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# Trace Elements and Missouri Soils

## II. The Interaction of Copper Ores With Putnam Clay

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### ABSTRACT

A study of the decomposition of different copper ores was undertaken by using colloidal Putnam clay. Two systems of a four percent suspension of clay were used, an H-clay and a Ca-H-clay (35% saturated with respect to calcium). The ore was in contact with the clay for 40 days. The exchangeable and non-exchangeable Cu were determined using Ca acetate treatments.

The results obtained in this study show the effectiveness of acid clay in the weathering of minerals. The ease of weathering of the materials used are in the decreasing order, azurite, malachite, copperpyrophosphate, chrysocolla, chalcocite, and chalcopyrite. The results show that the non-exchangeable copper exceeds the exchangeable in all cases. It is thought by the authors that a better understanding of the reactions between the soil and some added nutrient elements might be developed from the results of this study.

# Trace Elements and Missouri Soils

## II. The Interaction of Copper Ores With Putnam Clay<sup>1</sup>

O. E. GIBBS AND C. E. MARSHALL<sup>2</sup>

Copper is one of the trace elements that is frequently reported as being deficient in highly organic soils and in highly leached and sandy soils. The importance of copper as a nutrient for plants and animals has been well established. However, the relationship between the copper content of the soil and its availability for plant nutrition is not well understood.

Copper sulfate is used widely to correct copper deficiencies. In some instances large amounts are necessary to correct the deficiency. This suggests the fixation of copper; that is, that a fraction is unavailable for plant nutrition. Copper sulfate is an expensive source of copper and in time of war is scarce. By using copper-bearing ores to correct copper deficiencies, the cost may be reduced. The water-soluble copper from copper-bearing ores is very small. However, the weathering effect of acid clay may conceivably release significant amounts of copper. Acid clay is an important factor in the weathering-out of nutrients from the reserve minerals that occur naturally in the soil or those added as fertilizers.

It was the purpose of this study to investigate the release of copper from different copper ores and copper-pyrophosphate by colloidal Putnam clay, and to determine whether part of this may be fixed by the clay.

### REVIEW OF PREVIOUS INVESTIGATIONS

Extensive studies have been made of the availability and fixation of copper by soils. However, there is no literature dealing with the weathering of copper ores by colloidal clay. The copper content of various soils has been determined and different sources of copper have been used to correct copper deficient soils. A little work has been done using copper in the determination of the base-exchange capacity

<sup>1</sup>The material of this bulletin was taken from the thesis presented by O. E. Gibbs, for the degree of M.S., University of Missouri, August 1952. It is a report on Department of Soils project number 51 entitled "Fertility Level of Soils."

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of certain colloidal clays, and on the sorption of copper by colloidal clays.

Copper was used by Bower and Truog (1)\* in a study of the base-exchange capacity of purified Miami and montmorillonite clay fractions. The clay was saturated with copper acetate, washed with methyl alcohol, and the adsorbed copper displaced with N ammonium acetate. Therefore, the copper was in contact with the clay for only a short time. In comparison with ammonium acetate, copper gave high results for the exchange capacity. As a conclusion, it was found that the weak base-forming polyvalent cations form basic salts with the relatively weak clay acid to a varying degree, depending upon the strength of base which the cation in question forms. In this way high results for exchange capacity are produced.

Sieling (2) used copper acetate in determinations of the base-exchange capacity of electro dialyzed H-Bentonite, H-Miami, and H-humus. The copper acetate gave values which agreed satisfactorily with extraction methods employing ammonium acetate and calcium acetate. The exchange capacity was found by measuring quantitatively the amount of copper in the filtrate and deducting this from the amount added originally. Sieling did not use a concentration of copper acetate greater than twice the exchange capacity of the material used.

Menzel and Jackson (16) postulated three types of reaction which greatly influence the availability of native or applied copper to plants.

- (1) The precipitation of cupric hydroxide and cupric carbonate under conditions likely to exist in neutral or calcareous soils.
- (2) The formation of hydroxylated copper ions when sorbed on layer silicates.
- (3) The formation of complexes of copper with organic compounds of the soil.

They studied the sorption of copper from acid systems of kaolinite and montmorillonite. The potassium-saturated clays were equilibrated with standardized cupric solutions in centrifuge tubes by slowly rotating them for 16 hours in an end-over-end shaker. The clay was then thrown out of suspension by centrifugation and the supernatant liquid analyzed. The results showed that when cupric ions were used to replace potassium ions on the clay, more cupric ions (m.e.) were adsorbed than potassium ions released. Also, it was found that simple exchange of cupric ions for potassium ions sorbed on kaolinite or montmorillonite occurred only in acid dilute copper solutions. Menzel and Jackson

\*Numerals in parentheses refer to the Bibliography on pages 25 and 26.

explained the excess copper sorbed over potassium released on the basis of the hydrolysis of the cupric ion, according to the reaction,  $\text{Cu}^{++} + \text{H}_2\text{O} = \text{CuOH}^+ + \text{H}^+$ .

Copper is related to zinc in several ways. Therefore, the fixation of zinc is of special interest. Elgabaly (17), reporting on the fixation of zinc by several different types of colloidal clays, came to the following conclusions.

"A fraction of the adsorbed zinc was found to be non-exchangeable with ammonium acetate and is considered as being fixed by the mineral. In minerals with Al in octahedral arrangement, zinc is thought to be fixed in the holes not occupied by Al ions. This type of fixation is accompanied by a decrease in the cation-adsorption capacity, and an increase in the anion-adsorption of the mineral. In minerals with Mg in the octahedral positions zinc substitutes for Mg. This process does not affect the adsorption properties of the mineral. Some of the zinc adsorbed on the surface (complex monovalent form) may enter the inner layer of the electrical double layer, where it cannot be exchanged with neutral inorganic salts. Magnesium cannot completely replace all the zinc taken up by the minerals. The data suggest that soils containing clays with low Si/Mg ratios may fix zinc in forms not readily available to plants."

