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Interaction of Monomeric Silicic Acid With Copper and Zinc and Chemical Changes of the Precipitates With Aging

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ABSTRACT

Precipitates were formed by titrating dilute, acidic solutions of monomeric silicic acid [$Si(OH)_4$] and copper (Cu) or zinc (Zn) to various pH values. Those containing Cu formed above pH 6.0; those containing Zn formed above pH 7.0. Periodically, during 2 years of aging in their mother liquor, the liquid phase was sampled and analyzed and the Cu/Si or Zn/Si molar ratios of the precipitates calculated. The Cu/Si ratios of those containing Cu stabilized readily near 0.78 and were unaffected by pH. The Zn/Si ratios of the Zn-containing precipitates, however, changed as a result of Si enrichment from near 1.80 soon after their formation to near 0.80 after aging 2 years. The systems with the lowest pH changed first and most rapidly and became stabilized within 6 months; those above pH 8.0 changed more slowly.

The Zn-containing precipitates gave diffuse X-ray diffraction patterns indicative of a 2:1 layer silicate, whereas those containing Cu were amorphous.

Additional Index Words: **layer silicate, Zn hydroxide, Zn silicate, Cu silicate, Cu/Si ratio, Zn/Si ratio.**

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MANY SOILS contain large quantities of soluble silicon (Si) that reacts with acidified ammonium molybdate solution within 2 min after mixing to form a yellow heterpoly acid. Silicon reacting in this manner is primarily monomeric silicic acid [$Si(OH)_4$] (Alexander, 1953). McKeague and Cline (1963), and later Elgawhary and Lindsay (1972), summarized the literature pertaining to Si in soils and soil solutions. Silicon reacts with many heavy metal cations at room temperature and atmospheric pressure (Britton, 1927; Hazel et al., 1949).

Recent work has dealt with reactions of Si with heavy metal cations where most if not all of the Si was present as $Si(OH)_4$. The maximum stable concentration of $Si(OH)_4$ in equilibrium with solid phase amorphous silica over the pH range 2 to 9 is about 0.002*M* at 25°C (Alexander et al., 1954). Aqueous systems containing solid phase amorphous silica maintain this equilibrium concentration of $Si(OH)_4$ through polymerization—depolymerization reactions. Both reactions occur slowly and may proceed for many days depending on conditions. The same kind of relationship exists between $(Si(OH)_4$ in solution and other solid-phase silica materials, except that the equilibrium solubilities differ, depending on the stability of the solid phase

(Elgawhary and Lindsay, 1972). Soluble aluminum (Al) removes $Si(OH)_4$ from solution and precipitates collodial silica above pH 4.0 (Okamoto et al., 1957). Trace amounts of Al precipitate relatively large amounts of collodial silica, but larger amounts are needed to precipitate $Si(OH)_4$. Soluble Al, and to a lesser extent soluble iron (Fe), were shown to react with the silica surfaces of diatoms by presumably forming protective coatings and thus preventing their dissolution in sea water undersaturated with $Si(OH)_4$ (Lewin, 1961).

Tiller (1968) showed that treating montorillonite with $Si(OH)_4$ increased its sorption of Zn. The effect was greater as the suspension pH was increased from 4.5 to 6.0. Recently, Tiller and Pickering (1974) synthesized at 20°C and atmospheric pressure a 2:1 layer silicate of the stevensite type containing Zn from solutions initially containing about 0.002*M* $Si(OH)_4$ with Si:Zn ratios ranging from 0.64 to 1.20. Initial reaction products were amorphous to x-rays, but they became crystalline after aging for about 1 year. Willemite was not formed in any of their systems, and hemimorphite was a minor constituent in only one. Thus, they concluded that these materials were not likely reaction products resulting from dilute solutions of $Si(OH)_4$ and Zn at room temperature. Zinc-containing silicates were synthesized from heated dilute solutions of Zn salts and $Si(OH)_4$ by Esquevin (1960), who extensively studied conditions affecting the formation, composition, and lattice structure of various Zn-silicate precipitates.

