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TYPE I PITTING OF COPPER TUBES FROM A WATER DISTRIBUTION SYSTEM

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Abstract—Samples of copper tubes from a cold water distribution system which had failed due to pitting whilst in service were subjected to a detailed failure investigation. Analysis of the tubes showed that failure was a result of Type I pitting attack. While the exact cause of pitting was unknown, it was hypothesised that it could have been due to changes in the water quality and/or content. The tubes were found to be made from phosphorus de-oxidised copper and no anomalies were evident in either the chemical composition or the microstructure which could have caused the pitting observed. It was recommended that the tubes be replaced and that due attention be given to ensure that the new tubes are free of internal carbonaceous deposits or other foreign matter. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Corrosion, pitting corrosion.

1. INTRODUCTION

Copper tubes are used extensively in water distribution systems due to their corrosion resistance and ease of installation. In Europe and North America they account for more than 80% of all tubes installed in water service [1], amounting to over 100 million metres of tubing. In spite of these large quantities, tube failures are relatively rare. Of the failures that do occur, pitting corrosion accounts for approximately 60%.

This study presents an investigation of the failure of copper tubes from a cold water distribution system carrying potable water in a shopping centre. The tubes, which were built into the brick walls, sprang leaks in several premises in the shopping centre after approximately 12 years' service, causing severe staining of the walls. Examination of the tubes revealed the presence of pin holes perforating the tube walls.

2.. EXPERIMENTAL PROCEDURE

2.1. *Visual examination*

Several tubes sections were received for analysis. These were sectioned to reveal the internal surfaces, which were found to be covered with a greenish-white scale (Fig. 1). Furthermore, localized deposits of green corrosion product in the form of tubercules were also evident (see arrow in Fig. 1). Some tubercules were carefully removed by light scrubbing to reveal the underlying metal. A shiny, black layer of an unidentified compound was found to exist beneath the greenish-white scale. Beneath this black layer, in turn, pits penetrating into the tube wall were found. An example of the various layers and the underlying corrosion pit is shown in Fig. 2. Some of the pits observed were relatively large and deep, as shown in Fig. 3.

2.2. *Chemical analysis of internal scale and corrosion products*

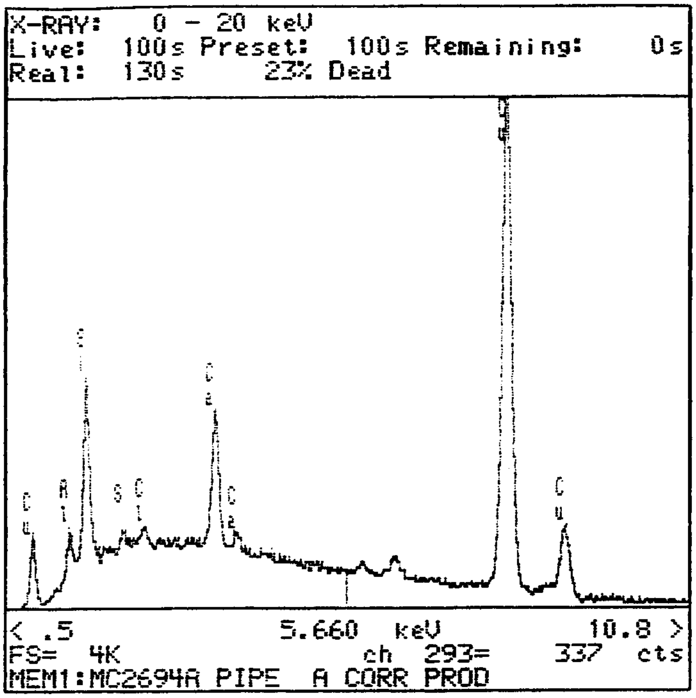
Samples of the tubes were examined in a scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy of X-rays (EDS) facility. The results of the EDS analysis of the greenish-white scale found on the internal surfaces of the tubes are shown in Fig. 4. The large copper

Fig. 1. The internal surface of a tube (×2). The arrow indicates the presence of a tubercule of corrosion product.

