

# Auto-Refrigeration/Brittle Fracture Analysis of Existing Olefins Plants—Translation of Lessons Learned to Other Processes

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## Abstract

This paper describes the use of process hazards analysis (PHA) techniques and “API 579 Recommended Practice for Fitness-for-Service, Assessment of Existing Equipment for Brittle Fracture” to evaluate existing olefins plants. It also examines some of the identified transient process excursions that can result in operations below vessel minimum allowable temperature (MAT), creating the potential for brittle fracture, and the methods of the evaluation are described. The importance of identifying transient process conditions and making materials-of-construction selections based on these conditions is emphasized. Translation of the typical findings and lessons learned to other processes handling light-liquid hydrocarbon materials in carbon steel equipment is discussed, as well as the importance of operator training and response.

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## 1. Introduction

Auto-refrigeration and the low temperatures that can result in brittle fracture of carbon steel equipment have been a concern since the industry experienced a number of failures. The American Society of Mechanical Engineers (ASME) revised the “Boiler and Pressure Vessel Code (BPVC), Section VIII, Division 1” in 1987 to reflect limitations of low temperature for new pressure vessels. An industry accepted method to analyze and evaluate existing pressure vessels for brittle fracture was not available until the American Petroleum Institute (API) issued “API 579 Recommended Practice for Fitness-for-Service” in January 2000. As a part of ongoing review of process risk, the potential for auto-refrigeration and associated brittle fracture was highlighted as one of the major potential risks associated with the Lyondell olefin plants. A program to analyze, evaluate and mitigate the risk of auto-refrigeration/brittle fracture in existing plants was initiated in 2001. After having evaluated several olefins and polymer plants, this paper reflects the techniques and methods used and also describe potential transient conditions that were identified during the analysis. Fig. 1 reflects the major steps in the auto-refrigeration/brittle fracture prevention program.

## 2. Brittle fracture basics

Carbon steel and other ferritic steels become susceptible to brittle fracture with decreasing temperatures. Brittle fracture is a particularly undesirable failure mode because it can occur without warning, and the damage may manifest itself in complete rupture of the equipment. Brittle fracture occurs in a break-before-leak mode, rather than the preferred leak-before-break mode of failure. For brittle fracture to occur, all three of the following elements must be present simultaneously:

- a susceptible steel (susceptibility increases as temperature decreases);
- a stress riser, such as a crack or a notch (as often is found in weld defects);
- a sufficient applied stress above a minimum stress level (~7000 psi [48 MPa] for carbon steels).

These three elements are often represented in the form of a Brittle Fracture Triangle (Fig. 2). All three sides of the triangle must be present for brittle fracture to occur. Remove any side and brittle fracture is not possible. For most pressure vessels under normal operating conditions, the stress is almost always above 7000 psi (48 MPa). Since no vessel is fabricated perfectly, there are always some weld flaws (cracks or notches). The net effect is that two sides of the triangle are always present during normal

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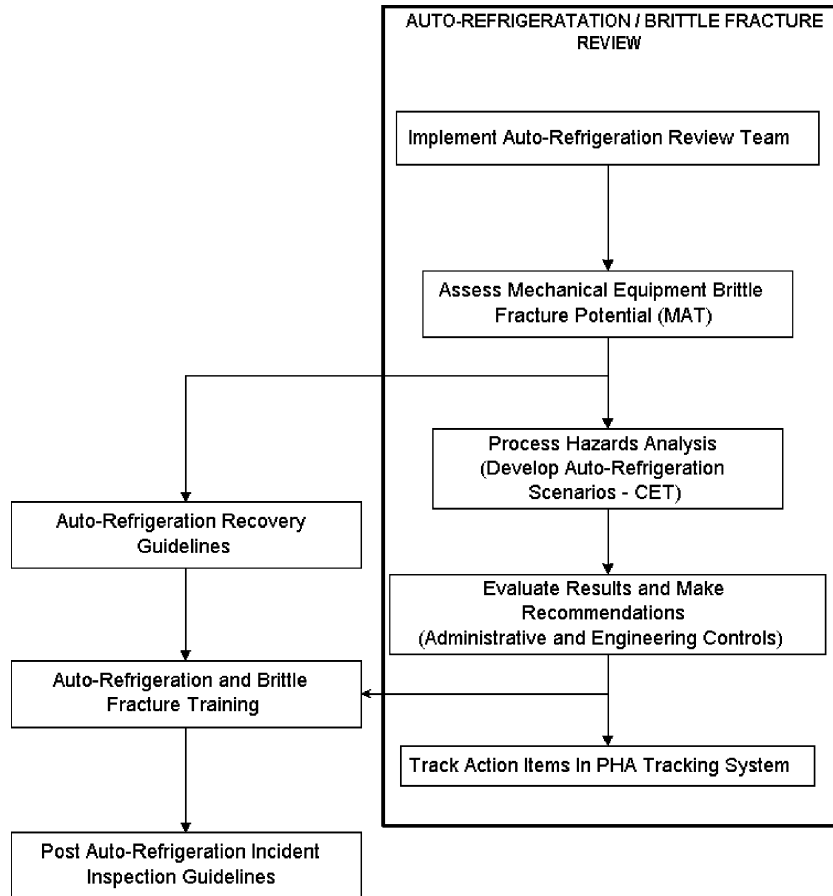


Fig. 1. Auto-Refrigeration/Brittle Fracture Prevention Program.

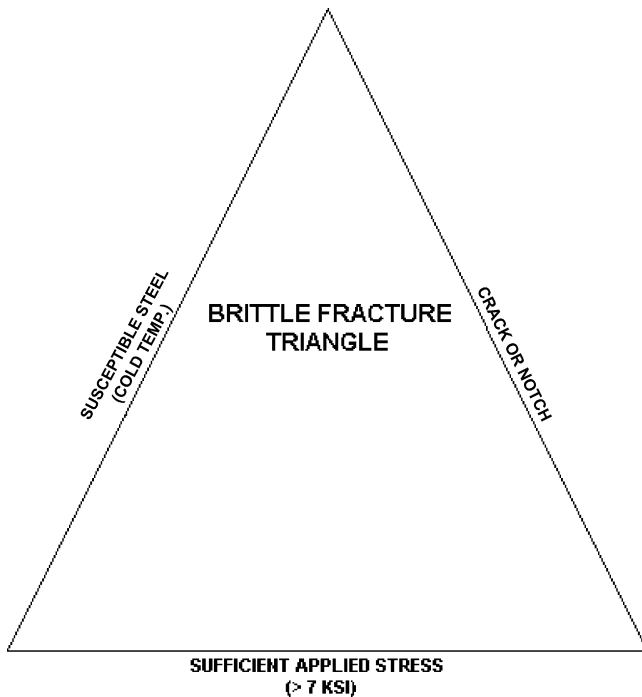


Fig. 2. Brittle Fracture Triangle.

operations. The best protection for preventing brittle fracture is not expose carbon steel vessels to cold enough temperatures to “close” the Brittle Fracture Triangle.

