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Subject: Hydrogen Embrittlement – IFI Endorsed Position

This document summarizes into “know-how” findings flowing out of scientific research at McGill University on hydrogen embrittlement (HE) as it relates to fasteners. The McGill University HE program began in 2006 as a collaborative research and development (CRD) project, co-sponsored by a number of industrial partners and the Government of Canada. The IFI has been a significant industrial sponsor and has a seat at the Advisory Committee that oversees the progress of the program. The ongoing research follows two distinct tracks: (i) fastener materials susceptibility, and (ii) interactions of fastener materials with coatings and coating processes.

One notable example of tangible outcomes is that the research has informed the revision of fastener electroplating standards ASTM F1941 and ISO 4042.

The IFI believes this paper explains in clear and practical terms the state-of-the-art knowledge about hydrogen embrittlement failures in fasteners, and highly recommends reading it in full as the basis for understanding this very important fastener topic.

Respectfully,

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**FUNDAMENTALS
OF
HYDROGEN EMBRITTLEMENT
IN STEEL FASTENERS**

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Introduction

High strength mechanical steel fasteners are broadly characterized by tensile strengths in the range of 1,000 – 2,000 MPa (150 – 300 ksi), and are often used in critical applications such as in bridges, vehicle engines, aircraft, where a fastener failure can have catastrophic consequences. Preventing failures due to hydrogen embrittlement (HE) and managing the risk of HE are fundamental considerations implicating the entire fastener supply chain, including: the steel mill, the fastener manufacturer, the coater, the application engineer, the joint designer, all the way to the end user. Hydrogen embrittlement has been studied for decades, yet the complex nature of HE phenomena and the many variables make the occurrence of fastener failures unpredictable. Research is typically conducted under simplified and/or idealized conditions that cannot be effectively translated into *know-how* prescribed in fastener industry standards and practices. Circumstances are further complicated by standards that are sometimes inadequate and at other times unnecessarily alarmist; in some cases they are both at the same time. Inconsistencies and even contradictions in fastener industry standards have led to much confusion and many preventable fastener failures. The fact that HE is very often mistakenly determined to be the *root cause* of failure as opposed to what it really is: a *mechanism* of failure, is a reflection of the confusion.

The objective of this paper is to distil the latest knowledge related to hydrogen embrittlement into *know-how* in a manner that is complete yet simple, and directly applicable to fasteners. The topic is divided into basic components. First is a description of the theory and mechanism of hydrogen damage, followed by a discussion of conditions that are necessary for hydrogen embrittlement failure to occur. The fundamentals are followed by a description of HE test methods, guidelines for processing, surface cleaning, coating (particularly electroplating), and baking.

The principal sources of the knowledge compiled in this publication are academic research supported by 25 years of real life experience with fastener hydrogen embrittlement. Research at McGill University in Montreal, Canada began in 2006 as a collaborative effort, co-sponsored by industry and the Government of Canada. Industrial partnership was led by the Industrial Fasteners Institute (IFI) and the Canadian Fasteners Institute (CFI). The ongoing research follows two distinct tracks: (i) fastener materials susceptibility to HE, and (ii) interactions of fastener materials with coatings and coating processes. Nearly ten years later, the project has evolved with great distinction into a center of expertise that is recognized around the world.

1. General description

A typical definition for hydrogen embrittlement in literature and consensus standards is as follows.

Hydrogen Embrittlement (HE) — a permanent loss of ductility in a metal or alloy caused by hydrogen in combination with stress, either externally applied or internal residual stress [1].

Generally, hydrogen embrittlement is classified under two broad categories based on the source of hydrogen: internal hydrogen embrittlement (IHE) and environmental hydrogen embrittlement (EHE). IHE is caused by residual hydrogen from steelmaking or from processing steps such as pickling and electroplating. EHE is caused by hydrogen introduced into the metal from external sources while it is under stress, such as is the case with an in-service fastener. The terms “Stress Corrosion Cracking” (SCC) and “Hydrogen Induced Stress Corrosion Cracking” (HiSCC) are used to define EHE that occurs when hydrogen is produced as a by-product of surface corrosion and is absorbed by the steel fastener. Cathodic hydrogen absorption (CHA) is a subset of SCC. Cathodic hydrogen absorption occurs in the presence of metallic coatings such as zinc or cadmium that are designed to sacrificially corrode to protect a steel fastener from rusting. If the underlying steel becomes exposed, a reduction process on the exposed steel surface simultaneously results in the evolution of hydrogen in quantities that are significantly higher than in the case of uncoated steel.

2. Hydrogen damage mechanism

High strength steel is broadly defined as having a tensile strength in the range of 1,000 – 2,000 MPa, (150 – 300 ksi). When high strength steel is tensile stressed, as is the case with a high strength fastener that is under tensile load from tightening, the stress causes atomic hydrogen within the steel to diffuse (move) to the location of *greatest stress* (e.g., at the first engaged thread or at the fillet radius under the head of a bolt). As increasingly higher concentrations of hydrogen collect at this location, steel that is normally ductile gradually becomes brittle. Eventually, the concentration of stress and hydrogen in one location causes a hydrogen induced (brittle) microcrack. The brittle microcrack continues to grow as hydrogen moves to follow the tip of the progressing crack, until the fastener is overloaded and finally ruptures. This hydrogen damage mechanism can cause the fastener

to fail at stresses that are significantly lower than the basic strength of the fastener as determined by a standard tensile test.

Theoretical models that describe hydrogen damage mechanisms under idealized conditions have been proposed since the 1960's. In the case of high strength steel, these models are based primarily on two complementary theories of *Decohesion* and *hydrogen enhanced local plasticity (HELP)*. Given the complexity of HE phenomena, hydrogen damage models continue to evolve and be refined thanks to the efforts of theoretical and experimental researchers around the world. A detailed discussion of the theory of hydrogen damage is outside the scope of this paper.

