

COPPER CONTENTS IN TAP WATERS - SOME THOUGHTS ABOUT CAUSES AND RELEASE MECHANISMS

Claes Taxén and Mats Linder, Swedish Corrosion Institute, Kraeftriket 23 A, SE 104 05 Stockholm

ABSTRACT

The copper content in tap waters is discussed starting from equilibrium conditions. The hydroxide model is compared with the 'true equilibrium'. Arguments that could explain the formation of the hydroxide $\text{Cu}(\text{OH})_2(\text{s})$ rather than more stable compounds such as $\text{CuO}(\text{s})$ and $\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s})$ are found to include surface energy, mechanism of precipitation and mechanism of formation from $\text{Cu}_2\text{O}(\text{s})$.

The copper content at various times of stagnation is discussed in relation to the precipitation of cupric phases and to a reductive mechanism involving metallic copper. At equilibrium in aerated water, the most stable cupric phase limits the solubility of copper and the amounts of organic and inorganic complex forming agents determine the total copper contents of the water. In oxygen poor water, exposed metallic copper may behave as a reducing agent and limit the copper contents of the water. Calculations with EDTA as complex forming agent shows that also strongly bound cupric species may be reduced to cuprous and precipitate as cuprous oxide.

It is suggested that the observed stagnation curves may be a result of a production process of $\text{Cu}(\text{II})$ that is coupled to the consumption of oxygen, and the precipitation or reductive removal of $\text{Cu}(\text{II})$ from the water. The shape of the curve and the maximum copper content should then be a result of competing kinetics for the production and the depletion processes.

1. Background

Copper in tap waters originates from corrosion processes at the walls of the copper tubes. The corrosion of copper metal is of an electrochemical nature and basic electrochemical data for the corrosion process are required to give a model description of the corrosion process. However, the contents of copper in tap waters depend on many other factors than the corrosion process itself. Solubility of corrosion products plays a central role as do the kinetics of their formation and dissolution. The solubility of the corrosion product determines the

concentration or, to be more precise, the activity of the Cu^{2+} ion. The formation of dissolved complexes between the Cu^{2+} ions and components from the water determines the total dissolved copper contents. Inorganic complexes are primarily formed with the hydroxide ion and with carbonate. Organic complexes are formed with the humic and fulvic fractions, mainly, of the natural organic matter (NOM) in the water. The organic complexes are in general less well characterised than the inorganic, not least because the organic matter itself is not always well characterised. Possibly other constituents in NOM than the fulvic and humic acids take part in the complex formation. Frequently, the organic contents in the water is known only as the TOC- value (TOC = Total Organic Carbon) or COD (COD = Chemical Oxygen Demand).

Flowing waters in once-through systems generally have low values for the dissolved copper. Many investigators have found that immediately after stagnation the copper contents begin to increase. Several typical patterns or stagnation curves have been reported. At the same time as the copper contents start to increase, the oxygen concentrations in the initially air saturated water begins to decrease. Usually a first order dependence is observed giving an asymptotic approach to zero oxygen concentration. The concentrations of copper in the water during the stagnation period frequently exceeds the solubility limits for the corrosion products (Cu(II) as well as Cu(I) and the sum of the two).

Organic complexes are suspected to play an important role in the occurrence of these apparently super saturated waters. The organic copper complexes are likely to be relatively stable. The stagnation curves frequently show a period where the copper contents decrease towards a level close to the solubility value. This observation of decreasing copper concentrations is not entirely consistent with stable aqueous organic complexes. Many authors have discussed the stagnation curves and the high copper concentrations in terms of kinetics of formation of the stable solid corrosion products. In a short perspective it is possible that for example $\text{Cu}(\text{OH})_2(\text{s})$ is formed rather than the more stable $\text{CuO}(\text{s})$ or malachite in carbonate rich waters. Indeed the existence of $\text{Cu}(\text{OH})_2(\text{s})$ has in some cases been confirmed by X-ray analysis. $\text{Cu}(\text{OH})_2(\text{s})$ has, because of its instability, a higher solubility than $\text{CuO}(\text{s})$. In spite of the efforts of many researchers, there is yet no generally accepted method of predicting the resulting copper content in a tap water from its composition.

