In Situ Verification Techniques for Multipoint Thermocouples in Pressure Vessels

White Paper

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Table of Contents

Introduction:

Thermocouples are used extensively to monitor the temperature of pressure vessels used in catalytic reactions. Without accurate and reliable temperature readings, reaction efficiency is reduced and the risk of process upset and vessel damage increases. Pressure vessel thermometry faces unique challenges given that thermocouples are located inside a fixed isolated environment, in which the tools used to test functionality are limited during production cycles, potentially requiring several years. During turnaround and catalyst changes, users are offered limited time to determine whether thermocouple sensors are still functional or whether they should be reused or replaced. Determining their functionality can prove difficult because even experienced users are often unfamiliar with thermocouple failure mechanisms. Given that the thermocouples supplied from the factory are supplied in a quasi-homogeneous state, calibration test results are typically provided via a representative sample probe. Thermocouples may become inhomogeneous once they have been in service, rendering a representative test no longer appropriate, and necessitating a true in situ calibration as a result. The question then becomes, how does one perform a true in situ calibration?

What is Thermocouple Calibration?

Calibration is achieved by comparing the unit under test (UUT) with a reference at a given temperature, and adjusting the output so that it will provide an accurate reading. Given that thermocouples are analog devices that self-generate their own outputs, it is not possible to change their readings for greater accuracy. The industry standard approach for the thermocouple calibration of base materials (Type K, J, E) is to compare the output to a calibrated reference probe, typically a noble metal thermocouple (Type R or S) or a resistance temperature detector (RTD). If the test thermocouple reads within a certain range of accuracy, it is deemed either standard limits of error or special limits of error.

How Thermocouples Are Calibrated from the Factory:

Manufacturers fabricate thermocouple assemblies from raw mineral-insulated metal-sheathed cable that has been annealed and is in a semi-stabilized state. During the manufacturing stage, it is important to perform testing on both the batch cable and each individual thermocouple. Calibration is an especially important qualifying test because critical processes, such as those for pressure vessels in the oil and gas industry, rely on accurate and reliable temperature measurements to ensure both the efficiency of the process and the safety of the vessels.

Thermocouples are only accurate if they are homogeneous over time. Homogeneity for thermocouples refers to the chemical composition of the alloys which is responsible for their voltage output. For example, Type K typically remains homogeneous at lower temperatures, but once heated beyond a certain temperature its calibration is likely to change. The changes may be minor, but standard practice is to avoid overheating a thermocouple during the calibration process. ASTM E839, section 5.3, and ASTM E608, section 4.4 caution manufacturers against calibrating thermocouples at certain temperatures prior to use.

The preferred method of calibration for higher temperatures is to prepare a sample from each batch of material. This sample is then calibrated using reference temperatures that are similar to process conditions. This testing method establishes the overall homogeneity and calibration for a batch of material.

Thermocouple Accuracy after Service:

When thermocouples lose homogeneity over time, they may also lose accuracy. It is difficult for users to predict when the accuracy of thermocouple readings has changed beyond an acceptable limit. A new unused thermocouple, such as one from Daily Thermetrics, is supplied in a stabilized state and is homogeneous along the entire length of the probe.

Once in service within a reactor, a probe is subjected to high temperatures, high pressure, and a corrosive atmosphere. The challenge is to mitigate the factors that reduce the homogeneity of thermocouple conductor wires and, where possible, to verify the reliability of the thermocouple.

Drift:

Thermocouples are accurate for as long as their voltage output is consistent with their predicted applicable voltage output. Drift is the term used to denote when a thermocouple's output changes over time relative to the predicted voltage. This can occur via various chemical processes, such as corrosion (oxidation or sulphidation), or through mechanical processes such as strain.

When standard mineral-insulated cable is manufactured, it is usually drawn repeatedly, resulting in irregularities in the surface of the conductor wire, as shown in Figure 1. These irregularities are more susceptible to corrosion such as oxidation. An example of oxidation on the exterior of the conductor wires is shown in Figure 2. Once oxidation starts to occur on the thermocouple conductor, its chemical makeup changes and the output is expected to "drift" away from the predicted output. The oxidation process tends to become progressively worse over time, gradually affecting the thermocouple output to a greater extent as well.

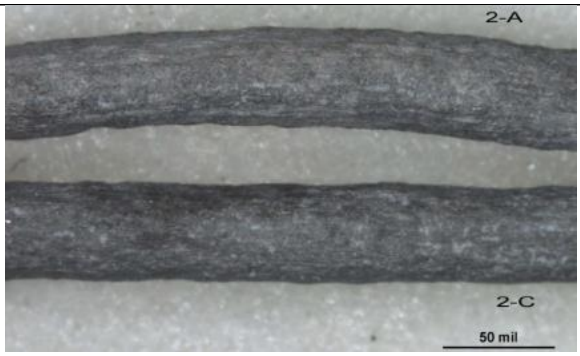


Figure 1. Thermocouple Conductors prior to Service

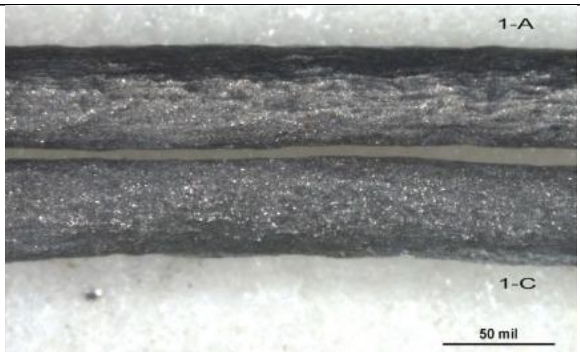


Figure 2. Thermocouple Conductors after Service

Thermocouple drift is considered different from other effects such as cold work or aging, which are typically reversible and are not present on a fully stabilized thermocouple supplied by a manufacturer.