Hydrogen "traps" refer to metallurgical features within the steel microstructure such as grain boundaries, dislocations, precipitates, inclusions, etc., to which hydrogen atoms may become bonded. Hydrogen thus "trapped" is no longer free to diffuse (i.e., move) to areas of high stress where it can participate in the mechanism of HIC. Traps are typically classified as *reversible* or *non-reversible* based on their bonding energies. Reversible traps are characterized by low bonding energies; in other words hydrogen is more easily released from the trap. Non-reversible traps are characterized by high bonding energies; in other words hydrogen requires a great deal of energy (e.g., heat) to be released from the trap. Hydrogen that is not trapped is called *interstitial* hydrogen; it is *free* to move in the metal lattice. Interstitial hydrogen is also called *diffusible* hydrogen.

NOTE: for the purpose of describing hydrogen embrittlement in high strength steel mechanical fasteners, this paper uses the term "hydrogen" to refer to atomic hydrogen and not molecular H₂ gas.

3. Fracture morphology

With quenched and tempered high strength steels, the fracture surface resulting from hydrogen induced cracking is typically characterized by *brittle intergranular* morphology which is caused by a crack growth path that follows the grain boundaries (Fig. 1). The morphology of a fracture surface will vary based on the susceptibility of the material and the degree of embrittlement. Clearly defined grain facets (i.e., sharp and angular features) and/or a high proportion of brittle vs. ductile features are indicative of high degree of embrittlement. Figure 1 illustrates a fracture surface that is 100% intergranular with very well defined grain facets.

With a tensile loaded fastener, a crack typically grows up to a point where the reduced cross section of the fastener can no longer withstand the applied load. At this point the fastener ruptures rapidly (i.e., *fast fracture*). A normal fracture surface corresponding to rapid rupture is ductile, characterized by *ductile dimple* morphology. Figure 2 illustrates a fracture surface where the brittle hydrogen induced crack propagation ended (i.e., final crack tip) prior to final rapid rupture of the fastener.

Other forms of embrittlement failure resulting from phenomena not related to the presence of hydrogen such as temper embrittlement, quench embrittlement, quench cracking, etc. should be distinguished from hydrogen embrittlement failures. These other types of embrittlement can exhibit similar intergranular fracture surfaces but are principally distinguished from *hydrogen embrittlement* by the fact that they are *not time dependent*.

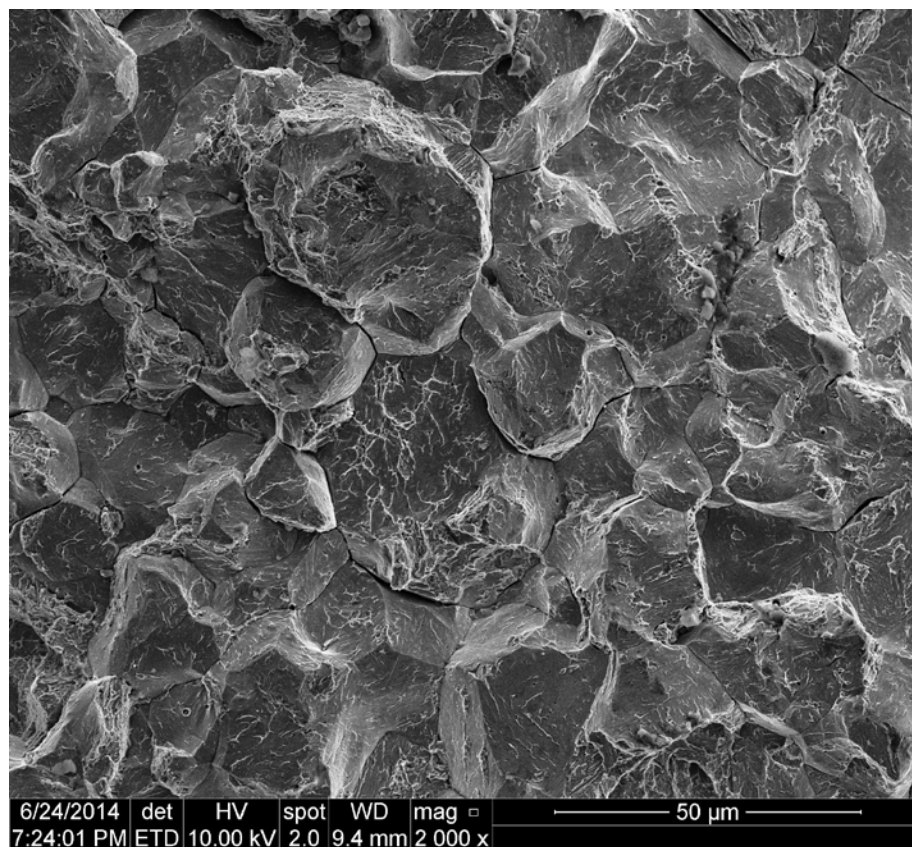


Figure 1 – Fracture surface showing 100% well defined brittle intergranular morphology – Cr-Mo alloy steel (AISI 4135), quench and tempered to 51 HRC, zinc electroplated

(Source: Brahim 2014)

