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Naval Oceanographic and Atmospheric Research Laboratory
Stennis Space Center, MS 39529-5004

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**13. Abstract** *(Maximum 200 words).*

Sections of CDA 706 piping and Monel 400 tubing were severely pitted after exposure to marine and estuarine waters, respectively. Surfaces of both alloys were uniformly covered with thick surface deposits, ranging in color from blue-green to reddish brown to black. Pits developed under surface deposits containing $10^4$-$10^5$ sulfate-reducing bacteria (SRB) in association with other bacteria. Pits were irregular in shape, lacking a consistent morphology. The observed corrosion was attributed to a combination of differential aeration cells, a large cathode::small anode surface area, concentration of chlorides, development of acidity within the pits, and the specific reactions of the base metals with sulfides produced by the SRB. Chlorine and sulfur appear to have reacted selectively with iron and nickel in the alloys. Nickel has been selectively removed from pitted areas leaving a copper rich spongy pit interior.
SRB isolated from in-service failures were used to inoculate copper-containing foils in an attempt to identify mineralogical fingerprints that could be used as diagnostic for SRB influenced corrosion of copper alloys. The thickness and tenacity of the resulting sulfide deposits varied among the metals and cultures. Strongly adherent corrosion products contained major amounts of djurleite ($Cu_{1.96}S$). Chalcocite ($Cu_2S$) as well as traces of covellite (CuS) and digenite ($Cu_9S_5$) were also identified. Djurleite and the high temperature polymorph of chalcocite may be mineralogical fingerprints for the SRB influenced corrosion of copper-containing metals.

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25

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# The First Annual Navy Corrosion Control Workshop

UNITED STATES NAVY

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**Naval Research Laboratory** ◊ **Naval Sea Systems Command**

- Marine Corrosion Facility
- Corrosion Control Branch

## 29 – 31 October, 1990

## Key West, Florida

# Microbiologically Influenced Corrosion in Copper and Nickel Seawater Piping Systems

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## Executive Summary

Sections of CDA 706 piping and Monel 400 tubing were severely pitted after exposure to marine and estuarine waters, respectively. Surfaces of both alloys were uniformly covered with thick surface deposits, ranging in color from blue-green to reddish brown to black. Pits developed under surface deposits containing $10^4$-$10^5$ sulfate-reducing bacteria (SRB) in association with other bacteria. Pits were irregular in shape, lacking a consistent morphology. The observed corrosion was attributed to a combination of differential aeration cells, a large cathode::small anode surface area, concentration of chlorides, development of acidity within the pits, and the specific reactions of the base metals with sulfides produced by the SRB. Chlorine and sulfur appear to have reacted selectively with iron and nickel in the alloys. Nickel had been selectively removed from pitted areas leaving a copper-rich spongy pit interior.

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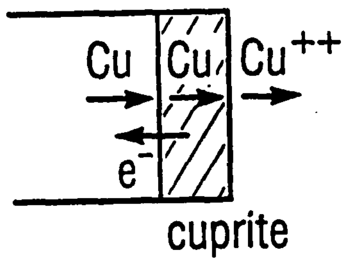
**ANODIC SITES**




**Primary Oxide-Forming Reactions**

$4\ Cu + O_2\ (\text{adsorbed}) \rightarrow 2\ Cu_2O\ (\text{cuprite})$

$2\ Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-$

**Primary Oxidation Reactions for $Cu_2O$ - Covered Metal**

$Cu \rightarrow Cu^{++}(aq) + 2e^-$

**Follow-Up Reactions**

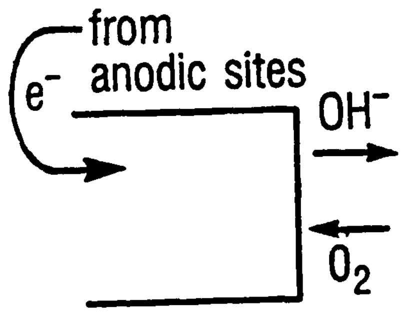
In Seawater:

$2\ Cu^{++} + 3\ OH^- + Cl^- \rightarrow Cu(OH)_3Cl\downarrow$

In Fresh Water:

