THE BIOCORROSION OF COPPER BY BIOPOLYMERS AS EXAMINED IN SITU, IN REAL TIME FT-IR/CIR/ATR IN CONJUNCTION WITH PRE AND POST XPS/AES

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ABSTRACT

Thin films of copper [2.0 nm on germanium internal reflection elements (IREs) and 3.4 nm on germanium discs] were exposed to 10% gum arabic (aqueous solution), 2% alginic acid (aqueous solution), 1% bacterial culture supernatant (BCS, simulated seawater solution) and 0.5% Pseudomonas atlantica exopolymer (simulated seawater solution). The IREs were monitored *in situ*, in real time using fourier transform infrared/cylindrical internal reflection/attenuated total reflection spectroscopy as a function of time at ambient conditions. The discs were characterized (pre- and post-exposure) by X-ray photoelectron and Auger electron spectroscopies. Ancillary graphite furnace atomic absorption spectroscopy was used to monitor the removal process of the copper thin film from the germanium substrates. Results indicate that Cu was oxidized by gum arabic, alginic acid and BCS. Furthermore, Cu was removed from the Cu/Ge interface by all four polymers. The Cu was found associated with the polymer solutions.

INTRODUCTION

Biogeochemical cycling of metals has been recognized for many years. Cyclic paths facilitated by microbes activities include concentration of metals, change of oxidation state and dissolution of metals. Interactions between microbes and metals are of economic importance. The activity of microbes on metallic surfaces can be beneficial as in dump leaching. Uranium and copper mines use microorganisms to enhance the metals release from ores. In contrast, the solubilization of metals by microorganisms can have deleterious effects in many industrial (and other) processes. Fundamental to control and exploitation of these microbial activities is understanding the near surface chemistry (nm range of interaction). Knowledge of the reactions that occur at the microbe/metal interface is limited. Hence, techniques are needed which will exploit the phenomena occurring at the near surface interface. In this region bacterial exopolymers secreted by attached organisms anchor cells to the metallic surface, and also promote the destruction of the surface. The acidic quality usually associated with the polysaccharides exhibit the capacity to bind metallic surfaces and therefore, influence the stability of ground state metal atoms that are in contact with the polysaccharides.[4-6] It is believed that the polysaccharides are vital to the initial reactions that take place between the microbe/metal interface.

The intent of the present research was to develop methodology for studying chemical species, kinetics and reactions that take place at the near surface between the microbial polysaccharides and the metallic surface. Fourier transform infrared/ cylindrical internal reflection/attenuated total reflection spectroscopy (FT-IR/CIR/ATR) gives insight in real time on the reactions that take place between the biofilms and the metallic surface.[8,9] X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) make it possible to examine metallic surfaces (nm range of interaction) before and after exposure to polymers.[11,16,18]

EXPERIMENTAL

Saturated polysaccharide suspensions were prepared from dehydrated preparations, gum arabic (Aldrich, 26,077-0) as a 10% w:v solution, alginic acid (Sigma, A-7003) as 2% w:v solution, a 0.5% suspension of P. atlantica dissolved in nanopure (np) water and simulated seawater (ss) and a 1% suspension of BCS[10] in np and ss. The germanium (Ge) internal reflection elements (IREs) and Ge discs were sputter coated with 2.0 and 3.4 nm of copper (Cu) (see Jolley et al.[10-12] for preparation details). Copper deposited Ge discs were placed into analytically cleaned vials. One mL (pipetted by Eppendorf pipet) of the polymer solution (np water was used as the control) was placed into a corresponding vial for copper/polymer exposure (24 hr duration) at

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ambient temperature. At the end of the exposure time period, the Ge discs were removed from the vials with analytically cleaned plastic hemostats. The discs were rinsed with np water to remove residual polymer solution (rinse was not placed into vials). Excess water was wicked away from Ge discs using Kimwipes and the discs were dried with N_2 gas stream from liquid N_2 boiloff. Within 30 min after disc removal, the Ge discs were placed in the sample introduction system of the XPS/AES analysis system. Exposed polymer and water solutions were kept for subsequent graphite furnace atomic absorption spectroscopy analysis.

