

Anti-scaling properties of copper

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ABSTRACT

The nature of the materials employed in water distribution circuits has a decisive influence on the extent of scaling. The liberation of Cu^{2+} ions into the water inhibits the nucleation and growth of calcium carbonate crystals. Thus, compared to other metals and polymers, copper shows a much lower scaling tendency. Furthermore, the presence of copper ions in the water, at concentrations well below the maximum permissible limits, decreases the scaling potential of the water with respect to other materials situated downstream.

The present study shows that copper becomes coated in calcium carbonate much less readily than other materials. This prevents the proliferation of bacteria such as those responsible for legionnaire's disease, which is generally facilitated by scale deposits. The influence of copper ions on the scaling potential of water was therefore determined first of all, followed by a study on the scaling behaviour of polyethylene. Real scaling was then studied on tubes of various types, in waters with widely different scaling potentials.

Key words | copper, inhibition, scaling, water

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INTRODUCTION

Because of the increasing awareness of public health problems, managers of cold and hot water distribution networks are facing the need to replace their circuits in order to meet current regulations. 'Old' installations widely used traditional materials such as galvanised steel, copper and lead. The use of lead is coming to an end, due to the very low permissible limits. Galvanised steel and copper can still be used, but are now in competition with stainless steel and certain polymers suitable for water for human consumption. Among the advantages mentioned for these new materials, it is said that they do not corrode, that they therefore cause no contamination and that consequently they are better for public health. It is sometimes even added, particularly for polymers, that they have excellent scaling behaviour. However, in this debate, it is quickly forgotten that, while the material is effectively in contact with water when it is first put into service, this is no longer true after a certain length of time, since corrosion products, scale or biofilms then separate the water and the installation material.

In practice, it is interesting to observe that, after being put in contact with a calcifying water for a certain time, a circuit in stainless steel or in polymers is always coated by a layer of CaCO_3 , whereas a circuit in copper usually has no scaling problem. In fact, copper is obviously not inert in contact with water. Immediately after immersion, various electrochemical oxidation and reduction reactions occur, leading to the regular release of limited amounts of Cu^{2+} ions into the water. According to European legislation, the maximum permissible concentrations of copper ions in waters intended for human consumption are $200 \mu\text{g/l}$ at the treatment plant and $2000 \mu\text{g/l}$ at the consumer's tap. The difference between these maximum permissible levels takes into account the possibility of a slight enrichment in Cu^{2+} ions during transport in contact with copper-containing materials. This slight dissolution has two effects. First, the water in the boundary layer is enriched with cupric ions and therefore could affect the nucleation of CaCO_3 directly on the copper. Secondly, it modifies the scaling potential of the water

downstream of the copper or copper alloy installations. The scaling kinetics on other materials could thus be modified. It is these two aspects that will be considered in this study of the influence of copper on scaling.

EQUIPMENT AND EXPERIMENTAL METHODS

Waters studied

Since it was not possible to obtain a water whose scaling potential remained rigorously constant, it was decided to work with a natural water of artesian origin (water A), used to supply Paris (Vanne and Loing aqueducts). Its initial copper content is of the order of 10 µg/l. This water, whose typical composition is given in Table 1, has a strong tendency to cause scaling, and its behaviour in this respect is well established (Leroy *et al.* 1993). For the same reasons, another natural water (water B), surface water from the river Seine, was used for tests in a weakly scaling environment.

Rapid controlled precipitation (RCP) tests

For the precipitation of solid calcium carbonate to effectively appear from a liquid phase, nuclei must be able to form and grow. The process starts with the formation of pairs of hydrated CO_3^{2-} and Ca^{2+} ions, which group together to create a colloidal nucleus possessing an electrical charge, characterised by its potential ζ . This nucleus grows and at the same time gradually loses its hydrate molecules, to finally form a crystal, which then has its own growth phase.