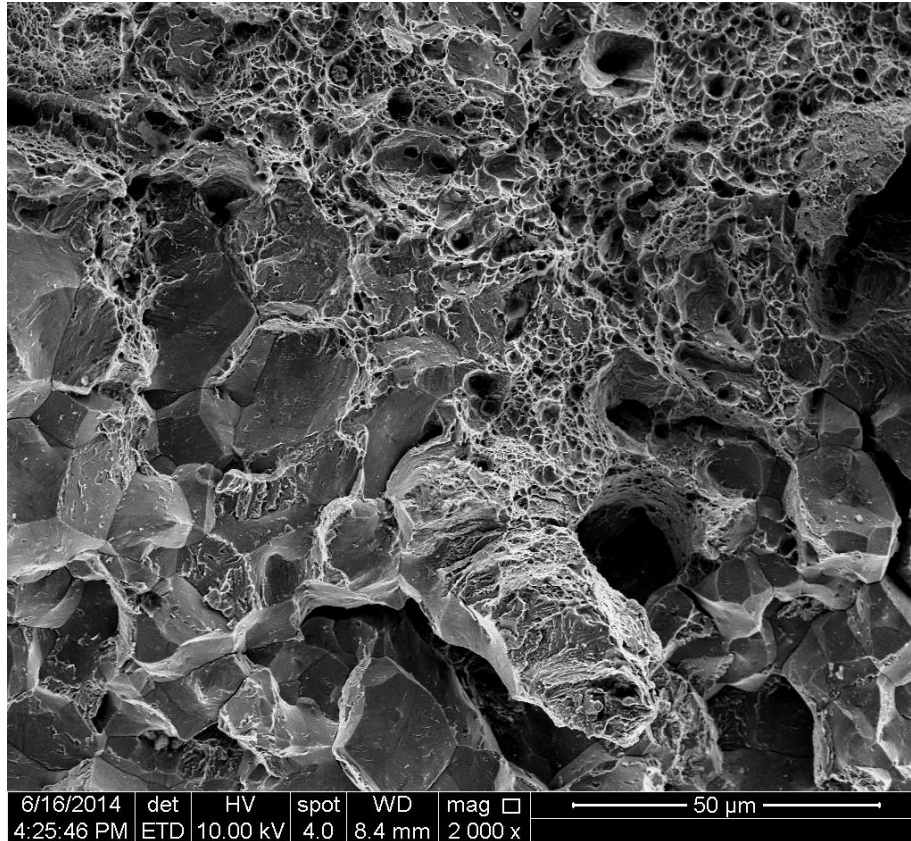


Figure 2 – Fracture surface showing both brittle intergranular morphology resulting from hydrogen induced cracking (HIC) and ductile dimple morphology indicative of final rupture. More precisely, the image shows where the brittle hydrogen induced crack propagation ended (i.e., final crack tip) prior to final rapid rupture of the fastener – Cr-Mo alloy steel (AISI 4135) at 51 HRC, zinc electroplated (Source: Brahim 2014)

4. Conditions at the tip of a crack

A microcrack can be initiated in a loaded fastener by a number of mechanisms that are not necessarily related to HIC (e.g., fatigue, overloading). However, once a crack is initiated by any mechanism including HIC, the conditions at the tip of the crack, notably the concentration of stress, are often much more severe than initial conditions. The crack can propagate readily by a single or a combination of mechanisms that seek to relieve the stress at the tip of the crack. If it happens that a sufficient quantity of hydrogen is available to interact with the crack tip, then the propagation of the crack may be facilitated by HIC (Fig. 3). For example, even in low susceptibility materials, an

existing crack under static or cyclic load exposed to a corrosive environment can propagate in part by stress corrosion cracking.

In the case where HIC is the mechanism of an initial microcrack, the time to failure is significantly shortened as available hydrogen continues to interact with and follow the tip of the progressing crack. In such a scenario, HIC is the primary failure mechanism. On the other hand, a failure investigation must distinguish the scenario where HIC is the mechanism of an initial microcrack from a scenario where the mechanism of the initial crack is not related to HIC. The fracture surface presented by the latter scenario can nevertheless exhibit intergranular features if hydrogen becomes available to interact with the crack tip. In such a scenario, HIC must be considered only as a secondary fracture mechanism.

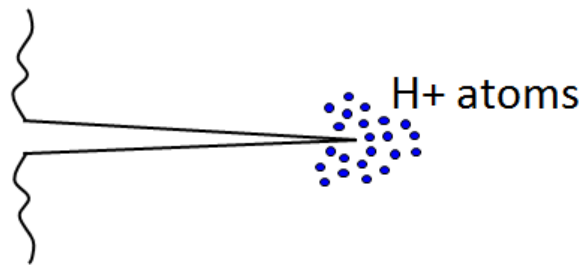


Figure 3 – Illustration of an existing sharp crack surrounded by atomic hydrogen that can interact with the crack tip to cause hydrogen induced crack propagation

5. Conditions for hydrogen embrittlement failure

Three conditions must be met to cause hydrogen embrittlement failure: (i) steel that is *susceptible* to hydrogen damage, (ii) *stress* (typically as an applied load), and (iii) atomic *hydrogen* (Fig. 4). If all three of these elements are present in sufficient quantities, and given *time*, hydrogen damage results in crack initiation and growth until the occurrence of fracture. *Time to failure* can vary, depending on the severity of the conditions and the source of hydrogen.

