R AD-A254 467 GE

Form Approved
OBM No. 0704-0188

2

1. Agency Use Only *(Leave blank).*

2. Report Date.
1991

3. Report Type and Dates Covered.
Final - Journal Article

4. Title and Subtitle.
Production of Sulfide Minerals by Sulfate-Reducing Bacteria During Microbiologically Influenced Corrosion of Copper

5. Funding Numbers.

Contract	
Program Element No.	0601153N
Project No.	03102, 00101
Task No.	310, 109
Accession No.	DN094463, DN250058
Work Unit No.	11331A, 93330F

DTIC
ELECTE
AUG 2 5 1992
S C D

6. Author(s).
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7. Performing Organization Name(s) and Address(es).

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

8. Performing Organization Report Number.
JA 333:011:91

9. Sponsoring/Monitoring Agency Name(s) and Address(es).

Naval Oceanographic and Atmospheric Research Laboratory, Basic Research
Management Office, Stennis Space Center, MS 39529-5004
and Naval Coastal Syatems Center, Panama City, FL 32407-5000

10. Sponsoring/Monitoring Agency Report Number.
JA 333:011:91

11. Supplementary Notes.
Published in CORROSION
*Naval Coastal Systems Center, Panama City, FL 32407-5000, **Naval Surface Warfare Center, Silver Spring, MD 20903-5000

12a. Distribution/Availability Statement.
Approved for public release; distribution is unlimited.

12b. Distribution Code.

13. Abstract *(Maximum 200 words).*

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421485 5pg

92-23533

92 8 24 039

14. Subject Terms.
Biofouling, corrosion, biodeterioration, electrochemistry

15. Number of Pages.
4

16. Price Code.

17. Security Classification of Report.
Unclassified

18. Security Classification of This Page.
Unclassified

19. Security Classification of Abstract.
Unclassified

20. Limitation of Abstract.
SAR

Production of Sulfide Minerals by Sulfate-Reducing Bacteria During Microbiologically Influenced Corrosion of Copper☆

M.B. McNeil, J.M. Jones,** and B.J. Little****

ABSTRACT

Mineralogical data, thermodynamic stability (Pourbaix) diagrams, and the simplexity principle for precipitation reactions were used to evaluate corrosion product mineralogy on copper alloys exposed to sulfate-reducing bacteria. The formation of copper sulfides as corrosion products in natural surface environments is suggestive of microbiologically influenced corrosion. Sulfide corrosion products other than chalcocite (Cu_2S) indicate that reactions within a biofilm induced corrosion.

KEY WORDS: microbiologically influenced corrosion, sulfate-reducing bacteria, corrosion product mineralogy, copper

INTRODUCTION

Microbiologically influenced corrosion (MIC) can be divided into two subsets: (1) microbiologically intermediated corrosion caused by chemical intermediates produced by microorganisms which are not in direct contact with the corroding surface and (2) microbiologically induced corrosion caused by chemical species generated within a biofilm at a metal/biofilm interface. Microbiologically intermediated and induced corrosion of copper-containing metals in waters <10 m or in shallow land burial (–20 and 35°C) will be addressed in this paper. Peat bogs, volcanic environments, acid mine waters, and artificial environments including chemical process equipment have been excluded. Since all sulfides in the environments defined in this paper are biological in origin, sulfide corrosion of copper was considered to be either intermediated or induced by microbial processes. It is the purpose of this paper to differentiate microbiologically induced corrosion by identifying minerals that form only in the presence of a biofilm containing sulfate-reducing bacteria (SRB).

METHODS AND MATERIALS

Coupons (1 by 3 cm) of 99Cu, 90Cu:10Ni, and 70Cu:30Ni were exposed for four months to seven mixed cultures of facultative and obligate anaerobic bacteria containing SRB and to three natural waters

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☆ Submitted for publication November 1990; in revised form, April 1991.

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Reprinted from CORROSION, Vol. 47, No. 9, pp. 674-677 (1991) September

from the Gulf of Mexico, a lake, and a salt marsh. Isolation, culturing, and maintenance techniques have been reported elsewhere.[1] Uninoculated controls were maintained under identical conditions. Surface topography and chemistry were documented using an Electroscan(1) model E-30 environmental scanning electron microscope and a Tracor Northern(2) model 5502 energy-dispersive x-ray spectrometer (ESEM/EDAX). Coupons were removed from culture medium, washed through a series of salt water/distilled water washes, and examined directly from distilled water. X-ray diffraction patterns of the corrosion products were measured using copper $k\,\alpha$ radiation in a Phillips(3) model XRG 3100 x-ray diffraction system and interpreted with an APD 3720 Mod 3 data analysis system, verified by manual indexing. Mineral patterns of the Joint Committee on Powder Diffraction(4) were used both in software and manual indexing.

