

INTELLIGENTLY PREDICT AND MANAGE SOUR WATER CORROSION IN REFINERY APPLICATIONS

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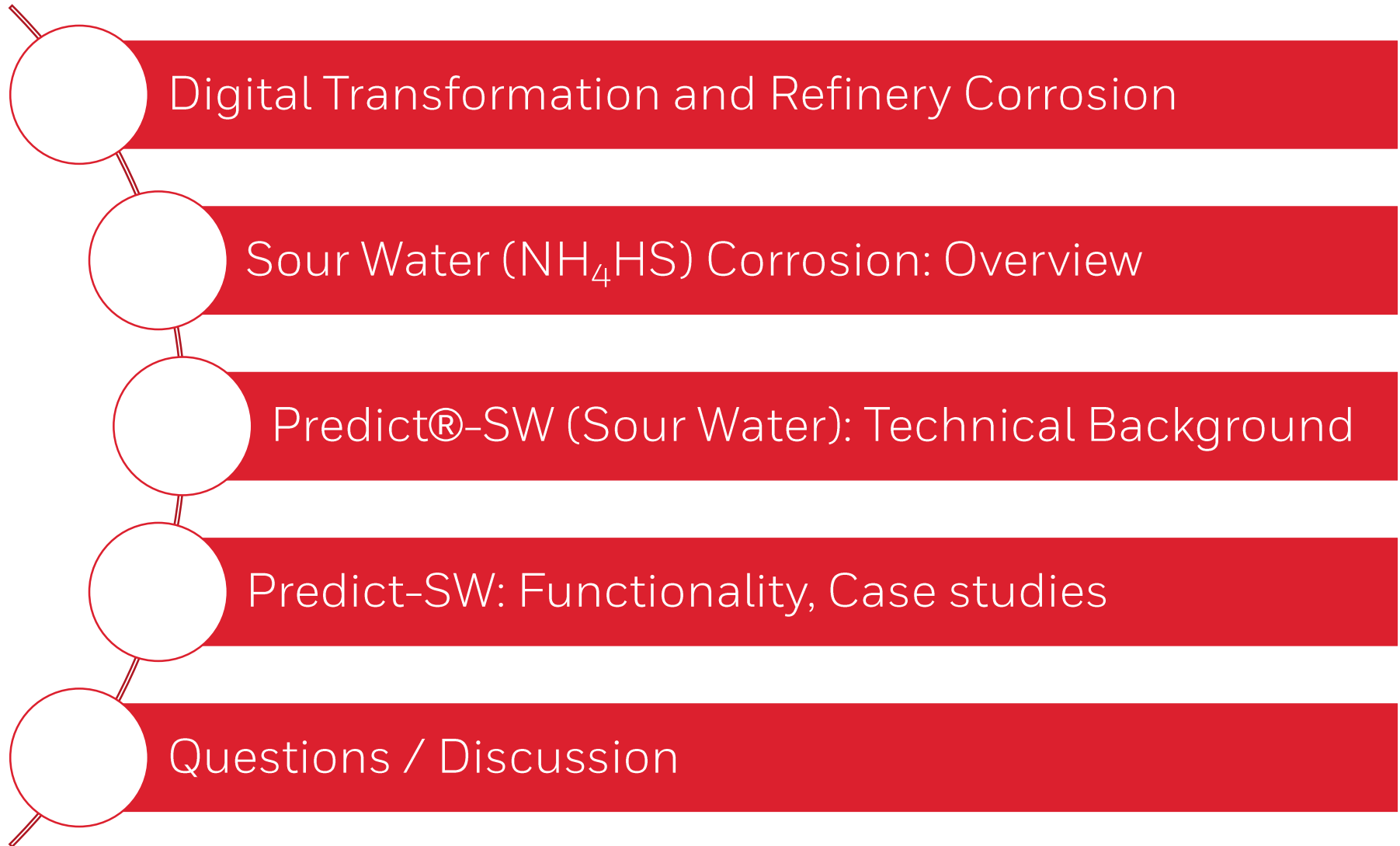
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AGENDA



DIGITAL TRANSFORMATION

- It is the process of using *digital* technologies to create new — or modify existing — business and manufacturing processes, culture, and customer experiences to meet changing business and market requirements.
- Example: Paper document vs an electronic/digital doc, digital images vs film, etc.
- In Refining, this includes examples such as Advanced Process Control, Predictive analytics, Software-based sensing for process control etc.
- Foundation for creation of the intelligent refinery and enhanced *operational excellence*



Advanced Process Control



Cybersecurity



Predictive Safety /Reliability and Intelligent Analytics

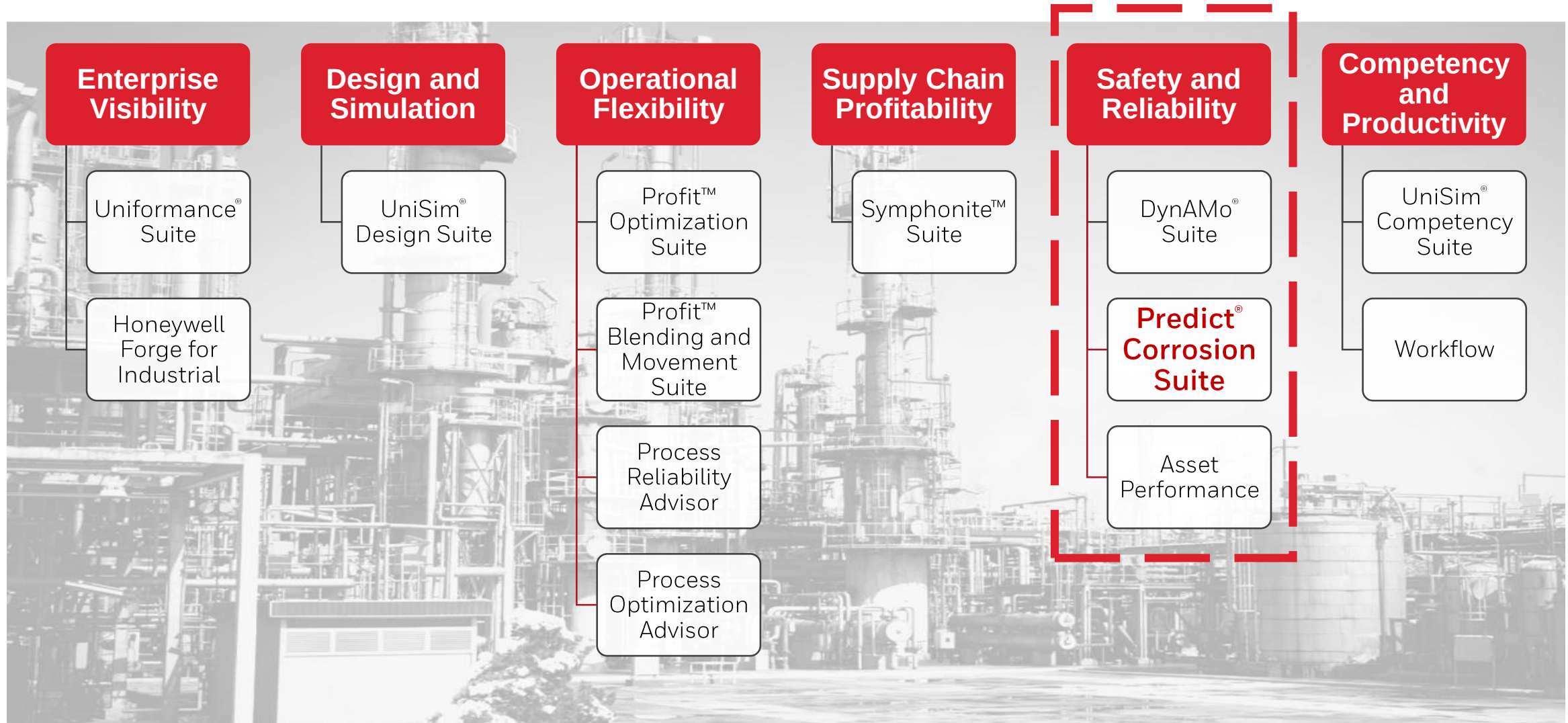


Cloud-based data and Tools

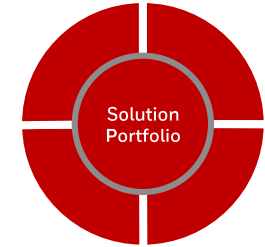
REFINING SOLUTIONS



REFINING SOLUTIONS FOR DIGITAL TRANSFORMATION



REFINERY JOINT INDUSTRY PROGRAMS (JIP)



- **Typical Sponsors**

- Operating Companies
- Chemicals Providers
- Service Providers
- Engineering & Design Companies

- **Aggregated Funding (\$2M to \$4M)**

- **2 to 3 Years Research Effort**

- **JIPs**

- \$24M+ cumulative refinery JIP funding since 2000
- 20+ Sponsor Companies

- **Joint Industry Projects:**

- CDU Overhead
- Nap Acid Corrosion
- Rich Amine Corrosion
- Lean Amine Corrosion
- Sour Water Corrosion
- Sulfuric Acid Corrosion

JOINT INDUSTRY PROGRAMS FOR REFINERY CORROSION

Sour Water Corrosion (Hydroprocessing / Hydrocracking / Sour Water Strippers / FCCU): Phase I – III between 2000-2013 (Predict®-SW)

Rich Amine and Lean Amine Corrosion: Corrosion due to different amine solvents (MEA, DEA, DGA and MDEA) – three programs between 2003-2012 (Predict®-Amine)

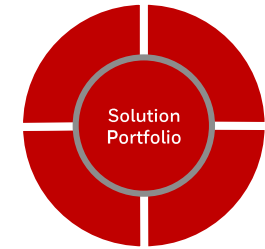
Crude Oil Corrosivity: Phase I completed in 2011 (Naphthenic Acid and Sulfidic Corrosion), Phase II complete in 2018 (sulfur speciation and transfer line/high WSS effects) (Predict®-Crude)

CDU OH JIP Phase I for NH_4Cl corrosion – complete in 2018 – CDU-OH-Phase II slated for Q1 2019 start up (Predict®-CDU-OH)

Sulfuric Acid Alkylation: Program complete with development of first prediction model to correlate fresh acid concentration, temperature and wall shear stress to corrosion rates (Predict®-SA)

