MIC and Internal Corrosion

Brenda Little

49CFR Part 195

(d) If you install an insulating device in an area where a combustible atmosphere is reasonable to foresee, you must take precautions to prevent arcing.

(e) If a pipeline is in close proximity to electrical transmission tower footings, ground cables, or counterpoise, or in other areas where it is reasonable to foresee fault currents or an unusual risk of lightning, you must protect the pipeline against damage from fault currents or lightning and take protective measures at insulating devices.

§ 195.577 What must I do to alleviate interference currents?

(a) For pipelines exposed to stray currents, you must have a program to identify, test for, and minimize the detrimental effects of such currents.

(b) You must design and install each impressed current or galvanic anode system to minimize any adverse effects on existing adjacent metallic structures.

§ 195.579 What must I do to mitigate internal corrosion?

(a) *General.* If you transport any hazardous liquid or carbon dioxide that would corrode the pipeline, you must investigate the corrosive effect of the hazardous liquid or carbon dioxide on the pipeline and take adequate steps to mitigate internal corrosion.

(b) *Inhibitors.* If you use corrosion inhibitors to mitigate internal corrosion, you must—

(1) Use inhibitors in sufficient quantity to protect the entire part of the pipeline system that the inhibitors are designed to protect;

(2) Use coupons or other monitoring equipment to determine the effectiveness of the inhibitors in mitigating internal corrosion; and

(3) Examine the coupons or other monitoring equipment at least twice each calendar year, but with intervals not exceeding 7½ months.

(c) *Removing pipe.* Whenever you remove pipe from a pipeline, you must inspect the internal surface of the pipe for evidence of corrosion. If you find internal corrosion requiring corrective action under § 195.585, you must investigate circumferentially and longitudinally beyond the removed pipe (by visual examination, indirect method, or both) to determine whether additional corrosion requiring remedial action exists in the vicinity of the removed pipe.

(d) *Breakout tanks.* After October 2, 2000, when you install a tank bottom lining in an aboveground breakout tank built to API Specification 12F, API Standard 620, or API Standard 650 (or its predecessor Standard 12C), you must install the lining in accordance with API Recommended Practice 652. However, installation of the lining need not comply with API Recommended Practice 652 on any tank for which you note in the corrosion control procedures established under § 195.402(c)(3) why compliance with all or certain provisions of API Recommended Practice 652 is not necessary for the safety of the tank.

§ 195.581 Which pipelines must I protect against atmospheric corrosion and what coating material may I use?

(a) You must clean and coat each pipeline or portion of pipeline that is exposed to the atmosphere, except pipelines under paragraph (c) of this section.

(b) Coating material must be suitable for the prevention of atmospheric corrosion.

(c) Except portions of pipelines in offshore splash zones or soil-to-air interfaces, you need not protect against atmospheric corrosion any pipeline for which you demonstrate by test, investigation, or experience appropriate to the environment of the pipeline that corrosion will—

(1) Only be a light surface oxide; or

(2) Not affect the safe operation of the pipeline before the next scheduled inspection.

§ 195.583 What must I do to monitor atmospheric corrosion control?

(a) You must inspect each pipeline or portion of pipeline that is exposed to the atmosphere for evidence of atmospheric corrosion, as follows:

Federal hazardous liquid and carbon dioxide pipeline safety regulations are provided in 49 CFR 195

Subpart H prescribes minimum requirements for protecting steel pipelines against corrosion. Regulations in this subpart require operators to have a thorough understanding of the corrosive properties of the fluids being transported and knowledge about how those properties change over space and time. Furthermore, the operator is responsible for inhibiting potentially disastrous internal corrosion and monitoring the effectiveness of remediation strategies.

Federal hazardous liquid and carbon dioxide pipeline safety regulations are provided in 49 CFR 195, a performance-based standard. Performance requirements have the following advantages:

- Based on measurable, quantifiable parameters that are directly related to safety
- Allow timing of measurements to be specified
- Permit numerical performance criteria to be set for each parameter
- Require corrective actions to be taken whenever performance criteria are not met
- Permit monitoring to establish performance trends
- Allow adjustment of performance criteria and corrective actions based on performance trends

The following operational variables make it difficult to thoroughly characterize fluids:

- Crude oils vary in composition and chemistry
- Injection waters vary in pH, salinity, microbial constituents, and sulfate concentration
- Operating procedures (e.g. accumulations of drilling mud, reinjection of light gases into the formation, and flow rates) affect corrosion and the effectiveness of corrosion control measures

NACE Standard TM0194-2004
Item No. 21224

Standard
Test Method

Field Monitoring of Bacterial Growth in Oil and Gas Systems

Revised 2004-11-15
Approved 1994
NACE International
1440 South Creek Dr.
Houston, Texas 77084-4906
+1 281/228-6200

ISBN 1-57590-197-7

Liquid Culture Techniques

"equal to or greater than" (≥) the highest dilution used in the testing.

RESULTS INTERPRETATION TABLE

Number of Positive Vials	Actual Dilution of Sample	Growth (+) Indicates Bacteria per mL	Reported Bacteria per mL
1	1:10	1 to 9	10
2	1:100	10 to 99	100
3	1:1,000	100 to 999	1,000
4	1:10,000	1,000 to 9,999	10,000
5	1:100,000	10,000 to 99,999	100,000
6	1:1,000,000	100,000 to 999,999	1,000,000

Problems with Liquid Culture Techniques for Bacteria:

- Only about 1% of naturally occurring bacteria can be cultured.
- There is no relationship between numbers of bacteria and the likelihood that MIC has occurred or will occur.
- Not all sulfide-producing microorganisms are bacteria. Sulfide- producing prokaryotes (SPP)

Standard
Test Method

Detection, Testing, and Evaluation of Microbiologically Influenced Corrosion (MIC) on External Surfaces of Buried Pipelines

Approved 2006-06-23
NACE International
1440 South Creek Drive
Houston, Texas 77084-4906
+1 281/228-6200

ISBN 1-57590-206-0

Types of microorganisms routinely enumerated using liquid culture techniques:

- General aerobic heterotrophs
- General anaerobic heterotrophs
- Sulfate – reducing bacteria
- Acid – producing bacteria

Other important groups

- Metal reducing bacteria
- Metal oxidizing bacteria
- Fungi
- Methanogens
- Archaea

CT article cover

Detecting and Monitoring Bacteria in Seawater Injection Systems

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Biocide treatments and monitoring of bacteria in offshore oil production have been based on the use of conventional culture techniques that may not be reliable. This article describes molecular biology techniques that precisely assess microbial contaminants of a seawater injection system in the Gulf of Mexico.

