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## **Positive Material Identification**

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## **Introduction**

There are many points in the supply chain that material can be mixed up. Mistakes can happen during shipment of raw materials, manufacturing, shipping, installation, and repair, just to name a few points in the supply chain. A mistake can be disastrous to a company. Positive Material Identification (PMI) is a way that engineers or technicians can verify that a part was manufactured out of the correct material or that the correct material is being installed. It is also commonly referred to as Alloy Verification (AV) or Positive Material Verification. There are several methods of PMI commonly used. One important fact that many engineers get wrong is that PMI is not a chemical analysis. A chemical analysis is, however, a method of PMI.

Positive Material Identification is used in mining, jewelry analysis, manufacturing, and in the refining industry to prevent material mismatches. It can be used when receiving materials to make sure what was ordered is what was received. Random testing can also find where a bar may have been cut and incorrectly marked afterwards. Parts being shipped to a refinery are often required to be PMI verified.

An accident at the BP Texas City refinery on July 28, 2005 demonstrated how material mismatches could be disastrous. The accident occurred when a contractor accidentally switched an 8-inch carbon steel pipe elbow with an alloy steel one during turnaround maintenance in February 2005. The carbon steel elbow was severely weakened and failed due to high temperature hydrogen attack (HTHA) in a Resid Hydrotreater Unit (RHU) hydrogen gas heat exchanger. The U.S. Chemical Safety and Hazard Investigation Board recommended PMI to prevent improper substitutions of alloys in hazardous process systems. At the time of the incident, the BP procedures required PMI testing of materials received in the warehouse or shipped from the warehouse for new construction. The procedures did not require PMI testing during maintenance, even if there was a risk of switching components.

The July 28, 2005 incident came approximately four months after an explosion and fire in the Isomerization unit at the refinery. The March 23, 2005 incident killed 15 workers and injured

180 others. The explosion and fire occurred after a heavier than air hydrocarbon vapor cloud was ignited, which sparked the explosion. The incident in July may not have been made an issue if it was not for the March explosion, which led up to a \$21 million fine. This was OSHA's largest fine in its history at the time, where there were over 300 safety violations found.

The RHU system design had different specifications for high temperature and low temperature hydrogen gas service. The high-temperature service required 1.25% chrome low alloy steel (example F11/P11) to resist HTHA. The low-temperature service required carbon steel to minimize the cost factor. The components were installed in the correct locations when the RHU unit was built and the components were dimensionally identical. They were placed into service in 1984. Component interchangeability and the components being visually identical combined to make it necessary to distinguish between the components to prevent switching them during maintenance. Maintenance and inspection was conducted in 1989 and 1991 and the components were removed and reinstalled at those times. An investigation concluded that the components were switched during the winter 2005 heat exchanger overhaul.

API Recommended Practice 578 is an often-cited standard for Positive Material Identification. Many end user specifications or standards reference this API publication and it discusses three methods of PMI. The standard also mentions that there are other qualitative and are appropriate for limited applications that are not discussed in the API standard. Mill Test Reports (MTR) are not a substitute for PMI. API Recommended Practice 578 identifies several quantitative and qualitative methods of Positive Material Identification.

## Methods

API 578 identifies three primary quantitative test methods for PMI. The first method is portable X-ray fluorescence (XRF), which is the least destructive of the methods. The second method is portable optical emission spectrometry (OES), which leaves a small mark on the area tested. The third is chemical laboratory chemical analysis that requires a sample of the material to be tested.

The most common methods of Positive Material Identification include X-ray fluorescence (XRF) and optical emission spectrometry (OES), which is also called Spark Emission Spectrography. The method of PMI to be used depends on the alloys and elements that we are trying to identify. Laboratory chemical analysis is also a method of PMI. The most common method of PMI is XRF. XRF equipment can use either a source of an x-ray tube. Licensing requirements vary with the equipment and the state. For example, the State of Texas requires equipment with a source be licensed and equipment with a tube be registered.