The objectives of this work were to more clearly define the extent to which $Si(OH)_4$ reacts with Cu and Zn in dilute solutions under conditions of temperature, pressure, and concentration that approach those existing in soil systems and to determine changes in Cu/Si and Zn/Si ratios of products with aging.

MATERIALS AND METHODS

Reagents and Solutions

All water used in these studies was prepared by passing distilled water through a commercial mixed-bed demineralization cartridge to remove soluble inorganic contaminants. Acidic solutions that were approximately 0.1*M* in Zn or Cu were prepared by dissolving the oxides in a slight excess of perchloric acid. Silicic acid was prepared by passing a solution of $Na_2SiO_3 \cdot 9H_2O$ through a H-saturated cation exchange resin column (Alexander, 1954) so that the resulting solution was about 0.002*M* $Si(OH)_4$.

These solutions were added to polycarbonate or polyethylene bottles containing sufficient water and 2*M* $NaClO_4$ to give volumes a few milliliters less than that desired to allow for the titrant to be added. The resulting solutions were approximately 0.001*M* in $Si(OH)_4$, 0.0005*M* in the desired metal cation, 0.1*M* in $NaClO_4$, and were near pH 3.2.

Formation of Precipitates

About 10 to 12 bottles containing all constituents were prepared for each metal cation. They were titrated serially to the desired pH by adding NaOH dropwise, to vigorously stirred solutions. At the desired pH, the contents were stirred an additional 30 min before equilibrating at 23 ± 1°C. The pH of each system was adjusted daily to the original titrated value for a few days until the pH became somewhat stable. Water was added to make a specific volume; some systems were diluted to 200 ml, whereas others were diluted to 2,000 ml, depending on the amounts of precipitate and solution desired. No attempt was made to exclude CO_2 from the containers. They were open to the atmosphere during titration and pH adjustment, and tightly closed during aging to prevent evaporation.

Periodically, the clear supernatant was sampled after standing unstirred for at least 2 days. The pH of the stirred suspension was measured immediately after sampling using an all-glass combination electrode standardized with buffers at pH 4.01, 7.00, and 9.18.

The metal cations in the supernatant samples were determined by using an atomic absorption spectrophotometer. The $Si(OH)_4$ concentration was determined by the reduced molybdenum blue method (American Public Health Association, 1960).

X-ray diffraction patterns were obtained using Cu Kα radiation on glycerated material oriented on glass slides and on powder samples dried at 40°C.

RESULTS

Electrometric Titrations

Electrometric titration curves (Fig. 1) of 0.0005*M* solutions of the metal cations in the presence of 0.001*M* $Si(OH)_4$ show that at these concentrations Cu precipitated above pH 6 and Zn above pH 7. The Si-containing precipitates form at a slightly lower pH (about 0.7 pH unit less for the Zn series, and about 0.3 pH unit less for the Cu series) than do their corresponding hydroxides. These results were similar to those of Britton (1927), who showed that generally the pH difference was greater for those metals precipitating above pH 7 than for those precipitating under acid conditions.

Effect of Aging

The liquid phase concentration changes in systems initially 0.0005*M* in Cu or Zn, and 0.001*M* in $Si(OH)_4$, aged in the mother liquor for about 2 years are shown in Fig. 2. Precipitation of Cu removes more $Si(OH)_4$ from solution than does Zn, with Cu being about twice as effective as Zn through 4 months aging.

The major effect of aging the Cu series was that the pH decreased. The general shape of the curves and the amounts of $Si(OH)_4$ and Cu removed from solution changed very little over the 2-year period. The decrease in pH was most evident in those systems containing precipitates. In fact, after 6 months aging the pH values of some systems containing precipitates were lower than in others without precipitates.

