Novel Corrosion Inhibitors for High Temperature Applications

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Goals

- To design and develop a series of novel water-soluble and oil soluble-corrosion inhibitors and evaluate them as a new class of high-temperature effective corrosion inhibitors.

Overview

- Introduction
- Experimental
- Results and Discussion
- Field Application
- Conclusions
- Acknowledgements

Introduction

- Electrochemical cell
- Corrosion types
- Factors affecting corrosion rates
- Effects of temperature in corrosion rates

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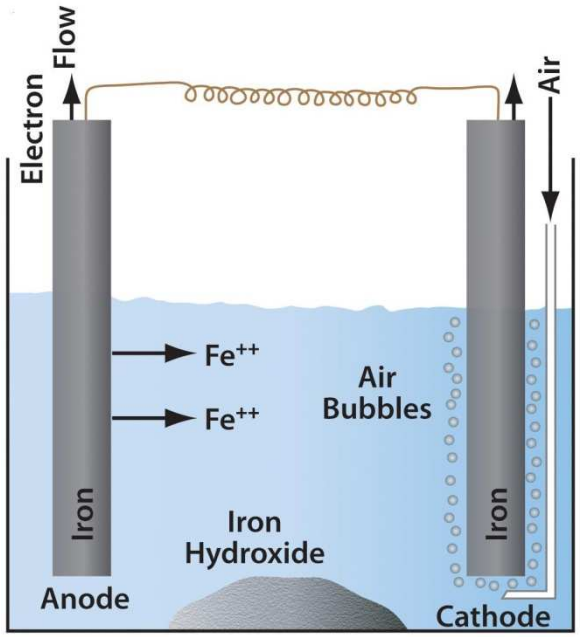
Factors Required For Electrochemical Corrosion

- Anode
- Cathode
- Electrolyte
- External Connection

The severity of corrosion depends upon the potential energy generated between the anode and the cathode.

Corrosion Cell



Iron - Iron Cell

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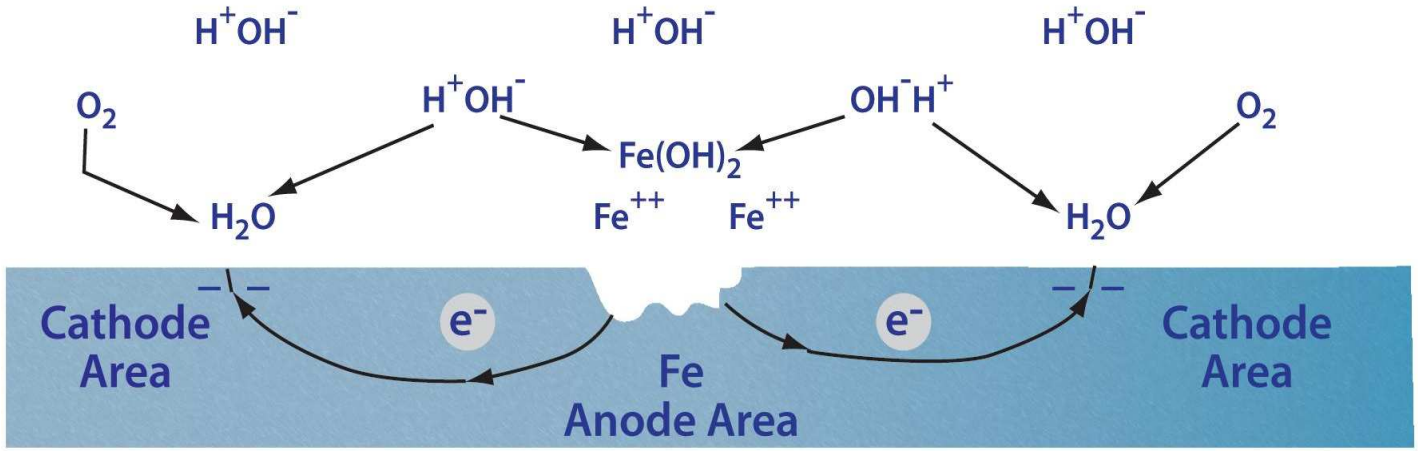
Corrosion Mechanism



Anode Reactions

$Fe \longrightarrow Fe^{++} + 2e$

$Fe^{++} + 2OH^- \longrightarrow Fe(OH)_2$

Cathode Reactions

$2H^+ + {}^1/_2\ O_2 + 2e^- \longrightarrow H_2O$

$H_2O + {}^1/_2\ O_2 + 2e^- \longrightarrow 2OH$

Corrosion Types

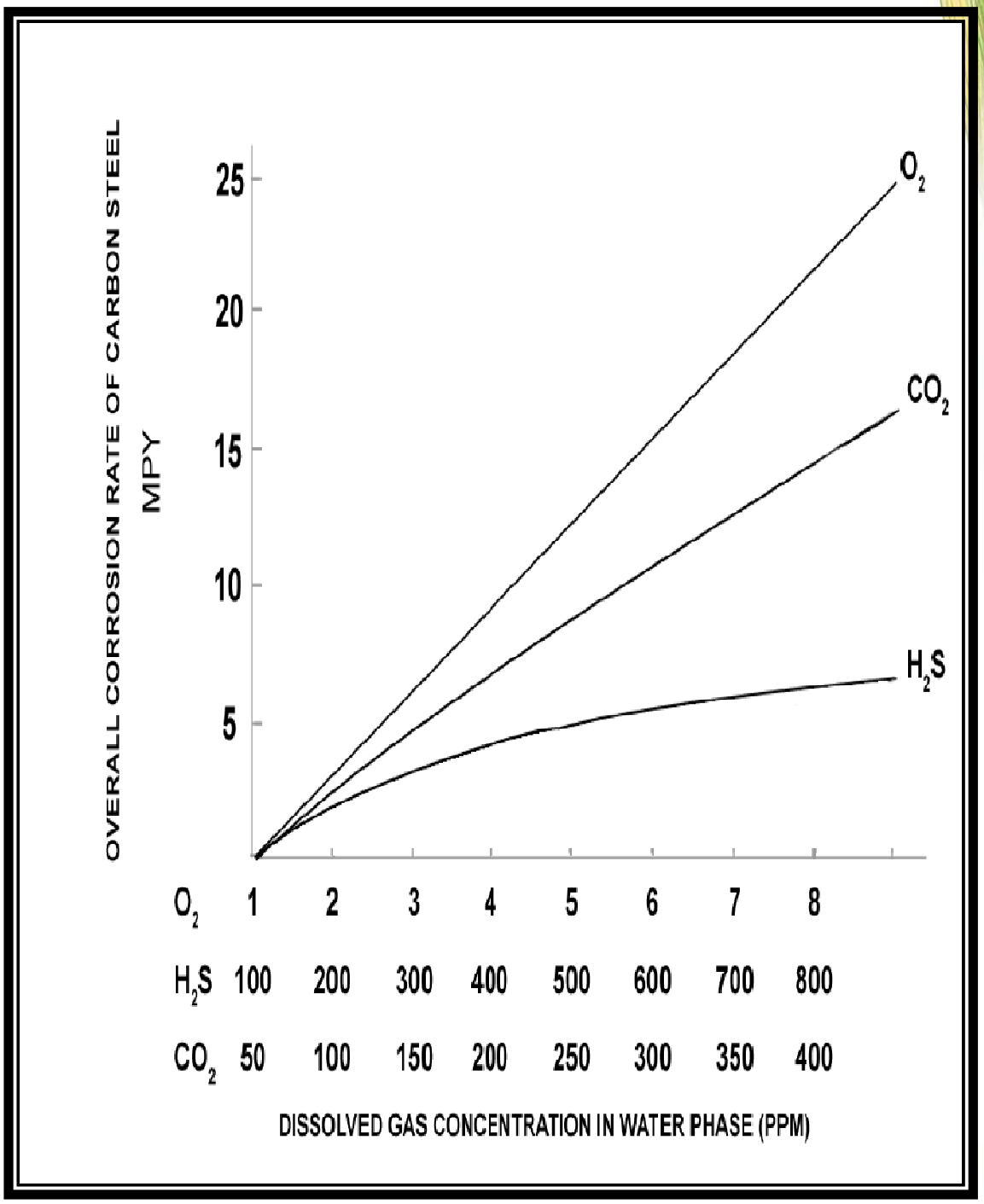
- Generalized Corrosion
- Pitting Corrosion

