CHARACTERIZATION OF ALUMINUM AND PHOSPHORUS IN IRON ORE[1]

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Abstract

It is well known the undesirable effect that impurities such as phosphorus and aluminum cause in pig iron and steel. The presence of phosphorus in high amounts in the iron ores can make the steel brittle, favoring the appearance of cracks. In the present study eight samples of iron ores coming from Vale's mines were used. Sequential extractions were made to remove specific forms of phosphorus. The residues of these extractions, as well as the original samples, were characterized by X-ray diffraction, Mössbauer spectroscopy (at room temperature) and chemical analyses. The results of the chemical extractions suggest that phosphorus and aluminum are extracted simultaneously and hence they are associated to the iron oxides. For most samples there is a correlation between the presence of phosphorus and goethite (α-FeOOH), but some samples do not contain goethite but present high contents of phosphorus. The association of aluminum to the iron oxides suggests that it might not be possible to remove it by physical methods. These correlations are still being investigated.

Key words: Iron ore; Mössbauer spectroscopy; Aluminum; Phosphorus.

CARACTERIZAÇÃO DE ALUMÍNIO E FÓSFORO EM MINÉRIO DE FERRO

Resumo

É bem conhecido o efeito indesejável que impurezas como o fósforo e alumínio causam ao ferro gusa e aço. A presença de fósforo em valores elevados torna o aço quebradiço e com fraturas, o que influencia o valor de mercado do minério de ferro. O presente estudo foi realizado com o objetivo de se estudar a forma de ocorrência de alumínio e fósforo em oito tipos de minérios de ferro provenientes de minas da Vale. Extrações seqüenciais visando a remoção de formas específicas do fósforo foram realizadas. Os resíduos destas extrações, bem como as amostras originais, foram caracterizados por difração de raios-X, espectroscopia Mössbauer à temperatura ambiente e análises químicas. Os resultados das extrações químicas sugerem que o fósforo e o alumínio presentes estão associados aos óxidos de ferro. Observou-se uma correlação nítida entre a presença de fósforo e do mineral goethita para a maioria das amostras. Entretanto, algumas amostras não contêm goethita, mas possuem um teor elevado de fósforo. A associação do alumínio aos óxidos de ferro sugere que talvez não seja possível remove-lo totalmente por métodos físicos no beneficiamento.

Palavras-chave: Minério de ferro; Espectroscopia Mössbauer; Alumínio; Fósforo.

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1 INTRODUCTION

It is well known the undesirable effect that impurities such as phosphorus and aluminum cause in pig iron and steel. The presence of phosphorus in high amounts in the iron ores can make the steel brittle, favoring the appearance of cracks, and hence the market price for the iron ore is strongly influenced by the phosphorus content. Routine methods of concentration usually are not capable of removing the phosphorus present in some types of iron ores in order to lower the content below the limit of about 0.1%.(1) It is not known exactly how both phosphorus and aluminum are present in iron ores, but based on results found for synthetic samples of hematite (α-Fe_2O_3) and goethite (α-FeOOH), we can infer that phosphorus, probably in the form of phosphate, is adsorbed onto the surface of the particles or occluded in micro pores. Another possibility is that it is located inside the structure of the oxy-hydroxides. Finally, it might be present as a phosphate mineral.(2-4) For synthetic samples it was found that goethite presents a much higher sorption capacity than hematite, certainly because of the larger surface area and porosity of the goethite particles.(2) It is very likely that also in iron ores goethite will present this behavior. Currently there is no technology that is technically and economically viable to remove phosphorus and aluminum in iron ores. The comprehension of the way in which these two elements are associated to iron ores will bring new insights that eventually will subsidize the developments of methods for the removal of these elements. Therefore, in this work we present the results for the characterization of P and Al in eight samples of iron ores from different mines from Vale.