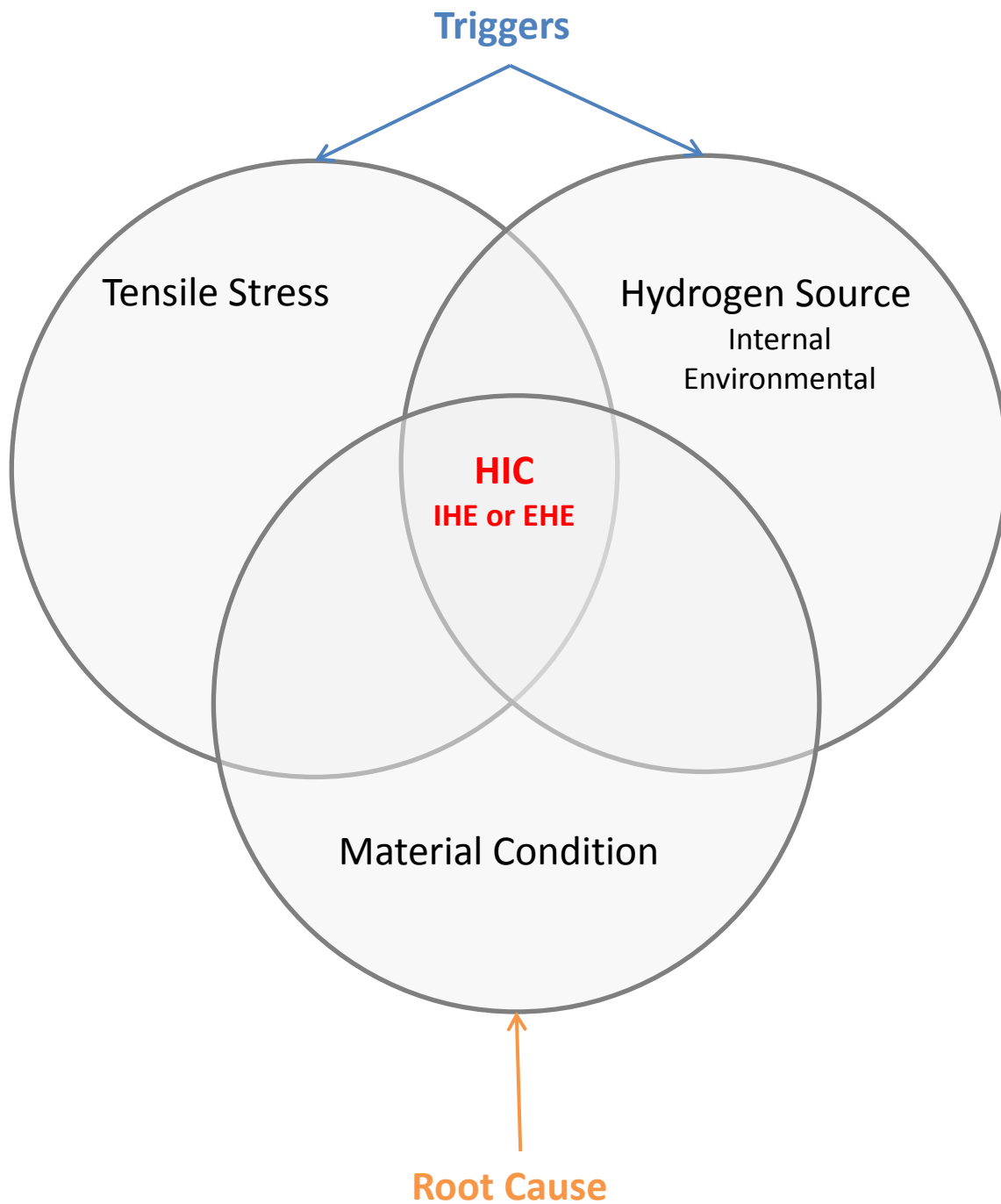


Figure 4 – Given time, three conditions must be met in sufficient and overlapping quantities for HE failure to occur. Stress and hydrogen are *triggers*, whereas material susceptibility is the fundamental requirement for HE to occur and is therefore associated with the *root cause*.

5.1. Material susceptibility

Hydrogen embrittlement susceptibility is a function of the *material condition*, which is comprehensively described by the metallurgical and mechanical properties of a material such as steel. Therein lies the fundamental basis for understanding HE phenomena, which when simply stated is the study of how a stressed material performs in the absence and then in the presence of absorbed hydrogen. Material strength (i.e., tensile strength and/or hardness) has a first order effect on HE susceptibility. As strength increases, steel becomes harder, less ductile, less tough and more susceptible to HE. By the same token, at *equal strength*, steel that exhibits lower toughness and less ductility is inherently more brittle and more susceptible to HE. The susceptibility of steel fasteners increases significantly when the specified hardness is above 39 HRC (380 HV). Steel fasteners with a specified hardness below 39 HRC (380 HV), *normally* have no significant susceptibility to hydrogen embrittlement failure. In other words, they can tolerate the presence of hydrogen without any delayed degradation of their mechanical strength. This assertion assumes that the fasteners were produced by well controlled manufacturing processes using appropriately selected steel of adequate quality. Examples of such fasteners are SAE J429 Grade 8 [2] and ISO 898-1 property class 10.9 [3] products.

The critical hardness threshold for heat treated quench and tempered steel fasteners will vary for a given product due to second order effects of *chemistry*, *tempering temperature* and *sub-microstructure*. These second order effects may vary the threshold value by as much as ± 1.0 HRC ($\sim \pm 10$ HV). Additionally, *non-homogeneity* of the metallurgical structure resulting from poorly controlled heat treatment, impurities and non-metallic inclusions can dramatically increase the susceptibility of steel in ways that are measurable but unpredictable.

With respect to internal hydrogen embrittlement (IHE) avoidance, some standards have defined critical hardness limits that are lower, ranging from 31 to 35 HRC. However, these values are largely unsupported by data, and have been adopted primarily as a precaution against manufacturing errors that could render the material significantly more susceptible than it should be. Rather, it is appropriate to classify “susceptible fastener products” as those having specified hardness above 39 HRC (380 HV). As a point of reference, ASTM F1941 [4], which is the recommended standard for electroplating fasteners in North America, classifies susceptible fastener products as those having minimum specified hardness above 39 HRC (380 HV). This recommendation is based on both scientific research and *longstanding fastener industry practice*.

Similarly, ISO 898-1 (Table 2, footnote i) [3] contains a cautionary statement about the risk of stress corrosion cracking for property class 12.9 fasteners, which have a specified hardness range of 39-44 HRC (385-435 HV).

