Case Study: Failure Analysis of Sulfuric Acid Supply Line

Introduction

VGO Testing & Inspection Engineers was retained by an industrial client to determine the cause of failure of a 1-inch diameter carbon steel pipe used to convey 93% sulfuric acid to a demineralizer in the steam plant. The client reported that the line, which was thought to be several years old, failed by developing a hole at an elbow between the discharge pump at the acid supply tank and an automatic valve which controls the flow to the demineralizer. Several months earlier, the same line reportedly developed another leak, downstream of the current failure.

VGO's client indicated that the acid flow through the line was intermittent, to the extent that several days might pass without flow, followed by a few minutes of active flow when the system called for acid. Additionally, the client reported that downstream of the failure was a second automatic ball valve, and beyond that was another line that injected water into the acid supply line (which at that location consisted of lined pipe to prevent corrosion).
VGO's assignment was to examine the failed section of pipe and establish the mechanism of failure.

Methodology

An 8-foot long section of the failed line, including the leaking elbow, two other elbows, and four sections of straight pipe, was submitted to VGO for analysis. VGO's analysis included the following steps:

- Ultrasonic thickness survey of the line to characterize extent and location of thinning
- Longitudinal sectioning of line to expose interior surface for visual examination
- Low power microscopic examination of corroded areas to establish corrosion morphology
- Metallographic examination of cross sections removed from line
- Microhardness testing to estimate physical properties

Results

The leak was caused by a localized hole in the pipe adjacent to an elbow and was the result of acid-induced corrosion. Although the line had only been penetrated by corrosion at one location, the corrosion damage was widespread in the line.

The corrosion damage exhibited two distinct morphologies and was the result of two, related corrosion mechanisms. That is, the pipe exhibited both general thinning, caused by the corrosive attack of sulfuric acid due to excessive flow velocities and/or turbulence, and highly-directional, localized grooves, caused by “hydrogen-grooving”, a corrosion mechanism associated with intermittent flow.

In particular, in the area just beyond the leak, the pipe had been thinned to less than 0.020 inch. Elsewhere, the entire length of the submitted section of line had also been thinned, with minimum thicknesses ranging from 0.060 to 0.080 inch, compared to an original thickness of 0.133 inch (i.e., nominal wall thickness for 1-inch, Schedule 40 pipe). The general thinning was due to flow-induced destruction of the passive protective surface film which forms on carbon steel in concentrated sulfuric acid service and protects it from corrosion.

In addition to the general thinning, the line also exhibited numerous, fine, diagonal (helical) grooves, characteristic of hydrogen grooving, a corrosion mechanism caused by the alternate formation of hydrogen bubbles, which collect on the surface of the pipe during stagnant conditions, followed by flushing of the bubbles during periods of flow, resulting in localized destruction of the passive protective surface film.

The pipe material exhibited a microstructure and hardness typical of carbon steel pipe. No welding defects or other flaws were observed that would have been contributory to the failure.

Discussion

Although sulfuric acid is highly corrosive, carbon steel is a suitable material for use in tanks and piping in concentrated sulfuric acid service due to the presence of a ferrous sulfate film that forms on the surface of the steel upon exposure to the acid. This film, which itself is a corrosion product, protects the underlying steel from further corrosion, but only within certain ranges of acid concentration, temperature, and flow rate. If the film breaks down or fails to form, rapid corrosion of the underlying steel will result.

The iron sulfate film is relatively fragile and can be eroded away, or prevented from fully forming, by turbulence or excessive flow velocities. If this occurs, the underlying metal rapidly corrodes until a new film is formed and becomes stable. The general corrosion attack present along most of the line in this project was most likely the result of corrosion caused by excessive flow velocities and turbulence. As a general rule of thumb, the flow velocity should be less than about 2 to 3 ft/sec to prevent destruction of the iron sulfate film and the resulting corrosion of the underlying steel. However, even within this range of velocities, turbulence effects at elbows, flanges, and other disruptions can destroy the film and lead to accelerated corrosion.