Fig. 2. A high magnification photograph of the region beneath a corrosion tubercule ($\approx \times 50$). Note the presence of the greenish-white scale, the underlying black layer and the corrosion pit.

peak originates from the base metal. The large silicon and calcium peaks, and the smaller aluminium peak are due to the presence of these elements in the scale. These elements are readily oxidised and are therefore frequently detected in scale deposits. A minor chloride peak was also detected. This ion is usually associated with pitting attack but the quantity of chloride in this case does not appear to be large.

Fig. 3. The internal surface of a tube showing extensive pitting (×3).



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X-RAY:    0 - 20 keV
Live:   100s Preset:   100s Remaining:     0s
Real:   130s      23% Dead
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FS=  4K                ch  293=      337  cts
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Fig. 4. The EDS results of the greenish-white deposits found on the internal surfaces of the tubes.

3. METALLOGRAPHY

Samples from the tubes examined were prepared for metallographic analysis using standard grinding and polishing techniques. Etching was carried out in acidified ferric chloride. The typical microstructure observed in all cases consisted of large equi-axed grains, indicating that the tubes were in the annealed condition.

3.1. *Chemical analysis*

An analysis of the chemical composition of the tubes was carried out using a wet chemical analysis method. From the high phosphorus content it was evident that the tubes were made from phosphorus de-oxidised copper.

4. TYPE I PITTING

Pitting corrosion is the most common failure mechanism for copper tubes in water distribution systems. Essentially two different types of pitting attack have been identified, and these are referred to in the literature as Type I and Type II pitting*. The former is known as cold water pitting and occurs more frequently than the latter.

Type I pitting is usually encountered in cold water systems carrying borehole or well waters free from organic matter [1]. It occurs sporadically and can result in tube wall penetration within a few months. In some cases, however, penetration occurs only after 15 years or more. The internal surfaces of tubes undergoing Type I pitting are usually covered with a greenish scale of a copper compound called malachite. Beneath this scale, the tube surface is covered with a smooth, shiny layer of dark cuprite which is very friable and easily spalled off. Pits are usually associated with the presence of tubercules which form over pin hole defects in the cuprite layer.

The characteristics of Type I pitting attack are such that many pits at all stages of development can usually be found [1]. Larger pits are generally linearly arranged along the bottom half of horizontal water lines. When pits are very close together, tubercules can extend over a number of pits to form one long tubercule. Although pitting has been observed in annealed, half-hard and hard-drawn tube, susceptibility is generally greatest in the annealed condition. The pits formed are usually saucer-shaped and relatively wide.

A number of causes of Type I pitting have been identified [1]. Firstly, the incidence of pitting has been associated with the presence of carbonaceous films on the internal surface of the tube. These films are residues of the lubricant used for the drawing operation and which are carbonized during annealing. The quantity and distribution of these films on the internal surface appears to affect the severity of pitting. The problems arising from the presence of these carbonaceous films can be overcome in practice by scouring the tubes with a water–sand or a water–air blast.

Secondly, pitting has been associated with the presence of foreign matter deposits on the bottom half of horizontal tubes [1]. This is in agreement with observations on the preferential location of pits discussed above. The foreign matter deposits can be introduced into the water lines in a number of ways. Metal chips and filings and dirt can be allowed to contaminate the system during installation. If these are not properly removed before service, they may deposit along sections of the water lines where the water velocity is low. Foreign matter deposits may also be introduced into the system in the water or may be due to corrosion products formed during surface corrosion of the tubes during service. The concentration of these deposits, and hence their deleterious effects, can be reduced by the installation of filters in the water line.

Thirdly, another factor said to cause pitting attack is the presence of soldering pastes on the insides of the tubes. This generally results from bad workmanship and can be avoided by ensuring that adequate quality standards are maintained during installation. The soldering pastes may act as deposits in the same way as foreign matter. Alternatively, during soldering or brazing these pastes may be converted to oxides which form as a thin film on the copper surface. These oxides are generally cathodic to copper and can therefore give rise to pitting corrosion.

The effect of water quality on the incidence of Type I pitting is the subject of some controversy and no consensus has been reached in this regard. Some general observations have been made, however, on the effects of various constituents and characteristics of water on the extent of pitting,

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*Some researchers have also reported the existence of Type III and Type IV pitting, but these appear to be variations of Type I pitting [1].

