



Fountain Quail
ENERGY SERVICES

Corrosion Study

Corrosivity of Chlorine Dioxide on Typical Oilfield Iron

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Introduction

- Background
- Test Goals and Procedure
- Summary
- Equipment
- Fluid System
- Test Execution
- Results and Analysis

Background

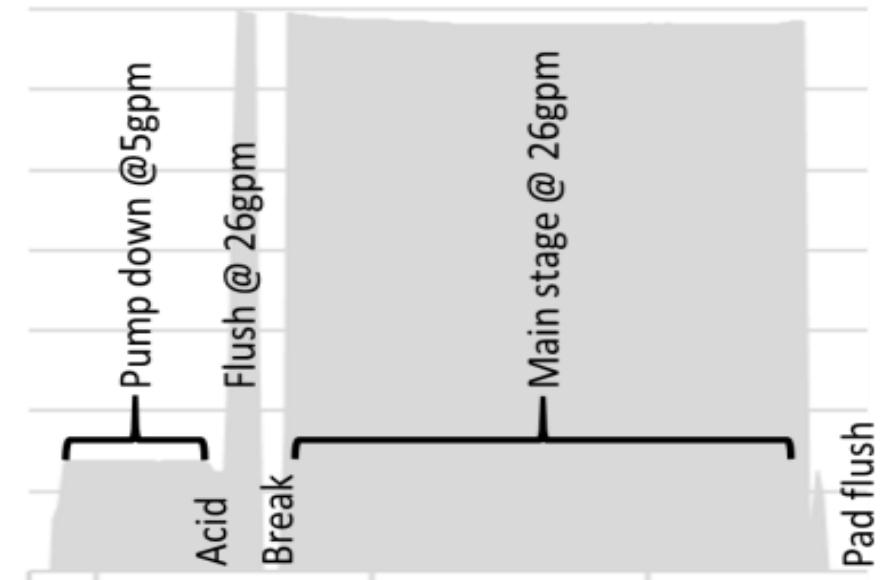
- Concern about impact of chlorine dioxide ClO_2 on fluid ends and flow iron
- Current corrosion studies unrepresentative (static vs. dynamic tests)
- A test was needed that simulated flow conditions, fluid chemistry, and typical alloys used in hydraulic fracturing



Goal

Determine the effect chlorine dioxide (ClO_2) has on common field iron used in hydraulic fracturing flow and pressure pumping equipment at

- a. Typical dose rates
- b. In a traditional slick water hydraulic fracturing fluid chemistry
- c. Using both fresh and brine water solutions
- d. In a dynamic flow environment

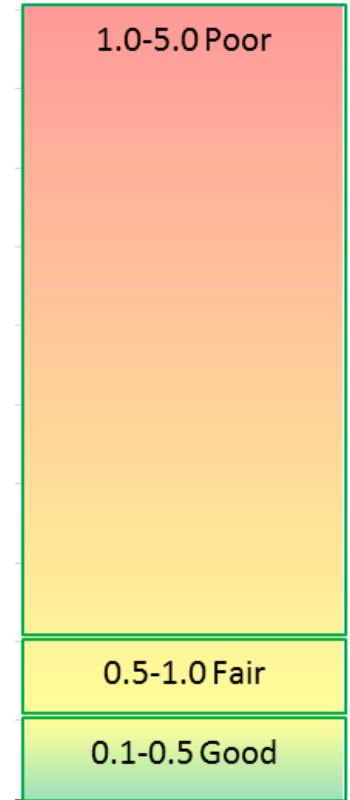


Plan

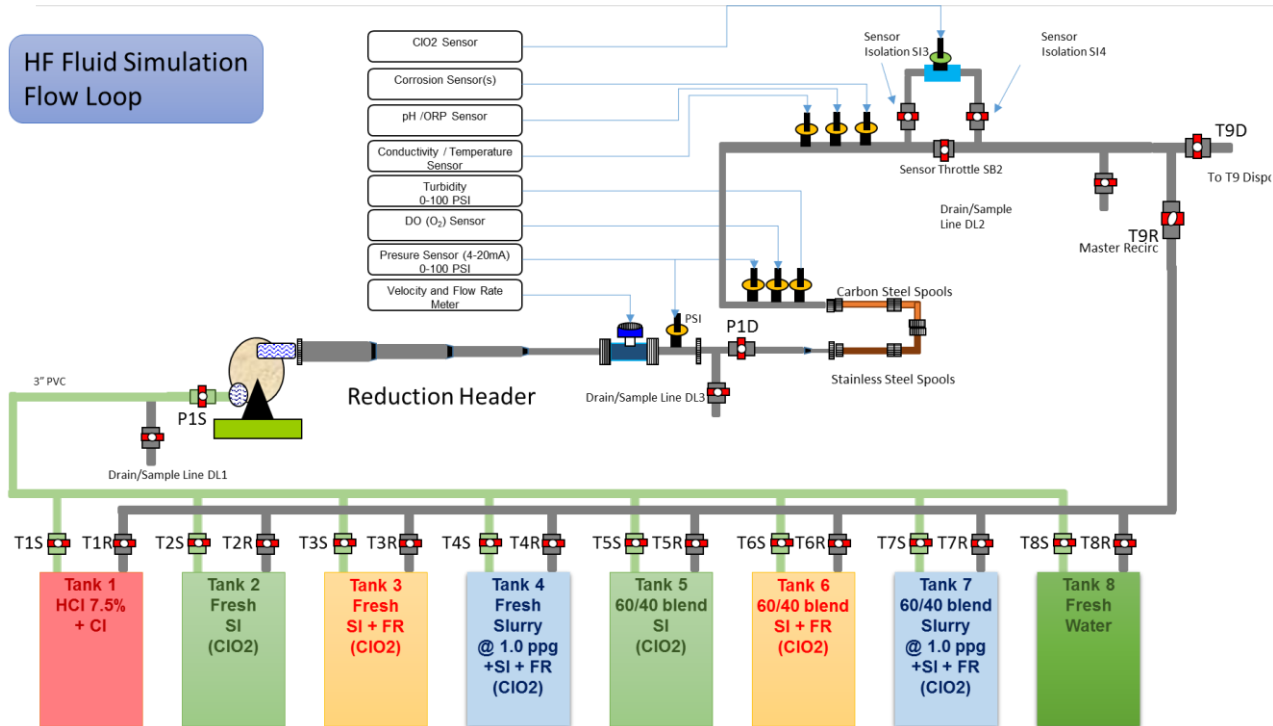
- Design a test to simulate flow conditions, alloys, and typical fluid chemistries
- Use fresh and brine solutions
- Mimic the steps in a conventional frac stage
- Establish a baseline using fluid systems without ClO_2 , then repeat with ClO_2
- Repeat each stage and fluid system to reduce uncertainty
- Measure critical parameters to ensure consistency between stages
- Quantify corrosion rates using multiple sensors
- Analyze data to assess impact of ClO_2 on selected alloys

Summary

- Carbon steel (CS) corrosion rates were poor (1-5 mm/yr)
- Stainless steel (SS) corrosion rates were good (<0.5 mm/yr)
- Corrosion rates of CS in brine were over 30% higher than fresh
- Overall there does not appear to be any statistically significant impact of the ClO_2 in either fresh nor brine water solutions
- ClO_2 did not increase O_2 levels in any of the fluid systems used



