

NOTES

EFFECT OF SURFACE AREA AND MINERALOGY OF IRON OXIDES ON THEIR SURFACE CHARGE AND ANION-ADSORPTION PROPERTIES

Key Words—Adsorption, Fluoride, Iron oxide, Phosphate, Surface area, Surface charge, Zero point of charge.

The chemical and physical properties of soil iron oxides are though more to be a function of their surface area than of their mineralogical form (Greenland and Mott, 1978; Schwertmann, 1979). Based on published data, this statement is, however, difficult to confirm, because different experimental conditions have been used. In order to evaluate the above statement under controlled conditions, the surface charge and anion-adsorption properties of twelve synthetic iron oxide samples covering seven different minerals have been investigated under the same set of standard experimental conditions.

EXPERIMENTAL

Material

The iron oxides were prepared by slightly modified literature methods. Amorphous (noncrystalline) iron oxides were prepared by mixing solutions of iron(III) nitrate and sodium hydroxide ($\text{OH/Fe} = 3.0$) at room temperature (Borggaard, 1982a). Goethite B was prepared by keeping a mixture of iron(III) nitrate and sodium hydroxide solutions ($\text{OH/Fe} = 1.0$) 3 days at room temperature, then adding sodium hydroxide until pH 12.3 and aging this mixture for 2 days at 55°C (Atkinson *et al.*, 1968). Goethite 1 was prepared by aging a mixture of iron(III) nitrate and sodium hydroxide solutions ($\text{OH/Fe} = 3.5$) at 60°C for 2 days. Akaganéite ($\beta\text{-FeOOH}$) was prepared by refluxing 0.2 M iron(III) chloride 24 hr (McLaughlin *et al.*, 1981). Lepidocrocite 1 was prepared by shaking a mixture of iron(III) sulfate, sodium thiosulfate, and potassium iodate in an end-over-end shaker 1 day (Greenland and Oades, 1968). Lepidocrocite 3 was prepared by bubbling CO_2 -free air for 3 hr through a mixture of 0.06 M iron(II) chloride and an ammonia buffer (pH ~ 7.5) at 45°C maintained at pH ~ 6 during the oxidation by adding ammonia solution (Giovannoli and Brüttsch, 1974). Feroxyhite ($\delta\text{-FeOOH}$) was prepared by simultaneous rapid addition of hydrogen peroxide and sodium hydroxide solutions to an iron(II) chloride solution at room temperature and pH 5–8 (Carlson and Schwertmann, 1980). Maghemite 2 was prepared by a procedure resembling that for lepidocrocite 3 (Giovannoli and Brüttsch, 1974), except for higher pH (~ 7) and iron concentration (0.1 M) and lower oxidation rate (6 hr), as these changes have been shown (Taylor and Schwertmann, 1974) to favor maghemite formation. After formation of the iron oxides the suspensions were centrifuged, and the precipitates were washed once with water, twice with ethanol, and once with acetone and then dried at 65°C. Maghemite 1 was prepared by heating magnetite at 200°C for 10 days as described previously (Borggaard, 1982a). Hematite 1, hematite 3, and hematite 4 were prepared by heating goethite 1, lepidocrocite 1, and feroxyhite, respectively, at 560°C for 20 hr.

The mineralogy of the oxides was assessed by X-ray powder diffraction using Fe-filtered $\text{CoK}\alpha$ -radiation. Small amounts ($<10\%$) of goethite and maghemite were found in maghemite 2 and lepidocrocite 3, respectively. The poorly crystalline samples, especially lepidocrocite 1 and feroxyhite, may contain amorphous iron oxides.

All the samples were stored for at least 3 weeks in an evacuated desiccator over sodium hydroxide before use to reduce or prevent CO_2 contamination.

Analytical methods

The surface area determinations were carried out as described previously for soil (Borggaard, 1982b), i.e., the N_2/BET area was determined by applying the BET equation to nitrogen adsorption after outgassing for 20 hr at 60°C and 1 mPa, and the H_2O area was determined by measuring the water adsorption at 19% RH.

