



# 2017 API TANKS, VALVES, AND PIPING CONFERENCE & EXPO

**Developments in HHXRF Technology**

Latest PMI Tools and Applications

## The Latest Developments in PMI Tools and Applications

- Analysis of microalloying elements in high strength low alloy steels
- Measuring residual element (RE) content in carbon steels
- Low level silicon detection in steel piping to predict sulfidation corrosion
- Calculating equivalency factor (EQF) using pseudo elements
- Application demonstration

## Microalloys

- A family of materials strengthened by the addition of “micro” alloy concentrations to low-carbon mild steel
- Pipeline steels historically used do not contain elements found in similar carbon-manganese steels
- More recently the addition of microalloying elements such as vanadium, niobium and/or titanium
- Facilitating grain refinement increasing strength and toughness

## Microalloy Applications

- Oil & gas pipelines
- Offshore & subsea
- Automotive industry
- Pressure vessels
- Shipbuilding/Naval vessels
- Building structures
- Bridges/suspension components
- Heavy equipment



## Microalloy Advantages

- Weight reduction more than 25% over hot-rolled carbon steel
- Operational savings through increased pumping capacity in line pipe
- Lower fabrication costs from weight savings in transport and handling
- Reduced carbon content improves weldability and weldment toughness
- Lower CE minimizes heat treatment and susceptibility to cracking

## PHMSA Bulletin

- 2009 PHMSA bulletin ADB-09-01 advises pipeline operators of inconsistent chemical and mechanical properties
- Piping from the same heat exhibited variable chemical and mechanical properties including mill test reports not meeting recorded values (Nb, V, Ti)
- Suggesting that pipeline operators closely review manufacturing specifications for the production and rolling of steel plate

***“Trust, but verify.”***

## PHMSA Bulletin

- PHMSA investigated seven pipelines with five confirmed containing defective piping
- Use of substandard steel by U.S. from 2007 to 2009
- A number of pipe mills provided pipeline suppliers from India, Ukraine, Korea, China and Mexico sub-standard API 5L X70 piping with:  
***“Low and variable yield and tensile strength and chemical composition properties in high strength line pipe”***

## Plains Justice Report 2009

- Improper steel chemistry reported  
***“LOW or NO, manganese, vanadium niobium,  
molybdenum or titanium”***
- Improper rolling of steel plate
- A lack of proper segregation of steel slabs  
of different grades of steel at the steel mills





## Sulfidation Corrosion

- Thins pressure boundary wall of piping, components and welds exposed to hydrocarbon containing sulfur compounds at elevated temperatures
- Carbon steels with low-silicon ( $<0.10\%$ ) content can corrode at an accelerated rate
- Refinery units including crude, cat cracker, coker, hydrocracker and others
- Retro-PMI per API 578 as best practice (RAGAGEP)

## API 939-C Guidelines

- According to the (API) Recommended Practice 939-C (Guidelines for Avoiding Sulfidation Corrosion Failures in Oil Refineries), one-third of high-temperature sulfidic corrosion failures are the result of low silicon content
- Applicable to hydrocarbon process streams containing sulfur compounds operating at temperatures above 450F up to 1000F
- Sulfidation corrosion of piping and equipment continues to be a significant risk for incidents potentially resulting in loss of property and injury to workers

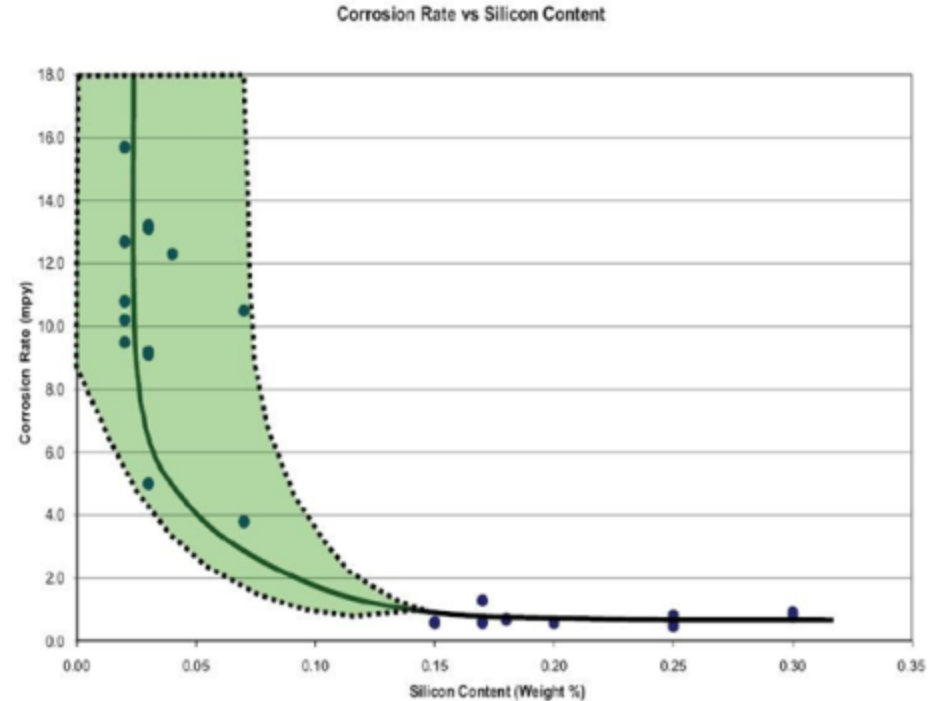
Guidelines for Avoiding Sulfidation  
(Sulfidic) Corrosion Failures in Oil  
Refineries