For nucleation to occur, the reaction $\text{CO}_3^{2-} + \text{Ca}^{2+} \rightarrow \text{CaCO}_3\downarrow$ must be thermodynamically possible. This will be the case when the product of the ionic concentrations exceeds the solubility product. In particular, it depends on the temperature and the ionic force of all the other species present in the water. At any point in a water circuit, the local conditions can be defined by:

$$[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] = \delta K'_s \quad (1)$$

Table 1 | Physical-chemical characteristics of the waters studied (A: groundwater; B: surface water)

Parameter	Water A	Water B
Temperature (°C)	11.6	10.0
Electrical conductivity (µS/cm)	506	448
pH	7.5	7.8
Hardness (degrees F)	27.1	22.6
Alkalinity (degrees F)	22.1	16.7
Calcium (mg/l)	106.4	85.0
Magnesium (mg/l)	2.4	3.3
Sodium (mg/l)	6.9	10.0
Potassium (mg/l)	1.8	2.9
Total cations (meq/l)	5.86	5.03
Bicarbonate (mg/l)	269.6	203.7
Sulphate (mg/l)	21.0	29.0
Chloride (mg/l)	18.0	24.0
Nitrate (mg/l)	32.0	24.0
Total anions (meq/l)	5.88	5.01
Degree of supersaturation (δ) (Legrand-Poirier calculation)	1.16	1.32

where K'_s is the solubility product. When $\delta < 1$ the water is locally *aggressive*. When $\delta = 1$ the water is locally *in thermodynamic equilibrium*. When $\delta > 1$ the water is *calcifying* and calcium carbonate is thermodynamically liable to precipitate. The value of δ can be calculated by the Legrand-Poirier method (Legrand *et al.* 1981). However, both thermodynamic considerations and experience show that it is not sufficient for δ to be just greater than 1 for detectable nucleation to occur. For massive irreversible nucleation leading to precipitation, δ must attain a value of the order of 40 (Tarits 1990). Above this value, precipitation in the water is virtually certain. For

values between 1 and 40, precipitation remains possible, with an increasing probability as δ approaches 40. In other words, when $\delta > 40$, the water is completely unstable, if $1 < \delta < 40$ it is simply metastable. The deliberate or accidental presence of certain substances (e.g. Fe^{2+}) (Bornhauser *et al.* 2000) can increase the probability of nucleation occurring at δ values between 1 and 40. On the contrary, other species, such as Cu^{2+} and Zn^{2+} ions, decrease the probability (Abouali *et al.* 1996).

For a test intended to representatively evaluate the scaling potential of water, the supersaturation coefficient δ must not be too high. The rapid controlled precipitation (RCP) test was developed for this purpose in the course of a previous study (Lédion *et al.* 1997). For most common waters, the value of δ must be between 1 and 40. At higher levels, spontaneous precipitation is liable to occur and the thermodynamic conditions are then no longer those prevailing during scaling. The value of δ is therefore adjusted using the Legrand-Poirier method (Legrand *et al.* 1981), by varying the temperature and the pH of the water in equilibrium with the atmosphere.

Required test conditions

In order to obtain the target δ value of about 25 in the waters studied, in a reasonable time of not more than 25 to 45 min, the temperature and degree of stirring must be appropriately adjusted. Since there is no temperature control system, an initial temperature of 25°C is used to accelerate degassing. The pH in equilibrium with the atmosphere is between 8.5 and 8.6 and this enables a δ value of 25 to be obtained for a temperature of 23°C.

Test equipment

Since the tests are comparative, two identical 1 litre capacity borosilicate glass flasks are employed, equipped with PTFE-coated magnetic stirrer rods. The rods can be rotated at a speed up to 800 rpm with the aid of Tacussel Agimax magnetic stirrers, the velocity being adjusted using a Digital Instruments digital stroboscope. The pH and electrical conductivity are measured using Tacussel pHM 210 pH-meters and Radiometer CDM 210 conductimeters

