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Microbiologically influenced copper corrosion in potable water with emphasis on practical relevance

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Abstract

The physical and chemical properties of biofilms, in combination with metabolic and degradation products of biological origin, influence the nature and local chemistry of the aqueous phase at the copper/biofilm phase boundary. The pitting susceptibility of copper is determined by this change of water composition at the copper/biofilm phase boundary and is supported by the mixture of solid corrosion products and the biofilm at the copper surface. Several factors influence the susceptibility of copper to MIC: commissioning, design and operating conditions; the chemical composition of the water and the relevant biological activity. Field experience and theory showed that a combination of methods should be used to protect existing copper installations. In summary, water chemistry seems to be a major influencing parameter for the described corrosion problems. Raising the alkalinity of the potable water whilst optimising the chloride/sulphate ratio is considered as the most promising preventative measure to overcome the described problems.

Introduction

Copper is an excellent material for plumbing purposes. Despite the widespread use only a few corrosion failures have occurred under special circumstances (Ferguson et al. 1996; Japan Copper Developm. Assoc. 1982; Winkler 1990). Pitting corrosion of copper has been extensively investigated during the last fifty years. Pitting corrosion was shown to be promoted by carbonaceous films which were formed by cracking lubricants during the bright annealing process (Campbell 1954; Lucey 1967). Later it was found that a special type of oxide layer also resulted in pitting corrosion in certain types of water (Baukloh et al. 1990). Such oxides grow when copper tubes – especially hard-drawn tubes – are jointed by brazing. The manufacturers made successful efforts to produce copper tubes free from carbonaceous films. This quality is today required by the relevant standards and specifications (DVGW GW392). Different methods based on surface treatments e.g. grit blasting and preoxidizing processes were used to achieve such a high quality (Baukloh et al. 1982; Cornwell 1973, 1976; Gilbert 1966).

Despite these measures, potable water installations in mainly institutional buildings in different regions of the world were affected by an unexpected pitting of copper pipework. No specific type of tubing (hard, halfhard, soft annealed) showed a particular susceptibility to this type of pitting. Microbiologically influenced corrosion (MIC) has been identified as causing the observed problems (Angell et al. 1990; Campbell et al. 1993; Fischer et al. 1988; Geesey et al. 1987, 1994; Nuttall 1993; Wollmann 1994). This type of corrosion of metals and alloys is now generally accepted and considered to be a major concern in terms of economic losses and pollution (Characklis et al. 1990; Dowling et al. 1990; Heitz et al. 1996; Houghton et al. 1988). However, experience and scientifically-based knowledge did not indicate a remarkable susceptibility of copper to pitting in the respective water distribution areas. Causes and mechanisms of these microbiologically influenced corrosion processes were by no means

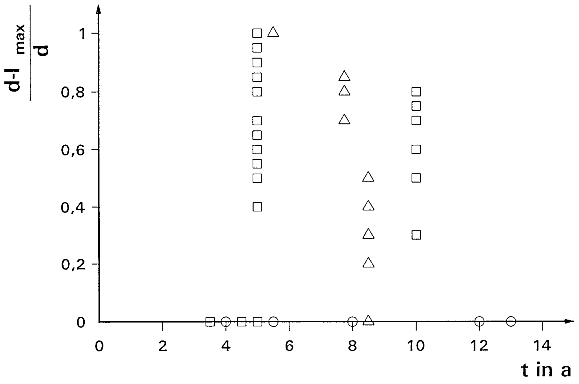

Figure 1. Evaluation of the maximum pit depth of the installed copper tubes for different public buildings in the same water distribution area as a function of operating time of the installations in years; d (in μm) is the thickness of the copper tube wall (usually 1000 μm), l_{max} the maximum pit depth observed in a copper tube removed from the installation after a certain operating time. Consequently, d – l_{max}/d = 0 means the perforation of the tube. □ Building A; △ Building B; ○ Building C

understood at their first occurrence. The scope and objective of this contribution is to provide an overview about factors that influence the susceptibility of copper to MIC and to assess the relevant influencing parameters yielding an overview about the present state of knowledge.