The final metallurgical condition of products such as Grade 8 and property class 10.9 fasteners is obtained during the heat treatment process (i.e., quenching and tempering). From the perspective of fastener manufacturing, heat treatment is the most critical and defining process if the parts are to achieve the required mechanical and metallurgical characteristics making them fit for purpose. The root causes of hydrogen embrittlement fastener failures are very often linked to improper quenching and tempering. Some consequences of improper heat treatment include, higher than expected hardness, unintended carburization and incomplete martensite transformation. Therefore it is imperative that the heat treatment process produces fasteners that satisfy the *explicit and implied* requirements specified in material standards [2, 3, 5-8].

5.2. Tensile stress

Load induced stress is a normal service condition for mechanical fasteners. Tensile loaded fasteners such as screws and bolts are primarily subject to tensile stress and a varying amount of torsional stress during tightening. In some cases, fasteners may be subject to shear loads, typically in the body. In some rare but critical cases, fasteners may also be subject to unintended bending loads. Given time, the tensile component of loading systems in a fastened joint can result in HE failure of a *bolt if the tensile stresses exceed the HE threshold stress of the material*. Hydrogen embrittlement *threshold* is defined as the critical stress below which HE does *not* occur. Otherwise stated, HE threshold is a measure of the degree of susceptibility of the steel for a given quantity of available hydrogen. *Time to failure* is dependent on the amount by which the threshold stress is exceeded. Time to failure decreases with increasing stress.

The applied stress in a bolt or screw is a function of the loading conditions in the joint. These loading conditions are a combination of the joint design (i.e., service loads) and tightening conditions (i.e., installation preload) of a fastener assembly. Under normal conditions, preloaded bolts are installed to preloads ranging from 50% to 70 % of ultimate tensile strength (UTS) (a.k.a., R_m). For Grade 8 and property class 10.9 fasteners which normally have no significant susceptibility to HE, this amount of loading is below the HE threshold of the material. However, if

the same fastener has hardness above the specified limit or other defects such as poor microstructure or low fracture toughness (see paragraph 5.1), it will also exhibit an abnormally high degree of HE susceptibility. The HE threshold load of such a fastener material is correspondingly lowered and may be exceeded by the installation preload. Under these conditions, given the *same concentration of hydrogen* and *normal tightening conditions*, the probability of exceeding the HE threshold stress of the material becomes significantly greater, thus increasing the risk of hydrogen induced cracking (HIC).

NOTE: As with all failure mechanisms, hydrogen induced cracking (HIC) is normally initiated at the points of greatest concentration of stress:

- *In the case of screws and bolts, this corresponds to the root of the first engaged thread or at the fillet radius under the head.*
- *In the case of nuts, the distribution of load in internal threads makes it significantly less likely that the HE threshold can be exceeded. Consequently, HE failure of a nut, although theoretically possible, is extremely rare.*
- *In the case spring washers, a significant tensile stress component is present as the washer is compressed. It is not unusual for electroplated high-hardness spring washers to fail as a result of HIC, unless they are adequately baked.*

As a final point of discussion, unintended geometrical irregularities such as angles, sharp radii, unintended flaws, surface discontinuities or pits can arise from bad fastener design, poor manufacturing, over-pickling or corrosive service conditions. Notably, poor radii and thread laps at the thread root are highly localized concentrators of stress. These irregularities can often lead to unexpected crack initiation, thus exacerbating the conditions, particularly for a material that is already susceptible to HE.

5.3. Atomic hydrogen

There are two possible sources of hydrogen: *internal* and *environmental*.

i. *Internal hydrogen*

Steel inherently retains a small amount of *residual* hydrogen as it is produced. Vacuum degassing techniques have been improved to the extent where steel of standard quality will contain

hydrogen concentrations *roughly* in the order of 1 ppm. As will be described later, this residual hydrogen is not normally cause for concern. Internal hydrogen can also be introduced into fasteners during the manufacturing processes. For example, during austenizing hydrogen may be absorbed by the fasteners; it is subsequently “*baked out*” during tempering. In a steel fastener that has been properly quenched and tempered, any remaining residual hydrogen is typically trapped and innocuous.

NOTE: Secondary processes such as welding and brazing may also introduce hydrogen into the heat affected zone.

The most relevant manufacturing processes to consider with respect to internal hydrogen embrittlement are primarily coating processes and related surface cleaning and preparation processes (e.g., pickling). The reasons these processes are significant is that they are the final manufacturing step, and coating materials (e.g., zinc) act as a barrier to hydrogen effusion. In other words, the coating prevents hydrogen’s natural tendency to diffuse out of the steel at room temperature.

Typical cleaning for electroplating comprises hot alkaline degreasing followed by electrolytic (i.e., anodic) alkaline cleaning and inhibited acid pickling. Acid pickling is a significant source of hydrogen in coating processes. Therefore a suitable inhibitor and minimum cleaning cycle time should be used to minimize the risk of internal hydrogen embrittlement (IHE). For fasteners with hardness greater than 39 HRC (380 HV), such as ASTM A574 [8] socket head cap screws and property class 12.9 fasteners, special pre-treatments are advisable using non-acidic methods such as mechanical cleaning or alkaline de-rusting.

NOTE: Inhibitors reduce corrosive attack on the steel and the generation and/or absorption of hydrogen. Quench and tempered steel fasteners should ideally be supplied with a surface that can be cleaned with a minimum immersion time when pickling is used.