Some interesting observations have been made on the response of different soils to copper sulfate applications. Piper (5) investigated some soils of South Australia and found that lateritic gravelly soils and white siliceous sands required only  $3\frac{1}{2}$  to 7 lbs. per acre of copper sulfate, while heavier soils required 21-42 lbs. per acre. This study included a Robe soil, which is a heavy soil. (The clay content was not given.) The heavier application necessary to obtain satisfactory crops and the absence of any depressing effect at the relatively high rate of application of 100 lbs. per acre distinguish the behavior of the Robe soil from the other soils studied. Piper concluded that it is apparent that some factor is operating on this soil which rapidly lowers the availability of copper so that large applications are required, and that furthermore these large applications do not produce toxic effects. What this factor is still requires elucidation. Soil moisture is certainly important, since the pot experiments have shown that the toxic effects of copper are accentuated under acid conditions. Adsorption by clay minerals and organic matter might also be expected to play a part. Such adsorption would be greater in Robe soil than in the comparatively inert sandy gravelly types.

The adsorption and fixation of copper in some sandy soils of Central Florida were investigated by Jamison (3). He used the same method as Sieling; that is, deducting the amount of copper in the filtrate from that added. He found that three of the four soils tested adsorbed copper continuously as the concentration of copper acetate increased. He suggested that Sieling (2) might have found this true had he gone to a higher concentration of copper acetate. Jamison also studied the

fixation of copper by Norfolk fine sand. He concluded that the presence of iron in this soil, at a pH value where it would tend to be active and tie up active phosphate groups, had no effect on the fixation of copper. The presence of phosphate groups in relatively small quantities in the soil has no measurable influence on its retention of copper. He also concluded that although finely divided quartz may fix copper at pH 5.0, the amounts are small as compared with those fixed by the natural soil. Jamison stated, "The fixation of copper in acid soils must be due to the formation of slowly soluble organic copper compounds. Where pH is 6.0 or above, copper fixation can be partly due to the precipitation of basic copper compounds."

Peech (4), in determining the availability of ions in some Florida soils, found that the recovery of copper was considerably lower than the recovery of zinc at any given pH, indicating that copper is fixed the more strongly of the two cations. Normal sodium chloride solution was used to extract the ions. He concluded that two of the important factors that govern the availability and, consequently, the utilization of ions in light sandy soils under field conditions are leaching and fixation, which in turn are controlled by soil reaction. If the amount of an element utilized by the plant may be taken as a measure of availability of that particular element, then solubility is not necessarily a good criterion of availability.

Wood (8) made some copper studies with Oregon soils. Four surface soils which had indicated an erratic response to copper sulphate fertilization were used in these studies: the Olympic silty clay loam, Hammond sand, Powell silt loam, and Labish peat. The Olympic silty clay loam gave the most consistent field response to copper addition, but on chemical analysis it contained more than twice as much total copper as the other three soils. Wood pointed out that his data leads one to suggest that the response obtained is not due to the added copper, but rather to some other factor or factors. In a fixation study, when neutral ammonium acetate was used as an agent to extract exchangeable copper, the Olympic clay loam soil retained added copper to a much greater degree than the other soils.

The different responses to copper sulfate application are very noticeable for heavy and light soils. Sommer (9) observed that increases in yield may be obtained on heavy soils with amounts which would be toxic if applied to lighter soils. Manns, Churchman, and Manns (10) obtained increases in yield with application up to 300 pounds of copper sulfate on heavier soils, but found that 150 pounds per acre decreased yields on the lighter soils. Wild and Teakle (11) reported that bluestone applied at the rate of 10 pounds per acre to very sandy or

gravelly soil proved harmful. Plots receiving 2½ pounds per acre gave best results.

Lundblad, Svanberg, and Ekman (12) in studying Swedish soils found that in the peat soils the fixation of copper, as measured by its availability to the plants, was distinctly less pronounced than in the mineral soils. On the peat soils, a top dressing of 25-125 kg. of copper sulfate per hectare brought about progressively increasing yields up to normal values, whereas on the mineral soils a much larger quantity (250 kg) was unable to give this effect in the years 1944-46. Nevertheless, the migration of copper down into the soil, was slightly more rapid in the mineral than in the peat soils. Thus, the copper, fixed chemically in the peat, seems to be more available to the plant than copper fixed in the mineral particles. These investigators concluded that on mineral soils the action of a copper dressing appears to be diminished by the mineral material. Another explanation would be that the organic matter of mineral soils is better able to fix the metal than the organic matter in peat soils. That organic matter in a mineral soil is of relatively small significance in the availability of copper to the plants was concluded from the observation that there was little or no difference between the results on mineral soil with different content of organic matter. The results, that copper in peat soils is slightly more available than is the copper in mineral soils, are a direct contradiction to the conception in some earlier literature on the subject that fixation of copper by humus in the soil is the main cause of copper deficiency in crops. According to the opinion of these Swedish investigators the main cause is a low copper content in the soil itself. A high content of humus can hardly be the "reason" for copper deficiency in crops, but it may be a "result" of copper deficiency in the soil.

Lucas (15) found that a large portion of the copper in organic soils could be extracted with normal nitric or hydrochloric acid, but very little with ammonium acetate.

Vermaat and Van Der Bie (14) investigated the occurrence of copper in tropical soils. Two soils from the lixivial types of weathering were studied: (1) a brown and red lixivial weathered soil which contained a large to a very large clay fraction (Kaolinite type), a moderate loam fraction, a very small sand fraction, and a 3% (average) organic matter; (2) a bleached lixivial soil which contained a small to moderate sand fraction, a fairly large loam fraction, a small clay (meta halloysite) fraction, and a 9 to 20% organic matter. Vermaat and Van Der Bie concluded from the analysis of these two soil types that the major part of the copper adsorbed in the exchangeable form is adsorbed by clay and not by organic colloids.

Holmes (6) investigated the copper and zinc content of several United States soils. He drew the following conclusions:

"The variations found in different soils and within the profile of a single soil are thought to be due to differences in contents of clay and organic matter. The intensity of soil acidity developed and the composition of the parent material influence the content of copper and zinc retained in the soil. The composition of the parent material has a varying influence upon the zinc and copper content of a soil depending in a large measure upon conditions existing during soil formation."

