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Raise the Bar

Latest Advancements in Positive Material Identification (PMI) for Handheld X-Ray Fluorescence (XRF) and Handheld Laser-Induced Breakdown Spectroscopy (LIBS)

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Why PMI?

How it Works

Carbon Equivalency

HF Alky Residual Elements – API 751

Sulfidation Corrosion – API 939C

PHMSA Mega Rule

Flow-Accelerated Corrosion



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Why PMI?

- Positive Material Identification (PMI) is the analysis of any material, generally a metallic alloy, to establish composition by reading the quantities by percentage of the constituent elements
- These specifications include the levels of various alloying elements that comprise a specific ASTM or AISI grade
- PMI and verification applications include any installed, inventoried, or in-process fabricated items whose properties must meet strict engineering specifications to avoid potentially catastrophic consequences



Why PMI?

“41% of the 170 largest losses in the hydro-carbon process industry resulted from failures of piping systems...”



Equipment Type and Percentage of Large Losses

Piping 30%

Tanks 15%

Reactors 13%

Drums 7%

Pumps and Compressors 6%

Heat Exchangers 4%

Towers 4%

Heaters/Boilers 3%

Others 18%

Source: Marsh and McLennen (property protection and risk consultants)

Common Technologies Used in PMI

Three technologies typically used for alloy grade ID and chemical analysis



- 40-year-old mobile Optical Emission Spectroscopy (**OES**)



- 40-year-old portable X-Ray Fluorescence (**XRF**)
 - Over 60,000 Thermo Fisher Scientific Niton handheld **XRF** alloy analyzers installed globally



- **New LIBS** Technology
 - Over 3,000 HH LIBS installed
 - Can supplement XRF for carbon applications
 - Can replace OES for most applications

Why PMI?

- LIBS is a minimally destructive test – leaves a small burn on the surface
- Relatively small spot size (50u) means alloy must be homogeneous (representative) at that spot
- Requires sample prep (grinding)
- Routine set-up procedure
- May need occasional cleaning of optics
- Need to purchase consumables
 - Mainly argon cartridges and grinding media
- Laser Safety vs Radiation Safety



Why PMI?

- XRF is completely non-destructive
- Standard measurement beam area is 8mm; Optional small-spot feature collimates the beam down to 3mm for smaller samples
- Sample prep (grinding) is generally not required, unless removing paint, scale, coatings, etc. from the sample surface, or when light element analysis (S, P, Mg, Al, & Si) is required
- Fast set-up procedure via internal System Check
- May need occasional cleaning/changing of aperture window, which is the only consumable
- Radiation Safety Training required





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How it Works

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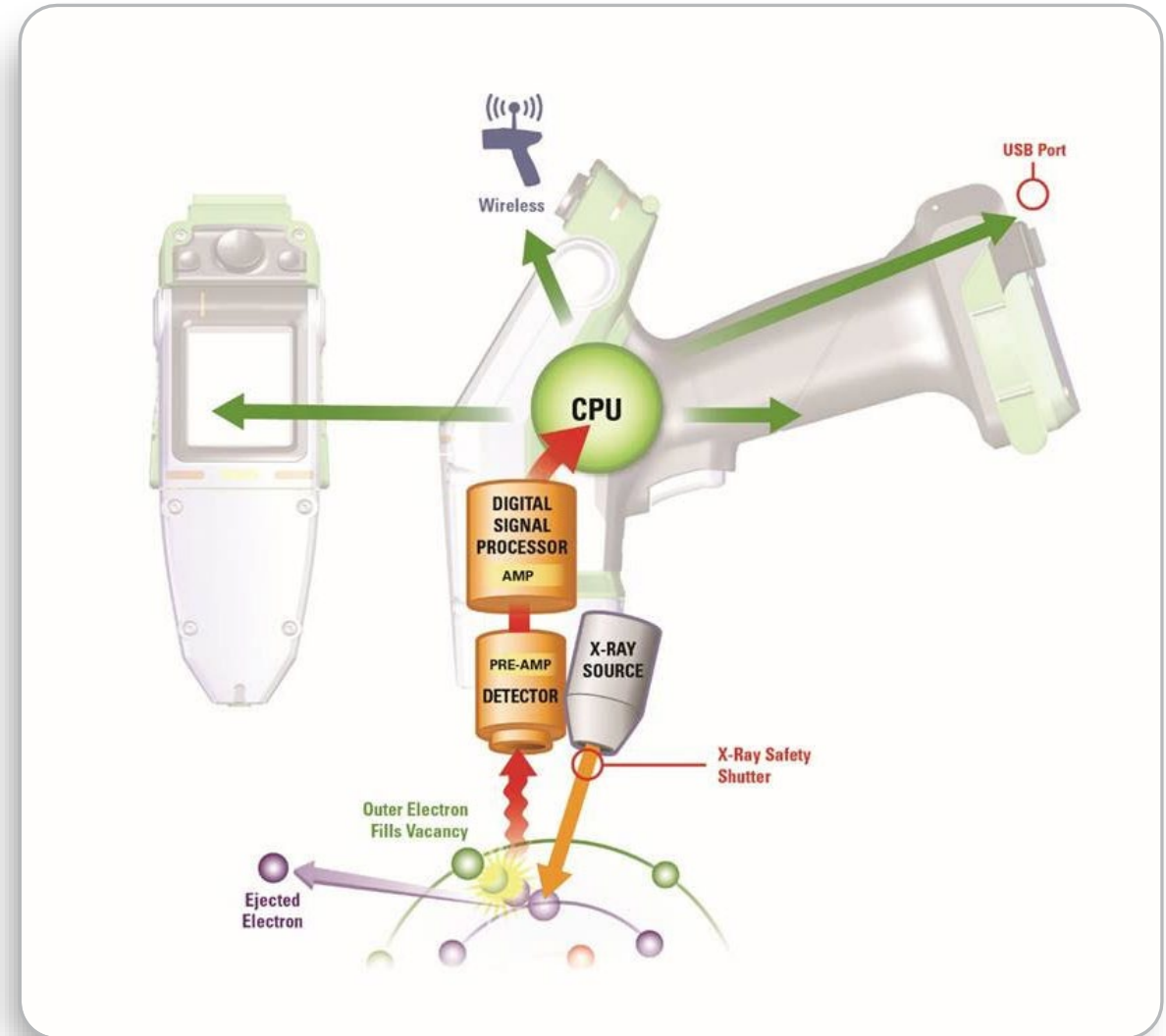
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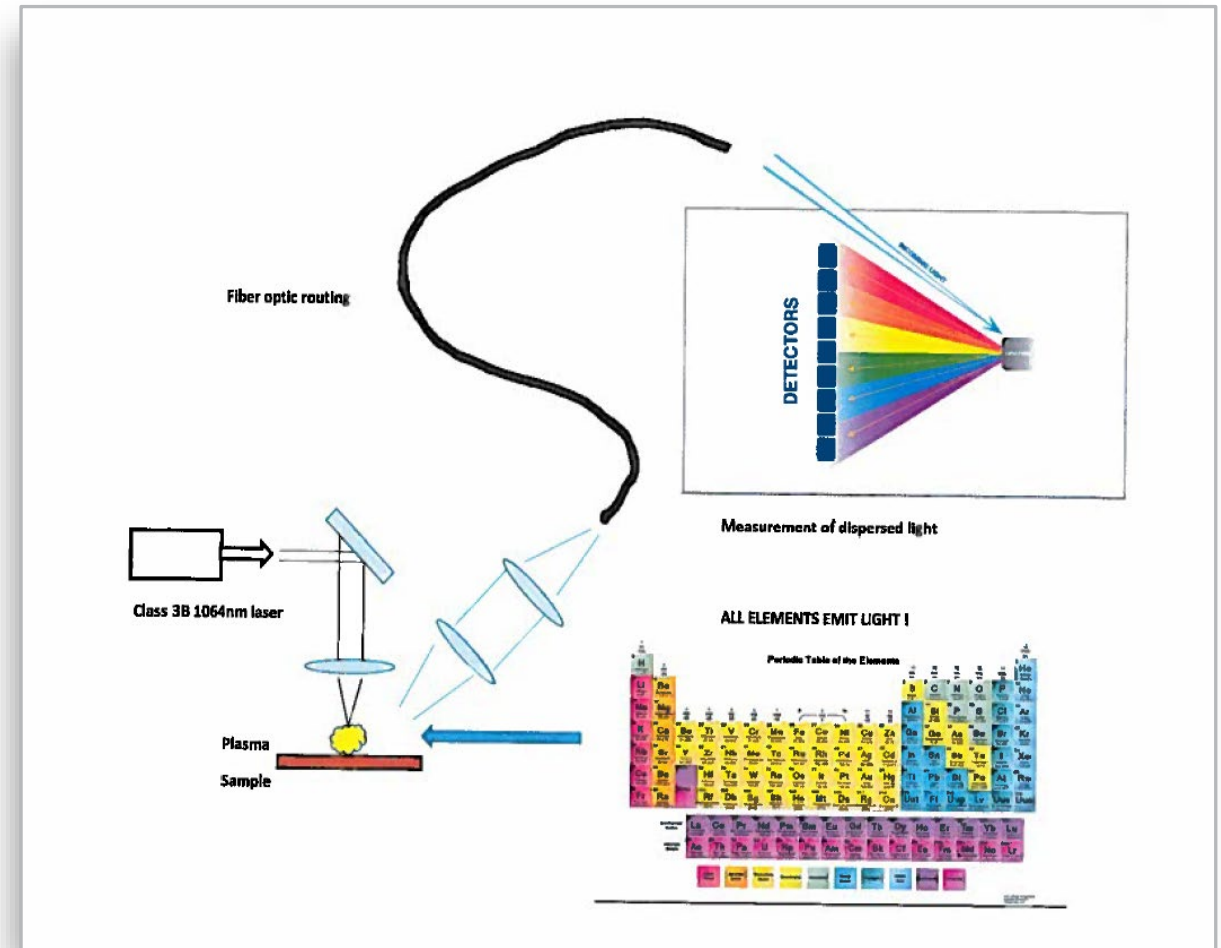
How it Works - XRF