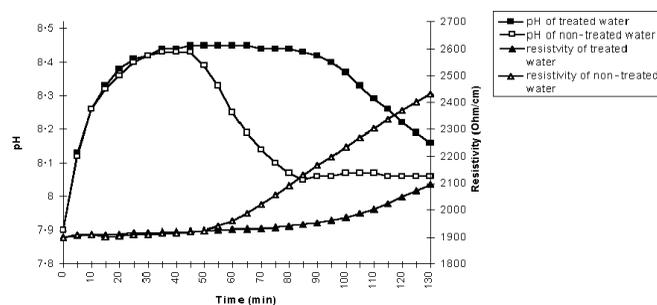


Figure 1 | Variation of pH and resistivity with time.

respectively. The resistivity is automatically corrected to 20°C.

RCP test procedure

The treated water and the reference water (untreated) are stirred simultaneously in sequences of 5 or 10 min. After each sequence, the pH and resistivity of the two waters are measured. Figure 1 shows an example of the variation of the pH and resistivity with time for a non-treated reference water and the same water treated with a physical antiscaling procedure (Lédion *et al.* 1999). The maximum in the pH-time curves corresponds to the precipitation threshold in the water concerned. The start of precipitation is also indicated by a change in slope of the resistivity-time curves, while the slope beyond the inflection characterises the kinetics of the phenomenon. However, experience shows that the onset of precipitation is determined more accurately from the pH curves, the resistivity curves being used essentially to analyse the rate of reaction (Lédion *et al.* 1997).

Evaluation of the efficiency of a treatment using the RCP test

The measured efficiency must incorporate both the nucleation and growth phases. The test time is therefore fixed, e.g. 150 min, and the area between the resistivity curves for treated and non-treated water is compared to the area beneath the resistivity curve for non-treated water (Figure 1). The efficiency E is then defined by:

$$E(\%) = \frac{\int_0^t (\rho_{NT} - \rho_0) dt - \int_0^t (\rho_T - \rho_0) dt}{\int_0^t (\rho_{NT} - \rho_0) dt} \times 100 \quad (2)$$

where ρ_0 is the initial resistivity, ρ_{NT} is the resistivity of the non-treated water, and ρ_T is the resistivity of the treated water, at time t .

Scaling tests on polyethylene

Choice of material

In order to verify the influence of copper on the scaling potential of water with respect to materials other than copper and its alloys, it is not possible to apply conventional methods where scaling is electrochemically accelerated (Lédion *et al.* 1985; Gabrielli *et al.* 1996a,b, 1997, 1998, 1999; Euvrard *et al.* 1997; Deslouis *et al.* 1997). However, a polymer scaling test is feasible. Since scaling phenomena involve nucleation and growth mechanisms, the technique employed is based on electrostatic trapping of CaCO_3 nuclei by an insulating polyethylene wall. In a previous study (Lédion *et al.* 1993), it was shown for a given water that scaling on an insulating substrate is easier when the difference in relative permittivity (dielectric constant) between the water ($\epsilon = 80$) and the insulator (polyethylene $\epsilon = 2.34$) increases. Furthermore, it is preferable to choose a polymer with little tendency to hydrate, since hydration modifies the dielectric behaviour. That is why polyethylene is particularly well suited for use as a nucleus trap.

Effect on deposit weights

If copper has an effect on scaling, a difference will be observed in the scale masses deposited during the tests when the scaling of an untreated water is compared with a water containing copper (treated water). The tests must always be comparative and must be performed simultaneously on the two waters since scaling takes a certain time and the scaling potential of the two distributed waters can vary with time. Parallel tests were therefore carried out on 'copper-treated' and 'untreated' waters. The

