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APPLICATION NOTE

Conducting Retroactive PMI

Using the Thermo Scientific Niton XL5 XRF Analyzer

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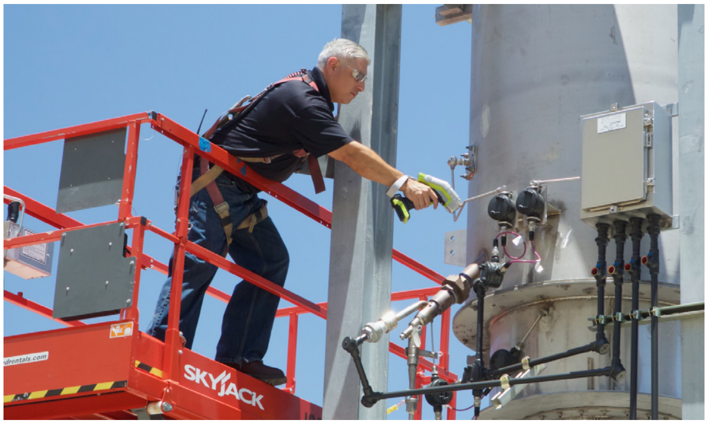
Introduction

Petroleum refining and petrochemical industries continue to be of central importance to the global economy, delivering products such as gasoline, diesel, heating fuel, rubber, plastic, detergents, fertilizers, solvents, cosmetics and many more indispensible consumables. Refineries and petrochemical plants may be considered among the most prized industrial assets in the world, however, the hydrocarbon processing business is also a high-hazard industry in that there are potential exposures to risk in all operations due to the nature of the materials being extracted, transported and processed.

Health and safety have been and continue to be the number one priority for the petroleum refining and petrochemical industry and the emphasis for process safety management (PSM) and asset integrity is to prevent unplanned releases which could result in a major accident. Across the global oil and gas industry, considerable effort has been focused on minimizing the risk of personnel exposure and equipment loss by preventing the release of highly hazard chemicals and toxic substances. Fatal accidents and injuries, as well as leaks, premature pipe replacements, loss of property, and unplanned outages at refineries, chemical plants and gas processing facilities often can be traced back to inadvertent substitution of construction materials.

A primary cause for losses at refineries, chemical plants, pipeline networks and gas processing facilities is equipment failures. Mechanical Integrity (MI) consistently remains a contributing factor and enforcement policies



A technician performs positive material identification on pressure vessel components using the Thermo Scientific Niton XL5 analyzer.

such as 29 CFR 1910.119 “Process Safety Management of Highly Hazardous Chemicals” issued by the Occupational Health and Safety Administration (OSHA), identifies certain requirements for preventing or minimizing the consequences of catastrophic releases. Under OSHA’s National Emphasis Program (NEP), policies were launched to safeguard against catastrophic releases:

- *Enforcement Directive Number CPL 03-00-004* effective June 7, 2007
- *Petroleum Refinery Process Safety Management National Emphasis Program and Directive Number CPL 03-00-014* effective November 29, 2011

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Application

Industry reported data suggests a probability that as much as 3% of rogue material will make its way into the field as part of a final fabricated assembly, piping circuit, pressure vessel or other critical process equipment. Routes of entry as an inadvertent material substitution may have several undesirable paths of travel:

- Component manufacturer applies the incorrect material stamp to the finished part
- Fabricator uses unmarked, unknown material during the fabrication process (i.e. loose stock, drops, cutouts)
- Material traceability is not maintained during fabrication when multiple pieces are made from a single stock (i.e. gussets, lift lugs, stiffener rings, support clips, pipe pups, gasket rings)
- Warehouse stocks inventory in the wrong location and error gets carried forward
- Welder uses incorrect filler metal by selecting from wrong rod box, improper labeling or stocking of inventory or even borrowing weld rods from a fellow welder
- Welder or pipefitter selects the wrong component during fabrication process
- Integrity of the original mill test report (MTR) is compromised during the procurement and supply cycle as ownerships exchanges and data is transposed or even manipulated
- Maintenance occurring outside normal operating hours not subjected to typical QA/QC inspection practice
- Improper tagging or marking of materials during maintenance removal and lack of verification prior to re-installation

The U.S. Chemical Safety and Hazardous Investigation Board (CSB) report No. 2005-04-B offers the following lesson learned following an incident investigation of a major fire at one of the nation's largest refining complexes, which caused a reported $30 million in property damage and minor injuries.

Positive Material Verification Programs

In-situ alloy steel material verification using x-ray fluorescence, or other nondestructive material testing, is an accurate, inexpensive, and fast PMI test method. Facility owners, operators, and maintenance contractors should ensure that the verification program requires PMI testing, such as specified in American Petroleum Institute Recommended Practice (API RP) 578[1], or other suitable verification process, for all critical service alloy steel piping components that are removed and reinstalled during maintenance.[2]

One study focusing on corrosion-related accidents in petroleum refineries in both the European Union (EU) and Organization for Economic Cooperation and Development (OECD) countries' reports, the inadequacy of material composition was identified as the key component of failure in 9 of 99 significant refinery accidents. While history and experience reveal that inadvertent material substitutions continue to be a considerable problem in the refining and petrochemical industry, applying the principles and guidelines published in recommended practice API RP 578 "Material Verification Program for New and Existing Alloy Piping Systems" supports applying Recognized and Generally Accepted Good Engineering Practices (RAGAGEP) in instituting an effective material verification program (MVP). Owner-users adopting a 100% PMI practice for pressure-containing components and welds for in-service equipment, new construction materials, or during maintenance activities can significantly reduce the likelihood of material mix-up and avoid the consequences of failure while mitigating corporate risk.

