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PROJECT
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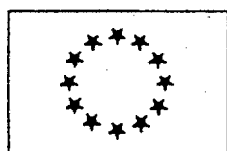
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NEW TYPES OF CORROSION IMPAIRING THE RELIABILITY OF COPPER IN POTABLE WATER INSTALLATIONS CAUSED BY MICROORGANISMS

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ABSTRACT

Generally, copper tube is considered the material of choice for most domestic and institutional plumbing requirements. In a few instances problems have arisen which have been shown to involve microbiological activity. The objective of this programme was to examine the interactions between microorganisms and their secreted products and the copper tube surface.

Bacterial communities associated with the pitted copper pipes were sampled in various ways and over 70 taxa were isolated, purified and identified provisionally prior to screening for extracellular polymer (EPS) secretion using a range of carbon sources. Three organisms, an *Acidovorax sp.*, a *Sphingomonas sp.* and a *Moraxella sp.* were finally used to investigate optimum culture conditions, using batch and continuous culture, for final bulk production of EPS. The polymers were isolated, purified and given preliminary analyses to show that they were acidic polysaccharides carrying pyruvyl and acetyl side chains, and also contained uronic acid moieties. Varying levels of proteinaceous material were also present and impossible to eliminate completely.

Preliminary studies showed that xanthan had a very similar composition to the culture biopolymers, so this was used as a model biopolymer to develop the 'electrochemical methods. It was also used to investigate the interactions at a molecular level between such polymers and copper surfaces. It was demonstrated that on adsorption it created a strongly hydrophilic surface. A simple electrochemical ceil was developed based on the modification of Nernst potential measurements yielding a potential value which indicated whether polymers exhibited cation- or anion selective behaviour, or no selectivity at all. The xanthan and some of the bacterial polymers *were* cation selective but this could be abolished or even reversed to anion selectivity by chemical treatments to remove polymer acetyl groups or by the addition of proteins.

Two linked electrodes, one bare and the other coated, were shown to establish a corrosion element. The covered areas acted as the cathode whilst the bare areas were anodic. This was also seen in single metal samples with disrupted polymer coatings giving bare patches depending on the transport properties of the coating. The polymer properties were of importance in two ways:
a)   preventing the formation of the usual chloride-generated passivating layers on the bare surface, and,
b)   acting as a partial barrier to oxygen diffusion.

In anodic areas the corrosion follows the chloride induced mechanism leading to repassivation of the surface. Sulphate ions inhibit this expected passivation process and normally copper surfaces also become passivated in the presence of bicarbonate ions, following a different but poorly understood mechanism. However, in the presence of some types of bacterial polymer this repassivation does not occur. The basic corrosion process appears to follow the chloride model, but this can become overshadowed by the effects of additional anions such as sulphate and bicarbonate, and the interaction of these anions with only some microbial polymers.

In summary, these results, drawing on the cross-disciplinary experience of the partnership, have demonstrated for the first time that some microbial biopolymers have ion permselective properties and that this can be used to explain a mechanism for the observed form of MIC of copper water tubes. On this basis, proposals to overcome this microbially influenced corrosion process can be formulated.

1   INTRODUCTION

Copper as a metal is used widely because of its good resistance to corrosion combined with mechanical workability, excellent electrical and thermal conductivity, and ease in soldering and brazing. Vast quantities of copper tube are in service as potable water distribution systems [1].

Several types of pitting corrosion have been reported but the level of failures is remarkably low. Reiber [2] indicated that copper corrosion is in general uniform, with pitting only occurring under limited and rare conditions. A range of well-defined types of pitting corrosion of copper were reviewed by Mattsson [3], but none of these was considered to be associated with microbial activity. However, since then two forms of pitting have been reported which do appear to have microbial origins. One of these, termed "pepper-pot pitting" was reported from large institutional buildings in S.W. Scotland, U.K. [4] whilst the other, frequently termed Type 1½ pitting, has been observed in tubes from Saudi Arabia, Germany, England, and fittings in power stations, where one of the most important applications is for tubular-type heat exchangers, particularly in the US [5, 6]. Most of the observations described so far are associated with the presence of copious biofilms, and 'microorganisms residing in the film which are identified by electron microscopic techniques, biochemical activities *in vivo* and *in vitro* [7, 8].

There are many possible roles for these polymers in the corrosion of metals including the formation of occluded regions with limited oxygen diffusion - creating aeration cells [9], ion concentration cells involving binding of the metallic cation at different affinities by adjacent polymers [10, 11] and, as demonstrated in this work, the restricted formation of appropriate corrosion products [1 2].' Binding reactions are also of importance in the adsorption of biofilm matrix materials onto metallic surfaces, A physico-chemical model for the explanation of the manifestations of corrosion observed in' the attacked pipes is offered in this contribution taking into account membrane properties and heterogeneities of these properties, and the distribution of the exopolymeric material on the surface of the pipes [1 2].

Two prerequisites have been considered to ensure the practical relevance of the work.

* The chemical composition of synthesized polymeric material consists mostly of the same chemical substances as the polymeric material detected in the perforated copper pipes.
* The microorganisms used for the production of the biopolymeric materials are isolated and cultured from the perforated copper pipes.

