BWA™
Water Additives

Use of Biocides to Mitigate MIC in Oil & Gas Applications

Presentation Outline

- Introduction
- Biofilm test method
- Results
  - Biocidal activity
  - Biofilm removal activity
- Case history
- Summary

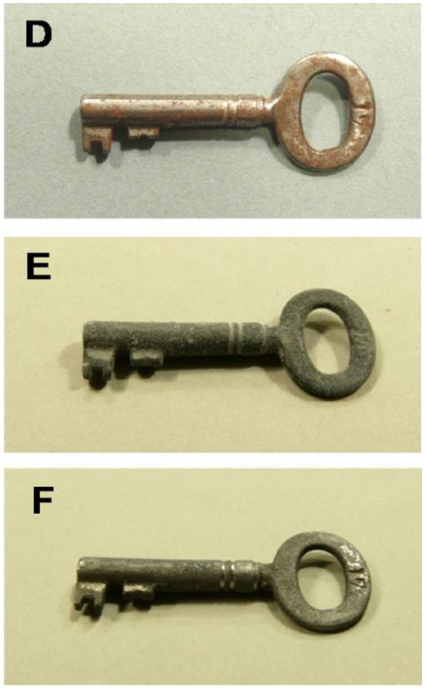
Introduction to MIC

Microbial Corrosion

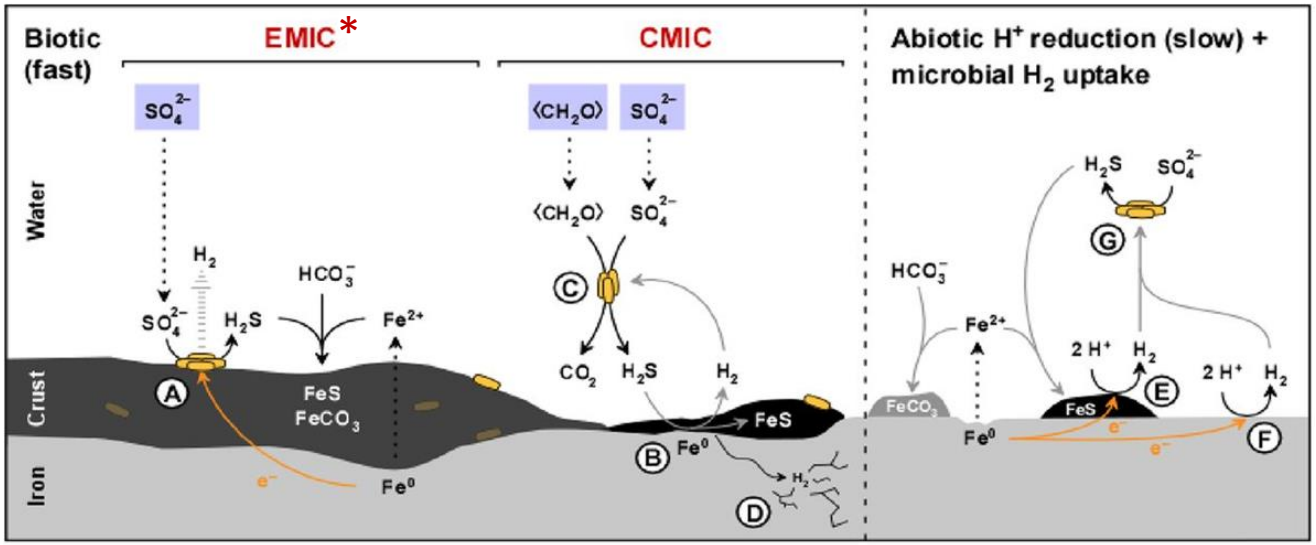
- Can proceed at very high rates
- Can occur under conditions not normally considered corrosive
- Tends to occur localized
- May involve several different species and mechanisms
- Often driven by sulfate-reducing bacteria (SRB)

Sterile

27 months



MIC by Sulfate-Reducing Bacteria (SRB)



Stoichiometry of corrosive reactions

Electrical Microbially Influenced Corrosion (EMIC):

(A) $4\,Fe^0 + SO_4^{2-} + 3\,HCO_3^- + 5\,H^+ \rightarrow FeS + 3\,FeCO_3 + 4\,H_2O$

Chemical Microbially Influenced Corrosion (CMIC):

(B) $H_2S + Fe^0 \rightarrow H_2 + FeS$

(C) $3\langle CH_2O\rangle + 2\,Fe^0 + 2\,SO_4^{2-} + H^+ \rightarrow 3\,HCO_3^- + 2\,FeS + 2\,H_2O$

