

Changes in Physical and Chemical Properties of Sandy Loam Soils by Hematite Addition

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ABSTRACT : Pedogenic hematite is a well known agent for sink of pollutants and nutrients and for aggregation of particles in soils. Changes in physical and chemical properties of two sandy loam soils (Anahuac and Crowley soils) from the Southern Coastal Plain, the United States of America, were tested after adding finely ground crystalline hematite prepared for drilling fluid weighting material. There was an increase in hydraulic conductivity (HC) of the soils with addition of up to 3% by weight of hematite but a decrease in HC with addition of more hematite. The aggregate stability (AS) of the soils was not affected by adding hematite. Anahuac soil with higher content of organic matter and lower sodium adsorption ratio (SAR) had higher values of HC and AS than Crowley soil. Adding hematite also resulted in a slight increase in zinc (Zn) adsorption by the soils, but had no influence on the adsorption of phosphate.

INTRODUCTION

Soil stability is a measurement of its ability to retain structure against changes of chemical and physical environments. It depends on several soil properties such as SAR, organic matter content, clay content and mineralogy, pH, and iron (Fe) oxide content.

Many red soils have a structure favorable to plant growth (Deshpande *et al.*, 1968). This structure has been most commonly attributed to the Fe oxides (Chesters *et al.*, 1957). The high proportion of Fe in laterite, the common occurrence of Fe oxide cemented nodules in soils, and the Fe oxide coating on quartz grains indicate that Fe oxides can be aggregating and cementing agents (Deshpande *et al.*, 1968; Shadfan *et al.*, 1985). Positive relationship exists between Fe oxide content, and HC and AS of soils (Arca, Weed, 1966; Gu, Doner, 1993; Keren, Singer, 1990). The aggregating and cementing actions of Fe oxides reduce the dispersion of clay in soils (McNeal *et al.*, 1968).

The particle size of pedogenic hematite ranges from 2 to 5×10^{-8} m in width and 1 to 2×10^{-8} m in thickness (Schwertman, Taylor, 1989). The fine particles of hematite in soils may act as aggregating agents of other soil particles. In cementation, hematite fills the pores between particles by crystal growth (Shadfan *et al.*, 1985). The cemented mass can be detrimental to plant rooting and to water movement

in soils. Iron oxide precipitated in clay suspensions of kaolinite, illite, or smectite had an aggregating effect (Balckmore, 1973).

Soil Fe oxides also acts as a sink for nutrients and contaminants such as phosphate, arsenate (AsO_4^{3-}), nitrate (NO_3^-), Zn, cobalt (Co), and herbicides via specific or nonspecific adsorption. The amount of a particular ion adsorbed depends on its activity, and the pH and ionic strength of the soil solution (Schwertman, Taylor, 1989). Generally, chloride (Cl^-), NO_3^- , perchlorate (ClO_4^-), and alkali cations are nonspecifically adsorbed on Fe oxides. Zinc and Co are specifically adsorbed on Fe oxides (McKenzie, 1980; Music *et al.*, 1979). Regarding adsorption of heavy metals on Fe oxides, hydrolyzed species are preferentially adsorbed over unhydrolyzed species (Music *et al.*, 1979). Phosphate and AsO_4^{3-} are also specifically adsorbed on Fe oxides (McKeague, Cline, 1963). Iron oxides also adsorb soil organic matter which is supported by the high content of organic matter in Fe oxide rich horizons in humid temperate area soils (Evans, Russell, 1959).

Extensive research has been conducted to improve low stability of soils which are naturally occurring or are formed by human activity such as irrigation and waste disposal using gypsum, calcium carbonate, calcium chloride, sulfuric acid, and synthetic organic polymers (Loveday, 1984). However, hematite as an amendment to improve soil stability has not been reported in literature. The objective of this study was to examine changes in physical and chemical properties of soils by addition of mined and finely ground hematite prepared for drilling fluid weighting material which is contained in waste drilling fluid.