The susceptibility of carbon steel to brittle fracture is related to temperature. As temperature decreases, the susceptibility to brittle fracture increases. Auto-refrigeration can provide the mechanism for low temperature exposure. When a particular grade of steel becomes susceptible depends on its grain size and the melting practices used. The best grades of carbon steel used for pressure vessel construction can be applied at the allowable stress down to approximately  $-50^{\circ}\text{F}$  ( $-45.5^{\circ}\text{C}$ ). These steels are specially processed to obtain good resistance to brittle fracture. Carbon steels that are not specially processed for brittle fracture resistance may become susceptible at room temperature and above. The specific temperature where a pressure vessel becomes susceptible to brittle fracture can be captured in the concept of minimum allowable temperature (MAT). The MAT is the lower temperature boundary at all possible vessel pressures (stresses) to ensure brittle fracture does not occur. The MAT at maximum allowable working pressure (MAWP) is defined as the minimum design metal temperature (MDMT).

Other types of ferritic steels, such as chrome-moly and carbon-moly steels, behave similarly to carbon steels, which are not specially processed for resistance to brittle fracture. Even nickel steels can become susceptible to brittle fracture at low enough temperature. Austenitic stainless steels, nickel-base

alloys, aluminum alloys and copper alloys are essentially resistant to brittle fracture.

One key concept for complete understanding of brittle fracture is that a minimum level of applied stress is needed to propagate a brittle fracture. For the crack tip to propagate through the carbon steel, it must have sufficient energy. For carbon steel, this minimum level of applied stress (energy) is about 7000 psi (48 MPa). This equates to about 40% of the MAWP for pressure vessels built to the ASME Section VIII, Division 1, 1998 or earlier code (35% for vessels built to the 1999 or later code). The potential for catastrophic failure is reduced when the pressure is brought below the 7000 psi (48 MPa) stress level (<40% MAWP). If an auto-refrigeration excursion has occurred and the brittle fracture triangle is “closed”, the vessel is at risk of failure. The only fail-safe response is to “open” the triangle by dropping the pressure on the vessel, thereby lowering the stress to less than 7000 psi (48 MPa). This may induce additional auto-refrigeration, resulting in lowering the vessel temperature. But, as long as the stress is reduced, the potential for a catastrophic failure is diminished. The vessel may crack and leak from secondary stresses, but the primary stresses, the stresses that cause vessels to rupture, have been reduced.

### 3. Analysis approach

The Auto-Refrigeration/Brittle Fracture Review process involves two major analysis methods:

- (1) Mechanical Evaluation: In the mechanical evaluation, the equipment is analyzed for brittle fracture potential using API 579, Section 3 [1]. For most equipment, a Level 2 method A, B or C analysis is used. The result of this evaluation is to generate a curve that reflects a vessel’s MAT for all pressure conditions.
- (2) Process Hazards Analysis (PHA): The PHA evaluates the process for possible auto-refrigeration excursions. The purpose of this analysis is to generate a CET for all vessels subject to exposure to light hydrocarbon materials. The CET is represented by a curve of process temperature conditions for pressures below the MAWP of the vessel.

#### 3.1. Mechanical Evaluation

The mechanical evaluation uses the methods described in API 579 [1,2]. Since most auto-refrigeration excursions occur under upset/non-steady state conditions, the MAT is calculated for all pressure conditions of the vessel. API 579 allows the MAT to decrease as the primary (pressure) stress on the vessel falls. The MAT is allowed to decrease to as low as  $-155^{\circ}\text{F}$  ( $-104^{\circ}\text{C}$ ) for carbon steels. To facilitate the analysis, a spreadsheet was developed that takes vessel information (material of construction, MAWP, corrosion allowance, weld joint efficiency, impact test data, etc.) and calculates the MAT. The spreadsheet also has pure component pressure/temperature equilibrium curves for the more common light hydrocarbon materials encountered in an olefins plant. The pure component curves can be used to approximate the expected process temperatures (CET) for

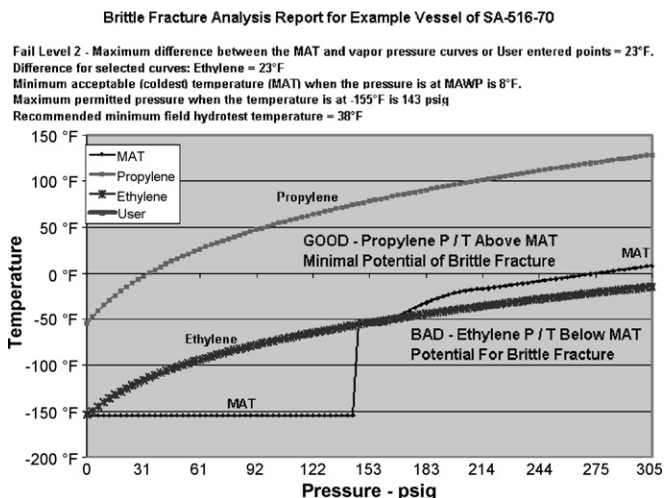


Fig. 3. Example of Vessel MAT.

equipment. Input of process simulation results (flash temperature and pressure) can also provide a more exact picture of the expected process conditions. If the CET curve is at or below the MAT curve, then the vessel is at risk of brittle fracture. Fig. 3 represents the MAT curve calculated for a non-PWHT SA516-70 carbon steel vessel with an MAWP of 305 psig (2.1 MPa). The MAT at MAWP is  $+8^{\circ}\text{F}$  ( $-13^{\circ}\text{C}$ ). For the example vessel, the vapor pressure (CET) curve for the ethylene goes below the MAT for the vessel. In this case, the vessel is acceptable for containing liquid propylene, but is unacceptable for containing liquid ethylene.

#### 3.2. Process Hazards Analysis (PHA)

The purpose of the PHA is to identify all possible scenarios that could result in auto-refrigeration of the light hydrocarbon process material. The analysis may use any of U.S. Occupational Safety and Health Administration (OSHA)/Environmental Protection Agency (EPA) accepted PHA methods. Because auto-refrigeration most often occurs during transient conditions, the analysis must: (1) evaluate the unit during each of the following operating modes and (2) evaluate the transition between operating modes.