The Zn series changed only slightly during the first 4 months of aging; except for some systems initially above pH 7.75, the pH decreased a few tenths of a unit. Between

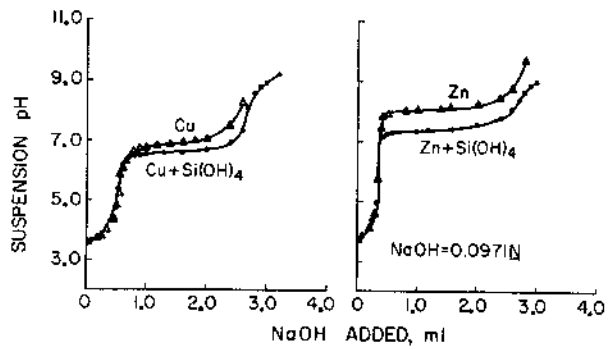

Fig. 1—Electrometric titration curves for 0.0005*M* Cu or Zn with and without 0.001*M* $Si(OH)_4$.

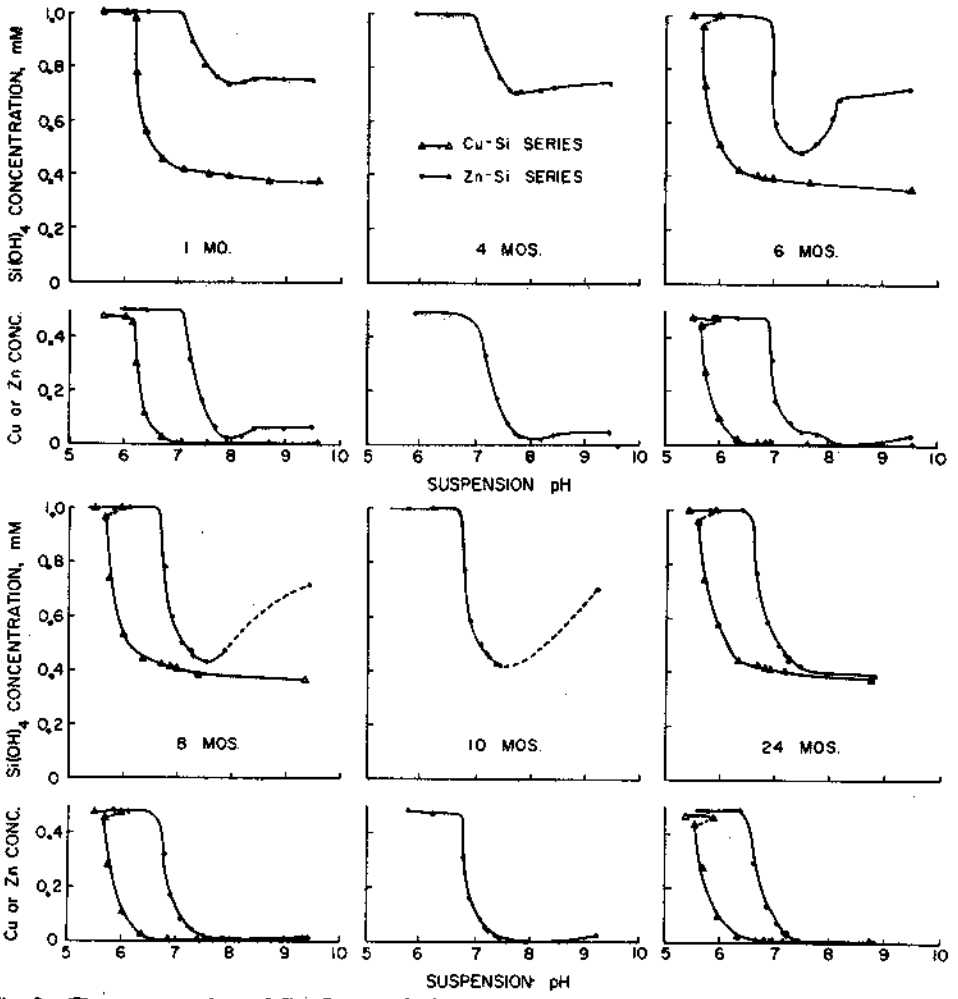

Fig. 2—The concentrations of Cu, Zn, and $Si(OH)_4$ remaining in solution as affected by pH and aging.

