MICROBIOLOGICALLY INFLUENCED CORROSION IN THE NATURAL GAS INDUSTRY

ANNUAL REPORT (January 1989 - December 1989)

Prepared by

Dr. Daniel H. Pope Bioindustrial Technologies, Inc. P.O. Box 323 Grafton, NY 12082

Dr. Henry C. Aldrich Institute of Food & Agricultural Sciences University of Florida Gainesville, FL 32611 Dr. David C. White Institute of Applied Technology University of Tennesseee 10515 Research Drive Knoxville, TN 37932

Dr. Danny R. Jackson Radian Corporation P.O. Box 201088 Austin, TX 78720-1088

Dr. David R. Boone Oregon Graduate Center 19600 NW Von Neumann Drive Beaverton, OR 97006-1999

DCN 90-263-031-02

FOR
GAS RESEARCH INSTITUTE
Contract No. 5088-260-1747

GRI Project Managers James R. Frank Bioengineering

Thomas M. Steinbauer Transmissions Operations Research

GRI DISCLAIMER

LEGAL NOTICE This report was prepared by Radian Corporation as an account of work sponsored by the Gas Research Institute (GRI). Neither GRI, members of GRI, nor any person acting on behalf of either:

- a. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- b. Assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

<u> 50272 - 101</u>							
REPORT DOCUMENTATION PAGE	1. REPORT NO. GRI 90-0237	2	PB91-130328				
4. Title and Subtitle			S. Report Date				
Microbiologically In:	fluenced Corrosion in	the Natural Gas	July 1990				
Industry			•				
7. Author(s) D.H. Pope, D	.C. White, H.C. Aldric	ch, D.R. Jackson,	8. Performing Organization Rept. No.				
D.R. Boone		•	DCN: 90-263-031-01				
9. Performing Organization Name a	nd Address		10. Project/Task/Work Unit No.				
Radian Corporation			\				
P.O. Box 201088			11. Contract(C) or Grant(G) No.				
Austin, Texas 78720-	1088		(c) 5088-260-1747				
nabelity longs (1)			അ				
12. Sponsering Organization Name	and Address		13. Type of Report & Period Covered				
Gas Research Institu	te		Annual Report				
8600 West Bryn Mawr			(Jan.1989-Dec. 1989)				
Chicago, Illinois 600			14.				

15. Supplementary Notes

16. Abstract (Limit: 200 words)

This report presents the results of a continuing program funded and managed by the Gas Research Institute to investigate microbiologically influenced corrosion (MIC) in the natural gas industry.

The program consists of four phases. In Phase I, the objective was to develop methods of defining MIC and to test assumptions about MIC which were the basis for operating protocols developed by industry and the research community. Initial investigations demonstrated that MIC results from the activities of a microbial community rather than just sulfate reducing bacteria (SRB's). A metallurgical "fingerprint" for MIC was discovered in field samples and reproduced in the laboratory. Test kits and a field guide for identifying MIC were developed for use by gas industry personnel. The Phase II objective was to determine whether existing methods of controlling internal MIC were effective and how treatments could be improved. Protocols and sidestream test devices were developed to assess whether internal MIC was a problem and which mitigation strategies were effective. Phase III studies are examining external corrosion and investigating mechanisms in more detail. Models are being used to develop testable predictions about corrosion processes. Phase IV will focus on the development of new detection, prevention, and mitigation strategies.

17. Document Analysis a. Descriptors

Natural Gas Corrosion Sulfate-reducing bacteria Pitting

b. Identifiers/Open-Ended Terms

Biocorrosion Microbiologically-influenced corrosion

Field 6. Biological and Medical Sciences/Microbiology

Field 7. Chemistry		
8. Availability Statemen:	19. Security Class (This Report)	21. No. of Pages
•	Unclassified	118
Unlimited Distribution	20. Security Class (This Page)	22. Price
	Unclassified	

See Instructions on Reverse

OFTIONAL FORM 272 (4-7) (Formerly NTIS-35)

RESEARCH SUMMARY

Title

Microbiologically Influenced Corrosion in the Natural Gas Industry

Radian Corporation

GRI Contract Number: 5088-260-1747

Principal Investigator

Contractor

D.H. Pope, D.R. Jackson, D.C. White, H.C. Aldrich, and D. R. Boone

Report Period January 1989 - December 1989

Annual Report

Objective

Determine the nature of MIC in the natural gas industry and develop improved methods of detection and treatment.

