III : RESULTS AND DISCUSSION

1 : GREENHOUSE AND LABORATORY EXPERIMENTS ON IRON NUTRITION AND MOVEMENT IN SOIL

A : GREENHOUSE EXPERIMENT

This study was conducted to investigate the effects of P fertilizers on availability of applied inorganic Fe sources to sorghum plants in a greenhouse experiment. The Fe sources [$FeSO_4$ and $Fe_2(SO_4)_3$] were applied at rates of 0, 25, and 50 mg Fe kg^{-1}. The P fertilizers (UP 10-30-0, UPS 10-30-0-7S, DAP, and MCP) were applied at rates of 0 and 50 mg P kg^{-1} soil. Sorghum plants were grown in pots for two successive crops to determine residual effects.

PLANTS

Yield:

The influence of Fe applied alone and with P fertilizers on dry matter yield of first and second crop sorghum is shown in Fig. 1 and Table 1A. The statistical comparisons of the means are shown in the Appendix (Table 1A). Yield of first crop increased linearly with application of $FeSO_4$ up to the highest rate applied (50 ppm Fe). The dry matter yield increased even more with addition of P fertilizers with $FeSO_4$. This result is in agreement with that of Mortvedt and Giordano (1971), that $FeSO_4$ and $Fe_2(SO_4)_3$ were effective at much lower application rates if applied with fluid polyphosphate fertilizers. The results also agreed with Mortvedt and Kelsoe, (1988) who found that sorghum yields and Fe uptake were increased with band application of $FeS0_4$ alone or with the following commerical fertilizers (10-30-0, 10-30-0-7S, and TCP). They stated that the commerical fertilizers used contained iron impurities. The P fertilizers applied with $FeS0_4$ generally increased dry matter yield in the following order : MCP> 10-30-0-7S> DAP> 10-30-0.The sharp decrease in yield when MCP was applied with 50 ppm Fe (compared with 25 ppm Fe) may be attributed to a coprecipitation between soluble ions of Fe and $H_2PO_4^-$ which would be enhanced by increased Fe^{3+} activity as a result of adding more Fe (50 ppm) which in turn would affect P availability. Part of the beneficial effect of P fertilizers may be due to their acidity which would increase Fe availability. This interpretation is corroborated by the DTPA extractable Fe data taken after first crop which is discussed later.

Regarding the $Fe_2(S0_4)_3$ source (Fig. 1B), sorghum dry matter yield tended to increase somewhat with the rate of Fe added, although significantly only in some cases. However, the ferric source was inferior to the ferrous source.

The residual effect of Fe on yield was determined in a subsequent second crop planted in the same rows of the first crop. Dry matter yields were considerably lower than in the first crop for both Fe sources, however, they still tended to increase with applied Fe and P fertilizers (Fig. 1C &D). The reduced yield of the subsequent crop is more than can be attributed to the lower number of plants per pot (6 in 1st crop and 4 in 2nd crop due to poor stand); therefore, depletion of Fe must have been a factor. In the subsequent crop, as in the first crop, the ferric source again was inferior to the ferrous source.

Plant materials were chemically analyzed to determine concentration and uptake of Fe, Mn, and Zn..

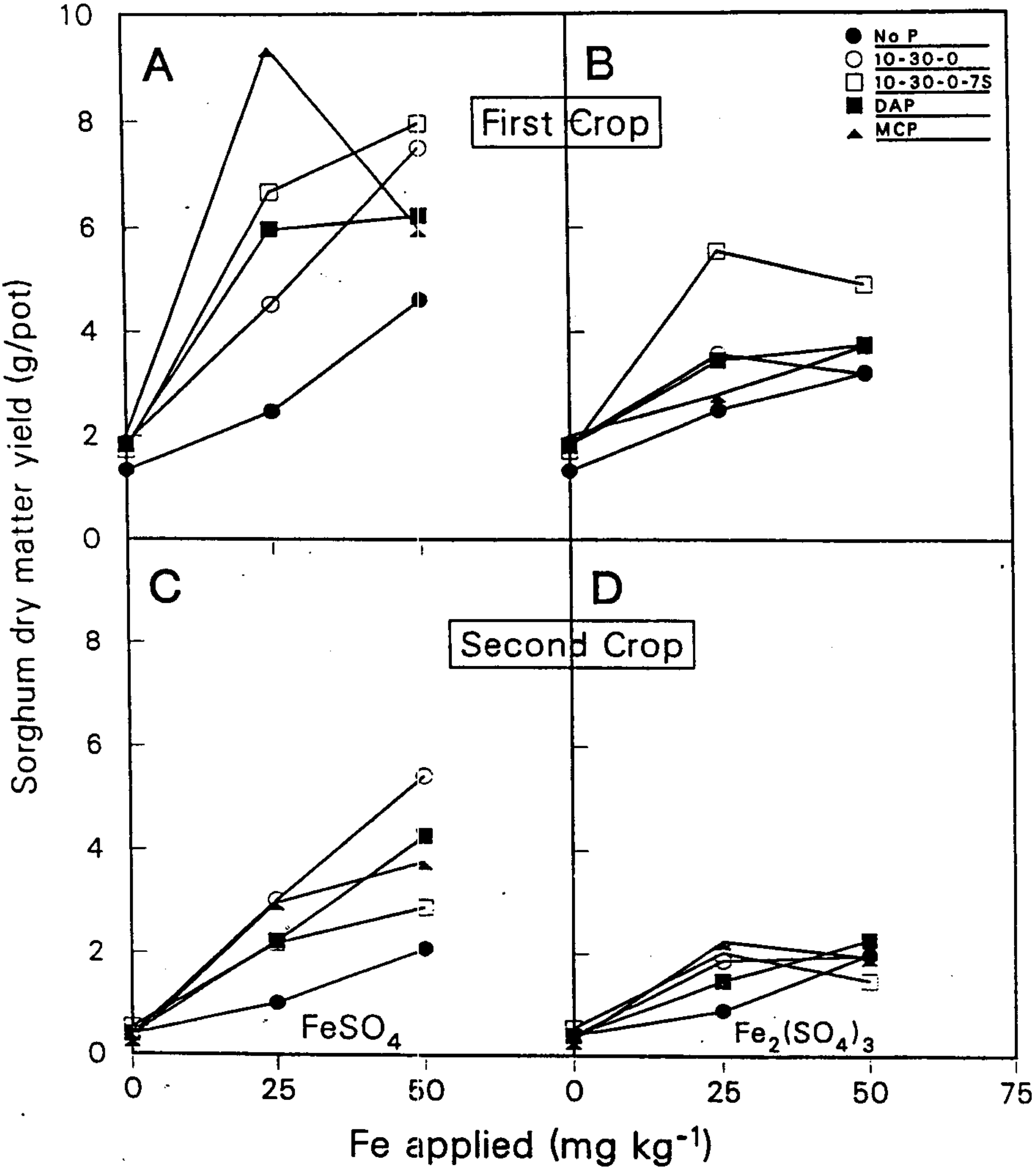

Fig. 1. Dry matter yield of first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

Iron :

The Fe concentration in the first crop tended to increase by applying $FeSO_4$ or $Fe_2(SO_4)_3$ alone or with P fertilizers. The increase was higher with 50 ppm Fe as $FeSO_4$ (Fig. 2 A,B and Table 2A). The Fe concentration showed little response in the second crop (Fig. 2 C,D).

The Fe uptake by first crop was increased when both Fe sources, (especially $FeSO_4$) were added alone or with P fertilizers (Fig. 3 and Table 3A). The P fertilizers generally increased Fe uptake more when applied with Fe treatments than when alone. Mortvedt and Giordano (1973) found that $FeSO_4$ banded with polyphosphates increased yield and Fe uptake of sorghum 200% over applications of polyphosphates alone. On the other hand, Mortvedt and Kelsoe (1988) pointed out that Fe uptake was increased by the acid-type commercial fertilizers as much as when FeSO4 was added, presumably because of Fe contaminants in those acid-type commercial fertilizers. In the present study, where analytical-grade acid fertilizers were used, the results showed that the acid type UPS 10-30-0-7S with 25 ppm Fe as $Fe_2(SO_4)_3$ increased Fe uptake significantly over the other of P fertilizers with Fe^{+3}. This shows that the beneficial effect of acid-type fertilizers is mainly due to increased availability of Fe.

The Fe uptake by second crop tended to increase by applying $FeSO_4$ and P fertilizers more than using $FeSO_4$ alone (Fig. 3C, D and Table 3). The increase was higher with 50 ppm Fe than 25 ppm. The most effective fertilizer was UP 10-30-0 followed by DAP. Also, uptake increased by applying $Fe_2(SO_4)_3$ and P only slightly compared with application of $Fe_2(SO_4)_3$ alone; there was little effect by increasing Fe^{+3} rate.

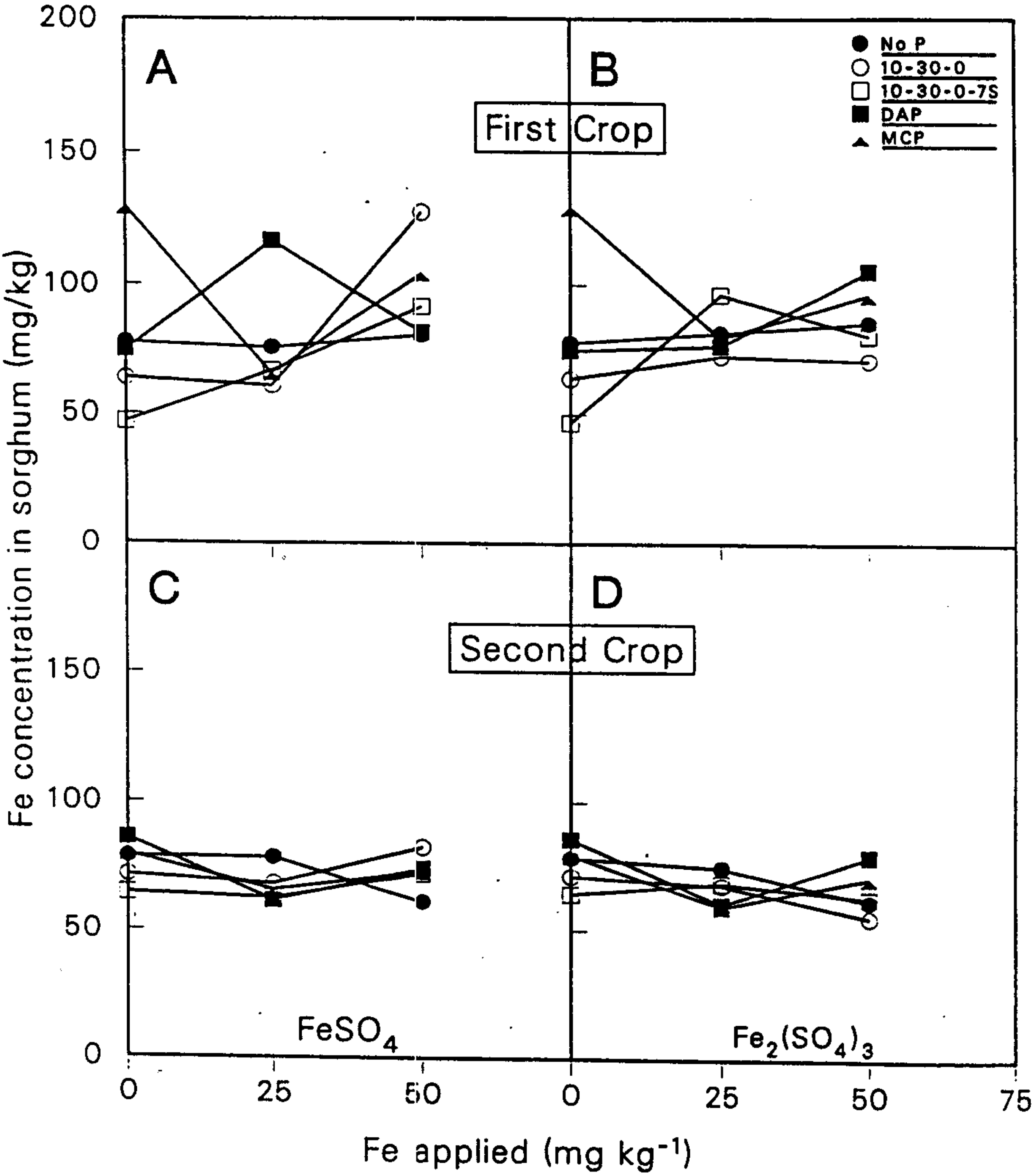

Fig. 2. Fe concentration in first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

The ferrous source was thus superior to the ferric source in both crops. Availability of Fe to plant roots would be lower by adding ferric rather than ferrous iron to the soil. The theory of Hodgson et al. (1972) that soluble iron ions adsorbed on colloidal soil surface reduces iron-precipitation and helps Fe-availability to plants seems viable.

The lower Fe uptake in the second crop as compared with the first crop indicate a reduced availability of Fe with time duration following its application.

Manganese:

The Mn concentration in the first crop was decreased significantly by applying $FeSO_4$ or $Fe_2(SO_4)_3$ alone or with P fertilizers, as shown in Fig. 4 and Table 4A. Significant differences were found between the treatments which received P fertilizers alone and the others which received P fertilizers and 25 or 50 ppm Fe as $FeSO_4$ or 50 ppm Fe as $Fe_2(SO_4)_3$. Treatments receiving P alone showed more Mn concentration than those receiving both P and Fe. The decrease in Mn concentration may be due to the antagonism effect between Fe and Mn. This trend also was noticed by Somers and Chive (1942), Tiffin (1967), Ohno et al. (1978), and Haleem (1985) who observed an inverse relation between Fe and Mn concentration in plants, supporting the Fe and Mn antagonistic relationship. The Fe-Mn interactions occur at two levels: at the uptake level where Fe hampers manganese uptake, and at the metabolic level where Mn inactivates Fe metabolic activity by decreasing Fe^{2+} concentration in plants.

The Mn concentration in the second crop was decreased significantly by adding $FeSO_4$ (Fig.4 C,D and Table 4A)). The Mn concentration in second crop was higher than the concentration in first crop which may be due to the dilution effect since plant growth of the 1st crop was much greater than that of the 2nd crop. The highest dry matter yield (given by the 10-30-0 P fertilizer) had the lowest Mn concentration (compared to the other

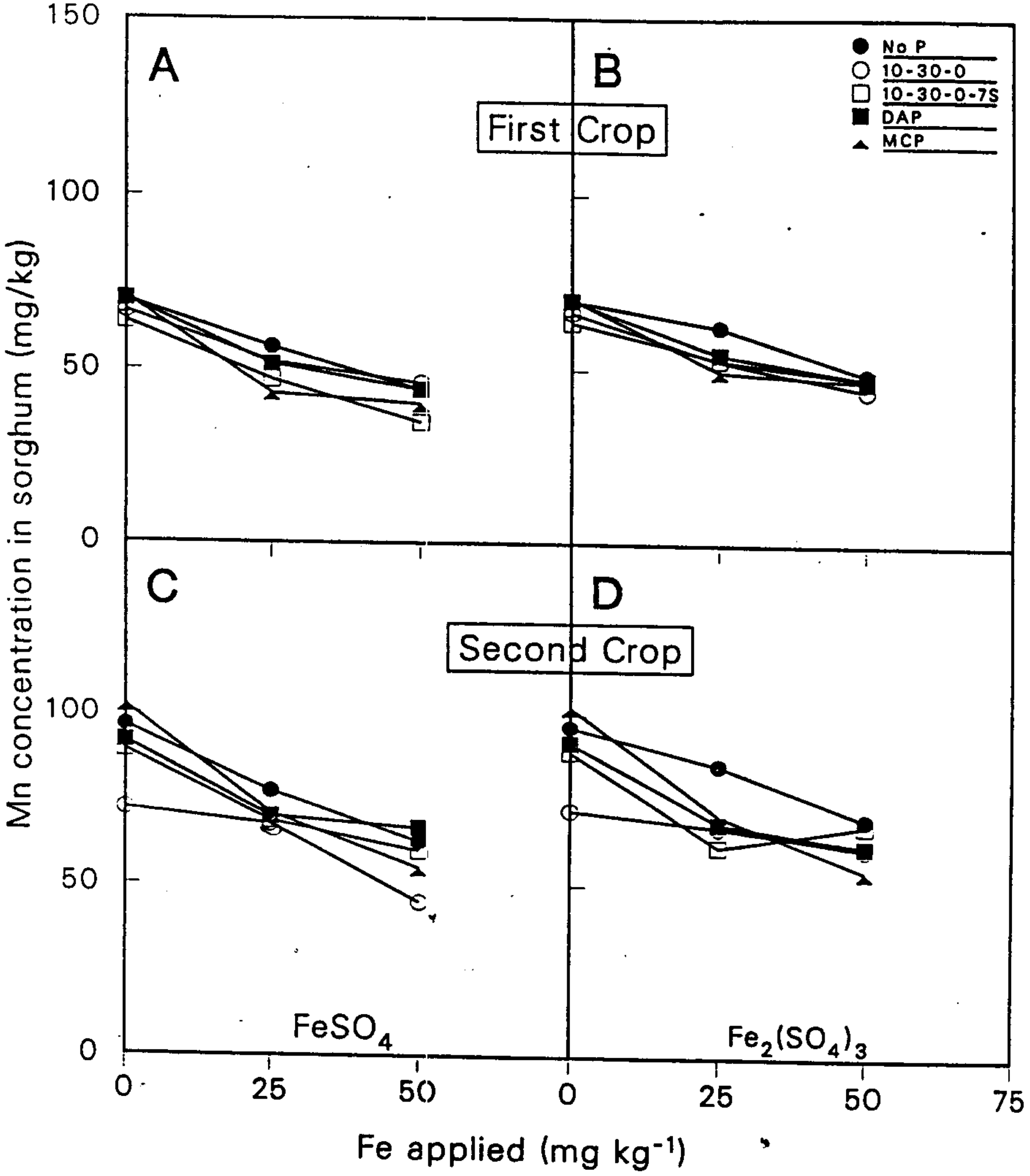

Fig. 4. Mn concentration in first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

P fertilizers). All the P fertilizers had similar effect on Mn concentration except 10-30-0, which significantly reduced the concentration of Mn . The antagonistic Fe-Mn interaction theory is shown by this particular treatment (10-30-0) which showed a significant increase in Fe concentration.

The Mn uptake in the first crop was increased significantly over $FeSO_4$ alone by applying P fertilizers with $FeSO_4$. (Fig. 5 and Table 5A). This increase was generally higher with 25 than with 50 ppm Fe. Mortvedt and Kelsoe (1988) found that uptake of Mn generally decreased with high rate of FeS04 banded with acid type fertilizers. This suggests that the large supply of available Fe with these fertilizers antagonized Mn uptake. In the case of using $Fe(S0_4)_3$ alone or with P fertilizers, Mn uptake was little affected. When 10-30-0-7S was applied particularly with 25 ppm Fe, the Mn uptake was increased significantly more than with the other fertilizers.

In the second crop, applied $FeS0_4$ with P fertilizers increased Mn uptake quite significantly. However, applied $Fe_2(SO_4)_3$ was not very effective for increasing Mn uptake and P fertilizers had little effect on the Mn uptake. In general, Mn uptake was more clearly related to biomass of the plant material than to Mn concentration. This is shown by the higher Mn-uptake of the MCP source which also gave higher yield compared with the other sources.