2 MATERIAL AND METHODS

Eight iron-ore samples from different mines from Vale were investigated. Chemical analysis showed that in general phosphorus and aluminum were more concentrated in the +0.15 e +0.045 mm fractions, and hence these two fractions were chosen to be further investigated. The characterization was performed by chemical analysis (chemical methods and inductively coupled plasma, ICP), X-ray diffraction and Mössbauer spectroscopy. Sequential extractions using the procedure described by Ruttenberg(5) were done for all samples. This method consists of a sequence of extractions that are meant to extract specific forms of phosphorus. Extractions with magnesium chloride (step I) and sodium acetate (step II) supposedly remove labile phosphorus and carbonate/apatite phosphorus, respectively. In step III the extractions are done with the well-known dithionite-citrate-bicarbonate (DCB) system. In principle, only phosphorus and aluminum linked to the iron oxides are removed with this treatment. The iron contents of the original samples were determined by titration with potassium dichromate, which is the standard method recommended and adopted by the industry. Due to limitation in the masses, the iron contents for the residues of the extractions were determined by ICP. The average error between the wet-chemical results and those from ICP for the original samples is about 1 % absolute, which can be considered acceptable for the purpose of this work. X-ray diffractograms were obtained in a Shimadzu XRD 6000 diffractometer equipped with iron tube and a graphite monochromator. The scans were done between 5-75° (2θ) with a scanning speed of 1°/min using silicon as an internal standard. The integrated intensities and widths of the peaks were obtained by fitting the profiles with a Pearson function after subtracting the background and the $K_{\alpha 2}$ contribution.(6) Mössbauer spectra were obtained in a conventional spectrometer operating at room temperature. The spectra were computer-fitted with symmetric sextets and/or doublets or with distributions of magnetic hyperfine fields.(7)

3 RESULTS AND DISCUSSION

All samples present more than 50 % w/w of iron (Table 1), except sample AM4 for which there is only 36 % w/w. Samples presenting the highest amounts of aluminum (above 1 % w/w) are AM3 and AM5, whereas samples AM2, AM5 and AM8 possess phosphorus above 0.11 % w/w.

Table 1. Chemical analysis of the +0.150 mm and +0.045 mm fractions.

Sample	Fe (%)	Al (%)	P (%)
AM1-150	63.8	0.198	0.062
AM1-45	65.0	0.171	0.058
AM2-150	68.5	0.673	0.118
AM2-45	68.1	0.314	0.114
AM3-150	56.8	1.366	0.049
AM3-45	56.7	1.264	0.055
AM4-150	36.0	0.046	0.032
AM4-45	36.4	0.090	0.055
AM5-150	61.9	1.143	0.127
AM5-45	62.0	0.957	0.119
AM6-250	64.7	0.676	0.057
AM7-150	68.1	0.177	0.071
AM7-45	67.7	0.391	0.087
AM8-150	64.6	0.117	0.169
AM8-45	57.5	0.101	0.129

The mineralogy of all samples is basically hematite, goethite, quartz and magnetite. In several samples the mean particle-size of the goethite is below 1000 Å, and in samples AM3 is around 200-300 Å. The particle-size of the hematite is generally above 1000 Å, except for sample AM5 which has a mean size of 700 Å.

No significant amounts of phosphorus or aluminum were extracted during steps I and II of the Ruttenberg procedure, meaning that the amounts of labile or carbonate phosphorus is small.

The treatment with DCB (step III) was done twice in order to guarantee the dissolution of all iron-bearing phases, but even after two extractions the residue showed the presence of iron oxides (see below). The literature reports that oxides with high crystallinity or high Al-for-Fe isomorphic substitution are more resistant to dissolution with respect to the DCB treatment.(8) The iron contents determined by ICP for the +0.045 mm samples before and after the treatment with DCB, as well as the percentages of extraction, are shown in Table 2. The behavior with respect to the extraction with DCB is quite different from sample to sample, varying from only 21 % for sample AM2-45 up to 98 % for sample AM3-45. The reasons for such large differences are not clear yet. The removal of both phosphorus and aluminum is shown in Figure 1, from which it can be seen that a significant proportion of both elements were extracted.