Sulfidation corrosion affects steel piping and equipment and continues to be a significant cause of leaks in the refining industry. When exposed to hydrocarbon containing sulfur compounds at elevated temperatures, carbon steels with low silicon content (<0.10%) can corrode at an accelerated rate. Sulfidation thins the pressure boundary wall and can result in a leak releasing highly hazardous chemicals to the atmosphere. API RP 939C "Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries" recognizes implementing Retrospective PMI into a Material Verification Program (per API RP 578) as an inspection method to detect and track sulfidation corrosion.[3]

HF alkylation is an increasingly central process in the refining industry for the production of petrochemical products. With the principal materials of construction being carbon steel, Monel™ 400, copper-nickel, and other nickel based alloys such as Hastelloy™ C-276 and B-2, the proper selection, application and placement of the alloys within the process piping envelope is critical to avoid unexpected corrosion and deterioration of pressure equipment components. Carbon steel in the HF alkylation process has demonstrated satisfactory corrosion resistance to HF corrosion when residual element (RE) content is controlled. Case studies have shown that REs in carbon steel can contribute to accelerated HF corrosion, primarily elements Cr, Ni, Cu. A recognized guideline is that for base metal of C> 0.18 % wt % and Cu + Ni + Cr, 0.15 % wt % is optimum. These values are critical as the type and concentrations to be measured will directly affect the analytical methods operations need to adopt.[4]

Handheld X-ray fluorescence (HHXRF) is a fast and accurate non-destructive testing method that provides confirmation of alloy composition to material specifications and positive grade identification. HHXRF offers proof positive that correctly purchased materials are received; confirms QA/QC for in-process fabrication; meets end user material requirements of outgoing products and that installed components and welds match the engineering design and application for which they are intended.

For best performance and most reliable data, the operator should carefully consider the most suitable surface preparation methods, tools and grinding media for the task.

Thermo Scientific™ Niton™ XL5 XRF Analyzer

The new Niton XL5 is the smallest and lightest high performance XRF alloy analyzer in the market. The Niton XL5 couples world class performance with its smaller size and light weight, enabling access to more test points typically inaccessible to larger HHXRF equipment while reducing operator fatigue. Compact measurement geometry and new powerful mini X-ray tube provides highest performance and best light element sensitivity for the most demanding applications such as low silicon measurement. Niton XL5 delivers fast, accurate elemental analysis in demanding refinery environments. The Niton XL5 provides the refining industry with the following key benefits:

- New powerful 5W X-ray tube provides highest performance level and best light element sensitivity
- Smallest HHXRF enables testing in tights spaces and internal components, increasing productivity
- Lightest HHXRF at 2.8 lbs (1.3 kg); designed for optimal user comfort and balance without operator fatigue
- Flexible user interface enables custom workflow solutions and easy optimization for specific applications such as low silicon measurement, residual and trace element analysis
- Unparalleled chemistry and grade identification accuracy for confident results every time
- Excellent light element detection (Mg, Al, Si, P, S) without vacuum or helium (He) purge
- Integrated 1.2M micro and 5M macro cameras and small spot analysis for accurate sample positioning and image capture for improved reference and data integrity
- Swiping, tilting and vivid touch screen display can be used even while wearing gloves
- Rugged housing is waterproof and dustproof for harsh environments
- Extended field use with hot swappable battery and battery life indicator display

The Niton XL5 is designed with a rugged aluminum housing, dissipating primary heat sources from within the analyzer. Internal temperature is monitored and controlled through electronic fail-safe protection preventing the analyzer from overuse by suspending measurement activity until cooled to a safe working temperature.

The Niton XL5 takes advantage of its smaller size and increased component interface by offering a new miniature Hot Work Standoff allowing standard operations at high testing temperatures without impeding the increased value of component accessibility. Equipped with a Kapton window, the new Hot Work Standoff easily snaps in place with an improved, tool less window bracket design allowing the operator a maximum sample temperature of 900° F (480° C). It's important to note that the user should wear appropriate personal protective equipment (PPE) when performing surface preparation and sample measurements at elevated temperatures. Ideally suited for rope access PMI inspection, the Niton XL5 offers technicians a reduced weight burden and smaller footprint that typically takes up valuable space whether attached via lanyard or secured in a backpack.

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Conclusion

Aging infrastructure more often provides the challenge of "in-situ" or retro-PMI testing to confirm existing assets are fit for service. Typically this requires performing measurements at elevated temperatures under normal process operating conditions ranging from 200° F up to 900° F. Such conditions require an analyzer that meets all of the demanding aspects of retro-PMI testing. The Thermo Scientific Ntion XL5 XRF analyzer is specifically designed and purpose-built to perform in this harsh environment with a feature set making it the instrument of choice for refinery, petrochemical and all other process facility inspectors who demand the best tool for the job.

With a considerable reduction in size and weight, coupled with the highest analytical performance available in a rugged, well balanced package, the Niton XL5 is a product driven by industry demand and client input. It is designed to meet the requirements of asset owners from all industry segments from refining and petrochemical to power generation, gas processing, offshore and pipeline transportation.

To discuss your particular applications and performance requirements, or to schedule an on-site demonstration and see for yourself how Thermo Scientific portable XRF analyzers can help save you time and money, please contact your local Thermo Scientific representative or visit our website at thermofisher.com/portableid.

Additional Resources

To learn more about Sulfidation Corrosion or to identify Residual Elements, visit www.thermofisher.com/oilandgas and read our latest application notes on these topics.

Reference

1. API RP 578 – Material Verification Program for New and Existing Alloy Piping Systems
2. "Safety Bulletin," U.S. Chemical and Safety Hazard Investigation Board, CSB report No. 2005-04-B, October 12, 2006, page 7.
3. API RP 939C – Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries
4. API RP 751 – Safe Operation of Hydrofluoric Acid Alkylation Units

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