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Selective Seam Weld Corrosion Literature Review

Pipeline and Hazardous Materials Safety Administration
U.S. Department of Transportation

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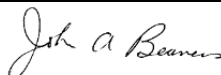



Selective Seam Weld Corrosion Literature Review	DET NORSKE VERITAS (U.S.A.), INC. Materials & Corrosion Technology Center 5777 Frantz Road Dublin, OH 43017-1386, United States Tel: (614) 761-1214 Fax: (614) 761-1633 http://www.dnv.com
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EXECUTIVE SUMMARY

Over the past few years, a number of catastrophic, high profile pipeline failures have occurred wherein fracture of the longitudinal seam weld took place. These include failure of a liquid propane pipeline operated by Dixie Pipeline Company in Carmichael, Mississippi in 2007. In both cases, there seems to be some evidence that seam-integrity assessments, in-line inspection (ILI), and hydrotesting did not identify or detect the presence of high risk weld seam defects.

The formation of ERW seam weld defects can arise due to a variety of reasons and causes. Lack of fusion weld defects can originate during the initial pipe fabrication process typically resulting from a loss of electrical contact between the runners and the parent steel plate, lack of proper plate edge preparation, and lack of sufficient gap closing force exerted on the plate. Selective seam weld corrosion (SSWC) is another mechanism by which defects can be introduced at the seam weld. In this report, the open literature related to selective seam weld corrosion of line pipe steel is summarized.

Based on the available literature, it is evident that SSWC is an integrity threat not only for ERW welded pipe but also for pipe fabricated using other seam weld methods as well. Several mechanisms have been proposed to explain how and why SSWC takes place including:

- galvanic interactions between the weldment and the base metal
- differences in dissolution/corrosion rates for different steel phases
- inclusions and chemistry segregation in the weldment
- crevices that form between inclusions and the steel or are present due to lack of fusion

Of the mechanisms posed, sulfur enrichment and sulfide inclusions leading to localized corrosion in the weldment seem to have the greatest merit and the largest body of supporting evidence. In addition to controlling the level of sulfur and inclusion shape and composition, the overall steel composition and microstructure, weld heat input, and post-weld seam or full pipe body heat treatment are important considerations to minimizing SSWC susceptibility. Once installed, the environmental factors that influence SSWC are essentially the same as would be observed for other forms of corrosion. Similarly, the same approaches that are used to mitigate and control other forms of corrosion have also been the subject of limited studies to mitigate SSWC including chemical treatments, coatings, and cathodic protection.

Despite efforts to evaluate SSWC for pipe steels, many gaps still exist regarding the various potential influential factors that may promote or mitigate SSWC susceptibility. These include the need to determine if a critical steel sulfur concentration exists below which SSWC is not a threat, determination and evaluation of CP levels to establish guidelines for mitigating SSWC in susceptible pipe, and better quantification of the effects of soil and coating properties on SSWC susceptibility. It is proposed that filling in these gaps will greatly strengthen and enhance the technical and cost effectiveness of pipeline integrity plans that consider the threat of SSWC.

1 INTRODUCTION AND BACKGROUND

Over the past few years, a number of catastrophic, high profile pipeline failures have occurred wherein fracture initiated at the longitudinal seam weld. These include failure of a liquid propane pipeline operated by Dixie Pipeline Company in Carmichael, Mississippi in 2007. In some cases, there seems to be some evidence that seam-integrity assessments, in-line inspection (ILI), and hydrotesting did not identify or detect the presence of high risk weld seam defects. As a result of these observations, the National Transportation Safety Board (NTSB) recommended [1] that the U.S. Department of Transportation (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA) conduct a comprehensive study to identify actions that can be used by operators to eliminate catastrophic longitudinal seam failures in pipelines.

The formation of ERW seam weld defects can arise due to a variety of reasons and causes. Lack of fusion weld defects can originate during the initial pipe fabrication process typically resulting from a loss of electrical contact between the runners and the parent steel plate, lack of proper plate edge preparation, and lack of sufficient gap closing force exerted on the plate or skelp. Selective seam weld corrosion is another mechanism by which defects can be introduced at the seam weld. In this report, the open literature related to selective seam weld corrosion of line pipe steel is summarized. The reported findings are organized based on the effects of environmental conditions, the effects of steel chemistry and metallurgy, the effects of welding parameters, and mitigation of selective seam weld corrosion in susceptible pipe. First, however, an overview of the phenomenology and proposed mechanisms of selective seam weld corrosion is presented.

2 PHENOMENOLOGY AND MECHANISM

Selective seam weld corrosion (SSWC) is a form of corrosion attack that preferentially occurs along the weld bond line/fusion zone (FZ) of line pipe and often has the appearance of a wedge shaped groove (leading to the term grooving corrosion). Figure 1 provides an example metallographic cross section that illustrates the appearance of SSWC. To characterize the relative corrosion rate of SSWC compared to the corrosion rate and associated overall metal loss by the base metal, the grooving factor is sometimes used as given by:

$$\alpha = \frac{d_1}{d_2} = 1 + \frac{a}{d_2}$$

where α is the grooving factor, d_1 is the distance from the original metal surface prior to the onset of corrosion to the depth of the weld groove, and d_2 quantifies overall metal loss of the material [2]. These parameters are shown schematically in Figure 2. Thus, a grooving factor of 1.0 would indicate that no SSWC had occurred and that all metal loss was general and uniform across the surface. Grooving factor values greater than 2 (that is the seam weld is corroding at a rate that is

twice that of the rest of the surface) are typically considered to indicate susceptibility and threat of SSWC [2], though the rationale for selecting this value is unclear.

In some cases, in addition to rapid dissolution at the FZ, high corrosion rates have also been observed at the heat affected zone (HAZ)/FZ boundary. An example illustrating this situation is shown in Figure 3. Because of a number of factors, the weldment tends to corrode at a faster rate than the surrounding metal with rates as high as 400 mpy being reported [3]. Furthermore, it has been observed that pipe failures that result from SSWC often tend to occur fairly early in service. For example, one study of 68 SSWC in-service failures noted that 70% of the failures occurred within the first four years of pipeline installation and 90% had failed within seven years [3].

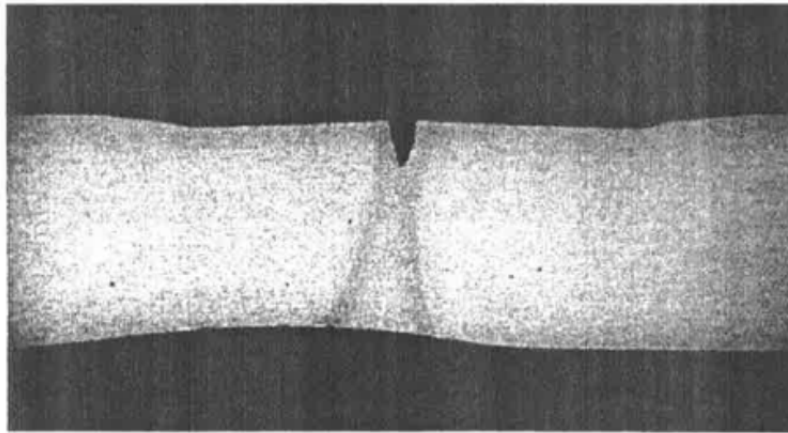


Figure 1: Metallographic cross section illustrating SSWC (6.5X magnification).[4]

