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# CORROSION OF MILD STEEL BY THERMOPHILIC ANAEROBES

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## ABSTRACT

The effect of thermophilic anaerobes upon corrosion of AISI C1020 carbon steel in synthetic oilfield produced water has been investigated. Electrochemical techniques such as: corrosion and pitting potential measurements, linear polarization resistance, and electrochemical impedance spectroscopy were applied to evaluate microbiologically influenced corrosion. Passivity retardation and breakdown of mild steel are accomplished easily in the produced water containing thermophilic anaerobes.

## INTRODUCTION

Microorganisms in aqueous solutions are known to induce or enhance corrosion of metals and alloys. When this occurs, the phenomenon is known as microbiologically influenced corrosion (MIC). It is generally recognized that oxygen concentration cells as a result of an uneven bacterial colonization on the metal surface may lead to localized corrosion (1). Metabolic products such as sulfides produced by sulfate reducing bacteria in anaerobic environment can also enhance the corrosion (2).

The involvement of mesophilic microorganisms in the corrosion of seawater and fresh water has been the subject of considerable investigation (3-5). However, little attention has, as yet, been received for corrosion by thermophilic bacteria. The ubiquity of thermophiles in hot water systems has been characterized by Brock et al (6). Ford (7) suggested that whenever hot water is produced, the potential exists for thermophilic microorganism growth and, therefore, in the presence of metals, microbially mediated corrosion. In the present study, thermophilic anaerobes were cultivated from Prudhoe Bay's oilfield produced water and corrosion coupons; and electrochemical techniques associated with viable bacteria cell counts were employed to investigate MIC of mild steel.

## EXPERIMENTAL PROCEDURE

Specimens. The test specimens (AISI C1020 carbon steel), 16 mm diameter disks, were supplied by Metal Samples (Munford, Alabama). The specified composition of this steel was 0.20 C, 0.47 Mn, 0.012 P, and 0.013 S, wt%. A multi-electrode probe was fabricated to simplify experimental design by combining four steel disks into one probe as illustrated in Figure 1. The surfaces were wet polished in sequence with 240, 400 and 600 grit SiC paper, ultrasonically cleaned with distilled water, degreased with acetone and sterilized with 70% alcohol for 30 minutes.

Electrochemical Cell. A sterilized, flow-through electrochemical cell, as shown in Figure 2, consists of a 600 ml glass beaker and includes 1) a four sided working electrode probe, 2) a Pt coated Nb mesh counter electrode, 3) a saturated calomel reference electrode, 4) a 0.2 $\mu$m sterile filter ventilation port, 5) a gas dispersion tube and 6) solution inlet and outlet. Test solution was synthetic Prudhoe Bay's produced water and contained (in g/l) NaCl 17.03, $Na_2SO_4$ 0.725, $CaCl_2$ 0.637, $MgCl_2.6H_2O$ 1.67, $B_2O_3$ 0.354, KCl 0.2, $SrCl_2.6H_2O$ 0.064, $BaCl_2.2H_2O$ 0.003, KI 0.016, $NaHCO_3$ 2.26 and $Na_2S_2O_5$ 0.434. The solution was sterilized by autoclaving at 121 °C for 2 hours, and allowed to cool with air equilibration by a 0.2 $\mu$m filter vent. A solution containing (g/l) $NaCH_3COOH$ 0.237, $NaC_2H_5COOH$ 0.033 was also sterilized by filtration through Gelman membranes (0.2 $\mu$m pore diameter) and added under aseptic conditions before starting an experiment. The pH was adjusted to 7.5 using either 0.1 M NaOH or HCl.