Download Segment

API RECOMMENDED PRACTICE 939-C  
FIRST EDITION MAY 2009

## Corrosion Rate

- API 939-C chart shows one company's corrosion rate vs. silicon content
- All A53-B piping and operating approximately at same temperature
- 10-15 mpy vs. 1 mpy makes a big difference after decades of service



A105

Si 0.10-0.35

## Common Materials

Flange

Valve

Olet

A234-WPB

Si 0.10 min

Elbow

Tee

Reducer

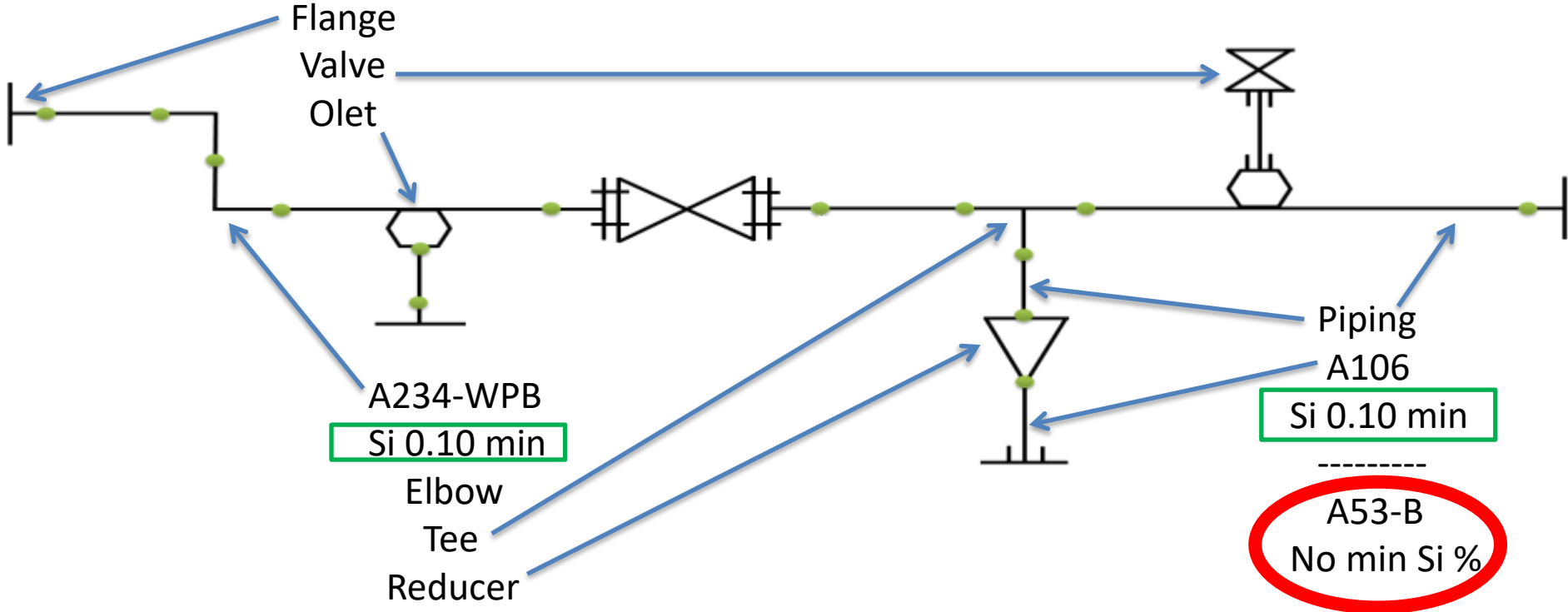
Piping

A106

Si 0.10 min

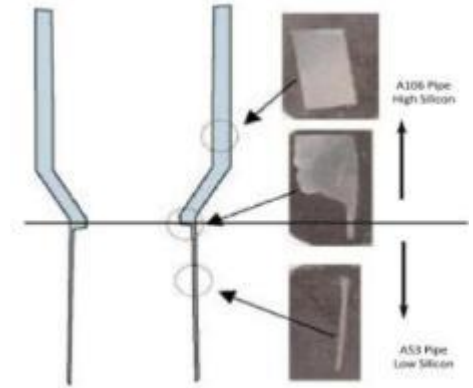
A53-B

No min Si %



## A-53 Piping

- Most material of concern installed before 1985 as A53 piping may have lower silicon content
- A53 and A106 piping used interchangeably
- Current typical practice is triple certification piping A106/A53/API 5L



