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ROLES OF H₂S IN THE BEHAVIOR OF ENGINEERING ALLOYS: A REVIEW OF LITERATURE AND EXPERIENCE

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ABSTRACT

Hydrogen sulfide (H_2S) has long been associated with the cause of corrosion damage and sulfide stress cracking (SSC) in high strength steels and high hardness weldments used in oil and gas production, petroleum refining, and petrochemical/chemical processing. Other applications where sulfide species have produced environmental cracking include heavy water production, electric power, marine applications and many others where sulfate reducing bacteria can flourish and oftentimes produce substantial amounts of H_2S. H_2S has also been associated with internal blistering, hydrogen induced cracking (HIC) and stress oriented hydrogen induced cracking (SOHIC) of carbon steels used in refinery vessels in wet H_2S service and pipelines containing sour (H_2S-containing) fluids. In recent years, new stainless alloys have been implemented in lieu of conventional steels in many applications where H_2S corrosion is particularly severe. These materials have been used along with chemical inhibitors to mitigate corrosion. These alloys, however, may in some cases also be susceptible to SSC, localized corrosion and anodic stress corrosion cracking (SCC) in sour environments. In this review, the behavior of carbon and low-alloy steels, stainless steels, and nickel alloys in sour environments is discussed. Emphasis is placed on the identification of the various types of H_2S-related corrosion and environmental cracking that can occur, the origin and mechanisms, and the methods of control.

Keywords: sulfide stress cracking, SSC, hydrogen induced cracking, HIC, stress oriented hydrogen induced cracking, SOHIC, steel, stainless steel, nickel base alloy

INTRODUCTION

For over five decades there has been a continual need to develop new materials technology for use in industrial applications involving exposure to H_2S. Much of this effort has centered around the need for higher strength and more corrosion and/or embrittlement resistant materials that can withstand high temperature, high pressure, and increasing aggressive service environments. More recent research has

been directed at identifying materials that can withstand service conditions where pressures and temperatures are in excess of 135 MPa and 200 C, in the presence of significant quantities of corrosive gases such as H_2S and CO_2 and aggressive species such as chlorides and sulfur compounds.[1] Of even greater importance is the need for more economic stainless steels with high strength and corrosion resistance to handle service applications involving exposure to high CO_2 partial pressures in combination with low to moderate levels of H_2S (<100 kPa). [2]

Additionally, downstream petroleum refining and petrochemical environments are subject to higher levels of corrosivity as a result of processing a greater variety of impure hydrocarbon feedstocks. Impurities such as H_2S, organic sulfide compounds, and nitrogen compounds, result in high levels of H_2S, cyanide and ammonia which can also produce conditions for SSC and HIC of steels used in plant pressure vessels and piping. [3]

Understanding of the role of H_2S in the degradation of engineering has remained paramount over the past several decades in research. In addition to being extremely toxic, H_2S is responsible for corrosion and environmental embrittlement in common materials of construction. Consequently, it has been necessary to develop special materials and processing methods that minimize the effects of corrosive degradation and maximize the integrity of these systems. Furthermore, through an understanding of H_2S-related cracking mechanisms, it has been possible to monitor and make adjustments to process environments to minimize H_2S corrosion and embrittlement.

This paper reviews the roles of H_2S in the following corrosion phenomena:

1. Corrosion of steel
2. Sulfide stress cracking (SSC)
3. Hydrogen induced cracking (HIC)
4. Stress oriented hydrogen induced cracking (SOHIC)
5. Environmental cracking of stainless and Ni-base alloys.

HYDROGEN SULFIDE CORROSION

Acidic Environments

H_2S as well as CO_2 can be dissolved in aqueous environments to form acidic, corrosive solutions (see Figure 1).[4] From this behavior, these gases derive their commonly used name: acid gases. Depending on the temperature, pressure, and pH of the environment, aqueous environments containing H_2S and/or CO_2 can be aggressive to carbon and low-alloy steels by causing severe weight-loss corrosion. Corrosion rates for low-alloy steels in acidic H_2S-containing environments tend to increase with decreasing pH of the aqueous solutions.[5] Corrosion in these environments under anaerobic conditions commonly found in oilfield production typically occurs by the following processes: [6]

anode:
$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

cathode:
$$H_2S + H_2O \rightarrow H^+ + HS^- + H_2O \qquad (2)$$
$$HS^- + H_2O \rightarrow H^+ + S^{2-} + H_2O \qquad (3)$$

net reaction:

$$Fe + H_2S \ H_2O \rightarrow FeS + 2H^0 \tag{4}$$

Under acidic conditions, H_2S is stable (See Figure 2) and can dissolve into the aqueous solution. [7] In practice, iron sulfide corrosion products are based on FeS as shown above but can take other molecular forms such as FeS_2, Fe_7S_8, or Fe_9S_8 depending on the pH, H_2S partial pressure and oxidizing potential of the environment.

Alkaline Environments

Many downstream hydrocarbon refining and petrochemical process environments operate at alkaline pH levels (>pH 7) by virtue of the chemical equilibrium established between dissolved H_2S and ammonia in aqueous solutions. Corrosion processes tend to be different and more complex in these conditions versus those found in acidic environments. Typical corrosion reactions for iron in alkaline sour water environments are similar to those shown for acidic conditions in Equations 1-4.

For sulfide corrosion mechanisms which operate in the limited pH range common to many alkaline wet H_2S processes (pH 7-10), the active sulfide species are bisulfide (HS⁻) and soluble sulfide (S^{-2}). As in acidic environments, sulfide corrosion products can be both stoichiometric and non-stoichiometric depending the conditions that prevail. In many cases, these sulfide films can impart protection from corrosion resulting in reduced corrosion rates. However, cyanide compounds can also be present in many cases and enter in the corrosion reaction according to the following equation:

$$FeS + 6CN^- \rightarrow Fe(CN)_6^{4-} + S^{2-} \tag{5}$$

This reaction is significant because it results in a complex between iron and cyanide being formed and a destruction of the normally pseudo-passive sulfide films. It also results in the production of atomic hydrogen as shown below:

$$Fe + 2H^+ + 6CN_6^{4-} \rightarrow Fe(CN)_6^{4-} + 2H^0 \tag{6}$$
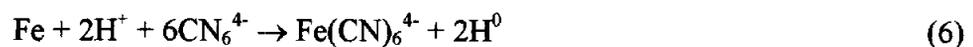
Production of Atomic Hydrogen

One of the natural byproducts of corrosion is the production of atomic hydrogen at local cathodic sites. Atomic hydrogen (H^0) is readily *adsorbed* onto the metal surface. In most corrosive environments, the vast majority of this atomic hydrogen recombines on the metal surface to form hydrogen gas (H_2) which harmlessly bubbles off of the metal surface. However, in the presence of environments that contain sulfur species resulting from H_2S (i.e. dissolved H_2S, HS⁻ and S^{-2}), the kinetics of recombination can be significantly retarded resulting in increased *absorption* of atomic hydrogen by the substrate material. This behavior results because sulfur is a highly effective hydrogen recombination "poison" which acts similarly to species such as Sn, Pb, Sb, P which increase the efficiency of hydrogen charging (α) defined by the following equation:

$$\alpha = H_P/H_A \tag{7}$$

where: H_P = hydrogen produced by corrosion and H_A = hydrogen absorbed into the material.

Under steady state conditions, in the absence of internal trapping of hydrogen, the efficiency of hydrogen charging can be represented as the simple ratio of the permeation current determined in a simple hydrogen permeation experiment[8] and the corrosion current on the exposed surface. Additionally, the overall severity of hydrogen charging can usually be represented by the product of the corrosion current and the efficiency of hydrogen charging which is proportional to the hydrogen flux.

In most cases for sour environments, the hydrogen permeation flux versus time curve has the characteristic behavior shown in Figure 3. It increases and reaches a maximum value (J_{max}) and then the flux decreases to an intermediate steady state value (J_{ss}) or slowly continues to decrease with time as semi-protective sulfide films form on the metal surface. However, if these films are disrupted due to chemical upsets in the service environment, flow induced shear stress or periodic surface inspection, another episode of high flux can ensue. From this figure, it can be seen that peak hydrogen flux may only be a passing situation. In some cases, chemical additions or inhibitors may be utilized to mitigate such transient situations; however, in others careful attention to metallurgical processing of the material must be utilized to prevent environmental cracking associated with these events.

As shown in the following sections, the absorbed hydrogen produced by exposure to H_2S-containing environments can have a significant influence on the embrittlement and environmental cracking of materials. When evaluating the impact of hydrogen charging environments on materials, another meaningful parameter is the subsurface hydrogen concentration (C_o) on the surface exposed to an H_2S environment. It is derived from the steady state hydrogen permeation current (J_{ss}) and effective diffusivity of hydrogen (D_{eff}) in the material as shown below[8]

$$J_{ss} = D_{eff}C_0/L \tag{8}$$

where L = metal thickness. This approach, shown schematically in Figure 4,[9] allows for determination of critical values of hydrogen concentration (C^*) for cracking of particular materials so that the role of metallurgical condition and processing can be understood and used to optimize service performance.

SULFIDE STRESS CRACKING OF STEELS

It is generally accepted that SSC is a form of hydrogen embrittlement cracking in most high strength steels. Admittedly, direct evidence to this effect is limited; but this is only due to the limited number of fundamental mechanistic studies that have been conducted in sour environments. Sulfide stress cracking can be induced in susceptible materials by the simultaneous presence of tensile stresses and a corrosive environment containing a sufficient level of H_2S. The role of H_2S in this phenomenon is generally considered to be two-fold: (1) it increases the rate of corrosion of steel in aqueous solutions, and (2) it poisons the hydrogen recombination/evolution reaction as discussed previously. Consequently, H_2S results in increases in the severity of hydrogen charging versus similar environments without H_2S.

Mechanisms of Sulfide Stress Cracking

From the above discussion, it would appear fortuitous that hydrogen is intimately connected with SSC failure. Most of the attributions of the role of hydrogen in SSC are based on similar cracking tendencies observed in SSC and hydrogen embrittlement tests on carbon and low-alloy steels in non-H_2S containing environments.[10] However, differences in SSC in Ni-containing, low-alloy steels have been observed which suggest that an anodic SCC mechanism is also possible in these materials.

<u>Hydrogen Embrittlement Cracking Mechanisms.</u> A comprehensive mechanistic SSC study was conducted to identify specifically the mechanism of SSC in AISI 4130 steel which is the basis of most high strength steels used in oilfield service.[11] Tests were conducted both with and without H_2S under conditions of applied potential to produce equivalent hydrogen permeation currents. As shown in Figure 5, susceptibility to SSC was found to be directly related to the amount of hydrogen available, not the presence or absence of H_2S. In the case where the hydrogen-embrittlement mechanism prevails, hydrogen atoms (H^0) produced by corrosion or cathodic charging can recombine to form molecular hydrogen or can be adsorbed onto the metal surface and diffuse into the metal. In an H_2S-containing environment, the absorption of atomic hydrogen into the metal is enhanced by the poisoning effect of S-containing species indicated previously. This effect is shown in Figure 6, where the hydrogen charging characteristics of a low-alloy steel in an aqueous medium are shown both as a function of pH and H_2S concentration. [12] Once in the material, atomic hydrogen readily diffuses at ambient temperatures to sites of high internal stress (i.e. grain boundaries, inclusions, and regions of triaxial stress at notches). In the presence of tensile stresses, these locations become sites for embrittlement and the initiation of brittle cracking failure.