4 and 6 months aging a marked minimum in $Si(OH)_4$ concentration occurred between pH 6.5 and 7.75. This resulted from a slow reaction whereby the precipitates were enriched with Si from the mother liquor at different rates. The enrichment began and finished first in the low pH systems, and thus some of these systems stabilized before the high pH systems changed noticeably. The action was complete below pH 7.75 within 8 months, below pH 9 within 10 months, and in all systems in the study within 24 months. More $Si(OH)_4$ was removed from solution by means of this enrichment reaction than was removed during the initial precipitation. As a result of the two reactions, Zn became as effective as Cu in removing $Si(OH)_4$ from solution.

The concentration of Zn remaining in solution 1 month after precipitation shows a minimum near pH 8.0. In contrast, Cu concentrations were uniformly low above pH 6.5 (see Fig. 2). As aging progressed, the Zn concentration minimum tended to disappear except above pH 9.0, where the increased concentration persisted even after 10 months. This effect is seen easier in Fig. 3 where the Zn concentrations after 1 and 10 months are plotted against the suspension pH. A marked decrease in pH with aging is evident for all systems containing precipitates. Zinc concentrations decreased in the three systems above pH 8.2, increased in those between pH 7.7 and 8.2 and did not change in those below pH 7.7. The minimum Zn concentration measured after 10 months was $1.8 \times 10^{-5}M$, and was barely lower than the lowest concentration measured after 1 month. The major effect of aging seems to have been a migration of the points by a decrease in pH to the 10-month line, and then a shifting up the line with further slight pH decrease.

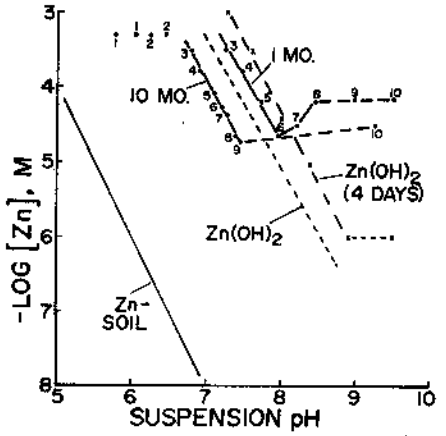

Fig. 3—The solubility of precipitates containing Zn and Si as affected by pH and aging. Included for convenience are data for Zn $(OH)_2$ aged 4 days (these studies) and $Zn(OH)_2$ and soil-Zn (Lindsay, 1972). Corresponding numbers are for the same system aged different times.

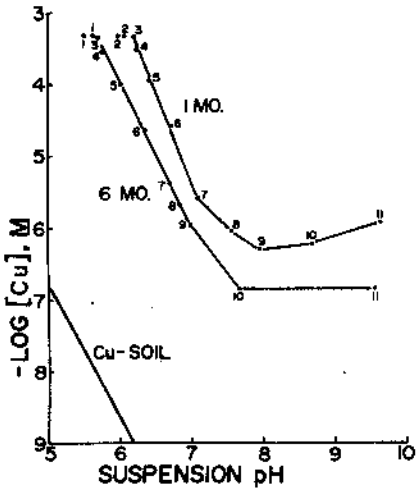

Fig. 4—The solubility of precipitates containing Cu and Si as affected by pH and aging. Included for convenience are soil-Cu data from Lindsay (1972). Corresponding numbers are for the same system aged different times.

