

THIS MONTH: CORROSION IN THE CHEMICAL PROCESSING INDUSTRY

DECEMBER 2009

# MIP MATERIALS PERFORMANCE

CORROSION PREVENTION AND CONTROL WORLDWIDE



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## Handheld x-ray technology identifies alloy composition of critical metal piping in petrochemical plants

In the petrochemical industry, metal alloy parts and piping systems that are constructed of the incorrect alloy grade or an out-of-specification alloy can experience accelerated corrosion that may result in failures and loss of containment of hazardous liquids and/or vapors. According to American Petroleum Institute (API) recommended practice (RP) 578,<sup>1</sup> which addresses material verification, confirming that the actual composition of alloys in a piping system is consistent with the construction material specification minimizes the potential for catastrophic release. Using handheld x-ray fluorescence (XRF) spectroscopy technology, nondestructive positive material identification (PMI) testing of piping and components can be done in situ without

shutting down process equipment or sending material samples off site.

Several major corrosion problems at refineries have been associated with carbon steel (CS) parts and piping that do not fall within specified material content guidelines, says Don Mears, president of Analytical Training Consultants (Kingwood, Texas) and an API-certified training provider. Mears is also an oil and gas industry consultant with Thermo Scientific Niton Analyzers (Billerica, Massachusetts) and author of an API RP 578 PMI certification course. In a recent presentation at Corrosion Technology Week 2009,<sup>2</sup> Mears explained that over the years the refining industry has found that corrosion increases dramatically in hydrofluoric acid (HF) alkylation units

where CS piping and components contain elevated levels of residual elements (RE)—Cr, Ni, and Cu. This is due to material incompatibility with the chemical reaction. He adds that a guideline for acceptable residual element content found in API RP 571,<sup>3</sup> which focuses on damage mechanisms that affect fixed refinery equipment, says that corrosion can be minimized based on the carbon content and the sum of the RE (Cr, Ni, and Cu) content. The optimum conditions for nonuniform corrosion in a CS piping system call for a carbon content of <0.18%, and a sum of the RE content to be <0.15%. If the sum of the RE is >0.2% (2,000 ppm), then nonuniform corrosion could be up to five times greater when compared to moderate rates of corrosion.

*With the recent advancements in handheld XRF analyzer technology, it is now possible, in situ, to measure low levels (ppm) of trace elements in metal pipes as well as light elements with atomic numbers as low as 12 (magnesium).*

“The objective of material verification is to discern whether the material contains a RE sum that is <2,000 ppm. An RE sum above that level can be an indicator of accelerated corrosion susceptibility. Inspectors want to ensure that RE sums are <2,000 ppm to avoid excessive accelerated HF corrosion and possible system failure,” Mears explains, adding that piping identified as having high RE content can be further examined for indications of corrosion and metal loss using ultrasonic thickness testing.

Another problem, he says, is that CS piping with low silicon content (<0.10%) in the crude, fluid catalytic cracker (FCC), coker, and other units can corrode at an



An inspector uses a handheld XRF analyzer to check weld chemistry on an existing piping system as part of a retroactive PMI program in accordance with API RP 578. Photo courtesy of Thermo Fisher Scientific.

accelerated rate when exposed to hydrogen-free sulfidation conditions between 450 and 650 °F (232 to 343 °C), which is also addressed in API RP 571 and API RP 939-C.<sup>5</sup> “Operators with assets at risk from this type of degradation should consider the risks and the requirements to apply PMI control in order to determine silicon levels and the extent to which the material may corrode,” Mears notes.

With the recent advancements in handheld XRF analyzer technology, it is now possible, in situ, to measure low levels (ppm) of trace elements in metal pipes as well as light elements with atomic numbers as low as 12 (magnesium), and determine whether or not the composition of CS piping has elevated levels of RE or low silicon content.

XRF spectroscopy technology, first used in the 1960s, analyzes the composition of a sample by measuring the spectrum of the fluorescent x-rays emitted by the different elements in the sample when it is bombarded with high-energy x-rays. Each of the elements present in a sample produces a unique set of characteristic x-rays that is a “fingerprint” for that specific element.<sup>4</sup> Over the years, improvements in the technology have led to the current handheld instruments that use x-rays emitted from either a miniaturized x-ray tube or a small, sealed capsule of radioactive material.

“When the user pulls the trigger on an XRF analyzer, the x-ray tube powers up and sends a primary x-ray beam into the sample,” says Jon Shein, director, marketing communications for Thermo Scientific Niton Analyzers. “When the primary x-ray beam strikes the sample—in this case we’re talking about metal alloys—a spontaneous process takes place at the atomic level that releases energy in the form of fluorescent x-rays. Similar to a radio tuner where different frequencies correspond to different radio stations, different frequencies of x-ray energy correspond to the different elements contained in the sample. Based on the