The oil industry is severely affected by microbiologically influenced corrosion (MIC) and biofouling during oil recovery, processing, transport, and storage. MIC and reservoir souring is linked to the settlement of sulfate-reducing bacteria (SRB) biofilms in different parts of the oil recovery system.[1] Monitoring industrial systems for MIC and treating them with biocides and corrosion inhibitors includes the use of culture techniques to identify problematic microorganisms in waters or on surfaces and detect changes in total viable bacterial numbers.[2-3] Samples of water or surface deposits are inoculated into selective artificial culture media for culturing problematic bacterial physiological groups (aerobic heterotrophic bacteria (HB), facultative anaerobic bacteria, SRB, and acid-producing bacteria). Culture techniques may be time-consuming, since culture media are typically observed for ~30 days, and also require relatively large amounts of samples.

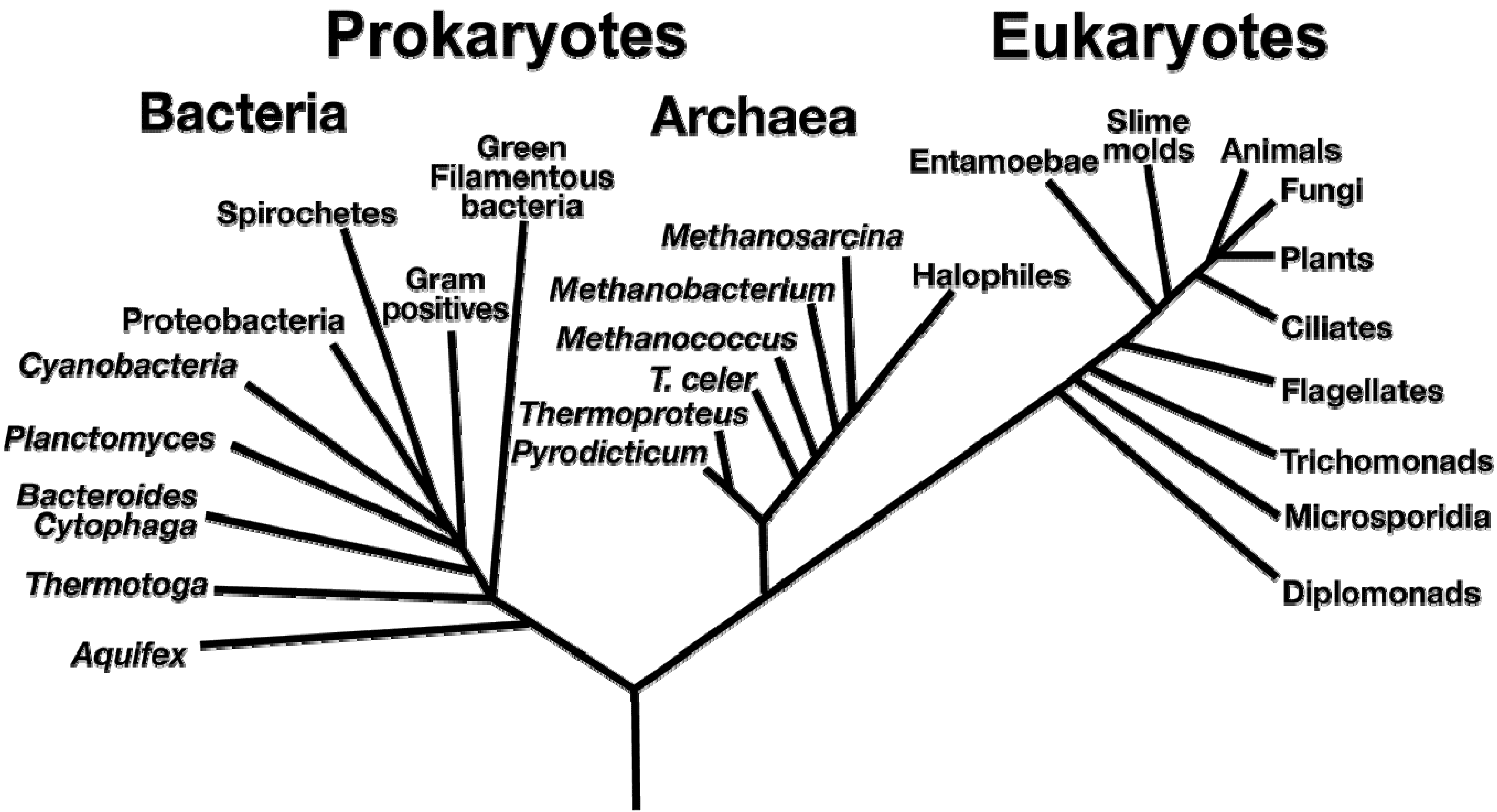
Recent advances in microbial ecology, however, show that only 1 to 10% of the microorganisms present in a natural system can be cultured using conventional culture techniques. Molecular techniques, which involve the direct analysis of microbial populations from their genetic material without the need of culturing, are promising in MIC monitoring since they offer the potential to:

- Identify dominant bacteria in industrial ecosystems without the limitations of culture techniques.
- Determine the proportion of corrosion-contributing bacteria in the total bacterial population.
- Identify bacteria susceptible and resistant to biocides.
- Assess the changes in the overall composition of bacterial populations caused by the use of biocides or due to fluids composition modifications.

