Practical Aspects of Industrial Sulfuric Acid Corrosion

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Sulfuric Acid is a high volume important inorganic acid commonly used by industry. Practical aspects of dealing with sulfuric acid in industrial service will be discussed. The discussion will be limited to stainless steels and nickel base alloys. The effects of contaminants, temperature, inhibitors, and aeration of the acid solution shall be discussed. Welding fabrication concerns will be identified. Both physical defects and metallurgical considerations of welding will be addressed.

Seemingly small variations in conditions can result in major changes in corrosion. Minor levels of impurities, parts per million of halides, may significantly affect actual service corrosion rates. Halides, such as chlorine, are among the most potent impurities encountered. Not only may impurities accelerate corrosion but they may also change the type of corrosion (e.g., stress corrosion cracking). Aeration can increase or decrease the rate of corrosion depending on the materials involved. Hot wall effects are frequently overlooked even though they may have a pronounced effect on actual service.

It is highly recommended that published corrosion data be considered as a relative guide for ranking of performance. However, it is important to note that actual service corrosion rates and rankings may vary significantly from published data. Slight changes in plant environment may cause a change from passive to active corrosion behavior. Materials that may work well in one plant for years may quickly corrode in weeks or months in a similar plant even though conditions appear to be similar.

Stainless Steels and Nickel Alloys

The alloys being considered here are 300 series stainless steels as well as more highly alloyed austenitic stainless steels. In the passive region stainless steel can corrode at less than 0.13 mm/year (0.005 inches/year). Nickel base alloys are considered as alternatives. While nickel base alloys are more expensive than stainless steels they have unique properties that make them more suitable in certain applications.

Stainless steels obtain their corrosion resistance by forming a chromium oxide passive layer on the surface of the steel. The corrosion resistance of an alloy increases with increasing chromium content. Aeration or an oxidizing environment is generally beneficial to stainless steels. It is the presence of oxygen that promotes the formation of the passive layer. If the passive layer is damaged by abrasion or some other means in service, oxygen is needed to repassivate the stainless steel. An alternative to stainless steels in non-aerated environments are nickel-copper alloys.

If the passive layer is compromised then active or active-passive corrosion behavior will occur. Corrosion rates are much higher in the active region. For example testing in 93 to 98% sulfuric acid has shown that many common austenitic stainless steels show passive behavior. This passive behavior has been demonstrated from 30 to 70 °C (86 to 158 °F) for some commonly used austenitic stainless steels. With increasing temperature passive behavior changes to active-passive or active behavior (see figure 1).
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Many high chromium nickel base alloys also form a passive layer in oxidizing environments. Frequently these high chromium nickel base alloys have relatively low corrosion rates in both active and passive corrosion states. Another nickel base alloy alternative is the nickel-copper alloys such as Monel alloy 400. Nickel-copper alloys perform well under reducing conditions such as non aerated environments.

Stress Corrosion Cracking

Impurities may significantly affect corrosion.. Chlorine can significantly accelerate the corrosion rate of components in service (see figure 1). Even more troublesome chlorine may lead to stress corrosion cracking (SCC) of stainless steel (see figure 2). The necessary ingredients for stress corrosion cracking are stress, a susceptible material, temperature, and corrosive agent. If the corrosive agent can not be eliminated or reduced then steps to control the other factors are required.