Technical Perspective Researchers estimate that corrosion costs all types of industry up to \$126 billion annually. Of this, it is estimated that 10 to 30% results from microbiologically influenced corrosion (MIC). Often the cost of MIC is greater than these numbers reflect because most MIC consists of pitting which results in pipe or other equipment failure. Recognizing the seriousness of this problem in several other industries, the Gas Research Institute (GRI) initiated a research program to investigate MIC in the natural gas industry.

Results

The first phase of the program provided biological, chemical, and metallurgical "fingerprints" of MIC. Studies showed that MIC was associated with internal deposits, pitting corrosion, a type of corrosion which can result in through-wall failures of equipment. The work also demonstrated that MIC results from the activities of a microbial community rather than a single type of bacteria. Specific field test kits and a field guide for investigation of MIC were developed for use by gas industry personnel.

The second phase focused on internal MIC. Results showed that many treatment protocols are ineffective. Field surveys showed that sometimes "hot spots" in systems can contribute to the contamination of downstream operating systems. Treatment strategies targeting these spots have been applied to some field sites and appear to work well.

The third phase is focusing on external MIC and the detailed mechanisms associated with MIC so that new detection and mitigation approaches can be developed.

Technical Approach In Phase I, initial field investigations demonstrated that the microbial community associated with cases of MIC of gas pipelines was complex and dominated by organic acid-producing bacteria. Laboratory experiments were conducted to determine the extent of growth and acid production by MIC community members when growing on carbon steel coupons singly or in combination. The results clearly show that the slime formers, APB, and SRB grew much better and produced more organic acids when grown as a community. It was also determined that the metallurgical 'fingerprint' could be reproduced by either adding a microbial community, organic acids, or hydrochloric acid in laboratory experiments. A database was developed from these field site tests and laboratory experiments.

Phase II involved monitoring of gas facilities over a two-year period. Chemical, biological, and operational factors were studied to determine if significant relationships existed between these factors and MIC severity. Available test protocols and mitigation strategies were assessed and determined to not always be effective. In response, new protocols and sidestream test devices were developed. Targeted treatment strategies were applied at some field sites. These protocols will be published as Field Guides.

Studies in Phase III are focused on both laboratory and field investigations on the effects of MIC on coatings, cathodic protection, and metallurgy. Laboratory tests of mechanisms are underway to examine the effects of environmental gradients and conditions under a corrosion nodule. These studies will be useful in the development of new detection, prevention, and mitigation strategies.

Phase IV will focus on the development of methods for detection and mitigation. Mitigation approaches will be investigated which are more effective and do not require large chemical inputs.

Project Implications

This program on microbiologically influenced corrosion (MIC) has changed the thinking of much of the research community and industry on the role bacteria play in corrosion processes. It has also led to methods of detection and mitigation which are now widely used by the gas industry (and increasingly by other industries as well). This program is one of the few research efforts focused primarily on carbon steel rather than stainless steel or copper/aluminum alloys.

The current focus of the program is to finish documenting the results on internal mitigation developed in Phase II as useable field guides and videotapes. The Phase III activities are well underway and focus on external corrosion and a more detailed examination of how both microbial and 'classical' corrosion mechanisms are related with environmental factors. This should result in the development of better detection and mitigation approaches than those currently available.

The GRI MIC program will continue to include field and laboratory studies. It is recognized that field studies are essential to ensure that the results of laboratory studies are relevant and to facilitate the transfer of new methods to gas industry operating personnel which can be used in 'real-world' operating conditions. Laboratory studies are needed to interpret field data and develop new detection and mitigation approaches.

A crucial aspect of this program is the transfer of information and technology from the research team to the gas industry. This will be accomplished through refereed publications, field guides, videotapes, workshops, and the MIC Users Group which has guided this program. In fact, without the day to day participation in the program by gas industry corrosion control experts in the field (and laboratory) the progress which has been made in understanding and mitigating MIC in the gas industry would have been severely limited.