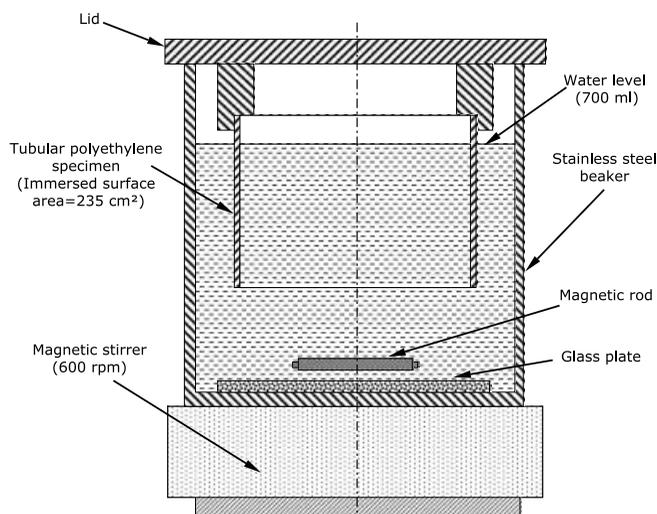


Figure 2 | Experimental set-up.

weights deposited depend on the duration of the tests and on how fast they are carried out (see below).

Experimental set-up

The experimental set-up is described in Figure 2. The specimen is a polyethylene tube (diameter 75 mm, length 50 mm and wall thickness 1 mm, weight about 12 g). It is immersed in an austenitic stainless steel beaker containing 700 cm^3 of water. The volume is mixed by magnetic stirrer at 600 rpm.

Specimen preparation

All specimens are cleaned by immersion in 50% hydrochloric acid solution prior to use, followed by rinsing in tap water, then in demineralized water. After removal of drips, they are dried in a ventilated oven at 50°C for 10 min. Then they are placed in the balance room, where they are left for at least 40 min to allow their temperature to stabilise before being weighed. Weighing is performed on a balance accurate to a tenth of a milligram. One of the specimens serves as a reference and is weighed during each measurement series. Its variations in weight, due to changes in air hygrometry, are used to correct the weights of the test specimens.

Test procedure

In order to take into account inevitable variations in the scaling potential of the water supplies (the laboratory is supplied by the Vanne and Loing aqueducts), parallel tests were always performed on samples taken at the same time, with and without metal ion treatment. The copper ions were introduced in the form of cupric sulphate, the corresponding weights being measured on a Mettler MT5 balance accurate to 1 µg. In general, nine specimens were studied at the same time, one reference sample, four in treated water and four in untreated water. For higher accuracy, the number of specimens was sometimes doubled (eight plus eight).

The beakers were filled and placed on magnetic stirrers previously adjusted with a stroboscope. The specimens were attached to the beaker lids and the test started when they were immersed in the water. The heating of the thermostatically controlled baths was then switched on. The test duration depended on:

- the nature of the water used;
- whether a rapid or slow test was performed;
- the water temperature;
- the stirring speed.

For example, for the reference water used in the present study (water A from the Vanne and Loing aqueducts), the rapid tests lasted 2.5 h at 50°C and the slow tests 15 h at 20°C.

Evaluation of treatment efficiency

After testing, the specimens were removed from the beaker lids, drip dried, then oven dried for 10 min at 50°C, stabilised for at least 40 min in the balance room and weighed, together with the reference sample. The weight gain due to the deposit was determined, taking into account the weight variation of the reference specimen. Average values were calculated for the treated and untreated waters, the efficiency E' being defined by the relation:

$$E'\% = 100 \times [W_1 - W_2]/W_1 \quad (3)$$

where W_1 is the weight of untreated water and W_2 is the weight of treated water. If E' is positive, the treatment

inhibits scaling, while if E' is negative, the treatment promotes scaling.

Continuous test rig

Materials employed

The materials used for these tests were various types of copper tubing with a length of 10 cm. The tubes were sufficiently small to be weighed on a precision balance. For purposes of comparison, polyethylene, stainless steel and tin-plated tubes were also studied. The different materials employed and their designations are shown in Table 2.

In order to produce scaling by hot water, we used a test system which is shown schematically in Figure 3.