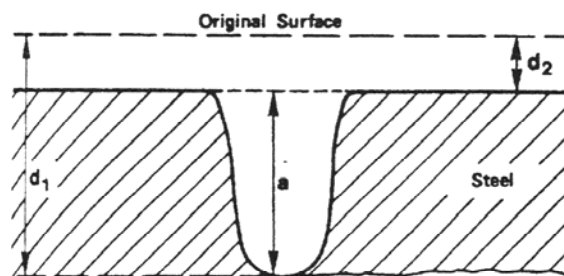


Figure 2: Schematic illustration of SSWC and the parameters used to calculate the grooving factor.[2]

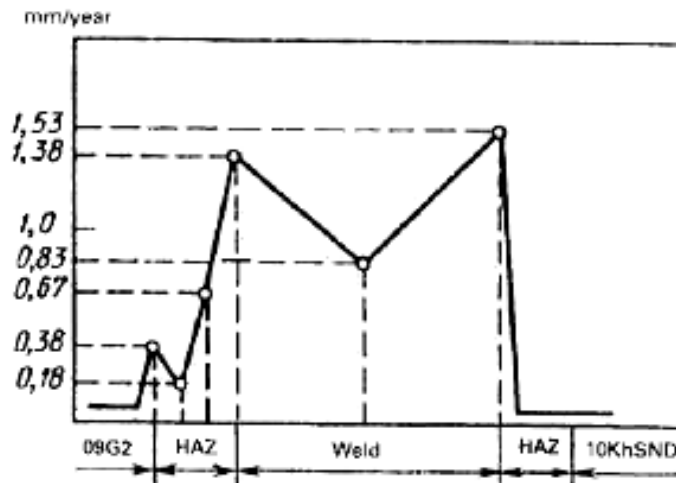


Figure 3: Corrosion rate profile measured for steel illustrating an example case where the HAZ/FZ boundary exhibited the highest corrosion rates.[5]

Even though the reported pipeline failure rate due directly to SSWC is low with approximately 1% of pipeline failure incidents in the PHMSA pipeline failure database [6], SSWC is still of concern because it results in the formation of long, sharp V-notch or crevice-like defects. As a result, SSWC may not necessarily directly lead to pipeline failure in and of itself but instead may lead to conditions where other failure modes such as stress corrosion cracking, brittle fracture, fatigue, outside force impacts, and overpressure events may become enabled due to the introduction of localized thinning and/or stress risers [7, 8].

SSWC is most often associated with ERW and similar welding methods, with low frequency ERW considered to be more susceptible than high frequency ERW. Examination of the open literature, however, demonstrates that SSWC has been observed for steels using a variety of welding methods. These welding methods, in addition to ERW, include:

- Submerged arc welding (SAW) [5, 9-12]
- Double-submerged arc welding (DSAW) [13]
- Tungsten inert gas (TIG) [14, 15]
- Shielded metal arc welding (SMAW) [10, 11, 16]
- Gas metal arc welding (GMAW) [10]

Beyond the observation that SSWC can occur for steels welded by a variety of different methods, observance of preferential weld corrosion is not limited to buried pipeline systems. Examples where SSWC has been observed include seawater [2, 5, 9, 10, 12, 17] and liquid hydrocarbon pipelines [8, 18] where internal corrosion was experienced, process piping and reinjection systems [16, 19], ship hulls [11], heat exchanger tubes [7], and oil well casings and tubulars [20]. In each of these examples, the weldment fusion zone and/or the heat affected zone preferentially experienced rapid corrosion compared to the base metal.

The mechanism of SSWC has been the subject of several studies in order to determine viable methods to mitigate and minimize its occurrence. SSWC has been attributed to several root cause mechanisms, including:

- galvanic interactions between the weldment and the base metal
- differences in dissolution/corrosion rates for different steel phases
- inclusions and chemistry segregation in the weldment
- crevices that form between inclusions and the steel or are present due to lack of fusion

In the galvanic interaction argument, the weldment acts as the anode while the base metal acts as the cathode. Typical potential differences on the order of 30 to 70 mV have been reported [17, 21, 22] with galvanic currents as high as $350 \mu\text{A}/\text{cm}^2$ reported [15]. Though these potential differences are relatively modest, the effects of the relative areas of the weldment compared to the base metal needs to be considered. That is, in situations such as this where a small anode is coupled to a large cathode, high corrosion rates are often observed even with small potential differences. This is further exacerbated if shallow Tafel slopes¹ indicating that significant changes in the reaction rate are possible with small shifts in potential are also present.

Related to the concept of galvanic interactions between the base metal and weld metal, some investigators have studied the polarization behavior of the base metal, FZ, and HAZ. Several investigators have observed differences in Tafel slopes or different exchange current densities for these different regions [14, 15, 22-24]. In these cases, the net result is that, at any given potential, the corrosion current for the FZ is greater than the corrosion current for the base metal. In Figure 4, the case of a shift in the exchange current density for steel dissolution is schematically illustrated. It should be noted, however, that Hemmingsen et al. [23] showed that, in chloride environments at moderate to low pH values (between 6.4 and 1.8), the FZ, HAZ, and base metal all exhibited comparable Tafel slopes within 3 mV/decade of each other. This seems to indicate that, though changes in Tafel response are possible, they may not be present in all instances. In addition to studying the different polarization behaviors of the base metal and FZ, Masamura and Matsushima [3] showed that, during crevice corrosion and under-deposit corrosion in different chloride solutions, the rate of dissolution was higher for the FZ than the base metal. Both metal phases experienced corrosion; however, the rate for the FZ was higher. The shift in polarization behavior to higher currents for the FZ has mostly been explained in terms of sulfur enrichment [25] in the ferrite phase in regions immediately adjacent to FeS inclusions [22].

Sulfide inclusions have been recognized as preferential sites for localized corrosion of steels since the 1910's [26]. As a result, this well-known phenomenon has been cited as the primary cause of SSWC [4, 12, 15, 17, 19, 27, 28]. Beyond the inclusions themselves, there is evidence to suggest that the parent metal surrounding the inclusions can become enriched in sulfur up to levels that represent supersaturation [29-31]. For example, Heitmann et al. [28] using scanning tunneling electron microanalysis, showed that the ferrite surrounding MnS inclusions in

¹ In this case, small changes in potential result in large changes in the current associated with anodic dissolution (corrosion).

the FZ was enriched in sulfur out to a distance of over 1 μm past the inclusion/ferrite interface. The role of inclusions on localized corrosion has been explained from several vantage points. Kato et al. [17] postulated that pits form due to active dissolution around Fe/MnS mixed inclusions in the FZ. Sulfide inclusions and the metal just adjacent have also been proposed to act as sites for preferential adsorption of chloride ions [30, 32]. Sulfur in the metal lattice has been proposed to weaken interatomic metal-metal bonds [33, 34]. The dissolution of sulfide inclusions is also known to result in the creation of corrosive species such as sulfide [31, 35], sulfate with concomitant production of acid (H^+) [36], elemental sulfur which is then oxidized to bisulfite and acid [32], and thiosulfate and acid [37] depending on the conditions studied. Regardless of the mechanism, because sulfide inclusions are known to induce rapid localized corrosion, it is logical to expect them, if present in the FZ and HAZ, to play a significant role in SSWC as well.