Table 2. Iron contents in the original and DCB-treated samples.

Sample	Fe_t (%)	Fe_{DCB} (%)	Dissolved mass (%)
AM1-45	65.4	63.9	73
AM2-45	68.3	69.0	21
AM3-45	56.0	*	98
AM4-45	36,7	19.1	48
AM5-45	61.1	63.2	55
AM6-45	62.1	63.6	53
AM7-45	66.8	52.2	48
AM8-45	57.9	51.3	60

** The mass of the residue was insufficient to perform the chemical analysis.*

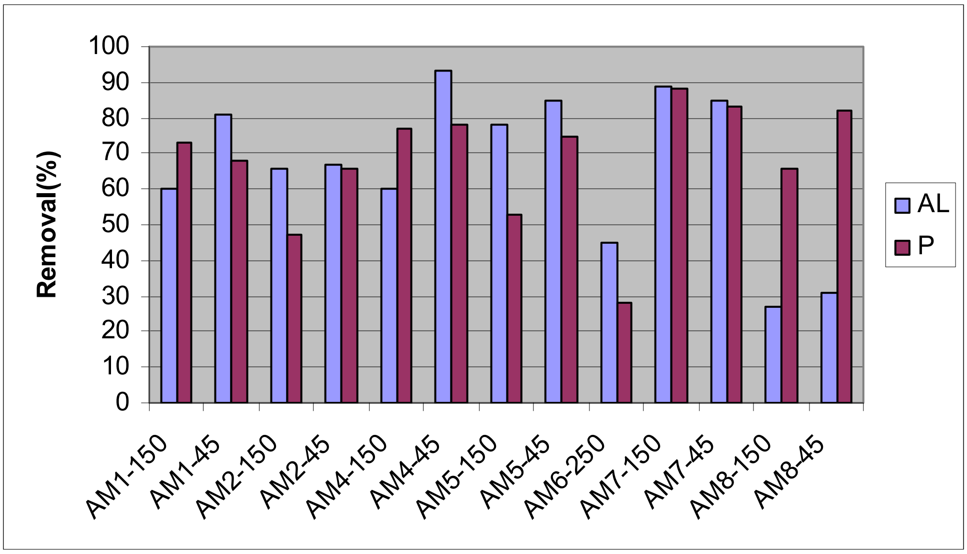

Figure 1. Removal (%) of phosphorus and aluminum in step III of the Ruttenberg procedure.

Mössbauer spectra of all but AM3 +0.045 mm samples before and after the DCB extractions are shown in Figures 2, 3 and 4. The relative areas obtained from fitting these spectra and the results of the chemical analysis for the residues allow the calculation of the mineralogy. It can be seen from the numerical results in Table 3 that for most samples the DCB treatment preferentially removes goethite. It is interesting to comment that sample AM2 practically has no goethite but it contains 0.12% of phosphorus, This observation proves that high amounts of phosphorus does not necessarily means high contents of goethite.

Table 3. Hematite, goethite, magnetite and quartz (%) before and after step III of the Ruttenberg procedure.

Sample	Before				After			
	H	G	Mt	Qz	H	G	Mt	Qz
AM1-45	36	63	-	1	63	31	-	6
AM2-45	97	-	-	3	99	-	-	1
AM3-45	2	88	-	10	1	89	-	10
AM4-45	33	21	-	46	24	3	-	73
AM5-45	74	10	6	10	79	0	10	11
AM6-250	93	-	-	7	93	-	-	7
AM7-45	86	2	8	4	81	1	13	5
AM8-45	64	20	-	16	67	6	-	27

