

Brittle Fracture Risk in Legacy Refinery Assets from LPG Auto-Refrigeration: Assessment, Mitigation, and Case Studies

Executive Summary

The petroleum refining industry is confronting an emergent, high-consequence risk associated with the brittle fracture of aging assets, particularly those in Liquefied Petroleum Gas (LPG) service. This risk stems from a critical design gap: pressure equipment fabricated before the comprehensive code revisions of 1987 was often not designed to withstand the severe, transient low temperatures induced by the auto-refrigeration of LPG during process upsets, leaks, or depressurization events. While the underlying physics is not new, the industry-wide recognition of this latent threat is a recent and urgent development, demanding a paradigm shift in asset integrity management.

This report provides an exhaustive technical analysis of this complex hazard. It begins by elucidating the fundamental principles of brittle fracture in steel and the thermodynamics of LPG auto-refrigeration, establishing the critical link between these two phenomena. It then delivers a comprehensive guide to quantifying the risk, detailing methodologies for calculating the potential auto-refrigeration temperature—the Critical Exposure Temperature (CET)—ranging from foundational thermodynamic principles to advanced computational simulation.

The cornerstone of a modern response to this hazard is the API 579-1/ASME FFS-1 "Fitness-For-Service" standard. This report provides a detailed, step-by-step walkthrough of the three-level brittle fracture assessment procedure outlined in Part 3 of this standard, which forms the definitive framework for evaluating the suitability of legacy equipment for continued operation.

To ground the analysis in empirical evidence, the report presents a series of detailed case studies. These include catastrophic failures, such as the Husky Superior Refinery explosion and various LPG tank ruptures, which serve as stark reminders of the potential consequences when safety barriers fail. Conversely, case studies of

successful proactive assessments demonstrate how the FFS framework can be leveraged not only to ensure safety but also to optimize operations and reduce maintenance costs, transforming a compliance requirement into a value-adding activity.

Finally, the report formulates a robust set of actionable mitigation strategies based on a defense-in-depth philosophy. These strategies encompass engineering solutions such as material upgrades and Post-Weld Heat Treatment (PWHT), as well as critical operational and procedural controls, including the development of safe operating envelopes and rigorous operator training. The strategic recommendations provided are designed to guide refinery management in implementing a comprehensive, proactive, and "evergreen" asset integrity program to address this specific and significant hazard, ensuring both the safety and long-term reliability of legacy assets.

Section 1: The Confluence of Hazards: Brittle Fracture and Auto-Refrigeration

The threat to aging refinery assets from LPG service arises from the dangerous intersection of a well-understood material failure mechanism—brittle fracture—and a specific thermodynamic process—auto-refrigeration. While individually recognized for decades, it is the growing awareness of their potential to combine during process upsets that constitutes a significant and previously underestimated risk to equipment designed under older codes.

1.1 The Nature of Brittle Fracture in Steels

Brittle fracture is characterized as the sudden, catastrophic failure of a component under stress, where the material exhibits little to no measurable plastic deformation before breaking.¹ Unlike a ductile failure, which provides warning through yielding and thinning, a brittle fracture is an instantaneous event, with cracks propagating at speeds approaching the velocity of sound in steel, up to 7,000 feet per second.¹ This can result in the equipment shattering into multiple pieces, leading to a massive and uncontrolled release of hazardous materials.⁴ The occurrence of this phenomenon is

governed by the convergence of three specific conditions, often conceptualized as the "brittle fracture triangle".⁵ The potential for brittle fracture exists when this triangle is "closed," meaning all three conditions are met simultaneously.

1. **Sufficient Stress:** The first side of the triangle is the presence of adequate stress to drive crack propagation. A particularly insidious aspect of brittle fracture is that the required stress can be well below the material's nominal yield strength, often a load that the component has successfully withstood numerous times before.¹ The total stress acting on a potential flaw is a combination of primary stresses from internal pressure, and secondary stresses, which include residual stresses locked into the material from fabrication and welding, and thermal stresses induced by rapid temperature changes.⁸ Residual stresses from welding, in particular, can be near yield-strength magnitude and are a major contributor to the risk, especially in non-post-weld heat-treated components.¹⁰
2. **A Critical Flaw:** Brittle fractures do not initiate in perfect material; they almost invariably originate from a pre-existing flaw or stress concentrator.¹ These flaws can be macroscopic or microscopic and can be introduced during the original manufacturing of the equipment. Common fabrication flaws include lack of weld fusion, slag inclusions, porosity, or undercuts.¹¹ Flaws can also be created during the equipment's service life through damage mechanisms such as fatigue cracking, stress corrosion cracking, or hydrogen-induced cracking.¹⁰ The challenge is that many of these critical flaws can be small, tightly closed, and difficult to detect with standard in-service inspection methods, creating a hidden vulnerability within the asset.¹⁰ The catastrophic failure of an LPG tank in one case study was traced directly to a full-length axial crack introduced by improper weld repair during fabrication decades earlier.¹²
3. **Susceptible Material at Low Temperature:** The final and most critical condition is that the material itself must be in a "brittle" state, meaning its fracture toughness is low. For carbon and low-alloy steels, which constitute the bulk of older refinery equipment, fracture toughness is not a constant property but is highly dependent on temperature.² As the temperature of the steel decreases, its ability to deform plastically and absorb energy is reduced, making it more susceptible to fracture.

