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CHEMICAL AND ELECTROCHEMICAL CHARACTERIZATION OF COBALT BEARING FERRITES ORIGINATING FROM THE PURIFICATION OF COBALT CONTAINING WASTEWATER

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Abstract

In this research, the efficiency of the "ferrite process" for the purification of wastewater heavily contaminated with Cobalt (99.99% in the optimal conditions) was verified, and the three cobalt-bearing ferrites produced using three different Fe²⁺/Co²⁺ molar ratios (15/1, 7/1 and 3/1) were characterized by chemical analysis (ICP-AES and potentiometric titration), XRF, XRD and DSC, indicating Co_xFe^{II}_{1-x}Fe^{III}₂O₄ (x = 0.16, 0.35, and 0.65 respectively) as the most probable structure of the solids. Electrochemical analysis of the solid cobalt ferrites was performed using a carbon paste electrode in HClO₄ and HCl media. In each case, the first cyclic-voltammogram showed the participation of solid species in the electrochemical transformation process. In second and successive scans, the voltammograms indicated the redox couples Fe³⁺_{ads} + 1e⁻ ⇌ Fe²⁺_{ads} (E = 0.525 V vs. AgCl/Ag) and Co²⁺ + 2e⁻ ⇌ Co(s) (E = -0.230 V) in HClO₄, and FeCl₂⁺_{ads} + 1e⁻ ⇌ FeCl⁺_{ads} + Cl⁻ (E = 0.475 V) and CoCl_x^{(x-2)-} + 2e⁻ ⇌ Co(s) + x Cl⁻ (E = -0.320 V) in HCl.

Keywords: Cobalt, Wastewater treatment; Metal removal, Cobalt-ferrites, Voltammetry, Carbon paste electrode.

INTRODUCTION

Uncontrolled industrial and agricultural practices, combustion processes and mining have led to the accumulation of toxic heavy elements into the environment [1,2]. The growing concern of increasing environmental levels has prompted rigorous restriction

measures including the establishment of limit indices for each metal.

Cobalt is rare but widely distributed in nature [3]. Its abundance in the earth's crust is 0,0001-0,0002%, and range from 0.1 to 13 $\mu\text{g}\cdot\text{g}^{-1}$ in soils, from 0.1 to 5 $\mu\text{g}\cdot\text{L}^{-1}$ in drinking water and from 0.3 to 2.3 $\text{ng}\cdot\text{m}^{-3}$ in ambient air [4]. Cobalt is used in manufacture of alloys with a high melting point, in nuclear technology, in aeronautical and car industries [3] and the cobalt salts in the glass industry, for paints and coloured pottery [5].

Prompted by the need to ensure that permissible levels of heavy metals are not surpassed, in previous works we optimised a procedure for metal removal from wastewater involving their precipitation from alkaline solutions containing Fe(II) [6], a procedure described by Tamaura et al [7]. The ultimate aim was to achieve maximum purification and an end-product, or "ferrite sludge", with magnetic properties [8]. Using a 5 L reactor, the conditions giving rise to a high purification efficiency and a ferrite sludge of maximum magnetic permeability were: pH 10, temperature 60°C, air flow 30 l/min, stirrer rate 560 rpm and treatment time 1 h. The total amount of Fe(II) added to the solution to be treated had a notable effect on the degree of purification and also on the stoichiometry and properties of the ferrite [6].

The present investigation was designed to confirm the efficiency of the ferrite process for the purification of cobalt-containing wastewater, and to characterize the resultant cobalt ferrites produced using three different $\text{Fe}^{2+}/\text{Co}^{2+}$ molar ratios (15/1, 7/1 and 3/1), as previously described for Pb [9], Cu [10] and Cd [11]. In order to gain knowledge on the stability and possible reuse of these residues, the composition and stoichiometry of the ferrites were determined by chemical analysis (ICP-AES and potentiometric titration), X-ray fluorescence (XRF), X-ray diffractometry (XRD) and differential scanning calorimetry (DSC). The electrochemical behaviour of the solid species was also analysed using a carbon paste electrode (CPE) and an electrolyte binder [12]. Voltammograms of the cobalt ferrites were obtained in both HClO_4 and HCl media, and the oxidation and reduction peaks were interpreted by comparison with spectra corresponding to a pure iron ferrite sludge [13], iron oxides [14], magnetite [15] and a cobalt oxide.