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MATERIALS AND METHODS

Materials

Two surface soils (0~15 cm in depth) were collected from the Southern Coastal Plain, USA: Anahuac soil (Fine, mixed, active, hyperthermic Oxyaquic Glossuadalfs) from Jefferson county, Texas and Crowley soil (Fine, montmorillonitic, thermic Typic Albaqualfs) from Cameron parish, Louisiana. The collected soil samples were air-dried and gently ground with a rubber stopper to pass a 2 mm sieve. Mined and ground hematite (coarse hematite) which was prepared for drilling fluid weighting material by Triton USA Co. and additionally ground hematite sample in laboratory (fine hematite) to reduce particle size (coarse hematite: 1% sand, 93% silt, and 6% clay and fine hematite: 70% silt and 30% clay) were used as soil amendments.

Soil Analysis

Physical property

Soil samples were fractionated into sand, silt, coarse clay ($0.2\sim 2 \times 10^{-6}$ m), and fine clay ($< 0.2 \times 10^{-6}$ m) fractions using wet sieving and sedimentation after removal of water soluble salts, carbonates, and organic matter with pH 5 sodium acetate (NaOAc) and hydrogen peroxide (H_2O_2) (Jackson, 1974). Texture of the soils was determined based on the weight of each fraction. The field capacity of the soils was determined using a small core method and applying $-1/3$ bar for drainage (Cassel, Nielson, 1982).

Mineralogy

The mineralogical composition of each fraction was determined by X-ray analysis with a Philips X-ray diffractometer (XRD) producing $CuK\alpha$ radiation at 30 kV and 18 mA and by infrared absorption with a Perkin Elmer System 2000 FT-IR spectrometer. Sand and silt fractions were finely ground and mounted in aluminum sample holders and clay fractions were magnesium (Mg) saturated, glycerol solvated, and potassium (K) saturated and heated successively at 25°C, 300°C, and 550°C. Clay fractions were mounted on glass slides to obtain preferred particle orientation. Glycerol was sprayed on the Mg-saturated mount. Diffuse reflectance method was used for the infrared analysis of clay fractions. Iron oxide contents in the soils were determined with dithionite-citrate-bicarbonate extraction method (Jackson, 1974). The concentration of Fe in extractants was determined with a Perkin Elmer 3100 atomic

absorption spectrometer.

Chemical Property

Organic matter contents of bulk soil samples were determined by the Walkley-Black procedure (Nelson and Sommers, 1982). pH (1 : 1 soil-water method), cation exchange capacity (CEC: Na^+ for saturation and NH_4^+ for exchange), and SAR and electrical conductivity (EC) of saturate paste were determined (US Salinity Laboratory Staff, 1954). A pH meter (Corning Scientific Instruments, Model 12) and a conductivity meter (CDM3, Radiometer Copenhagen) were used for the determination of pH and EC, respectively. Concentration of sodium (Na), K, calcium (Ca), and Mg in solutions for CEC and SAR were determined with a Varian AA-475 atomic absorption spectrometer.

Experimental Procedure

Changes in physical properties by hematite addition

Soil and coarse hematite or fine hematite were mixed at different concentrations of hematite (0, 1, 3, 5, or 7% by weight). The soil-hematite mixtures were incubated at 25°C during five wetting and drying cycles with water. Distilled water and distilled water adjusted to pH 9 with sodium hydroxide (NaOH), so called pH 9 NaOH solution, were employed. Water (50% of sample weight) was added at each wetting. The incubated samples were air-dried and gently ground with a rubber stopper to pass a 2 mm sieve to provide thorough mixing and homogeneity.

Two hundred grams of the ground sample was packed in permeameter with double ring bottom (5 cm of inner ring and 7.6 cm of outer ring in diameter) by gentle tapping on a rubber stopper. Each sample column was 4 cm in height and 1.1 g/cm^3 in bulk density. A filter paper (Whatmann No. 40) was placed on the bottom of the permeameter before packing. A constant head of 10 cm above the column with 0.01 N calcium sulfate ($CaSO_4$) solution was maintained to measure HC. Effluent was collected after each time interval to determine average HC. The HC test continued until HC reached steady state.

