

CONDITIONS GOVERNING THE FORMATION OF ATACAMITE AND PARATACAMITE¹

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ABSTRACT

Synthetic atacamite or paratacamite in contact with pure water, CuCl_2 or NaCl solutions at temperatures from 25 to 100°C, at times up to 70 days, did not convert to the other polymorph. In various methods of preparation, the copper hydroxychloride formed as paratacamite where the CuCl_2 concentration was sufficiently small, and as a mixture with atacamite at higher concentrations. Apparently nucleation of atacamite is favored by CuCl^+ complex in solution.

INTRODUCTION

Copper (II) trihydroxychloride, $\text{Cu}_2(\text{OH})_3\text{Cl}$, is encountered in mineral deposits, metal corrosion products, industrial products, and art and archeological objects (Lewin and Alexander, 1968). It occurs in three different crystal forms: botallackite (monoclinic), atacamite (orthorhombic), and paratacamite (rhombohedral). Although paratacamite appears to be the thermodynamically stable phase at 100°C and higher temperatures at ordinary pressures, and atacamite may be more stable at room temperature (Oswald and Feitknecht, 1964), both dimorphs have been reported as the end products of corrosion, oxidation, and hydrolysis processes.

When a solid phase forming from a solution can adopt either of several alternative crystalline arrangements, the composition of the final product is determined by the relative rates of nucleation and growth of the several species under the prevailing conditions, rather than by their relative thermodynamic stabilities. These relative rates may be sensitive to the temperature, pH, type of mass transport, velocity of crystallization, presence of adsorbable species, concentrations of complexing agents, and other solution parameters.

The present investigation seeks to elucidate the way in which such parameters control the crystallographic nature of solid deposits of copper (II) hydroxychloride. Although unstable hydrates (Walter-Levy and Goreaud, 1969), or the unstable hydroxychloride, botallackite (Feitknecht and Maget, 1949; Aebi, 1950; Voronova and Vainshtein, 1958) may form at first, under most conditions of mineral deposition these phases transform readily into paratacamite and/or atacamite. It is shown in the present work that the conditions necessary for the forma-

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tion of deposits of paratacamite alone, atacamite alone, and mixtures of these phases can be fully specified. As a consequence, determinations of the crystal character of a mineral deposit or corrosion patina involving these species can provide the key to disclosing the conditions which prevailed during its formation.

EXPERIMENTAL

Paratacamite. A powder consisting of fine particles (*ca.* 0.1–1 μm in linear dimensions) of pure paratacamite was prepared by allowing 100 ml of 1.0 *F* NaOH to drip slowly into an equal volume of a vigorously stirred solution of 1.0 *F* CuCl_2 ; yield was 7.0 g. This method is particularly convenient and rapid, for the product consists of pure paratacamite at all concentrations of the reagents, at all temperatures up to the boiling point, and at all rates of addition and stirring.

Pure paratacamite may also be prepared by immersing either copper, copper (I) oxide, or copper (I) chloride in a NaCl solution of any concentration, or a CuCl_2 solution more dilute than 0.025 *F*, and allowing the mixture to stand, exposed to air, for an extended period of time (days to weeks). Similar procedures have been reported by Feitknecht and Maget (1949).

Atacamite. A powder composed of pure atacamite (particle size *ca.* 0.1–1 μm in linear dimensions) was prepared most conveniently as follows. One gram of finely divided CaCO_3 (e.g., precipitated chalk) was added to 1000 ml of 0.1 *F* CuCl_2 and the mixture was stirred for 2–4 hours. At the end of this period, the CaCO_3 had completely dissolved, and about 3.6 g of atacamite powder could be filtered from the solution.

Pure atacamite has also been reported as formed in small amounts by allowing a solution of CuCl_2 +urea to stand for one year or longer, by the slow removal of ammonia vapors from 1 *F* CuCl_2 containing an excess of ammonium hydroxide (Oswald and Feitknecht, 1964), or as a surface deposit on magnesite or calcite spar crystals which have been kept immersed in dilute CuCl_2 for extended periods (Garrels and Stine, 1948). These procedures have given rise to the assumption that pure atacamite can only be prepared by very slow precipitation (Oswald and Feitknecht, 1964), but the technique given in the preceding paragraph permits, by suitable scale-up, very large amounts of pure atacamite to be prepared in short times and with great convenience.

Analysis of Mixtures. The proportions of the constituents in atacamite/paratacamite mixtures were determined from the relative intensities of nearby X-ray diffraction peaks recorded with a Norelco Geiger Counter Diffractometer. The peaks utilized were the $\text{CuK}\alpha$ reflections at $31.0^\circ 2\theta$ ($d=2.88$; $I/I_1=0.5$) for paratacamite, and $31.6^\circ 2\theta$ ($d=2.83$; $I/I_1=1.0$) for atacamite. The intensity ratios of these peaks were calibrated by means of standard mixtures of the two pure crystal phases, produced via the synthetic methods described above.