- X-rays from a primary beam (X-ray tube) are fired into the sample
- Excited electrons in the atoms return to ground state, emitting characteristic energy element x-rays
- The energies are picked up by a detector and produce spectral data
- Software and calibrations in the CPU compare the energies and intensity of spectral lines to quantify the concentrations of elements
- Composition and grade data are displayed and stored in memory for recall or printing



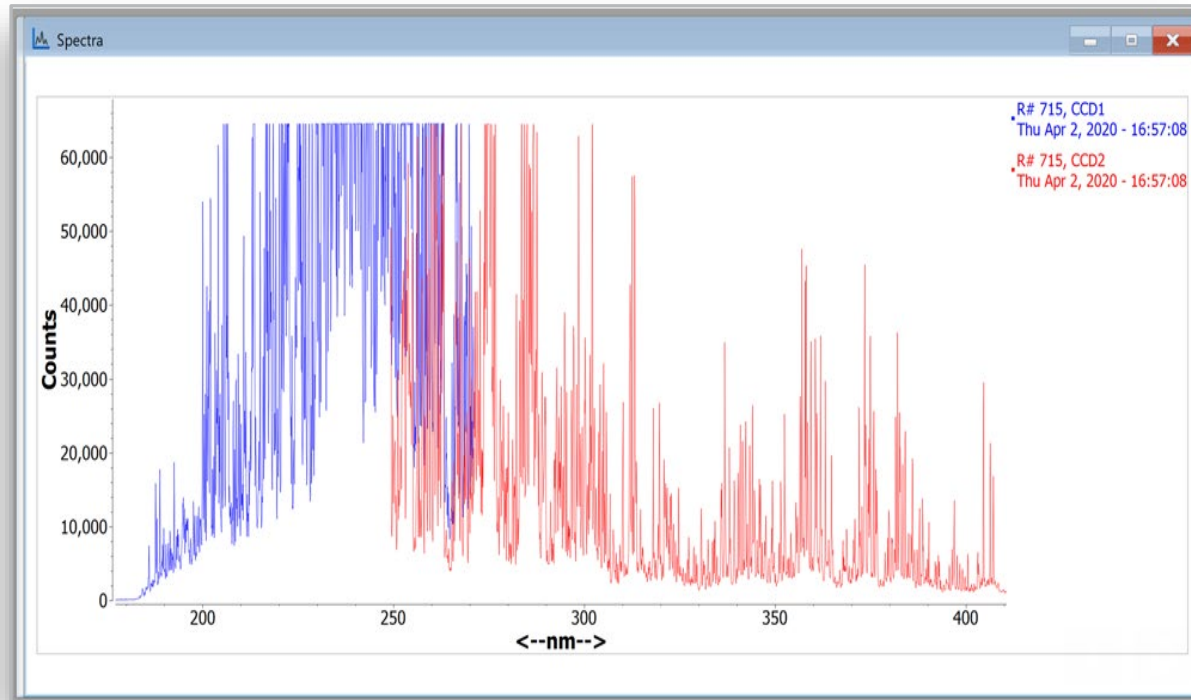
How it Works - LIBS

- Pulsed laser is fired into the sample and vaporizes the metal to form a plasma on the surface
- Excited electrons in the plasma return to ground state in atoms and ions, emitting light which is diffracted by a grating into component wavelengths
- The wavelengths are transferred to a detector and produce spectral data
- Software and calibrations in the CPU compare the wavelengths and intensity of spectral lines to quantify the concentrations of elements
- Composition and grade data are displayed and stored in memory for recall or printing

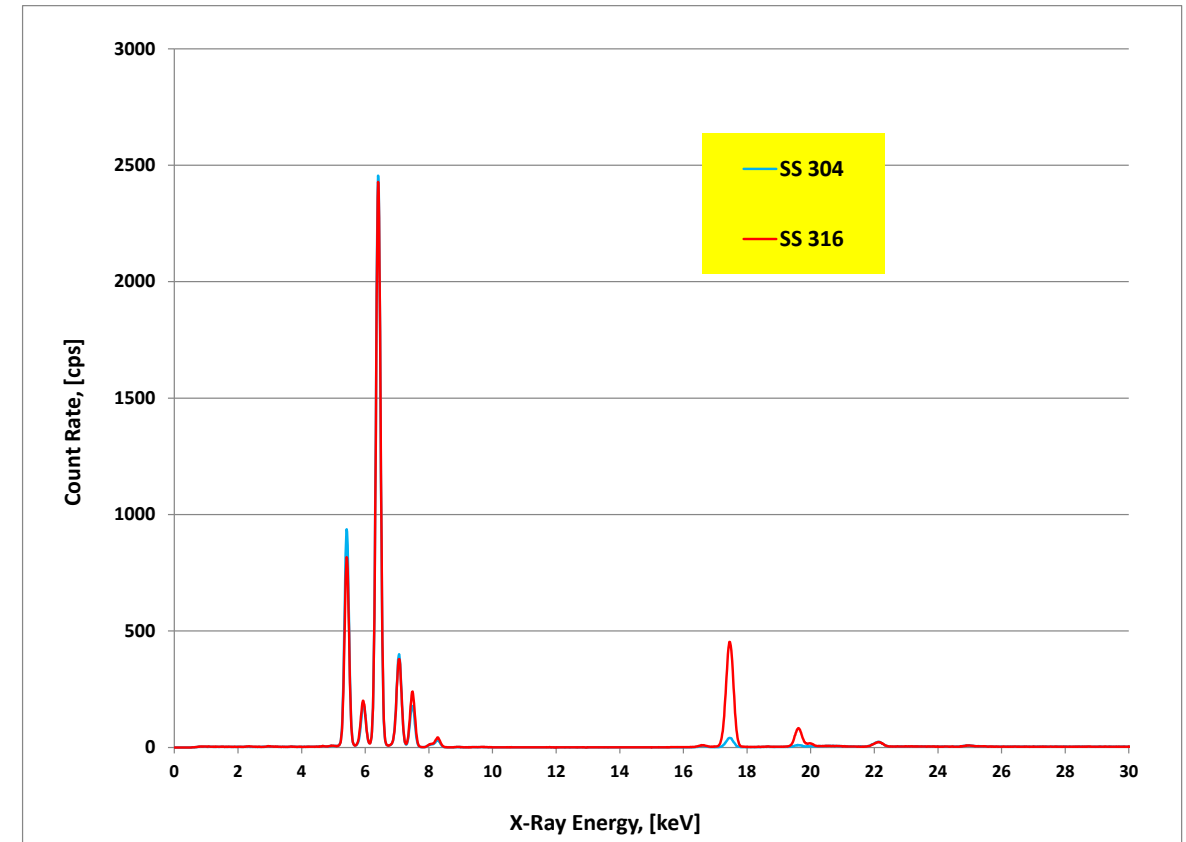


How it Works – LIBS & XRF Spectra of Same Alloy

The LIBS spectra contains more information, meaning we see more detectable elements, but with greater complexity in the analytical determination of those extra elements



