



CANADA

COPPER IN DOMESTIC WATER SYSTEMS
(A REVIEW)

by

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The following errata slip is forwarded for inclusion in Mines Branch Information Circular IC-107 "Copper in Domestic Water Systems (A Review)" recently forwarded to you.

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ERRATA

- Page iii - Last line - Change to read "Bibliography"
- Page 2 - Lines 1 and 2 - delete "Mr. H. S. Campbell of the British Non-Ferrous Metals Research Association and"
- Page 2 - Line 3 - delete "both of"
- Page 5 - Paragraph 3, last line - add "for domestic pipe in new buildings."
- Page 6 - Paragraphs 2 and 3, last line - delete "(33)"
- Page 8 - Paragraph 3 - Replace paragraph with following "Green staining has been noted even in waters having 2 to 7 ppm free carbon dioxide and hardness below 75 ppm."
- Page 10 - Paragraph 5 - Change 0.1 - 0.15 ppm to read "0.1 - 0.5 ppm".
- Page 11 - Second last line - delete "(44)"
- Page 13 - Change title to read "Bibliography"
- Page 15 - Reference 36 - change (1938) to "(1939)"

Mines Branch Information Circular IC 107
COPPER IN DOMESTIC WATER SYSTEMS
(A Review)

by

John Ungar*

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ABSTRACT

Some of the available published information on the subject of the use of copper pipe and fittings in domestic water supply systems is reviewed, and 50 references are listed. The cause of corrosion of copper pipes, the cause of green staining (cupro-solvency), and the inhibition of these difficulties are discussed.

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Direction des Mines
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APERÇU SUR LE CUIVRE EMPLOYÉ DANS
LES CANALISATIONS D'EAU DE MÉNAGE

par

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RÉSUMÉ

L'auteur donne un aperçu de certains des renseignements disponibles qui ont été publiés, dans 50 ouvrages énumérés auxquels on renvoie le lecteur, au sujet de l'emploi de tuyaux et de raccords en cuivre de canalisations d'eau de ménage. Il traite de la cause de la corrosion et de la formation de taches vertes (cuprosolvabilité) et de l'inhibition de ces difficultés.

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INTRODUCTION

Copper water pipes have been used by man for, literally, thousands of years. In our modern buildings of today they are becoming increasingly popular for the construction of water supply lines. However, as the use of copper piping increases, so does the occurrence of copper corrosion and of green staining of baths, sinks and clothes.

Complaints of green staining are fairly common where certain types of water are supplied through copper piping. The phenomenon is caused by copper dissolved in the water, derived either from pitting or from general corrosion.

Less frequent is the pitting corrosion of copper pipes, which, since it may cause costly failure and at the same time lends itself more easily to laboratory investigation, has been discussed in a considerable number of articles. However, green staining, which is the more annoying problem for the general public, is only lightly touched upon in the literature. As the two problems obviously overlap, they are reviewed jointly in the following pages.

These problems are of primary interest to the householder, the builder, the plumber, and the water treatment specialist. On the other hand, most large industrial plants would consult the water treatment specialist in the first place, and should therefore not be troubled by this problem.

A list of literature references is appended to this review. In addition to these, comments were also received, in private

communications, from Mr. H. S. Campbell of the British Non-Ferrous Metals Research Association and Mr. B. A. Sard of the United Water Softeners Ltd., both of London, England, and from Mr. A. W. Tracy of the American Brass Company, Waterbury, Connecticut, U. S. A.

OCCURRENCE OF COPPER CORROSION AND GREEN STAINING IN CANADA

The Industrial Waters Section of the Mineral Processing Division has, for some time, been conducting a survey of the chemical quality of municipal water supplies across Canada. During the course of this survey a number of municipalities in various parts of the country have reported the occurrence, in varying degrees, of attack by water on copper tanks, pipes and fittings. Others have reported the absence of such problems.