The main goal of this project is experimental validation of this theoretical model and the explanation of relevant corrosion mechanisms,

The objectives of this project are summarised as follows:
i.)   **To produce appropriate model and natural polymer coatings to simulate biofilms.**
ii.)   **To characterise the phase boundary, copper/biopolymer.**
iii.)   **To demonstrate that certain polymers can affect the electrochemical behaviour of copper leading to corrosion in aqueous environments.**
iv.}   **To elucidate the mechanism(s).**
v.)   **To relate these laboratory observations with those made' on "real" systems.**

2   TECHNICAL DESCRIPTION

General - The aim of the project is the formation of a corrosion element at a copper electrode with a membrane modified surface leading to pitting corrosion to determine the corrosion mechanism responsible for the observed breakdowns in water installations. A macro-element was created by two electrodes one of them being coated with a biopolymeric film. For the formation of a micro-element the physico-chemical properties" of the coating on a single mixed electrode was locally changed. These coatings were synthesized chemically to get model biopolymers and biologically to get culture biopolymers. The chemical composition and the physical properties of both types of biopolymers was partially established. The diffusion properties of these biopolymeric coatings was examined. The corrosion behaviour of these coated electrodes was examined by electrochemical measurements.

The means used to achieve the objectives are summarised in Fig. 1.
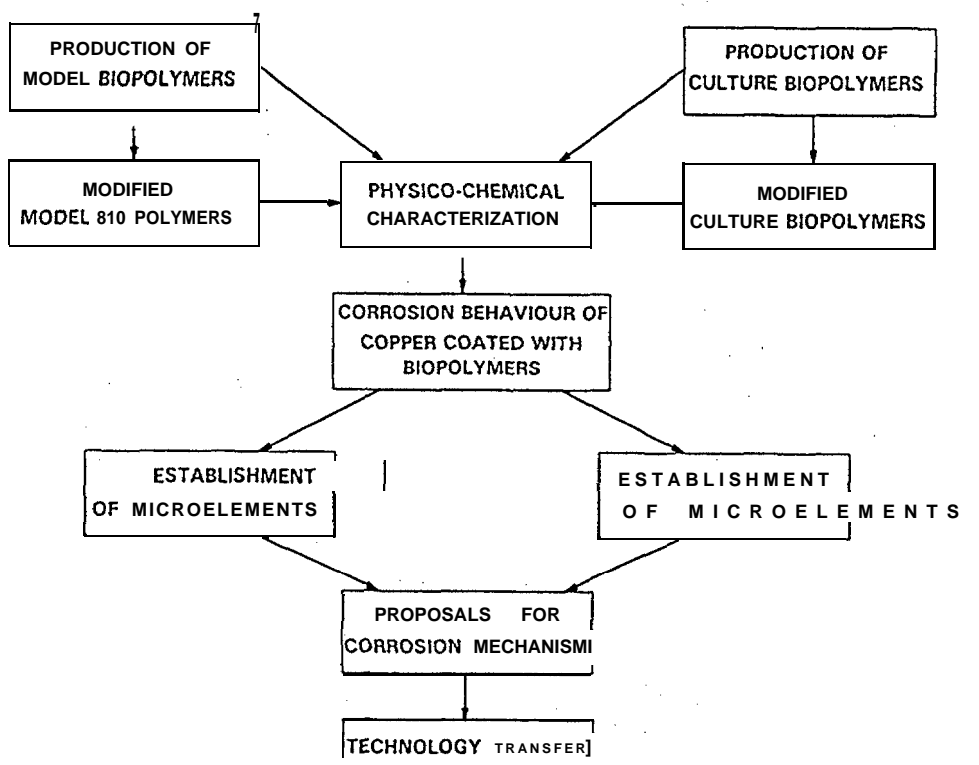
Model Biopolymer - The chemical composition of the biofilm isolated from failed copper tubes taken from the water supplies of an affected county hospital was partially characterized. The structure may be described as linear and/or crosslinked acidic or non-ionic polysaccharides. The primary composition consist of materials with similar structures to that found for xanthan e.g. presence of pyruvate and acetyl 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. Based on this analysis a model biopolymer was developed comprising xanthan as model substance, agarose as matrix substance and alginate as a stabilizer.

Culture Biopolymer - Naturally occurring biopolymers and these produced by microorganisms in culture are unlikely (except under closely defined conditions) to be homogeneous. Heterogeneity may be evidenced by different saccharides moieties in the back bone structure; in the presence of different repeat units, side-chains; and also in the presence of protein sub-units. [t is likely therefore that in naturally occurring biofilms present in potable water systems that any or ` all of these variations may be present within the polysaccharide matrix.

With this in mind, it was important that biopolymers used in these investigations were representative of those occurring under normal operating conditions. To achieve this, bacteria present within the standing water and biofilm of corroding systems were isolated, subculture and characterised, In addition, their propensity to produce exopolymer was determined by a screening test.

As a result, a small number of strains, isolated from tubing systems exhibiting hemispherical pitting were grown both in batch and continuous culture in a synthetic pitting water medium supplemented with glucose or other carbon source, together with ammonium phosphate designed to maintain a nitrogen-limited balance, and the polymer produced harvested.

Collected culture, typically 20 L was harvested, Bacterial cells and large debris were removed by tangential-flow filtration (0.22 μm membrane) to yield a clean filtrate containing the exopolymer. This was then concentrated by passage across a second filter with a 10000 nominal molecular weight cut-off membrane and on this occasion the concentrate retained. Alcohol precipitation from the concentrate by 4 volumes cold propan-2-ol gave a white precipitate which was harvested by centrifugation (5000 x g x 30 rein) yielding a loose polymer-gel which was either employed for electrochemical experiments or dialysed and lyophilised for chemical analysis.

A basic biochemical profile of the polymers was determined by FTIR-spectroscopy, together with biochemical analysis for reactive side chains, acetyl, pyruvyl together with uronic acid and protein content.