Moisture:

The insulation of mineral-insulated metal-sheathed thermocouples is most often composed of magnesium oxide (MgO). This form of insulation is hygroscopic, which means that it will absorb moisture from ambient air. This moisture can be evenly distributed, such as when it is introduced during manufacturing, or unevenly distributed, such as when there is a breach of the sheath in service. ASTM E608 specifies a minimum of one GΩ insulation resistance at room temperature for ungrounded thermocouples. One GΩ insulation resistance is sufficient to keeping the circuits properly isolated in a controlled environment and for shorter lengths, but it may not be sufficient for a demanding application. Insulation resistance has an exponential inverse relationship with temperature, hence probes subjected to higher temperatures will have a much lower insulation resistance while in service. Insulation resistance is also a function of length and shows the path of least resistance of the voltage. A probe with an evenly distributed and absorbed moisture content that is partially subjected to a higher temperature would see moisture migrate to a lower temperature area. This migration could sustainably lower the insulation resistance.

Moisture inside a mineral-insulated cable can cause inaccuracy in the thermocouple circuit. If moisture is sufficiently high at a single location, a ghost junction or spurious junction may form. The extra junction would act as a partial thermocouple and would contribute to the thermocouple output. Based on the strength of this junction, the output could be adjusted by a fraction of a degree or the ghost junction may control the entire output.

Moisture can also cause chemical changes in the conductors by corroding the wires and thus altering their composition over time. Figure 3 shows a lateral section of conductor wires that failed following use in a high-temperature service. Oxidation, which may have been instigated either by moisture in the cable, permeation or a breach, causes the grain boundaries to become brittle. The brittle nature of the conductor wire can lead to a total break and loss of thermocouple output, or it can contribute to inaccuracy in the conductor wire.

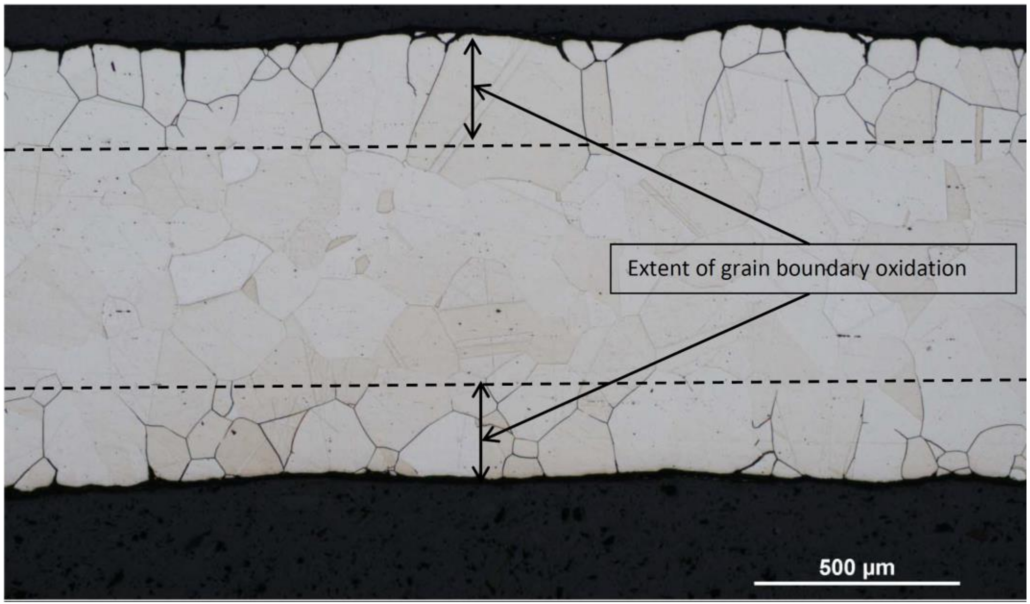


Figure 3. Lateral Section View of Thermocouple Conductor after Service

In Situ Calibration Methods:

In situ calibration is used to proof-test whether a thermocouple sensor remains accurate after it has been in service. Many users have misconceptions regarding the practice and reliability of in situ calibration, resulting in a false positive proof test of thermocouple accuracy and repeatability. Industry standards reference the unreliable nature of in situ calibration for thermocouples and discourage it. ASTM E608, section 4.4, states that the temperature profile along a nonhomogeneous section can affect the output of a calibration test (ASTM Standard E608/E608M, 2013).

Industry-Accepted In Situ Calibration Methods:

It is possible to calibrate a thermocouple in situ (in place) through various different methods depending on the accessibility of the thermocouple. ASTM E2846, Standard Guide for Thermocouple Verification, represents a good guide with options for users to calibrate their thermocouples in situ (ASTM Standard E2846, 2014).

One of the most common in situ calibration techniques once the UUT has been removed from the process and been replaced by a reference sensor or referee thermocouple (Figures 4 and 5). A referee thermocouple is an unused thermocouple from the batch of thermocouples installed. The measurement of the reference sensor or referee thermocouple is subsequently compared with the UUT, and if it falls within an acceptable range, the UUT is deemed calibrated. This method is suitable for processes with thermowells or other protection tubes that do not directly subject the UUT to the process. *This technique is not feasible for multipoint thermocouples in a pressure vessel with a fixed installation*.