2. Equilibrium concentrations of copper in tap waters.

2.1 'True equilibrium'

By performing equilibrium calculations for the system $\text{Cu}^{2+} - \text{OH}^- - \text{Cl}^- - \text{SO}_4^{2-} - \text{HCO}_3^-$ for a series of tap waters we have identified the pH of the water and the total carbonate contents as the main factors that control the contents of dissolved copper at saturation. Figure 1 shows a diagram with iso-concentration curves for the total dissolved copper. Depending on the pH and the total carbonate concentrations, cupric oxide or different basic cupric salts control the solubility. Table I shows the composition of the waters considered. The pH and carbonate contents of the water were varied. The concentration of Cu(II) was adjusted to saturation with respect to the most stable solid. The sodium concentrations were adjusted to electroneutrality. Thermodynamic data for 25°C were used [1] and Davies' model for calculation of activity concentrations applied.

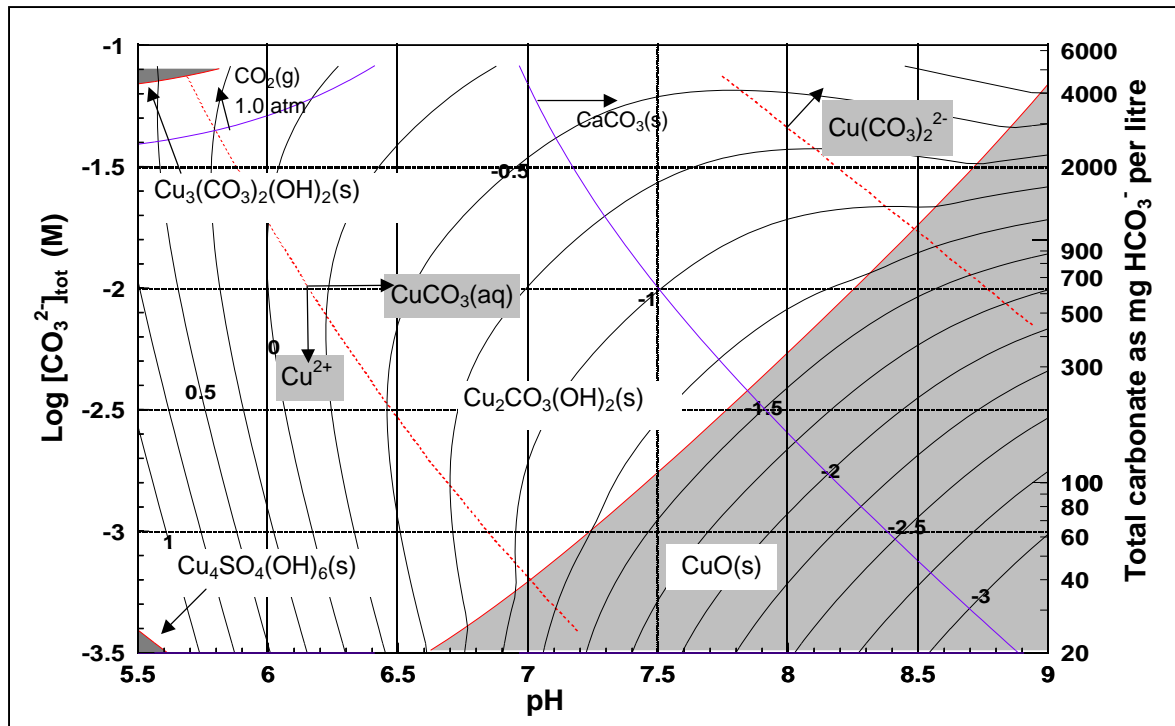


Figure 1. Result of equilibrium calculations for a water composition according to table I. All relevant solid phases considered.

Curved thin lines: iso-concentration lines for equilibrium content of copper in solution as function of pH and total carbonate content. The logarithm of the total concentration in mg/l dissolved copper is indicated with bold figures on every second line.

White field: malachite limits the copper solubility.

Left grey field in lower corner: basic copper sulphate (brochantite) limits the copper solubility.

Left grey field close to upper corner: azurite limits the copper solubility.

Right grey field: CuO, (tenorite) limits the copper solubility.

Dotted lines: enclosure area where CuCO₃(aq) is the dominating form of dissolved copper

Below left dotted line: Cu²⁺ is the dominating form of dissolved copper.

Above right dotted line: Cu(CO₃)₂²⁻ is the dominating form of dissolved copper.

Solid line in the upper left hand corner: saturation limit of CO₂(g) at 1.0 bar.