Working Model - The typical manifestation characteristics of this corrosion process have been evaluated based on a failure analysis performed in a German institutional building affected by this special type of corrosion [13]. It was possible to simulate this corrosion process in the laboratory under accelerated conditions performing potentiostatic series [14], Chloride ions have been identified as a further important influencing parameter [1 5],

Electrolyte (pH 7-9)
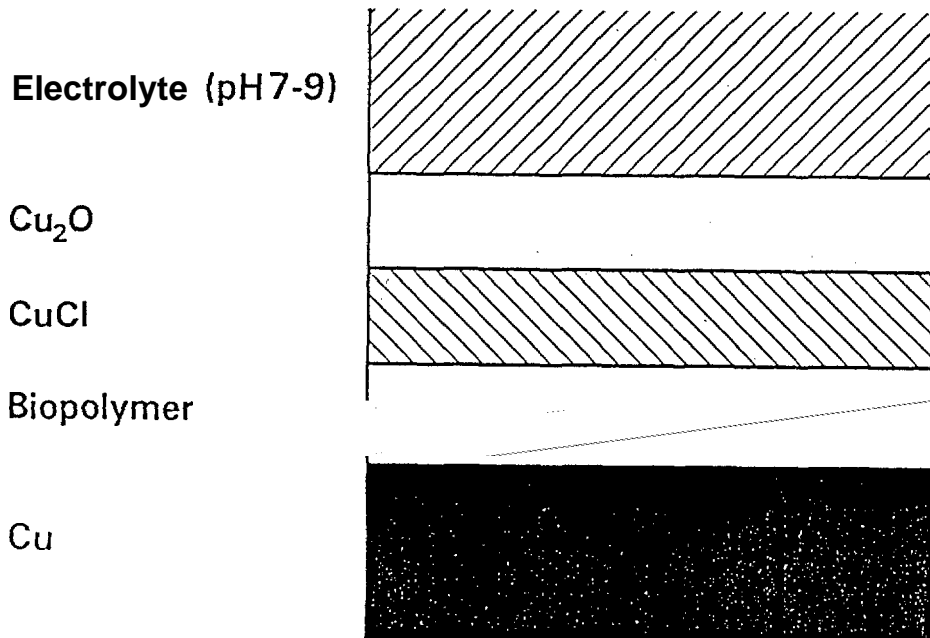
Cu_2O

CuCl

Biopolymer

Cu

Fig. 2:   A working model of microbially influenced corrosion of copper.

Based on these considerations a working model was developed for a chloride ion containing electrolyte (Fig. 2) [1 6]. Copper(II)-corrosion products formed via secondary precipitation reactions have not been taken into account in this working model, Based on. the results of the failure analysis it is assumed, that the electrode areas corresponding to this model act as a cathode whilst in the pitting areas (tubercules) the biopolymer is either partially disrupted or not present, The only manifestations of corrosion observed underneath the biopolymeric coating is general attack.

The formation of the layered structure of corrosion products on a copper surface as described in Fig. 2 was acknowledged as one of the most important criteria. A possible solution is offered in the model as shown in Fig. 3, that is based on the assumed cation selectivity of the biopolymeric coating due to its high number of fixed negative charges and its membrane properties. The heterogeneity of these coatings was detected applying staining techniques [1 7].
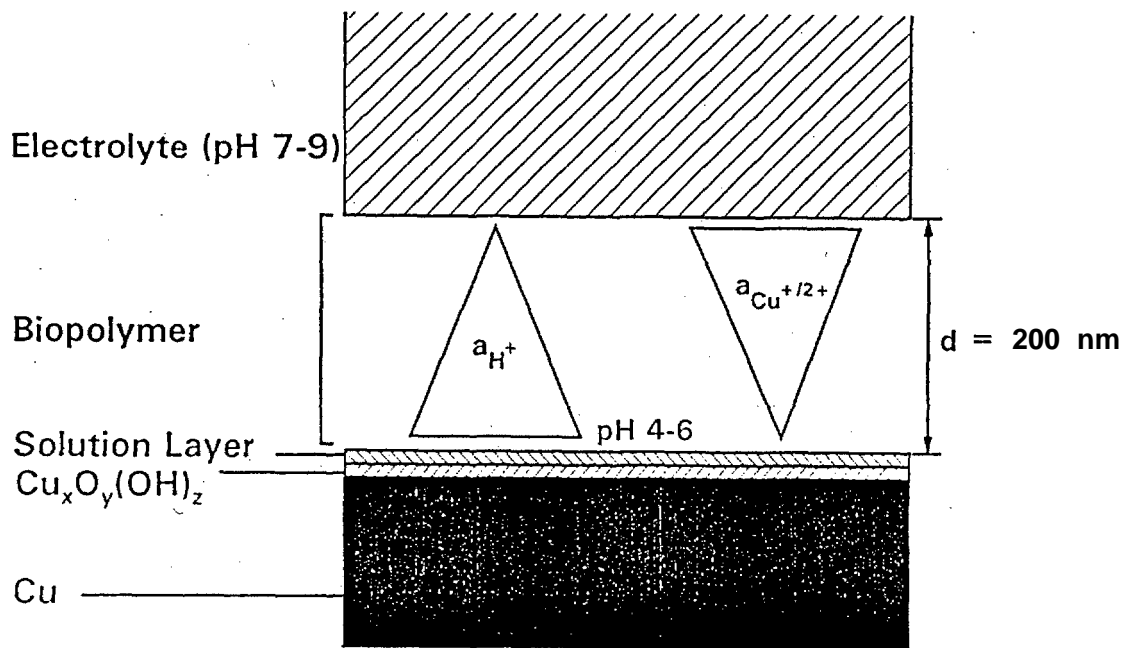
Fig. 3:   A working model for the formation of reaction layers.