GRI Project Manager James R. Frank Manager, Bioengineering

TABLE OF CONTENTS

Section	<u>n</u>	<u>Page</u>												
1.0	EXECUTIVE SUMMARY	1-1												
2.0	BACKGROUND INFORMATION ON MIC													
	2.1 MIC Mechanisms	2-2												
	2.1.1 Cathodic Depolarization	2-2												
	2.1.2 Formation of Occluded Area on Metal Surface	2-4												
	2.1.3 Fixing the Anodic Sites	2-4												
	2.1.4 Under Deposit Acid Attack	2-5												
	2.2 Monitoring for MIC	2-5												
	2.2 Monitoring for Mic													
	2.2.1 Microscopic Techniques	2-7												
	2.2.2 Fluorescently Labeled Antibodies	2-7												
	2.2.3 Culture Methods	2-9												
	2.2.4 On-line Monitoring	2-9												
	2.3 Prevention and Treatment of MIC	2-11												
3.0	SUMMARY OF WORK PERFORMED DURING PHASE 1 (1986-1988)	3-1												
	3.1 Extent of MIC in the Gas Industry	3-1												
	3.2 Roles of Microorganisms in MIC	3-2												
	3.3 Metallurgical Picture for MIC	3-3												
	3.4 Importance of Chemical Factors in MIC Processes	3-5												
		3-11												
		3-11												
		3-11 3-15												
	3.7 Monitoring Methods for MIC	3-15												
4.0	RESULTS OF PHASE II	4-1												
	4.1 Results of Laboratory Tests of Mitigation Measures	4-1												
	4.2 Results of Field Tests of Mitigation Measures	4-5												
	4.3 Final Results of Long-Term Monitoring of Systems for													
	Factors Contributing to MIC Susceptibility	4-10												
		4-19												
5.0	RESULTS OF PHASE III	5-1												
	5.1 Use of Sidestream Devices and Field Laboratory Systems													
	in Determining Effects of Metallurgical Features and													
	Chemical Factors on MIC	5-1												
		5-13												
		5-23												
	5.4 Tests of Electrochemical Methods for Investigating and	2.3												
		5-26												
		5-31												
	5.6 Technology Transfer	5-38												
6.0	DISCUSSION AND CONCLUSIONS	6-1												

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>on</u>																	<u>Page</u>
7.0	FUTUR	E PLANS FOR	THE MIC	P	RO	GR	AM											7-1
	7.1	Field Stud:	ies															7-1
	7.2	Laboratory	Studies															7-3
	7.3	Monitoring	Methods															7-3
	7.4	Mitigation	Measure	s														7-4
	7.5	Technology	Transfe	r	•	•				•	•	٠		•	•	•		7-4
8.0	REFER	ENCES			_													8-1

LIST OF FIGURES

Figure		<u>Page</u>
1-1	Major milestones and deliverables	1-4
2-1	Diagram of proposed cathodic depolarization model for acceleration of corrosion by sulfate-reducing bacteria	2-3
2-2	Photomicrograph of MIC community growing on a steel coupon after several days exposure to city water, stained with fluorescein isothiocyanate, and observed using an epifluorescence microscope (1600x magnification)	2-8
2-3	Photomicrograph of sulfate-reducing bacteria (SRB stained with fluorescent antibodies specific to sulfate-reducing bacteria (SRB-FA) and observed using an epifluorescence microscope (1600x magnification)	2-8
3-1	Internal failure located in the bottom of a pipe located in a low spot of a gathering/transmission pipeline in the Southwest where low pH water containing acid-producing bacteria was collected	3-6
3-2	External corrosion on a transmission pipeline in the Midwest exhibiting large pits containing striations and tunnels which is characteristic of the MIC metallurgical picture	3-6
3-3	Discrete pits on the external surface of a transmission pipeline in the Midwest containing black corrosion deposits	3-7
3-4	Same pits after removing deposits for microbiological and chemical analyses and cleaning with water and a nylon brush	3-7
3-5	Photomicrograph of "tunnels" in a pit from a carbon steel pipe (20x magnification)	3-8
3-6	Scanning electron microscope (SEM) photomicrograph of tunnels in a pit in a carbon steel gas pipeline oriented in the direction of rolling of the steel (100x magnification)	3-8
3-7	Coupons prepared from new and old types of gas pipeline and exposed to 10,000 ppm acetic acid with or without 10,000 ppm added chloride	3-10
3-8	Example of severely disbonded coal-tar coating with localized external corrosion on a transmission pipeline in the eastern United States	3-12
	DIDGITUG IN LUG CASICIN UNILCU DIALES	J-12