Case studies of copper pipe corrosion

Potable water installations

Potable water installations were affected by MIC, namely in Germany, Saudi-Arabia, Southwest-England, Scotland and Sweden in the mid eighties. A further confirmed case of MIC has been reported from Australia (Wallace 1996). Failure analyses were performed (Campbell et al. 1993; Fischer et al. 1992b, 1994, 1995; Linder et al. 1983) and test rigs were set up in affected buildings and in the laboratory to simulate and understand the corrosion process (Angell et al. 1990; Wagner et al. 1992a, 1994a, 1995b, 1996c, 1996b, 1996e, 1996f) as a basis for the evaluation of countermeasures.

From practical experience it could be assumed that in cold water installations no failure within an installation is to be expected when no failures occur in the first few years after commissioning. About three years after commissioning of the installation this likelihood usually decreases (Franqué von 1968a, 1968b, 1972; Kruse 1991). This does not hold true for this microbiologically influenced copper corrosion process as depicted in Figure 1 (Wagner et al. 1996c). In Figure 1 the corrosion progress occurring in copper installations in three large institutional buildings and situated in the same water distribution area was validated by performing inspections of copper tubes affected by MIC using the maximum pit depth as the evaluation criterion. A relative measure for the pit depth d-l_{max}/d (d: thickness of the copper tube in μm; l_{max}: maximum pit depth in μm) was plotted as a function of operating time after set-up of the installation. The zero line means a perforation, the ‘one’ a tube without any pitting attack. Wall thickness was usually 1 mm. The inspections were performed in installations with service lives of up to thirteen years. Figure 1 reveals the following facts:

- The likelihood of failure did not exhibit a relative maximum between the years one and three;
- perforations occurred even after a use of thirteen years, eg in building C;
- pit depths measured on different samples after a certain time of use varied between zero and perforation, that is 1 mm (see especially after 4.5 years for building A);
- a change for the worse could be observed within the installation of building A after 10 years despite the performance of countermeasures (Fischer et al. 1995). This indicates that the MIC process could be slowed down considerably, but not eliminated completely by these measures.

Since these results were evaluated for three different buildings in the same water distribution area, also taking into account the described characteristics of this corrosion process, the relevance of MIC being a special mode of corrosion could be established. The typical further characteristics for the MIC process under consideration are the occurrence of

- copper by-products in a dissolved or particulate state and
- extra-cellular polymeric substances mixed with solid corrosion products usually consisiting of black copper(II) oxide and/or posniakite/malachite.

Complex biofilms are ubiquitous at interfaces in nature (Ellwood et al. 1982). One possible cause of the pitting and consequent perforation of the copper pipes was the presence of extra-cellular polymeric material (Wagner et al. 1992a). These extra-cellular polymeric substances comprise different organic materials, i.e. polysaccharides, glycolipids and oligopeptides (Bremer et al. 1992; Ford et al. 1977; Little et al. 1986). These biofilms are possibly formed as a consequence of the growth of copper resistant microorganisms (Cornwell et al. 1973; Cooksey et al. 1992).

The biofilm observed here on copper comprised extra-cellular polymeric material with a high water content and included bacteria, fungi and adventitious algae. The biofilm was either situated underneath or mixed with solid copper corrosion products. The chemical composition of the solid corrosion products and parts of the biofilm were investigated in more detail for a representative German case (Fischer et al. 1992). Dark-red copper(I)-oxide, black copper(II)-oxide, blue-green posniakite and malachite were identified. The structure of the extra-cellular polymeric substances was described as linear and/or cross-linked acidic or partly non-ionic polysaccharides (Fischer et al. 1988; Paradies et al. 1992). In some other cases, the copper pipes were covered with a polysilicate film which was insoluble in acids (Fischer et al. 1995). This film was not of biological origin. However, because the manifestations of corrosion were the same, this material was not differentiated from the biofilm described above. Therefore, the authors consider the physicochemical properties of the biofilm to play an essential role in this MIC process (Siedlarek et al. 1994; Wagner et al. 1996a).