Factors Affecting Corrosion Rates

- Brine concentration
- Type of hydrocarbons
- Temperature
- Pressure of producing system
- Velocity of fluids
- Solids production
- Oxygen, H2S, CO2, elemental sulfur, organic acids, chlorides

Effect of Temperature

- Rule of thumb – chemical reaction rates double with 10ºC rise in temperature.
- Metal in presence of corrosive gas in open container CR ↓ as temp ↑ (solubility of a gas decreases as temp increases)
- In a closed system with corrosive gas CR↑ as temp ↑



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Experimental Procedure

- Chemical Formulation
- Heat stability tests
- RCE Test Methods
- HP/HT Autoclave Tests
- Field Tests

Chemical Formulation

- Three new chemical compounds were used in the formulations
- More than fifty formulations were tested
- The chemicals were blended using solvents with high boiling points

Heat Stability Tests

- Selected chemicals were heated in a sealed tube under inert conditions at 400˚F for six hours and a sample of each was taken for Fourier Transformed Infra Red Spectroscopy (FTIR) followed by RCE tests

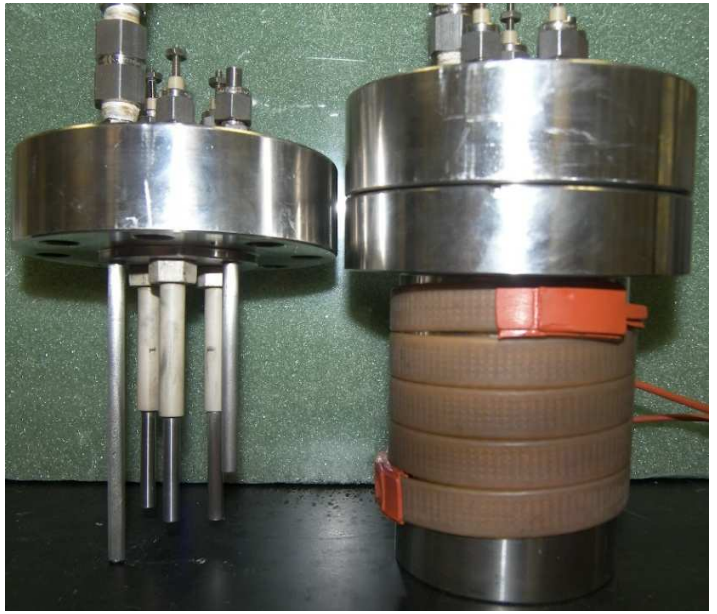
- The chemicals that were stable continued to heat at 400˚F for 24 hours and tested by FTIR and RCE tests

Rotating Cylinder Electrode (RCE)

- All tests were conducted at 15 ppm of the chemical
- The fluids are synthetic brine and kerosene (90:10)
- Continuous CO_2 sparge at 150˚F and rotation at 2000 rpm

HP/HT Stirred Autoclave

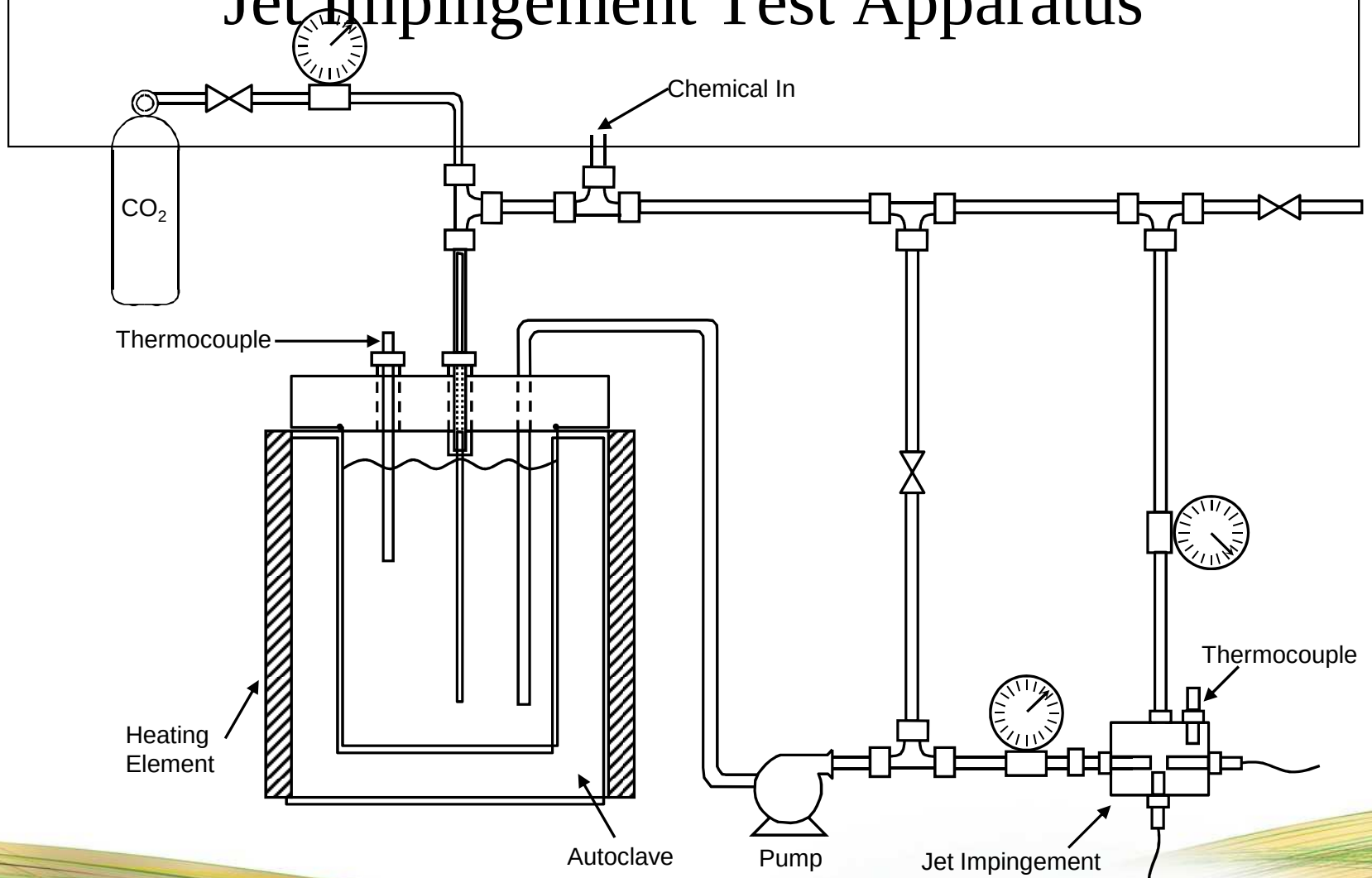
- Capable of operating at or below 575F and Pressure 5,000 psi
- Sweet or Sour Testing
- Can use under static or stirred conditions
- Corrosion rates are calculated using LPR data and mass loss data