Bacteria. Bacterial samples from Prudhoe Bay's produced water and corrosion coupons were cultured in two media: the thioglycolate general anaerobe medium and the lactate/acetate SRB medium. The thioglycolate general anaerobe medium consists of (g/l) yeast extract 5.0, casitone 15.0, dextrose 5.5, NaCl 2.5, L-cystine 0.5 and sodium thioglycolate 0.5 for general thermophilic anaerobe growth. The lactate/acetate SRB medium contains (g/l) sodium acetate 2.8, sodium lactate (60% solution) 2.91, yeast extract 1.0, ascorbic acid 0.1, $MgSO_4.7H_2O$ 0.5, $Na_2SO_4$ 0.5, $K_2HPO_4$ 0.5, $NH_4Cl$ 0.5, $FeSO_4.7H_2O$ 0.1, NaCl 7.0 and sodium thioglycolate 0.1 for thermophilic sulfate reducer growth. The cultures were incubated at 55 °C for 7 days prior to inoculation.

Since some samples from the SRB cultures have consistently given a positive result for SRB growth, two treatments were performed in the present study. This involved 1) inoculation

of consortia of bacteria into an electrochemical cell, and 2) inoculation of bacteria from the SRB cultures into another cell. Before inoculation, bacterial cultures were centrifuged at 5000 rpm for 20 minutes and replaced with fresh synthetic produced water. Inocula were then added at specimen exposure time of 0, 50, 175, 330 and 520 hours.

Bacteria cell counts from bulk solutions and specimen surface were determined by acridine orange direct counts (AODC). Also, the thiolglycolate medium and most probable number's technique (MPN) were employed to estimate the total number of viable general anaerobic bacteria and SRB, respectively.

Test Conditions. Prior to the start of each experiment the electrochemical cell was sterilized with ethylene oxide using the precautions defined previously (8). All lines to and from the cell were autoclaved to achieve sterilization. A combination of 5% hydrogen and 95% nitrogen gas was continuously pumped through a copper column and sparged in the solution to achieve adequate anaerobic conditions. During the test period the solution temperature ranged from 55 to 60 °C by means of a water bath. A dual- channel peristaltic pump was used to control flow rate through the cell at $60 \pm 5$ ml/hr.

Electrochemical Analyses. Open circuit potential (OCP) of test specimens was monitored at an interval of 1 hour by a HP 3458A multimeter via a Keithley 706 scanner controlled by a computer. DC measurements were conducted by Softcorr corrosion measurement software associated with EG & G model 273 (option 92) potentiostat. For linear polarization resistance, current densities were monitored within $\pm 30$ mV versus open circuit potential with a scan rate of 0.17 mV/sec; and for potentiodynamic polarization, the same scan rate was applied and started at -50 mV versus free corrosion potential. Electrochemical impedance spectroscopy (EIS) analysis was performed by a microcomputer using the Zplot software (Scribner Associates Inc.), a Solartron 1255 HF frequency response analyzer, and a potentiostat/ galvanostat 273 (option 92) from EG & G Princeton Applied Research. The applied voltage amplitude was 5 mV at frequencies between 5 mHz and 10 KHz. Five frequencies were examined per decade. An Etec Autoscan Scanning Electron Microscope (SEM) was used to examine the morphology of corrosion products and bacteria.

## RESULTS AND DISCUSSION

Open Circuit Corrosion Potential. Figure 3 presents the open circuit potential (OCP) versus time plots for specimens exposed to the produced water with different bacteria inoculations for time up to 650 hours. In all cases, the OCP increased to approximately -625 mV (SCE) after certain periods of exposure. However, for the sterile control the potentials maintained steady between -620 and -640 mV (SCE) throughout the rest of exposure, while in the non-sterile control, a significant decrease in OCP after 300 hours of exposure was observed. It was noticed that with direct deaeration of the produced water using the 5% hydrogen + 95% nitrogen gas, the pH of the solution increased from 7.5 to 8.5 during the duration of the tests. Therefore, it is possible to infer that the increase of OCP toward more positive values is attributed to the formation of passive film on the metal surface; but the decrease in OCP might

be related to the passivity breakdown of the specimen due to bacterial activity.