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
3-9	Localized external corrosion with deposits, pits, craters and general attack found under the disbonded coating in Figure 3-8	3-12
3-10	Growth in fluids and on surfaces of MIC community on various coating materials immersed in a minimal medium solution	3-13
3-11	MICKIT III test kit for culturing bacteria present in corrosion, water, and soil samples	3-16
3-12	Sidestream test system at an onshore processing facility for gas produced offshore	3-17
4-1	Recolonization of acid-producing and sulfate-reducing bacteria on pipe surfaces during a seven-hour period following treatment with glutaraldehyde at a concentration of 100 ppm	4-6
4-2	Effect of intermittent glutaraldehyde treatment on the surface populations of acid-producing and sulfate-reducing bacteria in carbon steel spool pieces	4-7
4-3	Effect of temperature on microorganisms on the surface of carbon steel spool pieces in a field sidestream device	4-8
4-4	Effect of heat treatment on MIC bacteria in water and hydrocarbon phases	4-9
4-5	Diagram of offshore gas production, gathering, and transmission system studied in GRI program	4-11
4-6	Microbial levels in pipeline system A	4-12
4-7	Microbial levels in pipeline system C	4-13
4-8	Microbial levels in pipeline system D before treatment	4-14
4-9	Example of the distribution of MIC bacteria in water and hydrocarbon phases in an offshore production separator	4-16
4-10	System shown in Figure 4-8 after treatment	4-20
5-1	Block diagram of system used in biocide and corrosion inhibitor tests	5-2
5-2	Levels of viable SRB and APB in fluids and on surfaces of coupons in test system 1, control (non-treated) test loop	5-3

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
5-3	Levels of viable SRB and APB in fluids and on surfaces of coupons in test system 1, corrosion inhibitor treated test loop	5-4
5-4	Levels of viable SRB and APB in fluids and on surfaces of coupons in test system, glutaraldehyde treated test loop	5-5
5-5	Scanning electron microscope (SEM) photomicrograph of a cross-section through a nodule on a X-42 grade carbon steel coupon (125x magnification)	5-7
5-6	Same as Figure 5-5 (250x magnification)	5-7
5-7	SEM photomicrograph of a cross-section through a nodule on a B grade carbon steel coupon (125x magnification)	5-8
5-8	Same as Figure 5-7 (250x magnification)	5-8
5-9A	Light micrograph of bacteria on surface of coupon in test 1, control loop	5-10
5-9B	Transmission electron micrograph of section through the edge of plastic removed from coupon surface in Figure 5-9A	5-10
5-10A	Light micrograph of surface of plastic replica of coupon from a test 1, corrosion inhibitor-treated loop	5-11
5-10B	As in Figure 5-9B, except that coupon was taken from a test 1, corrosion inhibitor-treated loop	5-11
5-11A	As for Figures 5-9A and 5-10A, this light micrograph shows a test 1, glutaraldehyde-treated loop	5-12
5-11B	As for Figure 5-9B, except that the coupon was from test 1, glutaraldehyde-treated loop	5-12
5-12	SEM of bacteria on coupon 5 hours after exposure	5-15
5-13	SEM view of bacterial colony (arrowhead) on coupon after 8 hours of exposure	5-15
5-14	SEM view of corrosion on surface of coupon exposed for 24 hours	5-16
5-15	SEM of large corrosion pit on coupon after 1 week exposure (8000x magnification)	5-16
5-16	Growth on bacteria on the working electrode surface	5-17

LIST OF FIGURES (Continued)

