solid-solution between Co cations and goethite, as previously observed for other systems (Lloyd *et al.*, 1995).

More interesting from our point of view is the examination of the $Co-L_{2,3}$ edge (Figure 5, right). The positions of the Co edges for sample $Co-G_{FeII}$ are the same as those of the CoO reference, while these peaks are shifted to higher energy (~ 2 eV) for sample $Co-G_{FeIII}$, this position being similar to that found for the $CoOOH$ reference. These results confirm that the cobalt cations are divalent for the sample prepared from $Fe(II)$ solutions ($Co-G_{FeII}$), whereas in that obtained from $Fe(III)$ solution ($Co-G_{FeIII}$) are in a trivalent state.

The different oxidation state observed for Co in the two goethite samples can be largely explained by their different pH of formation (pH = 12.5 for the sample

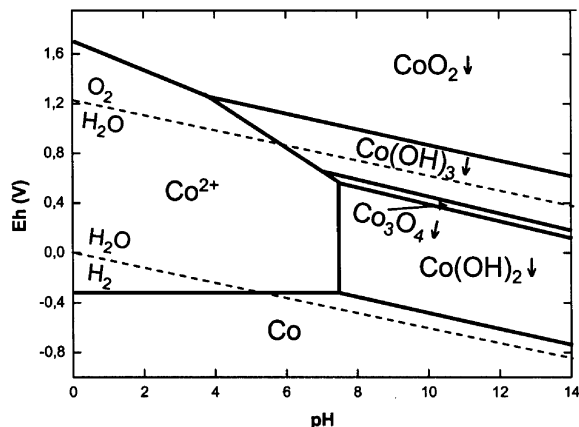


Figure 6. Eh vs. pH diagram for Co taken from Burriel *et al.* (1983).

synthesized following the method involving Fe(III) solutions and pH = 9 for that obtained by the method starting from Fe(II) solutions). Thus, it is well known that the oxidation of Co(II) cations to Co(III) is favored by the pH increase, as observed in the Eh-pH diagram of this system which is shown in Figure 6 (Burriel *et al.*, 1983). In agreement, the Co cations were only incorporated in their divalent state in the Co-substituted goethite sample obtained at the lower pH.

CONCLUSIONS

We have found that the path followed for the synthesis of Co-goethite determines the oxidation state of Co in the Co-goethite solid-solution. Thus, when such solid-solutions are prepared at pH ~9 by precipitation-oxidation from Fe(II) and Co(II) solutions, the Co cations are divalent, whereas trivalent Co was incorporated in those obtained at pH 12.5 from Fe(III) and Co(II) solutions precipitated. This different behavior can be largely attributed to the fact that the oxidation of Co(II) to Co(III) is favored as the pH of goethite formation increases.

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