Potentiodynamic Polarization. To study passive behaviors of AISI C1020 steel in synthetic produced water, potentiodynamic polarization scans were made in different pHs, where sterile media were degased for 0, 3, and 10 days and pH was 7.5, 8.2 and 8.5, respectively. Figure 4 presents potentiodynamic polarization curves for steels in the deaerated sterile media after one hour of exposure. It suggests that the passive region of the steel increased with increasing solution pH. At pH of 7.5, the active to passive region cannot be observed, while at pH of 8.5 three regions are identified: the first one, ranging between -800 and -710 mV (SCE) is an active region. At more positive potentials, a decrease in the current density corresponding to a passive region can be found, while at potential more noble than -600 mV (SCE), the increase in the current density is associated with a pitting process. The presence of pits on the specimen surface was confirmed through visual and microscopic observations after the potentiodynamic scan.

Figure 5 shows potentiodynamic polarization curves for steels in the sterile solutions with and without addition of consortia of bacteria after 3 days of incubation. It is apparent that the pitting potential of mild steel changed to a more negative value (-665 mV) in the solution containing thermophilic bacteria. Therefore, the breakdown of passivity accomplished easily by the presence of bacteria could be projected.

Linear Polarization Resistance. The average corrosion rate, in terms of polarization resistance $R_pT$measured by linear polarization resistance technique ($\pm$30 mV vs. OCP) for steels in the different solutions is shown in Figure 6 as a function of time. In general, the corrosion rate of a steel in the sterile solution is less than that in the non-sterile solutions. Such an observation is consistent with the phenomena of microbiologically influenced corrosion. In addition, higher corrosion of a steel in the sterile+consortia medium was observed in comparison to a specimen in the sterile+SRB medium. A possible explanation could be that underneath biofilms microbial consortia of different kinds of bacteria and SRB enhanced the corrosion induced by SRB due to drastic changes in the pH, redox potentials, and concentrations of ions at restricted areas beneath the biofilm. Viable cell counts by MPN from coupon surfaces supported this hypothesis since higher SRB populations (1.0E+03 cells/cm$^2$) were detected from coupons in the sterile+consortia medium compared to those (1.0E+02 cells/cm$^2$) in the sterile+SRB medium upon termination of experiments. Moreover, bacterial populations on the coupon surfaces determined by AODC showed 1.0E+07 and 5.0E+05 cells/cm$^2$ for specimens in the sterile+consortia and sterile+SRB medium, respectively. Therefore, it is also possible to infer that not only thermophilic SRB play an important role to influence steel corrosion but other microorganisms in the consortia could enhance the metal corrosion. Figure 7 presents the morphology of microbial consortia which have been inoculated into test cells.

Electrochemical Impedance Spectroscopy. Figures 8-10 present Nyquist impedance plot measured by EIS for specimens in the solutions at various immersion times. It is apparent that for a long term exposure (time > 5 days) Nyquist plots do not permit a reasonably accurate extrapolation of charge transfer resistances. In other words, the corrosion reactions in the present study are complicated by diffusion constraints. However, Bode plots, as shown in Figures 11-13, could imply the defects of passive film formation influenced by bacteria.

A comparison of the phase angle at 5 mHz for specimens in the solutions with different bacteria inoculations indicates that in the presence of thermophilic bacteria, longer exposure times were required for the completion of passive film on the steel surface. It is generally recognized that the formation of surface films such as passive film and biofilm on the metal surface increases the metal/solution interfacial capacitance and that the maximum phase angle moves to low frequencies. As a result, an increase of the phase angle at the lowest frequency (5 mHz) can reflect the formation of surface films. However, in the presence of bacteria, kinetics of passive film formation could be modified: bacteria locally defects the passive film and retards the completion of passive film formation. This was confirmed by corrosion rate measurement (Figure 6), which showed approximately two times more corrosion rate detected from a specimen exposed to the sterile+consortia medium compared to that in the sterile control after 5 days of exposure.

Visual and SEM observations. Figures 14-18 present photographs of specimens exposed to different treated solutions for 650 hours before and after the removal of surface films. For the sterile control (Figure 14), no corrosion is evident on the coupon surface, while in the sterile+SRB and sterile+consortia media (Figures 15-18), tubercles associated with pitting corrosion are apparent. Figures 19-20 show micrographs for bacteria formed in the sterile+SRB and sterile+consortia medium, respectively. This is consistent with AODC data which demonstrated higher bacterial populations in the sterile+consortia medium than those in the sterile+SRB medium.

