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TEMPERATURE EFFECTS ON THE POINT OF ZERO CHARGE AND ISOELECTRIC POINT OF A RED SOIL RICH IN KAOLINITE AND IRON MINERALS

R. M. Torres Sánchez and E. L. Tavani

Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) C.C., 49, (1897) M.B. Gonnet, Argentina

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Abstract

The effects of temperature (373–1373 K) on the point of zero charge (PZC) and isoelectric point (IEP) of a red soil rich in kaolinite and iron minerals were studied. PZC values of the soil treated at 373 and 573 K indicated the presence of iron oxide. The soil calcined between 773 and 1173 K shows a PZC almost coincident with the respective values of kaolinite. At 1373 K, the PZC of the soil is nearer to the value of iron oxide. In the entire temperature range studied the PZC values were lower than the IEP values. An approach of PZC and IEP values was observed after a partial removal of iron oxide by the dithionite-citrate-bicarbonate (DCB) method. The analyses of the PZC and IEP values, of electron probe micro analysis (EPMA) data and of specific surface areas evidence a specific adsorption of iron oxide on kaolinite. Finally, the dissolution sequence of iron and aluminium contained in soil was determined using hydrochloric acid.

Keywords: point of zero charge, iron minerals, isoelectric point, kaolinite, red soil

Introduction

The effects of surface charges on clay and iron minerals have been widely studied. This property affects the behaviour of the suspensions (flocculation, viscosity, tixotropy) and the association of mineral species (physical adsorption, specific adsorption) [1–4].

The direct relation between the PZC of oxide mixtures and the chemical composition is known after Parks [5]. Some authors proposed that the PZC of an oxide mixture varies linearly with the weight fractions of the oxide components [5–6]. Other authors [7–8], taking oxides of similar specific surface areas, mentioned the importance of the sensitivity of the oxide components to *pH* changes. More recently, Kuo and Yen [9] stated that in a mixture the types of oxides behave independently.

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In the above mentioned relations the specific adsorption of ions was not taken into consideration. Several authors analysed the relationship between specific adsorption and surface charges of particles [10–12]. With regard to this aspect, we mention the study performed by Escudey and Galindo (1983) in Chilean volcanic ash soils. In such soils the iron oxide covers mainly the external surface of the other components. Iron oxide was partially removed by the DCB method. Important variations of surface charges for each of these residues were determined by the authors [11].

The terminology used in our work defines the PZC as the *pH* where σ_o (net adsorption density of H^+ and OH^-) is zero and the IEP as the *pH* at which the charge from all sources is zero. PZC = IEP only when the specific adsorption of chemical species is absent [11, 13].

Red soils of the northeast area of Argentina are a natural complex association of kaolinite and iron minerals, characterized by high content of aluminium and iron [14]. The main components are: kaolinite, silica, iron and titaniferous oxides. They are formed by a weathering process of basalts [15–16]. These soils constitute the main known potential source of aluminium in our country [17–18]. Nevertheless, the separation of its components is difficult. A knowledge of its behaviour within a wide temperature range is very important in order to determine the use of these mineral sources in several processes of extractive metallurgy.

In view of the ideas mentioned above, the temperature effects on the PZC and IEP of a soil rich in kaolinite and iron minerals were studied.

Experimental

Equipment and methods

PZC determinations were carried out in a Metrohm Universal titration vessel EA 880. The *pH* measurements (electrodes of Metrohm) were performed with a Metrohm *pH*-meter E 516, with a teflon-coated stirrer, in a nitrogen atmosphere. The fast adsorption method of titration [19] was used to determine the PZC with 10^{-3} mol/l and 10^{-1} mol/l KCl as supporting electrolyte, and successive additions of 0.1 mol/l HCl, at 15 min intervals. The amounts of acid required to adjust the *pH* of the blanks were substracted from the experimental values measured for the samples.