Test Fixture and Flow Plan



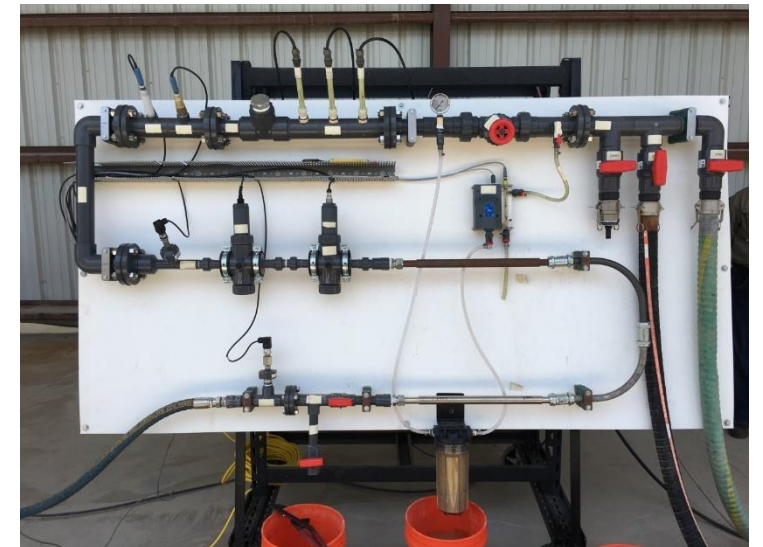
	4" Pipe		¾" Pipe		Flow Loop	
Stage Simulation	Flow (BPM)	Velocity (FPS)	Flow (GPM)	Velocity (FPS)	Run Time (Minutes)	Volume (gal)
Water only	2.0	2.1	3.0	2.2	3.0	9.0
Pump Down	3.5	3.8	5.0	3.6	32.0	160.0
Break	3.0	3.2	4.5	3.3	2.0	9.0
Acid Phase	7.0	7.5	10.5	7.3	1.0	10.5
Flush	17.5	18.8	26.0	18.8	6.0	156.0
Pause	5.00					
Water Pad	17.5	18.8	26.0	18.8	5.0	130.0
Slurry	17.5	18.8	26.0	18.8	100.0	2,600.0
Flush	17.5	18.8	26.0	18.8	6.0	156.0
Total	160.0					

Test Facility



Instrumentation

- Chlorine Dioxide (ClO₂): Kuntze Zircon™ DIS Sensor Model No: 231512110
- Dissolved Oxygen (DO): Endress+Hauser: Oxymax COS61D Model No: COS61D-1014/0
- Conductivity: Endress+Hauser: Condumax CLS21D Model No: CLS21D-C1N1
- Turbidity: Endress+Hauser: Turbimax CUS51D Model No: CUS51D-10V6/0
- pH & ORP: Endress+Hauser: Memosens CPS16D Model No: CPSD16D-1009/0
- Pressure: Burkert Type 8323 S 0-200psig
- Flow: Endress+Hauser ProMass 100 Flowmeter



Corrosion Monitoring

Three methods of measuring corrosion were used



LPR Probes using 304SS, 316SS, and 4130CS electrodes



Seven cylinder coupons (4130CS, 4140CS, 4150CS, 4340CS, 17-4SS, 304SS, 316SS)



7.3ft of 0.75" ID tubular components (CS, 304SS)

Test Plan – Fluid Summary

- The simulated frac fluid consisted of friction reducer, scale inhibitor, and 100 mesh sand at 1ppg
- The acid phase used 7.5% HCl with corrosion inhibitor @ 2.5 gpt
- On Day 3 and 4 water was treated with ClO_2 to a 5ppm residual before beginning each stage

Scale Inhibitor @ 0.25gpt

SC-30 sourced from X-CHEM (0.25gpt)

0.5 – 1.5% Sodium hydroxide

Friction Reducer @ 1.0gpt

TFR-24La sourced from Tucker Energy Services (1.0gpt)

15-20% Petroleum Distillate

< 1% Ammonium Chloride

<1% Oleic Acid Diethanolaide

50 -60% Water

Corrosion Inhibitor @ 2.5gpt

TCA-6038 sourced from X-CHEM (2.5gpt)

50 -70% Methanol

20-30% Pyridine Benzyl Quaternary Ammonium Chloride

5-10% Water

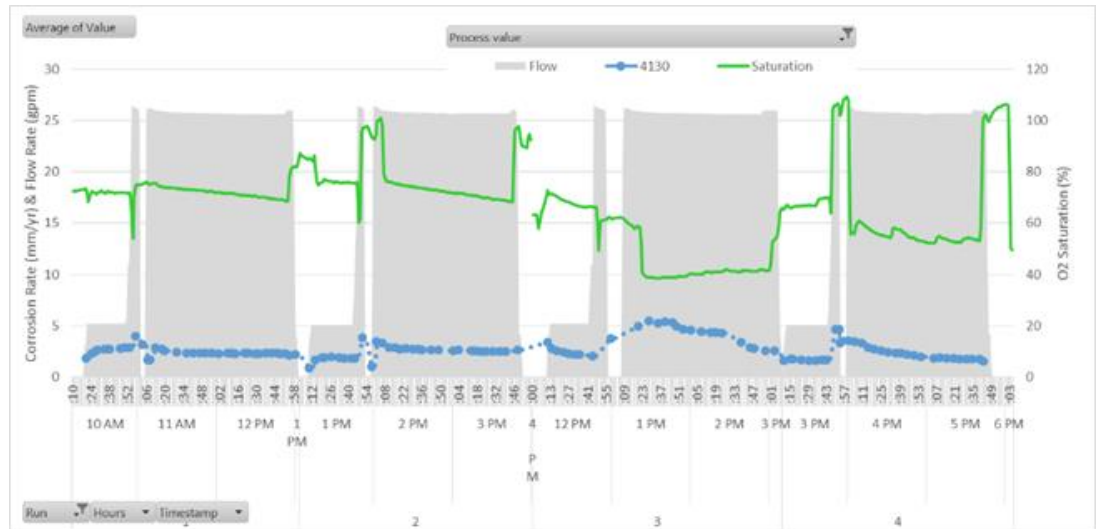
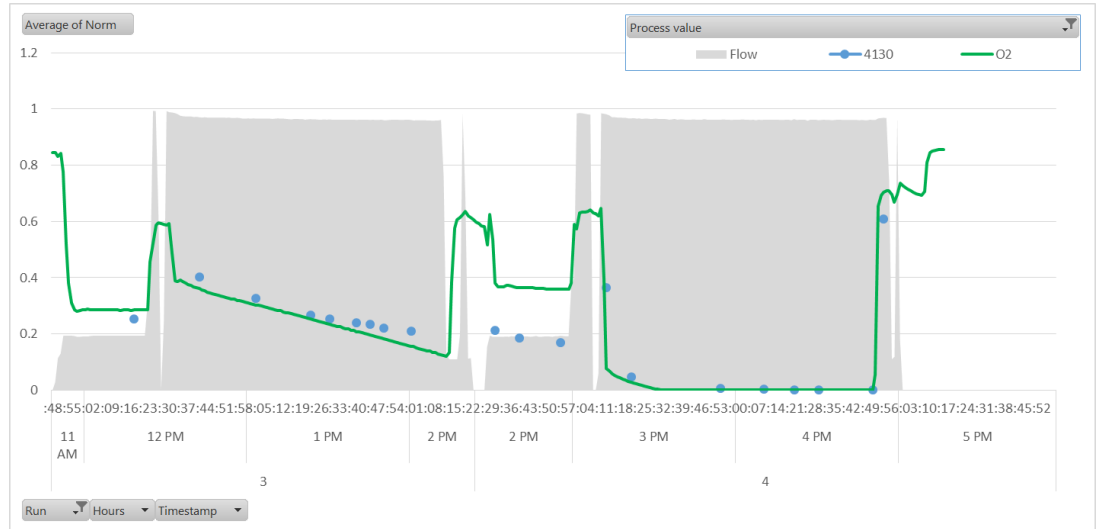
Test Summary

- Testing conducted on Monday, July 24, 2017 through Thursday, July 27, 2017
- Four days of testing divided into two simulated frac stages per day
- Each stage was approximately 3 hours and consisted of six phases
 - ① pump down
 - ② acid
 - ③ flush
 - ④ pad
 - ⑤ proppant
 - ⑥ final flush
- Flow loop was flushed each day and left full to keep sensors wet.