Well crystallized specimens of synthetic atacamite and paratacamite were obtained by heating 1.0 g samples of the precipitated material in the presence of several drops of water in a sealed tube at 150°C for about 160 hours. The observed X-ray diffraction patterns are substantially equivalent to XRDF patterns 2-146 and 15-694, except for lines at $d=2.78$ (100), 2.74(40), 2.71(20), 2.28(100) and, 1.76(60) for atacamite which are absent in XRDF 2-146; and lines at $d=2.88$ (50), 2.76(100), 2.71(40), 2.34(40), 2.24(50), and 1.81(60) for paratacamite, which are not reported in XRDF 15-694.

Non-Interconvertibility of Dimorphs. Standard mixtures of atacamite and paratacamite, prepared by mixing weighed samples of the pure powder specimens described above, were

stirred in contact with water; as well as with CuCl_2 solutions ranging from 0.020 F to 2.00 F ; and with NaCl solutions ranging from 0.10 F to 2.00 F , at temperatures from 25°C to the boiling point, and for periods of time up to 70 days. The solid phase remaining after these treatments was in every case found to be identical with the starting mixture, within the precision of the X-ray method of analysis ($\pm 2\%$).

Standard mixtures were stirred at 25°C for 4 days with solutions of 0.001 F Na_2CO_3 . This reagent slowly hydrolyzes copper (II) trihydroxychloride to copper (II) oxide. The volume of solution was adjusted in relation to the quantity of solid introduced so that only a part, ranging from 20 to 80 percent, of the atacamite/paratacamite mixture was subject to the hydrolytic reaction. Analysis of the residues showed that in every case the relative proportion of atacamite to paratacamite remaining at the end of the experiment was the same as it had been at the start. That is, the attack by the alkali did not discriminate between the dimorphs.

Hence, there appears to be no interconversion of one of the dimorphs into the other in aqueous systems at ordinary pressures. This implies either that equilibrium is not established between the solid phase and its ions in solution, or the free energies of the two crystal forms are so similar that they have substantially identical solubilities and reactivities. The latter appears unlikely in view of the fact that atacamite can be converted into paratacamite by heating the former solid in a sealed tube at 200°C for 3 days (Oswald and Feitknecht, 1964).

Direct Precipitation. Copper (II) hydroxychloride was precipitated by direct mixing of equal volumes of CuCl_2 and NaOH solutions of equal concentrations under the following conditions. The NaOH solution was added to the CuCl_2 solution, and *vice versa*; rapid stirring, no stirring; concentrations ranging from 0.020 F to 5.00 F ; reaction at 25°, or at 100°C. In every case, the product consisted only of paratacamite. These results do not entirely accord with the conclusions of Strelets and Orlyanskaya (1957) based on refractometric measurements; these authors have reported that when the reagents are more concentrated than 0.5 F , only copper (II) hydroxide precipitates.

Metal Corrosion Product. Copper foil, 0.010" thick and 99.99 percent pure, was cleaned by immersion in dilute HNO_3 followed by thorough rinsing in distilled water. Squares of the foil, 2.5×2.5 cm., were suspended in one to three liters of the solution of interest, and the air-equilibrated liquid phase was stirred for 46 hours, after which the green corrosion product was collected and analyzed. The volume of solution was made large enough that the corrosion of the copper did not cause the concentrations of the reactants to be changed by more than 2–3 percent from their initial values. Change of volume due to evaporation during the run was also kept within this limit. These considerations apply to all the following experiments as well.

In NaCl solutions ranging from 0.010 to 6.00 F and at 25° and 100°C, as well as in CuCl_2 solutions between 0.001 and 0.020 F , the only green corrosion product was paratacamite. In CuCl_2 solutions between 0.050 and 2.00 F , the product was a mixture of atacamite and paratacamite, the proportions varying as a function of the CuCl_2 concentration in the manner shown in Figure 1A. The addition of NaCl to a CuCl_2 solution led to an increase in the atacamite yield and a corresponding decrease in the paratacamite (Fig. 2A). Increase in the temperature of the solution favored paratacamite at the expense of the atacamite.