EXPERIMENTAL

Equipment and Reagents

The equipment used in the ferrite-forming treatment process and the instruments for XRD, XRF and DSC have been described elsewhere [6, 9-11].

Electrochemical characterization of the samples was performed using an EG&G 273-A Princeton Applied Research potentiostat/galvanostat, equipped with model 270/250

Research Electrochemistry software (v. 4.23). A carbon paste electrode (prepared as indicated in the Procedures section), a Pt rod and an $\text{AgCl}|\text{Ag}|\text{KCl}_{\text{sat}}$ ($E^\circ = 0.222$ V vs. SHE, $[\text{KCl}] = 3$ M) electrode were used as the working, auxiliary and reference electrodes, respectively. All potential values are expressed with respect to this reference electrode.

Procedures

The cobalt ferrite samples were obtained by placing 2.43; 5.20 and 12.15 g of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ in a 5 L reactor and diluting to 2 L with water. Subsequently, 36.04 g of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ were added to the Co solution to yield $\text{Fe}^{2+}/\text{Co}^{2+}$ molar ratios of 15/1, 7/1 and 3/1, respectively. The pH was adjusted to 10 by the addition of NaOH solution. The reactor was then closed and the electric stirrer, temperature probe, pH electrode and air-supply tube connected. After 1 h, the liquid was separated from the solid ferrite by decanting and pressure filtration. The resulting solids were desiccated at 100°C for 2 h and powdered in an agate mortar. These solid products are hereafter referred to as Fe_xCo ($x = 15, 7$ or 3).

The Co(II) ($\lambda = 228.616$ nm) and total Fe ($\lambda = 259.940$ nm) levels remaining in the treated solutions and those of dissolved solid ferrite samples were determined by ICP-AES. The Co(II) and total iron contents of the solid ferrites were also estimated by XRF. For the determination of Fe(II), a 0.200 g sample of cobalt ferrite was dissolved with a solution containing 10 mL of 25% (v/v) HCl and 10.00 ml of $1.0\cdot 10^{-3}$ M $\text{K}_2\text{Cr}_2\text{O}_7$ in a nitrogen atmosphere. The excess of $\text{K}_2\text{Cr}_2\text{O}_7$ was determined by potentiometric titration using a standard solution of Fe(II) prepared from ferrous ammonium sulphate $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$. The J-shaped carbon paste electrode was prepared using ultra-pure graphite powder (particle size 200 mesh) supplied by Carbone Lorraine. Graphite powder (ca. 100 mg) and a small amount of ferrite (1-2 mg) were mixed with 1-2 drops (50-100 μl) of electrolyte binder. The mixture was then thoroughly homogenised and placed in the electrode reservoir. Voltammograms were obtained at a scan rate of 1.0 $\text{mV}\cdot\text{s}^{-1}$; potential slits were set by the supporting electrolyte. A linear scan was performed from the open-circuit potential in the positive direction (LSV), followed by successive cyclic scans towards negative potentials and back (CV1, CV2 etc).

RESULTS AND DISCUSSION

The residual average Co^{2+} concentration of the processed wastewater solutions determined by ICP ranged from 0.005 to 0.63 mg/l and corresponded to a Co^{2+} removal efficiency from 99.99 to 99.80 %. These values are of the same order as those obtained for

other heavy metals removed from wastewater samples from educational laboratories [6], and demonstrate the suitability of the ferrite precipitation method for the purification of wastewater highly polluted with cobalt.