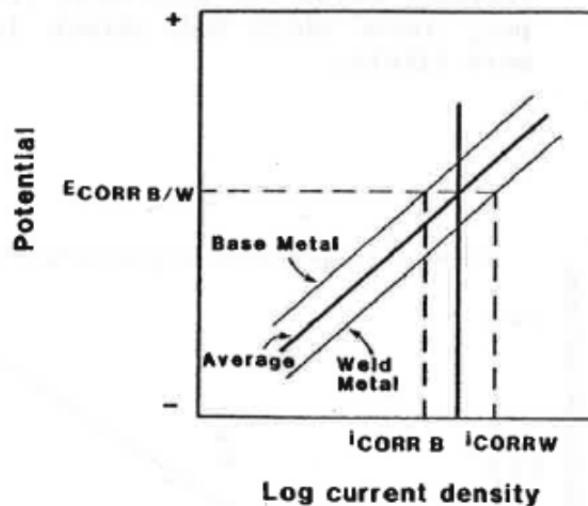


Figure 4: Illustration of different polarization behavior for weldment and base metal used to explain SSWC.[38]

The formation of micro-crevices has also been proposed to explain SSWC [7, 12, 17]. In this scenario, micro-crevices can be formed at lack of fusion defects within the FZ. Once formed and exposed at the metal surface, traditional occluded/concentration cell crevice corrosion mechanisms are then invoked to explain SSWC initiation and propagation. It has also been proposed that sulfide inclusions create micro-crevices due to a difference in thermal expansion compared to steel [39]. Because of this difference in thermal expansion, decohesion between the metal matrix and inclusions may occur during heating and cooling. Creation of such micro-crevices between the parent steel and the inclusions would then likely result in a combination of inclusion-related mechanisms and traditional crevice corrosion thereby leading to SSWC.

The mechanism of SSWC may vary depending on the environment that the pipeline is exposed to, the steel that was used to fabricate the pipe, and the welding parameters used. A combination of mechanisms may also occur in which one or more processes are taking place simultaneously or in sequence. Regardless of the precise mechanism that is taking place during SSWC, it is important to recognize that very rapid dissolution of the FZ and/or HAZ takes place, which then leads to the formation of long, V-like defects that can act as precursors for other failure modes.

3 EFFECT OF ENVIRONMENTAL VARIABLES

As with all forms of corrosion, the environment that the pipeline is exposed to plays a significant role in determining both the susceptibility to and rate of SSWC. Thus, in general, the same environmental variables that influence corrosion of pipelines in buried and other in-service conditions from an external corrosion perspective as well as those variables that influence internal corrosion should be considered relevant. These would include temperature, flow, pH, chloride concentration, soil type and conductivity, microbial activity, sulfate concentration, oxygen, carbon dioxide, hydrogen sulfide, and so forth. To illustrate this, in Figure 5, the average measured SSWC penetration rates for 32 different in-service ERW seam welded pipelines are shown. From these data, two factors are clearly evident. First, the observed corrosion rate is higher in high conductivity environments such as brine and seawater. This is likely explainable due to both an overall increase in dissolution kinetics in these environments and due to better communication between anodic and cathodic sites (i.e., the effective cathodic area is larger in high conductivity media because the IR drop in the environment is lower).

The second factor that is evident is the effect of oxygen. Though not specifically stated by Masamura and Matsushima [3], it seems likely that the water chemistry in the closed and open recycled systems is similar. The main expected difference between these two systems would be the oxygen level. As shown in Figure 5, the observed SSWC rate in the open system was almost a factor of 5x higher. Miyasaka et al. [41] evaluated the effect of oxygen over a 60 day period in tests aimed at examining SSWC susceptibility of both seam normalized and full body heat treated high frequency ERW linepipe in simulated completion fluids and drilling muds. The effect of oxygen level on the depth of SSWC attack is shown in Figure 6. At oxygen concentrations less than 0.45 ppm, SSWC was not observed in 3% NaCl at pH 9 and 50 °C. Above this oxygen level, SSWC was observed and the nominal penetration rates were quite high, being on the order of 65 – 85 mpy if it is assumed that SSWC took place at a constant rate throughout the 60 day test period. The most likely explanation for the role of oxygen in these cases is through an additional cathodic reaction that increases the corrosion potential of the steel thereby shifting to higher dissolution rates. Because of the similarities between SSWC and other forms of localized corrosion (e.g., pitting and crevice corrosion), a critical potential above which SSWC is possible and below which it does not occur may exist. If such a critical potential exists, then the role of oxygen, and any oxidant, if present at sufficient concentrations, could be to increase the corrosion potential above the critical potential for SSWC. It is also interesting to

note that the pH in the work by Miyasaka et al. [40] was above the reported critical pH for carbon steel to develop passive films [41]. In the presence of a reasonably stable passive film, pitting of carbon steels would tend to follow the classical localized corrosion models and mechanisms, which perhaps provides some additional insights into the SSWC mechanism under these conditions.

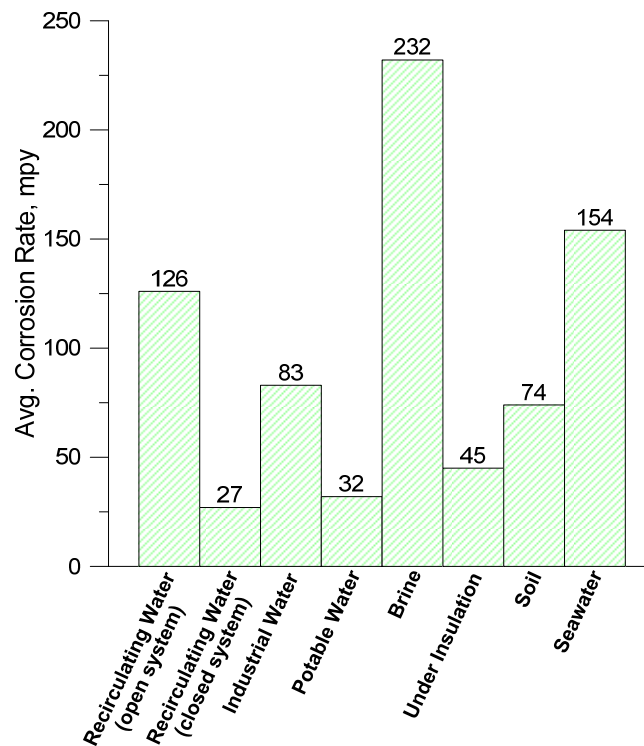


Figure 5: Average SSWC penetration rates for 32 different ERW line pipe steels in a range of environmental conditions.[3]