Solid diagonal line: saturation limit of CaCO₃(s)

Table I. Composition of the model water

	Total Concentrations	
	moles/dm ³	mg/dm ³
Cl ⁻	0.001	35.5
SO ₄ ²⁻	0.001	96.1
Ca ²⁺	0.0005	20.0
CO ₃ ²⁻	Varied	
pH	Varied	
Cu ²⁺	To saturation	
Na ⁺	To electroneutrality	

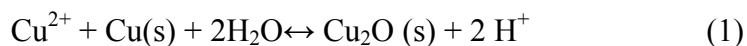
2.2 Inhibited Equilibrium- The hydroxide model

Many authors have observed higher concentrations than predicted by 'true equilibrium' and cupric hydroxide has in some cases been identified by X-ray. These observations together with observations of a strong increase in copper contents with increasing carbonate

formation. Frequently, the organic content in the water is known only as the TOC- value (TOC=Total Organic Carbon) or COD (COD = Chemical Oxygen Demand). Various models for complex formation between NOM and Cu^{2+} have been applied. Edwards [5] found that one single complex constant for the NOM- Cu^{2+} interaction gave good agreement with experimental observations. Elfström-Broo and coworkers [6] applied a model for complex formation developed by Cabaniss and Schuman [7]. Using median values of copper contents, they found a significantly improved correlation when NOM was included. The improvement is drastic in 6 of 6 waters with median values below 0.5 mg/l. However, in 3 of 4 waters with median values above 1 mg/l, the NOM model overestimates the copper contents.

2.4 *Equilibrium in a system with organic matter.*

In the construction of the diagrams in figures 1 and 2, only divalent copper was considered. It was however verified that monovalent copper gives a negligible contribution to the total concentration of dissolved copper. The work of Werner [8] suggests that the equilibrium system in a copper tube in some cases also includes metallic copper in contact with the water. The contents of cupric ions in the water is then determined by the electrochemical equilibrium in reaction 1. This process was considered also by Tronstad and Veimo [9].



Complex formation with available ligands determines the total concentration of copper in the water at equilibrium. This electrochemical condition for equilibrium gives an additional constraint for the copper contents. The contents of copper at equilibrium can still not exceed that given by solubility of cupric salts and oxide. Reaction 1 becomes relevant only for cases where bare copper metal is exposed to the water. For carbonate and hydroxide as complex forming agents at levels relevant for tap waters, the content of copper is low. But organic complexes with copper can be quite strong. Does reaction 1 limit the copper contents to lower values than those given by cupric solubility also in the presence of very strong complex forming agents? Figures 3 and 4 show results for a case where EDTA is present. The same water composition was used as in figure 1 with a fixed total carbonate concentration of 30 mM $\sim 200 \text{ mg/dm}^3$ as HCO_3^- . All solid cupric species were considered. Figure 3 shows results for pH 6.0 and figure 4 shows results for pH 9.0. Equilibrium constants for the various complexes and protolysis products of EDTA were taken from ref. [10].

At pH 9.0 the solubility curve, in the absence of Cu(s) shows that the total copper concentration increases strongly with increasing concentrations of EDTA. Almost all of the EDTA is present as a copper complex. If Cu(s) is exposed however, the total copper content is much lower. Nevertheless, 10^{-4} M EDTA would increase the copper contents with a factor of about 100. At pH 6.0 the solubility of the stable cupric solid is higher. Consequently, the total concentration of the dissolved copper is relatively insensitive to the EDTA contents at low levels. Also at pH 6.0 the electrochemical equilibrium reduces the total amounts of copper significantly at low EDTA concentrations. Comparing the results for pH 6.0 and 9.0 we find that the reducing power of metallic copper is weaker at pH 6.0 than at pH 9.0.

During the calculations it was observed that at low copper contents, EDTA tends to bind to the available calcium instead. NOM has also been found to interact strongly with calcium [7]. The complex formation between copper and NOM can, at least to some extent, be described as an ion exchange. It is to be expected that copper ions replace not only protons but also ions like calcium and magnesium.