Over \$21 million in refinery research IP built into Honeywell prediction models – over 16 years of data development

SOFTWARE APPLICATIONS



Accurate quantification

Optimized Inspection
Planning

Identification of
critical loops

Savings in material
upgrades and inhibitor
costs

Software Models - Refining

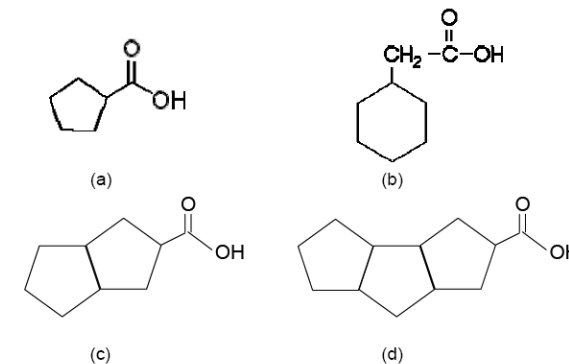
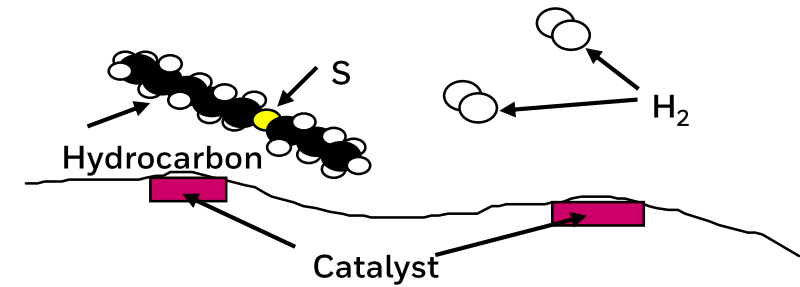
- Predict®-RT *(online)*
- Predict®-SW
- Predict®-Crude
- Predict®-Amine
- Predict®-SA

Software Models – O&G

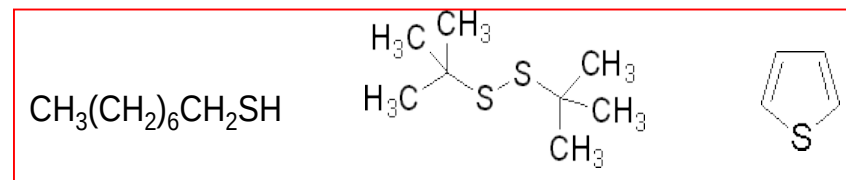
- Socrates™
- Predict®-Pipe
- Predict®-O&G
- Predict®-Amine

Complex Refinery Processes

- Sour Water (NH_4HS) Corrosion
 - A multi-variable control problem requiring accurate assessment of different inter-linked parameters – NH_4HS , H_2S , NH_3 , Cyanides, Wall shear stress, temperature
 - No quantified data to connect corrosion rates to process parameters
- Naphthenic Acid and Sulfidic Corrosion in Crude Units
 - Naphthenic acids, a group of organic molecules with cycloaliphatic rings and an attached carboxylic acid group ($\text{R}(\text{CH}_2)_n\text{COOH}$) where R is a single or multiple cyclopentane or cyclohexane ring(s)
 - Sulfur compounds (Mercaptans/Thiols, disulfides, thiophenes primary active sulfur species



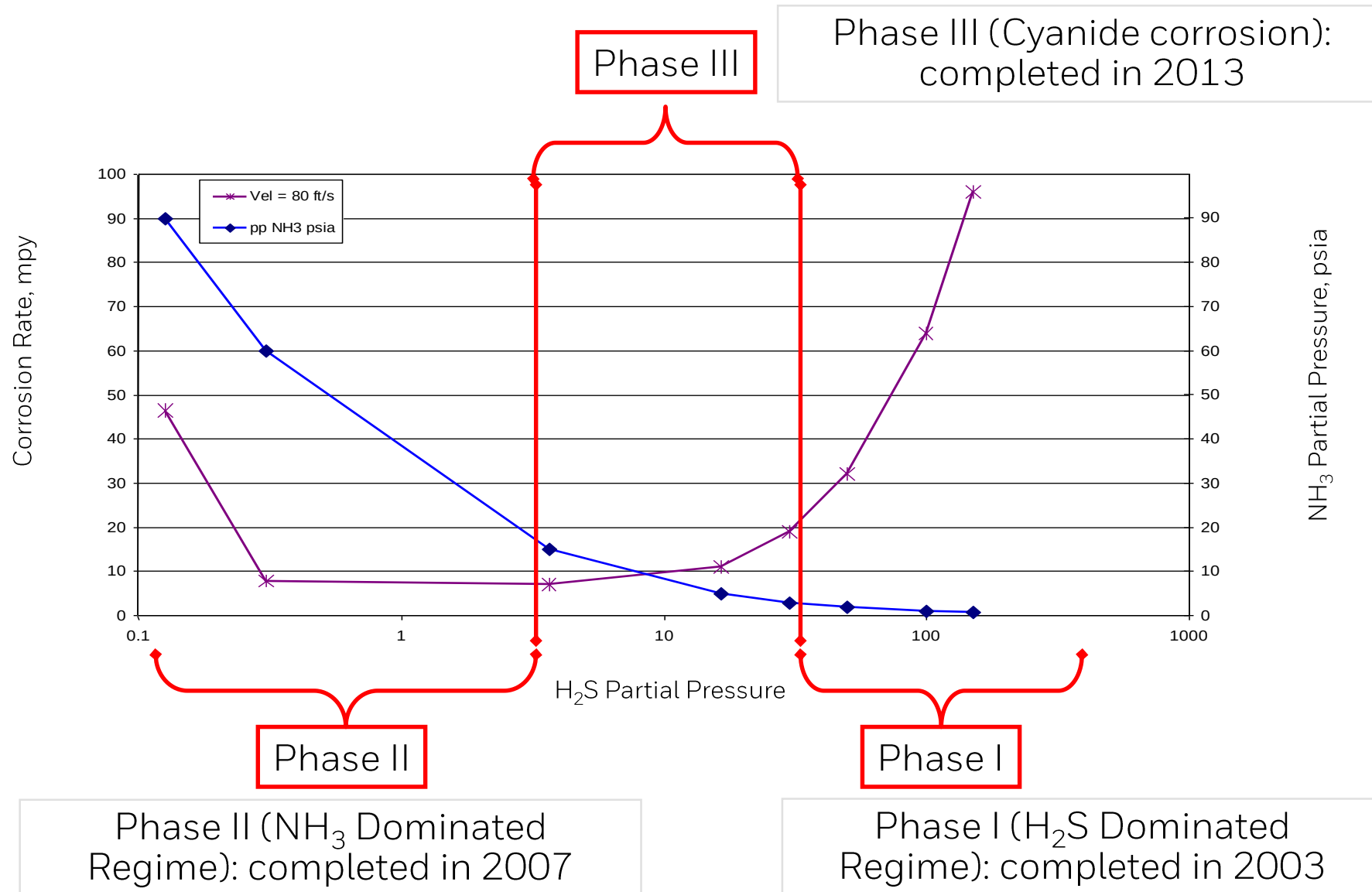
ACTIVITY
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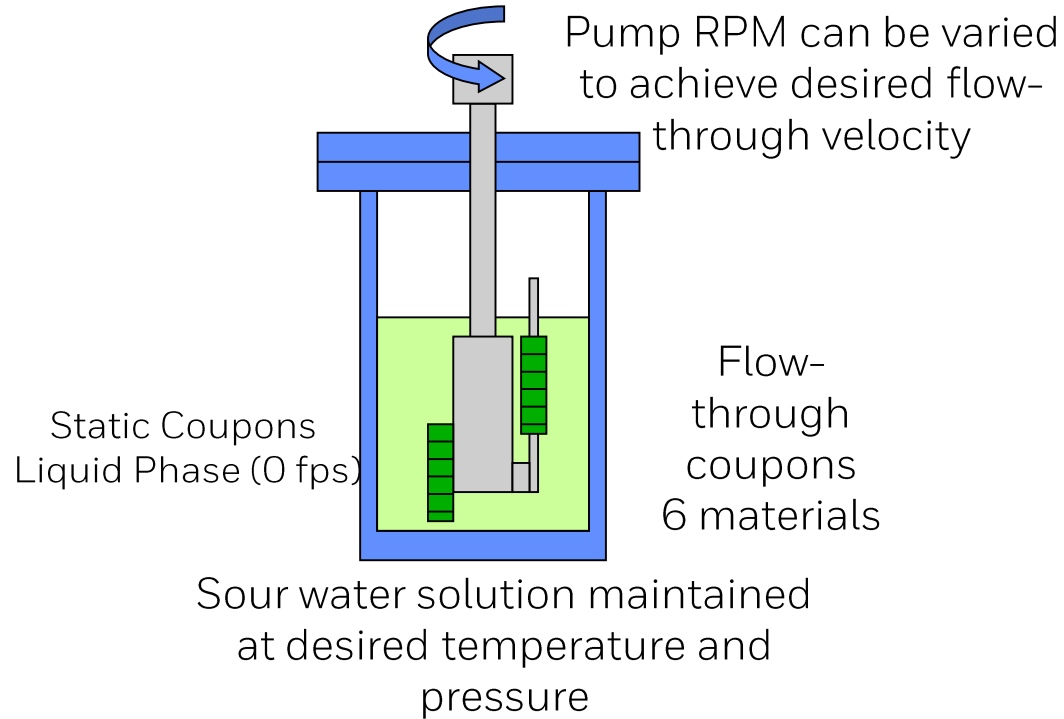
PREDICT-SW MODEL DEVELOPMENT – HISTORICAL RECAP

- Absence of quantified data made SW corrosion prediction / prevention of failure difficult
- In 2000, Shell Global Solutions and other large operating companies commissioned Honeywell to run a Joint Industry Project designed to generate data for ammonium bisulfide corrosion
- Purpose: To create a definitive, engineering basis for dealing with sour water corrosion
- **Phase I** (H_2S Dominated Regime): was completed in June 2003
- **Phase II** (NH_3 Dominated Regime): was completed in March 2007
- **Phase III** (Completing the picture – Cyanide corrosion): Program testing completed in 2012– Final report released in 2013

