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THE DANGERS OF TEMPER EMBRITTLEMENT IN VINTAGE VESSELS

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THE DANGERS OF TEMPER EMBRITTLEMENT IN VINTAGE VESSELS

TEMPER EMBRITTLEMENT: WHAT IS IT AND WHY DO I CARE?

Some low-alloy steels, such as 2 ¼ Cr - 1Mo, can experience a phenomenon known as temper embrittlement. This is the reduction in toughness due to metallurgical embrittlement that results from long-term exposure to high-temperature. Temper embrittlement occurs from 650°F to 1070°F (343°C to 577°C) and is most commonly of concern in hydrotreating reactors and exchangers, although it can occur in other locations (API 571) [4].

Why such a big deal? Well, for those in industry with 1960-70s vintage vessels still in operation, this phenomenon can cause concern whenever the vessel approaches a shutdown. In order for the vessel to be shut down and started back up safely, it must have an established minimum pressurization temperature, (MPT), which considers the material's toughness. This temperature defines the "danger zone" of operation where risk of brittle fracture is increased. Unlike Kenny Loggins, refinery engineers want to avoid "riding into the danger zone" – The "danger zone" being the range of temperatures at which the material is most likely to experience cracking, such as subcritical hydrogen cracking, or total brittle fracture. In order to determine this danger zone, a material's FATT must be established. A materials fracture appearance transition temperature, FATT, is when a material experiences 50% ductile fracture and 50% cleavage. This can be most accurately determined through a series of Charpy impact tests; however, since the 1970s, researchers have been trying to establish a simpler chemical composition method for finding the FATT. A summary of current equations for establishing a FATT based on chemical composition can be found in WRC 562 [6]. Though there have been several factors proposed for calculating or screening a material's FATT based on chemical composition, none have been more widely accepted then XBar and J*.

Recently, the American Petroleum Institute Subcommittee Corrosion and Materials (API SCCM) has undertaken the development of MPT guidance for aging Cr-Mo equipment. The draft documents produced by this effort, to be published as 934F, are significantly more conservative than the guidance in WRC 562 with regards to temper embrittlement. Furthermore, the methods available to owner-users for estimating a material's FATT after significant time in service will be limited. Both a Recommended Practice (RP) and Technical Report (TR) will be released for 934F in the coming months. These documents will be considered industry practice and could affect how your refinery operates Cr-Mo equipment unless alternate guidance can be justified.

WHAT TO FACTOR IN: TEMPER EMBRITTLEMENT

Before explaining any further, it should be noted that both XBar and J* were established in the early 1970s to introduce a new approach to quantifying temper embrittlement in pressure vessels. XBar was originally proposed in Robert Bruscato's study [1] on temper and creep embrittlement of 2 ¼ Cr – 1Mo Shield Metal Arc Weld (SMAW) deposits. In the 1970 article, Bruscato outlines the earlier works about temper embrittlement from Low et al. and Steven & Balajiva and summarizes the trace elements that have the largest effect in promoting temper embrittlement. Notably, the embrittlement factor, called XBar, (and sometimes referred to as the Bruscato Factor) was developed based on data for low-alloy Cr steel, not the more common low-alloy Cr-Mo used in refineries. Nonetheless, XBar is used to evaluate 2 ¼ Cr – 1Mo weldments by controlling tramp elements in the welding consumables in order to reduce the tendency toward temper embrittlement and brittle failure.

$$\overline{X} \text{ or } X_{bar} = \frac{(10P + 5Sb + 4Sn + As)}{100}$$

P = Phosphorus (ppm)
Sb = Antimony (ppm)
Sn = Tin (ppm)
As = Arsenic (ppm)

Bruscato conducted his research on weldments rather than base material because weldments were known to be the region most susceptible to the damage, which holds true for today's low-impurity base materials (API 571). Of the 30 weldments studied, over 90% of the temper embrittlement in the step aged material can be connected to four elements: manganese, silicon, phosphorous, and tin! So, why were the "key culprits" of manganese and silicon left out of this calculation? In SMAW weldments, manganese and silicon enhance the weldability of a material, promote higher toughness, and in the case of the latter, act as a deoxidizer. Thus, there are limits to how much these elements can be reduced in welds.