RESULTS

All copper-containing metals exposed to SRB (laboratory cultures and natural waters) were covered with black, porous, sulfur-containing corrosion products. Controls showed little corrosion and no surface-bound sulfides. Corrosion products on 99Cu were consistently nonadherent, while corrosion products on 90Cu:10Ni and 70Cu:30Ni specimens were adherent. Corrosion product mineralogy is summarized in Table 1. Primary corrosion products were independent of culture type or source. Type and amount of minor corrosion products and corrosion rate varied among cultures and metals. Diffraction patterns from 99Cu specimens indicated that corrosion product layers were primarily monoclinic chalcocite, with minor amounts of other minerals, including digenite (Cu_9S_5). Diffraction patterns from 90Cu:10Ni and 70Cu:30Ni specimens indicated layers of monoclinic chalcocite, hexagonal chalcocite (stable above 103°C), and djurleite ($Cu_{1.93}S$–$Cu_{1.97}S$). Spionkopite ($Cu_{39}S_{28}$), a rare mineral not previously synthesized, appeared occasionally as a minor corrosion product on both 99Cu and copper-containing alloys.

Cocci, bacilli, and filamentous bacteria were documented throughout the corrosion layers with the ESEM (Figure 1). Sulfide minerals precipitated along cell walls (Figure 2), contributing to the observed microporosity of the surface-bound biogenic sulfides.

DISCUSSION

Figure 3 shows a copper-sulfur stability diagram for 10^{-2} M total sulfide incorporating thermodynamic data for chalcocite and covellite (CuS).[2] A 10^{-2} M sulfide concentration is three to five orders of magnitude above concentrations reported for bulk seawater,[3] but can be achieved by SRB within biofilms.[4] The upper hatched parallelogram represents acidity/redox conditions found in near-surface waters.[5] The lower (oppositely hatched) parallelogram represents conditions existing in natural environments but not characteristic of near-surface waters. The pH limits are those found in natural bulk waters.

If surface bulk water is near equilibrium with regard to reduced sulfides, the diagram indicates that all sulfiding corrosion must be microbiologically induced. In deep water, it is possible to form chalcocite, but not covellite, by intermediated corrosion. This observation agrees with experimental observations that despite the ubiquity of sulfate in surface waters, sulfating corrosion of copper was observed only when SRB were absent or inactive and chalcocite was usually the primary corrosion product for pure copper.[6-8]

Corrosion in waters containing sulfates and bulk sulfide concentrations below detection limits (i.e., SRB-induced corrosion) has been studied since the 19th century.[9-11] Baas-Becking and Moore[11] reported digenite, monoclinic chalcocite (the polymorph stable below 103°C), and covellite as corrosion products of SRB-induced corrosion under laboratory conditions. They reported that chalcocite could not be prepared abiotically at room temperature and conjectured that the initial product of SRB-induced corrosion was digenite, which altered to other minerals. Digenite, monoclinic chalcocite, covellite, and djurleite have been found in field corrosion studies. Djurleite, unlike other sulfides, has been reported to provide corrosion protection.[6]

Three significant experimental observations for copper-containing materials exposed to SRB are as follows: (1) the absence of detectable amounts of covellite, (2) the formation of chalcocite in thick, porous, friable, nonadherent films on 99Cu at room temperature, and (3) the formation of hexagonal chalcocite on Cu:Ni alloys. Covellite, a characteristic corrosion product in long-term field studies, is difficult to produce with small electrolyte to surface area ratios in short times.

Hexagonal chalcocite is metastable at room temperature. Its presence can be understood by using the simplexity principle.[12] Crystallization from solutions containing cations which may substitute for the principal cation in a mineral favors the formation of high-entropy structures, typically the high-temperature polymorphs, including hexagonal chalcocite. Djurleite, present in small amounts on 99Cu, was a major corrosion product on copper-nickel alloys. Formation of djurleite may be stabilized by nickel ions. This hypothesis has not been evaluated. Alternatively, its formation may reflect different sulfidation kinetics.[13]

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(1) Electroscan, 66 Concord St., Wilmington, MA.
(2) Tracor Northern, Inc., Middleton, WI.
(3) Phillips Electronics Co., Eindhoven, Netherlands.
(4) American Society for Testing and Materials (ASTM), Philadelphia, PA.

