

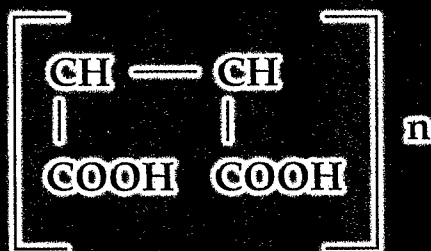
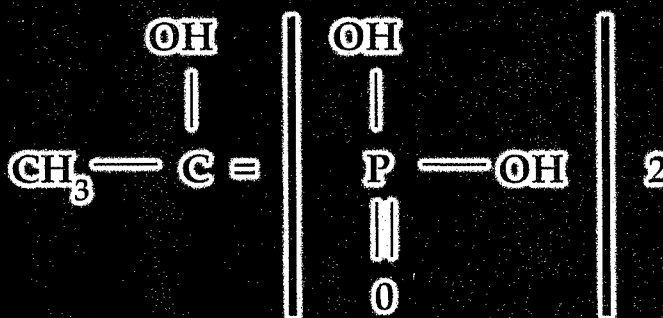
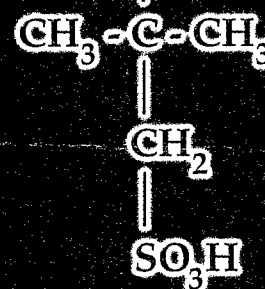
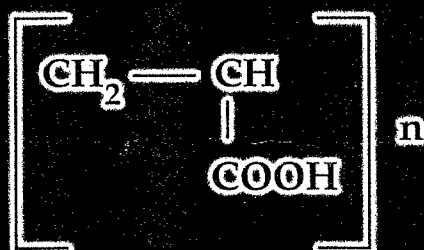
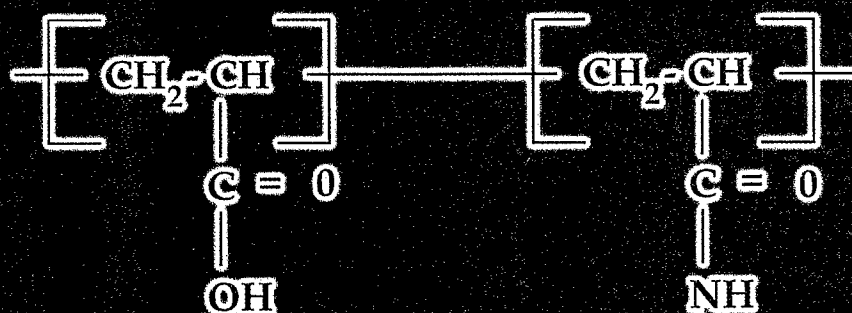
the ANALYST

THE VOICE OF THE WATER TREATMENT INDUSTRY

**Expert Consensus
on MIC**

**Factors Influencing the
Precipitation of
Calcium**

An Overview of FIFRA



SCALING AND CORROSION

Presorted Standard
U.S. POSTAGE
PAID
PERMIT No. 48
MERRIFIELD, VA

Expert Consensus on MIC – Prevention and Monitoring, Part 1

BY P.J.B. SCOTT, CARIAD CONSULTANTS

ABSTRACT

Originally produced by NACE Task Group 304 as a report on industrial practice currently recommended by experts in the field of microbiologically influenced corrosion (MIC), this article discusses the best available techniques and strategies for handling MIC problems. It summarizes prevention and monitoring, and provides references where detailed descriptions of useful techniques may be found. Failure analysis and control will be outlined in part two of this article, which will appear in the spring issue of *The Analyst*.

Introduction

20060130 274

There has been a growing cry among industry professionals that the message of MIC experts has not been adequately disseminated in the industrial community. Concerns were raised during a meeting of the technical committee on MIC at Corrosion/2003 in San Diego that industrial practice was falling far short of appropriate action in the MIC field even though experts have tremendous knowledge of how to monitor, diagnose, and control MIC.