- (a) Normal operation,
- (b) upset conditions,
- (c) normal startup,
- (d) normal shutdown,
- (e) emergency shutdown,
- (f) air freeing/nitrogen freeing,
- (g) inventory,
- (h) de-inventory,
- (i) not in operation/maintenance-in-progress,
- (j) commissioning/leak testing.

Because of the transient, unsteady state conditions that may exist during all operating modes, the PHA team must have an extremely good understanding of the operations of the plant.

Additionally, they need knowledge of operational steps that occur when making transitions from one mode to another. For each scenario identified, the CET and coincident pressure are determined. The CET is the lowest expected temperature possible, given the scenario developed and the process material contained in the vessel. The scenarios must take into account the possibility of having light hydrocarbon materials in vessels that do not normally contain such materials. Overflowing of separation drums, recycle streams, cross-connections via common headers, and cross-heat exchange in exchangers must all be considered. Subsequent actions executed by the process controls or by operating personnel must be anticipated and evaluated.

Of particular concern is the ability to increase operating pressure after an auto-refrigeration excursion prior to the equipment warming. This has the potential to place the vessel well below the MAT. Scenarios involving increasing pressure were evaluated. This was done by considering a limiting case scenario where the equipment temperature was considered to remain constant at the CET as the pressure increases. Dynamic process simulation and finite element analysis confirmed that this simplifying evaluation assumption was conservative. As a result of rapid re-pressurization, separator vessels (compressor suction and discharge drums, reflux drums, and chilling train separators), that normally contain liquid inventory are vulnerable to excursions below the MAT. When such a vessel is de-pressurized, the liquid in contact with the vessel wall vaporizes, creating a very effective mechanism to rapidly cool the vessel wall to the process equilibrium temperature. As the vessel is re-pressurized, the temperature of the wall that is in contact with the liquid lags well behind the process equilibrium temperature. This is because heat transfer is limited by less effective convective and conductive mechanisms.

The PHA techniques most often used during the analysis are the fault tree and guide-list methods. In all cases, the two methods were used in combination to ensure complete identification of potential process auto-refrigeration excursions. The fault tree method was implemented only to the extent that the PHA team had an adequate grasp on both the initiating events and the process sequence that potentially could result in auto-refrigeration/brittle fracture. The fault tree method allows the PHA team to identify and assess the measures in place to minimize the likelihood of occurrence of initiating events and to make judgements about the adequacy of protective measures. The guide-list provides a structured analysis of all operating modes of the plant and ensures that all transient conditions are evaluated. The developed guide-list is frequently updated to reflect what is learned from the previously completed evaluations.

#### 4. Findings

Based on the experience gained from several reviews, a number of generalized findings can be made in the evaluation of an existing olefins plant. These olefins plant findings can readily be translated to other processes that contain light-liquid hydrocarbons. While these generalized findings are based in part on the Lyondell studies, they do not represent the exact detailed findings of the studies. The findings described below and the

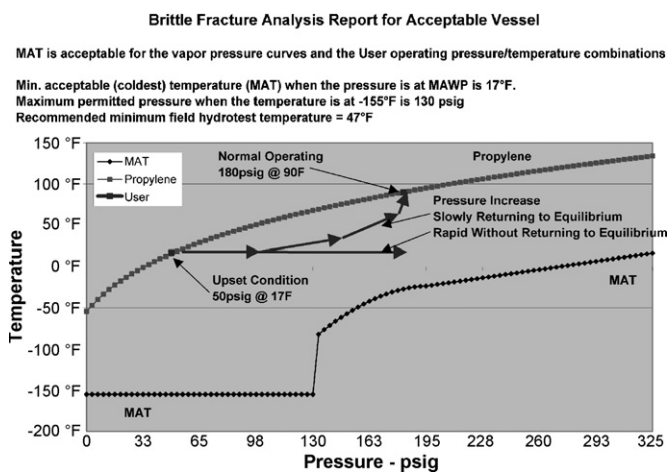


Fig. 4. Example of Acceptable Vessel.

associated vessels are purely examples of some of the possible excursion scenarios that may be encountered when undertaking an auto-refrigeration/brittle fracture PHA.

#### 4.1. Acceptable Vessels

Many of the vessels/scenarios evaluated did not result in any substantial findings or recommendations. These vessels were acceptable for continued operation for the process services being contained. The SA516-70 carbon steel example vessel (illustrated in Fig. 4) reflects the typical MAT results and upset scenarios encountered.

Loss in system pressure with a subsequent return to normal operating pressure (or even up to the MAWP) does not result in conditions at or under the MAT. The rate at which the pressure increases determines the transient upset conditions. Large systems or where pressure increase is based on heat transfer, result in a slow pressure increase with vessel wall conditions tracking near equilibrium. Systems, like compression trains, result in a rapid pressure increase and the vessel walls can deviate substantially from the equilibrium temperature. In most cases, the final upset conditions do not approach the MAT and no mitigation is required. This represents the majority of vessels evaluated.

#### 4.2. Three-and-One-Half Percent Nickel Vessels in Liquid Methane Service

Vessels fabricated from 3.5% nickel low temperature steels (SA203 Grades B and E, SA350—LF3) have substantial impact resistance even at very low temperatures. These alloys however are still limited to  $-155^{\circ}\text{F}$  ( $-130^{\circ}\text{C}$ ) MAT. When containing liquid methane, as in the de-methanizer feed separator and the de-methanizer reflux drum, the auto-refrigeration CET can be well below the MAT. See Fig. 5 for an example of MAT analysis results for a nickel vessel.

With liquid methane in this example, if the pressure is dropped much below 320 psig (2.2 MPa), the CET will be lower than the MAT of the 3.5% nickel vessel. The vessel is

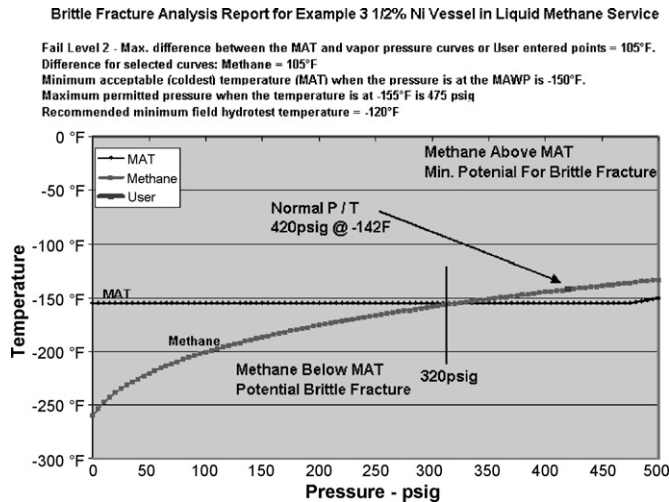


Fig. 5. Example of 3.5% Nickel Vessel MAT—Liquid Methane Service.

acceptable for “normal” process conditions, but is not acceptable under “upset” conditions where the pressure is lost and auto-refrigeration occurs. Replacement of the vessel using stainless steel is one option for correcting this situation. This example reflects the common error of selecting materials-of-construction based solely on the normal operating conditions of pressure and temperature without consideration for other operating modes.