LIBS Spectra 316L



XRF Spectra 304 and 316

How it Works - XRF, OES and LIBS Element Ranges

H																He	
Li	Be										B	C	N	O	F	Ne	
Na	Mg										Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89-10															
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Technology Choice: Handheld XRF and/or LIBS Analyzer

Type of Alloy Family	Best Technology (preferred type listed first)
Stainless steel	XRF or LIBS ¹
C-steel	LIBS
Low alloy and Cr-Mo steel	LIBS or XRF
Tool Steel	XRF or LIBS
Ni, Ni/Co and Co alloy	XRF or LIBS
Cu alloy	XRF or LIBS ²
Al alloy	LIBS or XRF
Ti alloy	XRF or LIBS ³
Zn alloy	XRF or LIBS ³
Exotic and refractory alloy	XRF
Precious metals	XRF or LIBS
Rare earth alloys	XRF

¹ If L-grades are needed (C)
LIBS is the only HH solution

² HH LIBS best if sorting ECu,
Be-Cu or Al-Si bronze

³ HH LIBS best if sorting based
on Al content



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Carbon Equivalency

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Carbon Equivalency

- Formula developed to assign a numerical value to the hardenability of a steel
- Predict the susceptibility of a steel to Hydrogen (cold) cracking
- Heat Affected Zone (HAZ) hardenability in welding
- Elements C, Mn, Ni, Cr, Cu, Mo, V influence overall CE value
- Recycled steel more common today in steel production
- Modern high strength steels will have lower carbon with micro alloying elements such as Nb, V, Ti added for desired strength

Common CE Value Classifications	
Carbon Equivalent (CE)	Weldability
Up to 0.35	Excellent
0.36-0.40	Very Good
0.41-0.45	Good
0.46-0.50	Fair
Over 0.50	Poor

International Institute of Welding (IIW)

$$CE = C + Mn/6 + (Cr + Mo + V)/5 + (Cu + Ni)/15$$

American Welding Society (AWS)

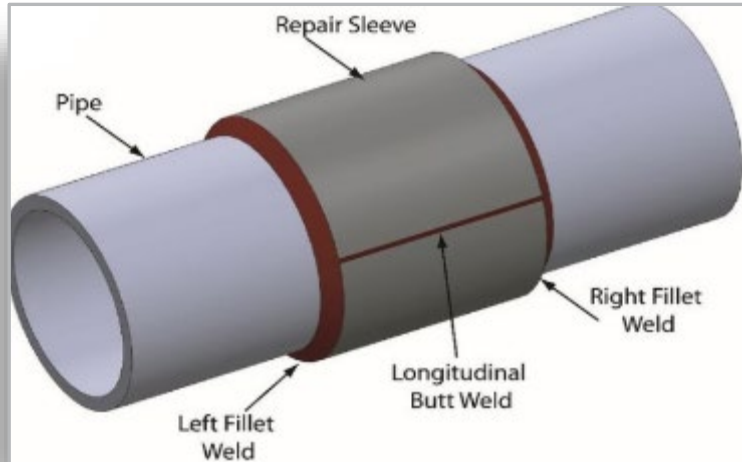
$$CE = C + (Mn + Si)/8 + (Cr + Mo + V)/5 + (Cu + Ni)/15$$

$$P_{cm} = C + \frac{Si}{30} + \frac{Mn + Cu + Cr}{20} + \frac{Ni}{60} + \frac{Mo}{15} + \frac{V}{10} + 5B$$

$$CE (CAN) = \%C + F * [\%Mn/6 + \%Si/24 + \%Cu/15 + \%Ni/20 + (\%Cr + \%Mo + \%V + \%Nb)/5 + 5*\%B]$$

Carbon Equivalency

- Used in all O&G sectors (upstream, mid, downstream)
- Energy markets – nuclear, power gen, fossil fuel
- Casting repairs (i.e. valves, pumps, turbine casing)
- Pipeline welding, containment sleeve
- Hot tap for flow meter, bypass line
- Offshore riser reinforcement
- Shaft, flange face machining & weld build-up



Carbon Equivalency

Sample	CE-IIW	CE-AWS	C	Mn	Cu	Si	Ni	Cr	Mo	V	Ti	Al
X65	0.287	0.335	0.049	1.061	0.118	0.286	0.117	0.090	0.056	0.081	0.005	0.038
X65	0.306	0.352	0.042	1.209	0.118	0.279	0.095	0.087	0.064	0.087	0.005	0.024
X65	0.291	0.338	0.040	1.134	0.125	0.277	0.105	0.091	0.061	0.085	0.005	0.030
X65	0.290	0.338	0.042	1.116	0.118	0.284	0.112	0.096	0.065	0.077	0.005	0.031
X65	0.300	0.346	0.039	1.196	0.116	0.276	0.094	0.080	0.068	0.088	0.005	0.028
X65	0.294	0.341	0.034	1.171	0.113	0.280	0.102	0.092	0.078	0.083	0.005	0.030
X65	0.278	0.326	0.039	1.091	0.124	0.289	0.106	0.090	0.049	0.069	0.006	0.032
X65	0.295	0.340	0.046	1.127	0.116	0.273	0.109	0.087	0.063	0.081	0.005	0.034
X65	0.282	0.333	0.041	1.078	0.117	0.310	0.107	0.095	0.059	0.075	0.004	0.038
X65	0.280	0.325	0.036	1.115	0.110	0.275	0.098	0.089	0.053	0.079	0.005	0.034
AVG	0.290	0.337	0.041	1.130	0.118	0.283	0.105	0.090	0.062	0.080	0.005	0.032
STDEV	0.009	0.008	0.004	0.049	0.004	0.011	0.007	0.005	0.008	0.006	0.000	0.004
RSD	3.1%	2.4%	10.7%	4.3%	3.8%	3.8%	7.1%	5.1%	13.3%	7.2%	9.1%	13.7%

Fe #218 Avg(20) 196-204,206-...

Low Alloy

Sample: IMZ112

Ele	A:20	218	217	215
RES	0.174	0.170	0.181	0.185
CE	0.319	0.318	0.291	0.285
C	0.201	0.204	0.175	0.167
Mn	0.464	0.454	0.465	0.460
Si	0.274	0.256	0.273	0.280
Cu	0.067	0.067	0.067	0.064
Ni	0.060	0.057	0.069	0.069
Cr	0.047	0.046	0.045	0.051
Mo	0.057	0.049	0.052	0.054
Ti	0.020	0.015	0.017	0.016
Al	0.031	0.025	0.026	0.027
V	0.057	0.052	0.054	0.059
Fe	98.72	98.77	98.76	98.75

Carbon Equivalency



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PERFORMANCE CHARACTERISTICS

Thermo Scientific Niton Apollo LIBS Analyzer

Low Alloy and Carbon Steel Performance Characteristics

Using the Niton Apollo Handheld LIBS Analyzer

Introduction

The Thermo Scientific Niton Apollo handheld LIBS analyzer is built for your most demanding applications. When low detection limits and high sample throughput are critical, the Niton Apollo's combination of hardware and software provides you with solutions designed to meet your most difficult analytical requirements. Featuring an effective laser and high purity argon purge, the Niton Apollo accurately measures carbon in about 10 seconds. Weighing just 6.4 lbs. (2.9 kg), the Niton Apollo transforms a traditional laboratory, or cart-mounted Optical Emission Spectroscopy (OES) system, into a highly portable handheld analyzer.