Chemical analysis, revealed that the biofilm consists predominantly polysaccharides [18]. The completing properties of the biopolymer due to its functional groups (carbonyl-, carboxy-, amino-, N-acetyl-amino, axial hydroxy groups, and aromatic hydroxy and groups of the lignic and humic acids) are not regarded in this contribution, because investigations have shown that these complexes 'in the biopolymer are saturated in much smaller time constants [19].

The cation selective coating prevents the formation of protective layers on a metal surface, A pH-gradient is established in such a biopolymer following a model proposed by Geesey [10]. The extra-cellular coating stabilizes a low pH at the phase boundary copper/electrolyte due to its acidic functions. The copper ions formed during electrolytic corrosion are transported through this coating to the phase boundary biofilm/electrolyte, where insoluble reaction layers consisting of copper corrosion products are formed due to the high pi-i in the electrolyte. The pH-gradient causes the formation of a concentration cell acting as an electrochemical force for the transport of the copper ions to the phase boundary biofilm/ electrolyte. Additionally, it keeps the copper ion activity low at the copper surface,

This'simplified working model was validated with complementary experimental methods. The physico-chemical properties of both the model and culture biopolymers were characterised by performing contact angle measurements, diffusion potential measurements, transference number experiments and cyclic voltammetry. Methods were developed to coat copper electrodes with either of the two types, of biopolymers. A macro-element was created by electrically connecting two electrodes, only one of which was coated with a biopolymer and performing contact element measurements, Micro-elements comprised single electrodes which were coated with polymers and had inhomogeneities introduced at the surface by a range of methods, such as potentiostatic or galvanostatic series. Control corrosion experiments were performed in electrolytes containing single anion salts with bare copper electrodes to produce data sets that allowed comparisons with -the results obtained with copper electrodes coated with biopolymers and exposed to the same electrolytes. Further corrosion experiments were also performed in potable water taken for a building affected by MIC to validate the proposed corrosion mechanisms.

3   R E S U L T S

Contact Angle Measurements - Changes or chemical modifications of the surfaces, e.g. metallic or oxidized surfaces as well as of the biopolymers, change the free energy of interaction with contacting solids or liquids while leaving the bulk physical properties largely unchanged, The ability to control interracial interactions by chemical modification of a surface is important for adhesion, biocompatibility and static discharge, all depending on wetting and/or on hydrophilicity. Studying nettability through measuring contact angles enabled' us to evaluate the relations between the structures of the surface and of surface-modified exopolymers by treating the investigated biopolymers as surfactant m o l e c u l e s .

It has long been known that the surfaces of synthetic and biological polymers carrying polar groups as well as functional groups are capable of reorientation, when in contact with polar condensed phases, to expose the polar functionality. Alginic acid and xanthan provide remarkable examples of this behaviour: the sensitivity of wetting to confirmational changes within the contact angle interface revealing a surprisingly large change with pH in the nettability by water (Fig. 4). At low pH (4.0 - 6.5), the advancing contact angle of water is approximately 80°, i.e. the surface is more hydrophobic than "unfunctionalized Cu/CuO-surface". At pH above 6.0, the advancing contact angle is approximately 40°. The differences in the contact angles of water at low pH between Cu/CuO and the pH-dependence of the exopolymers cannot be interpreted solely in terms of hydrophobicity, since the surface of Cu/CuO is rougher than. that of the biological polymers. Table 1 lists the measured contact angles relevant for solids adhering at copper surfaces.

Table 1: Selected Contact Angle Data Obtained Experimentally by the Static Method

Liquid γ(mN/m)	Solid	Θ Degrees (20°C)	Remarks
H$_2$O (72)	Cu	115	clean, UHV,
H$_2$O (72)	Cu '	95	exposed to air
H$_2$O (72)	Cu	45	exposed H$_2$O
pH ,7.5, (60)	Xanthan	7.0-12.5	deposited on Cu
pH 7.0, (60)	Alginic Acid	7.5-15.0	deposited on Cu
pH 7.0, (60)	Agarose	17-21	deposited on Cu

It is assumed that the large decrease in the contact angle measured with a, Krüss tensiometer applying the static method, e.g. change of approx 30°, of water on the Cu/CuO surface as the pH of the contacting ring is varied from 4.0 to 8.0 is due to confirmational changes of the 1,4-linked ß-D-mannuronic acid. residues protonated or deprotonated, respectively in the alginic acid (Fig, ,4).
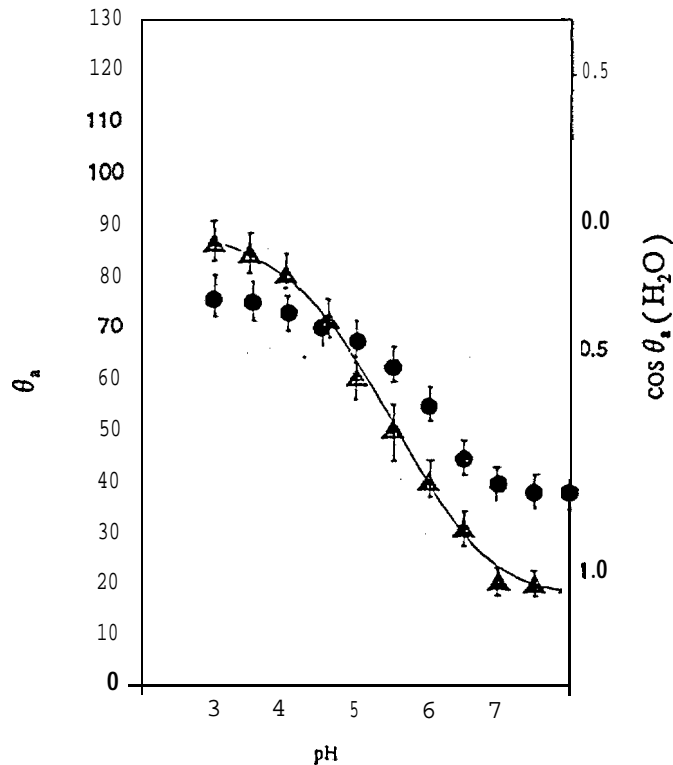

Fig. 4: Variation of the advancing contact angle Θ$_a$ of water as a function of pH of alginic acid on Cu-surfaces at 20° C (A----A alginic acid, ●----● xanthan).