IEP determinations were carried out by measuring the diffusion potential (E_d) [20]. In this method, due to the existence of surface charges, when two solutions with different concentrations are brought into contact, a diffusion potential (E_d) appears. The IEP was obtained from the E_d *vs.* *pH* curve, as the *pH* where E_d was zero.

Micrographs were taken and electron probe micro analysis (EPMA) was performed with a Philips 505 scanning electron microscope (SEM) and EDAX microprobe.

Diffractograms were obtained in a Philips diffractometer, Model PW 1140/00, with CuK_α radiation and nickel filter.

Chemical analyses were performed by volumetric and gravimetric methods for the main components and plasma spectrometry for the minor elements. Plasma spectrometry was carried out in an Instrumental Laboratory IL '200' equipment.

Differential thermal analyses (DTA) were carried out in a NETZSCH equipment. Calcination was performed in an electric furnace in static air atmosphere.

Magnetic separation was performed in a low intensity (1000 Gauss) magnetic separator that can be dry-operated. Gravity separation of minerals was made with a jig and on a shaking table.

Specific surface areas were determined by nitrogen adsorption using the BET method.

Hydrochloric acid leaching tests were carried out at the boiling temperature of the system (378–381 K), in closed Pyrex flasks, with mechanical stirring and reflux. The acid volumes used were calculated on the basis of the chemical composition of the sample, and were expressed as a stoichiometric molar ratio (r = volume used/volume required to achieve a complete dissolution of the sample).

Raw material

The natural red soil used was collected from arable land from the area around Posadas, province of Misiones, Argentina. The sample was crushed and screened for elimination of plant residues and gravel, treated with hydrogen peroxide 30% w/w to eliminate organic matter, leached with distilled water and air dried. Table 1 shows the chemical analyses of the natural soil without organic matter.

The sample was further calcined during different times (20, 40 and 60 minutes) at temperatures: 373, 573, 773, 973, 1173 and 1373 K to determine the mass loss. It was found that from 60 minutes onward mass losses were maintained without significant variations and it was chosen as the best time to calcine the soil. Table 2 shows the mass loss and specific surface area of the sample treated at different temperatures during 60 minutes. Samples obtained from this thermal treatment were identified by its calcination temperature. Each of these samples was washed with distilled water, air dried and crushed in an agate mortar. Mass losses were due to dehydroxylation of goethite and minerals of the kaolinite group, between 373 and 973 K. Accordingly, specific surface area variations were minimal. Between 1173 and 1373 K, there were no structural modifications associated with mass loss, but sintering started which caused an abrupt decrease in the specific surface area (from 28 m^2/g to 2 m^2/g at 1173 and 1373 K, respectively).

Semiquantitative determination of the mineral species was done by means of various analysis techniques such as: EPMA, SEM, XRD, DTA, plasma spectrometry, gravity separation, magnetic classification, chemical analyses, selective acid leaching and mass loss at different temperatures. Table 3 shows the minerals contained in the sample studied.

Table 1 Chemical analyses of the red soil without organic matter

	w/w (%)		*w/w* (%)
SiO_2	41.23	Na_2O	0.93
Al_2O_3	22.51	K_2O	0.21
Fe_2O_3	19.19	MgO	0.51
FeO	2.02	CaO	0.08
TiO_2	2.90	LOI (1373 K)	10.30
		Total	99.88

Table 2 Mass loss and specific surface area of the sample at different temperatures (60 min)

Temperature/ K	Mass loss/ %	Specific surface area/ m^2/g
373	0.0	55
573	3.0	50
773	5.6	46
973	9.6	44
1173	10.1	28
1373	10.3	2

Finally, a soil fraction without calcination (50 g) was treated by the DCB method to remove iron oxide partially [21]. The process was performed in three stages at 353 K. In each stage 400 ml of 0.3 mol/l citrate, 50 ml of 1 mol/l bicarbonate and 10 g of dithionite were added. The residues obtained were treated with hydrogen peroxide to eliminate the possible adsorption of organic anions [22].