Characterization of the Cobalt ferrites

To determine the Co^{2+} concentration and total Fe in the solid ferrites, 0.025 g of the solid product was dissolved in 9.00 mL of 25% HCl and diluted to 25.00 mL in deionized water. Co^{2+} and total Fe (Fe(III)+Fe(II)) contents were determined by ICP-AES, and Fe^{2+} levels were estimated by potentiometric titration as described in the experimental section. Table 1 shows the values obtained and also provide the percentage total Fe(II plus III) and Co^{2+} levels of the solid samples directly determined by XRF. Based on these values, stoichiometries and formula weights were proposed for the cobalt-bearing ferrites and are shown in Table 2.

TABLE 1

Estimation of Fe and Co in the cobalt-ferrites (%)

Ferrite	ICP - AES and			XRF	
	Fe(II)	Fe(III)*	Co	Total Fe	Co
Fe15Co	20,10 ±	48,13 ±	4,19 ± 0,03	68,23 ±	4,20 ± 0,02
Fe7Co	15,61 ±	48,02 ±	8,87 ± 0,04	63,62 ±	8,80 ± 0,06
Fe3Co	8,25 ± 0,09	47,82 ±	16,52 ±	56,08 ±	16,60 ±

TABLE 2

Stoichiometries and formula weights of cobalt-ferrites

Fe^{2+}/Co^{2+} Ratio	Stoichiometries	formula weight (g/mol)
15	$Co_{0,16}Fe^{II}_{0,84}Fe^{III}_2O_4$	232,05
7	$Co_{0,35}Fe^{II}_{0,65}Fe^{III}_2O_4$	232,62
3	$Co_{0,65}Fe^{II}_{0,35}Fe^{III}_2O_4$	233,56

To confirm the stoichiometry of these ferrites, solid samples were subjected to XRD and DSC analysis. Figure 1 shows the XRD patterns corresponding to the compounds Fe15Co, Fe7Co and Fe3Co, respectively. It can be observed only the presence of a major magnetite phase (a) and the displacement of the peaks corresponding to this phase reflecting a slight increment in interplanar distances as the Fe^{2+}/Co^{2+} relationship diminishes. This occurs since Co^{2+} ions progressively substitute the Fe(II) ions occupying the octahedral positions of the magnetite structure, tending towards the stoichiometry of the Cobalt ferrite $CoFe_2O_4$.

Figure 2 presents the DSC curves of the three compounds showing two exothermic {1 and 3} and one or two {2} endothermic peaks. The first exothermic peak {1} recorded from 154-187 to 234-247 °C, with a maximum value at 217-230 °C, corresponds to the transformation of magnetite into maghemite by atmospheric oxygen, according to the reaction:



Consequently, during the ferrite sludge formation process and given the alkaline medium employed, it is possible to predict the formation of amorphous hydrated cobalt oxide according to:



The one or two endothermic peaks {2} observed from approximately 236 to 391°C could, therefore, correspond to the loss of water of crystallization molecules by the hydrated cobalt oxide, with a total energy exchange of 27-63 J·g⁻¹ which would appear to occur in one or two very close stages:



The presence of the hydrated cobalt oxides was confirmed by XRD analysis of the solids heated at 300°C for 4 h. Figure 1 shows also the diffractogram corresponding to Fe7Co after heating. In addition to the maghemite phase, $\gamma-Fe_2O_3$ (b), it is now possible to identify cobalt oxide, CoO (c) corresponding to anhydrous crystalline structures.

Finally, the second exothermic peak {3} of the DSC curve starts at 400°C and corresponds to the transformation of maghemite into hematite ($\alpha-Fe_2O_3$) according to:



The following simplified reaction is thus suggested for the cobalt ferrite formation process under the optimal conditions proposed:



the solids composing the cobalt ferrite being $Co_xFe_{3-x}O_4$, magnetite, Fe_3O_4 and hydrated cobalt oxide, $CoO\cdot nH_2O$.