Early in 1958, the Mines Branch was asked by the Division of Building Research of the National Research Council of Canada, at Ottawa, to look into the problem of "blue water" or "green staining". Both the Division of Building Research and the Vancouver regional station of the National Research Council had been receiving complaints for some time with regard to copper hot-water systems. Background notes on this problem in the Vancouver area were made available to the Industrial Waters Section.

In May, 1958, an enquiry was received through the National Research Council, from New Westminster, B. C., accompanied by a piece of cloth, originally white, which had suffered intensive green

staining in a washing machine installed in a new house where the water system consisted of copper piping.

This piece of cloth was stained uniformly, the discoloration having penetrated into the fibres themselves. Microscopic examination of the material showed that there was no film adhering to any of the fibres, nor were there any particles occluded between the fibres.

The intensity of the discoloration indicated that this piece of cloth had been subjected to a number of washes in a copper-bearing water. Soaking in strong ammonia solution removed practically all of the stain within a few minutes; the ammoniacal extract thus obtained was then evaporated to dryness, and an X-ray diffraction study of the residue confirmed that the stain was caused by a copper compound.

GREEN STAINING OR BLUE WATER

Green staining problems (sometimes known as "blue water" problems) occur chiefly with waters that are regarded as corrosive to copper, or "cuprosolvent", and complaints usually mention one or more of the following observations:

1. Blue tint in water drawn from pipe.
2. Green stains on clothes being washed.
3. Green soap scum on baths, sinks, etc.
4. Greenish stains on porcelain or enamelled surfaces.

It has been reported that such complaints arise where the water contains as little as 1 part of copper (by weight) dissolved in one million parts of water.

All the authorities consulted seem to agree that the problem of green staining of fabrics occurs chiefly when soap is used, since precipitated copper soaps will intensify the colour, and that staining is less likely to occur when soapless detergent products are used.

Quiescent water, which may occur in so-called "dead-ends" of pipes, will intensify the effect of a cuprosolvent water, because of the prolonged contact time between such a water and the copper piping.

Finally, staining may also be encountered with a normally non-corrosive water and new copper pipework, during the time it takes for a continuous protective coating to be formed on the inside of the pipe.

GENERAL CORROSION AND PITTING

While green staining is a form of slow, general corrosion, instances of more serious localized corrosion--particularly pitting--occur from time to time, causing leaks which at times can result in quite considerable material damage. In this type of attack on copper pipe, the cause may involve not only the chemical action to which blue water problems are due, but also, or instead, physical, mechanical, or electrochemical effects.

Effect of Faulty Pipework Construction and Design

In a number of cases it has been found that corrosion of copper pipes has been promoted or enhanced by poor workmanship or design, such as bad joints, use of the wrong solder, or unnecessary "dead-ends".

It must also be recognized that copper has a poor impingement resistance and that, consequently, high water velocity may cause increased pitting due to erosion.

Impurities and Galvanic Action

Impurities present in the copper used for the manufacture of the copper pipe may be the cause of the formation of local elements (i. e. the setting-up of minute electrical cells) which cause corrosion. Thus, in the past, different batches of copper tubing have been affected in varying degrees by the same water. The manufacturers realise this and now adhere to very stringent, self-imposed specifications.

A number of cases of pitting corrosion, investigated by various workers, particularly in Europe, were shown to be due to a film of carbon which acted as a cathode. Such carbon films are caused by charring of residues of the drawing lubricant used in the manufacture of copper tubing. A similar effect is sometimes caused by a thin film of vitreous copper oxide, formed during annealing of tubing after drawing. These methods of manufacture are not generally used on the North American continent.

Arrangements involving two or more different metals in a water system should be avoided in construction, as galvanic couples may be set up which will cause corrosion of pipes and fittings. In hot water lines, as little as one-tenth of a part of dissolved copper per million parts of water is said to be sufficient to form a deposit of copper on galvanized coating, causing pitting of the zinc coating and,

eventually, corrosion of the steel underneath. Deposition of metallic copper from a cuprosolvent water will also accelerate corrosion of aluminium kettles, iron pipes, and hot water tanks.

