IRON OXIDE REMOVAL FROM SOILS AND CLAYS BY A DITHIONITE–CITRATE SYSTEM BUFFERED WITH SODIUM BICARBONATE

by

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ABSTRACT

The oxidation potential of dithionite ($Na_2S_2O_4$) increases from 0.37 V to 0.73 V with increase in pH from 6 to 9, because hydroxyl is consumed during oxidation of dithionite. At the same time the amount of iron oxide dissolved in 15 minutes falls off (from 100 percent to less than 1 percent extracted) with increase in pH from 6 to 12 owing to solubility product relationships of iron oxides. An optimum pH for maximum reaction kinetics occurs at approximately pH 7.3. A buffer is needed to hold the pH at the optimum level because 4 moles of OH are used up in reaction with each mole of $Na_2S_2O_4$ oxidized. Tests show that $NaHCO_3$ effectively serves as a buffer in this application. Crystalline hematite dissolved in amounts of several hundred milligrams in 2 min. Crystalline goethite dissolved more slowly, but dissolved during the two or three 15 min treatments normally given for iron oxide removal from soils and clays.

A series of methods for the extraction of iron oxides from soils and clays was tested with soils high in free iron oxides and with nontronite and other iron-bearing clays. It was found that the bicarbonate-buffered $Na_2S_2O_4$-citrate system was the most effective in removal of free iron oxides from latosolic soils, and the least destructive of iron silicate clays as indicated by least loss in cation exchange capacity after the iron oxide removal treatment. With soils the decrease was very little but with the very susceptible Woody district nontronite, the decrease was about 17 percent as contrasted to 35–80 percent with other methods.

INTRODUCTION

The removal of amorphous coatings and crystals of free iron oxides, particularly hematite and goethite, which act as cementing agents, is important in many types of analysis of soils and clay minerals. The removal of free iron oxides aids in dispersion of the silicate portion, which is essential for effective segregation into different particle size fractions. For x-ray diffraction studies the removal of free iron oxides greatly enhances the parallel orientation of layer silicate clays and brings out some x-ray diffraction peaks that are otherwise difficult or impossible to detect. Differential and integral thermal analysis, electron micrographs and cation exchange capacity are greatly improved after removal of free iron oxides. Use of citrate chelating agent (Aguilera and Jackson, 1953) with $Na_2S_2O_4$ not only helps with iron extraction but removes some coatings of alumina and thereby assists in the dissolution of free silica cements that are stabilized by alumina coatings, as will be shown in the present paper.

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In 1877 Bemmelen and others (reviewed by Jackson, 1956, p. 47) dissolved iron oxide and other soil colloids by the use of mineral acids and alkalies. Tamm (1922) used acid $Na_2C_2O_4 \cdot$ to remove iron oxide. In an attempt to speed up the reaction, Drosdoff and Truog (1935) used H_2S and oxalic acid to reduce and chelate the iron. Truog *et al.* (1937) modified this method by the use of Na_2S and oxalic acid as a source of nascent H_2S. They reported a considerable decrease in cation exchange capacity of nontronite, Miami silt loam, and certain other soils. Allison and Scarseth (1942) removed the iron oxide by microbiological reduction in the presence of sucrose. Jeffries (1941) used nascent hydrogen produced by Al acted on by oxalic acid. Dion (1944) made a comparative study of destructive effects of oxalic acid and tartaric acid (with nascent hydrogen from Al) and showed less destruction at pH 6 than at a lower pH. However, partial destruction of mineral colloids still resulted with this procedure. He reported up to 45 percent loss in cation exchange capacity by both montmorillonite and kaolinite clays by this and several methods with which it was compared. This loss could be attributed only to the breakdown of mineral structure. Jeffries (1947) employed nascent hydrogen produced by the action of oxalic acid on magnesium. Haldane (1956) substituted Zn for Mg because iron was deposited on the Mg ribbon, and thus its dissolution was not complete. Deb (1950) proposed the use of $Na_2S_2O_4$ with H_2O, or with sodium tartrate and sodium acetate in pH ranges from 2.9 to 6.0 at 40°C. Essentially the Deb method ($Na_2S_2O_4$ in water solution) was used by Mitchell and Mackenzie (1954) at pH 5.8 to 6.0 and Mackenzie (1954) at pH 3.5 to 6.5. Removal of iron oxide from latosols by these methods was very slow and incomplete. Also there was unwanted precipitation of FeS and S, 0.02 to 0.05 N HCl being used to dissolve the FeS and CS_2 being used to dissolve the S. Considerable decrease in cation-exchange capacity occurred with some soils (31.8 meq/g decreased to 24.6 at pH 5.8, Mitchell and Mackenzie, 1954).

