Stress-Corrosion Cracking

The following is a portion of a technical brief prepared for the Essential Services Task Force by Professor Karl Sieradzki of the Ira A. Fulton School of Engineering, Arizona State University. Professor Sieradzki is Professor of Mechanical and Aerospace Engineering and Professor of Materials and Chemical Engineering

The technical brief describes in detail the phenomenon known as Stress Corrosion Cracking (SCC), which was determined to be the cause of Kinder Morgan Energy Partners, LLC's July 30, 2003 East pipeline failure.

Background Phenomenology of SCC in Steel Pipelines

Stress-corrosion cracking relates to the environmental degradation of the mechanical integrity of structural components. Stress-corrosion failures are well known in a variety of industries such as electrical power generation including nuclear, aircraft, petrochemical, and underground pipeline transmission systems. In order for a component to undergo SCC a combination of 3 factors must be in place, a susceptible material, a corrosive environment and an appropriate level of tensile stress. Figure 1 is a Venn diagram showing the intersection of these three factors and resultant SCC. As shown schematically in Figure 2, there are two variants of SCC, so classified owing to the difference in the microscopic crack-advance mechanism. In one mechanism, that for purposes herein we will call *active path dissolution*, crack advance occurs by a localized corrosion process during which metal is actually dissolved (corroded) locally from the tip of an advancing crack. In the second mechanism hydrogen gas (made available by an electrochemical process) actually absorbs into the metal (a bit like a sponge soaking up water) and reduces the cohesive energy of the solid, which is a measure of how much work is required to pull the solid apart. This second mechanism called *hydrogen embrittlement* (HE) is differentiated from the first in that there is no requirement of metal dissolution for crack advance to occur. Each of these crack-advance mechanisms can result in two different metallurgical classifications of cracking, intergranular SCC and transgranular SCC. We discuss these

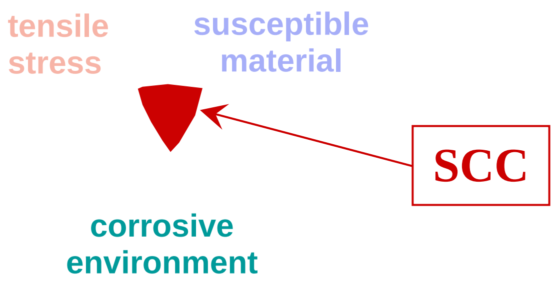

Figure 1. Venn diagram illustrating the factors that control the onset of stress-corrosion cracking.

metallurgical classifications below following some introductory comments on metallurgy and corrosion.

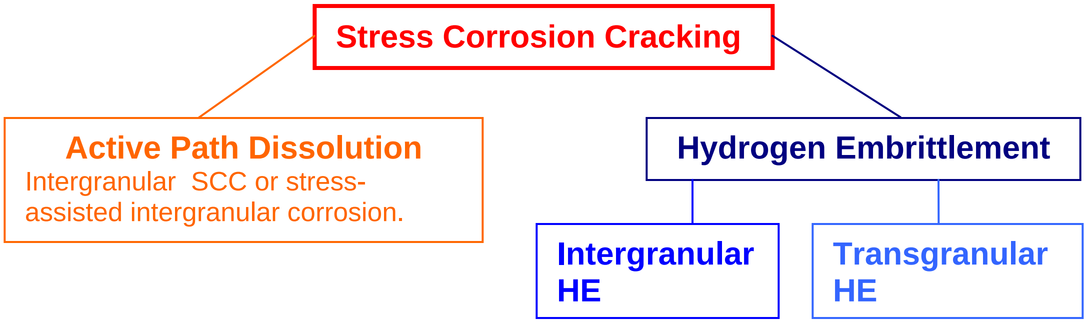

Figure 2. The phenomenon of stress-corrosion cracking is complex and has many variants. Two main variants of stress-corrosion cracking are active path dissolution and hydrogen embrittlement. Active path dissolution always refers to intergranular cracking along an electrochemically active grain boundary path. Hydrogen embrittlement (HE) can result in either an intergranular or a transgranular crack path. The determining factor is often the strength of the steel. HE induced cracking in high strength steel is usually intergranular and whereas in low strength steel such as those used in pipelines HE cracking is transgranular.