Aggregates (1~2 mm in diameter) of the incubated sample containing coarse hematite were collected using dry sieving. Aggregate stability was tested with mechanical wet sieving machine operating for five minutes. Fifteen grams of aggregate for one test and distilled water as wetting medium were used. All treatments and HC tests were duplicated and AS test was conducted with five replicates.

Changes in Chemical Properties by Hematite Addition. Soils and coarse hematite were mixed at different concentration (0, 1, 3, 5, or 7% of hematite by weight). Five grams of soil-hematite mixture and 30 ml of 1 mM zinc sulfate ($ZnSO_4$) or 30 ml of 500 mg/l of phosphorus (P) in 0.1 M KCl matrix solution were placed in 50 ml glass tubes and shook for 16 hours using a horizontal shaker to equilibrate. After equilibration, samples were centrifuged at 10,000 g for 10 minutes. The pH of the filtered solutions was recorded with a pH meter (Corning Scientific Instruments, Model 12). Concentrations of P and Zn in the solutions were determined with the colorimetric method described by Murphy, Riley (1962) and a Perkin Elmer 3100 atomic absorption spectrometer, respectively.

RESULTS

Both soils are acidic (about pH 6), and have similar EC, texture (sandy loam), Fe oxide content, and mineralogy (Table 1). Anahuac soil has higher content of organic matter, higher CEC, and lower SAR than Crowley soil. Anahuac soil had greater HC and AS than Crowley soil at same level of added hematite. Hematite addition up to 3% to both soils increased HC but the larger amounts decreased it regardless the pH of incubating solution (Fig. 1).

The treatment of soils with coarse hematite increased HC more than the treatment with fine hematite regardless the pH of incubating solution. The soil-hematite mixtures incubated with distilled water had greater HC and AS than the soil-hematite mixtures incubated with pH 9 NaOH solution. The red color of leachates increased with increasing concentration of both coarse and fine hematite in the mixtures, and the soils treated fine hematite had deeper red color of leachate than the soils treated with coarse hematite at same concentration. Aggregate stability of soils was not affected by addition of coarse hematite (Fig. 2).

The adsorption of Zn by soils treated with coarse

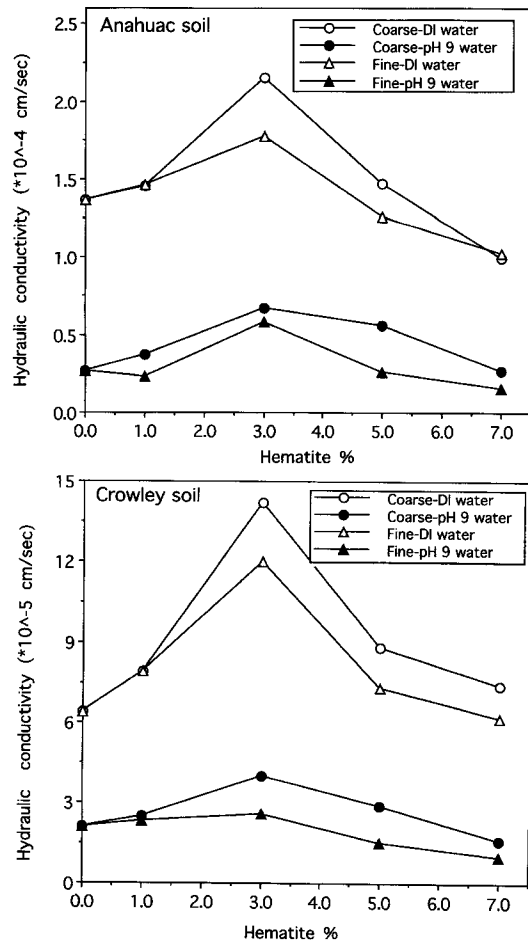


Fig. 1. Hydraulic conductivity of Anahuac and Crowley soils treated with coarse or fine hematite and incubated in distilled water or pH 9 solution.

hematite increased slightly as more hematite was added (Fig. 3). Anahuac soil-hematite mixtures had greater amount of adsorbed Zn than Crowley soil-hematite mixtures at same concentration of hematite. The pHs of equilibrated solutions for the Zn adsorption were 5.80. The adsorption of P by soils did not