Electroplating processes generate hydrogen; however the quantity of hydrogen generated is not directly related to the amount of hydrogen absorbed by the fasteners. The amount of hydrogen which may be absorbed depends on the process type (e.g., alkaline zinc, acid zinc, zinc alloy, etc.) and process parameters (e.g., current density, electroplating time, rack/barrel, etc.). The most important factor that influences the quantity of hydrogen that remains in a fastener is *permeability* of the coating material to hydrogen diffusion. Otherwise stated, permeability determines if the coating is porous enough to allow hydrogen to effuse outward or if it is an effective barrier that blocks

hydrogen effusion, thus forcing it to stay in the steel. For example, studies have shown that the risk of IHE is non-existent with phosphate coatings because they are very porous. Similarly, studies have shown that the risk of IHE is significantly lower for low hydrogen embrittlement cadmium (LHE-Cd) electroplating and certain zinc-nickel (Zn-Ni) electroplating processes containing 12 to 16 % nickel. Such coating materials are more permeable than zinc (Zn) or zinc-iron (Zn-Fe) electroplated coatings.

Common industry practice is to heat (i.e., *bake*) the fasteners after the coating process with the intention to extract any diffusible hydrogen that was introduced in the course of such processes. Baking will be discussed in greater detail below (see paragraph 9).

NOTE: Typically, IHE failures occur within hours or days after installation.

ii. Environmental hydrogen

Environmental hydrogen is introduced as a result of corrosion. More precisely, galvanic corrosion of a sacrificial cathodically protecting coating (e.g., Zn, Zn-Ni, Cd) generates hydrogen, which may then be absorbed by exposed steel surface areas of a fastener (i.e., cathode). This condition occurs when the coating is damaged, cracked, porous or partially consumed by corrosion. The quantity of hydrogen absorbed in this manner is orders of magnitude higher than under normal anodic corrosion conditions (i.e., without a coating). These conditions can lead to what is commonly described as stress corrosion cracking (SCC) or hydrogen induced stress corrosion cracking (HiSCC), a subset of environmental hydrogen embrittlement (EHE).

From a failure analysis perspective, any amount of corrosion prior to failure of an in-service fastener can lead to EHE as the dominant failure mechanism, even in the presence of internal hydrogen. With the passage of time, the localized contribution of corrosion generated hydrogen is cumulative, and the relative contribution of internal hydrogen becomes negligible.

NOTE: Typically, EHE failures require longer times than IHE failures (weeks to years), as hydrogen is absorbed during corrosion processes.

6. Case-hardened fasteners

Case-hardened screws present additional challenges in that the surface is intentionally hardened to fulfill a self-drilling and/or self-tapping function. These products vary greatly depending

on the market and purpose for which they are supplied. They are used for joining wood, steel, galvanized steel, aluminum, or combinations of these materials; consequently they can be supplied with core hardness ranging from 25 to 45 HRC and surface hardness up to 600 HV (~55 HRC). The combination of high surface and core hardness can make case-hardened screw materials very susceptible to both IHE and EHE. Case-hardened screws are sometimes coated with zinc rich organic coatings, but are very often coated by zinc electroplating. The availability of hydrogen provides ample triggers for HE to occur. The possible sources of hydrogen are: (i) internal hydrogen introduced during zinc electroplating, (ii) corrosion generated environmental hydrogen resulting from the sacrificial corrosion of cathodic protective coatings, and (iii) corrosion generated environmental hydrogen resulting from galvanic mismatches of materials being joined.

NOTE: Most chemicals preservatives used in pressure treatment of lumber are copper-based and can significantly accelerate the corrosion of screws. This accelerated corrosion process begins with rapid corrosion of zinc or zinc rich coatings, followed by an equally rapid corrosion of the underlying steel. These complex galvanic couples further increase the rate of hydrogen generated by corrosion.

Fortunately the function of case-hardened screws does not require a great degree of tensioning, which is why they don't often fail as a result of HE; they are loaded below their HE threshold stress. On the other hand given such little margin for error, case hardened screws do sometimes fail. Slight variations in hardness, loading conditions or corrosive environment can lead to relatively rapid failure (i.e., hours to days after installation). Case-hardened screws are low value added commodity products and are sometimes manufactured under poor process control conditions, making prevention a challenge.

From the perspective of preventing HE failure, the key product characteristics that must be controlled are: (i) core hardness, (ii) case hardness, and (iii) case depth.

- Core hardness – Experience has shown that core hardness is the most critical characteristic and should be kept below 38 HRC.
- Surface hardness – surface hardness should be selected in accordance with the intended purpose of the screw, but not more. Similar to core hardness, surface hardness should be specified as a range (i.e., min. – max.), and not only as a minimum requirement.

- Case depth – Experience has shown that case depth should not exceed the values given in ASME B18.6.3 [9] or ISO 2702 [10].

Additional preventive measures include selection of an appropriate coating. For example, although zinc electroplating is very economical and readily available, it may not be appropriate for case hardened screws at a high hardness range. Other precautions include specifying and overseeing the use of appropriate installation methods. For example, the use of impact wrenches might not be appropriate for some products and applications.

7. Hot dip galvanizing – effect of thermal up-quenching

A recently revealed phenomenon has been very useful in explaining some failures of hot dip galvanized high strength fasteners. Historically, such failures were either attributed to IHE caused by acid pickling prior to galvanizing or to stress corrosion cracking caused by in-service corrosion. In the 1970's, failures of hot dip galvanized high strength fasteners attributed to SCC prompted ASTM Committee F16 on Fasteners to ban hot dip galvanizing of ASTM A490 [7] structural bolts, used primarily in North America. In Europe and elsewhere, galvanizing of ISO 898-1 property class 10.9 [3] structural bolts has remained a standard practice. In 1999, the German Fastener Association (i.e., Deutscher Schraubenverband – DSV) issued a detailed guide aimed at mitigating both risks of IHE and SCC by prescribing material and processing requirements for galvanizing high strength fasteners [11]. Notably, the DSV guide prescribes surface preparation by mechanical cleaning instead of acid pickling.