Zinc:

The concentration of Zn in first crop sorghum plants was generally decreased when P fertilizers were applied, whether alone or with Fe. (Fig 6A and Table 6A). The lowest Zn concentration value was associated with MCP especially when applied with 50 ppm Fe. (Fig. 6B). Applying Fe decreased Zn concentration. Adding MCP as compared with other P fertilizers resulted in a decrease in Zn concentration. These results are in harmony

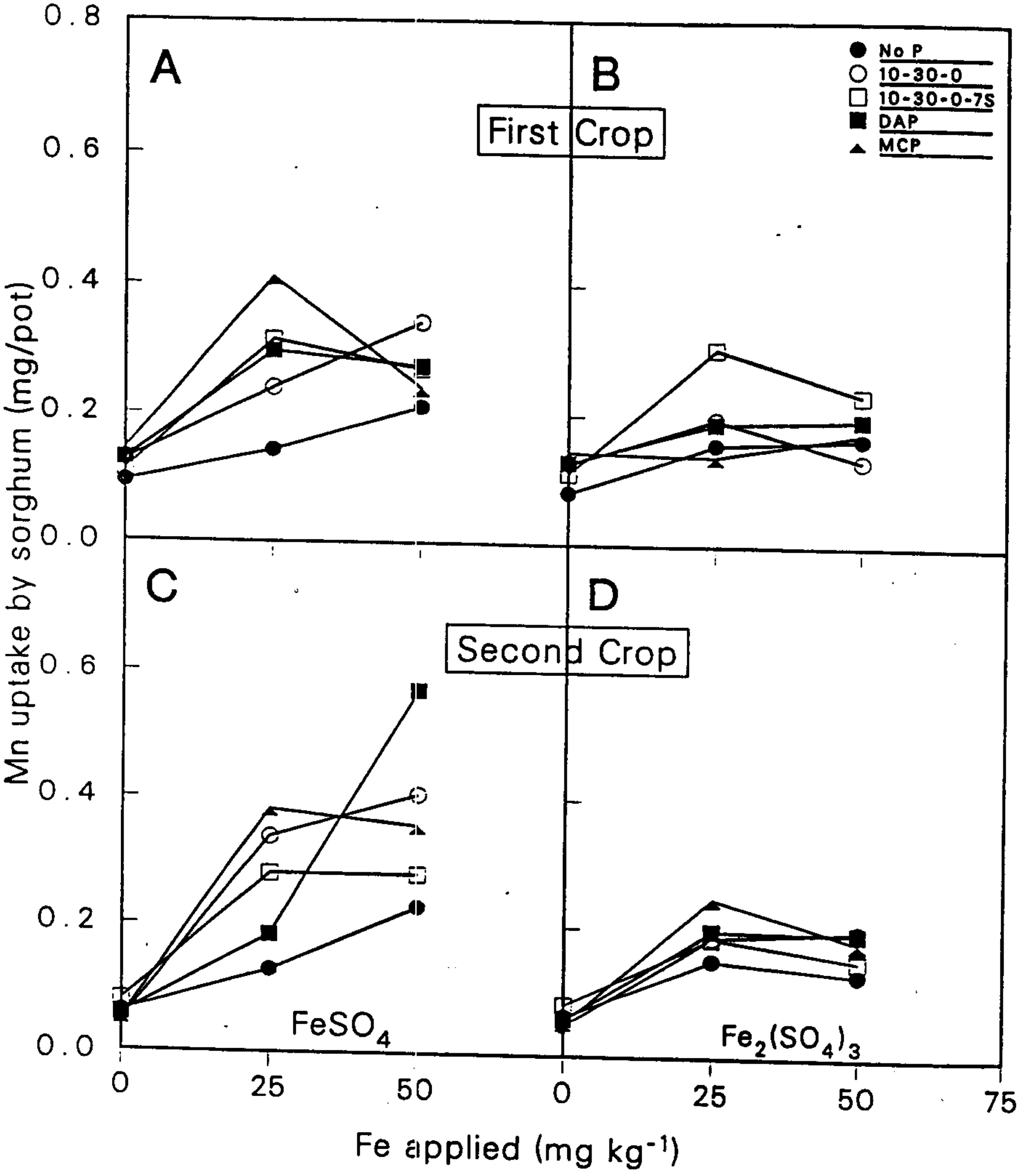

Fig. 5. Mn uptake by first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

with the results obtained by Wallace and Cha (1986) who reported that addition of Fe decreased Zn and Mn concentrations in leaves, while addition of both Fe and P decreased Zn concentration even more.

The concentration of Zn in the second crop was also decreased by applying P fertilizers (Fig. 6 C,D) especially with 10-30-0. The $FeSO_4$ or $Fe_2(SO_4)_3$ applied alone had little effect on Zn concentration.

The Zn uptake data of the first crop which are illustrated in Fig. 7 and Table 7A, showed that Zn uptake was generally increased by applying either Fe source. Adding P fertilizers plus Fe significantly increased uptake above that of Fe alone in most cases.

The uptake of Zn by second crop increased linearly with applied $FeSO_4$, and adding P fertilizers gave further significant increases. In the case of applying $Fe_2(SO_4)_3$ with P fertilizers, Zn uptake increased more than from $Fe_2(SO_4)_3$ alone. However, Fe rate had little effect on Zn uptake. These results were contrary to those of Mortvedt and Kelsoe (1988) who reported that uptake of Mn and Zn generally decreased with the high rate of $FeSO_4$ banded with acid type fertilizers.

SOILS

The influence of band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with P fertilizers, on levels of Fe, Mn, and Zn extracted by DTPA was determined.

Iron:

Levels of DTPA-extractable Fe after first crop significantly increased with increasing rate of $FeSO_4$ banded alone or with each fertilizer (Fig. 8 and Table 8A).

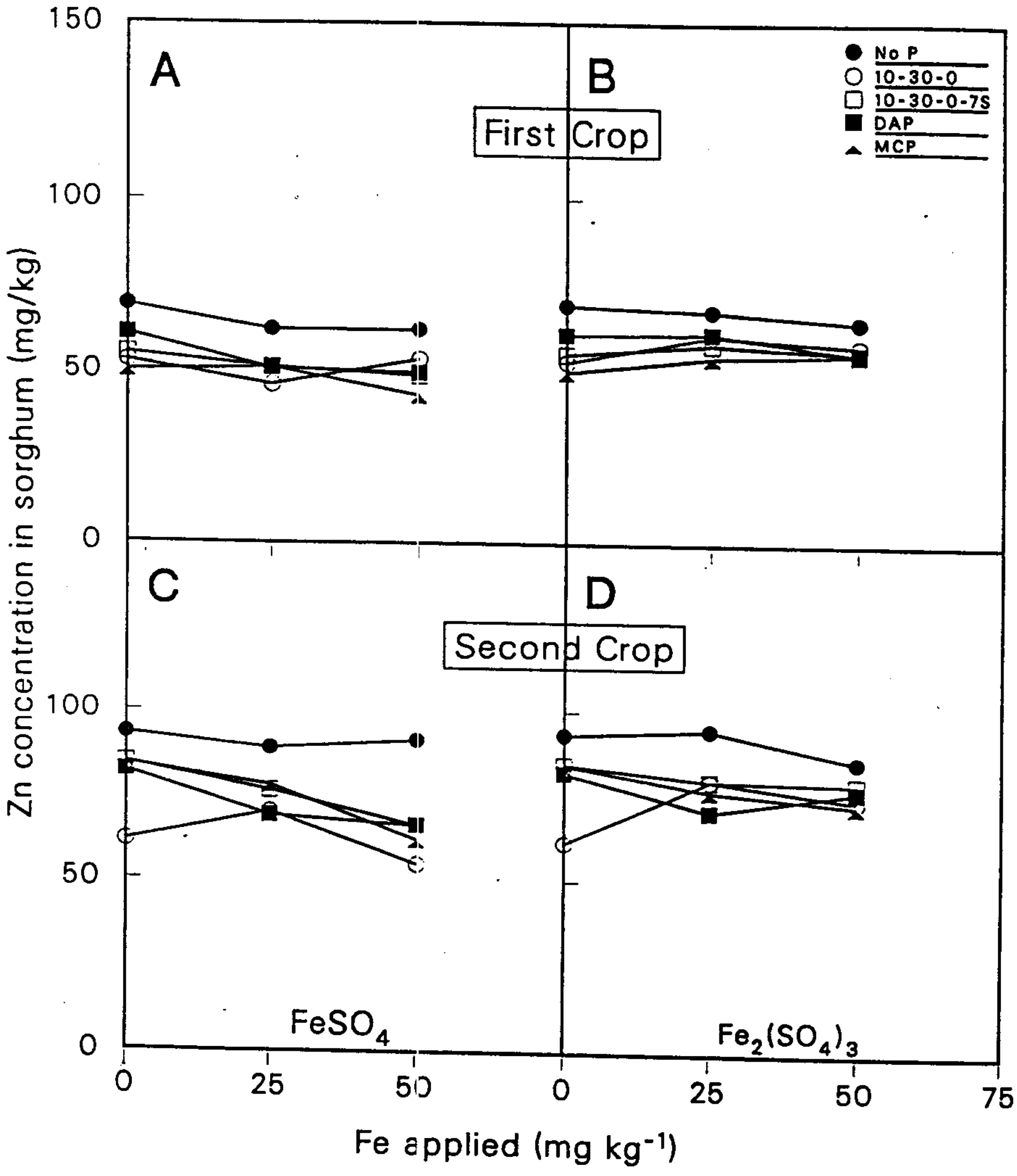

Fig. 6. Zn concentration in first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

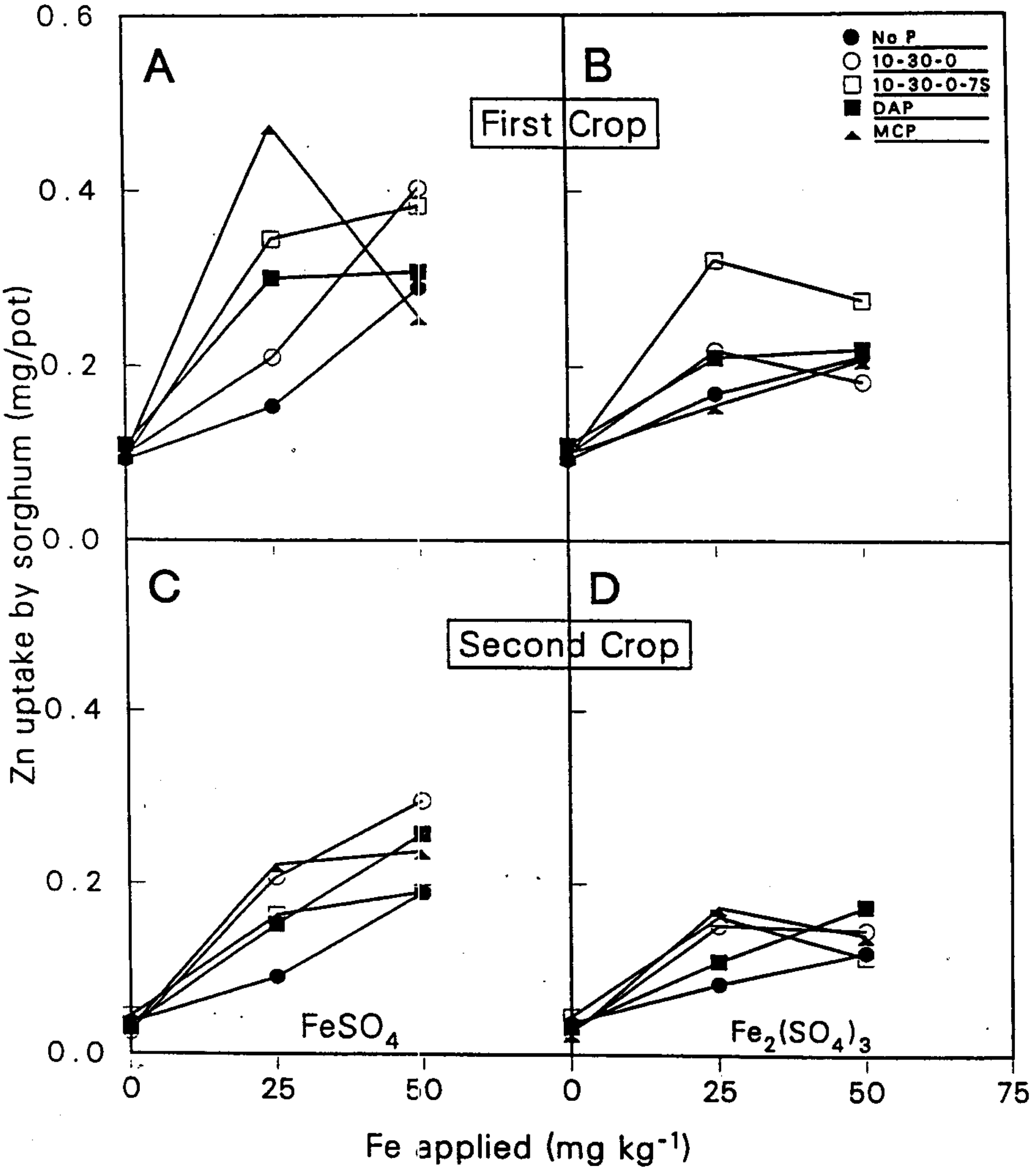

Fig. 7. Zn uptake by first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

Extractable Fe varied with each fertilizer and at each Fe rate. For example, there was a significant difference between DAP and the other P fertilizers and between 10-30-0 and treatments which received Fe alone (No-P). The effect of P fertilizers on DTPA extractable Fe followed the order: DAP> 10-30-0> 10-30-0-7S> MCP> No-P. The DTPA-extractable Fe was higher with P fertilizer and $FeSO_4$ than $FeSO_4$ alone. This may be due to the acidity of these fertilizers which may have maintained Fe available for a long period of time. These results corroborate those of Westfall and Hanson (1985) who found that injecting 10-34-0 into a moderately acid soil (pH 6.6) and a calcareous soil resulted in increased levels of extractable Fe. Also, the results are in agreement with Mortvedt and Kelsoe (1988) who demonstrated that levels of DTPA-extractable Fe generally increased with rate of $FeSO_4$ banded alone or with P fertilizers (10-30-0, 10-30-0-7S, 10-34-0, and TSP).

The DTPA-extractable soil Fe, after second crop, was increased significantly more by applying P fertilizers with $FeSO_4$ than from $FeSO_4$ alone. The effect of Fe rate on extractable Fe varied with P fertilizer source. In general, increasing Fe rate increased extractable Fe. The effect of P fertilizers on DTPA - extractable Fe followed the order: DAP> 10-30-0> 10-30-0-7S> MCP> No-P.

Adding $Fe_2(SO_4)_3$ source increased the Fe which was extracted by DTPA. There were no significant differences between the treatments which received 25 or 50 Fe rates and little affect from adding P fertilizers.

There appears to be a trend that when MCP was applied with the high Fe rate it depressed extractable Fe, perhaps from coprecipitation with calcium phosphate , whereas the other fertilizer may have formed more soluble products.

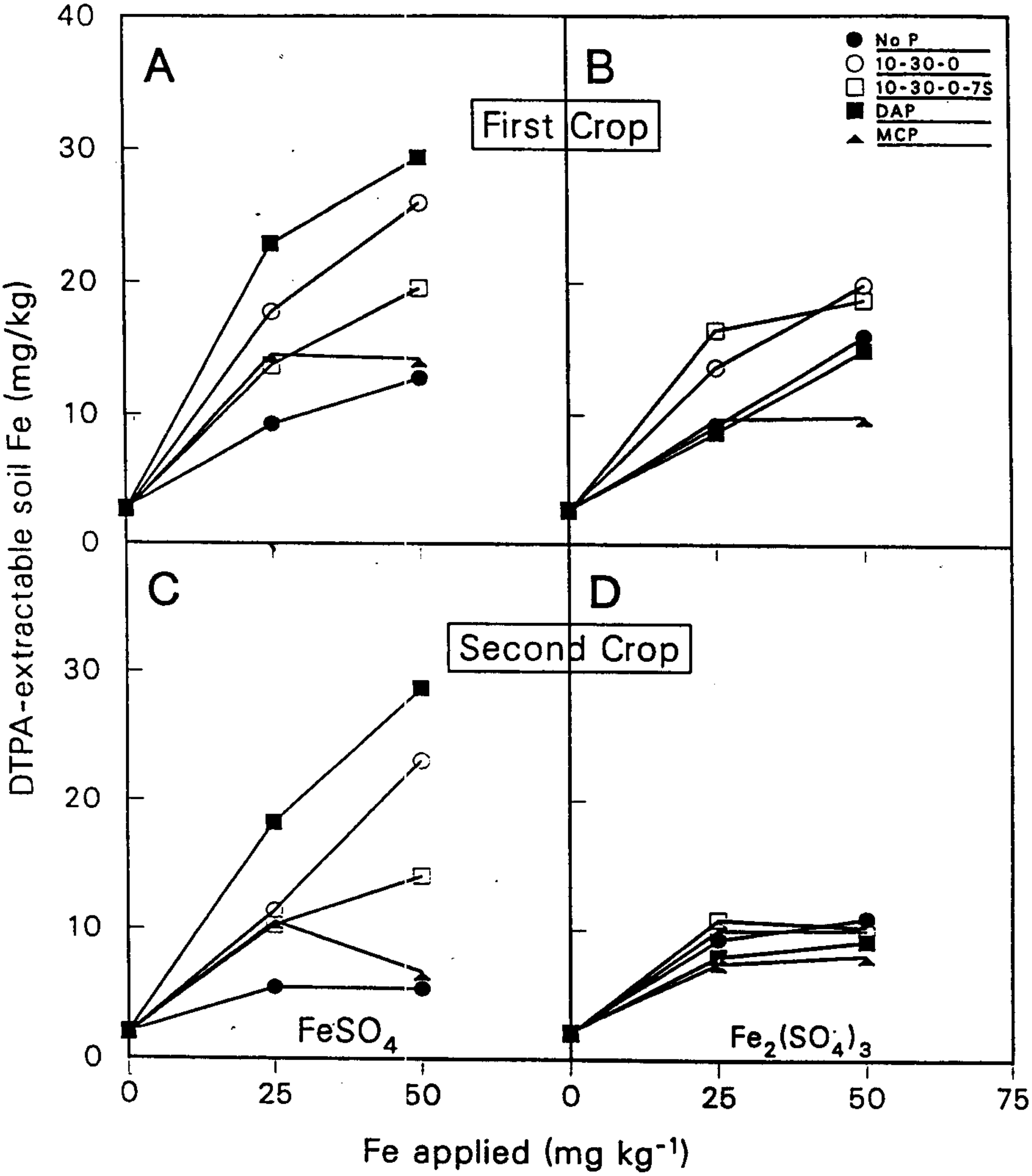

Fig. 8. Soil Fe extracted by DTPA after first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

Manganese

The $FeSO_4$ applied alone had little effect on levels of DTPA-extractable Mn (Fig. 9 and Table 9A). Adding ferrous sulfate did not affect solubility of Mn in the soil. Also, the P fertilizers added alone or with $FeSO_4$ had inconsistent effect on DTPA-extractable Mn after first and second crop and gave no significant results. There was one exception, the MCP decreased extractable Mn, but not significantly and when applied with FeSO4 tended to depress Mn even more. Addition of calcium associated with the phosphate ion seems to cause immobilization to Mn ion.

Zinc

The DTPA-extractable Zn levels after first and second crop as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with P fertilizers are presented in Fig. 10 and Table 10A. After first crop, DTPA-extractable Zn was decreased with increasing Fe rate either as $FeSO_4$ or $Fe_2(SO_4)_3$ alone or with P fertilizers. Applied $FeSO_4$ with MCP resulted in depression of DTPA-extractable Zn. The DTPA-extractable Zn after the second crop was also decreased with increasing $FeSO_4$ rate. The P fertilizers had a negative effect on extractable Zn. In the case of using $Fe_2(SO_4)_3$, the DTPA-extractable Zn did not follow a specific trend.