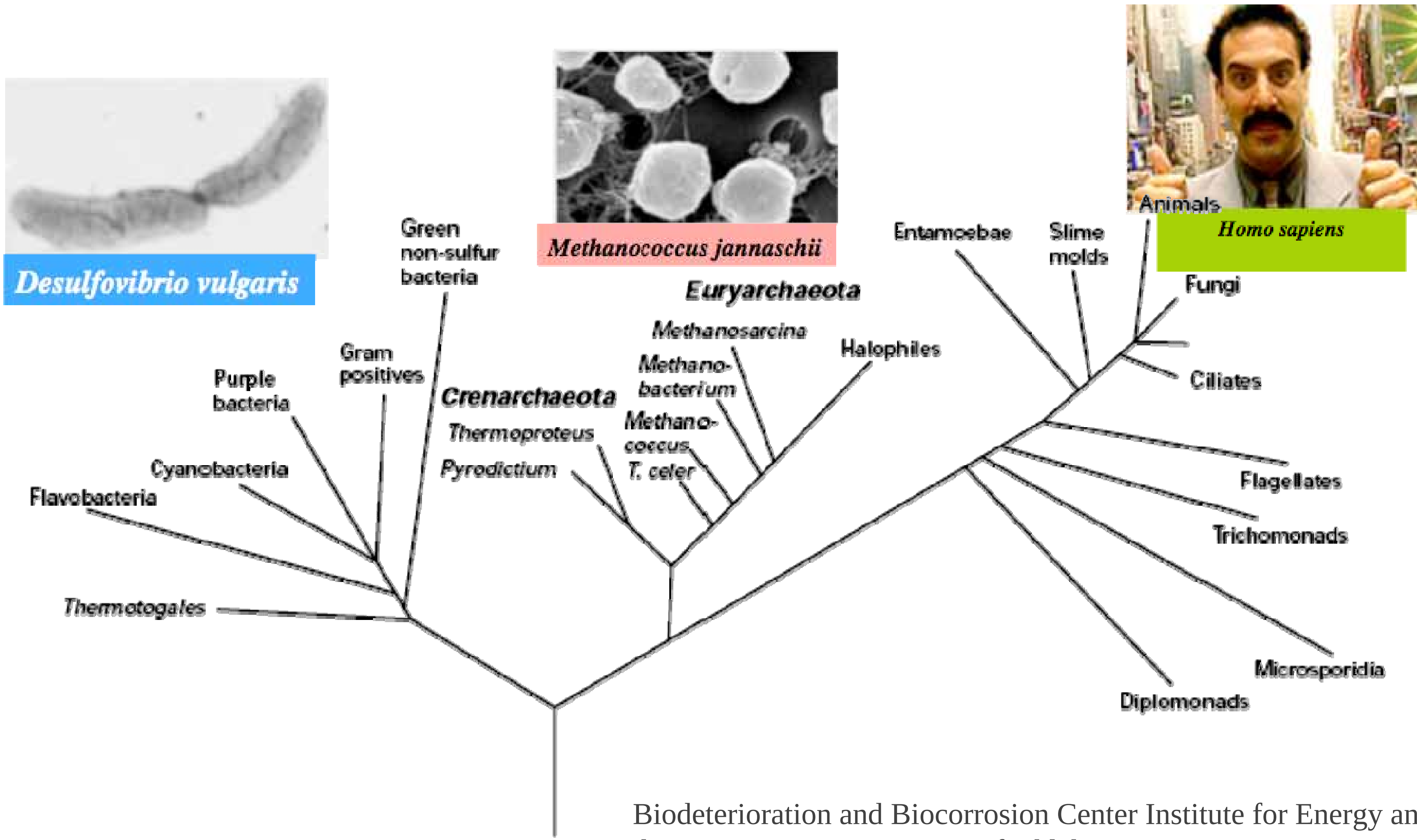
TM0194-2004

Section 1.1.3 “This standard deals with only bacteria and does not consider other microorganisms that may be found in oilfield fluids, such as archaebacteria, phytoplankton (algae), protozoa or fungi.”

The Organisms - Three Domains of Life



The Organisms - Three Domains of Life



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DNA-based detection:

Bacteria in samples broken open, DNA extracted, specific genes amplified (PCR), cloned, and sequenced

Characterizing Microbial Diversity in Production Water from an Alaskan Mesothermic Petroleum Reservoir with two independent Molecular Methods

Phan et al.,2008

"…near absence of culturable SRB in other samples from this well, the low or transient level of sulfate detected and the inversely high relative abundance of methanogens."

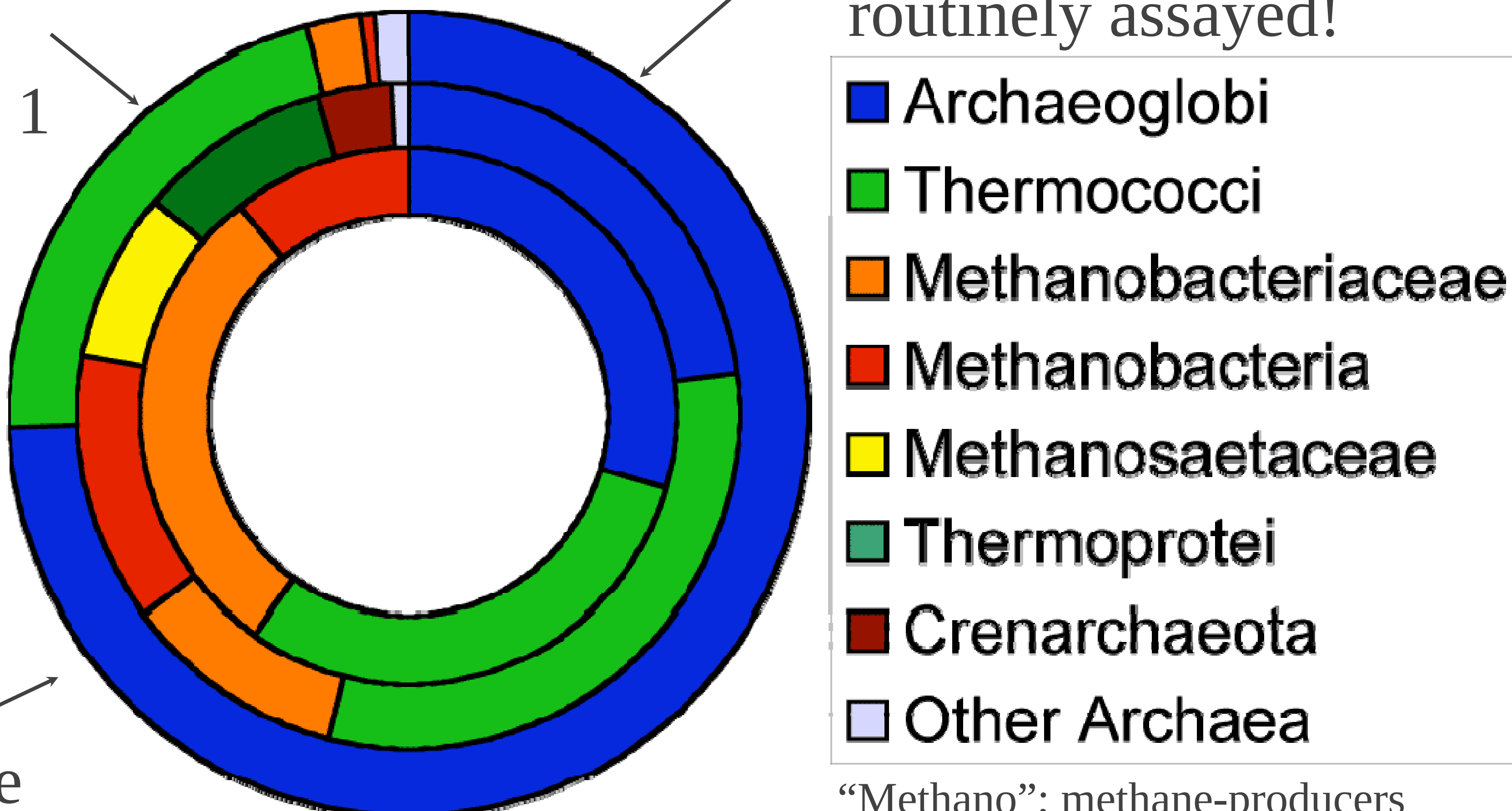
Hot samples are rich in Archaea!