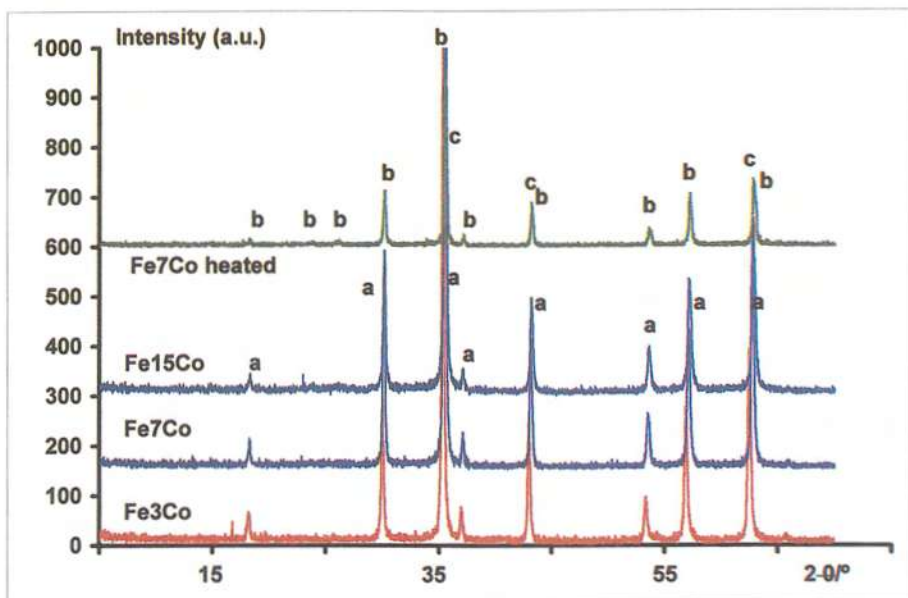


Figure 1. XRD patterns corresponding to the compounds Fe15Co, Fe7Co and Fe3Co desiccated at 100°C. Peaks correspond to displaced magnetite (a), maghemite (b) and cobalt oxides dehydrated at 300°C for 4 h (c).

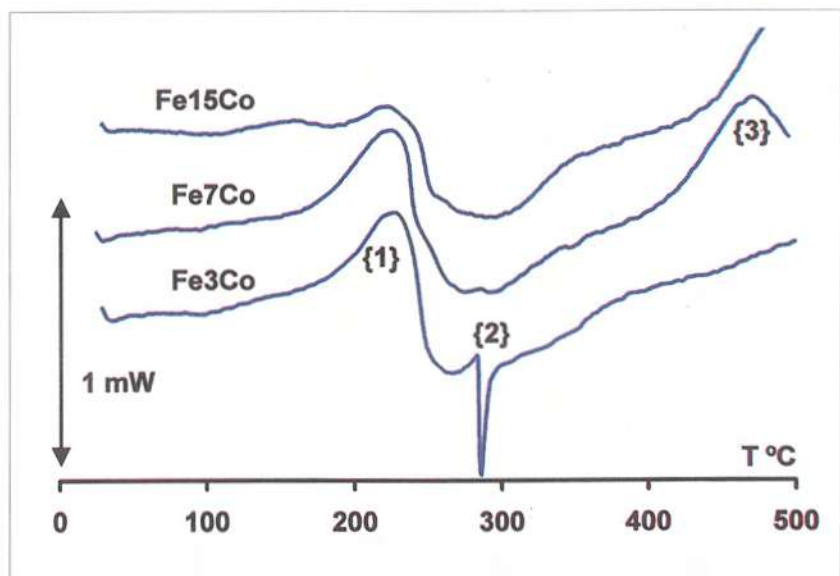


Figure 2. DSC curves obtained from room temperature to 500 °C showing one endothermic and two exothermic peaks, named {1}, {2} and {3}.

