

FERRIHYDRITE AS A POTENTIAL IRON AMENDMENT IN CALCAREOUS SOILS

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ABSTRACT

A Series of laboratory and greenhouse experiment were conducted to evaluate ferrihydrite product and they effects on growth and some chemical composition of wheat plants. Results were noticed that, infrared examination indicated that decreasing level of silica gave a weak band at 860 Cm^{-1} particularly at 0.125. However higher silica content gave a lower degree of polymerization as indicating by a reduction in band intensity at 800cm^{-1} and enhancement at 760cm^{-1} . Micro structural views of ferrihydrite showed the best developed of the crystal particularly when Si / Fe ratio increased. Successive extraction of Fe with DTPA showed that, cumulative amounts of Fe extracted from the ferrihydrite products were ranged between 17.5 and 44.2% for Fe- 0.125 Si and Fe-1.0 Si respectively, indicating that poorly crystalline materials had a supplying power for Fe status particularly in calcareous soils. Application of Fe- 0.5 Si and Fe-1.0 Si to the soil stimulate the yield production (grain and straw) of wheat plant as compared with other treatments. Increasing levels of Fe from 25 to 100 mg/kg gradually increased the yield production. Ferrihydrite products added to the soil gave a remarkable effects on Fe and N uptake. Results also showed that, increasing ratio of Fe / Si had a positive effect for both Fe and N uptake as well as total content. Total chlorophyll content were gradually increased with ferrihydrite addition. It evident that poorly crystalline materials had a good scope of residual effects which seems to substantial the slow release properties of these was immobilized.

Keywords : Ferrihydrite, IR, TEM examination, wheat production, calcareous soil.

INTRODUCTION

Iron deficiency is still one of the major problems in calcareous soils, the dynamic of iron (Fe) in calcareous soils is largely controlled by the dissolution-precipitation equilibrium of more or less crystalline iron oxides (Lindsay, 1979; Schwertmann, 1991). These minerals are characterised by a poor solubility products that is decrease which increasing pH (Isabelle and Philippe, 2000). The total concentration of soluble Fe in solution is thus always far below the level required for adequate growth of crop species (Marschner, 1995), Unless pH is very low as occurs in the reducing conditions of waterlogged soils (Hinsinger, 1993). In calcareous soils, because of high pH, Fe concentrations in soil solution are very low and plants often develop severe symptoms of Fe chlorosis (Romheld, 1987; Marschner, 1995).

From the iron chemistry thermodynamics, it is well known that Fe compounds are very insoluble (Lindsay, 1988). The rate of this solubility depends on the specific surface of the solid (Schwertmann and Taylor, 1989). Amorphous materials dissolve very fast whereas crystalline materials are quite slow. These factors may act to mobilize labile Fe from soil phase Fe-containing compounds in the soil. The most readily available labile sources of

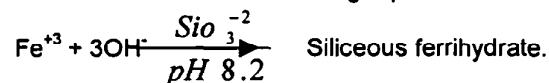
Fe are likely the poorly crystalline Fe oxides, i.e., ferrihydrite, which have high reactive surface areas. This was corroborated in the recent study by *Loeppert and Hallmark (1985)* in which a high negative correlation was observed between incidence of chlorosis and the amorphous Fe oxide content.

The objective of this study was to evaluate the effectiveness of ferrihydrite as fertilizer value particularly in calcareous soil and their effects on growth and some chemical composition of wheat plants.

MATERIALS AND METHODS

Properties and preparation of siliceous ferrihydrite:

The poorly crystalline Fe oxide was prepared by addition of NaOH to a Fe(III) salt as is summarized in the following equation :



The presence of silicate influences the poorly crystalline product to have smaller crystal sizes and a higher surface area (*Carlson and Schwertmann, 1980, and Vempati and Loeppert, 1985*). The rate of transformation of ferrihydrite to goethite is inversely related to silica content (*Schwertmann and Thalmann, 1976*). Ferrihydrite (Without any silica) transforms rapidly at room temperature and high pH into a crystalline phase, e.g., goethite, but it has been observed that in the presence of silicate the transformation of these materials is inhibited due to silicate anion sorption at the surfaces of the crystal nuclei and the retardation of crystal growth processes (*Vempati and Loeppert, 1985*). Therefore, in the soil it is likely that silicate anions in the ferrihydrite structure will inhibit the transformation to more crystalline phase and thus will enable the product to maintain the labile pool of Fe for subsequent crops.

The ferrihydrite samples were prepared at initial molar ratios of Si to Fe of 0.125, 0.25, 0.5 and 1.0 by the procedure described below. For simplicity, the ratios of siliceous ferrihydrite will be referred to as Fe-0.125 Si, Fe-0.25 Si, Fe-0.5 Si and Fe-1.0 Si, respectively. To a 100ml erlenmeyer flask containing 100 ml of water, 150ml of sodium silicate (concentration was dependent upon the desired Si: Fe ratio) was added simultaneously with 242 ml of 0.714M ferric sulfate under conditions of vigorous stirring. The pH was adjusted to 8.2 with NaOH, and the products were incubated for four days, then dialyzed to remove excess salt. The final concentration of Fe in the sample was adjusted to 4 gm per liter with deionized water. Samples for transmission electron microscopy (TEM) were prepared by diluting the aqueous suspension to 20mg Fe per liter with deionized water. One drop of the diluted suspension was placed on a 400-mesh Cu TEM grid with pur carbon as the support film. The samples were viewed with a Hitachi HVLLE TEM operated at 50KeV. Infrared spectrograms of the ferrihydrite treatments samples were recorded with a Backman IR-4250 spectrometer using KBr-pellets.