Thermophiles, hyperthermophiles

Archaeal 16S clone libraries

Archaeal SRB and not routinely assayed!

Sample 1



Sample 2

Similar sequences, different proportions

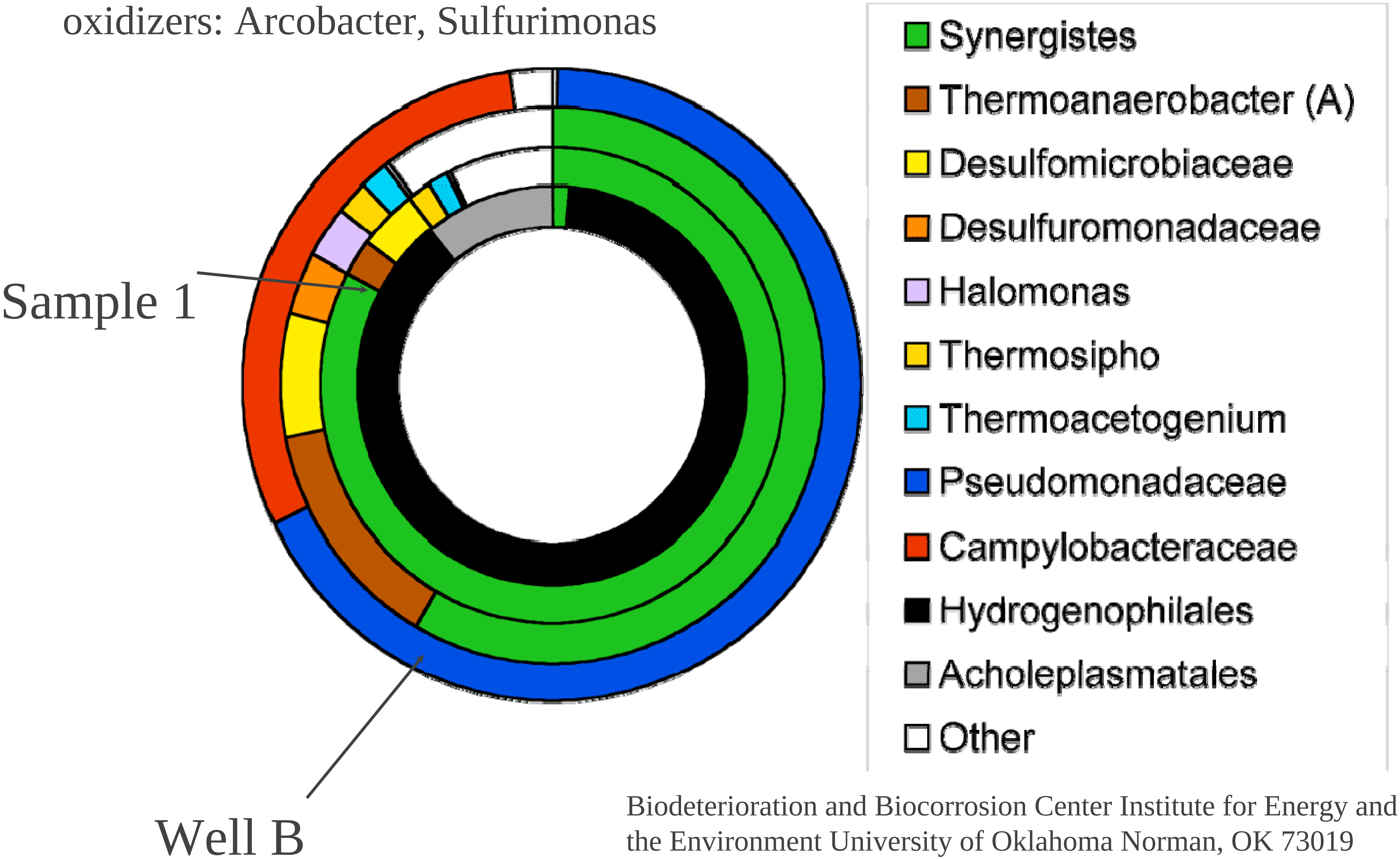
“Methano”; methane-producers

Methanothermobacter thermautotrophicus

Most numerically dominant H_2 utilizer

Bacterial clone libraries

Seawater community is different: *Pseudomonas stutzeri*, Sulfur-, thiosulfate-oxidizers: Arcobacter, Sulfurimonas



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•Molecular analysis showed the presence of thermophilic anaerobes such as eubacterial SRB, archaeal SRB, thiosulfate-users, fermentors (acid producers), methanogens, H_2 users.

Metabolic evidence for anaerobic hydrocarbon biodegradation!

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Detection Techniques

Coupons

a. Location – Failure to properly locate coupons may lead to poor correlation of monitored corrosion rates with actual system rates (ref. RP0775-2005).

b. Exposure Time – Aggravating conditions (i.e. bacterial fouling) may take time to develop and will require longer exposure times. Multiple holders can be used so that both long-term and short-term effects can be monitored (ref. RP0775-2005).

c. Evaluation – Corrosion rates calculated from mass loss can be misleading. If corrosion occurs in the form of pitting or crevice corrosion, the depth, size, and distribution should also be evaluated.