<u>Figure</u>		<u>Page</u>
5-17	Bode plot of the corrosion rates measured by EIS on pipeline steel	5-18
5-18	Frequency of the maximum shift in the phase angle between applied potential and the induced currents in EIS analysis	5-19
5-19	Corrosion rates of combinations of anaerobic bacteria with times of exposure	5-20
5-20	Diagram of gradient film reactor (GFRxr)	5-21
5-21	Example of data obtained from the GFRxr	5-22
5-22	Example of pits formed in test spool piece in the GFRxr during a test run	5-24
5-23	The open cell potential of carbon steel with the bacteria \underline{H} . \underline{alvei} , \underline{D} . \underline{gigas} , \underline{H} . \underline{alvei} plus \underline{D} . \underline{gigas} , and $\underline{Bacillus}$, \underline{H} . \underline{alvei} plus \underline{D} . \underline{gigas} versus sterile control	5-27
5-24	The effect of <u>Bacillus</u> , <u>Bacillus</u> plus <u>H</u> . <u>alvei</u> , and <u>Bacillus</u> plus <u>D</u> . <u>gigas</u> on the open cell potential of carbon steel compared to sterile control	5-27
5-25	Admittance versus time with the bacterial combinations <u>D. gigas</u> , <u>H. alvei</u> , <u>D. gigas</u> , <u>H. alvei</u> plus <u>D. gigas</u> , <u>H. alvei</u> plus <u>D. gigas</u> and control	5-28
5-26	The effects of bacterial combinations on the admittance of carbon steel over time	5-28
5-27	Experiment using scanning vibrating electrode to monitor surface of coupons exposed to a solution with and without bacteria	5-29
5-28	Experiment showing the level of low frequency noise on coupled carbon steel coupons before and after the addition of MIC bacteria	5-30
5-29	Measurement of potential noise and high and low frequency current noise	5-32
5-30	Model of MIC of carbon steels, Phase 1	5-34
5-31	Model for MIC of carbon steels, Phase 2	5-35
5-32	Model for MIC of carbon steels, Phase 3	5-36

LIST OF TABLES

lable		<u>rage</u>
2-1	Comparison of Media for Detection of MIC Bacteria Results of Round-Robin Testing on Various Samples, Fall Committee Week (9/25/89)	2-10
3-1	Bacterial Populations and Organic Acids in Test Loops Containing Various Bacteria and Carbon Steel Coupons	3-4
3-2	Model Sequence for MIC External Sampling - Uncoated Pipe	3-9
4-1	Effectiveness of Biocide Formulations on Bulk Fluid and Surface Microbial Populations after 24 Hour Exposure	4-2
4-2	Tests of Corrosion Inhibitors on Surface Microbial Populations in the Test Loops	4-4
4-3	Summary Statistics for Offshore Microbiological and Chemical Measurements	4-17
4-4	Pearson Correlation Matrix for Offshore Microbiological & Chemical Measurements	4-18
4-5	Cost Analysis of Targeted Treatment vs. Treatment of an Entire Pipeline in an Offshore Gathering System	4-22
5-1	Semi-Quantitative Results of Chemical Composition of Nodules (from EDAX)	5-9
5-2	Enumeration of Non-Standard Microorganisms from Some Gas Industry Sites	5-25

1.0 EXECUTIVE SUMMARY

It is estimated that corrosion costs industry of all types up to \$126 billion annually. Some corrosion experts have estimated that 10 to 30% of total corrosion results from microbiologically influenced corrosion (MIC). The actual cost of MIC is far greater than would be predicted by the percentage of corrosion attributed to MIC. This is because MIC leads most often to localized pitting which sometimes results in failures of the pipe or other equipment even though the total amount of corrosion is relatively minor. Recognizing that MIC had been documented as a serious problem in several other industries, the Gas Research Institute (GRI) in 1986 instituted a program to investigate MIC in the gas industry.

The objectives of Phase I of the program were to define which, if any, types of MIC occurred in the gas industry, determine how to best identify those types of MIC which occurred in the gas industry, and using these techniques, determine the characteristics of MIC in various aspects of gas production, processing, transmission and distribution. The results of this phase provided biological, chemical, and metallurgical "fingerprints" for MIC. Studies also showed that most MIC was of the pitting type, which is more likely to result in through-wall failures than are many other types of corrosion. This work also demonstrated that MIC resulted from the activities of microbial communities—not single types of microbes—as had been previously believed. Specific test kits and a field guide for investigation of MIC were developed for use by gas industry personnel. The work of the research team and the data generated by gas industry personnel demonstrated that MIC was an important mechanism of corrosion in the gas industry.