Sulfide Stress Cracking (SSC):

(D) $2\,H_{abs} \rightarrow H_2$

Abiotic:

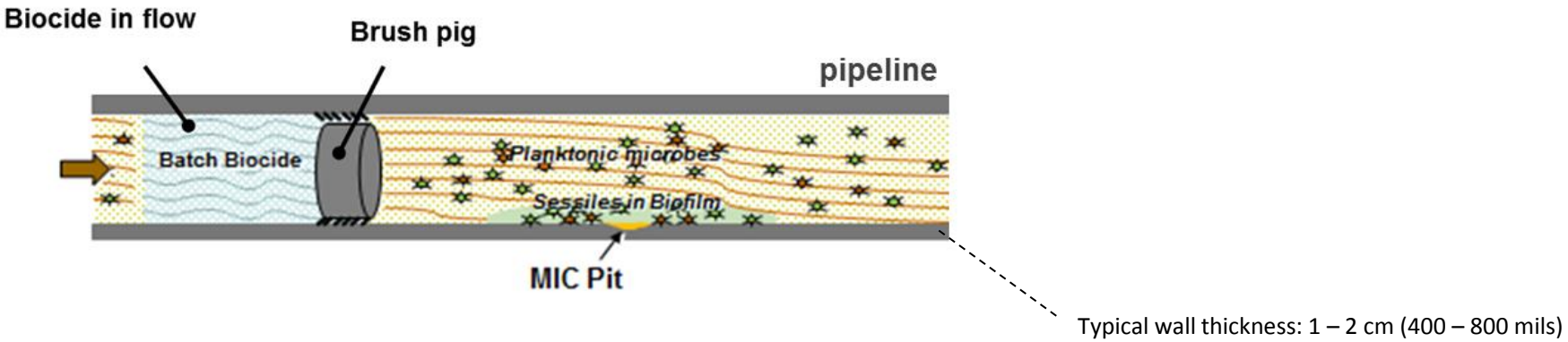
(E) $Fe^0 + 2\,H^+ \xrightarrow{FeS} Fe^{2+} + H_2$

(F) $Fe^0 + 2\,H^+ \rightarrow Fe^{2+} + H_2$

(G) Same as (A), but slower

* Not all SRB capable of EMIC mechanism; similar mechanism detected for certain methanogenic archaea

Mitigation of MIC in Oil and Gas Pipelines



Mitigation of internal MIC in petroleum pipelines

- (Mechanical cleaning / 'pigging') **+ biocide**
- Biocide is applied in batch mode, e.g. once a week for a few hours
- Purpose: Reduce corrosion of pipeline

Efficacy of Biocides against Biofilm

- The effect of biocides on the viability of biofilm organisms has been extensively studied
- Information on the ability of biocides to remove biofilm is limited
  - Eager, et. al. showed that glutaraldehyde was able to remove a *Pseudomonas fluorescens* biofilm
- The biocidal activity ***and*** biofilm removal properties of common oilfield biocides was investigated

Methodology

Biofilm Test Method

- Biofouled coupons transferred to buffer containing biocide
- At appropriate times coupons removed, rinsed and transferred to sterile saline
- Coupons sonicated to release bacteria
- Viable bacteria determined by plate counting and results reported as CFU/cm^2
- Duplicate coupons stained and viewed microscopically to assess biofilm removal

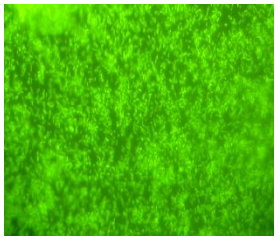
Results

Comparative Biocidal Efficacy against Biofilm

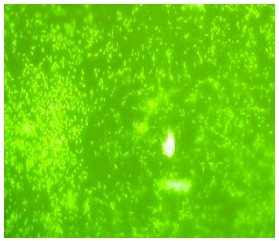
Biocide	Concentration, ppm active	Viable Count, CFU/cm^2	
		1 hour	4 hours
Control	0	5.3×10^6	4.3×10^6
ADBAC	25	4.3×10^6	9.3×10^5
	50	3.3×10^3	1.3×10^3
Glutaraldehyde	25	6.0×10^6	3.7×10^5
	50	1.1×10^4	1.9×10^2
Glutaraldehyde + ADBAC	25	1.7×10^5	2.5×10^4
	50	6.8×10^2	$<1.6 \times 10^1$
THPS	25	1.2×10^6	1.2×10^5
	50	1.1×10^5	3.4×10^2
	100	6.8×10^2	4.7×10^1
TTPC	25	1.4×10^6	1.3×10^5
	50	5.1×10^2	3.1×10^1