Two milliliter aliquots of each of the ferrihydrite (8 mg Fe) samples, in triplicate, were transferred to polypropylene test tubes and extracted successively for two hours (six times) with 20ml of 0.005M DTPA (diethylenetriamine-pentaacetic acid) according to the methods described by Black (1982).

Greenhouse experiment:

Pot experiment was conducted in the National Research Center and designed as randomized complete block with three replicates in plastic pots 40cm height, 25 cm diameter, each one containing 10kg of air dried soil. The investigated soil was characterized by pH 8.72, E.C. 0.36 ds.m⁻¹, CaCO₃ 11.3% organic matter 0.12%, total-N 0.012% available -Fe 5.3 ppm, clay 1.73%, silt 6.58% and sand 91.69%. Soil were treated with ferrous sulfate (Fe⁺²), ferric sulfate (Fe⁺³) and ferrihydrite with three doses 25, 50 and 100 mg Fe kg⁻¹. The investigated treatments were used as follows :

| Treatment | mg Fe kg ⁻¹ . | Treatment | mg Fe kg ⁻¹ . |
|------------------|--------------------------|------------|--------------------------|
| Control | | | |
| Fe ⁺² | 25 | Fe-0.25 Si | 25 |
| Fe ⁺² | 50 | Fe-0.25 Si | 50 |
| Fe ⁺² | 100 | Fe-0.25 Si | 100 |
| Fe ⁺³ | 25 | Fe-0.5 Si | 25 |
| Fe ⁺³ | 50 | Fe-0.5 Si | 50 |
| Fe ⁺³ | 100 | Fe-0.5 Si | 100 |
| Fe-0.125 Si | 25 | Fe-1.0 Si | 25 |
| Fe-0.125 Si | 50 | Fe-1.0 Si | 50 |
| Fe-0.125 Si | 100 | Fe-1.0 Si | 100 |

Nitrogen, phosphorous and potassium were applied at rates of 120mg N, 50mg P₂O₅ and 40mg k₂O/kg as slow release nitrogen fertilizer, superphosphate and potassium sulphate respectively. Wheat (*Triticum aestivum* L.C.V. Sakha 69) were planted, after 10 days the plants were thinned to six plants per pot. Plant samples were taken at 30,45 and 60 days from seedling. Fresh, dry weight, total chlorophyll, ferrous (Fe⁺²), nitrogen and iron were determine in plant as described by *Cottenie et al., (1982)* and *Black (1982)*.

At physiological maturity, plants were harvested and separated into straw and grains, dry weight were recorded, and biomass ground and prepared for analysis. Total-N and iron were determined in grain and straw by the method described by *Cotteni et al. (1982)*.

Soil samples were taken from each pot after harvesting and air dried. Fractionation of iron were carried out according to the method described by *Miller et al., (1986)* (Table 1). The extraction sequence procedure, were observed in Table (1). 10 gm of soil sample was placed in centrifuge tube and

20 ml of extracting solution was added, shaken for 16h and centrifuged. The remaining solid was washed twice with water and then the next extraction solution was added. Aliquots of extractants from steps 5 and 6 were evaporated to dryness, ashed and taken up in 1 M HNO₃ for analysis. The extraction solutions were filtered and the filtrates were analyzed. Each soil sample was taken entirely through to procedure in triplicate.

Table (1) : Extraction conditions for sequential extraction procedure used in determining Fe forms in soil (after Miller *et al.*, 1986)

| Extracting solution | | Conditions | |
|----------------------------|--|------------|---------------|
| | | Time h | Temp. °C |
| Water soluble exchangeable | 0.5 M Ca (NO ₃) ₂ . | 16 | 22 |
| Acid soluble | 0.44M CH ₃ COOH + 0.1M Ca(NO ₃) ₂ pH 5 | 8 | 22 |
| Associated with Mn oxides | 0.01M NH ₂ OH.HCl+ 0.1MHNO ₃ pH 2 | 0.5 | 22 |
| Organically bound | 0.1M K ₄ P ₂ O ₇ pH 10 | 24 | 22 |
| Amorphous oxides | Oxalate reagent | 0.5 | 80.water both |
| Crystalline oxides | Oxalate reagent + ascorbic acid | 0.5 | 80waterboth |
| Residual | 10mL HF+ HNO ₃ | 2 | 110 |

RESULTS AND DISCUSSION

Infrared spectroscopy:

Infrared examination in Fig. (1) showed that, in the presence of lowering silica concentration (Fe-0.125 Si) the ferrihydrites product has a higher degree of polymerization. However, higher silica content gave a lower degree of polymerization as indicating by reducing the band intensity at 800 and enhancement of 760 cm⁻¹ band.

It was observed that silica addition at rate of 0.5 Si gave the broad band at about 800 cm⁻¹, and increasing Si at rate of 1.0 the intensity of this band is doubled and its position is shifted to 760 cm⁻¹ i.e., the lower wave numbers. However decreasing the level of Si to 0.125, the band becomes weaker and is shifted to 860 cm⁻¹ i.e., to higher wave number Fig. (1). The shift towards lower wave numbers is therefore explained by Si bound to Fe-OH functional groups of the surface, thereby forming Si-O-Fe bonds i.e., to nonpolymerized silica (Wijnija and Schulthess, 2001).

The ferrihydrites preparation without Si does not show any band between $760\text{-}860\text{ cm}^{-1}$ (Fig. 1). In contrast, in all Si containing preparations, a band with a maximum at 860 cm^{-1} exists which intensifies approximately linearly with Si content. The broad I.R. band of the Si containing ferrihydrite can be attributed to Si-O stretching. A shift this band towards lower frequencies has been observed in Fe-Si ferrihydrite (Shuman, 1991) and interpreted as due to Si-O-Fe instead of Si-O-Si bonds in the structure.