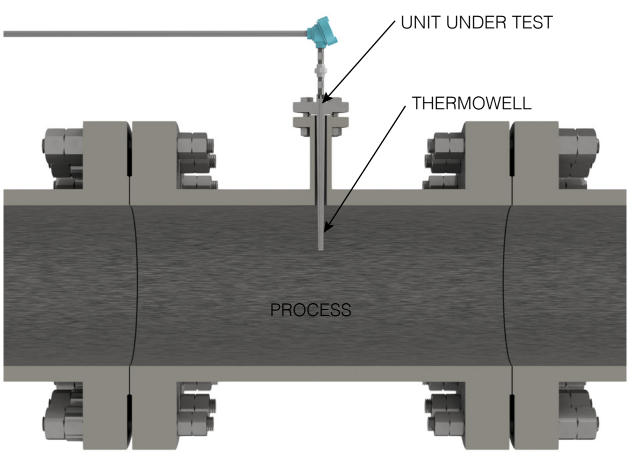


Figure 4. Typical In Situ Calibration Test - UUT

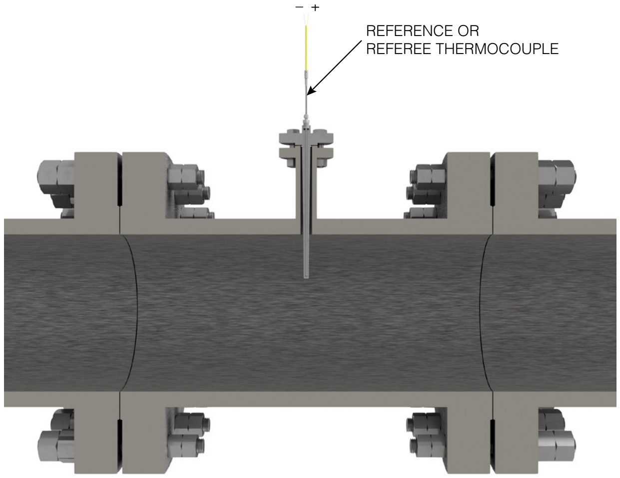


Figure 5. Typical In Situ Calibration Test - Reference

Another common in situ calibration technique is to leave the UUT in place during service but to insert a reference probe in an adjacent location. The reference probe verifies the accuracy of the UUT, and if it falls within an acceptable range, the UUT is considered to be within calibration. This method is suitable for processing conditions that allow a probe to be inserted while live. Pressure vessels do not permit a second sensor to be inserted during service and so this is not an acceptable in situ calibration method.

Tip-Sensitive Calibration:

Some users attempt to verify the functionality of a thermocouple following a period of time in service by heating the thermocouple measuring junction and comparing it to a reference. The theory is that by heating the thermocouple junction, a user can verify the accuracy of the sensor for future process conditions. The flaw in this methodology is that the voltage generated by the Seebeck effect (the means by which thermocouples function) is caused by a temperature gradient along the conductors rather than the tip itself. In the case of long thermocouple sensors, the temperature gradient is often not located close to the junction. A typical installation of multipoint thermocouples inside vessels is presented in Figure 6.

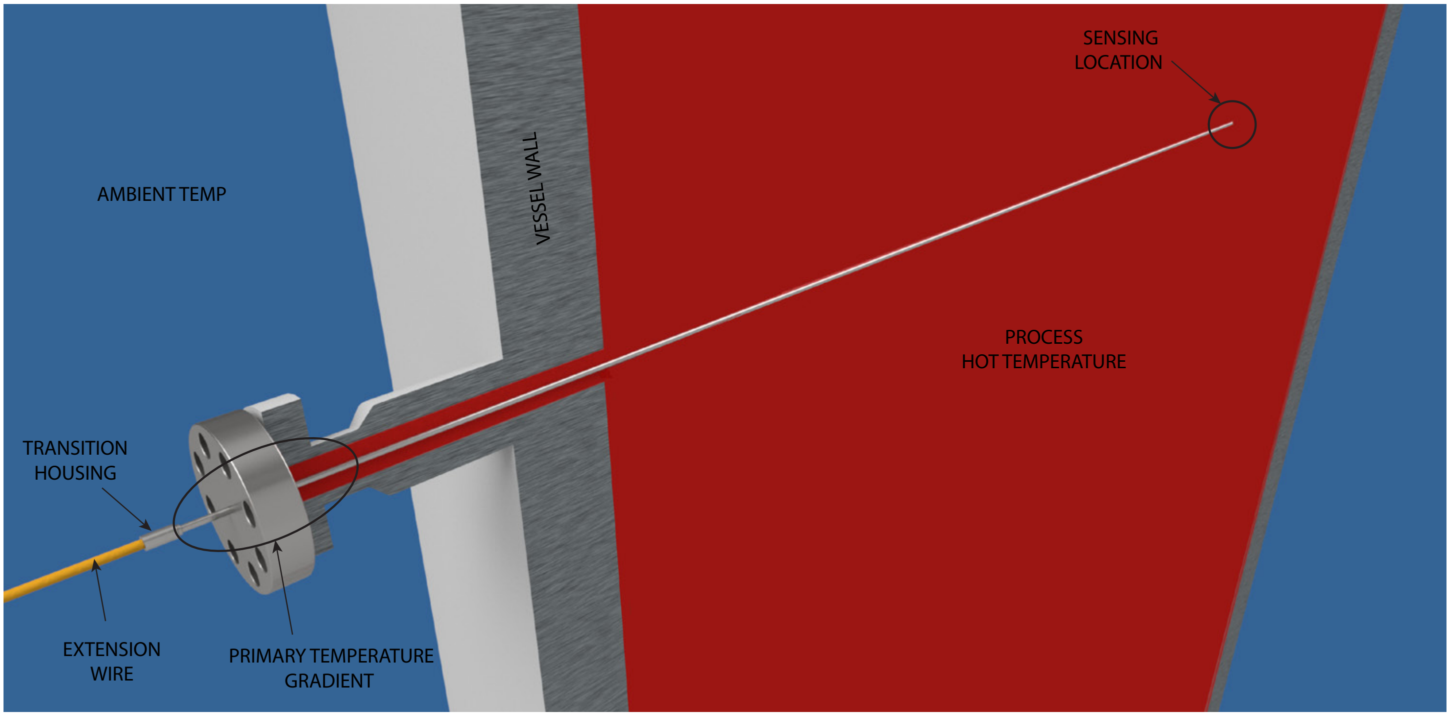


Figure 6. Simplified View of the Thermometry in a Pressure Vessel

During service, the thermocouple diagram (Figure 7) can be simplified into three zones. The temperature inside the vessel is elevated and is fairly uniform across the cross-section perpendicular to the flow. The thermocouple junction is located in this zone and it is critical to determining whether temperature fluctuations occur during the process. The next zone is the gradient zone, which is where the temperature transitions from the process zone through the vessel wall and into the ambient zone. The transition zone contains the majority of the temperature gradient and thus contributes most of the thermocouple output. The final zone is beyond the vessel, where the temperature reaches ambient temperature and transitions to an extension wire to be routed to a control panel.