TABLE 1

Minerals in Corrosion Products(A)

	Bacterial Cultures							Natural Waters		
	I	II	III	IV	V	VI	VII	Gulf of Mexico	Lake Water	Salt Marsh
99Cu	Low chalcocite Digenite (C)	Low chalcocite Digenite	Low chalcocite Djurleite(B)	Low chalcocite Digenite(B) Spionkopite(B)		Low chalcocite Digenite	Low chalcocite Djurleite(B)	Low chalcocite	Low chalcocite	Low chalcocite
90Cu 10Ni	Low chalcocite Djurleite	Low chalcocite High chalcocite Covellite(B) Digenite(B)	Low chalcocite Spionkopite(B) (C)	Low chalcocite High chalcocite Djurleite(B)	Low chalcocite High chalcocite Djurleite	Low chalcocite Geerite	Low chalcocite High chalcocite Djurleite Digenite(B)	Low chalcocite High chalcocite Djurleite Digenite(B)	Low chalcocite High chalcocite Djurleite Digenite(B)	Low chalcocite High chalcocite Djurleite Digenite(B)
70Cu 30Ni						Low chalcocite High chalcocite Djurleite Anilite(B)	Low chalcocite Djurleite	(C)	Low chalcocite High chalcocite Djurleite	Low chalcocite High chalcocite Djurleite

(A)Formulae:

Low chalcocite	Cu_2S
High chalcocite	Cu_2S
Digenite	Cu_9S_5
Djurleite	$Cu_{1.93}S\text{-}Cu_{1.97}S$
Anilite	Cu_7S_4
Spionkopite	$Cu_{39}S_{28}$
Covellite	CuS
Geerite	Cu_8S_5

(B)Very low concentration.

(C)Pattern has many poorly defined peaks.

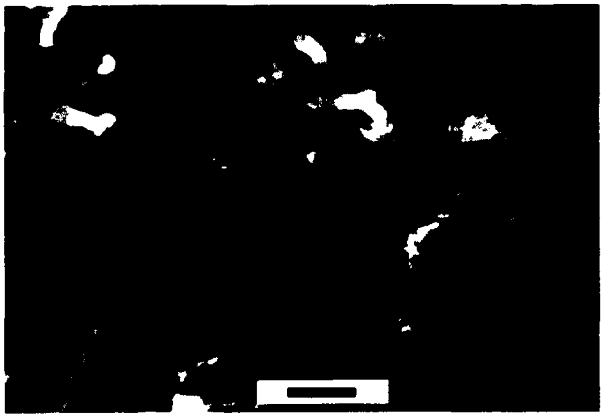

FIGURE 1. *Bacteria associated with corrosion products.*

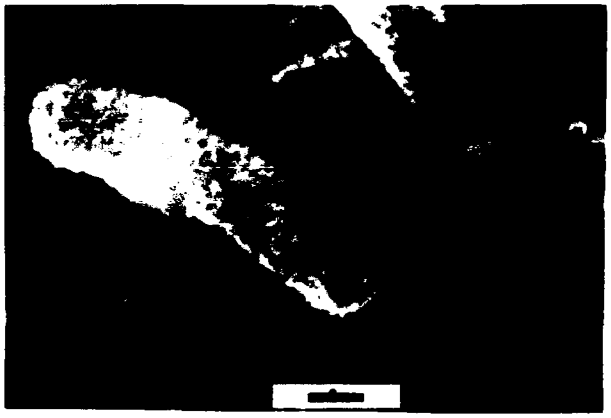

FIGURE 2. *Encrustations of copper sulfide along cell wall.*

CONCLUSION

In near-surface waters, the formation of thick, nonadherent layers of chalcocite or the formation of hexagonal chalcocite is indicative of SRB induced corrosion of copper and copper alloys.

ACKNOWLEDGMENTS

This work was funded by the Office of Naval Research (Codes 1123MB and 121D), Program Element 61153N through the NOARL Defense Research Program and NAVCOASTSYSCEN (NCSC) internal research

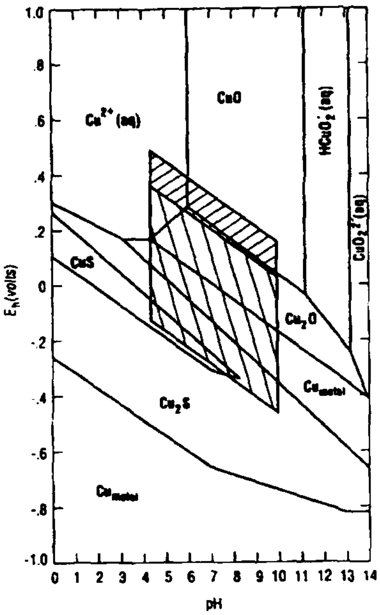

FIGURE 3. *Thermodynamic stability diagram for copper in fresh water with parallelograms bounding natural environmental conditions. Total reduced sulfide = 10^{-2} M; total dissolved copper ≈ 10^{-6} M.*

funds. The authors thank Dr. David Mohr (NCSC) and Robert Pope (University of Southern Mississippi) for technical assistance. NOARL Contribution No. 333:011:91.

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