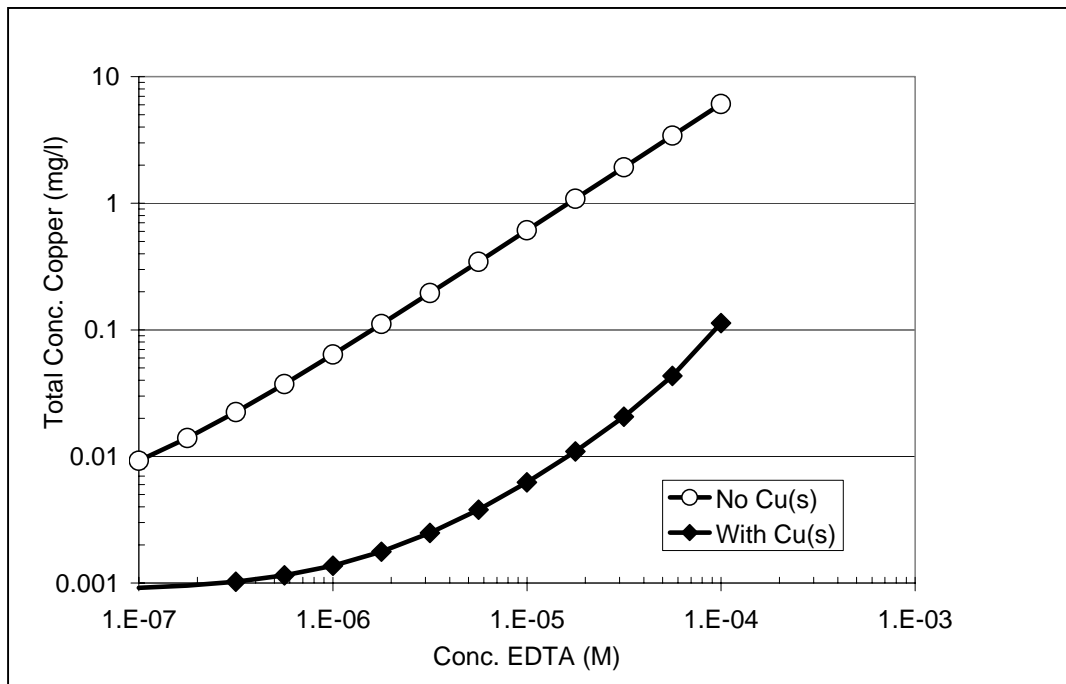


Figure 3. Equilibrium copper concentrations at pH 9. With and without metallic copper exposed to the water.

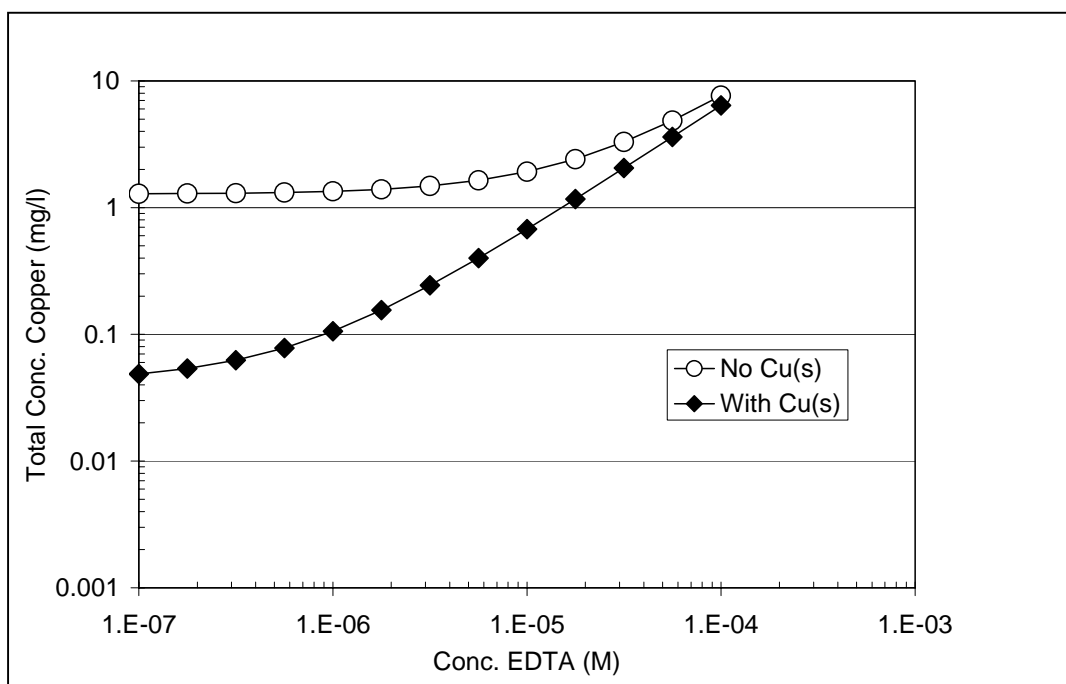


Figure 4. Equilibrium copper concentrations at pH 6. With and without metallic copper exposed to the water.

3. Stagnation curves

When the copper contents of the water in the tube is followed as function of the time of stagnation, a complicated pattern can be observed. [8, 9, 11, 12, 13] Figures 5 and 6 show examples.

