

EFFECT OF IRON OXIDE DISSOLUTION TREATMENT ON THE ISOELECTRIC POINT OF ALLOPHANIC SOILS

Key Words—Allophane, Anion adsorption, Dissolution, Iron oxide, Isoelectric point, Soils.

Selective dissolution of iron and aluminum oxide coatings and of free iron oxides is used in mineralogical studies of soil clays (Wada and Harward, 1974) and their surface properties (Cavallaro and McBride, 1984). The usual dissolution techniques are the ammonium oxalate method (McKeague and Day, 1966) and the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960). Both methods use organic anions that can be adsorbed on the clay surfaces (Appelt *et al.*, 1975) and thus change the charge properties of those surfaces. The effect of these adsorbed anions on determinations of the isoelectric point (IEP) of clay particles can be important because the electrophoretic mobility is very sensitive to external surface composition (Gil-Llambías and Escudey-Castro, 1982). The objective of the present work is to study the effect of the DCB treatment on the IEP of allophanic clays.

EXPERIMENTAL

The <2- μm fraction was extracted from a sample of subsurface soil collected from an uncultivated Andept from south-central Chile. This soil (Osorno) was previously described by Galindo (1974). Organic matter from the soil was eliminated by treatment with 30% hydrogen peroxide until no dark residues remained (Kunze, 1965) and no changes in the IEP were noted with further hydrogen peroxide additions.

The clay-size fraction was obtained by sedimentation procedures based on Stoke's Law. The organic matter-free sample was suspended in a liter of doubly distilled water, the suspension pH was adjusted to 5 with 0.1 M HCl, and the sample was dispersed with an ultrasonic vibrator for a period of 5 min twice. After mixing, the <2- μm material was removed with a siphon from a depth of 20 cm after a period of 30 hr; this sample was labeled Osorno 0.

A 30-g portion of Osorno 0 was placed in each of 10 plastic 250-ml centrifuge bottles. These samples were treated for iron oxide removal by the DCB procedure, employing the volumes proposed by Mehra and Jackson (1960), in an 80°C water bath. After the first DCB treatment, one bottle was removed from the bath and a 3-g portion of treated clay was labeled Osorno 1. The other bottles were treated again with DCB, and a second bottle was removed from the bath, and a 3-g portion of the clay was labeled Osorno 2. Similarly, Osorno 3-10 samples were obtained after further DCB treatments.

Each of the 3-g portions was washed 5 times with doubly distilled water, centrifuged, resuspended in 20 ml of doubly distilled water, and treated with 0.5 ml of 30% hydrogen peroxide per gram of sample. The tubes were held in a 55°C water bath. After 12 hr about 20 mg of sample was removed, washed 5 times with doubly distilled water, and used for IEP determination. The remaining sample in each tube was then treated with hydrogen peroxide for another 12 hr and another sample for IEP taken. This procedure was repeated 7 times for a total of 3.5 ml of 30% hydrogen peroxide per gram of sample.

The IEP values were determined by microelectrophoresis. Electrophoretic mobilities were measured with a zeta meter (ZM-77) apparatus. Dilute dispersions (0.05 g/liter) were prepared in 10^{-3} M KCl. The pH was adjusted with 10^{-2} M HCl or NaOH. The mobilities were averaged and the zeta potential calculated using the Helmholtz-Smoluchowski equation (Hunter, 1981).

X-ray powder diffractograms were obtained using a Philips-Norelco instrument with $\text{CuK}\alpha$ radiation and a carbon crystal monochromator. Al, Si, and Fe of the clay-size fractions dissolved in Teflon bombs (Bernas, 1968) were determined on a Perkin-Elmer model 5000 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

X-ray powder diffraction (XRD) patterns and chemical composition (Table 1) show that the clay-sized material was composed largely of non-crystalline species similar to allophane and oxides of iron and aluminum (Escudey and Galindo, 1983). Small XRD peaks at 4.04, 3.33, and 2.52 Å suggested small amounts of α -cristobalite, quartz, and goethite, respectively.

Table 2 shows the shift of the IEP values for the Osorno 2, 6, and 10 samples as a result of increasing additions of hydrogen peroxide. In each sample a constant IEP was obtained after the addition of 1.5 ml of H_2O_2 per gram of sample. Zeta potential vs. pH curves

Table 1. Chemical analyses (wt. %) of selected samples.