In addition to the biofilms, an exceptional level of biological activity within the failed copper tubes was observed in some cases. This was either indicated by the chemical composition of the biofilm mentioned above (Fischer et al. 1988) or by tremendous oxygen consumption during periods of stagnation (Angell 1992; Nuttall 1993). This was interpreted as indirect evidence of metabolic activities leading to the formation of biofilms. Many investigations dealing with MIC in potable water installations report on the influence of living microorganisms leading to the formation of a biofilm (Hadley 1948; Walker et al. 1990). Microorganisms live and die, and their metabolism changes as they progress along the growth curve. Consequently, the biosynthesis of extra-cellular materials as well as many biochemical processes cannot be considered as constant. No specific types of microorganisms can be confirmed as having a detrimental influence on the corrosion process because no validated, generally accepted model for the description of the relevant corrosion process is available. Nevertheless, it has been suggested that some bacteria will attack copper when they become sessile on the copper surface (Arens et al. 1995, 1996; Dutkiewicz et al. 1996; Geesey et al. 1986; Webster et al. 1996).

General attack was detected in the failed piping of all cases. Pitting attack was also detectable. The pits had a hemi-spherical shape in the majority of cases, however, in one case pinhole-shaped pits were also found. Although the copper surface was usually covered with a biofilm mixed with solid corrosion products, parts of the stained copper tubes were shiny without detectable signs of attack in some cases. This was observed when either the biofilm showed a heterogeneous structure and stabilized corrosion elements or the chemical and physical status of the corrosion products or their adherence were not uniform (Angell et al. 1990; Wagner et al. 1992b).

In all cases involving this type of MIC the distributed potable water was a soft, weakly buffered and slightly alkaline water prepared from surface water (Fischer et al. 1995). The probability of copper pitting in these types of fresh water under these conditions is negligible using the available knowledge described in the literature (Lucey 1975, 1982) or given in a DIN Standard (DIN 50930). This indicated that other factors were responsible for the corrosion damage. In three countries (Germany, Saudi-Arabia, Scotland) both the cold and warm water circuits showed the same manifestations of corrosion and failure. These manifestations could be attributed to Type I pitting corrosion (Lucey 1975, 1982). This means that no effect of water temperature could be evaluated.

Large plumbing systems

There is significant evidence that large plumbing systems are more prone to MIC. The highest failure rate occurs where a high degree of branching and long horizontal runs are present in the installation. The likelihood of MIC pitting increases when the water stagnates and is replenished infrequently, and is at a maximum under intermittent flow conditions when periods of stagnation are prolonged. Usually, domestic houses are affected to a much lesser extent by this type of corrosion.

An installation is much more susceptible to pitting with increasing contamination of the water supply, e.g. by the use of open water tanks and dirty filters. A long delay between the running of the installation and the initial commissioning and pressure testing can affect the likelihood of corrosion, especially when water remains in the copper tubes due to incomplete drain-down.

The hospital water systems under investigation were primarily aerobic but evidence of transient anaerobic conditions has been reported (Nuttall, 1993). A wide range of bacteria has been isolated from waters and copper tube surfaces associated with pitting corrosion. The copper (II) ion is very toxic for many organisms but those associated with the pitting showed a range of tolerance levels with some evidence (Angell & Chamberlain, 1991) that those with low tolerance may be protected by other more tolerant strains when in mixed culture.

Factors affecting copper pipe corrosion

Design, installation and operating conditions

The installation and operating conditions were evaluated as possible causes for the damage (Fischer et al. 1992, 1995; Wagner et al. 1992a, 1994a, 1994b, 1996c, 1996b). The conditions of the installation after the pressure test and operation determine the likelihood of corrosion. Other factors to consider are the pipe sizes and actual flow rates, storage vessel size, conditions of maintenance/cleanliness and temperature control.

The role of microorganisms

There are numerous ways in which organisms, particularly microorganisms can play a role in corrosion processes. The number of organisms for copper is rather larger than for many other metals as it is susceptible to such a wide range of chemical reactions (Pope et al., 1984). Thus the corrosion can be initiated by localised breakdown of the normal passivating surface coatings, primarily Cu_2O. Classes of active compounds produced by microorganisms include:

- Inorganic acids, such as dissolved CO_2; organic acids, e.g. acetic, butyric; acidic polysaccharides, e.g. alginate, xanthan; ammonia; sulphur-containing compounds like cysteine or H_2S.
- Proteins, unless exceedingly acidic or rich in sulphur amino acids are frequently protective, the amino nitrogen and copper having a high affinity and effectively acting as a corrosion inhibitor.