## CONCLUSIONS

1. Corrosion of mild steel in synthetic Prudhoe Bay's produced water is enhanced by the presence of thermophilic anaerobes.

2. Mild steel can be passivated by direct deaeration of produced water using a 5% hydrogen + 95% nitrogen gas.

3. Passivity retardation and breakdown of mild steel are accomplished easily in the produced water containing thermophilic anaerobes.

## ACKNOWLEDGEMENT

The authors are indebted to BP America Inc. for financial support and the supply of bacterial samples as well as formula of Prudhoe Bay's produced water.

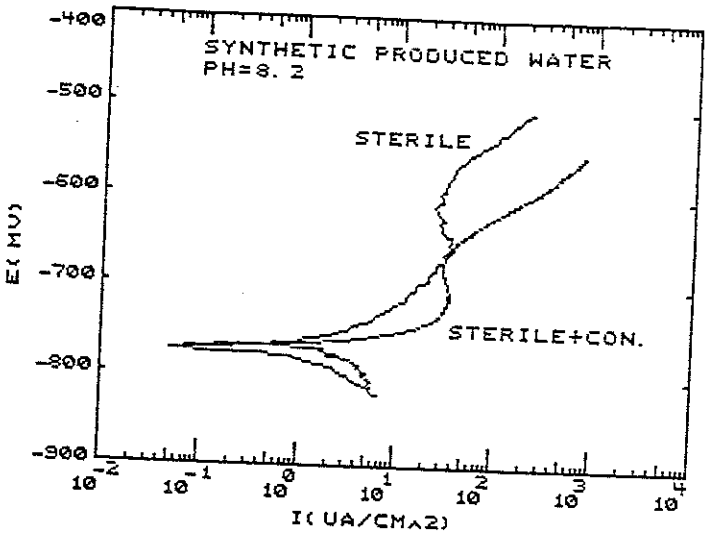


Figure 5. Potentiodynamic polarization curves for C1020 carbon steel in deaerated synthetic produced water with and without addition of consortia of bacteria after 3 days of incubation.

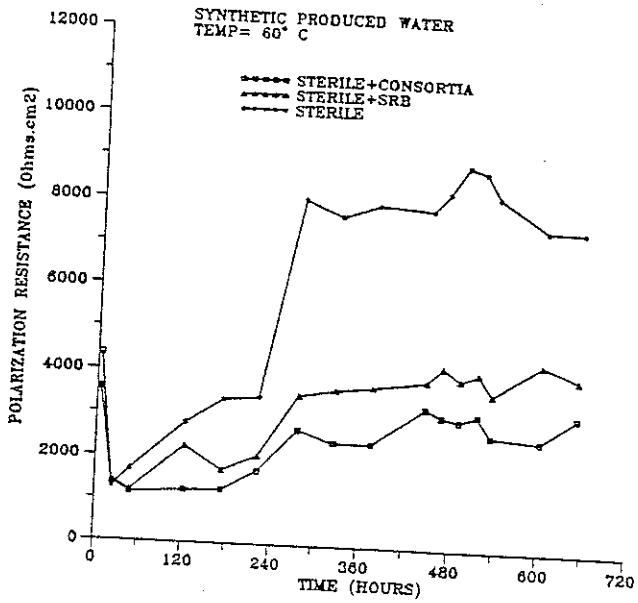


Figure 6. Polarization resistance versus time plots for specimens in the different treated solutions.