The major portions of the 1- and 10-month Zn lines are very nearly parallel; and they, in turn, are parallel to the soil-Zn line given by Lindsay (1972). Both lines lie below the Zn concentration from freshly precipitated $Zn(OH)_2$, but the equilibrium concentrations for $Zn(OH)_2$ (Lindsay, 1972) lie between the two. The reason for the Zn concentrations being higher above pH 8.0 for the Si-containing precipitates than for the freshly precipitated $Zn(OH)_2$ is not known. Possibly peptization of extremely small particles containing Zn and Si could have been a factor because the liquid samples were not filtered before analysis.

A similar comparison for the 1-month and 6-month data for Cu (Fig. 4) also indicates a general decrease in pH with aging. The minimum Cu concentration, however, decreased from $5 \times 10^{-7}M$ after 1 month to $1.5 \times 10^{-7}M$ after 6 months. With aging, the Cu concentrations decreased above pH 8.0, increased between pH 6.7 and 8.0, and were essentially unchanged below pH 6.7.

Effect of Chloride

Initial attempts at precipitation were made in $0.1M$ NaCl solutions. The reaction of Zn with $Si(OH)_4$ in that medium did not differ from that in $0.1M$ $NaClO_4$ presented here. Copper, however, would not react with $Si(OH)_4$ in the $0.1M$ NaCl solutions until the pH was > 9.0. Titration of the acid solutions containing Cu proceeded normally until about pH 6.3, when the solution became dark blue-green and strongly buffered. Within a few minutes and without

Table 1—The effects of chloride concentration on the removal of $Si(OH)_4$ from solution by Cu as affected by pH.

Cl concentration	$Si(OH)_4$ removal at pH of:			
	6.0	7.0	8.0	9.0
meq/liter	% of added †			
Nil	0	60	85	93
0.01	0	40	53	65
0.10	0	0	0	2

† Solution initially contained approximately $0.001M$ Cu and $0.001M$ $Si(OH)_4$.

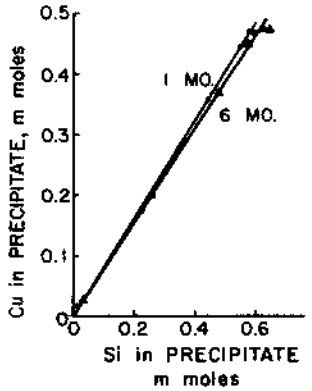

Fig. 5—The relationship between the Cu and Si contents of precipitates aged 1 and 6 months.

adding more NaOH, the pH began to drift downward and finally after 3 to 4 min became stabilized near pH 5.2. During the pH change, a precipitate formed that did not contain $Si(OH)_4$ which was tentatively identified as $Cu_2(OH)_3Cl$ by X-ray diffraction. The effect of Cl concentration on the removal of $Si(OH)_4$ from solution by Cu is shown in Table 1. The effect of aging on these systems is not known.

Effect of $Si(OH)_4$

Another interesting feature observed in the Cu series was that in the absence of $Si(OH)_4$ a fluffy blue precipitate formed that was possibly the hydroxide. Within a few minutes after its formation, however, CuO separated forming a dark, chocolate-colored precipitate. In contrast, the Si-containing precipitate remained bright blue indefinitely, even after it was separated from the solution and dried.

Calculated Cu/Si and Zn ratios of the Precipitates

From the analysis of the liquid phase and the known initial concentrations and volumes, the amounts of Cu or Zn and Si in the solid phase were calculated. After 1 and 6 months aging the amounts of Cu and $Si(OH)_4$ in the precipitates are shown in Fig. 5. Data obtained after aging longer are not given because they were essentially identical to the 6-month data. The data clearly indicated linear relationships between the two constituents in all precipitates formed in this series. The average Cu/Si ratio was 0.79 after aging 1 month, 0.78 after 6 months, and 0.75 after 2 years. Samples analyzed between mixing and aging 1 month indicated only slight Cu/Si ratio changes.

X-ray diffraction patterns of precipitates aged 2 years indicated the Cu-containing materials were amorphous.

Because chloride interferes with the reaction of Cu and $Si(OH)_4$, no additional work was done with reactions and products formed from these two constituents.