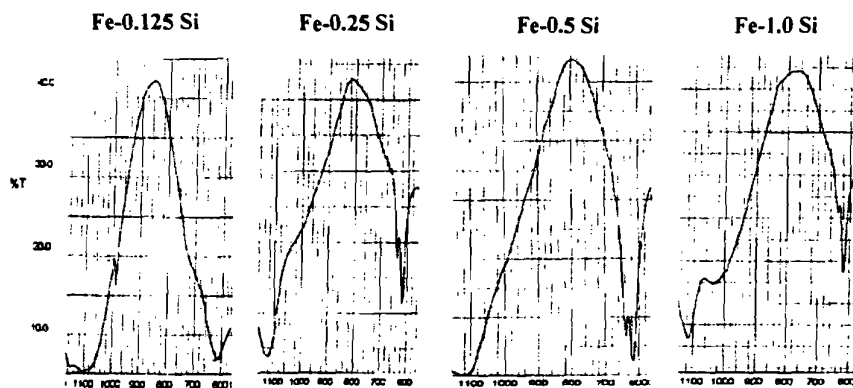


Fig. (1) : I.r. spectra of ferrihydrites containing increasing amounts of Si.

Transmission electron microscopy :

Micro-structural views of ferrihydrite in Fig. (2) observed a best developed crystal of ferrihydrite at increasing ratio of Si/Fe, very small spherical particles as well as small acicular crystals of ferrihydrite are formed. However decreasing ratio of Si/Fe gave a highly aggregated of ferrihydrite. This may be explained by the partial inaccessibility of the internal surface to formation the crystallization (Schwertmann and Cornell, 1991).

A negative linear correlation exists between the proportion of ferrihydrite and the silica content of the ferrihydrite mixture formed. High Si/Fe ratio (Fe-1.0 Si), less crystalline was formed which have rather rough surfaces. Minimizing aggregation mainly due to sorption of silicate anion at the surfaces of the crystal nuclei and the retardation of crystal growth processes (Vempati and Loeppert, 1985).

Serrated and shorter plates are formed at increasing Si/Fe ratios, decreasing the level of Si/Fe non serrated laths are formed and minimize with an increasing content of spherical of ferrihydrite. It is therefore believed that during the precipitation processes ferrihydrite were formed, first and then takes up most of the Si and thereby purified the solution. This concept is supported by the fact that at the higher initial of Si/Fe ratio, ferrihydrite crystals are formed because the maximum amount of ferrihydrite which can be formed obviously is high enough to purify the solution sufficiently.

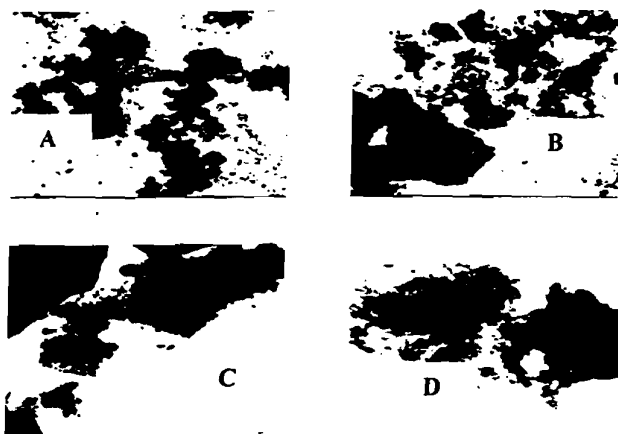


Fig. (2) : Electron micrographs of four ferrihydrites sample : A- Fe-1.0 Si, B-Fe-0.5 Si, C-Fe-0.25 Si and D-Fe- 0.125 Si

DTPA extraction :

Several successive extraction with DTPA were examined (Fig. 3) in order to evaluate the supplement value of the ferrihydrite product was slow release Fe- fertilizer particularly in calcareous soil. Results observed that during the first extraction the Fe-0.125 Si gave the lowest value of iron release as compared with other treatments. Increasing Fe/Si ratio enhanced the release of iron, this results may be due to the presence of silicate which influences on the poorly crystalline produce to have smaller crystal size and higher surface area (Carlson and Schwertmann, 1980 and Vempati and Loeppert, 1985).

The cumulative amount of Fe removed from the materials ranged from 17.5 for (Fe-0.125 Si) to 44.2% for (Fe-1.0 Si), indicating that, poorly crystalline materials had a good scope of residual effect, which seems to substantial the slow release properties of these materials.

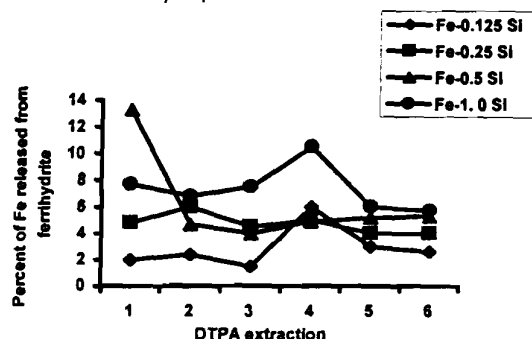


Fig. (3) : Quantity of Fe extracted during successive DTPA extractions of synthetic ferrihydrites

Plant growth :

Table (2) observed that the addition of ferrihydrite increased both fresh and dry weight of wheat plants at different stages of plant growth. The ameliorative effect of ferrihydrite depends on the level of Si/Fe ratios and the rate of Fe application. For Fe-1.0 Si was more effective as compared with other treatments. This result may be due to the solubilization of the amorphous ferric hydroxide or ferrihydrite which gave higher amounts of Fe in the soil solution than those caused by crystalline hydroxides (*Lindsay, 1979 and Perez-Sanz and Lucena, 1994*).