Detection Techniques

Electrical Resistance (ER) Probes

a. ER probes determine metal loss by directly measuring the increase in resistance of a metal as its cross-sectional area is reduced by corrosion.

b. Where pitting is the only form of attack, the probes may yield unreliable results [ASTM G96-90(2008)]. This is particularly relevant in sour oil/gas systems and certain forms of microbial corrosion such as SRB attack.

Detection Techniques

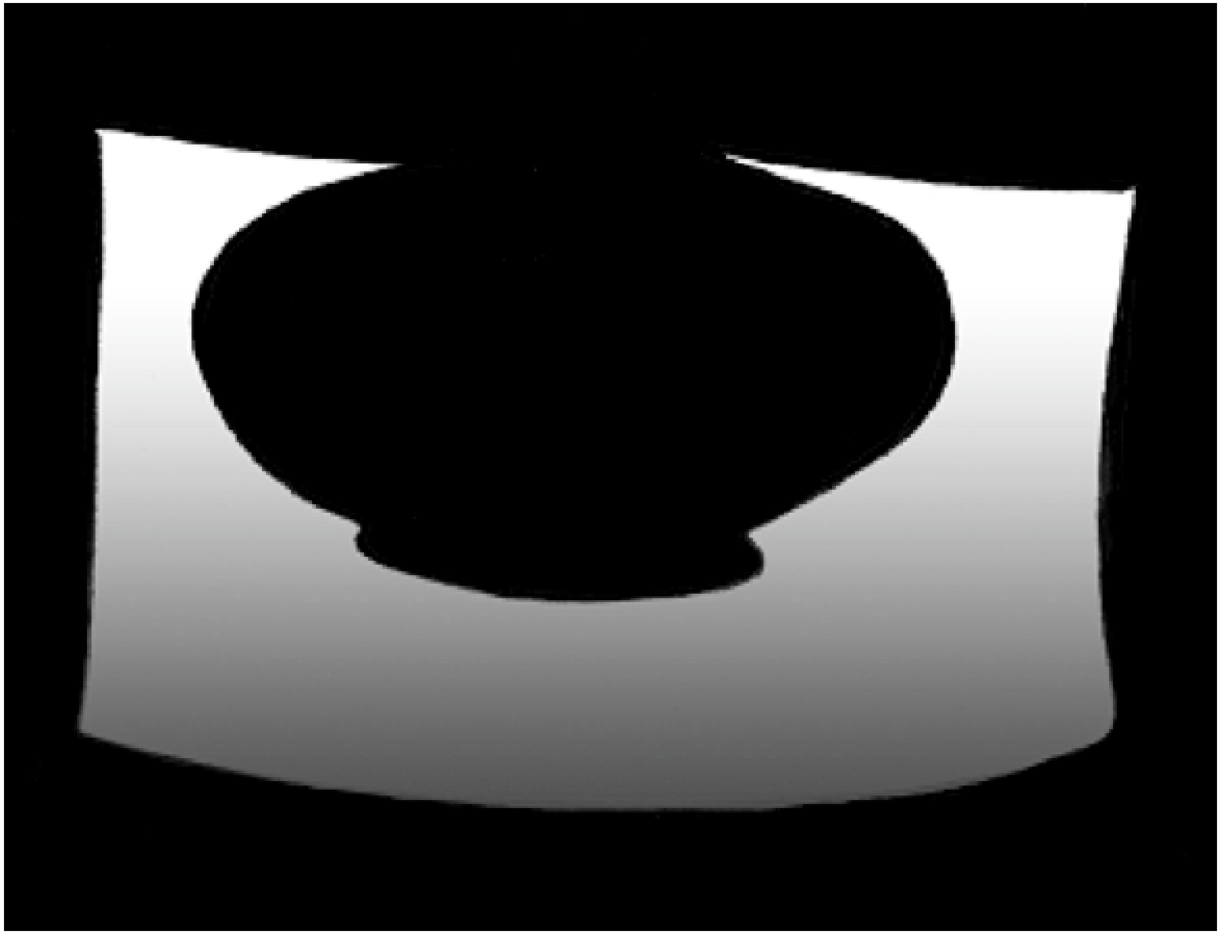
Nondestructive Testing (NDE)

a. Typically volumetric methods are used such as radiography or ultrasonic testing.

b. Used for detecting damage and irregularities in pipe walls.