Two key material properties govern this behavior:

- **Ductile-to-Brittle Transition Temperature (DBTT):** Also referred to as the Nil Ductility Temperature (NDT), the DBTT represents a temperature range over which the failure mode of steel transitions from ductile (tearing with significant energy absorption) to brittle (cleavage with very little energy absorption).²

Operating a piece of equipment at or below its DBTT places it at high risk for brittle fracture.² The failure of an LPG storage vessel during a hydrotest was attributed in part to the vessel metal having turned brittle in service from repeated chilling, lowering its temperature into the transition range.⁹

- **Fracture Toughness (KIC):** This is a quantitative measure of a material's intrinsic resistance to the propagation of a pre-existing sharp crack.³ A material with high fracture toughness is resistant to fracture, while one with low toughness is not. For ferritic steels, fracture toughness decreases dramatically as the temperature drops, meaning a flaw that is stable and benign at operating temperature can become critical and lead to catastrophic failure if the equipment is sufficiently chilled.³ The quality of the steel and its processing history are paramount; heat treatments like normalization can produce a more uniform, fine-grained microstructure that significantly improves fracture toughness and lowers the DBTT.¹⁰

The history of engineering is marked by catastrophic brittle fractures, from the failures of Liberty ships in the cold waters of the North Atlantic during World War II to the rupture of a molasses tank in Boston in 1919.³ These events serve as powerful reminders of the devastating potential when the three sides of the fracture triangle—stress, a flaw, and low-temperature material susceptibility—align.

1.2 The Auto-Refrigeration Phenomenon in LPG Service

Auto-refrigeration is the thermodynamic process responsible for creating the low-temperature condition that can render steel equipment brittle. It is an unintentional, uncontrolled, and rapid chilling effect that occurs when a liquefied compressed gas, such as LPG, undergoes a phase change from a liquid to a vapor.⁵

The process is fundamentally an isenthalpic (constant enthalpy) flash evaporation, analogous to a Joule-Thomson expansion.¹⁴ When a vessel or pipe containing pressurized liquid LPG is suddenly depressurized (e.g., through a leak or an open valve), the pressure drops abruptly. To reach a new equilibrium at the lower pressure, a portion of the liquid must flash into vapor. This phase change requires a significant amount of energy, known as the latent heat of vaporization. In an uncontrolled event, this energy is drawn rapidly from the most immediate source: the remaining liquid itself and the metal walls of the containing equipment.⁸ This rapid extraction of heat causes a dramatic drop in the temperature of the liquid and the equipment. A

common visual manifestation of this effect is the formation of frost on the outside of a propane tank during high rates of gas withdrawal, as the tank surface is chilled below the dew point of the surrounding air.⁸

While this cooling effect is harnessed intentionally in refrigeration cycles, its unintentional occurrence in a process environment can be extremely hazardous. Several common scenarios within a refinery can trigger auto-refrigeration in LPG and other light hydrocarbon services ⁵:

- **Depressurization Events:** The controlled or emergency depressurization of a vessel or piping system to a low-pressure flare header is a primary cause. The rapid venting of vapor causes the liquid in the vessel to boil vigorously, chilling the system.¹¹
- **Leaks and Ruptures:** A leak through a failing valve, flange gasket, or a crack in a pipe can lead to flashing if the downstream pressure (e.g., atmospheric) is below the boiling point of the LPG at that pressure.¹¹
- **Operational Upsets:** A variety of process deviations can lead to auto-refrigeration. These include the loss of heat input to a distillation column's reboiler, which stops vapor generation and can cause a pressure and temperature drop. Another example is overfilling a vessel, which can cause liquid to be carried over into a gas outlet line and flash across a control valve. Backflow from common headers, such as flare or liquid drain systems, can also introduce cold, flashing liquid into equipment not designed for it.¹¹
- **Pressure Safety Valve (PSV) Operation:** The activation of a PSV involves a very rapid, high-volume release of fluid. This can severely chill the valve body and the downstream flare piping, potentially compromising their integrity if they are not made of suitable low-temperature materials.¹⁸

1.3 The Latent Threat in Older Assets: The MDMT Design Gap

The core of the problem addressed in this report lies in the disconnect between the historical design practices for pressure equipment and the now-recognized reality of auto-refrigeration as a credible low-temperature event. The physics of brittle fracture and auto-refrigeration have been understood for many decades. The "new trend" is not a change in science, but rather a crucial shift in industry awareness. There is a growing recognition that a vast inventory of aging equipment, designed and built before modern code revisions, carries a latent, unassessed vulnerability. The risk was

always present; what is new is the widespread understanding of its significance and the development of formal engineering frameworks, like API 579-1/ASME FFS-1, to address it.

The critical turning point in design philosophy occurred with the December 1987 addenda to the ASME Boiler and Pressure Vessel Code, Section VIII, Division 1.¹⁹ Before this date, the code generally permitted the use of common carbon steel pressure vessels for service temperatures as low as -20°F (-29°C) without requiring any formal impact testing to verify their toughness.⁴ This exemption was based on a long history of successful service under

normal operating conditions.

This created a critical design gap. The Minimum Design Metal Temperature (MDMT) stamped on the nameplate of a pre-1987 vessel was typically based on the lowest anticipated ambient temperature or normal process temperature.²³ It almost certainly did not account for the possibility of a severe, transient low-temperature excursion caused by auto-refrigeration.¹¹ An upset event involving the depressurization of propane can easily chill the equipment metal to its atmospheric boiling point of -42°C (-44°F).²⁵ This temperature is significantly colder than the -29°C (-20°F) for which the vessel was implicitly deemed safe, placing the equipment squarely within its potential brittle fracture range and creating the conditions for a catastrophic failure.²¹ This gap between the original design basis and a credible upset scenario is the central reason why a systematic reassessment of these legacy assets is imperative for ensuring plant safety.