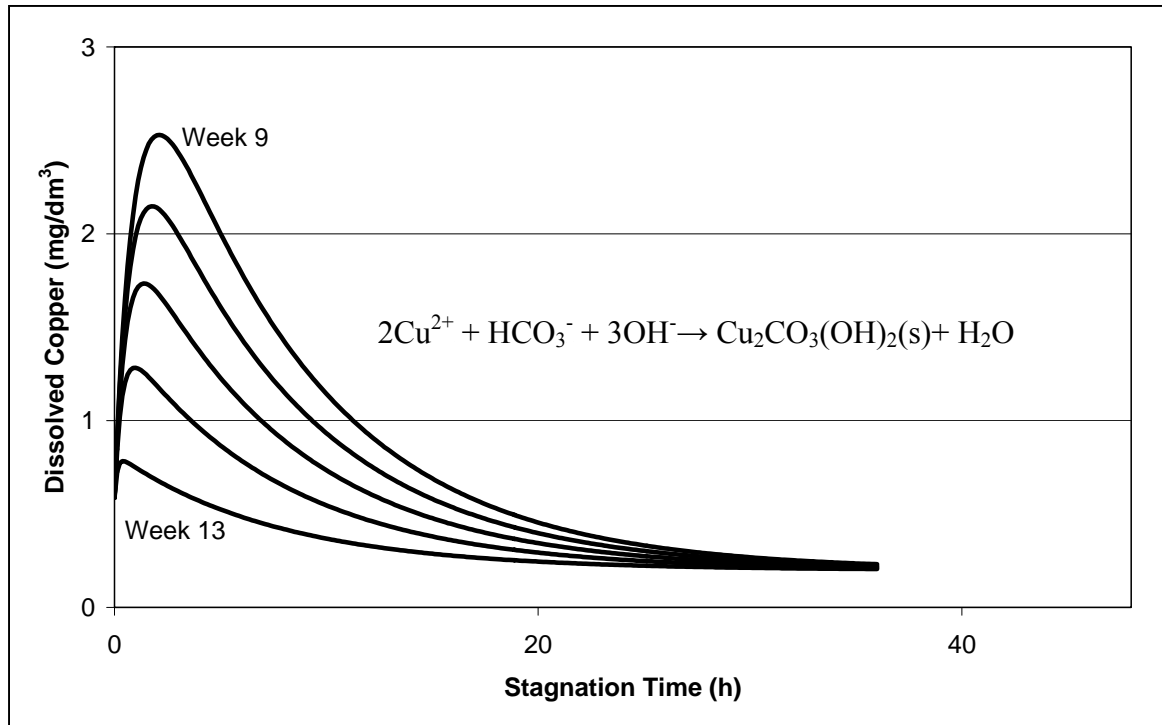


Figure 5. Stagnation curves. Free after Merkel [12]. pH 7.5

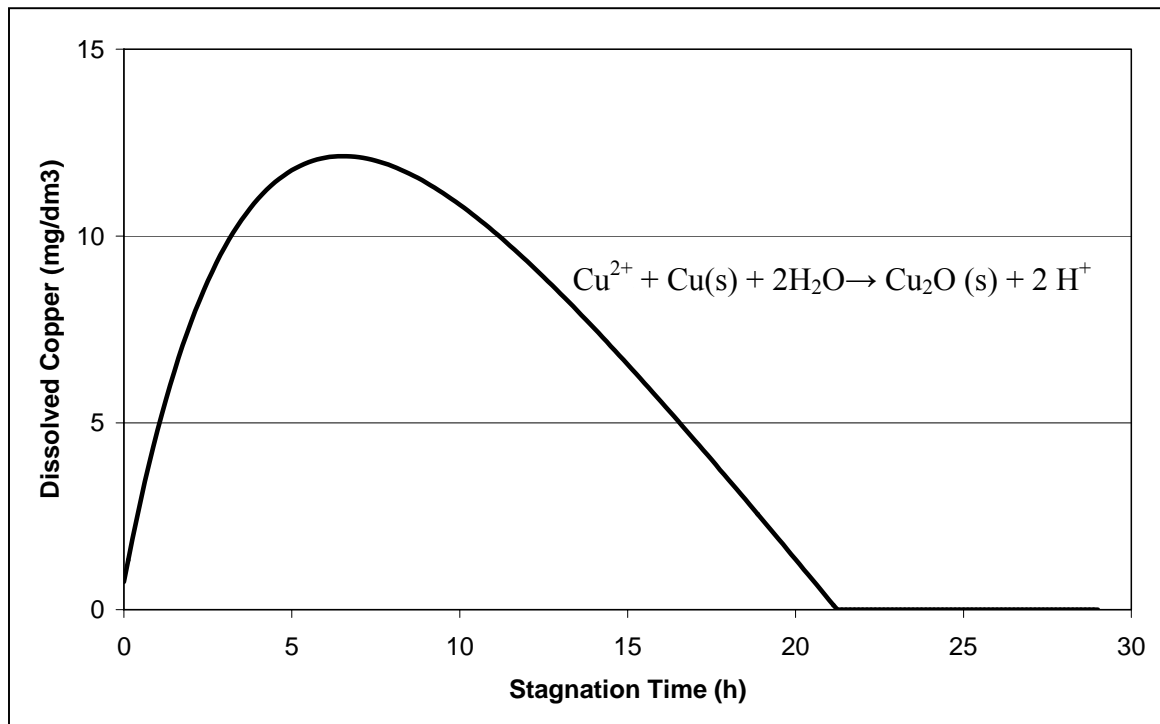


Figure 6. Stagnation curve. Free after Werner [8]. pH ~6

In figure 5, the concentrations show peak values a few hours after stagnation. After the peak, the copper contents decrease asymptotically towards a value that seems to agree well with the inorganic malachite equilibrium for the water. Repeating the sequence a week later gives similar shapes of the stagnation curve but with consistently lower peak values. Since the copper concentrations consistently decrease towards the malachite equilibrium, it seems likely that the process responsible for the decrease is indeed precipitation of malachite at the tube walls. The presence of malachite at the tube walls was confirmed by X-ray analysis [12]. Figure 6 shows a similar peak in copper contents as the curves in figure 5. The main difference is that the copper content in figure 6 drops to a much lower value. The value is lower than any Cu(II) equilibrium and it has been concluded that the copper contents decrease towards the $\text{Cu}_2\text{O(s)}/\text{Cu(s)}$ equilibrium. From our calculations with EDTA we find that the reducing power of metallic copper is so strong that, at equilibrium, only small amounts of Cu(II) is present in the solution. Another difference is that, whereas the curves in figure 5 fall off with a rate proportional to the degree of super saturation, the curve in figure 6 falls off with a constant rate.

4. Tentative explanations

4.1 *'The hydroxide-NOM explanation'*

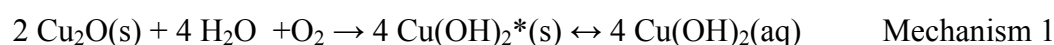
The rising part of the stagnation curves could be explained by dissolution of $\text{Cu(OH)}_2\text{(s)}$ from the tube wall. Augmented by organic complex formation, freshly precipitated cupric hydroxide may have a solubility that explains the peak levels. The decrease in copper contents after the peak may be explained by a precipitation process which removes copper as well as NOM from the water [5]. To our knowledge, this explanation has never been systematically applied to describe stagnation curves. There are a few questions that it leaves unanswered and where it could be more explicit. E. g. what is the specific advantage that Cu(OH)_2 