Oxidation Reaction Product. Samples of copper (I) oxide and of copper (I) chloride were allowed to undergo oxidation by dissolved air in NaCl or CuCl_2 solutions at room temperature. Ten millimoles of starting material were completely converted to copper (II) hydroxychloride within 46 hours. The relation between the crystal character of the oxidation

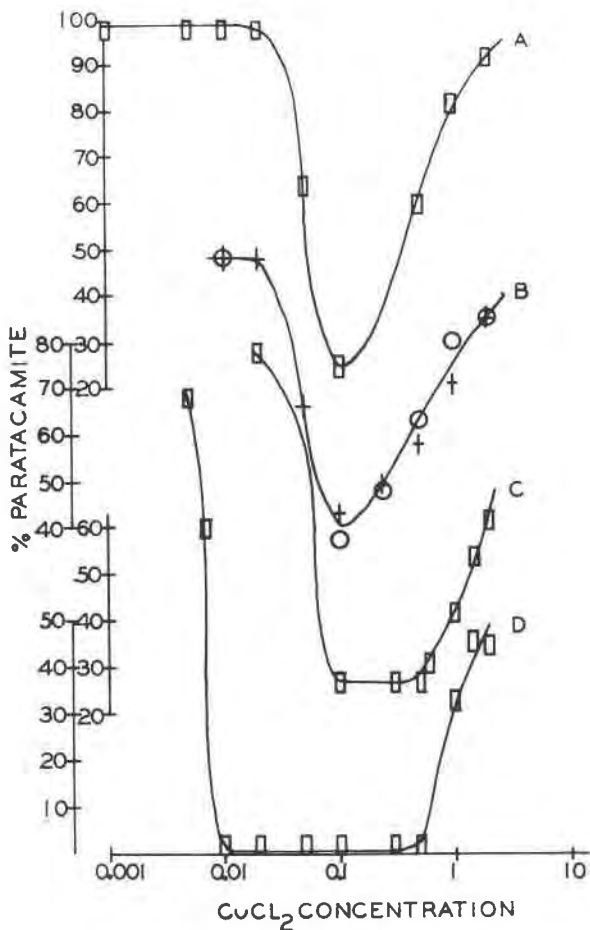


FIG. 1. The crystal character of the copper (II) trihydroxychloride formed in aqueous CuCl_2 solutions by five different reaction schemes: *A*, corrosion of copper metal; *B*, oxidation of $\text{Cu}_2\text{O}(+)$ and $\text{CuCl}(0)$; *C*, replacement of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (malachite); *D*, indirect precipitation product of CaCO_3 .

product and the composition of the solution is shown in Figure 1B. Addition of NaCl to 0.02 *F* CuCl_2 solution in which CuCl is oxidizing markedly favors the formation of atacamite at low NaCl concentrations; the effect falls off with increasing NaCl concentration (Fig. 2B). The product formed in the oxidation of copper (I) chloride in NaCl solution alone was identical to that formed by the corrosion of copper metal in NaCl (Fig. 2A), paratacamite being formed at all chloride concentrations.

Replacement Reaction Product. Ten millimole samples of copper (II) hydroxycarbonate (malachite) powder, $\text{Cu}_2(\text{OH})_2\text{CO}_3$, were suspended in NaCl or CuCl_2 solutions and main-

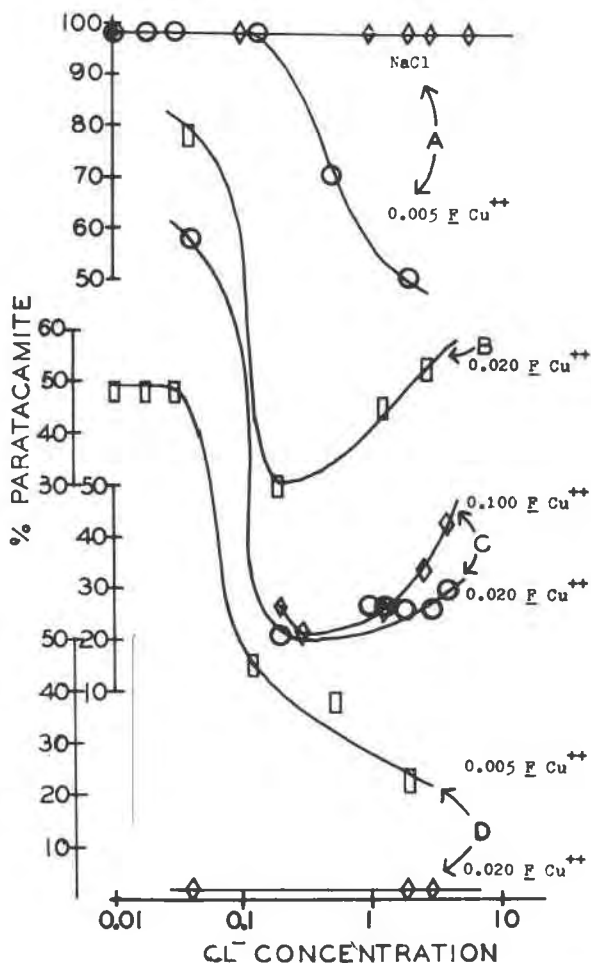
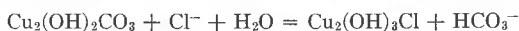