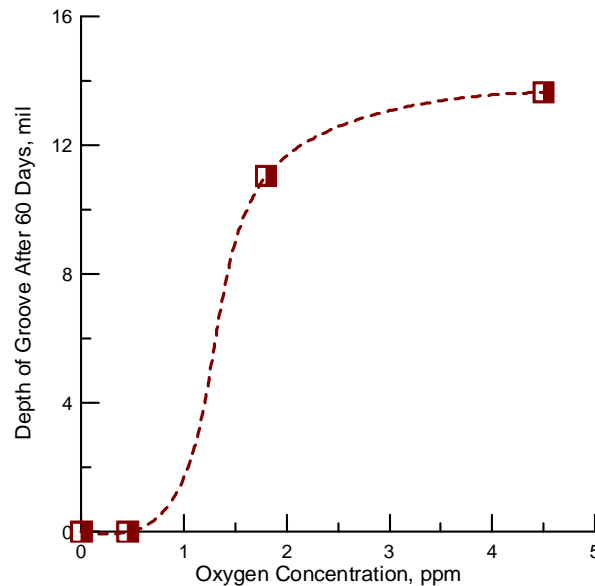


Figure 6: Effect of oxygen concentration on groove depth after 60 day testing in alkaline solutions simulating completion fluids and drilling muds.[40]

In addition to the effects of oxygen, Miyasaka et al. [40] also investigated the effects of CO_2 and H_2S in brine solutions on SSWC of ERW line pipe to simulate sweet and sour oil and gas production environments. In their studies, they observed that in simulated seawater at pH values near 5 and temperatures of 25, 50, and 70 °C, very little effect of CO_2 saturation on SSWC was evident. They attributed the negligible effect of CO_2 on SSWC to being equivalent to small pH changes. It seems, however, that no effort was made to investigate if protective or semi-protective carbonate films had formed. Olsen et al. [16] showed that, in a water injection system containing brine with CO_2 , that protective carbonate layers form that tended to limit SSWC. Olsen et al. did urge some caution, however, stating that there were sometimes significant differences in the adherence of the carbonate layer on the FZ compared to the base metal. In these cases, the adhesion in the FZ was lower than in the base metal thereby setting up a situation where the unprotected weld would be coupled to a large protected cathode area thereby accelerating SSWC.

In the presence of H_2S , Miyasaka et al. [40] noted that no SSWC took place in their tests. This was attributed to H_2S adsorption on the metal surface thereby creating a situation where the hydrogen evolution reaction occurred uniformly on the FZ, HAZ, and base metal surfaces. As a result of uniform cathodic reaction kinetics, the dissolution of the steel was also uniform. Similar to their interpretation of their CO_2 results, there did not seem to be an evaluation of the possibility of the formation of sulfide films that could form and be protective thereby explaining the lack of SSWC in the simulated sour oil production environment.

The pH has also been shown to have some influence on SSWC, mainly in establishing tendencies for which areas and regions were anodic or cathodic. Hemmingsen et al. [23] showed that, in chloride solutions at pH values less than 2.5, the base metal tended to be anodic to the FZ and HAZ. At higher pH values, however, a reversal of the anode and cathode took place. They also showed that the addition of FeCl_3 acted essentially as a chemical potentiostat; similar shifts of the relative anode arrangement from the base metal to the FZ/HAZ could take place. These results illustrate that the relationship between the weldment and the base metal can be a complex function of environmental conditions that is not easy to predict a priori.

Lastly, though not strictly an environmental variable, test duration has been shown to be an important consideration in determining SSWC susceptibility. In tests in 0.5% NaCl saturated with CO_2 over a range of temperatures from 22 to 180 °C, Joosten et al. [9] showed that the weldments on X60 and X65 steels, when coupled with the base metal, were often the cathode at the start of exposure but eventually became the anode. The time for the weldment to transition from cathode to anode took up to 200 hours. This observation highlights the importance of conducting tests for sufficient lengths of time to allow steady state conditions to develop. Failing to do so could lead to non-conservative, false negative assessments of SSWC susceptibility and eventually to potential catastrophic field failures.

4 EFFECT OF STEEL METALLURGY

Because there is a well-recognized link between the metallurgy and chemistry of the base metal and the resultant properties of the weldment, considerable effort has been expended to understand and improve SSWC resistance through these means. These efforts tend to fall into the following four main avenues of emphasis: general chemistry and microstructure control, limits on sulfur content and sulfide inclusion control, limits on carbon and carbide control, and other steel chemistry modifications. Each of these topics is discussed below.

4.1 Steel Microstructure and General Composition

Several investigators have examined SSWC from the perspective that different steel phases might exhibit different corrosion rates. For example, Hemmingsen et al. [23] examined the resultant microstructure and corrosion rate for a SAW welded ASTM A350-LF2 steel. In their study, they showed that the FZ and HAZ tended to be a mixture of ferrite, pearlite, bainite, martensite, and retained austenite depending on the temperature and cooling rates during welding and solidification. In 0.5M NaCl over a range of pH from 6.4 to 1.85, they noted that the corrosion rate of low transformation temperature products such as martensite and upper and lower bainite exhibited higher corrosion rates. Rothwell [14] similarly noted different corrosion rates for different microstructures when examining TIG welded pipe steel. In Rothwell's work, however, upper and lower bainite exhibited the lowest corrosion rates and the fully normalized steel microstructure exhibited the highest corrosion rates (Figure 7). In the context of SSWC, Rothwell's results appear to be contrary to expectations as the normalized microstructure would likely best represent the base metal which showed the highest corrosion rates with the more

weld-related microstructures showing corrosion rates a factor of 3 – 6 times smaller. No satisfactory explanation for this behavior was provided by Rothwell, though it was suggested that specifying a very narrow compositional range on the parent steel plate would likely improve resistance to SSWC.

Sephton and Pistorius [15] examined the effect of sulfur levels in addition to different heat treatment methods to study the effect of steel microstructure on corrosion rates measured in 3.5% NaCl. In this study, they were focused on bainite, fresh martensite, tempered martensite, and ferrite/pearlite mixed microstructures. In analyzing the corrosion rate data, they noted that initially, the corrosion rate of bainite tended to be greater than other steel phases. Over long time periods (typically > 200 hrs), they noted that the corrosion rate of all phases tended to converge to nearly the same value. Instead of different corrosion rates for the different steel microstructures, they showed that sulfur content was still the most important variable with higher sulfur regions exhibiting lower (more negative) corrosion potentials and higher corrosion rates.

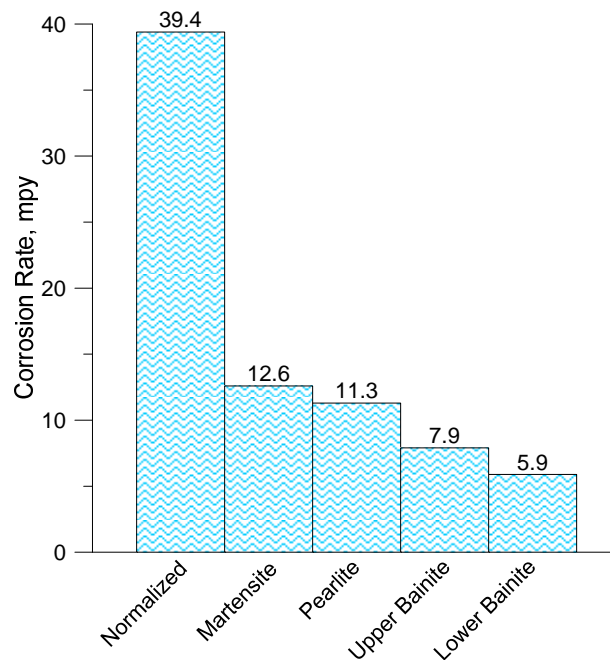


Figure 7: Corrosion rates measured for different steel microstructures in simulated seawater.[14]

4.2 Sulfur Level and Sulfide Inclusion Control

The most often cited reason for SSWC has been sulfur and consequently sulfide inclusions in the FZ and HAZ. As was discussed previously regarding the mechanism of SSWC,

the role of sulfur in accelerating corrosion has been linked to not only particles and inclusions but also to its presence in the steel lattice sometimes at concentrations exceeding its solubility.