has over other cupric solids? The higher surface energies should be overcome by precipitation at the tube wall, particularly when the stable solid is already present there. What is the process responsible for the decrease in oxygen concentration? Is it just a coincidence that the rate of the oxygen reduction is very similar to that of the initial increase in copper contents?

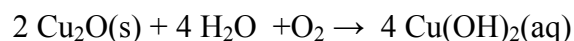
A tentative explanation that we like to put forwards is not necessarily in conflict with all details in the description above. For lack of a better name we will call this alternative the 'dynamic explanation'

4.2 *'The dynamic explanation'*

The rate of increase in copper contents

The works of Werner [8] and Merkel [12] and others indicate that there is a strong correlation between the rate of oxygen consumption and the initial rate of increase in copper content. It seems likely that the freshly produced Cu(II) (produced by oxidation of $\text{Cu}_2\text{O(s)}$) make up the major part of the dissolved copper and that initially the same reaction that consumes oxygen, also produces dissolved Cu(II). There are several mechanisms through which oxygen consumption can be coupled to the production of dissolved Cu(II).





Mechanism 3

The asterisk in $\text{Cu}(\text{OH})_2^*(\text{s})$ indicates that we consider this compound to be an unstable reaction intermediate and that it does not necessarily have the same properties as crystalline $\text{Cu}(\text{OH})_2(\text{s})$. Although the mechanisms as they are written imply that dissolved $\text{Cu}(\text{II})$ is formed as cupric ions or as cupric hydroxide complexes, this is a consequence of the chosen stoichiometry only and equilibrium between the various dissolved forms may be assumed. Mechanism 3 is very similar to mechanism 1. The main difference is that mechanism 1 implies a dissolution reaction of a cupric solid intermediate whereas mechanism 3 produces the divalent copper directly in the dissolved state. Mechanism 2 involves the homogeneous oxidation of dissolved $\text{Cu}(\text{I})$ by molecular oxygen. This process is known to take place and to be relatively fast [14]. Sharma and Millero [15, 16] determined rate constants for this process in natural waters and in artificial solutions.

