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<sup>298-102</sup> 



Key West, Florida

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### 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<sup>4</sup>-10<sup>5</sup> sulfate-reducing bacteria (SRB) in association with other Pits were irregular in shape, lacking a consistent bacteria. 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 and the specific reactions of the base metals with sulfides pits. 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.

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<sub>1.96</sub>S). Chalcocite (Cu<sub>2</sub>S) as well as traces of covellite (CuS) and digenite (Cu<sub>9</sub>S<sub>5</sub>) were also identified. Djurleite and the high temperature polymorph of chalcocite may be mineralogical fingerprints for the SRB influenced corrosion of copper-containing metals.

## **ANODIC SITES**



Primary Oxide-Forming Reactions 4  $Cu + 0_2$  (adsorbed)  $\rightarrow 2 Cu_2 0$  (cuprite) 2  $Cu + H_2 0 \rightarrow Cu_2 0 + 2H^+ + 2e^-$ 

Primary Oxidation Reactions for  $Cu_2O$  – Covered Metal  $Cu \rightarrow Cu^{++}(aq) + 2e^-$ 

Follow-Up Reactions In Seawater:  $2 \text{ Cu}^{++} + 3 \text{ OH}^- + \text{Cl}^- \rightarrow \text{Cu} (\text{OH})_3 \text{Cl} \downarrow$ 

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

CATHODIC SITES from e<sup>-</sup> anodic sites OH<sup>-</sup> 0<sub>2</sub> **Pre-Reduction Step**  $0_2$  (solution)  $\rightarrow 0_2$  (adsorbed)

Primary Reduction Reaction  $0_2 + H_20 + 4e^- \rightarrow 4 0H^-$ 

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.

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A. EDAX SPECTRUM OF UNEXPOSED NICKEL ALLOY.

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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.



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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.

**Bacterial Cultures** 

# **Minerals in Corrosion Products**

Augmented Natural Waters

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	=	Ξ	≥	>	2	- IIV	Gulf of Mexico	Lake Water	Salt Marsh
Low-Chalcocite Digenite Djurleite*			Low-Chalcocite Digenite* Aniite		Low Chalcocite High Chalcocite*		Low-Chalcocite	Low-Chalcocite	Low-Chalcocite
Low Chalcocite High Chalcocite Covellite*			Low Chalœcite High Chalcocite Djurleite*			Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*
					Low Chalcocite Djurleite*	Low Chalcocite Djurleite*			

Formulae

Low Chalcocite Cu<sub>2</sub>S High Chalcocite Cu<sub>2</sub>S Digenite Cu<sub>9</sub>S<sub>5</sub> Djurleite Cu<sub>1.93</sub>S-Cu<sub>1.97</sub>S Anilite Cu<sub>7</sub>S<sub>5</sub> Covellite CuS

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\* low concentration

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Blanks indicate work that has not been completed

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### BACTERIA ASSOCIATED WITH CORROSION PRODUCTS.

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975571 0 000 eV t 4 T T K28 2 207: 0 202 . . . .. 5 Ξ ויח ġ : ţ \$ F -: ..... - 1 In Ti 8 8 ŝ C •. ,:::**X** 0.000 VFS = 102410.240 100 COPPER FOIL WITH 114 FLAT TOP LAYER SQ: QUANTIFY OPPER FOIL WITH 114 FLAT TOP LAYER Standardless Analysis 20.0 KV 62.0 Degrees Chi-sqd = 1.02ŝ, Rel. K-ratio Net Counts Element 76 0.01801 +/- 0.00113 1214 +/-Cu-L Mg-K 0.00345 +/- 0.00093 333 +/-90 218 P -K 0.02056 +/- 0.00203 2204 +/-S-K 0.09776 +/- 0.00284 9663 +/-281 822 +/-Ca-K 0.01003 +/- 0.00198 162 220 0.19403 +/- 0.00568 7521 +/-Fe-K 286 Cu-K 0.65616 +/- 0.01292 14625 +/-. ZAF Correction 20.00 kV 61.96 deg No.of Iterations = 3F Wt% Ζ Α Atom% Element K-ratio 0.003 0.909 3.484 0.999 2.31 1.05 Ma-K **₽ -**K 0.938 2.93 0.020 1.586 Ø.994 5.03 1.407 S-K 0.094 0.913 0.998 20.06 12.10 1.29 0.97 Ca-K 0.010 0.919 1.109 0.985 15.95 16.76 Fe-K 0.187 1.002 1.011 0.884 55.37 66.18 0.600 Cu-K 1.031 1.014 1.000

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EDAX SPECTRUM OF 99CU COLONIZED BY CULTURE IV.

Tota! = 100.00%

University of Scutherr (lissission) TIE 21-ALG-PC | C0148 Sunson: 0.000kev = 0 👘 F:01 (2) 0.000; 0.000 . : : - -í τ. : ..... ال F Ξ D 1 高興 C Ξ ā. ...... ai a dilla a sui - a s -----10.240 VFS = 2048 0.000 COPPER FOIL WITH 114 GRENULER BOTTOM LEVER 100 D: QUANTIFY JOPPER FOIL WITH 114 GRANULAR BOTTOM LAYER Standardless Analysis 20.0 KV 62.0 Degrees ÷. Chi-sad = 1.16Re). M-matio Net Counts 2 emant 10367 +/-173 0.09590 +/- 0.00160 CL-L 190 0.00259 +/- 0.00111 445 +/- $\mathfrak{D} = \mathcal{H}_{\mathcal{L}}$ 253 0.07937 +/- 0.00179 12581 +/-3 -K 2508 +/-**26**2 Fe-IC 0.04034 +/- 0.00261 346 Cu-K 0.78177 +/- 0.00968 27941 +/-TAP Connection 20.00 KV 51.95 dee No.of Iterations = 3 F Atom% WEX. Z A Element K-natio 4.47 0,929 1.650 0.905 0.77 0.003 10.52 9.905 1.430 19.33 0.085 ÷ +< 0,043 0.991 0.318 3.59 0.52 1.011 *≣ ⊒-* K 76.26 85.14 0.832 1.019 1.004 1.000

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

Tetal= 100.00%

Cu∸K



# ENCRUSTATIONS OF COPPER SULFIDE ALONG BACTERIAL CELL.

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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).