Comparative Biofilm Removal Activity

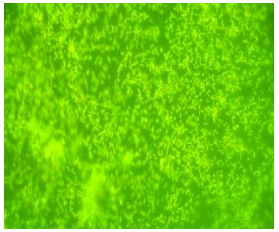
1 Hour Exposure



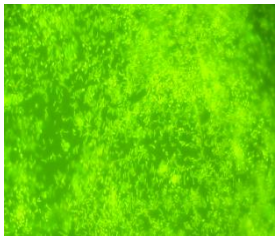
Control
1.1 x 10^7 CFU/cm^2



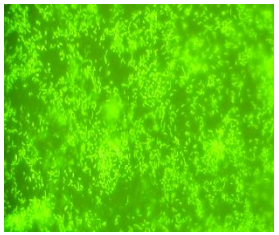
ADBAC
3.3 x 10^3



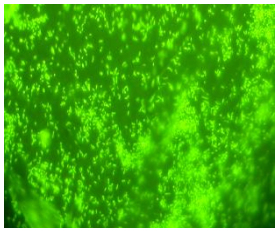
Glutaraldehyde (GA)
2.8 x 10^5



GA/ADBAC
3.7 x 10^4

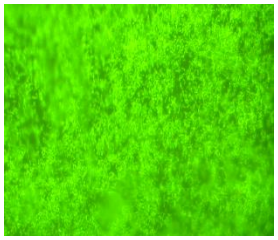


THPS
7.8 x 10^4

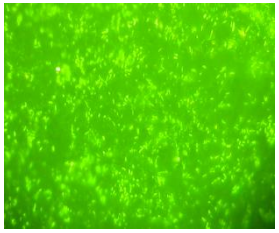


TTPC
1.9 x 10^3

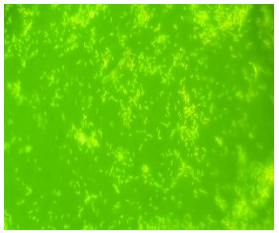
4 Hour Exposure



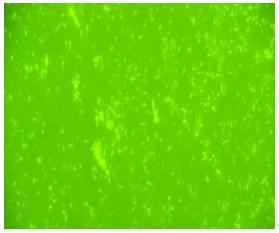
Control
1.3 x 10^7 CFU/cm^2



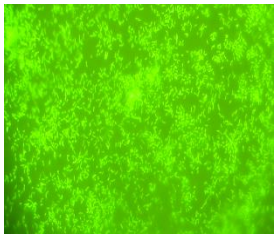
ADBAC
1.3 x 10^3



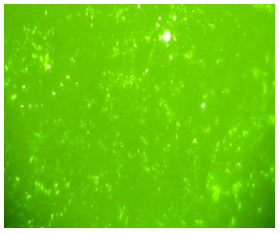
Glutaraldehyde (GA)
<1.6 x 10^1



GA/ADBAC
<1.6 x 10^1



THPS
1.9 x 10^2



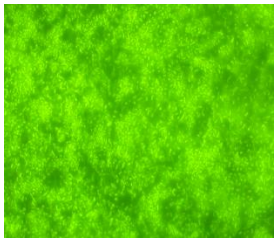
TTPC
<1.6 x 10^1

Comparative Biocidal Efficacy against Biofilm of Phosphonium Biocides

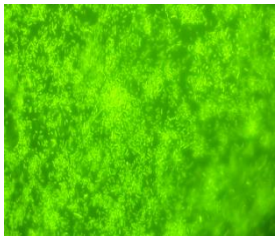
Biocide	Concentration, ppm active	Viable Count, CFU/cm²	
		1 hour	4 hours
Control	0	2.9×10^6	5.7×10^6
THPS	50	3.9×10^6	7.8×10^3
	100	4.7×10^3	1.1×10^2
TTPC	25	7.9×10^6	4.8×10^4
	50	6.5×10^2	1.4×10^2
THPS/TTPC	50/25	2.0×10^3	$<1.6 \times 10^1$