4.3. Chilling Train Vessels

Fig. 6 represents a simplified diagram of an example process gas chilling train. Loss of forward process gas flow due to a trip of the process gas compressor or from flaring process gas going forward (lower streams flowing from left to right) results in low-flow/stagnant flow of the process gas in the core exchangers. If the liquid/vapor methane and hydrogen chilling streams (upper streams flowing from right to left) continue flowing through the

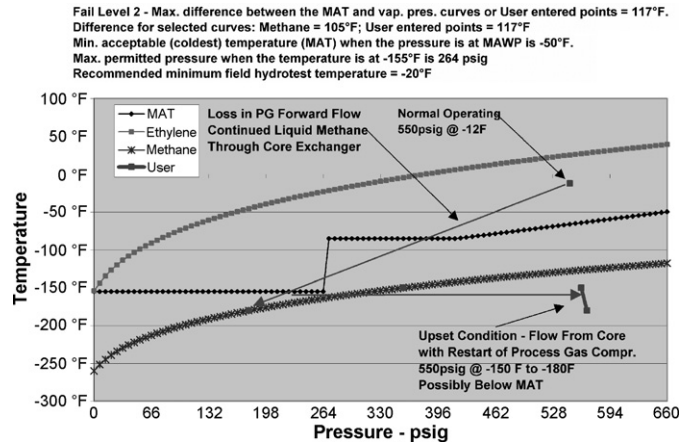


Fig. 7. Example of Chilling Train Vessel MAT—Continued Chilling Streams Through Core Exchangers.

core exchangers, process gas is condensed at a temperature lower than normal. This condensed process liquid either: (1) gravity-flows to the next drum or (2) in some instances may back-flow into the previous drum. The direction of flow of the condensed liquid depends on the physical arrangement of the cores and separator drums. Due to process gas composition and the associated reduced pressures in the chilling train during the excursion, liquid temperatures can be suppressed significantly below normal operating conditions. This auto-refrigeration excursion has the potential to have 3.5% nickel drums below the  $-155^{\circ}\text{F}$  ( $-103^{\circ}\text{C}$ ) limit. Additionally, vessel conditions could be below MAT if normal process pressures are re-established (restart process gas compressor) prior to warming of the vessels. Fig. 7 reflects an example vessel where the vessel is chilled followed by subsequent re-establishing of normal process pressure.

The vessel is acceptable for “normal” process conditions, but is not acceptable under “upset” conditions where forward process gas flow is lost and the cold liquid methane/hydrogen

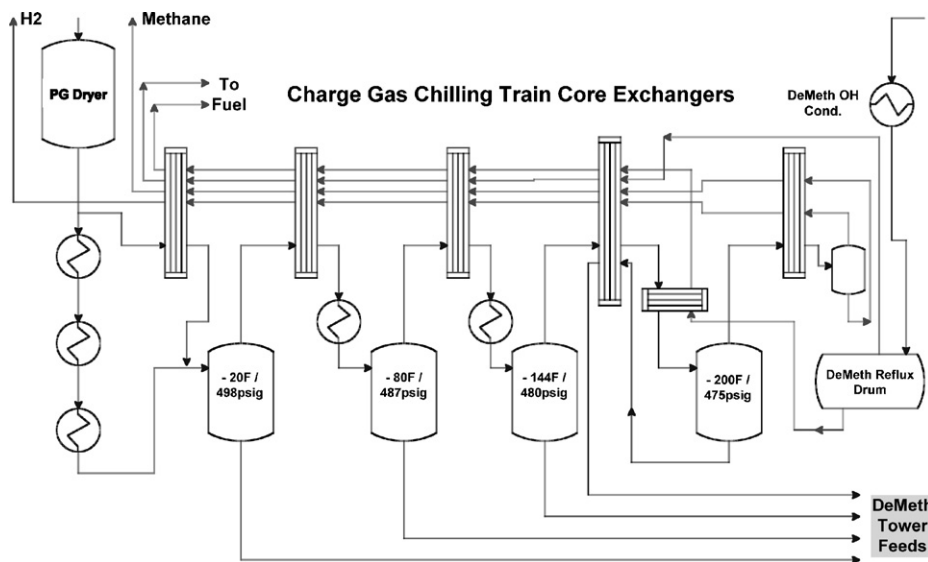


Fig. 6. Simplified Process Gas Chilling Train.



streams continue flowing through the core exchangers. Possible options for correcting this situation are replacement of the vessel using stainless steel or installation of protective interlocks. This same scenario can occur on standard shell-and-tube-heat-exchangers in other process positions where an auto-refrigeration excursion on one side of the exchanger has the potential to chill the other side to conditions below the MAT. This type of scenario (continued forward flow with loss of heat input) was one cause of the gas processing plant brittle fracture that occurred at Longford, Australia in 1998.

4.4. Distillation Towers and Peripherals

Process upsets in distillation towers may result in the potential for exposure of the tower or any of its peripheral equipment (re-boiler, overhead condenser, or reflux drum) to conditions below the equipment MAT. Fig. 8 represents an example of a de-ethanizer reflux drum.

Under normal operating conditions, the vessel operates above its MAT. Upsets in operating pressure to values either higher or lower than normal may result in excursions below the vessel MAT. Rapid increase in pressure can result in excursions below the MAT. Possible initiating events include loss of condensing or pressure controller failure. An excursion to low pressure does not initially result in exposure below the MAT. Initiating events include loss of re-boil or pressure controller failure. However, if the operations response to the upset is to attempt to quickly return to normal pressure, the CET may be lower than the MAT. The vessel wall temperature will always lag the process temperature. One alternative for avoiding this scenario is to install controls/interlocks to limit the source of the pressure (re-boil), thus preventing operation below the MAT.