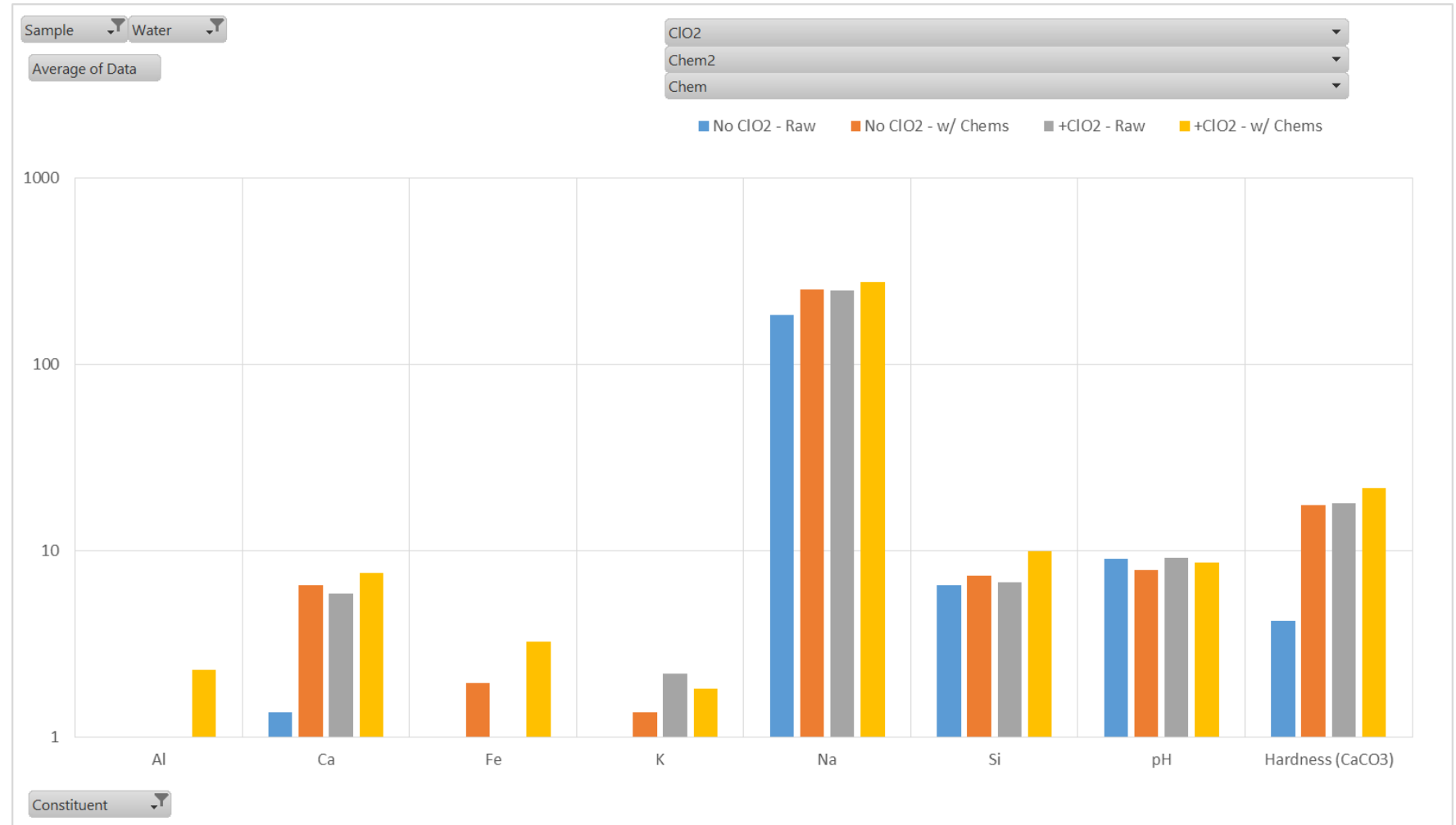
Test Plan B

- O₂ in Slurry Tank dropped unexpectedly
- Corrosion rates were significantly lower
- Corrosion data was compromised resulting in the loss of a baseline
- A “recycle” of the 60/40 test was needed
- “Fresh” produced water was acquired
- Brine test was run again on Oct 3-4
- O₂ Levels were consistent