The zero point of charge (ZPC) was determined by the salt-addition-technique (Pyman *et al.*, 1979). An aqueous iron oxide suspension adjusted to pH 6.5 was purged overnight with CO_2 -free nitrogen and titrated with 1 M NaCl. The suspension was then diluted with water, the pH adjusted to 8 (5.5 for hematite 3 and lepidocrocite 1), and the suspension titrated again with 1 M NaCl. Except for hematite 3 and lepidocrocite, pH increased during the initial titration and decreased during the titration following dilution with water and adjustment to pH 8. pH was plotted against volume of 1 M NaCl, the two titration curves for each oxide were drawn, and the point towards which these titration curves tended was taken as the ZPC.

The hydroxyl buffering (McLaughlin *et al.*, 1981) was determined by titrating a suspension of iron oxide in 0.3 M NaCl with 0.1 M NaOH from pH 4.5 to 9. The slope of the curve obtained by plotting amount of OH adsorbed against pH was taken as the hydroxyl buffering.

The fluoride adsorption capacity was taken as the mean of the fluoride adsorbed by shaking two suspensions of iron oxide in 0.1 M NaCl made to contain 0.002 M and 0.004 M NaF, respectively, 4 days at pH 3.5 (pH was readjusted to 3.5 after shaking for 1 day). After centrifugation the fluoride concentration in the clear supernatant was measured by a fluoride selective electrode as recommended in the supplier's manual after adding a buffer containing 1 M KNO_3 , 0.01 M DCTA (*trans*-1,2-diaminocyclohexanetetraacetic acid), 0.3 M potassium hydrogenphthalate, and 0.21 M KOH.

The phosphate adsorption capacity was determined by shaking four portions of each oxide sample with various phosphate solutions for 4 days at pH 7.0 (pH was readjusted to 7.0 after shaking for 1 day). The phosphate solutions were prepared to contain 0.1 M NaCl and 6.5×10^{-4} , 1.3×10^{-3} , 2.6×10^{-3} , and 5.2×10^{-3} M Na_2HPO_4 . After centrifugation the phosphate concentration in the clear supernatant was determined by the molybdenum blue method (Watanabe and Olsen, 1965). The adsorption data were fitted to the Langmuir equation, and the calculated adsorption maximum was taken as the phosphate adsorption capacity.

RESULTS AND DISCUSSION

For all iron oxides examined except akaganéite and lepidocrocite 3 the results (Table 1) show good agreement between the surface areas determined by the N_2/BET method and those determined by water adsorption at 19% RH, indicating that the iron oxides possess external surfaces only. Previously, Pyman and Posner (1978) found the same specific surface for amorphous iron oxides by these two methods.

Except for hematite 3 and lepidocrocite 1, all of the samples displayed a ZPC near pH 7 in agreement with previously reported values for several iron oxides, although in the lower end (Parks, 1965; Cabrera *et al.*, 1981). The slightly lower ZPCs

Table 1. Specific surface, zero point of charge, and anion-adsorption properties of various synthetic iron oxides.

Sample ¹	Specific surface (m ² /g)		Hydroxyl buffering ³		Adsorption capacity ³ (μmole/g)		Anion adsorption ⁴ (μmole/m ²)		
	H ₂ O	N ₂ /BET	ZPC ² (pH)	(μmole OH/ (pH·g))	Fluoride	Phosphate	Hydroxyl	Fluoride	Phosphate
Hematite 1	11	14	7.3	10	92	33	0.71	6.6	2.4
Hematite 3	37	36	5.9	26	287	—	0.72	8.0	—
Hematite 4	66	64	7.1	34	326	135	0.53	5.1	2.1
Maghemite 1	8	8	7.2	8	54	24	1.00	6.7	3.0
Maghemite 2	32	30	7.3	24	251	53	0.80	8.4	1.8
Goethite 1	13	16	7.2	13	117	34	0.81	7.3	2.1
Goethite B	94	82	7.6	53	613	216	0.65	7.5	2.6
Akaganéite	44	31	7.2	75	554	193	2.4	17.9	6.2
Lepidocrocite 1	191	221	5.8	198	1306	525	0.89	5.9	2.4
Lepidocrocite 3	30	50	7.1	33	255	128	0.66	5.1	2.6
Feroxyhite	234	235	7.5	130	1293	598	0.55	5.5	2.5
Amorphous iron oxides	316	348	7.2	183	2018	1068	0.53	5.8	3.1

¹ For preparation conditions, see text.

² Zero point of charge, standard deviation ± 0.3 pH units.