4.5. Bimetallic De-Methanizer

De-methanizers made from two different materials present a significant challenge in terms of auto-refrigeration and brittle fracture potential. Vessel designers have historically handled the wide differences in tower process temperatures with an overhead temperature of  $-140^{\circ}\text{F}$  ( $-95^{\circ}\text{C}$ ) and a bottom temperature of

Brittle Fracture Analysis Report for Example - Lower C.S. Sect. Of a De-Methanizer

Fail Level 2 - Maximum difference between the MAT and vap. pres. curves or User points = 105°F.  
 Difference for selected curves: Methane = 105°F; User entered points = 55°F  
 Minimum acceptable (coldest) temperature (MAT) when the pressure is at the MAWP is -75°F.  
 Maximum permitted pressure when the temperature is at -155°F is 220 psig  
 Recommended minimum field hydrotest temperature = -45°F

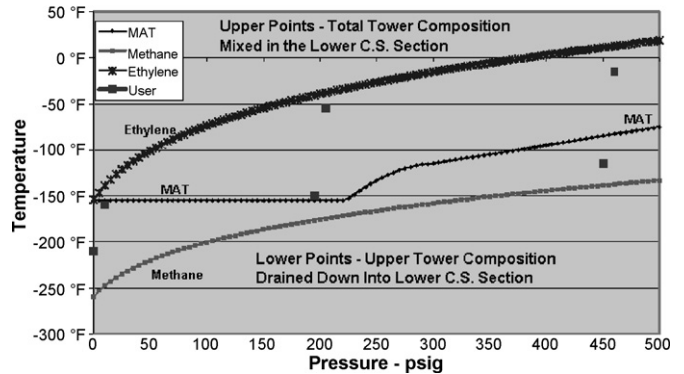


Fig. 9. Example of De-Methanizer—CS Bottom Section MAT.

$+20^{\circ}\text{F}$  ( $-7^{\circ}\text{C}$ ) by using a bimetallic construction. The top section of the tower is typically made of 3.5% nickel steel, while the bottom may be fabricated from a Charpy impact-tested carbon steel. During process upsets that result in loss of vapor flow up the tower (loss of re-boil, etc.), the tower slumps and the cold process material from the upper section of the tower cascades down into the lower section. Depending on the process composition and the materials-of-construction, this tower upset can represent a significant potential for brittle fracture. Fig. 9 represents an example analysis of the lower carbon steel section of a bimetallic de-methanizer. The points below the ethylene equilibrium curve represent the process material vapor/liquid equilibrium (CET) if all of the tower inventory, both upper and lower sections, were combined and well mixed. The points near the methane equilibrium curve represent the vapor/liquid equilibrium (CET) for the average composition of the material in the upper section of the tower. If the process material from the upper section is allowed to drain into the lower section, there is a potential for conditions to be below the MAT of the lower section.

API 579 uses a bimetallic de-methanizer as the Level 3 analysis example [1,3]. This method uses fracture mechanics, statistical application of NDT methods and finite element analysis to evaluate and inspect the vessel for continued service. While certainly an API 579 Level 3 analysis may provide assurance for fitness-for-service, there is no guarantee that a particular vessel will pass such a rigorous analysis. Another approach to mitigating the risk of operations below the MAT is to prevent the cold material in the upper section of the tower from reaching the lower carbon steel section of the tower. This can be accomplished by modifications to the tower internals and the installation of controls/interlocks. This will divert the upper section process material out of the tower, if the lower section conditions approach the MAT.

4.6. Nitrogen Freeing of Equipment

During inventory of the unit, light hydrocarbon liquids can be introduced into a process environment inerted with nitrogen.

Fail Level 2 - Maximum difference between the MAT and vapor pressure curves or User entered points = 18°F.  
 Difference for selected curves: User entered points = 18°F  
 Minimum acceptable (coldest) temperature (MAT) when the pressure is at the MAWP is 7°F.  
 Maximum permitted pressure when the temperature is at -155°F is 170 psig  
 Recommended minimum field hydrotest temperature = 37°F

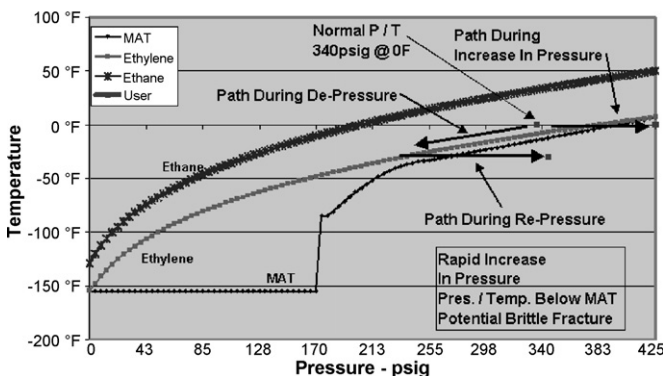


Fig. 8. Example of De-Ethanizer Reflux Drum MAT.

## Brittle Fracture Analysis Report for Example: Nitrogen in a Vessel

Fail Level 2 - Maximum difference between the MAT and vapor pressure curves or User entered points = 37°F.  
 Difference for selected curves: User entered points = 37°F  
 Minimum acceptable (coldest) temperature (MAT) when the pressure is at the MAWP is 37°F.  
 Maximum permitted pressure when the temperature is at -155°F is 148 psig  
 Recommended minimum field hydrotest temperature = 67°F

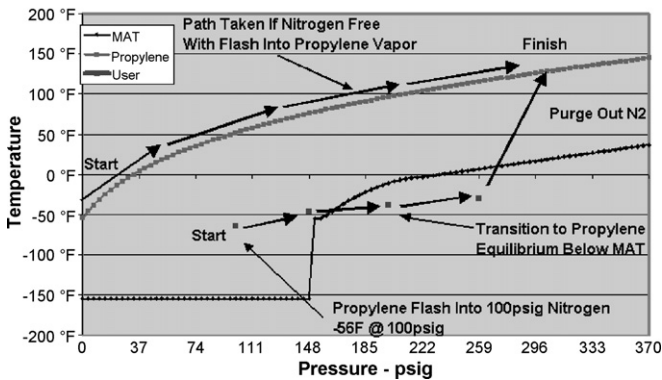


Fig. 10. Example of Nitrogen-Filled Vessel During Inventory.