In recent years there have been substantial efforts for the transportation industry directed toward maximizing resistance to SSC in high strength steels used in oilfield casing and tubing and canisters used to contain pressurized natural gas. It appears that quenching and tempering (Q&T) is a preferred process for producing high strength steels with higher resistance to SSC than that obtained with other processing methods (e.g. annealing, normalizing and normalizing and tempering). Even more importantly, steels with a high percentage of transformation to martensite upon quenching exhibit maximum resistance to SSC following tempering (See Figure 7). [13] This effect has been associated with two major benefits of the Q&T process: (1) production of a martensitic structure in the material by balancing steel composition and the critical cooling rate to produce complete martensitic transformation, and (2) a fully martensitic, as-quenched structure allows tempering to be conducted at higher temperatures leading to production of a high SSC resistant spheroidized carbide structure while retaining high strength.

The use of AISI 4130 steels and its modifications with increased Mo is particularly noteworthy since the C-Cr-Mo composition promotes both through-wall hardenability (i.e. martensitic transformation) and even higher tempering temperatures. This technology has been utilized to produce steels with up to 650 - 750 MPa yield strength with high resistance to SSC. Moreover, further innovations have been made to increase the SSC resistance of steels even farther. Studies show that grain refinement produced through a combination of thermo-mechanically controlled processing (TMCP), microalloying additions of Nb, Ti, V and B, and high tempering temperatures can increase the SSC resistance of steels in the range of 750 - 860 MPa yield strength. [14,15]

<u>Stress Corrosion Cracking Mechanisms.</u> Ni-containing steels exhibit a different environmental cracking tendency to that of Ni-free steels as discussed previously. [16] Generally, steels with >1% Ni exhibit a greater susceptibility to environmental cracking in sour environments, (see Figure 8). However, some controversy still exists regarding this matter. More interesting still is the fact that these Ni-containing steels show a reduced tendency for environmental cracking with applied cathodic potentials. [17] This is opposite to the effect expected if hydrogen embrittlement cracking mechanisms were operating, but indicative of the behavior that would persist if anodic SCC mechanisms were present.

SSC Fractography

In low-alloy steels, SSC appears as both transgranular and intergranular cracking. [18] It is generally observed that SSC in high strength steels (>700 MPa yield strength) appears predominantly as

intergranular cracking except where steels have been processed to maximize SSC resistance. Lower strength steels (<700 MPa yield strength) as well as high strength steels using enhanced processing to improve SSC resistance, have predominantly transgranular features. In low strength steels, the failure mode incorporates short blister cracks which are linked by transgranular cleavage cracks. This mechanism is more commonly described by the term stress oriented hydrogen induced cracking (SOHIC) and will be discussed in more detail in a later section of this paper. In the enhanced high strength steels, the transgranular mode is noted on the primary fracture surface with intergranular secondary cracks along prior austenite grain boundaries.

SSC - Environmental Variables

The three paramount environmental variables are solution pH, environment temperature, and H_2S concentration.

pH and H_2S Partial Pressure. In most environments, tendencies toward SSC of low-alloy steels generally decrease with increasing pH of the aqueous environment between pH 0 and 7. The reason for this behavior appears to be the decrease in availability of the hydrogen ion in aqueous media with increasing pH. It has also been commonly observed that SSC of low-alloy steels increases with increasing H_2S concentration. Standard laboratory tests have been developed for SSC which evaluate materials in solutions adjusted to pH values in the range of 3 to 5 by varying H_2S partial pressure and additions of acid and buffering agents such as bicarbonate or acetate. [19, 20] Figure 9 shows the regimes of serviceability over this range for a typical API casing grade, low alloy steel with a specified minimum yield strength of 760 MPa. It demonstrates the strong relationships among SSC, pH and H_2S partial pressure. [19]

Temperature. Sulfide stress cracking is a highly temperature dependent phenomenon and has been used effectively in the design of some components that operate continuously at high temperatures in sour oil and gas applications (i.e. downhole tubing and casing). As shown in Figure 10, SSC susceptibility reaches a maximum at about room temperature and then decreases with increasing temperature over the range 25-200 C. [21]

HYDROGEN BLISTERING, HIC AND SOHIC

As previously discussed, one of the consequences of H_2S corrosion is absorption of atomic hydrogen into the steel. Another manifestation of this behavior is the formation of internal blisters, HIC and SOHIC in susceptible steels. They are characterized by separations that generally run parallel to the surface of the material and are caused by the accumulation of molecular hydrogen. These separations may occur as large blisters or as a series of thin, blister cracks (referred to as hydrogen induced cracking - HIC) that step through the material. These parallel blister cracks may link up and propagate in a steplike manner until catastrophic failure occurs when the effective thickness of the material is sufficiently reduced.

One of the main distinctions between SSC discussed in the previous section and those cracking mechanisms involving hydrogen blistering indicated above is that SSC is a solid state embrittlement reaction resulting from the interaction between the metal lattice and the atomic hydrogen. On the contrary, blistering and HIC involves the recombination of atomic hydrogen to molecular hydrogen at weak internal interfaces (e.g. inclusions, and laminations) in the material. The blistering and HIC processes do not need the presence of externally applied tensile stress to occur. Under the influence of

applied or residual tensile stress, however, the short blister cracks normally associated with HIC can form a stacked array in the through thickness direction. This phenomenon is referred to as stress oriented hydrogen induced cracking (SOHIC). When linked by short transgranular cleavage cracks, SOHIC can lead to failure by reducing the effective thickness. Blistering, HIC and SOHIC are generally observed in lower strength steels used in plate and pipe products with <700 MPa yield strength.

Examples of SSC, HIC and SOHIC are shown in Figures 11 through 13, respectively.

Environmental Factors

The three paramount environmental factors in determining susceptibility of steels to blistering, HIC and SOHIC, are generally the same as those involved with SSC discussed previously in this paper - pH, H_2S concentration and service temperature. This is not surprising since both types of phenomena are based on the materials response to absorbed hydrogen produced by the sulfide corrosion reaction. Susceptibility to cracking increases in acidic solutions with decreasing pH and increasing H_2S concentration. However, the influence of service temperature differs between the hydrogen blistering-type cracking mechanism and SSC. Laboratory studies show that susceptibility to stepwise cracking increases with increasing temperature up to a maximum around 50 C and then decreases with further increases in environment temperature (*see* Figure 14). [22] While the reasons for this behavior has not totally been confirmed, it is believed to be related to changes in hydrogen charging efficiency with temperature in aqueous, acidic solutions.

Since welded, low strength plate steels are more extensively utilized in downstream refinery applications, more extensive research has been conducted in alkaline (pH 7-10) sour water solutions found in these applications. As shown in Figures 15 through 17,[23] hydrogen flux increases with H_2S, cyanide and chloride concentration and increasing service temperature. This is primarily due to the synergistic effects observed among these variables in increasing the hydrogen charging efficiencies to exceptionally high values when high levels of all variables are imposed, thus leading to severe conditions for HIC, SOHIC and SSC. In fact, one of the surprising aspects of these alkaline sour water environments is that, despite their high pH, hydrogen charging levels can be obtained that exceed those typically associated with severe acid solutions (i.e. TM0177 solution at pH 3).

Metallurgical Factors Influencing HIC and SOHIC

Susceptibility to HIC is highly dependent on the impurity content of the material, heat treatment and metallurgical processing. These variables influence the distribution of hydrogen in the material and the nature of the internal sites where hydrogen can recombine to form molecular hydrogen and accumulate. For example, susceptibility to HIC decreases with a reduction in the level of S in the steel (See Figure 18). [24] A similar but lesser influence of P has also been identified. The predominance of the sulfur effect is related to the increase in number, size and aspect ratio of MnS inclusions with increasing S content. These inclusions act as primary sites for HIC at medium to high levels of sulfur in the steel. In some cases, Cu and Ca additions also appear to be beneficial in reducing HIC susceptibility. Cu additions greater than 0.2 wt. percent reduce hydrogen absorption from sulfide corrosion in intermediate pH environments (4.8 - 5.2). [25] Ca additions help improve HIC resistance through sulfide inclusion shape control by breaking up the normally elongated inclusions to a more spherical shape (i.e. reduce the inclusion aspect ratio). This shape is less conducive to the initiation of the planar blisters typical of HIC. [26] However, when S contents are very low, over-treatment by Ca can increase susceptibility to HIC by the formation of Ca containing inclusions (See Figure 19).

Resistance to HIC can also change with the metallurgical processing method used in steel production. Highest susceptibility is associated with hot rolled structures. Normalizing, quenching and tempering have been shown to increase HIC resistance (See Figure 18) particularly at lower S content. Thermo-mechanically controlled processing (TMCP) of pipe and plate steels, combined with lower S levels and carbon equivalents has resulted in a high resistance to HIC. This effect is considered to be the result of a reduction of the microstructural (ferrite/pearlite) banding in the material with normalizing and quenching and tempering processing methods. The carbide-rich bands are considered secondary sites that can predominate once sulfur levels are reduced.

One very important aspect of susceptibility to SOHIC does not follow all of the same relationships commonly observed for HIC. Maximum susceptibility to SOHIC is associated with low to intermediate sulfur levels (0.002 to 0.010 wt. percent S). As the susceptibility to HIC decreases with decreased S content of the steel, the tendency to form through thickness arrays of blister cracks (i.e. SOHIC) under applied tensile stress increases with reduced sulfur content until ultra-low sulfur levels ($\leq$0.001 wt. percent S) are reached (See Figure 20).[27] In most cases, attention to design and post weld heat treatment can be utilized to reduce operating stresses in welded equipment to levels below those required to produce SOHIC. However, in some cases, the combined effects of low to intermediate sulfur levels and microstructural banding can combine to result in SOHIC at stress levels around ASME allowables. Therefore, careful attention to metallurgical processing and materials qualification are required to assure resistance to SOHIC.

ENVIRONMENTAL CRACKING OF HIGH-ALLOY MATERIALS

Stainless steels and Ni-base alloys offer great potential in engineering design by eliminating the dependence on corrosion inhibitors. However, it must be realized that these materials can, in some cases, act very differently than steels and are subject to a different set of engineering limitations. In addition, in order to justify corrosion resistance alloys (CRAs) for many applications, they must also have high strength. In addition, these materials must be able to overcome the detrimental effects of H_2S, CO_2 gas, sulfur compounds, and concentrated brine solutions. To obtain high strength and corrosion resistance, there has been increased use of materials containing high levels of chromium, nickel, and molybdenum (Table 1).

Two important areas of concern for CRAs are that their corrosion and cracking behavior is generally more complex than that observed for conventional steels. For example, some stainless and nickel alloys may be susceptible to cracking by either a hydrogen-embrittlement-cracking (HEC) process or by anodic SCC in chloride-containing aqueous environments, or by both mechanisms. The mechanisms involved in hydrogen-related HEC and anodic SCC processes are contrasted in Figure 21. [28]

To understand the behavior of high-alloy materials in oilfield production environments, four classifications of materials need to be made. They are (1) martensitic stainless steels, (2) duplex stainless steels, (3) high-alloy austenitic stainless steels, and (4) Ni-base alloys. Typically, conventional austenitic stainless (AISI 3XX series) steels do not have adequate strength or resistance from SCC for use in most H_2S applications. Each classification has different ranges of composition, microstructure, strengthening mechanism, and performance in corrosive production environments. As a rule, CRAs do not behave as one class of materials.