Johnson (20) studied a large number of soil types in Missouri and concluded: "The copper levels of the soil are a function of the parent material from which the soil is derived, the conditions prevailing during the period of soil development, the amount of organic matter present in the soil, the soil texture, and the soil reactions."

Steenbjerg and Boken (13) collected three groups of soils:

- (1) severe copper deficiency
- (2) copper deficiency
- (3) sound crops

The soil samples taken where the crops were sound were almost exclusively represented by clay soils. These soils were used in determining the value of various copper fertilizers. It was concluded that malachite is on a level with copper sulfate from a fertilizing point of view. Copper sulfide might be used after a suitable grinding. The effect of copper pyrites was slightly inferior to that of copper sulfate, but further grinding, which is usually a relatively cheap process, would undoubtedly increase its effect to the level of that of copper sulfate. Cupric oxide gave excellent effects both in pot experiments and field experiments.

Steenbjerg (19) used chalcopyrite, chalcocite, malachite, and copper sulfate in a three year (1939-41) study of the surface effect of fertilizers. The copper content of the ores was determined by Low's method. Chalcopyrite contained 20.5, chalcocite 58.9, malachite 49.5, and copper sulfate 25.5% copper. In the first year of the experiment, the ratio of dry matter produced to the relative copper surface added was much higher for the malachite, followed by the chalcocite, and then the chalcopyrite. Steenbjerg concluded that in the first year the adsorption of copper and especially the production of dry matter depended on the different lattice structure of the various copper minerals. However, in the second year and to a still higher degree the third year the various copper minerals seem to have been transformed, at least in part, into another sparingly soluble compound. On the basis of three year's pot experiments with these copper minerals, Steenbjerg concluded that it is possible to set up two main types of action of sparingly

soluble fertilizers added to, or developed in, the soil. The two types are termed the "copper type" and the "potassium type". In the case of the "copper type", the absorption of the plant nutrient in question and the production of dry matter soon come to depend upon the physical and chemical properties of the sparingly soluble compound, or compounds, developed in the soil. Gradually the newly formed compound dominates in the production of dry matter. This occurs because it is accumulated in relatively large quantities, plants absorb comparatively small amounts, and it is not leached.

The copper activity of the copper bearing ores would be of special interest, but no data on this are available. Dawson and Nair (18) reported the pCu value of various suspensions. They found the following pCu values: CuS 17.6,  $\text{CuCO}_3(\text{CuOH})_2$  2.7,  $\text{Cu}(\text{OH})_2$  6.8. These values were obtained by using the copper amalgam electrode, and they compare satisfactorily with other published data.

In summary, therefore, one can say that extensive field studies show large variations in the amount of copper necessary to correct copper deficiencies. However, there are differences of opinion as to the cause of these wide variations. Fixation by mineral matter is strongly suggested. A small amount of work has been done with copper solutions and colloidal clays in the determination of the exchange capacity. The results did not suggest the fixation of copper by clay. Different copper ores used in pot and field experiments reached after one year about the same efficiency as sources of copper for plants.

### PLAN OF THIS INVESTIGATION

In order to get significant amounts of weathering in a short time, the copper ores, chalcocite, chalcopyrite, malachite, azurite, and chrysocolla, and the copper-pyrophosphate<sup>1</sup> were placed in direct contact with the electro-dialyzed Putnam clay. Two different amounts of each ore were used in this study. A quantity of ore containing one m.e. of copper was used in one case and four times this amount in the other. The ores were ground, sieved, examined under the microscope, and total copper determinations made. Only that fraction between 150 and 200 mesh was used; therefore, the particle size for each ore was constant. The ore, plus 75 milliliters of a four per cent clay suspension was contained in a 100 m.e. plastic tube. The period of contact was 40 days. This was thought to be long enough to observe the relative effects of the clay on weathering the different ores.

The pH value of the soil, in regard to copper available for plant nutrition, has received some attention in the literature. The use of ores

<sup>1</sup>Hereafter the term ores will include the copper-pyrophosphate.

containing various impurities makes the meaning of the pH values of the different systems difficult to interpret. It was thought that some conclusions might be drawn if two systems were set up with different initial pH values. One system was electrodialed Putnam clay with an initial pH of 3.78. The second system was a Ca-H-clay, with 35% of the exchange capacity saturated with respect to calcium, and an initial pH of 4.98.

After the 40 days of weathering the ore was separated from the clay by repeated centrifuging. The clay suspension was treated in centrifuge tubes, four times successively with a saturated solution of calcium acetate. The super-natant liquid was analyzed for copper by the standard iodimetric method. Following the removal of the exchangeable copper, the clay was analyzed for total copper. Duplicates were set up in all cases.

## PROCEDURES

### General Laboratory Technique

Common sense precautions were taken in the laboratory to eliminate contamination from dust, copper, or brass equipment. All glassware was washed thoroughly with soap and hot water and rinsed with distilled water. The inside and outside were washed down with water redistilled in an all-glass still, twice before using. All the water used in the analysis, making up solution, etc., was so prepared. A blank was run for each procedure.

### Preparation of Colloidal Clay

Clay from Putnam subsoil was used. The separation and the electro dialysis were carried out as outlined by Albrecht (22). After the first electro dialysis, it was decided to electro dialyze the clay again, using double distilled water from pyrex glass. Electro dialysis was continued until a negative test was obtained for chloride and sulfate ions in the anode chamber. The concentration of the colloidal clay was determined (percentage by volume), and a four percent stock suspension made. The Ca-H-clay was prepared by adding equivalents of calcium oxide to the H-clay to make the clay 35% saturated with respect to calcium. The equivalence was taken as 70 m.e. per 100 gm.

### Preparation of Ores

The ores were crushed in an iron hammer mill, followed by a grinding with an agate mortar and pestle and sieving with standard brass sieves. Only that quantity between 150 and 200 mesh was used in this study. According to Tyler's Standard Screen Scale (23) the particles collected between 150 and 200 mesh are .104 to .074 millimeters in diameter.