Results and discussion

Figure 1 shows the titration curves obtained for the calcined soil at different temperatures. At 773 K an increase of the *pH* value of PZC was observed. Between 773 and 1173 K the PZC values were similar and at 1373 K the PZC again increased. The PZC variations of the samples with thermal treatment showed a close relationship with the consecutive chemical transformations of kaolinite. These changes were:

$$\underset{\text{kaolinite}}{\mathrm{Al_2Si_2O_5(OH)_4}} \xrightarrow{T_1\downarrow} \underset{\text{metakaolinite}}{\mathrm{Al_2Si_2O_7+2H_2O}} \xrightarrow{T_2\downarrow} \underset{\text{spinel phase}}{\mathrm{Al_4Si_3O_{12}+xSiO_2}} \xrightarrow{T_3\downarrow}$$

$$\rightarrow \underset{\text{mullite}}{\mathrm{Al_6Si_2O_{13}+ySiO_2}}$$

T_1, T_2 and T_3 were determined from DTA curves (heating rate: 10deg·min^{-1}) and XRD measurements: T_1 = 833 K; T_2 = 1193 K and T_3 = 1373 K. In our experiments, the sample showed a good reaction development (mass loss in Table 2) within 60 minutes of calcination at 773; 1173 and 1373 K, respectively.

Table 3 Mineralogical analyses of the soil without organic matter

Mineral species	*w/w* (%)
Kaolinite (kaolinite and halloysite)	48–56
Silica (quartz and colloidal silica)	8–13
Feldspars (albite and orthoclase)	8–13
Iron (colloidal and granular hematite, magnetite and goethite)	17–23
Titaniferous (ilmenite, rutile and leucoxene)	2–4

Nevertheless, it was not possible to explain all the variations observed assuming that kaolinite is the only mineral which determines the PZC of the soil. On account of the variety of minerals present in the soil (Table 3), its main mineral components were joined in two fractions: a) kaolinite-silica and b) iron-titaniferous minerals. In each fraction, the major components having surface charges of similar behaviour at the same *pH* were included. Within this context,