Table 1. Chemical, physical, and mineralogical data of Anahuac and Crowley soils.

	pH	EC ¹	SAR ²	CEC ³	OM ⁴	Fe ₂ O ₃ ⁵	FC ⁶	Texture	Mineralogy ⁷		
									Sand	Silt	Clay
Anahuac	6.0	1.3	1.0	10.8	2.0	0.21	17.5	Sandy loam	Q, F	Q, F	S, K, M
Crowley	5.9	1.6	3.0	5.6	1.1	0.17	16.4	Sandy loam	Q, F	Q, F	S, K, M

1; Electrical conductivity (dS/m), 2; Sodium adsorption ratio ($SAR = [Na^+] / \{1/2([Ca^{2+}] + [Mg^{2+}])\}^{1/2}$), 3; Cation exchange capacity (cmol/kg), 4; Organic matter content (%), 5; Iron oxide content (%), 6; Field capacity (%), 7; Mineral identification was based on XRD and FTIR data. Q; quartz, F; feldspar, S; smectite, K; kaolinite, M; mica.

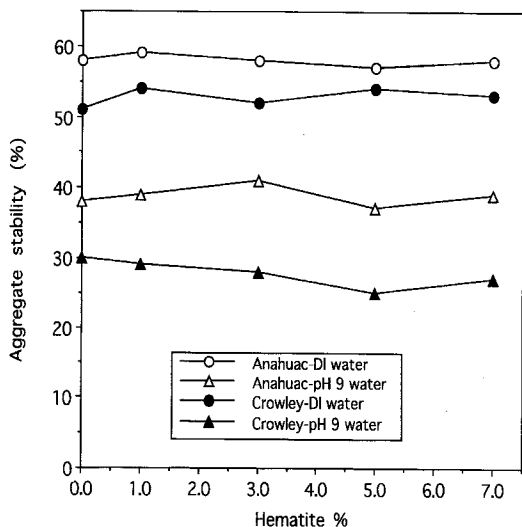


Fig. 2. Aggregate stability of Anahuac and Crowley soils treated with coarse hematite and incubated in distilled water or pH 9 NaOH solution.

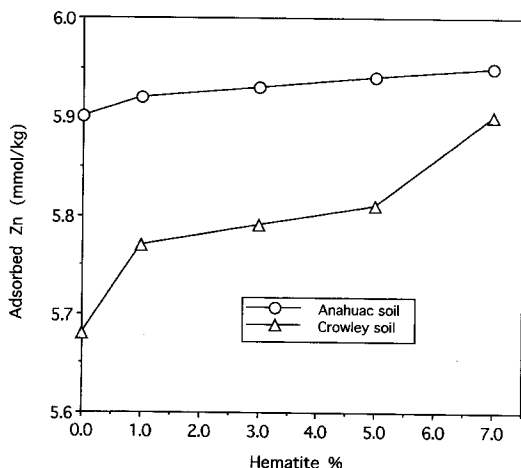


Fig. 3. Zinc (Zn) adsorption by Anahuac and Crowley soils treated with coarse hematite. Five grams of coarse hematite-soil mixtures and 30 ml of 1 mM of $ZnSO_4$ were used. All recorded pHs of solutions after equilibration were 5.80.

changed by hematite addition and amount of adsorbed P by both soils treated hematite was similar (Fig. 4). The pHs of equilibrated solutions for the phosphate adsorption test were 5.40.

DISCUSSION

Higher HC and AS of Anahuac soil than Crowley soil at same concentration of hematite may be due to its higher content of organic matter and lower SAR.