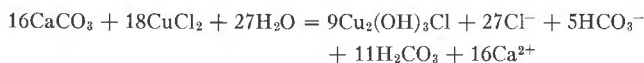
FIG. 2. The crystal character of the $\text{Cu}_2(\text{OH})_3\text{Cl}$ formed in a given CuCl_2 solution as a function of added NaCl . A, corrosion of copper metal; B, oxidation of CuCl ; C, replacement of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (malachite); D, indirect precipitation product of CaCO_3 .

tained at room temperature for 46 hours, during which time the hydroxycarbonate was completely converted to the hydroxychloride, according to the following stoichiometry.

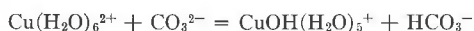


As in the previous cases, the crystal character of the hydroxychloride was found to be a function of the CuCl_2 and NaCl concentrations; the relationship is shown in Figure 1C. In pure NaCl solutions, only paratacamite was formed, as was the case with copper metal in NaCl (Fig. 2A). The addition of low concentrations of NaCl to CuCl_2 solutions favored the formation of atacamite; high concentrations, however, reduced the yield of atacamite and favored the production of paratacamite (Fig. 2C).

Indirect Precipitation. The term "indirect precipitation" will be employed to designate the reaction in which copper (II) hydroxychloride is produced due to the rise in pH accompanying the slow dissolution of a sparingly soluble alkaline material in the initially acidic (pH 1.5-3, depending on the concentration) copper (II) chloride solution. In the case of CaCO_3 powder suspended in an initially 0.100 *F* CuCl_2 solution, the stoichiometry of the reaction is close to the following:



The role of the CaCO_3 is to react with the hydronium ions resulting from the hydrolysis of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, thus displacing the hydrolysis equilibrium in favor of $\text{CuOH}(\text{H}_2\text{O})_5^+$, according to:



As the $\text{CuOH}(\text{H}_2\text{O})_5^+$ is removed from the solution by precipitation as $\text{Cu}_2(\text{OH})_3\text{Cl}$, more CaCO_3 dissolves. This process tends to buffer the solution at a pH of 4.0 (*cf.* Vorob'ev, Rykova and Shternina, 1968). The complicated stoichiometry shown in the above equations merely expresses the fact that under the concentration conditions given, about two-thirds of the carbonate which enter the solution from the dissolving calcium carbonate are converted to carbonic acid, which decomposes and releases CO_2 , while about one-third remains as bicarbonate ions.

One gram samples of precipitated chalk were suspended in 1-3 liters of CuCl_2 solutions of various concentrations and stirred at 25° or 100°C until reaction was complete (several hours). The precipitate was filtered off and analyzed. Its crystal character was found to be a function of the CuCl_2 concentration, as shown in Figure 1D. The addition of NaCl to 0.005 *F* CuCl_2 reduced the proportion of paratacamite and correspondingly raised the proportion of atacamite in the precipitate. However, at a CuCl_2 concentration of 0.5 *F*, the addition of NaCl had the opposite effect (Fig. 2D).

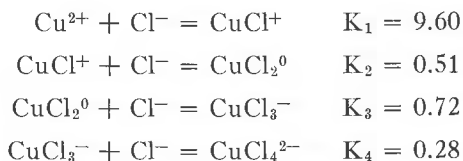
Increase in temperature from 25° to 100°C resulted in an increased yield of paratacamite at the expense of atacamite.

DISCUSSION

Role of Copper (II) Ions. The air/aqueous corrosion of pure copper, the oxidation of copper (I) oxide or copper (I) chloride, the replacement of CO_3^{2-} in malachite by Cl^- , and the indirect precipitation by or on calcite in chloride solution, all result in the production of pure paratacamite when the CuCl_2 concentration is sufficiently small. Furthermore, in each of these cases a transition to mixtures of atacamite/paratacamite occurs as the CuCl_2 concentration is raised, and a maximum proportion of atacamite is achieved at an intermediate CuCl_2 concentration (around 0.1 *F*). It is clear from these observations that the crystal character of the hydroxychloride is governed by the composition of the solution phase, and not by the properties or structure of the substrate on or near which the corrosion, oxidation, hydrolysis, or replacement product is formed. This conclusion also provides the rationale for the observations of Walter-Levy and Goreaud (1969), who noted that when $\text{Cu}(\text{OH})_2$ or CuO is acted upon by a CuCl_2 solution, pure paratacamite results if

the CuCl_2 concentration is 0.04 F , but atacamite predominates in the product if the concentration is between about 0.17 and 0.22 F .