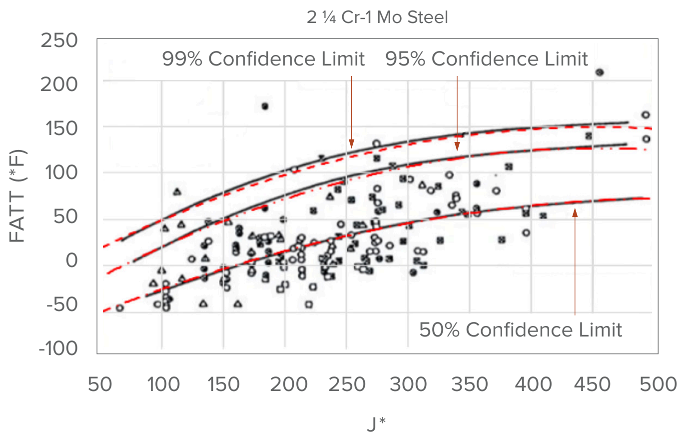
Of course, the culprit temper embrittlement elements do not affect 2 ¼ Cr – 1Mo plate material the same as they do welds. Hence, a different factor better-suited to base material and HAZ was needed. Watanabe et al. [2] introduced J* as a separate embrittlement factor four years later at an ASME conference on Petroleum Mechanics in order to address this issue.

$$J = (Mn + Si) \cdot (P + Sn) \cdot 10^4$$

where, J is a constant based on chemical impurities

P = Phosphorus (wt%)
Si = Silicon (wt%)
Sn = Tin (wt%)
Mn = Manganese (wt%)

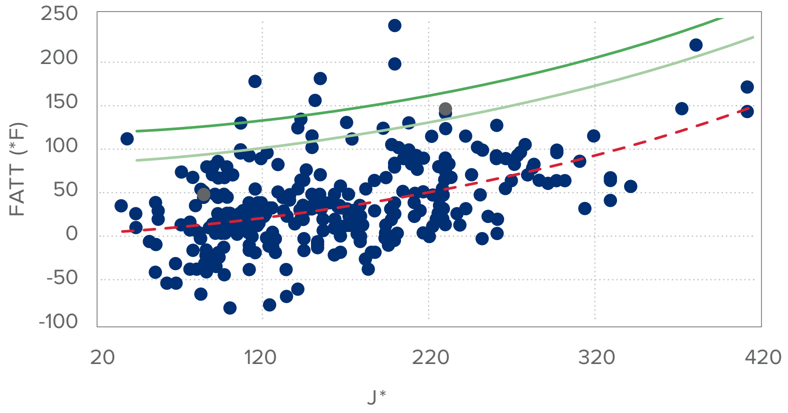
This factor was developed from separate research conducted by Japan Steel Works., Watanabe et al. compared the pros and cons of both XBar and J* at ASME's 29th Petroleum Mechanical Engineering Conference. As shown in the equation, the researchers developing J* felt it was important to incorporate the key culprits, manganese and silicon, that Bruscato left out of his XBar formula. The difference between XBar and J* can be attributed to the difference between weldments and base metals. Deoxidizing (capping, killing, etc.) and microstructural refinement are more straightforward in plate manufacturing than in welding. Watanabe et al. included manganese and silicon in J*because these elements can be limited without detriment to the material, and because they can typically be more prevalent than the other tramp elements affecting temper embrittlement.