Martensitic Stainless Steels

Martensitic stainless steels have been used in oilfield production for many years. These have been nominally 12%Cr stainless steels based on wrought AISI 410 or cast CA15 stainless steels. AISI 410 and similar alloys have been found to be more susceptible to SSC in severe H_2S environments than low-alloy steels at corresponding strength levels (see Figure 22).[29] However, when used within their limiting conditions of pH and H_2S partial pressure, they can provide exceptional serviceability.

Recently, new grades of martensitic stainless steels with improved mechanical properties have been introduced. For example, high-strength tubular grades of martensitic stainless steels with yield strengths up to 760 MPa have been developed for oilfield tubulars. They are nominally 13%Cr stainless steels and are used in the quenched and tempered condition. Newer materials also contain additions of 4 to 6 percent Ni and 1.5 to 2 percent Mo for added resistance to localized corrosion superior to the straight 13Cr alloys. They also show better SSC resistance than the more commonly used AISI 410 steels and 13Cr steels (See Figure 23). [30] As indicated for SSC (and also true for high temperature corrosion resistance), performance is highly dependent on pH leading to a major increase in performance above pH 4.

Maximum susceptibility to cracking in martensitic stainless steels typically occurs near room temperature with decreasing cracking susceptibility with increasing service temperature. This is consistent with the mechanisms of SSC in carbon and low alloy steels. Resistance to environmental cracking is dependent on pH, H_2S partial pressure and chloride concentration in the environment. Resistance to cracking is dependent on the material remaining essentially passive. Once the environmental severity increases beyond certain limits (which are characteristically different for each material composition and material condition), passivity is lost and sulfide corrosion commences. This corrosion is usually of a localized nature which can generate atomic hydrogen at sufficient levels to produce SSC.

Duplex Stainless Steels

Duplex stainless steels are a mixture of two microstructural constituents, ferrite and austenite. They can be produced in both cast and wrought conditions and typically have 22 to 25 percent Cr with yield strengths of 350-620 MPa when in the cast or annealed conditions. These steels derive their mechanical properties and microstructure from a balanced chemical composition which contains alloying additions of chromium, nickel, molybdenum and nitrogen. This results in a material with a corrosion resistance generally superior to those of the martensitic stainless steels in H_2S, CO_2, and brine environments together with a material strength, which is greater than conventional austenitic stainless steels.

Wrought duplex stainless steels have been introduced with strength capabilities between 400 and 900 MPa yield strength. Unlike low-alloy steels and martensitic stainless steels, duplex stainless steels can be strengthened by cold working during processing to reach maximum conditions. While this cold working has a generally negative effect on susceptibility to environmental cracking, the effect appears to be of secondary importance in most cases when it is limited to no more than about 30 percent cold reduction in tubular materials.

Laboratory tests indicate that these materials can be susceptible to cracking in environments containing H_2S and brine. The studies also indicate that the cracking behavior of these materials is somewhat different from that observed for low-alloy steels. Duplex stainless steels tend to be susceptible

to environmental cracking at both low and high temperatures whereas SSC of high-strength steels and martensitic stainless steels tends to be a low-temperature, hydrogen-related phenomenon. The cracking of duplex stainless steels in brine solutions with H_2S and CO_2 results from environmental cracking of the ferrite phase by HEC at low temperatures, and by anodic SCC at high temperature. [31] This results in a maximum susceptibility to environmental cracking at intermediate temperatures generally found in the range 60 to 120 C depending on the specific alloy and test method utilized for evaluation (See Figure 24). [32] The maximum allowable H_2S content for crack-free behavior with duplex stainless steels appears to be only slightly higher than that observed for more corrosion resistant martensitic stainless steels (e.g. 13Cr-5Ni-2Mo steels). However, as with the martensitic stainless steels, serviceability is still very dependent on pH with pH 4 being a major dividing line in performance. Research on the 22-25% Cr duplex stainless steels indicates that this limiting level of H_2S is between 0.7 and 35 kPa partial pressure H_2S. [33] Due to the increased cost of duplex stainless steels, their main advantage appears to be their higher strength capabilities when coldworked.

Austenitic Stainless Steels

High-alloy austenitic stainless steels are being introduced into H_2S service applications primarily for use as high-strength tubular materials. These materials have a fully austenitic microstructure with high levels of Ni, Cr, Mo and N. This austenitic structure is stable even after high levels of cold working during processing. Highly alloyed austenitic stainless steels in tubular form can be cold worked in the range of 30 to 50 percent cold reduction to strength levels in tubular material between 750 and 1,000 MPa yield strength.

High-alloy austenitic stainless steels have exceptionally good corrosion resistance. In an H_2S and chloride containing environment, high levels of Cr and Mo offer these materials resistance to both general and localized corrosive attack. Alloying additions of N also benefit by increasing pitting resistance. However, it appears that the benefit of N in high alloy austenitic stainless steels exposed to H_2S-containing environments is not as great as observed in non-sulfide containing, oxidizing, chloride-containing environments (e.g. aerated seawater).

There are many materials that fall into this alloy classification which have varying concentrations of Cr, Mo and N. Their corrosion behavior can vary substantially depending on actual composition. Generally, these are correlated based on pitting resistance equivalent number (PREN) given by the following equation[34]:

$$PREN = Cr + 3.3Mo + 11N + 1.5(W+Cb) \qquad (9)$$

where the constant associated with N is 11 which is lower than 30 commonly utilized in non-sulfide containing oxidizing environments (recalling the above discussion). [35] Additionally, benefit is also assigned to alloying additions of W and Cb. Nickel also appears to have benefit in these materials even though it does not appear in the pitting resistance as indicated in Equation 9. [36] This most likely results from an increase in general corrosion resistance associated with the substitution of nickel for iron which delays the onset of localized corrosion and SCC to higher temperatures and more aggressive environments (See section on Ni-Base Alloys).

Laboratory tests on these materials indicate they are very resistant to HEC at low temperatures. However, they can be susceptible to cracking in severe, high-temperature brine environments by an anodic cracking mechanism similar to that of chloride SCC of AISI 304 and 316 stainless steels.

Hydrogen sulfide and other sulfur compounds appear to accelerate anodic SCC in much the same way that oxidizing agents increase the severity of SCC in non-sulfide containing environments. Susceptibility to SCC increases with the strength level and level of cold work of the material. Laboratory tests also indicate that the limiting conditions of H_2S for these materials may be on the order of 70-700 kPa partial pressure H_2S, at temperatures up to 220 C. [37]

Ni-Base Alloys

Two groups of Ni-base alloys are being employed in equipment primarily for use in service environments containing high H_2S partial pressures. Both offer extremely high resistance to SSC and corrosion by virtue of their alloy composition that contains high levels of Ni, Cr and Mo. These materials typically have between 5 and 20% iron. The distinction between the two groups of Ni-base alloys is made on the basis of how the high-strengthening is obtained. For tubular goods, Ni-base alloys can be cold worked to strength levels in excess of 1,000 MPa yield strength. For other components, such as valves and specialized equipment which often require more complex shapes or welding, precipitation hardened Ni-base alloys, which obtain their strength via aging heat treatments, are available with nearly the same strength levels.

High-strength Ni-base alloys exhibit environmental cracking in H_2S and brine environments at temperatures ranging from 25 C to higher than 220 C. [37,38] At low temperatures, Ni-base alloys with less than 5 percent Fe can exhibit HEC. Failures result from cathodic (hydrogen) charging of Ni-base alloys in environments containing aqueous H_2S accelerated by galvanic contact with steel or other less noble alloys. The amount of hydrogen charging produced by the Ni alloy/steel galvanic couple in aqueous H_2S environments is sufficient, in many cases, to produce HEC in a susceptible material. However, the material conditions where HEC is observed is limited to hardnesses in excess of HRC 40 produced by cold working and/or heat treatment and may vary with alloy composition and microstructure. Maximum susceptibility to cracking occurs as a result of low temperature heat treatments or prolonged high temperature service exposures (between 250 and 550 C) in combination with transverse stresses relative to the cold working direction used in metallurgical processing. Similarly to SSC in steels, HEC in Ni-base alloys is less severe at elevated temperatures, see Figure 25. [38] The current use of these materials is based on the control of strength and hardness levels, eliminating low-temperature heat treatment, and control of the environment by minimizing galvanic interactions.

Nickel-base alloys can also exhibit SCC at temperatures greater than 150 C. [37,38] This phenomenon is essentially the same as that observed for austenitic stainless steel in high-temperature chloride-containing environments (see Figure 21). But, it is generally limited to only very severe corrosive conditions for these alloys, often those that contain very high levels of H_2S in combination with near saturated brine solutions and sometimes the presence of elemental sulfur. Resistance to cracking is related to alloy composition based on the PRE values as indicated previously. Benefits in terms of SCC resistance are obtained with increased Ni, Mo and W content as shown in Figures 26 and 27. [39, 40]

SUMMARY

H_2S is associated with corrosion damage and contributes to several forms of environmental embrittlement. These forms of embrittlement include internal hydrogen blistering, HIC and SOHIC of carbon steel plate and pipe material and SSC in high strength steels or hard weld zones. It can also contribute to SSC, HEC, localized corrosion and anodic SCC stainless and Ni-base alloys. In many cases, these phenomena are controlled by similar environmental and metallurgical parameters (e.g. pH,

temperature, H_2S partial pressure, material composition, metallurgical processing and microstructure). However, the influence of these parameters may vary depending on the specific material and phenomenon in question. Consequently, they need to be considered separately for accurate prediction and assessment.

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TABLE 1
STAINLESS STEELS AND NICKEL-BASE ALLOYS COMPARISON

Stainless Steels
Nominal compositions, wt%

Designation	Fe	Ni	Cr	Mo	N	Other	Comments
Martensitic SS							
13Cr	Bal	-	13	-	-	-	low cost/resists CO_2 corrosion
Modified 13Cr*	Bal	5.0	13	2.0	-	-	improved corrosion resistance (esp. in H_2S) and strength over 13Cr
15Cr	Bal	1.5	14.5	0.5	-	-	improved corrosion resistance over 13Cr
Duplex SS							
18Cr*	Bal	4.5	18.5	2.5	00.7	-	lower cost than 22/25Cr alloy
22Cr	Bal	5.5	22.0	3.0	0.10	-	resists CO_2 and low/mod H_2S
25Cr	Bal	6.0	25.0	3.5	0.20	W	higher corrosion and SCC resistance than 22Cr esp w/added Mo and W
High alloy austenitic SS							
Alloy 28	Bal	31.0	27.0	3.5	-	-	higher resistance to CO_2, mod H_2S and Cl⁻
Alloy 254*	Bal	18.0	20.0	6.0	0.20	-	low Ni and Cr content but high Mo and N for pitting resistance
Alloy 904*	Bal	25.0	21.0	4.5	-	-	low Ni and Cr content but high Mo and N for pitting resistance
Alloy 6XN*	Bal	24.0	21.0	6.5	0.20	-	low Ni and Cr content but high Mo and N for pitting resistance