The rig is designed so that the waters studied (water A from the Vanne and Loing aqueducts, and water B from the Seine) begin to precipitate slightly. This enables tests with a hot water circuit leading to scaling of studied materials. The tubes are mounted in series with plastic joints and their positions are changed every day by circular permutation, to compensate for possible variations in copper ion concentration that could modify the scaling potential of the water at different points in the circuit. The temperature of the water was controlled at 52°C for the water A which has a higher scaling potential, and at 60°C for the water B with lower scaling potential, and the outlet flow rate was maintained at about 35 l/h. For each series of specimens, the tests lasted 30 days, with 8 h exposure per day, i.e. a total of 240 h. Scaling was evaluated by weighing on a balance accurate to a tenth of a milligram. To avoid unwanted scale nucleation due to water evaporation, the specimens were withdrawn after each exposure period, when the water had cooled to ambient temperature. They were then rinsed in demineralized water and oven dried for 20 min at 50°C. Weighing was performed after the tubes had cooled to the temperature of the balance room.

Test procedure

Each day, the water was heated to the test temperature and the flow rate was established once the tubes had been

Table 2 | Characteristics of the tubes employed in the scaling tests

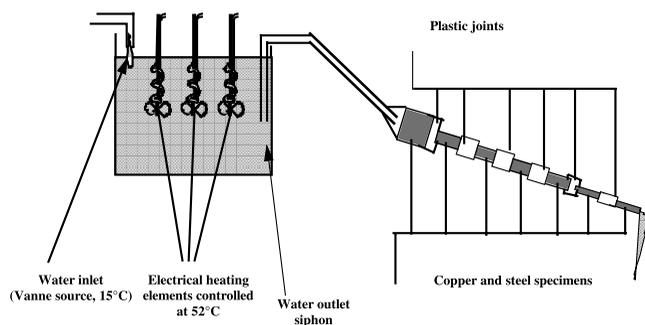
Nature of tubes	Length (cm)	Diameter (mm)	Thickness (mm)	Designation
Sanco [®] annealed copper	10	12	1	S
Annealed copper tubes with a bright inside surface	10	13	0.75	R
Semi-hard copper	10	12	1	DD
Drawn copper	10	12.9	0.7	E
Tin-plated	10	12	1	Sn
Ugine F18 ferritic stainless steel	10	15	1.3	F18
Mannesmann Pressfitting austenitic stainless steel	10	15	1	A
Inconel 600	10	22.2	1.2	Inco 600
Polyethylene	10	12	1	PER

put in place. Following each daily period of 8 h of exposure, the specimens were weighed after the withdrawal, rinsing and drying procedure described above.

RESULTS

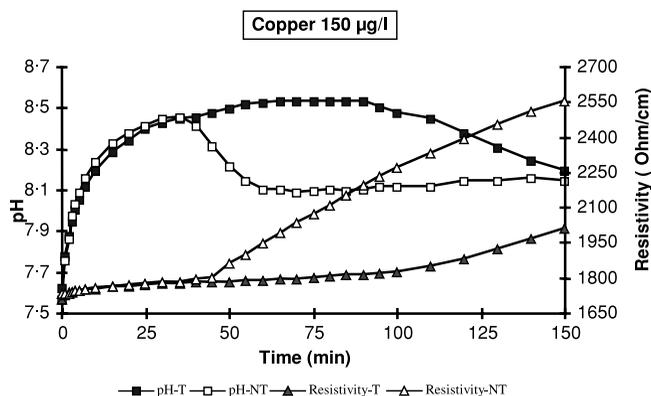
Rapid controlled precipitation tests

This method was used to study the variation of the scaling potential of water due to copper additions in the form of

**Figure 3** | Principle of the continuous test rig.

copper sulphate. Figure 4 shows that an addition of 150 µg/l significantly retards the precipitation of calcium carbonate. In the treated water, the pH begins to fall 80 min later than in the non-treated water, and the rate of precipitation, indicated by the slope of the resistivity curve, is considerably reduced.

Figure 5 shows the calculated efficiency of treatment with copper ions on the scaling potential of the Vanne

**Figure 4** | RCP test results showing the effect of an addition of 150 µg/l of Cu²⁺ on the precipitation kinetics in Vanne water (A).