In spite of these precautions, failures have occurred with galvanized fasteners that: (i) were never in contact with acid prior to galvanizing, (ii) failed shortly after installation, and (iii) were not subject to environmental corrosion. The hot dip galvanizing process itself does not introduce hydrogen therefore another source of hydrogen must be considered. It has been proved that a significant source of hydrogen is the freeing of trapped residual hydrogen as a result of thermal shock (i.e., *up-quenching*) that occurs when the fasteners are immersed in molten zinc during galvanizing. The presence of a thick zinc coating prevents hydrogen escaping, instead causing it to accumulate at grain boundaries [12]. The release of trapped hydrogen by up-quenching is therefore a third and potentially very significant source of hydrogen in addition to conventional sources of internal and environmental hydrogen. This source of hydrogen is likely to have played a primary

role in failures of hot dip galvanized high strength fasteners that were inadequately attributed to conventional IHE or SCC.

NOTE: Fasteners with a specified hardness range of 25-39 HRC (240-380 HV) are not normally embrittled by the galvanizing process, as evidenced by the fact that high strength structural fasteners, including ASTM A354 BD and ISO 898-1 property class 10.9 bolts, are routinely and safely galvanized. As shown in Figure 4, hydrogen is a trigger, and not the root cause. The root cause of failures of hot dip galvanized high strength fasteners is invariably related to poor material condition resulting in higher than normal susceptibility to HE for a given lot of fasteners (see paragraph 5.1). A dramatic example of such a case is the failure of A354 Grade BD anchor rods on the San Francisco-Oakland Bay Bridge in 2013. The root cause of these failures was attributed to poor material condition of one lot of anchor rods [13].

8. Stress relief prior to electroplating

Residual tensile stress in quenched and tempered fasteners that are work hardened prior to electroplating can lead to the initiation of hydrogen induced microcracks (*after* electroplating). As was described above, HIC can only occur *provided all three conditions for hydrogen embrittlement are met*: notably the material is susceptible *and* there is sufficient hydrogen *and* the residual stress resulting from work hardening exceeds the HE threshold of the steel. In such a scenario, it is beneficial to perform a stress relief operation prior to electroplating.

Standard secondary machining operations such as grinding, turning, tapping and milling are *not* normally problematic. Also, stress relief is not necessary or desirable for fasteners that are thread rolled after heat treatment, or generally where compressive residual stresses are intentionally introduced. Only operations that result in significant plastic deformation resulting in tensile stresses, such as cold forming, cold bending cold straightening, and some drilling and welding operations may justify stress relief before electroplating.

The effectiveness of stress relief increases with increasing temperature and time, however, the temperature must not alter the mechanical properties of the fasteners; more precisely it must not exceed their tempering temperature. The selection of appropriate temperature and duration for a stress relief operation is specific to each case and depends on an assessment by the fastener manufacturer of the likelihood of the three conditions for HE being met. Achieving a well-founded

and effective stress relief strategy should be based on empirical data obtained by product inspection or testing; any such method should consider the time dependence of HE.

NOTE: The requirement for stress relief prior to electroplating is not relevant or appropriate for fasteners that are quenched and tempered without further alteration; tempering effectively relieves residual stress.

9. Hydrogen embrittlement test methods

Given the “time-dependency” of hydrogen embrittlement failures, test methods designed to either detect or measure any mechanical loss of strength resulting from the effect of hydrogen must incorporate a *time* component.

Typically, hydrogen embrittlement testing is performed by means of *sustained load* (SL) tests. Sustained load testing is intended as a post-production (e.g., after electroplating) quality assurance step for testing high strength fasteners that are susceptible to IHE. Sustained load testing consists of applying a specific static load for a fixed period of time ranging from 24 to 200 hours, depending on the specification. The qualitative nature of the sustained load test is such that a fastener will either pass or fail at the given point in time as a result of being subjected to the test conditions. It is not a quantitative measure of how close a fastener is to failure. There are a number of method variations of the sustained load test. The methods most often used to test threaded fasteners are described in ASTM F606, Section 7 [14], ASTM F519 [15] and ISO 15330 [16]. For case-hardened fasteners a more applicable test procedure is described in ASME B18.6.3, Section 4.11.5 [9].

NOTE: Sustained load tests are suitable for testing large numbers of samples from a given lot, making it applicable for production testing. Standard sustained load test specifications are not intended for testing parts after removal from service.

More analytical alternatives to sustained load testing are *slow strain rate* (SSR) tests such as those described in ASTM G129 [17] and ISO 7539-7 [18], or the incremental step load (ISL) test such as in ASTM F1624 [19]. The basis for these tests is a slow increase of the applied load until rupture of the sample, thus incorporating the time component in the test. Given a slow enough loading rate, it is possible to measure the HE threshold stress for a given material under a given concentration of hydrogen.

NOTE: Analytical test methods described in ASTM G129, ISO 7539-7, and ASTM F1624 are not suitable for embrittlement testing of parts on a production scale due to the time and cost associated with performing the test. These test methods are often used for research and development.

10. Baking

The potentially deleterious effects of hydrogen absorbed during surface cleaning or plating can usually be eliminated by “baking” the fasteners after processing. Baking is a low temperature heat treatment that has been shown to either extract hydrogen by effusion or cause it to migrate to trap sites, thus making it immobile. As interstitial (free) hydrogen content is reduced by baking, both time-to-failure and threshold stress increase.