Phase II focused on internal MIC as it was agreed that this form of MIC might be easier to understand and control than external MIC. Accordingly, extensive monitoring of gas facilities (e.g., wells, separators, pipelines) was done over a two-year period. Chemical, biological, and operational factors were studied to determine if significant relationships existed between these factors and MIC severity. Available test protocols and mitigation strategies were assessed. The results showed that many test protocols in use

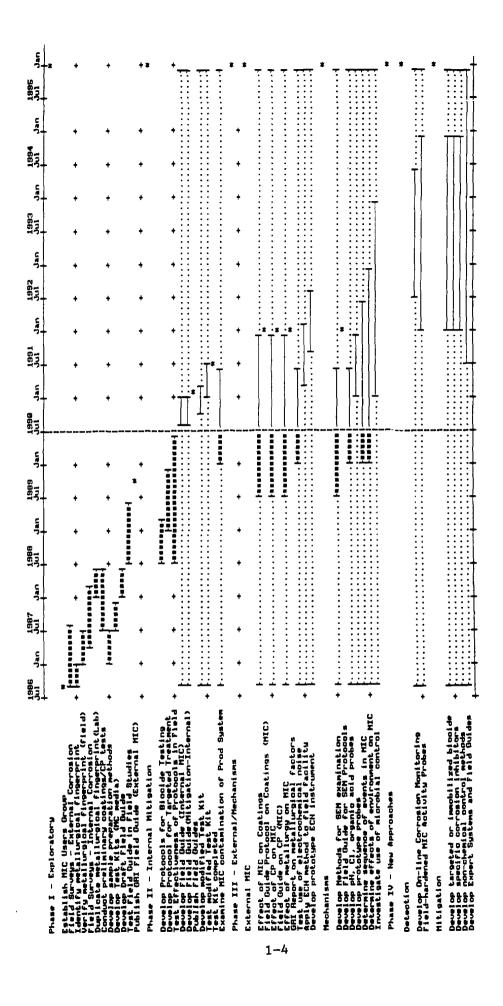
fail to accurately assess the extent of MIC in the gas industry and the effectiveness of mitigation strategies. New protocols and test devices were developed. The survey also demonstrated that there were often "hot spots" in systems (e.g., some separators) which contributed greatly to the contamination of entire operating systems. Targeted treatment strategies were proposed for treating these components which would provide effective treatment at reduced cost and with reduced use of potentially hazardous chemicals. These have been applied to some field sites and appear to be working well. Additional field guides, for investigation of internal MIC and use of sidestream devices as well as protocols for testing of biocides, will be produced by the end of 1990. Additional test kits incorporating tests for chemical and biological factors will be produced.

The work in Phase III focuses on investigating the factors causing external MIC, testing the effectiveness of currently available mitigation measures (coatings and cathodic protection), developing on-line methods for monitoring MIC, and attaining a better understanding of the basic mechanisms whereby MIC occurs. Considerable evidence suggests that at least some types of coatings may be subject to biodegradation and possibly contribute to the occurrence of MIC. The influence of cathodic protection on MIC under various conditions will be investigated. Such techniques as alternating current (AC) impedance and electrochemical noise are showing promise as techniques for online monitoring. Current studies have demonstrated that metallurgical factors may influence the attachment of MIC bacteria and subsequent corrosion. Models have also been developed which make it possible to test predictions with regard to the MIC processes. (That is, the pH in a mature pit will be less than 4 and viable microbes will be largely absent from the interior of the pit.) Tests of these predictions are under way. These tests are important in the development of new detection, prevention, and mitigation strategies.

Phase IV is concerned with developing better methods for detection, mitigation and prevention of MIC. This will include attempts to develop metallurgies which might be MIC resistant, corrosion inhibitors which mask specific targets for MIC bacteria, and methods for <u>in situ</u> mitigation of

external MIC (e.g., by altering the chemical environment surrounding the buried pipe).

Figure 1-1 shows the major milestones and deliverables for each phase of the project, including work for 1990 and beyond.



GRI MIC Program Plan - Major Milestones and Deliverables Figure 1-1.