In solutions containing Cu^{2+} and Cl^- , the following association reactions have been shown to occur; the values for the equilibrium constants determined by Morris and Short (1962) for 0.691 F HClO_4 solutions may be taken as adequate for the present purposes.



In solutions made up by dissolving CuCl_2 in water, the concentrations of each of the above species can be calculated from the total solute formality and the equilibrium constants. Figure 3 depicts the results of such calculations (only the relative proportions of the various species are of interest; no other significance should be attached to the precise values given).

The precipitation of $\text{Cu}_2(\text{OH})_3\text{Cl}$ starts at a pH of approximately 4.

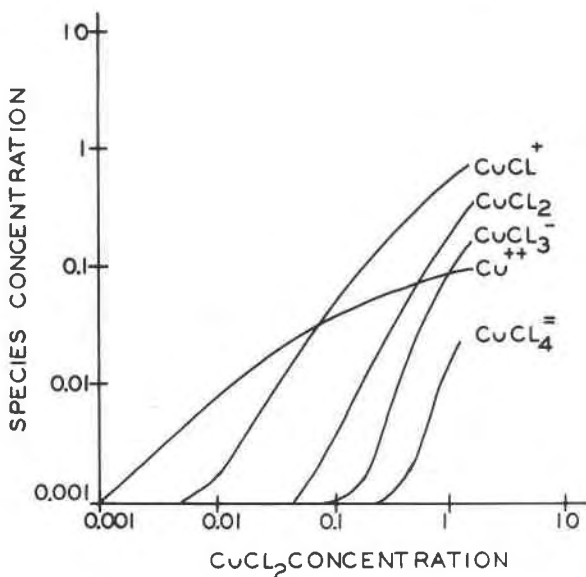
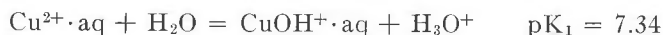


FIG. 3. The concentrations of the principal copper-containing species in aqueous CuCl_2 solutions as a function of the total solute formality. Calculated from equilibrium constant data of Morris and Short (1962).

If we take the value given by Achenza (1964) for the pK_1 of the copper (II) ion:



then at the precipitation pH,

$$\frac{[\text{CuOH}^+ \cdot \text{aq}]}{[\text{Cu}^{2+} \cdot \text{aq}]} = 4.6 \times 10^{-4} = 1/2200$$

Thus the hydrolysis of the copper (II) ion at pH's up to those necessary to cause the slow precipitation of $\text{Cu}_2(\text{OH})_3\text{Cl}$, as in the indirect precipitation experiments, displaces the Cu/Cl association reactions by a negligible amount.

At low concentrations of the solute (0.001 *F* and below), the hydrated copper (II) ion is the principal species present; CuCl^+ is less than 2 percent of the total copper content. Under these conditions, paratacamite is the crystal form which deposits from the solution. As the solute is made more concentrated, the proportion of CuCl^+ begins to be significant. The results of the phase analyses of the deposits show that when the CuCl^+ concentration reaches or exceeds about 20–30 percent of the total copper (II) content at a pH of 4, atacamite forms in preference to paratacamite. This suggests that CuCl^+ directs the nucleation and growth of atacamite crystals (or, equivalently, inhibits the nucleation and growth of paratacamite crystals), and this hypothesis is supported by the observation that at CuCl_2 concentrations in the low range, where only paratacamite forms, the addition of NaCl to the solution causes atacamite to form instead. Clearly, the additional Cl^- has displaced the association equilibrium in these solutions toward the formation of significant concentrations of CuCl^+ .

At higher concentrations of the solute (above 0.1–0.5 *F*), the higher association products, CuCl_2^0 , CuCl_3^- , and CuCl_4^{2-} , become important. The data show that when these species reach 3–20 percent of the total copper (II) content at pH 4, they either repress the effect of CuCl^+ , or themselves take over control of the phase-building processes, and direct the formation of paratacamite. This explains why the addition of NaCl to solutions which already contain considerable concentrations of CuCl^+ results in a *decreased* proportion of atacamite. For, although the additional Cl^- displaces the equilibria toward the formation of more CuCl^+ , it also produces CuCl_2^0 , CuCl_3^- , and CuCl_4^{2-} . Since the phenomena of nucleation and growth involve specific surface effects (e.g., chemisorption), causing the concentration of a species already present in adsorption saturation amounts (*i.e.*, CuCl^+) to increase still more is less im-