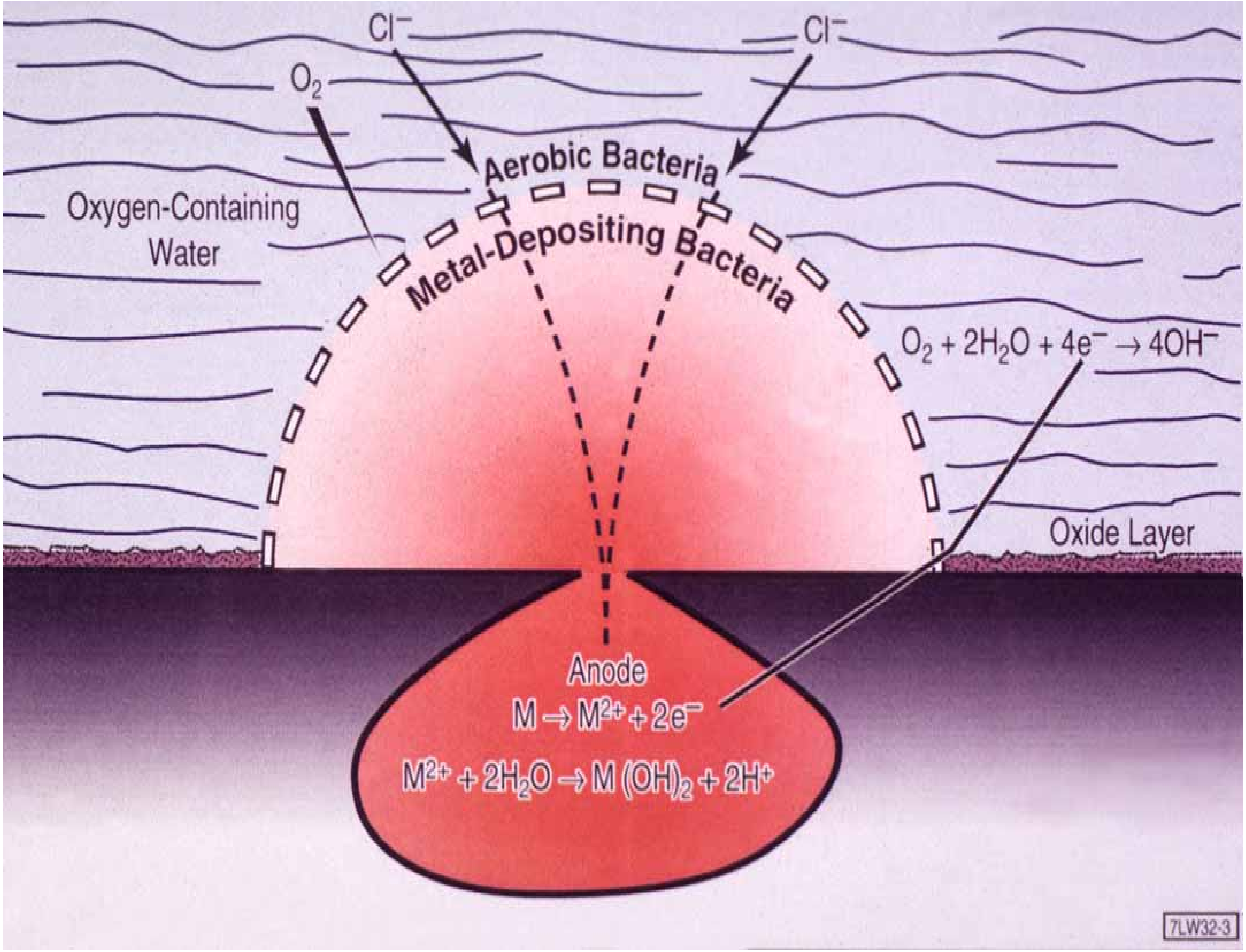
c. All NDE methods require acceptable performance demonstration on known flaws. If actual flaws vary from test conditions errors are likely to occur.

Interpretation of Pit Morphology

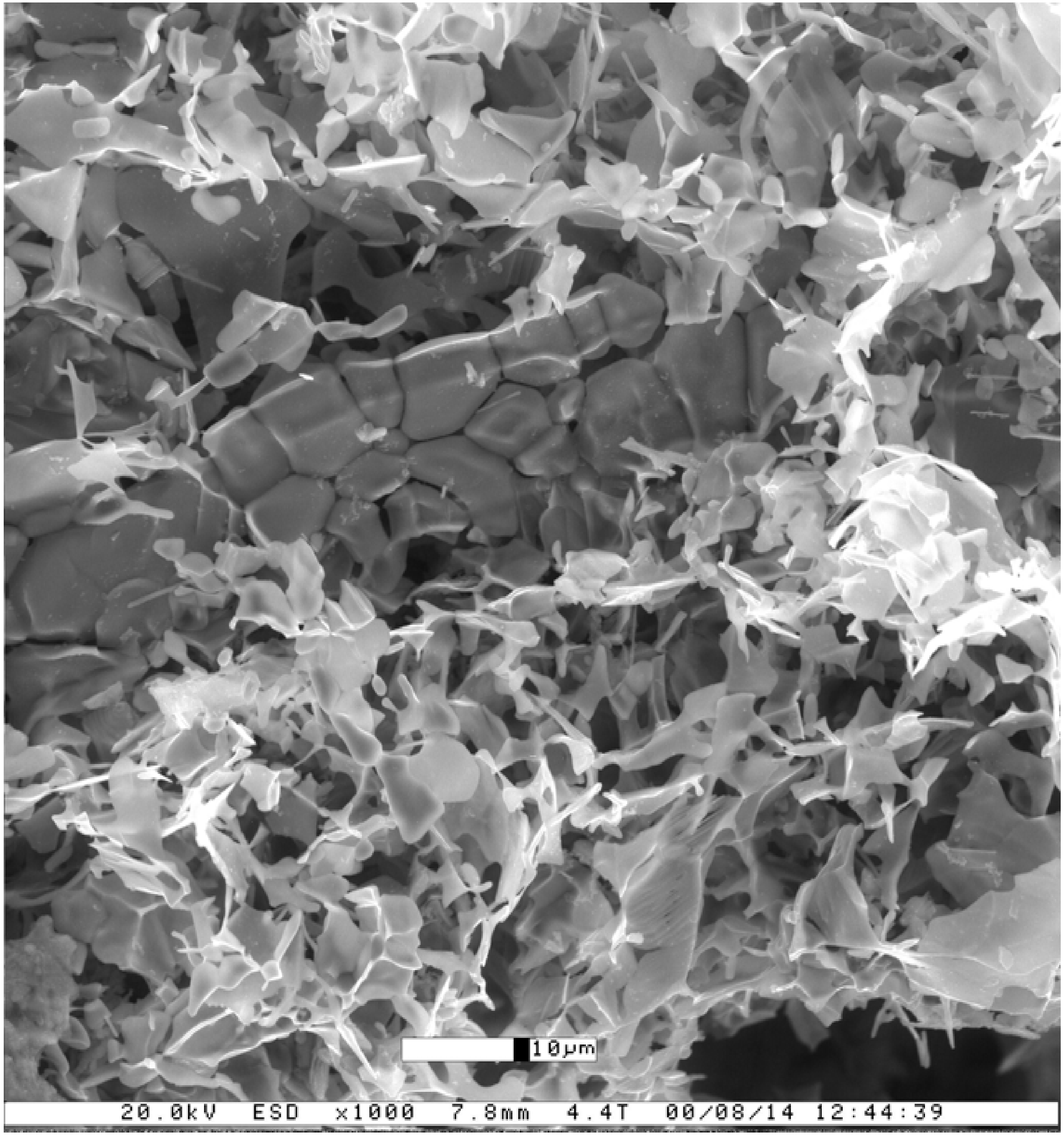


An illustration of an ink bottle-type pit noted in many cases of MIC and commonly found in the Type 904L tubes from failed heat exchangers.