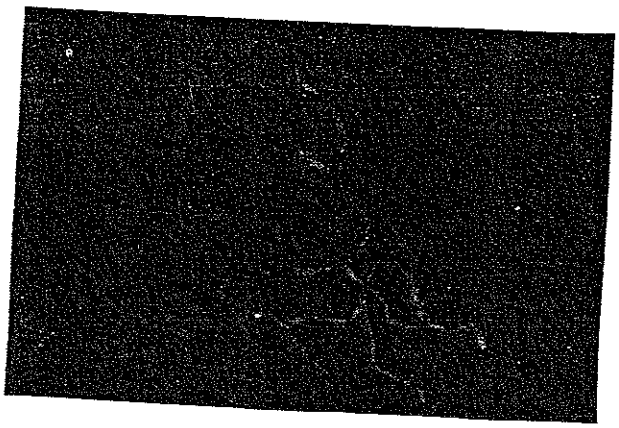

Figure 7. Micrograph of bacteria which have been inoculated into test cells.

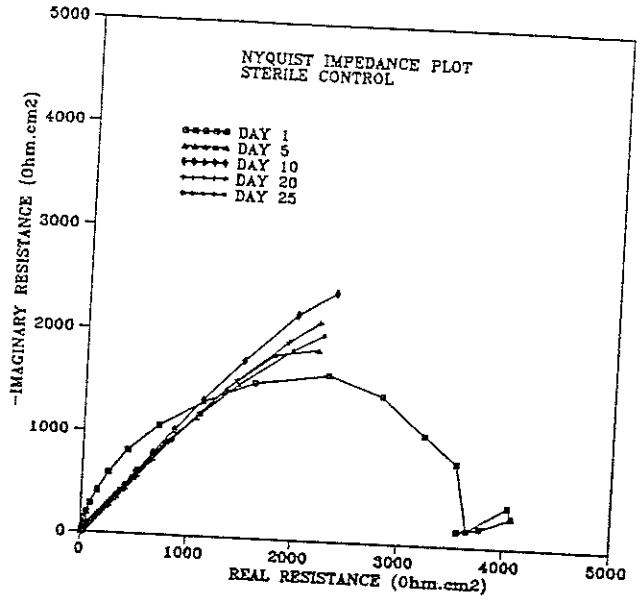


Figure 8. Nyquist impedance plots for a specimen in the sterile medium at various exposure times.

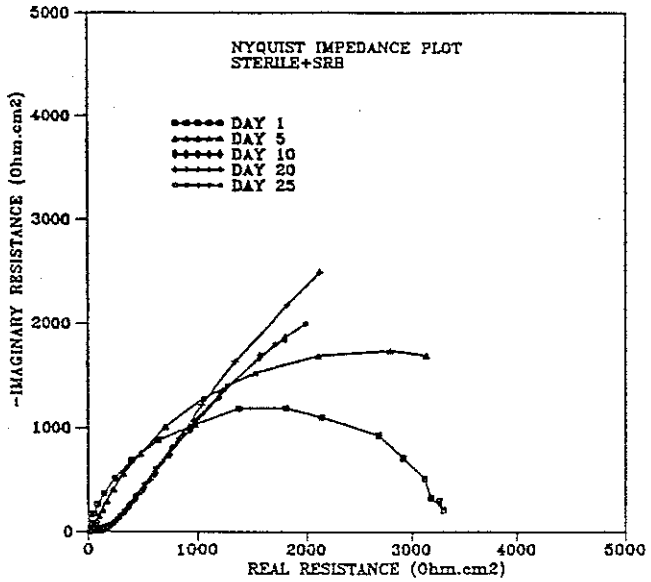


Figure 9. Nyquist impedance plots for a specimen in the sterile+SRB medium at various exposure times.