Aguilera and Jackson (1953) proposed the use of $Na_2S_2O_4$ with sodium citrate (with or without ferric iron specific Versene) adjusted to pH 7.3 by 10 percent NaOH at 80°C for very complete and rapid removal of iron oxides from soils. Almost immediately after publication in 1953, the more convenient practice of adding the $Na_2S_2O_4$ as 1 g of dry powder was adopted (as reported by Jackson, 1956, p. 57), and this increased difficulty in keeping the pH up to 7.3 since no NaOH was added with the $Na_2S_2O_4$. Careful pH adjustments were required to keep FeS and elemental S from precipitating which happened if the pH were allowed to drop much. To stabilize the pH at 7.3, the method was modified in the present study by addition of $NaHCO_3$ buffer (as described by Jackson, 1956, p. 57) with highly satisfactory results.

MATERIALS

Soils rich in free iron oxides and soils and clay minerals containing iron-bearing 2 : 1 layer silicates were studied. The samples included : Fajardo clay (8–16 in.), Red-Yellow Podzolic soil from Puerto Rico (courtesy J. A. Bonnet) ; Bayamon clay (10–28 in.), Reddish Brown lateritic soil from Puerto

Rico (courtesy J. A. Bonnet); Miami silt loam B_2 (14–27 in.), Gray-Brown Podzolic soils from Sun Prairie, Wis. (courtesy R. W. Simonson); Waipiata B (6–10 in.), dark yellow brown soil developed from olivine basalt, from near Waipiata, New Zealand (courtesy L. D. Swindale), vermiculite weathered from granite, Manitou Experimental Forest, Colo. (courtesy J. L. Retzer); nontronite from Woody district, Calif. (from R. M. Wilke, Palo Alto, Calif.); glauconite from Cambrian sandstone at Shot Tower State Park, Spring Green, Wis.; Kuroishibaru (6–10 in.) allophanic Ando soil from Japan (courtesy S. Aomine).

PROCEDURE

Methods of Iron Oxide Removal

Sodium dithionite–sodium citrate with $NaHCO_3$ *buffer (proposed method).*— This technique is a modification of the method of Aguilera and Jackson (1953) by the inclusion of $NaHCO_3$ as a source of hydroxyl, thereby stabilizing the oxidation potential and pH, giving more effective removal of iron oxides. The procedure has been detailed elsewhere (Jackson, 1956, pp. 57–58), and is modified in part as follows:

A suitable amount of the sample (4 g of many soils or 1 g of clay per 100 ml tube) containing 0.5 g of extractable Fe_2O_3 or less, is placed in a 100 ml centrifuge tube and 40 ml of 0.3 M Na-citrate solution and 5 ml. of 1 M $NaHCO_3$ solution are added. The temperature is brought to 80°C in a water bath, then 1 g of solid $Na_2S_2O_4$ ($\frac{1}{2}$ g suffices for clays low in free iron oxides) is added by means of a spoon, and the mixture is stirred constantly for 1 min and then occasionally for a total of 15 min. At the end of the 15 min digestion period, 10 ml of saturated NaCl solution (and 10 ml of acetone, particularly needed for allophanic soils) is added to the tube to promote flocculation. The suspension is then mixed, warmed in a water bath, and centrifuged for 5 min at 1600–2200 rev/min. The clear supernatant is decanted into a 500 ml volumetric flask (or a 1000 ml flask if the volume exceeds 500 ml) and the solution is kept for Fe, Al and Si determinations.