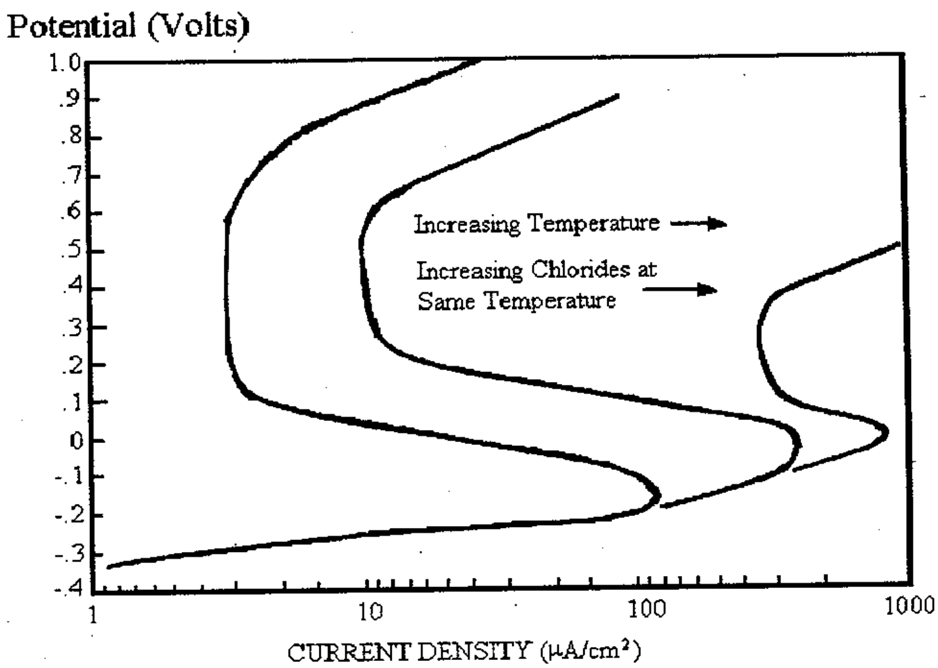

Figure 1 Effect of temperature and chlorides on corrosion rate

Stresses due to design, fabrication, welding and thermal cycling can induce SCC. Depending on the application, controlling residual stresses may be sufficient to preclude SCC. For more severe applications (high chloride concentration or high temperature) additional steps may be required.

For more severe applications it may be necessary to use materials with higher nickel content. Super austenitic stainless steels containing greater than 25% nickel and nickel base alloys have superior resistance to chloride stress corrosion cracking (see figure 3).

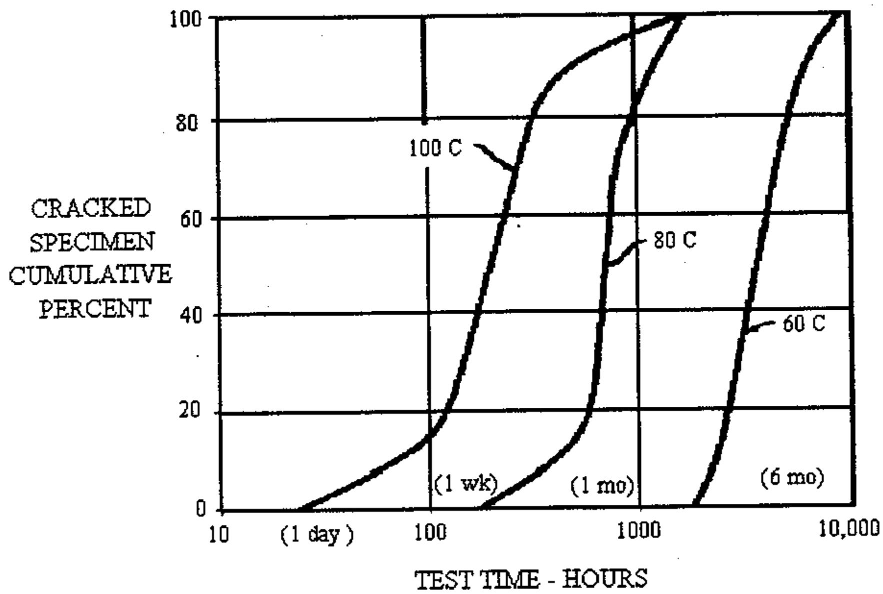

Figure 2 Temperature versus time to SCC for 304 stainless steel in 100 ppm chloride by wick test. U-bend specimens, applied stress 90% of yield strength, tests performed under concentrating conditions