The relative amount of uronic acid groups in alginic acid is considerably higher than in xanthan. These pH effects tell us that carboxyl groups may play an important role in the adsorption process. This infers that the low pH at the phase boundary copper/electrolyte differs from the pH in the bulk electrolyte supporting the introduced working model.

Diffusion Potential Measurements - **As mentioned 'earlier, because the "biofilm" matrix material carries negative charges the materials under consideration could be expected to show a cation selective behaviour. Therefore, for a cation selective membrane, the potential difference can be measured for a potassium chloride electrolyte with a concentration difference of 10-fold taking into consideration a membrane contribution and a concentration contribution, using an** $Ag/AgCl/Cl^-$ **reference electrode:**

$$A U = \Delta U_{Ag/AgCl\,Cl^-} + \Delta U_{Membrane} = 118\ mV$$

with

$$Lu_{AdAgctQ}^- = 2.3\ (RT/zF)\ log\ [a_1(Cl^-)/a_2(Cl^-)] = 59\ m$$

and

$$\Delta U_{Membrane} = 2.3\ (RT/zF)\ log\ [a_2(K^+)/a_1(K^+)] = 59\ mV$$

where ΔU **is the potential difference,** R **the gas constant, Temperature,** z **the ionic charge,** F **the Faraday constant, and** a_1, a_2 **are the ionic activities in the two compartments. Using saturated calomel reference electrodes** $(Hg/Hg_2Cl_2/KCl_{sat.})$ **the membrane potential difference will be measured only,**

Fig. 5 shows the potential values of AU = 120 $mV \pm 5\ mV$ **obtained for the model biopolymer xanthan/agarose/algi nate and the culture biopolymer #930520F2 as a function of time, The slight continuous decrease is assigned to the continuous dissolution of alginate into solution as observed with the unaided eye. The culture biopolymer revealed values of about 100** mV **also indicating the cation selective behaviour. However, after about 15 h exposure time a slight, but continuous decrease of these values was observed.**

The contribution of the membrane and concentration difference to the potential difference could be separated by the use of the two types of reference electrodes as already described. This was investigated for the model biopolymer agarose/xanthan using **the obtained potential values after 40 h. The results are summarised in Table 2, for potential differences obtained as a function of different electrolyte concentrations of potassium chloride in the two compartments [20]. The contribution of" the membrane decreases with increasing electrolyte concentration, whilst the contribution made by the concentration to the potential difference remains stable.**

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— 3% (w/w) xanthan, 1% (w/w) agarose, 0,5% (w/w) K-alginate

----- #930520F2 culture biopolymer
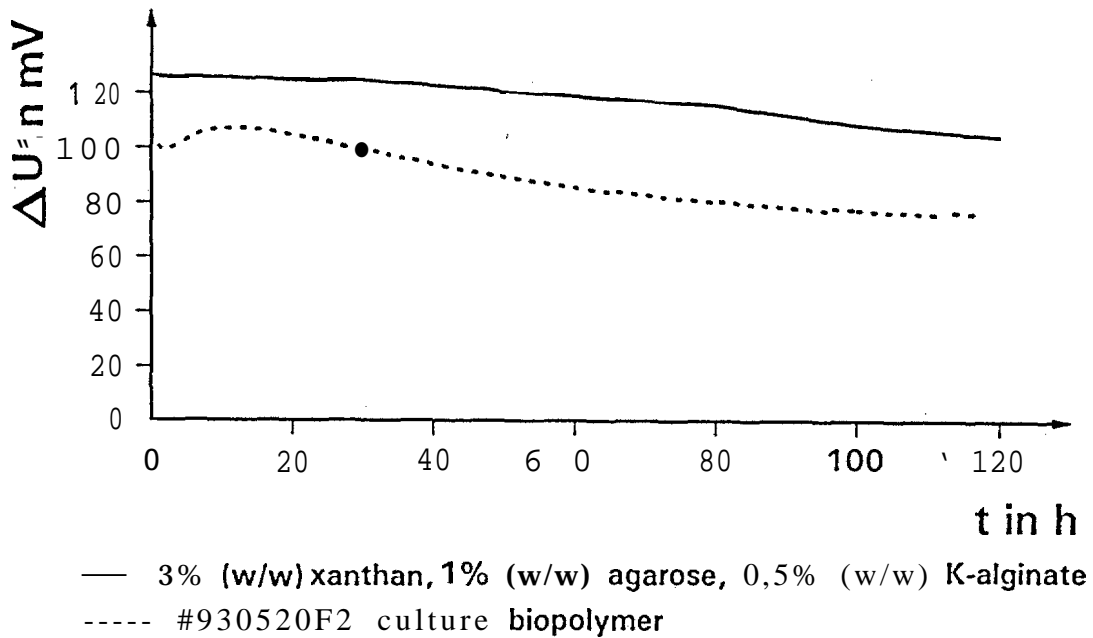
Fig. 5: **Potential difference values for the** model biopolymer 3 % **(w/w)** ·xanthan/1% **(w/w)** agarose/0.5% **(w/w)** alginate **and the culture** biopolymer #930520F2 **in** 5 · 10^{-4} M / 5 · 10^{-5} M **p o t a s s i u m chloride solutions as a function of time.**

Table 2: **Potentials After** 40h **Obtained with 1** % Agarose/3% Xanthan **as a Separating Membrane** ['l 6, 20].