For samples which originally contained more than 5 percent of extractable Fe_2O_3, the treatment in the previous paragraph is repeated once or twice (sample combined into fewer tubes for the second treatment), with decantation into the same 500 ml volumetric flask as before. A final washing (two or more for samples of more than 1 g of residue) is made with the Na-citrate solution (with NaCl and acetone if necessary for flocculation), which is combined with the previous decantates for Fe determination. If the colloid does not flocculate, 10 ml of acetone is added (HCl and $CaCl_2$ solutions are avoided). The solution is mixed and warmed in a water bath. Care is taken that solutions containing acetone do not boil. Centrifugation for 5 min is repeated. A pure white color of the residue generally should not be expected, as some soils and colloids contain cream or green colored colloids and coarse, black mineral particles. The sample is kept in methanol, acetone or water, without drying. The sample, freed of extractable Fe_2O_3 but not dried at any time during the procedure, is ready for cation exchange capacity determination or (Jackson, 1956, p. 72) boiling in 2 percent Na_2CO_3 for dispersion and segregation for x-ray diffraction analysis, differential and integral thermal analysis, infrared analysis, elemental analysis, electron microscope examination, or other procedures.

Sodium sulfide–oxalic acid (comparison method).—This method was proposed by Truog *et al.* (1937). It is taken as representative of the various

H_2S methods. A 4 g soil sample is placed in 650 ml of distilled water, 5 ml of 20 percent $Na_2S \cdot 9H_2O$ solution is added, and the sample is boiled for 5 min ; 10 g of NH_4Cl is added and the sample is kept at 80°–90°C during the treatments. Oxalic acid is added to bring to pH 6.0 with vigorous stirring. Then 10 ml more of 20 percent $Na_2S \cdot 9H_2O$ solution is added. Oxalic acid is added rapidly until pH 7 is reached and then slowly to pH 6 and again rapidly to pH 3.5. The mixture is stirred and allowed to stand for a few minutes as the black FeS is dissolving, then is brought back to pH 7 with 2 N NH_4OH. The pH is slowly brought down to 6 and then rapidly to 3.5 with 2 N HCl. After digestion for a few minutes, the sample is centrifuged and washed twice with 0.001 N HCl. The extract is used for Fe, Si and Al analysis.

Sodium dithionite in acid system (comparison method).—Deb (1950) proposed three methods for the removal of free iron oxide : ammonium oxalate and oxalic acid in sunlight (pH 3.8) ; $Na_2S_2O_4$ in sodium acetate and sodium tartarate system at pH 5–6 ; and sodium dithionite in water at pH 3.5. The last was considered by Deb to be faster and less destructive than the first two and is taken as representative of $Na_2S_2O_4$ methods previous to that of Aguilera and Jackson (1953). A 4 g soil sample is dispersed thoroughly in 50 ml of distilled water, 2 g of $Na_2S_2O_4$ is added, and the mixture is digested for 30–50 min in a water bath at 40°C. The sample is centrifuged and treated twice again with 0.02 N HCl for 10–15 min, centrifuged, and the extract is taken for Fe analysis.

Zinc–ammonium oxalate (comparison method).—This is a modification (Haldane, 1956) of the Jeffries nascent H methods, substituting Zn for Al (Jeffries, 1941) or Mg (Jeffries, 1947). This modification is said to avoid precipitation of Fe on the metal and avoids introduction of Mg and Al ions which are also present in clay. To a 4 g soil sample placed in a 100 ml evaporating dish, 1 ml of 0.5 N NaOH is added and the mixture is ground into a paste with a rubber pestle (2–3 min). The suspension is neutralized with 1 ml of 0.5 N oxalic acid. Using 40 ml of ammonium oxalate buffer and continuous grinding, the sample is transferred to a 100 ml volumetric flask. Then 0.5 g of Zn powder (300-mesh) is added. The sample is allowed to stand for 1 hr with intermittent shaking, made up to volume, filtered, and the filtrate is used for Fe and Si analysis.

Determination of Fe, Al and Si dissolved.—An aliquot of the supernatant citrate solution was prepared (Jackson, 1958, p. 169 ; 1956, p. 58) for Fe analysis by H_2O_2 treatment and color development with KSCN. A second aliquot was similarly prepared, then given a double NaOH separation in a Ni beaker to obtain a Si and Al solution (Jackson, 1956, p. 59) from which aliquots were analyzed colorimetrically, Si by molybdate (Jackson, 1958, p. 296) and Al by aluminon (Jackson, 1958, p. 300).