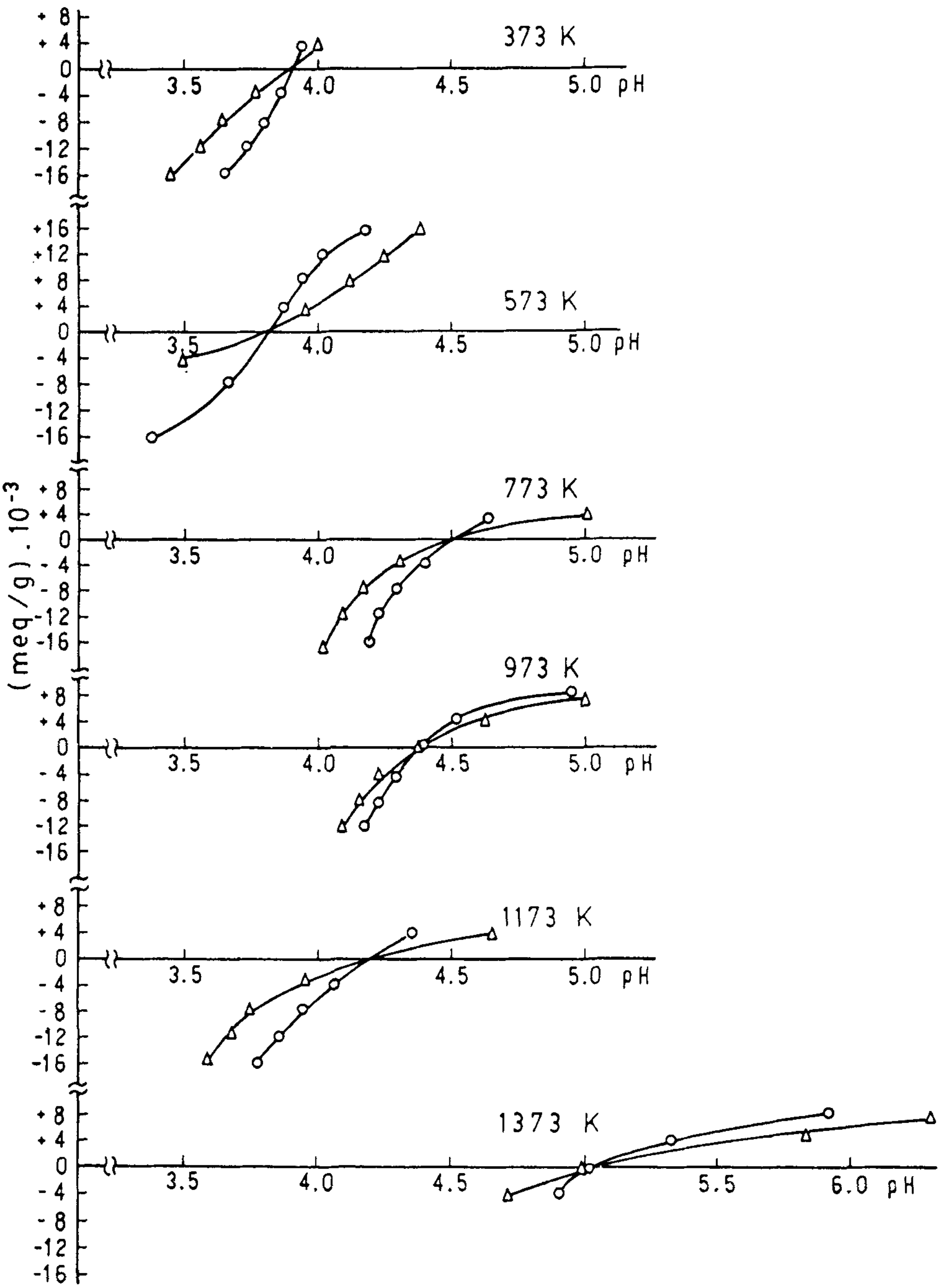

Fig. 1 Curves of titration of the soil treated at different temperatures (Δ KCl 10^{-3} mol/l and o KCl 10^{-1} mol/l)

the PZC values of calcined soil at different temperatures were compared with the values of kaolinite and of pure iron oxide.

Between 373 and 573 K the PZC values of the sample were 0.5 *pH* units higher than those of kaolinite determined by Tschapek *et al.* [7]. This behaviour indicated the existence of iron and titanium oxides whose PZC values were higher than those of kaolinite. A good agreement was observed between the PZC values of kaolinite and soil between 773 and 1173 K. At 1373 K, the PZC of the sample did not coincide with the value of kaolinite but it was similar to the IEP of pure α-Fe_2O_3 [23]. The IEP of pure α-Fe_2O_3 was considered to be equal to its PZC [11, 13].

Table 4 Iron(II) oxidation by thermal treatment

Temperature / K	Iron(II) content / *w/w* /%
373	2.02
573	0.58
773	0.46
973	0.30
1173	0.27
1373	0.25

In order to evaluate the association type (mixture or specific adsorption) between iron oxide and kaolinite, the IEP values of the calcined sample at different temperatures were determined. The presence of specific adsorption may be supported by a difference between PZC and IEP values [11, 13]. It is important to note that in our study, the only chemical changes of iron compounds were: the dehydroxylation of goethite and the progressive oxidation of iron (II) (Table 4). In both cases the final product was iron (III) oxide.

Figure 2 shows the IEP and PZC values for the soil calcined at different temperatures. In the entire range studied the PZC values were lower than the IEP values. The greater differences were determined at 373, 573, 1173 and 1373 K.

In the sample treated at 373 K the PZC and IEP values differed by 0.4 *pH* units (Fig. 2). By selective acid leaching of this soil and subsequent gravity separation, a heavy fraction (granular hematite, magnetite, goethite and titaniferous minerals) was obtained. This fraction had a great quantity of particles constituted by more than one mineral species (solid solutions and segregations) as it was determined by us (XRD, SEM and EPMA). PZC and IEP values were similar for the heavy fraction minerals. For this reason, the difference between the PZC and IEP values of the sample was attributed to the association type of the minerals which are not present in the heavy fraction.