Although the general corrosion was considered to have been most likely the result of this particular corrosion mechanism, another possibility was also considered, namely, contact with diluted sulfuric acid. That is, in lower concentrations of sulfuric acid, the iron sulfate film fails to form sufficiently, leading to general corrosion and thinning of the material. This suggests the possibility that water may have back flowed into the line from the water injection point. Note that sulfuric acid is highly hygroscopic, meaning it readily absorbs moisture, either directly from the air or from contact with liquid water. Thus, it is important that the acid in the line be prevented from coming into contact with water, either in liquid or vapor form. Although the failure was upstream of two automatic ball valves, which were presumably intended to prevent the backflow of water into the concentrated-acid portion of the line, the possibility of reverse leakage past the valves should be considered a possibility.

The other mechanism of corrosion that was apparent in the line was hydrogen grooving, as evidenced by the helical grooves present in all sections of the line, and especially in the top half of the horizontal sections. Hydrogen grooving is a form of corrosion that occurs to carbon steel in concentrated sulfuric acid service when the iron sulfate film is scrubbed off the pipe wall by hydrogen bubbles, which form as a reaction product when carbon steel is exposed to concentrated sulfuric acid. When the film is scrubbed off the wall, the wall is subject to renewed corrosion until a new film forms and stabilizes.

This mechanism generally occurs only under conditions of intermittent flow. During normal flow, the hydrogen gas bubbles are very small and are carried downstream without causing a problem. However, when the acid stops flowing, the gas bubbles rise, and in the case of horizontal sections of the line, accumulate on the interior pipe wall in the top half of the pipe. When the flow resumes, the gas bubbles are dislodged and flow downstream, rising along the surface of the pipe in a curved pattern, scrubbing off the protective iron sulfate film along the way. The freshly-exposed carbon steel then rapidly corrodes, forming a new film of iron sulfate.

Continued repetition of this process results in a series of curved grooves in the top half of the pipe. The classical pattern of attack is represented by a series of symmetrical, curved grooves in the two upper quadrants of the pipe, all radiating toward a central longitudinal groove at the very top. In the case of this failure, the pattern of attack was somewhat different, consisting of a series of helical—and at some locations, criss-crossed–grooves, without the central longitudinal groove. This pattern was probably the result of a spiral flow pattern in the pipe, induced by the change in flow direction at the elbows.

Potential solutions to the failure include changing the geometry of the line to reduce turbulence at elbows, increasing the diameter of the line to reduce the flow velocity, changing the material to an alloy more resistant to attack by concentrated sulfuric acid, and assuring the function of check valves upstream of the water injection port to avoid dilution of the acid by water.

Details of the analysis are in the following figures and captions.

Figure 1. Sulfuric acid tank and piping

Figure 1 shows the 93% sulfuric acid storage tank (left, behind clear plastic screen) and the piping to the demineralizer after the failed pipe had been removed from service and replaced with new pipe. The new pipe, which was reportedly Type 316 stainless steel, was routed through the wall in back of the tank (middle arrow) approximately 18 inches above the location where the failed line had been routed (bottom arrow).