The addition of Fe⁺² or Fe⁺³ slightly improved fresh and dry weight of plant growth as compared with the control. While the application of low level of Fe from Fe-0.25 Si was more pronounced effect on fresh and dry weight of wheat plants than high level of Fe from Fe⁺² or Fe⁺³ respectively. This result may be related to a possible contribution of some other mechanisms for the mobilization of Fe ions from ferrihydrite which can regulate the Fe status in the soil, when excreted at large rate in the rhizosphere, these organic anions can dissolve substantial amount of Fe from Fe-bearing solid phases and eventually supply thereby enough Fe to meet plant's demand, at least when Fe is supplied as an amorphous Fe phase (*Jones et al., 1996 ; Isabelle and Philippe, 2000*).

Grain and Straw yield :

Data in table (2) show that the addition of Fe treatments increased grain and straw yield as compared with control. However the application of Fe⁺² and Fe⁺³ does not effective as compared with Fe/Si at different ratios. This could be due to the sorption mechanisms particularly in calcareous soil which characterized by high both of pH and CaCO₃ %.

The addition of Fe-0.5 Si and Fe-1.0 Si stimulate the yield production for both grain and straw yield as compared with Fe-0.125 Si and Fe-0.25 Si. Increasing the levels of Fe from 25 to 100 mg Fe kg⁻¹ gradually increased the grain and straw yield production of wheat plants.

It was observed that the addition of Fe⁺³ were more pronounced effect on the grain and straw yield of wheat plants as compared with Fe⁺². This results may be related to the Fe⁺² reaction with calcium carbonate to form lepidocrocite and goethite, whereas Fe⁺³ polymerizes in solution to form a poorly crystalline phase (ferrihydrite), seems to substantial the slow release properties of these and also to avoid the precipitated of the soluble fraction of Fe in soil- water system (*Loeppert and Hossner, 1984*).

Table (2) shows that grain/ straw ratio could be affected by the ferrihydrite and the level of Fe addition. It has been noticed that Fe treated with silica was markedly increased grain/ straw ratio as compared with other treatments. Increasing levels of Fe increased the grain/straw ratio of wheat plants. Therefore data in grain/ straw ratio confirmed that the forms of poorly crystalline Fe oxide i.e., ferrihydrite, which have high reactive surface areas.

Table (2) : Effect of ferrihydrite on fresh, dry weight and total yield of wheat plant growing in calcareous soil (gm/plant)

| Treatment | Fe level mg Fe kg ⁻¹ | Fresh weight | | | Dry weight | | | Grain yield g/plant | Straw yield g/ plant | Grain/ straw ratio |
|------------------|---------------------------------------|--------------|-------|-------|------------|------|-------|---------------------------|----------------------------|--------------------------|
| | | 30 | 45 | 60 | 30 | 45 | 60 | | | |
| Control | | 6.30 | 10.40 | 15.22 | 1.91 | 4.31 | 6.32 | 1.41 | 6.32 | 0.22 |
| Fe ⁺² | 25 | 6.92 | 11.03 | 17.34 | 2.0 | 4.62 | 6.90 | 2.53 | 8.13 | 0.311 |
| Fe ⁺² | 50 | 7.03 | 12.60 | 17.66 | 2.22 | 4.90 | 6.92 | 2.86 | 8.72 | 0.32 |
| Fe ⁺² | 100 | 7.15 | 12.65 | 18.20 | 2.31 | 4.95 | 6.99 | 3.0 | 9.0 | 0.33 |
| Fe ⁺³ | 25 | 7.0 | 12.13 | 17.96 | 2.0 | 4.90 | 6.96 | 3.03 | 9.16 | 0.33 |
| Fe ⁺³ | 50 | 7.33 | 12.90 | 18.53 | 2.42 | 4.93 | 7.12 | 3.42 | 9.83 | 0.34 |
| Fe ⁺³ | 100 | 7.92 | 13.40 | 18.92 | 2.66 | 5.0 | 7.52 | 3.86 | 10.12 | 0.38 |
| Fe-0.125 Si | 25 | 7.56 | 14.16 | 20.15 | 2.35 | 5.50 | 8.36 | 4.76 | 12.56 | 0.37 |
| Fe-0.125 Si | 50 | 8.12 | 14.35 | 21.23 | 3.02 | 5.66 | 8.45 | 4.94 | 13.03 | 0.37 |
| Fe-0.125 Si | 100 | 8.64 | 15.28 | 22.24 | 3.14 | 5.91 | 8.93 | 5.29 | 13.91 | 0.38 |
| Fe-0.25 Si | 25 | 8.29 | 15.31 | 22.20 | 3.0 | 5.34 | 8.66 | 4.92 | 14.42 | 0.34 |
| Fe-0.25 Si | 50 | 8.75 | 16.72 | 23.07 | 3.22 | 6.12 | 9.01 | 5.49 | 14.93 | 0.36 |
| Fe-0.25 Si | 100 | 9.03 | 16.93 | 24.81 | 3.60 | 6.72 | 9.32 | 5.76 | 15.23 | 0.37 |
| Fe-0.5 Si | 25 | 9.10 | 16.82 | 23.52 | 3.62 | 6.55 | 8.91 | 5.31 | 16.63 | 0.31 |
| Fe-0.5 Si | 50 | 9.34 | 17.64 | 24.61 | 3.71 | 6.93 | 9.22 | 5.86 | 17.18 | 0.34 |
| Fe-0.5 Si | 100 | 10.50 | 18.30 | 25.90 | 4.11 | 7.06 | 9.96 | 5.93 | 17.86 | 0.33 |
| Fe-1.0 Si | 25 | 10.0 | 18.21 | 24.82 | 3.90 | 7.0 | 9.35 | 6.10 | 19.13 | 0.31 |
| Fe-1.0 Si | 50 | 10.61 | 18.90 | 26.32 | 4.26 | 7.21 | 10.31 | 6.67 | 19.68 | 0.33 |
| Fe-1.0 Si | 100 | 11.03 | 19.65 | 26.93 | 4.43 | 7.82 | 10.46 | 6.92 | 20.23 | 0.34 |

Nutrient uptake :

a-N and Fe uptake at different stages of plant growth :

Data in table (3) showed that the addition of ferric sulfate increased the uptake of N and Fe than ferrous sulfate. Whereas different ratios of Fe/Si enhanced the N and Fe uptake by wheat plant as compared with Fe⁺² or Fe⁺³ treated soil. This result may be due to forms and crystallinity of the precipitated Fe oxide.