The Effects of Temperature and Flow Rate

The cuprosolvency of any water increases with rising temperature, and it is generally accepted that temperatures in excess of 140°F will increase the tendency towards attack. If the rate of corrosion of copper is plotted against water temperature, there is a sharp rise just above 140°F, and a maximum in the curve at about 170°F (33).

Additional troubles may be caused in copper hot-water lines by fluctuating temperature, generally indicative of poor maintenance. Such fluctuations may cause breaks in any protective coating which may have formed on the inside of the pipe, thus setting up galvanic couples and increasing the rate of corrosion.

Flow rate and temperature will exert a combined effect on copper pipe corrosion. As mentioned above, high water velocity may cause erosion, while high temperature at low water velocity may produce pitting. On the other hand, high temperature combined with high flow rate can cause increased attack, in the form of horseshoe-type pitting.

Some authorities claim that there is a peak in this combined effect. For 1/2 in. copper tubing this peak would be about 170°F and at 8 fps or above (33).

EFFECT OF WATER QUALITY

Because water quality affects all types of copper corrosion, it is discussed separately in the following rather than under the previous two main headings.

Assuming that any suspended matter will have been removed from domestic waters prior to distribution, the effect of dissolved substances in the water must be considered.

Water Hardness

This property of water is due chiefly to dissolved calcium and magnesium salts, which may cause deposits and will precipitate soaps to form a curd instead of a lather. Such curds give rise to the greenish scum noted on baths, sinks, etc.

Hard waters, particularly those that have a high carbonate (temporary) hardness, tend to deposit a protective scale of calcium carbonate, possibly together with some basic copper carbonate formed from the copper initially dissolved from the tubing. Such a scale would not be permanent, however, if a water of relatively high carbon dioxide content passed through the pipe. On the other hand, very hard waters may cause excessive deposition and thus clog the pipes.

Soft waters tend to be corrosive, and where ion exchange (base exchange) softening is used for treating domestic supplies it is usual to recommend blending the fully softened water with raw, unsoftened water to a final hardness of between 3 and 7 grains per gallon (40-100 ppm in terms of calcium carbonate).

In the case of most naturally occurring, low-hardness waters, treatment is the only answer if copper is to be used in pipe-work.

Acidity of Water

It is generally recognized that the use of waters of low pH value (higher concentration of hydrogen ions) with copper piping results in trouble, and that such acid waters, e. g. those with high carbon dioxide content, should be treated before use.

Some authorities state that to avoid attack the carbon dioxide concentration should be less than 2 ppm.

It has been reported that no difficulties whatsoever were encountered, over a period of more than 3 years, in an all-copper hot water system where the water was consistently maintained at a pH of 9 to 9.5.

With a view to inhibiting attack in domestic systems, the pH may be raised to between 8 and 9.5 by the addition of sodium silicate solution, or by percolating the water through a filter containing alkaline materials such as granulated sodium silicate-alkaline glass or granulated, sintered magnesite. Glassy phosphates, e. g. sodium hexametaphosphate, are sometimes used as inhibitors.

Dissolved Oxygen

In most blue-water complaints, it has been found that the water is more or less saturated with oxygen. Dissolved oxygen promotes the corrosion of copper, and in short-term experiments the

effect of oxygen concentration is very pronounced.

In industrial plants, various methods of de-aeration can be employed to combat this oxygen attack, including the simple expedient of adding reducing agents, but neither the use of additives nor the other methods are practical in domestic systems. In the latter case, the elevation of pH by the use of phosphates, referred to above, is generally adequate protection.

Other Dissolved Gases

Hydrogen sulphide, found in some natural waters, attacks copper. Corrosion due to the presence of excessive amounts of chlorine is increased by agitation and the presence of air, and it must be noted that hypochlorites in dilute solution are strongly corrosive.