This complaint is not new. In 1993, a "Viewpoint" article in *Materials Performance* (NACE International monthly magazine) bemoaned the discrepancy between the extensive knowledge of MIC experts and the actual practice of MIC monitoring and control in industry. In recent years there have been tremendous advances in our knowledge of the causes and mechanisms of biological corrosion, in monitoring techniques, biocides, and other control measures. The article stated:

"The problem with all these advances is that the message is being rehearsed in the inner circles of MIC conferences but is not being taken swiftly enough to the people who would benefit most at the design, engineering, and plant levels. Although many have jumped on the buzz-word bandwagon, there are too few instances of the difficult task of sampling and diagnosing of MIC being taken seriously."

*"It is no surprise that some people would prefer to ignore the fact that biological corrosion is a complex and difficult field. A reluctance to delve into the unpredictable realm of biology is no excuse, however, for ignoring unexplained corrosion problems; and it is no reason to avoid adequate diagnosis, monitoring and treatment of MIC. We, as practitioners of solutions to MIC problems, are using these new advances but have not succeeded in encouraging their widespread understanding and use."*¹

As a result of the technical meeting, a task group was established to write a state of the art report on industrial practice currently recommended by experts in the field of MIC and to publish it where it may be widely available to industrial practitioners. This article is the first in a two part series providing recommendations on the best practice in MIC prevention and monitoring.

Where MIC Problems Are Likely To Occur

Although MIC can occur in unexpected places, it tends to occur repeatedly at certain locations. Table 1 lists potential problem areas by industry application. (See Table 1 on page 10)

In general, MIC problem areas for many industries occur more frequently when:

- Associated with welds and heat affected zones.
- Found under deposits.
- Equipment is not drained and dried after hydrotesting.
- Cooling systems are not passivated after turnarounds are complete.

How To Prevent MIC

The keys to MIC control are system design, maintenance/cleanliness, and water quality.² System design should include, if possible:

- Appropriate materials selection (Stainless steel, for example, is less susceptible to general corrosion, but more susceptible to pitting than carbon steel; titanium has been found to be resistant.).
- Accessibility for cleaning (including access ports for pigs and blasting/water or jetting).
- Accessibility for water treatment, including systems for filtration and settling of suspended solids, chemical additions, and monitoring equipment.
- Provision for drains, traps, recycle circuits, and monitoring equipment.
- Control of water velocity and elimination of stagnant, low flow areas and dead legs.
- Minimization of crevices and welds.

Good housekeeping is often the key to MIC prevention and control. The system should be as free as possible of sludge, deposits, and foulants. Routine cleaning, including chemical and mechanical cleaning, should be part of operating routine. Vigilance is essential in keeping the system clean so monitoring programs should be instigated and maintained.

Good housekeeping can also sometimes mean keeping the system dry. MIC is a common problem when the system is not completely dried after hydrotesting. During wet lay-ups and outages, when it is not possible to dry the system, it may be necessary to add a long acting biocide immediately prior to shutdown.