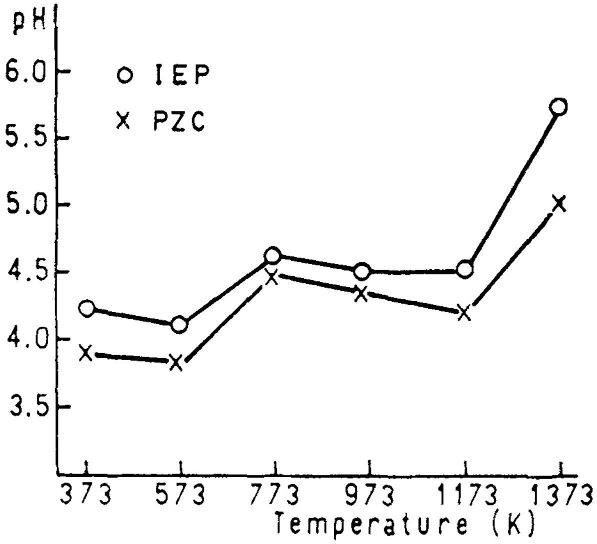

Fig. 2 Temperature effects on IEP and PZC of the soil

This fact was ascertained by the partial removal of iron oxide (DCB method) for the soil treated at 373 K. The degree of iron oxide extraction was 60% after three stages. The residual iron oxide corresponded, mainly, to minerals of the heavy fraction. The PZC and IEP values of the sample were nearer while the iron oxide content decreased. The PZC and IEP values agreed in $pH = 3.5$ for a 60% removal of iron oxide. This behaviour was attributed to the association type (specific adsorption) between the partially removed iron oxide and kaolinite.

According to the results described above, it would be possible to infer that iron oxide partially covers the kaolinite mineral. This iron oxide is distributed as small particles which ensures a high specific surface area of the original sample ($Sg = 55\ m^2/g$). At 1373 K, the specific surface area decreased to $2\ m^2/g$. The sintering of the iron oxide which covers the kaolinite started as the temperature rose and produced an increase of particle sizes (SEM-EPMA). PZC and IEP values of the calcined soil at 1373 K differed by 0.7 pH units. This difference was modified by partial iron oxide removal (DCB method) as in the sample at 373 K.

Table 5 shows the results of electron probe micro analysis (EPMA) performed on the bulk sample calcined at different temperatures. The Fe_2O_3/Al_2O_3 ratio for different temperatures confirms the above suggestions. Besides, at 1373 K an important increase of surface SiO_2 was observed (EPMA). This change was produced by the formation of mullite (XRD) [24].

Table 5 Analyses by EPMA on the bulk sample treated at different temperatures

Temperature/K	Fe_2O_3/Al_2O_3	Fe_2O_3/SiO_2	SiO_2/Al_2O_3
373	2.86	1.64	1.74
773	3.10	1.92	1.61
1373	3.86	1.74	2.20

The acid leaching of the sample treated at 373 K was carried out to study the dissolution sequence of the iron and aluminium contents in the red soil. Figure 3 shows the dissolution ratio of iron(III)/aluminium for the original soil versus the reaction time and the acid volume used. For a reaction time of 5 minutes the dissolution ratio of iron(III)/aluminium was constant for different volumes of 6 mol/l hydrochloric acid added. Under these conditions the dissolutions of iron(III), aluminium and titanium were: 65%; 10% and 6%, respectively. After the acid attack the soil lost the characteristic red colour which evidences the removal of free iron oxide Besides, the PZC of the sample decreased by 0.5 *pH* units (*pH* of original soil = 3.9 and *pH* of residues = 3.4). The contribution of titaniferous oxides to the PZC of the sample was minimum due to the small specific surface area of the original oxide determined by us ($Sg = 7\ m^2/g$).