Cation exchange capacity measurement.—The cation exchange capacity was determined by Ca with centrifuge method (Jackson, 1958, p. 59). Five washings are given with $CaCl_2$ and CaOAc solutions ; and five with water, alcohol and acetone. The exchangeable Ca is replaced in NaOAc and deter-

mined by the Beckman DU flame emission spectrophotometer using a wave length of 424 mμ. Na was used to avoid any fixation of NH_4 or K by vermiculite samples (Sawhney *et al.*, 1959).

RESULTS AND DISCUSSION
Oxidation Potential

Prerequisite to a good method for free iron oxide removal is a high oxidation potential (high tendency to become oxidized, hence a good reducing agent, Jackson (1956), p. 651). In each dithionite system compared in this section, the hydroxyl source and other variables were applied to 40 ml of Na citrate, with 1 g of dithionite. The oxidation potential of these dithionite systems increases with the increase in pH (Table 1) owing to use of four OH

TABLE 1.—pH AND OXIDATION POTENTIAL OF DITHIONITE-CITRATE SYSTEMS WITH VARYING AMOUNTS OF $NaHCO_3$ OR NaOH

| Volume (ml) | Addition of 1 M $NaHCO_3$ | | | | Volume (ml) | Addition of 10 percent NaOH | | | |
| | After 2 min | | After 15 min | | | After 2 min | | After 15 min | |
	pH	Ox. pot. (V)	pH	Ox. pot. (V)		pH	Ox. pot. (V)	pH	Ox. pot. (V)
0.0	6.50	0.37	6.00	0.36	0.0	6.50	0.37	5.95	0.34
2.5	7.10	0.65	6.70	0.61	1.0	11.30	0.51	6.45	0.50
3.7	7.50	0.68	6.90	0.65	1.5	11.70	0.58	6.75	0.56
5.0	7.75	0.72	7.25	0.69	2.0	11.90	0.58	7.65	0.56
10.0	8.35	0.73	8.15	0.73	4.0	12.15	0.59	12.10	0.61

groups in oxidation of each dithionite molecule. The earlier dithionite methods, which used a low pH, did not give effective removal of iron oxides because of the low oxidation potential of the system.

The required OH may be obtained either from NaOH or $NaHCO_3$. In the NaOH system, there were sudden increases and decreases in pH (Table 1, column 7) and oxidation potential (Table 1, column 8), whereas in $NaHCO_3$ system (highly buffered) there were gradual changes in pH (Table 1, columns 2 and 4) and a well regulated, high oxidation potential of 0.7 V (Table 1, columns 3 and 5). The theoretical value of 1.12 V for the alkaline reaction (Latimer, 1952; Jackson, 1956, p. 48) was not reached in the presently proposed method.

Correlation of Oxidation Potential with Solubility of Iron Oxides and Reaction Products

The order in which the reagents were mixed and the resulting pH greatly influenced the rate of dissolution of iron oxides and the precipitation or nonprecipitation of S and FeS. In one method (Table 2, procedure 1), both

Table 2.—Solubility of Fe_2O_3 with Different Procedures and pH Levels, During a 15 min Reaction Time

No.	10% NaOH (ml)	Procedure	Initial[1] pH	pH after 15 min	Fe dissolved (p.p.m.)	Fe dissolved (%)	Precipitation S	Precipitation FeS	Precipitation Rate
1.	1.8	$NaCt^2$ (pH 7.3) + $Na_2S_2O_4$ solution (pH 7.3) + sample + heat	7.20	6.90	163.5	84.1	No	Little	Fast
2.	nil	NaCt (pH 7.3) + sample + heat + $Na_2S_2O_4$ solid	6.30	6.25	180.7[3]	92.7	Yes	Yes	Fast
3.	nil	NaCt + sample + heat + $Na_2S_2O_4$ solid	6.35	6.20	197.5[3]	101.0	Yes	Yes	V. fast[4]
4.	0.5	NaCt + NaOH + sample + heat + $Na_2S_2O_4$ solid	6.40	6.25	195.0[3]	100.0	Yes	Yes	V. fast[4]
5.	1.0	NaCt + NaOH + $Na_2S_2O_4$ solid + sample + heat	6.80	6.45	162.5	83.6	No	No	Fast
6.	1.0	NaCt + NaOH + sample + $Na_2S_2O_4$ solid + heat	6.80	6.35	177.0[3]	90.8	No	No	Fast
7.	2.0	Same	7.40	6.50	127.0	65.1	No	No	Slow
8.	2.5	Same	8.20	6.80	31.5	16.4	No	No	Slow
9.	3.5	Same	10.50	6.95	9.0	4.7	No	No	Slow
10.	4.0	Same	12.08	8.15	0.2	0.1	No	No	V. slow
11.	8.0	Same	12.15	8.40	0.2	0.1	No	No	V. slow
12.	16.0	Same	12.17	8.45	0.2	0.1	No	No	V. slow
13.	32.0	Same	12.16	8.55	0.2	0.1	No	No	V. slow