## Sample Preparation

Accuracy affected by other contaminants

- Moisture
- Dust
- Fingerprints
- Aerosols
- Atmospheric debris
- Perspiration
- Condensation



## Sample Preparation

- Consider composition and grit when selecting abrasives
- Lower chromium content likely heavier oxidation
- 60-80 grit for CS/LA
- ZrAlO recommended
- Do not use silicon carbide

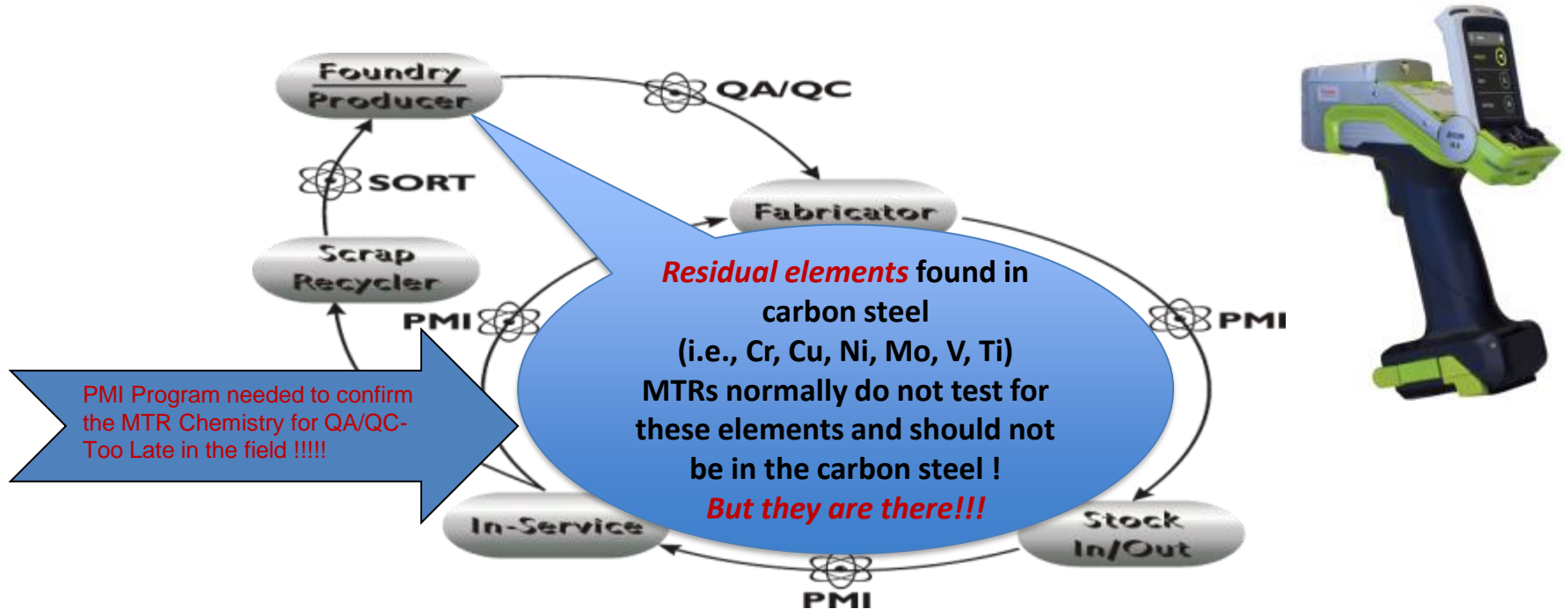


## Residual Elements

- Manufacturing of carbon steel is becoming more dependent on recycled metal scrap increasing residual element concentrations in finished materials
- Residual element concentrations in carbon steel can be a critical indicator in the expected life and performance of pipes and components used in petrochemical applications
- Particular elements of interest include Cu, Ni, and Cr, as well as Mo, Sn, V, Sb, As, and Pb

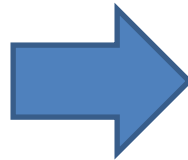


## PMI Cycle Overview – Renewed & Now Required Emphasis



## Residual Elements

- Challenge for mills to completely remove tramp elements from melted scrap
- Mills do provide material test reports (MTR) although not always listing the minor, undesirable element concentrations