Applying the rate constants of Sharma and Millero [16] to the water studied by Merkel [12] we find that the rate of oxidation is indeed sufficient to explain the observed time constants for the consumption of oxygen. But, because of the low solubility of $\text{Cu}_2\text{O}(\text{s})$ the rate of diffusion of $\text{Cu}(\text{I})$ from the tube wall to the bulk water is low. When also this process is included the rate of mechanism 2 does not seem to explain the observed time constants. The rate of mechanism 2 is influenced by the concentrations of chloride, amines and other complexing agents for $\text{Cu}(\text{I})$, by pH and by the solubility of the $\text{Cu}_2\text{O}(\text{s})$.

At present we cannot exclude any of these mechanisms and more than one may be operative. Actually, all three may be operative depending on the composition of the water. The main feature is shared between all three: $\text{Cu}(\text{II})$ is formed in the solution, albeit in mechanism 1 via a solid or adsorbed intermediary product.

The depletion stage

Because of the continuous production of dissolved $\text{Cu}(\text{II})$, the contents in the water increases. If there is bare copper metal exposed to the water, $\text{Cu}(\text{II})$ can be reduced and precipitated on the tube walls as $\text{Cu}_2\text{O}(\text{s})$. If metallic copper is not exposed to the water, precipitation of the stable cupric solids may start at sufficient super saturation. Dissolved cupric complexes with available NOM are undoubtedly formed. Solid cupric hydroxide can probably form in the water. The more stable cupric oxide and the basic salts seem to require a site of nucleation and precipitate at the tube wall. Even there, at least malachite seems to grow from a few centres [12]. These precipitation reactions start while the production processes are still active. The observation of decreasing copper contents signals the point where the production no longer can keep up with the precipitation or the reducing reaction. Eventually, the production rate becomes insignificant because most of the oxygen has been consumed or the $\text{Cu}_2\text{O}(\text{s})$ surface is completely covered by cupric phases. The copper content then approaches the equilibrium value.

The equilibrium value will be that of the most stable cupric solid. Complex formation with NOM will contribute to the observed amounts of dissolved copper.

The main difference between the two models; 'the hydroxide-NOM model' and 'the dynamic model' is that in the latter we emphasise the dynamic nature of the process. There is no cupric solid whose stability regulates the copper contents in the water. Instead, the observed stagnation curves are results of two competing processes; production of $\text{Cu}(\text{II})$ coupled to oxygen reduction and depletion from $\text{Cu}(\text{II})$ through precipitation or reduction. The kinetics of these processes coupled to mass transport through diffusion determine the shapes of the curves and the levels of copper contents attained.

5. Colloidal solutions- 'blue water'.

Colloidal solutions of copper containing particles are the likely cause for the blue water syndrome. The copper concentration can be so high that the water attains a bluish colour. Several studies have been performed with a water composition that has been found to give blue water[5, 17,18]. The composition of this water is shown in table II.

Table II. Composition of a water known to cause 'blue water' [17, 18]

Ion	Concentration (mg/l)
Magnesium	3
Chloride	9
Calcium	5
Nitrate	16
Sulfate	16
Sodium	17
Silica	20
Alkalinity	5

Compared to most tap waters, the water in table II may be described as soft and thin. The ionic contents as well as the alkalinity is low. The stability of colloidal solutions relies on the electrostatic repulsion between the particles. In waters with low ionic strength the electrostatic forces are long range whereas at higher ionic strength the electrostatic field is contracted and the repulsive forces are short range only. Short range repulsion is easier overcome by attractive forces than long range repulsion. Thus, the blue water phenomenon observed for the water in table II may be promoted by the low ionic strength that prevents coagulation and sedimentation of the particles. The effective radius of the ionic atmosphere around a charged particle; the Debye length, for some aqueous solutions is shown in table III.

Table III. Debye length (nm) in aqueous solutions at 25°C [19].