Nickel-Base Alloys
Nominal composition, wt%

Designation	Fe	Ni	Cr	Mo	N	Other	Comments
Cold worked							
2535*	Bal	38.0	25.0	3.0	-	-	lower nickel content than 825, higher, higher pitting resistance
825	Bal	42.0	21.0	3.0	-	-	good resistance to CO_2/high H_2S and Cl⁻/moderate temperature
G-30*	20	Bal	22.0	7.0	-	-	good resistance to CO_2/high H_2S and Cl⁻/high temperature
2550*	20	50.0	25.0	6.0	-	2.5W	better resistance than G3 to CO_2/high H_2S and Cl⁻
G-50	17	50.0	20.0	9.0	-	-	better resistance than G3 to CO_2/high H_2S and Cl⁻
C-22*	4.0	Bal	21.0	13.5	-	3.0W	alternative to C-276 in some environments
C-276	5.5	Bal	15.0	16.0	-	3.5W	excellent resistance to CO_2/high H_2S and Cl⁻/very high temperature and sulfur
Precipitation hardened							
925*	Bal	42.0	21.0	3.0	-	2.0Ti	lower Ni and cost option to alloy 718
718	Bal	52.0	19.0	3.0	-	1.0Ti/ 5.0Cb	good resistance to CO_2/mod H_2S and Cl⁻
725*	8.0	Bal	21.0	8.0	-	3.4	better pitting and SCC resistance than 718
625 plus*	5.0	Bal	21.0	8.0	-	1.5Ti/ 3.5Cb	better pitting and SCC resistance than 718