Sample	Fe_2O_3	Al_2O_3	SiO_2
Osorno 0	16.0	28.3	36.2
Osorno 7	6.2	30.1	40.8
Osorno 10	4.0	28.2	49.6

Table 2. Effect of hydrogen peroxide on isoelectric point of Osorno 2, 6, and 10 samples after dithionite-citrate-bicarbonate treatment.

Amount of H ₂ O ₂ added (ml H ₂ O ₂ /g sample)	Sample		
	Osorno 2	Osorno 6	Osorno 10
	Isoelectric Point (pH)		
0	6.7	3.6	3.1
0.5	7.4	4.9	3.8
1.5	9.0	7.9	5.3
2.5	8.9	7.8	5.2
3.5	9.0	8.1	5.3

Table 3. Isoelectric point (IEP) of dithionite-citrate-bicarbonate treated samples before and after H₂O₂ treatment.

Sample	IEP before H ₂ O ₂	IEP after H ₂ O ₂
Osorno 0	8.6	8.7
Osorno 1	6.0	7.3
Osorno 2	6.7	9.0
Osorno 3	6.5	8.0
Osorno 4	6.8	7.5
Osorno 5	6.2	7.9
Osorno 6	3.7	8.1
Osorno 7	4.2	6.8
Osorno 8	3.0	6.5
Osorno 9	3.0	5.3
Osorno 10	3.1	5.3

before and after H₂O₂ treatments are presented in Figure 1.

As a result of the DCB treatment the IEP shifted to more acid values due to sample composition. Thus, the high IEP of the Osorno 0 samples is probably due to the effect of the coatings of iron oxide (IEP = 9.3, after Escudey and Galindo, 1983) and aluminum oxide (IEP = 8.8, after Gil-Llambías and Escudey-Castro, 1982). The Osorno 10 sample showed a lower IEP value, close to those previously reported by Escudey and Galindo (1983) for similar materials due to an increased silica/alumina ratio, resulting from the removal of iron oxides and aluminum oxides (Cavallaro and McBride, 1984), and the dissolution of allophan-like compounds (Wada and Gunjigake, 1979) by the DCB treatment.

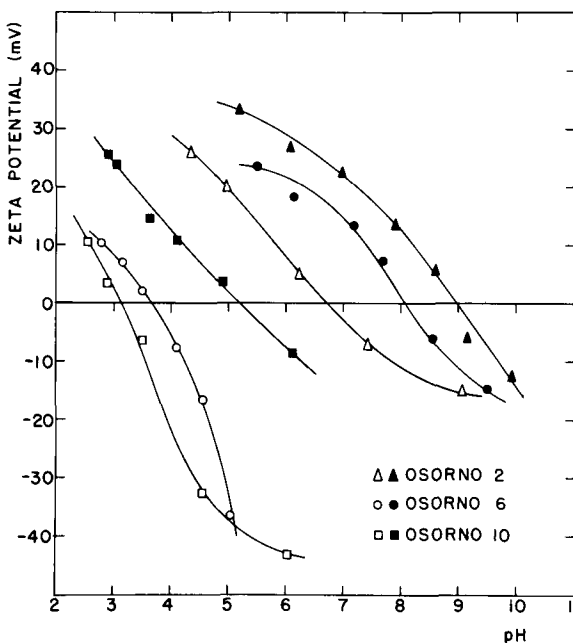


Figure 1. Zeta potential vs. pH curves for Osorno 2, Osorno 6, and Osorno 10 samples after (filled points) and before (open points) treatment with H₂O₂.

In all experiments, wide differences were observed between the IEP measured on washed samples after DCB treatments and the same samples further treated with H₂O₂ to remove adsorbed citrate.

We conclude that organic anions of reagents used in selective dissolution procedures (such as citrate or oxalate) were adsorbed on surfaces too strongly to be washed off. Inasmuch as electrophoretic mobility is very sensitive to external surface composition, the IEP measurements of washed samples following these treatments were lower than the clean inorganic surfaces would be, showing a characteristic shift to acid pHs attributable to specific anion adsorption (Stumm and Morgan, 1981). Thus, reproducible and reliable IEP values were obtained after a new hydrogen peroxide treatment.

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