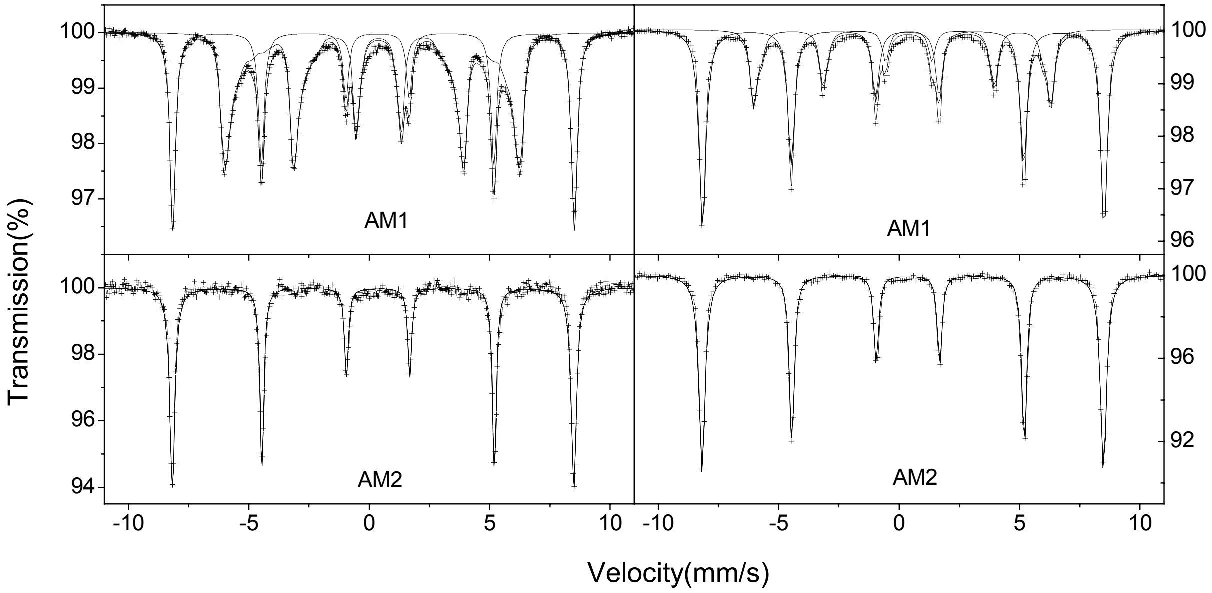

Figure 2. Room-temperature Mössbauer spectra of samples AM1 and AM2 (left) and after extractions with DCB (right).