Jet Impingement System

- Maximum temp. 350F
- Calculated Wall Shear Stress Value (3% TDS brine):
  - τ = 60-960 Pascal or
  - 0.087-1.49 psi(high shear stress)

Jet Impingement Test Apparatus



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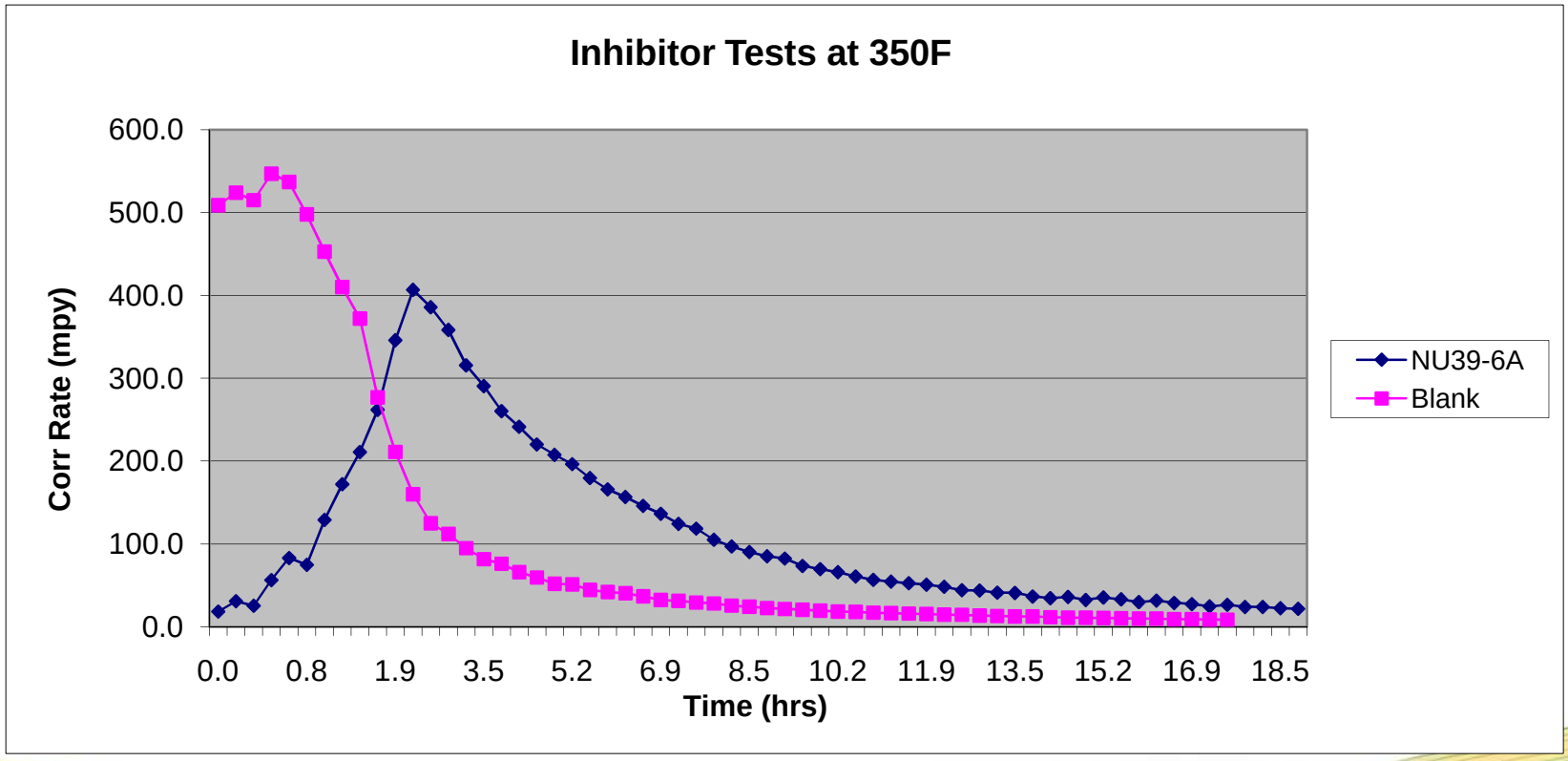
Results and Discussion