Section 2: Quantifying the Chill: Calculation of Auto-Refrigeration Temperatures

To assess the risk of brittle fracture, the first step is to accurately determine the lowest metal temperature the equipment could experience during an upset. This is known as the Critical Exposure Temperature (CET).¹¹ There is no single "unified method" for this calculation; rather, a spectrum of methods exists, ranging from simple, conservative estimations to complex, high-fidelity simulations. The selection of a method is not merely a technical choice but a strategic one, balancing the cost and effort of the analysis against the potential cost of unnecessarily replacing or

modifying equipment based on an overly conservative temperature prediction.

2.1 Foundational Thermodynamic Methods

These methods rely on fundamental thermodynamic principles and are suitable for initial screening or for simple, single-component systems.

- **Vapor-Pressure Relationship:** This is the most straightforward and conservative approach. It assumes that upon depressurization, the liquid will cool to its boiling point corresponding to the final pressure of the system.⁸ For an LPG vessel leaking or venting to the atmosphere, the final pressure is 1 atm. The CET is therefore assumed to be the atmospheric boiling point of the LPG. For pure propane, this is -42°C (-44°F).²⁵ This method provides a quick, worst-case estimate that requires only a vapor-pressure curve for the substance. While simple, its high conservatism may lead to disqualifying equipment that would be deemed safe by a more detailed analysis.
- **Isenthalpic Flash Calculations (Joule-Thomson Expansion):** This method provides a more accurate thermodynamic model of the flash evaporation process. It is based on the First Law of Thermodynamics, assuming the expansion is adiabatic (no heat exchange with the surroundings) and therefore occurs at constant enthalpy (an isenthalpic process).¹⁴ The calculation procedure is as follows:
 1. Determine the specific enthalpy (h_{initial}) of the liquid at its initial temperature and pressure, just upstream of the pressure drop. This can be found using thermodynamic property tables or software.
 2. Recognize that the final state will be a two-phase mixture of liquid and vapor at the lower downstream pressure. The enthalpy of this mixture (h_{final}) is equal to the initial enthalpy (h_{initial}).
 3. The final temperature is the saturation temperature corresponding to the final pressure. The quality, or vapor fraction (x), of the mixture can be calculated using the formula $h_{\text{final}} = h_{\text{liquid}} + x \cdot h_{\text{vaporization}}$, where h_{liquid} and $h_{\text{vaporization}}$ are the enthalpy of the saturated liquid and the latent heat of vaporization at the final pressure, respectively.

This calculation can be performed graphically using a $\log(p)$ - h (pressure-enthalpy) diagram, a standard tool in refrigeration engineering.²⁶ For multi-component mixtures, which are common in refinery LPG streams, a more complex iterative calculation, such as the Rachford-Rice method, is required to solve for the equilibrium temperature,

pressure, and phase compositions.²⁷

2.2 Advanced Simulation and Computational Methods

For complex systems or when a more realistic result is needed to avoid unnecessary capital expenditure, advanced modeling tools are employed.

- **Dynamic Process Simulation:** Using commercial process simulators like Aspen HYSYS is the industry-standard approach for analyzing system-wide depressurization scenarios.²⁸ Unlike a simple adiabatic flash, a dynamic simulation models the process over time and can incorporate crucial real-world effects, most importantly, heat transfer.³¹ The model can account for the heat stored in the mass of the vessel walls and insulation, as well as heat ingress from the ambient environment. This heat transfer counteracts the chilling effect of the auto-refrigeration, resulting in a more realistic and typically warmer (less severe) prediction for the minimum metal temperature.³² These simulations are essential for accurately designing depressurization systems and for FFS assessments of high-value assets where a conservative estimate would lead to costly and unnecessary modifications.²⁹
- **Computational Fluid Dynamics (CFD) and Finite Element Analysis (FEA):** For components with intricate geometries and complex flow patterns, such as control valves or pressure safety valves (PSVs), a bulk fluid temperature calculation is often insufficient. High-velocity flow through the valve can create localized cold spots due to the Joule-Thomson effect that are much colder than the average fluid temperature.¹⁸ In these cases, a multi-physics approach is used:
 1. **CFD:** A CFD model is created to simulate the detailed fluid flow, pressure drop, and temperature distribution within the valve body during the depressurization event. This identifies the precise location and magnitude of the minimum temperature.¹⁸
 2. **FEA:** The detailed temperature profile from the CFD analysis is then applied as a thermal load to a Finite Element Analysis (FEA) model of the valve body. The FEA model calculates the resulting thermal stresses caused by the sharp temperature gradients.This combined CFD-FEA approach is a highly specialized, Level 3 FFS technique. It is often used to justify the continued service of critical and expensive components that might be conservatively disqualified by simpler methods, thereby avoiding costly replacements.¹⁸

2.3 Comparison of Methodologies and Selection Guidance

The choice of calculation method is a critical decision that directly influences the outcome of the brittle fracture assessment. Opting for a simple, highly conservative method is inexpensive but carries the risk of condemning a perfectly safe piece of equipment, potentially triggering millions of dollars in unnecessary replacement or modification costs. Conversely, investing in a more complex and accurate analysis, like a dynamic simulation, requires more engineering effort but can provide the rigorous justification needed to keep a valuable asset in service safely. This trade-off between analysis cost and potential capital expenditure means the selection process is a strategic engineering and business decision.