The Importance of Sample Preparation

Good sample preparation is essential to obtaining reliable results when using the Niton Apollo. Trace amounts of contaminants, such as paint, grease or scale may yield unreliable outcomes. This is because the Niton Apollo uses a laser to ablate the surface of the sample. When this occurs, only a small portion of the sample (a few nanograms) is removed. If the surface is diluted, then there is not a representative sample of the metal to provide accurate results.

Instrument Performance

The results listed are obtained from well-prepared samples and are an indication of the best performance to be expected from the Niton Apollo. Accuracy and precision are typical ways of determining instrument performance. Accuracy describes how close the read values (concentration) are to the certified or true value. Precision is an indication of how close multiple readings are to one another on any given sample.

Accuracy is dependent on the calibration of the instrument and sample preparation. Precision is dependent on both the instrument performance in terms of stability and equality on the homogeneity of the sample analyzed. Due to the small amount of material being ablated, spot to spot variation can occur increasing (worsening) the measured precision. It is highly recommended to perform at least three (3) or more analysis and average the results. Users may also delete questionable burns if they occur.

The Niton Apollo has an easy to read average screen (Image 1). The on-board carbon equivalency (CE) equation is based on

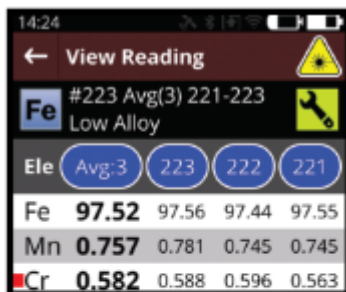


Image 1

$$CE = C + \frac{Mn}{8} + \frac{Cr + Mo + V}{5} + \frac{Ni + Cu}{15}$$

Image 2

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APPLICATION NOTE

Thermo Scientific Niton Apollo LIBS Analyzer

Analysis of Carbon Equivalents in Steel Components

Using the Niton Apollo Handheld LIBS Analyzer

Author: Brian Wilson, Thermo Fisher Scientific, Tewksbury, MA USA

Application

The weldability of a steel is primarily influenced by its carbon content. Additionally, the contribution of other elements, such as manganese (Mn), chromium (Cr), molybdenum (Mo), vanadium (V), copper (Cu), nickel (Ni), and silicon (Si) can also impact its carbon equivalency (CE). These additional elements add up in scrap fed electric arc furnace steels that now predominate the market and carry over into finished goods.

Carbon equivalency was originally developed to assign a numerical value for a given steel composition indicating the carbon content which would contribute to an equivalent level of hardenability for that steel. Even further, carbon equivalency represents the contribution of the materials composition to cold-cracking (hydrogen cracking) susceptibility of the steel.

In welding, carbon equivalent calculations are used to predict heat affected zone (HAZ) hardenability. By understanding any differences in chemistry through the carbon equivalency calculation, it can be determined if the properties of two materials being joined together via a filler metal component are compatible for the process. If the components are too dissimilar, or if the carbon equivalent approaches a higher, undesirable value (Table 1), then special precautions may be needed prior to and during the welding process.

Welding precautions may include prescriptive heat treatment, use of low hydrogen electrodes, and controlling heat input. Many of these guidelines are published in the NACE (National Association of Corrosion Engineers) standards



Carbon equivalency (CE) is an essential calculation prior to performing welding.

(NACE MR0175/ISO 16156 and NACE MR0103/ISO 17945). These standards were developed for offshore, petrochemical, and natural gas applications where carbon steels in the presence of hydrogen sulfide (H₂S, sour service) are susceptible to sulfide stress cracking (SSC) or hydrogen stress cracking (HSC).

There are two commonly used equations for expressing carbon equivalency developed by the International Institute of Welding (IIW), and American Welding Society (AWS).

$$\begin{aligned} \text{International Institute of Welding (IIW)} \\ CE &= C + Mn/8 + Cr + Mo + V/5 + Cu + Ni/15 \\ \text{American Welding Society (AWS)} \\ CE &= C + (Mn + Si)/8 + (Cr + Mo + V)/5 + Cu + Ni/15 \end{aligned}$$

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HF Alky Residual Elements – API 751

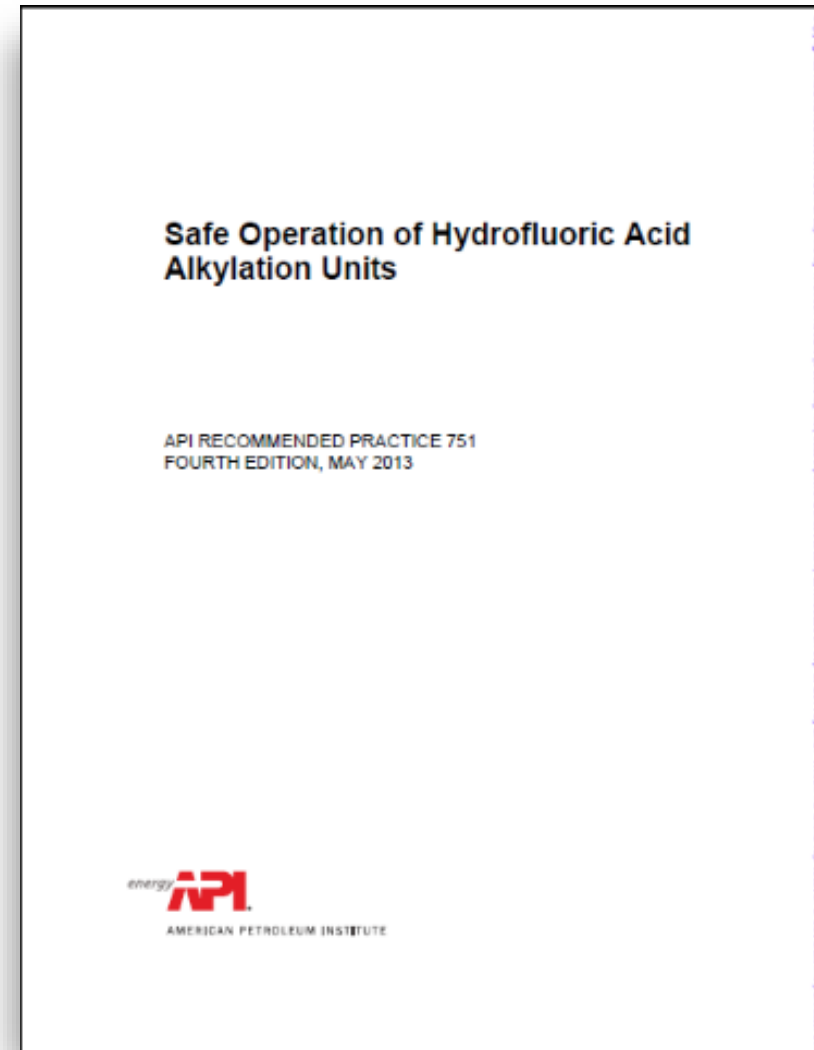
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- Alkylation units convert isobutane into alkylate, a gasoline component
- Most refineries use HFAU while others use SAAU. SAAU is not subject to this app.
- Residual element concentrations in carbon steel can be a critical indicator in the expected life and performance
- Manufacturing of carbon steel is becoming more dependent on recycled metal scrap
- NACE 03651 suggests the combination of carbon and RE content (Cu, Ni, Cr) could increase corrosion by 5 times



HF Alky Residual Elements

- Cu+Ni<0.15
- **Cu+Ni+Cr<0.15**
- C>0.18%
- CE<0.43
- Nb<.02 V<.02
- Nb+V<.03



TABLE 2 Tensile Requirements

	Grade			
	55 [380]	60 [415]	65 [450]	70 [485]
Tensile strength, ksi [MPa]	55–75 [380–515]	60–80 [415–550]	65–85 [450–585]	70–90 [485–620]
Yield strength, min. ^A ksi [MPa]	30 [205]	32 [220]	35 [240]	38 [260]
Elongation in 8 in. [200 mm], min, % ^B	23	21	19	17
Elongation in 2 in. [50 mm], min, % ^B	27	25	23	21

ADDITIONAL SUPPLEMENTARY REQUIREMENTS

In addition, the following supplementary requirement is suitable for this application.