Regardless of the precise mechanism, steel sulfur levels have been strongly linked to SSWC susceptibility. Figure 8 illustrates the effect of sulfur levels on SSWC as represented by the grooving factor [2]. Recall that a grooving factor of unity indicates no susceptibility to SSWC as the base metal, FZ, and HAZ would all experience the same dissolution rate. As shown in Figure 8, higher sulfur levels tend to lead to higher grooving factors. In interpreting these results along with those presented by Masamura and Matsushima [3], Duran et al. [2] concluded that steel sulfur levels below 0.02 wt% could be considered to be of little risk for SSWC failure in pipelines. This conclusion is predominantly based on the somewhat arbitrary assignment of a critical grooving factor value of less than 2 indicating no risk for SSWC. That is, if the grooving factor is less than 2 in laboratory tests, indicating that the dissolution rate of the FZ/HAZ was less than twice the dissolution rate of the base metal, it could be assumed that the risk of in-service SSWC failure is negligible. Though Masamura and Matsushima showed that lower sulfur steels showed lower grooving factors than high sulfur steels, they still observed grooving factors greater than 2 for steels with as little as 0.006 wt% sulfur [3]. In an evaluation of sixty reported in-service SSWC penetration failures of ERW pipeline systems (Figure 9), the reported steel sulfur levels ranged from 0.007 – 0.028 wt% [3]. These observations imply two significant conclusions. First, sulfur level, though a critical factor, is not sufficient to accurately describe and predict SSWC susceptibility. Second, even steels that have grooving factors on the order of 2 or less can still experience in-service failures by SSWC. It is also logical to assume that grooving factors determined in laboratory tests may not accurately predict actual in-service performance. Thus, though the steel sulfur content is critical and lower sulfur levels are beneficial, there may not be a critical level below which immunity to SSWC can be assumed with confidence.

Beyond the sulfur level in and of itself, efforts to control sulfide inclusion size, shape, and composition have also been explored in order to minimize the risk of SSWC. To control MnS inclusions, additions of Ca, Ti, Nb, Co, Zr, V, and rare earths such as Ce can be added to the molten steel as a part of ladle refining [3, 4, 10, 19, 22, 25, 28, 38, 42, 43]. When examining the effect of sulfur on SSWC of EWR pipe material, Masamura and Matsushima [3] showed that the addition of 0.003 wt% Ca to the steel in combination with small Cu and Ni additions and limiting the sulfur concentration resulted in a material that was essentially immune to SSWC in the as-welded state. Endo et al. [10] similarly showed that additions of Ca on the order of 0.003 – 0.006 wt% in combination with small additions of Cu and Ni resulted in the base metal and weldment exhibiting nearly identical polarization behaviors. When differences between the base metal and the weldment were observed by Endo et al., the weldment was slightly anodic to the base metal. When Ca was added in isolation without Cu and Ni, the benefits of Ca were much less pronounced. In work by Katoh et al. [22], the effects of adding small amounts of Ti, Nb, and V (on the order of 0.02-0.04 wt %) were studied and shown to result in effectively eliminating SSWC in both short term and long term (6 month) tests over a range of environmental conditions. Rare earth additions, such as Ce, at levels on the order of 1.7 times the sulfur concentration have been shown to result in near immunity for X70 steels to SSWC [28].

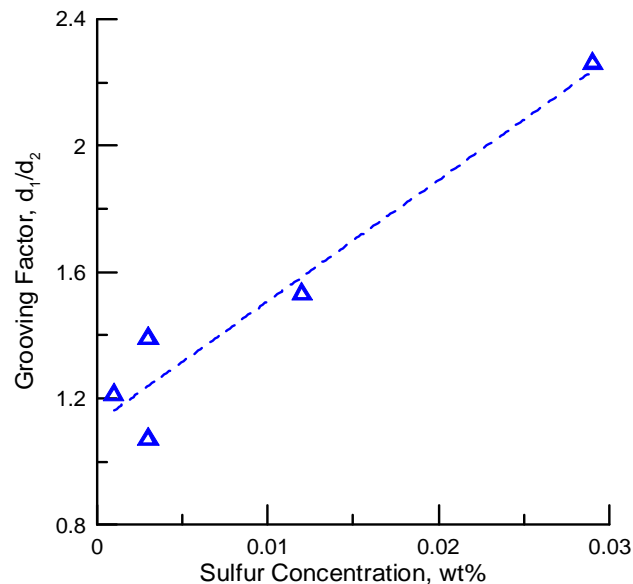


Figure 8: Effect of sulfur concentration in steel on ERW grooving factor. Data taken from Duran et al. [2]

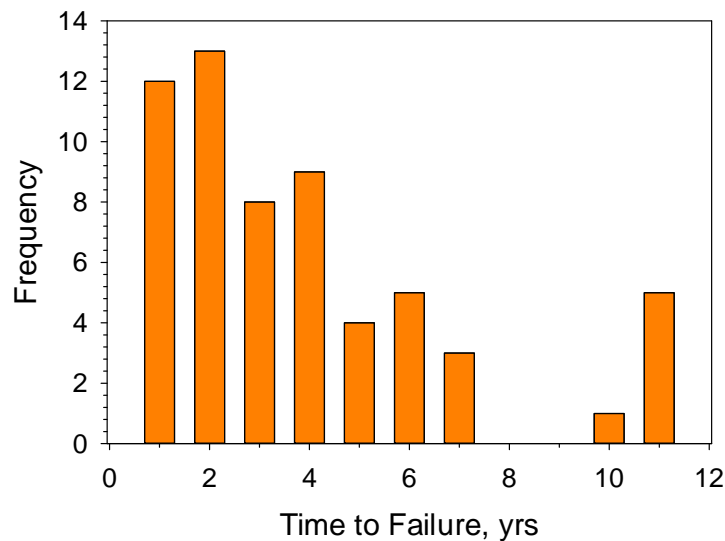


Figure 9: Time to in-service failure due to SSWC for ERW pipe with a range of sulfur levels from 0.007 to 0.028 wt%.[3]

The mechanism by which the addition of these elements improves SSWC resistance is most likely through modification of the properties and in some cases the composition of sulfide inclusions. The most typical sulfide inclusion found in line pipe steels is MnS inclusions.