### Total Copper Analysis of Ores

The standard method as outlined by Park (21) was used in the determination of total copper in the ores. Concentrated  $\text{HNO}_3$  followed by 12 N  $\text{HCl}$  and 18 N  $\text{H}_2\text{SO}_4$  was used to get the copper in the ores into solution, with the exception of the silicate ore. The silicate ore was treated with concentrated  $\text{HClO}_4$  and  $\text{HNO}_3$  mixture (3:1). The insoluble sulfates and silica were filtered off. Ammonium hydroxide was added to the filtrate until a permanent blue color persisted. Ammonium bifluoride was used to tie up the iron present. Potassium acid phthalate was added to buffer the solution between pH 3 and 4. Potassium iodide was added and the solution titrated with sodium thio-sulfate.

### Microscopic Examination of Ores

**Pyrite ore (cupric compound):** This ore contained two major types of crystalline particles, clear and dark. Both the clear and dark particles had a refractive index above 1.62. The clear material had a medium birefringence of .025. A small amount of greenish colored material was present, which had a refractive index below 1.62 and very little birefringence. The greenish and clear materials were considered as impurities, and dark material as mostly chalcopyrite.

**Sulfide ore (cuprous compound):** This ore contained a high proportion of chalcocite crystals. Some white crystalline material was present, with a refractive index below 1.64.

**Carbonate ore (contains malachite):** This ore contained a large amount of impurities. Evidence of this was the lack of birefringence and a refractive index below 1.64 for a large percentage of the material. Calcite was present in small amount. The ore contained a small percentage of the green malachite mineral.

**Carbonate ore (containing azurite):** The ore contained a high percentage of the azurite mineral. The azurite had a refractive index above 1.64, high birefringence, and a blue color. Some brown colored material was present, with a refractive index below 1.64. No carbonates of Ca were present.

**Silicate ore:** The ore contained two major constituents, colorless material and bluish material. The colorless material had a refractive index below 1.55 and a weak birefringence; therefore, it was not chrysocolla. The bluish material was the chrysocolla mineral with a measured birefringence of .045 and a mean refractive index of 1.58.

**Copper-pyrophosphate (spent catalyst):** Most of the material was thought to be charcoal. A great deal of very black material was present. A few white and brown particles were present. The white particles had a refractive index between 1.55 and 1.62, and a birefringence of

approximately .005. The brown particles were not birefringent and had a refractive index of approximately 1.7. The shape of the brown particles suggested a crystalline form.

#### **Separation of Ore from Clay**

A large percentage of the ore remained after the 40 days in contact with the clay. It was found that by centrifuging at a high speed the ore was thrown down, along with considerable clay. By repeated centrifuging at a decreasing speed, and decanting, a satisfactory separation was obtained. Four centrifugings at the following speed and time were found satisfactory.

- (1) 2400 RPM for 15 minutes
- (2) 1600 RPM " " "
- (3) 1200 RPM " 10 "
- (4) 800 RPM " 10 "

#### **Determination of Calcium-Exchangeable Copper**

The plastic tubes containing the clay were filled approximately one-half full with saturated calcium acetate, stirred with an electric stirrer, and filled with the saturated calcium acetate solution. This was done before each centrifuging. The centrifuging was repeated four times, and between the third and fourth there was a time interval of 12 hours. The centrifuging was done at 2000 RPM for 15 minutes each time. The copper in the supernatant liquid was determined by the standard iodimetric method. During the period between the centrifuging and the titration of the copper in the supernatant liquid, a mold grew in the solutions. In the process of trying to destroy this growth, all the copper-pyrophosphate samples and one of the duplicates in several of the ores were lost. By making very acid with concentrated HCl, allowing to stand for several days, and heating on a steam plate the molds were destroyed in the remaining samples.

#### **Determination of Copper not Exchanged by Calcium Acetate**

Samples of suspension containing between one and two grams of clay were quantitatively transferred to 100 ml. beakers. Thirty milliliters of a 3:1 nitric-perchloric acid mixture were added to each beaker. After two hours of digestion the clay was heated on the steam plate until the dense white fumes ceased to come off (approx. 8 hrs.). Ten milliliters of approximately 18N  $H_2SO_4$  were added and the residue macerated with a stirring rod. Ten to fifteen milliliters of water were added and the solution heated to boiling. After cooling and diluting the solution up to 75 cc., the residue was filtered and the copper determined in the filtrate by the standard iodimetric method.

## RESULTS

## Total Copper Analysis of Ores

The results of duplicate determinations and the average percentage copper of the ores, as determined by Park's method, are presented in Table 1. The theoretical values are calculated from the formulae given by Mellor (24).

TABLE 1 -- TOTAL COPPER CONTENT OF ORES

Ores	% Copper Chem. Analysis	Theoretical % Copper from Formula
Chalcopyrite ( $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ )	29.68	34.63
Chalcocite ( $\text{Cu}_2\text{S}$ )	58.93	79.85
Malachite ( $\text{CuCO}_3 \cdot \text{CuOH}_2\text{O}$ )	12.92	57.20
Azurite ( $2 \text{CuCO}_3 \cdot \text{CuOH}_2\text{O}$ )	48.23	55.25
Chrysocolla ( $\text{CuO} \cdot \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$ )	16.94	36.21
Copper-Pyrophosphate ( $\text{Cu}_2\text{P}_2\text{O}_7$ )	15.40	63.22

## pH Values During Weathering Period

The pH values were obtained by the Beckman pH meter. The pH values for the H-clay and the Ca-H-clay, with the ore containing four m.e. of copper, are shown graphically in Figures 1 and 2.

The pH values for the H-clay and Ca-H-clay with ore containing one m.e. of copper, are shown in Figures 3 and 4.

**Exchangeable Copper and Copper not Exchanged by Calcium**  
(milligrams for three grams of clay)

The milligrams of copper that were exchanged and those which were not exchanged, from the 3 grams of clay, by the calcium acetate, are presented in Table 2. The milligrams of ore added, containing 1 m.e. (31.8 mgs) and four m.e. (127.2 mgs) of copper, are also shown both for the H-clay and the Ca-H-clay.