Table 1. Where MIC Problems Are Most Likely To Occur

Industry/Application	Potential Problem Sites for MIC	Organisms Responsible
Pipelines - Oil, Gas, Water, Wastewater	- Internal corrosion primarily at the bottom (six o'clock) position - Dead ends and stagnant areas - Low points in long distance pipes - Waste pipes: internal corrosion at the liquid/air interface - Buried pipelines: on the exterior of the pipe, especially in wet, clay environments under disbonded coating	- Aerobic and anaerobic acid producers, sulfate reducing bacteria, manganese and iron oxidizing bacteria, sulfur oxidizing bacteria
Chemical Process Industry	- Heat exchangers and condensers - Storage tanks, especially at the bottom where there is sludge build-up - Water distribution systems - See also Cooling Water Systems, Fire Protection Systems, and Piping	- Aerobic and anaerobic acid producers, SRB, manganese and iron oxidizing bacteria - In oil storage tanks, also methanogens, oil-hydrolyzing bacteria
Cooling Water Systems	- Cooling towers - Heat exchangers: in tubes and welded areas and on shell where water is on shell side - Storage tanks: especially at the bottom where there is sludge build-up	- Algae, fungi, and other microorganisms in cooling towers - Slime forming bacteria, aerobic and anaerobic bacteria, metal oxidizing bacteria, and other microorganisms and invertebrates
Fire Protection Systems	- Dead ends and stagnant areas	- Anaerobic bacteria, including SRB
Docks, Piers, Oil Platforms, Other Aquatic Structures	- Just below the low tide line - Splash zone	- SRB below barnacles, mussels, and other areas sequestered from oxygen
Pulp and Paper	- Rotating cylinder machines - White water clarifiers	- Slime forming bacteria and fungi on paper making machines - Iron oxidizing bacteria - SRB in wastewater
Power Generation Plants	- Heat exchangers and condensers - Firewater distribution systems - Intakes	- As above for heat exchangers and fire protection systems - Under mussels and other fouling organisms on intakes
Desalination	- Biofilm development on RO membranes	- Slime forming bacteria

Water quality should be maintained at a high level. Methods to enhance water quality may include:

- Selecting the cleanest possible water source.
- Using settling tanks and filtration systems to remove particulates.
- Removing contaminants and nutrients such as oils, iron, phosphate, and nitrate.
- Chemically treating to reduce hardness, remove oxygen, or alter pH.
- Adding biocide and inhibitor.

Detecting MIC Problems in Your System

Early detection of MIC problems is an important component in cost effective MIC management. Whether your system has already had MIC problems or whether MIC is just a known problem in your industry and you want to test for it in your new installation, following is the recommended best practice. Details of these procedures are given below.

- In the bulk liquids it is necessary to monitor physical, chemical, and biological characteristics on an on-going basis.
- Corrosion coupons should be installed for regular monitoring of surfaces and, in addition, the actual equipment surfaces should be checked when the equipment is opened or exposed.

Monitoring Bacteria in Bulk Waters/Liquids

The aim of water monitoring is to identify factors in the bulk water/liquids that may promote bacterial growth and attack, which result in an increase of corrosion and/or pitting rates; to identify

potential problem organisms; and to detect trends in their quantity/abundance as they enter the system.

All water quality parameters considered important to understanding internal corrosion and MIC for a particular type of industrial system should be routinely and frequently monitored (approximately weekly). Temperature, pH, anions, cations/metals, alkalinity, total suspended solids (TSS) and total dissolved solids (TDS), dissolved gases (CO₂, H₂S, O₂, etc.), total organic carbon (TOC) and dissolved organic carbon (DOC), turbidity, and microorganisms (bacteria, algae, and fungi) may all be useful in obtaining clues to the health of a particular system.

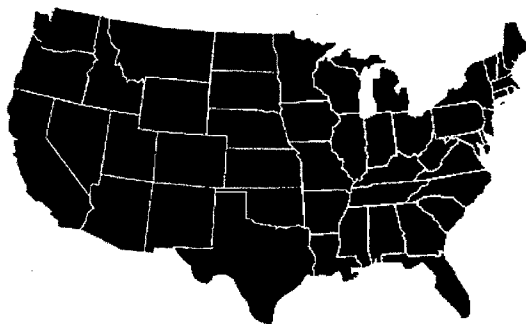
Note that dissolved oxygen is often not particularly representative of the microenvironments where corrosion may be occurring. Biofilms can sequester anaerobic bacteria in deoxygenated environments even in waters supersaturated with oxygen. Some workers have also found that chemical oxygen demand (COD) may be a useful indicator of water quality in cooling water systems. COD content may measure the concentration of electron donors available for sulfate or metal reduction. Hence, low COD means a low risk for sulfate reduction (SRB), iron reduction (IRB), etc.