Typically, to exert an effect organisms need to be held in close proximity to the metallic surface and for the localised changes in chemistry to be prolonged by reduced diffusion away from the localised site. The establishment of microcolonies or a matrix-enveloped biofilm will both achieve this effect. Thus, unless planktonic bacteria can produce a very significant shift in the bathing medium, for example through pH changes or H_2S production they are unlikely to be involved in MIC. In practice, this is fairly unlikely in any flowing system, although partial or complete stagnation could allow development of significant levels to affect corrosion (Angell, 1992). Very dense populations of bacteria on a metal surface can lead to corrosion inhibition in aerobic systems due to competition for oxygen, so a patchy, heterogeneous biofilm is more likely to cause corrosion.

Bacterial copper tolerance

Extracellularly secreted materials, either copper binding proteins (Gordon et al., 1992) or acidic polysaccharides (Bremer & Geesey, 1993) can play major roles in microbiologically influenced copper corrosion processes. Those extracellular polysaccharides secreted in response to the presence of copper had a higher level of uronic acid substituents. The copper stimulus also increases the levels of polysaccharide secreted by many bacteria. In practice over 40 isolates of different organisms were obtained from pitted copper tubes but many were expected natural water flora organisms such as *Pseudomonas vesicularis*, *Ps. stutzeri*, *Sphingomonas-paucimobilis*, *Comamonas testosteroni*, *Flavobacterium breve* together with a large amount of *Moraxella lacunata* and *Moraxella sp*. (Chamberlain et al., in preparation).

Biofilms

The presence of a biofilm is a key feature in the majority of cases of microbially influenced corrosion. These films comprise microorganisms, organic and inorganic particulates and a binding matrix which is usually predominantly polysaccharide with additional proteins and other cell-derived organic compounds, such as nucleic acids. These biofilms have been the subject of considerable study in recent years (Chamberlain et al., 1988), in particular those associated with the occurrence of pitting corrosion of copper. The first indication that a biofilm matrix containing polysaccharides may be of importance in the case of copper MIC was reported by Fischer et al. (1988). This was based initially on the staining reaction with Gentian Violet, essentially a non-specific polysaccharide stain, but was subsequently supported by detailed chemical analyses. The major component was a xanthan-like material together with polymers resembling bacterial alginate, which show acetylation of the uronic acid residues, unlike the brown algal versions.

The role of polysaccharides

Most polysaccharides associated with microbial corrosion have some form of anionic group on the molecule and this has lead to several models of how such materials could produce pitting. Thus, Mittelman and Geesey (1985) showed that polymer from a river bacterium was capable of binding copper and could be effective at establishing copper concentration cells on a copper surface. This basic concept was evolved by Bremer and Geesey (1991) into a laboratory-based model of MIC of copper. Geesey and Bremer (1992) demonstrated that the *(Pseudomonas) Sphingomonas paucimobilis* isolated by Angell and Chamberlain (1991) from pitted copper tubes from a German Hospital were capable of dissolving thin, (6–7nm) vapour-deposited copper films on germanium internal reflection elements examined by ATR/FTIR. Subsequent work with isolates from copper tube from the USA confirmed that some strains of bacteria, which were stimulated to produce extracellular polysaccharides by the presence of copper, could show varied behaviour towards the thin copper films. Thus, some polymers dissolved it whilst others did not, and those which did were usually rather acidic in their reaction due to uronic acid carboxyl residues. However, the presence of a non-dissolving strain could protect the copper surface against the actions of the aggressive polymer.

On the basis of an extensive series of papers relating to copper binding by bacterial polymers (Geesey et al., 1987; Jolley et al., 1989; Geesey and Bremer, 1990) they suggested that some polysaccharides with acidic groups such as uronic acid or pyruvyl substituents were known to frequently possess high affinity binding sites for copper (Geesey et al., 1986) thereby promoting the removal of further metallic copper ions. The juxtaposition of two such polymers of differing copper binding affinity could allow the development of a differential concentration cell, resulting in the establishment of an anodic site beneath the polymer binding the most copper (Geesey and Mittelman, 1985).