Phosphorus

Soil P extracted by $NaHCO_3$ after second crop as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with P fertilizers is illustrated in Fig. 11 and tabulated in Table 11A.

Soil P was increased with added P fertilizers. Native extracted soil P was decreased with increasing Fe rate either as $FeSO_4$ or $Fe_2(SO_4)_3$ when they were applied alone. The only P fertilizer in the presence of which, Fe caused a decrease in extractable

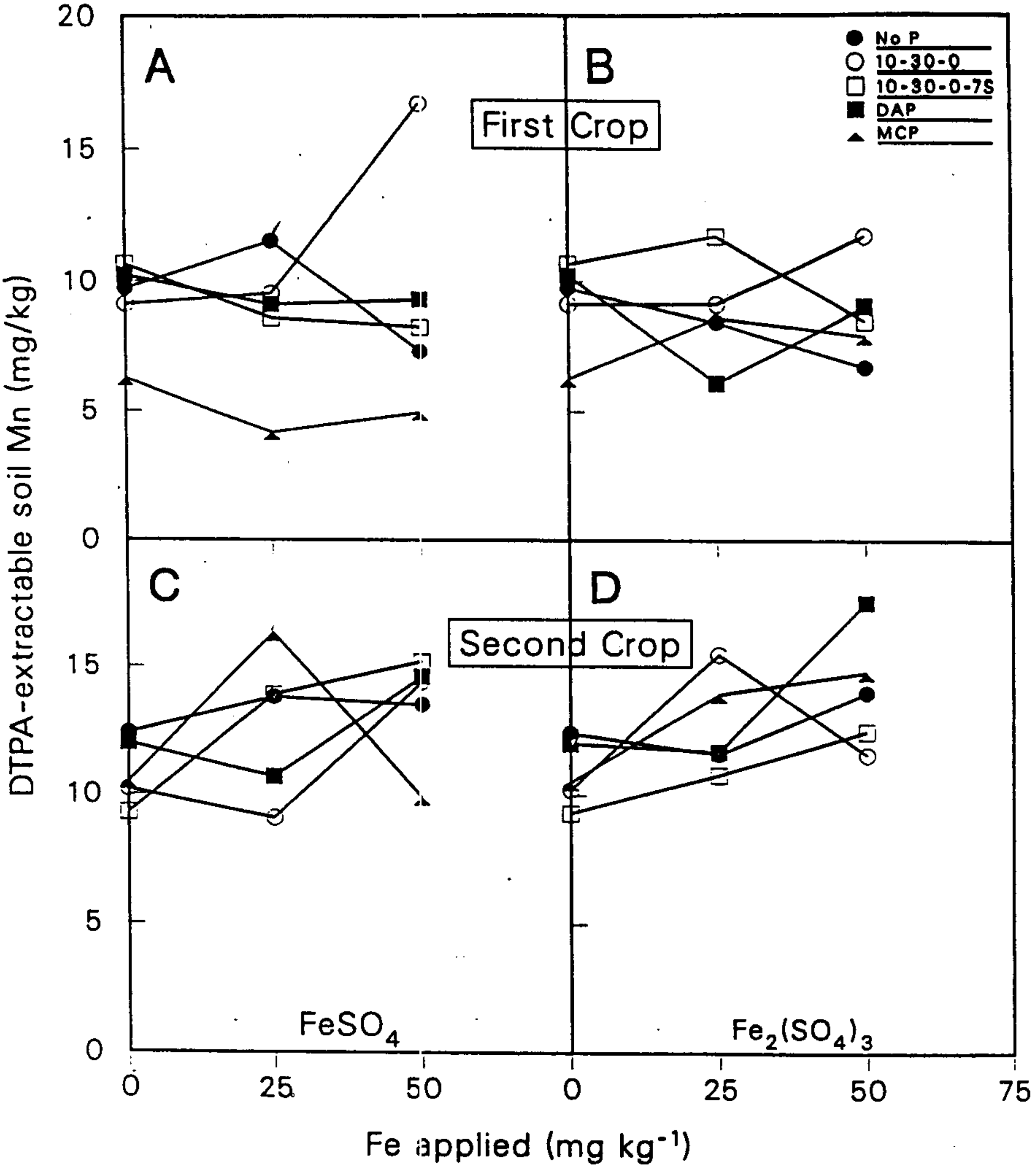

Fig. 9. Soil Mn extracted by DTPA after first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

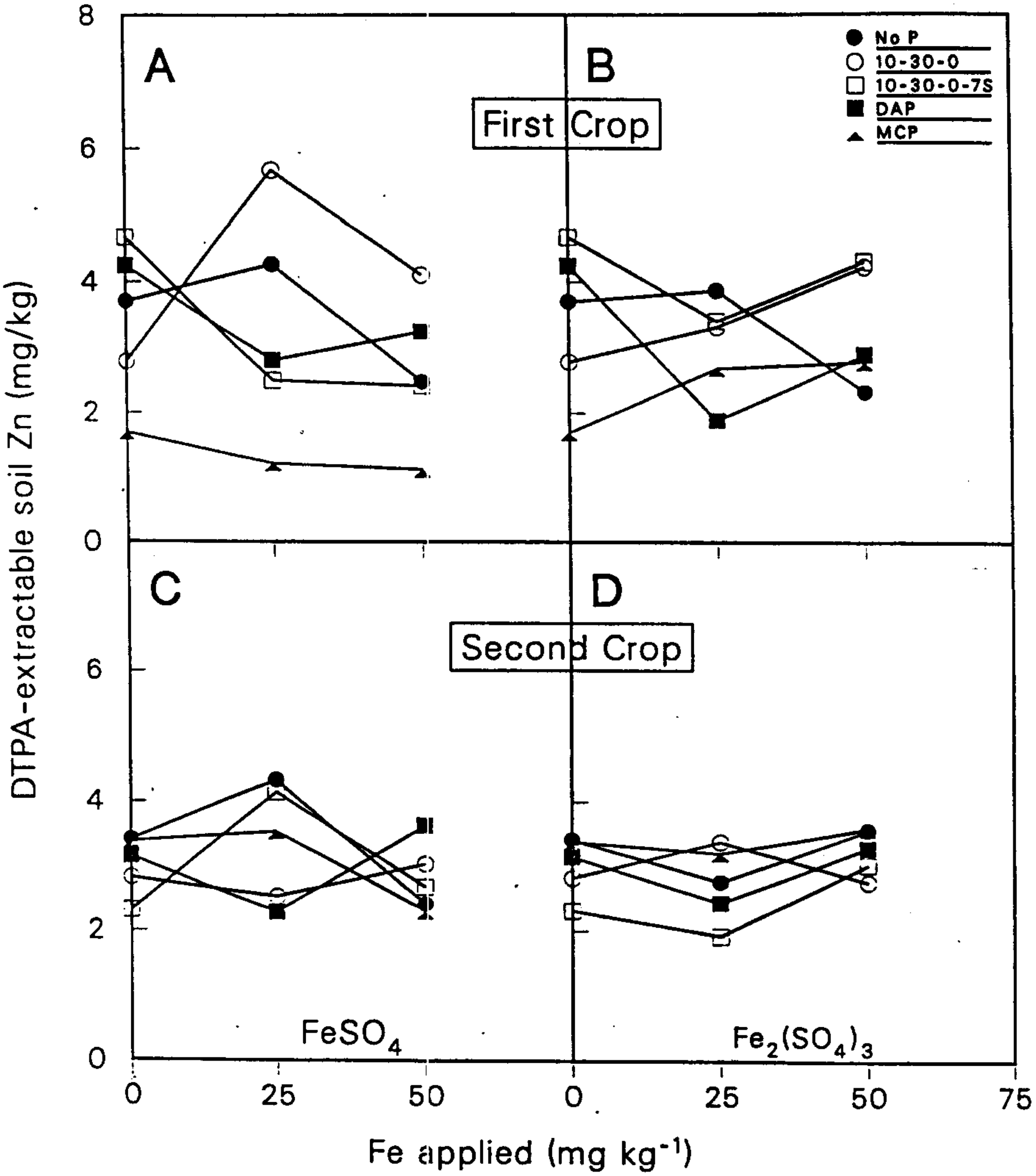

Fig. 10. Soil Zn extracted by DTPA after first and second crop sorghum as affected by band application of $FeSO_4$ and $Fe_2(SO_4)_3$ alone or with fluid P fertilizers.

P, was MCP. With other P fertilizers, application of Fe caused an increase in extractable P. Banding $FeSO_4$ with MCP at 50 ppm Fe in particular, gave a profound and significant decrease in extractable P from the soil. This result may be attributed to the co-precipition between phosphate and ferric ions. The effect of MCP on soil P in the case of using $Fe_2(SO_4)_3$ followed the same trend as $FeSO_4$. Banding 10-30-0 and 10-30-0-7S with $FeSO_4$ or $Fe_2(SO_4)_3$ at a rate of 25 or 50 ppm Fe showed slight but not significant increase in extractable P. This result suggests that these two acid-type P fertilizers did not enhance much interaction between phosphate ions and ferrous or ferric ions or other metal ions. The DAP apparently increased soil P availability when banded with $FeSO_4$ and this increase was accentuated with increasing of $FeSO_4$ rate. A similar trend was obtained when DAP was banded with 25 ppm Fe as $Fe_2(SO_4)_3$. Nitrification of ammonium associated with this DAP by soil micro-organisms and a consequent possible formation of iron phosphate may have contributed to increased available P.

B : LABORATORY EXPERIMENT

The experiment was conducted to investigate the effect of P fertilizers on Fe availability and movement from a fertilizer band as well as on availability of indigenous Mn and Zn. Soil was sampled at varied distance from the band and at different times of incubation.

Iron

The DTPA-extractable Fe, after 7 days incubation varied from one fertilizer to another (Fig. 12 and Table 12A). The DAP appeared to have a superior effect on Fe availability, particularly at 0 to 1.0 cm from the band, followed by MCP. Both fertilizers

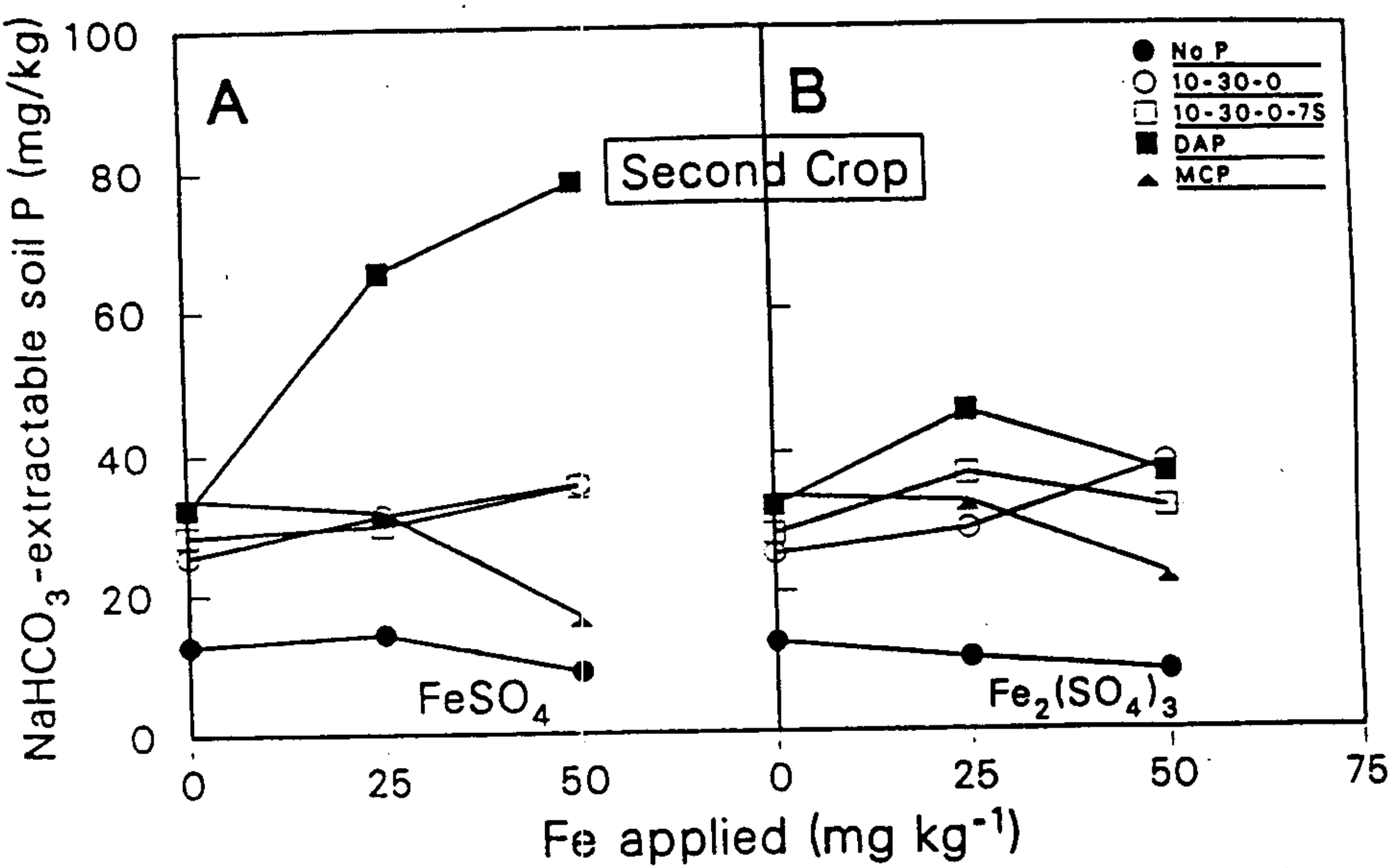

Fig.11. Soil P extracted by NaHCO3 after second crop sorghum as affected by band application of FeSO$_4$ and Fe$_2$(SO$_4$)$_3$ alone or with fluid P fertilizers.

were superior to UPS 10-30-0-7S, and UP 10-30-0. Within 0.0 to 0.5 cm of the band, there was a significant difference between DAP and either 10-30-0-7S or 10-30-0.

Levels of DTPA-extractable Fe were highest in the fertilizer band and decreased sharply with distance away from the band, especially at 1.5 cm away from the band. A similar result was obtained by Mortvedt and Kelsoe (1988).

The extractable Fe after 21 days showed that DAP still had a beneficial effect especially within 0.0 to 0.5 cm, but its effect decreased sharply and became inferior source at 1 cm and beyond. The 10-30-0-7S tended to show the most Fe movement of all treatments.

Levels of DTPA-extractable Fe after 35 days also decreased sharply with distance from the fertilizer band. However, compared with earlier samplings, there was greater extractable Fe at this sampling. The Fe levels were highest with DAP followed by 10-30-0-7S. At any of the 3 sampling times, there was not much Fe movement beyond 1.5 cm with any fertilizer. Also, at all times, the non fertilized treatment showed nearly the same amount of extractable Fe at all distances.

The overall effects of P fertilizers and incubation time on Fe movement from a fertilizer band showed that Fe concentration was highest near the center of the band (0-0 to 0.5 cm) at all three sampling times (7, 21, and 35 days), and declined sharply with distance from the band. In most cases, iron availability declined at 21 days, compared with at 7 days, then increased at 35 days. Effect of soil micro-organisms in this respect may not be ruled out. Also, it seems that adding P fertilizers in form of phosphates increased Fe-availability, since both DAP and MCP fertilizers showed greater levels of available Fe than UP and UPS. After 35 days, the increased levels of extractable Fe compared with the 7-

and 21-days, particularly with DAP, may be the result of enhanced activities of nitrification and mineralization by soil micro-organisms and a possible subsequent acidification.

Ryan, et. al.(1986) found that NH_4^+ rapidly increased during the first week of incubation with phosphate fertilizers (UP, UP+Fe-EDDHA, and UP+Iron Sul) and reached a plateau, then declined rapidly over the next 15 days.

In the present study, the effect of P fertilizers on Fe movement followed a rather consistent order of: DAP > MCP > 10-30-0-7S > 10-30-0. The superiority of DAP over the other P sources may be due to its greater N content resulting in greater acidification with time. Nelson (1974) reported that acid is formed during the nitrification process to the extent that about 1.8 pounds of pure $CaCO_3$ is required to neutralize the acidity produced in converting one pound of ammonium N to nitrate.

Manganese

The DTPA-extractable soil Mn as affected by P fertilizers is shown in Fig. 13 and Table 13A. After 7 days incubation, comparing the control with fertilizers, there were slight decrease in extractable Mn caused by the 2 acidic urea-acid fertilizers as well as MCP, but an increase was caused by the DAP fertilizer. After 21 days the extractable Mn in all fertilized treatments was generally less than the non fertilized. After 35 days, there tended to be more extractable Mn in the treatment over the control, as ocurred with the 7 days sampling. The main observed trends in Fig. 13 were: the extractable Mn was decreased with time of incubation, DAP was the superior P fertilizer, and MCP the inferior one.

The decrease in extractable Mn with time may be due to the precipitation of Mn with phosphate. A similar result was obtained by Mortvedt and kelsoe (1987).

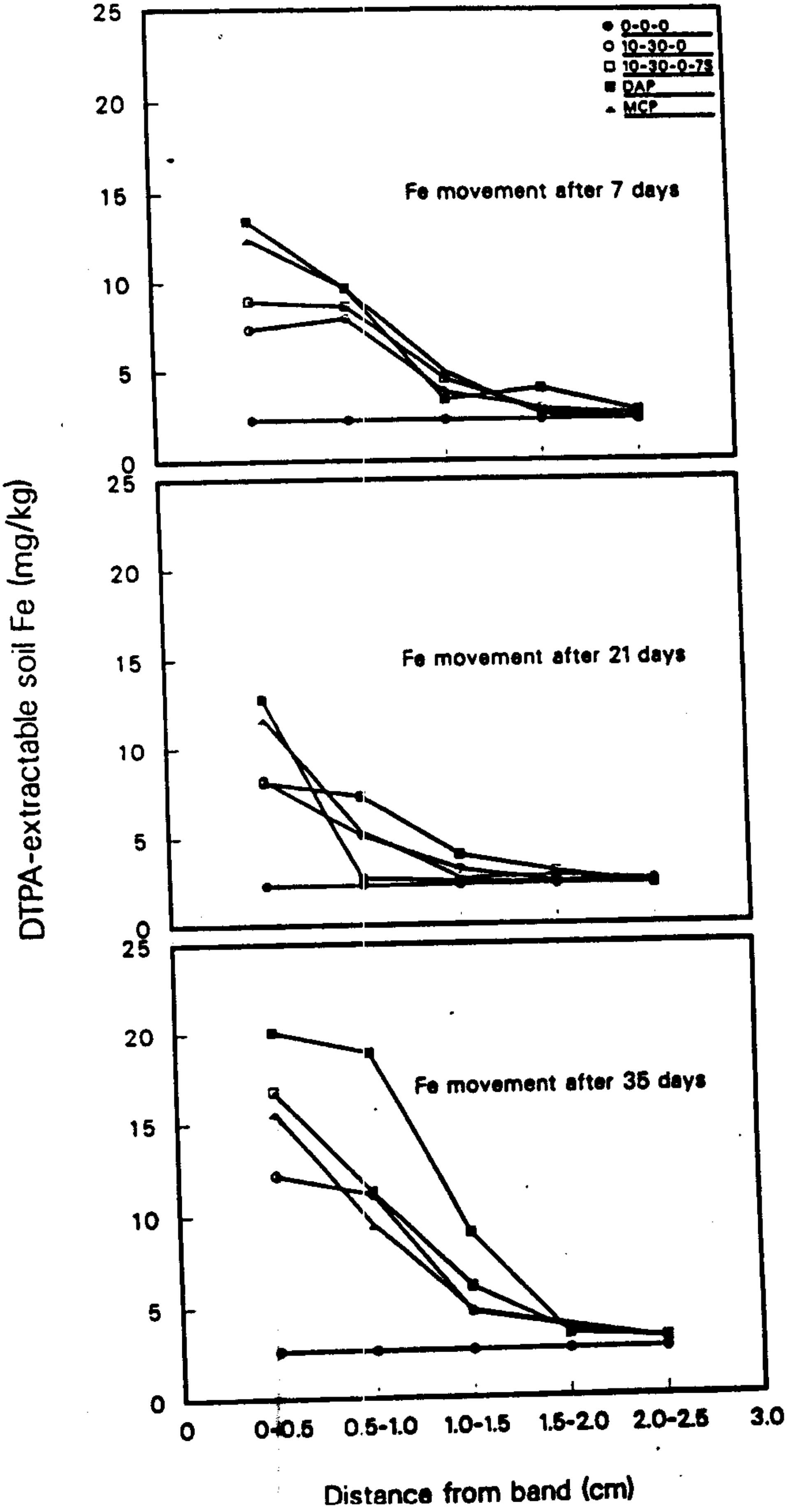

Fig.12. Fe movement from a fertilizer band as affected by P source and time.