Additional parameters may be measured in specific systems, for example, sulfide, nitrite, ammonia, and product in chemical process and oil and gas industries. Changes in these numbers, especially long-term trends in one direction or large anomalies, should be cause for further investigation. Correlate water quality measurements with microbial counts. Bacteria may increase, for example, during influxes



PRODUCTS

Phosphonates
Biocides
Dispersants
Specialty Polymers
Corrosion Inhibitors
Flocculants
Coagulants
Defoamers
Polyphosphates
Amines
Acids & Alkalis



9 Branch Locations

SERVICES

Rail
Dry Bagging
Dry Blending to Spec.
Liquid Blending to Spec.
Private Labeling
Transloading
Mini-Bulk Deliveries
Tank Installations



Corporate Office
LOS ANGELES
Phone: (323) 832-9500 • Fax: (323) 773-0909
For more information: www.lachem.com



of particulates into the cooling water system in the windy season. Bacterial numbers are also usually strongly correlated with temperature.

Equipment required for water monitoring is readily available from commercial sources and standard practices are available. Online monitoring of these parameters is ideal, but the equipment is more expensive and may have limitations in gas or liquid hydrocarbon environments. Many operators reduce costs by measuring conditions such as temperature, pH, conductivity, and TDS with online monitors and using portable or laboratory spectrophotometers and kits for the rest.

The most important thing to remember about bacterial counts is that the actual numbers are often virtually meaningless. Culture media provide optimum growth conditions for only a small percentage of known bacteria. Under the best conditions, media usually only count about 10% of the viable bacteria present and 1% may be more typical. Some other direct count techniques determine numbers of bacteria, but do not distinguish between live and dead cells. Also, direct counts can be difficult or impossible in turbid waters, and most direct counting techniques require a microscope and stains, which many plants do not have. Far more important is the trend of increasing or decreasing numbers, which can only be established by consistent and conscientious monitoring. When applied carefully and consistently, monitoring of bacteria in waters can be a useful technique. For example, the limits for total viable counts (TVC) almost universally applied as < 10 per mL at 37 °C for 24 hours incubation on yeast extract media has been very successfully applied for monitoring and control of potable water contamination.

As a tool for predicting the occurrence of bacterial corrosion, planktonic bacterial counts have been much maligned in recent reviews of bacterial monitoring. At least some of the bad experiences with planktonic counts, however, are a result of poor techniques and practices. In counting bacteria, technician training and consistent sampling/culture methods are a vital aspect of program success. As a measure of changing system conditions, planktonic counts can provide useful data, but only if measured rigorously. Samples should be collected in the same way, from the same place, incubated for the same time, at the same temperature, in the same medium, and counted by the same operator. Errors introduced by changing these variables can be so large that they can override or confuse any actual changes in the system, rendering the monitoring program useless. Correct procedures carried out by trained technicians are important, but are rarely recognized by technicians or even management in the field.

Do not change the method of collection, culture, or measurement of the system unless necessary. There is a very poor correlation between bacterial numbers counted when using various commonly used culture media, and the resulting differences are not consistent or predictable. If necessary, check the effect of the new conditions by overlapping the two methods until the relationship between the two results is clear for your system.

One of the most common counting methods for aerobic systems is measurement of the number of colony forming units (CFU) per mL of bulk water on standard culture plates or dip slides. These generally count the number of heterotrophic, aerobic bacteria culturable on standard media plates (such as Trypticase Soy Agar [TSA] or in nutrient broth). Dip slides are more convenient because they eliminate the need to measure accurately a known quantity of water, but are more expensive. Results are usually obtained in one to three days. Anaerobic bacteria are usually cultured in liquid media, in which it is easier to

exclude oxygen, at least at the bottom of the culture tube. Results are obtained in a few days, longer for SRB (up to 28 days). While the most widely used techniques for counting bacteria in liquid cultures is the "most probable number" (MPN) technique, it may be difficult to use in very turbid liquids.