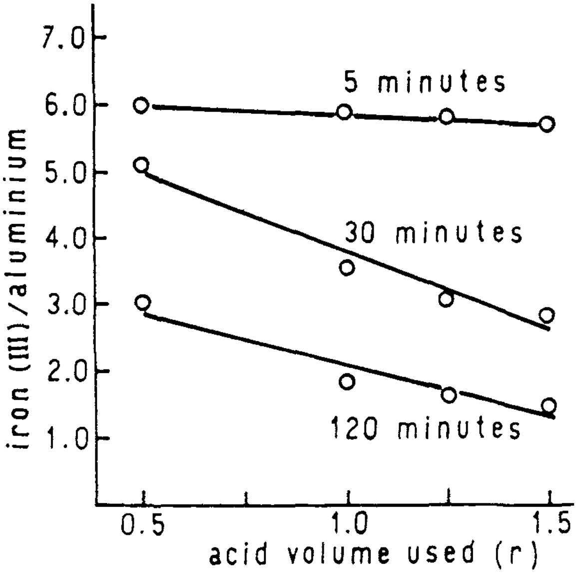

Fig. 3 Influence of the reaction time and of the acid volume used on the dissolution of iron(III) and aluminium for the original soil

For longer reaction times (30 and 120 minutes) the ratio of iron(III)/aluminium decreased with the increase of the acid volume used. This was produced because the massive dissolution of aluminium started when 65% of iron(III) had been removed. Consequently, if the volume of acid added is greater than the one required for the dissolution of the mentioned quantity of iron(III) and if the leaching time is sufficient, the changes mentioned are produced.

Conclusions

The PZC values of the soil treated at 373 and 573 K indicated the presence of iron oxide. The PZC values of the calcined soil between 773 and 1173 K were nearer to the respective values of the kaolinite at the same temperatures. At 1373 K, the PZC of the soil was almost coincident with the value of iron oxide.

The sintering of iron oxide partially covering the kaolinite started as the temperature rose. The specific surface area of the calcined sample decreased significantly at 1373 K (*Sg* of original soil=55 m^2/g and *Sg* of calcined soil= 2 m^2/g) due to an increase of the iron oxide particle size. This change increased the kaolinite surface covered with iron oxide and caused that the PZC of the calcined soil at 1373 K was nearer to the value of iron oxide.

In the entire temperature range studied the PZC values were lower than the IEP values. An approach of PZC and IEP values was observed after partial iron oxide removal (DCB method). This behaviour was attributed to the existence of a specific adsorption of iron oxide on the kaolinite.

PZC and IEP measurements constitute a simple method to establish the specific adsorption of iron oxide on kaolinite in red soil.

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Zusammenfassung — Es wurde der Temperatureinfluß (373–1373 K) auf den Nulladungspunkt (PZC) und den isoelektrischen Punkt (IEP) von Roterde mit einem hohen Gehalt an Kaolinit und Eisenmineralien untersucht. Die PZC-Werte der bei 373 und 573 K behandelten Bodenprobe zeigen die Gegenwart von Eisenoxid. Von 773 bis 1173 kalzinierte Boden zeigt einen PZC, der fast mit dem entsprechenden PZC-Wert von Kaolinit übereinstimmt. Bei 1373 K liegt der PZC-Wert der Bodenprobe näher am Wert von Eisenoxid. Im gesamten untersuchten Temperaturbereich lagen die PZC-Werte unter den IEP-Werten. Eine Annäherung von PZC- und IEP-Werten konnte beobachtet werden, nachdem Eisenoxid teilweise mit Hilfe der Dithionit-Zitrat-Bikarbonat-Methode (DCB) entfernt worden war. Aus der Analyse der PZC- und IEP-Werte, der EPMA-Angaben und der spezifischen Oberflächen ergibt sich der Schluß auf eine spezifische Adsorption von Eisenoxid auf Kaolinit. Letztlich wurde mittels Salzsäure die Lösungsabfolge des im Erdboden enthaltenen Eisens und Aluminiums bestimmt.