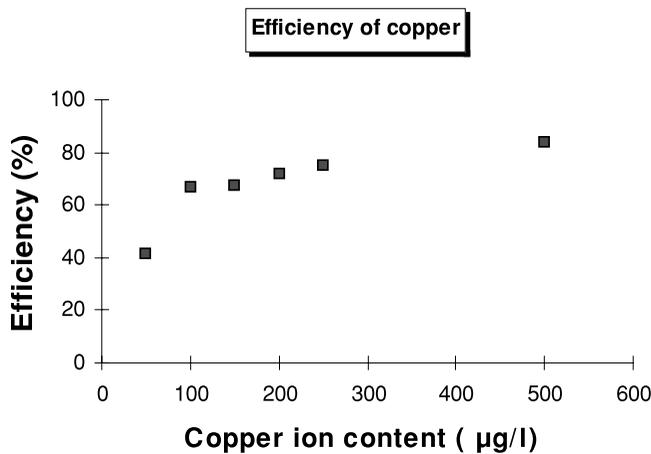


Figure 5 | Influence of copper content on the kinetics of precipitation in Vanne water (A). RCP tests at room temperature.

water. With the mode of calculation employed, the efficiency of inhibition attains 80% for a copper ion content greater than 250 µg/l.

Scaling tests on polyethylene

Figure 6 shows the results of RCP tests at 20°C and 50°C. It can be seen that a concentration of 250 µg/l of copper is sufficient to fully inhibit scaling at 20°C. At 50°C, scaling is almost completely inhibited for copper contents greater than 500 µg/l. In both cases, maximum inhibition is obtained for copper concentrations well below the permissible limits stipulated by European and French legislation (respectively 2000 µg/l and 1000 µg/l).

Direct scaling of tubes in the continuous test rig

The results obtained from the first test series concern various copper tubes, which were compared to F18 ferritic stainless steel tubes and tin-plated tubes. The medium used was water A from the Vanne and Loing aqueducts, which has a high scaling potential. It can be seen in Figure 7 that the ferritic stainless steel and tin-plated tubes show rapid weight gains, whereas no increase in weight is observed for copper. Indeed, for the copper tubes, a very

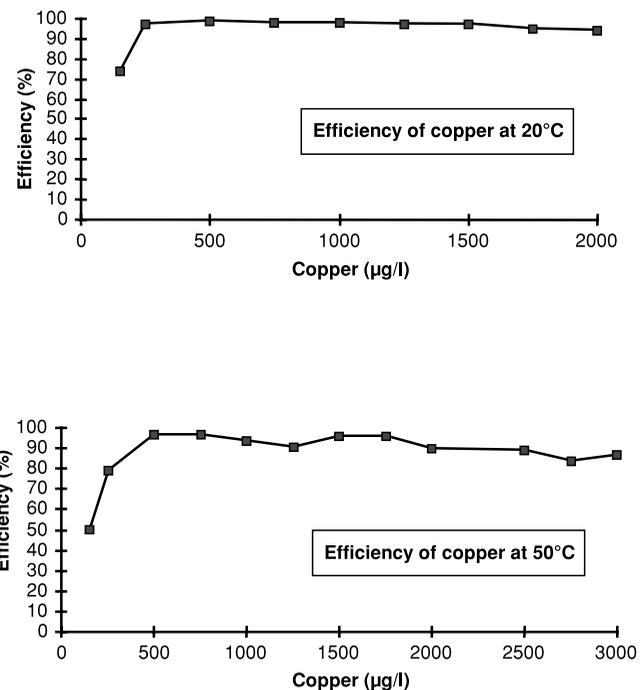


Figure 6 | Influence of Cu^{2+} additions on scaling of polyethylene at 20°C and 50°C.