It was noticed that the addition of Fe-0.5 Si and Fe-1.0 Si were more pronounced effect on the uptake of N and Fe of wheat plants than the other treatments. Increasing the levels of Fe up to 100 mg kg⁻¹ increased the uptake of N and Fe of wheat plants. the addition of Fe-1.0 Si at a rate of 100 mg kg⁻¹ gave a remarkable effect on N and Fe as compared with other treatments. This result can be explained by the interactions of nitrogen with iron through changes in pH. When ammonium nitrogen is absorbed, plants release protons causing the growth medium to become more acid and iron availability is increased (Marscher *et al.*, 1982).

Table (3) : Nitrogen and iron uptake (mg/plant) as affected by the addition of ferrihydrite to wheat plant at different stages of plant growth.

| Treatment | Fe level mg Fe kg ⁻¹ | N mg/plant | | | Fe mg/plant | | |
|------------------|------------------------------------|------------|-------|--------|-------------|-------|-------|
| | | 30 | 45 | 60 | 30 | 45 | 60 |
| Control | | 14.29 | 43.1 | 56.88 | 0.19 | 0.43 | 0.63 |
| Fe ⁺² | 25 | 21.8 | 51.74 | 77.97 | 0.40 | 0.92 | 4.14 |
| Fe ⁺² | 50 | 24.42 | 55.37 | 78.88 | 0.66 | 3.43 | 5.53 |
| Fe ⁺² | 100 | 25.87 | 56.43 | 80.38 | 0.69 | 4.45 | 6.99 |
| Fe ⁺³ | 25 | 23.0 | 56.84 | 81.43 | 0.80 | 3.92 | 5.56 |
| Fe ⁺³ | 50 | 28.79 | 59.16 | 92.56 | 1.21 | 4.43 | 6.40 |
| Fe ⁺³ | 100 | 31.92 | 62.5 | 99.26 | 1.59 | 5.0 | 8.27 |
| Fe-0.125 Si | 25 | 28.67 | 68.2 | 105.3 | 1.17 | 4.95 | 7.52 |
| Fe-0.125 Si | 50 | 37.75 | 71.88 | 109.0 | 1.81 | 5.66 | 9.29 |
| Fe-0.125 Si | 100 | 39.87 | 74.49 | 116.0 | 2.19 | 6.37 | 10.72 |
| Fe-0.25 Si | 25 | 38.7 | 70.59 | 114.31 | 1.80 | 5.34 | 9.52 |
| Fe-0.25 Si | 50 | 40.89 | 80.17 | 119.8 | 2.25 | 7.95 | 10.81 |
| Fe-0.25 Si | 100 | 46.8 | 89.37 | 125.8 | 2.88 | 10.08 | 12.11 |
| Fe-0.5 Si | 25 | 47.78 | 87.77 | 121.7 | 2.53 | 9.17 | 10.69 |
| Fe-0.5 Si | 50 | 49.34 | 94.24 | 128.1 | 2.96 | 11.08 | 11.98 |
| Fe-0.5 Si | 100 | 55.07 | 97.42 | 139.4 | 3.69 | 12.00 | 13.94 |
| Fe-1.0 Si | 25 | 52.65 | 95.9 | 129.9 | 3.12 | 11.2 | 12.15 |
| Fe-1.0 Si | 50 | 57.93 | 99.49 | 146.4 | 3.82 | 12.97 | 14.43 |
| Fe-1.0 Si | 100 | 60.24 | 108.6 | 156.9 | 5.44 | 14.85 | 15.69 |

b-N and Fe content in grain and straw :

Table (4) noticed that the addition of ferrihydrite at different ratios of silica gave a remarkable effect on N and Fe content in grain and straw. Whereas increasing the ratio of silicate were more pronounced effect on N and particularly Fe content in grain and straw of wheat plant. This result may be probably due to, most soluble fraction of iron was depleted to some extent only in the rhizosphere, caused an increase systematically through mobilizing Fe from ferrihydrite and not only dissolved amorphous Fe but also some Fe from the ferrihydrite it self (Schwertmann, 1991). Results showed that increasing the rate of Fe increased the content N and Fe grain and straw. The percentage of increasing in Fe for both grain and straw at 100 mg kg⁻¹ of Fe-1.0 Si and Fe-0.5 Si were 14.26, 10.34 and 11.34, 15.05% as compared with the same treatments at a rate of 25 mg kg⁻¹. Whereas the percentage of increasing Fe in Fe-1.0 Si and Fe- 0.5 Si at a rate of 25 mg kg⁻¹ were 52.11, 49.4 and 42.91, 36.19% as compared with Fe-0.125 Si at the same rate.

There is a relationship between Fe and N, data observed that increasing ratios of Fe/Si the N uptake increased. While increasing levels of Fe enhanced the nitrogen content in both grain and straw of wheat plant. Similar result were observed by (Kafkafi and Ruth, 1985).