Electrochemical analysis

Electrochemical analysis of the cobalt ferrites was performed using a J-shaped carbon paste electrode [12]. The voltammograms obtained were compared with those corresponding to an iron ferrite [13], iron oxides [14], magnetite [15], and also with scans corresponding to cobalt oxide. The voltammetric peaks shown in successive scans were labelled R_{xy} and O_{xy} , where R and O refer to reduction and oxidation, and the subscripts x and y indicate the figure and peak number, respectively.

HClO₄ medium

Linear scans from the open circuit potential to +1.0 V, and several cyclic scans from +1.0 V to negative potential (-1.0 V) and back to +1.0 V were recorded using CPEs. These electrodes were prepared by loading the reservoir with a mixture of approximately 0.0020 g solid cobalt ferrite, 0.100 g graphite power and 2 drops of electrolyte binder (HClO₄), and immersing the electrode into a solution of the same electrolyte.

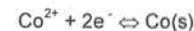
Figure 3 shows the voltammograms obtained using CPEs containing Fe3Co and 1M HClO₄. One oxidation peak, O_{31} , was observed in the linear scan voltammogram (LSV), while three reduction peaks R_{31} , R_{32} and R_{33} and two oxidation peaks O_{33} and O_{30} were recorded in the first cyclic voltammogram (CV1). In previous works [13-15] the following mechanisms were established:



The cathodic peak R_{32} corresponds to the electrochemical solubilization of the ferrite [16]:



The R_{33} and O_{33} peaks are specific to the cobalt ferrite. The potential of the associated redox system, calculated as the semisum of the potentials of the anodic and cathodic peaks, is -0.230 V (vs. Ag/AgCl) and corresponds to the redox couple Co^{2+}/Co^0 whose potential, according to Maki et al [17], is -0.403 V vs. SHE. Therefore, the most probable electrochemical reaction that can be assigned to these peaks is:



The peaks R_{30} and O_{30} correspond to the system [14,16]:



Second and successive cyclic scans (CV2...) only yielded the peaks R_{30}/O_{30} and R_{33}/O_{33} . The bigger current and area of these peaks can be explained taking into account the dissolution of the ferrite in the previous scan, and therefore the increased dissolved concentration of both iron and cobalt in the electrode and hence the increased adsorbed concentrations.

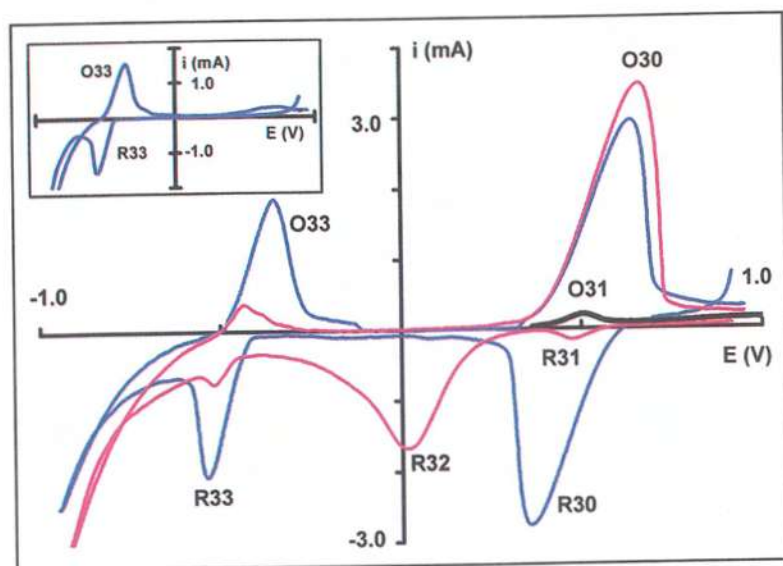


Figure 3. Cyclic voltammograms obtained at a CPE containing Fe₃Co ferrite and 1 M HClO₄ as electrolyte. The left corner of the figure shows the voltammogram of a CPE containing CoO in 1 M HClO₄.