The following table provides a comparative overview to guide the selection of the most appropriate method for a given situation.

Method	Underlying Principle	Data Requirements	Typical Application	Relative Cost	Conservatism Level
Vapor-Pressure Curve	Thermodynamic Equilibrium	Fluid identity, final pressure, vapor-pressure data ¹⁶	Initial, rapid screening of many components; worst-case scenario definition.	Very Low	Very High
Isenthalpic Flash Calculation	First Law of Thermodynamics (Constant Enthalpy)	Initial T&P, final P, fluid composition, enthalpy data (or log(p)-h chart) ¹⁴	FFS Level 1/2 screening; simple, single-vessel depressurization analysis.	Low	High
Dynamic Process Simulation	Energy & Mass Balance over	Full process data, equipment	System-wide PHA studies; FFS Level 2/3	Medium	Medium

(e.g., HYSYS)	Time	geometry, material properties, insulation details ²⁹	assessments ; justifying continued service of high-value assets.		
CFD / FEA	Fluid Dynamics & Structural Mechanics	Detailed 3D geometry, fluid properties, material properties, boundary conditions ¹⁸	FFS Level 3 assessment of complex components (e.g., PSVs, control valves); resolving highly localized cooling/stress issues.	High	Low

Section 3: A Framework for Reassessment: API 579-1/ASME FFS-1, Part 3

Once the potential for low-temperature excursions has been identified and the Critical Exposure Temperature (CET) has been quantified, a formal engineering assessment is required to determine if the existing equipment is "fit for service" under these conditions. The definitive industry standard for this task is the joint American Petroleum Institute (API) and American Society of Mechanical Engineers (ASME) document, API 579-1/ASME FFS-1, "Fitness-For-Service".¹¹

3.1 Introduction to Fitness-For-Service (FFS)

The FFS standard provides a comprehensive set of quantitative engineering evaluation procedures to demonstrate the structural integrity of in-service components that may contain flaws, have sustained damage, or are being subjected to conditions outside their original design basis.³⁶ It is the industry-accepted methodology for making

rational, data-driven decisions to run, repair, re-rate, or replace equipment.¹¹ The standard is perfectly suited for addressing the brittle fracture risk from auto-refrigeration, as this represents a classic case of an existing asset facing a hazard that was not contemplated in its original design.¹¹

The core principle of a brittle fracture assessment under Part 3 of the standard is the comparison of the demand placed on the equipment with its capability. The demand is the lowest potential metal temperature the component could experience, the CET. The capability is the material's inherent resistance to brittle fracture, expressed as the Minimum Allowable Temperature (MAT). The fundamental acceptance criterion is that for all credible operating and upset scenarios, the equipment must satisfy the condition:

$$\text{CET} \geq \text{MAT}$$

If this condition is met, the equipment is considered fit for service with respect to brittle fracture.⁵

3.2 The Three-Level Assessment Approach

API 579 Part 3 provides a tiered assessment methodology. This approach allows users to start with a simple, conservative screening and only proceed to more complex and data-intensive analyses if necessary. This graduated approach efficiently focuses engineering resources on the most critical or borderline cases.³⁹

- **Level 1 Assessment:**

- **Procedure:** This is a conservative screening assessment that can be performed by a qualified inspector or engineer with minimal data.⁴⁰ It utilizes a set of exemption curves, similar to those found in the ASME design codes, which define a single MAT value for a given material and its governing thickness.⁴² This MAT is then compared to the CET. The assessment is typically performed assuming the vessel is at its Maximum Allowable Working Pressure (MAWP).
- **Application:** Level 1 is ideal for rapidly screening a large inventory of vessels and piping systems. Its simplicity allows for the quick identification of equipment that is clearly acceptable (CET is much warmer than MAT) and those that are clearly problematic or require a more detailed evaluation. Various software tools are available that can automate this check, making it a

highly efficient first pass in a facility-wide assessment program.⁴⁴

- **Level 2 Assessment:**

- **Procedure:** If a component fails the Level 1 assessment, or if a more flexible operating window is desired, a Level 2 assessment is performed. This is a more detailed engineering analysis that requires more data and calculation but yields a less conservative result.⁴⁰ The key output of a Level 2 assessment is not a single temperature but a complete MAT versus pressure curve.⁵ This curve defines a safe operating envelope, explicitly taking credit for the fact that material can safely withstand colder temperatures if the stresses (i.e., internal pressure) are also reduced.
- **Application:** This is the most common assessment level performed in practice. It provides a practical and valuable tool for operations, as the resulting safe operating envelope can be used to develop specific procedures for startup, shutdown, and depressurization that ensure the asset remains outside the brittle fracture risk zone.⁵