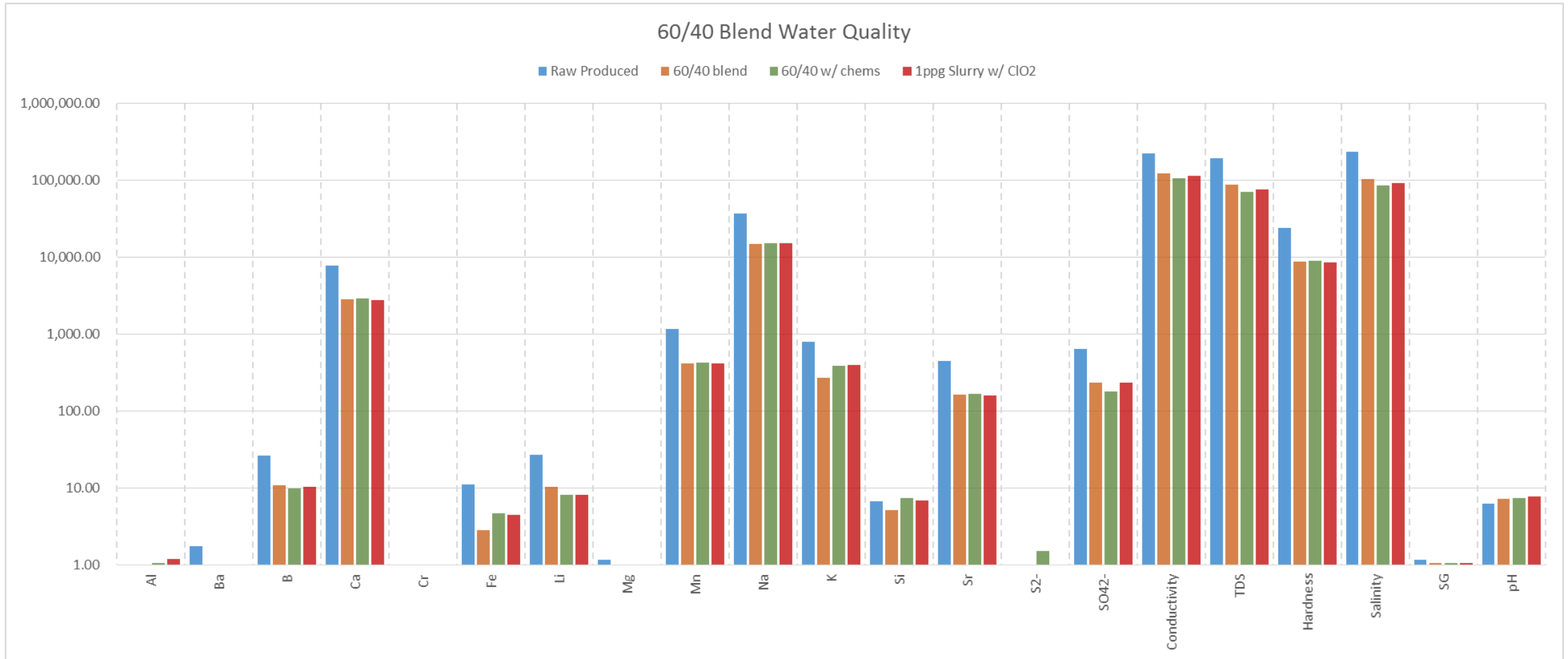


Fresh Water Quality

- Elements with concentrations < 1.0 are not shown



Produced Water Quality



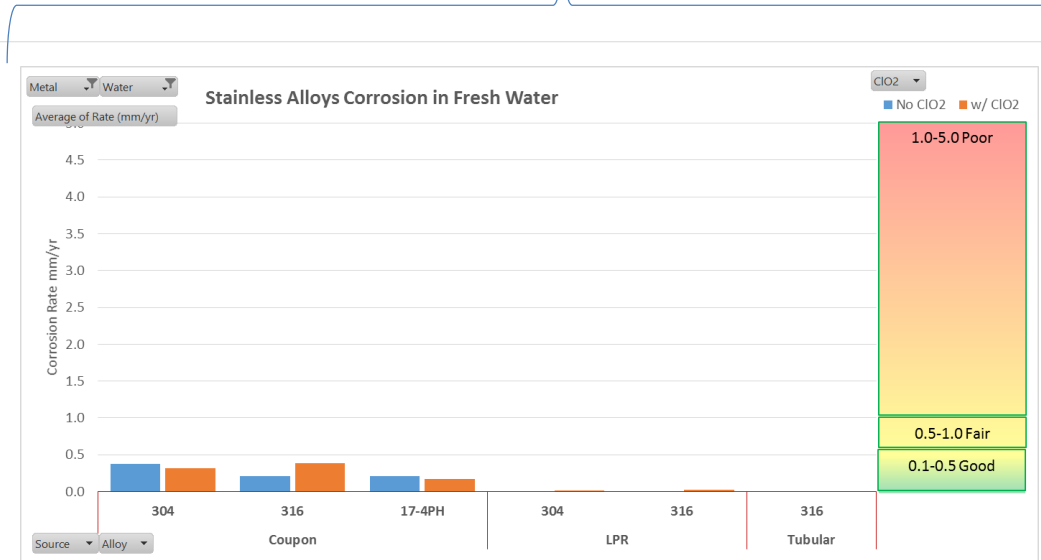
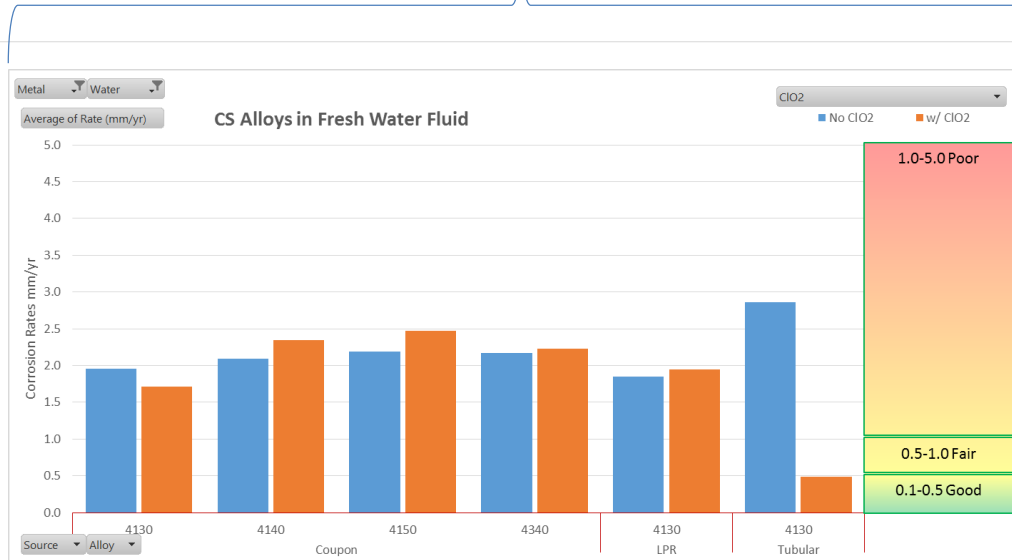
Results and Analysis

Results

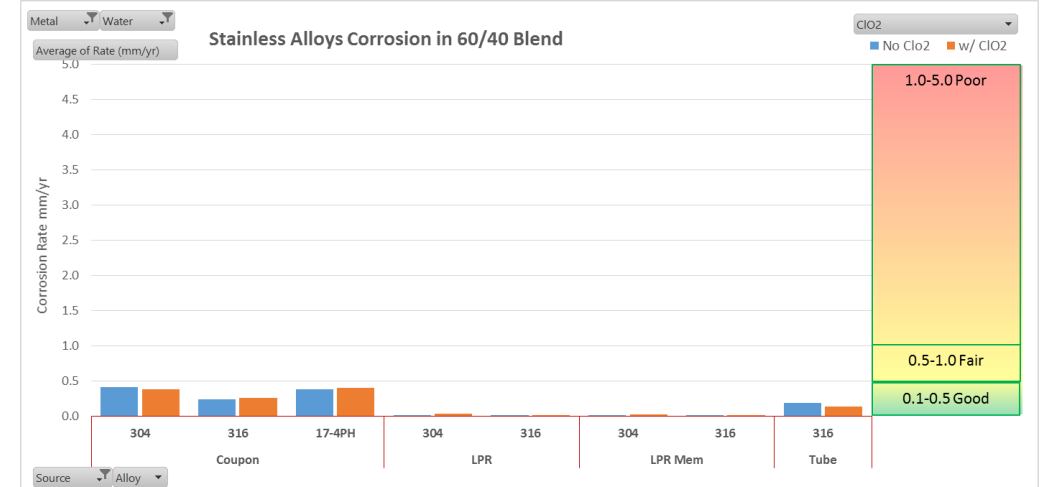
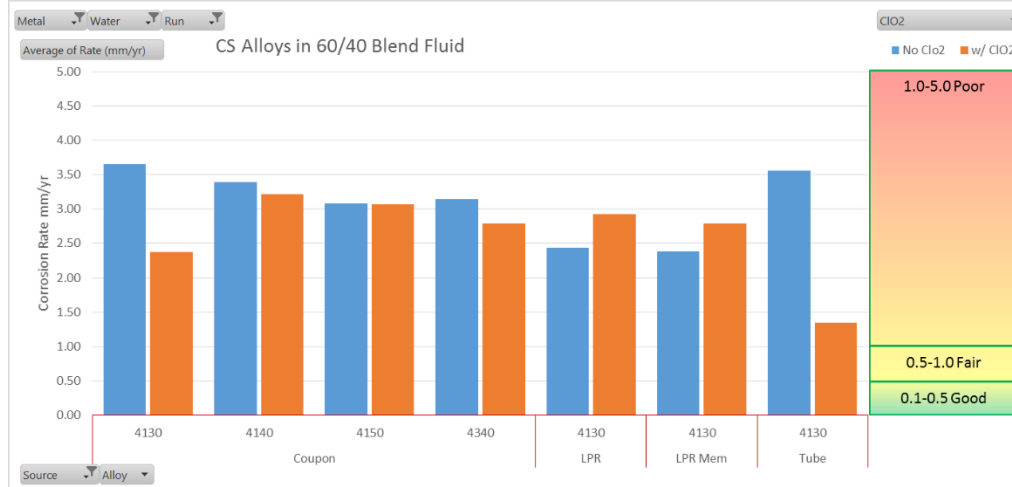
Carbon Steel Alloys