S54. Requirements for Carbon Steel Plate for Hydrofluoric Acid Alkylation Service

S54.1 Plates shall be provided in the normalized heat-treated condition.

S54.2 The maximum carbon equivalent shall be as follows:
Plate thickness less than or equal to 1 in. [25 mm]: CE maximum = 0.43

Plate thickness greater than 1 in. [25 mm]: CE maximum = 0.45

S54.3 Determine the carbon equivalent (CE) as follows:

$$CE = C + Mn/6 + (Cr + Mo + V)/5 + (Ni + Cu)/15$$

S54.4 Vanadium and niobium maximum content based on heat analysis shall be:

Maximum vanadium = 0.02 %

Maximum niobium = 0.02 %



Maximum vanadium plus niobium = 0.03 %



(Note: niobium = columbium)

S54.5 The maximum composition based on heat analysis of Ni + Cu shall be 0.15 %.

S54.6 The minimum C content based on heat analysis shall be 0.18 %. The maximum C content shall be as specified for the ordered grade.

S54.7 Welding consumables for repair welds shall be of the low-hydrogen type. E60XX electrodes shall not be used and the resulting weld chemistry shall meet the same chemistry requirements as the base metal.

S54.8 In addition to the requirements for product marking in the specification, an “HF-N” stamp or marking shall be provided on each plate to identify that the plate complies with this supplementary requirement.

HF Alky Residual Elements

- Common material specifications
- A106 pressure retaining piping
- A105 flange, valve forging
- A234-WPB wrought fitting (elbow, tee)
- A516-70 pressure vessel plate
- A216-WCB valve casting
- Weld consumables typ.
 - E60XX, low hydrogen
 - Very important to remove protective copper coating from outside of filler wire
 - >30% copper can be detected using XRF



HF Alky Residual Elements

- XL5 is great solution for Cu, Ni, Cr, Nb, V
- Typ. 45-60 seconds (main, low)
- No carbon or CE detected
- Apollo is preferred with 10s measurement
- Able to measure C/CE and possibly relax RE total criteria (Cu+Ni)
- Same sample process with more data output

CERTIFICATE OF ANALYSIS
IMZ-112

SPECTROMETRIC REFERENCE MATERIAL OF LOW-ALLOY STEEL

Analysis listed as percent by weight [% m/m]

C	0.195	Mo	0.043
Mn	0.43	V	0.045
Si	0.27	Ti	0.010
P	0.022	Nb	0.013
S	0.016	Al	0.034
Cr	0.034	Al _{sol.}	0.024
Ni	0.046	Sn	0.15
Cu	0.055	N	0.010

brian.k.wilson

Cu+Ni = 0.101
 Cu+Ni+Cr = 0.135
 Nb+V = 0.058
 Nb+V+Ti = 0.068
 EQF = 0.103
 CE IIW = 0.298
 CE PCM = 0.238

Certificate Number 352

#218 Avg(20) 196-204,206-...
Fe Low Alloy

Sample: IMZ112

Ele	A:20	218	217	215
RES	0.174	0.170	0.181	0.185
CE	0.319	0.318	0.291	0.285
C	0.201	0.204	0.175	0.167
Mn	0.464	0.454	0.465	0.460
Si	0.274	0.256	0.273	0.280
Cu	0.067	0.067	0.067	0.064
Ni	0.060	0.057	0.069	0.069
Cr	0.047	0.046	0.045	0.051
Mo	0.057	0.049	0.052	0.054
Ti	0.020	0.015	0.017	0.016
Al	0.031	0.025	0.026	0.027
V	0.057	0.052	0.054	0.059
Fe	98.72	98.77	98.76	98.75



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Sulfidation Corrosion – API 939C

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Sulfidation Corrosion

- Thins pressure boundary wall of piping, components and welds exposed to hydrocarbon containing sulfur compounds at elevated temperatures
- Accelerated corrosion for carbon steels containing less than 0.10wt% silicon
- One third of high temperature sulfidation corrosion failures result from low silicon content

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

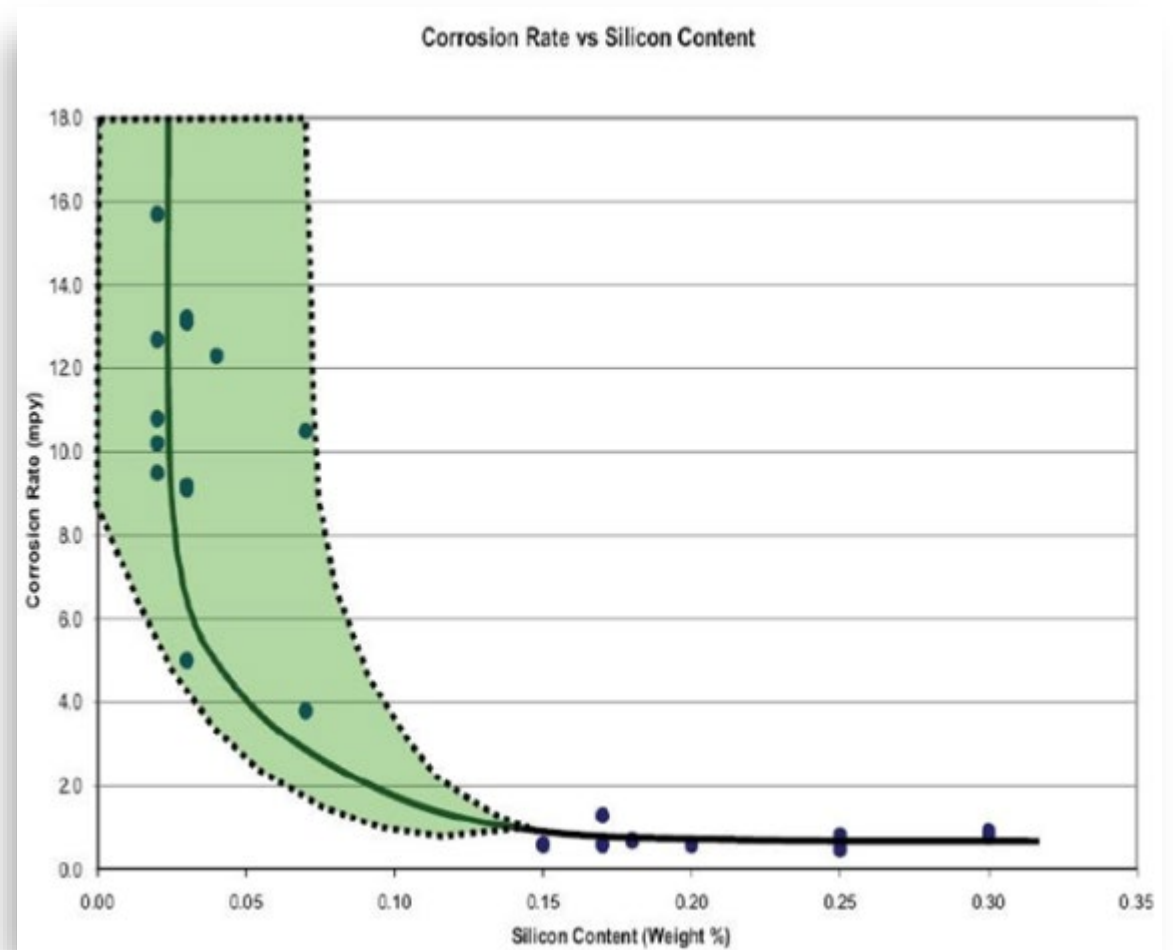
Downstream Segment

API RECOMMENDED PRACTICE 939-C
FIRST EDITION, MAY 2009



Sulfidation Corrosion

- Mechanism ranges from 450-1000F
- This chart from API 939C shows one company's corrosion rate
- All A53 B piping circuit and operating at the same approximate temperature
- 10 to 15 mpy versus 1 mpy makes a big difference after decades of service
- More than 700 refineries worldwide
- ~200 refineries in N. America
- Identify the refinery shutdown periods and key in on service providers