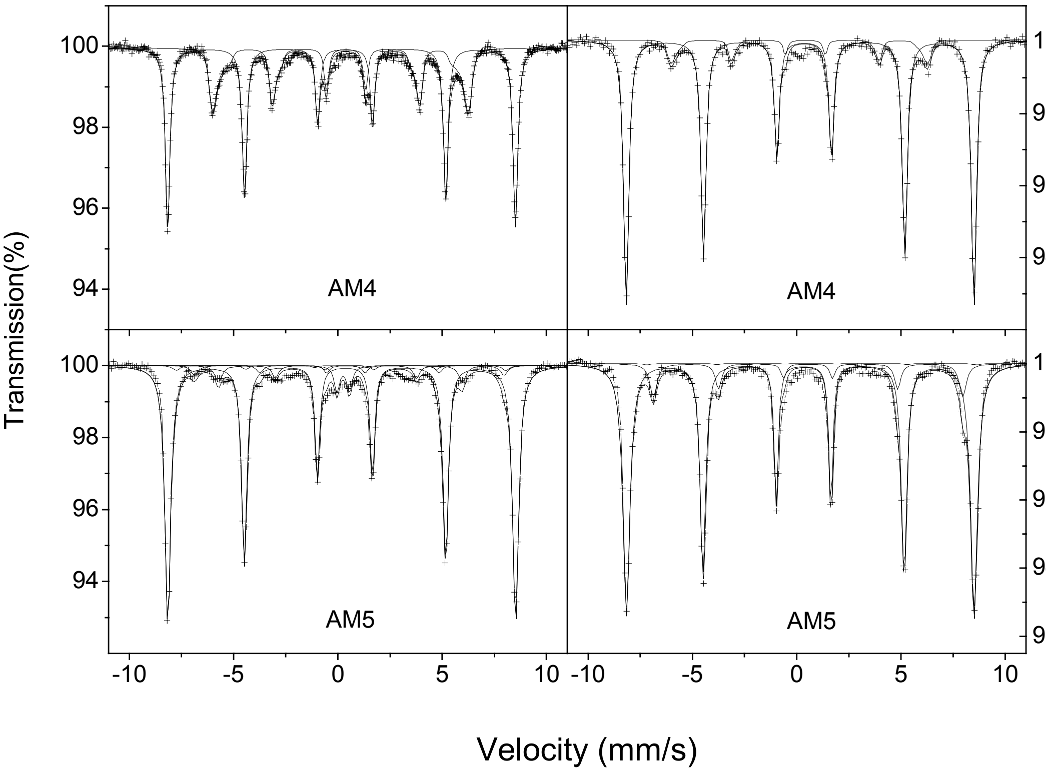

Figure 3. Room-temperature Mössbauer spectra of samples AM4 and AM5 (left), and after extractions with DCB (right).

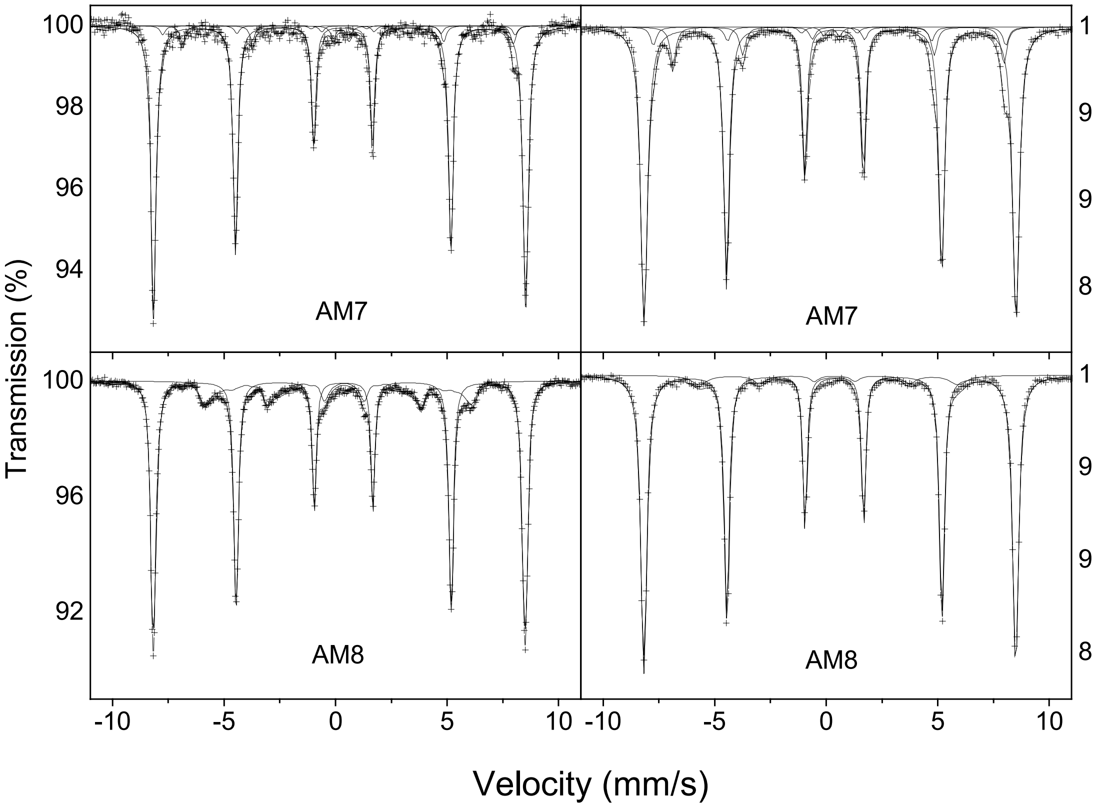

Figure 4. Room-temperature Mössbauer spectra of samples AM7 and AM8 (left), and after extractions with DCB (right).