Since microorganisms grow selectively on various media, it is necessary to culture a wide variety of potential corrosion-causing microbes, at least initially. Depending on the environment being tested, monitoring programs may include media for general aerobic bacteria, general anaerobic bacteria, acid producing bacteria, sulfur oxidizing bacteria, sulfate reducing bacteria (SRB), fungi, algae, and any other groups that are suspected to be a problem in the system. If some of the media routinely produce negative results, they can be dropped from the regular monitoring program, but should still be checked occasionally. General aerobic or anaerobic bacteria counts and SRB counts should be continued in most cases, however.

Because of the limitations of culture techniques, bacterial culturing is not the only method recommended for monitoring MIC. Non-assay techniques should also be used, including coupons, visual inspection, linear polarization probes and any other clues available.³

ATP (adenosine triphosphate) photometry, respirometry, fluorescent dyes, specific antibody tests, and redox indicator tests are faster techniques, measuring biomass in about 10 minutes, but are more expensive, require sophisticated equipment and/or techniques and have detection limits that are quite high. Recently, fluorescent bio-reporters have also been used to measure total biological activity online.

Monitoring Surfaces

Although sessile bacteria are recruited initially from bulk liquids, there is usually little correlation between the planktonic and sessile bacterial numbers. Therefore, sessile bacteria need to be monitored separately from the bulk water bacteria.

Sessile bacterial numbers should be sampled in the areas that are most susceptible to corrosion problems. Many monitoring programs include removable, in-process coupons or probes. They are typically inserted into system piping/components or in devices added to the system, such as tubular flow systems, Robbins® devices, or Renaprobe®. These programs provide real-time data on the system conditions and can be used to gain information on biofilm development and corrosion rates. The probes may also be located in a side-stream device. Side-stream devices have the additional advantage that biocide levels and process conditions can be altered experimentally under controlled conditions, giving reasonably fast and reliable information on their effects on the system. Coupons have been found to be a useful and effective field monitoring technique for MIC as in other corrosion problems, especially when included in a larger monitoring program using several other supplementary techniques. Although it is not always possible to distinguish between MIC and other corrosion mechanisms, extended analysis of coupons using microscopic techniques can yield important evidence with regard to pit initiation mechanism(s). Analysis can also identify the severity of localized attack through the measurement of pitting (pit densities, depths, and diameters) and calculation of pitting rates by bacteria or other corrosive components.⁴

One problem encountered with many coupon and probe devices is that they are destructive and time consuming to analyze. To obtain information on long-term buildup of biofilms, coupons must be

removed sequentially, requiring placement of numerous coupons in the same location. They must then be cultured for various bacterial groups. These shortcomings have led to many recent attempts to develop faster, more user-friendly methods of monitoring biofilm development. The HMB-IV-S Test Kit®, originally established for testing metal working fluids, has been modified for measuring biofilm activity in cooling water. The test measures the level of the peroxidase enzymes produced in aerobic metabolism. This 15-minute, non-destructive test uses a plastic coupon that has been placed in the system for at least two weeks and reagents that do not require refrigeration or special storage.⁵

Probes using DNA hybridization show considerable promise as an alternative to culture methods, although they can only detect total bacteria and/or specific genera of bacteria.⁶ Probes have been developed to target:

- all eubacteria,
- *Desulfovibrio desulfuricans* and SRB of the genus *Desulfotomaculum*
- SRB of the genus *Desulfobacter*, or
- *Desulfovibrio desulfuricans* and SRB of the genus *Desulfobacter*.

Because the use of multiple probes requires repeated analysis of a sample, reverse probe protocols have been explored in which a number of probes are immobilized on a chip and hybridized to labeled components of the sample. For example, reverse sample genome probing (RSGP), in which whole genome probes are immobilized, has allowed determination of multiple SRB species on a corrosion coupon in a single DNA hybridization assay.^{7,8} The greatest breakthrough will come when samples can be assayed rapidly without prior growth. Bioinformatic analysis of sequenced microbial genomes and sequencing of all bacterial genomes in selected microbial communities, which may be expected in the near future, will spur development of increasingly useful chips with thousands of DNA probes that can be used to analyze the microbial community composition of corrosion coupons.