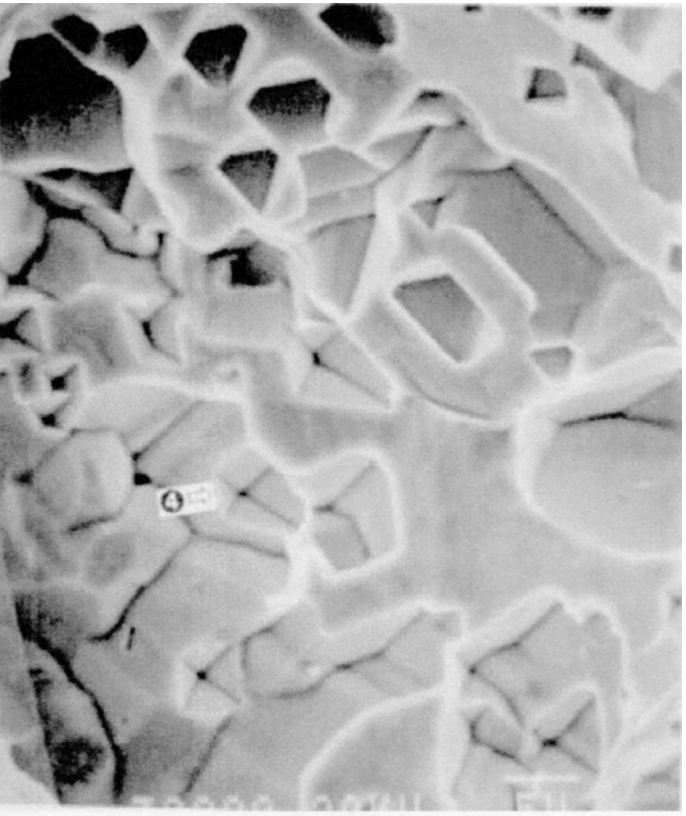
Scott, P.J.B. and Davies, M. 1993 A Practical Manual on MIC NACE International



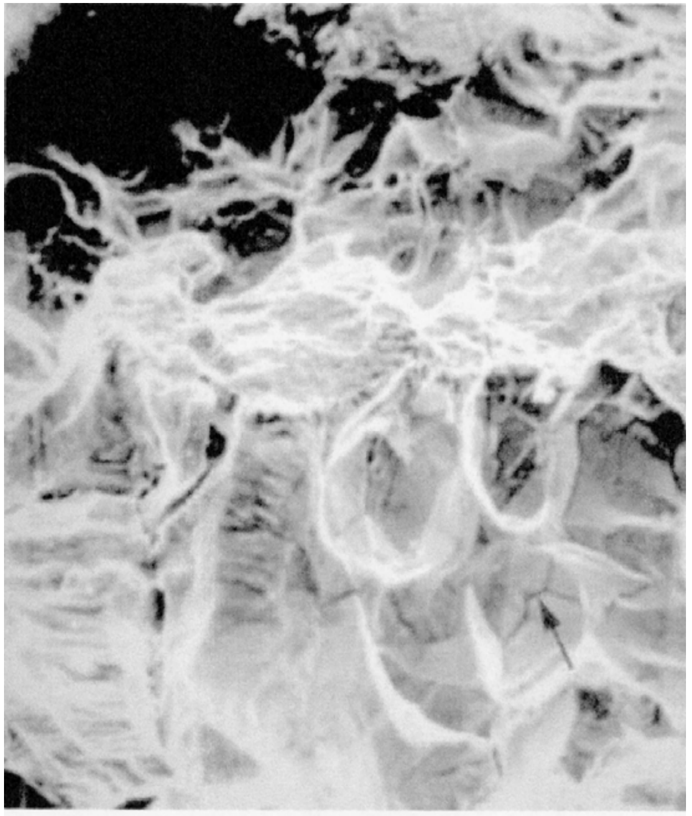
Cl⁻
Cl⁻
O2
Aerobic Bacteria
Oxygen-Containing Water
Metal-Depositing Bacteria
O2 + 2H2O + 4e⁻ → 4OH⁻
Oxide Layer
Anode
M → M2+ + 2e⁻
M2+ + 2H2O → M (OH)2 + 2H+
7LW32-3



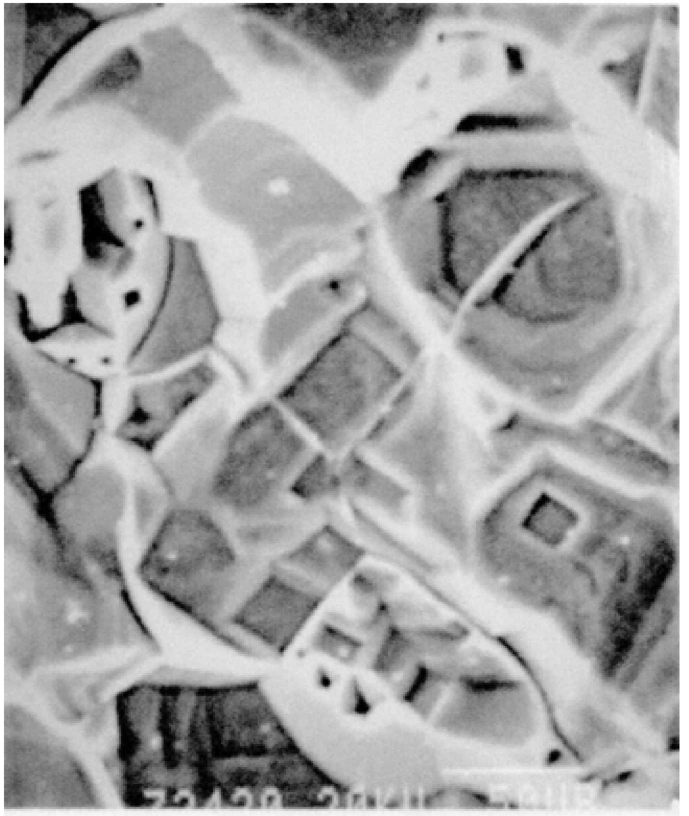
ESEM image of dendritic skeletons in MIC cavities of 316L stainless steel weld (1000X)