[1] All reagents added and mixed. [3] Average of duplicates.
[2] Ct represents citrate. [4] Time given = 10 min.

the Na citrate and the $Na_2S_2O_4$ solutions were adjusted to pH 7.3, yet Fe dissolution was not complete in 15 min. In another system (Table 2, procedure 2) when only the Na citrate solution was adjusted to pH 7.3, the recovery was more nearly complete but S and FeS were precipitated.

As the pH was increased to 6.4, the Fe_2O_3 dissolved completely (Table 2, column 7), but FeS and S precipitation occurred. As the pH was increased further the percentage of Fe dissolved went down steadily. This relationship is brought out clearly by the curves of Fe_2O_3 solubility and oxidation potential against pH (Fig. 1). The oxidation potential increases sharply up to pH 8 and then levels off. The solubility of Fe_2O_3 decreases rapidly above pH 7. The two curves intersect at about pH 7.3, suggesting this as the optimum pH for the most effective and rapid removal of free iron oxides. The order of addition of reagents in the adopted procedure was based on procedures 3 and 4 (Table 2) because they were the most effective. Substitution of 5 ml

of 1 M $NaHCO_3$ buffer for NaOH in the adjustment of the usual 40 ml of Na citrate solution to pH 7.3 overcame the difficulty of S and FeS precipitation, maintained a high oxidation potential (Table 1, column 5), and was completely effective for dissolution of free iron oxides (Table 3).

Solubility of Hematite and Goethite in Proposed Method

A 0.2 g sample of finely ground crystalline hematite was dissolved completely (Table 3, column 3) in 2 min, whereas with an excess of $NaHCO_3$ or NaOH (i.e. at higher pH values), a longer treatment was required. Moreover, the rate of dissolution of goethite decreased even more sharply (Table 3, column 4) with increase in pH. The recovery was complete in two or three treatments of 15 min each. Therefore, for soils with a high content of free iron oxides, two or three treatments of 15 min each are given.
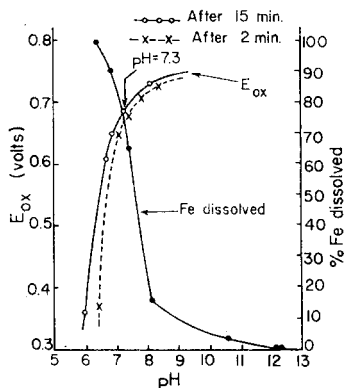

Figure 1.—Curves of pH against oxidation potential of $Na_2S_2O_4$–Na citrate systems buffered with $NaHCO_3$, and associated solubility of Fe_2O_3. NaOH was added to obtain the three solutions above pH 9.

Comparative Study of Iron Oxide Removal Methods

Since 1877, when Bemmelen and others used mineral acids and alkalies to dissolve iron oxides (and clays as well) in order to clean the sand and silt for petrographic study, various methods have been developed which are more selective. Most of them lack some of the essential requirements of a desirable iron oxide removal method; namely, the method should be (a) effective, (b) rapid, (c) free of analytical difficulties, and above all (d) should not attack iron silicate minerals in clays. Three types of methods are compared with the proposed buffered dithionite method in the present study, namely one using H_2S, one using unbuffered dithionite and one using nascent hydrogen, as described in the procedure section.