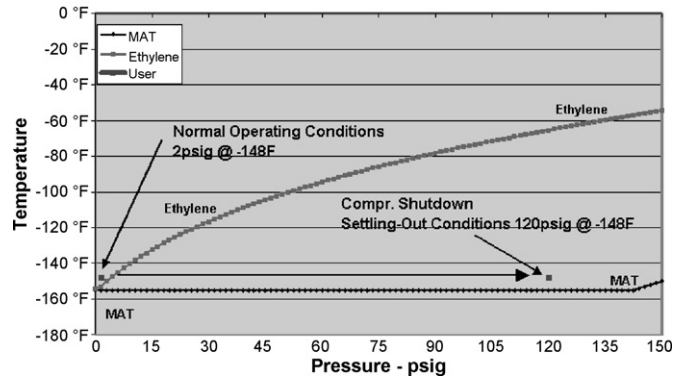
The nitrogen contained in the process is free of any hydrocarbon. The effect is to lower the partial pressure of the hydrocarbon below the expected flash temperature (CET) for the hydrocarbon at the measured process pressure. Process simulation indicates that ethylene can flash to as low as  $-190^{\circ}\text{F}$  ( $-123^{\circ}\text{C}$ ) when it is at equilibrium with nitrogen at atmospheric pressure. This is  $40^{\circ}\text{F}$  ( $22^{\circ}\text{C}$ ) lower than the normal atmospheric flash temperature of  $-150^{\circ}\text{F}$  ( $-101^{\circ}\text{C}$ ). Propylene can flash to as low as  $-110^{\circ}\text{F}$  ( $-79^{\circ}\text{C}$ ) in nitrogen, compared to its normal atmospheric flash temperature of  $-53^{\circ}\text{F}$  ( $-47^{\circ}\text{C}$ ). These substantially suppressed temperatures present lower CETs than would be expected based solely on the light hydrocarbon material being contained. Because the temperature reduction is due to the presence of the nitrogen, the CET can occur while substantial pressure is applied to the vessel. Such suppressed CETs at substantial pressure can present a brittle fracture potential for the exposed vessel as the pressure builds during the introduction of the light hydrocarbon. Fig. 10 shows an example using propylene as the light hydrocarbon. The MAT is for a vessel made from SA516-70 non-PWHT. It can be seen that introducing propylene into the nitrogen-filled vessel padded at 100 psig (0.689 MPa) results in a flash temperature of  $-56^{\circ}\text{F}$  ( $-49^{\circ}\text{C}$ ). As the vessel builds pressure and the nitrogen is vented off, the propylene moves to its vapor/liquid equilibrium temperature, but not without being substantially below the MAT. Freeing the vessel of nitrogen by purging with propylene vapor prevents exposure below the MAT.

This same effect can occur during other process steps where nitrogen is introduced into the process and where there is sufficient mixing to allow the light hydrocarbon and the nitrogen to reach equilibrium. Process equipment, such as dryer or catalyst beds are at risk if nitrogen or other non-condensable vapors, such as methane or hydrogen are used as a purge or drying media. Such auto-refrigeration excursions can occur at substantial pressures and place the vessel at risk of brittle fracture.

## Brittle Fracture Analysis Report for Example Compr. Suction Drum (-150F Charpy)

MAT is acceptable for the vapor pressure curves and the User operating pressure/temperature combinations

Minimum acceptable (coldest) temperature (MAT) when the pressure is at MAWP -150°F.  
 Maximum permitted pressure when the temperature is at -155°F is 143 psig  
 Recommended minimum field hydrotest temperature = -120°F

Fig. 11. Example of Compressor Suction Drum MAT ( $-150^{\circ}\text{F}$  Charpy).

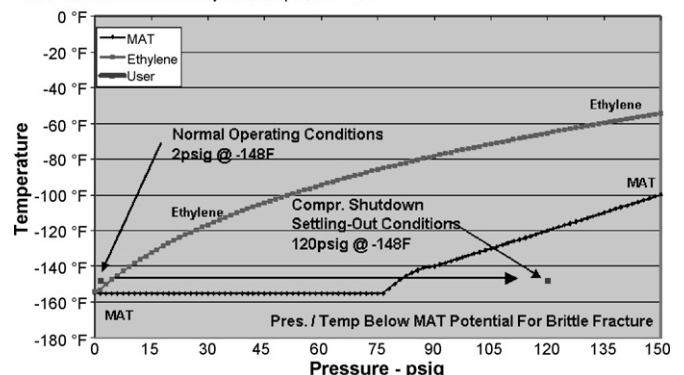
## 4.7. Compressor Suction Drums

Multi-stage compressor trains represent an unusual case for evaluation. The normal operating pressure can be substantially different than the “settling out pressure” that occurs when the compressor is stopped. For compressor suction drums, the normal operating temperature can be rather low at a correspondingly low pressure. When the compressor stops, the settling out pressure can be substantially higher as the pressure equalizes across all of the compressor stages. With the pressure rise being rather rapid and the suction drum being filled only with vapor, there is insufficient time to allow the vessel wall temperature to maintain equilibrium with the rise in pressure. If the vessel material-of-construction is not specified correctly, this increase in pressure can result in vessel conditions being below the MAT. Two examples are presented that reflect these potential results.

Fig. 11 represents the transient shutdown for a compressor suction drum made of material specified with a  $-150^{\circ}\text{F}$  ( $-101^{\circ}\text{C}$ ) Charpy impact temperature. It can be seen that the sudden rise in the pressure conditions results in a CET above

## Brittle Fracture Analysis Report for Example Compr. Suction Drum (-100F Charpy)

Fail Level 2 - Maximum difference between the MAT and vapor pressure curves or User entered points = 28°F.  
 Difference for selected curves: User entered points = 28°F  
 Minimum acceptable (coldest) temperature (MAT) when the pressure is at MAWP is -100°F.  
 Maximum permitted pressure when the temperature is at -155°F is 77 psig  
 Recommended minimum field hydrotest temperature = -70°F

Fig. 12. Example of Compressor Suction Drum MAT ( $-100^{\circ}\text{F}$  Charpy).

the MAT of the vessel, making this example acceptable for service. Fig. 12 represents the same design, but specified with a  $-100^{\circ}\text{F}$  ( $-73.3^{\circ}\text{C}$ ) Charpy impact temperature. Using ASME BPVC Section VIII, Division 1 and Division 2 Code rules [4], this material-of-construction selection would be acceptable for the normal operating condition due to the reduced stress condition. For the vessel in Fig. 12, the CET is below the MAT at the settling out upset conditions, making the vessel susceptible to brittle fracture.