**Exchangeable Copper and Copper not Exchanged by Calcium**  
(m.e./100 grams of clay)

The copper exchanged by the calcium and that which is not exchanged by the calcium, (calculated on a m.e./100 grams of clay basis) are presented in Table 3. These data are calculated from the results obtained using 3 grams of clay and 1 and 4 m.e. respectively of copper added as the ore.

TABLE 2 -- EXCHANGEABLE COPPER AND COPPER NOT EXCHANGEABLE BY CALCIUM  
(milligrams per three grams of clay)

	Mgs. of Ore Added	Mgs. of Copper Added	Mgs. of Copper Exchanged by Calcium		Mgs. of Copper not Exchanged by Calcium		Total Mgs. Copper Weathered from Ore	
			H-clay	Ca-H-clay	H-clay	Ca-H-clay	H-clay	Ca-H-clay
Chalcopyrite	107.2	31.8	0	0	.5	.3	.5	.3
Chalcopyrite	428.7	127.2	0	0	5.0	4.1	5.0	4.1
Chalcocite	53.9	31.8	.4	0	1.8	2.0	2.1	2.0
Chalcocite	215.6	127.2	.9	1.4	6.7	5.0	7.6	6.4
Malachite	245.9	31.8	2.6	.9	13.8	13.5	16.4	14.4
Malachite	983.6	127.2	5.6	*	27.8	24.6	33.4	24.6
Azurite	65.9	31.8	2.7	1.8	12.3	7.9	14.0	9.7
Azurite	263.5	127.2	9.2	7.7	39.2	34.6	48.4	43.7
Chrysocolla	187.5	31.8	.4	0	4.9	2.3	5.3	2.3
Chrysocolla	750.2	127.2	.9	.5	7.4	7.2	8.3	7.7
Cu-Pyrophosphate	206.3	31.8	*	*	6.7	4.5	6.7*	4.5*
Cu-Pyrophosphate	825.2	127.2	*	*	12.2	10.8	12.2*	10.8*

\*The calcium exchangeable copper was lost for this sample.

**Percentage of Total Copper Weathered out  
that is Calcium Exchangeable**

The percentage of copper that is calcium exchangeable, of the total copper weathered from the ores, is presented in Table 4. These data are calculated from the results obtained with the 3 grams of clay.

**TABLE 3 -- EXCHANGEABLE COPPER AND COPPER NOT EXCHANGED BY CALCIUM  
(milli-equivalent (31.77 mgs.) per 100 grams of clay)**

Source of Copper	Copper Added m.e./100 gms. of clay	Ca-Exchange- able Copper m.e./100 gms. of Clay		Copper not Exchangeable by Calcium m.e./100 gms. of clay	
		H-clay	Ca-H-clay	H-clay	Ca-H-clay
		Chalcopyrite	33-1/3	0	0
Chalcopyrite	133-1/3	0	0	5.0	4.0
Chalcocite	33-1/3	.4	0	1.9	2.1
Chalcocite	133-1/3	.9	1.4	7.1	5.2
Malachite	33-1/3	2.7	.9	14.5	14.2
Malachite	133-1/3	5.9	*	29.1	25.8
Azurite	33-1/3	2.9	1.9	12.9	8.9
Azurite	133-1/3	9.6	8.0	41.2	36.3
Chrysocolla	33-1/3	.4	0	5.2	2.4
Chrysocolla	133-1/3	.9	.5	8.0	7.5
Copper-Pyrophosphate	33-1/3	*	*	7.1	4.7
Copper-Pyrophosphate	133-1/3	*	*	12.8	11.3

\*This sample was lost.

**TABLE 4 -- PERCENTAGE OF TOTAL COPPER WEATHERED FROM ORES  
THAT IS Ca-EXCHANGEABLE**

Source of Copper	Copper added (m.e.)	H-clay	Ca-H-clay
Azurite	1	18.0	18.5
Azurite	4	19.0	18.2
Malachite	1	15.8	6.3
Malachite	4	16.7	
Chrysocolla	1	7.5	
Chrysocolla	4	10.8	6.4
Chalcocite	1	18.2	
Chalcocite	4	11.8	21.9

## DISCUSSION OF RESULTS

## pH Values During Weathering

The order of the ores in relation to their final pH values is the same for the H-clay and Ca-H-clay systems containing 4 m.e. of copper. This is seen in Figures 1 and 2. The decrease in the pH value the first day with the Ca-H-clay might be explained by the calcium that was added to the clay, not having established equilibrium with the clay at