Fourier Transform Infrared Spectroscopy

Cu deposited Ge IREs were placed into the stainless steel open boat CIRCLE cell (from Spectra-Tech). The cell was installed into the CIRCLE mirror assembly in the FT-IR optical bench (while under purge with liquid N_2 boil off). Individual samples of the polymers were placed into the CIRCLE cell to completely cover the IRE. After the CIRCLE cell cover was installed, infrared spectra were immediately collected by a Digilab FTS-15C FT-IR spectrometer at one min intervals for one hr; 15 min intervals for the next two hr; and one hr intervals for a total of 24 hours.

Peak areas for the 1640 cm^{-1} water absorbance band were determined. For normalization of the spectra as a function of time, a 6 mm wide strip of Parafilm (manufactured by American Can Co.) was placed in the infrared light path after the CIRCLE attachment to serve as an internal standard. The resulting data were plotted as a function of time.

X-ray Photoelectron

Qualitative and semi-quantitative analyses of the Cu coated Ge substrates were completed on a Perkin Elmer Physical Electronics Model 548 XPS system which was equipped with a Model 04-151 Mg Kα X-ray source. The peak positions for the non-polymer exposed samples were referenced to the carbon 1s line (284.6 eV). The peak positions for the exposed polymer samples were referenced to the Ge 3d line (29.8 eV) rather than the C 1s line due to the molecular complexity of the polymer.[19] No peak position corrections were needed. The XPS spectra were smoothed once using a three point weighted average computer program. After the XPS analyses, samples were moved using a carousel manipulator to the opposite side of the vacuum chamber for Auger depth profile analysis.

Auger Depth Profile Analysis

Semi-quantitative depth profile analyses were performed using a Perkin Elmer PHI Model 590 Scanning Auger Microprobe and Model 04-177 sputter ion gun with argon gas. For standardization, a 3.4 nm thick copper film on a germanium disc was used with each sample set. The spectral ranges (monitored while simultaneously sputtering) were 240 to 290 eV (for carbon KLL @ 272 eV), 900 to 930 eV (for copper LMM @ 920 eV) and 1130 to 1160 eV (for germanium LMM @ 1147 eV). Peak-to-peak heights were measured and plotted versus sputtering time.[1] The C_p (crossover point) results were calculated by determining the time when the half distance (0.5y, where y equals the total distance between the maximum and minimum peak-to-peak heights) crosses the trace of the data.

Graphite Furnace Atomic Absorption Spectroscopy

A Perkin Elmer HGA-400 graphite furnace installed in a Perkin Elmer 703 atomic absorption spectrometer (GFAAS) was used for analysis and calibration of samples. Calibration of film thickness and separation techniques of metal/polymer are published in Jolley, *et al.*[10-12] Matrix effects (light scatter from polymer smoke) exhibited by the polymers made it necessary to isolate the copper from the bulk of the exposed polymer solution.[25] Concentration determinations from the GFAAS data were used to calculate the yield of Cu which was associated with the exposed polymer solution.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy

The ATR measurements are based upon Harrick's equation for the approximate depth of penetration of the evanescent wave.[7,8,17] A discussion of the effects by addition of a metal to the IRE surface is available in Jolley, *et al.*[10] As the copper thin film is removed from the IRE, the effective cell path length is increased, resulting in an increased 1640 cm^{-1} water absorbance band. Thus, the copper removal from the IRE by test solutions can be profiled by monitoring the change (Δ) in the 1640 cm^{-1} water absorbance band peak area as a function of time.

The water absorption profiles and data of the removal of Cu by water (np and ss), and gum arabic, alginic acid, BCS (in ss water) and P. atlantica (in ss water) solutions are shown in Fig. 1 . The C_p values were calculated as before. The np water C_p value was not detectable and the ss C_p value was 27.8 min. The Δ peak areas were np < 0.1 and ss 0.3 abs cm^{-1}. These data indicate that the Cu thin film was relatively stable while being exposed to np water but was attacked to a limited extent by the ss water during the 24 hr exposure time.