Chemistry Requirements A106 vs A53

TABLE 1 Chemical Requirements

	Composition, %		
	Grade A	Grade B	Grade C
Carbon, max	0.25 ^A	0.30 ^B	0.35 ^B
Manganese	0.27–0.93	0.29–1.06	0.29–1.06
Phosphorus, max	0.035	0.035	0.035
Sulfur, max	0.035	0.035	0.035
Silicon, min	0.10	0.10	0.10
Chrome, max ^C	0.40	0.40	0.40
Copper, max ^C	0.40	0.40	0.40
Molybdenum, max ^C	0.15	0.15	0.15
Nickel, max ^C	0.40	0.40	0.40
Vanadium, max ^C	0.08	0.08	0.08



A53/A53M – 12

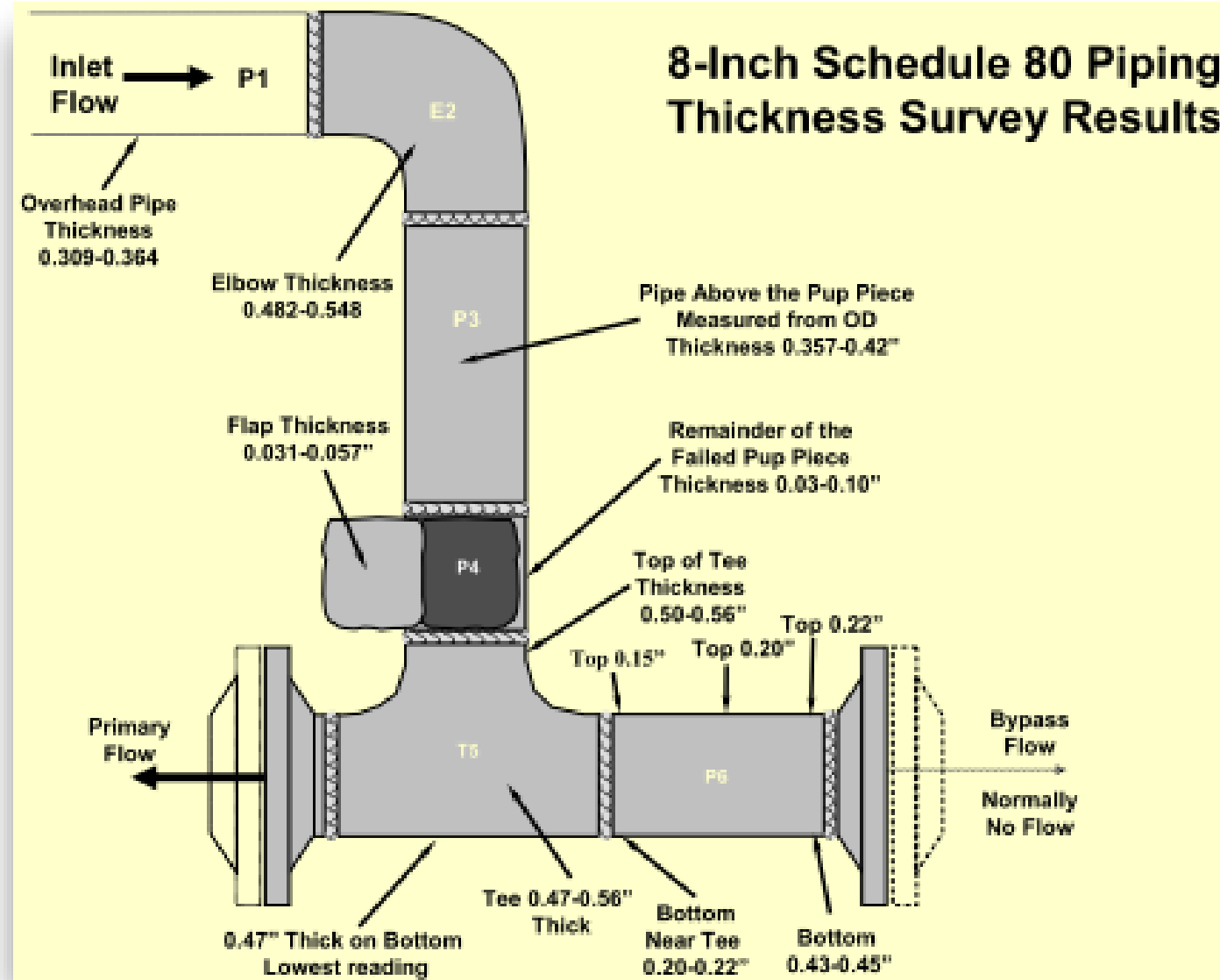
TABLE 1 Chemical Requirements

	Composition, max, %								
	Carbon	Manganese	Phosphorus	Sulfur	Copper ^A	Nickel ^A	Chromium ^A	Molybdenum ^A	Vanadium ^A
Type S (seamless pipe)									
Grade A	0.25 ^B	0.95	0.05	0.045	0.40	0.40	0.40	0.15	0.08
Grade B	0.30 ^C	1.20	0.05	0.045	0.40	0.40	0.40	0.15	0.08
Type E (electric-resistance-welded)									
Grade A	0.25 ^B	0.95	0.05	0.045	0.40	0.40	0.40	0.15	0.08
Grade B	0.30 ^C	1.20	0.05	0.045	0.40	0.40	0.40	0.15	0.08
Type F (furnace-welded pipe)									
Grade A	0.30 ^B	1.20	0.05	0.045	0.40	0.40	0.40	0.15	0.08

Chevron Richmond Incident

- On August 6, 2012, the Chevron Refinery in Richmond, CA experienced a catastrophic rupture in the #4 Crude Unit
- At the time of the incident, light gas oil was flowing through the line at a rate of approximately 10,800 barrels per day
- The ruptured line released flammable, high temperature light gas oil which partially vaporized into a large cloud that engulfed 19 Chevron employees. A few minutes later, the release fluid ignited.
- [Chevron Refinery Incident](#)





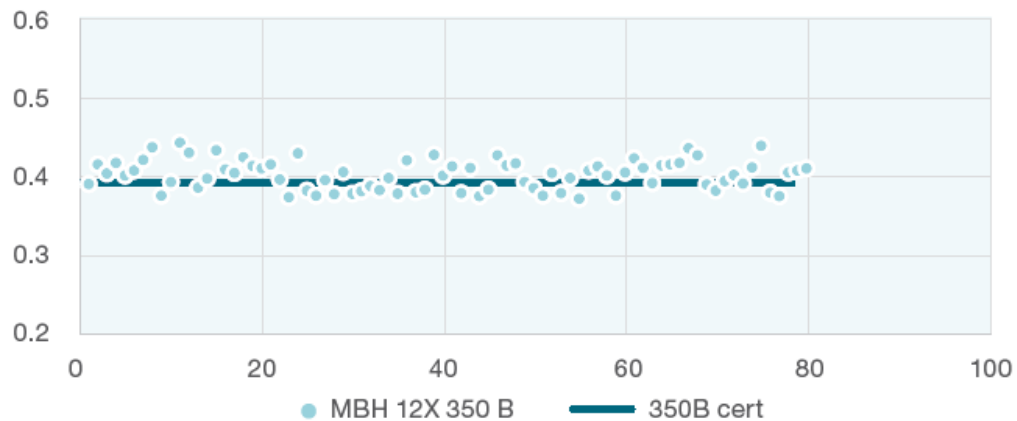
Silicon, Carbon Stability

Multiple samples analyzed eighty (80) times over a period of approximately four (4) hours to determine the stability of individual instruments.

The following illustrates examples of single instrument repeatability, all showing good precision for silicon (Si) and carbon (C).