Stainless Steel Alloys

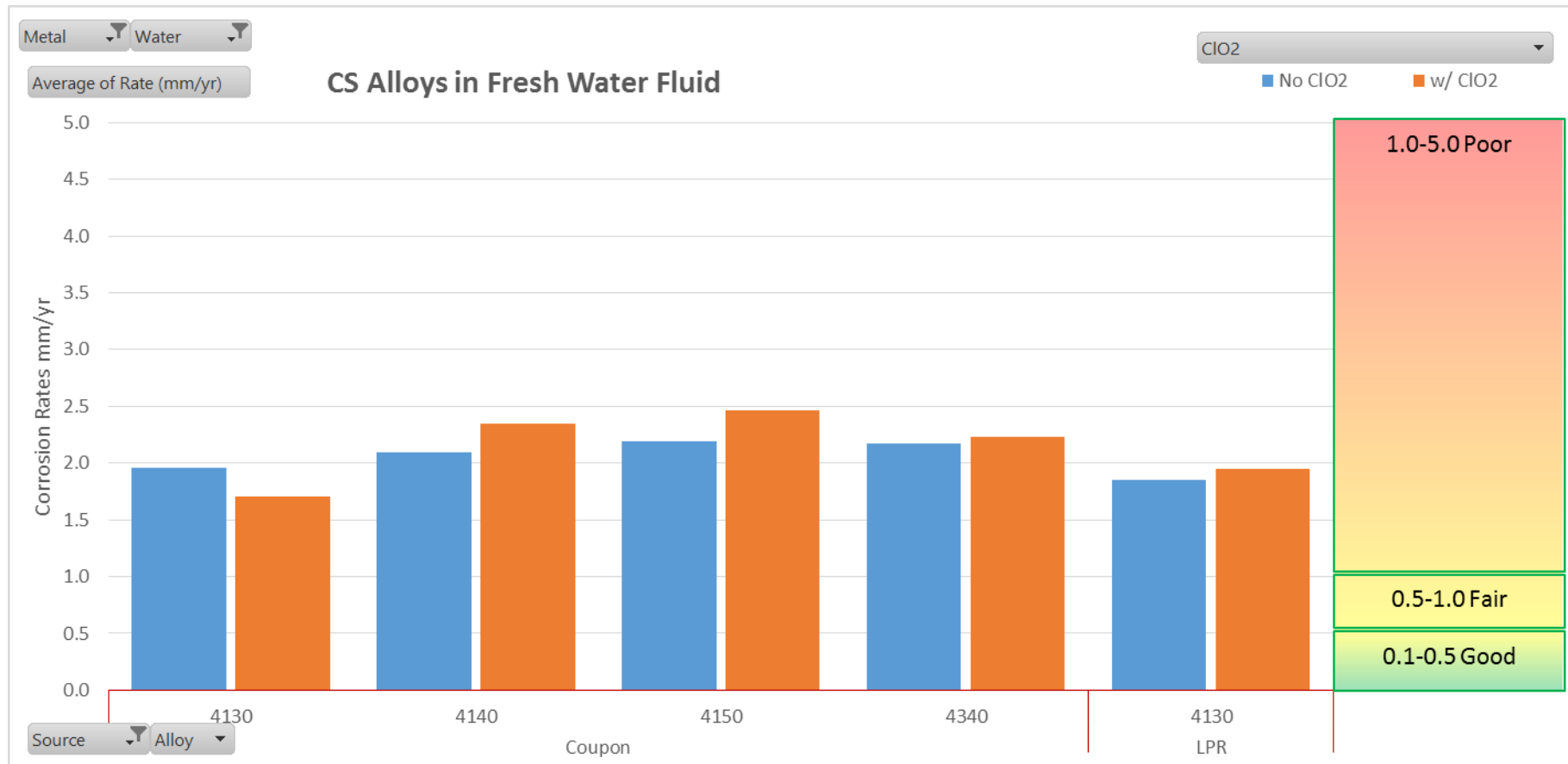
Fresh Water



60/40 Blend

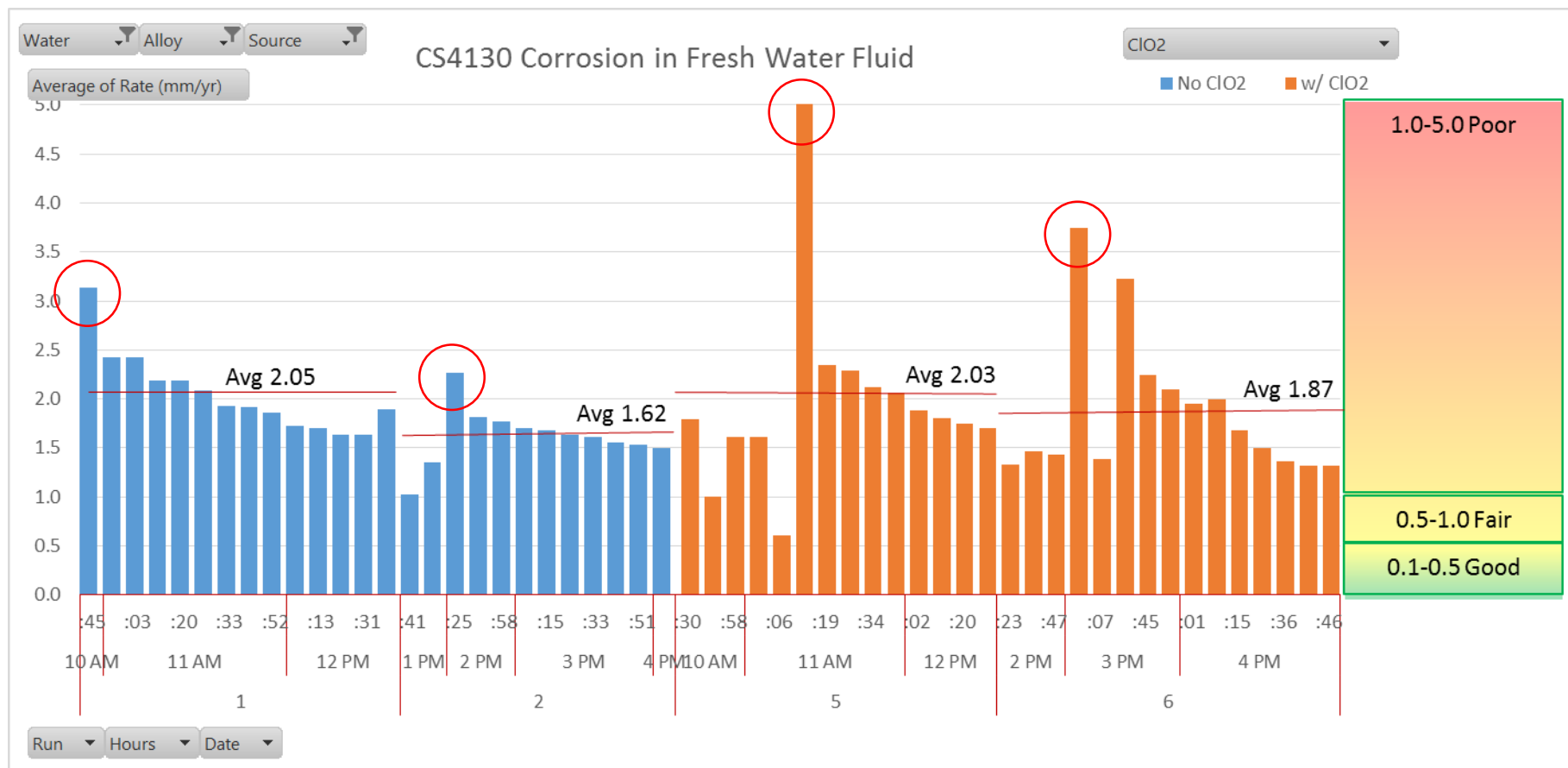


Carbon Steel Individual Coupons (Fresh Water)