Preliminary results for the Zn series indicated slight, if any liquid phase composition changes from 1 week to 1 month after the precipitates were formed. Consequently, sampling was not begun until after the systems were aged 1 month. At that time, the Zn/Si ratios of the precipitates ranged from 1.71 to 1.83, and averaged 1.76. Initially, the Zn and Si in the precipitates (Fig. 6) clearly indicated a

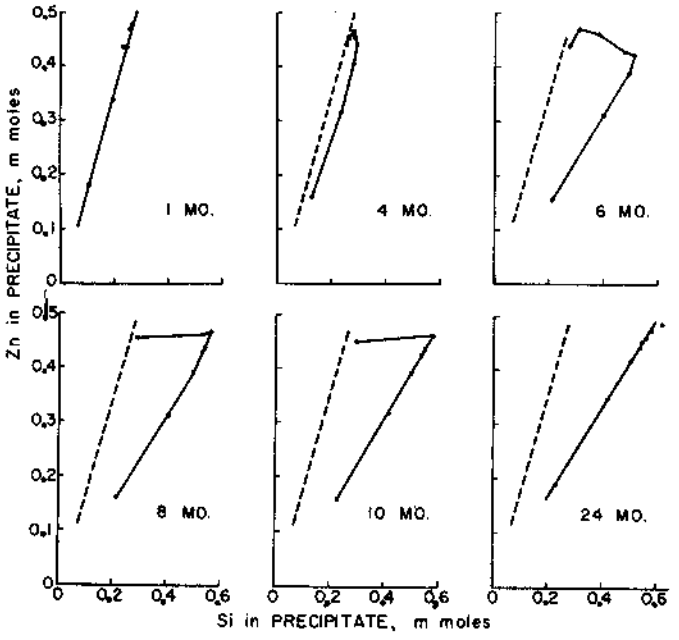

Fig. 6—The Zn and Si contained in the precipitate as influenced by aging. (The dashed lines indicate the position of the 1-month line. The system numbers given in Table 2 relate to the datum points as follows: Beginning with the lowest point on each line, the corresponding numbers increase consecutively along the lines, except for the 1-month line.)

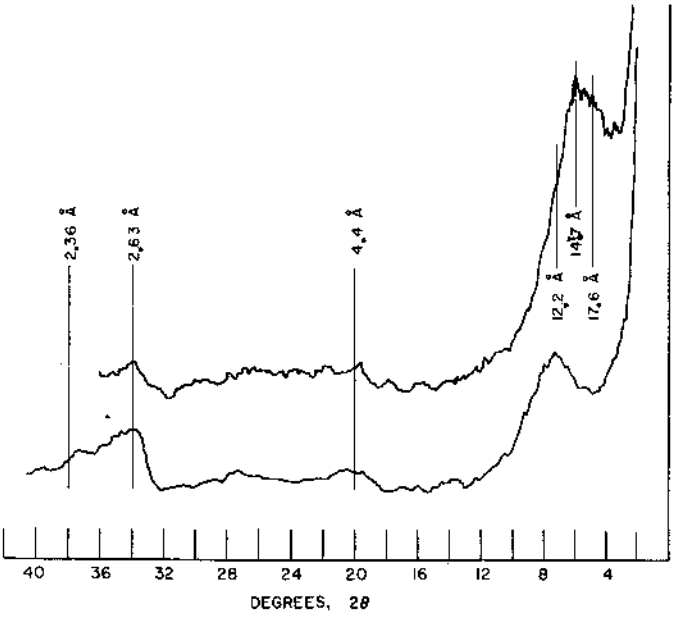

Fig. 7—X-ray diffraction patterns for glycerated-oriented precipitate *(upper curve)* and powder diagram for material dried at 45°C *(lower curve)*.