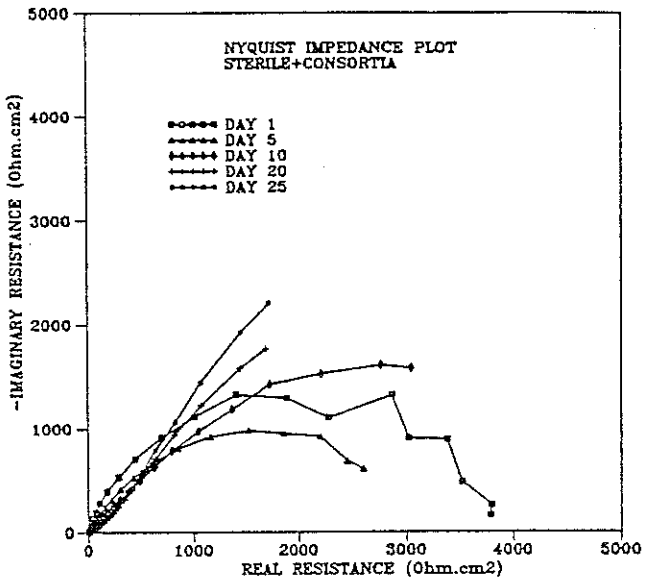


Figure 10. Nyquist impedance plots for a specimen in the sterile+consortia medium at various exposure times.

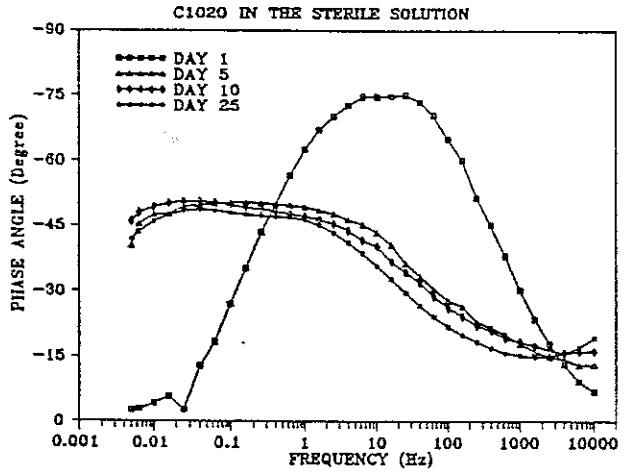


Figure 11. Bode plots for a specimen in the sterile medium at various exposure times.

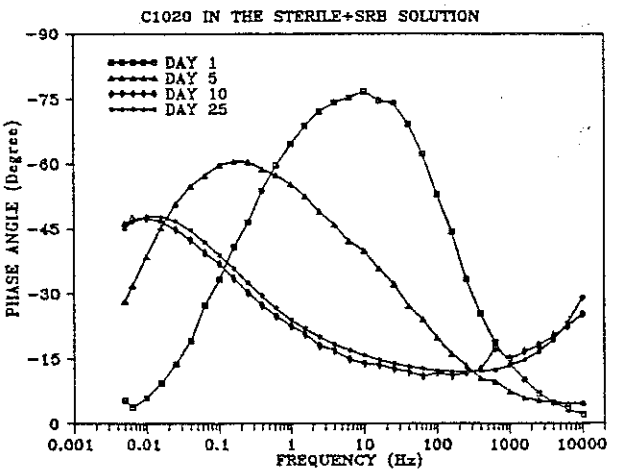


Figure 12. Bode plots for a specimen in the sterile+SRB medium at various exposure times.

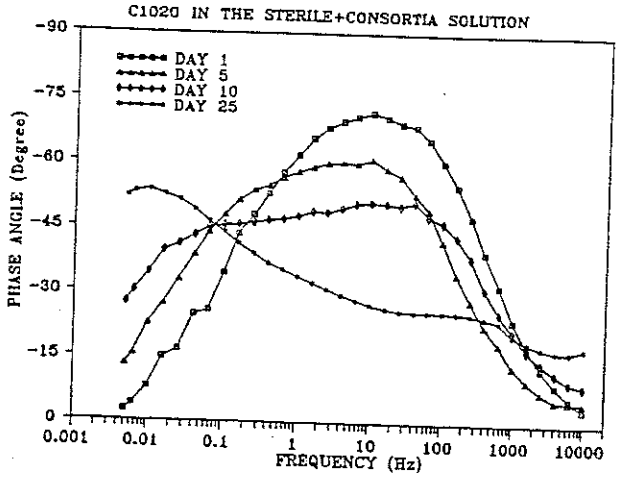


Figure 13. Bode plots for a specimen in the sterile+consortia medium at various exposure times.