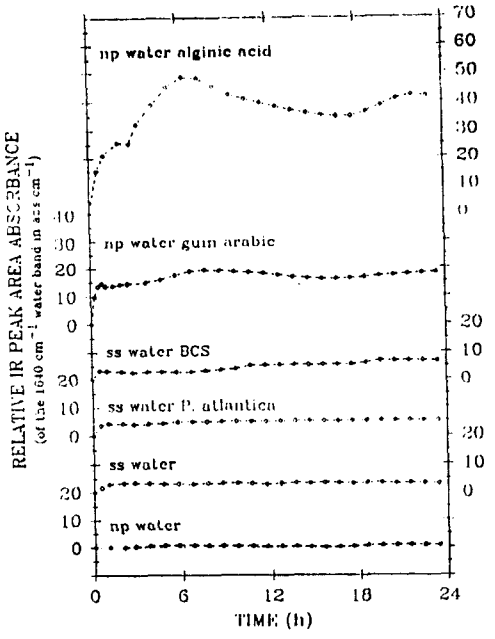

Fig 1. Relative IR peak area absorbance of the 1640 cm^{-1} water band as a function of Cu/polymer solution exposure time.

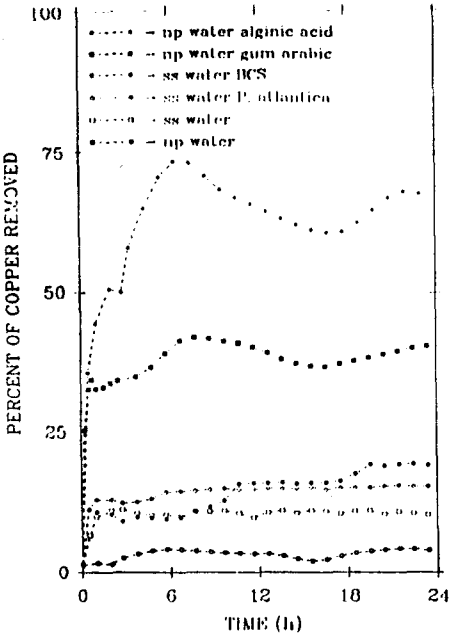

Fig. 2. Percent of copper removed as a function of time.

The P. atlantica, BCS (both in ss water), gum arabic and alginic acid C_p values were 21.2, 29.4, 14.9 and 55.2 min, respectively. The Δ peak areas were 0.5, 6.7, 17.7 and 40.3 abs cm^{-1}, respectively. The data indicate that the four polymer solutions were able to remove some of the deposited Cu. The percents of total Cu available that were removed by the alginic acid solution, gum arabic solution, BCS solution, P. atlantica exopolymer solution, ss water and np water, respectively were 64, 38, 19, 14, 11 and < 5%. These data indicate that the four polymer solutions were able to remove deposited Cu in the order: alginic acid > gum arabic > BCS > P. atlantica (see Fig. 2).

X-ray Photoelectron Spectroscopy

The XPS spectra of the uncoated Ge disc, a metallic copper reference, copper reference compounds and samples are shown in Fig. 3, 4, 5. The Cu° was a standard left inside of the AES/XPS vacuum chamber for instrumental calibration. Prior to analysis, Ar^+ sputtering was used to remove any oxide layers. The Cu $2p_{1/2,3/2}$ binding and LVV kinetic energy (LVV refers to $L_3M_{4,5}M_{4,5}$) positions were 951.2, 931.4 and 919.4 eV, respectively.

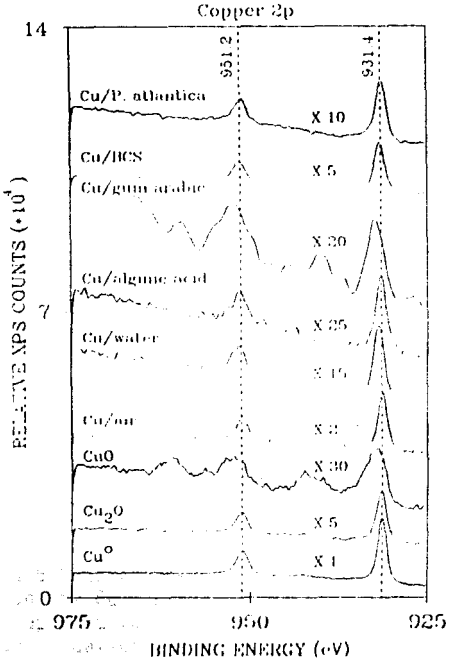

Fig. 3. Cu 2p photoelectron lines.