Comparative Biofilm Removal Activity of Phosphonium Biocides

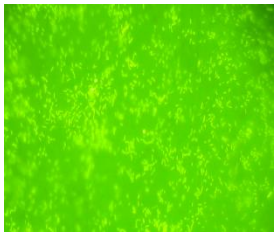
1 Hour Exposure



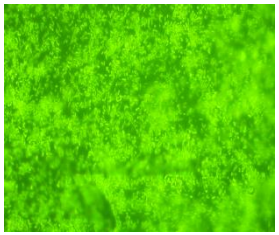
Control
2.9 x 10^6 CFU/cm^2



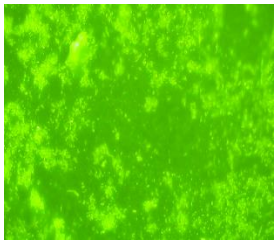
THPS, 50 ppm
3.9 x 10^6



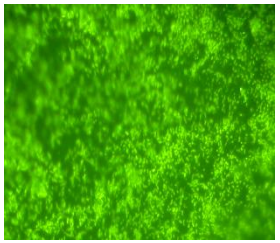
THPS, 100ppm
4.7 x 10^3



TTPC, 25 ppm
7.9 x 10^6

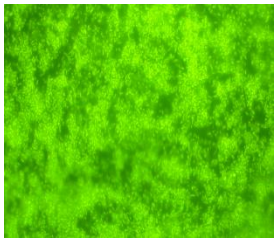


TTPC, 50 ppm
6.5 x 10^2

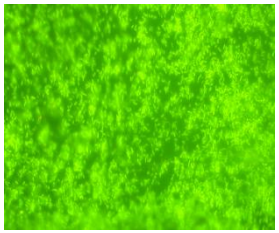


THPS/TTPC,
50/25 ppm
2.0 x 10^3

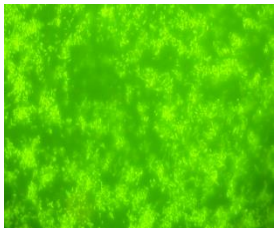
4 Hour Exposure



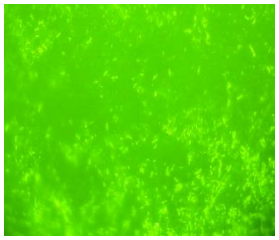
Control
5.7 x 10^6 CFU/cm^2



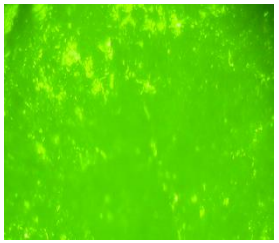
THPS, 50 ppm
7.8 x 10^3



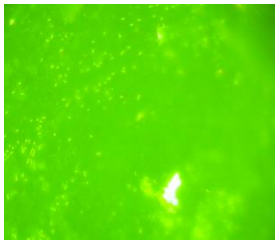
THPS, 100 ppm
1.1 x 10^2



TTPC, 25 ppm
4.8 x 10^4



TTPC, 50 ppm
1.4 x 10^2



THPS/TTPC,
50/25 ppm
<1.6 x 10^1

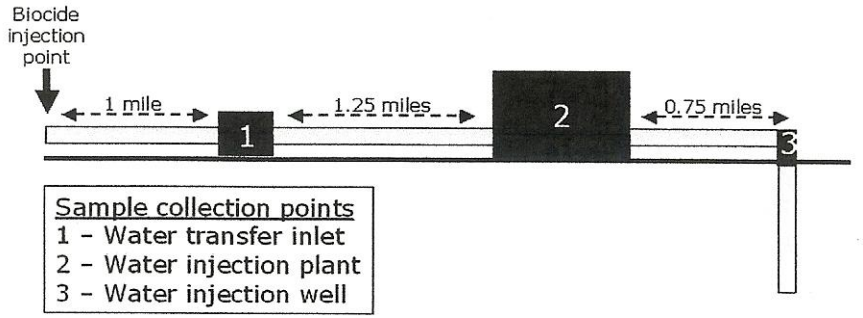
Case History

Bakken Water Injection Well Trial*

- **Problem: Using THPS to control bacteria, but observing incomplete kill and high corrosion rates**
- **Solution: Use low levels of TTPC to secure both additional kill and lower corrosion rates**
- **Results: Improved kill and lower corrosion rates**

*Keasler, V.; et.al. SPE 121082, 2009 International Symposium on Oilfield Chemistry