## Residual Elements

- Select ASTM standards include supplementary requirements for HF service providing limits on maximum RE content – A516, A106, A333, A960, A961
- NACE paper 03651 concluded an optimal RE concentration could be:

$Cu + Ni < 0.15\%$  for base materials

$Cu + Ni + Cr < 0.15\%$  for weld materials

API RP 751 para. D.1.2



## Residual Elements

- Pipelines, chemical composition of PSL1
  - Cu < 0.5%
  - Ni < 0.5%
  - Cr < 0.5%
  - Mo < 0.15%
  - Nb + V < 0.06%
  - Nb + V + Ti < 0.15%
- Flow Accelerated Corrosion (FAC)
  - Cr > 0.1%, Cu, Mo



## Carbon Equivalency (CE)

- CE is a formula used to assess weldability, hardenability and susceptibility to Stress Cracking Corrosion for CS in H<sub>2</sub>S service
- Elements C, Mn, Ni, Cr, Cu, Mo, V influence overall CE value
- Residual elements Ni, Cu, Cr found in recycled steel also influence SSC probability and recommended controls < 0.15% SUM

$$CE_{IIW} = C + \frac{Mn}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Ni + Cu)}{15}$$

## Carbon Equivalency (CE)

- Microalloys Nb, V, Ti offer desirable mechanical properties such as precipitation hardening and toughness (aka Hi Strength Low Alloys)
- Adding Nb, V, Ti allows for reduction in carbon necessary to achieve properties such as yield strength
- Reducing carbon % reduces Carbon equivalent which increases weldability while reducing hardness, specifically heat affected zone HAZ

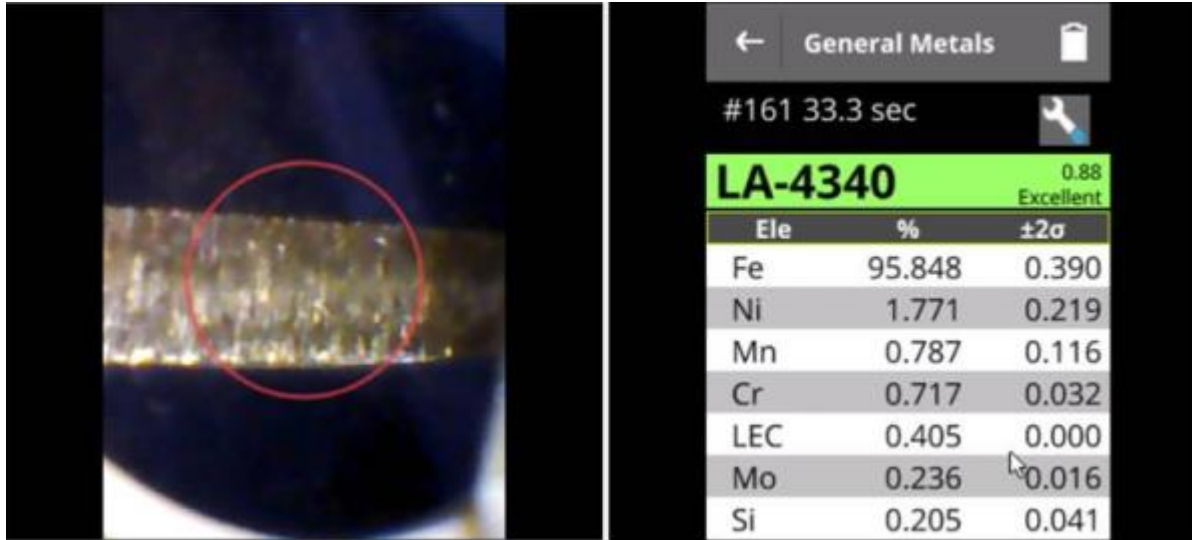
## Equivalency Factor (EQF)


- Modern HHXRF can input and process any common pseudo element equation including EQF
- Evaluating EQF can allow the user to assess what special welding precautions may be required:
  - Hot taps
  - Line pipe sleeve
  - Casting repairs (valves, pumps)




Ele	%	±2σ
LEC	0.060	0
EQF	0.196	0.010
Cu+Ni+Cr	0.107	0.039
Cu	0.029	0.006
Ni	<LOD=	0.050
Cr	0.047	0.007
Nb	0.044	0.001
V	<LOD=	0.018
Ti	<LOD=	0.032
Fe	98.623	0.069
Mn	1.085	0.026
Mo	0.008	0.001
Pb	0.026	0.003
Zr	0.020	0.001

## Live Demonstration



← General Metals 

#161 33.3 sec 

**LA-4340** 0.88  
Excellent

Ele	%	±2σ
Fe	95.848	0.390
Ni	1.771	0.219
Mn	0.787	0.116
Cr	0.717	0.032
LEC	0.405	0.000
Mo	0.236	0.016
Si	0.205	0.041



## Questions and Comments

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