Concentration KC1	Potential Difference Ag/AgCl/Cl⁻ ΔU/mV	Potential Difference $Hg/Hg_2Cl_2/KCl_{sat.}$ ΔU/mV	ΔU/mV
		Contribution of Membrane	Contribution of Concentration
5 · 10^{-2} M 5 " 10^{-3}M	59	1	5 8
5 · 10^{-3} M/ 5 " 10^{-4} M	76	21	5 5
5 · 10^{-4} M/ 5 " 10^{-5}M	98	4 4	55

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Cyclic Voltammetry - Characteristic peaks in cyclic voltammograms correspond to the formation and reduction of reaction layers, [n an electrolyte containing chloride ions one oxidation peak and one reduction peak occur that can be attributed to the influence of these chloride ions within the corrosion process on a bare copper electrode. These peaks did not occur when the electrode is coated with a biopolymer. " **Fig. 6** depicts the cyclic voltammograms of a bare electrode and an electrode coated with the culture biopolymer **EPS 930630FI.**
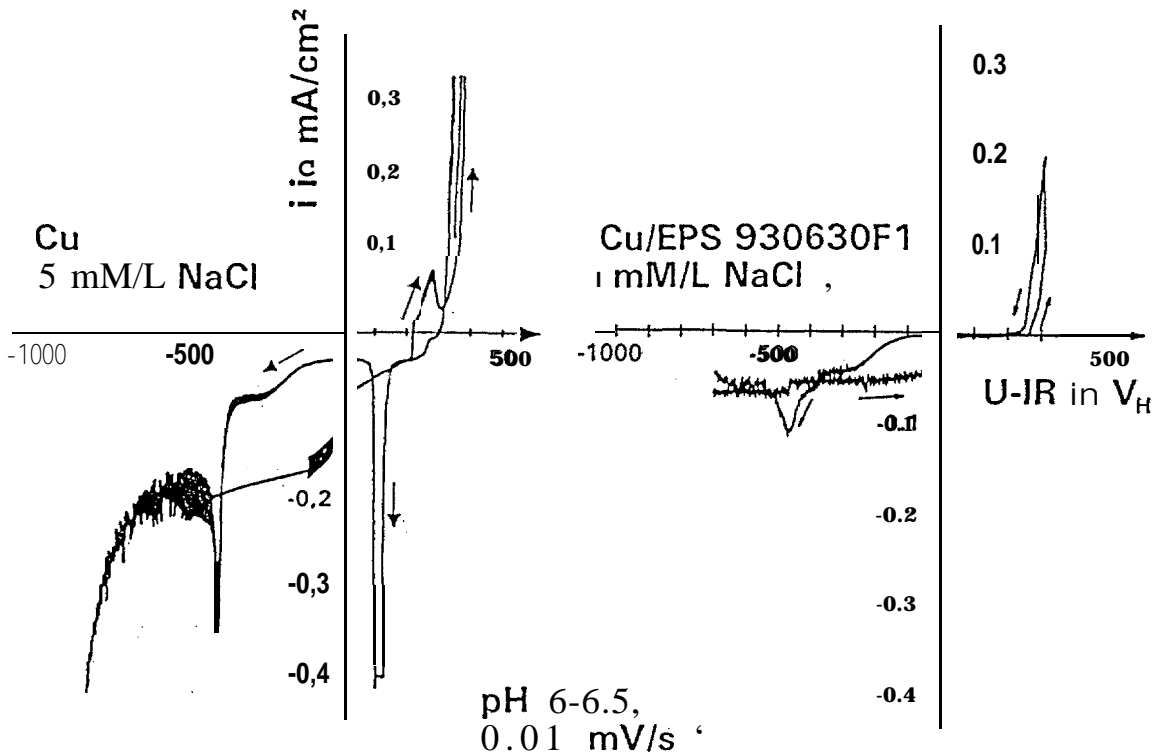

Fig. 6: Cyclic voltammograms of bare (left) and biopolymer coated copper electrodes in aerated NaCl solutions,

These show:

i.) Chloride ions could not pass the coating of biopolymer within the time scale of the experiment.

ii.) No marked influence of the coating on the anodic partial reaction was observable.

iii.) The coating acts as a diffusion barrier.

iv.) The much smaller integral charge of the reduction peak obtained with the coated electrode indicated a smaller amount of Cu_2O at the metal surface. This infers that the pi-i underneath the coating is smaller than in the bulk electrolyte.

v.) A reduction of reaction layers formed on top of the biopolymeric coating is not possible, because the coating does not possess conductive properties.

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Establishment of Macro-Elements - The separation of the corrosion reactions occurring at local anodes and local cathodes in a copper piping system was achieved by performing contact element measurements. This separation is described as the establishment of a macro-element, A typical example result is shown in Fig, 7.