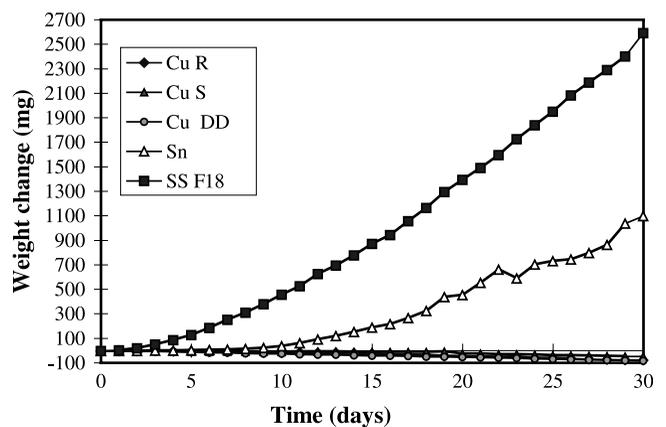


Figure 7 | Weight changes measured in a highly scaling water at 52°C (1 day=8 h exposure).

slight weight loss is measured, due to the normal uniform corrosion necessary to maintain the protective Cu_2O layer.

The second test series used water B, from the Seine, which supplies Paris and is only lightly scaling. Figure 8, which has a much more expanded weight scale compared

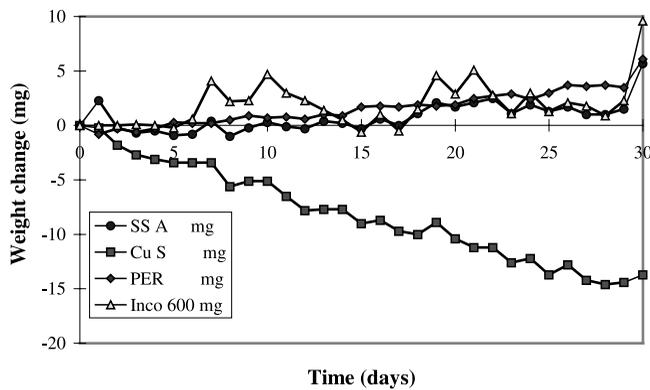


Figure 8 | Weight changes measured in a lightly scaling water at 62°C (1 day=8 h exposure).

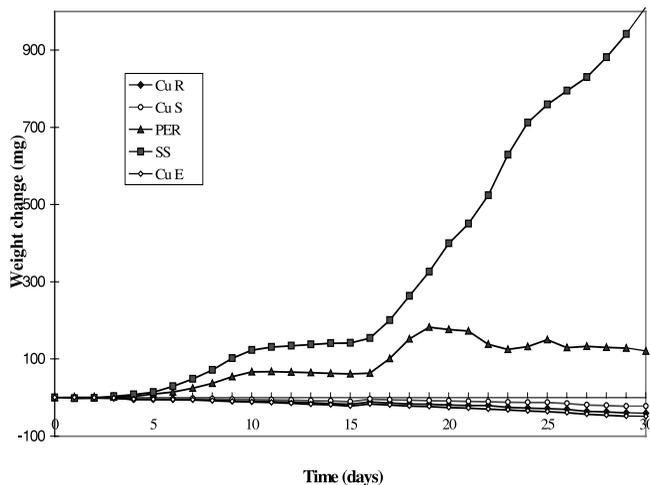


Figure 9 | Weight changes measured in a moderately scaling water mixture at 52°C (1 day=8 h exposure).

with Figure 7, shows that the copper used (annealed Sanco copper with an oxide layer) does not scale, and slightly loses weight for the reasons indicated above. In contrast, the other materials employed (Inconel 600, austenitic stainless steel, polyethylene) show slight but definite scaling. The last test series was performed using a 50–50 mixture of waters A and B for 16 days, which was then replaced by the highly scaling water A for the remainder of the test (Figure 9). It can be seen that scaling on the austenitic stainless steel and polyethylene is much less marked in the mixture than in water A alone, and that there is a tendency for the weight loss to level off at a

maximum value. This is probably related to poor scale adhesion. When the mixture is replaced by water A, scaling increases up to the end of the test for the stainless steel, but levels off for the polyethylene. Again, this latter observation is probably due to poor adhesion and to spalling during the daily handling operations. The three copper specimens (bright and oxidised Sanco copper and drawn copper) show no scaling at all, with only a slight loss in weight due to corrosion.