Table (4) : Nitrogen and iron uptake (mg/plant) in grain and straw of wheat plant as affected by of ferrihydrite treated soil

| Treatment | Fe level mg Fe kg ⁻¹ | Grain | | Straw | |
|------------------|---------------------------------|-------|-------|-------|------|
| | | N | Fe | N | Fe |
| Control | | 26.79 | 2.36 | 31.6 | 0.92 |
| Fe ⁺² | 25 | 53.88 | 3.15 | 36.09 | 1.03 |
| Fe ⁺² | 50 | 61.20 | 3.63 | 38.04 | 1.52 |
| Fe ⁺² | 100 | 64.5 | 3.94 | 39.8 | 1.93 |
| Fe ⁺³ | 25 | 65.75 | 3.78 | 40.7 | 1.67 |
| Fe ⁺³ | 50 | 78.66 | 5.31 | 42.6 | 1.78 |
| Fe ⁺³ | 100 | 89.55 | 5.62 | 45.96 | 2.65 |
| Fe-0.125 Si | 25 | 107.5 | 5.44 | 56.9 | 3.42 |
| Fe-0.125 Si | 50 | 113.1 | 6.81 | 62.7 | 3.85 |
| Fe-0.125 Si | 100 | 121.4 | 6.96 | 66.0 | 3.91 |
| Fe-0.25 Si | 25 | 114.1 | 7.24 | 70.1 | 4.06 |
| Fe-0.25 Si | 50 | 127.9 | 8.32 | 76.3 | 4.62 |
| Fe-0.25 Si | 100 | 135.3 | 9.01 | 80.7 | 4.91 |
| Fe-0.5 Si | 25 | 125.3 | 9.53 | 81.3 | 5.36 |
| Fe-0.5 Si | 50 | 140.0 | 10.2 | 86.2 | 5.91 |
| Fe-0.5 Si | 100 | 142.3 | 10.75 | 88.6 | 6.31 |
| Fe-1.0 Si | 25 | 145.7 | 11.36 | 91.7 | 6.76 |
| Fe-1.0 Si | 50 | 161.4 | 12.17 | 93.4 | 7.09 |
| Fe-1.0 Si | 100 | 173.0 | 13.25 | 98.6 | 7.54 |

Total chlorophyll and ferrous content :

a-Total chlorophyll content :

Chlorophyll content as a measure of Fe-stress in plants is presented in table (5). It was noticed that the addition of ferrihydrite with different ratios of silica increased the total chlorophyll as compared with ferrous and or ferric treated soil. The addition of Fe-1.0 Si enhanced the chlorophyll content in wheat plants at different stages of plant growth. This phenomena may be due to the formation of poorly crystalline product to have smaller crystal size and higher surface area maintaining Fe in available forms as observed in Fig. (2) (Carlson and Schwertmann, 1980 ; Vempati and Loeppertk, 1985)

It was observed that increasing the rate of ferric sulfate from 25 to 100 mg kg⁻¹ increased the total chlorophyll. Whereas the application of Fe⁺² treatments did not alleviate the Fe stress. The addition of Fe-0.125 Si and Fe-0.25 Si treatments were more effective for mitigating chlorosis at different stages of plant growth. Whereas the addition of Fe-0.5 Si and Fe-1.0 Si were more pronounced effect on the total chlorophyll.

It was concluded that Fe supplying ability of the treatments particularly at a rate of 100mg Fe/kg decreased in the following order : ferrihydrite (1.0 Si) > ferrihydrite (0.5 Si) > ferrihydrite (0.25 Si) > ferrihydrite (0.125 Si) > Fe⁺³ > Fe⁺².

b-Ferrous content :

Concerning ferrous leaves content, the results in table (5), observed that the addition of ferrihydrite with different ratios of silicate had a positive effect on ferrous content in leaves of wheat plants at different stages of plant growth. The effect of silicate were capable to forms smaller crystal sizes with ferric sulfate which retardation the transformation of ferrihydrite to goethite, and was more effective in the availability of ferrous to the grown plant (Sidhu et al., 1981, Schwertmann and Cornell, 1991; Ionoue et al., 1993).

With respect to the levels of silicate, it was observed that increasing the levels of silicate had matching amelorative effect in ferrous leaves content. However decreasing the levels of Fe mg kg⁻¹ decreased the ferrous content in the leaves of plant at 30, 45 and 60 days. Results also observed that there is a good relation between the chlorophyll content and the ferrous content in the plant tissue as noticed in table (5).

It may be concluded that the application of ferrihydrite had a positive effect for maintaining Fe in an active form as Fe⁺² in leaves of the wheat plants and furthermore, on the of chlorophyll content to an extent of healthy plants. The ability to overcome the adverse effects of high pH particularly in calcareous soil and other ions and then correcting iron chlorosis.

Table (5): Total chlorophyll and ferrous content (mg/plant) as affected by ferrihydrite to wheat plant at 30, 45 and 60 days of transplanting