Sometimes, after welding, these inclusions transform into mixed FeS/MnS inclusions. MnS inclusions start off as nominally spherical particles during steel ingot casting. Because these inclusions have anisotropic mechanical properties, they have a tendency to become flattened, elongated pancake-like stringers during hot rolling of the steel. The addition of Ca and other elements can serve multiple functions. First, they can create sulfides themselves. MnS is one of the last sulfides to form in the molten steel ingot because it has a lower melting temperature than many others [44]. Thus, the addition of Ca leads to the formation of CaS inclusions, tying up sulfur in preference to MnS because it precipitates at a higher temperature. Calcium sulfide inclusions also tend to be more globular and are less deformable during hot rolling so stringers are less likely to be formed [42, 43, 45]. Ti, Zr, Co, and rare earth additions have also been noted to function in a similar manner to Ca, forming less deformable sulfides at higher precipitation temperatures than MnS [45]. In some cases, Ti, Zr, Nb, and V form nitrides that then act as precipitation sites for MnS inclusions, which tends to make the inclusions smaller and more uniformly distributed in addition to making them less prone to elongation during mechanical deformation [45]. The formation of nitrides at MnS precipitation sites has also been shown to reduce the formation of FeS in the FZ of weldments [22]. Even though the addition of these elements has proven useful and highly beneficial for control of MnS and FeS inclusions and thus increased resistance to SSWC, their presence does not guarantee immunity in all cases [4]. Thus, each steel chemistry should be examined and considered to determine SSWC susceptibility.

4.3 Carbon Level and Carbides

In modern, low-S steels, some have claimed that SSWC susceptibility is not controlled by sulfur content or sulfide inclusions but rather through the effects of the carbon content and carbide formation [4, 7, 40]. In examining SSWC of ERW pipes in simulated oil and gas production environments, Miyasaka and Ogawa [40] showed that higher steel bulk carbon contents tended to result in slightly lower concentrations of pearlite formation in the weldment. This in turn shifted the corrosion potential of the weldment to more negative values. As discussed previously with respect to the mechanism of SSWC, this negative shift in the corrosion potential would result in galvanic coupling between the base metal (cathode) and the weldment (anode) and thereby cause the weldment to experience higher dissolution currents at any given fixed potential. They did not, however, observe any effect of carbon on the Tafel slopes of the weldment or the base metal.

Mueller [7] also speculated that carbon and carbide formation was the primary cause of SSWC. It was suggested that epsilon carbides in the steel decompose into finely divided carbides from the heating and cooling that occurs during welding. The creation of these finely divided carbides in effect increased the local net cathode surface area adjacent to and within the FZ. As a result, additional cathode sites are created leading to numerous local anode-cathode couples. These local anode-cathode couples then become the initiation sites for SSWC. Propagation of SSWC then would follow the traditional concentration cell (or occluded site chemistry) mechanism for propagation of localized corrosion.

Groeneveld et al. [4] also examined the effects of carbon content on SSWC for 32 different pipe steels that had either low frequency or high frequency ERW seam welds. The parent steels investigated included Grade B, X42, X46, X52, X60, and X65 and spanned pipe fabrication and production from 1931 through 1990. They also noted that higher carbon contents tended to exhibit a higher grooving factor. They attributed the beneficial effect of lower carbon to a reduction in the heterogeneities and differences between the FZ and base metal. By reducing the heterogeneities and the compositional and microstructural differences to a minimum, the net effect was a reduction in the corrosion rate and a reduction in SSWC susceptibility. Careful examination of the data they presented, however, shows that, if there really is an effect of carbon on SSWC, it is tenuous at best and much less pronounced than the effect of sulfur and sulfide inclusions. In some cases, identical carbon contents gave grooving factors that differed by factors as large as four. This clearly indicates that other factors and considerations must be accounted for and that carbon content is not the sole contributing factor.

4.4 Other Compositional Effects

In an effort to try to predict the corrosion potential of the base metal and weld metal, Skvortsov [5] developed an empirical expression to relate the corrosion potential with composition for heat treated steels in seawater used for ship hulls as shown below as E_1 . The goal of this effort was to estimate a priori if a strong galvanic interaction would occur given the composition of the steel, the likely composition of the weldment, and the likely heat input for the welding operation.

$$E_1(V \text{ vs } SHE) = k[(-7.4Mn - 0.46Si + 2.53Ni + 2.52Cr + 3.25Cu + 0.53Nb - 3.22Al + 3.8Mo)10^2 - (4.99Fe \times 10^{-3})]$$

In the above expression, the constant k is approximately 0.86 for steels and is 0.91 for the weldment; this difference in the constant k is to account for microstructural differences. To account for the heat input during welding, the following expression was proposed for predicting the corrosion potential of the weldment:

$$E_2 = E_1 - 0.43(Q - 8.38)$$

where E_1 is calculated using a k of 0.91 and Q is the welding heat input in kJ/cm. The calculated values for corrosion potentials of both base plate steel and weldments showed reasonably good agreement with experimentally measured potentials, with most deviations on the order of a 10-40 mV. Though this approach is intriguing, the practical value is unclear since making an accurate prediction of the weldment composition could be challenging for non-ERW welds given all the potential variables. For ERW welds, however, this approach may have merit since the weld and the base metal compositions are identical and only the microstructure and heat input effects need to be included.

In examining the corrosion potential expression developed by Skvortsov, it is interesting to note that Mn and Si tend to cause the corrosion potential to be more negative whereas Ni, Cr, Cu, Nb, and Mo promote increases in the corrosion potential. Therefore, if the intent is for the weldment to have a higher corrosion potential than the base metal and thus be the cathode in a galvanic couple, minimizing Mn and Si while maximizing Ni, Cr and Cu in the weldment should prove beneficial for SSWC resistance. Numerous investigations examining these elements have demonstrated that this approach has merit for reducing SSWC susceptibility, especially when introduced as alloyed filler materials for SAW, SMAW, and GMAW welding [3, 9-11, 16, 19, 25, 46, 47]. For example, Joosten et al., [9] showed that additions of Cr and Ni resulted in the weldments being net cathodes when galvanically coupled to the base metal in 0.5% NaCl saturated with CO₂ at 75 °C. Mitrovic-Scepanovic and Bringham [11] found an 80% reduction in the rate of SSWC with the addition of copper and nickel to the base metal at levels of 0.3 – 0.5 and 0.5 – 1.6 wt% respectively. Similar results have been reported by Endo et al. [10] who demonstrated that the corrosion potential of the weldment/HAZ region moved more noble by as much as 10 mV compared to the parent metal by adding small concentrations of nickel and copper in combination with reducing the overall sulfur concentration of the parent steel. The precise mechanisms for the observed improvements to SSWC susceptibility are unclear and little speculation has been put forward, however, the phenomenology of this approach seems to be well validated and established.

5 EFFECT OF WELD PARAMETERS AND POST-WELD PROCESSING

Because of the inherent differences between the parent metal and the weldment that usually develop regardless of the welding process, all welding methods have been shown to exhibit some susceptibility to SSWC. In addition to controlling the chemistry of the parent steel and the weldment, the effects of welding parameters and the potential beneficial effects of post-weld seam heat treatment and post-weld full body heat treatment on SSWC susceptibility have been extensively studied [2, 9-11, 17, 19, 22, 28, 40, 48]. In general, good edge surface preparation, the application of adequate pressure on the plate forming the weld joint, and minimal electrical contact resistance (for ERW) are critical to minimizing the possibility of generating lack of fusion defects which can serve as nucleation points for SSWC [8]. It has also been generally noted [9, 10] that SSWC is more severe when the composition of the weldment is leaner in key beneficial elements or enriched in deleterious elements than the base metal. As was discussed previously, higher levels of Ni, Cr, and Cu in the weldment when filler is used have been shown to be beneficial in minimizing SSWC. Manipulation of the weld chemistry is much more applicable to welding processes for which a filler is used but the principles can and do also apply to ERW in the context of element segregation.