$2\ Cu^{++} + HCO_3^- + 2\ OH^- \rightarrow Cu_2CO_3(OH)_2\downarrow + H^+$

**CATHODIC SITES**



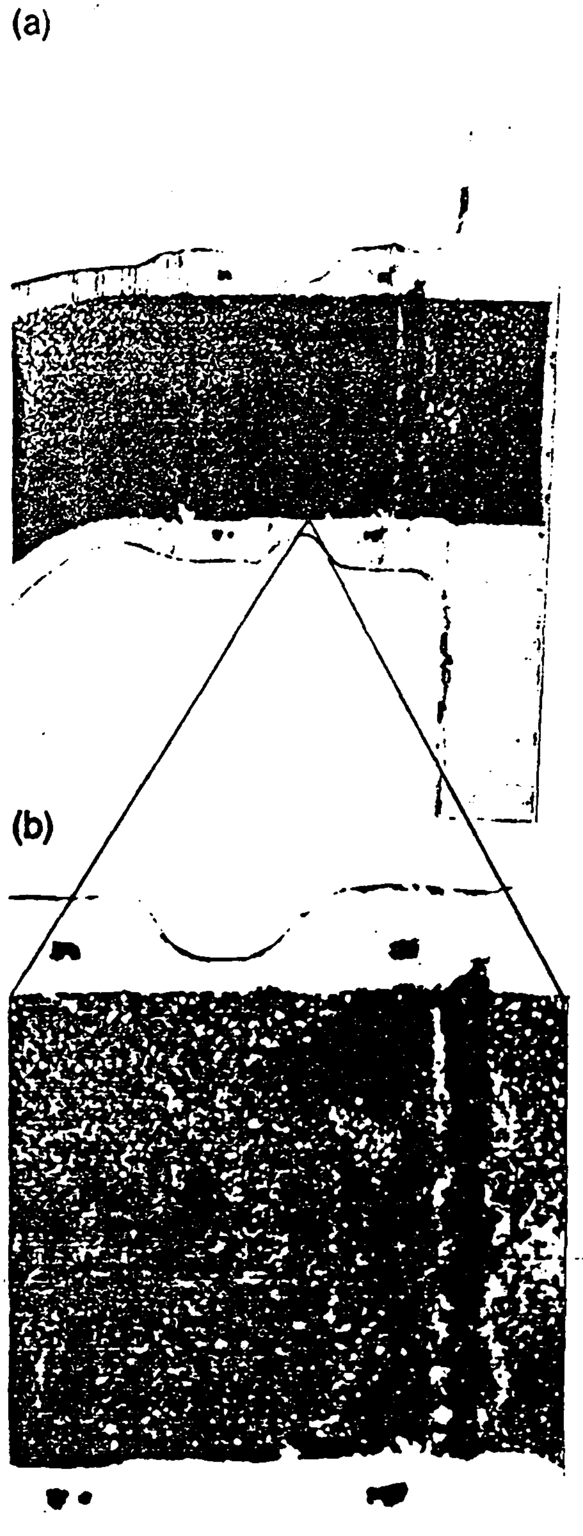

**Pre-Reduction Step**

$O_2\ (\text{solution}) \rightarrow O_2\ (\text{adsorbed})$

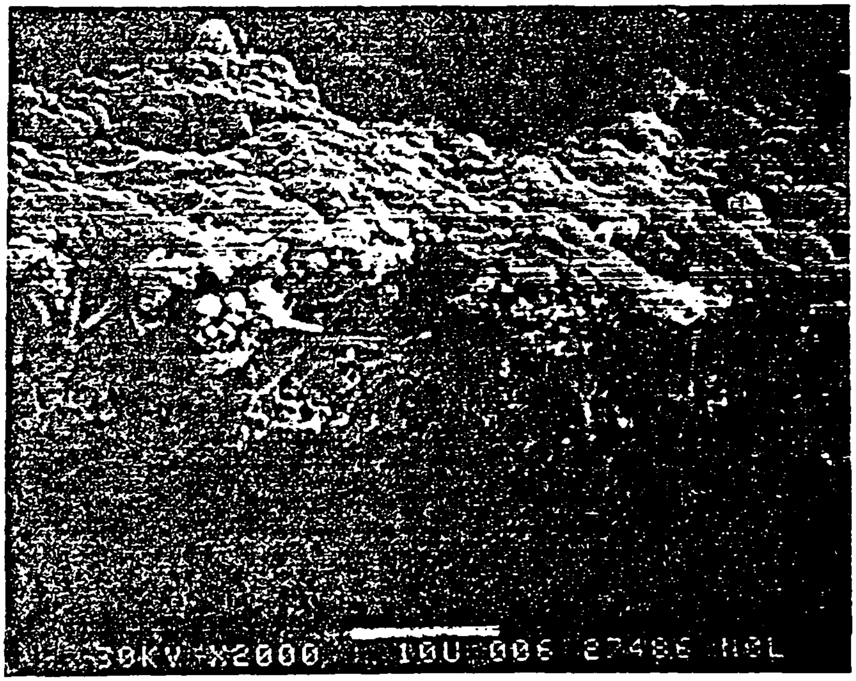
**Primary Reduction Reaction**

$O_2 + H_2O + 4e^- \rightarrow 4\ OH^-$

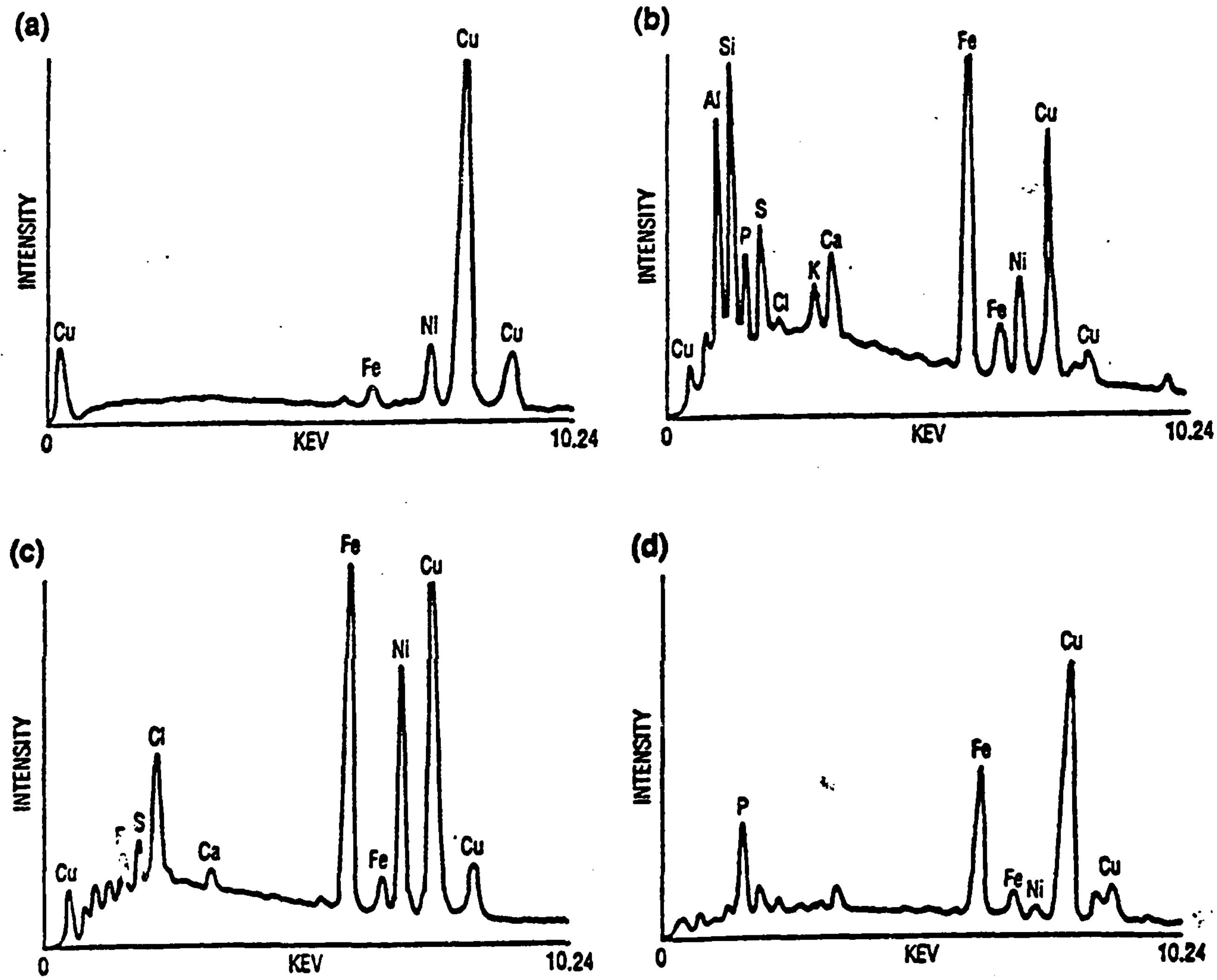
**TYPICAL CATHODIC AND ANODIC REACTIONS ON COPPER ALLOYS IN OXYGENATED SEAWATER AND FRESH WATER.**