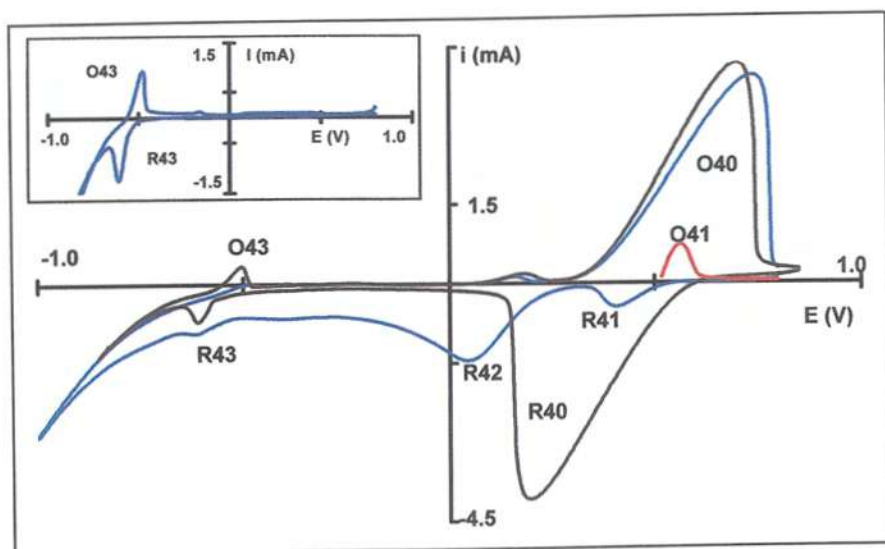


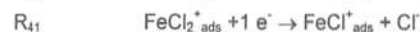
Figure 4. Cyclic voltammograms obtained at a CPE containing Fe₃Co ferrite and 1 M HCl as electrolyte. The left corner of the figure shows the voltammogram of a CPE containing CoO in 1 M HCl.

It has been observed that the height and area of the O₃₃ and R₃₃ peaks increase with the amount of cobalt in the ferrite. These results are in good agreement with the stoichiometry proposed for these solids.

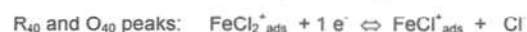
In order to confirm this mechanism, a new CPE was prepared by mixing 0.0020 g of cobalt oxide with 0.982 g of graphite powder, and using two drops of 1 M perchloric acid as binder. The voltammogram registered in 1 M perchloric acid (see left up corner of Figure 3) showed only the O₃₃/R₃₃ peaks at -0.230 V (vs. Ag/AgCl reference electrode), i.e., the system assigned to the Co²⁺/Co⁰ couple.

HCl medium

The voltammograms shown in Figure 4 corresponding to the Fe₃Co ferrite were obtained using a CPE prepared as described for the perchloric medium, but in this case 1 M HCl was used as electrolyte and binder. All peaks registered were similar to those recorded for the iron ferrite (magnetite) in the same medium [13-15], with the exception of O₄₃ and R₄₃ corresponding to cobalt, as seen in perchloric medium. The potential of the O₄₀/R₄₀ system corresponding to the Fe³⁺/Fe²⁺ redox couple is now 0.475 V, showing a shift of -55 mV with respect to the value obtained in perchloric acid. This may be explained by the participation of chloride ions in the electrochemical reactions. These results are in accordance with those obtained for similar compounds [9-11], and suggest the following reactions related to the peaks:



and in the second and subsequent scans:



The O₄₃/R₄₃ peaks reflect the presence of cobalt in the ferrite. Their potential in 1 M HCl was -0.320 V, showing a 90 mV shift towards more negative values with respect to the value obtained in perchloric acid. Moreover, it was confirmed that the shift was dependent on the concentration of chloride ions present in the solution. The participation of chloride ions in the electrochemical process may consequently be expressed as [18]:



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