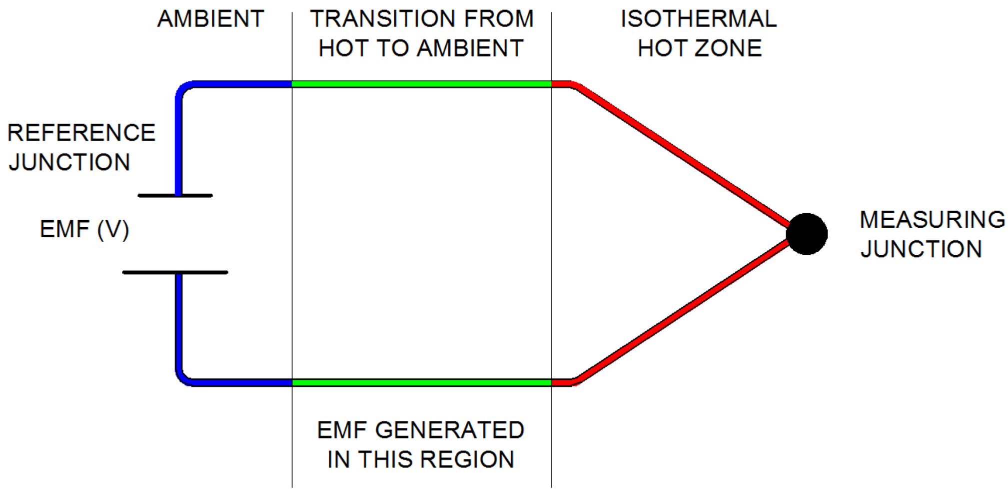


Figure 7. Simplifed Thermocouple Diagram

During tip-sensitive calibration, a heat source is applied to a general location at the thermocouple junction. This in turn generates a thermocouple signal that can be read at the end of the extension wire. The problem with this calibration technique is that, unlike during process conditions, the temperature gradient occurs within a section of cable that is within the process zone. As previously discussed, thermocouples are susceptible to multiple failure methods. Some of these failure methods do not typically occur inside a zone that is fairly isothermal during operation. For example, moisture accrued during manufacturing is typically spread through the mineral-insulated cable, but once the cable is heated, the moisture migrates toward the ambient zone and collects there. Furthermore, if a breach occurs in the transition housing, moisture can enter the cable and collect in the immediate ambient zone. Owing to these failure methods, moisture can progressively corrode the conductor wires and thus degrade the thermocouple's signal accuracy. If this type of failure occurs, a tip-sensitive calibration test would not recognize it as the normal gradient zone is isothermal during this calibration test.

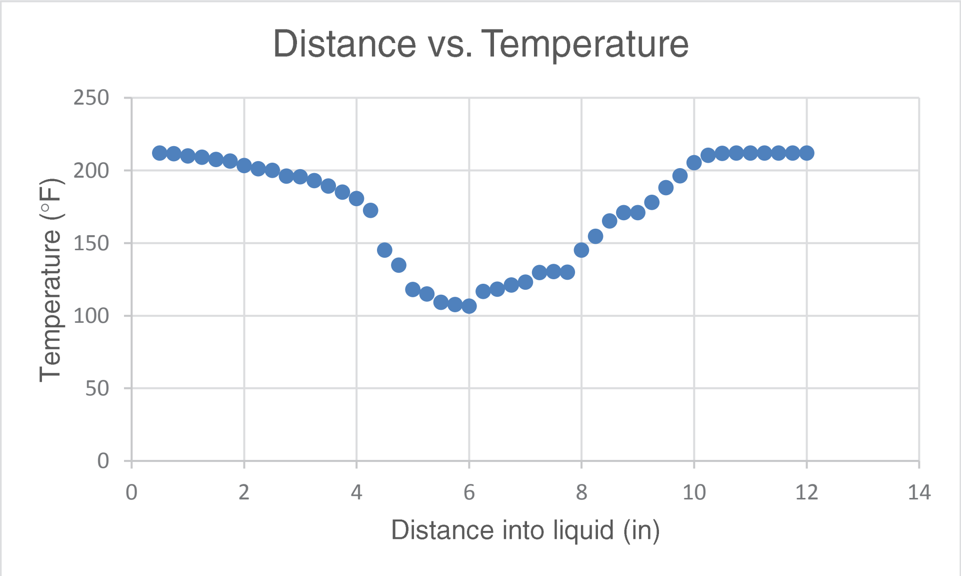
Tip-sensitive calibration represents a single point verification and is not a true test of inhomogeneity throughout the probe. The technique can mislead users into believing that the reliability of the thermocouple is legitimate, when in reality some common failure methods are not tested. Consequently, Daily Thermetrics' does not recommend in situ calibration unless a user can perform a true robust in situ calibration test.

Experimental Results Utilizing a Probe with Different Conductor Elements:

In order to reemphasize how the results of tip-sensitive calibration are not necessarily representative of the entire probe, an experiment was created in which a probe with a segment of incorrect extension wire was slowly lowered into a liquid bath oven. This probe had a base mineral-insulated metal sheath cable, although a section of the extension wire had been replaced with copper conductors rather than thermocouple-type conductors. As the probe was lowered into a hot bath set at 212.2ºF, temperature readings were taken with reference to how much of the probe was submerged in the fluid. The test concluded once the entire section of copper conductors had been fully submerged and the thermocouple was once again reading accurately.