**CROSS-SECTION OF 2.5 CM I.D. COPPER ALLOY PIPING AFTER ONE YEAR IN SEAWATER SERVICE, SHOWING THICK SURFACE DEPOSITS AND PITTING.**




SCANNING ELECTRON MICROGRAPH OF A CROSS-SECTION OF THE BLACK DEPOSIT WITHIN A PIT OF COPPER ALLOY. BACTERIA ARE WITHIN BLACK DEPOSIT. A SPONGY COPPER-RICH REGION IS BENEATH THE BACTERIA.

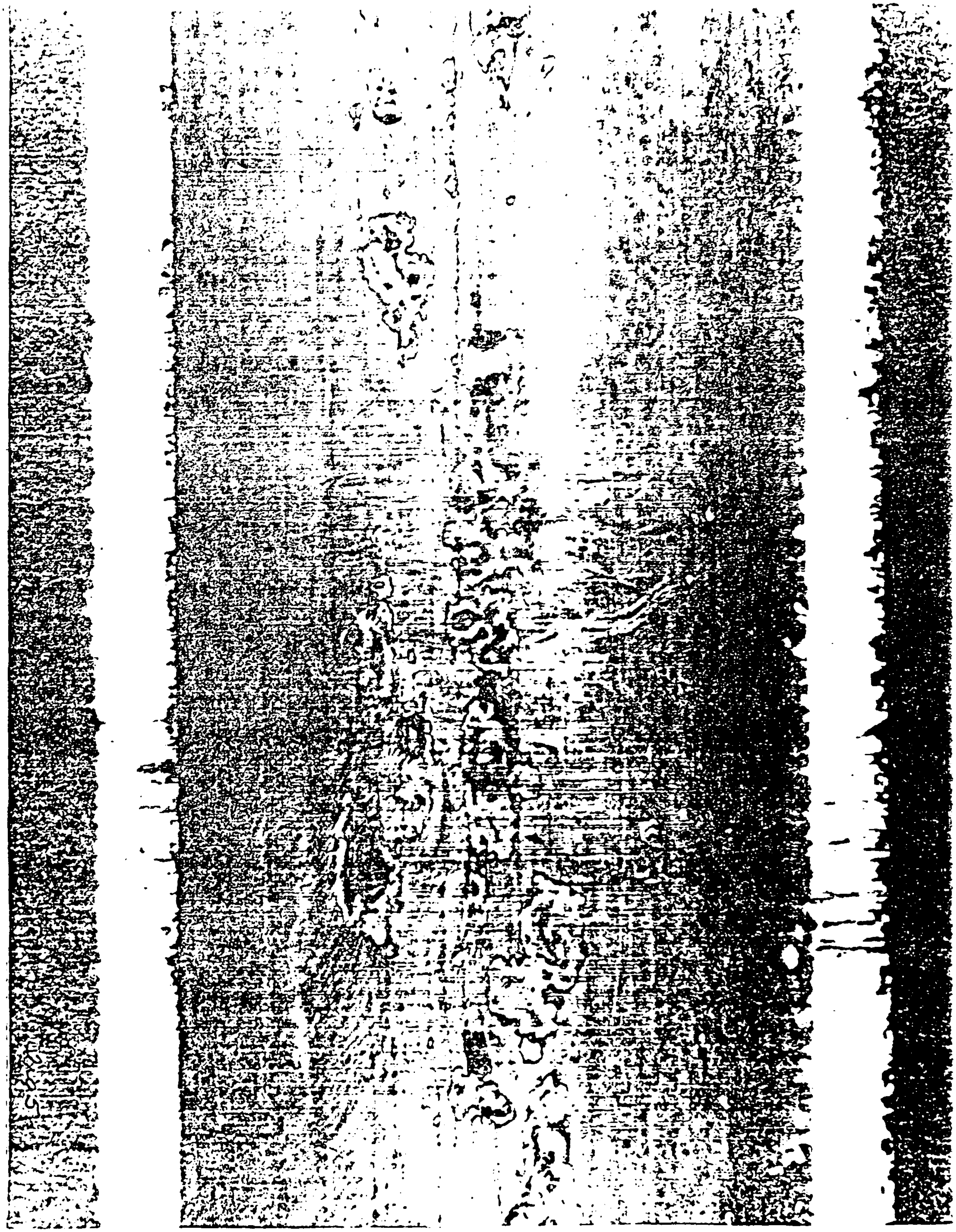



A. EDAX SPECTRUM OF CLEAN COPPER ALLOY BEFORE EXPOSURE

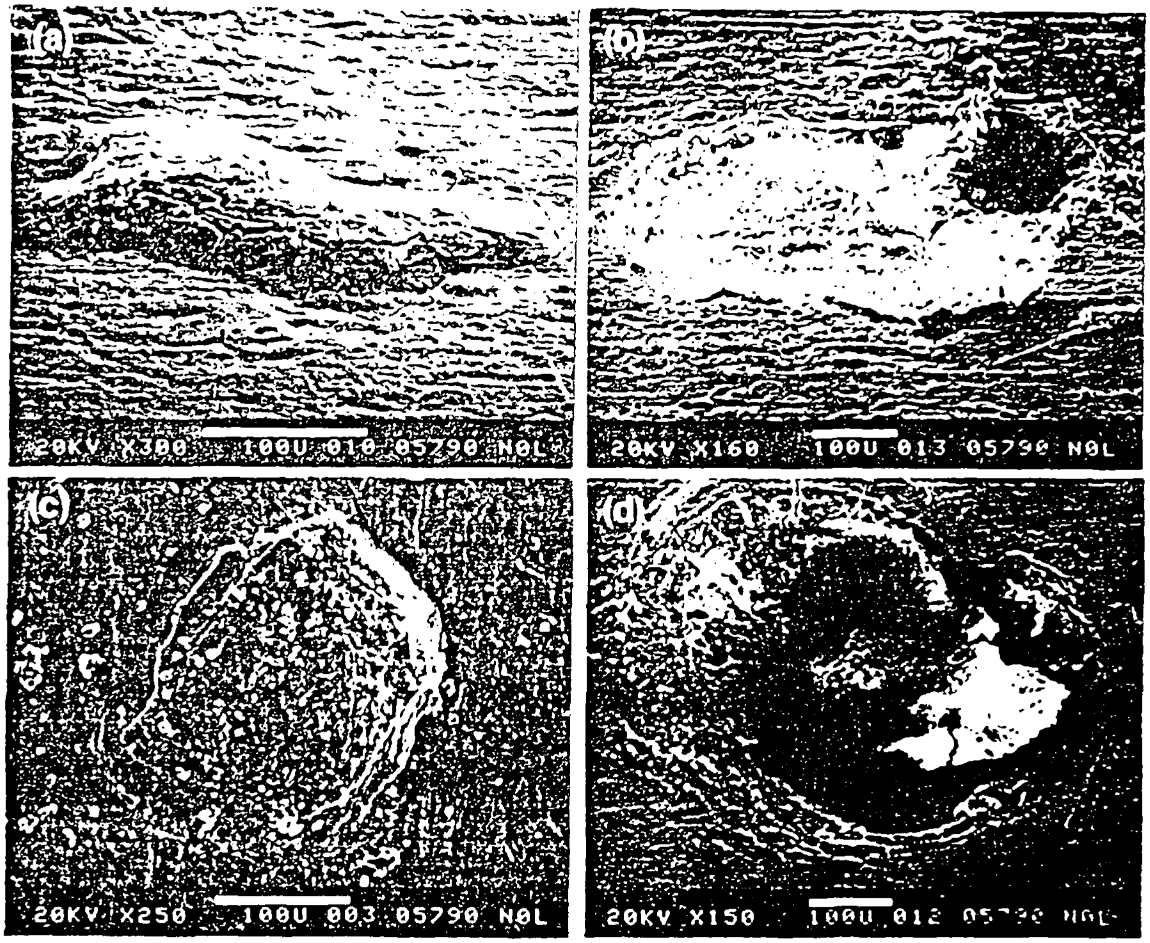
B. EDAX SPECTRUM OF PITTED REGION OF COPPER ALLOY, SHOWING ACCUMULATION OF ALUMINUM, SILICON, PHOSPHORUS, SULFUR, CALCIUM AND ELEVATED AMOUNTS OF IRON AND NICKEL.