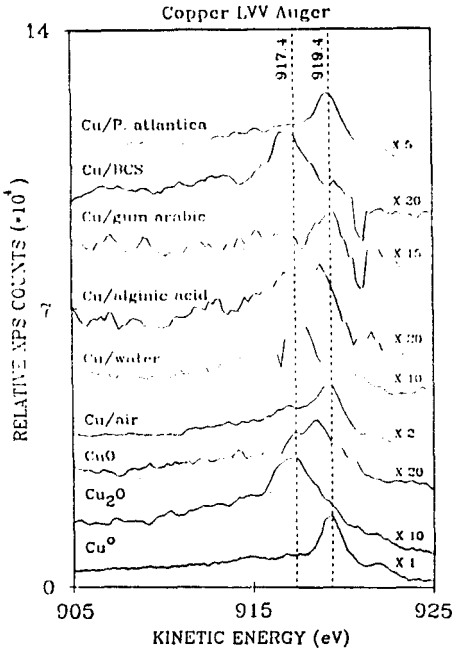

Fig. 4. Cu $L_3M_{4,5}M_{4,5}$ Auger electron lines

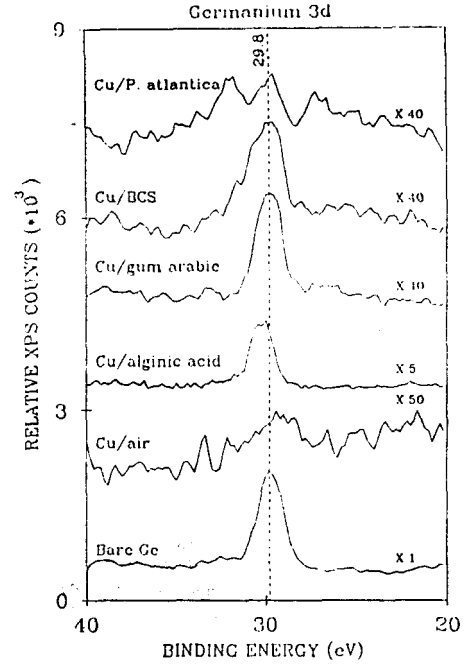

Fig. 5. Ge 3d photoelectron lines.

Cu_2O (Alfa Products) and CuO (Johnson Matthey) powders were mounted on indium foil and used as reference standards. The Cu $2p_{1/2}$ positions were 951.2 and 952.4 eV; the Cu $2p_{3/2}$ were 931.4 and 932.0 eV (Fig 2); and the Cu LVV were 917.4 and 918.6 eV (Fig 4), respectively. The Cu_2O had the characteristic Auger shift to lower energy while the CuO 2p showed the characteristic shake-up structure. The CuO LVV displayed a shoulder at 917.4 eV. These were in agreement with published findings.[2,3,13,14,18]

The Cu/air sample had 3.4 nm of Cu sputtered upon a Ge disc which was exposed to ambient air for five minutes. The Cu $2p_{1/2,3/2}$ and LVV positions were 951.2, 931.2 and 919.2 eV, respectively. Due to the similarity of the Cu/air and Cu^o, it was determined that the thin film of Cu had undergone negligible oxidation and was metallic in nature. This lack of oxidation agrees with results of kinetic investigations performed by Pinnel *et al.* which indicate that the rate of copper oxide film growth at ambient conditions is $< 10^{-4}$ nm/h.[18]

The Cu/water sample was prepared in the same manner as the Cu/air sample and exposed to np water for one hour. The Cu $2p_{1/2,3/2}$ and LVV positions were 951.6, 931.8 and 917.8 eV, respectively. Due to the similarity of the Cu/water and Cu_2O spectra, it appears that the Cu had oxidized to a +1 oxidation state. One would expect some oxidation since the total oxygen concentration in ambient water is approximately 3000 times greater than in ambient air, resulting in a greater interaction probability.