This test confirms a long-standing thermocouple principal: if a third metal is introduced into a thermocouple circuit, but both new junctions are at the same temperature, the thermocouple output is not affected. As the probe is lowered into the hot fluid, the measurement output reads accurately. Once the probe is submerged far enough into the fluid, the copper conductors enter the temperature gradient zone. Given that this is the zone where the output is generated, the readings change dramatically, reaching as low as 106.5ºF. As the probe is pushed even further into the process, the copper conductors are completely submerged and the output becomes accurate again.

This test effectively demonstrates why tip-sensitive calibration is not useful for determining the accuracy of a nonhomogeneous probe.



Graph 1. Test Results. Distance vs. Temperature

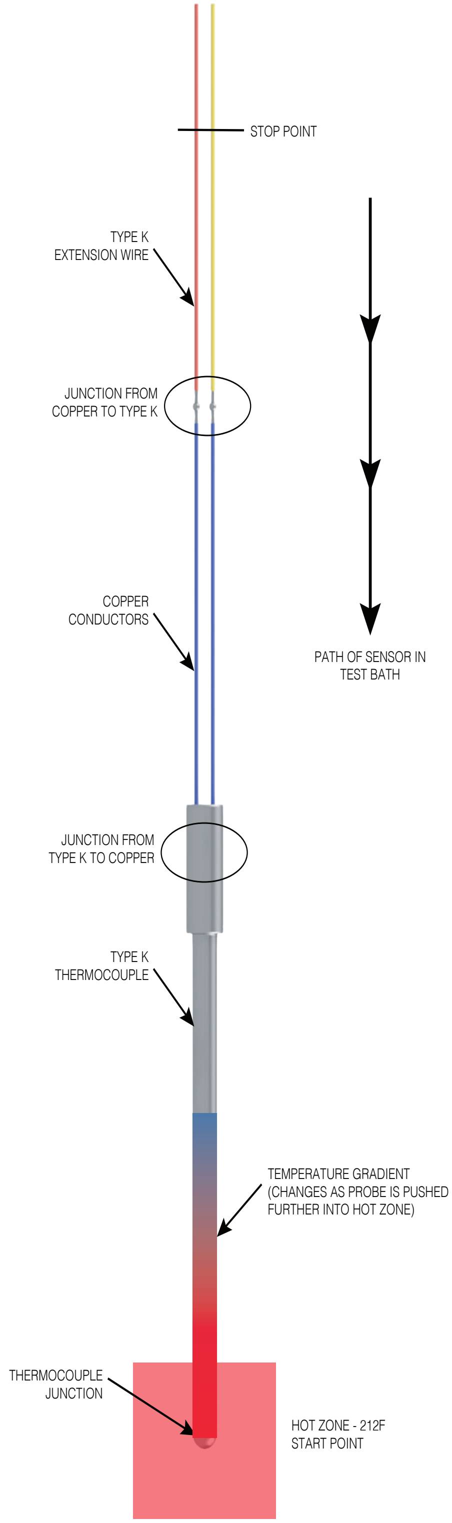


Figure 8. Test Setup

In Situ Verification Techniques:

When a thermocouple is in service and the junction cannot be accessed, a user still has options for verifying the functionality of the sensor. Thermocouple drift will leave evidence that can be measured using certain electrical tests, but the user needs to be familiar with the test methods and their limitations. A full procedure guide can be referenced in ASTM E1350 (ASTM Standard E1350, 2018).

Visual Inspection:

When possible, a full visual inspection of the thermocouple probes should be performed. During this inspection, the entire length of thermocouple probe subjected to process conditions ought to be evaluated. Pits, cracks and excessive corrosion should be noted and evaluated utilizing dye penetrant testing. Pits and cracks may appear to be small on the probe but can propagate throughout the sheath material and contaminate the conductors (Figures 9-12). Sample measurements of the thermocouple outside of the diameter should also be taken for comparison with the nominal. This measurement may indicate corrosion or erosion as well as whether the wall thickness is no longer appropriate for service conditions. All end closures should also be thoroughly inspected in order to detect any damage as well as all connections to terminal blocks or transmitters.

Figure 9. Pit on Exterior of Thermocouple Sheath

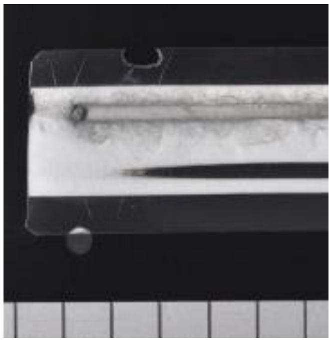


Figure 10. Lateral Section View of Pit

Figure 11. Crack on Exterior of Thermocouple Sheath

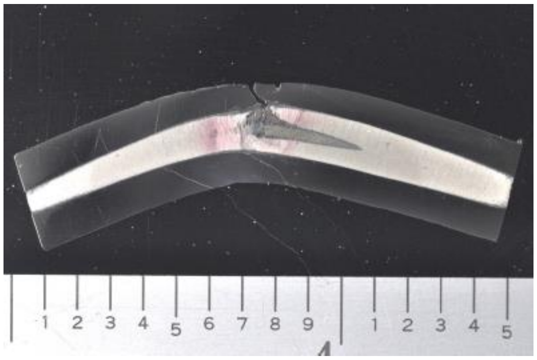


Figure 12. Lateral Section View of Crack

Loop Resistance:

Loop resistance is the electrical resistance of the joined thermocouple circuit and is measured from the reference junction of the thermocouple across the positive and negative legs (ASTM Standard E839, 2016).