C. EDAX SPECTRUM OF PITTED REGION OF COPPER ALLOY, SHOWING THE ACCUMULATION OF CHLORINE AND ELEVATED AMOUNTS OF IRON AND NICKEL.

D. EDAX SPECTRUM OF SPONGY MATERIAL BENEATH BACTERIA, SHOWING AN ACCUMULATION OF PHOSPHORUS, AN ENRICHMENT OF IRON AND A DEPLETION OF NICKEL IN THE BASE OF THE PIT.

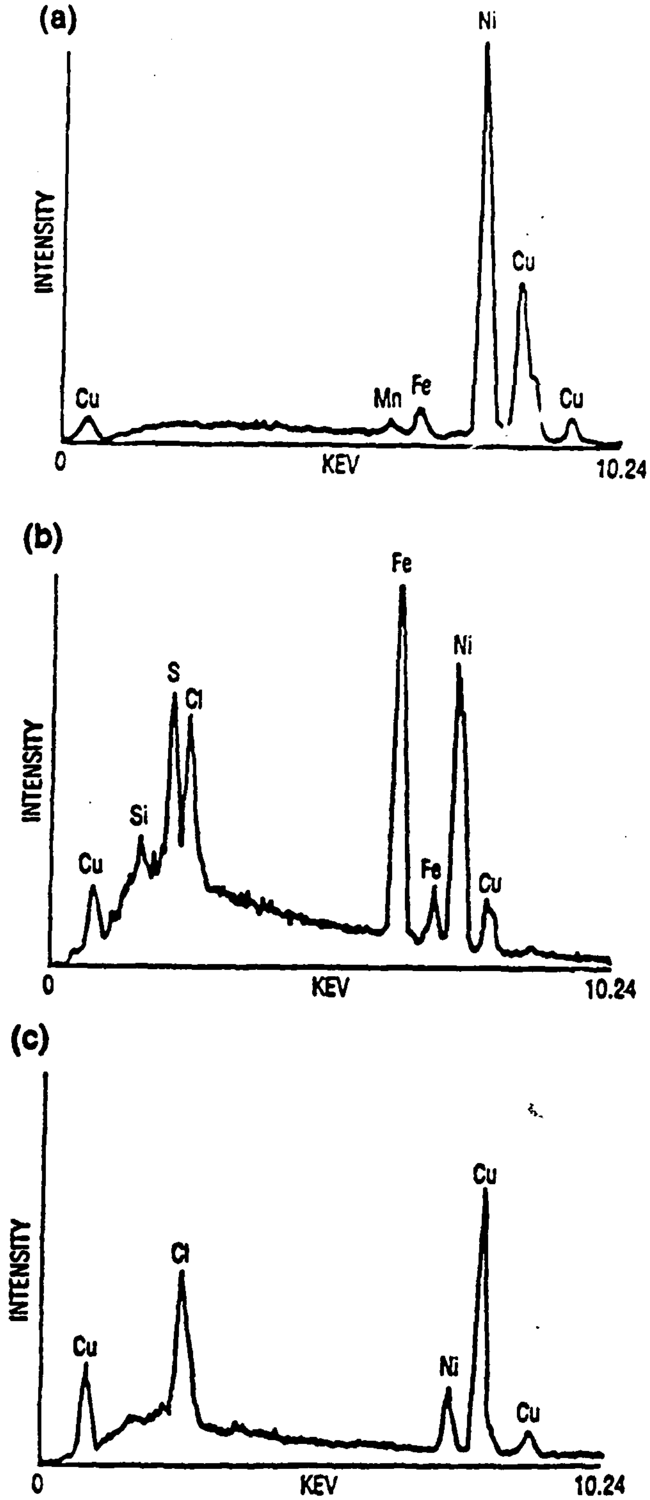


CROSS-SECTION OF 20 MM I.D. NICKEL TUBE AFTER EXPOSURE TO ESTUARINE WATER FOR 6 MONTHS SHOWING SURFACE DEPOSITS AND PITTING.




A AND C. BLISTERS ON THE SURFACE OF NICKEL TUBE.