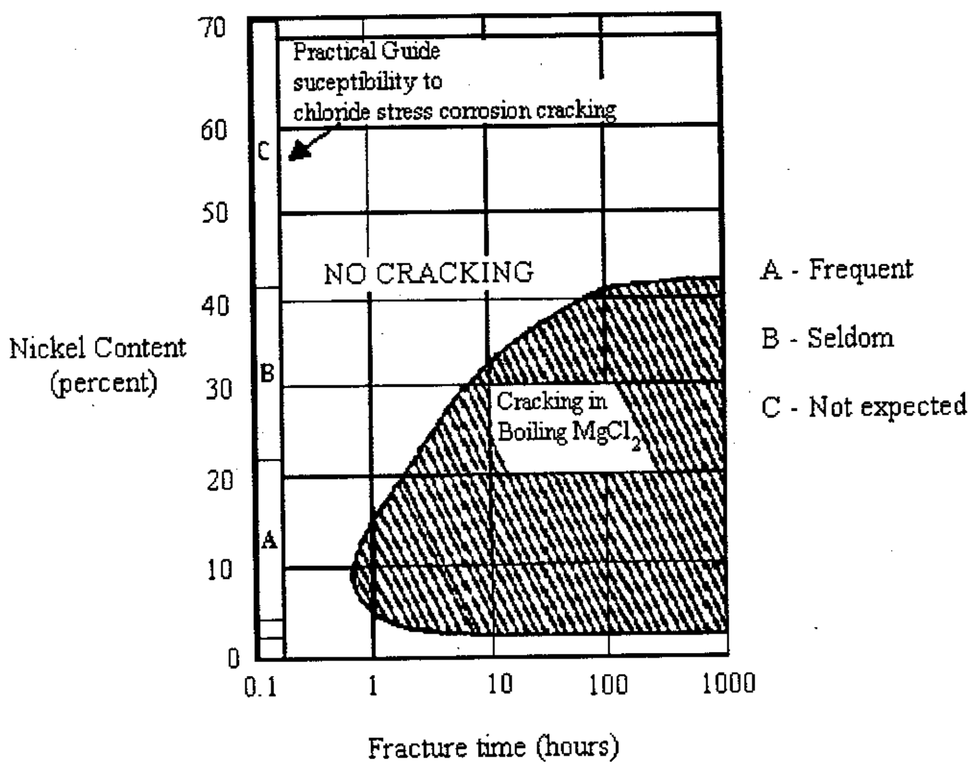

Figure 3 Time to fracture in boiling $MgCl_2$

Contaminants

Some impurities may actually reduce corrosion. Small additions of nitric or chromic acids can significantly reduce corrosion rates for stainless steels. The oxidizing effects of these agents enhance the passive oxide layers on the stainless steel surface (see figure 4).

