

MICRO-NUTRIENT FORMULATIONS FOR AGRICULTURE

Part I. Copper and Chromium Preparations

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Production of micronutrient carriers and their evaluation by controlled leaching of trace elements is described. Three sets of formulations have been prepared by mounting copper and chromium oxides separately on sintered, fritted and nonfritted compositions. They have been subjected to extraction with ammonium citrate solution and the release of metal monitored by using an atomic absorption spectrograph. The results show that released of copper can be controlled in the range of 2.45-5.74 and 18.75-19.60 ppm while that of chromium can be limited to 0.068-0.43 and 0.247-2.09 ppm by using fritted, sintered and non-fritted compositions respectively, large and instantaneous quantities of the two metals can be obtained by using nonfritted compositions. In both cases, the released of chromium is much smaller than that of copper.

Key words: Micro-nutrient, Agriculture, Copper, Chromium.

Introduction

It is now well established that yield of crops particularly those of wheat, cotton, rice, maize, sugarcane and potatoes is in general quite low in Pakistan. One of the main reasons for the low yield is that a proper and adequate mix of macro- and micro-nutrients is required for optimum growth of plants is not made available to the soils.

Status of the soil with respect to micronutrients in Pakistan is not yet established. Surveys reported to-date have suggested that 85% soil samples collected from the four provinces are either at marginal level or deficient in zinc and copper [1, 2, 3]. It was pointed out in an earlier paper that irrigation practice contributes to accumulation of salts in the soil and builds up salt stresses thus contributing to the deficiency in the micronutrients [4] in the macroenvironment of the plants leading to disturbance in the electrolyte balance in the microenvironment [5]. The stated conditions are therefore not conducive to healthy growth of crops and this is the predominant feature of Pakistani agriculture.

Quantitative relationship between micro and macronutrient additions on the one hand and growth and yield of crops on the other hand is already known to exist [6]. It is also established that a single element which compensates for the deficiency of a crop or crops cannot be suggested. However, it is found that some plant species benefit more from certain elements than the others. Estimates of critical levels of micro- and macro-nutrients in plants/crops show that 9 ppm Cu is the normal value for maximum wheat output while the range of critical values is 8-20 ppm and for maize the range is 5-30 ppm Cu [7].

In view of the importance of micronutrients certain

formulations were developed [8] and field tested for their role in correcting the deficiency [9]. The said formulations contained silicate melts of metal oxides. Having very low solubility in water, the release of the desired metal was low. Consequently there was need for the development of a formulation to mount the nutrients on suitable carriers and to study their release characteristics to offer specific quantities of nutrients under different conditions. A formulation such as the above would have the advantage of effecting sustained release of nutrients which may be sufficient for reasonably long periods. This might facilitate their uniform distribution and at the same time would avoid the building up of excessive quantities in the macroenvironment of the plant, thus reducing the consequent toxic effects.

This study reports the production and release characteristics of copper and chromium as micro-nutrients mounted separately on frits, red clay, plaster of paris, cement-sand mixture and plaster of paris-sand mixture.

Experimental

Four micronutrient compositions were prepared and fired at two different temperatures using carriers mentioned in Table 1. Compositions V to X were neither sintered nor fritted but were prepared by mixing the constituents thoroughly, wetting with water, drying and grinding the product to pass through a 200 mesh sieve.

The release of the micronutrients was studied by placing 2 gm each of the compositions in a plastic bottle filled with 450 ml of IN ammonium citrate solution. The contents of the bottles were occasionally stirred, allowed to settle for about half an hour and 5 ml solution was taken out of each bottle after 1, 2, 3, 4, 6, 24, 30, 48, 72 and 240 hours and

the two metals were analysed by atomic absorption spectrophotometry. The results are listed in Table 3, 4 and 5 and depicted in Figs. 1-4.

Results and Discussion

There are a number of alternatives to obtain a sustained release of metals, each of them devolves over preparation of insoluble compounds of the element concerned. Some of the methods listed in Tables 1 and 2 are concerned with (1) preparing frits by firing a mixture containing raw ores, soda ash and the oxide of the metal, to obtain a melt and quenching it by pouring over cold water; (2) sintering a mixture of red clay and the metal oxide with and without approximately 9% by weight of soda ash at 1000°; (3) preparing mixtures and metal oxide, and plaster of paris and metal oxide; sand plaster of paris and metal oxide, and plaster of paris and metal oxide and (4) taking a natural insoluble silicate viz. chromite ore. It would be observed from Table 3, 4 and 5 that the release of Cr in 240 hours from all the preparations is low ranging from 0.06 ppm in the sintered composition III to 2.09 ppm in VII containing sand and plaster of paris in a 1:1 ratio.