J-factor = $(Si + Mn)(P + Sn) \times 10^4$

BASE METAL	WELD METAL
○ OVER 30,000 Hrs	● OVER 30,000 Hrs
☐ 75,000 Hrs	■ 75,000 Hrs
△ 20,000 Hrs	▲ 20,000 Hrs

Figure 1. *Iwadate correlation between researched J* and FATT with WRC 562 equations. (Note: though data is shown for more than the 30,000 hours of collection, this was not used in the statistical analysis as stated in the original paper)*



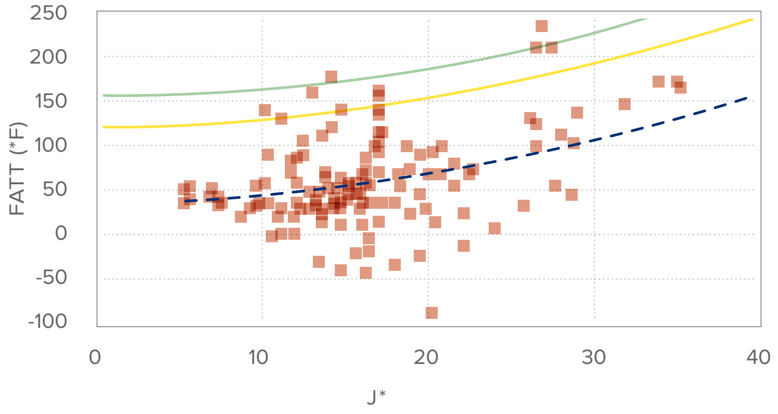
$J^* = (Mn + Si) \times (P + Sn) \times 10^4$

2nd poly mean fit: Statistical Analysis

$y = 0.0004x^2 + 0.051x + 5.4828$

$R^2 = 0.21049$

Figure 2. *FATT vs. J*: E²G has taken the collection of data from the aforementioned research and compiled it into a common database. The lines shown are the mean fit line 2nd degree polynomial and 95% and 99% prediction intervals, for comparison to the curves in WRC 562.*



$$X = \frac{(10P + 5Sb + 4Sn + As)}{100}$$

Trace Compositions measured in ***ppm***

$y = 0.0738x^2 + 0.527x + 6.98$

$R^2 = 0.1442$

Figure 3. *FATT vs. XBar: E²G's common database is shown, utilizing the XBar correlation. The lines shown are the same as in Figure 2.*

WHY DOES THIS MATTER?

Per API 571, materials manufactured before 1972 are more susceptible, since they were made before the knowledge and the technological abilities existed to limit XBar and J*. Nowadays, material with an XBar less than 10 and J* less than 100 is more common, which results in a low FATT, and therefore greatly reduces the severity of temper embrittlement. Since it is unrealistic to replace old vessels with higher XBar or J*, being able to predict their toughness during start-up and shut down is vital. Though some embrittlement may occur during fabrication, most damage it causes happens after years of the material being in the temperature range for embrittlement, and a material that was placed into service with adequate toughness may have degraded over time and now require a higher MPT.

Why are XBar and J* important in saving time and money? Optimizing start-ups and shutdowns can save hours or even days for some reactors, depending on thicknesses, heating and cooling rates, and operational limitations. This can shorten shutdown windows significantly, bringing millions of dollars of throughput back on-line more quickly, while managing the risk of brittle fracture during these times. Although developed for 2 ¼ Cr – 1Mo, the XBar and J* correlations are used today for the majority of low-alloy steel, from 1 ¼ Cr – ½ Mo to 3Cr – 1Mo.

E^{2}G is exploring the published literature from the last 5 decades to build a database of experimental toughness data for low-alloy steels. This effort will help us better understand the relation between FATT and tramp elements, and facilitate the optimization of MPTs for vessel start-ups and shutdowns. The WRC 562 bulletin summarizes the current correlations used for J* and XBar with the following established set of curves.

$$FATT_{mean} = -107.18 + 1.0363 \cdot J - 9.9265\,(10^{-4}) \cdot J^2 \quad (^\circ F)$$

$$FATT_{95\%} = -55.808 + 1.3942 \cdot J - 1.5376\,(10^{-3}) \cdot J^2 \quad (^\circ F)$$

$$FATT_{99\%} = 4.2512 + 1.3081 \cdot J - 1.4498\,(10^{-3}) \cdot J^2 \quad (^\circ F)$$