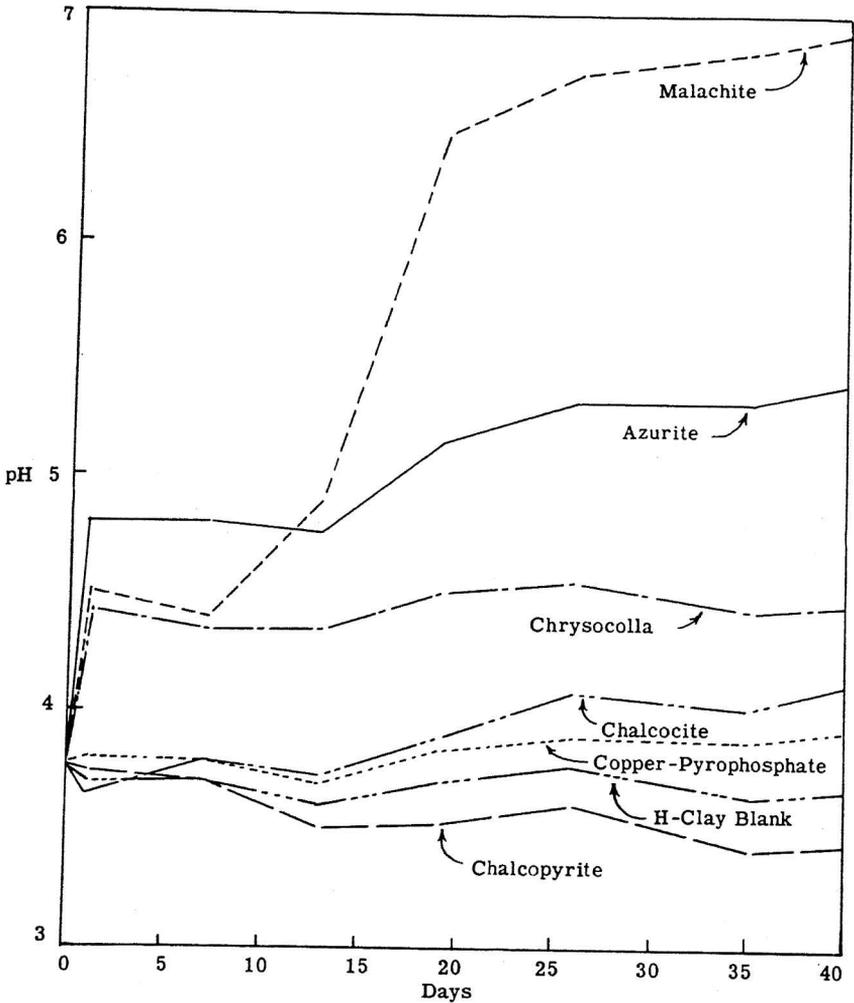


FIGURE 1.—pH VALUES DURING WEATHERING PERIOD OF H-CLAY CONTAINING 4 M.E. OF COPPER.

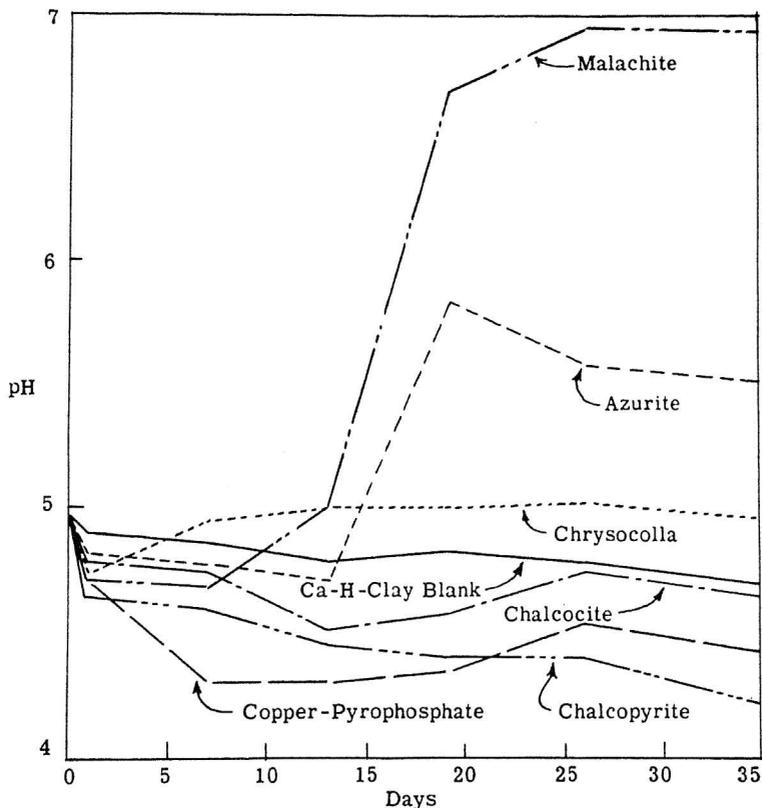


FIGURE 2.—pH VALUES DURING WEATHERING PERIOD OF CA-H-CLAY CONTAINING 4 M.E. OF COPPER.

the time the first pH measurement was made. The large increase in the pH of the malachite (Fig. 1 and 2) is probably due to the large amount of impurities (especially carbonates) present in the ore. The early increase in the pH of the H-clay (Fig. 1) system indicates the effectiveness of the acid clay in weathering the ores. The rapid rise in the pH values of the malachite and azurite on the thirteenth day of weathering is probably due to the fact that at this period the ore was mixed with the clay by bubbling air through the tubes. This method of mixing the ore and clay was done each time, thereafter, before the pH measurements were made.

It is seen in Figures 1 and 2 that the malachite has the same final pH value in the H-clay and the Ca-H-clay. The azurite has approximately the same final pH values. However, the other ores have significantly different final pH values for the H-clay and the Ca-H-clay systems. This might be expected since the two carbonate ores would be more easily

weathered than the sulfides, silicate, or copper-pyrophosphate. Therefore, the difference between the weathering ability of the H-clay and the Ca-H-clay would be less for the carbonate ores.

The wide differences in the final pH values of the different ores when four milli-equivalents of copper were added (Fig. 1 and 2) do not exist in the systems where one milli-equivalent of copper is added (Fig. 3 and 4). This is probably due to differences in the amount of ore

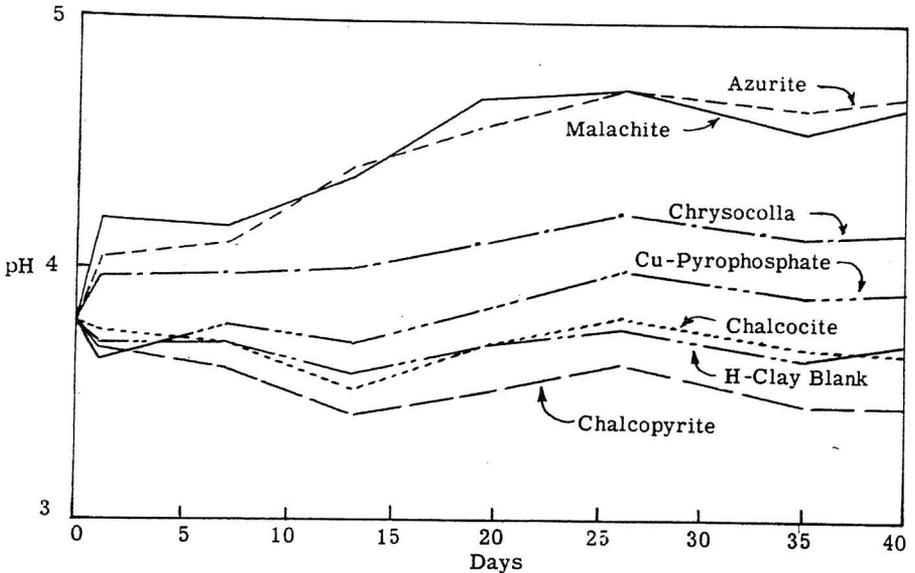


FIGURE 3.—pH DURING WEATHERING PERIOD OF H-CLAY CONTAINING 1 M.E. OF COPPER.