For a mineral-insulated metal sheath thermocouple with an extension wire, the total loop resistance is shown in Figure 13. Extension wire conductors are very close in size to nominal B&S wire awg sizing and values can be easily tabulated (ASTM MNL12-4TH, 1993). Process thermocouple conductors are mechanically worked and are considerably different from the nominal wire awg sizing. Therefore, they can also vary from tabulated results. The thermocouple junction and the addition of an extension wire via brazing may also cause potentially unpredictable errors in loop resistance readings. Consequently, Daily Thermetrics recommends against the use of calculated resistance values, preferring instead unique test results for each circuit.

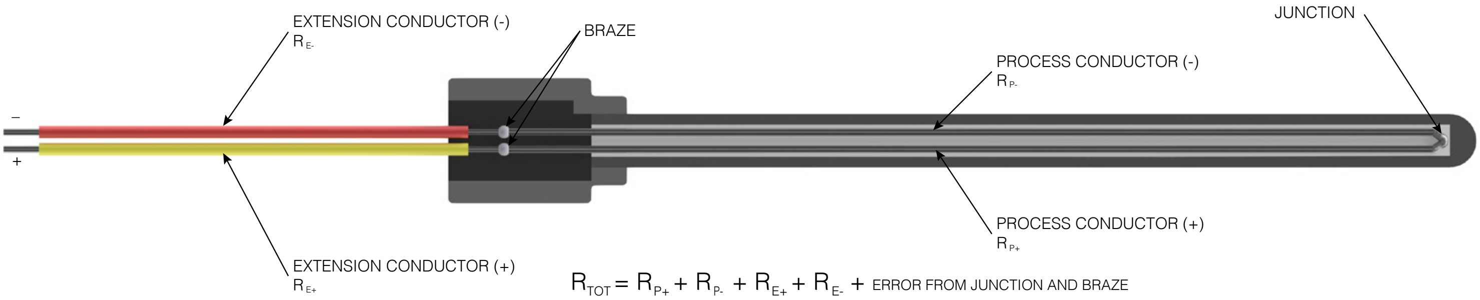


Figure 13. Thermocouple Loop Resistance Figure

If the end user intends to utilize loop resistance as a measure of thermocouple integrity, the use of resistance readings as manufactured is recommended. These readings can be used to identify damage during installation. It is important that all measurements start from the same place. For a typical multipoint thermocouple bundle supplied with a junction box, it is recommended that the thermocouple is disconnected from the terminal block inside the junction box (see Figure 14). This location has the first accessible bare connectors from the process, negating any errors from terminal blocks or the additional extension wire.

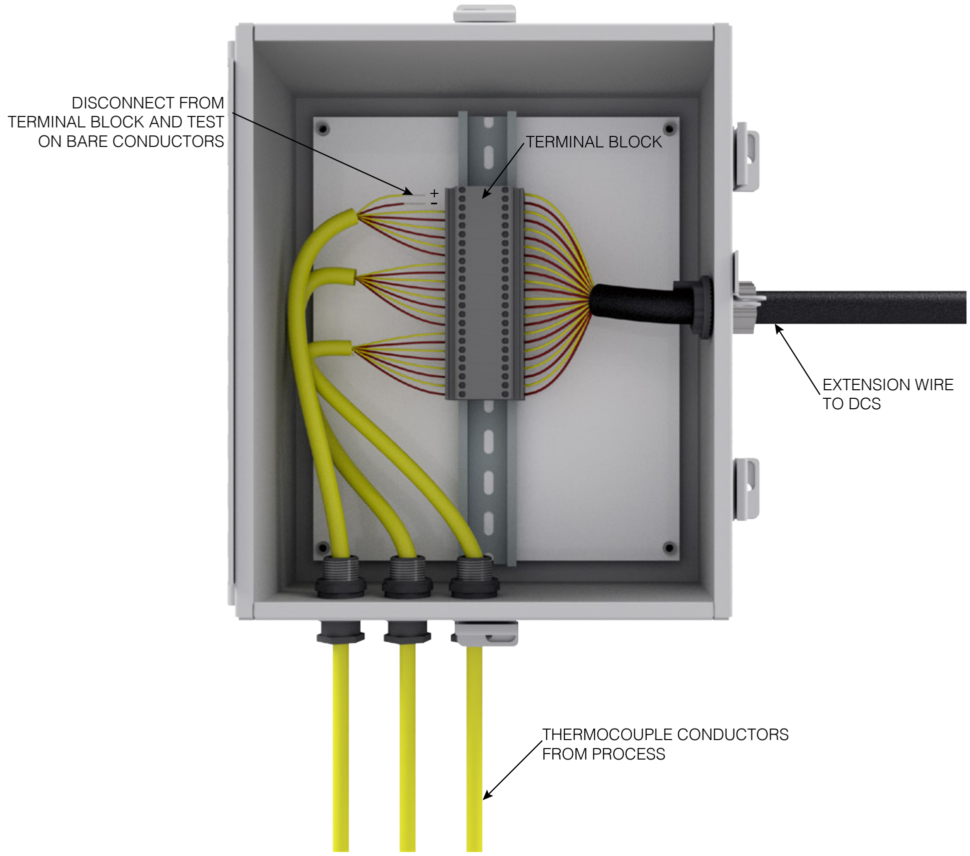


Figure 14. Example Loop Resistance Test Location Inside Junction Box

Once the values have been tabulated, a user can recognize whether significant changes occur either during installation or following service. While small changes are expected due to uncertainties in the equipment and temperature fluctuations, larger alterations may indicate damage. Changes greater than 20% should be flagged and replaced where possible, or verified by other means. Changes smaller than 20% but higher than other circuits should be noted and either verified by other means or flagged for additional testing at the next opportunity. Table 1 shows a sample set of recorded data that would demonstrate a proper installation; however, after service, one of the thermocouples has failed. Another thermocouple is an outlier and ought to be noted and either tested further or replaced. Each circuit should be tested via both directs and averaged to sample the circuit (ASTM Standard E839, 2016).