An important question from the industrial point of view is related to the possibility of removal of aluminum during the concentration steps of the iron ore. Besides being present as oxides, hydroxides or silicates, all or part of the aluminum might be isomorphically replacing iron in the structure of hematite and/or goethite. For natural samples the substitution limits for hematite and goethite are 15 mol % and 33 mol %, respectively.(9,10) These values correspond to 5.4 % and 10.2 % (w/w) of aluminum in the hematite and goethite, respectively. Therefore, the amounts found in the present samples (Table 1) are well below these solubility limits suggesting that all aluminum could be in the structure of the iron oxides. On the other hand, the DCB extractions give more precise information regarding the amounts of aluminum existing inside the iron oxides because in principle this treatment only removes iron oxides.(11) If we assume that all aluminum is in the hematite of samples AM2 and AM6, and in the goethite of the other samples, we can calculate x in the formulae $(Fe_{1-x}Al_x)_2O_3$ and $(Fe_{1-x}\,Al_xOOH)$. This calculation was done for all 0.045 mm samples using the aluminum amounts found in the original samples and in the residues of step III of the Ruttenberg extractions (Table 4). It is easily found that x varies between 0.1 mol % to a maximum of 2.5 mol %. For most of the samples there seem to exist a correlation between the amounts of extracted phosphorus and aluminum, suggesting that a large percentage of both elements are associated with the iron oxides, most probably to the goethite. However, samples AM2 and AM6 do not contain goethite but presented a high percentage of extraction. This behavior might be due to the presence of lithogenic iron oxides such as magnetite and hematite.(12) Although these kinds of oxides are considered more DCB-resistant, small amounts of surface iron can be extracted.(13) On the other hand, sample AM8 contains 20 % of goethite and showed an extraction of about 30 %. The reasons for these differences in behavior are still under investigation. For example, the existence of different amounts of martite and specularite certainly has a strong influence on the amount of hematite that is extracted by the DCB, but this effect is not known yet.

The values of Al_{Fe} and P_{Fe} in Table 4 mean the percentages of aluminum and phosphorus that are associated to the iron oxides with respect to the original samples. Considering that the DCB treatment did not completely remove the iron oxides (Table 3), it is possible that the aluminum existing in the residues of step III is also inside the structure of the iron oxides. In spite of that, it can be concluded that a significant percentage of aluminum and phosphorus cannot be removed from these samples by physical methods of concentration.

Table 4. Aluminum and phosphorus (%) before and after step III of the Ruttenberg extractions. Al_{Fe} and P_{Fe} mean the percentages of aluminum and phosphorus that are associated to the iron oxides with respect to the original samples

Sample	Al original (%)	Al residual (%)	Al_{Fe} (%)	P original (%)	P residual (%)	P_{Fe} (%)
AM1-45	0.171	0.033	81	0.058	0.018	68
AM2-45	0.314	0.102	68	0.114	0.038	67
AM3-45	1.264	*	*	0.055	*	*
AM4-45	0.090	0.006	93	0.055	0.009	84
AM5-45	0.957	0.141	85	0.119	0.035	75
AM6-250	0.676	0.374	45	0.057	0.041	28
AM7-45	0.391	0.057	85	0.087	0.015	83
AM8-45	0.101	0.070	31	0.129	0.023	82

** The mass of the residue was insufficient to perform the chemical analysis.*

4 CONCLUSIONS

The results of the Ruttenberg extractions suggest that a large proportion of the total aluminum is isomorphically replacing iron in the structure of the iron oxides, more likely, in the goethite. Phosphorus also seems to be associated to the iron oxides, and was removed simultaneously with aluminum, except in samples AM6 and AM8. The Mössbauer spectra showed a significant reduction in the amounts of goethite after the DCB extractions. As the phosphorus contents also decreased, it is reasonable to infer that this element is directly associated to goethite. Therefore, it can be concluded that a significant percentage of aluminum and phosphorus cannot be removed from these samples by physical methods of concentration.