SOUR WATER CORROSION JIP – DATA DEVELOPMENT



SOUR WATER CORROSION TESTS – STANDARD EXPERIMENTAL SETUP



Tested materials

- Carbon steel
- 410 SS
- 304 SS
- 316 SS
- Alloy 2205
- Alloy 2507
- Alloy 400
- Alloy 600
- Alloy 625
- Alloy 20Cb-3
- Alloy 800
- Alloy 825
- Alloy C-276
- AL6XN (6% Mo)

SOUR WATER PREDICTION DEVELOPMENT – PHASE I KEY FINDINGS

- Introduction of a new key parameter (H_2S partial pressure) for prediction of SW corrosion (not previously utilized)
- For the first time fluid dynamics (represented in terms of a WSS parameter) identified as critical element in determination of SW corrosion:
- Corrosion rate measured at any test velocity in the laboratory flow loop does not directly equate to the corrosion rate at the same velocity in a pipe or tube of different size.
- WSS chosen as the scalable parameter in order to make the appropriate comparison and to establish a linkage between the laboratory flow loop and actual service conditions.
- Defined the effect of hydrocarbons on corrosivity of sour water
- Determined the impact of SW corrosion inhibitors (ammonium polysulfide and imidazoline-based compounds)
- **Model applicable for hydrocracker / hydrotreater conditions**

SOUR WATER PREDICTION DEVELOPMENT – PHASE II

KEY FINDINGS

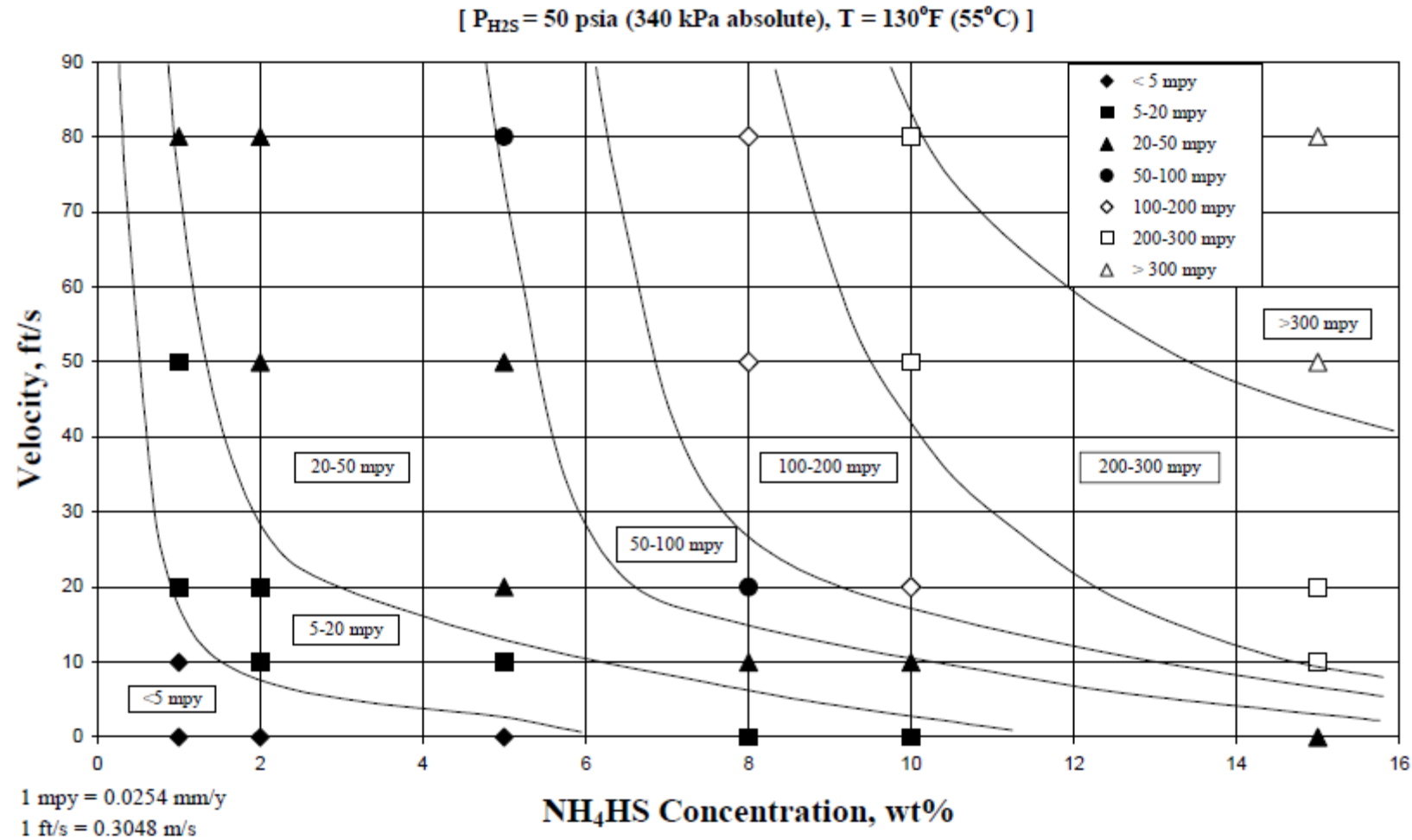
- Determined behavior of materials in NH_3 -dominated sour water environments — primarily high NH_3 partial pressure (in combination with very low H_2S partial pressure), temperature and free cyanide concentration
- Temperature found to be a major factor in corrosion determination for many of the materials examined
- Effect of temperature on thermodynamic equilibrium involving solubility of H_2S and NH_3 resulting in higher H_2S partial pressures at higher temperatures
- First observation of the impact of cyanide additions
- Corrosion rate increased on all materials, but varied in their extent depending on alloy and the conditions of NH_4HS concentration, WSS and NH_3 pp
- Determination of new iso-corrosion diagrams for different NH_3 pp versus NH_4HS concentration and velocity
- Extended applicability to SW Stripper and FCCU where NH_3 dominated NH_4HS speciation

SOUR WATER PREDICTION DEVELOPMENT – PHASE III

KEY FINDINGS

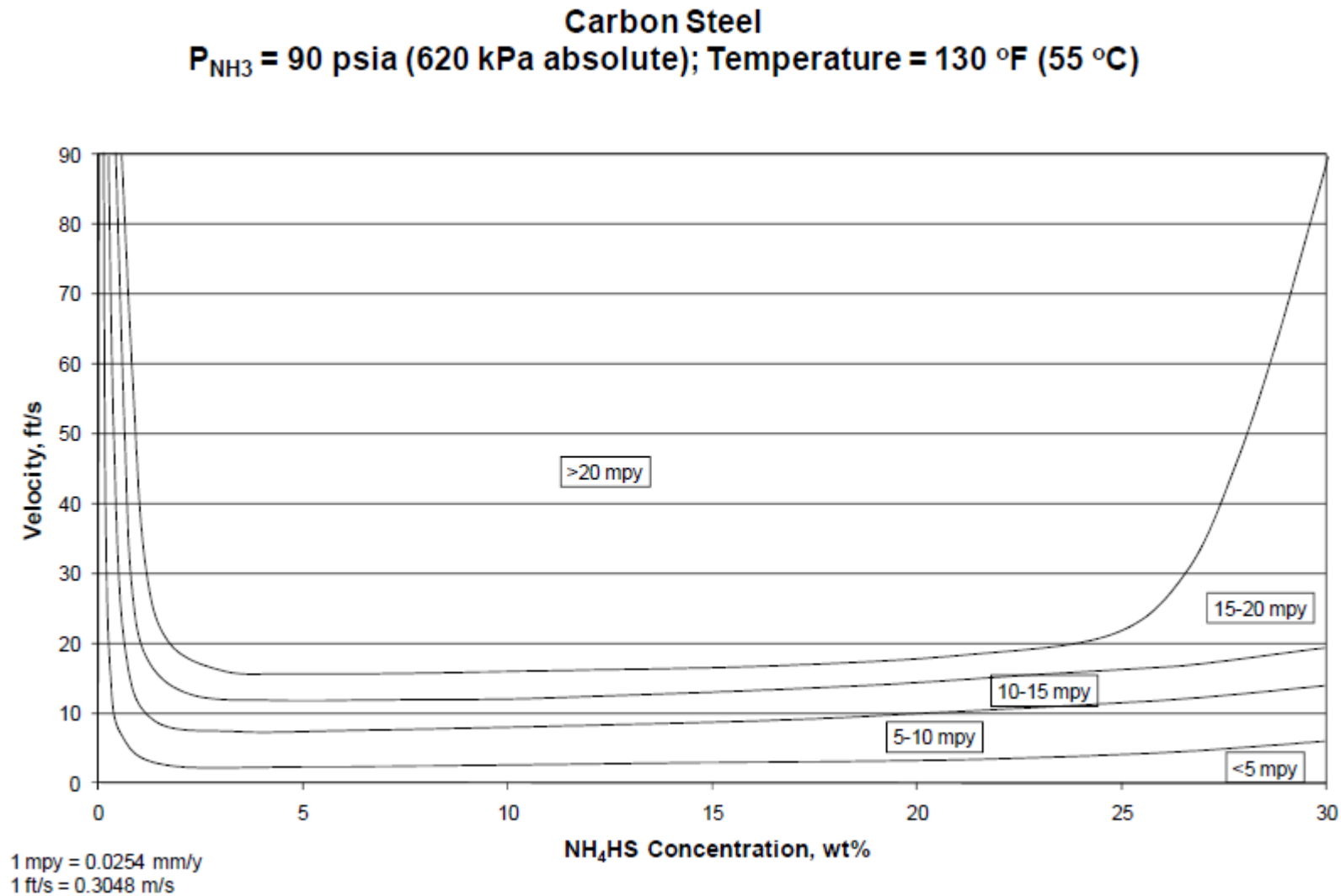
- Phase III results designed to address data gaps and identifying a new corrosion regime in the intermediate H_2S pp region between the H_2S - and NH_3 -dominated regions.
- Determined new iso-corrosion diagrams for intermediate H_2S pp region.
- NH_3 pp was considered a dependent variable (determined by the thermodynamic equilibrium as a function of NH_4HS concentration, H_2S pp, temperature and system total pressure).
- NH_4HS concentration, WSS, H_2S pp and free cyanide showed up as the most significant parameters in predicting sour water corrosion.
- New prediction approach using H_2S tie-in plots (eliminating over-conservatism and non-conservatism found in the Phase II “interpolation” region)
- Comprehensive model (over 1000 test data points) addresses all representative sour water corrosion conditions in refinery service