In general, it has been shown that low heat input during welding results in poor SSWC resistance [11]. Garner [38] et al. showed that for SAW welds the relative corrosion rate of the HAZ in relation to the base metal was highest at low heat inputs (Figure 10). At the lowest heat input values studied, the corrosion rate for the HAZ was on the order of twice that of the base

metal. Higher heat inputs reduced the relative difference between the HAZ and the base metal, though, in all cases studied, the dissolution rate for the HAZ was higher than the base metal. It should be noted that SAW tends to have higher heat inputs than many other welding methods. For example, the heat input values shown in Figure 10 are considerably higher than those typically encountered in ERW welding. Kusaka et al.,[49] demonstrated that X65 pipe steel welded using a high heat input laser process exhibited excellent corrosion resistance with no preferential corrosion of the weldment. Joosten et al.,[9] observed that higher heat inputs tended to result in eliminating selective attack in SAW and SMAW welds. They also observed a decrease in SSWC susceptibility when the weldment was preheated to temperatures of either 212 or 356 °F (100 or 180 °C). The improvements noted upon weld preheating and higher weld heat input were attributed to refining the microstructure of the weld root and HAZ, though this could also cause more grain growth can could result in coarser microstructures. Though not explicitly stated, the improvements observed could also be due to enhanced dissolution and refinement of any MnS or FeS inclusions present.

In contrast to the studies that show a beneficial effect of higher weld heat input on SSWC susceptibility, Lee et al., [48] observed no effect of weld heat input for ERW seam welded pipe. Evaluating heat input values ranging from approximately 13 – 18 BTU/in, they noted no significant effect of heat input on the corrosion rates of the weldments formed. One possible explanation for the apparent lack of dependence of SSWC susceptibility on weld heat input could be because the range of values studied was too small to note any significant effects. It could also be that heat input for ERW welds is less important with respect to SSWC susceptibility. Clarification and better understanding of this is necessary in order to quantify if and how heat input influences SSWC for ERW pipe.

Post weld heat treatment has been shown to provide some beneficial effects in reducing SSWC susceptibility. There is evidence that beneficial effects on SSWC can be obtained using either seam normalization or full pipe body heat treatment [40]. Mechanistically, post-weld heat treatment is thought to improve corrosion resistance through weld microstructure normalization, reduction of residual stresses in the weldment, improved bond line integrity via diffusion across the weld line, and refinement and redistribution of sulfur and sulfide inclusions [2, 7, 17, 22, 24, 28, 48]. Of these proposed mechanisms, changes in the weld microstructure are likely to only have a minor or secondary effect on SSWC susceptibility. Though residual stresses can lead to stress corrosion cracking and other forms of environmental cracking and have been shown to have some influence on corrosion rates, it seems unlikely that such stresses constitute a major influence on SSWC. Improved weld bond line integrity is certainly important to overall weld quality, but it is unclear how this might influence SSWC in any significant way as the temperatures and times are not sufficient to close lack of fusion defects.

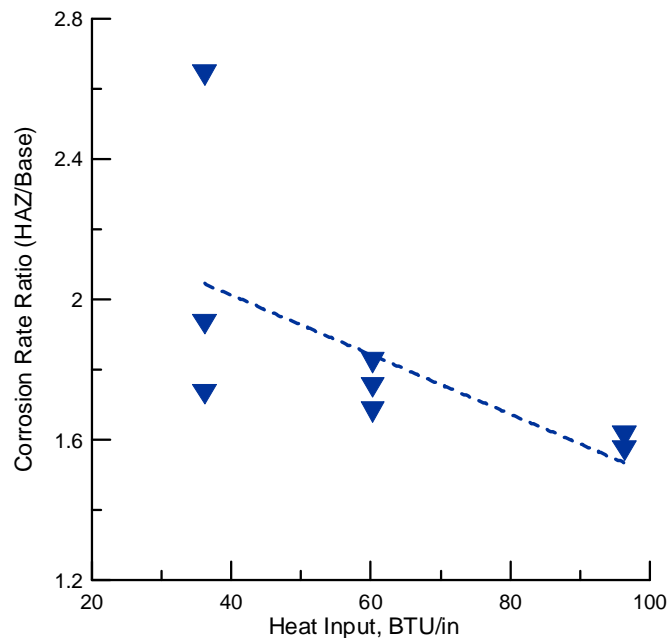


Figure 10: Effect of SAW weld heat input on the relative corrosion rate of the HAZ compared to the base metal. [38]

Refinement and redistribution of sulfide inclusions in the weldment and HAZ seems to be the most likely mechanism whereby SSWC susceptibility is improved through post-weld heat treatment. Lee et al., [48] showed a direct correlation of weld corrosion rate and post-weld heat treatment temperature for ERW pipe (Figure 11). In this study, the corrosion rate was determined by measuring the post-test thickness loss and grooving ratio after constant potential exposures for 48 hours in air-saturated 3% NaCl. Also shown in Figure 11, for comparison purposes, is the corrosion rate observed for the base metal. In addition to reducing the overall corrosion rate of the weldment, they also observed that the grooving factor began to approach unity with increasing heat treatment temperature. The benefits of post-weld heat treatment are evident, and Lee et al. correlated the observed improvements observed in corrosion rate reduction with a reduction of FeS inclusion size and quantity. Similar conclusions were drawn by Katoh et al. [22] and Masamura and Matsushima [3] who also showed that post-weld heat treatment of ERW welded pipe could reduce the number and density of sulfide inclusions in the weld region thereby improving resistance to SSWC.

It should be noted, however, that not all post-weld heat treatment procedures results in improvements to SSWC susceptibility. For example, in the same study showing the benefits of post-weld heat treatment, Lee et al., [48] also showed that, if the treatment temperature was less than 750 °C (1380 °F), the ERW welded pipe material was made more susceptible to SSWC. Similarly, Duran et al., [2] showed that 30 min post-weld heat treatments at temperatures less than 850 °C (1560 °F) gave unpredictable results for ERW pipe with a sulfur content of 0.029

wt%. In the case of Duran, they observed that a saw tooth type of response was noted as a function of temperature between 700 and 850 °C (1290 – 1560 °F) in which SSWC susceptibility would get better then worse repeatedly as the temperature was increased over this range. Kato et al., [17] and Heitmann et al., [28] also noted that post-weld heat treatments were most effective above 850 – 900 °C (1560 – 1650 °F).