The Cu thin films on the Ge substrates were prepared in the same manner as the Cu/air sample and then exposed to gum arabic, alginic acid, BCS (np water and ss water) and P. atlantica exopolymer solutions (np water and ss water) respectively, for 24 hours. The Cu film was also exposed to the gum arabic solution for a one hr period due to negligible detection of Cu in the 24 hr experiment (Fig. 4, 5 for data). The Cu/gum arabic Cu 2p showed a shake-up structure and a shoulder on the Cu LVV peak at 918.6 eV, which indicate a +2 oxidation state for the Cu. The Cu/alginic acid Cu 2p showed no shake-up structure while the Cu LVV peak was broadened and shifted down in kinetic energy with respect to Cu^o. The Cu appears to have +1 and zero oxidation state character. The np water and ss water versions of the Cu/BCS and Cu/P. atlantica were essentially identical in appearance and peak position; only the ss water versions were plotted. The Cu/BCS Cu LVV peak was shifted to lower energy than the Cu_2O and the Cu 2p showed no shake-up structure. Both results are indicative of an oxidation state in Cu of +1. Due to the similarity of the Cu/P. atlantica and the Cu^o it was determined that the thin film of Cu had negligible oxidation and was metallic in nature. Apparently, the P. atlantica exopolymer had inhibited oxidation of the Cu.

The semi-quantitative evaluations of the Cu removal by the polymers are shown in Fig. 5. The Ge 3d was essentially not detectable in the Cu/air and Cu/P. atlantica samples, whereas the Cu/gum arabic (24 hr exposure), Cu/alginic acid and Cu/BCS had strong signals. These spectra indicate that some of the Cu had been removed by the gum arabic, alginic acid and BCS (both np water and ss water) solutions, while the Cu removal was not detected by XPS in the P. atlantica (both np water and ss water) experiments.

Auger Depth Profile

The sputter depth profiles are shown in Fig. 6. The Cu/air sample was used for the Cu/Ge depth profile. The Cu, C and Ge maximum relative Auger (peak-to-peak height) signals were 6.3, 2.7 and 6.6, respectively. The Ge started at a minimum Auger signal of 1.5. The C_p values were 2.1, 3.0 and 3.3 min, respectively.

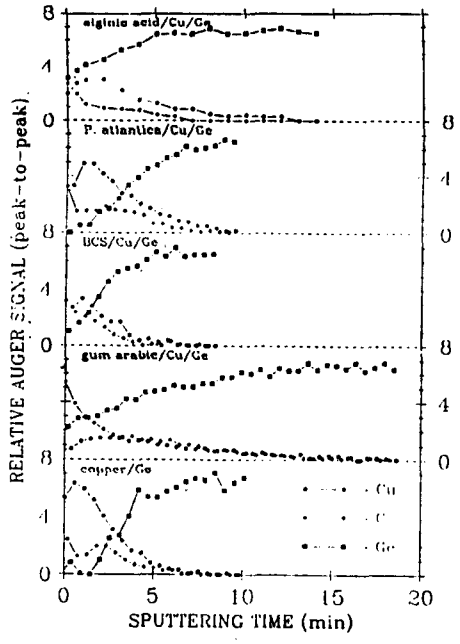

Fig. 6. Auger sputter depth profiles.

The Cu/gum arabic sample (24 hr exposure) was used for the gum arabic/Cu/Ge depth profile. The Cu, C and Ge maximum relative Auger signals (peak-to-peak height) were 1.5, 5.5 and 6.6, respectively. The Ge started at a minimum Auger signal of 1.5. The C_p values were 4.8, 1.2 and 3.3 minutes, respectively. The Cu/alginic acid sample (24 hr exposure) was used for the alginic acid/Cu/Ge depth profile. The Cu, C and Ge maximum relative Auger signals (peak-to-peak height) were 3.1, 2.7 and 6.6, respectively. The Ge started at a minimum Auger signal 3.2. The C_p values were 2.2, 0.9 and 2.5 minutes, respectively. The small initial Cu signal (49% less than the Cu/Ge value) and the larger starting Ge signal indicated that some of the Cu thin film had been removed by the polymer solution prior to analysis.