These data are indicative of a capability of some bacterial polysaccharides to dissolve thin copper films, however, it is still some way from the development of pitting in the accepted corrosion sense. This has been demonstrated subsequently (Campbell et al., 1993) using a mixed culture including the *Sphingomonas paucimobilis* mentioned above, plus a strain of *Sph. yanoikuae* and an *Acidovorax sp.* which originally appeared to be closely allied to *Ps. solanacearum*, a noted plant pathogen. The organisms were inoculated into packed beds of 1cm sections of 15mm copper tube and supplied with artificial tap water initially, followed by actual tap water from the supply which was associated with the copper corrosion incidence in SW England. Two systems were operated, one inoculated and one sterile. The inoculated system showed true pitting on both internal and external surfaces of the pipe rings, whereas the sterile system had a very low number of pits on external faces alone, but only where rings had been in contact to produce ‘crevices’. The process took approximately 2 years to occur and it is tempting to suggest that one or both of the two attendant bacterial strains may have acted as a partial protection system as described by Geesey et al. (1994). Final recovery of organisms at the termination of the experiment showed all three strains were still present with no other organisms as contaminants.

The role of oxygen differential cells

Other models have been put forward. Walker et al. (1994) proposed that the ‘pepper-pot’ pitting found in Scottish hospitals was essentially the footprint of the microcolony structure within the biofilm. It was suggested that the creation of oxygen differential cells with low oxygen levels beneath the organisms could create the required anodes. In our own research we have shown that a number of bacteria associated with MIC of copper are capable of producing polysaccharides which can interfere with the passage of chloride ions to the metal surface (Wagner et al., 1995a). The recent observations on biofilm structure described by Keevil et al. (1995) suggest that there are numerous channels which perforate the biofilm polymer mass allowing easier access to the regions close to the metal surface. Such a structure could raise serious objections to the cation selectivity mechanism if it were not for the fact that, as stated by Keevil, ‘the structure can also appear confluent because of the production of copious EPS gel **within** the channels’. Recent work with other bacterial polysaccharides has shown that anion migration can be limited by quite thin layers of dilute polymers (Hart et al., in preparation). However, even those biofilms with extensive channels still possess a basal layer, albeit only 5–10 μm thick, which covers the metal surface.

Physico-chemical aspects and their role

The physico-chemical properties of biofilms play a decisive role in the MIC process (Siedlarek et al. 1994c; Wagner et al. 1996a). These physical properties depend entirely on its chemical composition.As mentioned earlier, its primary composition consists of structures similar to that of xanthan, eg pyruvate residues, highly crosslinked and of high molecular weight. It also contains alginate like structures, a polysaccharide consisting of mannuronate and guluronate residues arranged in a non-regular clockwise pattern along a linear chain (Fischer et al. 1988; Paradies et al. 1992). Because of the accumulation of fixed negative charges within this biofilm due to its major components, this type of biofilm is expected to be cation selective yet permeable for components like water and oxygen.

The cation selectivity and permeability of this type of biofilm gave rise to the following arguments (Siedlarek et al. 1994c):

- Only cations and neutral components, eg water, oxygen and carbon dioxide, but no anions can pass through the coating consisting of extracellular polymeric substances with a high water content to a copper surface when in contact with potable water as observed in the failure cases. This allows the formation of copper oxides or copper hydroxides beneath the coating, but not the deposition of salt layers, e.g. copper(I)-chloride.
- The electrochemical force for the transport of copper ions through the biofilm is provided by the gradient of the electrochemical potential of ions produced through the anodic partial reaction of the corrosion reaction, i.e. copper oxidation.
- A very thin layer consisting of copper(I)-oxide is formed, when a bare copper surface comes into contact with an aqueous phase (Burke 1990; Strehblow 1984; Speckmann 1985, 1988).

A low pH can be assumed at the phase boundary copper/biofilm due to the dissociation constant of the carboxylic acid groups. Typical pK_a values of interest here are in the range of 4.2–5.6 according to titration experiments and conductivity measurements (Siedlarek et al. 1994c). The electrolyte at the phase boundary copper/biofilm becomes acidic if an adhering deposit of copper(I)-oxides or copper(I)-hydroxides is formed electrochemically through the reaction with water. Higher pH values in the range between 6.5 and 9.5 are established at the phase boundary biofilm/potable water corresponding to the pH range of potable water according to the German drinking water ordinance (Bundesgesetzblatt). These considerations infer the existence of a pH gradient across the biofilm coating (Wagner et al. 1991).