| Treatment | Fe level mg Fe kg ⁻¹ | Total chlorophyll mg/g F.W | | | Fe ⁺² mg/plant | | |
|------------------|---------------------------------|----------------------------|------|------|---------------------------|------|------|
| | | 30 | 45 | 60 | 30 | 45 | 60 |
| Control | | 0.55 | 0.32 | 0.26 | 0.20 | 0.18 | 0.15 |
| Fe ⁺² | 25 | 0.75 | 0.96 | 0.99 | 0.22 | 0.35 | 0.37 |
| Fe ⁺² | 50 | 0.77 | 0.96 | 1.0 | 0.25 | 0.36 | 0.37 |
| Fe ⁺² | 100 | 0.80 | 0.97 | 1.0 | 0.26 | 0.37 | 0.39 |
| Fe ⁺³ | 25 | 0.75 | 1.0 | 1.2 | 0.25 | 0.37 | 0.39 |
| Fe ⁺³ | 50 | 0.92 | 0.99 | 1.3 | 0.28 | 0.39 | 0.40 |
| Fe ⁺³ | 100 | 0.92 | 1.2 | 1.5 | 0.29 | 0.40 | 0.41 |
| Fe-0.125 Si | 25 | 0.79 | 1.2 | 1.35 | 0.25 | 0.38 | 0.4 |
| Fe-0.125 Si | 50 | 0.82 | 1.25 | 1.37 | 0.30 | 0.40 | 0.40 |
| Fe-0.125 Si | 100 | 0.98 | 1.32 | 1.39 | 0.32 | 0.42 | 0.45 |
| Fe-0.25 Si | 25 | 0.79 | 1.31 | 1.36 | 0.28 | 0.39 | 0.42 |
| Fe-0.25 Si | 50 | 1.02 | 1.33 | 1.42 | 0.33 | 0.42 | 0.43 |
| Fe-0.25 Si | 100 | 1.25 | 1.39 | 1.48 | 0.35 | 0.46 | 0.48 |
| Fe-0.5 Si | 25 | 0.96 | 1.45 | 1.50 | 0.31 | 0.43 | 0.45 |
| Fe-0.5 Si | 50 | 1.18 | 1.52 | 1.67 | 0.37 | 0.46 | 0.49 |
| Fe-0.5 Si | 100 | 2.06 | 1.46 | 2.19 | 0.46 | 0.50 | 0.52 |
| Fe-1.0 Si | 25 | 1.28 | 1.46 | 1.53 | 0.39 | 0.48 | 0.49 |
| Fe-1.0 Si | 50 | 1.69 | 2.02 | 2.35 | 0.41 | 0.44 | 0.53 |
| Fe-1.0 Si | 100 | 2.15 | 2.46 | 2.73 | 0.52 | 0.55 | 0.59 |

Fractionation of Fe in soil :

Sequential extraction of Fe are presented in table (6), were allowed to distinguish seven fraction of Fe, which differ in mobility and plant availability. The most available forms of Fe in soils are the water soluble and exchangeable fraction (*Shuman, 1991*). This fraction contains Fe which is loosely held by surface associations and therefore is the most mobile. Water extractable fraction is very low in all treatment and does not exceed $1.0 \text{ mg Fe kg}^{-1}$ soil. The largest amounts of the most mobile Fe forms were observed in Fe-1.0 Si 1.6 mg Fe/kg . Existence of such low amounts of plant available Fe is related to high pH and CaCO_3 . (*Olomu et al., 1973*).

In the second extracting step acid soluble Fe was determined through removing adsorbed and weakly bound of Fe, in calcareous soils only small amount of Fe is associated with carbonates. Fe concentration in this fraction is very low due to buffering capacity of the calcareous soil and ranged between 1.2 and 10.5 mg kg^{-1} soil.

Fraction-3 contains Fe bound to manganese oxides. The content of Fe associated with manganese oxides was low and did not exceed 59.4 mg kg^{-1} soil. Thus, this fraction, together with the previous two fractions, generally found to represent minor pool of the total metal concentration of the calcareous soil.

Substantial amounts of iron were found in the organically-bound fraction (Fe-4) was determined by extraction with a complexing agent (e.g., potassium pyrophosphate at 0.1 M concentration). The amounts of Fe associated with organically bound were in the range between 102.3 and 315.1 mg kg^{-1} soil. These data are in agreement with (*Shuman, 1991*).

Soil extractable fraction of Fe was predominantly present in the amorphous Fe oxide fraction (Fraction- 5). The amount of Fe in this fraction were ranged between 159.6 and $490.3 \text{ mg Fe kg}^{-1}$ soil. Amorphous Fe oxide; ferrihydrite and poorly- crystalline Fe phases have been identified as compounds that affect Fe solubility in near neutral, well aerated soils (*Schwertmann and Taylor, 1977, loeppert and Halmark, 1985*).

The crystalline Fe oxide fraction is smaller as compared to amorphous Fe oxides (table. 6). This phenomenon well explained by *schwertmann and Taylor (1977)*, they reported that soil organic and particularly humic substances may interact with surface bound Fe and this process could inhibit the formation of crystalline Fe-oxides in favour of amorphous Fe-oxides ferrihydrite. Also soil properties can play an important role for immobilization the Fe, under such condition with high pH and CaCO_3 content, iron is immobilized in form of hydroxide or hydrated oxides. It is believed that pH and CaCO_3 may be responsible for inhibit with formation of crystalline particularly in calcareous soil than organic matter effect. Since organic matter in our calcareous soil is quite low.

Iron held within silicate mineral structures, was extracted in the final step using an HF based method. The amounts of Fe that is fixed in the crystal lattice of minerals. This is in agreement with the result of (*Shumon, 1991*).

Inspite of the total content of Fe is quite abundant, the mobile fraction is low due to the specific properties of calcareous soil. Data also observed that amorphous and poorly crystalline of Fe phase influence the quantity of

plant available Fe (Geiger and Loeppert, 1986). The plant available Fe was correlated with the organic fraction (Loeppert and Halmark, 1985).

Table (6) : Effect of ferrihydrite on iron fraction (ppm) in calcareous soil after harresting of wheat plant