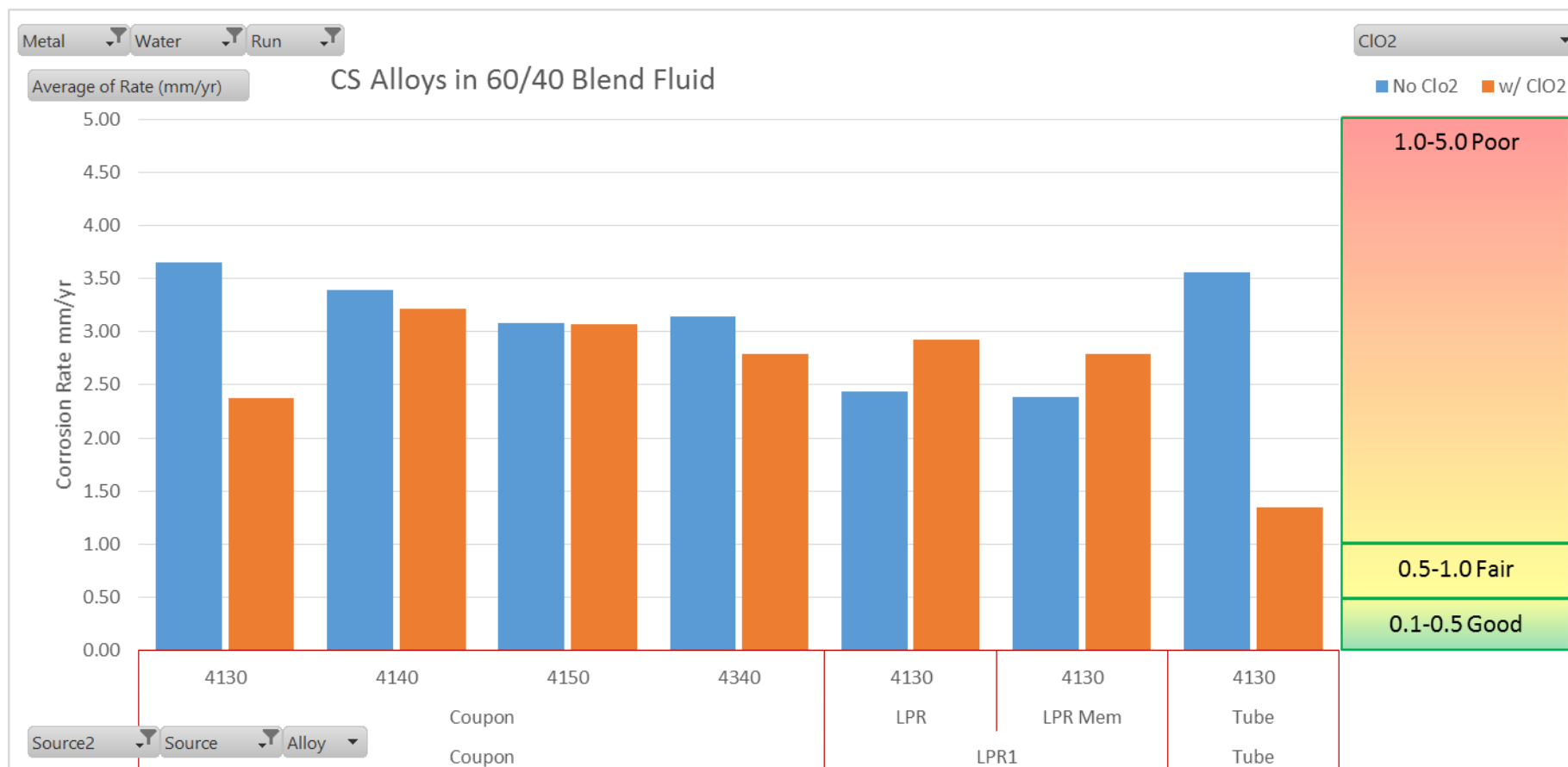


CS4130 Alloy (Fresh Water)

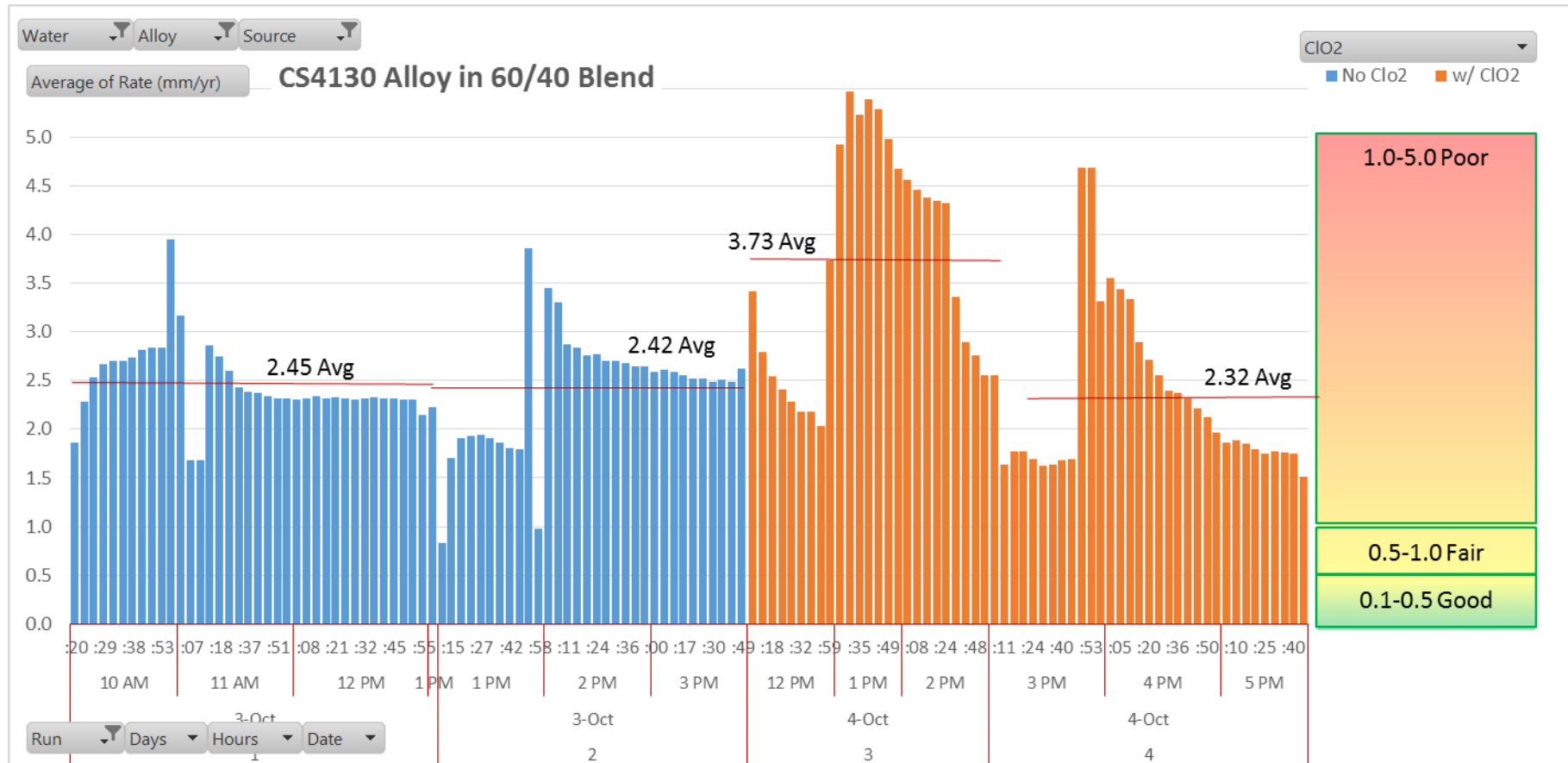
The spikes in corrosion are a reaction to the acid pad, but rates dropped back to a lower equilibrium each time.