#### 4.8. Compressor Discharge Drums

Compressor discharge drums present a similar challenge except that at normal operating conditions these drums contain condensed light hydrocarbon liquid at a substantial pressure. Upon shutdown of the compressor, the discharge side of the system will slowly lose pressure, resulting in auto-refrigeration of the liquid thus chilling the vessel. Upon restart of the compressor, the discharge pressure rises very rapidly, much faster than conductive heat transfer can warm the vessel wall. Under these conditions, steps must be taken to rid the vessel of the auto-refrigerating liquid or a different material-of-construction should be specified to prevent having the CET below the MAT. Fig. 13 represents an example compressor discharge drum undergoing a slow de-pressure event with subsequent compressor restart. It illustrates how the discharge drum ends up at CET conditions below the MAT, once the normal compressor discharge pressure is re-established.

#### 4.9. Loss in heat input

Vessels that normally receive a heated process stream may not be designed to accept the non-heated stream without conditions being below the MAT. Vessels such as acetylene guard beds/reactors and product surge drums are susceptible to being chilled if the heat source is lost to the primary heat exchanger. Fig. 14 represents an example product surge drum that depends on a pre-heat exchanger to keep process conditions above the

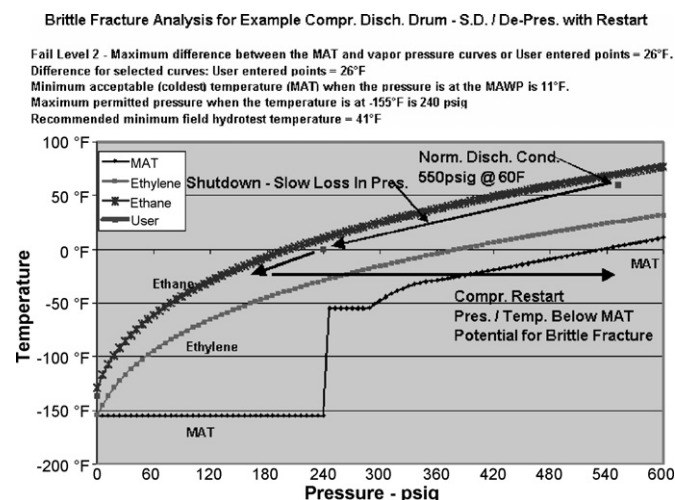


Fig. 13. Example of Compressor Discharge Drum MAT—Loss in Pressure with Restart.

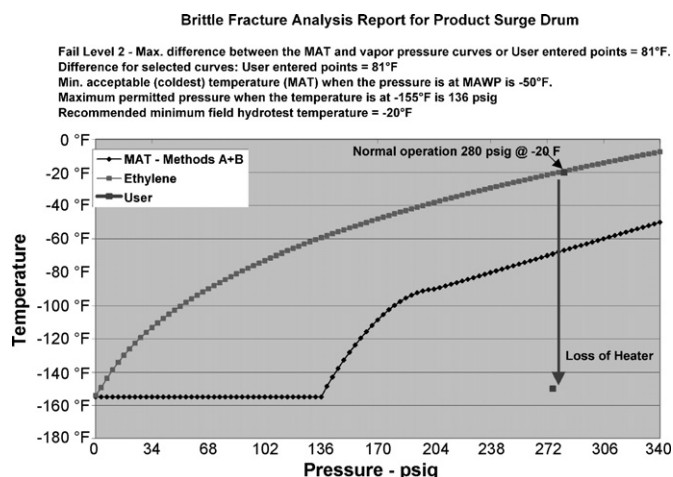


Fig. 14. Example of Product Drum MAT—Loss in Heat Input.

MAT. Failure of the heating source has the potential for process CET to be under the MAT.

The vessel is acceptable for “normal” process conditions but is not acceptable under “upset” conditions where heat input is lost. This scenario is very common for processing units that take a light-liquid hydrocarbon as a feedstock, but processes the hydrocarbon as a vapor. Options for mitigating this potential scenario are replacement of the vessel with one that has the appropriate MAT or installation of protective interlocks.

#### 4.10. Overflow/Transport of Liquid

Another potential scenario involves the overflow or transport of a light-liquid hydrocarbon into sections of the process that are not supposed to contain liquids. Typically, these type scenarios occur due to multiple failures during a chain of events, culminating in an auto-refrigeration excursion. The carry over of liquid into downstream systems can be an initiator or a consequence of the chain of events. A particular area of concern in an olefins plant equipped with a back-end acetylene converter is the carry over of liquid material out of the de-ethanizer reflux drum into the normally dry acetylene converter pre-heat exchanger train. For a brittle fracture potential to exist in this scenario, all three of the following conditions must occur:

- (1) The level in the de-ethanizer reflux drum must increase, overflowing the drum to the downstream exchanger train.
- (2) The pressure of the acetylene converter exchanger train must be reduced due to operations response or due to automated control actions, resulting in auto-refrigeration of the exchanger.
- (3) Through operator actions, normal process pressure is restored to the exchanger train after the exchangers are chilled due to auto-refrigeration.

If any one of the above items does not occur, the potential for brittle fracture, even under low temperature auto-refrigeration conditions is reduced.



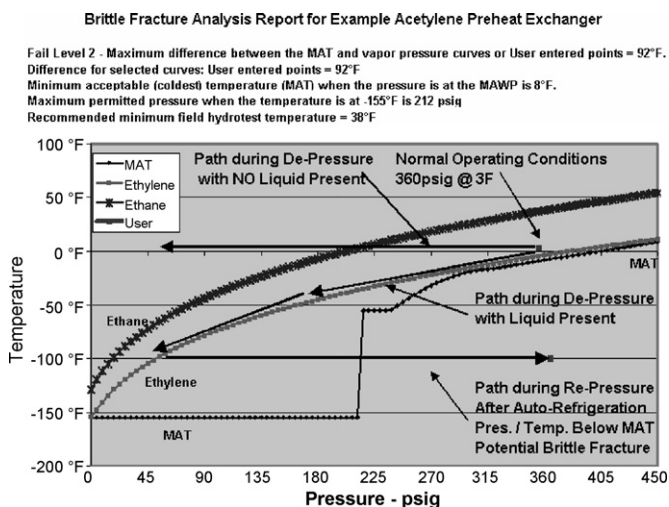


Fig. 15. Example of Acetylene Converter Preheat Exchanger MAT.

Fig. 15 represents an example of the MAT for a typical back-end acetylene converter pre-heat exchanger. For this example, the pressure/temperature (CET) conditions can be well below the MAT after operations re-establishes normal operating pressure.