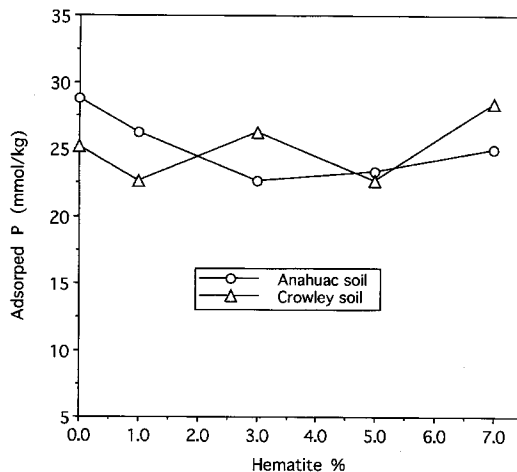


Fig. 4. Phosphate adsorption by Anahuac and Crowley soils treated with coarse hematite. Five grams of coarse hematite-soil mixtures and 30 ml of 500 ppm of phosphorus in 0.1 M KCl matrix solution were used. All recorded pHs of solutions after equilibration were 5.40.

Hydraulic conductivity and AS of a soil have positive relationship with its content of organic matter and negative relationship with its SAR (Perfect, Kay, 1990; Sumner, 1995). Aggregating effect of the added hematite increased the HC of the two soils at low concentration. However, the reduction of HC with greater than 3 % of hematite may be due to plugging macropores with excess hematite. The reduction of HC by plugging macropores may be greater than the aggregating effect of the added hematite at the high concentration. Observed red color of effluents suggests that a portion of the added hematite is mobile. Coarse hematite is less mobile in soils than fine hematite resulting in the higher HC. Lower HC and AS of the soil-hematite mixtures incubated in pH 9 NaOH solution than in distilled water may be due to higher pH and higher content of Na^+ from NaOH addition. The increased pH results in more negative charge of edge sites of clay minerals and surface of constant potential minerals (Sumner, 1995). The added Na^+ might increase dispersion of particles and swelling of clay minerals. No effect of the added hematite on AS of both soils conflicts with its aggregating effect indicated by the increased HC at low concentration of hematite. It might be related to severe shaking disrupting fragile aggregates during the AS test.

Pedogenic hematite is a well known sink for Zn and phosphate in soils (Schwertman, Taylor, 1989). However, the added hematite has a little impact on the adsorption of Zn and phosphate by the both soils. As indicated by Schwertman, Taylor (1989), pedo-

genic hematite has very small particle size and reactive. No significant impact of the added hematite on the adsorption may be due to its relatively large particle size which reduces its activity. Greater amount of adsorbed Zn by Anahuac soil than by Crowley soil may be due to the higher content of organic matter, providing more adsorption sites for Zn, of Anahuac soil.

CONCLUSION

Anahuac soil with higher content of organic matter and lower SAR had greater HC and AS than Crowley soil at same levels of hematite. Addition up to 3% hematite to the both soils increased HC but greater amounts of hematite reduced it. Both Anahuac and Crowley soils treated with coarse hematite had higher HC than the soils treated with fine hematite. Aggregate stability of the both soils was not influenced by addition of coarse hematite. The adsorption of Zn by the two soils increased slightly but the adsorption of phosphate was not influenced by the addition of hematite.

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적철석 첨가에 의한 사질양토의 물리·화학적 특성변화

김재곤 · Joe B. Dixon · 문희수

요 약 : 토양 적철석은 오염물질 및 영양분의 흡착과 미세한 입자들의 입단화 매개체로서 잘 알려져 있다. 미세하게 분말화 시킨 결정질 적철석을 두 사질 양토 (Anahuac and Crowley soils from the Southern Coastal Plain, USA)에 첨가하였을 때 나타나는 물리화학적 특성의 변화를 측정하였다. 적철석을 3% (무게비)까지 첨가하였을 때 토양의 투수율이 증가하였으나 그 이상 양을 첨가하였을 때 감소되었다. 토양의 입단안정도 (AS)는 적철석 첨가에 영향을 받지않았다. 같은 양의 적철석을 Anahuac soil과 Crowley soil에 첨가하였을 때 높은 유기물의 함량과 낮은 Na 흡착비 (SAR: sodium adsorption ratio)를 가진 Anahuac soil은 Crowley soil에 비해 상대적으로 높은 투수율과 입단안정도를 보여주었다. 두 토양 모두 Zn 흡착은 약간 증가하였으나 인산염 흡착은 영향을 받지않았다.