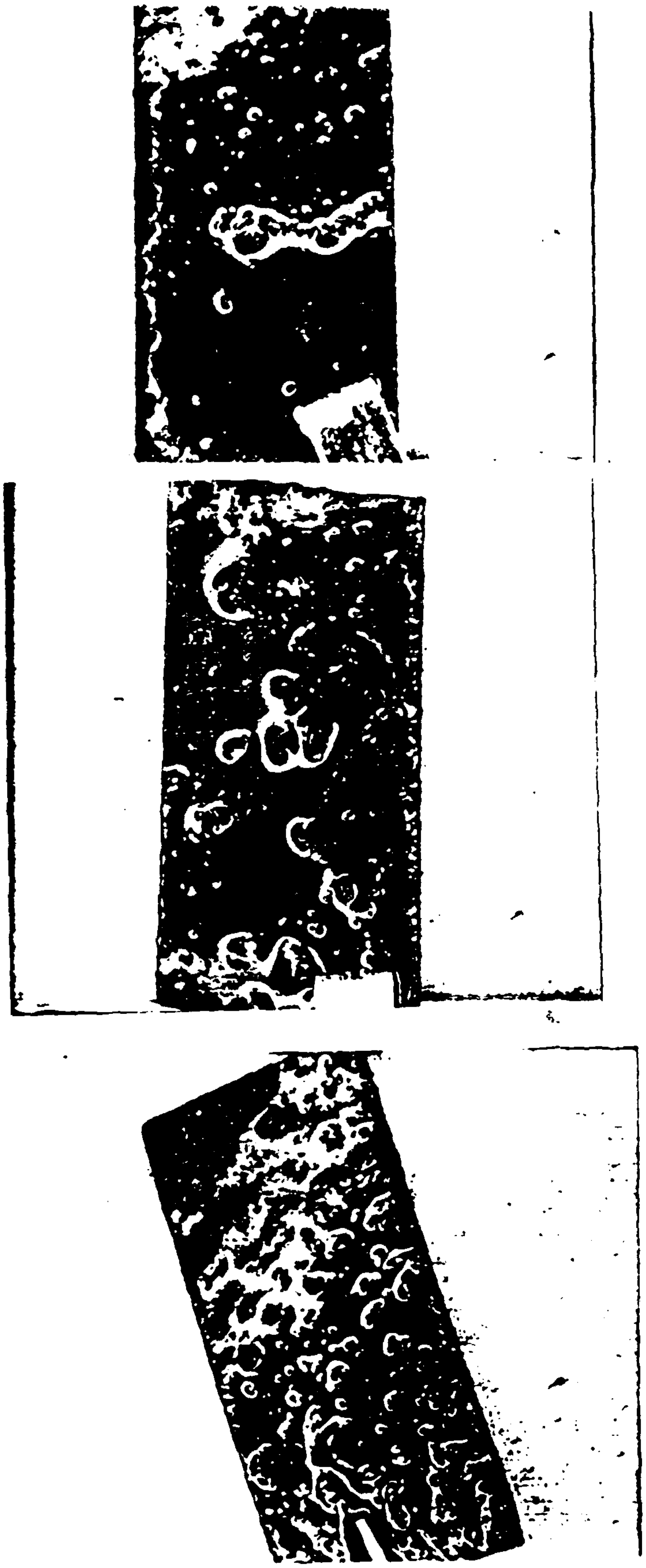
B AND D. PITS ON NICKEL TUBE.




A. EDAX SPECTRUM OF UNEXPOSED NICKEL ALLOY.

B. EDAX SPECTRUM OF NICKEL ALLOY AFTER EXPOSURE TO ESTUARINE WATER FOR 6 MONTHS SHOWING ACCUMULATIONS OF SILICON, SULFUR, AND CHLORINE WITH ELEVATED CONCENTRATIONS OF IRON AND NICKEL.

C. EDAX SPECTRUM OF THE RESIDUAL METAL IN THE BASE OF THE PIT SHOWING NICKEL DEPLETION AND COPPER ENRICHMENT.



**DEPOSITS ON 99CU AFTER FOUR MONTHS EXPOSURE TO SRB CULTURES.**

SURFACE OF 99CU AFTER FOUR MONTHS EXPOSURE TO CULTURE VI. CORROSION PRODUCTS HAVE SLOUGHED FROM SURFACE REVEALING PITTING.

# Minerals in Corrosion Products

| | Bacterial Cultures | | | | | | | Augmented Natural Waters | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI | VII | Gulf of Mexico | Lake Water | Salt Marsh |
| 99Cu | | Low-Chalcocite<br>Digenite<br>Djurleite* | | Low-Chalcocite<br>Digenite*<br>Anilite | | Low Chalcocite<br>High Chalcocite* | | Low-Chalcocite | Low-Chalcocite | Low-Chalcocite |
| 90Cu 10Ni | | Low Chalcocite<br>High Chalcocite<br>Covellite* | | Low Chalcocite<br>High Chalcocite<br>Djurleite* | | | Low-Chalcocite<br>High Chalcocite<br>Djurleite<br>Digenite* | Low-Chalcocite<br>High Chalcocite<br>Djurleite<br>Digenite* | Low-Chalcocite<br>High Chalcocite<br>Djurleite<br>Digenite* | Low-Chalcocite<br>High Chalcocite<br>Djurleite<br>Digenite* |
| 70Cu 30Ni | | | | | | Low Chalcocite<br>Djurleite* | Low Chalcocite<br>Djurleite* | | | |