These polynomial equations define FATT curves used in the WRC 562 methodology to develop an MPT envelope. This MPT defines a safe operating range of a vessel when starting it up or shutting it down, so that it does not fail as a result of brittle fracture. As shown in Figure 2, the WRC 562 FATT vs. J* polynomials were established from the research by Iwadate et al. [5] in 1994, and the curves defined by the equations match those drawn by the authors. In the article, Iwadate et al. use Weibull statistical analysis on data collected over the course of 30,000 hours by Japan Steel Works, to place 95% and 99% confidence intervals on the data.

When Charpy data are not available, these equations are what many in the industry currently use to estimate a conservative FATT and determine the MPT of a vessel. Finding the correct prediction interval is important; a more conservative MPT could cost more money in order to go through start-up and shutdown procedures, yet a non-conservative MPT may result in catastrophic brittle failure.

WHAT NOW?

E^{2}G is currently looking into multiple sets of research and databases used in the development of the XBar and J* factors. Both factors were proposed in the early 1970s and have since been reviewed by the works of many (e.g., Buscemi et al.[7], Shaw et al. [3], and Iwadate et al.) Though each review surrounds the study of XBar or J*, each generally relies on a separate database. For E^{2}G's literary review, we have been transcribing the databases from each applicable source and developing one database to use for the development and comparison of FATT correlations to XBar and J* factors.

By combining all data into one database, we can determine a mean curve and then develop prediction intervals similar to those found in WRC 562. The prediction intervals are essentially upward shifts of the mean curve that are used to bound either 95% or 99% of the points in the database; these prediction interval curves can be seen in Figures 2 and 3. For a given J* value, the proposed curves in Figures 2 and 3 would produce a slightly more conservative FATT result than the current WRC 562 equations. During this ongoing effort, the hope is that, as more points are added to our dataset, the 95% and 99% bounds can be lowered with confidence. Our next step is to focus efforts on commercial steels (rather than laboratory-created materials) and incorporate additional data into the analysis.

WHAT NEXT?

The next phase is to collect more data from outside resources and figure out questions such as: What more should be considered in the analytical breakdown? Do the XBar & J* factors make sense for broad generalizations (e.g., all low-alloy steels) or should there be a “case-by-case” calculation for each alloy? Are these the correct correlations to make between trace elements and FATTs? E^{2}G plans to work with WRC to publish a bulletin for the industry documenting the data collected and proposing a ‘best practice’. E^{2}G’s goal is either to reduce the variability in the predictive relationship of the current factors by adding more data, or to kindle the idea of finding a better relationship between chemical composition and FATT in order to both ensure safe operation and reduce shutdown time and cost.

WHAT ABOUT MY REACTOR?

Here at E^{2}G, we have specialized personnel experienced with vintage material and aging reactors and vessels. Our industry experts are available to evaluate your equipment using state-of-the-art fracture mechanics concepts. We have reviewed owner-users’ MPT procedures for countless pressure vessels, including those affected by temper embrittlement, hydrogen embrittlement, high-temperature hydrogen attack, and numerous other damage mechanisms which affect toughness. Many of our engineers helped to develop the techniques and material data currently relied upon by the petroleum and petrochemicals industries. If your facility uses rules-of-thumb guidance to set an MPT envelope for startup and shutdown, we can help optimize these procedures to shave hours or even days off of the ends of your turnaround window. Conversely, if your facility is using as-fabricated toughness data from an equipment file, such as a mill test report (MTR), to determine an MPT, we can help characterize the effects of embrittlement and develop a procedure for safely pressurizing equipment to reduce the risk of brittle fracture. If your site has an upcoming turnaround and wants to quantify brittle fracture risk, contact E^{2}G’s professionals in Fitness-for-Service and Materials & Corrosion engineering today. We can help you make sure the “metal under tension” at your refinery stays off the “highway to the danger zone.”

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