Sample 1 (MIC) 2000X

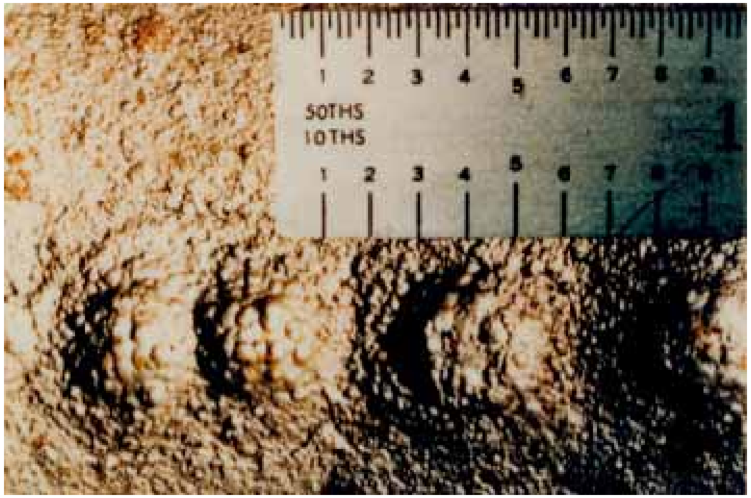


Sample 4 (Water with Cl') 750X



Sample 5 ($CuSO_4$+ Cl') 2000X

Y. Chung and L. K. Thomas; Paper 159; Corrosion '99



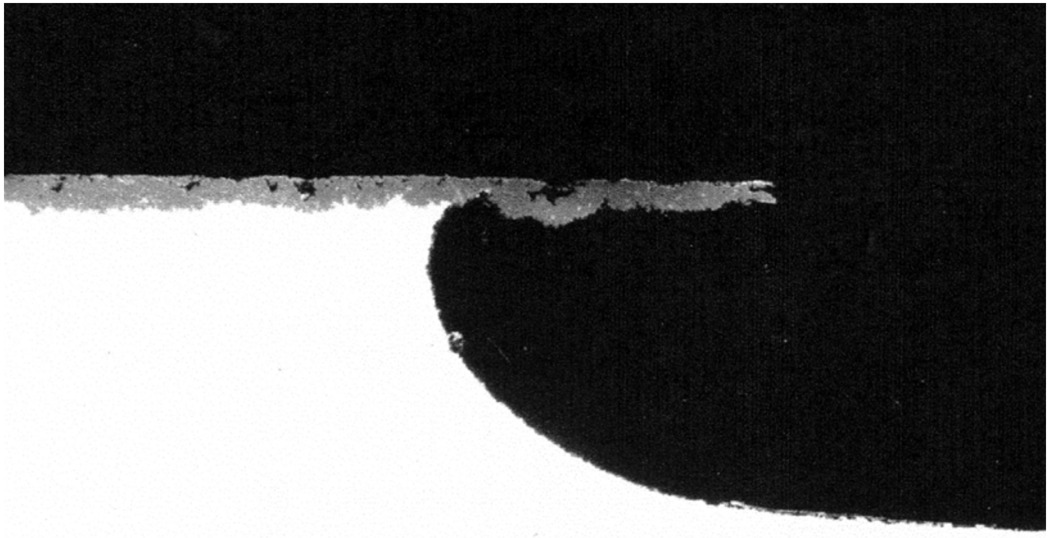
Cup-type scooped out hemispherical pits on flat surfaces with craters in pits

Close-up of sand-blasted surface showing MIC pattern

Corrosion pits with striations

Close-up view of tunnels (100X)

Pope, D. (1990) Method of Detection in the Field GRI Field Guide



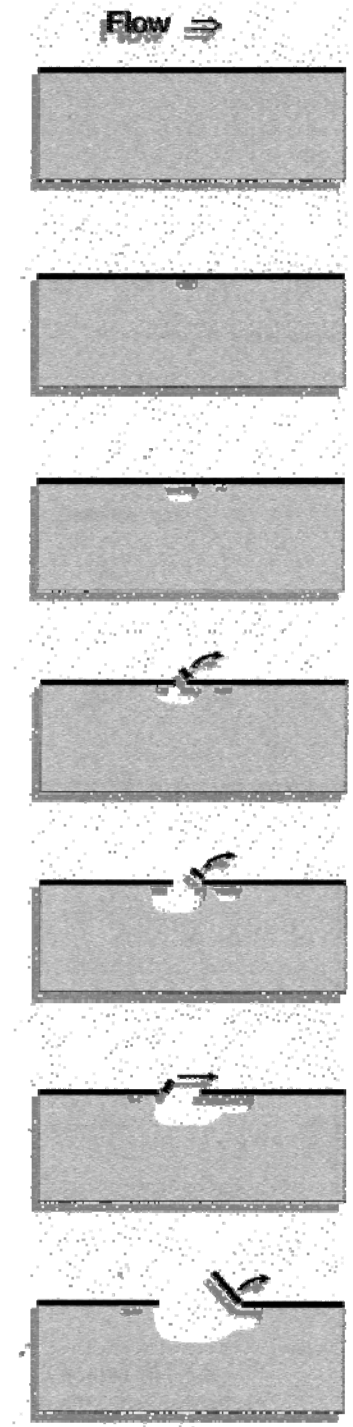
Deep mesa attack in carbon steel without chromium. 20x

2mm deep after 2-3 weeks exposure

80 C, 1.8 bar CO_2, pH 2.5 and flow 4 m sec^{-1}

Nyborg & Dugstad, 2003

Proposed mechanism for growth of mesa attack.



Nyborg & Dugstad, 2003

The following are required for an accurate diagnosis of MIC:

- A sample of the corrosion product or affected surface that has not been altered by collection or storage
- Identification of a corrosion mechanism
- Identification of microorganisms capable of growth and maintenance of the corrosion mechanism in the particular environment
- Demonstration of an association of the microorganisms with the observed corrosion

Corrosion Model Development

Bonis, Chevrot, and Stroe (2008) proposed a methodology for assessing potential corrosion mechanisms:

- What is the natural corrosion likelihood over the forecasted remaining period of operation, assuming that no mitigation measure is applied?

- Are mitigation measures applied? If yes, what level of confidence does one have in their consistency and efficiency at the time of the assessment and over future operation periods (rigorous implementation, corrosion monitoring results, inspection results)?

- What is the known or expected physical condition of the pipeline extrapolated from previous in-line inspection at the time of evaluation (as new, already damaged)?
  Is there any change in operating conditions which may significantly affect the corrosion and/or corrosion mitigation over the evaluation period?

Bonis, Chevrot, and Stroe (2008) have used this methodology to provide lifetime predictions for more than 400 existing pipelines.