* New alternative alloys
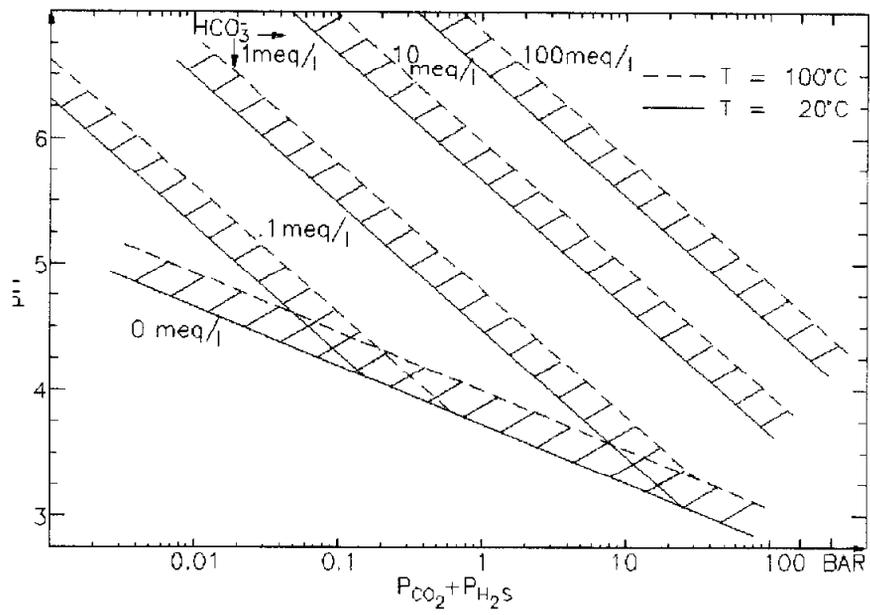
Figure 1 - Relationship of pH to acid gas partial pressure in acidic systems.[4]
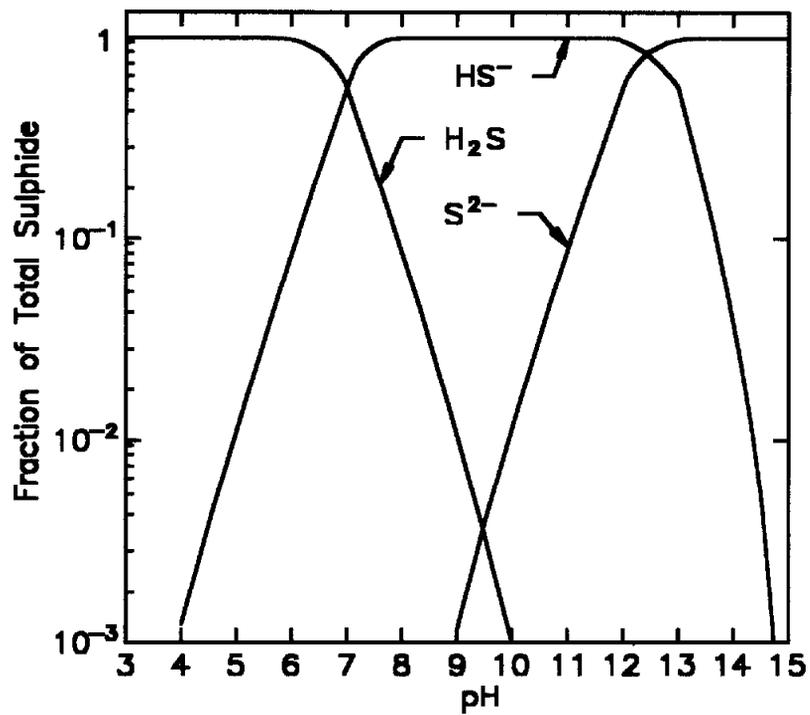
Figure 2 - Relative concentration of sulfide species versus pH.[7]
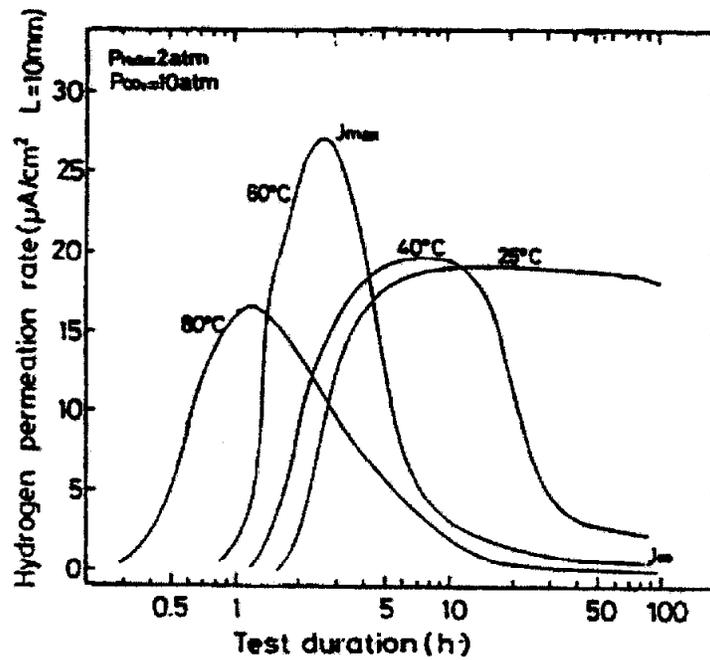
Figure 3 - Typical hydrogen flux time curves for steels exposed to H_2S-containing environments.
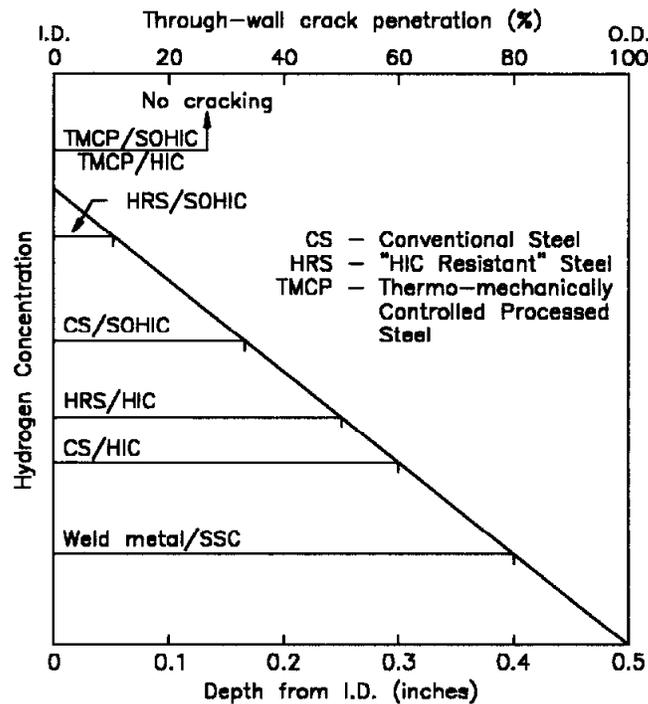
Figure 4 -Hydrogen concentration vs. thickness for one-side vessel exposure to TM0177 solution. Shows schematically critical hydrogen concentrations for HIC of various steels and SSC in weld metal.[9]
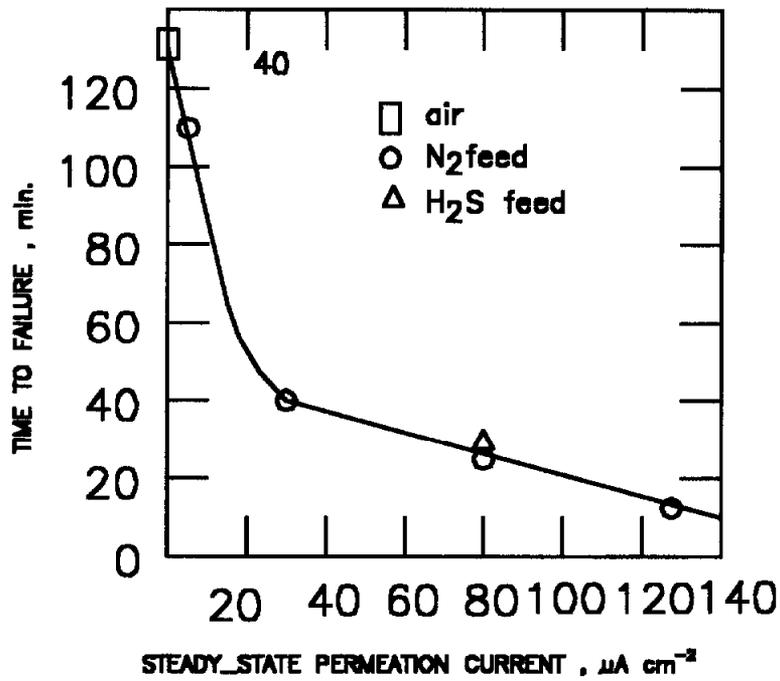
Figure 5 - Cracking susceptibility of AISI 4130 steel (HRC 32) in terms of time-to-failure versus hydrogen permeation current for various conditions with and without H_2S.[11]
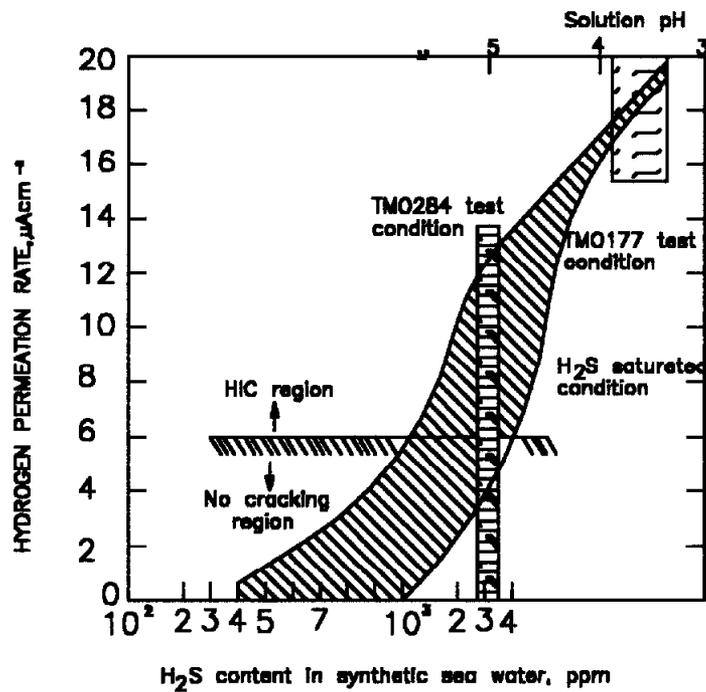
Figure 6 - Hydrogen penetration rate versus H_2S content in standard test solutions and region of HIC and HIC-free performance.[12]
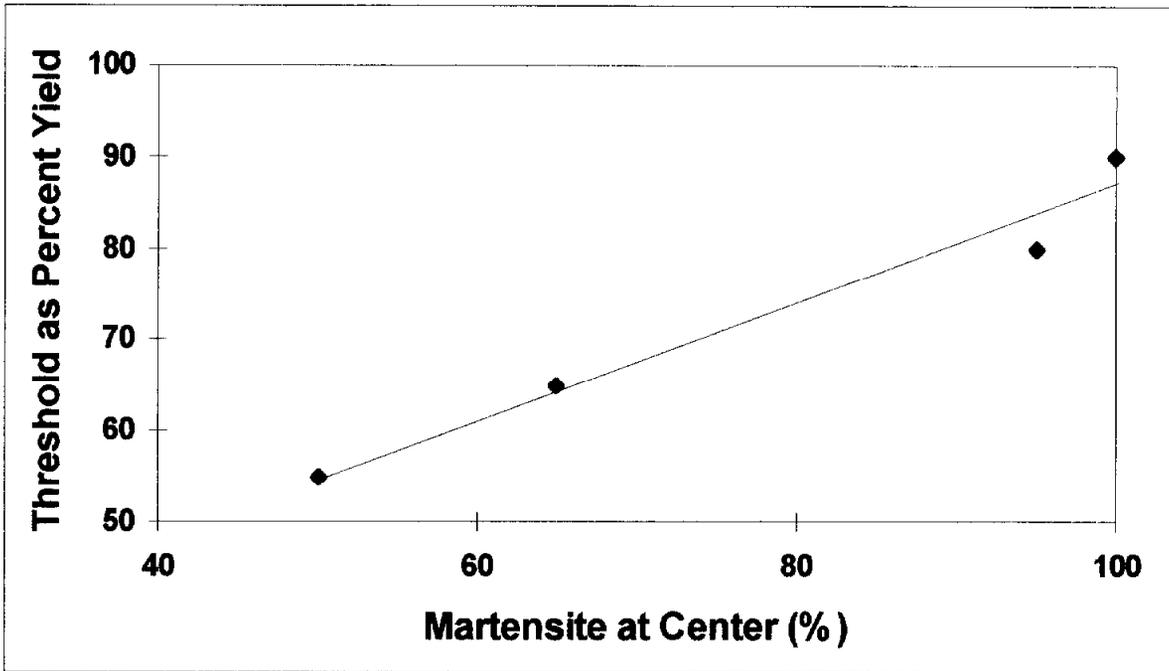
Figure 7 - Threshold stress for SSC versus percent as-quenched martensite for AISI 4130 Mod steels in the yield strength range 620 - 720 MPa.[13]
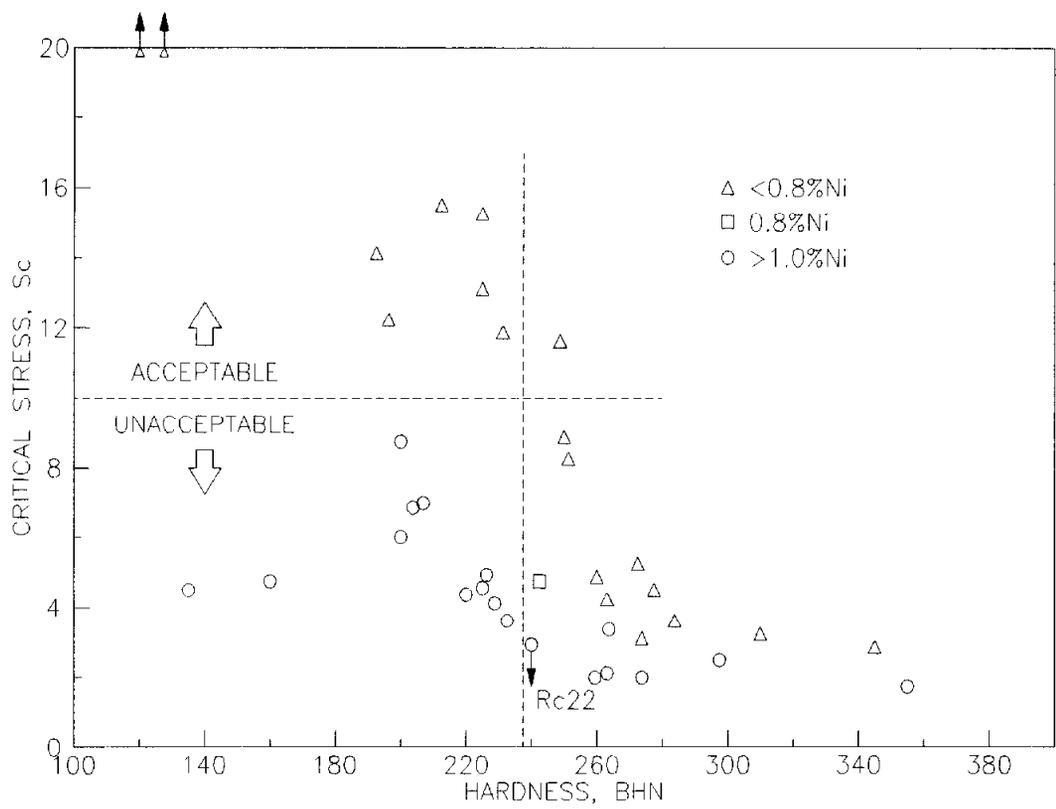
Figure 8 - Effect of Ni content on cracking susceptibility of a low-alloy (C-Cr-Mo) steel. Note reduced S_c values for steels with more than 1 percent Ni at less than BHN 240.[16]
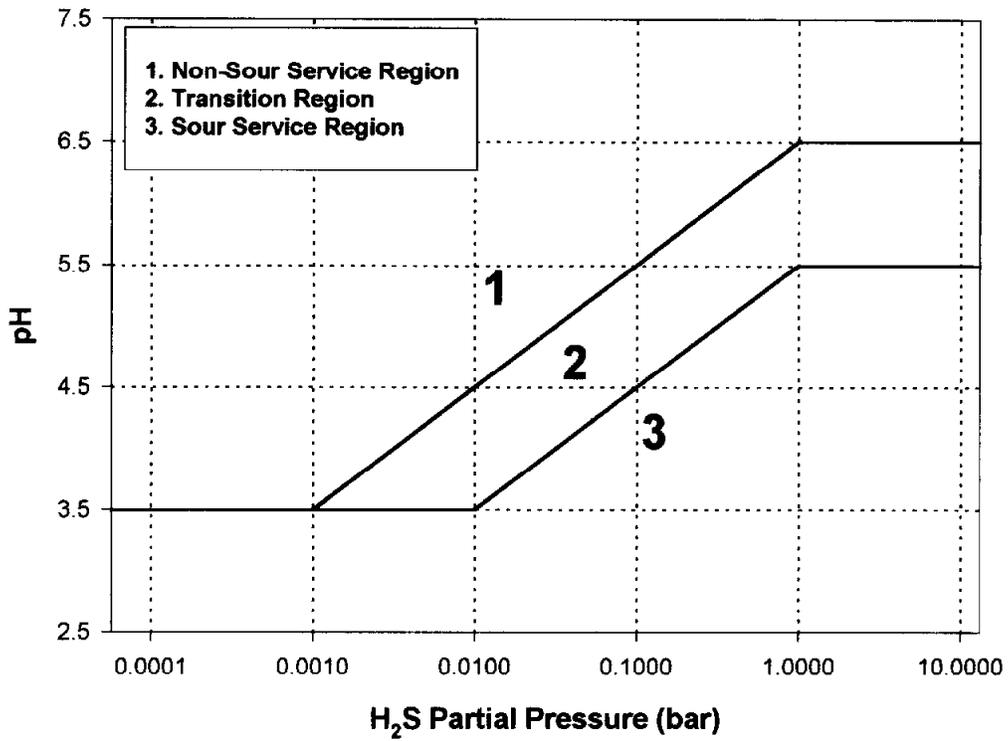
Figure 9 - SSC serviceability regimes based on pH and H₂S partial pressure.[20]
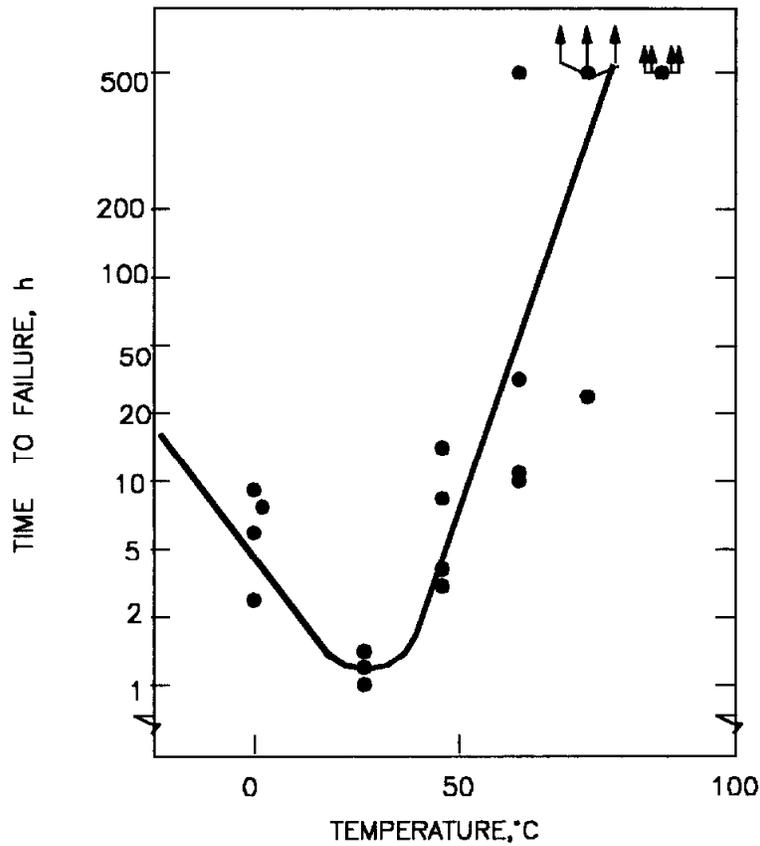
Figure 10 - Effect of pH value on sulfide stress cracking resistance of an API casing steel (C-Mn composition).[21]
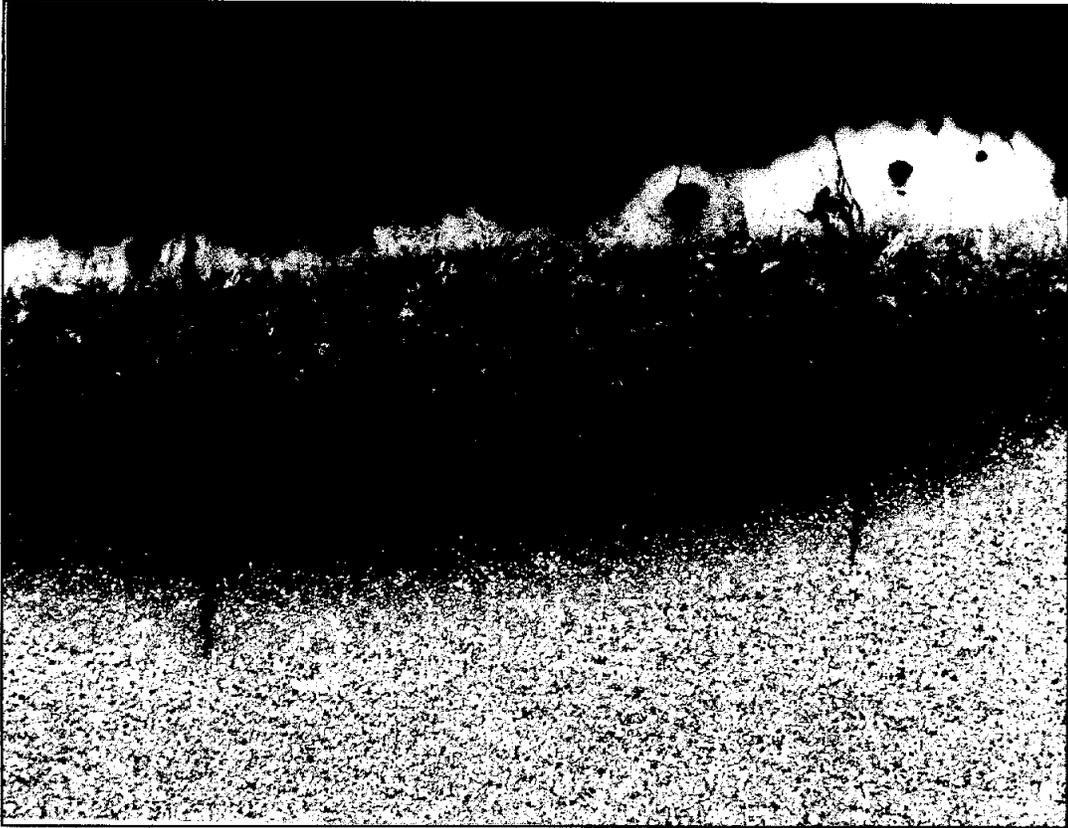
Figure 11 - SSC originating from a hard weld in ASTM A516-70 plate steel.