This scenario has been the cause for brittle fracture occurrences in ethylene plant acetylene converter pre-heat exchanger trains. Prevention of this type of excursion can take the form of high-level alarms and/or overhead isolation valves to prevent allowing the liquid-light hydrocarbon from entering the downstream equipment. This example is particularly important from an operator response/training perspective. This is a rather typical vessel made of SA516-70 non-PWHT carbon steel. Thousands of these types of vessels are in light-liquid hydrocarbon services. Operations personnel should be trained that anytime a de-pressure excursion occurs; the vessel temperature must be confirmed *prior* to re-establishing normal operating pressure. If it is determined that the vessel is cold due to auto-refrigeration, the pressure is *not* to be increased on the vessel until it has been warmed. Operations personnel should be trained to avoid the auto-refrigeration excursion. Failing that, they are *never* to increase the pressure on a cold vessel.

## 5. General observations

Based on the experience of executing several auto-refrigeration/brittle fracture reviews of existing olefins and polymer plants, a number of general observations can be made about the design and operation of a typical light-liquid hydrocarbon processing plant and about the evaluation process to identify potential scenarios.

(1) Plants were designed for steady-state operating conditions: Since many processing plants were built prior to full understanding of auto-refrigeration and potential brittle fracture, the current materials-of-construction do not reflect these now known temperature limitations. In many instances, the startup/shutdown or upset conditions were not fully evaluated when making vessel materials-of-construction deci-

sions. In many cases, the mere act of removing heat input from the process exposes vessels to a temperature potentially below the MAT.

- (2) A single event block: Using the described PHA methods indicate that in many instances operating mode sequences can result in auto-refrigeration. Often only one event block separates conditions from being at potential risk of brittle fracture. Additional protective measures to avoid the excursion or to prevent certain sequence of events are required to ensure adequate levels of protection.
- (3) Materials-of-construction selection for new vessels: In many instances, the materials-of-construction do not provide adequate separation between process CET and vessel MAT. For a vessel to be intrinsically safe, the MAT (MDMT) should be set at the lowest possible CET. For small vessels, there are minimal cost implications for this selection. For larger vessels, a more detailed analysis may allow selection of a lower-cost alloy as long as adequate separation is provided between the CET and MAT under all operating modes. Adequate separation must be provided to allow vessel wall temperature to return to equilibrium conditions with the process without reaching the MAT.
- (4) Key points for a successful Auto-Refrigeration/Brittle Fracture Review program:
  - (a) Management Support: Support of both the review process and the follow up recommendations.
  - (b) Analyze Equipment: *All* vessels that contain or have the potential to contain a light-liquid hydrocarbon must undergo an analysis.
  - (c) Simulate Process Conditions: In cases where the normal operation is close to the MAT curve, process simulation results may be necessary to accurately predict the behavior of the hydrocarbon mixture.
  - (d) Get the Right Team: Key to the success of the team is to have an operational expert. The operational expert is that key, highly-experienced operations representative (operator, supervisor or specialist) who understands how, when and why certain operational actions are taken.
  - (e) Have Dedicated Resources: A high-intensity, short-term effort is required to maintain focus and to bring about completion of the review.
  - (f) Acceptable Risk: Pre-define the level of acceptable risk (risk matrix—consequence and predicted frequency of occurrence) prior to the review.
  - (g) Risk Ranking: During the PHA, the team should rank each scenario that results in a recommendation to determine when sufficient levels of protection/mitigation have been attained. Ranking scenarios after the PHA results in substantial confusion by uninvolved project team members.
- (5) Evaluate abnormal operations: Auto-refrigeration excursions by their nature, do not occur during steady-state operations. In order to identify possible auto-refrigeration excursions, the team must consider process upset scenarios that are far removed from normal operations and likely outside the past operating history or experience. In addition to

normal operations, the team must consider:

- normal operation,
- upset conditions,
- normal startup,
- normal shutdown,
- emergency shutdown,
- air freeing/nitrogen freeing,
- inventory,
- de-inventory,
- not in operation/maintenance-in-progress,
- commissioning/leak testing.

The challenge to the review team members is to identify all of the ways the pressure and/or temperature excursions can occur and to develop appropriate action items to prevent or mitigate the risk. Use of the process data history to search for temperatures at or below the affected vessel MAT can assist in identification of past excursions that potentially could have resulted in brittle fracture.

- (6) Provide training: Key to a safe recovery from an auto-refrigeration excursion is for operations personnel to be well trained in the phenomenon of auto-refrigeration. How to prevent it from occurring, how to identify that it is occurring, what to do if confronted with auto-refrigeration, and just as important, what *not* to do if confronted with auto-refrigeration. Training provides the first line of defense in preventing auto-refrigeration excursions.
- (7) Inspection guidelines: Provide guidance to inspection personnel on the method and extent of postauto-refrigeration excursion inspection. The extent of the inspection is based on the excursion CET compared to the vessel MAT.

## 6. Concluding remarks

This description of an auto-refrigeration/brittle fracture review process is provided to encourage owner/operators of light-liquid hydrocarbon processing units to evaluate their existing units for auto-refrigeration/brittle fracture potential. The “Findings” and “General observations” are provided as thought-provoking examples of some of the potential scenarios that can be identified while undertaking such a review. Making appropriate process changes, installing alarms and interlocks and training operating personnel in how to properly respond has been emphasized. These actions should avoid excursions and ensure that the CET is above the MAT under all possible operating conditions. Replacement of equipment with upgraded materials-of-construction/metallurgy is suggested when an appropriate level of protection cannot be obtained by other means.

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## Glossary

*Auto-Refrigeration*: The UNINTENTIONAL and UNCONTROLLED phase change from a liquid to a vapor of a hydrocarbon that results in refrigeration.

*Brittle Fracture*: The sudden and often catastrophic fracture of a material with little or no plastic deformation. Failure occurs with minimum energy absorbed in the material prior to fracture. Occurs with rapid crack propagation through the material with no prior indication (leak-before-break).

*Critical Exposure Temperature (CET)*: The lowest temperature experienced by the piece of equipment as a result of auto-refrigeration.

*Maximum Allowable Working Pressure (MAWP)*: The maximum pressure the vessel may experience so as to keep within code-allowable stress.

*Minimum Allowable Temperature (MAT)*: The lowest temperature allowed at a coincidental pressure to ensure the vessel remains ductile.

*Minimum Design Metal Temperature (MDMT)*: The MAT at MAWP—the lowest temperature allowed at MAWP to ensure the vessel remains ductile.

*Post-weld Heat Treat (PWHT)*: Post-welding thermal heat treatment of the vessel to refine the weld metallurgy and to reduce residual stresses.