These theoretical considerations were substantiated by the performance of laboratory experiments, mainly in chloride-ion containing electrolytes using complementary electrochemical techniques (Siedlarek et al. 1994c; Wagner et al. 1996a). The biopolymers were directly situated on top of the bare copper surface. During exposure a layer of copper(I)-chloride was formed on top of the biopolymer, followed by a layer of copper(I)-oxide (Siedlarek et al. 1994a, 1994c; Wagner et al. 1996a, 1996d). The biopolymer coating stabilizes a low pH at the phase boundary copper/biopolymer due to its acidic functions leading to an enhanced copper by-product release compared to a copper electrode without biopolymer. In the pitting areas the biopolymer coating was either not present or partially disrupted during exposure. In these anodic areas the corrosion behaviour is determined by the anions and their ratios. Therefore, promising countermeasures should be based on the optimization of the anion ratios in the potable water with regard to chloride, sulphate and bicarbonate. These measures are also considered to be beneficial in terms of reducing cuprosolvency by supporting the formation of protective layers.

The mechanism of the formation of reaction layers must be well understood to describe promising countermeasures to overcome MIC problems. Anions like sulphate, chloride and bicarbonate together with protons are the main influencing parameters for the deposition of reaction layers of solid corrosion products during corrosion of copper when in contact with aerated cold water of potable quality.

The influence of chloride and sulphate ions on the corrosion reactions of copper is well understood (May 1953; Lucey 1967; Billiau 1983; Pourbaix 1976; Al-Kharafi et al. 1982; Shalaby et al. 1989; Siedlarek et al. 1993, 1994a; Fischer et al. 1992a, Edwards 1994b; Patel 1996). In sulphate-containing electrolytes, voluminous reaction layers of crystalline copper(I)-oxide are formed at potentials higher than the threshold potential. The deposited layers do not inhibit the anodic partial reaction to any observable extent. The only manifestation of corrosion is general attack. In electrolytes containing chloride, two reaction layers are formed, namely copper(I)-chloride underneath and an amorphous film of copper(I)-oxide on top of the copper(I)-chloride. This amorphous copper(I)-oxide is formed via hydrolysis of copper(I)-chloride, and inhibits the anodic metal dissolution. The observed manifestation of corrosion is therefore repassivating pitting with maximum pit depths of about 100 μm ± 30 μm. These observations for both chloride and sulphate ions are independent of pH in the range of $4 < \mathrm{pH} < 10$. In general, an increase in the sulphate concentration increases the pitting tendency of copper, whilst an increase in the chloride or nitrate concentration decreases the pitting tendency (Lucey 1968).

The available results concerning the system $Cu/H_2O/CO_2$ do not allow conclusive statements concerning the corrosion behaviour of copper (Edwards 1994a, 1994b, 1996; Thomas 1972, 1972a; Mattsson 1980, 1988; Adeloju 1986; Ushakova 1991, 1991a, Alhajji et al. 1996). Although bicarbonate has long been considered essential in the prevention of copper corrosion problems (Cruse et al. 1985), recent work has demonstrated that bicarbonate has a dual nature that is dependent on the solution pH (Edwards 1994a, 1994b, 1995, 1996; Majerowski et al. 1996). Contrary to expectations, a higher content of bicarbonate was found to increase copper corrosion rates below about pH 8.1. Above about pH 8.1, the presence of bicarbonate tends to passivate copper surfaces and decrease corrosion rates (Edwards 1995). In nearly all of the cases where bicarbonate was reported to have beneficial effects in practice, the solution pH was greater than pH 7.7 (Milosev et al. 1992; Thomas 1972; Drogowska et al. 1992; Mattson et al. 1968; Hongve et al. 1995; Nielsen 1995).