Metallurgical Basics

On a macroscopic scale (greater than about 0.1 millimeter) most metallic structural alloys such as steel appear homogeneous in chemical composition and isotropic in terms of physical properties such as mechanical strength. On a more microscopic scale these alloys are composed of tiny (less than 0.1 mm in diameter) crystallites or grains that are “stuck together” at the boundaries separating these crystallites. All materials have some level of impurities and in steels these are typically elements such as sulfur, phosphorous, antimony and tin. During solidification and other processing that an alloy receives, the chemical impurities are rejected from the interior of the crystallites (impurity segregation) and become highly concentrated at the grain boundaries. While owing to segregation impurity levels at grain boundaries can achieve 50 atomic percent or greater, the bulk level of impurities in the grain interior is very small (of order 0.1 atomic percent or less). Thus the chemical composition of the grain boundaries can be totally different from that of the grain interior and consequently the corrosion behavior of the grain boundary will be different from that of the interior of the grain.

Corrosion Basics

Corrosion is an electrochemical process involving chemical reactions and electron transfer. Electrochemical reactions always involve electron transfer while a simple chemical reaction does not. Metallic corrosion can occur along several different reactions paths and in the simplest case a metal such as iron (Fe) is oxidized into a soluble cation.

The corresponding electrochemical reaction is written as,

$$Fe \Leftrightarrow Fe^{2+} + 2e^{-}. \qquad (1)$$

Metallic iron starts off in a zero-valence state (Fe) and is oxidized to a soluble cation (Fe^{2+}) of positive charge $2+$. This necessarily involves the transfer of 2 electrons (per iron atom) in order to maintain charge balance. The 2 electrons/atom produced in the iron oxidation process are consumed in a corresponding reduction process. Typically in the corrosion of steel this involves reduction of dissolved oxygen and/or reduction of water. Reduction of dissolved oxygen increases the pH of the electrolyte while water reduction produces hydrogen gas (bubbles) on the surface of the corroding metal. The amount of metal corrosion and rate of the corrosion process is determined to great extent by two factors. One is simply the solubility of the metal cation in the electrolyte and this is governed by the identity and nature of the electrolyte. Issues such as anion identity (chloride, sulfate, phosphate, carbonate, nitrate, etc.), pH and temperature affect solubility. The other issue is transport of dissolved metal cations away from the corroding metal surface. If transport is slow or somehow impeded the electrolyte will eventually saturate in the dissolved metal cation and the corrosion process stops (Le Chatelier's Principle). Since corrosion is electrochemical in nature, reactions such as (1) above can be controlled by the application of a voltage or potential. Figure 3 illustrates the effects of applying both a positive voltage and a negative voltage to a sample of iron immersed in