Concentration	Salt type			
	1:1	1:2	2:2	1:3
10^{-1}	.96	.55	.48	0.39
10^{-2}	3.04	1.76	1.52	1.24
10^{-3}	9.6	5.55	4.81	3.93
10^{-4}	30.4	17.6	15.2	12.4

6. Possible implications for counter measures against high copper contents

The qualitative theory for the cause and mechanisms for copper release to tap water may have an impact on the choice of counter measures against high copper contents. Efforts aimed at reducing the amount of organic matter in the tap waters may not fully successful. While there is little doubt that NOM can contribute to the amounts of dissolved copper at equilibrium, the role of NOM in the processes that determine the shape of the stagnation curve is less clear. It seems possible that NOM plays a minor role for the peak values observed.

References

- 1 Thermodynamic data for copper. Implications for the corrosion of copper under repository conditions. Puigdomenech, I. and Taxén, C. Swedish Nuclear Fuel and Waste Management Co, SKB Technical Report TR-00-13 Stockholm 2000
- 2 Copper in tap waters. Literature study and equilibrium calculations. Mats Linder and Claes Taxén KI-report 2002:1E. Swedish Corrosion Institute, Stockholm 2002
- 3 Stumm, W. Chemistry of the Solid-Water Interface. Wiley, New York 1992.
- 4 Schindler, P.; Althaus, H; Hofer, F. and Minder, W. Löslichkeitsprodukte von Metalloxiden und -hydroxiden. Helvetica Chimica Acta vol. 48 p. 1204 (1965)
- 5 Edwards, M. and Sprague, N. Organic matter and copper corrosion by-product release: a mechanistic study. Corr. Sci., vol 43, pp 1–18. (2001)
- 6 Copper corrosion in water distribution systems- The influence of natural organic matter (NOM) on the solubility of copper corrosion products. Elfström Broo, A.; Berghult, B. and Hedberg, T. Corrosion Sci. vol 40 pp 1479-1489
- 7 Copper binding by dissolved organic matter:I Suwanne River fulvic acid equilibria. Cabaniss, S. E. and Schuman, M. S. Geochim. Cosmochim Acta vol 52 p 185-193 (1988) and Copper binding by dissolved organic matter:II Variation in type and source of organic matter. Cabaniss, S. E. and Schuman, M. S. Geochim. Cosmochim Acta vol 52 p 195-200 (1988)
- 8 Untersuchungen zum Mechanismus der Flächenkorrosion in Trinkwasserleitungen aus Kupfer. Werner, W., Dissertation, Karlsruhe 1992
- 9 Preliminary research on the action of water on copper pipes. Tronstad, L. and Veimo, R. Inst. Metals Journ 66 pp 17-32 (1940)
- 10 Martell and Smith 1997. Critically selected stability constants of metal complexes database. Version 3.0. Texas A & M University, College Station, Texas.
- 11 Resistance of copper tubes to pitting corrosion of type 1 and cuprosolvency. Harju, T. and Holm, R. 12th Scandinavian Corrosion Congress & Eurocorr '92. Espoo Finland. Proceedings p 759
- 12 Copper Corrosion By-product Release in Long-term Stagnation Experiments. Merkel, T.H.; Gross, H.J., Werner, W.; Dahlke, T.; Reicherter, S.; Beuchle, G. and Eberle, S.H. Water Research 36 pp. 1547-1555. (2002)
- 13 Impact of stagnation time on the dissolution of metal from plumbing material. Lytle, D. A. and Schock, M. R. , AWWA Annual Conf. June 15-19, 1997 Proceedings
- 14 Corrosion measurements by titration (CMT): Copper, Sn-Zn alloy and aluminium. Bech-Nielsen, G. and Juhl, A. D. Corr. Sci. vol 34, pp 785-796 (1993)
- 15 Oxidation of Copper(I) in Seawater. Sharma, V. K. and Millro, F. J., Environ Sci. Technol. vol 22 pp768-771 (1988.)
- 16 Redox reactions of metal ions at mineral surfaces. Wehrli, B. in Aquatic Chemical Kinetics. Reaction rates of Processes in Natural Waters. Ed. W. Stumm. Wiley, New York 1990.
- 17 Influence of organic matter on orthophosphate corrosion inhibition for copper pipe in soft water. Li, S.; Ni, L.; Sun, C. and Wang, L. Corr Sci vol 46 p 137 (2004)
- 18 Indicators for microbiologically induced corrosion of copper pipes in a cold-water plumbing system. Arens, P.; Tuschewitzki, G.; Wollman, M.; Follner, H. and Jacobi, H. Zentralbl. Hyg. Umweltmed. vol 196 p. 444 (1995)
- 19 Physical Chemistry 5th ed., Moore, W. J. Longman, London. 1972