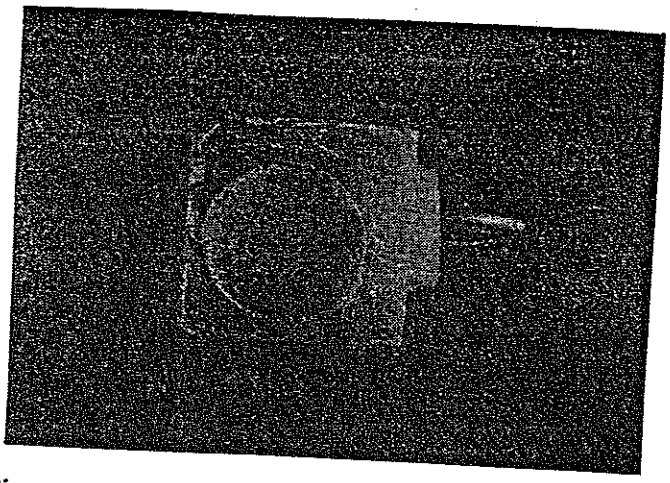

Figure 14. Specimen was exposed to the sterile medium for 650 hours.

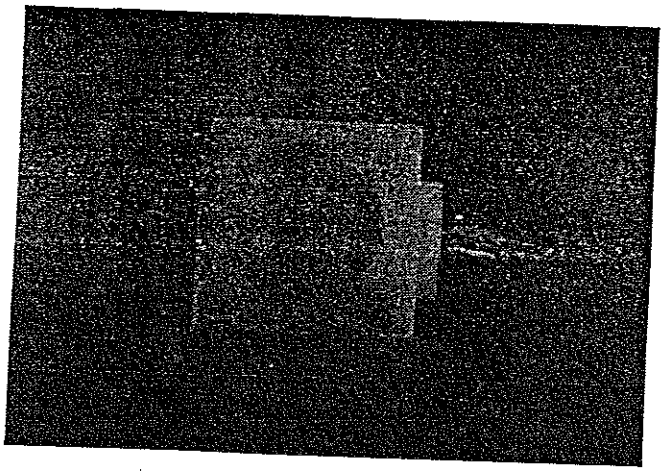

Figure 15. Specimen was exposed to the sterile+SRB medium for 650 hours.

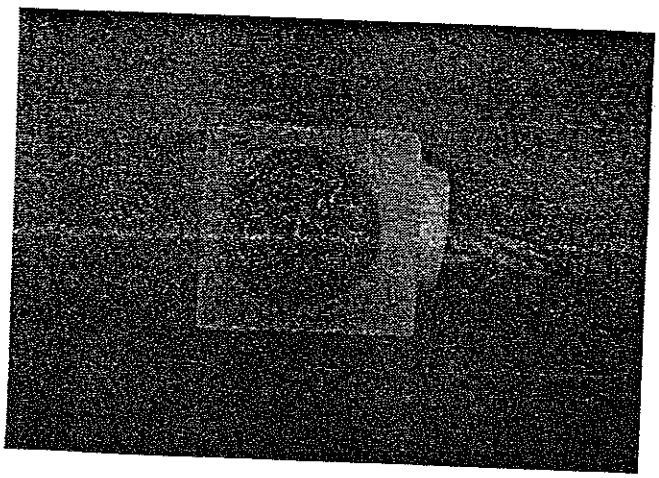

Figure 16. Specimen was exposed to the sterile+SRB medium for 650 hours followed by the removal of surface films.