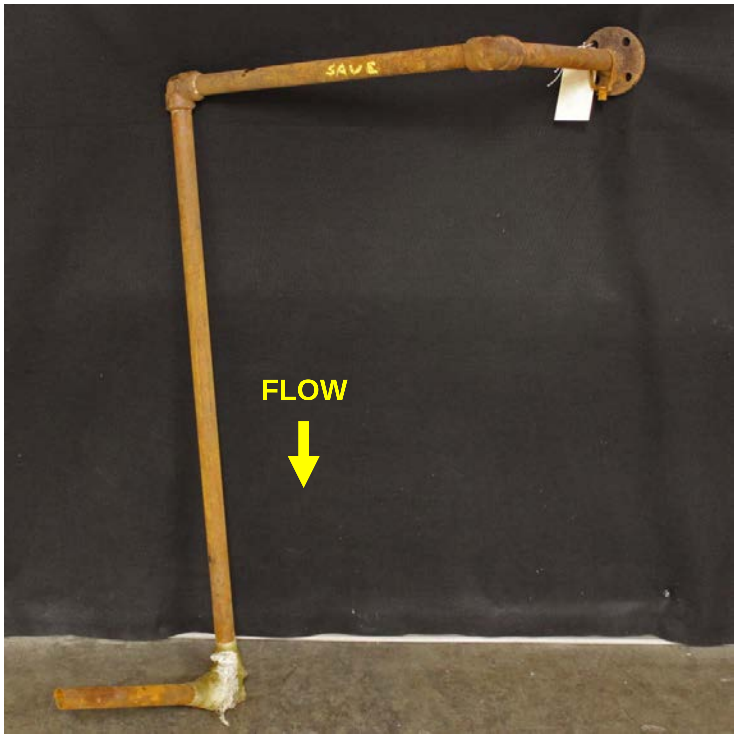

Figure 2. Submitted section of sulfuric acid piping

A section of the failed line, including the flange where it was attached to the outlet from the pump (top arrow, Figure 1), three elbows, and four sections of pipe, was submitted to VGO for analysis (Figure 2).

VGO's client reported that when the leak was first discovered, temporary repairs were made by wrapping the leak site with fiberglass tape, coated with polyurethane resin. The repair soon failed, and the leaking section, from the flange at the pump outlet to an unreported location downstream of the leak, was removed from service and replaced, reportedly with Type 316 stainless pipe.

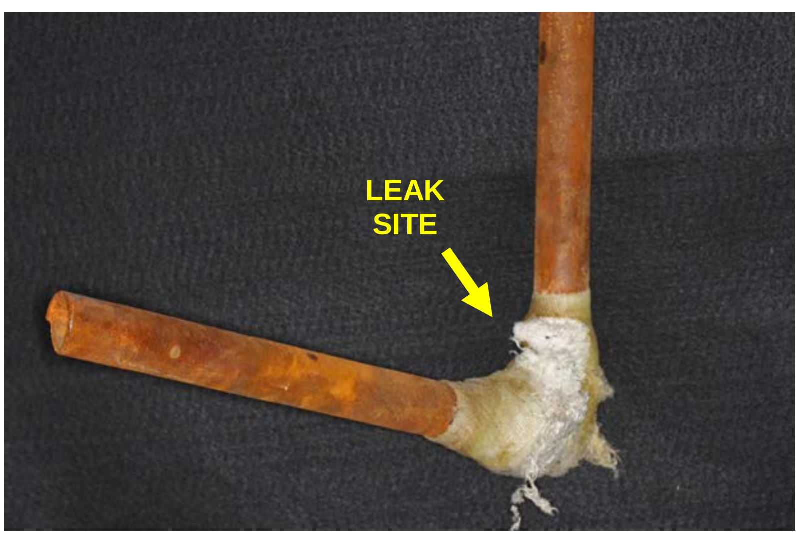

Figure 3. Location of leak in failed section of piping, as-repaired in field

Upon receipt of the submitted section of line at VGO, the pipe wall thickness was measured ultrasonically to assess the extent and pattern of thinning. The entire length of the submitted section of line was thinned. On the three horizontal sections of the line, the thinning was most pronounced on the top of the pipe, while on the vertical section of the line, the thinning was fairly uniform around the full circumference.

Excluding the area immediately surrounding the leak, the minimum thicknesses were generally in the range of 0.060 to 0.080 inch. Although the specified thickness (i.e., Schedule) of the line was not provided to VGO, several locations had thicknesses in the range of 0.130 to 0.137 inch, suggesting that the line was probably Schedule 40 pipe, corresponding to an original wall thickness of 0.133 inch (for a nominal 1-inch diameter pipe).

Figure 4. Leak site after removing fiberglass patch

Upon removing the fiberglass patch and wire brushing the line to remove the less adherent surface deposits, the leak—which was about ¼ inch in diameter--was readily apparent in the pipe wall, just above the elbow (Figures 4 and 5). The pipe wall surrounding the leak was only a few thousandths of an inch thick—so thin that the pipe had buckled, probably when the section of line was being removed from service.