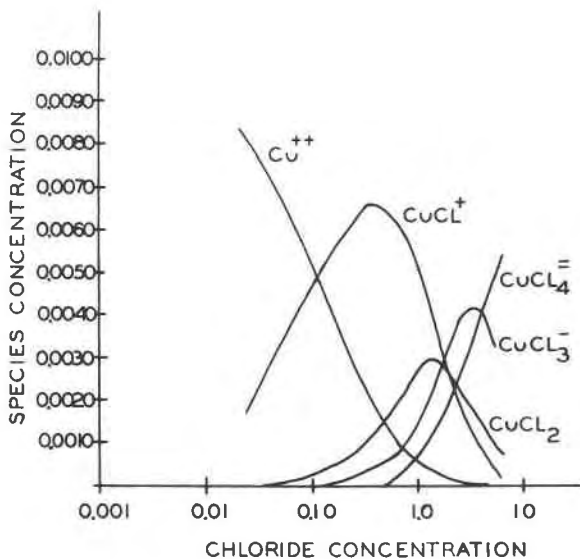


FIG. 4. The concentrations of the principal copper-containing species in 0.01 F CuCl_2 solution as a function of total chloride ion formality

portant than causing a species originally present in minor amounts (*i.e.*, CuCl_2^0 , *etc.*) to achieve significant concentrations.

Calculation of the concentrations of various solution species can be made for the general case where the total CuCl_2 formality is kept constant and the concentration of chloride varied (corresponding to the experiments involving the addition of NaCl). The results of such calculations for 0.01 F CuCl_2 are displayed in Figure 4. These results show that as the concentration of chloride increases, the concentration of copper (II) ion steadily decreases due to displacement of the association equilibria toward the formation of the Cu (II) complexes. It is clear that the total chloride formality where CuCl^+ is present in the greatest concentration corresponds very well with the chloride ion concentration where atacamite is produced in greatest amount relative to paratacamite (see Figure 2B, for example).

The rapid transition from pure paratacamite to atacamite-rich mixtures on the low concentration side of the system, the relatively small change in atacamite concentration associated with large changes in the CuCl^+ concentration, and the tendency for competing species to outweigh the effect of large concentrations of CuCl^+ , are all types of behavior characteristic of specific adsorption on solid surfaces, as, for

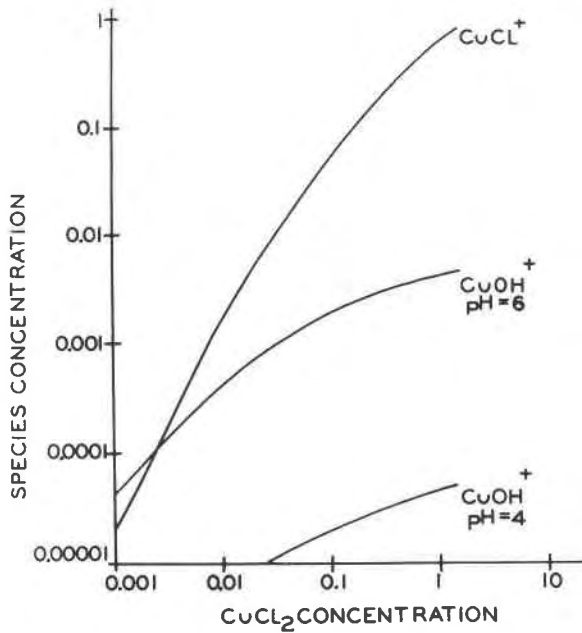


FIG. 5. The relative amounts of CuCl^+ and CuOH^+ as a function of the CuCl_2 formality during the corrosion reactions ($\text{pH}=6$), and in the indirect precipitation technique ($\text{pH}=4$).

example, are manifested in the "poisoning" phenomena shown by catalysts.

In the indirect precipitation technique, the formation of $\text{Cu}_2(\text{OH})_3\text{Cl}$ takes place at a pH of approximately 4. In the corrosion reactions, *i.e.*, Cu , Cu_2O , or CuCl undergoing oxidation and hydrolysis, the pH during precipitation of the trihydroxychloride is probably in the vicinity of 6. The relative amounts of CuCl^+ and CuOH^+ in the system under these conditions are shown in Figure 5 as a function of the total CuCl_2 formality.

These calculations show that at the lower pH , CuCl^+ predominates greatly over CuOH^+ at all CuCl_2 formalities, but at the higher pH , the CuCl^+ is present in only somewhat greater relative concentration than CuOH^+ at low CuCl_2 formalities.