Fe_2O_3, Al_2O_3, and SiO_2 dissolved by various methods.—In the latosolic soils, Fajardo and Bayamon from Puerto Rico, the proposed method removes about 6 and 8 percent of free iron oxides (Table 4, columns 2 and 5) as contrasted to less than 2 percent by the H_2S method and somewhat higher by

Table 3.—Fe_2O_3 Dissolved by Citrate–Dithionite Systems

Hydroxyl Source	Hematite (0.2 g)		Goethite (0.2 g) Fe recovered (%)			
	Time (min)	Fe Recovered (%)	15-min treatment			Total
			1st	2nd	3rd	
2.5 ml 1 M $NaHCO_3$	2	100	83.4	13.4	3.0	99.8
5 ml $NaHCO_3$	2	100	81.7	14.6	3.3	99.6
10 ml $NaHCO_3$	15	99.1	80.0	15.4	4.0	99.4
1 ml 10% NaOH	15	98.0	67.6	26.2	5.4	99.2

Table 4.—Percent Fe_2O_3, Al_2O_3 and SiO_2 Dissolved from Soils by Different Methods of Iron Oxide Removal

Method	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3	SiO_2
	Fajardo, P.R.			Bayamon, P.R.			Miami B_2, Wis.			Waipiata, N.Z.		
1.	5.5	2.2	7.2	7.9	1.8	8.6	1.0	1.8	7.5	1.8	2.2	8.0
2.	1.5	1.6	1.0	1.8	2.1	0.8	2.5	2.3	7.7	2.1	1.4	1.5
3.	4.8	—	—	5.3	—	—	1.5	—	—	2.6	—	—
4.	4.0	—	3.6	6.6	—	3.5	1.3	—	4.7	3.4	—	3.1
	Vermiculite, Colo.			Nontronite, Woody, Calif.			Glauconite, Wis.			Kuroishibaru, Japan		
1.	4.5	1.6	8.4	0.5	2.0	8.4	0.8	1.0	8.6	5.0	5.6	15.0
2.	6.0	3.8	10.2	2.9	1.5	1.1	0.6	0.5	2.3	6.1	10.3	10.2
3	4.2	—	—	2.8	—	—	0.7	—	—	4.7	—	—
4.	5.9	—	2.1	4.1	—	4.0	0.6	—	2.6	5.9	—	8.6

1. Proposed : $Na_2S_2O_4$–Na citrate–$NaHCO_3$; pH 7.3 ; temp. 80°C ; elapsed time, 1 hr.
2. Truog (1937) : Na_2S–NH_4Cl–oxalic acid ; pH 3.5–10 ; temp. 95°C ; elapsed time, 6 hr.
3. Deb (1950) : $Na_2S_2O_4$–H_2O ; pH 3.5 ; temp. 40°C ; elapsed time, 3 hr.
4. Haldane (1956) : Zn–oxalic acid–NH_4 oxalate ; pH 3.6 ; temp. 20°C ; elapsed time, 3 hr.

other methods. The greater effectiveness of the proposed method for removing free Fe_2O_3 from iron oxide rich soils is thereby shown. For Miami (Wis.) and Waipiata (New Zealand) nontronite-bearing soils, the H_2S, acid nascent H, and acid $Na_2S_2O_4$ methods attack and dissolve more of the combined iron than did the proposed method (Table 4). This effect is even more pronounced for nontronite and iron-rich vermiculite (Table 4).

The various methods dissolved a considerable amount of Al_2O_3 and SiO_2, especially from the allophane of the Japanese Ando (Kuroishibaru) soil. The

determination of Al and Si is very difficult in the Deb or Haldane extracts owing to the excess of $Na_2S_2O_4$ and oxalate, respectively. The time elapsed for removal of iron oxides from a set of eight samples is much higher (3–6 hr) for the comparison methods as compared to less than 1 hr for the proposed method (Table 4, footnote).