Sample Loop Resistance Recordings								
Tag	Factory Reading (ohm)		Installation Reading (ohm)		Deviation	Reading after Service (ohm)		Deviation
	+ to -	- to +	+ to -	- to +		+ to -	- to +	
TE-0001	12.45	12.47	12.48	12.52	0.32%	12.62	12.68	1.50%
TE-0002	12.46	12.48	12.49	12.56	0.44%	12.57	12.59	0.87%
TE-0003	12.38	12.41	12.41	12.48	0.40%	12.49	12.51	0.84%
TE-0004	12.51	12.52	12.57	12.58	0.48%	13.51	13.62	7.74%
TE-0005	12.47	12.48	12.52	12.54	0.44%	16.25	16.35	23.47%

Table 1. Sample Loop Resistance Recordings

Loop resistance is a function of temperature and this test should only be performed at ambient temperature. If results are required at process temperature, initial values should be taken once the vessel has reached and stabilized at process temperature. Local hazardous area codes and site-specific restrictions should be followed for this method because it is a potential source of ignition.

Insulation Resistance:

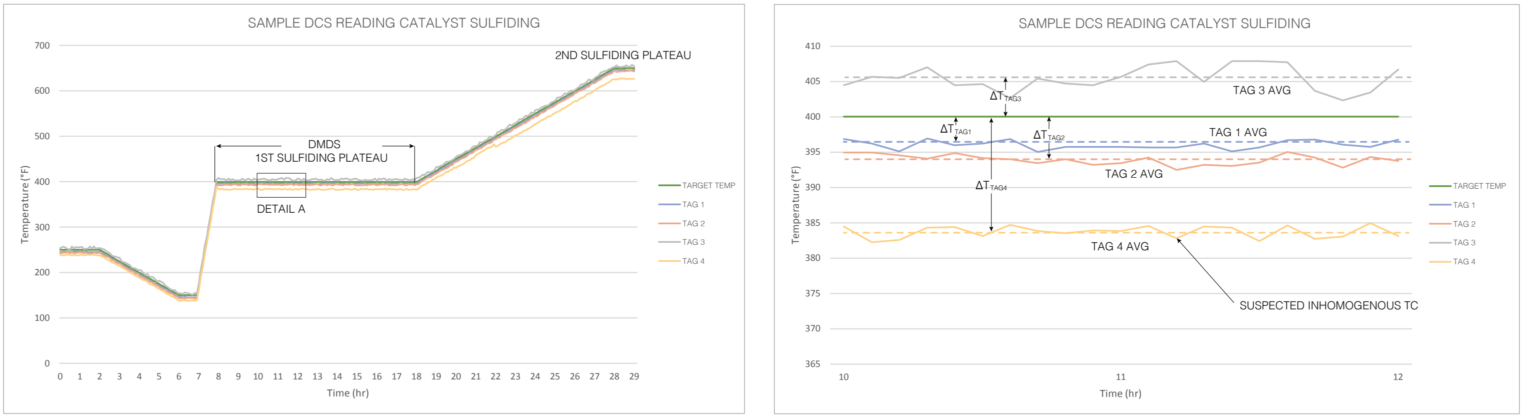
Insulation resistance is a measure of the effectiveness of the ceramic insulation inside the metal sheath, the epoxy in the transition housing and the pvc or Teflon of the extension wire. Akin to loop resistance, insulation resistance is inversely proportional to temperature, and so the test should only be performed at ambient temperature or the measures should be taken to correlate with the data at test temperature. Per ASTM, a factory thermocouple assembly should have an insulation resistance greater than 1,000 MΩ that is destined to a customer (ASTM Standard E608/E608M, 2013). Insulation resistance can degrade once a thermocouple is installed and while in service. If the insulation resistance degrades to lower than two orders of magnitude (100x) from the factory readings, corresponding to 10 MΩ, damage to the insulation or end seal is detected (ASTM Standard E1350, 2018). Given that the insulation resistance includes the extension wire, a reading below 10 MΩ does not necessarily signal a failure. It should be used in conjunction with other tests in order to determine whether future use is justified.

In Situ Calibration Techniques Utilizing Catalyst Phases:

The goal of an in situ calibration test is to replicate the temperature profile along the thermocouple probe during service. Operators have several options for accessing data during different catalyst phases, which can provide a better picture regarding the performance of the thermocouple. Operators should work with their catalyst suppliers to determine the appropriate phases at which a vessel should be near isothermal. Below are examples of certain times when an in situ test can be performed in conjunction with catalyst phases. Test data from these tests should not be the sole factor when determining acceptance, because variation occurs among catalytic processes. Although it is likely that a common cause could affect all thermocouples inside a vessel, the extent of damage to each thermocouple should be unique and apparent in such a condition.

In Situ Sulfiding:

In situ sulfiding includes two separate “sulfiding plateaus,” in which the vessel is held at a steady temperature for multiple hours (Reactor Resources, 2018). During these plateaus, the vessel becomes thermally stabilized and the thermocouples can be compared to one another as well as to the expected temperature based on available models or calculations. Figure 15 shows a sample analysis with a group of thermocouples during catalyst sulfiding. Small discrepancies from the target temperature can be expected, but major outliers should be recognized and noted as potential examples of inhomogeneity.



DETAIL A

Figure 15. Sample DCS Readings during Catalyst Sulfiding

Catalyst Hot Stripping:

Catalyst hot stripping uses hot hydrogen to remove the coke residue that has formed on a catalyst. During hot stripping, hydrogen is piped into the system for several hours until the temperature has stabilized, and it is then held for two hours. All sensors are expected to provide similar temperature readings based on available models or calculations. Given that this event takes place before the catalyst is unloaded, verification of the functionality of the thermocouples while the user has an opportunity to replace them is recommended.