These relationships show why the atacamite yield curves show a narrower and shallower maximum in the corrosion reactions (Fig. 1A-B) than in the indirect precipitation reaction (Fig. 1D). For in the former, the CuOH^+ interferes with the CuCl^+ (e.g., by competing for adsorption sites) at low CuCl_2 formalities, and the higher chloro-complexes interfere

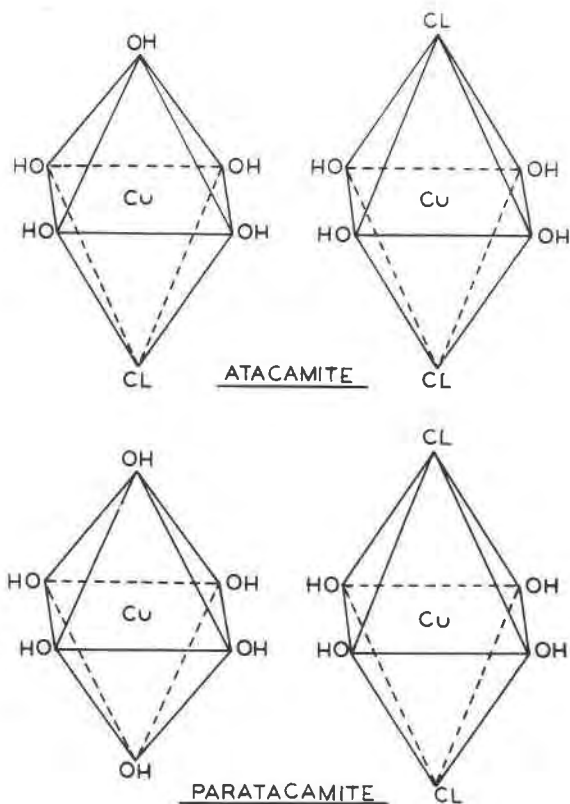


FIG. 6. The building blocks in the crystal structures of atacamite and paratacamite.

at the higher CuCl_2 formalities. Thus, the CuCl^+ is able to exert a significant effect only in the vicinity of 0.05–0.5 F CuCl_2 .

The hydrolysis reaction of malachite would be expected to produce a pH intermediate between that of the two reaction types discussed above, and the atacamite yield curve does indeed show an intermediate character (Fig. 1C).

The fact that direct precipitation of CuCl_2 solutions with NaOH always yielded paratacamite is a consequence of the great insolubility of $\text{Cu}_2(\text{OH})_2\text{Cl}$. The rate of precipitation when the reagents are mixed is so great that even with very vigorous stirring the effective concentration of the species CuCl^+ in the diffusion layer of liquid around a precipitation particle is always below the value requisite for atacamite production.

In the paratacamite lattice, the copper ions have an octahedral coordination, but with two different kinds of environment: one of every

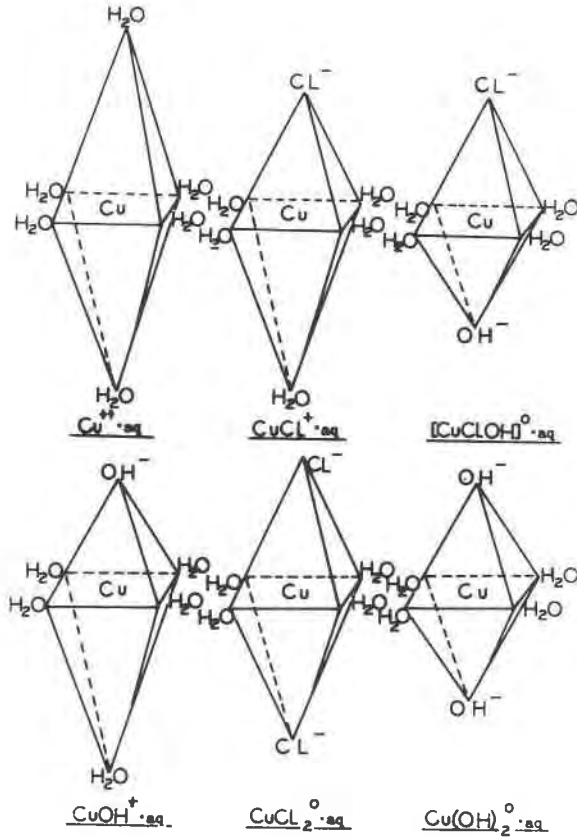


FIG. 7. The octahedrally coordinated copper (II) ions present in CuCl_2 solution.

four copper ions is surrounded by six OH groups; three of every four coppers have four OH and two Cl groups (Ludi and Feitknecht, 1963). In atacamite, the copper ions are also octahedrally surrounded, but half of them now have five OH and one Cl, while the other half have four OH and two Cl nearest neighbors (Wells, 1949). The contrast between the building blocks of these two crystal structures is illustrated in Figure 6.

It is noteworthy that the octahedrally coordinated solution species $\text{CuCl}^{+} \cdot \text{aq}$ and $[\text{CuOHCl}]^{0} \cdot \text{aq}$ (for which the formation constant is not available, but which must also be assumed to be present in significant amounts in solutions more concentrated than about 0.1 F CuCl_2 at $\text{pH} = 4$), shown in Figure 7, are closely related in structure and symmetry properties to one of the building blocks of atacamite but to neither of the building blocks of paratacamite. It is precisely in those solutions in

which the aforementioned species attain significant concentrations that atacamite nucleates and grows in preference to paratacamite. In more concentrated CuCl_2 solutions, or at higher pH's the ready availability of substantial quantities of the symmetrical solution species $[\text{CuCl}_2]^0 \cdot \text{aq}$ and $[\text{Cu}(\text{OH})_2]^0 \cdot \text{aq}$ promotes the buildup of the more symmetrical paratacamite lattice at the expense of atacamite.