The superiority of DAP (in particular) over the other P fertilizers may be attributed (partly at least) to its ammonium nitrogen and the subsequent nitrification with the resulting decrease in soil pH.

Zinc

The DTPA extractable Zn as affected by P fertilizer is shown in Fig.14 and Table 14A . After 7 days incubation, there was more extractable Zn in the 10-30-0 treatment over the control, and only within 1 cm from the band, beyond that there was less Zn . With other P fertilizers and at all distances, there was less Zn than in the non fertilized treatment. In all treatments extractable Zn sharply decreased with time; after 21 and 35 days DTPA-extractable Zn in all P fertilizers was very similar to the control and changed little with distance.

Mikkelsen and Jarrell (1987) found no increase in DTPA-extractable Zn in the soil as a result of applying urea phosphate or triple super phosphate. However, Ryan et al (1986) reported that extractable Zn was depressed by (urea phosphate + Fe) and decreased with time of incubation, from 8 ppm after 1 day to 0 after 30 days. Westfall and Hanson (1985) showed no consistent change in Zn availability in a calcareous soil from injected phosphate treatments.

Soil pH

Soil pH as affected by fertilizer treatments is shown in Fig. 15 and Table 15A. The soil pH after 7 days in all fertilized treatments was less by o.3 to 0.4 unit as compared to the non fertilized within 0.5 cm of the fertilizer band, but the effect decreased with distance. The effect was rather apparent with UP and DAP sources.

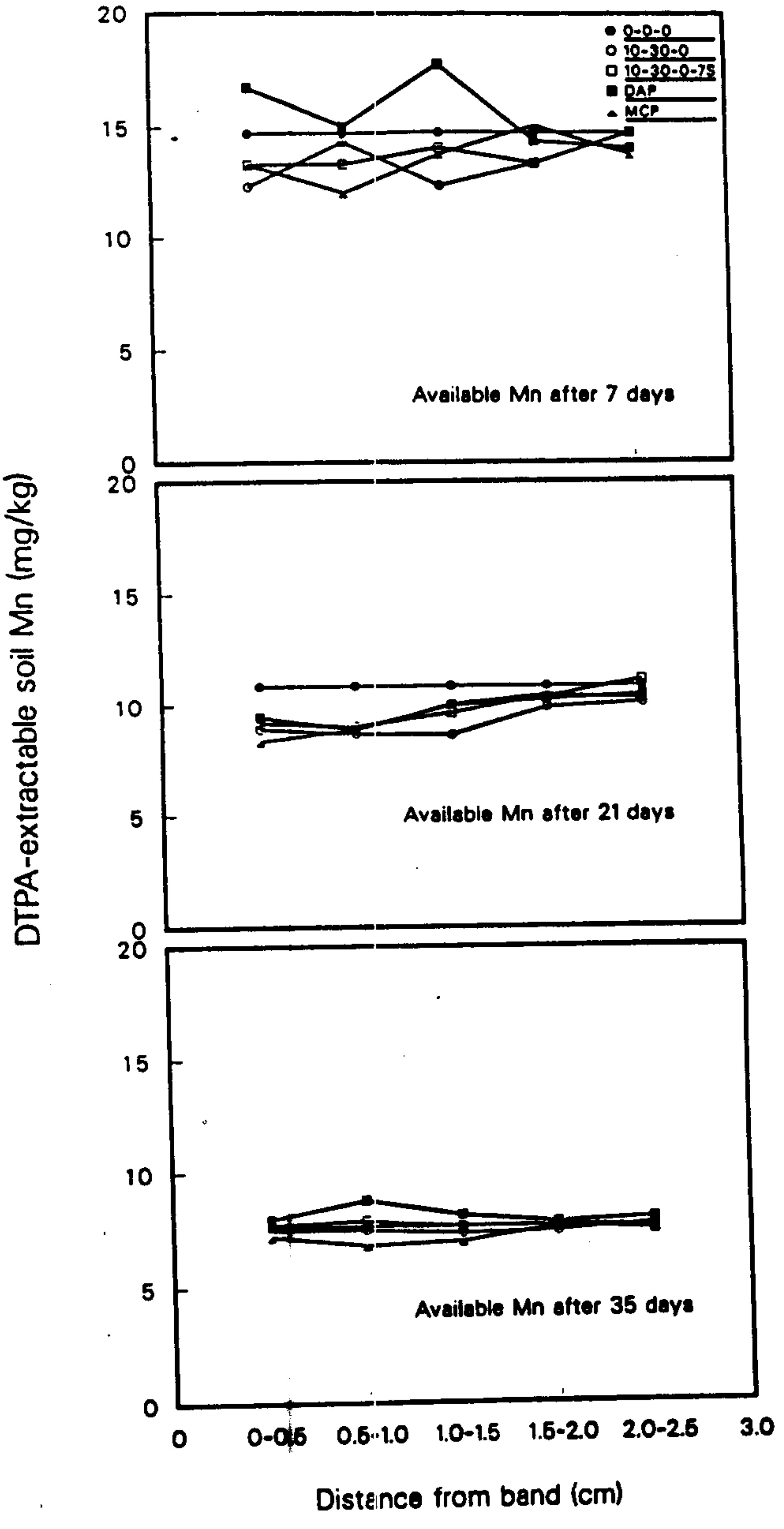

Fig.13. Indigenous soil Mn extracted by DTPA as affected by P source and time.

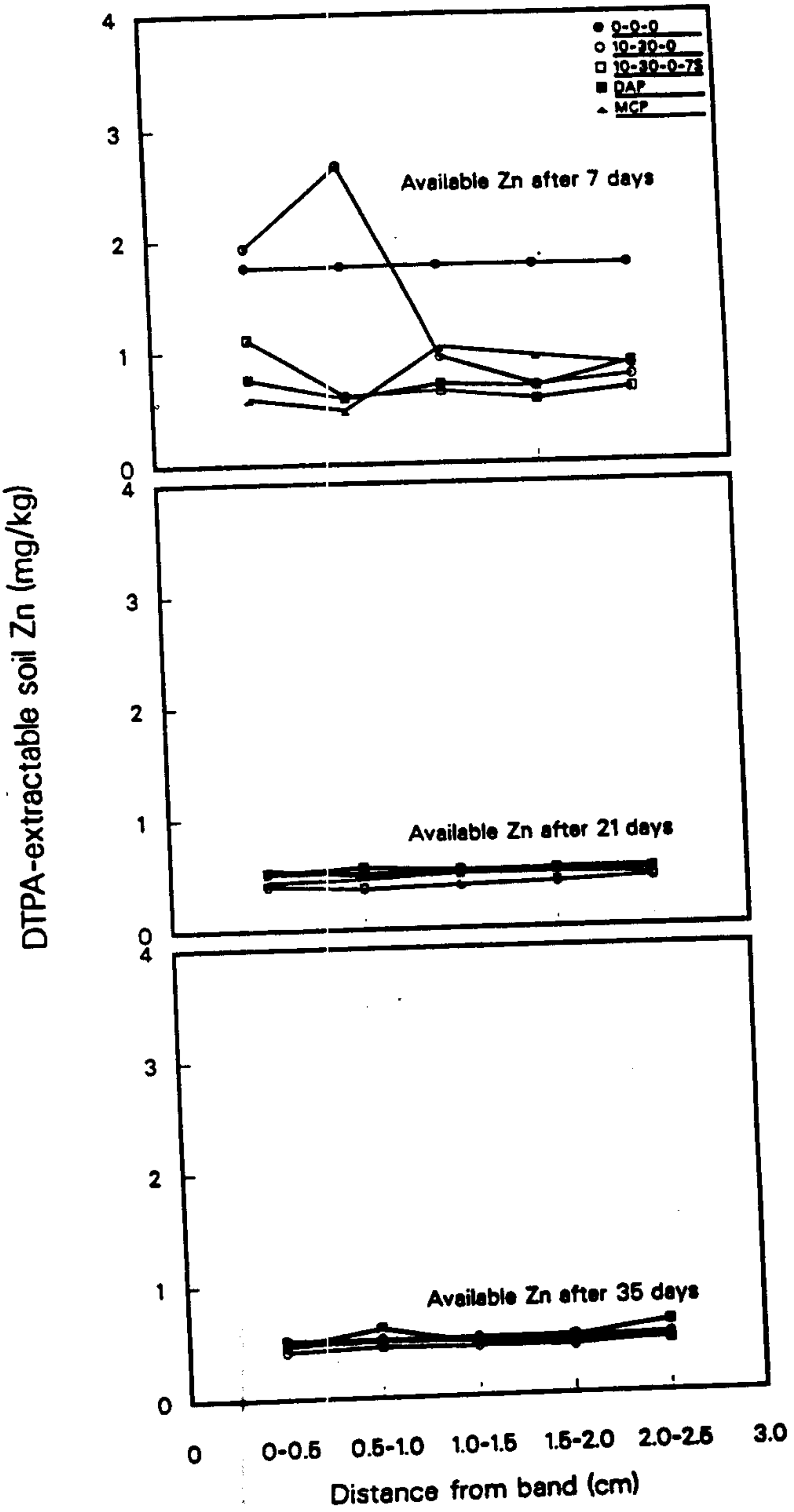

Fig.14. Indigenous soil Zn extracted by DTPA as affected by P source and time.

After 35 days, soil pH was decreased with all P fertilizers by 0.2 unit as compared with the non fertilized within 0.5 cm of the band. Also UP and DAP showed slightly more effect than the other 2 sources. In all treatments (fertilized and non fertilized) pH slightly decreased with time. The lower pH in fertilized treatments, as well as the decrease of pH with time indicate the increased biological activity occuring in the soil as a result of fertilizer application , and incubation. Urea hydrolysis and nitrification of ammonium are part of such activities. This result is in agreement with that of Mortvedt and Kelsoe (1987).

The acidifying effects caused by the P fertilizers, and the acidity from nitrification, reduced the pH 8.0 of this soil to a range of between 7.6 to 7.8 in most cases. In view of the large buffering capacity of such calcareous soils, greater reduction in soil pH would occur only when all soil carbonates were neutralized.

2 : THE ROLE OF SOIL $CaCO_3$ AND SOIL IRON IN IRON NUTRITION

In this particular study, the objective was to determine (i) the effective particle size fraction of soil calcium carbonate and (ii) the specific indigenous soil factors and their influence on Fe availability to soybean. Soybean [Glycine max.(L.) Merr.] was grown in a growth room in sand-soil mixes of 27 soils, collected from Egypt, and USA (Texas).

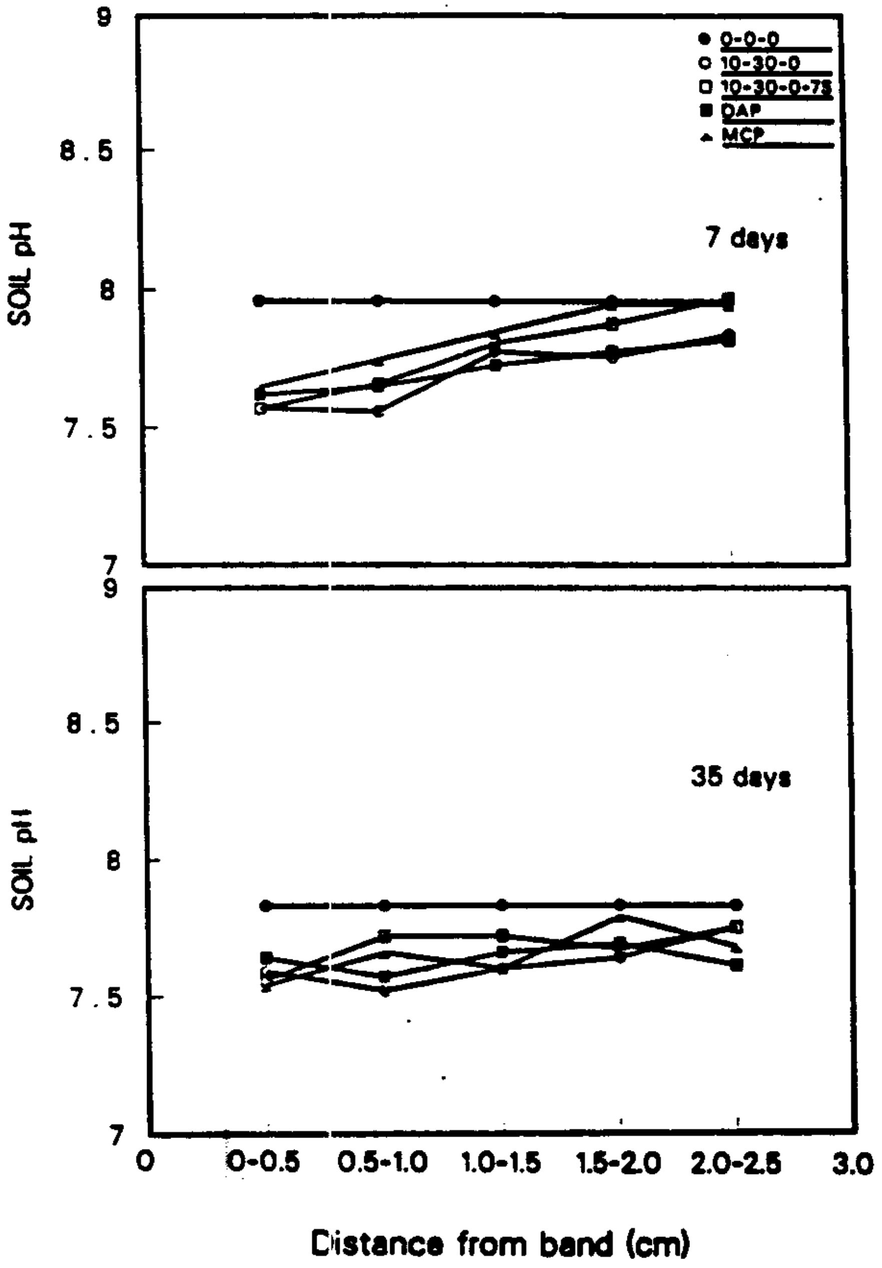

Fig.15. Soil pH as affected by distance from a fertilizer band and time

1- Determination of the effective particle-size distribution of soil carbonates by using steady-state procedure

Rate constants

The experiment rate constants K for the dissolution of Iceland-spar calcite are shown in table 5. At pH 3.0, rates were between 0.31 to 0.45 mg $min^{-1}cm^{-2}$ while at pH 5.0 they showed greater variability, being between 0.0039 and 0.0074 mg $min^{-1}cm^{-2}$. The dissolution rate of calcite at pH 3.0 is approximately 70 folds that at pH 5.0. The mean values of 0.371 and 0.00532 mg $min^{-1}cm^{-2}$ at pH 3.0 and 5.0, respectively, were used as the experimental rate constants for all subsequent models in this study.

Table 5. Rate constants (K) for the dissolution of Iceland-spar calcite.

particle-size range um	Rate of dissolution at pH 3.0	 pH 5
	mg min^{-1} cm^{-2}	
420-841	0.426	0.00739
250-420	0.448	0.00444
177-250	0.310	0.00620
149-177	0.324	0.00466
125-149	0.347	0.00389
Mean	0.371	0.00532

Effective particle-size distribution

The effective particle size distribution was determined by using the pH-stat dissolution procedure (Moore et al., 1990). The dissolution procedure made possible the quantitative estimation of the effective fine-clay size (0.1 - 1.1 um diameter) carbonate table 6. This highly reactive size fraction accounted for 0.0 to 32.3 % of the total calcium carbonate of soils. Total carbonate contents as determined by the pH-stat dissolution model and Chittick procedure showed some differences. The Chittick procedure yielded slightly lower values for 23 of the 27 soils. In a small number of cases, it gave greater values. These differences may be partially attributed to cumulative errors in the summing of the carbonate contents of the individual carbonate size fractions in the pH-stat procedure. The values obtained by the Chittick procedure were determined using whole-soil samples.

Estimation of effective particle size distribution by use of the pH-stat procedure requires certain fundamental assumptions. For example, an assumption of similar particle geometry (Moore et al., 1990). Previous studies have shown that the dissolution of liming materials (Schollenberger and Salter,1943; Elphick, 1955; Swartzendruber and Barber, 1965) and Iceland-spar calcite (Von Tress et al., 1985) can be effectively described with the assumption of spherical geometry and application of the equal-diameter reduction models as were used in this study. Crushed Iceland-spar calcite occurs as euhedral rhombus; however, upon dissolution , the edges and corners become increasingly rounded, especially at pH 3.0 , resulting in an increasing sphericity with continuing dissolution (Von Tress et al.,1985). Soil calcite usually occurs as aggregates of smaller rounded particles held together by carbonate cement or silicate clay (Bui et al., 1990).

In the current study, the reaction rate constants of soil carbonates were assumed to be equal to those of the geologic Iceland-spar calcite as postulated by Moore et al. (1990). The dissolution model requires the assignment of an assumed particle size for each effective particle-size class. In this study, initial radii of 0.05, 0.55, 2.0, 10.0, and 50.0 um (i.e. initial diameters of 0.1, 1.1, 4.0, 20.0, and 100 um) were assigned for the fine-clay, coarse-clay, fine-silt, coarse-silt, and sand fractions, respectively.

The frequency distribution of the carbonate of each particle size fraction as a percentage of total carbonate content for all 27 soils is presented in table 6, and figures 16, 17, 18, 19, and 20 . The fine-clay-size fraction (0.05 um radius) constituted less than tenth of soil carbonate in nearly all soils. The coarse-clay-size fraction (0.55 um radius) generally constituted from about one half to three quarters of soil carbonate in the vast majority of soils. Another small part of soil carbonate was that of the fine silt size as well as the coarse-silt size. The fine-silt size carbonate fraction (2.0 um radius) was constituted less than one-fifth of soil carbonates in most soils. The coarse-silt carbonate fraction (10 um radius) was constituted less than tenth of soil carbonates in the vast majority of soils. The sand-size-carbonate fraction (50 um radius) comprised one third of soil carbonates in 30 % of the cases, and one fifth of soil carbonates in 45 % of the cases. Therefore, in the soils of the current study, the major part of soil calcium carbonate was within the very fine size of < 4 um. Such is the size of clay particles. On the other hand, the coarse part of soil carbonate represents very little portion of soil carbonate. This makes the activity of soil carbonate caused mainly by its clay-size portion.