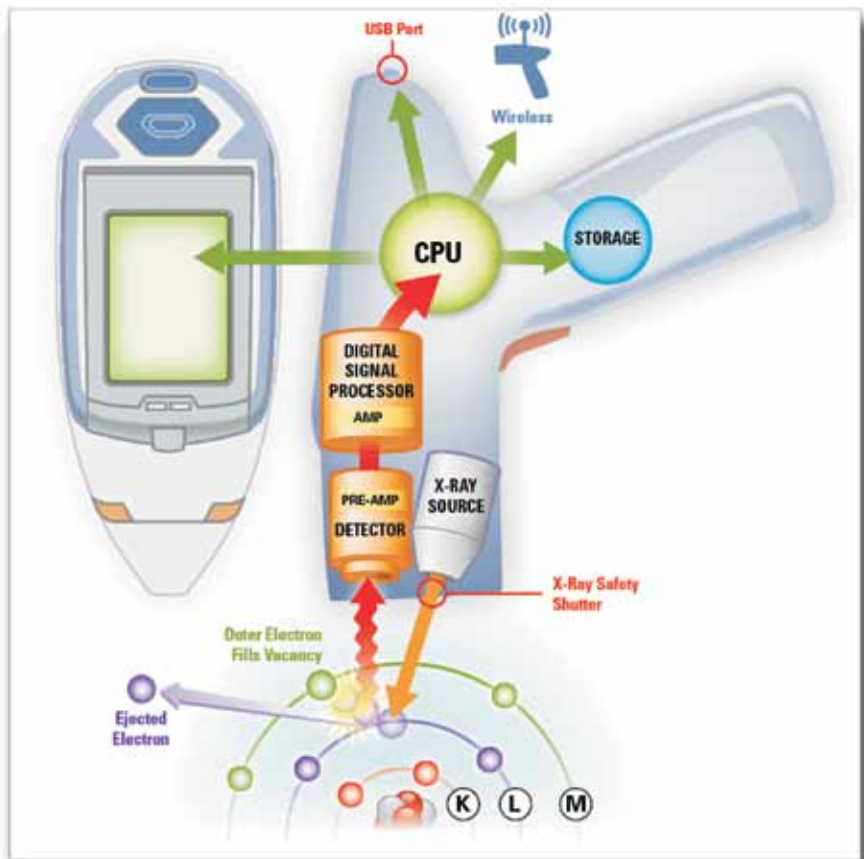
The elemental composition of a CS pipe in an HF alkylation unit at a Texas refinery is displayed on the screen of a handheld XRF analyzer. Photo courtesy of Thermo Fisher Scientific.

frequencies, we can identify the elements present, and based on the intensity of the returning fluorescent x-rays, we can quantify those elements.”

The handheld XRF analyzer technology developed by Thermo Scientific incorporates an x-ray source, detector, digital signal processor (DSP), central processing unit (CPU), and a data storage device. The x-ray energy emitted from the sample—from 1.25 keV up to 100 keV—enters the detector, which registers the individual x-ray events and sends electronic pulses to the DSP. The DSP collects and digitizes the x-ray events occurring over time, and sends the resulting spectral data to the main CPU for processing. Using various spectral processing algorithms, the CPU mathematically analyzes the spectral data to produce a detailed composition analysis. For metal alloy samples, the resulting data is then compared against an internal table or library of minimum/maximum specifications to determine an alloy grade or other designation for the tested material. The composition data and any resulting grade identification is then concurrently dis-

played on the instrument screen and stored in memory. The technology is capable of simultaneously identifying 30 of the most common elements, and can detect elements as light as magnesium (atomic no. 12) to those as heavy as uranium (atomic no. 92).

Mears points out that PMI and XRF spectroscopy can also determine whether or not pipe received in a warehouse meets specification. In a case study at a Texas refinery, CS pipe and components in a warehouse were tested for RE and low silicon content. The XRF readings showed that aside from a flange with a low silicon level of 0.09%, the silicon content of the materials met the specification. However, more than 33% of the pipe analyzed exceeded the RE specification limit, with RE content >2,000 ppm. Similarly, when test locations on CS pipes in the refinery’s crude unit were analyzed for silicon content, <3% of the test locations (one out of 37) had low silicon content (<0.10%). When CS pipes in the HF alkylation unit were analyzed for RE content, the readings determined that 33% of the test locations exceeded the



### About the Cover

An inspector uses a handheld x-ray fluorescence (XRF) analyzer to check weld chemistry on an existing piping system as part of a retroactive positive materials identification (PMI) program. XRF spectroscopy technology, first used in the 1960s, analyzes the composition of a sample by measuring the spectrum of the fluorescent x-rays emitted by the different elements in the sample when it is bombarded with high-energy x-rays. Using handheld XRF spectroscopy technology, nondestructive PMI testing of piping and components can be done in situ without shutting down process equipment or sending material samples off site. See p. 18 for an article on this topic. Photo courtesy of Thermo Fisher Scientific.

Handheld XRF spectroscopy technology analyzes the composition of a sample by measuring the spectrum of the characteristic fluorescent x-rays emitted by the different elements in the sample when it is bombarded with high-energy x-rays. Image courtesy of Thermo Fisher Scientific.



recommended RE content of <2,000 ppm (16 out of 44 locations). “The significant impact of the advancement in XRF technology is that now we can measure and determine very low element levels right in the plant process retroactively,” he says.

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### References

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- 2 D. Mears, J. Pasmore, “Positive Material Identification: Residual Elements in HF Alkylation Units and Sulfidation Corrosion with Low Si Levels Using PXRF Analyzers,” presented at NACE International Corrosion Technology Week, Houston, TX, 2009.
- 3 API RP 571, “Damage Mechanisms Affecting Fixed Equipment in the Refining Industry” (Washington, DC: API, 2003).
- 4 “How XRF Works,” Thermo Scientific, NITON® XRF Analyzers, <http://www.niton.com/portable-XRF-technology/how-xrf-works.aspx?sflang=en> (Oct. 19, 2009).
- 5 API RP 939-C, “Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries” (Washington, DC: API, 2009). **MP**