Figure 5. Additional views of elbow and leak after sectioning from line

The elbow material was considerably thicker than the pipe material; however, it too had been subjected to considerable thinning, particularly in the areas next to the welds joining the elbow to the pipe (Figure 6).

In addition to the thinning on the inside of the pipe, the outside of the pipe had been thinned where the pipe was inserted into the elbow. Although the corrosion at these locations may have been influenced by metallurgical changes in the material caused by the heat of welding, the major factor affecting the corrosion at these locations was most likely turbulence induced by the disruption in flow at the pipe-to-elbow joint.

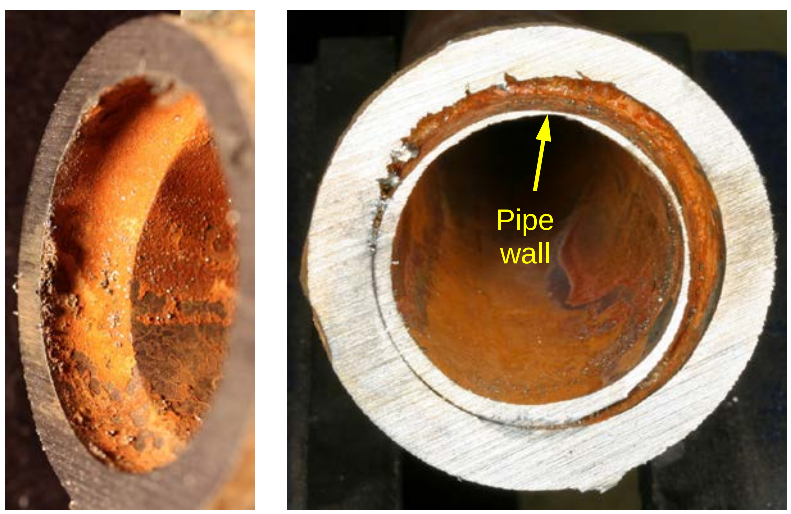

Figure 6. Transverse section thru pipe and elbow at elbow outlet

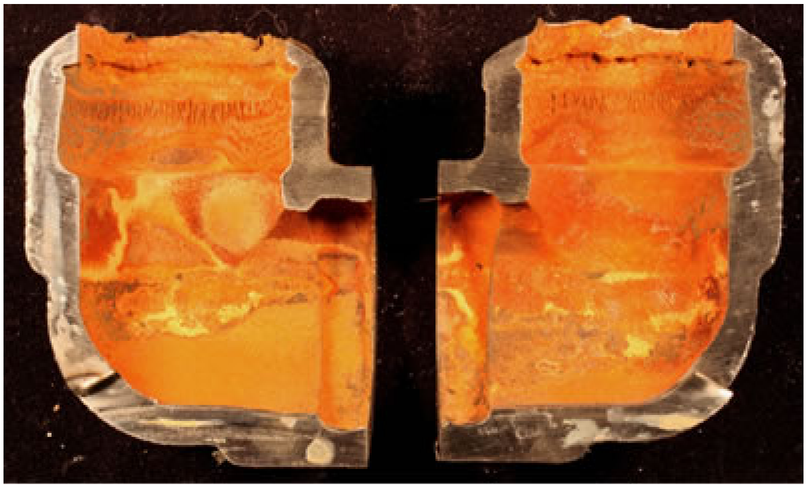

Figure 7. Longitudinal section thru elbow

Figure 8. Close-up view of elbow inlet

Figures 7 and 8 show a close-up view of the inside of the elbow after sectioning it longitudinally. The jagged edge at the top is the remnants of the pipe, which was only paper thin next to the elbow. The pipe wall had been completely consumed by corrosion in the area where it was inserted into the elbow, and the underlying elbow wall had also been thinned. The corrosion in the elbow consisted of a localized circumferential groove and pit-like depressions, caused by flow/turbulence-induced breakdown of the protective iron sulfate film, and sharp, crack-like, longitudinal grooves, likely caused by hydrogen-grooving.