2- The Indigenous soil factors that influence Fe availability

Twenty seven soils were collected from Egypt as well as from USA (Texas). Indiginous soil factors of $CaCO_3$ content, the effective particle size of $CaCO_3$, free Fe-oxide, amorphous Fe-oxide , and DTPA-extractable Fe, were determined. The correlation coefficients concerning plant parameters as well as those between soil parameters and plant parameters were calculated.

Chlorophyll concentrations ranged from 0.8 to 8.7 ug cm^{-2} (table 7). Visual chlorosis evaluation scores ranged from 0.0 to 4.0. The aboveground dry matter yield

Table 6. Carbonate particle-size distribution, as percentages of total carbonate content and contents of $CaCO_3$ in 27 soils.

Smple No.	Site	Size-distribution percentage of $CaCO_3$ as determined by pH-stat					$CaCO_3$ %	
		Clay-size		Silt-size		Sand-size	By pH-stat*	By Chittick**
		Fine	Coarse	Fine	Coarse			
				%				
1	El-Henwa (Egypt)	6.5	48.8	5.6	18.0	21.1	17.8	16.1
2	El-Mazrah ~	9.9	36.1	34.7	9.0	10.2	41.2	35.3
3	Tanta ~	0.0	46.3	17.5	6.4	29.8	3.9	2.2
4	Hoosh Essa ~	4.4	54.4	15.2	9.2	16.9	13.7	12.3
5	Kafer El-Dawar ~	7.6	61.6	11.2	5.3	14.1	16.4	15.1
6	West Noubaria 1 ~	0.5	13.3	3.2	13.4	70.1	9.7	8.9
7	West Noubaria 2 ~	0.2	14.9	1.4	15.4	68.4	15.4	9.4
8	East Noubaria ~	0.6	14.3	1.2	13,1	70.5	15.7	11.8
9	El-Amreea ~	3.0	64.4	4.5	11.3	17.0	32.3	38.1
10	Burg El-Arab ~	1.3	43.2	4.3	8.2	42.9	27.3	29.6
11	Reeves (USA)	0.0	70.7	18.4	8.4	2.6	12.2	12.3
12	Cameron ~	0.0	32.3	29.1	35.6	2.8	17.2	15.3
13	Bell ~	32.3	30.9	32.5	0.0	4.3	22.6	35.0
14	Coryell ~	2.4	45.2	16.2	24.0	12.2	26.1	25.6
15	Lubbock ~	5.6	56.5	12.6	0.0	12.7	3.4	1.4
16	Coryell ~	0.0	66.4	19.3	3.7	10.8	11.5	9.8
17	Reeves ~	7.7	73.3	10.2	5.5	3.6	29.2	25.9
18	Pecos ~	2.7	80.1	2.5	7.2	7.0	32.8	32.3
19	Hidalgo ~	5.5	64.5	11.1	0.0	18.3	2.9	1.6
20	Medina ~	0.5	66.5	13.0	8.5	11.3	15.8	13.7
21	Jones ~	0.7	77.3	0.0	4.2	17.9	8.5	6.8
22	Fisher ~	8.6	40.7	6.4	33.3	11.4	4.2	4.0
23	Coryell ~	1.6	50.3	47.6	1.1	1.6	24.6	22.1
24	Kleberg ~	3.0	0.0	96.5	0.0	0.5	14.1	1.0
25	Milam ~	4.7	67.0	17.0	1.3	10.1	14.1	11.6
26	Milam ~	0.0	57.5	26.7	3.0	12.5	3.2	2.3
27	Burleson ~	0.5	58.5	33.0	0.0	7.9	15.5	12

* See Moore *et al.* (1990); ** see Dreimanis (1962)

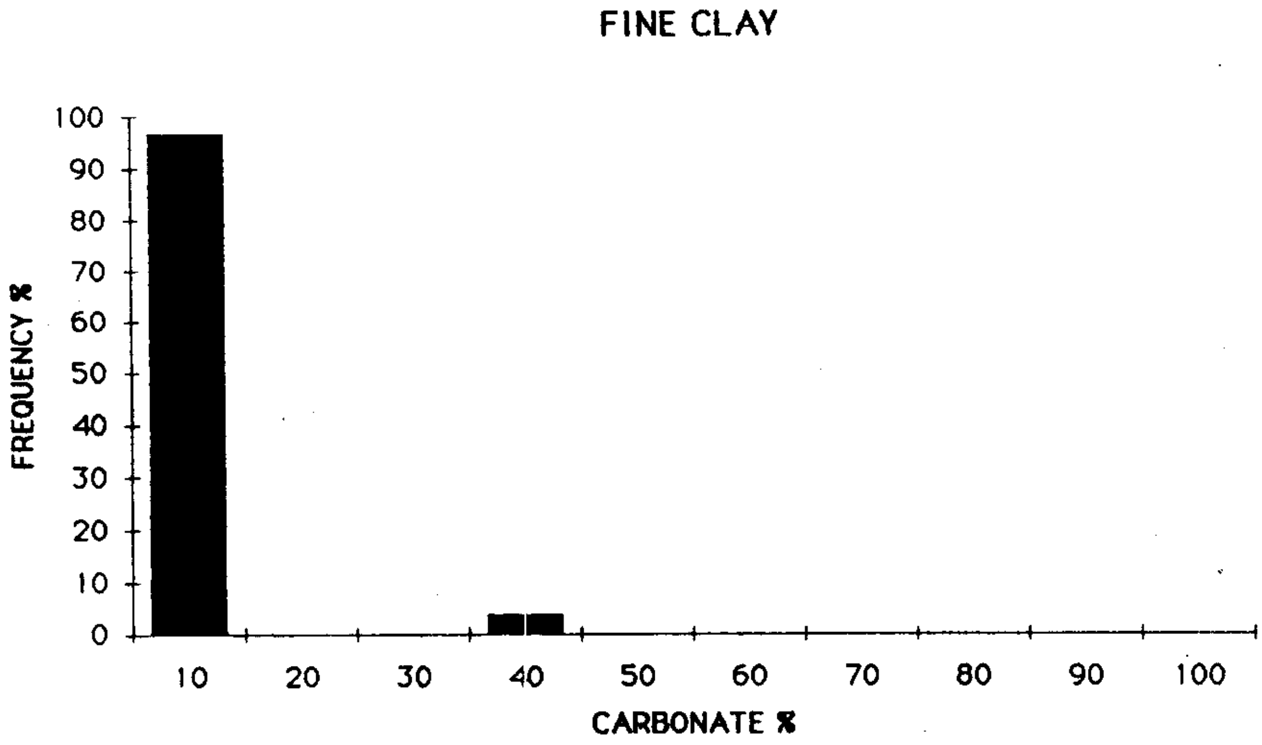

Fig.16. Frequency distribution of carbonate content of the fine-clay size fraction for 27 soils as a percentage of the total soil carbonate content, using the pH-stat dissolution procedure.

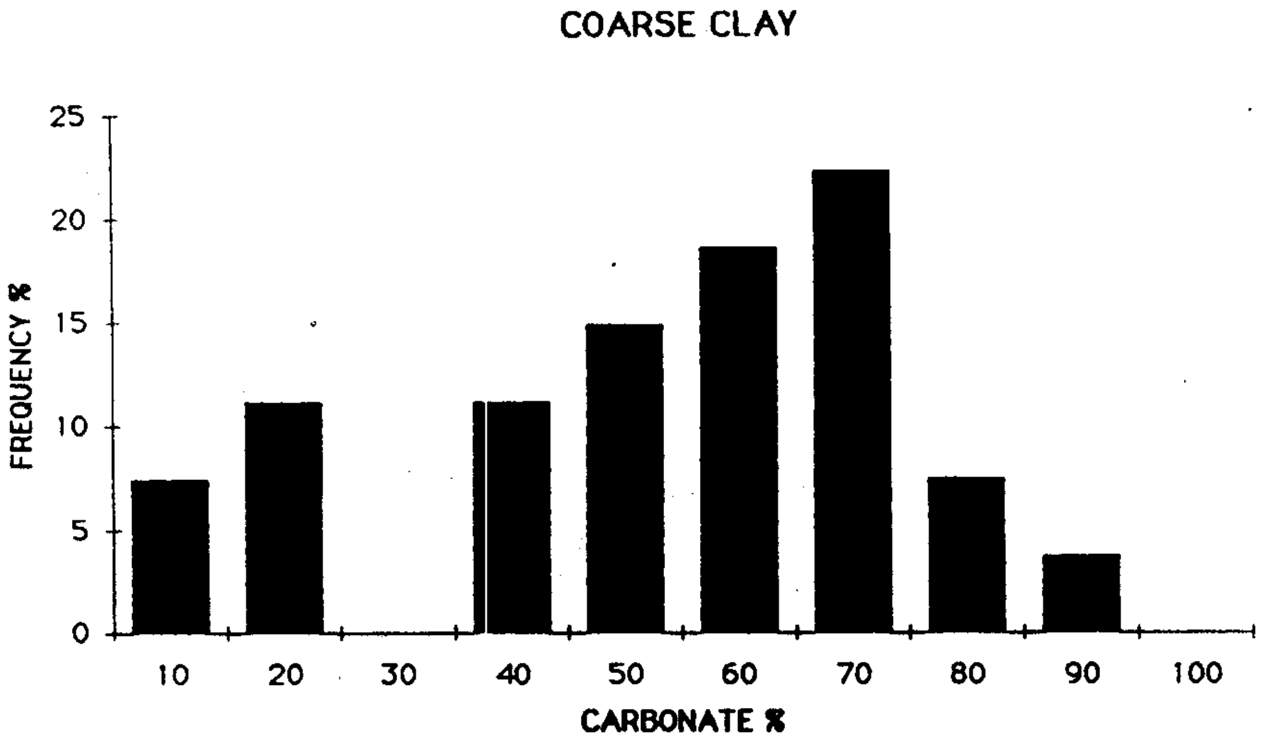

Fig.17. Frequency distribution of carbonate content of the coarse-clay size fraction for 27 soils as a percentage of the total soil carbonate content, using the pH-stat dissolution procedure.

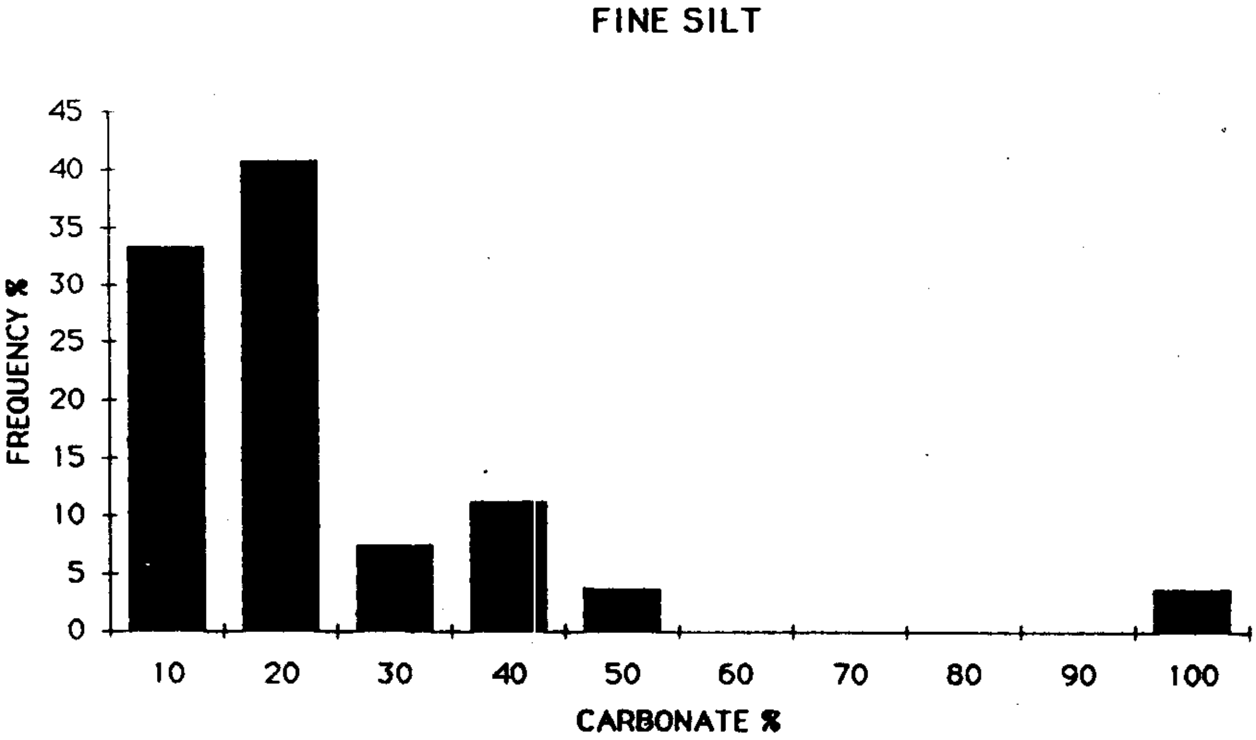

Fig.18. Frequency distribution of carbonate content of the fine-silt size fraction for 27 soils as a percentage of the total soil carbonate content, using the pH-stat dissolution procedure.

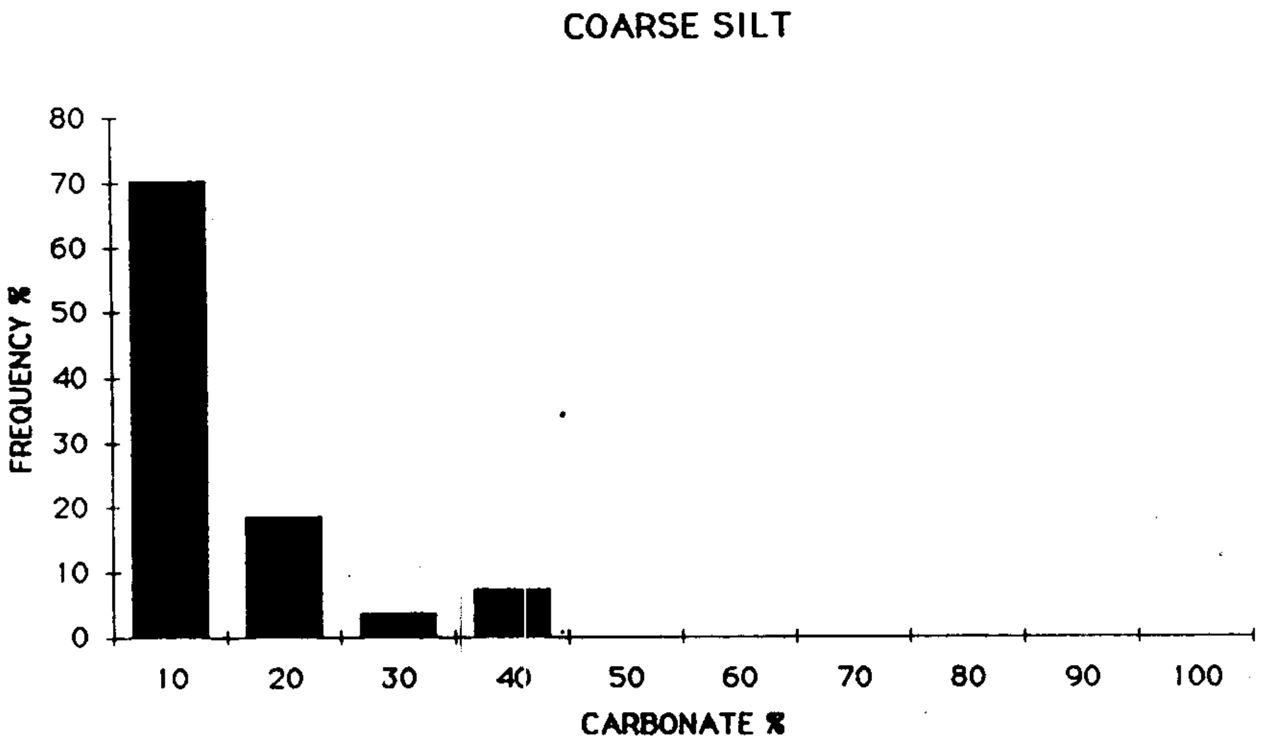

Fig.19. Frequency distribution of carbonate content of the coarse-silt size fraction for 27 soils as a percentage of the total soil carbonate content, using the pH-stat dissolution procedure.

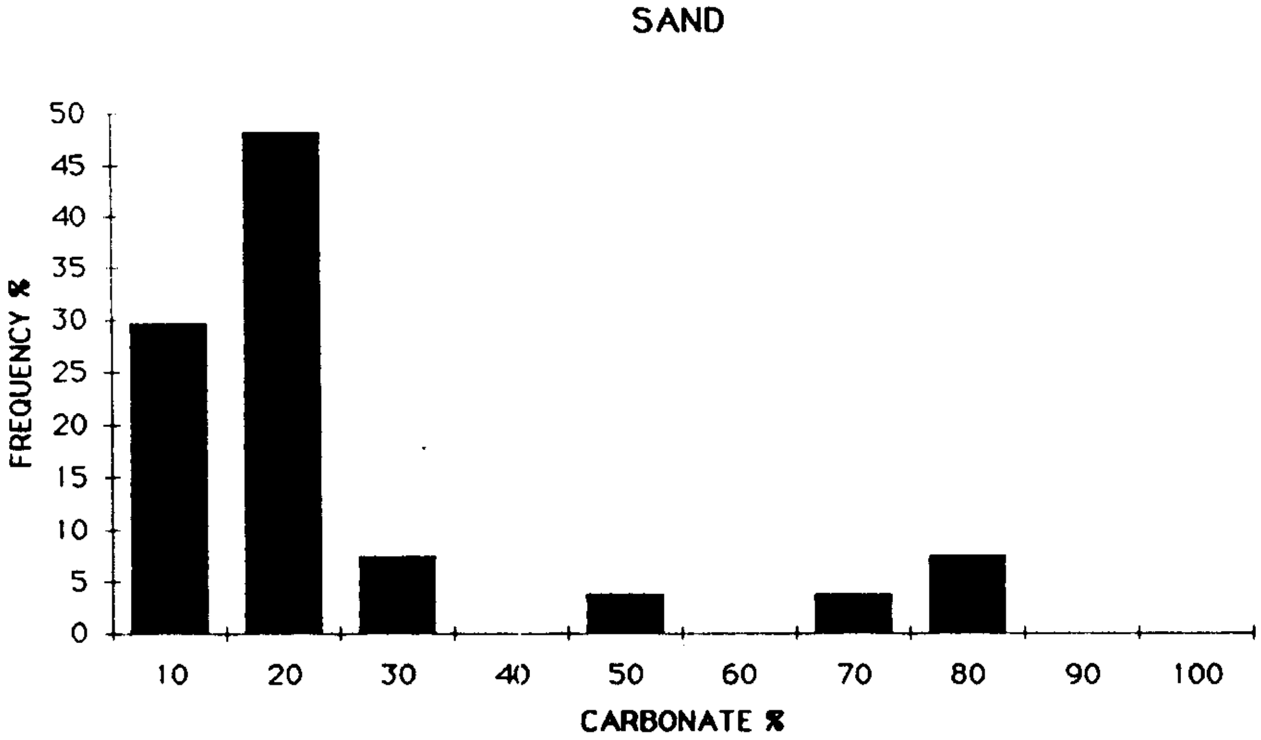

Fig.20. Frequency distribution of carbonate content of the sand size fraction for 27 soils as a percentage of the total soil carbonate content, using the pH-stat dissolution procedure.

ranged from 0.66 to 3.26 g pot^{-1}, Fe concentration ranged from 92 to 165 mg kg^{-1}, and Fe uptake by the plants ranged from 109 to 364 ug pot^{-1}.