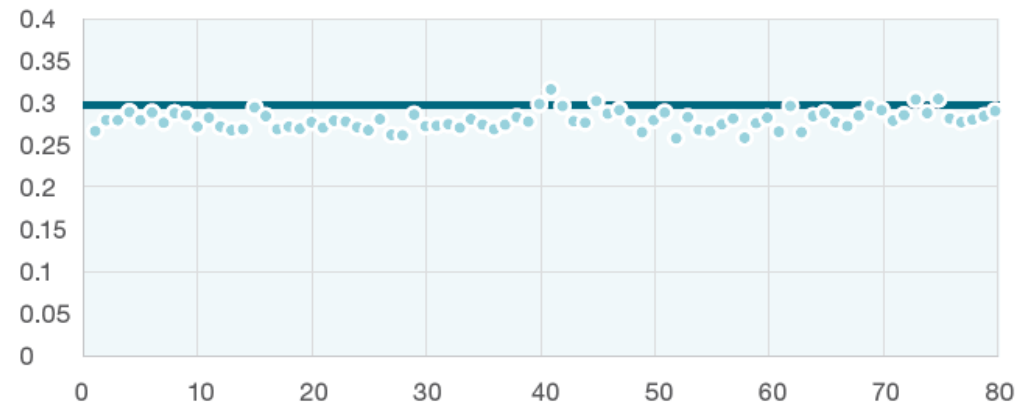
Chromium (Cr) Stability - Instrument 2

MBH 12X 350B Certified = 0.392%, avg = 0.401%



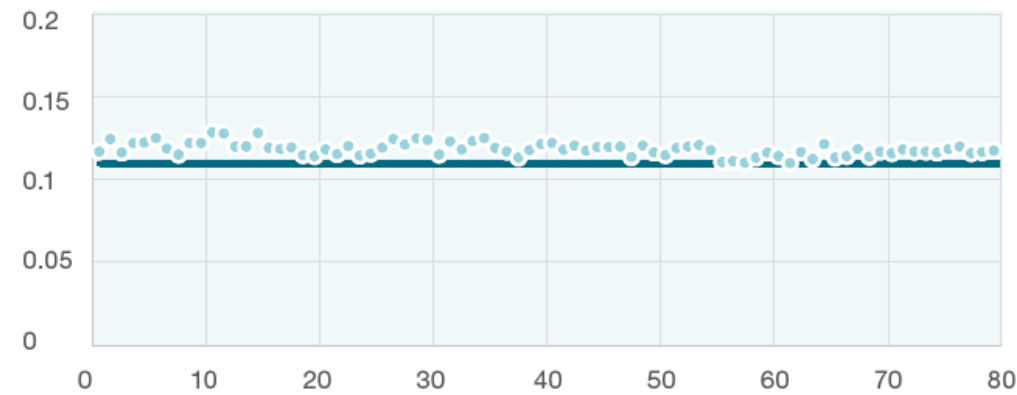
Silicon (Si) Stability - Instrument 12

MBH 12X 12749W Certified = 0.298%, avg = 0.28%



Carbon (C) Stability - Instrument 11

BS 48B Certified = 0.110%, avg = 0.118%



Typical Silicon Performance

0.058

Fe #110 Avg(5) 106-110 Low Alloy				
Sample: BS15A 0.058 Silicon				
Ele	Avg:5	110	109	108
CE	0.390	0.422	0.373	0.383
C	0.178	0.204	0.163	0.183
Mn	1.102	1.136	1.091	1.036
Si	0.053	0.052	0.053	0.048
Ni	0.096	0.101	0.097	0.099
Cr	0.065	0.066	0.068	0.060
Mo	-0.005	<0.034	<0.044	<0.033
Ti	0.075	0.075	0.076	0.075
Al	0.036	0.032	0.035	0.039
V	0.025	0.025	0.022	0.025

0.100

Fe #104 Avg(5) 100-104 Low Alloy				
Sample: IMZ113 0.10 Silicon				
Ele	Avg:5	104	103	102
CE	0.626	0.613	0.615	0.676
C	0.258	0.254	0.257	0.294
Mn	0.515	0.485	0.487	0.554
Si	0.113	0.108	0.111	0.120
Ni	0.177	0.172	0.167	0.178
Cr	1.209	1.192	1.187	1.244
Mo	0.060	0.062	0.062	0.060
Ti	0.070	0.070	0.070	0.069
Al	0.007	<0.013	<0.010	<0.011
V	0.042	0.042	0.041	0.042

0.270

Fe #117 Avg(5) 113-117 Low Alloy				
Sample: IMZ112 0.27 Silicon				
Ele	Avg:5	117	116	115
CE	0.352	0.333	0.367	0.323
C	0.245	0.225	0.261	0.215
Mn	0.407	0.409	0.379	0.417
Si	0.293	0.289	0.302	0.290
Ni	0.102	0.098	0.104	0.100
Cr	0.051	0.052	0.051	0.051
Mo	0.031	<0.037	<0.044	<0.039
Ti	0.076	0.076	0.075	0.076
Al	0.029	0.038	0.019	0.024
V	0.050	0.057	0.064	0.056

- XL5 is proven and approved solution for ambient conditions
- Typically, 20-60s measuring time depending on the concentration
- No carbon or CE detected
- Apollo is preferred with 10s measurement
- Able to measure C/CE
- Same sample process with more data output

Measuring Silicon in Carbon Steel at Ambient Temperature Using X-ray Fluorescence to Address Sulfidation Corrosion

Daniel Chapman*
Brian Wilson**

Chevron*
Thermo Scientific**



Materials Engineer*
Business Development Manager**



7TH BIENNIAL INSPECTION SUMMIT

JAN. 30-FEB. 02 | GALVESTON ISLAND | TEXAS



ASSET INTEGRITY THROUGH CORROSION MANAGEMENT,
INSPECTION AND ENGINEERING TECHNOLOGY



ThermoFisher
SCIENTIFIC



Raise the Bar

PHMSA Mega Rule

NDT Supply.com, Inc.

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- DOT regulatory initiative stemming from PG&E San Bruno incident Sept 9, 2010
- Effective date of final rule was July 1, 2020
- Applies to 500k miles of natural gas transmission pipelines across U.S.
- High Consequence Areas (HCA's) – interstates, freeways, expressways, etc.
- 49 Part 192.607 – Material Verification
 - Assets must be “traceable, verifiable and complete”

1. Summary of PHMSA's Proposal

The conventional method for determining the properties of unknown steel pipe material is to cut test specimens known as “coupons” out of the pipe and perform destructive testing. Because of the large amount of pipe operators reported in Annual Report submissions for which there are unknown or inadequately documented properties, the cost of such a conventional approach would likely be onerous. Therefore, PHMSA proposed standards in § 192.607 by which operators could develop a material properties verification plan and use an opportunistic sampling technique to reconstitute and document material properties in a more cost-effective manner. More specifically, PHMSA proposed to allow operators to use recently developed technology to perform *in situ*, non-destructive examinations for determining the properties of unknown steel pipe material.

PHMSA Mega Rule

This rule also requires operators of certain onshore steel gas transmission pipeline segments to reconfirm the MAOP of those segments and gather any necessary material property records they might need to do so, where the records needed to substantiate the MAOP are not traceable, verifiable, and complete. This includes previously untested pipelines, which are commonly referred to as “grandfathered” pipelines, operating at or above 30 percent of specified minimum yield strength (SMYS). Records to confirm MAOP include pressure test records or material property records (mechanical properties) that verify the MAOP is appropriate for the class location.^[7] Operators with missing records can choose one of six methods to reconfirm their MAOP and must keep the record that is generated by this exercise for the life of the pipeline. PHMSA has also created an opportunistic method by which operators with insufficient material property records can obtain such records. These physical material property and attribute records include the pipeline segment's diameter, wall thickness, seam type, grade (the minimum yield strength and ultimate tensile strength of the pipe), and Charpy V-notch toughness values (full-size specimen and based on the lowest operational temperatures),^[8] if applicable or required. PHMSA considers “insufficient” material property records to be those records where the pipeline's physical material properties and attributes are not documented in traceable, verifiable, and complete records.