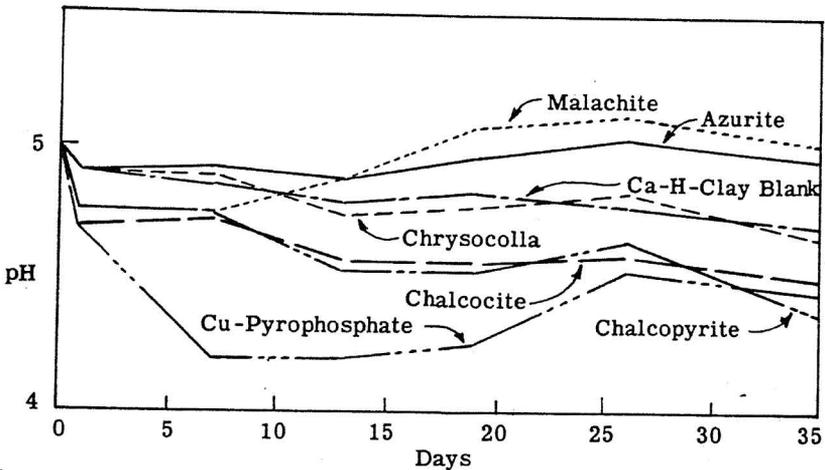


FIGURE 4.—pH DURING WEATHERING PERIOD OF CA-H-CLAY CONTAINING 1 M.E. OF COPPER.

necessary to supply the 4 m.e. of copper and 1 m.e. of copper. The order of the ores in relation to their final pH value is almost the same for the 1 m.e. as for the 4 m.e. of copper added. In the H-clay system (Fig. 3) the azurite has the highest pH (4.7) and the chalcopyrite the lowest pH (3.45). At these low pH values the possibility of copper hydroxide being precipitated is not very likely.

It is noticeable in all the Figures (1, 2, 3 and 4) that in the last 15 days of the weathering period the pH values did not vary much. If the pH curves can be used as a measure of the copper being weathered out of the ores, the major part of the copper was weathered out early in the weathering period.

### **Exchangeable Copper and Copper not Exchanged by Calcium**

From the data in Table 2 it is seen that the amount of copper exchanged from the clay by the calcium acetate is small. The absence of any copper being exchanged by the calcium, where the source of copper is chalcopyrite, is of interest. This study was not designed to determine the energy with which the clay holds the copper, but some interesting observations can be made regarding bonding energy of copper with clay. Calcium ions are divalent and are held relatively tightly by the clay. The copper, being held by the clay and not entering an exchange reaction with the calcium ions, is an indication of the energy with which the copper is held by the clay. The breaking of the high energy copper-sulphur bond is an indication of the energy with which copper might be held by the clay. These same things can be said about the chalcocite mineral as a source of copper. The results (Table 2) show very little calcium exchangeable copper when chalcocite or chrysocolla is the source of copper. The larger amounts of copper exchanged by the calcium, where the azurite and malachite are the sources of copper, might be explained by the differences in the energy with which the copper is held by the different copper minerals.

The slightly larger amount of copper weathered from the ores by the H-clay is reflected by a little larger amount of calcium exchangeable copper for the H-clay system over the Ca-H-clay system.

In Table 3 it is seen that the amount of copper not exchanged by the calcium might take up a considerable part of the exchange capacity if all the copper utilizes exchange seats on the clay.

The method employed in determining the copper not exchangeable by the calcium indicates that this copper is not from the original clay mineral or from ore that was not separated from the clay. Varying amounts of clay were taken in the determination, and the dupli-

cates checked when calculated on the basis of the three grams of clay used. This made the amount of copper found in the samples a function of the clay used for the determination. The blanks, containing varying amounts of clay, were the same. This indicated that no copper was coming from the clay mineral. Spectrographic analysis was run on the residue of a few samples after digestion and filtration. The small amount of copper present indicated that the digestion extracted practically all the copper coming from the ore that was held by the clay.

#### **Percentage of Total Copper Weathered from Ore that is Calcium Exchangeable**

For a percentage analysis, the azurite, having the most copper weathered from the ore, would be likely to show a relation if one existed between the total copper weathered from the ore and that which is exchanged by calcium. None of the samples of the exchangeable copper solutions was lost from this ore. An interesting relation does exist between the different samples of azurite. The results in Table 4 show that the percentage of total copper weathered from the ore that is exchanged by calcium is approximately the same for the 1 m.e. and 4 m.e. of copper added to the H-clay and Ca-H-clay. It may be concluded from these results that for the azurite mineral the percentage of copper weathered from the mineral that is calcium exchangeable is independent of the amount of azurite mineral added to the H-clay or Ca-H-clay. In two samples of the chalcocite mineral the percent calcium exchangeable copper of the total copper weathered from the mineral is approximately the same as the azurite mineral. The azurite and the chalcocite minerals contain the highest percentage of copper of the group. Since the azurite mineral is the only mineral that affords a good study of the percentage of calcium exchangeable copper, no significant conclusions can be drawn. The results do indicate a fair degree of accuracy in the various procedures.

## GENERAL DISCUSSION

The results of this study place the ease of weathering of the minerals used in the decreasing order, azurite, malachite, copper pyrophosphate, chrysocolla, chalcocite, and chalcopyrite. This is in agreement with the results of Steenbjerg and Boken (13) and Steenbjerg (19). Steenbjerg and Boken in using malachite, chalcocite, and chalcopyrite as copper fertilizer in pots and field experiments, found that malachite was on the level with copper sulfate, chalcocite slightly inferior, and chalcopyrite even more so. Steenbjerg (19) in a field study concluded that for the first year the malachite was superior to chalcopyrite.