CONCLUSIONS

The nucleation and growth of paratacamite crystals occur readily in aqueous systems when the concentration of CuCl^+ is very small, or when appreciable concentrations of that species are offset by the presence of molecular CuCl_2^0 or higher chloro-complexes in amounts greater than 3–20 percent of the total copper (II) content. The formation of atacamite crystals requires the presence of CuCl^+ to the extent of about 200 parts in 1000 of total copper (II) content, and the absence of large amounts of the higher chloro-complexes.

Occurrences of pure paratacamite as a mineral deposit, corrosion product, or in the patina of an art object are evidence that it formed under conditions of low CuCl_2 concentration, and, hence, deposited slowly. Crystals could grow to macroscopic dimensions in favorable cases.

However, occurrences of atacamite/paratacamite mixtures in the same circumstances imply that the concentration of dissolved copper present during the deposition was appreciable. The minimum concentration would be about 0.005 F —but this small a concentration would be effective only in the presence of both large amounts of dissolved Cl^- and intimate contact with a carbonate rock. In the absence of the latter two factors, the minimum concentration of copper (II) chloride in the corroding or mineralizing medium would have to be in excess of 0.02 F . Atacamite formed under these conditions would tend to precipitate rapidly and be powdery rather than crystalline in texture, unless some mechanism were operative to buffer the pH very close to the precipitation point.

REFERENCES

- ACHENZA, F. (1964) Hydrolysis of the copper (II) ion. *Ann. Chim. (Rome)*, **54**, 240–245.
- AEBI, F. (1950) Zur Struktur der basischer Salze mit pseudo-hexagonalen Schichtgittern. *Acta Crystallogr.* **3**, 370–372.
- FEITKNECHT, W., AND K. MAGET (1949) Zur Chemie und Morphologie der basischen Salze zweiwertiger Metalle. *Helv. Chim. Acta*, **32**, 1639–1653.
- GARRELS, R. M., AND L. O. STINE (1948) Replacement of calcite by atacamite in copper chloride solutions. *Econ. Geol.* **43**, 21–30.
- LEWIN, S. Z., AND S. M. ALEXANDER (1968) The composition and structure of natural patinas. *Art Archaeol. Technol. Abstr.* **6**, 201–283; **7**, 279–370.

- LUDI, A., AND W. FEITKNECHT (1963) Lichtabsorption und Struktur von Kristallverbindungen der Übergangsmetalle. *Helv. Chim. Acta*, **46**, 2238-2248.
- MORRIS, D. F. C., AND E. L. SHORT (1962) Stability constants of copper (II) chloride complexes. *J. Chem. Soc.* **1962**, 2672-2675.
- OSWALD, H. R., AND W. FEITKNECHT (1964) Über die Hydroxidhalogenide $Me_2(OH)_3Cl$, -Br, -J zweiwertiger Metalle. *Helv. Chim. Acta*, **47**, 272-289.
- STRELETS, N. L., AND A. K. ORLYANSKAYA (1957) Reactions of sodium hydroxide with metal salts in aqueous solutions (refractometric studies). *Tr. Pervoi Nauchn. Nauchn-Melod. Konf. Prepodavatelei Biol., Sel'sk.-Khoz. Khim. Distiplin Metodiki Prepodavaniya Ped. Inst. Ukr. S.S.R., Sinferopol*, 315-322.
- VOROB'EV, G. I., G. A. RYKOVA, AND E. B. SHTERNINA (1968) Influence of hydrogen ion concentration on the rate of dissolution of calcite in salt solutions containing carbon dioxide. *Russ. Jour. Inorg. Chem.* **13**, 1319-1322.
- VORONOVA, A. A., AND B. K. VAINSHEIN (1958) An electron-diffraction study of $CuCl_2 \cdot 3Cu(OH)_2$. *Kristallografiya* **3**, 444-451 [Transl. *Sov. Phys. Crystallogr.* **3**, 445-451.]
- WALTER-LEVY, L., AND M. GOREAUD (1969) Sur la formation des chlorures basiques cuivriques en solution aqueuse de 25 à 200°C. *Bull. Soc. Chim. Fr.* **8**, 2623-2634.
- WELLS, A. F. (1949) The crystal structure of atacamite and the crystal chemistry of cupric compounds. *Acta Crystallogr.* **2**, 175-180.

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