- HP/HT Tests
- RCE Tests
- Chemical Stability by FTIR

Water-Soluble High Temperature Stable Inhibitors



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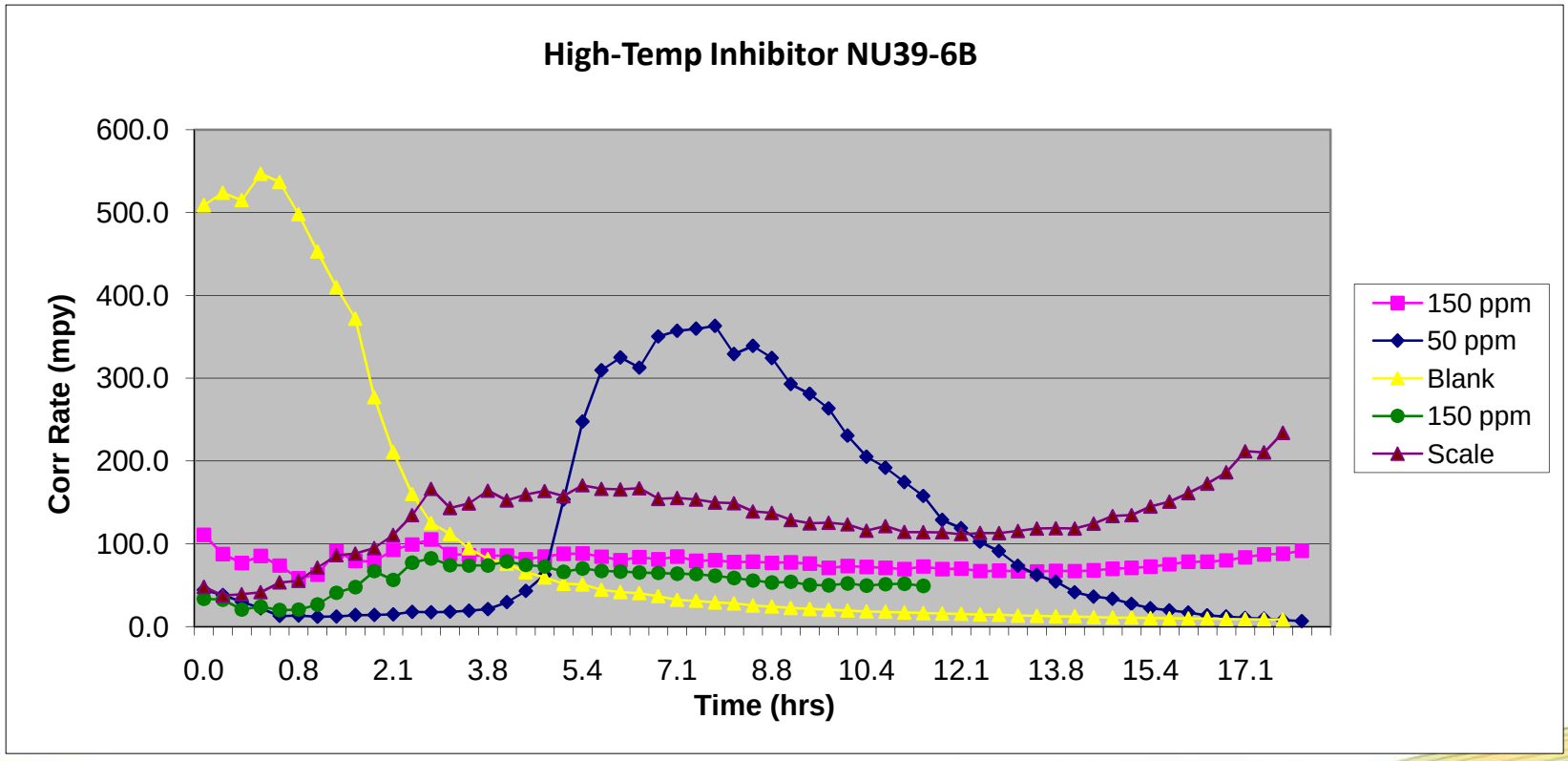
HP/HT Autoclave Tests @350F



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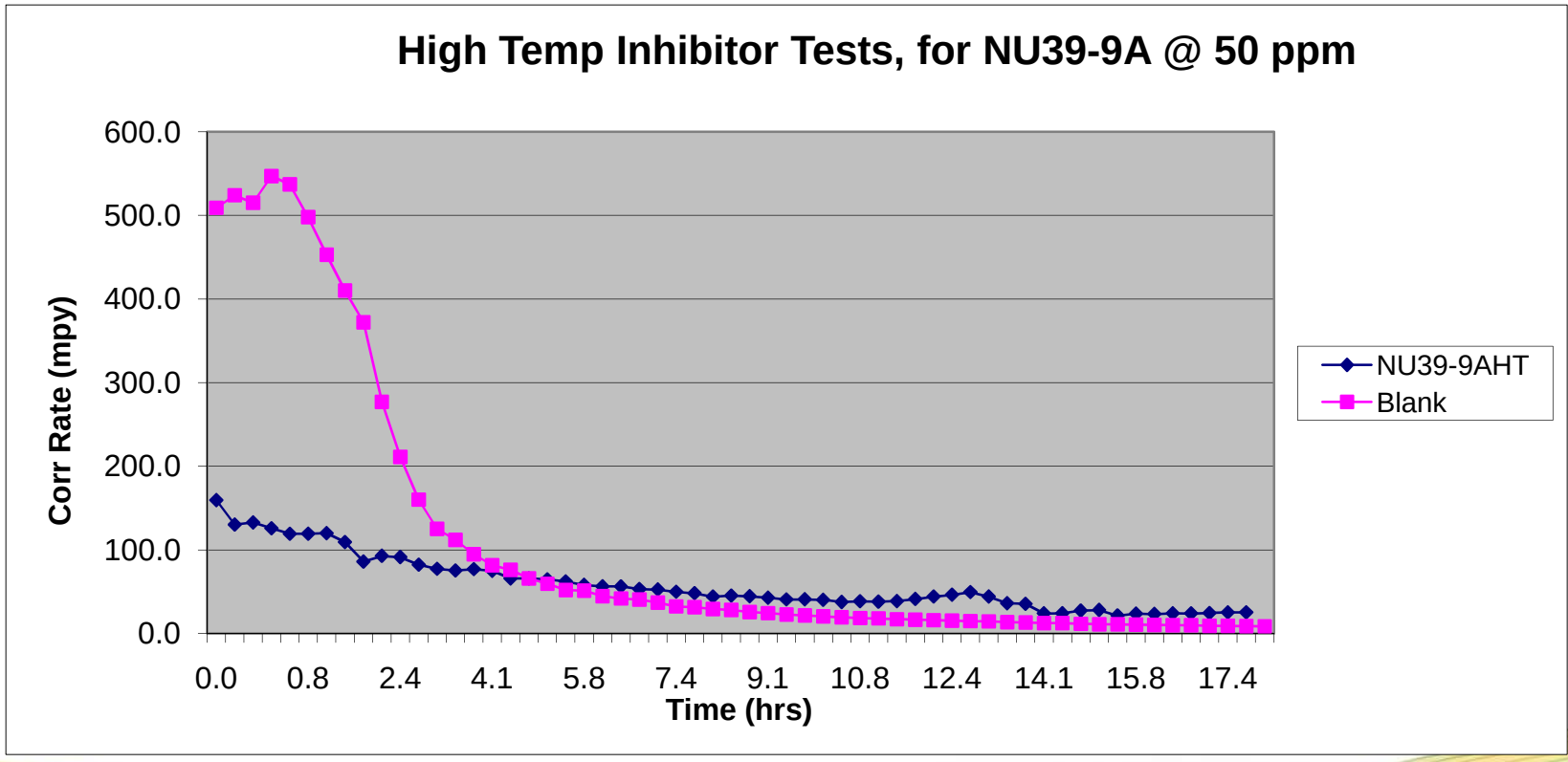
Water-Soluble HT/HP Pressure Inhibitor