In electrolytes with binary mixtures of anions (chloride/sulphate and bicarbonate/sulphate) the sulphate ions influence the repassivation of the copper material unfavourably (Project IVA5-20400789; Siedlarek et al. 1994b). Generally a tendency to pitting is favoured by a high sulphate/chloride ratio (Lucey 1968). For the corrosion system $Cu/CO_2/H_2O$ plus a second anion only isolated results are available (Thomas and Tiller 1972; Nishikata et al. 1990, Obrecht 1962, Wagner et al. 1996e). For example, copper pitting occurs in hard waters containing dissolved carbon dioxide and oxygen having a pH range of 7.0–7.8 and a sulphate/chloride concentration ratio of 3–4: 1 (Obrecht et al. 1969). However, it could be shown in recent work that a moderate increase of the bicarbonate level in a chloride/sulphate electrolyte leads to a considerable decrease of the manifestations of copper corrosion (Wagner et al. 1996e). A change of the chloride/sulphate ratio by increasing the chloride concentration yields a further reduction of the maximum pit depths of the copper (Wagner et al. 1996e).

Remedial and preventative measures

An MIC process as the cause for the breakdown of a copper potable water piping system must be clearly identified before discussing remedial measures. Staining procedures were developed to allow the rapid detection of biofilms that play a key role in this corrosion process (Chamberlain et al. 1988; Walker et al. 1994). Successful countermeasures were developed, substantiated and introduced into practice to protect the installations (Fischer et al. 1995; Wagner et al. 1996c, 1996b). This included the test of the suitability of alternative installation materials (Fischer 1993; Wagner 1995).

Design, installation and operating conditions

The following methods of remedial treatments should be considered when MIC is encountered (Fischer et al. 1995, Wagner et al. 1996b):

- Ensure cleanliness and minimize delays in starting operation after setting up the installation.
- Avoid pockets of air resulting in partly filled pipes.
- Clean the inner surface of the installation with citric acid and/or sulphamic acid and replace the damaged section. Without this additional treatment a simple replacement with copper is not a suitable countermeasure, as a higher likelihood of corrosion and, consequently, the occurrence of failures in a much shorter time period have to be expected (Wagner et al 1996c). Reinstallation with another material could also be a successful countermeasure.
- Insulate hot and cold water sections and maintain hot water at $T > 50$ °C and cold water at $T < 25$ °C.
- Increase the water circulation by using pumps.
- Reduce suspended solids and total organic carbon in the source water with filters.
- Minimize dead-ends in the system as well as long, horizontal sections.
- Install monitoring loops and sampling ports.
- Maintain the flow rates to establish a continually present oxygen concentration.
- Design the system in modular form to avoid problems caused by large single water systems.
- Make changes in more than one parameter to minimize the reappearance of pitting. This is the most important point.

Water treatment

Modulation of the water alkalinity is considered a most promising approach to overcoming corrosion problems in copper installations including MIC problems. This effect should be enhanced when the chloride/sulphate ratio is changed by the addition of chloride based on laboratory experiments (Wagner et al. 1996d). This approach is supported by experiences obtained in practice. The corrosion situation of copper tubes in contact with soft potable waters was improved satisfactorily in the Netherlands (Elzenga et al. 1981), in Sweden (Linder 1987), in the USA (Edwards et al. 1995) and in Australia (Majerowski et al. 1996) by the addition of bicarbonate. Nevertheless, microbial influences have not been reported in these cases. In a water distribution area in Germany affected by MIC and copper by-product release, bicarbonate dosing in combination with UV-treatment was shown in a test site to be a promising remedial measure (Baukloh A, personal communication). In another German case, the exchange of sulphate ions versus chloride ions resulted in a remarkable improvement of the pitting corrosion behaviour of copper (Kruse 1987).

As mentioned earlier, a moderate increase of the bicarbonate level in a chloride/sulphate electrolyte led to a considerable decrease in the manifestations of copper corrosion in laboratory experiments (Wagner et al. 1996e).

Conclusions

Several factors influence the susceptibility of copper to MIC: commissioning, design and operating conditions; the chemical composition of the water and the relevant biological activity. Field experience and theory showed that a combination of methods should be used to protect existing copper installations. In summary, water chemistry seems to be a major influencing parameter for the described corrosion problems. Modulating alkalinity of the potable water whilst optimising the chloride/sulphate ratio is considered as a most promising preventive measure to overcome the described problems.

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