- **Level 3 Assessment:**

- **Procedure:** This is the most rigorous, data-intensive, and least conservative assessment level. A Level 3 assessment is required if the component does not meet the criteria of Levels 1 or 2, or if there are complicating factors such as in-service embrittlement mechanisms (e.g., temper embrittlement in low-alloy steels or hydrogen embrittlement in hydroprocessing equipment).¹¹ The procedure involves a detailed fracture mechanics analysis, typically using the Failure Assessment Diagram (FAD) methodology described in API 579 Part 9.¹¹ This requires detailed stress analysis (often from an FEA model), assumptions or measurements of a postulated or actual flaw size, and specific material fracture toughness data (K_{IC}), which may need to be obtained from literature or through destructive testing of similar materials.
- **Application:** Level 3 assessments are reserved for highly critical or high-value equipment where the cost of the detailed analysis is justified by the need to avoid replacement or major modification. They are also necessary for complex scenarios involving multiple, interacting damage mechanisms where the simplified rules of lower levels do not apply.⁴⁶

3.3 Critical Considerations and Evolving Standards

Executing an FFS assessment requires careful attention to data quality and an understanding that the governing standards are not static. The accuracy of any FFS assessment is entirely dependent on the quality of the input data. This includes original design documents, certified material test reports (MTRs), fabrication records (especially verification of PWHT), detailed operating and maintenance history, and reliable inspection data.⁴⁰

Furthermore, it is crucial to recognize that the API 579-1/ASME FFS-1 standard is a living document. It is periodically updated, with new editions released every few years to incorporate new research, technology, and lessons learned from industry failures.⁴⁸ For example, subsequent editions of the standard have introduced more restrictive brittle fracture screening procedures for certain components, such as ASME B16.5 flanges and the reinforcement zones around pressure vessel nozzles, because the previous rules were found to be inadequate.⁴⁸

This has a profound implication for asset integrity management. An FFS assessment performed today based on the 2007 edition of the standard may no longer be considered acceptable or sufficiently conservative under the rules of the latest 2021 edition.⁴⁸ Therefore, a facility's FFS program cannot be a "one-and-done" project. It requires an "evergreen" process, likely managed through a formal Management of Change (MOC) system, to periodically review past assessments against the current version of the standard. This ensures ongoing compliance, reflects the state-of-the-art in safety engineering, and properly manages long-term risk and liability. A failure to maintain this vigilance can lead to a false sense of security based on outdated and potentially non-conservative analysis.

Section 4: Case Studies: Lessons from Industry Experience

The theoretical risks of brittle fracture become tangible when examined through the lens of real-world incidents. Case studies of both catastrophic failures and successful proactive interventions provide invaluable lessons for refinery operators and engineers, highlighting the critical importance of a robust asset integrity program.

4.1 Catastrophic Failures: Learning from Disaster

These incidents demonstrate the severe consequences that can result from the alignment of flaws, stress, and low-temperature conditions, often exacerbated by breakdowns in multiple safety barriers.

- **Case Study: Husky Superior Refinery Explosion (2018)**

- **Narrative:** In April 2018, an explosion within the Fluid Catalytic Cracking (FCC) unit at the Superior, Wisconsin, refinery resulted in the catastrophic brittle fracture of a large pressure vessel. The vessel shattered, launching a large fragment that struck and punctured a nearby asphalt storage tank, leading to a major fire.⁴⁹
- **Analysis:** The U.S. Chemical Safety Board (CSB) investigation found that the failed vessel was constructed from ASTM A-212, an older grade of carbon steel known to have poor fracture toughness and a higher susceptibility to brittle fracture compared to modern steels.⁴⁹ A critical finding was that while the vessel's design and operating conditions may have been acceptable under normal circumstances, the existing Fitness-for-Service standards did not require an evaluation for extreme, low-probability events like an internal explosion.⁴⁹ The CSB concluded that a vessel made from a more modern, tougher steel would likely have failed in a ductile "fish-mouth" rupture rather than shattering, which would have significantly reduced the consequential damage. Following the incident, the refinery was mandated by the Occupational Safety and Health Administration (OSHA) to conduct a comprehensive, facility-wide auto-refrigeration and brittle fracture Process Hazard Analysis (PHA). This review identified 35 at-risk scenarios and resulted in 132 specific recommendations for mitigation.⁴⁹
- **Key Takeaway:** This case underscores a limitation of standard FFS assessments: they are designed for expected operating and upset conditions, not necessarily for extreme events. It highlights the principle of Inherently Safer Design, where the selection of superior materials of construction acts as a fundamental and robust layer of protection that can mitigate the consequences of even unforeseen events.

- **Case Study: LPG Storage Tank Rupture (Fabrication Flaws & Operational Failure)**

- **Narrative:** A fatal accident occurred when an LPG tank, fabricated in 1949, ruptured violently while sitting in direct sunlight at a scrap metal junkyard.¹²
- **Analysis:** A detailed multidisciplinary investigation revealed a "perfect storm" of compounding deficiencies. The primary cause was a critical fabrication defect: the tank's longitudinal seam had been improperly repaired during its

original construction with a shallow, partial penetration weld, leaving a full-length crack-like flaw. This was compounded by two other failures: the pressure relief valve had become inoperative due to severe rusting (a maintenance failure), and the tank had been overfilled to approximately 93% capacity instead of the standard 80% (an operational failure). A thermodynamic and fracture mechanics analysis, supported by hydrostatic burst tests on similar flawed tanks, confirmed that the solar heating of the overfilled, hydraulically-locked liquid generated sufficient pressure to cause the flawed weld to fail via brittle fracture.¹²