Chlorides and Sulphates

High chloride concentrations are known to produce corrosion in copper pipes--at times, even through protective films. It has also been reported that attack on copper occurs in the presence of chloride even though the actual concentration may be relatively low, but in normal domestic supply waters the concentration of chloride ion does not usually affect the rate of corrosion.

While sulphate does not attack copper, preliminary tests seem to suggest that among the other factors discussed, the sulphate-chloride ratio may affect the copper-corrosive qualities of water. Examination of some analyses of waters of municipalities where either the occurrence or absence of copper corrosion has been reported seems

to support this theory. A high ratio apparently lessens the likelihood of cuprosolvency. More work, including laboratory tests, is planned on this subject.

Nitrogen Compounds

Although low concentrations of nitrate are sometimes used as inhibitors, high concentrations of nitrate and nitrite may attack copper, particularly since under suitable conditions they may break down to ammonia.

The cuprosolvent effect of ammonia and its compounds is so well-known that it need hardly be mentioned.

Manganese and Iron

The presence of manganese in a water will be conducive to attack on copper. Some authorities recommend that a maximum limit of 0.10 ppm manganese should be imposed and that, if at all practicable, the manganese should be completely removed from the water.

Other workers have recommended an upper limit of 0.1 - 0.15 ppm for the total concentration of manganese and iron.

Chemical Additives

The effect of chemicals added for cleaning the system, or for water conditioning, cannot be ignored, because without proper control they may cause more harm than good.

In one particular case reported, a circulating hot water system was dosed with various chemicals, including sodium sulphite. The latter was reduced by bacterial action to hydrogen sulphide, and

extensive corrosion of this copper system resulted.

Natural Inhibitors

Some waters--mainly surface waters--contain certain organic chemicals which apparently act as inhibitors of copper corrosion or cuprosolvency, so that a water which would normally be expected to corrode copper pipes does not do so. The precise mechanism of this protection has not been ascertained, but it has been suggested that these compounds induce formation of a cuprous oxide having a modified crystal structure which forms a protective film on the metal.

Although a number of papers have been published on the subject, these natural inhibitors have not been identified so far and it is not even certain whether they are of animal or vegetable origin. It has been established, however, that they show whitish-blue fluorescence in ultraviolet light and that there is some connection between the intensity of this fluorescence and the ammoniacal nitrogen content of the water containing the inhibitors. These inhibitors may be removed from the water by activated charcoal, or by coagulation followed by filtration through sand, but not by filtration alone.

DRINKING WATER STANDARDS

Even though a water may be corrosive to copper, normally it will not dissolve sufficient of the metal from the pipes to make it injurious to health. The upper limit recommended in the 5th edition (1943) of the standard text of Suckling⁽⁴⁴⁾ is 1.4 ppm as copper (Cu). The United States Public Health Service specifies a maximum tolerance

of 3 ppm copper. It has been noted that above about 5 ppm as Cu, a metallic taste in the water is apparent to most users.

SUMMARY AND CONCLUSIONS

Several factors have a tendency to cause attack on copper water pipes and fittings, and thus may promote green staining. The main chemical ones are: high carbon dioxide content, dissolved oxygen, high proportion of sodium to total cations, and the presence of iron or manganese. The presence of chloride ions will promote attack and the sulphate:chloride ratio ($\text{SO}_4:\text{Cl}$) may be one indication of the cuprosolvent qualities of a water.

Certain organic compounds, as yet unidentified, may act as natural inhibitors. Raising the pH value will also tend to inhibit attack. On the mechanical side, joints must be good, correct solder should be used, and films of carbon or of vitreous oxide (sometimes formed during manufacture of copper tubing) should be absent. Temperatures should not exceed 140°F , nor fluctuate, and flow-rates should not be excessively high.