The Cu/BCS ss water (the np water and ss water had similar depth profiles) was used for the BCS/Cu/Ge depth profile. The Cu, C and Ge maximum relative Auger signals (peak-to-peak height) were 3.3, 3.1 and 6.6, respectively. The Ge started at a minimum Auger signal of 0.5. The C_p values were 2.3, 1.7 and 1.4 minutes, respectively. The exposure to the BCS solution appeared to have little effect on increasing the C starting signal. The low intensity of the Cu signal (48% less than the Cu/Ge value) and the high intensity of the starting Ge signal indicated that some of the Cu thin film had been removed by the solution prior to analysis.

The Cu/P. atlantica ss water (the np water and ss water had similar depth profiles) was used for the P. atlantica/Cu/Ge depth profile. The Cu, C and Ge maximum relative Auger signals (peak-to-peak height) were 4.9, 3.1 and 6.6, respectively. The Ge Auger signal was not detectable at the start. The C_p values were 2.7, 4.7 and 3.3 minutes, respectively. The exposure to the P. atlantica exopolymer solution had little effect on increasing the C starting signal. Since the Cu maximum signal was approximately 22% less than the Cu/Ge reference and the Ge signal started to rise one min earlier, it appears that the P. atlantica exopolymer solution did remove some of the Cu thin film.

Graphite Furnace Atomic Absorption Spectroscopy

The quantitative evaluation by GFAAS of the removal of Cu for the water and four polymer solutions are summarized in Table I.

TABLE I . Graphite furnace atomic absorption spectroscopy yield

Sample	Exposure time (hr)	Percent Cu removed
Cu/AA	24	41
Cu/GA	24	36
Cu/BCS[a]	24	22
Cu/P. atlantica	24	6.0
Cu/H_2O[a]	24	3.5
Cu/H_2O	262	< 0.1

*a Simulated seawater.

Less than 0.1% of the total available Cu was removed from the substrate and solubilized into the water during 262 hr of exposure to np water. This result indicates that the Cu thin film was relatively stable while exposed to np water. The ss water was able to remove 3.5% of the copper from the substrate during the 24 hr exposure time.

Of the total Cu available 41, 36, 22 and 6.0% were removed by the alginic acid solution, gum arabic solution, BCS solution and P. atlantica exopolymer solution, respectively. The Cu removed from the substrate was associated with the polymer solution. These values correlated well with the FT-IR/CIR/ATR determinations. The four polymer solutions were able to remove various amounts of the deposited Cu in the order: alginic acid > gum arabic > BCS > P. atlantica; the same relative ordering as determined using the FT-IR/CIR/ATR technique.

SUMMARY

FT-IR data (supported by the GFAAS data) indicate that the Cu thin film was relatively stable while exposed to np water but a small amount was removed by the ss water. Some Cu was removed from the Cu/Ge interface by all four polymers and was found associated with the polymer solution.

The XPS, AES depth profile and GFAAS data indicate that the 10% w:v gum arabic solution was able to oxidize the Cu thin film to a +2 oxidation state. Copper was removed from the substrate and was found associated with the polymer solution.

The XPS, AES depth profile and GFAAS data indicate that the 2% w:v alginic acid polysaccharide solution and 1% w:v BCS solution (in ss) were able to oxidize the Cu thin film to a +1 oxidation state. In addition, Cu was removed from the substrate and was found associated with the polymer solution.

The XPS data for the 0.5% w:v P. atlantica exopolymer solution indicate no change in oxidation state of Cu and no detectable removal of copper. Since the np water had oxidized the Cu to +1 oxidation state, it appears that the polymer solution may have inhibited oxidation of the Cu. The AES depth profile and GFAAS data indicate that a small amount of the Cu was removed from the substrate by the polymer.

In conclusion, results indicate a removal of copper was exhibited by gum arabic, alginic acid, BCS and P. atlantica. The overall rates of Cu removal by the saturated solutions were in the order of alginic acid > gum arabic > BCS > P. atlantica.

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