Table 1. The effect of various water constituents and characteristics on Type I pitting

Chemical species	Effect
Sulphate (SO_4^{2-})	Assists pit initiation and growth, but its effect depends on the concentration of other chemical species.
Chloride (Cl^-)	Essential for pitting attack. Assists the breakdown of protective surface films and results in the formation of wide, shallow pits
Nitrate (NO_3^-)	Inhibits pitting
pH	Increases in pH generally decreasing the probability of pitting.
Dissolved oxygen (O_2)	Increased O_2 content increases the probability of pitting.
Carbon dioxide (CO_2)	Increased CO_2 content increases the probability of pitting due to a decrease in pH.

and these are summarised in Table 1. An empirical screening process has also been developed to assess the risk of Type I pitting in various waters [2] (Fig. 5). This process has been used extensively with reasonable success.

A number of characteristics of Type I pitting discussed above were evident in the failed copper tubes from the shopping centre. The presence of tubercules of corrosion product and the greenish scale on the internal surface of the tubes were clearly evident (Fig. 1). The friable underlying layer of shiny, dark cuprite was also observed (Fig. 2). The wide, saucer-shaped pits and their approximately linear distribution were also evident and are shown in Fig. 3. It is also evident that pits at various stages of development were observed.

5. CONCLUSIONS

It was concluded that the failure of the copper tubes was due to Type I pitting attack. It is not clear at this stage what the exact cause of pitting failure was, particularly given the fact that pitting only became evident after 12 years' service. It is highly unlikely that it may be due to the presence of foreign matter deposits introduced during installation of the system. The introduction of foreign matter in the water is, however, a possibility, particularly if the water is not filtered. A change in water quality or content (e.g. resulting from mixing of the water with borehole or well waters) could also be responsible for pitting.

Once initiated, pitting attack can in some cases be halted through the application of appropriate treatments of the water and the metal. The extent of pitting observed in the present case, however,

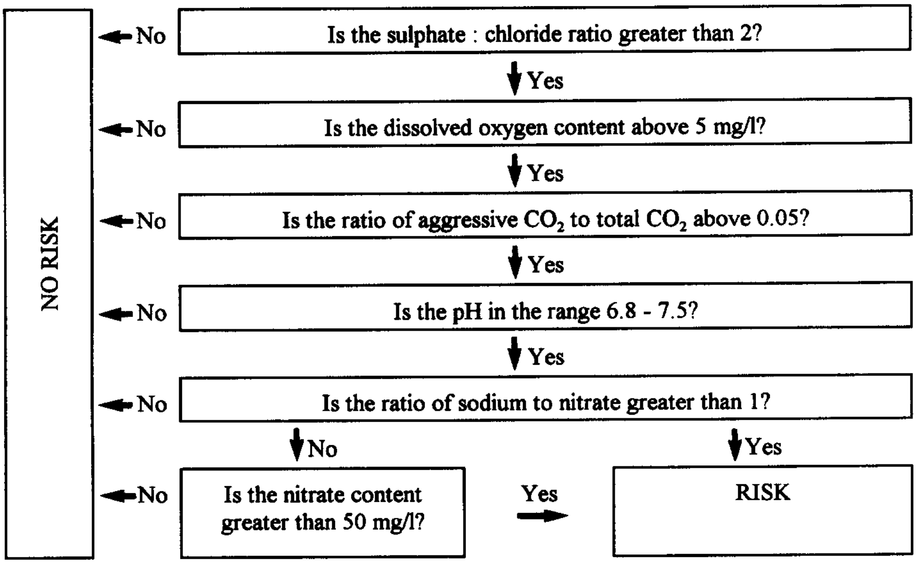

Fig. 5. Evaluation of waters for Type I pitting [2].

suggested that such treatment would be both unsuccessful and unfeasible. It was therefore recommended that the copper tubes be replaced. Careful attention should be given to the usual causes of Type I pitting. In particular, it should be ensured that all tubes be thoroughly cleaned and freed of any carbonaceous deposits prior to installation. The tubes should also be cleaned to ensure complete removal of any foreign matter deposits and solder pastes after installation. The use of water filters could also be considered to prevent the introduction of foreign matter in the water. Furthermore, the quality and content of the water should be determined and its potential to cause pitting assessed. The extent of replacement or modifications to the water distribution system would, to some degree, depend on the results of such water analyses.

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