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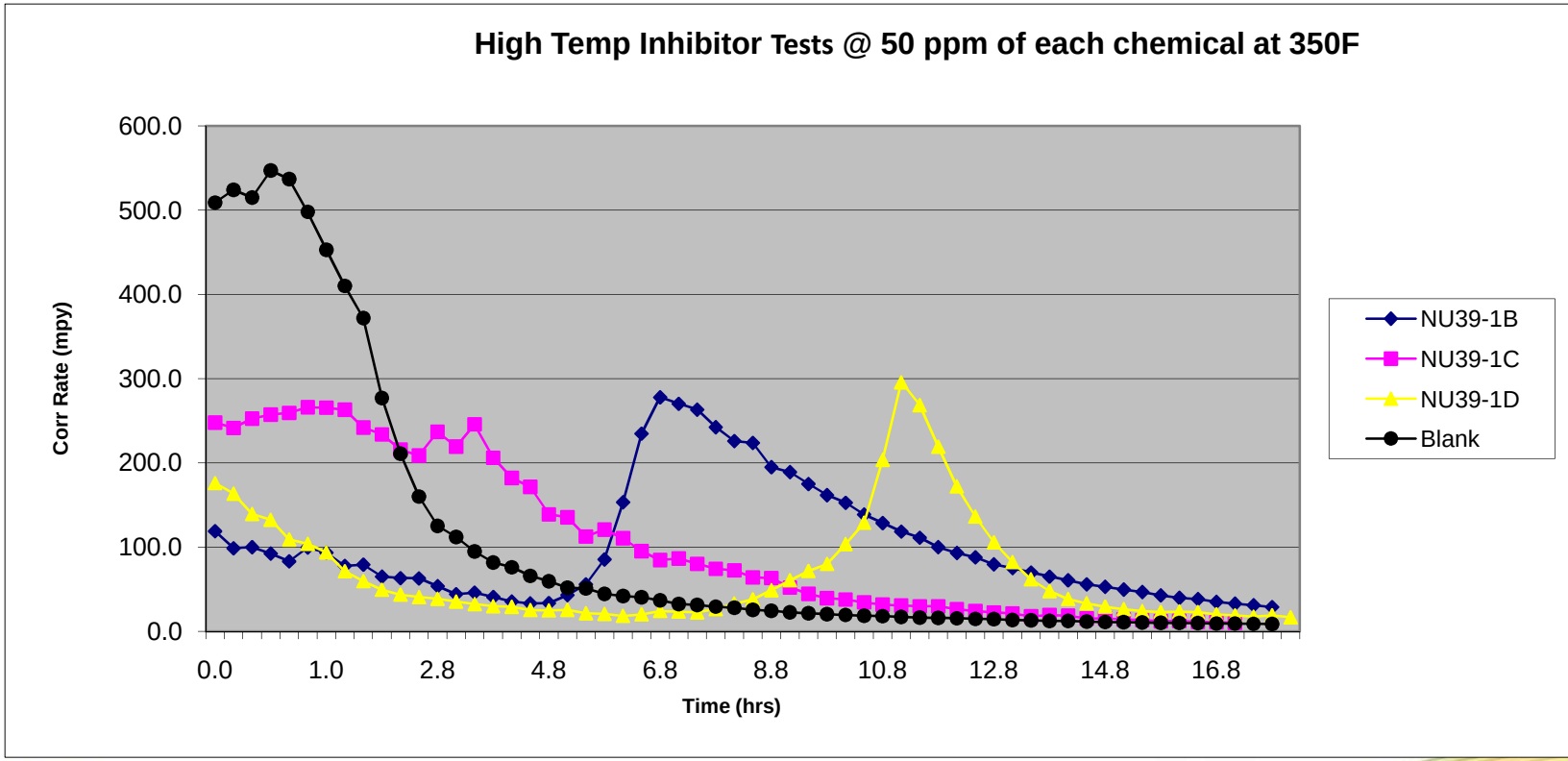
HP/HT Oil-Soluble CIs



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Selection

- NU39-9A was selected and commercialized as MC MX 725-6 (water soluble)
- NU39-1D was selected and commercialized as MC MX 793-6 (oil-soluble)