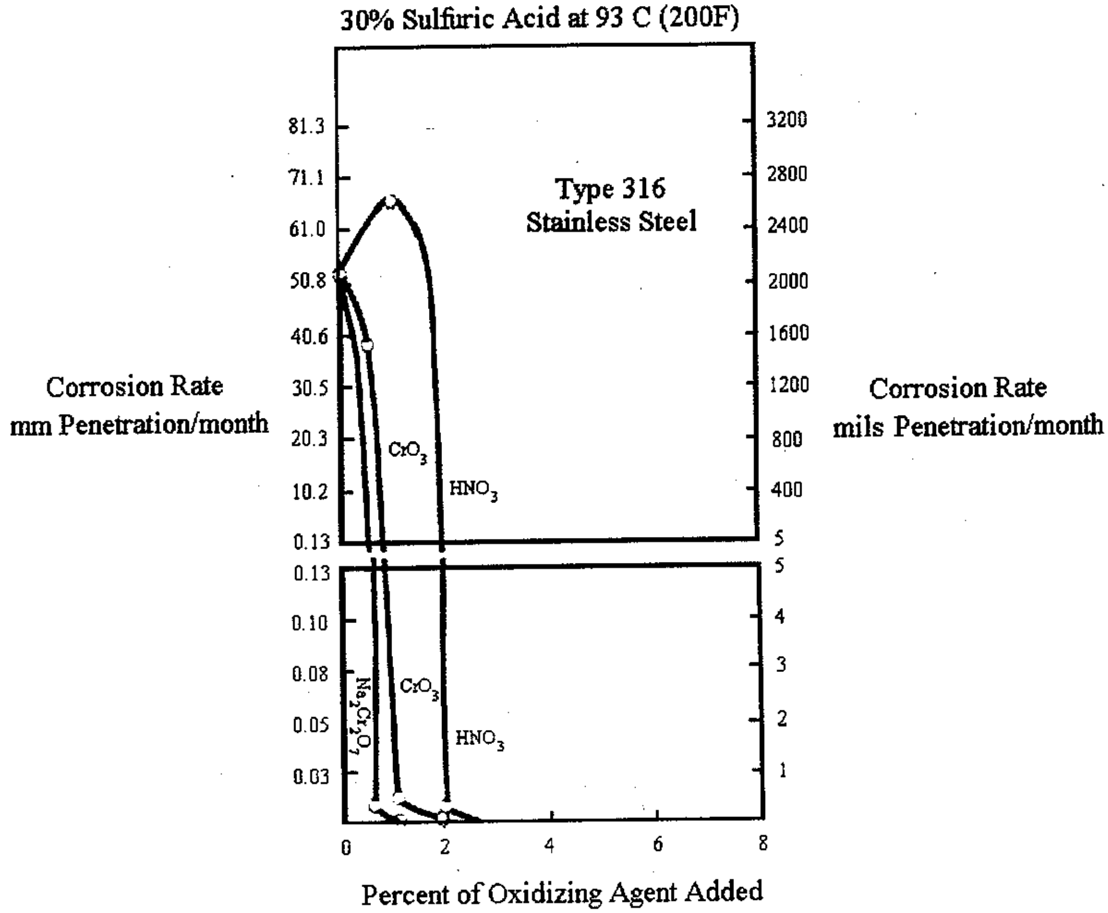

Figure 4 Effect of oxidizing agents on corrosion rate

Other agents also reduce corrosion of stainless steel (see figure 5). Copper sulfate is particularly effective at providing passivity to stainless steel. Many other impurities will slow corrosion to some degree simply by loading the solution and thereby retarding ionic movement. Thus, in some instances, actual in service corrosion rates can be less than the reported data.

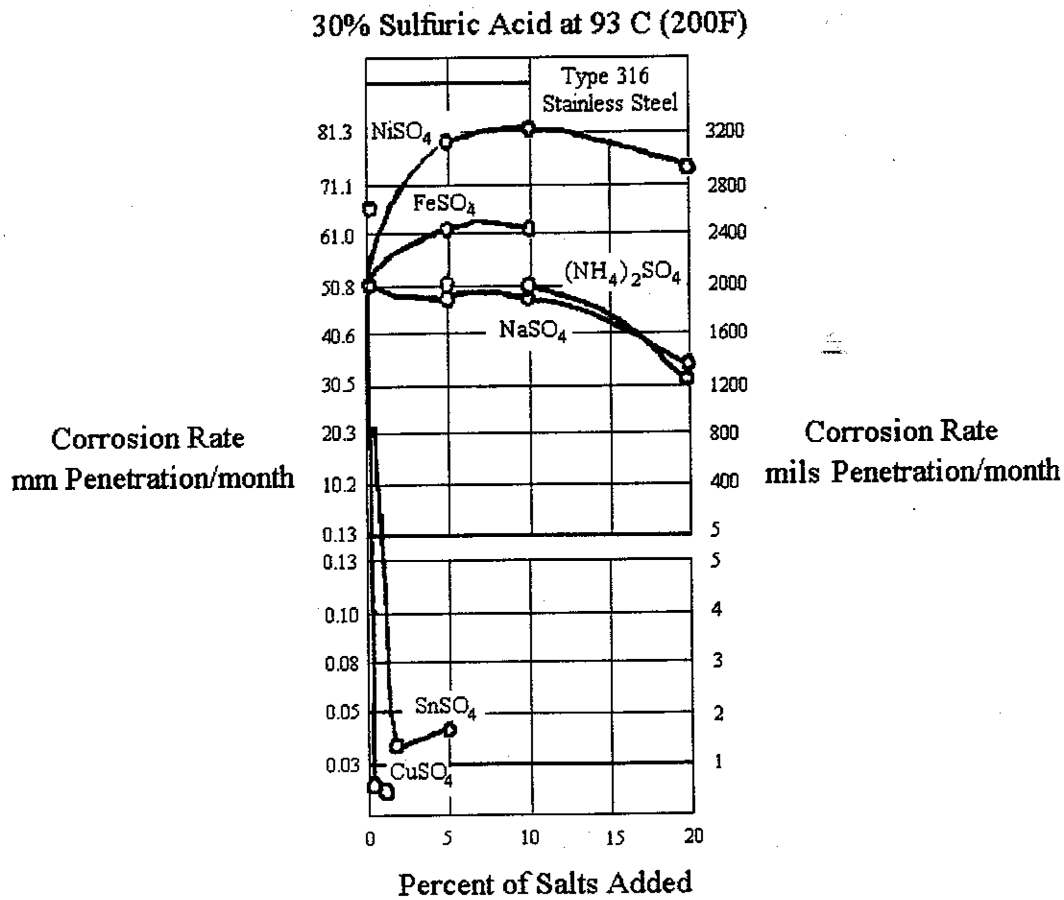

Figure 5 Effect of various impurities on corrosion rate

Temperature

Temperature is one of the most important factors affecting the corrosion rate. At higher temperatures passive behavior breaks down. High temperatures and strong acid conditions present the greatest challenges. These environments are where the most highly alloyed materials are used.