ISOCORROSION DIAGRAM – PHASE I



Published: NACE Paper 06576 (Part 1)
Figure 7 – API RP 932-B

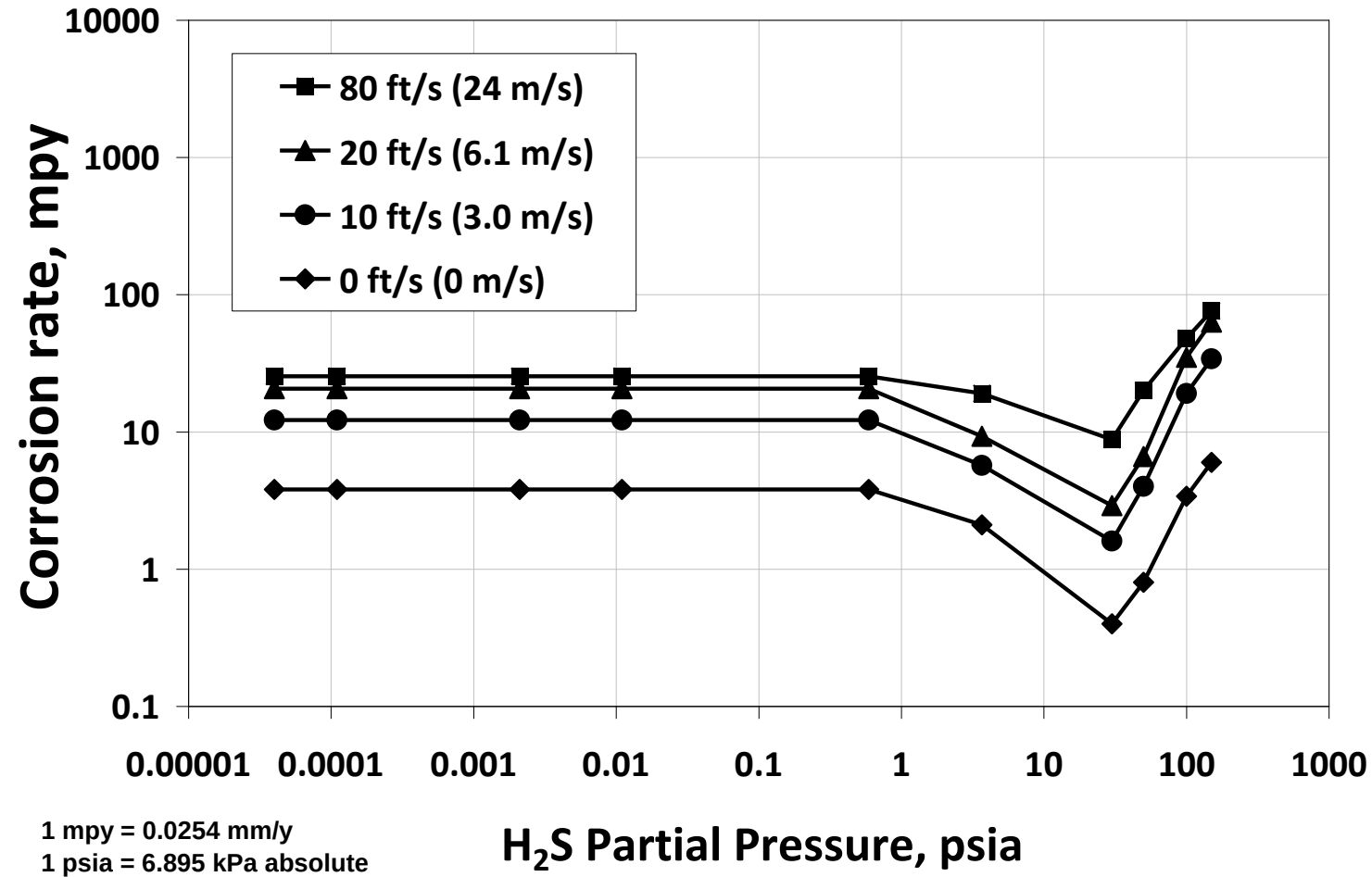
ISOCORROSION DIAGRAM – PHASE II



Published: NACE Paper 10349 (Part 2)

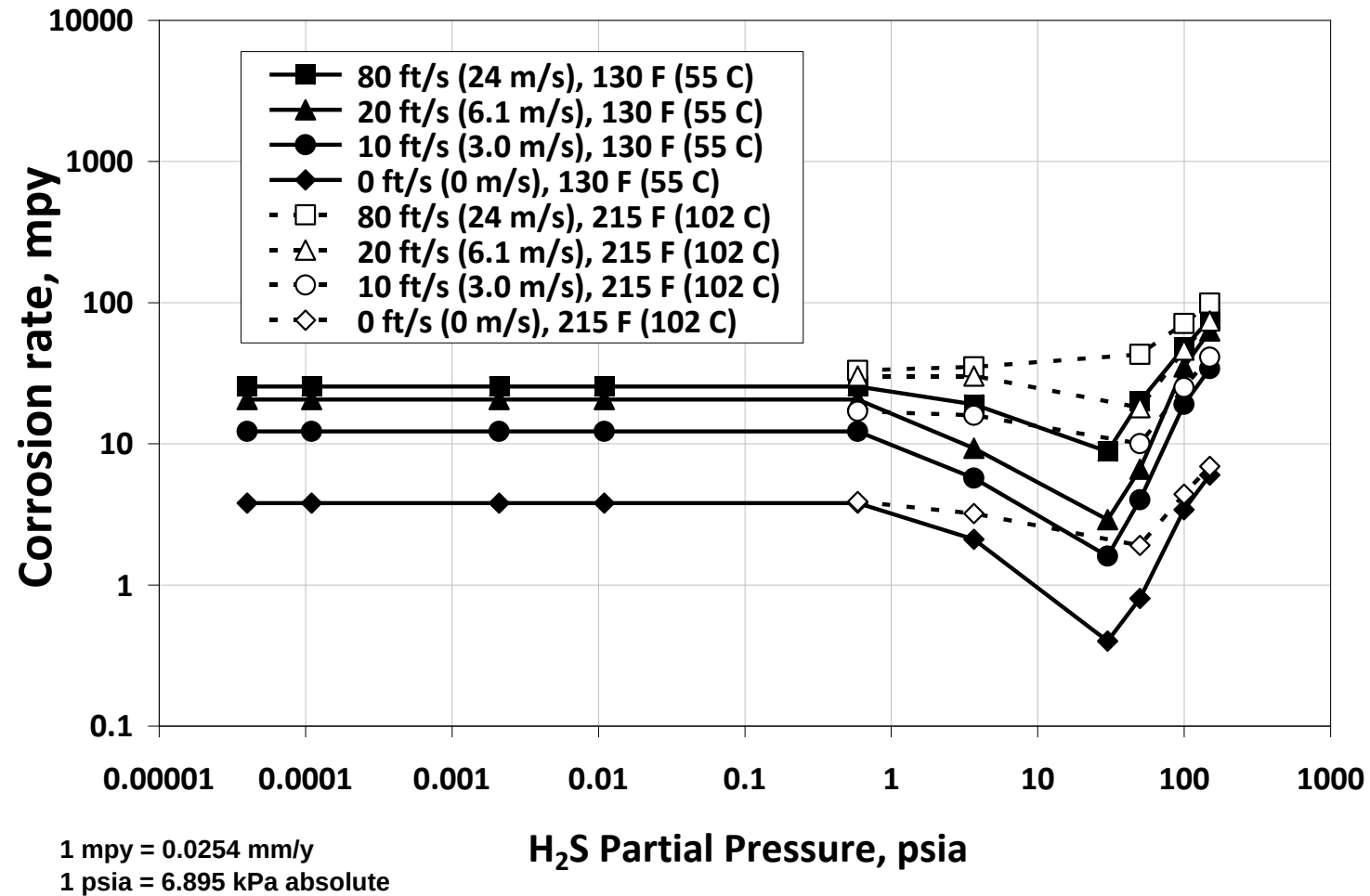
PHASE III – H₂S TIE-IN PLOTS

CS – 1 WT% NH₄HS – 130°F (55°C)



PHASE III – INTEGRATING DATA FROM ALL 3 PHASES

CS – 1 WT% NH_4HS – 215°F (102°C)



MODEL DEVELOPMENT - SUMMARY

- Identify typical operating condition boundaries for sour water in refining
- NH_4HS concentration, H_2S and NH_3 partial pressure, temperature, flow rates, cyanides etc.
- Simulate actual environment in laboratory tests
- Incorporate Ionic Modeling tools and extensive experimental design
- Expose typical material coupons (representative metallurgy) to simulated environment
- Based on statistically designed test matrix based on ionic modeling
- Measure corrosion rates reported and generate iso-corrosion curves, trends, tie-in plots
- Mathematical modeling of data and numerical interpolation
- Develop software model to predict corrosion (Predict-SW)
- Based on actual corrosion rates in simulated environments
- Validated through plant application and industry experience

NH₄HS CORROSION PREDICTION USING PREDICT-SW

Five key variables

NH₄HS concentration

Wall shear stress (not velocity)

H₂S partial pressure

NH₃ partial pressure

Temperature

Other relevant variables

Hydrocarbon content

Neutralizers / Chemical treatments (APS and Imidazoline)

CN content

SOUR WATER CORROSION PREDICTION WITH PREDICT-SW

Papers presented at NACE Corrosion Conferences

Paper Nos. 06576 and 06577)

(one by Shell Global and the other by Flint Hills Resources)

Paper Nos. 09377, 10349 and C2017-8929 (by Honeywell)