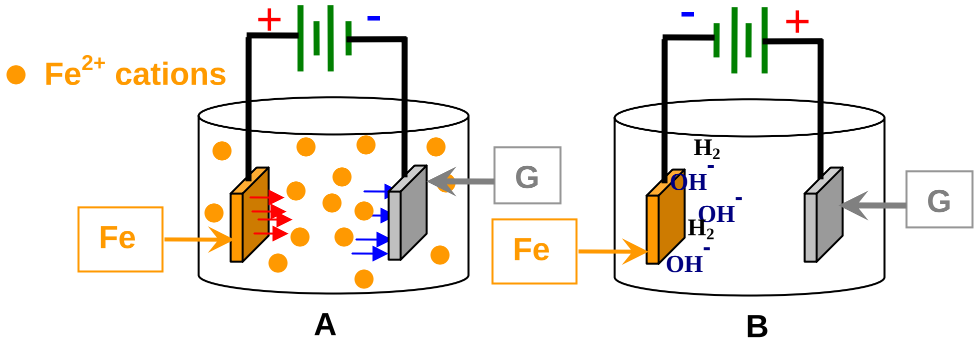

Figure 3. An iron sample is electrically connected to an inert counter electrode, G, such as graphite through a battery. Both electrodes are immersed in an electrolyte. (A) The iron is connected to the positive terminal of the battery and the counter electrode is connected to the negative terminal. The electrolyte contains iron cations. At the surface of the iron sample reaction (1) proceeds from left to right producing additional iron cations (red arrows). At the surface of the inert counter electrode the iron cations are reduced (blue arrows) and reaction (1) proceeds from right to left resulting in iron plating on to the surface of the graphite. (B) The iron sample is connected to the negative terminal of the battery and the inert electrode is connected to the positive terminal. There are no iron cations present in this electrolyte. At the surface of the iron electrode dissolved oxygen and water are reduced producing hydroxyl ions (OH^-) and hydrogen gas (H_2). When the iron sample is polarized in this manner it can not undergo a general corrosion process. This is the principle of cathodic protection.

different electrolytes. In effect, the applied voltage alters the solubility of the dissolved Fe^{2+} in the electrolyte. A positive voltage will increase the solubility and corresponding drive reaction (1) from left to right (iron oxidation) while a negative voltage will decrease the solubility and drive reaction (1) from right to left (iron reduction i.e., electroplating of iron). If there are no Fe^{2+} cations in the electrolyte other reduction processes occur such as oxygen and water reduction. This is the principle of cathodic protection (CP).

Stress-Corrosion Cracking of Pipeline Steels

Stress-corrosion cracking is a localized corrosion process. Generally there is no significant or measurable loss of metal. For example, in a buried pipeline the wall thickness of the pipe remains unchanged while the pipeline undergoes cracking. The cracking direction is nominally perpendicular to the tensile stress. As illustrated in Figure 4, stress-corrosion cracks can either be intergranular or transgranular. In appropriate electrolytes such as those that develop in naturally occurring groundwater, pipeline steels are susceptible to both co-called high and low pH SCC. The environment associated with high pH SCC is a relatively concentrated carbonate/bi-carbonate electrolyte. The chemical equilibrium between carbonate and bi-carbonate buffers the pH in these electrolytes forcing values in the vicinity of 9.5 – 10. These species develop over time owing to dissolved carbon dioxide and oxygen in the ground water. The high pH develops as a direct consequence of the cathodic protection used to protect the pipeline against general corrosion (severe rusting, loss of wall thickness, etc.). The electrolyte associated with the lower pH form of SCC contains many of the same species albeit at significantly reduced concentrations. Furthermore, in this case the pH is determined by a chemical equilibrium between carbonic acid and bi-carbonate which maintains the pH values in the vicinity of 6.4 (near neutral). Carbonate/bi-carbonate stress-corrosion cracking occurs by an active path dissolution mechanism and is intergranular in nature. This form of cracking shows some sensitivity to temperature and tends to be most severe around 40 ºC. SCC in the lower

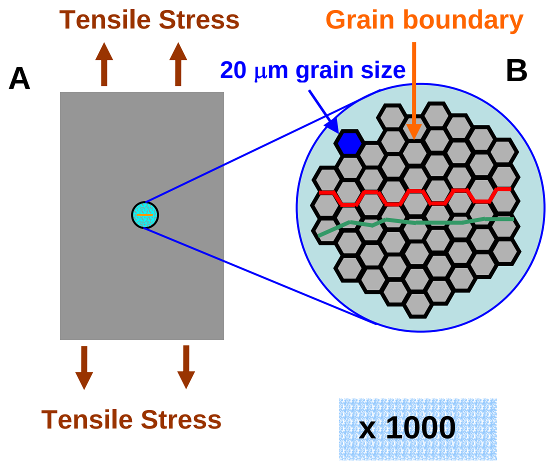

Figure 4. Illustration of crack morphologies associated with stress-corrosion cracking. (A) A sample is under tensile loading and a crack has developed in the center of the sample. (B) Under a magnification of about 1000 the crack morphology can be observed. Intergranular SCC follows a crack path along the grain boundaries (red) while in transgranular SCC the crack travels across the grains (green). Grain size corresponds to that of pipeline steels, about 20 micro – meters.

pH electrolyte occurs by a hydrogen embrittlement mechanism and is transgranular in nature.