Figure 12 - HIC in an ASTM A516-70 plate steel. Note crack
parallel to plate surface and ferrite/pearlite bands.
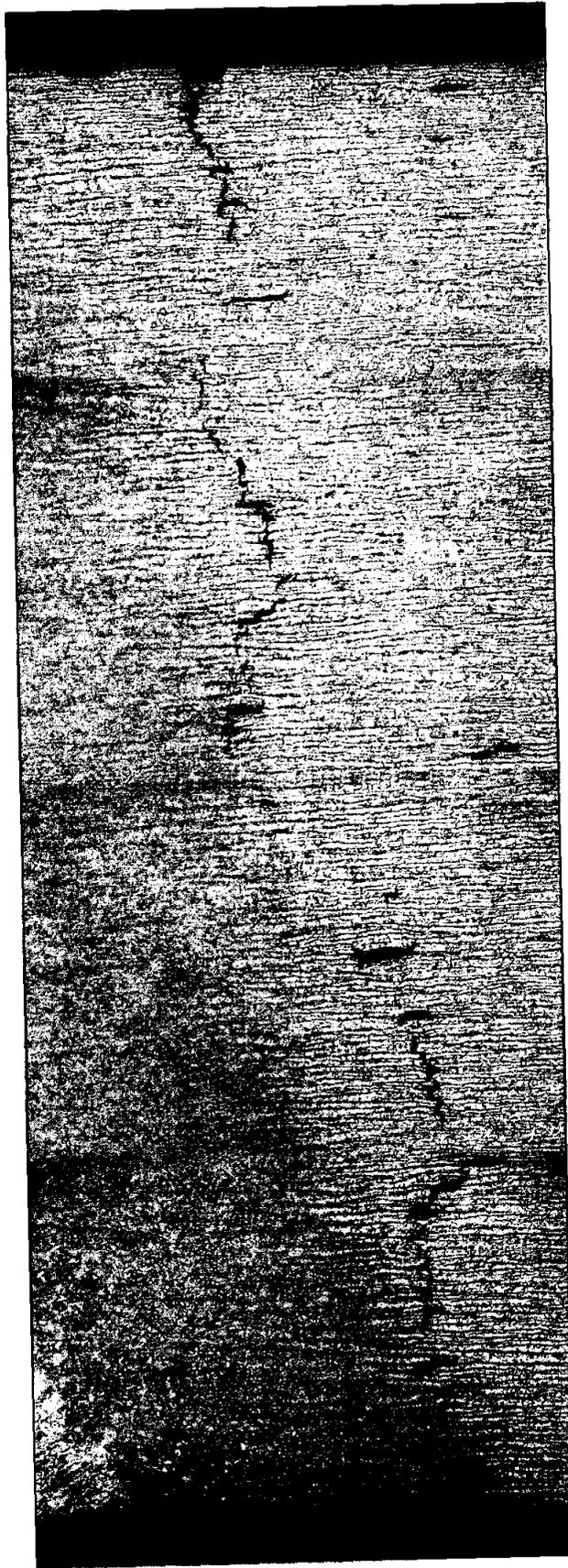
Figure 13 - SOHIC in the base metal adjacent to a weld heat affected zone
on an ASTM A516-70 plate steel.
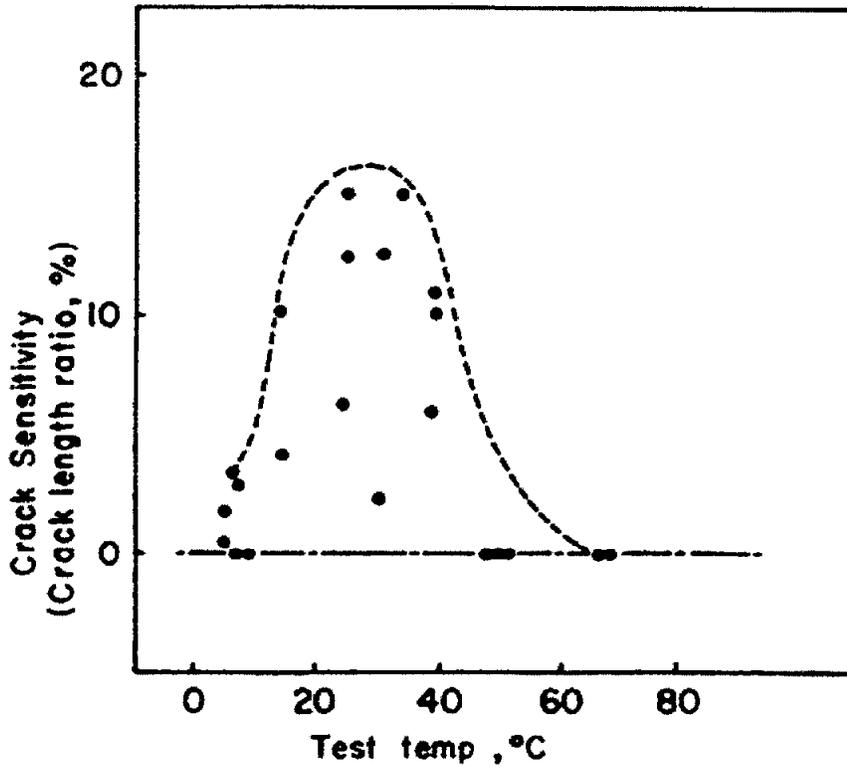
Figure 14 - HIC in pipeline steel versus testing temperature.[22]
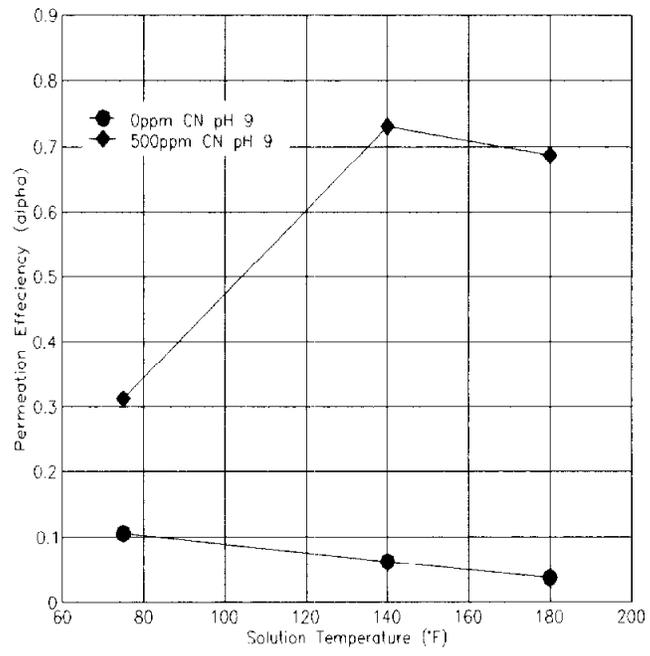
Figure 15 - Influence of cyanide on hydrogen permeation efficiency in alkaline wet H₂S environment.[23]
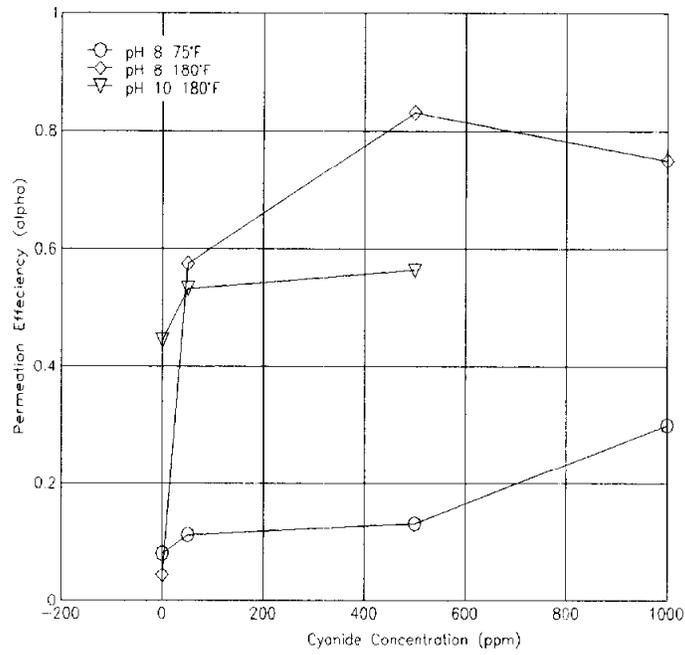
Figure 16 - Influence of pH on hydrogen permeation efficiency in alkaline wet H₂S environment.[23]
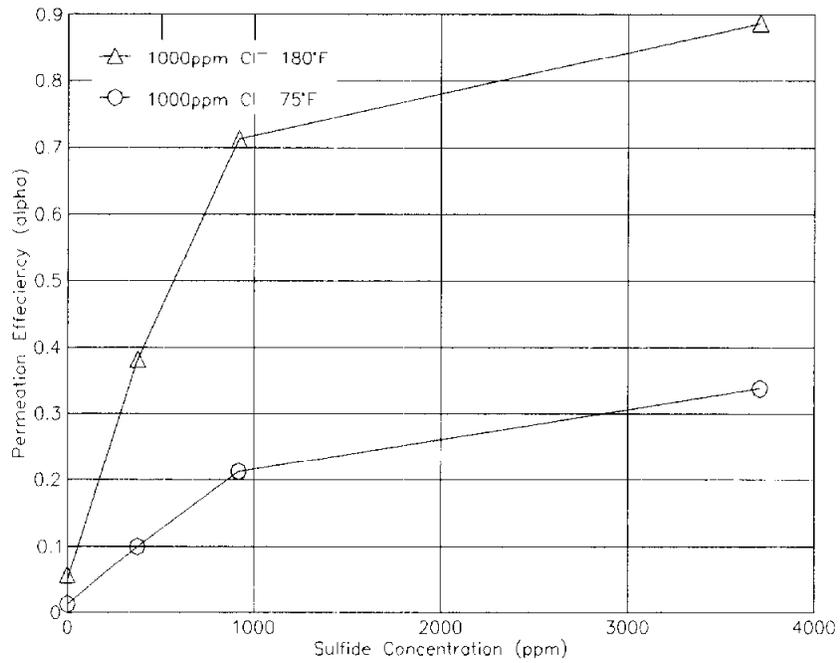
Figure 17 - Influence of chloride on hydrogen permeation efficiency in alkaline wet H₂S environment.[23]
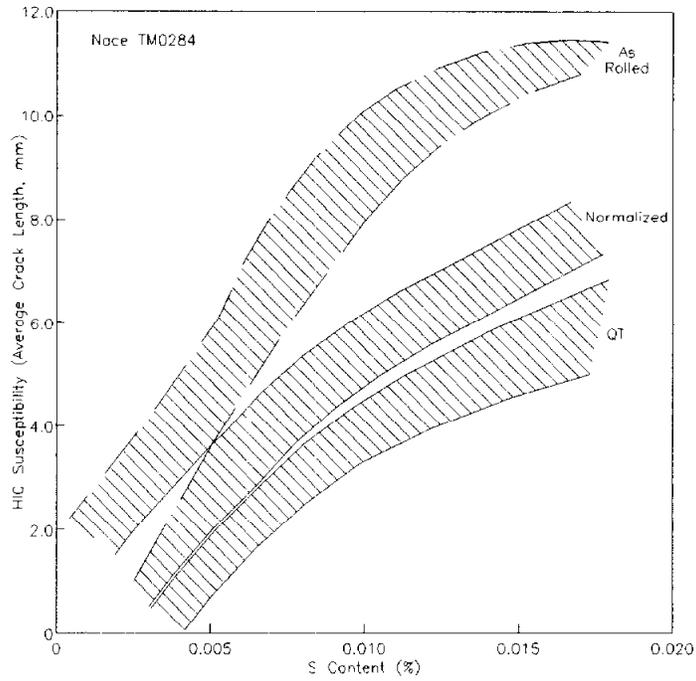
Figure 18 - HIC susceptibility versus S content and heat treatment.[24]
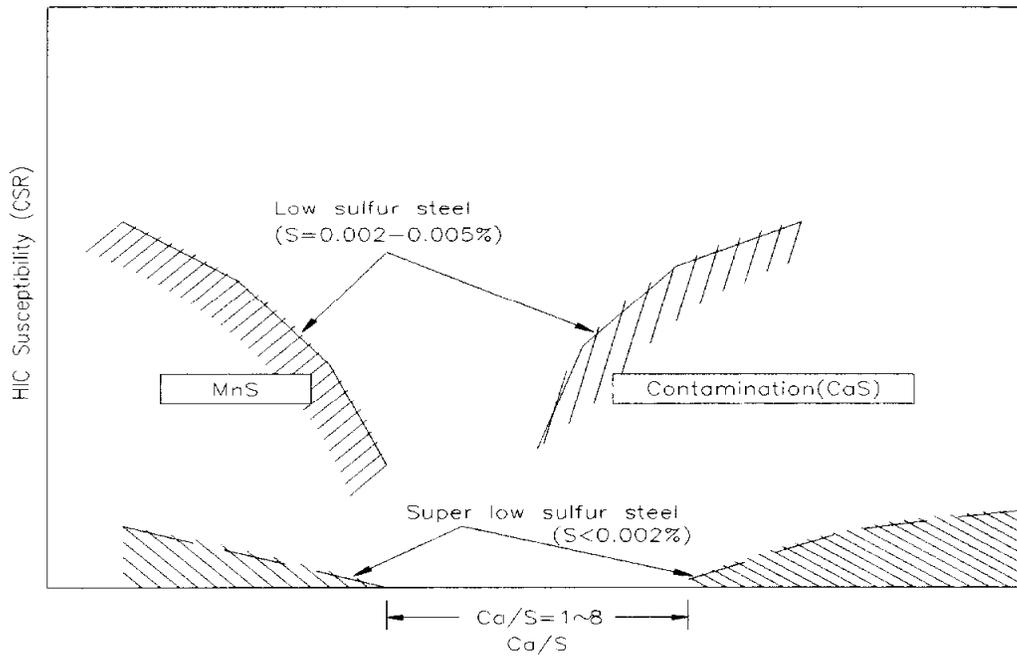