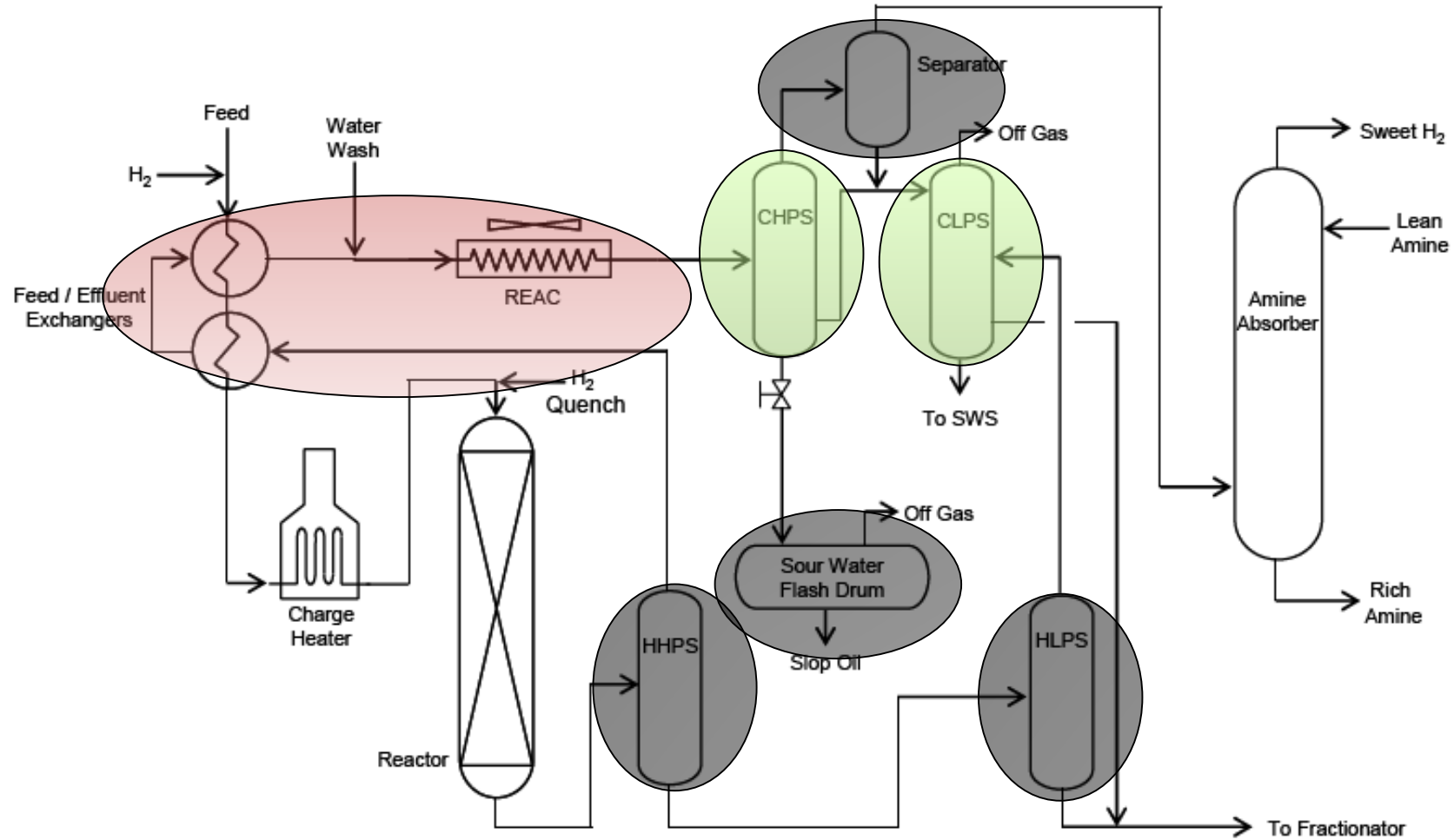
These papers include case studies correlating predicted corrosion rates with measured rates

Sour Water JIP guidelines built into API 932B – reinforces need for JIP model for accurate assessment

Some case studies (BP) were presented publically at non-corrosion focused events (Honeywell Users Group)

Over 45 refinery operators and engineering companies using Predict-SW for corrosion prediction / management

KEY PROBLEM AREAS IN SOUR WATER HANDLING



PREDICT-SW INTERFACE : INPUTS

Predict-SW 4.0 - Pro - Project1 Oirec

Home Reports Tools Help

Project List

- Project1 Oirec
 - Consultation1
 - Piping Model1
 - Piping Model2

Consultation1

Calculate Reset

Environment

Total Pressure: 1500.00 psig Temperature: 176.00 °F

H2S: 5 mol% H2S Partial Pressure: 75.735000 psia

NH4HS: Eval 8.00 wt% Free CN: 0.00 ppmw(aq)

Chemical Type: None Oil Type: User Defined

Application

Pipe Inner Diameter: 3.94 in CS Corrosion Allowance: 0.100 in

Design Life: 20.00 years Corrosion Allowance: 0.100 in

Pipe Roughness: Heavily Corroded Custom Roughness: 0.0000 in

Process Stream Conditions

☒ Custom Wall Shear Stress: 600.00 Pa

Regime: Horizontal Annular Mist Flow

Type of Flow: ☒ Horizontal ☐ Vertical

Configuration: 90 deg. Elbow

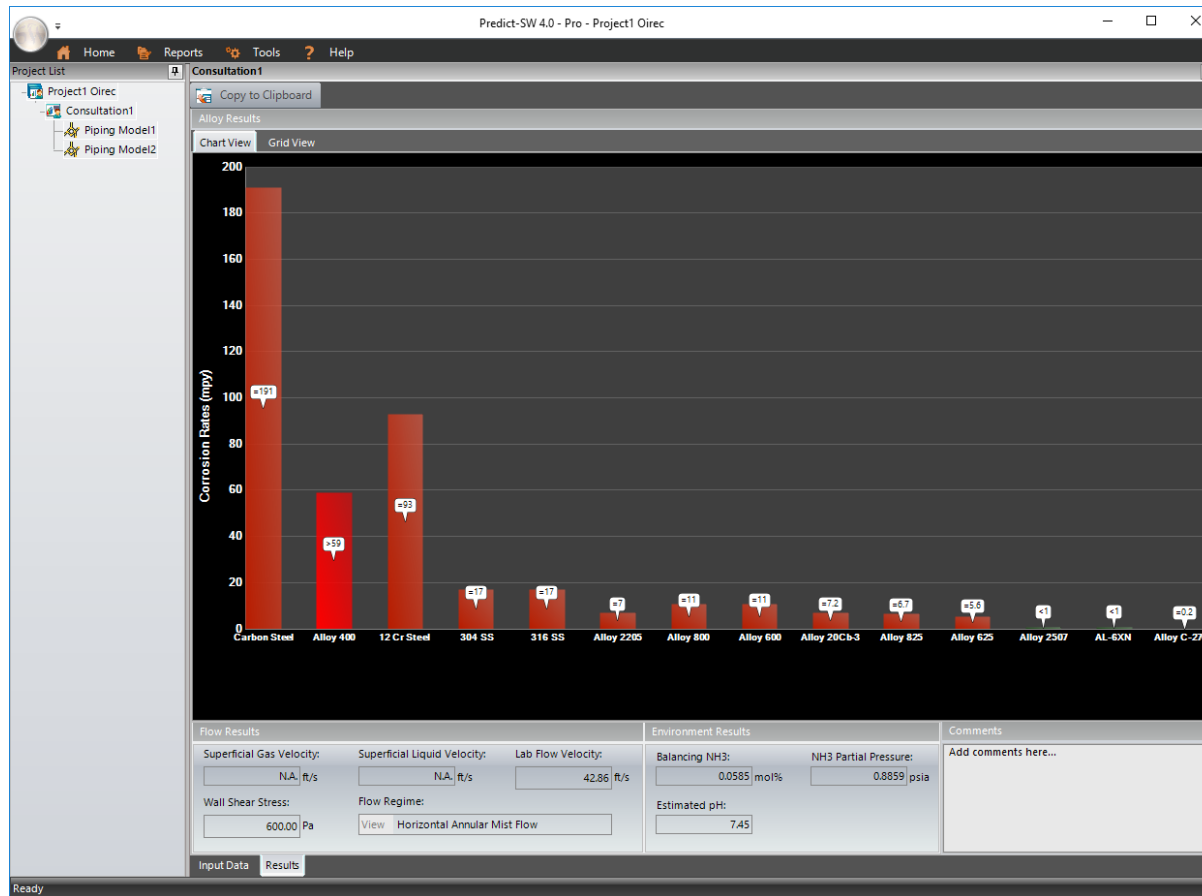
Process Flow Rates and Properties

Vapor Properties	Sour Water Properties	Liquid Hydrocarbon Properties
Flow Rate: ☒ Standard ☐ Actual 35.0000 MMSCFD	Flow Rate: 100.0000 GPM	Flow Rate: ☐ Override Hydrocarbon Protection 0.0000 bbls/d
Density: 0.99 lb/ft3	Density: 45.82 lb/ft3	Density: 53.10 lb/ft3
Viscosity: 0.0100 cP	Viscosity: 0.2500 cP	Viscosity: 5.0000 cP