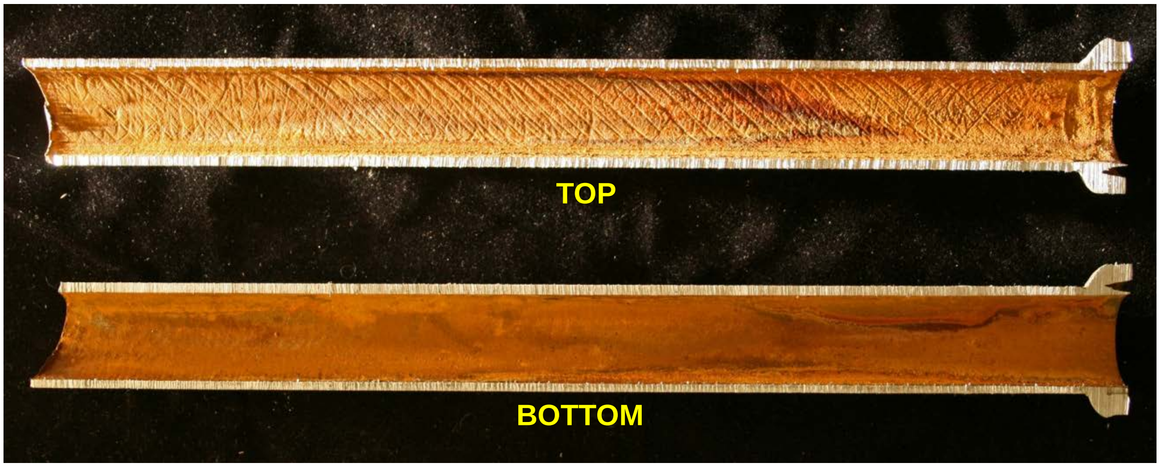

Figure 9. Longitudinal section thru pipe downstream from elbow

Figure 9 shows the inside of the pipe downstream of the elbow after sectioning the pipe longitudinally. The top half of the pipe exhibited a series of curved (helical) grooves, indicative of hydrogen grooving. These grooves are shown at higher magnification in Figures 10 and 11, both before and after cleaning to remove the surface corrosion products.

Figure 10. Close-up view of pipe internal surface before cleaning

The curved grooves are indicative of hydrogen grooving, a corrosion mechanism that occurs in carbon steel pipe in concentrated sulfuric acid service under conditions of intermittent flow. The grooves are caused by the scrubbing action of hydrogen gas bubbles, which form as a reaction byproduct between the acid and the steel and accumulate on the inside surface of the pipe during periods of non-flow. When flow resumes, the bubbles are carried downstream, scrubbing off the fragile, protective iron sulfate film that forms on the surface of the steel and protects it from further corrosion. The underlying steel then re-corrodes, forming a new layer of iron sulfate. Continued repetition of this action results in a series of grooves in the steel.

Figure 11. Close-up view of pipe internal surface after cleaning

In horizontal sections of pipe, the classical pattern of hydrogen grooving is a series of symmetrical, curved grooves in the two upper quadrants of the pipe, all radiating toward a central longitudinal groove at the very top. In the case of this failure, the pattern was somewhat different, consisting of a series of helical—and at some locations, criss-crossed–grooves, without the central longitudinal groove. The pattern was probably the result of a spiral flow pattern in the pipe, induced by the change in flow direction at the elbows.

The grooves were also present in the vertical section of pipe; however, rather than being concentrated in just one or two quadrants, they were present around the entire circumference.

The microstructure of the pipe material was examined in a transverse cross section through the pipe approximately 2 inches upstream from the leak (Figure 12). Although the pipe was slightly thicker at this location than it was at the leak, the pipe wall was still severely thinned, ranging in thickness from 0.020 to 0.050 inch. Further away from the hole, the pipe wall was somewhat thicker, with minimum wall thicknesses generally in the range of 0.060 to 0.080 inch; however, based on its original thickness of 0.133 inch, the thinning in these areas was still about 50 percent of the way through the wall.