Another new monitoring method allows determination of bacterial types using a quantitative polymerase chain reaction technique (Q-PCR) that does not require any culturing of organisms.⁹ This technique has the advantage of analyzing samples directly without any cultivation or other manipulation in the laboratory that would alter the composition of the microbial community. It can even be used on dried/poorly preserved samples that cannot be analyzed using microbial growth tests.

Some techniques have been developed for specific applications. An online monitoring system for corrosion and bacteria in oil and gas pipelines removes fluid from the pipe and separates the water for corrosion rate and bacterial analysis. Many techniques can be coupled to the system, including coupons, electrical resistance probes, galvanic probes, hydrogen probes, linear polarization resistance, alternating current impedance spectroscopy, electrochemical noise, pH, and conductivity. Electrochemical probes detect the changes in applied current caused by biofilm activity on coupled stainless steel electrodes. In addition, generated current is a more sensitive indicator of biofilm activity.¹⁰ These combined techniques have met with success in field applications.¹¹ Other, more complex electrochemical techniques, such as noise and impedance spectroscopy, are generally considered to be more suitable for research than field monitoring.

A final new online technique uses fluorogenic dye bioreporters, which react with planktonic and sessile microorganisms. Separate

signatures identify the products before and after interaction with microbes and are expressed as a ratio.¹²

This article was previously published in Materials Performance (April 2004, p.46). Reprinted with permission from NACE International, Houston.

MIC Monitoring References

A. E. Greenberg, L. S. Clesceri, and A. D. Eaton, *Standard Methods for the Examination for Water and Wastewater*, 18th ed. (American Public Health Association, American Water Works Association, and Water Environment Federation, 1992). (A very useful book.)

P. J. B. Scott and M. Davies, "Monitoring Bacteria in Waters: The Consequences of Incompetence," *Materials Performance* 38, no. 7 (1999): 40-43.

NACE International Standard TM0194-94, *Field Monitoring of Bacterial Growth in Oilfield Systems* (Houston, TX: NACE International). (Covers general, aerobic and anaerobic heterotrophic bacteria and SRB - both planktonic and sessile bacteria.)

NACE International Standard TPC 3, *Microbiologically Influenced Corrosion and Biofouling in Oilfield Equipment* (Houston, TX: NACE International, 1990). (This reference is restricted to monitoring of oilfield systems.)

D. H. Pope, R. J. Soracco, and E. W. Wilde, "Methods of Detecting, Enumerating and Determining Viability of Microorganisms Involved in Biologically Induced Corrosion" (Paper No. 8223 presented at CORROSION/82, NACE International, Houston, TX, 1982).

D. H. Pope and T. P. Zintel, "Methods for the Investigation of Under-Deposit Microbiologically Influenced Corrosion" (Paper No. 88249 presented at CORROSION/88, NACE International, Houston, TX, 1988).

1. P. J. B. Scott and M. Davies, "Viewpoint: State of the Art vs. State of Mind," *Materials Performance* 32, no. 9 (1993): 8-9.

2. R. W. Lutey, "Treatment for the Mitigation of MIC," in *A Practical Manual on Microbiologically Influenced Corrosion*, ed. J. G. Stoecker (Houston, TX: NACE International, 1993), 9.1-9.9.30.

3. F. E. Blackburn, "Non-Bioassay Techniques for Monitoring SRB" (Paper No. 04580 presented at CORROSION/04, NACE International, Houston, TX, 2004), 1-8.

4. R. B. Eckert, H. C. Aldrich, C. A. Edwards, and B. A. Cockingham, "Microscopic Differentiation of Internal Corrosion Initiation Mechanisms in a Natural Gas Gathering System" (Paper presented at CORROSION/03, NACE International, Houston, TX, 2003).