These forms of stress corrosion are related. All buried steel pipelines have a coating that serves as additional protection against general corrosion. Coatings are typically asphalt or if applied in the field polyethylene tape. If the coating has a local flaw, this is generally the location of SCC nucleation. Some coating flaws maintain cathodic protection at the steel surface thus allowing for a pH increase and eventual high pH stress corrosion cracking. Owing to detailed geometrical effects, other flaws cause a significant "iR drop" and cathodic protection is lost at the exposed steel at the bottom of the coating flaw. This situation will result in the lower pH form of SCC and hydrogen embrittlement. Any buried transmission steel pipeline whether carrying natural gas or gasoline can in principle undergo either form of cracking. The particular form of SCC that develops depends on subtle factors such as type of coating defect, temperature, and efficiency of the cathodic protection system.

Here we review in more detail the high pH form of SCC since this was the stated cause of the Kinder Morgan pipeline failure. As discussed above, the grain boundaries in the steel are more susceptible to corrosion owing to impurity segregation during solidification of the steel. The grain boundaries provide an "active – path" for the localized corrosion process. The role of the stress is to open up the crack and thus prevent corrosion products from shutting down the active corrosion process. If the tensile stress is too low and the crack remains very narrow, the electrolyte between the crack walls becomes saturated in corrosion product and SCC terminates. The stress results from fluid pressure in the pipeline and residual stresses from welding. Additionally, for sections of pipeline near enough to compressor stations, there may be a small cyclic stress component superimposed on the mean stress level (corrosion fatigue). Figure 5 summarizes the

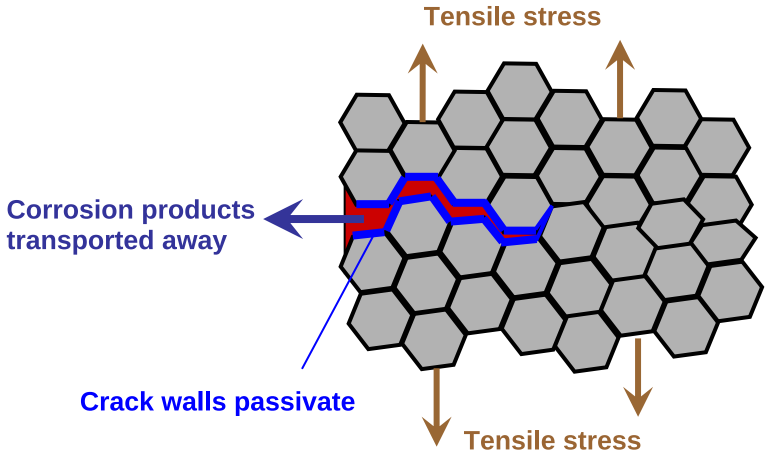

Figure 5. Details of high pH SCC which occurs by active path dissolution. The grain boundaries corrode owing to impurity segregation while the grain matrix remains passive. The crack walls which are comprised of exposed grain boundaries will corrode until the electrochemically active segregated impurities are exhausted at which point the walls passivate. The stress opens up the crack allowing for enhanced diffusive transport of the corrosion products. If the stress level is too low, the electrolyte between the crack walls becomes saturated in corrosion product and SCC terminates.

scenario for high pH stress-corrosion cracking. One final comment on this form of cracking is that its occurrence is always associated with multiple stress-corrosion cracks that are spaced relatively close to one another. If cracking proceeds long enough these cracks eventually coalesce and form a large connected crack that results in a catastrophic failure event (loss of operating pressure).