Cu/EPS 930820
— Cu
o.c. open circuit
s.c. short circuit

1 mM/L NaCl, aerated
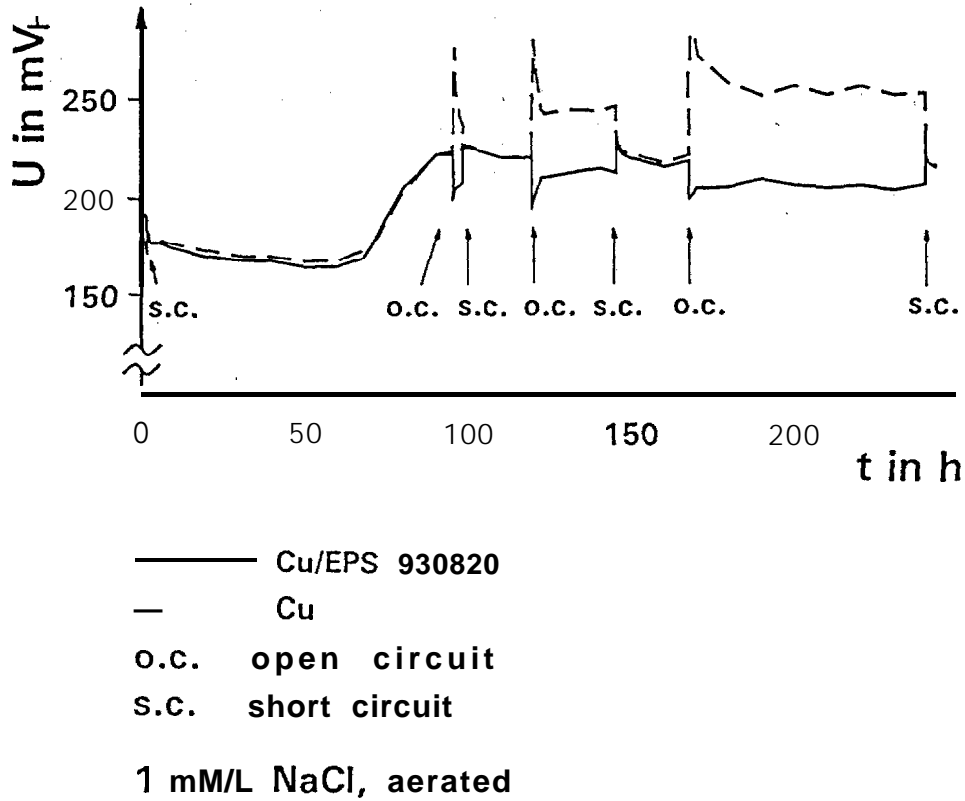
Fig., 7: Potential measurements of bare and EPS-coated copper electrodes over 250 hours showing polarisation behaviour on short circuit.

After short-circuiting, the bare copper electrode is polarized anodically and the copper electrode coated with EPS 930820 is polarized catholically. This indicates that the big areas of a copper pipe showing the layer structure in the presence of an adsorbed biofilm must be considered as a local cathode. In the pitting areas of the tube the biofilm on the surface is disrupted and allows anodic partial reactions occur [1 6].

Establishment of Micro-Elements - Potentiostatic series were performed to characterize the manifestations of corrosion obtained with the, macro-elements on two different electrode surfaces on a single copper surface. The successful performance is considered as the establishment of a micro-element. Furthermore, it is possible to characterise the long-term corrosion behaviour in this special corrosion process using the polarisation potential as an accelerating parameter. Pit depths were evaluated as pitting. leading to perforation is the feature responsible for most damage in potable water supplies [14].

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Fig. 8 shows the results obtained with bare copper electrodes in sodium chloride and in orginial potable water taken from an affected building and for a coated electrode in sodium chloride, In NaCl electrolytes repassivation of the pits was found with maximum pit depths of about 100 μm for both the bare and the coated copper electrode. After performing the potentiostatic series in chloride ion containing electrolytes the biopolymeric coating had become disrupted in the pitting areas. Therefore, the chloride induced pitting mechanism of copper took place on both bare and coated electrodes leading to a repassivation of the pits. This. is revealed schematically in Fig. 9.