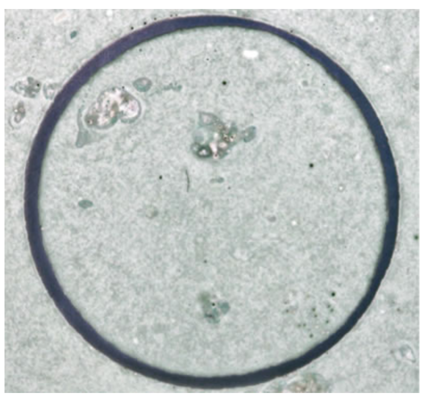

Figure 12. Transverse cross section thru pipe 2 inches upstream from leak

The microstructure was comprised of ferrite and pearlite, which is the expected microstructure for carbon steel pipe in this application (Figure 13). Microhardness of the pipe ranged from 79 to 89 on the Rockwell B scale (HRB), which is within the expected range for piping in this application. No metallurgical defects or other material-related flaws were observed that would be considered contributory to the failure.

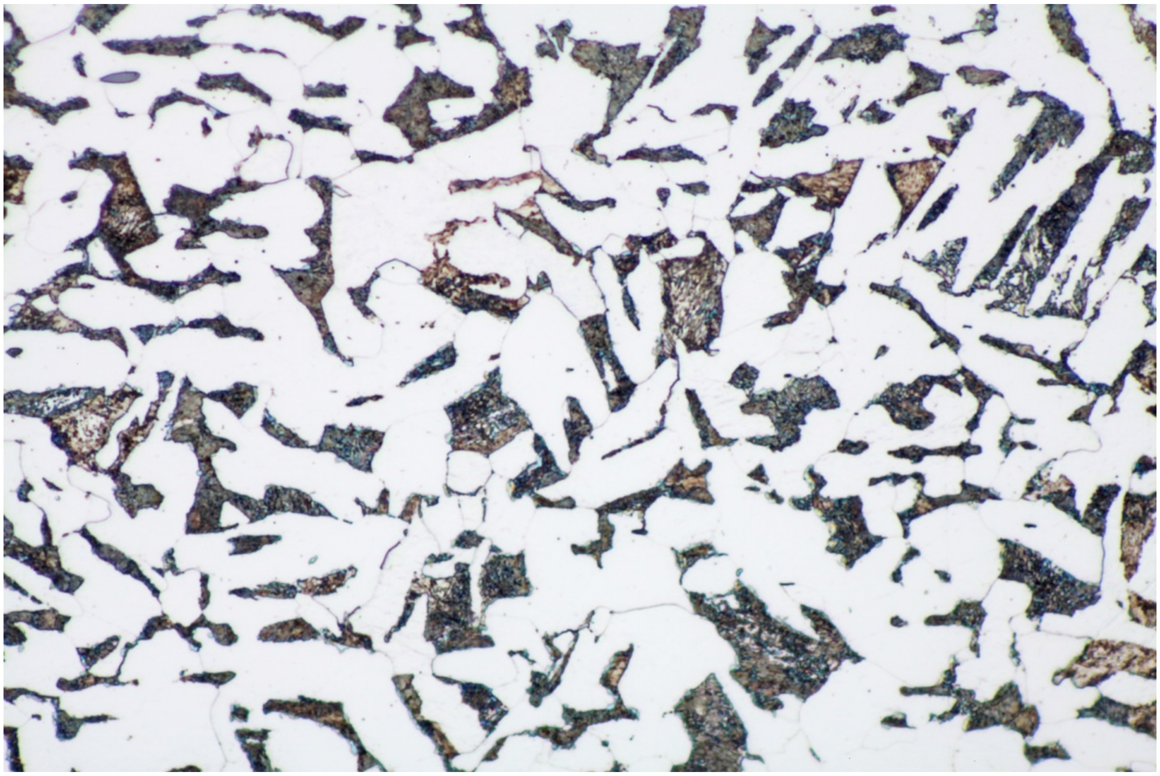

Figure 13. Ferrite (light constituent) and pearlite (dark constituent) pipe microstructure
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