In addition to in situ sulfiding and catalyst hot stripping, catalyst dry out can also be considered as a near isothermal event. It is recommended that users consult with their thermocouple manufacturer and catalyst supplier in advance of a shutdown in order to receive guidance and support for these types of verification methods.

Determining Acceptance Criteria:

Acceptance criteria will be determined by the operator with recommendation from the thermocouple manufacturer to determine the acceptance criteria for the verification methods outlined in this document. Depending on several factors, the end user may wish to keep a borderline thermocouple in place instead of replacing it. Outside factors to consider while determining replacement could be:

- Safety systems involved
- Licensor requirements
- Level of redundancy of thermocouple sensors inside the vessel
- Anticipated outage schedule

A sample acceptance flow chart is shown in Appendix 1 which explains the methodology that can be used while inspecting thermocouples in situ.

Conclusion:

Inspecting thermocouples that have been in service can be more complicated than expected. Once the thermocouple has been placed in service, the homogeneity of the conductors is affected and the output can change. Calibration techniques that are used on new thermocouples, like tip sensitive calibration, are no longer appropriate since it does not account for inhomogeneity of the conductors during operation. Other tests that are readily available, such as loop resistance, insulation resistance and visual inspection can provide an operator with much more actionable data than a tip sensitive calibration test. Loop resistance, in particular, can detect inhomogeneous sections of the thermocouple conductor, but values need to be recorded during manufacturing and installation to use as reference. Users still have opportunities for in situ calibration tests with the use of scheduled catalyst phases that place the sections of the vessel in an isothermal stabilized state. This form of verification will expose the entire thermocouple sheath to the same temperature profile as it would see during service and should be regarded as a true verification method. As discussed, there are options for customers to verify the life of their fixed installation thermocouples, but it is important to recognize poor verification techniques such as tip sensitive calibration as it is not a true test of homogeneity.

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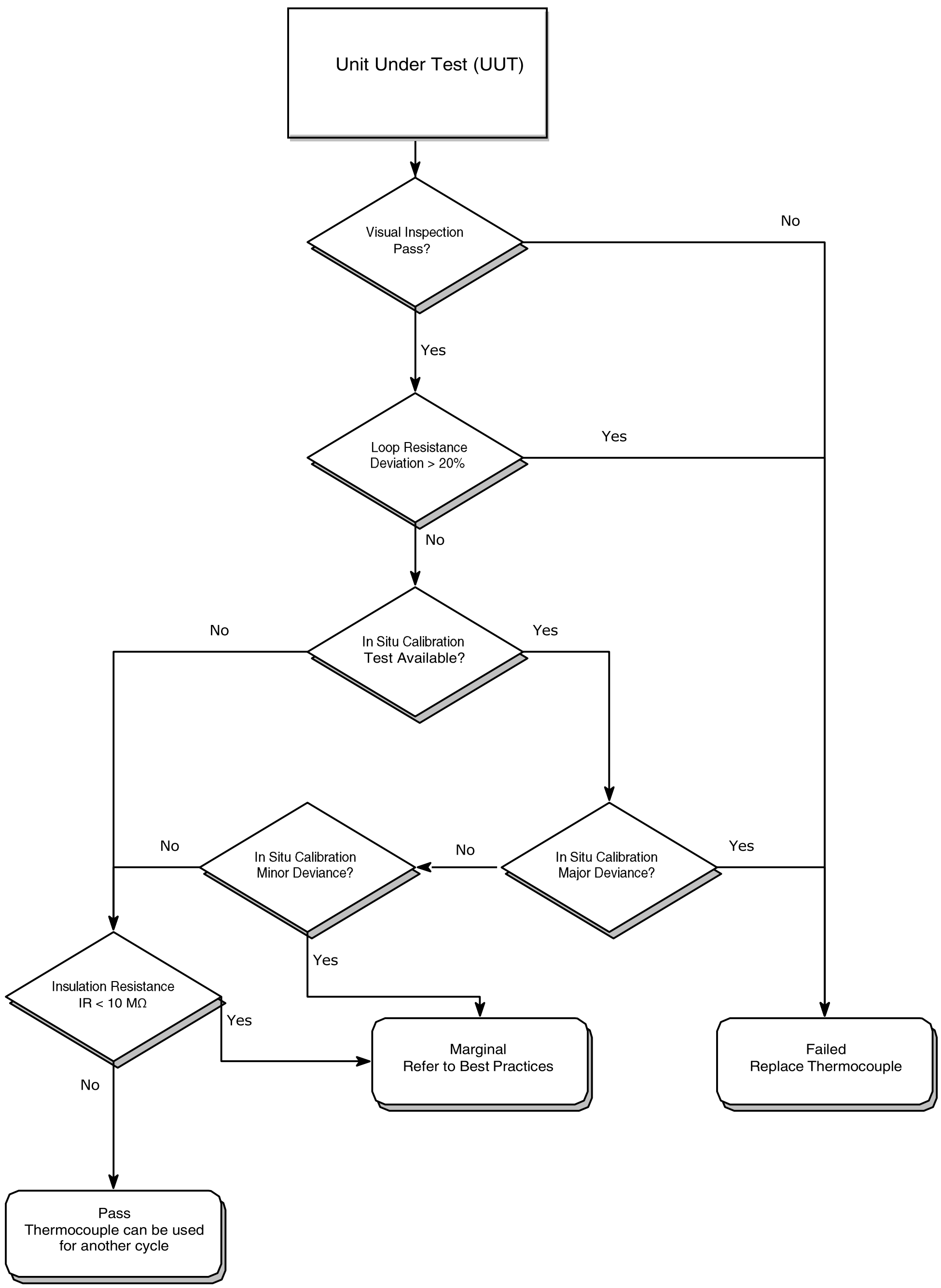
APPENDIX 1



Sample Acceptance Flow Chart