Formulae

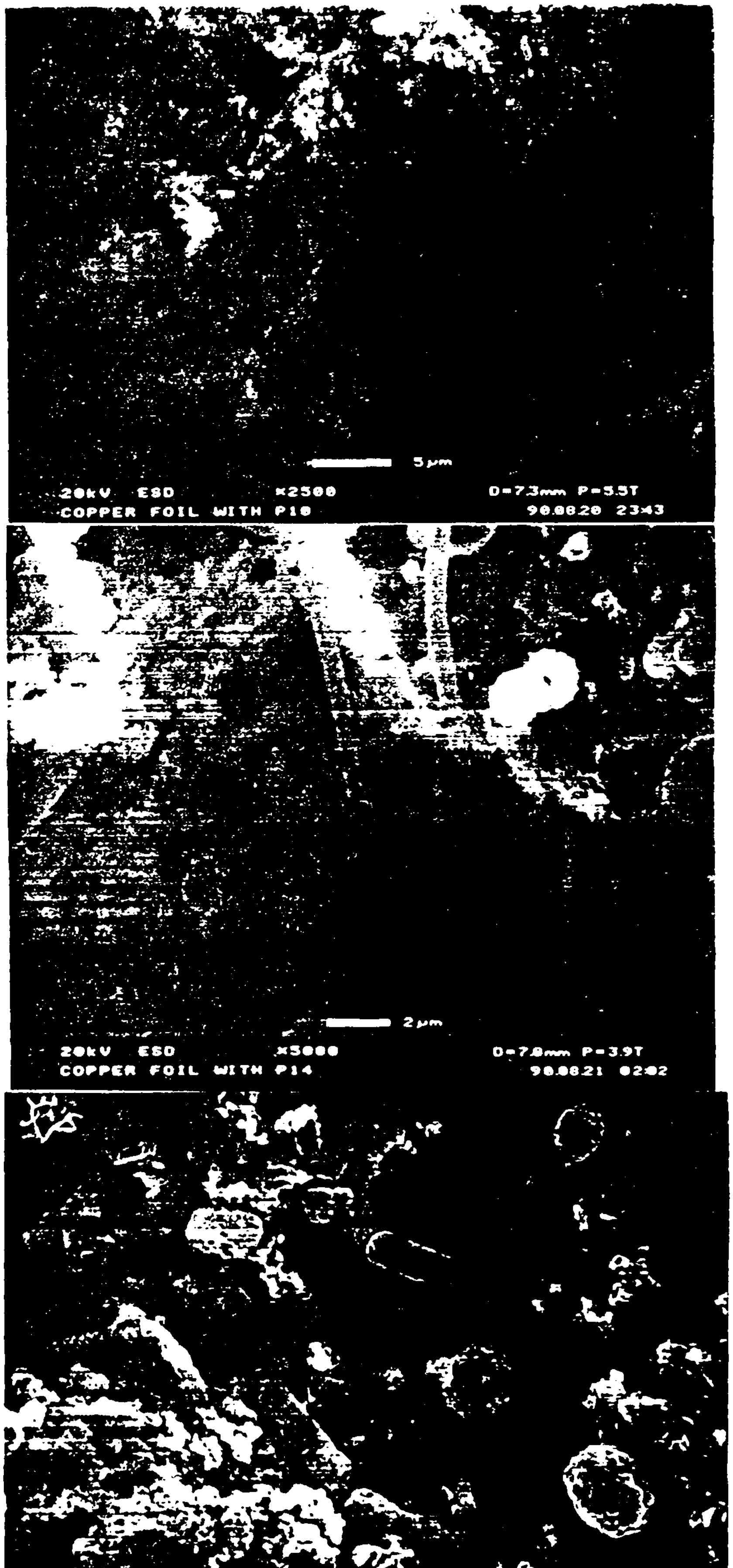
| | |
|---|---|
| Low Chalcocite | $Cu_2S$ |
| High Chalcocite | $Cu_2S$ |
| Digenite | $Cu_9S_5$ |
| Djurleite | $Cu_{1.93}S$-$Cu_{1.97}S$ |
| Anilite | $Cu_7S_5$ |
| Covellite | $CuS$ |

* low concentration

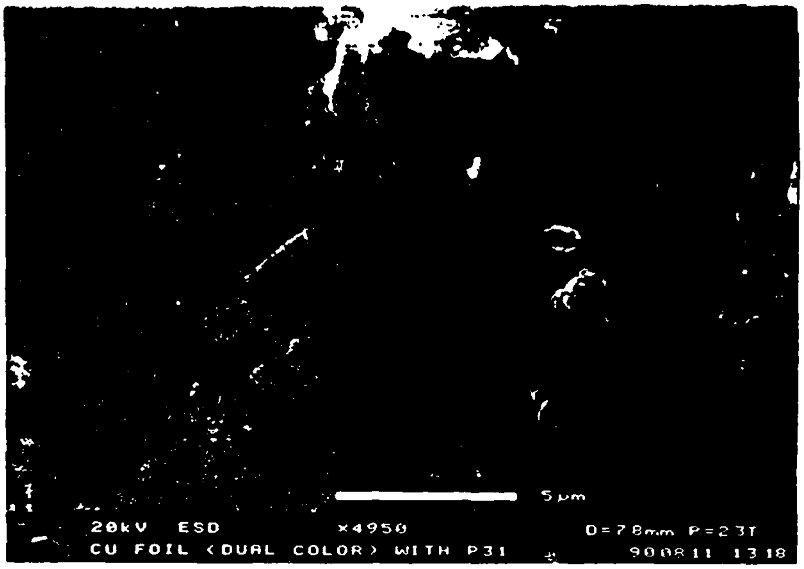
Blanks indicate work that has not been completed a