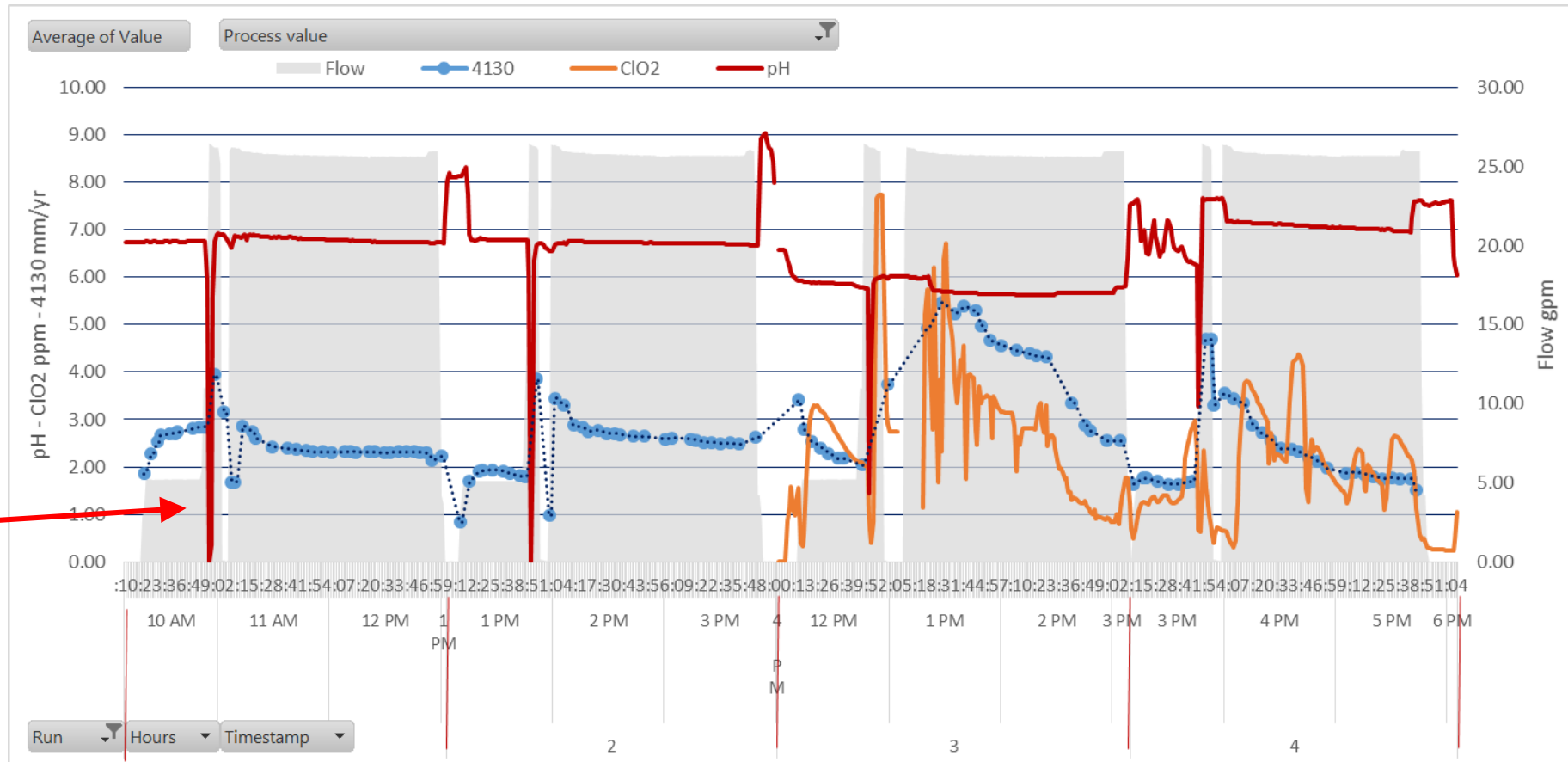
Carbon Steel Coupons Averages (A&B) (60/40)