Dry matter yield correlated positively with Fe uptake (r=0.911***), but negatively with Fe concentration (r=-0.476*) Table 8. The uptake of a nutrient would reflect the state of plant growth to a greater degree than its concentration. Greater yield usually leads to greater nutrient uptake, though the concentration of the nutrient may be decreased due to the expanded plant growth. This is referred to as "the dilution effect". Chlorophyll concentration (on a surface area basis) was also negatively correlated with the visual chlorosis evaluations (r=-0.742***). Also, dry matter yield and Fe-uptake correlated positively with chlorophyll concentration and negatively with visual chlorosis evaluations. Iron concentration in plant tissue did not show significant correlation with any of chlorosis, chlorophyll, or Fe uptake. It has previously been observed (Seckback,1982) that Fe concentration in plant was greater in chlorotic leaves than in none chlorotic leaves; and that plant Fe may be held in an inactive form as ferritinor Fe phosphate. Therefore, chlorophyll concentration and visual chlorosis evaluation are used as the main indicators for Fe stress.

Chlorosis along with other plant parameters and their correlations with soil parameters are summarized in table (9).

Soil iron oxide phase

Chlorophyll concentration of the plant tissue was positively correlated with Fe-oxides, especially with amorphous Fe-oxide where such a correlation was significant (r=0.457*), see table 9. These results agree with those obtained by Morris et al. (1990), who found that chlorophyll concentration in soybean was positively correlated with free Fe oxide and amorphous Fe oxide. Visual chlorosis evaluation showed a significant negative

Table 7. Means of the various plant growth indicators for soybean plants grown in sand-soil mixes.

Smple No.	Site	Chlorophyll ug cm^{-2}	Visual chlorosis ratings	Dry weight g pot^{-1}	Fe uptake ug pot^{-1}	Fe concentration mg kg^{-1}
1	El-Henwa (Egypt)	1.4	3.50	0.86	109	127
2	El-Mazrah ~	1.6	3.50	0.66	109	165
3	Tanta ~	8.7	0.00	2.75	336	122
4	Hoosh Essa ~	7.2	0.50	2.15	277	129
5	Kafer El-Dawar ~	6.3	0.00	1.79	211	118
6	West Noubaria 1 ~	3.3	1.25	2.48	229	92
7	West Noubaria 2 ~	6.0	1.50	2.54	289	114
8	East Noubaria ~	6.8	0.75	3.26	371	114
9	El-Amreea ~	1.8	4.00	0.90	120	133
10	Burg El-Arab ~	3.8	0.75	2.48	319	129
11	Reeves (USA)	2.4	1.50	2.14	211	99
12	Cameron ~	6.8	0.25	2.98	364	122
13	Bell ~	2.5	3.00	2.51	237	94
14	Coryell ~	5.3	0.25	2.02	242	120
15	Lubbock ~	6.4	0.75	3.19	349	109
16	Coryell ~	5.8	0.00	2.38	301	127
17	Reeves ~	1.4	2.00	1.52	176	116
18	Pecos ~	2.4	2.50	1.81	186	103
19	Hidalgo ~	8.0	0.50	2.66	274	103
20	Medina ~	4.7	0.75	2.19	212	97
21	Jones ~	4.1	0.50	2.46	275	112
22	Fisher ~	0.8	1.00	2.28	225	99
23	Coryell ~	6.3	0.25	2.77	239	105
24	Kleberg ~	3.5	1.25	2.43	266	109
25	Milam ~	4.6	0.50	2.19	230	105
26	Milam ~	5.2	0.00	2.68	356	133
27	Burleson ~	5.3	0.50	2.43	261	107

Table 8. Correlation coefficients (r) between various parameters of plant growth.

	Chlorophyll content	Dry weight	Fe uptake	Fe concentration
Visual evaluation of chlorosis	-0.742***	-0.723***	-0.745***	0.221
Chlorophyll content ug cm^{-2}		0.657***	0.723***	0.161
Dry weight			0.910**	-0.476*
Fe uptake				0.123

*, **, and *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively

Scored on a rating scale with 0 = no chlorosis, 4 = 100 % chlorosis.

correlation with amorphous Fe oxide (r = -0.468*) whereas with total free Fe oxide the correlation was not significant.

The processes involved in the dissolution and mobilization of soil Fe occur at the Fe-oxide particle surfaces ; therefore, the quantity, crystallinity , particle size and reactive surface area of the soil Fe oxides are important factors which influence availability of Fe to plants in calcareous soils . Since the amorphous Fe- oxide component has a high surface free energy and a high surface reactivity, it is therefore the most readily mobilized of the inorganic Fe sources within the soil (Vempati and Loeppert, 1988). The quantity of amorphous, or poorly crystalline Fe oxide has been shown to be a dominant factor influencing the availability of Fe to sorghum in calcareous soils (Loeppert and Hallmark, 1985). In the current study the correlation coefficients between the Fe-oxide parameters and the plant Fe-utilization parameters indicate that Fe-oxide reactivity plays an important role in influencing the availability of Fe to soybean.

Soil DTPA - extractable Fe.

Chlorophyll concentration in plant tissue showed positive correlation with DTPA-extractable Fe, r = 0.591**, table 9. Similar results were obtained by Morris et al. (1990). Visual chlorosis evaluations showed negative correlation with DTPA-extractable Fe (r = -0.528**). Similar results were obtained by Loeppert and Hallmark (1985) who assessed the growth of 2.5-week-old sorghum and found that DTPA-extractable Fe was negatively correlated with visual evaluation. Dissolution of soil Fe oxide by DTPA occurs as a kinetically controlled process at the oxide surface (Geiger and Loeppert, 1986), and the quantity of Fe extracted during the soil-test procedure is determined predominantly by the pH of the soil -DTPA suspension (Lindsay and Norvell, 1978) and the reactivity of the soil Fe-oxide phase (Geiger and Loeppert, 1986). Calcareous soils in the buffered DTPA solutions have similar pH values ; therefore the single most important factor influencing the

Table 9. Values of correlation coefficient (r) between some soil parameters and plant parametrs

Soil parameters	Plant parameters				
	Chlorophyll content	Dry weight	Fe uptake	Fe concentration	Visual evaluation of chlorosis
Total carbonate	-0.452*	-0.601***	-0.561**	0.398*	0.584**
Fine-clay ~~size-$CaCO_3$~~	-0.418*	-0.352	-0.400*	0.115	0.579***
Coarse-clay size ~	-0.455*	-0.643***	-0.624***	0.218	0.485*
Clay-size ~	-0.509**	-0.668***	-0.661***	0.225	0.571**
Fine-silt size ~	-0.166	0.193	-0.249	0.249	0.207
Coarse-silt size ~	-0.175	-0.363	-0.211	0.417*	0.286
Silt-size ~	-0.217	-0.315	-0.307	0.385*	0.297
Sand-size ~	-0.016	-0.016	0.077	0.211	0.191
pH (in H_2O)	0.299	0.326	0.354	-0.209	-0.607***
pH (in $CaCl_2$)	-0.290	-0.099	-0.096	0.002	0.355
Amorphous Fe oxide	0.457*	0.046	0.164	0.217	-0.468*
Total free Fe oxide	0.311	0.078	0.174	0.132	-0.378
DTPA-extractable Fe	0.591**	0.114	0.182	0.146	-0.528**

quantity of Fe extracted from calcareous soils during the DTPA soil test is reactivity of the Fe oxide phase. In the current study, DTPA-extractable Fe positively correlated with amorphous Fe-oxide content of the soil, r = 0.869***. The DTPA-extractable Fe is thus a relatively good quantitative indicator of the Fe oxide phase.

Soil $CaCO_3$

Chlorophyll concentration in plant tissue was significantly negatively correlated with total soil carbonate (r = -0.452*). Such a correlation was essentially brought about by the clay-size-fraction of carbonate (r = -0.599**), which constituted the greatest portion of soil carbonate (see table 6). Correlation coefficients between chlorophyll concentration and other size fractions of carbonate (silt and sand sizes) were not statistically significant. These sizes constitute little portion of soil carbonate (see table 6). Such an adverse effect of soil carbonate on plant was also shown when chlorosis was significantly positively correlated, with total soil carbonate content, which is caused mainly by the clay-size portion of carbonate. These results are in agreement with those by Inskeep and Bloom (1987) who found that total and clay-size calcium carbonates in soil, as well as, their surface area influence the extent of Fe chlorosis in soybean. However, such results are not in agreement with those on sorghum carried out by Loeppert et al. (1988) who reported no significant relationships between visual chlorosis ratings and both total soil carbonate content and clay-size carbonate content.

The rhizosphere pH in a calcareous soil is influenced by two important (and often competing) processes: (i) the modification of the root environment by plant and microbial exudates, and (ii) the production of HCO_3^- ions, hence the buffering influence of soil carbonates. Since the dissolution of soil carbonate minerals occurs as a surface reaction, the buffering influence of soil carbonates as well as soil pH are highly influenced by $CaCO_3$ reactive surface area. On the other hand, acidification of the rhizosphere by root exudates of soybean would be an important component of the membrane-bound Fe^{+3} reductase mechanism and the Fe-deficiency stress response of plants (Marschner et al., 1986).

The reactivity of the soil carbonate phase plays an important role in influencing the effectiveness of the Fe-stress with soybean. In their study with sorghum Loeppert and Hallmark (1985) reported that the concentration and reactivity of the soil carbonate phase in calcareous soils had no influence on the incidence of Fe chlorosis. They concluded that $CaCO_3$ equilibria play a more important role than carbonate reactivity in influencing the incidence of Fe chlorosis . When Marschner et al. (1986) grew sorghum under Fe-deficiency stress conditions, the rhizosphere pH was not significantly reduced ; i.e., acidification of the rhizosphere was not an important component of the Fe-stress response mechanism of sorghum. Therefore, with sorghum we could not expect carbonate reactivity to significantly influence the incidence of Fe deficiency chlorosis, compared with soybean, (Morris et al., 1990).

Soil pH.

As data shown in table 9, the chlorophyll concentration of the plant tissue was showed no significant correlation with soil pH in $CaCl_2$ suspension or with pH in H_2O suspension. Variations in soil pH among the 27 soils was not very pronounced. Values of pH in water suspension ranged from 7.7 to 8.2 and those of pH in $CaCl_2$ ranged from 7.1 to 7.9 (see table 2). However, visual chlorosis evaluation was negatively correlated with pH in water (r = -0.607***). Suitable pH range for prevention of chlorosis is usually that of near nutrality (Wallace and Mueller, 1978)

3 : REACTIONS BETWEEN IRON AND PHOSPHATE IN CALCAREOUS SYSTEMS

This particular study was conducted to (i) identify the predominant Fe-containing compounds formed under high pH and P conditions, and (ii) investigate the reactions of Fe^{3+} with phosphate in the presence of $CaCO_3$.

Powder x-ray diffraction (XRD)

The results of x-ray diffraction for the ferric hydroxide and ferric phosphate compounds are illustrated in Figures 21 to 25.

Fe-containing compounds formed under high pH

The Fe-containing compounds formed by reacting $Fe(ClO_4)_3$ and NaH_2PO_4 under high pH (8.0) conditions by using NaOH were subjected to XRD analysis. The results of x-ray diffraction for the ferric hydroxide and ferric phosphate compounds are illustrated in Figure 21 showing four peaks. Peak 1 concerns sample 1 of the 0:1 P:Fe molar ratio. Peaks 2, 3, and 4 are for samples 2, 3, and 4 with respective of P:Fe ratios of 0.11:1, 0.33:1 , and 3:1. The general shape of the broad peaks (Fig. 21) indicate amorphous compounds. Sample (1) which was prepared by reacting $Fe(ClO_4)_3$ with NaOH gave a peak with d spacing of 2.54 A° which is very close to the ferrihydrite peak (d = 2.56 A°). However, the other samples (2, 3 , and 4) gave broad peaks with d spacings of 2.6, 2.73, and 2.90 A° respectively. The widths of the half height (WHH) were 2.8, 2.8, 3.2, and 3.2 cm for samples 1, 2, 3, and 4 respectively.

Figure 22 shows the x-ray diffraction pattern of the other variation of sample 4 which had a 3:1 P:Fe molar ratio, but titrated with NaOH to the first inflection point only. While in the case of sample 4 which had a P:Fe molar ratio of 3 : 1, the d spacing was 2.90 A°, this other sample of the same P:Fe molar ratio has a broad band with d spacing 3.048 A°. Such differences between the two samples reflects the differences in the product composition and particle size.

With increasing P concentration, the major XRD band was shifted from 35.11 to 30.84 °2O (Fig. 21). This shift may be attributed to changes in both particle size and product composition.

Fe-containing compounds formed under calcareous system

The Fe-containing compounds which formed by reacting $Fe(ClO_4)_3$ with NaH_2PO_4 in presence of $CaCO_3$ (0.212 - 0.254 mm) were subjected to XRD analysis. The results of XRD are illustrated in Figures 23 - 25. The diffraction patterns of The two samples having P:Fe ratio of 0 1 are shown in figure 23. One of these samples represented the reaction between $Fe(ClO_4)_3$ with $CaCO_3$ and showed a pattern having 5-line peak with d spacing 2.51, 2.23, 1.91, 1.71, and 1.51 A°. This pattern is similar to that of 5-line ferrihydrite peak of 2.54, 2.24, 1.97, 1.73 and 1.47 A° (Dixon and Weed,1989).

With regard to samples having P:Fe molar ratios of 0.11:1 and 0.33:1 their patterns were rather similar whether with NaOH or with $CaCO_3$ (see figures 24 and 25).

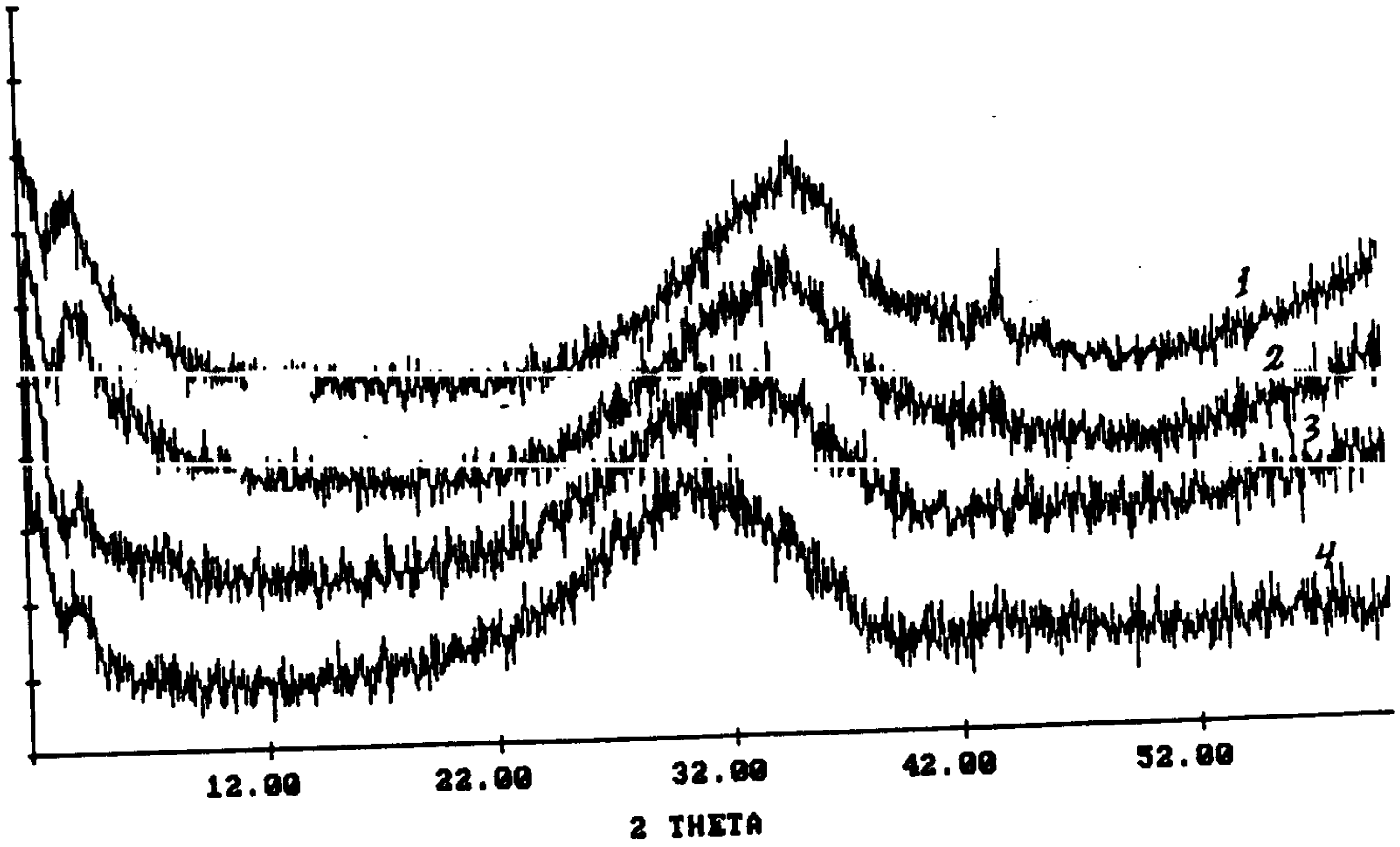

Fig.21. X-ray diffraction patterns of Fe-containing compounds:(1) 0:1, (2) 0.11:1, (3) 0.33:1, (4) 3:1 P:Fe molar ratio.

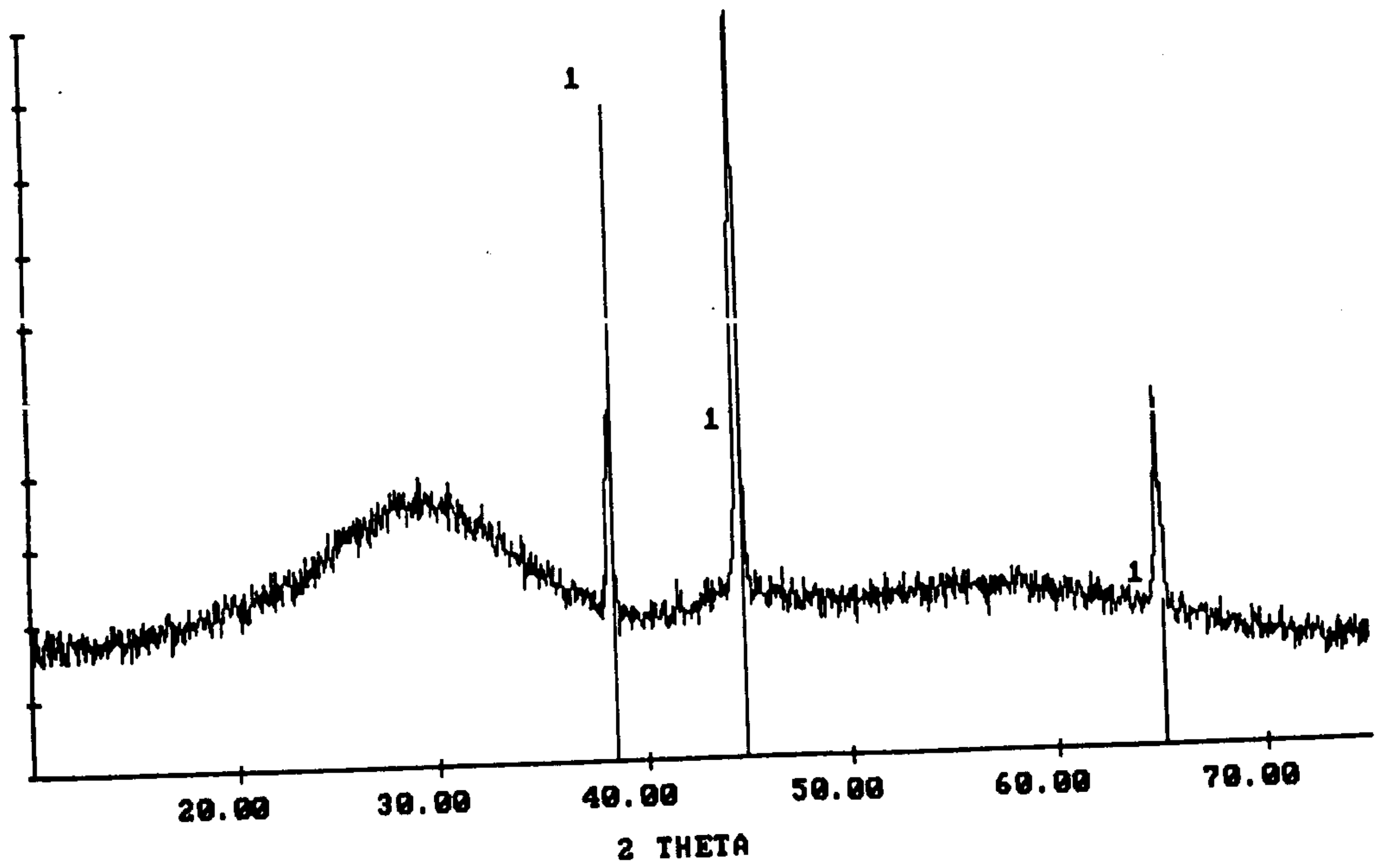

Fig.22. X-ray diffraction pattern of Fe-containing compound (3:1 P:Fe molar ratio, titrated with NaOH to first inflection point).