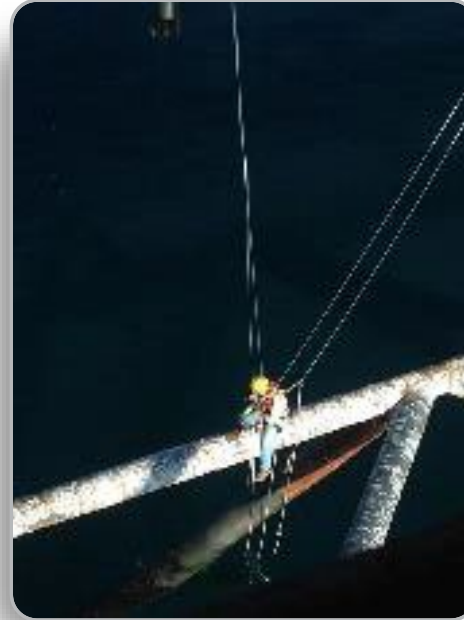
PHMSA Mega Rule Application

American Midstream Partners	Equitrans Midstream	Olin
Anadarko Petroleum	Evonik Corporation	ONEOK
Andeavor Logistics	Expro Midstream	Pacific Gas & Electric
Atmos Energy	Exxon Mobil	Pacific Northern Gas
Atmos International	Flint Hills Resources	Parker IFG Oil & Gas
BASF	Fluor Federal Petroleum Operations	Parkland Fuel
Black Hills Energy	FortisBC	Parsons Federal
Blade Energy Partners	Gate Energy	PBF Energy
Bluewing Midstream	Genesis Energy	Petrobras Transporte
Boardwalk Pipeline Partners	Golden Pass Pipeline	Phillips 66
BP	Grizzly Gas	Plains All American Pipeline
Buckeye Partners	Harvest Midstream	Plains Midstream Canada
Canyon Midstream Partners	Hawaiian Electric	Saudi Aramco
CenterPoint Energy	Hidden Star Energy	Shell
Centurion Pipeline	Hilcorp	SMUD
Cheniere Energy	Holly Energy Partners	SoCal Gas Company
Chevron	Husky Energy Midstream	Southern Company Gas
Cía. Operadora de Gas del	Imperial Oil	Southern Star Central Gas pipeline
Amazonas SAC	Interstate Energy	Southwest Gas Corporation
CITGO	Iroquois Gas Transmission	Spectra Energy Transmission
Colonial Pipeline Company	Kern River Gas Transmission	Suncor Energy
ConocoPhillips	Kinder Morgan	Superior Refining Company
Countrymark	Lavaca Pipeline	Tallgrass Energy
CPS Energy	LBC Houston	Talos Energy
Crestwood Midstream	Magellan Midstream	Targa
Crimson Midstream	Marathon Oil Company	TPE Midstream
Cypress Energy	Marathon Petroleum	Trans Mountain
DCP Midstream	MarkWest Energy Partners	TransCanada
Dominion Energy	Midcoast Energy	Trans-Northern Pipelines
DOPCO(Daehan Oil Pipeline	Momentum Midstream	Transpetro
Corporation)	Morrison Energy	Transportadora de Gas del Norte
Dow Chemical	Murphy Oil	UGI Utilities
DTE Energy	National Fuel Gas	Union Gas
Duke Energy	National Grid	Valero Energy
Easton Energy, LLC	Nextera Energy	Vectren Energy
Enable Midstream Partners	NIPSCO	Washington Gas
Enbridge	NiSource	West Texas Gas
EnCap Flatrock Midstream	Noble Energy	Williams
Energy Transfer	Northern Natural Gas	Xcel Energy
Enervest Operating LLC	NTS - Nova Transportadora do	Xisema S.A de C.V.
EnLink Midstream	Sudeste	
Enterprise Products	NuStar Energy	



PHMSA Mega Rule

- Users are the owner-operators and inspection firms that do pipeline inspection for them
- Key benefits:
 - Size, portability, ergonomics
 - Similar form factor to XRF
 - Simple to use, familiar user interface
 - Typically, lower purchase price vs OES
 - Lower cost of ownership (argon, maintenance)
 - SAFE and ideal for descending challenging excavation sites
 - Recognized methodology per API 578 3rd edition release



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Flow-Accelerated Corrosion (FAC)

NDT Supply.com, Inc.

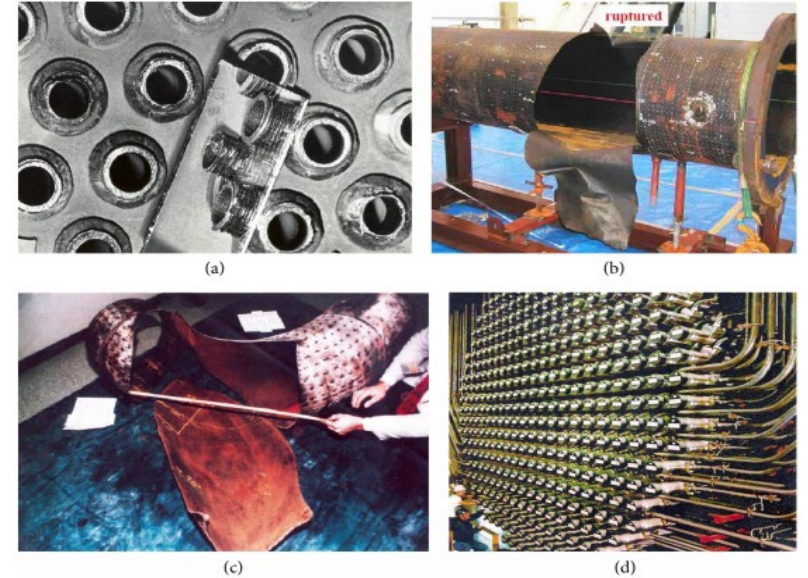
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Flow-Accelerated Corrosion (FAC)

- FAC is a corrosion mechanism that has been a concern in nuclear power production for 40 years, and it has led to accidents that have caused fatalities. There have been pipe ruptures leading to a release of steam and deaths of workers
- Accelerated loss of metal due the mechanical effect of fluid flow or velocity of a fluid combined with the corrosive action of the fluid. It is a complex process influenced by a number of variables:
 - The composition of the steel – principally the alloying elements of Chromium (Cr), copper (Cu) and molybdenum (Mo)
 - The water chemistry in use – pH at temperature in the water, dissolved oxygen, and temperature
 - The water flow variables – fluid velocity, diameter, fitting geometry, and upstream influences
- Of these variables, the material composition has been shown to exert the most influence of FAC through both plant experience and laboratory testing.¹



Plant	Component	Parameters				
		T (°C)	pH	O ₂	d (mm)	Re
a	Hinkley AGR ³ SG tube inlet with orifice $d/d_0 = 3.28$ AVT secondary water	155	9.1–9.4	~2 ppb	15.6	2×10^5
b	Mihama PWR ⁴ Condensate water pipe after orifice $d/d_0 = 1.612$	140–142	8.6–9.3	<5 ppb	540	5.8×10^6
c	Surry PWR ⁵ 90° bend after reducing T-piece in condensate system	190	8.9–9.0	4 ppb	305	10^7 ish
d	CANDU ⁶ Bend after end-fitting/outlet feeder pipe; primary water	305–315	10.2–10.8	~0	38–90	$3.5\text{--}7.7 \times 10^6$

1. Chexal, B., Goyette, L.F., Horowitz, J.S., Ruscak, M., Predicting the Impact of Chromium on Flow Accelerated Corrosion, PVP-Vol 338, Pressure

Flow-Accelerated Corrosion (FAC)

Measurement	Cr	Cu	Mo
1	0.079	0.051	0.0040
2	0.078	0.051	0.0047
3	0.071	0.055	0.0037
4	0.078	0.048	0.0044
5	0.081	0.053	0.0055
6	0.073	0.047	0.0040
7	0.072	0.057	0.0046
8	0.076	0.047	0.0042
9	0.083	0.047	0.0048
10	0.074	0.055	0.0044
Average	0.077	0.051	0.0044
Std. Dev.	0.004	0.004	0.0005
Ref Value	0.079	0.050	0.0047