Testing using the OES method, the SPectroPORT TPC-17, Arc-Met 900/930 (or equivalent OES equipment) is a common instrument used when carbon testing or expanded number of elements is required. The X-Met 880, Niton XLp 818, or Niton XL2 (or equivalent XRF equipment) is used for most other testing. New models are introduced often, but the basic theory is the same. A Niton XL2 used for X-ray fluorescence testing is shown below.



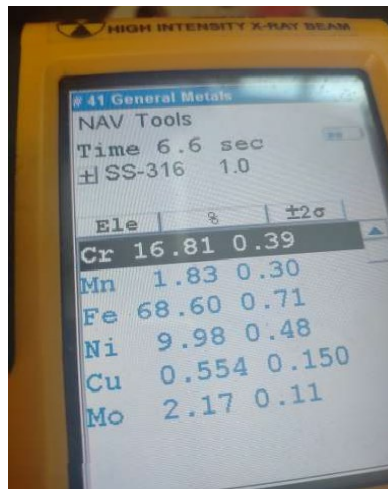
**Fig.1.** Niton XL2 used for X-ray fluorescence testing

The most common method of PMI is using the X-ray fluorescence method. The equipment is easy to use, but the user must be trained in radiation safety. Transportation training may be required for off-site use. The XRF method has the advantage over OES and Chemical Analysis because it allows testing without damaging the material.

The theory behind X-ray fluorescence is that a secondary x-ray is emitted from a sample that is excited by a primary x-ray source. The X-Ray Fluorescence (XRF) operates by emitting gamma rays from a radioisotope and then measuring the fluorescence gamma energy being emitted by the excited alloy atoms. These measurements can be compared with known standards for verification. Each element has its own characteristics, known as a fingerprint. The XRF technique has inherent limitations. It can only detect elements from Ti to U in the periodic table of elements, but this can vary between XRF models. This eliminates some of the alloying elements in some alloys. The XRF analyzer selects the material identification based on the element ranges programmed into its software. The indicated error on the report is +/- percentage on that particular element. The software programmed into the instrument selects the material match. The geometry of the part or the surface of the metal may affect the reading.

Operation requires allowing the test equipment to stabilize for a few minutes and selecting the model (alloy) that you are testing. Many refinery standards require that the instrument calibration be verified by checking against a reference standard of a known material. This known material is often a Certified Reference Material (CRM). A CRM has an alloy composition closely resembling the material to be tested. Surface preparation is usually not required for XRF testing, but the surface must be clean. Oxides, rust, grease, scale, paint (often has metal), and coatings or other non-representative material shall be removed, as they can interfere with test results.

A typical readout from an XRF test is shown below. For illustration purposes, 316 stainless steel (UNS S31600) was chosen for use in the General Metals Mode (most common use for engineering).



**Fig.2.** Readout from an XRF test

The above example shown the readout from testing the stem of a thermowell that was selected for illustration purposes. On the top of the display “SS-316” shows that the test shows that the material is 316 stainless steel based on the programming. An error is also shown on the display next to the reading. For example, the Chromium on the example shows 16.81 with an error of +0.39 percent. This means that the actual Chromium content could range from 16.42 to 17.20 percent by weight.

The above example was the analysis of an unknown. Examination of a known Material Test Report (MTR) can show the following: Chromium 16.89, Nickel 11.19, and Molybdenum 2.02. Using the XRF method of Positive Material Identification reveals the following results: Chromium 15.80 +0.97, Nickel 10.68 +1.31, and Molybdenum 2.17 +0.29. Based on the PMI reading the results of the Chromium can be from 14.83 to 16.77 percent, which is just below the stated MTR value. The Nickel value can be from 9.37 to 11.99 percent. The Molybdenum can range from 1.88 to 2.46 percent.

The ranges for determination of the alloy are programmed into the software in XRF equipment. Taking the example of 316SS (UNS S31600) shown above, the preprogrammed limits in the Niton XL2 are as follows: Chromium can range from 16 to 19, Nickel can range from 10 to 14, and Molybdenum can range from 1.9 to 2.8. We can observe that these numbers are not typical for 316SS. Typical standards for 316SS (UNS S31600) care as follows: Chromium can range

from 16 to 18, Nickel can range from 10 to 14, and Molybdenum can range from 2 to 3.