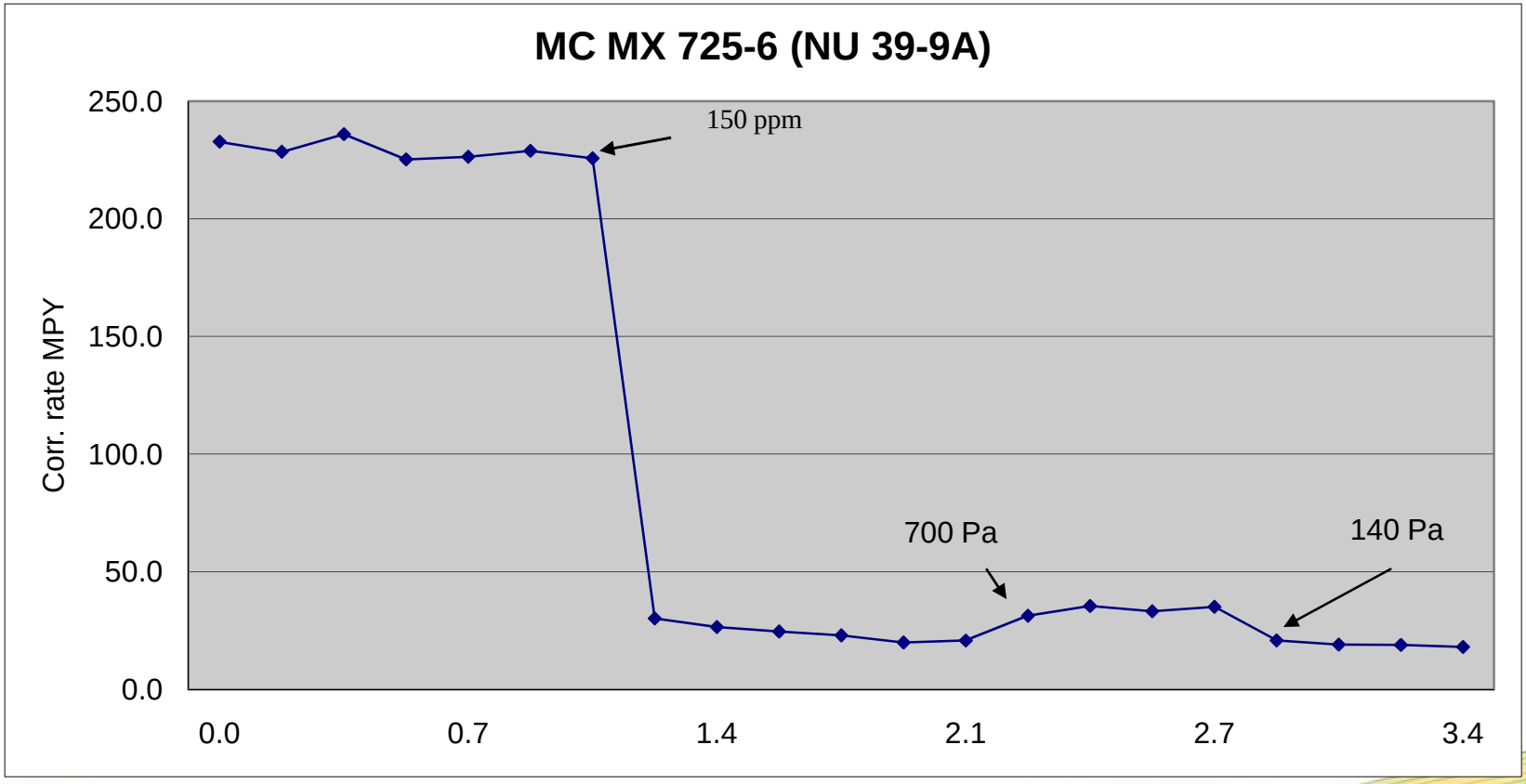
Chemical Degradation at Elevated Temperature

FTIR Comparison of Heated Chemical at 204°C with Unheated Chemical After Heating for Six Hours and for Twenty-Four Hours

Least degraded chemicals, after six hours:
MC MX 793-4 (oil soluble) < MC MX 725-6 (water-soluble)

After 24 hours:
MC MX 793-4 < MC MX 725-6

Jet Impingement Results at 350F



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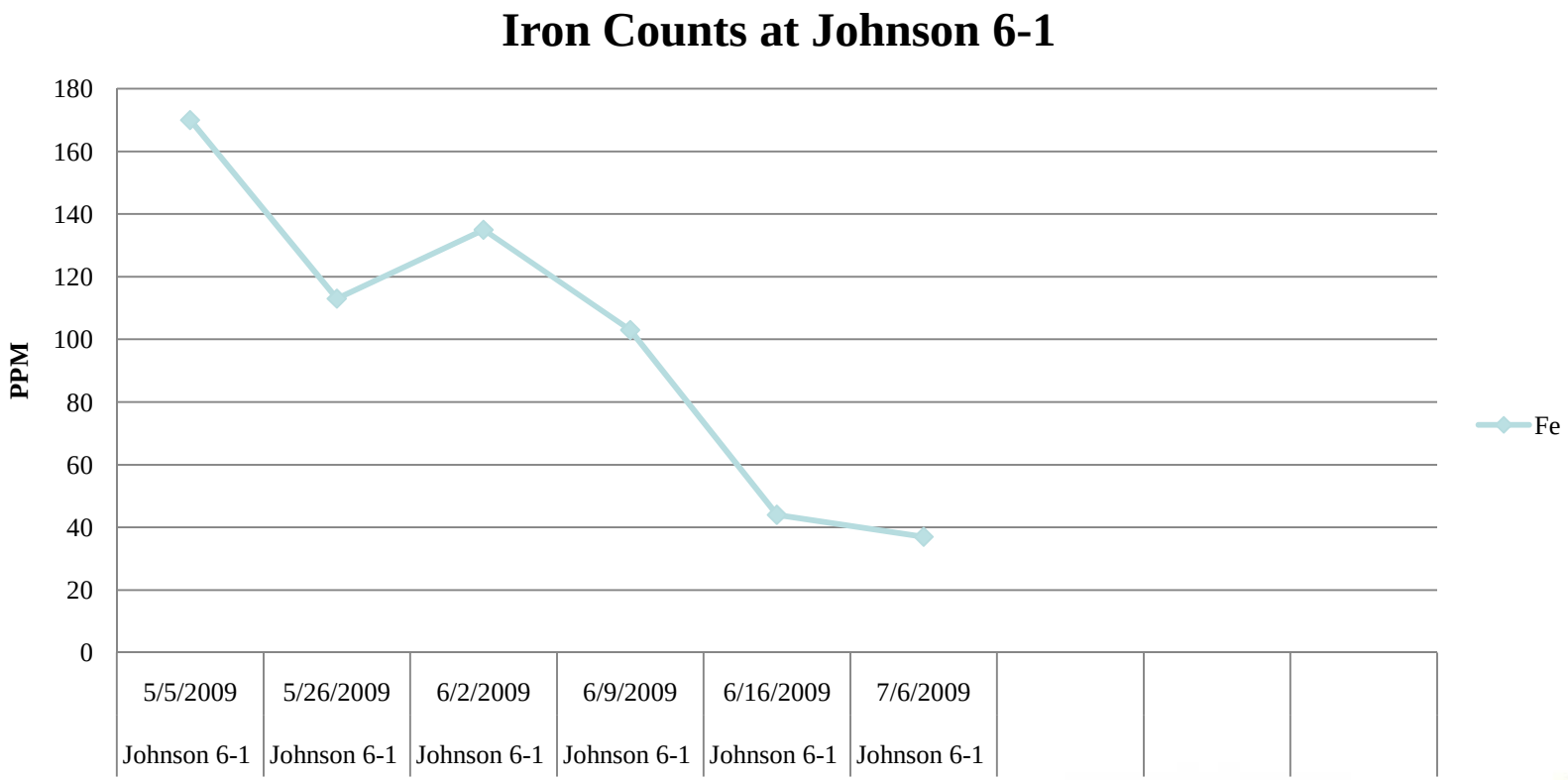
Field Conditions of Haynesville Shale

- 3-4% CO_2 and 100-300 ppm of H_2S
- BHT is 350-380F
- Average water production is 300 bbl/d
- Chemicals used in this field trial are: MC MX 725-6 (WS) and MC MX 793-6 (OS)
- Baseline iron count is 450-500 ppm