- **Key Takeaway:** Catastrophic failures are rarely the result of a single point of failure. They typically occur when multiple, independent safety barriers—in this case, design/fabrication, maintenance/inspection, and operations—fail simultaneously. This highlights the need for a holistic safety management system.
- **Case Study: LPG Bullet Failure During Hydrotest**
 - **Narrative:** A propane bullet, constructed in 1994, suffered a catastrophic brittle fracture during a routine hydrostatic pressure test, resulting in a fatality. This case is particularly alarming as the vessel was relatively modern.⁹
 - **Analysis:** The investigation concluded that the vessel material had likely become embrittled during its service life due to repeated low-temperature cycling from normal LPG withdrawal operations. This created a latent susceptibility to brittle fracture that was ultimately triggered by the high stresses of the hydrotest. Several contributing factors were identified, including the potential use of cold water for the test and an improper procedure that allowed air to be trapped, leading to a high-energy, pneumatic-like release upon failure. Furthermore, it was suspected that the steel plate (SA 516 Gr 70) may not have been supplied in the normalized condition, a critical heat treatment that improves low-temperature toughness and is often required for such service.⁹
 - **Key Takeaway:** Even equipment built after the 1987 code changes can be at risk if material specifications, fabrication quality control (like heat treatment), and testing procedures are not rigorously followed. A hydrostatic test is a significant stress event and must be treated as such, with strict controls on metal temperature (codes often require the test temperature to be at least 30°F above the MDMT) to prevent it from becoming the trigger for a brittle fracture.⁹

4.2 Proactive Assessments: Preventing Failure and Optimizing Operations

These case studies illustrate how a proactive approach using the FFS framework can not only prevent failures but also deliver significant operational and financial benefits.

- **Case Study: Refinery-Wide Proactive Brittle Fracture Assessment Program**
 - **Narrative:** This represents a composite case study based on the well-established practices of specialized engineering firms that conduct large-scale brittle fracture risk assessments for entire refineries or chemical plants.⁵
 - **Process:** The program is a systematic, multi-disciplinary effort. It begins with a comprehensive PHA to identify all equipment and piping systems that handle light hydrocarbons and could be subject to auto-refrigeration.⁵ For each identified asset, a Level 2 FFS assessment is performed to generate a detailed MAT versus pressure curve. This curve represents the equipment's capability. The PHA team then develops dynamic, sequence-driven scenarios to determine the CET for all credible upsets. By comparing the CETs (demand) with the MAT curves (capability), a formal, documented list of at-risk equipment is generated. This list becomes the basis for developing, prioritizing, and tracking specific mitigation actions, which can include engineering controls, administrative controls, and operator training.⁵
 - **Key Takeaway:** A systematic, proactive, and well-documented program is the most effective and legally defensible strategy for managing this complex risk on a facility-wide scale. It provides a clear, auditable trail that satisfies both internal process safety management (PSM) goals and external regulatory requirements.⁴¹
- **Case Study: Level 3 FFS on a Clad Hydroprocessing Reactor**
 - **Narrative:** An owner-operator needed to evaluate a heavy-walled hydroprocessing reactor that was subject to in-service degradation mechanisms—specifically, hydrogen embrittlement and long-term temper embrittlement. These conditions can significantly reduce material toughness and mandated a rigorous Level 3 FFS assessment.¹¹
 - **Analysis:** The Level 3 assessment, which employed advanced fracture mechanics using a Failure Assessment Diagram (FAD), yielded a new, less restrictive MAT curve for protection against fast, unstable fracture. The separate, but related, risk of slow, stable crack growth during startup/shutdown cycles was also evaluated. Rather than imposing overly conservative operating limits that would have severely hampered production,

the analysis showed this risk could be safely managed through an optimized, targeted inspection program focused on specific areas of the reactor.

- **Value Proposition:** This case perfectly illustrates that the goal of FFS is not simply to pass or fail a piece of equipment. By providing a precise, data-driven understanding of the true safe operating envelope, the assessment allowed the operator to dismantle unnecessary operational conservatism. The result was a significant reduction in costly unit start-up times without compromising safety.¹¹ This reframes the FFS process from a pure safety compliance cost into a powerful tool for asset optimization and improved profitability. Similarly, another case study on a piping program showed that a proactive FFS approach led to a 27.4% reduction in the number of required Condition Monitoring Locations (CMLs), focusing inspection resources where they were most needed and yielding a 3X return on investment.⁵³

Section 5: Mitigation and Modernization of Legacy Assets

For older refineries with a large inventory of potentially vulnerable equipment, a comprehensive mitigation strategy is essential. Since the complete replacement of major vessels is often economically prohibitive, a realistic approach must rely on a blended, defense-in-depth strategy. This involves implementing multiple, independent layers of protection that combine engineering solutions, material improvements, and robust operational controls.

5.1 Engineering and Material Solutions

These solutions aim to either eliminate the hazard or provide robust physical barriers to prevent failure, aligning with the higher tiers of the hierarchy of controls.