linear relationship between these two constituents. During the next 3 months, however, the precipitates for systems below pH 7.7 (Table 2) became noticeably enriched in Si, so that their Zn/Si ratios changed from 1.26 at pH 7.19 to 1.75 at pH 9.47. After 6 months aging, the three lowest points in Fig. 6, i.e., those of lowest pH, formed a new stabilized Zn/Si ratio of about 0.78. Precipitates aged at pH's > 7.8 changed progressively less as the pH increased; the system at pH 9.5 changed only slightly during the 6-month period. Further Si enrichment occurred during the 8- to 10-month period for the high pH system, resulting in stabilization of the Zn/Si ratios for all systems except one at values ranging from 0.74 to 0.80. For the system above pH 9.0, the Zn/Si ratio did not change much after aging 10 months and was still 1.53. A linear relationship between Zn and Si in the precipitates was evident for all except the high pH system. Within the next 14 months, it too became enriched with Si to the same extent as the other systems. The Zn/Si ratios of all precipitates ranged from 0.79 to 0.84, averaging 0.83, a slight increase from the average values of the stabilized precipitates aged 10 months.

Table 2—The pH of the stirred suspensions for the Zn series after various times of aging.

System no.	*Suspension pH after (months) 1	4	6	8	10	24
3	7.25	7.19	6.97	6.79	6.78	6.65
4	7.46	7.41	7.02	6.91	6.89	6.87
5	7.70	7.60	7.30	7.09	7.08	7.06
6	7.93	7.73	7.50	7.24	7.18	7.18
7	8.20	7.82	7.78	7.29	7.24	7.25
8	8.42	8.19	8.06	7.53	7.36	7.25
9	8.96	8.43	8.20	7.87	7.43	7.47
10	9.50	9.47	9.50	9.44	9.23	8.83

X-ray diffraction analysis of the Zn-containing samples indicate some crystallinity in all samples analyzed. The smooth diffraction patterns for one precipitate formed at pH 8 and aged 2 years are shown in Fig. 7. The pattern for the glycerated-oriented sample indicates a broad series of spacings over the range 14.2 to 18.6 Å. Also, there was a weak broad peak near 2.6Å. These patterns, although diffuse, indicate a 2:1 layer silicate. Diffraction patterns for a naturally occurring sauconite sample, not size-separated but otherwise treated in the same manner as the synthetic speciman (pattern not shown), had a major peak indicating spacing at 18.4Å and lesser peaks at 8.41 to 6.96Å. Neither of the last two spacings were evident for the precipitates, possibly because of the diffuse nature of the major spacings.

The pattern for the powdered synthetic material indicates a broad series of spacings near 12.2Å and weaker indications near 2.40 and 2.66Å and a still weaker response at about 4.4Å. These same spacings were reported (Tiller and Pickering, 1974) for a synthetic layer silicate containing Zn and Si formed under similar conditions as those used here. No other evidence of crystallinity was found in any of the samples.

DISCUSSION

A striking feature of the data presented is the contrast between the Cu and Zn series. At the time of precipitation, Cu was much more effective than Zn in removing $Si(OH)_4$ from solution. After aging the Cu series 1 month, the Cu/Si ratios of the precipitates averaged 0.78, whereas the Zn series aged under the same conditions gave Zn/Si ratios that averaged 1.81. After aging 10 months, however, the Cu series had changed only slightly, whereas the Zn series had changed markedly until the stabilized systems in both series had molar ratios near 0.78. Thus, with aging and with no interfering anions, the two metal cations appear equally

effective in removing $Si(OH)_4$ from solution.

During the prolonged aging, the precipitates in the five lowest pH systems in the Zn series changed first and became stabilized sooner than did those at higher pH. This was not surprising because of the smaller amounts of precipitates and the generally higher equilibrium concentrations of Zn and $Si(OH)_4$ at lower pH. It is difficult to understand, however, why the enrichment reaction started so slowly. The changes in the five lowest pH systems during the first 4 months of aging were only small fractions of those occurring over the next 2 months.