| Treatment | Fe level mg Fe kg ⁻¹ | Fe-1 (sol + exch) | Fe-2 (acid sol.) | Fe-3 (Mn- assoc.) | Fe-4 (OM- bound) | Fe-5 (amorph) | Fe-6 (Cryst) | Fe-7 (Resid.) |
|------------------|---------------------------------------|-------------------------|------------------------|-------------------------|------------------------|------------------|-----------------|------------------|
| Control | | 0.25 | 1.2 | 18.6 | 102.3 | 69.6 | 25.4 | 256 |
| Fe ⁺² | 25 | 0.30 | 2.4 | 20.4 | 110.0 | 156.2 | 40.1 | 348 |
| Fe ⁺² | 50 | 0.32 | 2.6 | 23.6 | 115.6 | 169.3 | 45.6 | 362 |
| Fe ⁺² | 100 | 0.33 | 3.5 | 26.8 | 120.0 | 201.4 | 48.1 | 396 |
| Fe ⁺³ | 25 | 0.32 | 2.4 | 25.2 | 135.6 | 222.9 | 46.1 | 418 |
| Fe ⁺³ | 50 | 0.34 | 2.9 | 29.3 | 142.8 | 243.5 | 49.3 | 426 |
| Fe ⁺³ | 100 | 0.35 | 3.9 | 35.2 | 150.9 | 269.7 | 52.7 | 435 |
| Fe-0.125 Si | 25 | 0.65 | 3.0 | 30.4 | 190.4 | 290.8 | 50.3 | 452 |
| Fe-0.125 Si | 50 | 0.69 | 3.6 | 36.7 | 220.6 | 310.1 | 59.4 | 466 |
| Fe-0.125 Si | 100 | 0.78 | 4.8 | 38.9 | 233.2 | 326.2 | 63.8 | 488 |
| Fe-0.25 Si | 25 | 0.70 | 4.0 | 37.3 | 242.4 | 352.1 | 61.2 | 474 |
| Fe-0.25 Si | 50 | 0.83 | 5.6 | 40.6 | 253.8 | 366.4 | 66.3 | 500 |
| Fe-0.25 Si | 100 | 0.95 | 6.7 | 45.4 | 260.9 | 384.8 | 72.9 | 525 |
| Fe-0.5 Si | 25 | 0.81 | 6.2 | 43.4 | 272.1 | 405.6 | 79.3 | 536 |
| Fe-0.5 Si | 50 | 0.46 | 6.9 | 48.9 | 279.6 | 435.8 | 52.1 | 566 |
| Fe-0.5 Si | 100 | 1.1 | 7.3 | 57.6 | 283.4 | 454.6 | 88.5 | 572 |
| Fe-1.0 Si | 25 | 0.94 | 7.1 | 50.1 | 246.7 | 466.3 | 40.3 | 589 |
| Fe-1.0 Si | 50 | 1.3 | 8.2 | 54.2 | 305.8 | 481.2 | 43.4 | 591 |
| Fe-1.0 Si | 100 | 1.6 | 10.5 | 54.4 | 315.1 | 490.3 | 96.7 | 612 |

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مركبات الـ Ferrihydrite كمحسن غذائي لتيسير عنصر الحديد فى الأراضى الجيرية

هشام إبراهيم العيلة

قسم تغذية النبات - المركز القومى للبحوث - الدقى - جيزة - مصر

- أقيمت عدة تجارب معملية و زراعية لتقييم مركب الفرى هيدرايت (ferrihydrite) تحت مستويات مختلفة من السليكا مع كبريتات الحديدك واثر ذلك على تكوين بلورات أكاسيد الحديد، النمو، المحصول والتركييب الكيماوى لنبات القمح المنزرع فى أرض جيرية حيث أظهرت النتائج ما يلى :
- أوضحت دراسة الأشعة تحت الحمراء (I.R) إلى ما يأتى :
 - أدى انخفاض مستوى السليكا (0.125) إلى تغيير طول الموجة للروابط بين السليكا والحديد (Si-O-Fe) لتأخذ مساحة أكبر 860 سم⁻¹ مما أدى إلى ضعف الروابط بين السليكا والحديد فى حين ارتفاع مستويات السليكا أظهر انخفاضاً ملحوظاً فى مساحة الروابط بين مجاميع السليكا والحديد Si-O-Fe لتقل من 860 إلى 800 إلى 760 سم⁻¹ مما يدل على انخفاض درجة البلورة لمركب الفرى هيدرايت وتكوين بلورات صغيرة الحجم ذات سطح نوعى كبير .
 - كما أظهرت الدراسة بالميكروسكوب الالكترونى أن زيادة نسبة السليكا/ الحديد أدت إلى حدوث أفضل نمو للورى جيد لبلورات الفرى هيدرايت (ferrihydrite) التى أخذت شكل بلورات صغيرة الحجم شبه دائرية .
 - أدى الاستخلاص المتتابع (successive extraction) لمركبات الـ ferrihydrite بواسطة الـ DTPA إلى انخفاض كمية الحديد المستخلصة إلى 17.5% مع (Fe-0.125 Si) بينما زادت كمية الحديد المستخلصة إلى 44.2% مع (Fe-1.0 Si) مما يشير إلى زيادة التأثير المتبقى لعنصر الحديد فى مركب الـ ferrihydrite .
 - أدت إضافة (Fe-0.5 Si)، (Fe-1.0 Si) إلى زيادة كل من محصول الحبوب والقش لنبات القمح مقارنة بإضافة (Fe-0.25 Si)، (Fe-0.125 Si) .
 - تشير النتائج إلى أن إضافة مركب الـ ferrihydrite بنسب مختلفة من السليكا أدت إلى زيادة كل من الحديد والنيتروجين خلال فترات نمو النبات المختلفة وكذلك فى الحبوب والقش أيضاً .
 - أدت زيادة مستوى الحديد من 25-100 ملليجرام/ كجم تربة إلى زيادة الكلوروفيل والحديدوز فى الأوراق خلال فترات نمو النبات المختلفة (30، 45، 60 يوم) .
 - كما تشير النتائج إلى أن أعلى قيمة للحديد المستخلص فى الأراضى الجيرية فى نهاية التجربة كانت على صورة أكاسيد حديد متبلورة أو مثبتة فى معادن السليكا .
 - أظهرت النتائج أن إضافة مركبات الـ ferrihydrite أدت إلى زيادة تيسر عنصر الحديد فى الأراضى الجيرية مما يعطى قيمة لهذا المخلوق كسماد بطى لعنصر الحديد .