Alloys with increased chromium content (see figure 6) or copper additions are commonly used in some of the more severe environments. Molybdenum alloying additions are also frequently used to maintain the passive oxide layer for better corrosion protection.

Hot wall effects are frequently over looked in heat transfer applications. Sulfuric acid temperature may be low enough for passive conditions to occur on most surfaces. Metal temperature of some hot components may be sufficient to be in transpassive region. Elevated temperature results in much higher corrosion rates on the surfaces of the hot wall in a heat exchanger.

Another commonly overlooked problem is a hot component causing the solution to evaporate. This can result in higher concentration of the acid and impurities than otherwise would have been expected. The combination of stronger acid and higher temperatures can result in accelerated corrosion rates. Alternatively, low levels of chlorine that may not be causing a problem throughout a plant can result in SCC and failure if concentrated by evaporation of solution on a hot component.

Velocity of the solution does not generally have a significant effect on the corrosion rate when stainless steel is in the passive condition. However, if elevated temperature, acid concentration, and impurities result in an environment where the metal is in the active-passive or active condition, solution velocity can effect corrosion rates.

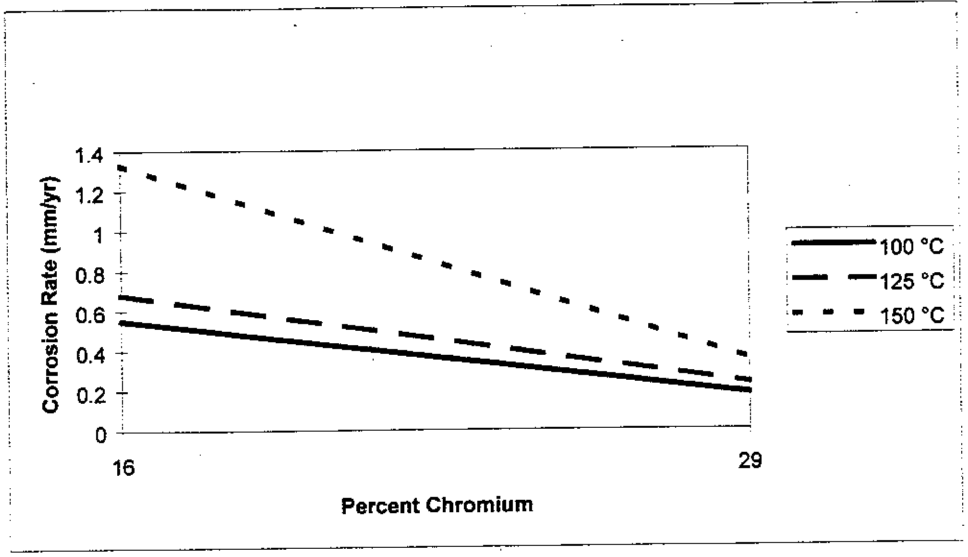

Figure 6 Effect of chromium on corrosion rate of stainless steel in 95% sulfuric acid

Crevices

Crevices are known to result in corrosion problems. Crevices are localized regions where corrosion conditions are different than in the bulk solution. For example, deaeration or impurity concentration may occur at crevices. Passive corrosion behavior usually breaks down more readily at crevices.

If crevices can not be eliminated by design then choosing an alloy more resistant to crevice corrosion may be required. Increased levels of molybdenum are frequently used to reduce crevice corrosion. Molybdenum increases the stability of the passive layer. Similarly increasing the level of Chromium increases the stability of the passive oxide layer thereby increasing resistance to crevice corrosion. Nickel also increases resistance to crevice corrosion. Improved crevice corrosion resistance is one of the advantages of using the super austenitic stainless steels or austenitic nickel base alloys for severe corrosion service.

Welding

Welding anomalies such as slag, surface porosity, laps, excessive penetration, lack of penetration, mismatch, cracks need to be controlled. These anomalies can result in lowering the corrosion resistance at the weld. Additionally, stress relief of the weldment may be required to eliminate residual stresses that can lead to SCC.