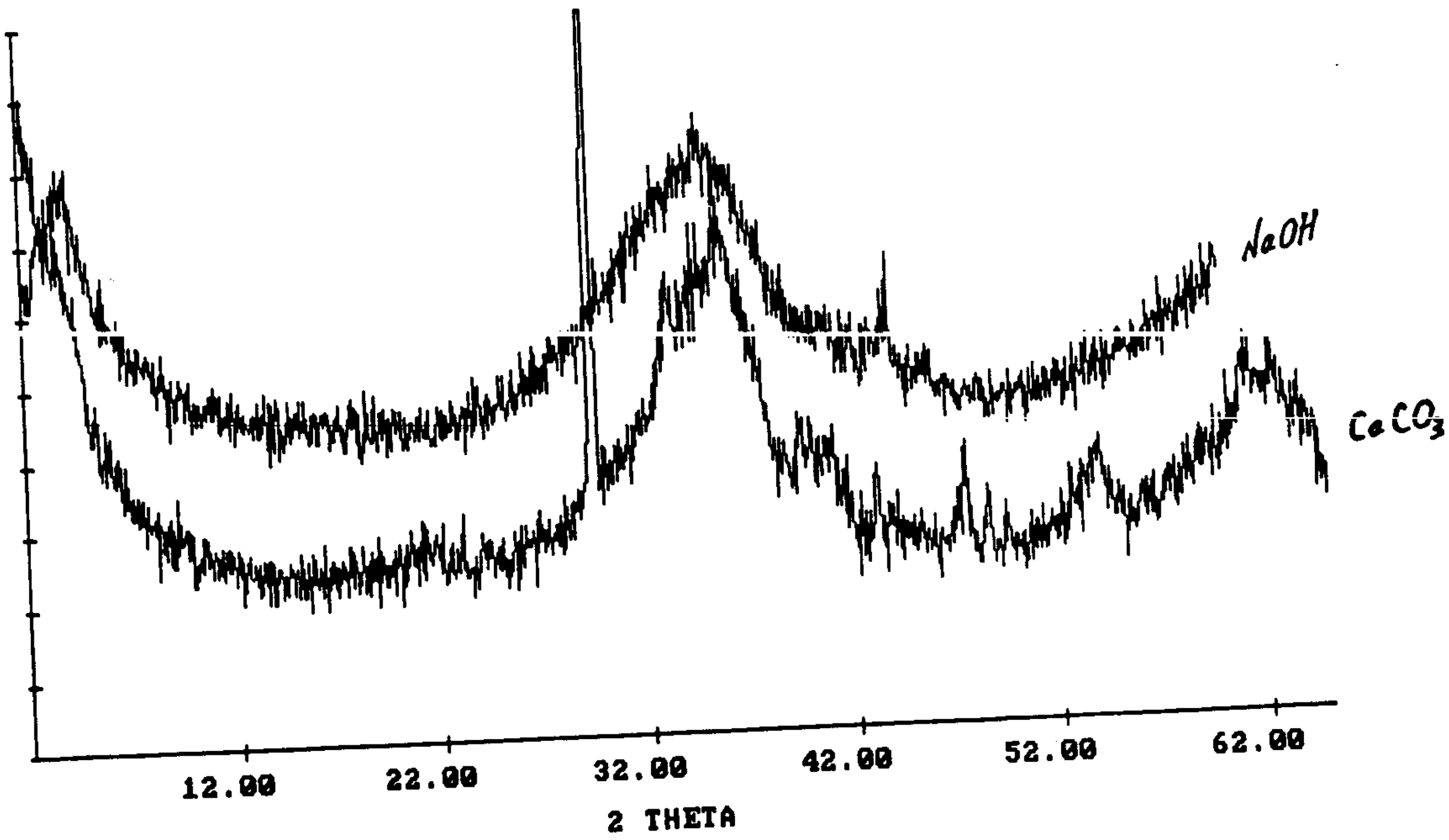

Fig.23. X-ray diffraction patterns of Fe-oxides (1) formed by reacting $Fe(ClO_4)_3$ with NaOH, and (2) formed by reacting $Fe(ClO_4)_3$ with $CaCO_3$.

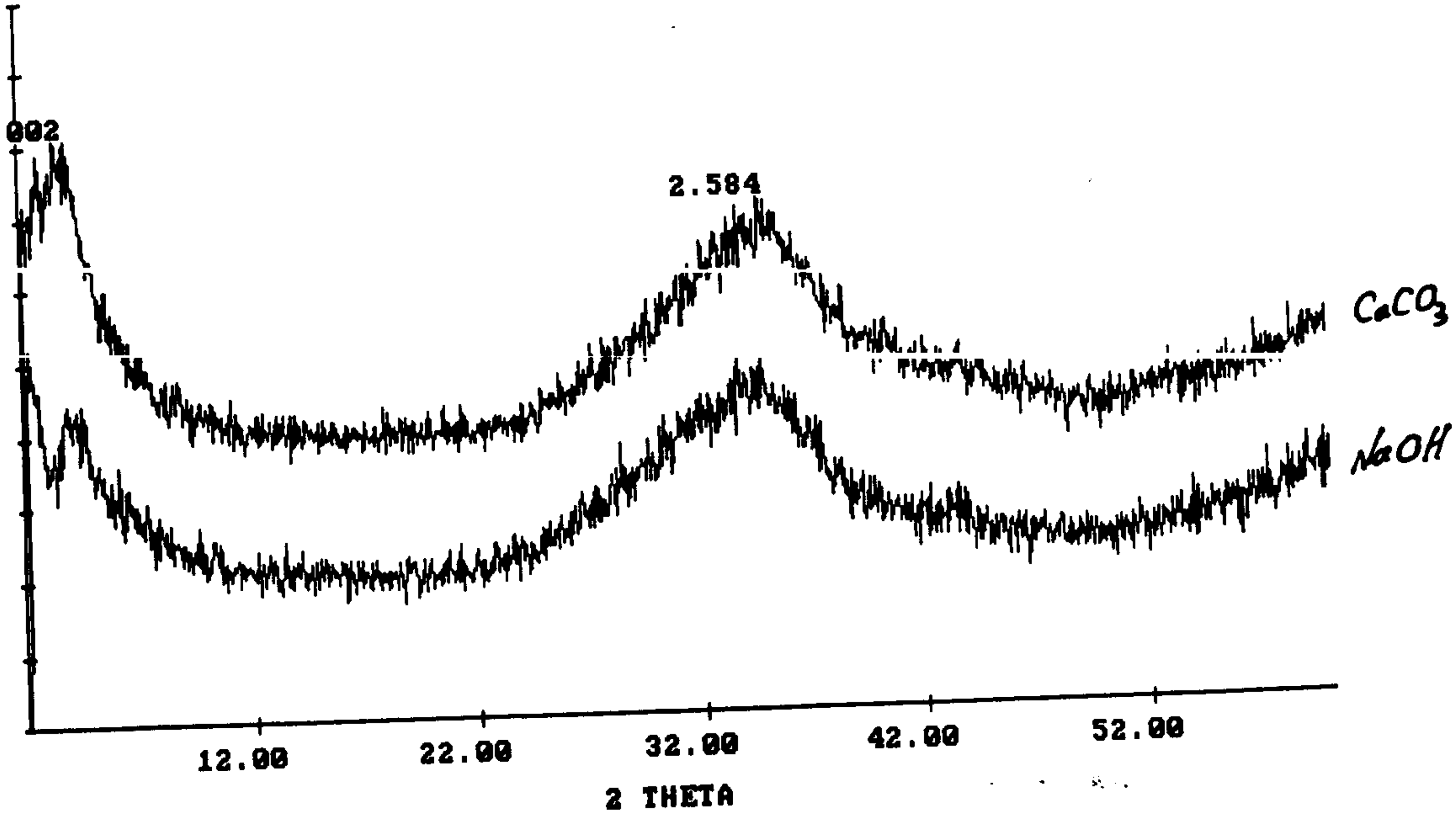

Fig.24. X-ray diffraction patterns of the Fe-containing compounds 0.11:1 P:Fe molar ratio, (1) formed by reacting with NaOH, (2) formed by reacting with $CaCO_3$.

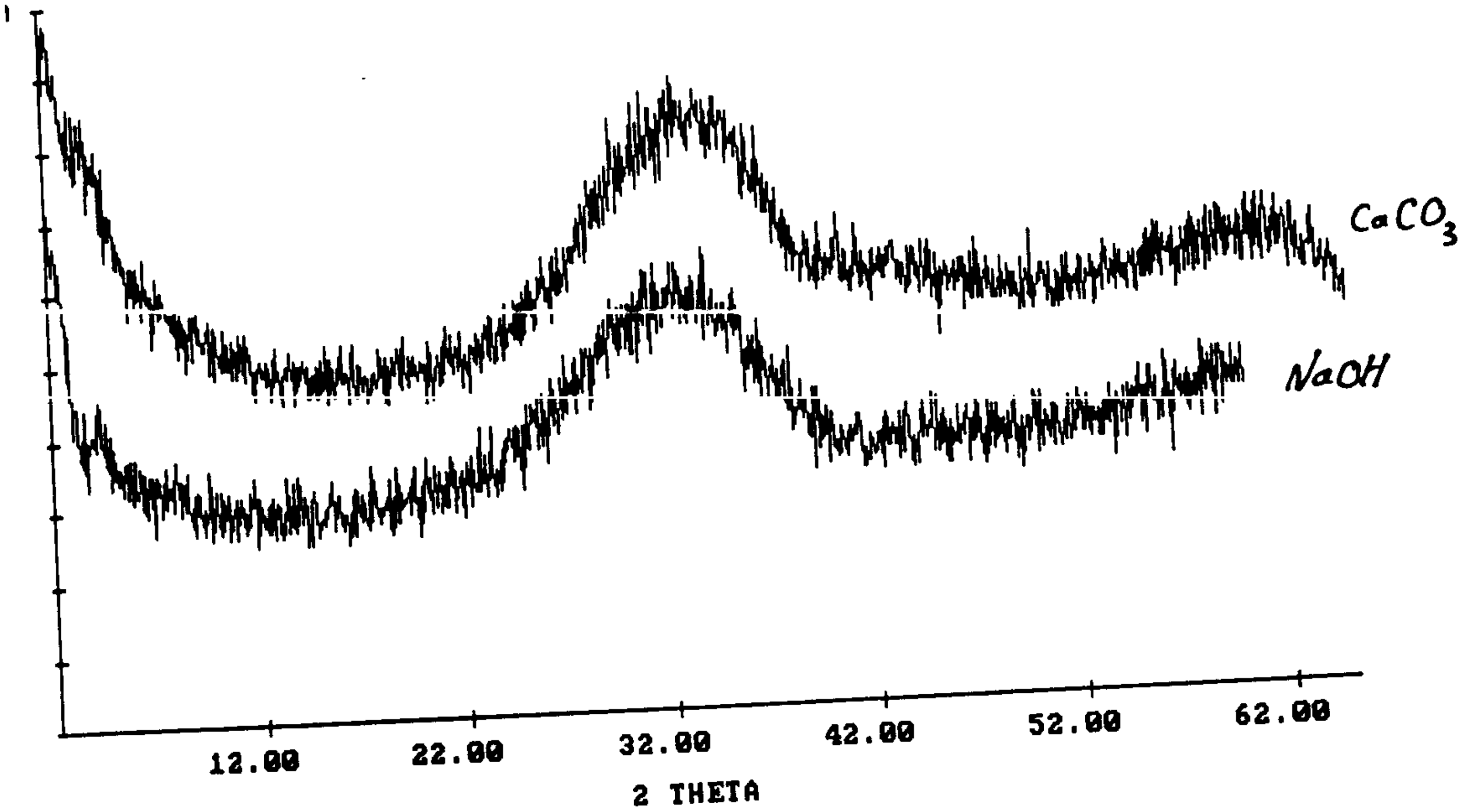

Fig.25. X-ray diffraction patterns of the Fe-containing compounds 0.33:1 P:Fe molar ratio, (1) formed by reacting with NaOH, (2) formed by reacting with CaCO$_3$.

Transmission Electron Microscopy (TEM)

The results of the TEM are shown in Figures 26 to 29. These results indicate that the particle size of Fe-containing compounds was influenced by P:Fe molar ratio. The dominant particle sizes are summarized below.

Sample number:

1- at P : Fe ratio 0:1 the dominant particle size is 5 - 10 nm

2- at P : Fe ratio 0.11:1 the dominant particle size is 5 nm

3- at P : Fe ratio 0.33:1 the dominant particle size is 2.5-7.5 nm

4- at P : Fe ratio 3:1 the dominant particle size is smaller particles 10 nm; with some larger ones around 50 to 100 nm.

From high phosphate to low phosphate concentration, the cluster morphology went from clusters of larger particles to those of smaller particles. The particle sizes in the samples of ratios of 0:1, up to 0.33:1 were around a range of 2.5 to 10 whereas with the high molar ratio of 3:1, the particle sizes were far greater. Especially notable is the bimodal particle size distribution of the 3.0 P:Fe molar ratio sample, the larger particles are likely to be ferric phosphate.

During observation of particles formed with molar ratios of 0:1 up to 0.33:1 P:Fe, it was difficult to find isolated particles, since most particles were aggregated. The presence of Fe and P is evidently shown by Electron diffraction pattern (EDP) analyses of some of the particles formed with the 3:1 P:Fe ratio (see figure 29).

Scanning Electron Microscopy (SEM) and energy-dispersive x-ray analysis

The sediment of calcite particles coated by Fe-containing compounds were examined by the scanning electron microscopy (SEM) and energy-dispresive x-ray analysis (EDXRA). The SEM for the 0:1 P:Fe molar ratio product revealed the presence of the

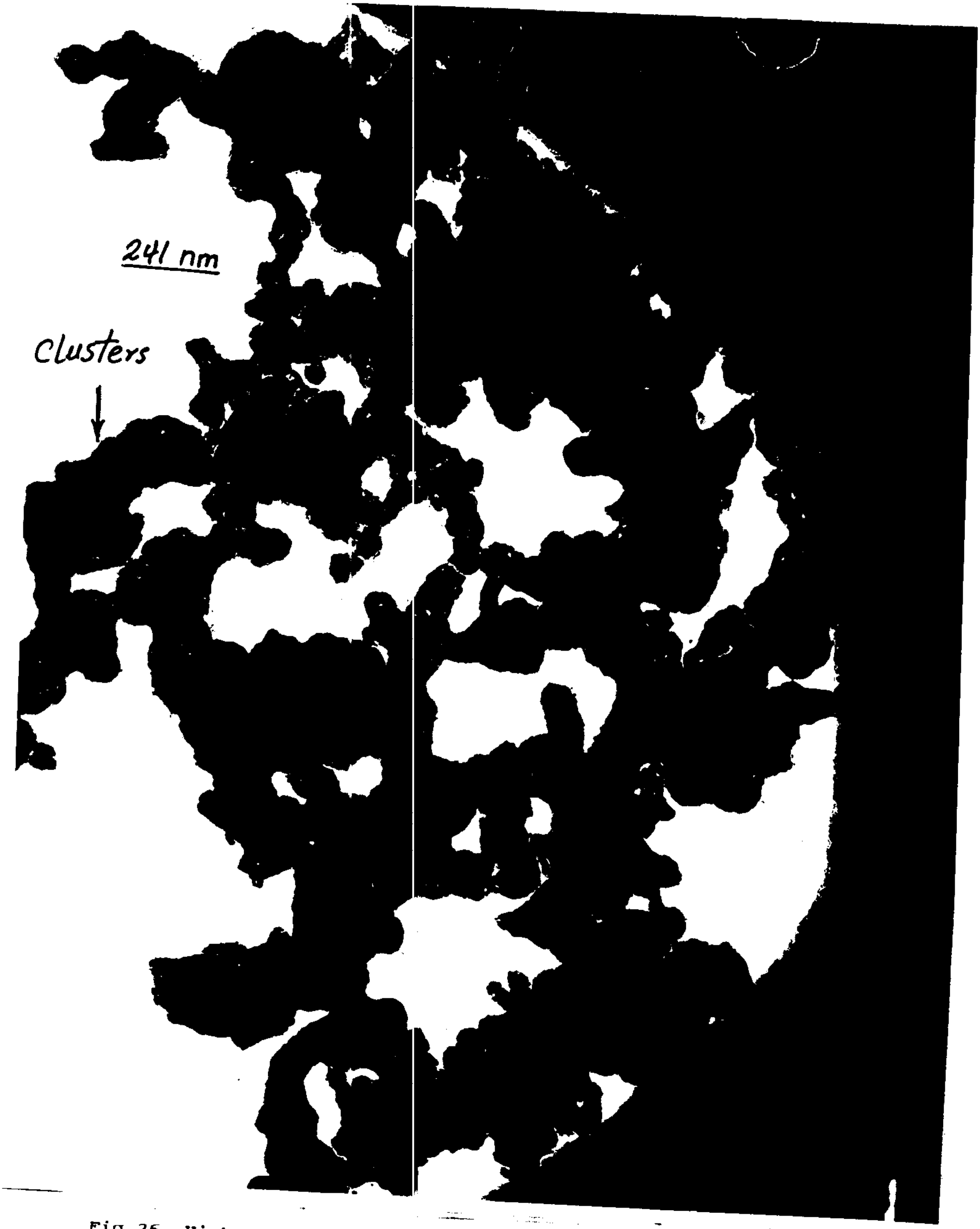

Fig.26. High magnification transmission electron micrograph of 3:1 P:Fe molar ratio product (clusters).