A discussion of the ranges above is necessary because many engineers make the mistake of having certain cutoffs that are incongruent with the models programmed into the instrument at the factory. Although the instrument is programmable, this is an advanced function. If the typical customer or end user has a different cutoff for a particular element, then a chemical analysis is probably a better choice.

Some elements cannot be detected using the XRF method. XRF cannot detect light elements like C, Si, and S. For example, carbon in alloys such as 316L stainless steel, 321H stainless steel, or Incoloy 800H/800HT. For these alloys, the OES method must be used if you need to know the carbon content.

When using the OES method, surface preparation is more involved than when using the XRF method. When using optical emission spectrometry (OES) equipment, the surface is prepared by sanding operations with various grit sandpapers. Rough grinding may be necessary prior to final sanding. The depth of the test is no greater than 1/32” below the metal surface.

After preparation of the surface, the OES probe is placed on the test surface in such a way as to cover the probe aperture completely. The switch on the probe is activated and the instrument counts down the pre-set time of approximately thirty seconds and the results are read from the display on the instrument.

The OES instrument generates an electric arc like a welding arc. The arc generates a spectrum of light as the sample surface is vaporized. The spectrum for each element in the sample being tested is unique.

When carbon content or an expanded number of elements to be analyzed is required, the OES method is typically used. In order to PMI weld wire when carbon testing is required, a weld pad must be prepared. To make a weld pad, cut a 3-inch piece of the barstock that is to be welded. The bar stock for the weld pad must be from the same bar to be used for the production parts.

Weld a few passes on one end of the bar sample until about 1/2-inch thick. ASME recommends a 5-layer weld pad for chemical analysis of undiluted weld consumables. Autogenous welds, where no filler metal is added, only require the base metal to be tested. Other methods of testing carbon content include the use of a carbon determinator.

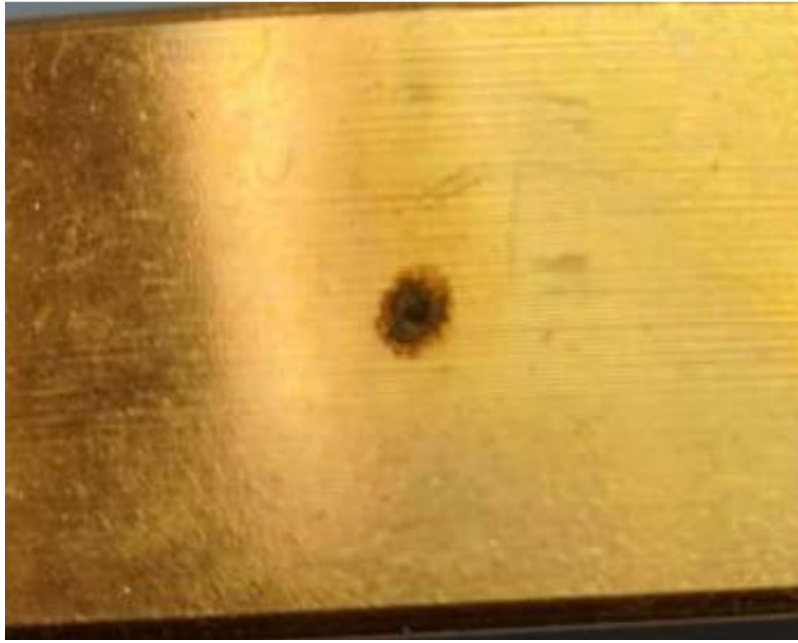
Accurate analysis depends on a good “burn”, which is characterized by a ¼” white circle containing several silver-gray spots encircled by a darker ring either wholly or partially. Any darkening or distortion of the “burn” area can be evidence of argon contamination, which may give erratic readings. It is important that the burn be removed via sanding or grinding, as it may change the grain structure of certain alloys. A typical “burn” area shown on stainless steel is shown below.



**Fig.3.** “Burn” Area on Stainless Steel

Often the burn can be seen when it has not been removed. This can often be seen on new flanges. An example is shown below.