Figure 19 - Schematic diagram of influence of Ca treatment on HIC through sulfide shape control and the effects of under- and over-Ca treatment.[26]
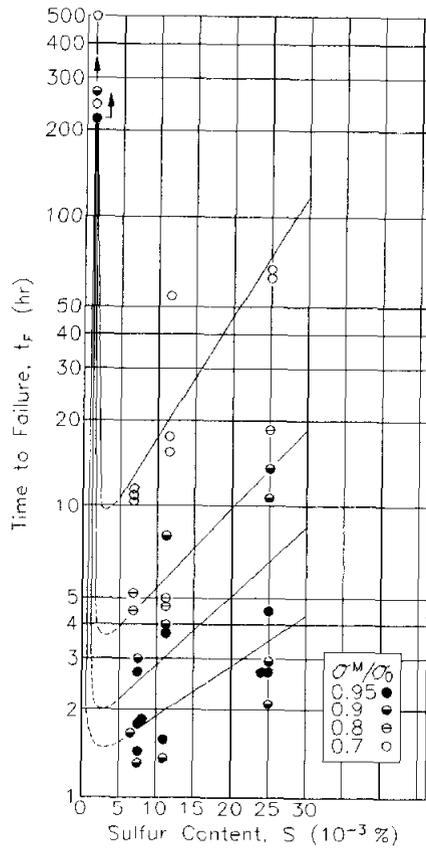
Figure 20 - Influence of sulfur content and applied stress (percent of yield stress) on SOHIC in carbon steel under cathodic hydrogen charging.[27]
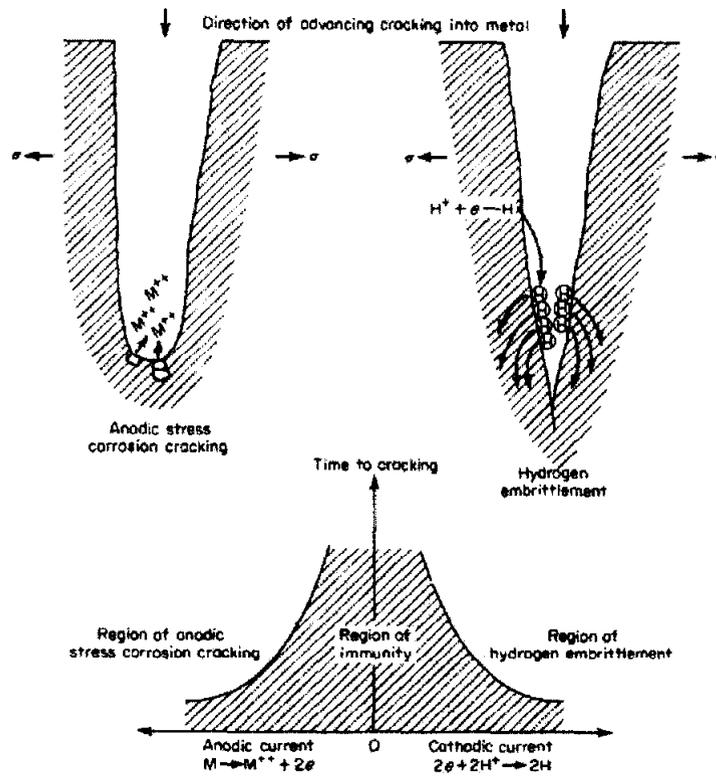
Figure 21 - Schematic comparison of (a) anodic SCC and (b) HEC cracking mechanisms.[28]
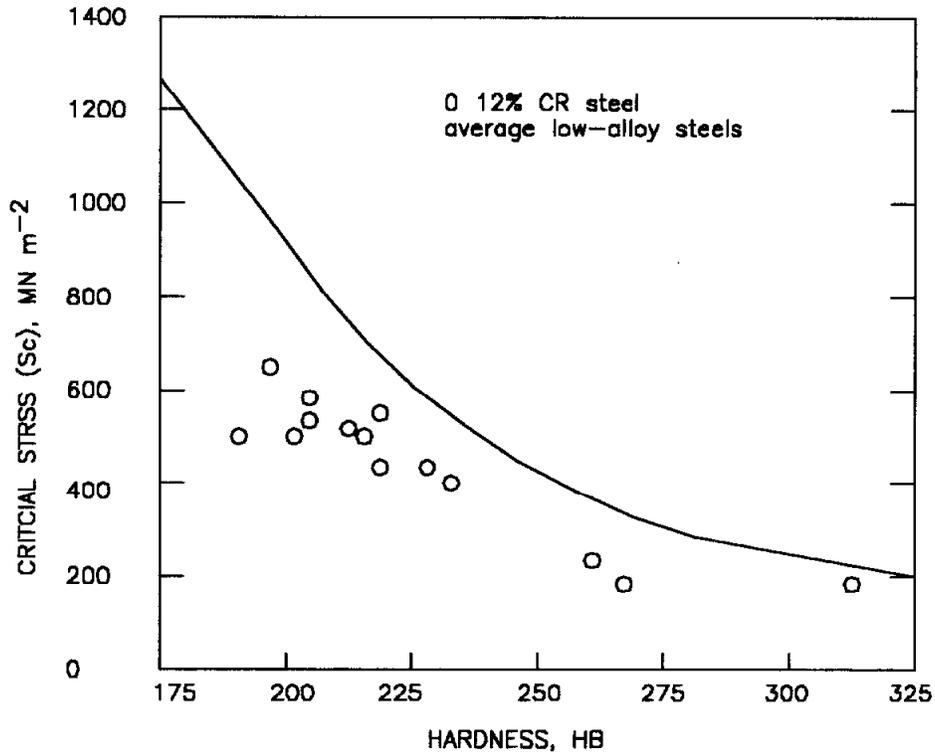
Figure 22 - Comparison of SSC threshold data (S_c) for low-alloy (AISI 4130) and 12% Cr (AISI 410) steels. Solid line is for low alloy steel; data points for 12% Cr steel.[29]
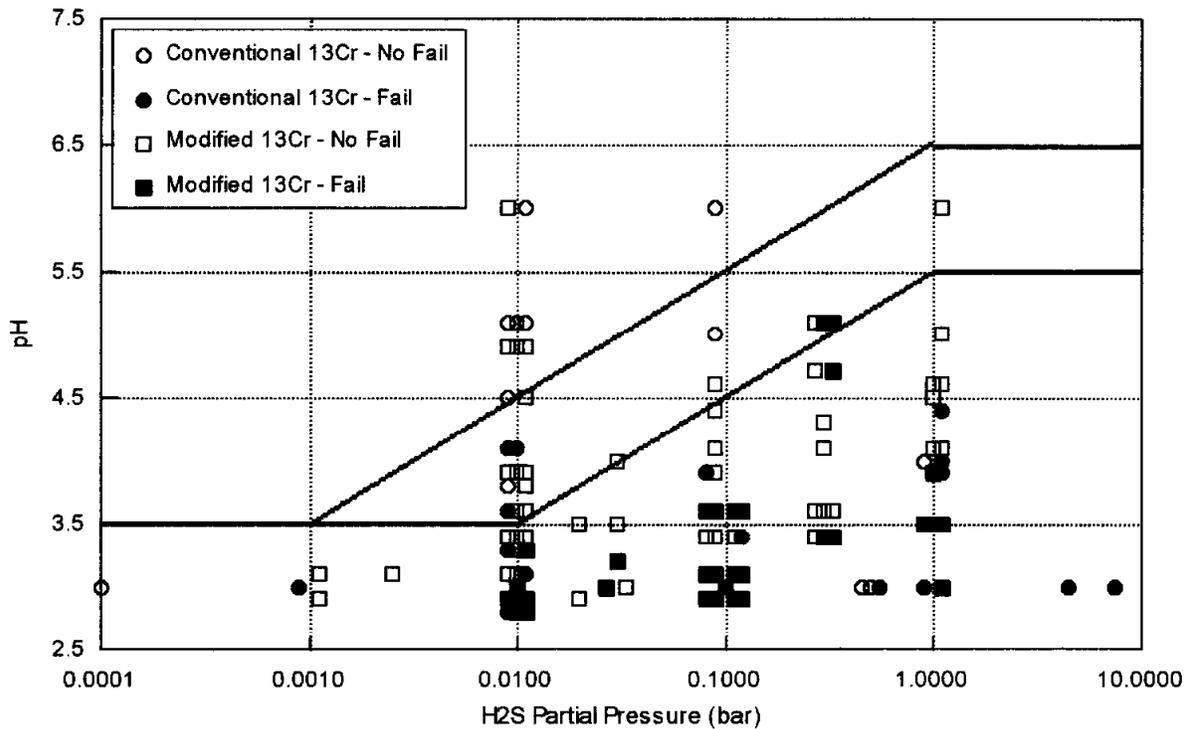
Figure 23 - SSC performance of conventional and modified 13 Cr as a function of pH and H_2S partial pressure.[30]
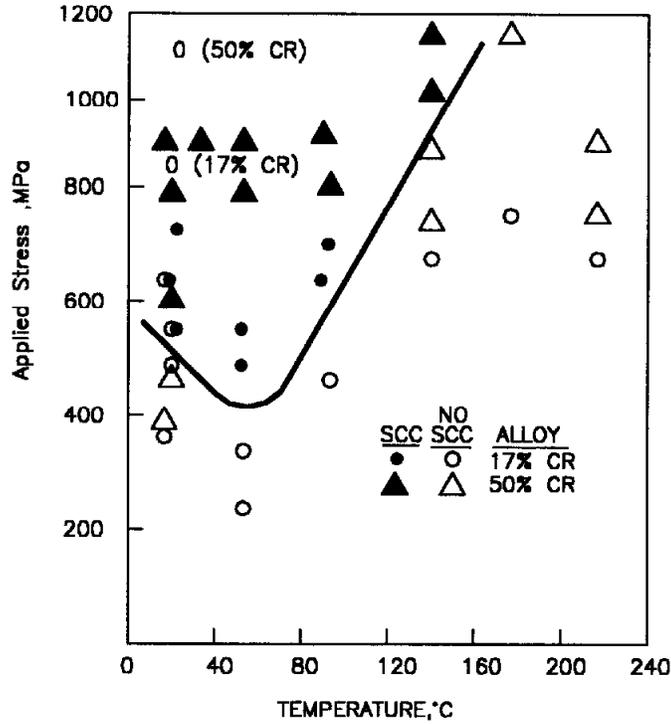
Figure 24 - SCC versus temperature for duplex SS showing maximum susceptibility at intermediate exposure temperatures resulting from combined effects of HEC and SCC.[32]
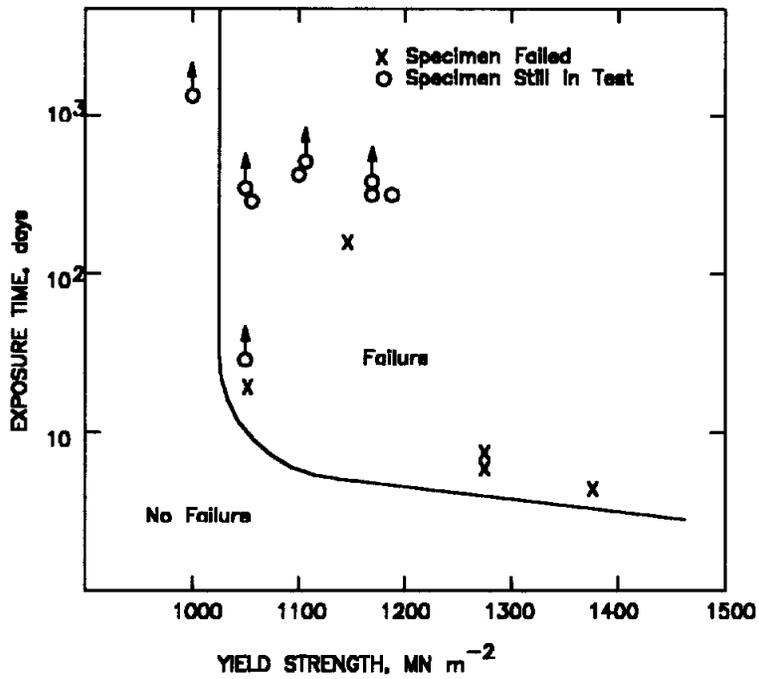