TABLE 1. COMPOSITION OF SINTERED/FRITTED FORMULATION.

Compo- sition No.	Red Clay (gm)	Soda ash (gm)	Serpen- tine (gm)	Phos- phate rock (gm)	Felspare (gm)	Cr ₂ O ₃ (gm)	CuO (gm)	Remarks
I	-	10	25	45	20	1	-	Fritted at 1250°
II	-	10	25	45	25	-	1	- do -
III	100	10	-	-	-	1	-	Sintered at 1000°
IV	200	-	-	-	-	-	2	- do -

TABLE 2. COMPOSITION OF UN-FIRED FORMULATIONS.

Composition No.	Sand (gm)	Portland cement (gm)	Plaster of Paris (gm)	Cr ₂ O ₃ (gm)	CuO (gm)
V	160	40	-	2	-
VI	160	40	-	-	2
VII	100	-	100	2	-
VIII	100	-	100	-	2
IX	-	-	200	2	-
X	Chromite ore (Cr ₂ O ₃ content 45%)				

TABLE 3. RELEASE OF CHROMIUM AND COPPER FROM COMPOSITIONS FRITTED AT 1250°.

Composition No.	2 hrs ppm	3 hrs ppm	4 hrs ppm	6 hrs ppm	24 hrs ppm	30 hrs ppm	48 hrs ppm	72 hrs ppm	240 hrs ppm
I Chromium	0.043	0.069	0.81	0.123	0.118	0.247	0.30	0.35	0.435
II Copper	1.43	1.48	1.50	1.50	1.70	1.78	2.054	2.12	2.45

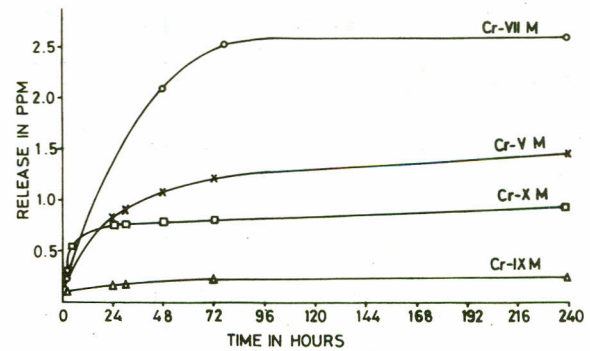


Fig. 1. Release of chromium from non-fritted composition.

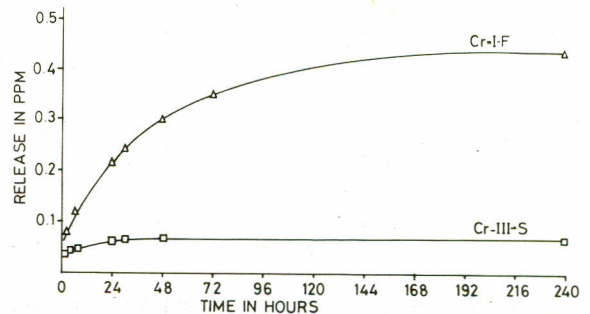


Fig. 2. Release of chromium from fritted and sintered composition.

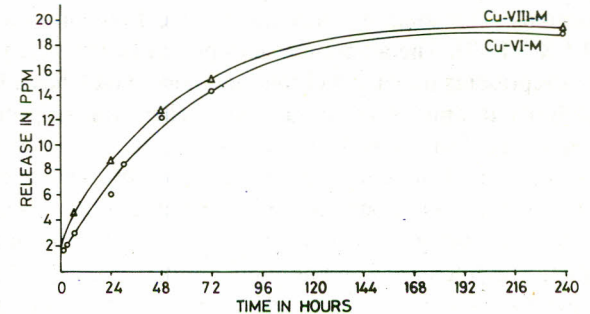


Fig. 3. Release of copper from non-fritted composition.

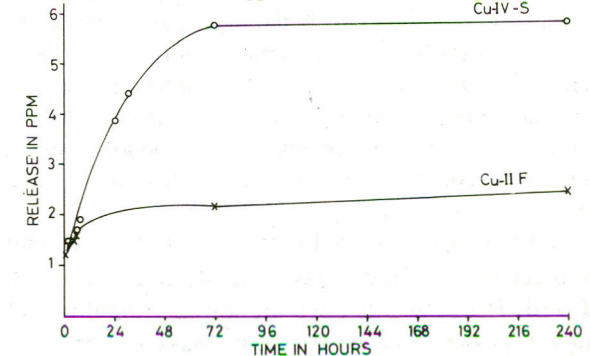


Fig. 4. Release of copper from fritted and sintered composition.

TABLE 4. RELEASE OF CHROMIUM AND COPPER FROM FORMULATIONS SINTERED AT 1000°.