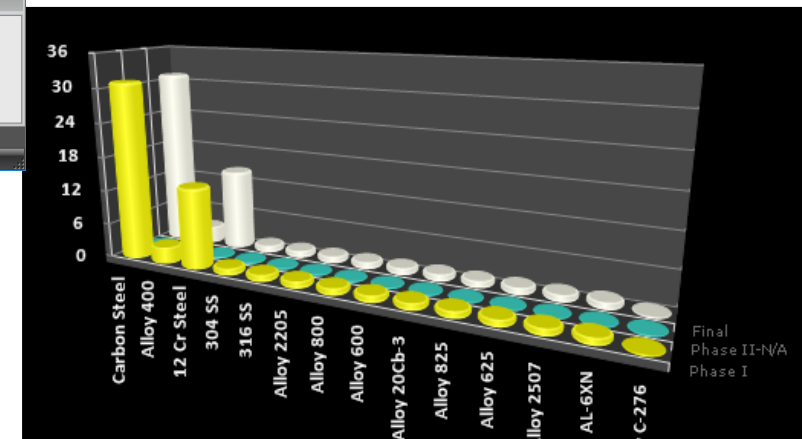
Input Data

Ready

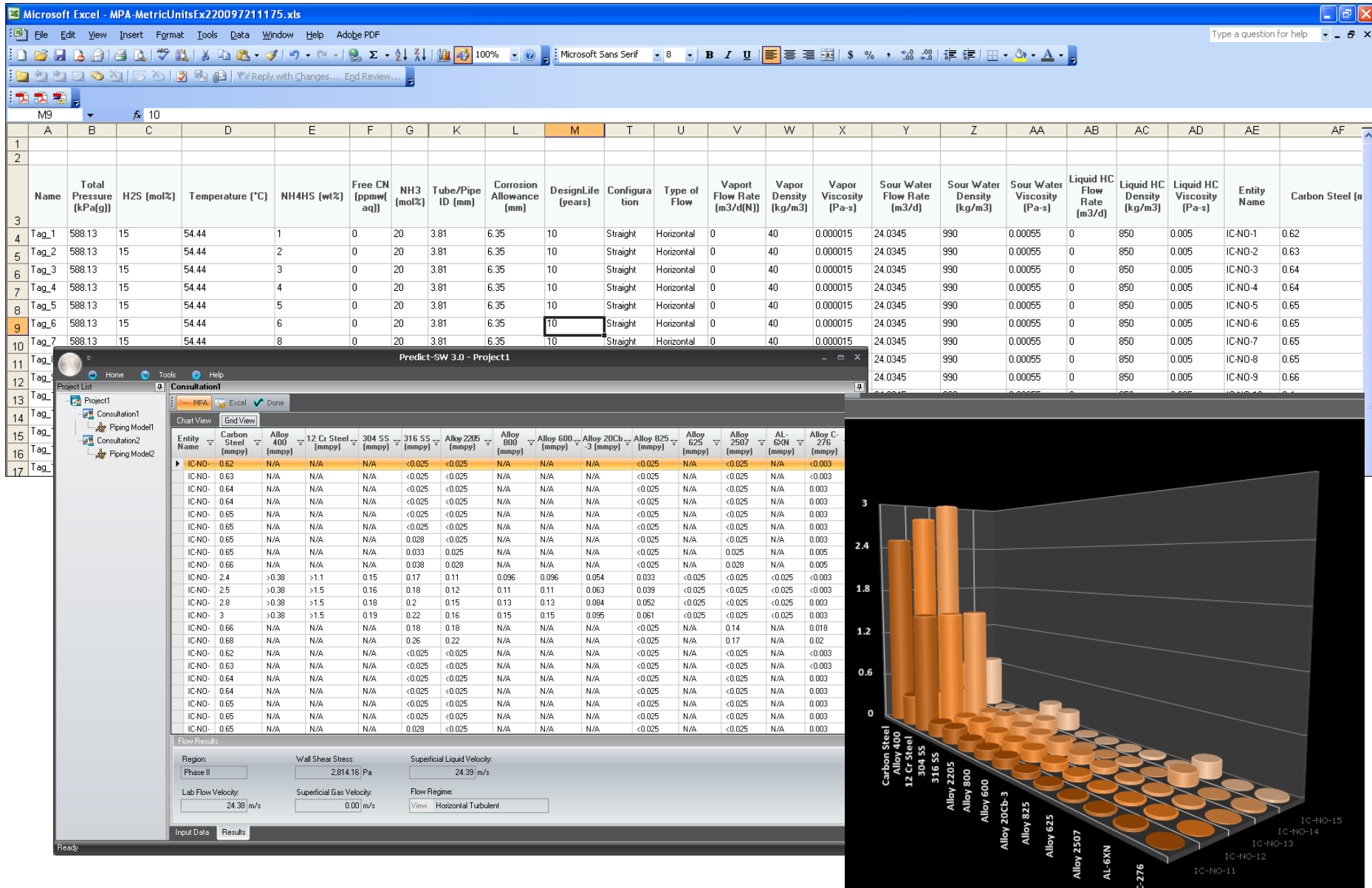
PREDICT-SW INTERFACE : RESULTS



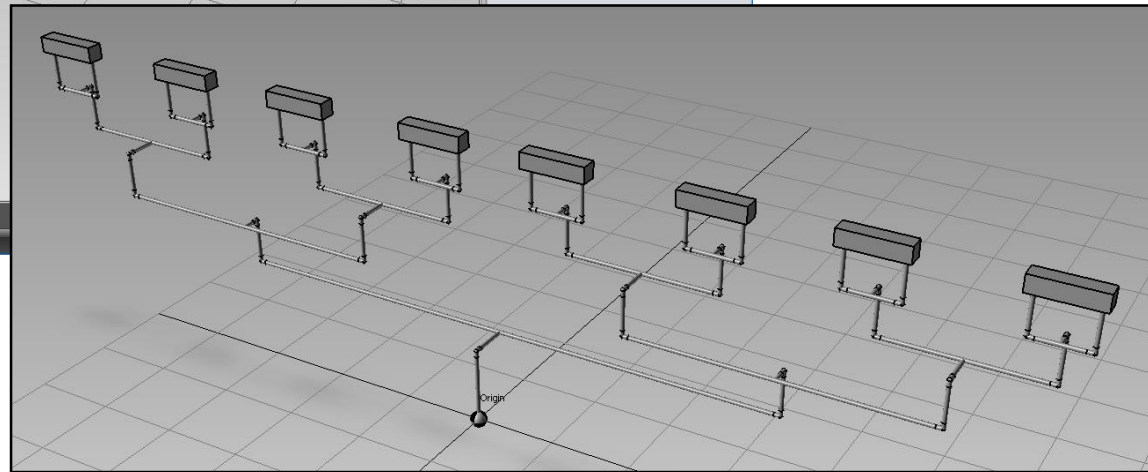
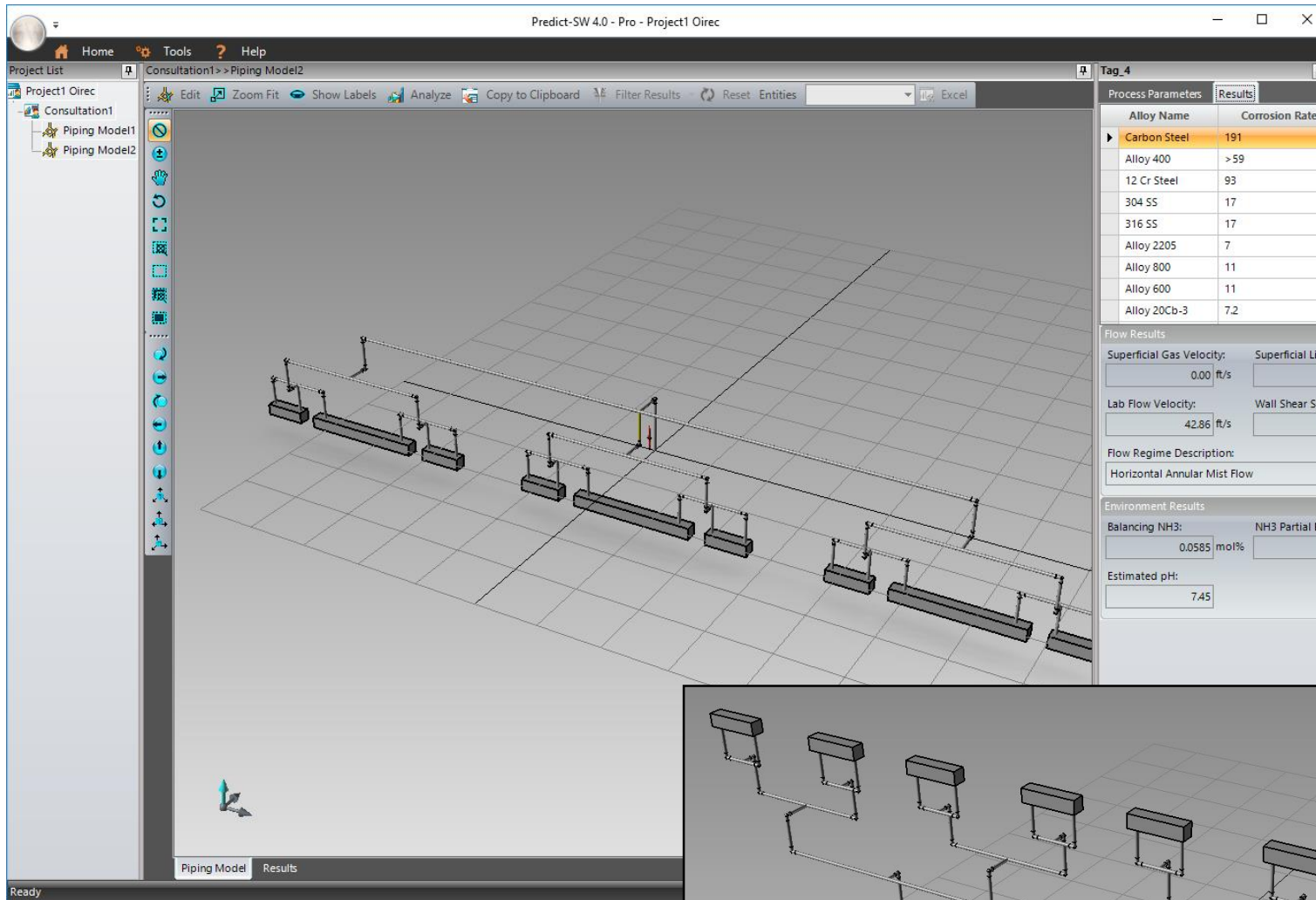
- Corrosion rates
- Flow regime
- Wall shear stress
- Flow parameters
- Phase comparisons
- Customizable Charts and Grids