Also significant is that the pH decreased during aging and stabilized as enrichment became complete. Except for the high pH system, pH changes were only minor after 10-months aging (Table 2). Thus, the initial precipitate was possibly a Zn-hydroxy silicate that hydrolyzed to form a basic ion which then reacted with $Si(OH)_4$ in solution to form a Si-enriched precipitate during aging, releasing H. This mechanism is discussed by Siffert (1962) for reactions of $Si(OH)_4$ with Al and Mg. Hazel et al. (1949), and Jones and Handreck (1963) report similar reactions for Fe systems.

Because the diffraction patterns were diffuse, it was not possible to determine whether the Zn-containing precipitates contained only a small percentage of layer silicate mixed with a relatively large amount of amorphous material, or if they were homogeneous but poorly crystalline. All materials visually appeared uniform except for a gradation in particle size in each sample. The chemical data, however, reflect a Zn/Si ratio indicative of sauconite which has an ideal Zn/Si ratio of 0.75. The final Zn/Si ratio for the synthetic materials was about 0.80. Tiller and Pickering (1974) presented chemical data for one of their products having a Zn/Si ratio of 1.0 that showed strong indications of a 2:1 layer silicate. They indicated that the layer silicate was mixed with other material having a high Zn/Si ratio or containing no Si at all, thus resulting in a higher Zn/Si ratio for the mixture than for the layer silicate alone. The precipitates formed here possibly are mixtures of amorphous Zn silicate and layer silicate having similar Zn/Si ratios, but with the layer silicate being a minor constituent. If such were the case, however, the amount of layer silicate might be expected to increase and its crystallinity to improve with continued aging. Aging the precipitates for 5 years as compared to 2 years did not improve the X-ray diffraction responses. Other possibilities are (i) mixtures of layer silicate and amorphous Zn silicate of various proportions admixed with a small amount of amorphous $Zn(OH)_2$, thus resulting in a slightly higher Zn/Si ratio than that for the silicate mixture alone; and (ii) a major component of poorly organized layer silicate mixed with a small amount of amorphous $Zn(OH)_2$. Changes in composition noted during aging (i.e., all materials had the same Zn/Si ratios initially and changed to another material having a different Zn/Si ratio, but at different rates under different pH conditions) support the concept of a single component solid phase. Such a component, however, need not be a simple compound.

The extent to which CO_2 may have affected the reactions is not known, since no attempt was made to exclude it from any of the experiments. The results of Tiller and Pickering (1974), however, indicate that carbonate-free precipitates were obtained in studies similar to those reported here when samples were not dialyzed to remove the unreacted $Si(OH)_4$. They indicated that $Si(OH)_4$ concentrations greater than $3 \times 10^{-5}M$ during aging were sufficient to inhibit zinc carbonate formation. The minimum $Si(OH)_4$ concentration shown in Fig. 2 for the Cu and Zn series that were aged for 2 years was $> 3 \times 10^{-4}M$, thus it was assumed that CO_2 did not directly affect the results of the experiments.

Although the Zn and Cu concentrations decreased as a result of precipitation with $Si(OH)_4$, they were much higher than Zn or Cu concentrations usually present in soil solutions. The Zn concentrations in the aged Zn series exceeded by a factor of 10^4 those for soil solutions shown by Lindsay (1972). A similar comparison for Cu indicates even a greater factor.

From the data presented here, it appears possible that Zn and $Si(OH)_4$ in soils may interact to affect the availability of Zn to plants by forming sparingly-soluble precipitates. The pH and the $Si(OH)_4$ concentration present in most calcareous soils are conducive to such precipitation reactions. Such a mechanism could explain the results presented by Boawn (1974), who showed that Zn fertilization resulted in a new equilibrium level of extractable Zn in a calcareous soil that persisted for at least 5 years. About half of the Zn applied under field conditions had reverted to a sparingly soluble form. Such a reversion seems possible by forming mixed precipitates containing Zn as a minor constituent rather than a pure two-component precipitate.

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