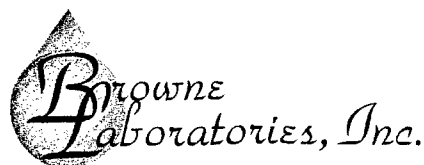
5. Eastern Technologies, Inc., Morgantown, PA. Water Test Kits and HMB Systems. Available at www.go2eti.com.
6. T. J. Tvedt and G. Aspery, "DNA Hybridization Using Genus-Specific Probes - A Powerful Tool for Solving Cooling Water Problems" (Paper presented at the International Water Conference, January 2001).
7. G. Voordouw, "Reverse Sample Genome Probing of Microbial Community Dynamics," *American Society for Microbiology News* 64 (1998): 627-633.
8. G. Voordouw, T. R. Jack, J. M. Foght, P. M. Fedorak, and D. W. S. Westlake, "Application of Reverse Sample Genome Probing to the Identification of Sulfate-Reducing Bacteria," in *Microbiologically Influenced Corrosion Testing*, eds. Jeffery R. Kearns and Brenda J. Little (Philadelphia, PA: American Society for Testing and Materials, 1994), 188-199.
9. X. Zhu, J. Lubeck, K. Lowe, A. Daram, and J. J. Kilbane II, "Improved Method for Monitoring Microbial Communities in Gas Pipelines" (Paper No. 04592 presented at CORROSION/04, NACE International, Houston, TX, 2004), 1-13.
10. M. H. Dorsey, G. J. Licina, B. J. Saldanha, and R. C. Eversole, "Monitoring for Corrosion and Microbiological Activity in a Cooling Water System," *Plant Power Chemistry* 4, no. 12 (2002): 721-731.
11. J. S. Smart and T. Pickhall, "A New System for On-Line Monitoring of Internal Corrosion and Bacteria in Pipelines" (Paper No. 9215 presented at CORROSION/92, NACE International, Houston, TX, 1992), 1-10.
12. Chattoraj, M. J. Fehr, S. R. Hatch, and E. J. Allain, "Online Measurement and Control of Microbiological Activity in Industrial Water Systems," *Materials Performance* 41, no. 4 (2002): 40-45.

About the Authors

P.J.B. Scott is a principal with CARIAD Consultants and can be reached by mail at Kato Asites, Heraklion, Crete 70013, Greece or by e-mail at cariad@her.forthnet.gr.

FOR THE WATER TREATMENT PROFESSIONAL WHO NEEDS AN EXPERIENCED PARTNER

BROWNE LABS CAPABILITIES – Over the last 25 years, the technical staff of Browne Laboratories has developed an extensive product line suitable for treating virtually any type of water and wastewater. We offer a complete line of house formulations; or, we can assist you with the development of custom formulations. Product quality is assured through our own in-house Quality Control Program. Browne Laboratories offers private labels with your company logo. We can assist with MSDS and Technical Bulletin preparation as well as provide assistance with laboratory services, test kits/reagents, external treatment equipment, and chemical feed equipment. All formulations can be prepared and shipped in packaging ranging from 5-gallon pails to bulk; and, in most instances, shipped to your customer within 24 hours.



CHEMISTRY TECHNOLOGIES AVAILABLE . . .

- Boiler Water Products
- Cooling Water Products
- Biocides
 - Isothiazoline
 - Carbamates
 - Polyquats
- Closed Loop Products
- Water & Wastewater Coagulants & Flocculants
- Heavy Metal Precipitants
- Defoamers
- Potable Water Products
- Mill Supply Treatment
- Paper Mill Preservatives
- Paper Mill Microbiocides

FOR ALL OF YOUR TOLL BLENDING NEEDS

P. O. Box 22817, Chattanooga, TN 37422 • phone: (423) 698-7777 • fax: (423) 698-8688
e-mail: sales@brownelabs.com • website: www.brownelabs.com