Potentiostatic series performed in potable water taken from an affected institutional building reveal the influence of the chloride induced mechanism of copper on this corrosion process, Nevertheless, a considerable variation in the obtained pit depths between O and about 150 μm was observed (Fig. 8). Repassivation occurred at considerably greater pit depths indicating the influence of further parameters on the corrosion process leading to failures in practice.
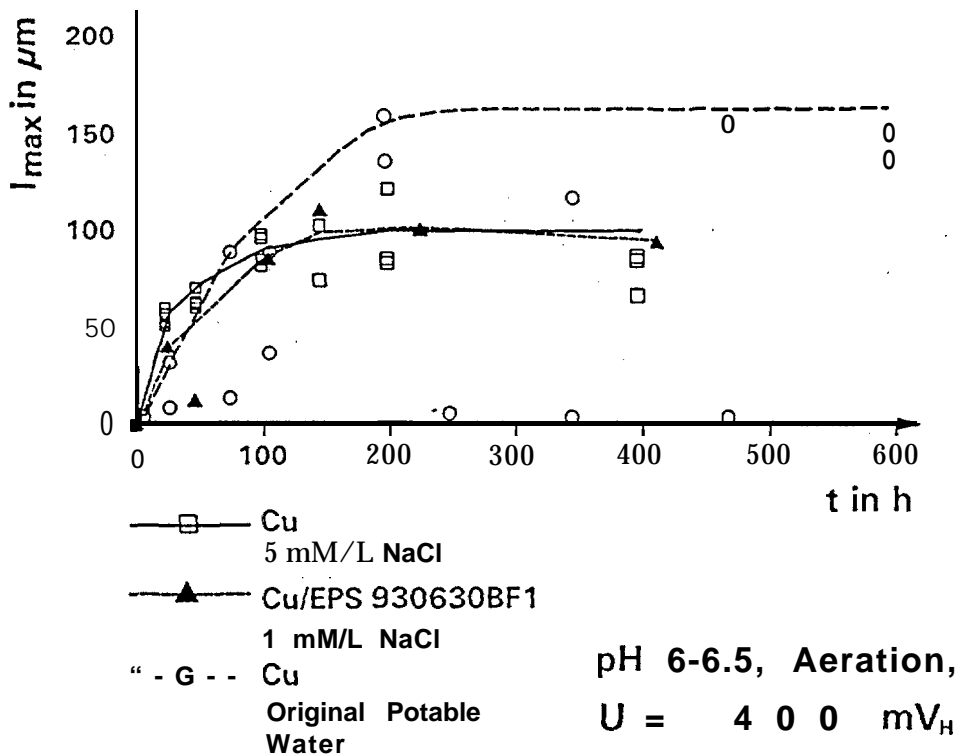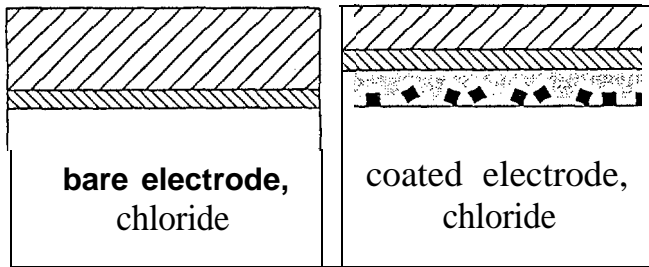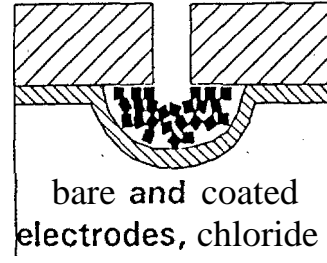

Fig. 8:   Extended potentiostatic series measurements on bare copper and EPS coated electrodes in chloride electrolytes and the original system water.

1 4

Areas of general attack

| bare electrode, chloride | coated electrode, chloride |

Pitting areas

bare and coated electrodes, chloride

Cu_2O ▨ $CuCl$ ▧ E P S ▣ Cu_2O-Crystals ▨ Copper ▢

Fig. 9: **Diagrammatic cross sections of corroded bare and coated electrodes with true electrodes for comparison.**

Technology Transfer - The analysis of the corrosion products in failed copper tubes identified posnjakite ($CuSO_4$ x $3Cu(OH)_2$) and malachite ($CuCO_3$ x $Cu(OH)_2$) in the areas of pitting. This' infers that sulphate and bicarbonate ions are further influencing parameters and that one has to take into account the interactions between different anions and the interactions of different types of biofilms with those anions, This is shown in Fig. 10 leading to the following results.

Sulphate interacting with chloride is able to prevent the observed repassivation of a copper surface. On the other hand, a combination of bicarbonate with a certain type of EPS yields pit depths of more than 450 μm whilst on bare copper electrodes pit depths of maximum 230 μm were obtained in the same electrolyte.

4 CONCLUSIONS

A variety of model and culture biopolymers, produced from bacteria isolated from pitted copper pipes, were shown" to possess cation selective and non-selective properties. A range of electrochemical techniques was applied to bare and coated electrodes and showed many of the responses found in corroding pipes. Therefore, it is believed that the heterogeneity in chemical composition and structure and hence ion selectivity of the polymers together with their .

patchy distribution over the surface creates the conditions necessary for continued corrosion once initiated by a range of anions, instead of the normal re-passivation process. Optimization of the alkalinity of potable water in combination with the assessment of the long-term performance of copper installation materials with different tempers and surface conditions is seen to be the most promising and economically feasible approach to overcome the described problems,
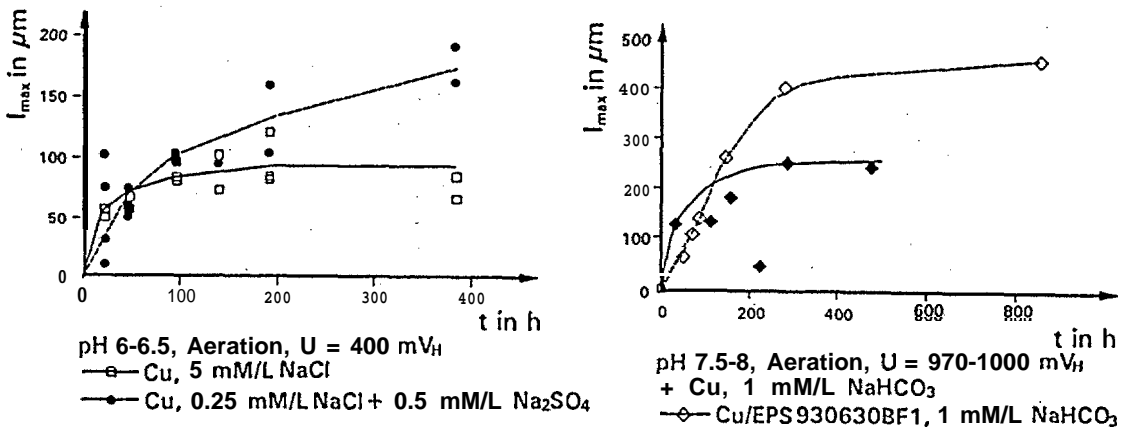

Fig. 10:   Potentiostatic series profiles for bare copper in chloride and chloride and sulphate ion containing solutions {left) and bare and coated electrodes in 0.1 mM sodium bicarbonate.

5   ACKNOWLEDGEMENTS

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