b

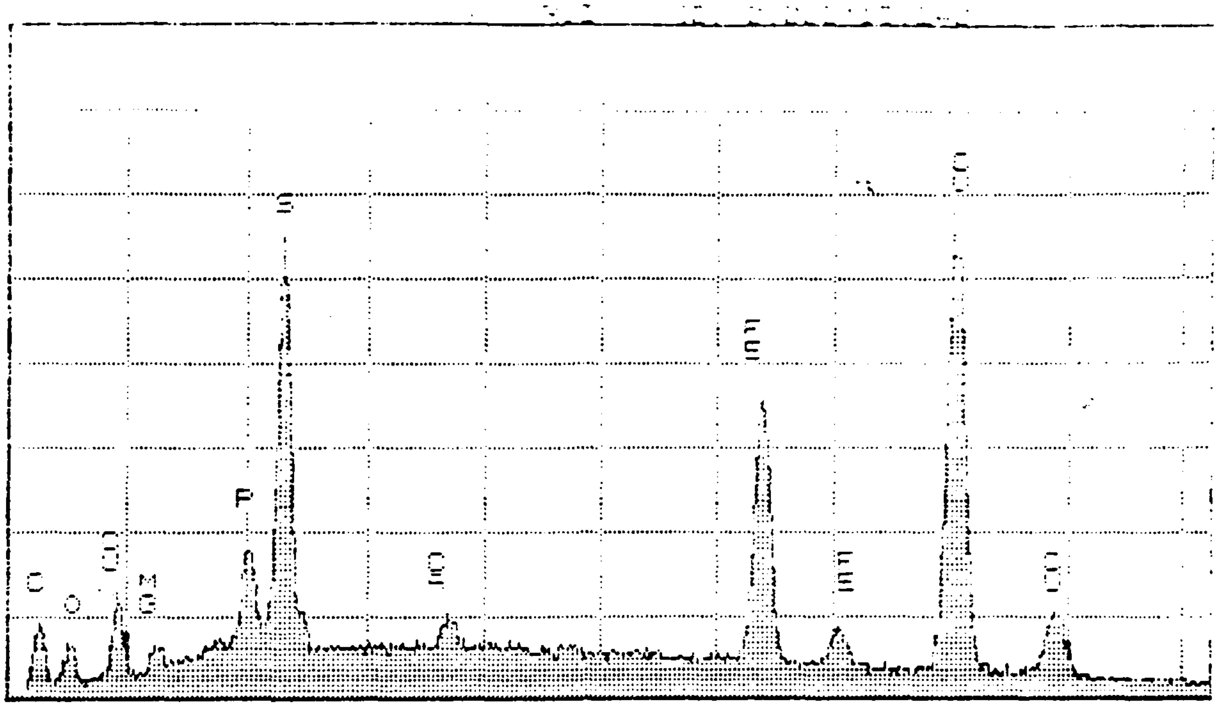
c


5μm
20kV ESD ×2500 D=7.3mm P=5.5T
COPPER FOIL WITH P10 90.08.20 23:43
2μm
20kV ESD ×5000 D=7.8mm P=3.9T
COPPER FOIL WITH P14 90.08.21 02:02
2μm
20kV ESD ×5000 D=8.2mm P=1.7T
COPPER FOIL WITH 492 90.08.20 02:10

d




**BACTERIA ASSOCIATED WITH CORROSION PRODUCTS.**




100 COPPER FOIL WITH I14 FLAT TOP LAYER

SQ: QUANTIFY

OPPER FOIL WITH I14 FLAT TOP LAYER
Standardless Analysis
20.0 KV 62.0 Degrees

Chi-sqd = 1.02

| Element | Rel. K-ratio | Net Counts |
|---|---|---|
| Cu-L | 0.01801 +/- 0.00113 | 1214 +/- 76 |
| Mg-K | 0.00345 +/- 0.00093 | 333 +/- 90 |
| P -K | 0.02056 +/- 0.00203 | 2204 +/- 218 |
| S -K | 0.09776 +/- 0.00284 | 9663 +/- 281 |
| Ca-K | 0.01003 +/- 0.00198 | 822 +/- 162 |
| Fe-K | 0.19403 +/- 0.00568 | 7521 +/- 220 |
| Cu-K | 0.65616 +/- 0.01292 | 14625 +/- 286 |

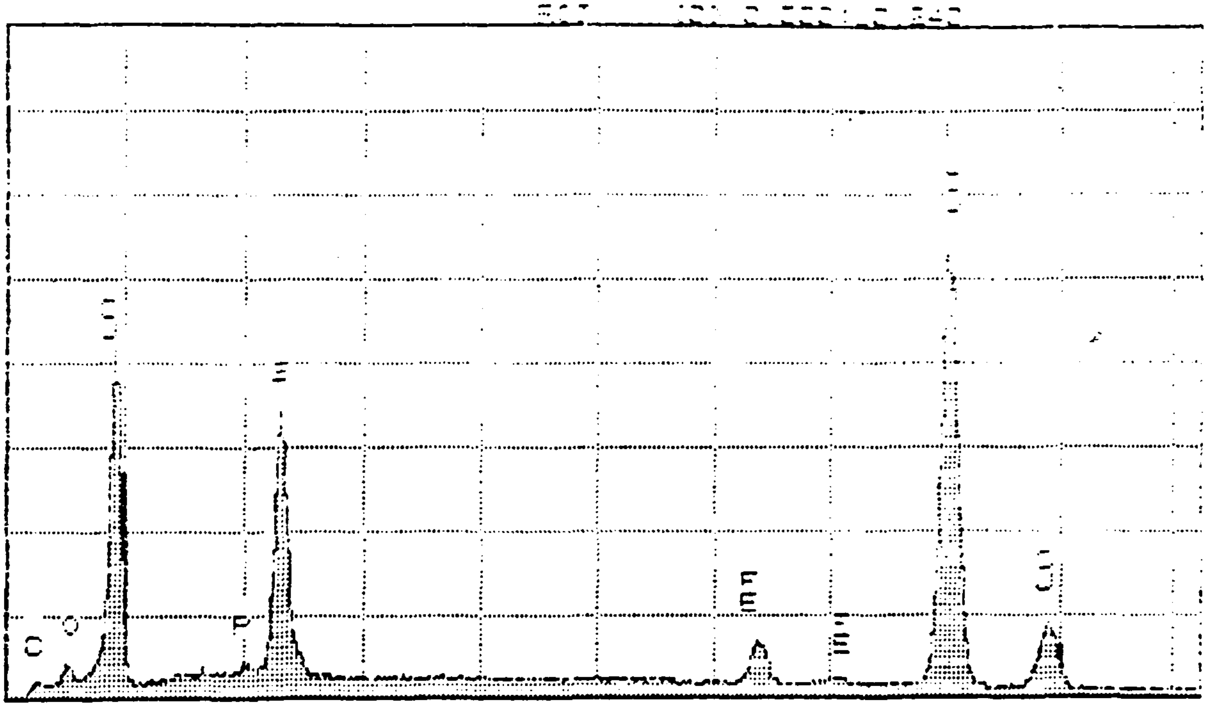
ZAF Correction 20.00 kV 61.96 deg
No.of Iterations = 3

| Element | K-ratio | Z | A | F | Atom% | Wt% |
|---|---|---|---|---|---|---|
| Mg-K | 0.003 | 0.909 | 3.484 | 0.999 | 2.31 | 1.05 |
| P -K | 0.020 | 0.938 | 1.586 | 0.994 | 5.03 | 2.93 |
| S -K | 0.094 | 0.913 | 1.407 | 0.998 | 20.06 | 12.10 |
| Ca-K | 0.010 | 0.919 | 1.109 | 0.985 | 1.29 | 0.97 |
| Fe-K | 0.187 | 1.002 | 1.011 | 0.884 | 15.95 | 16.76 |
| Cu-K | 0.633 | 1.031 | 1.014 | 1.000 | 55.37 | 66.18 |
| | | | | | Total= | 100.00% |