DISCUSSION

While the inhibiting effect of copper on scaling is undeniable, it is still necessary to determine the mechanism whereby copper ions affect the calcium carbonate nucleation and growth process. There are several possibilities:

- The Cu^{2+} ions could have a greater affinity for CO_3^{2-} ions than the Ca^{2+} ions. This would require the formation of a product more insoluble than calcium carbonate. A rapid thermodynamic calculation based on the different carbonates of copper shows that this hypothesis is not plausible, since the quantities of copper introduced are very small compared to the concentration of CO_3^{2-} ions. The same reasoning is valid for zinc (Abouali *et al.* 1996) which has a similar effect to copper.
- Copper ions could accelerate the formation of colloidal CaCO_3 nuclei, which would then have an anti-scaling effect, tending to promote sedimentation, as in the case of physical water treatments involving electrical, magnetic or electromagnetic fields. However, this explanation is also unlikely, since if it were true, nucleation would be promoted on copper-containing walls, leading to more rapid scaling on copper-based materials, whereas the opposite is observed in practice.
- Cu^{2+} ions could associate with Ca^{2+} ions to form a mixed carbonate of the type $\text{Cu}_x\text{Ca}_{1-x}\text{CO}_3$, in which copper is in solid solution in the cation sub-lattice. This is strongly supported by the suggestions in Parsiegla & Katz (1999). The

theoretical maximum copper content is 16%, but in practice the concentration could be much less. Inhibition would then be due to the fact that the activation energy for dehydration of Cu^{2+} ions is much higher than for Ca^{2+} ions, making growth of the nuclei more difficult. A single layer of copper ions would be sufficient to inhibit growth. This hypothesis is compatible with the thermodynamic data available for copper-calcium carbonate solid solutions (Roques 1990).

In long-term tests (120 h), it was found that the efficiency of copper additions decreased. Calcium carbonate finished by precipitating in the form of aragonite, for which the supersaturation was higher than for calcite. The presence of unidentified copper hydroxycarbonates, which have been considered as those of inhibiting species (Parsiegla & Katz 2000), was also revealed by Fourier transform infrared absorption spectrometry performed on 3 mm diameter scale specimens. This shows that the copper ions are effectively gradually consumed and that precipitation and scaling can occur when they are exhausted. This confirms the research findings in Parsiegla & Katz (1999). All tests were performed with very small copper additions, which can be assumed to have been present initially in the form of dissolved copper ions. Additional tests were performed with metallic copper in contact with the water and the inhibition effect was found to be identical. This equivalence between different sources of Cu^{2+} ions disproves the idea of a nucleation-inhibiting surface proposed by certain authors (Roques 1994). It is not only the emitting surface that does not scale, but also other surfaces of different materials placed in water containing copper ions dissolved during natural corrosion reactions. Both the RCP tests and the scaling tests on polyethylene substrates clearly show that the classical nucleation and growth process for calcium carbonate is inhibited by the presence of copper in the water.

CONCLUSIONS

When a lightly calcifying and weakly scaling water comes in contact with copper surfaces, no scaling is observed,

whereas other metallic and polymer materials can undergo slight scaling. In water with a higher scaling potential, deposition on copper still does not occur or remains negligible, whereas significant scaling can be observed on the other materials commonly employed for hot water distribution circuits (stainless steels and polyethylene).

The normal emission of copper ions associated with the classical electrochemical reactions between copper and water is sufficient to inhibit scaling. Water enriched in copper ions in this way has a much lower tendency to cause scaling on other materials placed downstream in the circuit, and this effect is observed at copper concentrations well below the maximum levels tolerated by current European regulations.

The absence of scaling and the consequent maintenance of 'clean' surfaces should help to limit the proliferation of bacteria, such as those responsible for legionnaire's disease (Fauris *et al.* 1993).

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