There is a relationship between the field experiments and the colloidal Putnam clay weathering of copper from the minerals malachite, chalcocite, and chalcopyrite. In other words, the response of crops to the different copper minerals follows the amount of copper weathered from the minerals. This relationship suggests the possibility of determining the relative fertilizer value of different materials in a short time by using colloidal clay.

The results of this study clearly show that colloidal Putnam clay holds copper with considerable energy. Much has been said about the copper-fixing power of organic matter, but the fixing-power of the clay fraction has only been implied by several workers in their observations of the response of different kinds of soils to copper applications. The idea of fixation has been generally thought of as a step following the adsorption of an exchangeable ion. Little thought has been given to the energy with which an ion is bound to the inorganic complex. The high energy with which the clay holds the copper is shown in the case of the chalcopyrite mineral. The high energy copper-sulphur bond is broken by the clay and none of the copper on the clay is exchangeable with calcium acetate.

The importance of the clay content of soils in relation to applied copper and its availability to plants is shown in this study. This is in agreement with the work of Lundblad, Svanberg, and Ekan (12) who concluded that the organic matter of mineral soils is of relatively small significance in the availability of copper to the plants. The large amount of copper that the clay is capable of holding is shown in Table 3. With this in mind the theory put forth by Steenbjerg (19), that malachite, chalcopyrite, chalcocite, and copper sulfate are transformed into another sparingly soluble compound, takes on more meaning. He does not attempt to describe what the sparingly soluble compound is. That sparingly soluble compound might well be the copper-hydrogen or copper-calcium clay fraction of many soils. The heavy applications of copper nec-

essary on heavy soils and the toxic effect on light soils also indicate that the clay fraction is the site of the sparingly soluble compound formed.

### BIBLIOGRAPHY

1. Bower, C. A. and E. Truog, "Base Exchange Capacity Determination as Influenced by Nature of Cation Employed and Formation of Basic Exchange Salts." *Soil Sci. Soc. Amer. Proc.*, 5:86-94, 1940.
2. Sieling, Dale H., "Base Exchange Capacity Determination of Soils by Means of a Rapid Colorimetric Copper Method." *J. Amer. Soc. Agron.*, 33:24-36, 1941.
3. Jamison, Vernon G., "Adsorption and Fixation of Copper in Some Sandy Soils of Central Florida." *Soil Sci.*, 53:287-297, 1942.
4. Peech, Michael, "Availability of Ions in Light Sandy Soils as Affected by Soil Reaction." *Soil Sci.* 51:473-485, 1941.
5. Piper, C. S., "Investigations on Copper Deficiency in Plants." *Soil Sci.* 32:10-177, 1942.
6. Holmes, R. S., "Copper and Zinc Contents of Certain United States Soils." *Soil Sci.*, 56:359-370, 1952.
7. Jamison, Vernon C., "The Effect of Particle Sizes of Copper — and Zinc — Source Materials and of Excessive Phosphates upon the Solubility of Copper and Zinc in a Norfolk Fine Sand." *Soil Sci. Soc. Amer. Proc.*, 8:323-326, 1943.
8. Wood, L. K., "Copper Studies with Oregon Soils." *J. Amer. Soc. Agron.*, 37: 282-291, 1945.
9. Sommer, Anna L., "Copper and Plant Growth." *Soil Sci.*, 60:71-77, 1945.
10. Manns, T. F., W. L. Churchman, and M. M. Manns, "The Influence of Minor Elements on the Soil Flora." *Del. Agr. Exp. Sta. Bul.* 207:45-46, 1937.
11. Wild, A. S., and L. J. H. Teakle, "Experiments with Micro-elements for the Growth of Crops in Western Australia." *J. Dept. Agr. West. Aust.*, 19 (ser.2):71-78, 1942.
12. Lundblad, Karl, Olof Svanberg, and Per Ekman, "The Availability and Fixation of Copper in Swedish Soils." *Plant and Soil*, Vol. 1, No. 4:277-302, 1949.
13. Steenbjerg, F. and Else Boken, "Copper Contents and Copper Deficiency in Danish Soil Types." *Plant and Soil*, Vol. II, No. 2:195-221, 1950.
14. Vermaat, J. G., and G. J. Van Der Bie, "On the Occurrence of Copper in Tropical Soils." *Plant and Soil*, Vol. II, No. 3:257-282, 1940.
15. Lucas, Robert E., "Chemical and Physical Behavior of Copper in Organic Soils." *Soil Sci.*, 66:119-129, 1948.
16. Menzel, R. G., and M. L. Jackson, "Sorption of Copper from Acid Systems by Kaolinite and Montmorillonite." *International Congress of Soil Science, 4th Amsterdam Transactions*, 125-132, 1950.
17. Elgabaly, M. M., "Mechanism of Zinc Fixation by Colloidal Clays and Related Minerals." *Soil Sci.*, 69:167-173, 1950.
18. Dawson, J. E., and E. K. N. Nair, "Copper Amalgam Electrode and its Applications: I. Construction and Calibration of the Electrode." *Soil Sci.*, 69: 239-249, 1950.
19. Steenbjerg, F., "On the Surface and Effect of Fertilizers." *Physiologia Plantarum*, Vol. 4:677-695, 1951.
20. Johnson, Frank E., "A Survey of the Trace Elements of Missouri Soils." *Thesis, Univ. of Mo.*, 1950.
21. Treadwell, F. P., and William T. Hall, "Analytical Chemistry," Vol. II, Ninth Edition, (John Wiley and Sons, New York), 1948.
22. Albrecht, Wm. A., "Colloidal Clay Cultures — Preparation of the Clay and Procedures of its Use as a Plant Growth Medium." *Soil Sci.*, 62:23-31, 1946.
23. "Testing Sieves" The W. S. Tyler Co., Catalogue 53, Cleveland, Ohio, U.S.A., 1930.
24. Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, (Longmans, Green and Co., New York), 1923.