**EDAX SPECTRUM OF 99CU COLONIZED BY CULTURE IV.**

University of Southern

Cursor: 0.000keV = 0 ROI (2) 0.000: 0.000




0.000 VFS = 2048 10.240

100 COPPER FOIL WITH I14 GRANULAR BOTTOM LAYER

Q: QUANTIFY

COPPER FOIL WITH I14 GRANULAR BOTTOM LAYER
Standardless Analysis
20.0 KV 62.0 Degrees

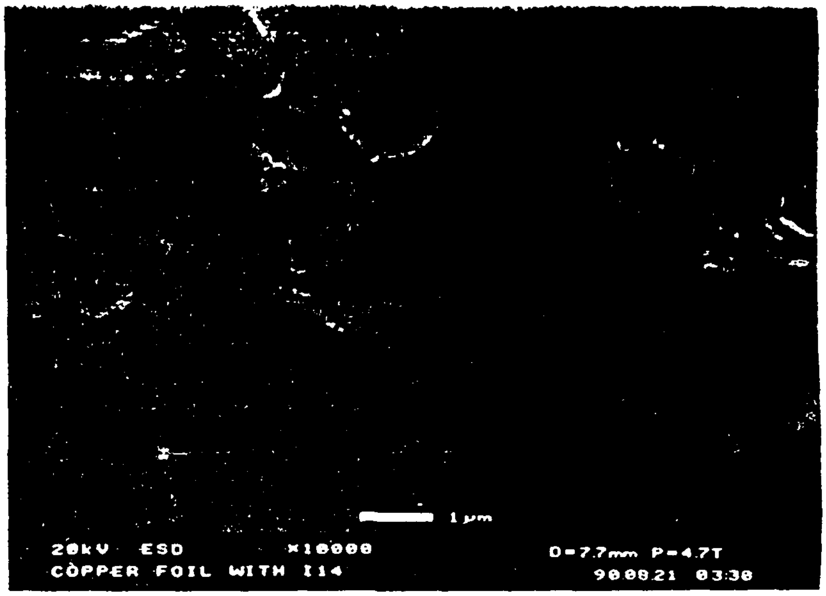
Chi-sqd = 1.16

| Element | Rel. K-ratio | Net Counts |
|---|---|---|
| Cu-L | 0.09590 +/- 0.00160 | 10367 +/- 173 |
| P -K | 0.00259 +/- 0.00111 | 446 +/- 190 |
| S -K | 0.07937 +/- 0.00179 | 12581 +/- 283 |
| Fe-K | 0.04034 +/- 0.00261 | 2508 +/- [illegible]2 |
| Cu-K | 0.78179 +/- 0.00968 | 27941 +/- 346 |

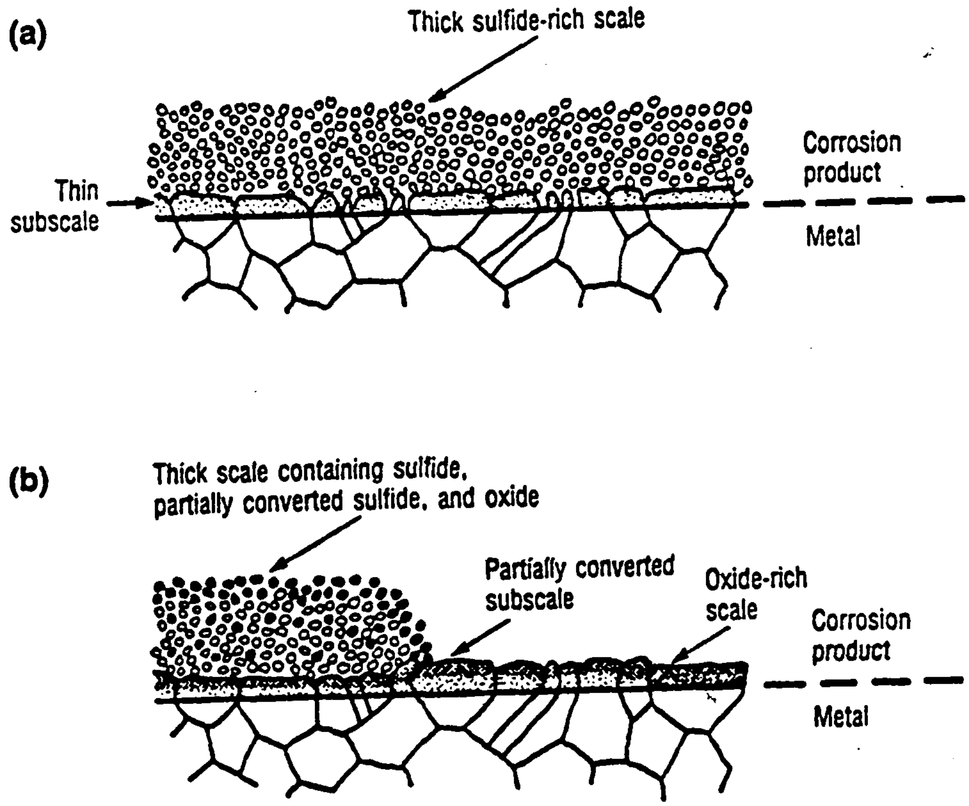
ZAF Correction 20.00 kV 61.96 deg
No.of Iterations = 3

| Element | K-ratio | Z | A | F | Atom% | Wt% |
|---|---|---|---|---|---|---|
| P -K | 0.003 | 0.929 | 1.650 | 1.995 | 0.77 | [illegible] |
| S -K | 0.085 | 0.905 | 1.430 | 1.799 | 19.38 | 10.51 |
| Fe-K | 0.043 | 0.991 | 1.011 | 0.818 | 3.59 | 3.52 |
| Cu-K | 0.832 | 1.019 | 1.004 | 1.000 | 76.26 | 85.14 |
| | | | | | Total= | 100.00% |

**EDAX SPECTRUM OF THE 99CU METAL SURFACE UNDER CULTURE IV.**




ENCRUSTATIONS OF COPPER SULFIDE ALONG BACTERIAL CELL.




**A. SCHEMATIC OF THICK SULFIDE-RICH SCALE FORMING ON COPPER ALLOY (TAKEN FROM SYRETT, 1980).**

**B. SCHEMATIC SHOWING DISRUPTION OF SULFIDE-RICH FILM ON COPPER ALLOY BY THE INTRODUCTION OF AERATED SEAWATER (TAKEN FROM SYRETT, 1980).**