MULTI-POINT ANALYSIS



3-D PIPING MODEL FOR BALANCED PIPING



CASE STUDIES – PREDICT-SW EXPERIENCE – FHR

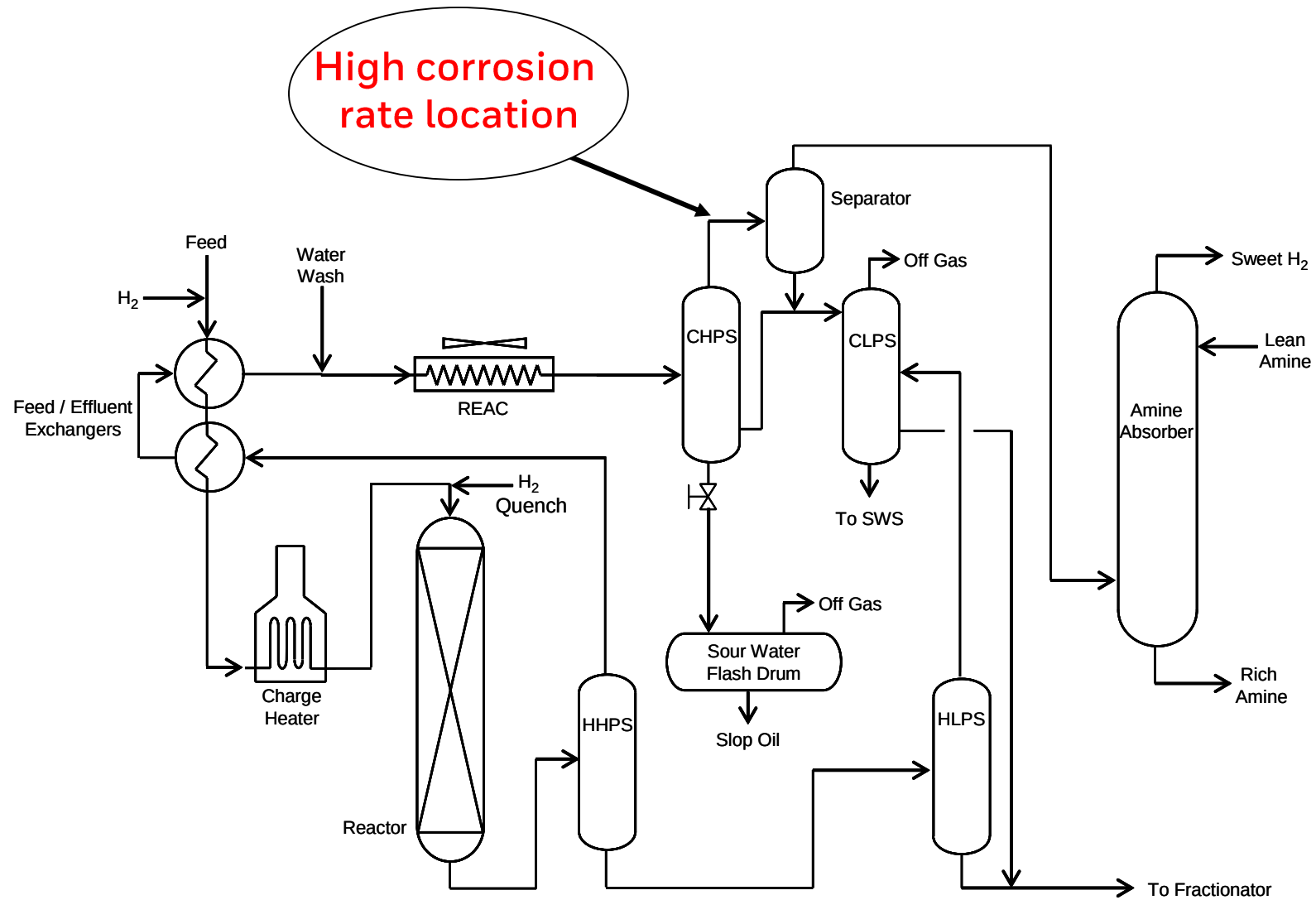
Flint Hills Hydrotreater A*

- Recycle gas piping from **CHPS (Cold Separator)** at 130 F – 54.5 C (sat. vapor)
- 10” Schedule 120 carbon steel elbow (not insulated)
- > 99% vapor, balance sour water
- 10 wt% NH_4HS
- 32 ft/s velocity
- 100 psia H_2S

Measured corrosion rate → ~ 68 mpy

*Paper No. 06577, Corrosion/06, San Diego, 2006

FHR HYDROTREATER A – PREDICT-SW EXPERIENCE



FHR HYDROTREATER A – PREDICT-SW EXPERIENCE

Predict-SW was used to predict the corrosion rate for this case

Churn Flow – 10 Pa wall shear stress

Measured CR of CS ~ 68 mpy

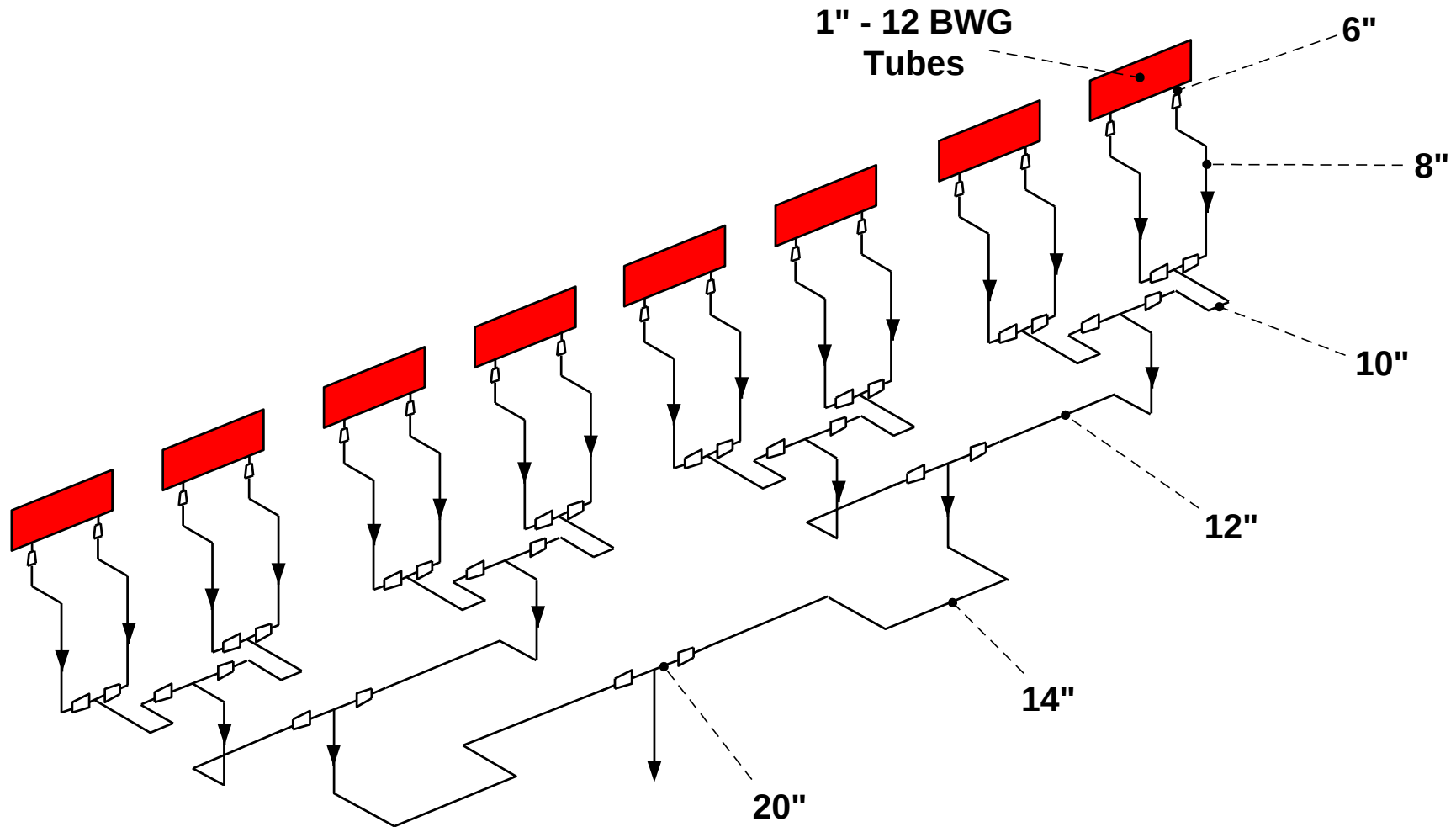
Predicted corrosion rate for CS = 65-75 mpy range

Predicted corrosion rate for 825 = 2 mpy

Line was replaced with carbon steel overlaid with alloy 825 (per Predict-SW recommendation)

The new line was not insulated and has not experienced any problems subsequently

FHR HYDROTREATER B: OUTLET REAC PIPING*



*Paper No. 06577, Corrosion/06, San Diego, 2006

FHR HYDROTREATER B - PREDICT-SW EXPERIENCE

Using old rules of thumb, there were serious concerns for corrosion in this REAC circuit

Carbon steel inlet / outlet piping and associated carbon steel air-fin exchangers

- 8 wt% NH_4HS at 130 F
- 27 psia H_2S
- Bulk velocities approaching 80 ft/s on the inlet and 30 ft/s on the outlet
- $K_p = 0.25$

Traditional rules of thumb indicated moderate to severe corrosion based on K_p , severe corrosion based on NH_4HS and velocity

FHR HYDROTREATER B - PREDICT-SW EXPERIENCE

No significant loss was detected by inspection

Plans made to replace CS piping with CS overlayed with alloy 825, plus upgrade of the fin-fans to alloy 2205