SELECTED REFERENCES

1. Am. Waterworks Assn, Interim Report on Investigations of American Research Committee on Grounding. J. A. W. W. A., 36, 383 (1944).
2. Anon., Unusual Corrosion Problem. Engineer, London, 204, 635 (1957) Water Pollution Abstr., #960, May 1958.
3. Anon., Pitting of Cooler Tubing. Maschinenschaden, 26, 119 (1953).
4. H. J. Antweiler, (Electrolyte Effects with Mercury Electrode). Z. Elektrochem., 43, 596 (1937)
44, 719 (1938)
44, 831 (1938)
44, 888 (1938)
5. S. Baker and E. Carr, Corrosion of Metals in Buildings-- The Behaviour of Copper in Buildings. Chem. and Ind., 1332 (1957).
6. G. D. Bengough, V. R. Evans, T. P. Hoar, and F. Wormwell, The Corrosion of Metals by Salt Solutions and Natural Waters: An Agreed Statement. Chem and Ind., 1043 (1938).
7. British Non-Ferrous Metals Research Association, Copper Water Pipes. Misc. Publ., #420 (1954).
8. H. S. Campbell, Pitting Corrosion in Copper Water Pipes Caused by Films of Carbonaceous Material Produced During Manufacture. J. Inst. Metals, 77, #4, 345 (1950).
9. H. S. Campbell, A Natural Inhibitor of Pitting Corrosion of Copper in Tap-Waters. J. Appl. Chem., 4, 633 (1954).
10. H. S. Campbell, The Influence of the Composition of Supply Waters, and Especially of Traces of Natural Inhibitor, on Pitting Corrosion of Copper Water Pipes. Proc. Soc. Water Treatmt. and Exam., 3, 100 (1954).
11. H. S. Campbell, The Use of Non-Ferrous Metals in Domestic Water Supply, Chem. and Ind., 692 (1955).
12. A. T. Dempster, Control of the Treatment of Water in Building Piping Systems. J. A. W. W. A., 45, 81 (1953).

(Selected References, cont'd) -

13. Dept. of Scientific and Industrial Research (London), Use of Copper and Galvanized Steel in Same Hot Water System. Digest of Bldg. Res. Sta., #8, (1949); Water Pollution Abstr. #1311, Nov. 1949.
14. V. R. Evans, "Metallic Corrosion, Passivity and Protection", 2nd Edition, Arnold's, London, 1946.
15. J. N. Frers, Treatment of Water for the Formation of Protective Layers. German Patent 813,976; Chem. Zbl., 123, 277 (1952); Water Pollution Abstr. #1817 (1953).
16. P. T. Gilbert, Corrosion of Copper, Lead and Lead-Alloy Specimens After Burial in a Number of Soils for Periods up to 10 Years. J. Inst. Metals, 73, 139 (1947).
17. L. W. Haase, Corrosion of Copper. Werkstoffe und Korrosion, 1, 139 (1950); Water Pollution Abstr. #537, May 1951.
18. J. J. Hamilton and M. E. Flentje, Colored Water--Red, Black or Blue. Water and Sewage Works, 188, May 1958.
19. H. M. Stationery Office (London), Non-Ferrous Metals. Post-War Bldg. Studies #13 (1944).
20. J. Heyrovsky (Polarographic Technique and Apparatus for Organic Substances and Minerals). Actualités Sci. Industr., #90 (1934).
21. G. R. Hill, Corrosion of Copper in Aqueous Solutions. Corrosion, 250-1a (1953).
22. D. Ilkovič (Polarographic Studies). Coll. Trav. Chim. Tchecosl., 8, 13 (1936).
23. H. Ingleson, M. A. Sage, and R. Wilkinson, Effect of Chlorination of Drinking Water on Brass Fittings. J. Inst. Water Eng., 3, 81 (1949).
24. Institution of Water Engineers, "Approved Methods for the Physical and Chemical Examination of Waters". W. Heffer and Sons Ltd., London (1949).
25. Institution of Water Engineers, J. Inst. Water Eng., 5, 700 (1951).