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REFERENCES

1 CURI, A. Estudos para redução do teor de fósforo em minérios de ferro. Dissertação de mestrado em Tecnologia Mineral. Universidade Federal de Minas Gerais. Belo Horizonte, 1991. 111p.

2 COLOMBO, C; BARRÓN, V. and TORRENT, J. Phosphate adsorption and desorption in relation to morphology and crystal properties of synthetic hematites...Geochimica et Cosmochimica Acta, V.58, n.4, p.1261-1269,1994.

3 GÁLVEZ, N; BARRÓN, V. and TORRENT, J. Preparation and properties of hematite with structural phosphorus. Clays and Clay Minerals., V.47, p. 375-385, 1999.

4 TORRENT, J; SCHWERTMANN, U. and BARRÓN, V. Fast and slow phosphate sorption by goethite-rich natural materials. Clays and Clay Minerals, V. 40, p.14-21, 1992.

5 RUTTENBERG, K.C. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol Oceanogr. Vol.37, n.7,, p.1460-1482, 1992,.

6 JENKINS R. and Snyder R.L., Introduction to X-ray Powder Diffractometry. John Wiley & Sons, Inc., 1996, 403p.

7 WIVEL, C. and MORUP, S. Improved computational procedure for evaluation of overlapping hyperfine parameter distributions in Mössbauer spectra. Journal of Physics, E14, p.605-610, 1981.

8 INDA JUNIOR, A.V. and KÄMPF, N. Avaliação de procedimentos de extração dos óxidos de ferro pedogênicos com ditionito-citrato-bicarbonato de sódio. R. Bras. Ci. Solo, Vol.27, p.1139-1147, 2003.

9 STANJEK, H. and SHWERTMANN, U. The influence of aluminum on iron oxides. Part XVI: Hidroxyl and aluminum substitution in syhthetic hematites. Clays and Clay Minerals, vol. 40, n.3, p.347-354, 1992.

10 FITZPATRICK, R.W. and SCHWERTMANN, U. Al-substituted goethite an indicator of pedogenic and other weathering environments in South Africa.in: MURAD, E. and SCHWERTMANN, U. The influence of aluminum substitution and crystallinity on the Mössbauer spectra of goethite. Clay Minerals, n.18, p.301-312, 1983.

11 MEHRA, O.P. and JACKSON M.L. Iron oxide removal from soils by a dithionite-citrate system buffered with sodium bicarbonate. In: Proceedings of 7th National Clay Conference (ed. A. Swineford), p. 317-327. Pergamon Press, New York. 1960.

12 RESENDE, M. Mineralogy, chemistry, morphology and geomorphology of some soils of the Central Plateau of Brazil. in*:* INDA JUNIOR, A.V. and KÄMPF, N. Avaliação de procedimentos de extração dos óxidos de ferro pedogênicos com ditionito-citrato-bicarbonato de sódio. R. Bras. Ci. Solo, Vol.27, p.1139-1147, 2003.

13 WALKER, A.L. The effects of magnetite on oxalate and dithionite-extractable iron. In: INDA JUNIOR, A.V. and KÄMPF, N. Avaliação de procedimentos de extração dos óxidos de ferro pedogênicos com ditionito-citrato-bicarbonato de sódio. R. Bras. Ci. Solo, Vol.27, p.1139-1147, 2003