Cost estimated at US\$10 million

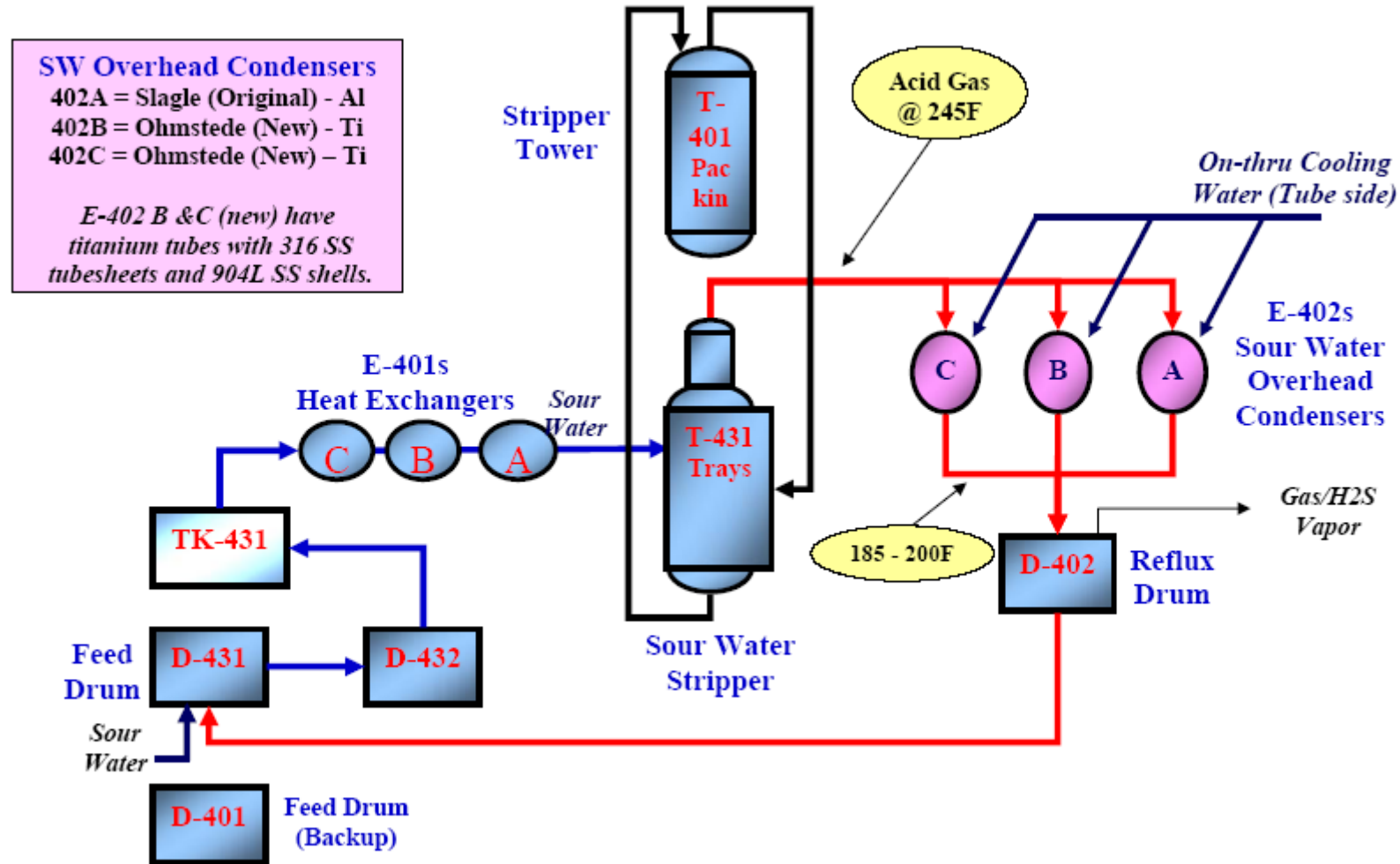
FHR HYDROTREATER B - PREDICT-SW EXPERIENCE

- **Predict-SW** used to predict the corrosion rate for the various inlet and outlet piping circuits
- Maximum of 25 Pa wall shear stress
- **Predicted corrosion was a maximum of 5 - 7 mpy**
- Plans to upgrade material were dropped, **\$10M material cost saving realized**
- Continued inspection has revealed an average of 5-6 mpy
- The low corrosion rates were the result of low wall shear stress combined with a low H₂S partial pressure

CASE STUDY C: BP SOUR WATER OH CONDENSERS

- Sour water Stripper overhead condensers with high end material (904L) were seeing corrosion problems
- Important need to identify the source of the problem and solution for effective mitigation
- Predict-SW utilized for process analyses and corrosion quantification

SOUR WATER STRIPPER PROCESS FLOWS



CASE STUDY C: DATA

NH4HS	H2S Partial Pressure	Temperature	Wall Shear Stress	CS Corrosion Rate	904L Corrosion Rate
wt%	psia	F	Pa	mpy	mpy
11.41	12.53	195	5	14	<1
11.41	12.53	195	10	16	<1
11.41	12.53	195	50	33	<1
11.41	12.53	195	100	51	<1
11.41	12.53	195	150	58	<1
11.41	12.53	195	200	62	<1
11.41	12.53	195	250	65	<1
11.41	12.53	195	500	68	<1
11.41	12.53	195	1000	72	<1
18	12.53	195	5	33	<1
18	12.53	195	10	38	<1
18	12.53	195	50	67	<1
18	12.53	195	100	78	<1
18	12.53	195	150	83	<1
18	12.53	195	200	88	<1
18	12.53	195	250	92	<1
18	12.53	195	500	96	<1
18	12.53	195	1000	99	<1

CASE STUDY C: INSIGHTS

- No corrosion on stainless alloy was indicated from ionic modeling and corrosion analyses
- However, inspection data was indicating corrosion propensity for 904L stainless steel
- So, what could contribute to corrosion here?
- Clearly, a factor was not considered in the analyses
- *One possibility was the presence of cyanides in the process stream, but not reported.*

CORROSION PREDICTION FOR SYSTEM WITH CN

NH4HS	NH3 PP	H2S PP	Temperature	CN	WSS	2205 CR	904L CR	CS CR
wt%	psia	psia	F	ppm	Pa	mpy	mpy	mpy
11.41	15.9	12.53	190	40	500	9.2	7.4	55
11.41	15.9	12.53	190	40	1000	13.3	11.2	74.7
11.41	15.9	12.53	190	40	1400	16	13.7	83.3
11.41	20	12.53	190	40	500	11.8	10.2	62.4
11.41	20	12.53	190	40	1000	16.1	14.3	84.4
11.41	20	12.53	190	40	1400	19	17.1	94.4
11.41	25	12.53	190	40	500	15.4	14.3	70.5
11.41	25	12.53	190	40	1000	20	18.8	94.9
11.41	25	12.53	190	40	1400	23.1	21.7	106.3
11.41	30	12.53	190	40	500	19.5	19.1	77.5
11.41	30	12.53	190	40	1000	24.5	23.9	103.7
11.41	30	12.53	190	40	1400	27.6	26.9	116.5

CASE STUDY C: SUMMARY

- No corrosion was anticipated under specified operating conditions for the system
- However, likely upset condition in the form of cyanide in the process stream was the likely candidate that contributed to corrosion propensity
- Analyses performed with Predict-SW facilitated identification of this problem and the appropriate material choice (Alloy C-276 with <1 mpy corrosion rate)

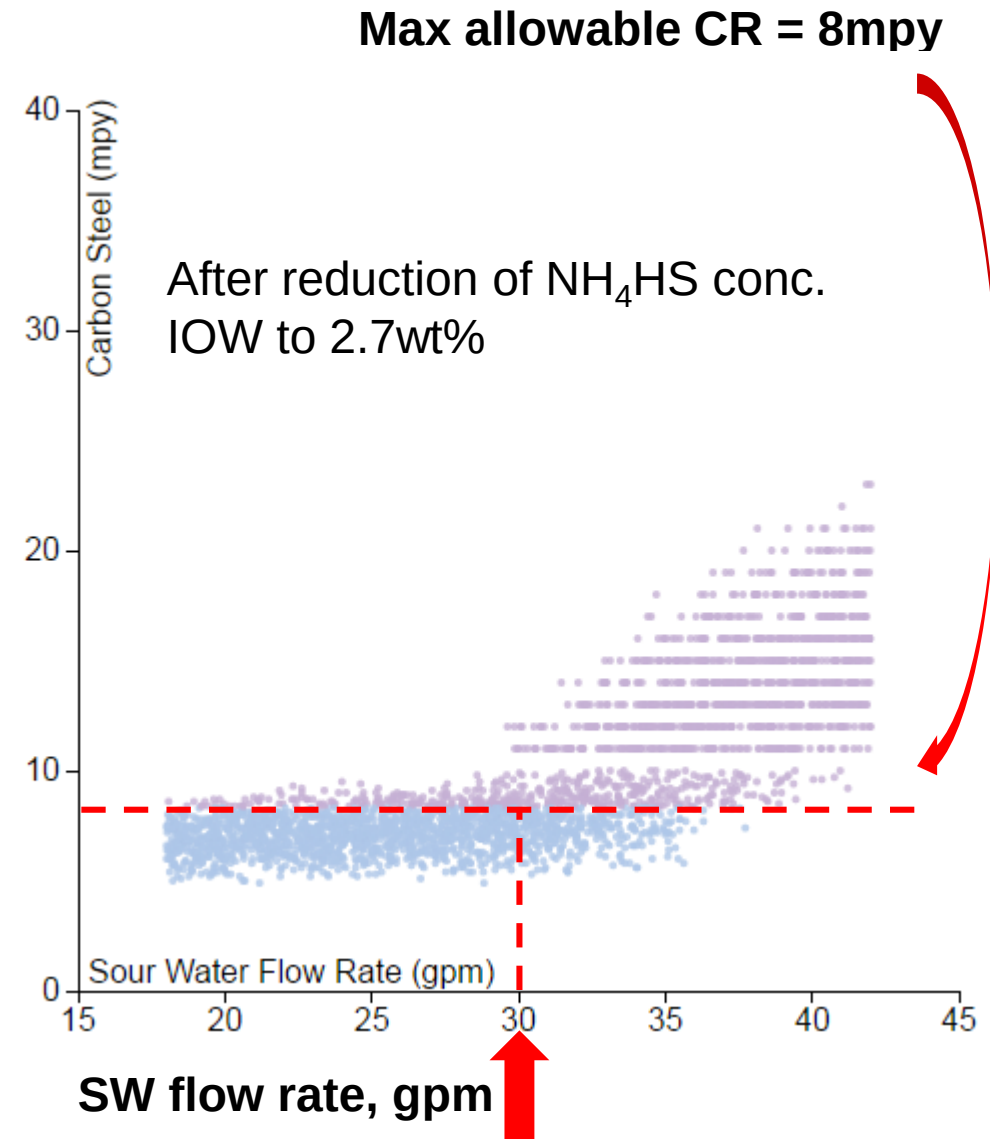
PREDICTIVE MULTI-PARAMETRIC ANALYSES MEANS DYNAMIC IOWS

Sour Water Flow Rate (gpm)	Value
Minimum	15
Maximum	45
Operating Point	30
IOW Low	15
IOW High	32

Max allowable CR = 8mpy

Multi-parametric analysis includes:

- Temperature
- NH_4HS conc.
- H_2S , NH_3 conc.
- Vapour flow rate
- Liquid HC flow rate
- Total pressure



CONCLUSIONS

- Sour water corrosion is a significant refinery reliability issue driven by multiple operating parameters
- Predict-SW is an accurate corrosion prediction model and material selection tool based on extensive JIP research and experimental corrosion data
- Predict-SW has also enabled development of effective IOW limits for monitoring corrosion
- Predict-RT-SW provides a real-time framework for optimizing operations as well as identifying corrosion hot spots and functions as a real-time software sensor.

THANK YOU

FOR MORE INFORMATION:

Please visit: www.honeywellprocess.com/Corrosion