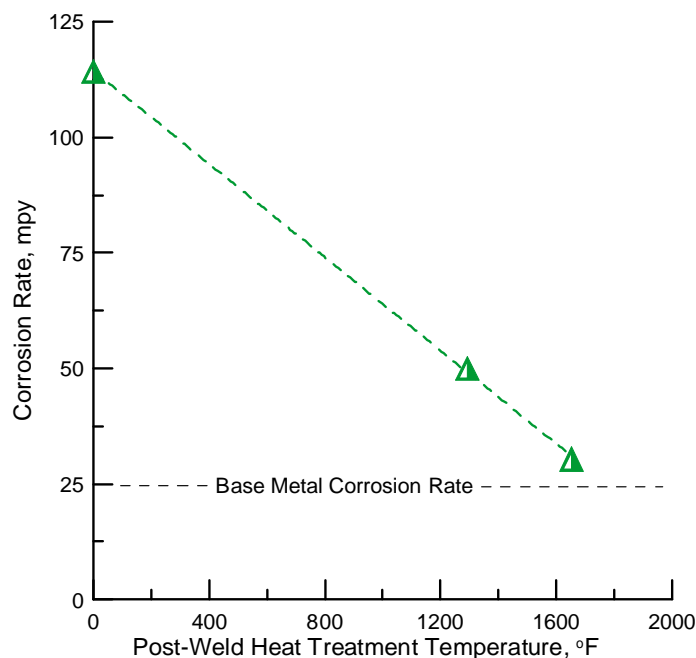


Figure 11: Effect of post-weld heat treatment on SSWC corrosion rate for ERW welds. [48]

6 MITIGATION OF SSWC SUSCEPTIBLE PIPE

Some study has also been focused on mitigating SSWC for susceptible pipe while in service. To date, the traditional methods used for nearly any form of corrosion have been explored including chemical treatment (inhibitors), coatings, and cathodic protection (for external corrosion of pipe). Winning et al., [18] showed that the use of some amine-based inhibitors in simulated oil and gas production environment resulted in reducing the SSWC rate to acceptable levels and values approaching those of the base metal. In this work, they also showed that they could achieve similar inhibitor efficiencies for the FZ, HAZ, and parent material within a few percent. There was, however, an instance where one inhibitor reduced the corrosion rate of the parent steel and the HAZ but the corrosion rate of the FZ increased by a factor of over 20x. Similarly, Walsh [50] showed that, while some chemical treatment inhibitors could reduce the SSWC rate in seawater injection lines, others resulted in accelerating SSWC compared to not injecting inhibitor. These observations indicate that inhibition of SSWC susceptible pipe is

possible but confirmation testing and follow up monitoring should be conducted to ensure that unexpected acceleration of SSWC is not taking place.

Kiefner [51] and Baker [52] both indicated that bare pipe or pipe with a poor or disbonded coating can result in possible locations for SSWC to occur. Thus, in areas that were bare and unprotected or where possible CP shielding might exist, SSWC should be considered a potential threat. Though no specific studies have addressed the efficacy of typical pipeline coatings on prevention of SSWC, aluminum thermal spray coatings have been shown to provide protection during 180-day tests for icebreaker hull plate applications [11]. In their testing, Mitrovic-Scepanovic and Brigham [11] showed that welded steel that was susceptible to SSWC but had a thermal sprayed aluminum coating on the order of 0.4 mm (0.015 in) thickness applied did not experience any measureable metal loss after long-term immersion in acidified artificial seawater and in salt spray testing. These results would seem to imply that other similar types of coatings such as galvanizing might also provide protection for SSWC susceptible pipe. Furthermore, since the mechanism by which aluminizing provides protection to the steel substrate is through sacrificial cathodic protection, these results would also seem to imply that protection using either impressed current or ribbon or bracelet anode cathodic protection should also be viable. Though it seems likely that the presence of a protective coating and effective cathodic protection can mitigate SSWC, there is a paucity of reported results that confirm these facts nor is there reported information quantifying the minimum level of CP needed.

7 SUMMARY AND CONCLUSIONS

Based on the available literature, it is evident that SSWC is an integrity threat not only for ERW welded pipe but also for other seam weld methods. Research efforts have assisted in developing a better understanding of the possible mechanisms and key factors that lead to SSWC. Of the mechanisms posed, sulfur enrichment and sulfide inclusions leading to localized corrosion in the weldment seem to have the greatest merit. There is ample phenomenological evidence as well as fundamental science that provide a basis for linking inclusions to localized corrosion. The presence of a higher concentration of inclusions could also explain the observed differences in corrosion potentials and the resultant galvanic interaction between the weldment and the base metal. Regardless of the mechanisms involved, it is clearly evident that limiting the sulfur content and including sulfide composition and shape-control elements is important to minimize the risk of SSWC.

In addition to controlling the level of sulfur and inclusion shape and composition, the overall steel composition and microstructure is important. Generally, Cu and Ni additions to the steel or to the weldment, in cases where a filler is used, have proven to be highly beneficial in improving SSWC resistance. In contrast, high levels of Mn and Si have been shown to be detrimental. Though there is no link between weld hardness and SSWC susceptibility, proper weld parameters and post-weld seam or full body heat treatment are beneficial. Higher weld heat

inputs and post-weld heat treatment above approximately 850 °C (1560 °F) tended to prove beneficial to SSWC resistance. These actions are also consistent with refining and redistributing sulfide inclusions.

Once installed, the environmental factors that influence SSWC are essentially the same as would be observed for other forms of corrosion. Thus, higher temperatures, more aggressive environments (e.g., lower pH, higher chloride), flow, and so forth tend to result in higher SSWC rates. Similarly, the same approaches that are used to mitigate and control other forms of corrosion have, at least to some extent, been examined for SSWC including chemical treatments, coatings, and cathodic protection. Chemical corrosion inhibitors have been shown to provide adequate reductions in the corrosion rate of the weldment of SSWC susceptible steels comparable to the base metal. However, in some cases, the opposite effect was observed with some inhibitors in that the corrosion rate of the weldment was accelerated. It seems that most typical pipeline coatings would be effective in minimizing SSWC through isolation from the environment (i.e., as a barrier coating), however this has not been conclusively shown. Flame sprayed aluminum has proven to prevent the onset of SSWC which seems to indicate that cathodic protection should be a viable approach to minimize the risk of SSWC.

Though research efforts have evaluated SSWC for pipe steels, many gaps still exist regarding the various potential influential factors that may promote or mitigate SSWC susceptibility. These include the need to determine if a critical steel sulfur concentration exists below which SSWC is not a threat, determination and evaluation of CP levels to establish guidelines for mitigating SSWC in susceptible pipe, and better quantification of the effects of soil and coating properties on SSWC susceptibility. It is proposed that filling in these gaps will greatly strengthen and enhance the technical and cost effectiveness of pipeline integrity plans that consider the threat of SSWC.

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APPENDIX

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Det Norske Veritas

DNV is a global provider of knowledge for managing risk. Today, safe and responsible business conduct is both a license to operate and a competitive advantage. Our core competence is to identify, assess, and advise on risk management, and so turn risks into rewards for our customers. From our leading position in certification, classification, verification, and training, we develop and apply standards and best practices. This helps our customers to safely and responsibly improve their business performance.

Our technology expertise, industry knowledge, and risk management approach, has been used to successfully manage numerous high-profile projects around the world.

DNV is an independent organization with dedicated risk professionals in more than 100 countries. Our purpose is to safeguard life, property, and the environment. DNV serves a range of industries, with a special focus on the maritime and energy sectors. Since 1864, DNV has balanced the needs of business and society based on our independence and integrity. Today, we have a global presence with a network of 300 offices in 100 countries, with headquarters in Oslo, Norway.

Global Impact for a Safe and Sustainable Future

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