The key factors that influence baking effectiveness are: (i) temperature, (ii) time, and (iii) permeability of the coating. In addition, increasing the rate of heating has also been shown to improve the effectiveness of baking. These factors lead to a great deal of variability for determining appropriate baking conditions. For susceptible parts (e.g., above 39 HRC, 380 HV) that are zinc electroplated, 8-10 hours at 190-220 °C (375-430 °F) is a minimum recommended baking duration. However, depending on size and strength level of the fasteners, they can require baking durations up to 24 hours to sufficiently reduce interstitial (free) hydrogen. A common practice of baking parts above 39 HRC (380 HV) for 4 hours is insufficient and leads to occasional failures.

NOTE: The practice of baking zinc electroplated parts for 4 hours at approximately 190 °C is inadequate for extracting hydrogen because zinc is an effective barrier to hydrogen diffusion. It has been shown that baking time of 4 hours may even be detrimental.

On the other hand, parts such as standard Grade 8 and property class 10.9 fasteners do not need to be baked, yet they are often unnecessarily required to be baked by specifications such as ASTM B633 [20]. Given our current understanding of baking effectiveness and material susceptibility, it is not the baking that prevents these fasteners from failing. Rather, Grade 8 and property class 10.9 fasteners that are correctly manufactured to the material and metallurgical properties intended (explicitly or implied) are not susceptible enough to fail due to IHE.

The maximum temperature used in a baking process is limited by three considerations: (i) it should not exceed the temperature at which the fasteners were originally tempered, (ii) it should not

impair the performance of the coating, and (iii) it should be selected such as to minimize the risk of solid or liquid metal embrittlement, which based on the melting point of the coating material.

NOTE: Zinc has a melting point of 419 °C (786 °F) and zinc electroplated parts are baked at 200-220 °C (390-430 °F). Cadmium has a melting point of 321 °C (610 °F) and cadmium electroplated parts are baked at 190-200 °C (375-390 °F).

The baking process is typically performed after electroplating, prior to application of a conversion coating or sealant and/or top coat. However, other sequences may be suitable depending on the specific properties of surface finishes.

The time between coating and baking should be kept short as a matter of good practice. The intent of such practice is to maximize the extraction of interstitial hydrogen; it is possible that a portion of the interstitial hydrogen may become trapped and more difficult to bake out. This phenomenon has been shown to be critical for electroplated steels at hardness above 50 HRC (510 HV), however, it is not as critical for most standard fasteners. The often used approach of specifying an exact time (e.g., 4 hours) is purely subjective and is intended as a practical operational time-frame and also as a quality assurance mechanism for monitoring good practice. Time between coating and baking should not be used as a rigid criterion for acceptability of a fastener lot and it definitely must not be used as the basis for assigning root cause to a fastener failure.

The electroplater should maintain close control of baking furnace conditions, including methods of loading, time in the furnace and uniformity of temperature. Achieving a well-founded and effective baking strategy should be validated by empirical test data obtained from sustained load testing of production parts described above, and/or process qualification tests such as those specified in ASTM F1940 [21] or DIN 50969-2 [22].

NOTE: It should not be assumed that baking will completely prevent hydrogen embrittlement in all cases.

References

1. ASTM F2078, Standard Terminology Relating to Hydrogen Embrittlement Testing.
2. SAE J429, Mechanical and Material Requirements for Externally Threaded Fasteners.
3. ISO 898-1, Mechanical properties of fasteners made of carbon steel and alloy steel Part 1: Bolts, screws and studs with specified property classes — Coarse thread and fine pitch thread.
4. ASTM F1941, Standard Specification for Electrodeposited Coatings on Threaded Fasteners (Unified Inch Screw Threads (UN/UNR)).
5. ASTM A354, Standard Specification for Quenched and Tempered Alloy Steel Bolts, Studs, and Other Externally Threaded Fasteners.
6. ASTM A325, Standard Specification for Structural Bolts, Steel, Heat Treated, 120/105 ksi Minimum Tensile Strength.
7. ASTM A490, Standard Specification for Structural Bolts, Alloy Steel, Heat Treated, 150 ksi Minimum Tensile Strength.
8. ASTM A574, Standard Specification for Alloy Steel Socket-Head Cap Screws.
9. ASME B18.6.3 - 2010, Machine Screws, Tapping Screws and Metallic Drive Screws (Inch Series).
10. ISO 2702, Heat-treated steel tapping screws - Mechanical properties.
11. Deutscher Schraubenverband E.V., DSV-GAV-Richtlinie Feuerverzinkte Schrauben 2009-07-01 - Technical delivery conditions for steel for fasteners with enhanced requirements.
12. Brahim, S., Yue S., Effect of surface processing variables on hydrogen embrittlement of steel fasteners Part 1: Hot dip galvanizing. *Canadian Metallurgical Quarterly* (2009). **48**(3): 293-301.
13. Brahim, S., Aguilar, R., and Christensen, C., Metallurgical analysis of Bay Bridge broken anchor rods S1-G1 & S2-A6, Joint Report, California Department of Transportation - American Bridge/Fluor, May 7, 2013.
14. ASTM F606, Standard Test Methods for Determining the Mechanical Properties of Externally and Internally Threaded Fasteners, Washers, Direct Tension Indicators, and Rivets.

15. ASTM F 519, Standard Test Method for mechanical hydrogen embrittlement evaluation of plating/coating processes and service environments.
16. ISO 15330, Fasteners — Preloading test for the detection of hydrogen embrittlement — Parallel bearing surface method.
17. ASTM G129, Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking.
18. ISO 7539-7, Corrosion of metals and alloys - Stress corrosion testing - Part 7: Method for slow strain rate testing.
19. ASTM F1624, Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique.
20. ASTM B633, Standard Specification for Electrodeposited Coatings of Zinc on Iron and Steel, ASTM International.
21. ASTM F1940, Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners.
22. DIN 50969-2, Prevention of hydrogen-induced brittle fracture of high-strength steel building elements - Part 2: Test methods.