Effect of iron oxide removal on cation exchange capacity of soils.—To measure the destructive effect of various methods of iron oxide removal on other iron silicate minerals in soils, their cation exchange capacity was determined before and after iron oxide removal treatment. After the treatments of Truog, Deb, and Haldane, there is a marked decrease in the cation exchange capacity of Miami and Waipiata soils (Table 5, columns 4 and 5). The decrease is even more pronounced for vermiculite and nontronite (Table 5, columns 6 and 7),

Table 5.—Effect of Different Iron Oxide Removal Methods on Cation Exchange Capacity of Whole Soils and Clayey Rocks (– 2 mm) High in Iron Silicates

Treatment[1]	Cation Exchange Capacity (meq/100 g)			
	Fajardo Soil	Bayamon Soil	Miami Soil	Waipiata Soil
None	37	33	42	49
1	58	59	53	52
2	59	69	32	31
3	49	35	41	39
4	45	48	50	45
	Vermiculite-rich Rock	Nontronite-rich Rock	Glauconite-rich Rock	Kuroishibaru Soil
None	108	44	10	83
1	107	50	18	93
2	54	23	11	25
3	55	47	10	65
4	73	43	37	125

[1] Details given in footnote of Table 4.

varying from 25 to 50 percent. This decrease is due to the breakdown of iron silicate minerals. For the Japanese Ando soil there is about 75 percent decrease after Truog's treatment and about 30 percent decrease after Deb's treatment, owing to the dissolution of allophane (Table 5, column 5). There is a slight increase in the exchange capacity after the proposed treatment, attributable to the removal of iron, aluminum and silica complexes which may have blocked some exchange sites. Also, possibly, there may have been reduction of some lattice iron which is not clearly shown up by earlier methods because of their destructive effect on iron silicate clays. There is a large apparent increase in the exchange capacity of glauconite and Ando soil after

the Haldane treatment (Table 5, columns 4 and 5), possibly owing to the precipitation of a voluminous zinc oxalate phase (quite noticeable to casual observation) and its exchange (precipitation) with Ca salts.

Iron oxide dissolved and its effect on cation exchange capacity of clays.—The effect of iron oxide removal is brought out more clearly with the clay size fraction (-2μ). The proposed method removes free iron oxides much more effectively from the latosolic soil clays as contrasted to other methods (Table 6, column 2). Methods 2, 3 and 4 attack the iron-rich silicate minerals (vermiculite and nontronite) and extract very large amounts of iron (Table 6,

TABLE 6.—Fe_2O_3 DISSOLVED AND THE EFFECT ON CATION EXCHANGE CAPACITY OF CLAYS (-2μ) BY VARIOUS METHODS OF IRON OXIDE REMOVAL

Method[1]	Bayamon		Vermiculite		Nontronite[3]		Allophane (Kuroishibaru)	
	Fe_2O_3 (%)	CEC[2]	Fe_2O_3 (%)	CEC	Fe_2O_3 (%)	CEC	Fe_2O_3 (%)	CEC
No treatment	—	42	—	130	—	64	—	128
1. Proposed	12.5	43	6.3	136	0.2	54	7.9	109
2. Truog	6.5	37	10.3	81	7.9	25	6.2	53
3. Deb	10.5	41	7.8	99	8.0	46	5.9	79
4. Haldane	2.2	47	8.7	120	2.3	50	7.1	69

[1] Details given in footnote of Table 4.
[2] Cation exchange capacity, meq/100 g of original -2μ clay sample.
[3] Contains some quartz in this -2μ fraction.

columns 4 and 6) from within the lattice of these minerals as shown by the sharp decrease in cation exchange capacity (Table 6, columns 5 and 7) after the treatment. There is also considerable decrease in the exchange capacity of Japanese Ando soil with the three comparison methods (Table 6, column 9).

CONCLUSIONS

The proposed method of buffering the dithionite–citrate system with $NaHCO_3$ gives freedom from S, FeS, zinc oxalate and other unwanted precipitates. It is very rapid, taking only 15–60 min as compared to several hours in earlier methods. It is highly effective in the dissolution of free iron oxides owing to maintenance of a slightly alkaline pH which keeps a high oxidation potential in the $Na_2S_2O_4$ system, in marked contrast to earlier acid or less buffered dithionite systems. The determination of Fe, Al and Si in the extract is much easier and simpler. Above all, the treatment has almost no destructive effect on iron silicate clay minerals.

ACKNOWLEDGMENTS

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