³ Coefficient of variation 5–10%.

⁴ Based on the N₂/BET area.

found in this investigation may be due to specific adsorption of small amounts of anions, e.g., carbonate and silicate, despite the precautions to prevent such adsorption. Hematite 3 and lepidocrocite 1 contained some sulfate because lepidocrocite 1 was prepared from a sulfate solution and hematite 3 was formed by heating lepidocrocite 1. Such sulfate may explain the lowering of their ZPC, as sulfate adsorption is known to decrease the ZPC of oxides (Pyman *et al.*, 1979).

The titration curve obtained by plotting OH adsorbed against pH generally becomes a straight line at high electrolyte concentrations. The slope of this curve (the hydroxyl buffering (McLaughlin *et al.*, 1981) is proportional to the electrical capacitance at the surface (Pyman and Posner, 1978). Nearly straight lines were obtained between amount of OH adsorbed and pH in the pH range 5–8.5. Hydroxyl buffering provides an estimate of titratable surface sites, and a close relation was found between hydroxyl buffering and the surface area (Table 2).

The amount of fluoride adsorbed at pH 3.5 is considered to be equal to the number of one-coordinated hydroxyl groups (A-type OH), which are the active groups in ligand exchange reactions, also called specific adsorption (Parfitt, 1978). The fluoride adsorption capacity was closely correlated with both the N₂/BET area and the H₂O area (Table 2).

Phosphate is thought to be adsorbed on various iron oxides as binuclear bridging complexes within a rather broad phos-

phate concentration range by replacing two one-coordinated hydroxyl groups per molecule of phosphate (Parfitt, 1978). Therefore, the high correlation coefficients shown in Table 2 between phosphate adsorption capacity and the surface area are not surprising.

The anion-adsorption properties expressed per unit of surface area, based on the N₂/BET area, are included in Table 1. For all of the iron oxides, except akaganéite, the values are comparable, i.e., titratable acidity and fluoride and phosphate adsorption are nearly independent of the mineralogical form of the iron oxides. The average ratio of hydroxyl buffering to specific surface is 0.71 ± 0.15 μmole OH/(pH·m²), largely in agreement with previously reported results (Pyman and Posner, 1978; Pyman *et al.*, 1979; McLaughlin *et al.*, 1981). The average ratios of fluoride and phosphate adsorption capacities to specific surface are 6.5 ± 1.2 μmole F/m² and 2.5 ± 0.4 μmole P/m², respectively, in good agreement with some (Atkinson *et al.*, 1972; Parfitt, 1978; Cabrera *et al.*, 1981) previously reported values but not with others (McLaughlin *et al.*, 1981). Based on the H₂O area, the corresponding figures are 0.79 ± 0.22 μmole OH/(pH·m²), 7.1 ± 1.3 μmole F/m², and 2.8 ± 0.7 μmole P/m², respectively.

The deviation of akaganéite is presumably due to an underestimation of the specific surface because of its poroid structure (Childs *et al.*, 1980), as the ratios between the fluoride and phosphate adsorption capacities and the hydroxyl buffering for akaganéite are similar to those for the other iron oxides.

For pure iron oxides, except akaganéite, the mineralogy does not seem to affect ZPC, and hydroxyl buffering and fluoride and phosphate adsorption capacities, when expressed per unit of surface area. If these results apply to soil iron oxides (akaganéite occurs rarely, if at all, in soil (Schwertmann, 1979)), it is then possible to calculate their anion-adsorption properties from the contents of amorphous iron oxides extractable by EDTA (Borggaard, 1981) and crystalline iron oxides extractable by dithionite-EDTA (Borggaard, 1982b), because these contents give a fair estimate of the surface area of soil iron oxides (Borggaard, 1982b). Such calculations have been carried out by Borggaard (1983) for phosphate adsorption by soil and show good agreement between calculated and measured phosphate adsorption.

Table 2. Correlation coefficients (r) between surface areas and various anion-adsorption properties for all iron oxides, except akaganéite.

	Surface area	
	N ₂ /BET	H ₂ O
Hydroxyl buffering	0.949	0.932
Fluoride adsorption	0.996	0.993
Phosphate adsorption	0.990	0.983

Correlation highly significant ($P < 0.001$) if $r > 0.847$ (9 d.f.).

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