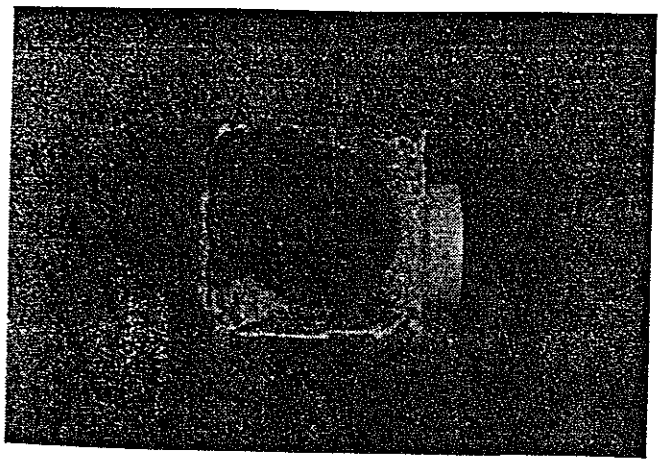

Figure 17. Specimen was exposed to the sterile+consortia medium for 650 hours.

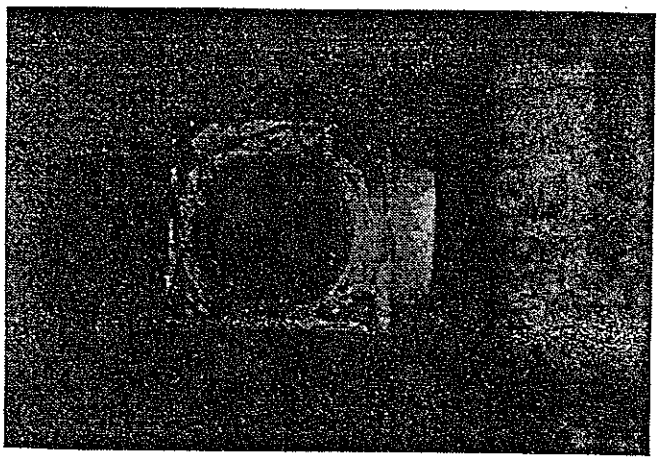

Figure 18. Specimen was exposed to the sterile+consortia medium for 650 hours followed by the removal of surface films.

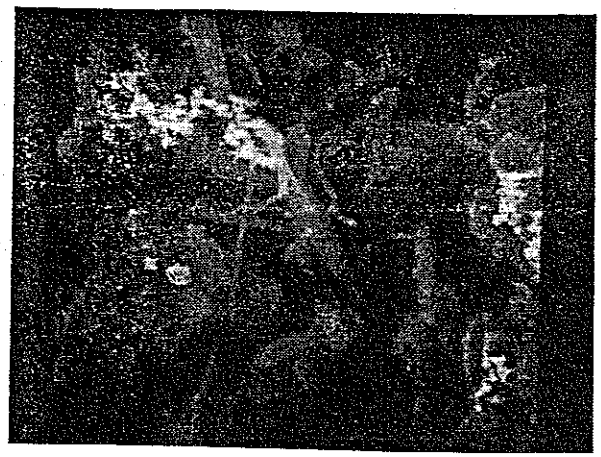

Figure 19. SEM micrograph of a specimen in the sterile+SRB solution. Sample exposure time is 650 hours. Magnification X2000.

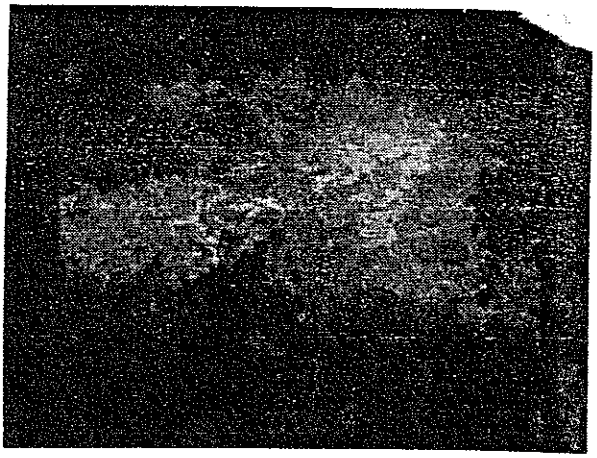

Figure 20. SEM micrograph of a specimen in the sterile+consortia solution. Sample exposure time is 650 hours. Magnification X2000.