CS4130 Alloy in 60/40 Blend

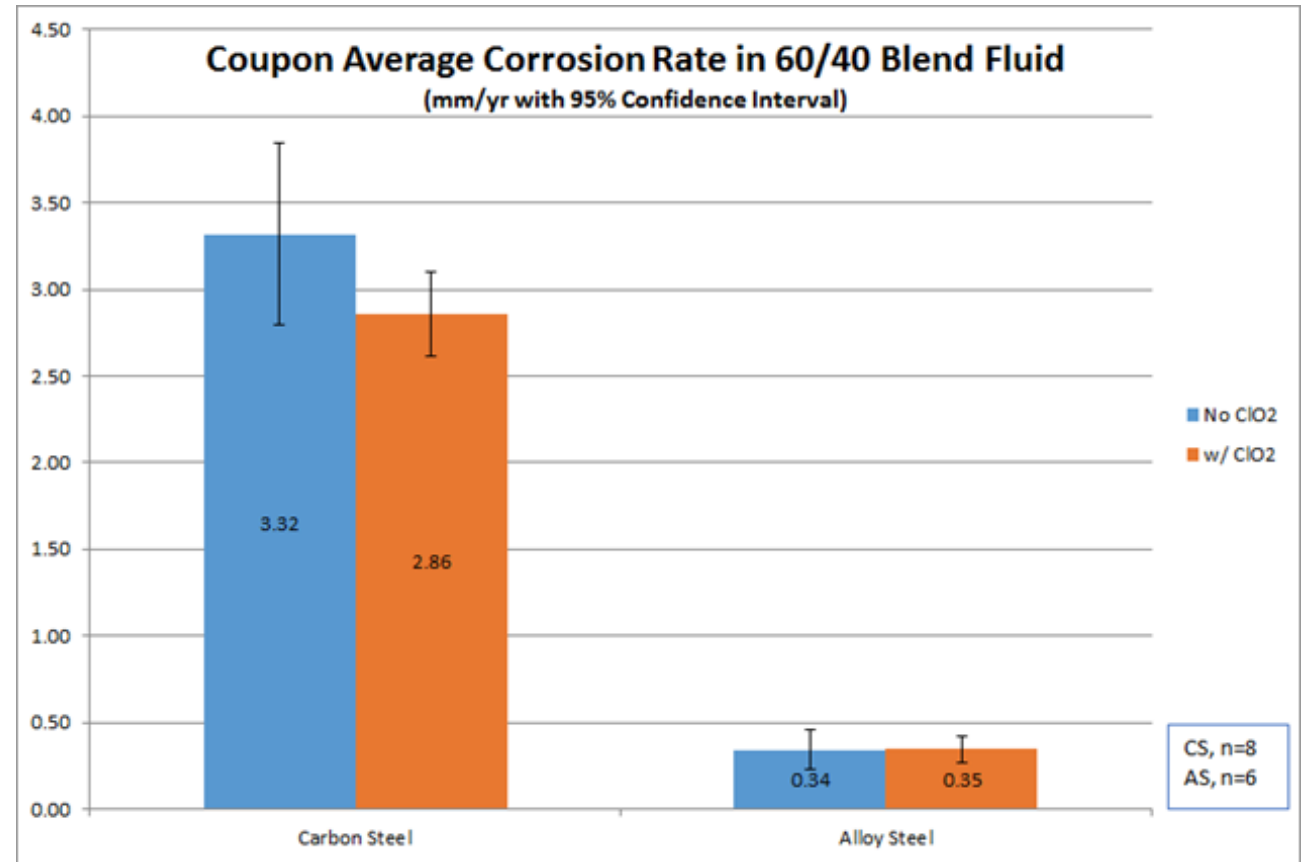


4130 Corrosion in 60/40 Blend w/ ClO2 Residuals & pH



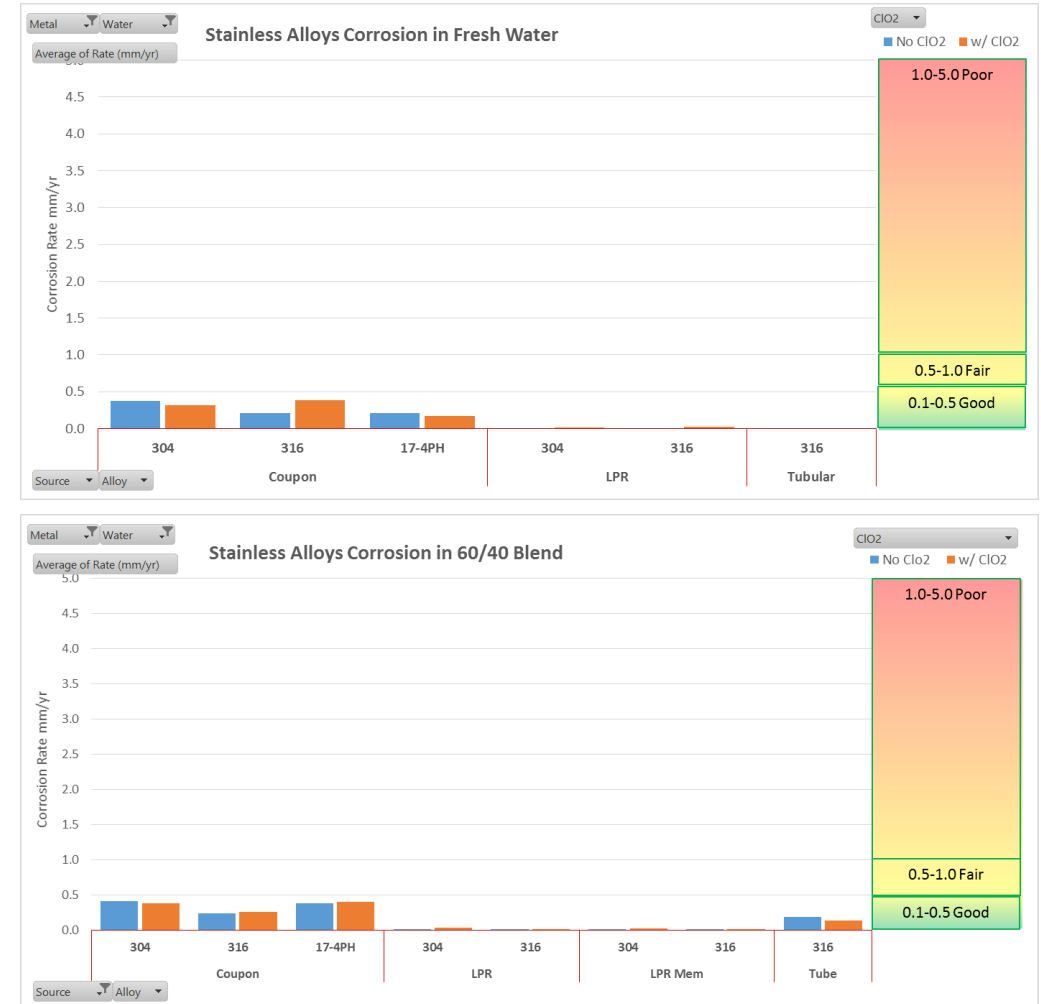
Carbon Steel Statistical Analysis

- Statistical analysis of the corrosion coupon data in the 60/40 blend shows no statistically significant difference with or without addition of ClO_2 in either group.
- This can be seen graphically in the overlap of confidence intervals.



Stainless Alloys

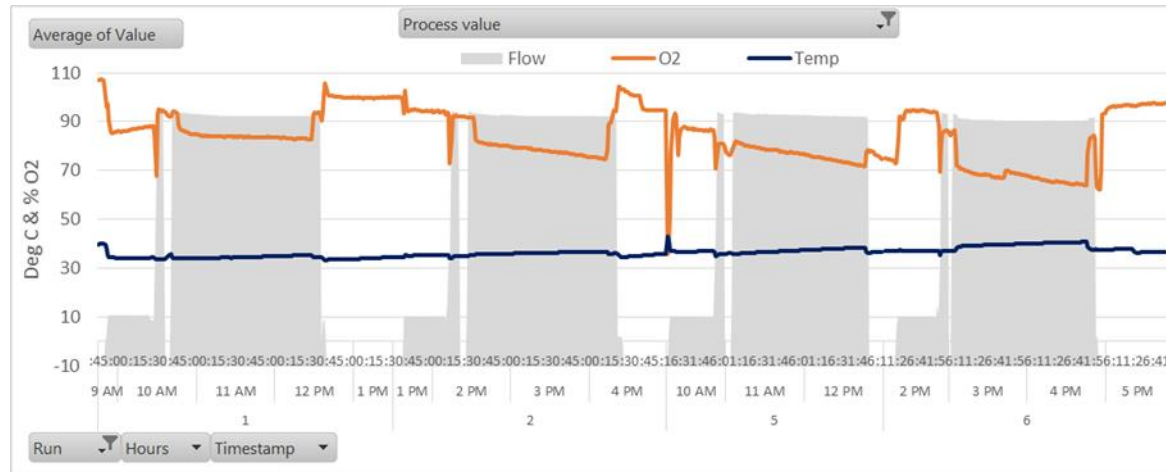
- Corrosion of the stainless alloys was consistently in the excellent to good range
- No statistically significant impact of the ClO_2 in either fresh nor brine water solutions
- The average of both observed and memory LPR data was <0.1 mm/yr while coupon corrosion rates were <0.29 mm/yr in fresh water and <0.35 mm/yr in the 60/40 blend



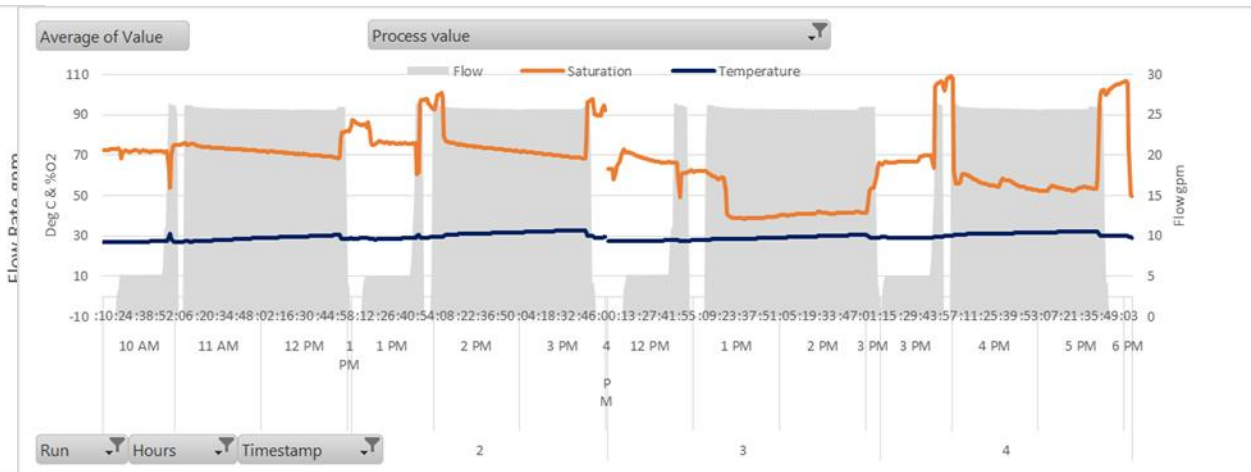
Conclusions

Conclusions – Water Chemistry

1. ClO_2 did not change water chemistry
2. ClO_2 did not increase O_2 saturation
3. Excess acid in poor quality ClO_2 effected carbon steel when $\text{pH} < 5.8$ and ClO_2 residuals > 3.0



Fresh Water O_2



Brine O_2

Conclusions - Corrosivity

Fresh Water

- 👍 The application of ClO_2 had very little effect on stainless alloys
- 👍 Carbon steel corrosion rates showed some slight increase but less than 4% overall

Brine Water

- 👍 The application of ClO_2 had very little effect on stainless alloys
- 👎 Carbon steel (CS) corrosion rates were over 30% higher than fresh water
- 👎 CS exposed to low pH and high ClO_2 residuals appears more susceptible to corrosion
- 👍 Adding ClO_2 shows no detrimental impact over a statistically significant population of CS samples and test runs

Acknowledgements

Many thanks to everyone who helped make this test possible

Flow loop fabrication and operational support

- Mark Thompson
- Jake Russell
- Terry Ballard
- Brian Bost

Water Analysis

- Xenco Labs

Metal Analysis

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- ERCO Worldwide

ClO₂ application and technical support

- International Dioxide (IDI)
 - Pete Garrison
 - Alan Burke
 - Scott Glynn
 - Bill Hulsman



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Questions?