- **Material Selection and Upgrades:** The most effective and permanent solution to brittle fracture risk is to use materials that are inherently tough at the lowest credible operating temperature. For any new equipment, or for repairs and alterations to existing assets, this is the preferred approach.¹⁷
 - **Carbon Steels:** For low-temperature carbon steel service, it is critical to specify materials that are supplied in the normalized condition (e.g., ASME

SA-516 grades). Normalization is a heat treatment that refines the grain structure of the steel, significantly improving its low-temperature toughness and lowering its DBTT.⁹

- **Low-Alloy and Stainless Steels:** For service temperatures below the practical limits of carbon steel, or for highly critical applications, other materials should be selected. Low-alloy steels containing a few percent of nickel (e.g., ASME SA-203) offer excellent toughness at cryogenic temperatures. For the most severe conditions, austenitic stainless steels (e.g., 304 or 316 grades) are an ideal choice as they have a face-centered cubic crystal structure and do not exhibit a ductile-to-brittle transition, remaining tough even at very low temperatures.¹⁷ It is important to note that recent editions of the ASME codes have re-categorized some previously exempt carbon steel specifications, now requiring them to undergo impact testing to be qualified for low-temperature service, reflecting an industry-wide tightening of requirements.⁵⁶
- **Post-Weld Heat Treatment (PWHT):** PWHT is one of the most critical remediation techniques for improving the brittle fracture resistance of welded carbon and low-alloy steel components, especially on older assets that may not have been heat-treated originally or have undergone weld repairs.⁵⁷ The process involves uniformly heating the weldment to a specific soak temperature, holding it for a prescribed duration, and then cooling it at a controlled rate.⁵⁹
 - **Procedure for Carbon Steel:** The typical soak temperature range for stress relieving carbon steel is 1,100°F to 1,250°F (600°C to 675°C).⁶¹ The holding time is generally based on the thickness of the material, with a common rule being 1 hour per inch (25 mm) of thickness.⁶¹
 - **Benefits:** PWHT provides two primary benefits for brittle fracture mitigation. First, it significantly reduces the high residual stresses introduced by the welding process, which are a major contributor to the total stress driving crack propagation.⁵⁸ Second, it tempers the hard, brittle microstructures that can form in the weld and heat-affected zone (HAZ), restoring ductility and toughness to the region.⁵⁹ PWHT is a mandatory requirement in many modern construction codes for thicker sections or critical service and is a vital tool for managing the integrity of weld repairs on legacy equipment.¹⁰ PWHT can be performed in large furnaces for entire vessels or locally for specific welds on piping or large structures using electrical resistance or induction heating methods.⁶³
- **Mechanical Re-rating:** If an FFS assessment shows that a vessel is at risk at its current design pressure, but would be safe at a lower pressure, it can be formally re-rated to a new, lower Maximum Allowable Working Pressure (MAWP). This is an

engineering control that permanently limits the stress on the vessel. The Level 2 FFS assessment directly provides the data needed for this, as the MAT vs. pressure curve shows the corresponding safe temperature for any given pressure. This can be a highly cost-effective mitigation that avoids physical modification to the asset.¹⁷

5.2 Operational and Procedural Controls

These controls form the administrative layers of protection, ensuring that the equipment is operated within the safe boundaries established by engineering analysis.

- **Developing Safe Operating Envelopes (Integrity Operating Windows - IOWs):** The MAT vs. pressure curve generated from a Level 2 FFS assessment is not just a calculation result; it is a critical operational tool. This curve should be used to establish a formal IOW, which defines the permissible boundaries of pressure and temperature for the equipment.⁵³ These IOWs must be clearly documented and communicated to operations personnel, forming the basis for safe operating procedures.⁴⁷
- **Process Controls and Interlocks:** Where feasible, engineering controls in the form of alarms and automated interlocks should be implemented as a robust layer of protection. This can include low-temperature alarms that alert operators to an impending auto-refrigeration event, or safety instrumented systems (SIS) that automatically intervene by closing a valve or shutting down a piece of equipment to prevent the temperature from dropping below the MAT.⁵²
- **Strict Procedural Controls:** Detailed, written procedures are required for all phases of operation, particularly those that carry a risk of low-temperature excursions. This includes procedures for startup, normal shutdown, and especially emergency shutdown and depressurization.⁴⁷ For example, a startup procedure for a vessel at risk must explicitly state that it cannot be pressurized above a certain low level (e.g., 25% of MAWP) until its metal temperature is verified to be above the MAT for that pressure level.⁴
- **Targeted Inspection and Monitoring:** The FFS assessment can be used to inform and optimize a facility's Risk-Based Inspection (RBI) program. Instead of performing generic, non-specific inspections, Nondestructive Examination (NDE) can be strategically focused on the areas of highest risk. This means using techniques like Ultrasonic Testing (UT), Magnetic Particle Testing (MT), or Liquid Penetrant Testing (PT) to inspect high-stress locations (e.g., nozzle-to-shell

welds, support lug welds) on the specific pieces of equipment identified as most vulnerable by the FFS analysis.¹⁷ This targeted approach increases the probability of finding critical flaws while optimizing the use of inspection resources.

- **Operator Training:** Repeatedly identified as a critical, non-negotiable safety barrier, rigorous operator training is essential.⁵ Operators are the first line of defense and must be thoroughly educated on the phenomenon of auto-refrigeration, the specific scenarios that can trigger it in their unit, and the precise actions to take to prevent it or safely manage it if it occurs. They must understand the "why" behind the procedural limits and IOWs to ensure compliance. This training is one of the most cost-effective risk reduction measures available.

Section 6: Conclusion and Strategic Recommendations

The potential for catastrophic brittle fracture in legacy refinery assets due to LPG auto-refrigeration is a significant and credible hazard. This risk is rooted in a historical design gap, where equipment fabricated prior to the 1987 ASME code revisions was not explicitly designed to withstand the severe, transient low temperatures that can occur during process upsets. The confluence of a susceptible material, a pre-existing flaw, and sufficient stress at a temperature below the material's ductile-to-brittle transition point creates the conditions for failure.