Figure 25 - HEC behavior of coldworked C-276 versus yield strength; environment H_2S/brine at room temperature coupled to steel; stress level 90% strength (YS); heat treatment 260 C for 250-550 h.[38]
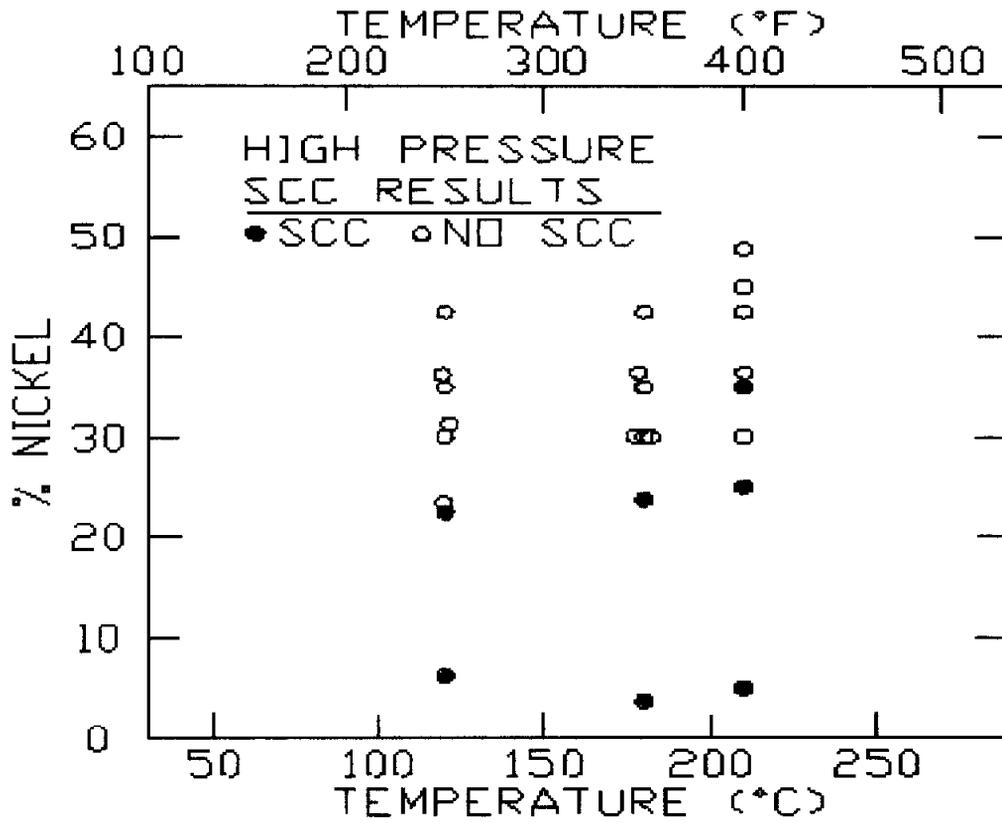
Figure 26 - Effect of Ni content on SCC of stainless and Ni-base alloys in H$_2$S/brine environment.[39]
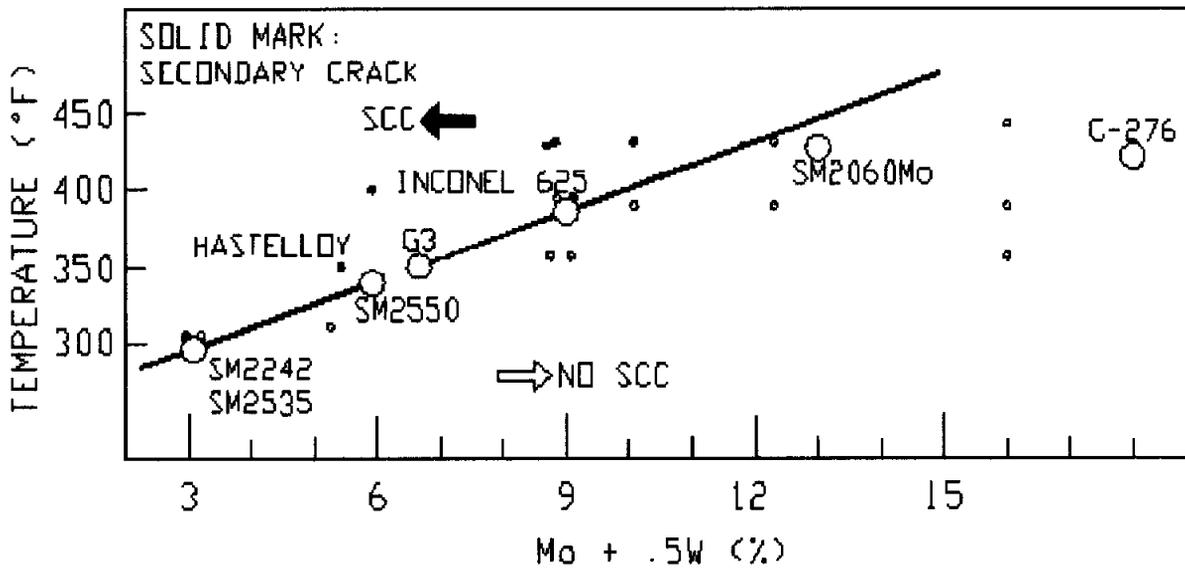

Figure 27 - Effect of Mo and W on SCC of stainless and Ni-base alloys in H$_2$S/brine environment.[40]