Composition No.	2 hrs ppm	3 hrs ppm	4 hrs ppm	6 hrs ppm	24 hrs ppm	30 hrs ppm	48 hrs ppm	72 hrs ppm	240 hrs ppm
III Chromium	0.035	0.037	0.037	0.043	0.06	0.065	0.068	—	0.068
IV Copper	1.37	1.41	1.54	1.74	1.87	3.85	4.45	5.80	5.74

TABLE 5. RELEASE OF CHROMIUM AND COPPER FROM ADMIXTURE.

Composition No.	2 hrs ppm	3 hrs ppm	4 hrs ppm	6 hrs ppm	24 hrs ppm	30 hrs ppm	48 hrs ppm	72 hrs ppm	240 hrs ppm
V	0.177	0.263	0.558	0.59	0.84	0.895	1.05	1.22	1.45
VI	2.05	2.51	2.56	2.91	7.11	8.52	12.32	14.10	18.75
VII	0.220	0.225	0.23	0.235	0.311	0.50	2.09	2.09	2.09
VIII	2.20	2.29	3.04	4.65	8.60	9.91	12.62	14.00	19.60
IX	0.126	0.128	0.128	0.128	0.150	0.163	0.247	0.247	0.247
X	0.30	0.521	0.72	0.72	0.725	0.757	0.78	0.789	0.896

It would be noted from Table 3 and 5 that the micro-environment for Cr ion is changed in each of the six compositions. The solubility increases in the following order: III I X VI VII. The admixture with plaster of paris IX perhaps represents unreacted chromium oxide which has a low solubility in ammonium citrate but higher with respect to III a silicate formed as result of sintering with red clay and soda ash. The fritty composition-I is also a silicate but with a higher ionic environment which perhaps offers an adequate leachability. Chromite ore is next to the frits in the quantity extracted by ammonium citrate leaching. These four formulations, it may be added, have a firm lattice and the metal is not sufficiently exposed to allow its solution. The next two formulations in the increasing order are V and VII which are simple admixtures, the former with portland cement and the latter with plaster of paris, each having an equal amount of sand. In both cases a firm lattice is not formed so that the solution may have to break it but apparently some compound is formed which is quite different from the silicate melts.

When copper is placed in the same micro-environment the order in which the release increase is as follows: II IV VI VIII. Here the frits have the lowest solubility and the sinter has twice as much. It appears that the copper atom is firmly encased into the silicate lattice while sintering with red clay has provided a similar environment only partially. The remaining two have not formed any such lattice and hence offer no resistance to the citrate leaching. The release in the two cases is almost similar.

The results plotted in Figs. 1 to 4 show that among the fritted chromium compositions, I has a regular increase ranging from 0.043 to 0.435 ppm from 2 hours to 240 hours respectively. The slope of the curves relating to the sintered

composition III and the non-fritted composition IX is very small which apparently bears out the suggestion that they have a firm lattice. It is of interest to mention that chromite ore releases chromium ions rapidly during the first six hours and the release obtained is approximately 0.7 ppm. Thereafter it levels off and reaches 0.896 ppm after 234 hours. The release of chromium from compositions V and VII is regular starting from 0.177, 0.22 ppm in the second hour to 1.2 and 2.09 ppm in 72 hours whereafter it levels off.

The copper composition IV sintered at 1000° has a regular increase from 1.37 to 5.80 ppm from 2 to 72 hours respectively whereafter it levels off. The fritted composition II on the other hand release from 1.43 to 2.45 ppm in 240 hours and the release is rapid only during the first six hours. The copper compositions VI and VIII on the other hand have much higher release values ranging gradually in each case from 2.05 and 2.20 to 18.75 and 19.60 ppm respectively.

It would be observed from the above set of data that it is possible to obtain different rates of release by suitable modification of the microenvironment of the metal and that its release can be minimised by preparing a frit or by sintering a mix containing soda ash. Such preparations would be useful in controlling the input to the crops because according to Reuther and Labanauske [10] and Jane [11] the concentration of Cu in different parts of a number of plants varies from 3 to 30 ppm while Robson and Reuter [12] report much lower critical values. It has also been observed that chromium added at the rate of 5 ppm increased the rate of nitrification in soils. Furthermore, in small amounts chromium in the form of phosphosphate slags, chromite, chro-

mium oxide or phosphate has been found to increase the yield of all plants tried and that dichromates were beneficial at lower but injurious at higher concentration [13, 14]. Accordingly it may be suggested that the raw or non-fritted, non-sintered compositions releasing higher quantities may be used for crops requiring higher concentration while the fired and fritted compositions would be suitable for crops/plants requiring low but regular amounts of the micro-nutrients in the macroenvironment.

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