Metallurgical considerations must also be considered. Sensitization, the precipitation of chromium carbides at grain boundaries, can occur due to improper heat treatment, stress relief, or welding. This can lead to preferential corrosion along the grain boundaries. This can easily go undetected during weight-loss corrosion testing. The total weight loss due to intergranular corrosion is small while the integrity of the component can be seriously degraded.

To prevent sensitization due to welding the following actions are frequently taken:

1. Resolution of the weldment
2. Use of low carbon materials
3. Use of carbide stabilized materials

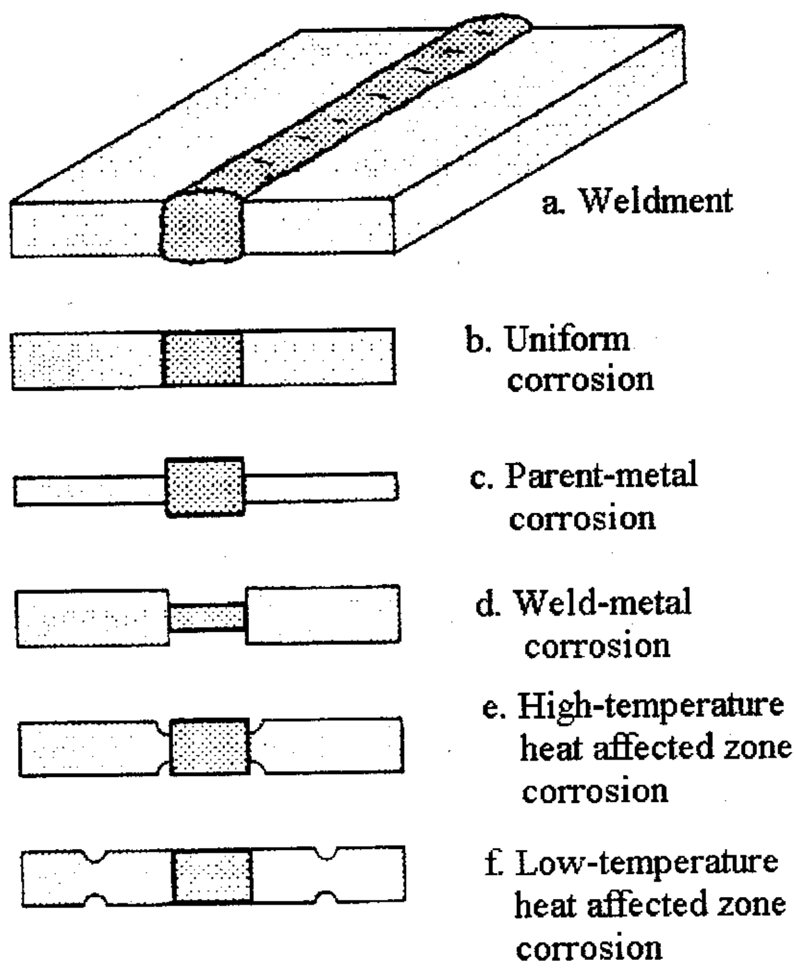

Figure 7 Schematic of corrosion effects at a weld

Weld metal corrosion testing should be conducted (see figure 7). Uniform corrosion of weld metal and parent metal is preferred. Preferential corrosion of the parent metal (parent metal anodic) is not usually a problem as the surface area of the parent metal is much larger than the weld metal.

Preferential corrosion of the weld metal (weld metal anodic) can be a significant problem. The ratio of parent metal to weld metal area is normally quite high resulting in high current density at the weld metal and correspondingly high corrosion rate of the weld.

The most significant problem is normally associated with preferential corrosion of the weld heat affected zone (HAZ). The heat of welding may cause changes in the metallurgical structure of the weld HAZ. These changes may result in preferential attack in a very localized region and may be difficult to detect using normal corrosion testing techniques. Care must be taken during fabrication to properly control the welding processes. Poor process control may result in unacceptable weld HAZ microstructure.

Summary

Stainless steels and nickel base alloys provide excellent sulfuric acid corrosion service as long as passive behavior is maintained. Acid concentration, temperature and impurities have a significant effect on corrosion behavior. SCC and crevice corrosion are frequently encountered in service conditions and need to be given adequate consideration. Selection of stainless steel or nickel alloys with proper alloying additions can eliminate or reduce corrosion commonly encountered in service conditions.

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