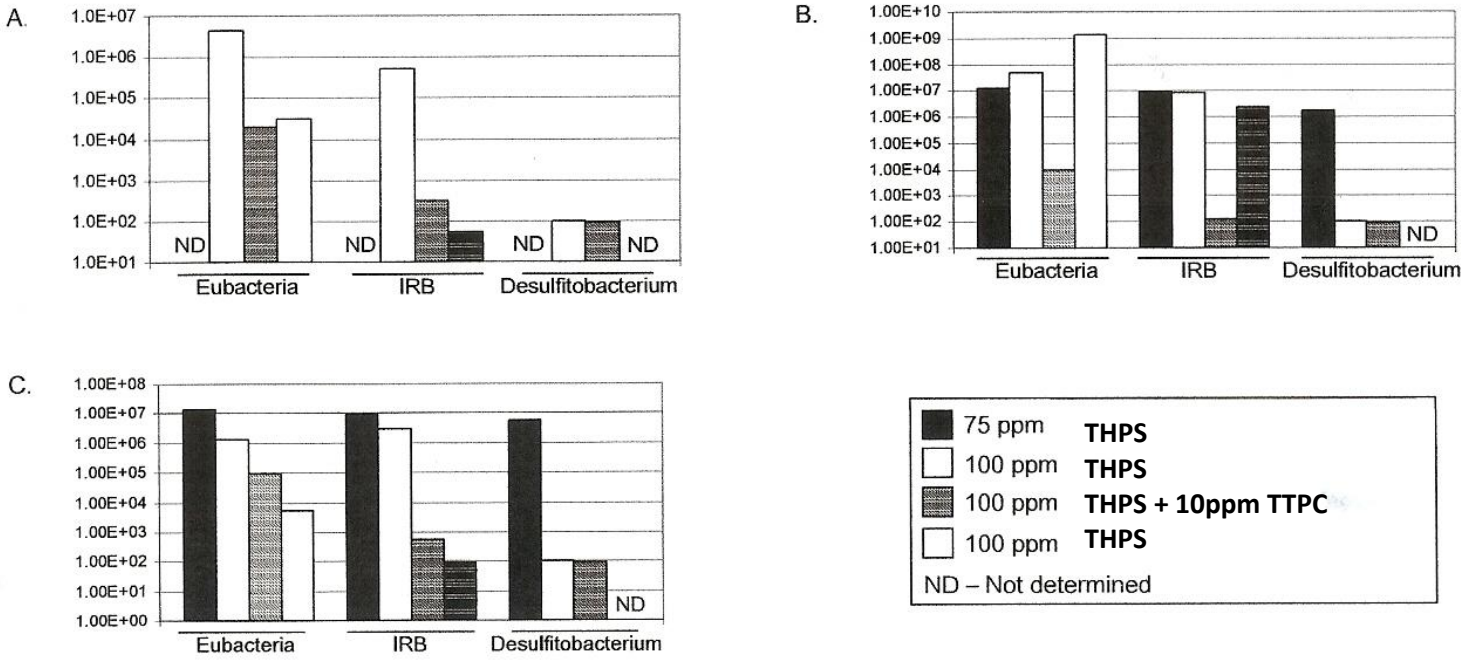
Trial Set-Up



Injected Biocide	Biocide Dose	Contact Time	Duration of Treatment
THPS	75 ppm	4 hrs/wk	7 months
THPS	100 ppm	4 hrs/wk	4 months
THPS plus TTPC	100 ppm + 10 ppm	4 hrs/wk	1 month
THPS	100 ppm	4 hrs/wk	3 months

Corrosion coupons pulled at the end of each treatment and replaced with new ones

Efficacy Results



Panel A: Bacterial Counts at Sample Point 1 (Water Transfer Inlet)
Panel B: Bacterial Counts at Sample Point 2 (Water Injection Plant)
Panel C: Bacterial Counts at Sample Point 3 (Water Injection Well)

Corrosion Coupon Results

Corrosion Coupons from SP 2:
(l to r), 75 ppm THPS, 100 ppm THPS, 100 ppm THPS + 10 ppm TTPC

	75 ppm THPS	100 ppm THPS	100 ppm THPS + 10 ppm TTPC	100 ppm THPS
Sample Point 1	**1.68 GC/P**	**1.60 GC**	**0.79 GC**	**1.19 GC**
Sample Point 2	**2.60 GC/P**	**3.09 GC**	**1.16 GC**	**2.65 GC**
Sample Point 3	**0.30 GC/P**	**1.15 GC**	**0.79 GC**	**1.05 GC**

GC = General Corrosion; P = Pitting. MPY results are time-normalized

Summary

- Biofilm control essential for the mitigation of MIC
- Biocides vary in their ability to kill and remove biofilm
- Biocide combinations which include a surface active biocide (ADBAC, TTPC) have improved activity compared to the individual biocides alone
- Biocide treatments which display both biocidal activity and biofilm removal properties would be expected to offer the best potential for MIC control