(Selected References, cont'd) -

26. L. Kenworthy, Corrosion Troubles--Practical Problems Associated With the Use of Particular Metals--Copper. J. Inst. Htg. and Vtg. Eng., 8, 23 (1940).
27. L. Kenworthy, The Problem of Copper and Galvanized Iron in the Same Water System. J. Inst. Metals, 69, #2, 67 (1943).
28. L. Lehrmann and H. L. Shuldener, Action of Sodium Silicate as a Corrosion Inhibitor in Water Piping. Ind. Eng. Chem., 44, 1765 (1952).
29. E. A. G. Liddiard and P. E. Bankes, The Action of Water on Lead. J. S. C. I., 63, 39 (1944).
30. F. Lieb, Concerning the Solvent Action of Water in Copper Pipes. Gas, Wasser, Wärme, 4, 212 (1950); J. A. W. W. A., 43, #6, 42 (1951); Water Pollution Abstr. #350 (1952).
31. K. H. Logan and M. Romanoff, Soil Corrosion Studies--Copper and Copper Alloy. J. Res. Nat. Bur. Stand., 33, 172 (1944).
32. E. Mattson, Staining of Copper and Brass. Corrosion, 14, #2 (1958).
33. R. May, Some Observations on the Mechanism of Pitting Corrosion. J. Inst. Metals, 82, 65 (1953).
34. Netherlands Waterworks Assn. (KIWA Ltd.), Report of the Copper Tube Committee, The Hague (1936).
35. M. F. Obrecht and L. L. Quill, Design of Test Systems for Studying the Corrosion of Copper and Copper Alloys by Various Types of Water. Proc., 19th Ann. Water Conf., Eng. Soc. W. Pennsylvania, 33 (1958).
36. J. L. Rice, Regulating Water Treatment in Buildings. J. A. W. W. A., 31, 81 (1938).
37. W. D. Robertson, V. F. Nole, W. H. Davenport, and F. P. Talboom, The Investigation of Chemical Variables Affecting the Corrosion of Copper. J. Electrochem. Soc., 105, #10, 569 (1958).
38. L. Rutter, Treatment of Paper for Chromatography of Some Colloidal Electrolytes. Nature, 166, 273 (1950).

(Selected References, concluded) -

39. W. Schaible, Metallic Corrosion by Water. *Angew. Chemie*, 68, 445 (1956).
40. G. Schikorr, The Cathodic Behavior of Zinc Versus Iron in Hot Tap Water. *Trans. Electrochem. Soc.*, 76, 247 (1939).
41. H. L. Shuldener, Water Pipe Corrosion Problems in Buildings. *Proc. 2nd Ann. Water Conf., Eng. Soc. W. Pennsylvania*, 71 (1941).
42. H. L. Shuldener, Effect of Operating Conditions on Corrosion of Hot Water Piping in Buildings. *Corrosion*, 10, #3 (1954).
43. F. N. Speller, "Corrosion--Causes and Prevention", 3rd ed., McGraw-Hill, New York, 1951.
44. E. V. Suckling, "The Examination of Waters and Water Supplies", 5th ed., J. and A. Churchill Ltd., London; 1943.
45. S. Sussman, Cooling Water Problems in the New York Metropolitan Area. *Ind. Eng. Chem.*, 44, 1740 (1952).
46. S. Sussman and J. B. Fullman, Corrosion in Closed Circulating Water Systems. *Htg. and Vtg.*, 50, #10, 77 (1953).
47. N. D. Tomaschov, Effect of Distribution and Dispersity of Local Cathodes on the Rate of Corrosion under Conditions of Oxygen Depolarization. *C. R. Acad. Sci. USSR*, 27, 987 (1940); *Water Pollution Abstr.* #1310, Nov. 1949.
48. H. H. Uhlig, "The Corrosion Handbook", 1st ed., John Wiley and Sons, New York, 1948.
49. U. S. Public Health Service (Public Health Service Drinking Water Standards). *Public Health Reports*, 58, #3, 69 (1943).
50. I. Vavruch,
 Chem. Obz., 17, #9, 151 (1942)
 19, #3, 45 (1944)
 19, #4, 69 (1944)

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