The analysis presented in this report demonstrates that a systematic, proactive approach is essential for managing this risk. The API 579-1/ASME FFS-1 "Fitness-For-Service" standard provides the definitive and industry-accepted framework for this task. By leveraging its tiered assessment procedures, refinery operators can quantitatively evaluate the vulnerability of their assets, moving beyond assumption-based conservatism to data-driven decision-making. Case studies of both failures and successful interventions confirm that while the consequences of inaction can be catastrophic, a proactive approach can not only ensure safety but also unlock significant operational and financial value by optimizing asset performance.

Effective mitigation for this complex hazard in an aging facility cannot rely on a single solution. It requires the implementation of a multi-layered, defense-in-depth strategy that integrates engineering controls, material improvements, and robust administrative

procedures.

6.1 Clarifying Key Technical Concepts

To further aid the reader, this section addresses common questions that arise from the technical distinctions central to a brittle fracture assessment.

- What is the Critical Exposure Temperature (CET) and is it a property of the metal or the liquid?

The CET is not an intrinsic property of the metal or the liquid. Instead, it is a property of the process or environment, representing the lowest anticipated temperature that the metal will be subjected to during any credible scenario, including normal operation, process upsets, or auto-refrigeration.¹¹ It is the "demand" placed upon the equipment.

- How is the Minimum Allowable Temperature (MAT) determined?

The MAT is the "capability" of the equipment's material, representing its inherent resistance to brittle fracture at a given pressure.¹¹ It is determined using the tiered assessment procedures in Part 3 of the API 579-1/ASME FFS-1 standard. A Level 1 assessment uses code-based exemption curves to find a single, conservative MAT value. A Level 2 assessment provides a more detailed MAT vs. pressure curve by factoring in stress ratios and fabrication history. A Level 3 assessment uses rigorous fracture mechanics, often requiring Finite Element Analysis (FEA) and specific material fracture toughness data, for the most precise determination.¹¹

- Shouldn't the Minimum Design Metal Temperature (MDMT) be equal to the MAT?

For older assets (pre-1987), the MDMT and MAT should not be assumed to be equal. The MDMT is a design parameter stamped on the nameplate, which under old code rules, was often based on normal conditions and did not account for upsets like auto-refrigeration.²⁰ The

MAT is an in-service parameter calculated using modern standards that reflects the material's *actual* toughness. Due to this historical design gap, the calculated MAT for a legacy asset is often significantly warmer (less safe) than its nameplate MDMT.²¹

- For newer equipment (e.g., post-2000), can the MDMT be considered equal to the MAT?

For newer equipment, the MDMT is a much more reliable value. Modern design codes require that the MDMT account for all credible low-temperature scenarios,

and the material's suitability must be proven through impact testing or strict exemption rules.²⁰ In a properly designed new vessel, the

MDMT is set to be equal to or warmer than the material's MAT at the time of construction. However, the distinction remains important, as the MDMT is a static design value, while the MAT can change over the equipment's life due to in-service degradation mechanisms like temper embrittlement, which would require a reassessment.¹¹

6.2 Strategic Recommendations

Based on this comprehensive analysis, the following strategic recommendations are provided for refinery management:

1. **Mandate a Proactive, Facility-Wide Brittle Fracture Screening Program:** Commission a systematic review of all pressure equipment in light hydrocarbon service (LPG, ethane, ethylene, etc.), with a priority on assets designed and fabricated before 1987. Utilize the API 579 Part 3 Level 1 and Level 2 assessment procedures as the primary screening tool. This will efficiently identify the most vulnerable equipment and focus engineering resources where they are needed most, establishing a clear, risk-based priority for mitigation efforts.
2. **Treat FFS as an Asset Optimization Tool:** Frame the investment in FFS assessments not merely as a compliance cost but as a strategic opportunity. By replacing historical assumptions with rigorous engineering analysis, FFS can precisely define the true safe operating envelope of an asset. As demonstrated in case studies, this can lead to tangible economic benefits, such as reduced startup times, optimized inspection programs, and the avoidance of unnecessary and costly equipment replacements.
3. **Establish an "Evergreen" FFS Management System:** Recognize that industry codes and best practices are dynamic and evolving. An FFS assessment performed to an outdated standard may no longer be considered adequate. Implement a formal Management of Change (MOC) or equivalent "evergreen" process to periodically review past FFS assessments against the latest edition of API 579-1/ASME FFS-1. This ensures that the facility's safety basis remains current, compliant, and reflective of the state-of-the-art in engineering practice, thereby managing long-term liability.
4. **Prioritize a "Defense-in-Depth" Mitigation Strategy:** For at-risk legacy assets where immediate replacement is not feasible, implement and document a robust

combination of controls. This strategy should integrate engineering solutions (e.g., ensuring any weld repairs include PWHT, mechanically re-rating vessels to lower pressures, upgrading safety instrumented systems) with strong administrative controls (e.g., formalizing Integrity Operating Windows, updating all relevant procedures, and implementing a targeted, risk-based inspection plan). This creates multiple, independent layers of protection against failure.

5. **Invest in High-Fidelity Operator Training:** Fund the development and recurring delivery of comprehensive training modules focused specifically on auto-refrigeration. This training must go beyond procedural steps to explain the underlying hazards, ensuring operators understand the critical importance of adhering to IOWs. Using process simulators to model upset scenarios can be a particularly effective tool. This represents one of the highest-impact and most cost-effective risk reduction measures a facility can undertake.

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