Field Trial with MX 725-6



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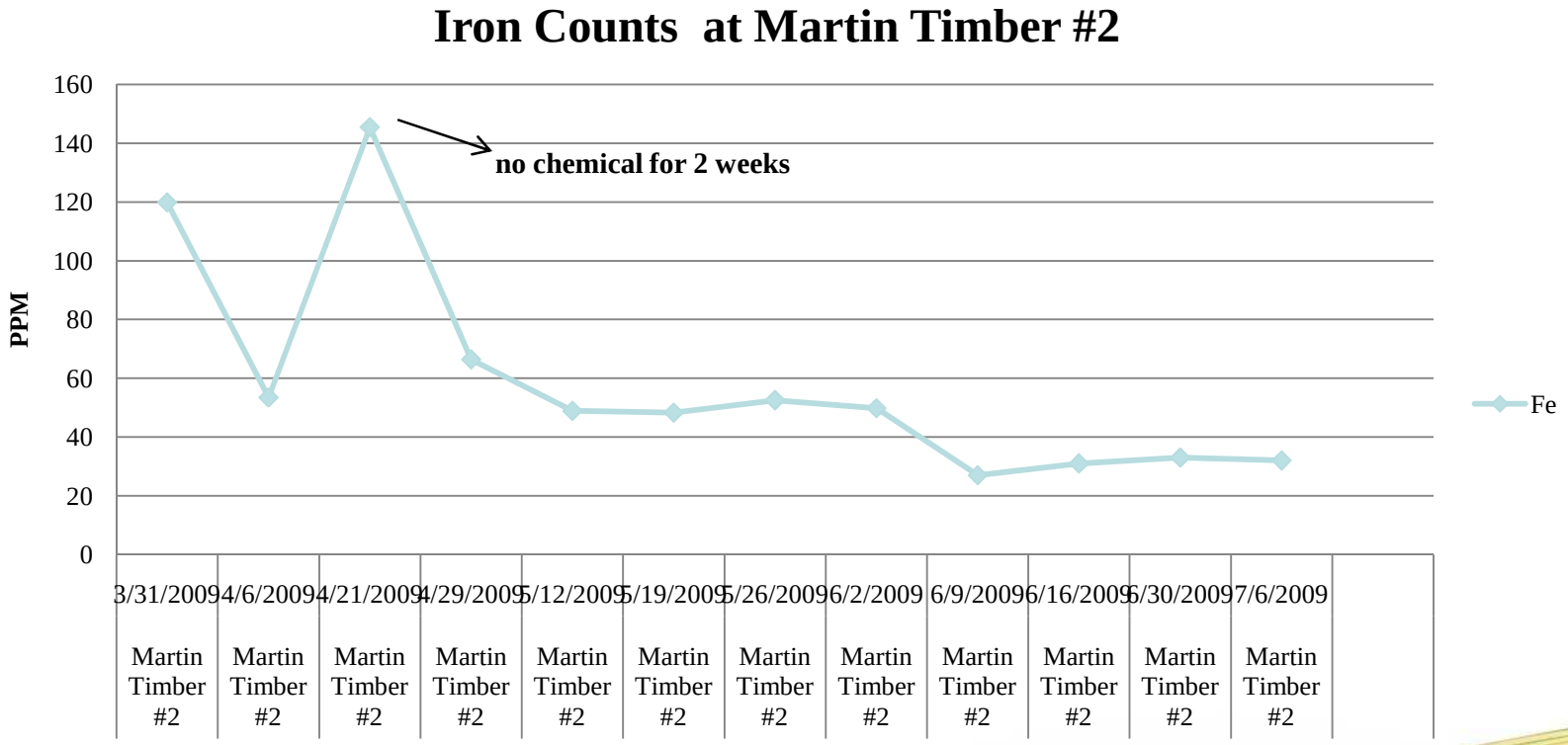
Corrosion Rates Measurement Using Iron Counts



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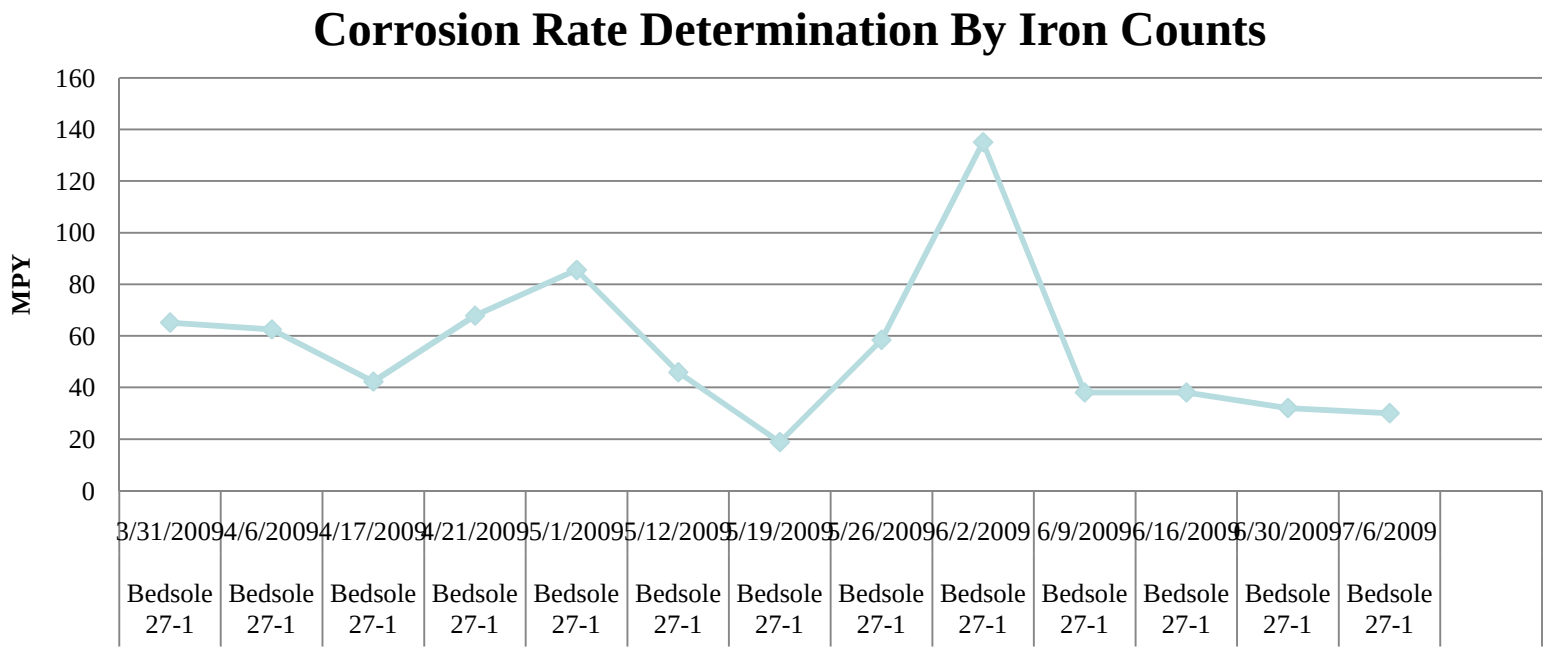