**Fig.4.** Burn on flanges

Alternate methods of testing such as laboratory chemical analysis may be used in obtaining a chemical breakdown for a sample of material unless specifically directed otherwise by customer or user requirements. Laboratory Chemical Analysis typically requires sectioning a sample to be tested. This destructive test usually makes bulk PMI testing using this method unfeasible for production parts. Shavings can be collected during machining; however, the practicality of doing so does not make sense if multiple parts are to be tested. It requires a larger sample, is more costly, and is slower and more time consuming than the other methods of Positive Material Identification. The accuracy is much higher using the laboratory chemical analysis method.

There are also other qualitative methods that API Recommended Practice 578. One of these methods is chemical spot testing. Chemical spot testing involves using a small amount of surface metal to test by depositing it on moistened filter paper. This is used to detect specific elements by adding reagents to the filter paper and examining a color change. The presence of certain elements will produce specific colors. This method tends to be slow and results can be subjective.

Another qualitative method discussed in API Recommended Practice 578 is resistivity testing. This method uses the same basic principle as a thermocouple. This principle is known as the

Seebeck Effect. Heating the junction of dissimilar metals creates a voltage. The voltage is unique to the alloy. This type of instrument is typically known as an alloy sorter. Typical instruments of this type are the Koslow TE-3000 Thermo-Electric Allot Sorter or the Walker Scientific ATS-6044T Alloy Sorter.

API Recommended Practice 578 also eludes to other methods as techniques for Positive Material Identification. These include the use of eddy-current sorters and electromagnetic alloy sorters.

Material verification programs can vary. Some programs are designed for new construction, while others are designed for existing construction, to include maintenance activities. This program is what was lacking at the BP Refinery in 2005. Many require 100 percent PMI. This is especially true for construction where higher risk systems, such as systems that contain many pressure containing components and attachment welds for them. When prioritizing these systems, the engineer must consider the consequences of a failure (i.e. fire or explosion potential) and/or the reason for a specified alloy. Lower risk systems usually require random sampling. These decisions are risk management decisions that engineers must make.

The extent of PMI testing will depend on many factors. Some of these factors are the historical inspection records. Other factors include the number of plant modifications and the material controls in place during the modifications as well as during the original plant construction. The consequences of a release and likelihood of component degradation must also be considered.

Each method of PMI can have safety issues that must be considered. As stated earlier, the operator should have radiation safety training when using the XRF method of PMI. Training is also required to use an instrument for off-site testing. This training is similar to FEMA IS-302, Modular Emergency Radiological Response Transportation Training. Some states require a swab test every six-months or require the user to wear a radiation dosage badge when using an XRF instrument. The OES method can have “hot spots” since it operates like a weld. OES can also have electrical arcing. Chemical spot testing also has precautions that must be taken, since it requires the handling of various chemicals.

Once a part or component is PMI tested, it should be marked. There are various ways of marking such as color coding by alloy or using a low-stress stamp. Both of these methods are acceptable when using API Publication 578 as a basis for testing. Color-coding, however, is not a substitute for permanent markings required by some material specifications (i.e. ASTM). Typical low-stress stamp marking include stamping the part with PMI, PMIV, or AV. Some company standards will also require the alloy to be stamped. The test record should be traceable to a part or component. The test record should have the date, procedure used for PMI, the PMI equipment used with serial number, results, and the operator. It also helps to have the heat number to make traceability to a Mill Test Report easier. When a part is rejected, it must be marked as such and segregated. A 100 percent PMI should then be conducted on the remaining components in the lot.

Positive Material Identification allows the engineer or field personnel to verify that a part being manufactured or installed is the correct material. Material mix-ups, like the one occurring at the BP Texas City refinery in 2005 can be costly to a company. The BP Texas City refinery incident came a few months after another unrelated accident that resulted in loss of life. There are three common quantitative methods identified in API Recommended Practice 578 used for PMI. I have given an overview of these methods. The engineer must keep in mind that there may be variations between equipment, but the basic operation is the same.

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