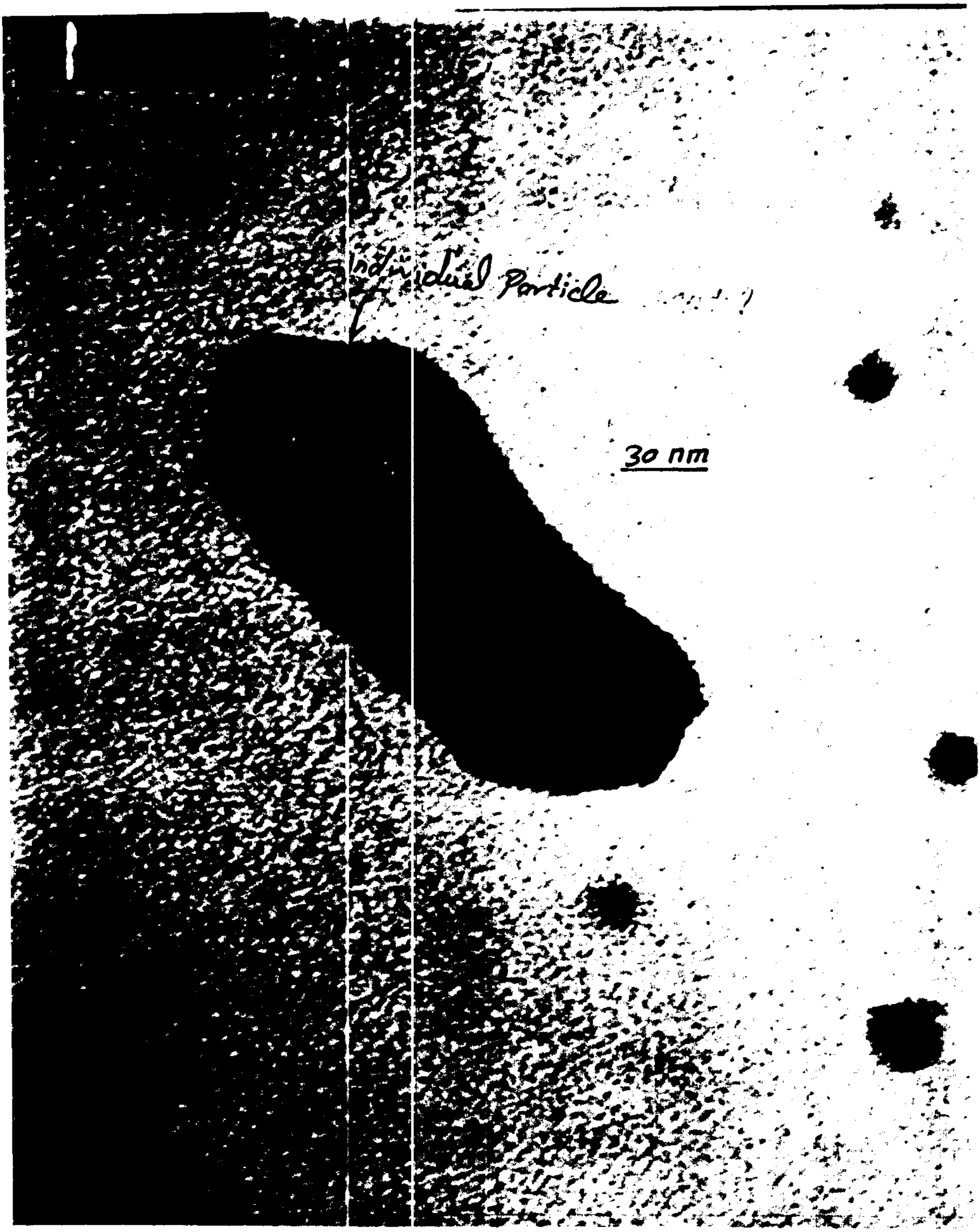

Fig.27. High magnification transmission electron micrograph of 3:1 P:Fe molar ratio product (individual particle).

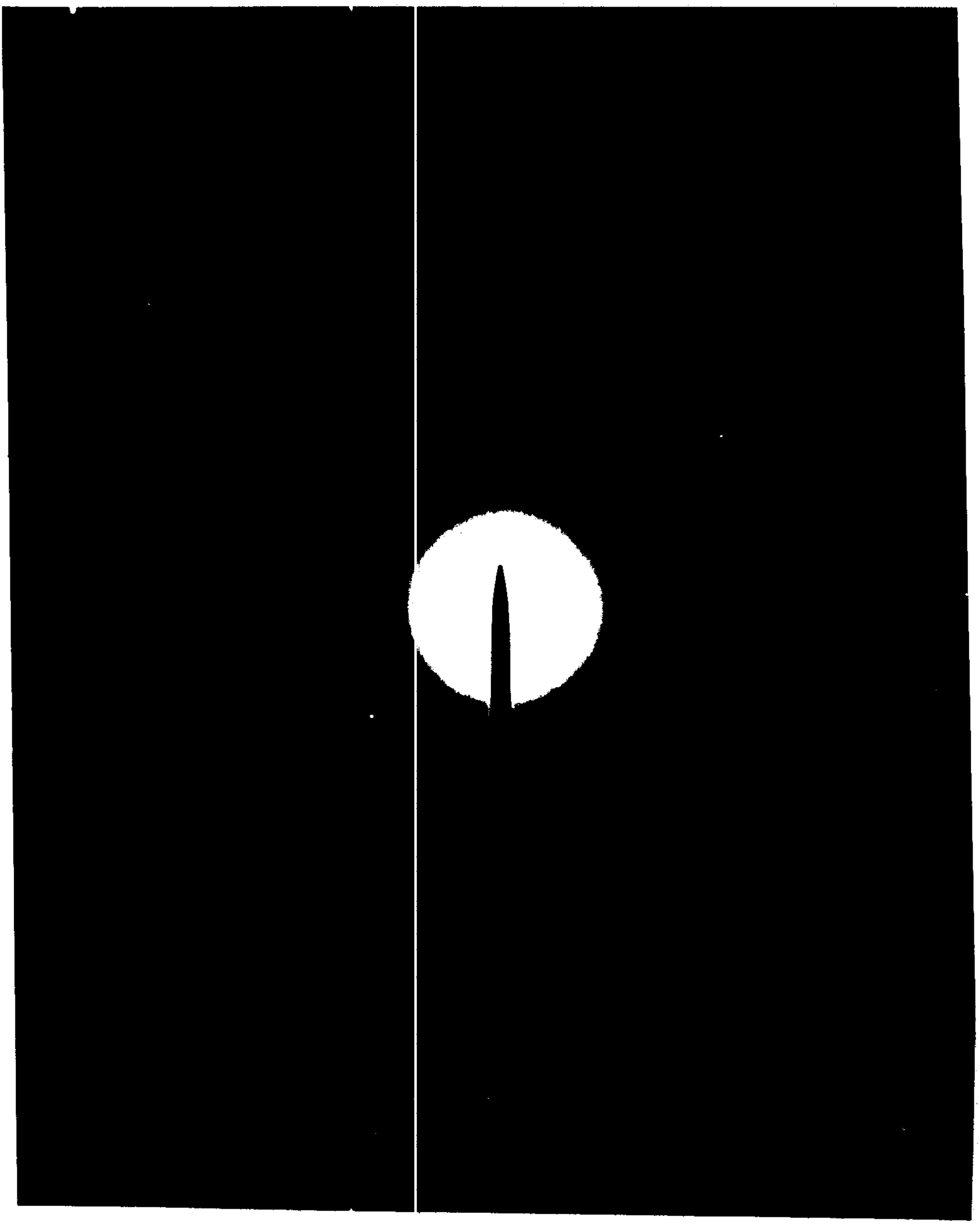

Fig.29. Electron diffraction pattern of 3:1 P:Fe molar ratio product.

ferrihydrite on the calcite particle as shown in Fig. 30. The EDXRA of the same sample shows the direct observation of Fe and Ca as shown in Fig.31.

In all samples having Fe^{+3} and H_2PO_4 ions, flakes of ferric calcium phosphate coatings on calcite particles were clearly shown (Fig. 30-37).

In the case of 0.11:1 P:Fe molar ratio product, the SEM revealed the presence of more flakes containing ferric calcium phosphate coating the calcite particles (Fig.32). The EDXRA of the sample (Fig. 33) resulted in the direct observation of Fe ,Ca, and PO_4^{-3}, with the concentration of Fe being such higher than those of Ca and P.

In the case of 0.33:1 P:Fe molar ratio product, the SEM study revealed the presence of rough flakes of ferric calcium phosphate as shown in Fig.34. The EDXRA of the sample (Fig. 35) resulted in direct observation of Fe, Ca, and PO_4^{-3}.

In the case of using 3:1 P:Fe molar ratio product, the SEM study revealed the presence of ferric calcium phosphate and coating the calcite (Fig.36). Also the EDXRA of the sample(Fig. 37) resulted in direct observation of Fe, Ca, and PO_4^{-3} , but the amount of P is high in this product compared with Fe or Ca.

DTPA extractable Fe as affected by P:Fe molar ratio

The DTPA- extractable Fe was affected by P:Fe molar ratio ranging from 0:1 to 2:1 (Table 10 and Fig.38). The amount of DTPA-extractable Fe increased with the increase in P level, and then decreased at the highest P level, i.e., 2:1 P:Fe molar ratio.

Phosphate ligand is readily bound to the Fe-oxide surface and may result in a reduction of normal polymerization and crystal growth. This results in Fe-oxide crystals of smaller particle size, from which Fe is more readily released upon reaction with DTPA.

Fig.30. Scanning electron microscopy for the 0:1 P:Fe molar ratio product, note the presence of ferrihydrite flakes on the cacite particle (arrow)..

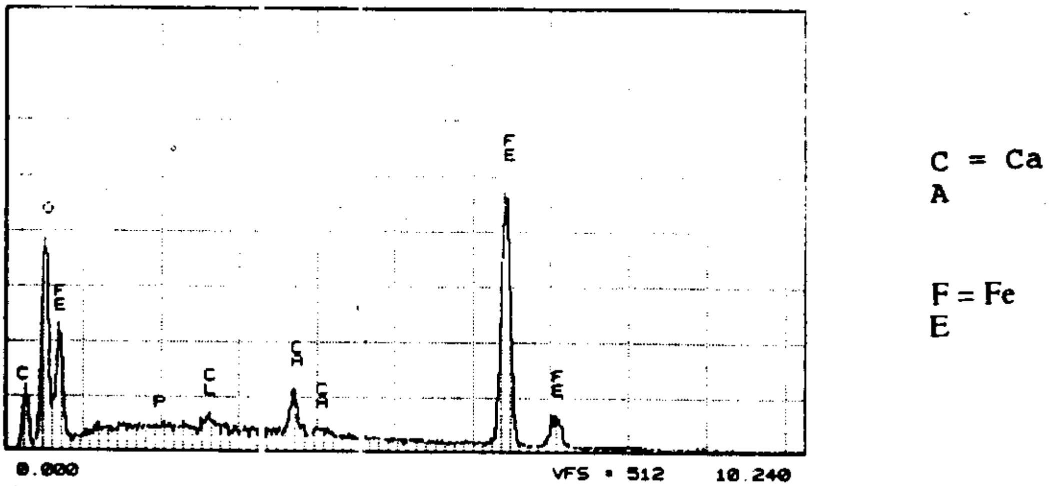

Fig.31. EDXRA spectra collected from particle shown in Fig.30., note the presence of Fe and Ca.

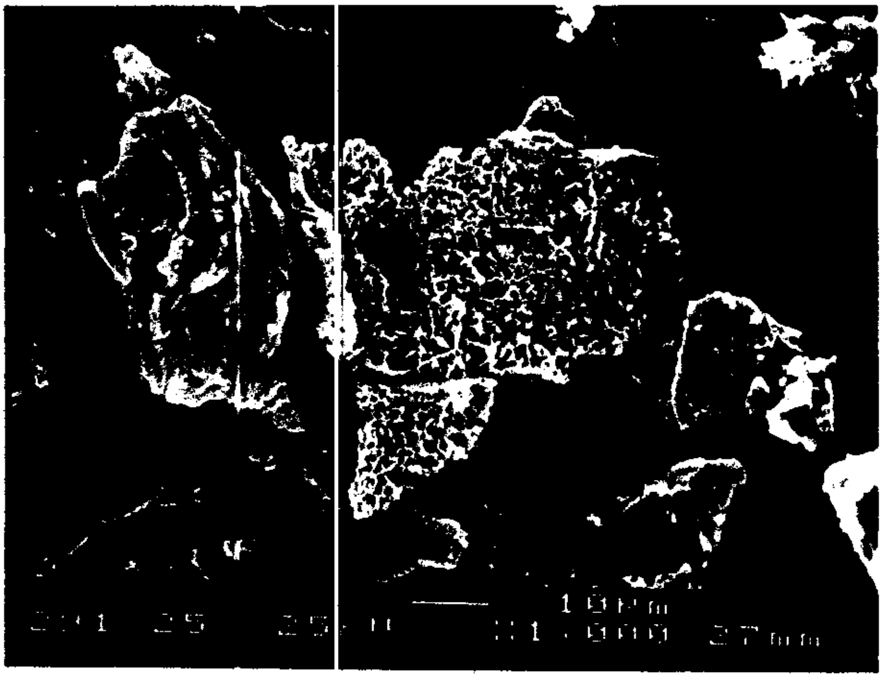

Fig.32. Scanning electron microscopy for the 0.11:1 P:Fe molar ratio product, showing flakes of material containing ferric-calcium phosphate coating the calcite particles.

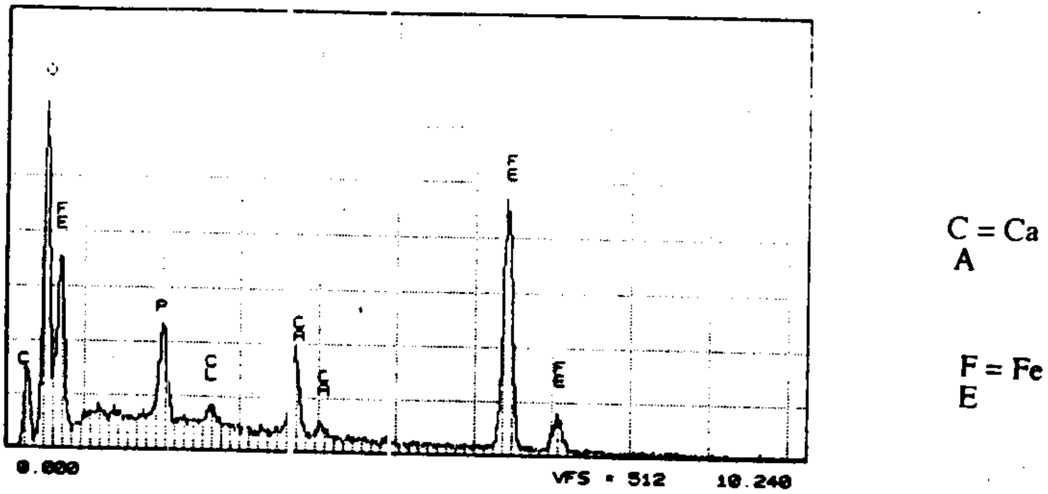

Fig.33. EDXRA spectra collected from particle shown in Fig.32., note the presence of Fe, Ca, and P.

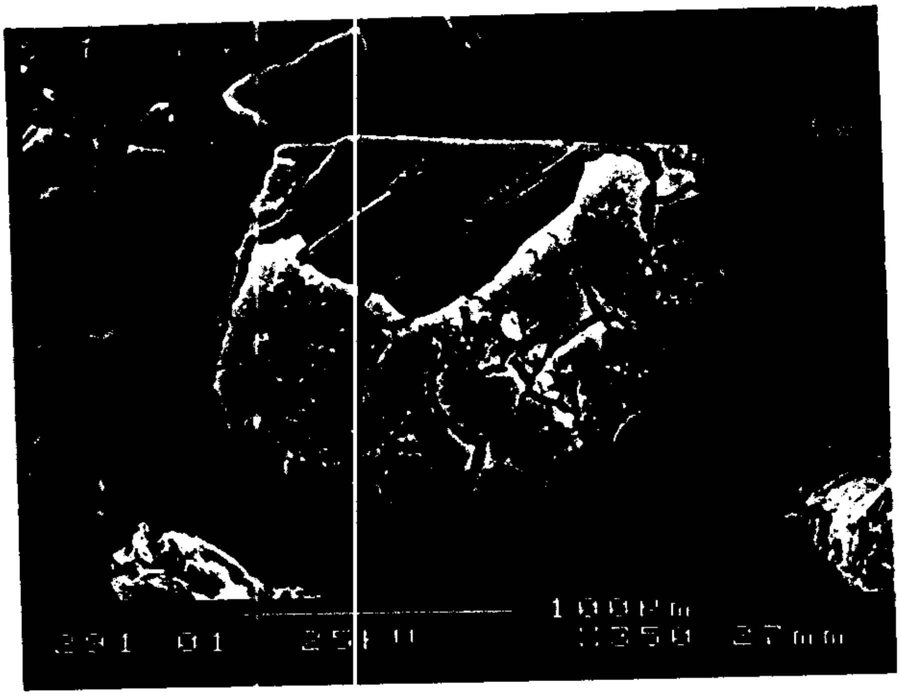

Fig.36. Scanning electron microscopy for the 3:1 P:Fe molar ratio product, showing flakes of material containing ferric-calcium phosphate coating the calcite particles

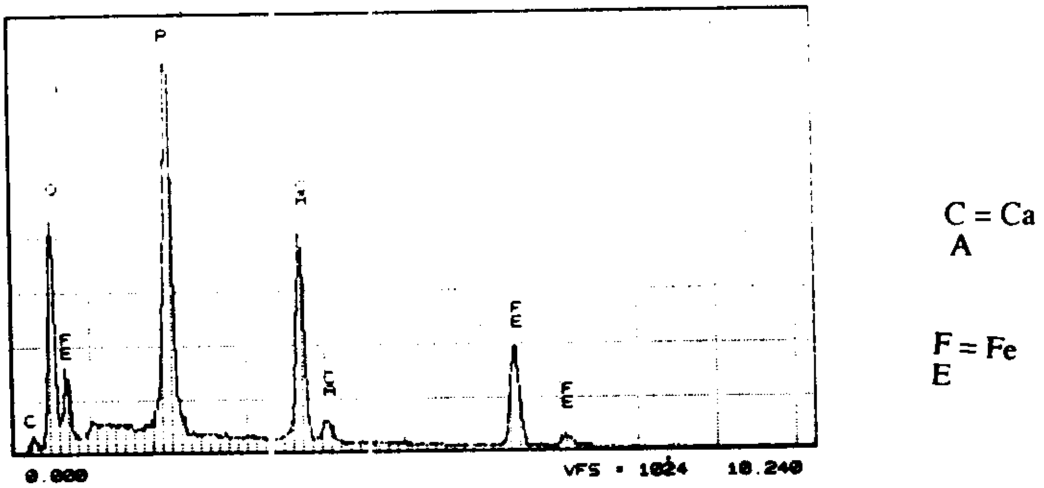

Fig.37. EDXRA spectra collected from particle shown in Fig.36., note the presence of Fe, Ca, and P.

When the amount of P was increased to the higher level, ferric phosphate was formed, with a resulting decrease in the rate of release of Fe.

Table 10. DTPA-extractable Fe as affected by P:Fe molar ratio.

Sample No.	$CaCO_3$ fraction mm	NaH_2PO_4 mmole	$Fe(ClO_4)_3$ mmole	P : Fe ratio	DTPA-extractable Fe mg
1	< 0.254	0.00	0.13	0 : 1	0.149
2	< 0.094	0.00	0.13	0 : 1	0.179
3	< 0.094	0.07	0.13	0.5 : 1	1.000
4	< 0.094	0.13	0.13	1 : 1	0.533
5	< 0.094	0.26	0.13	2 : 1	0.370