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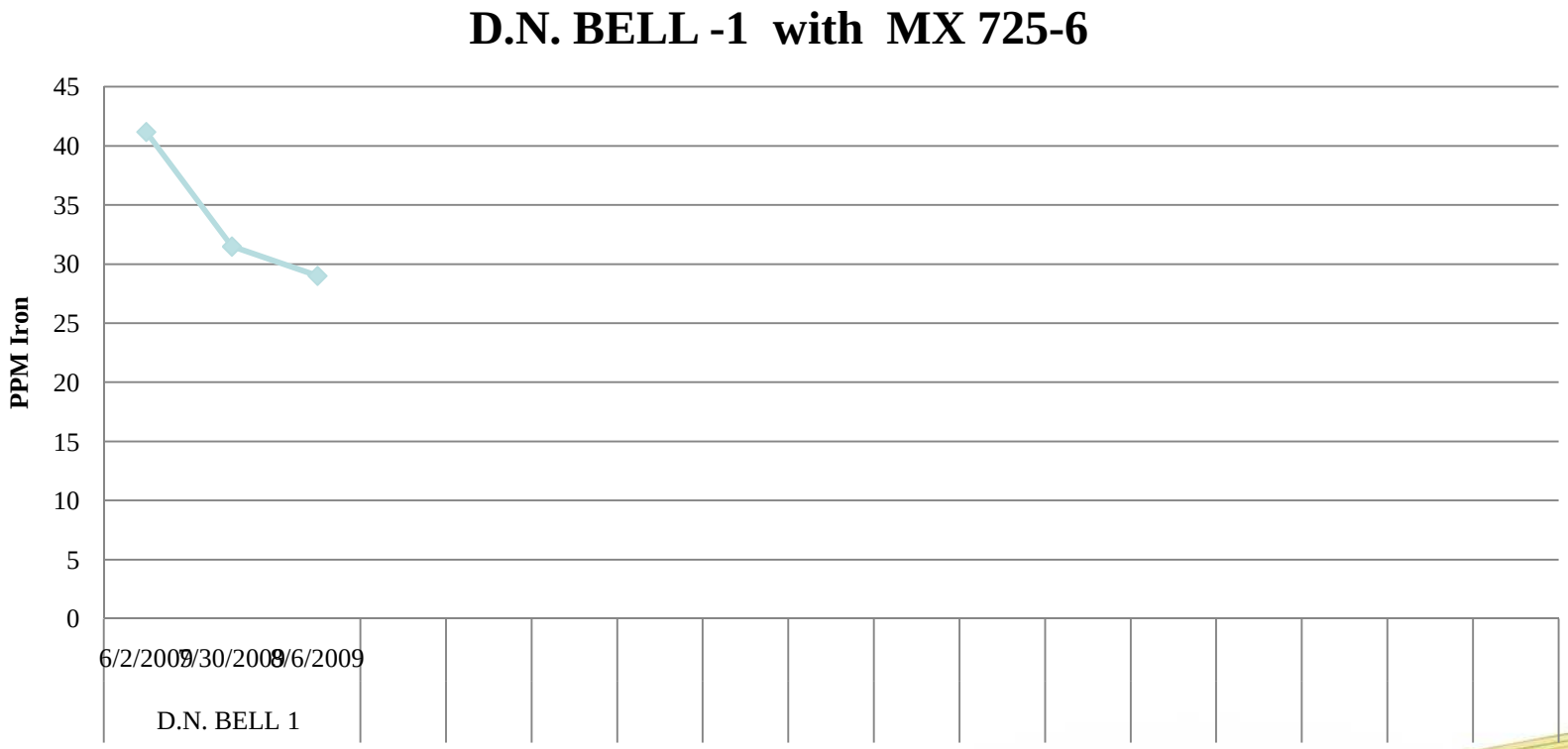

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Current Research: Development of Corrosion Inhibitors for Extreme High Temperatures

- Chemicals were tested using HT/HP stirred Autoclave
- Tested at 200 psig CO2 and 200 psig Oxygen
- Temperature at 560F and 400 psig total pressure
- 20,000 NaCl was used with kerosene (9/1)
- Two 1018CS coupons were used; one coupon was suspended in the gas cap and a second coupon was fully submerged in the test solution

Corrosion Inhibitors Tested at 572ºF

	NU48-42A		NU48-42B		NU48-42C	
	Gas	Liquid	Gas	Liquid	Gas	Liquid
Initial Weight (g)	23.6183	22.7865	22.9443	23.0793	23.1915	23.1935
Final Weight (g)	23.5742	22.7178	22.9125	23.0158	23.133	23.1441
Weight Loss (g)	0.0441	0.0687	0.0318	0.0635	0.0585	0.0494
Test Hours	7	7	7	7	7	7
Corrosion Rate (mpy)	123.73	192.76	89.22	178.17	164.14	138.61
Corrosion Rate (mm/y)	3.13	4.88	2.26	4.51	4.16	3.51

Inhibitors for Extreme Conditions

	NU48-42C		NU48-42D	
	Gas	Liquid	Gas	Liquid
Initial Weight (g)	22.4691	22.4595	22.6783	22.6815
Final Weight (g)	22.4335	22.4026	22.6379	22.546
Weight Loss (g)	0.0356	0.0569	0.0404	0.1355
Test Hours	63	63	63	63
Corrosion Rate (mpy)	11.10	17.74	12.59	42.24
Corrosion Rate (mm/y)	0.28	0.45	0.32	1.07

Conclusions

- We have developed several high-temperature stable corrosion Inhibitors for sweet or sour conditions
- Products MC MX 725-6 (water soluble) and MC MX 793-6 (oil soluble) are effective and stable at 400F
- The water-soluble MC MX 725-6 was applied in several very high-temperature wells successfully
- The oil soluble MX 793-6 currently undergoing field testing in Canada and South Texas

Conclusions (continued)

- Multi-Chem Corrosion Research Team developed a corrosion inhibitor (NU54-48C/MC MX 6-1412) for extremely corrosive and very high temperature environments
- The chemical is effective in the presence of high levels of O2 and CO2 , at 572F and high pressure

ACKNOWLEDGEMENTS

- East Texas Gas Producers Association (ETGPA)
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