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Your Source for Metallurgical Testing and Failure Analysis

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TESTING CERT #0510-01

MSi Investigative Summary

BACKGROUND

One (1) metal sample removed from a welded stainless steel pressure vessel was submitted to our laboratory for a metallurgical investigation. Reportedly, the ID surface of the sample exhibited a highly localized corrosion attack. It was also reported that the attack occurred in the form of dark, rounded recesses, and that the affected area was covered by an internal structural component. The ID surface of the sample was partially ground and dye-penetrant tested by maintenance personnel.

The service history of the vessel included exposure to caustic slurries, hydrogenated oils, surfactants and chlorides for an estimated period of 15-20 years. In the course of service, the ID of the vessel had been intermittently exposed to temperatures in the 200-300° F range. Our client purchased the vessel used and utilized it in Betaine (cocoamidopropyl dimethylamine) production. No further background information regarding unit construction or maintenance was available. We were requested to determine the mechanism responsible for the apparent corrosion degradation.

SAMPLE IDENTIFICATION

Part Description	Material	No. of Samples
Metal Sample Removed from a Pressure Vessel	Welded Stainless Steel Plate (~1/2"-thick)	1

PERFORMED TESTING

Visual and Stereoscopic Examination
Energy-Dispersive Spectroscopy (EDS)
Metallographic (Microstructural) Examination
Chemical Analysis
Hardness Testing

CONCLUSIONS

1. Based upon the performed tests and examinations, it is our opinion that the failure of the submitted pressure vessel section was caused by a microbiologically-influenced corrosion (MIC) attack followed by a MIC-related stress-corrosion cracking (SCC) attack. The MIC attack was most likely triggered by specific microorganisms, either aerobic (e.g., sulfur-oxidizing bacteria), or anaerobic (e.g., sulfate-reducing bacteria).
2. The bacteria typically grow on assorted organic nutrients, deposited on the ID surface of the components during periods of exposure to a stagnant aqueous environment. The stagnant conditions were most likely produced by the internal structural component covering the affected area. MIC-based attack is known to be highly localized and aggressive, with the adjacent areas being unaffected. Most MIC failures occur within a short period of time.
3. The phenomenon of MIC on metal surfaces can be described as follows:
 - First, the specific microorganisms that are present inside the system attach themselves to the areas coated with organic nutrients (slime, biofilm, etc.) and begin to grow. Microbial growth is most active at temperatures of 20-55°C (68-131°F).
 - Second, the microbial metabolic activity results in the formation of a growing nodule. Nodule growth is promoted by the sticky by-products that capture organic and inorganic substances. The growing nodule forms a concentration cell by setting up electrochemical potential differences between the underlying metal and the adjacent, nodule-free metal. Consequently, the metal below the deposits becomes anodic and dissolves preferentially. Other by-products may contain sulfur-bearing compounds and organic acids, which would contribute to the localized, under-the-nodule metal corrosion.
 - Finally, a combination of the concentration cell mechanism and the biological activity creates assorted pits. Weak organic acid by-products inside these pits can be converted to a strong hydrochloric acid, if chlorides are present in the water. At this point, the bacteria can survive only at the outer surface of the nodule and their contribution diminishes. Corrosion then continues predominantly as an electrochemical process.
 - It should be noted that the pits tend to accumulate and concentrate impurities, including chlorides, even when these impurities are present in very small amounts. If the rising under-the-nodule chloride concentration reaches the critical level, it may trigger a localized stress-corrosion cracking (SCC) attack in susceptible materials. Such highly-localized SCC attack was observed at the bottom of the MIC pits in the submitted sample, with the adjacent areas being unaffected.
4. The phenomenon of stress-corrosion cracking (SCC) occurs in metals when three conditions are met simultaneously. These conditions are: (1) corrosive environment, (2) presence of residual, or service-applied tensile stresses in the metal, and (3) susceptible material. Removal of one of these conditions will prevent SCC from occurring.
5. The described corrosion failure mechanisms were confirmed by SEM/EDS and metallographic examinations. The affected metal exhibited no evidence of pre-existing plate fabrication defects, excessive nonmetallic inclusions, or any other detrimental material conditions that could have contributed to the failures.

CONCLUSIONS (cont.)

6. Chemical testing identified the material of the submitted sample as a 300-series austenitic stainless steel similar to Type 316L, but with a slightly reduced molybdenum content. The slightly lower level of molybdenum was not considered to be a contributing factor to the corrosion attack.
7. Hardness testing results indicated that the sample was supplied in an annealed condition.
8. Once initiated, the MIC-related pitting and SCC will progress, due to the local electrochemical conditions that make the pitted areas anodic in relation to the adjacent, unaffected metal. Remedial maintenance can slow down the metal degradation process, but will not arrest it. To delay similar vessel failures in the future, we respectfully recommend the following measures:
 - Inspect, clean and flush the vessel, to remove any organic and inorganic debris that could stick to the interior vessel surfaces.
 - If practical, drain and dry the interior of the vessel during extensive shutdown periods.
 - Identify and remedy areas where stagnant or low-flow conditions could develop. Stagnation allows debris and corrosion products to settle and attach to the metal, facilitating the formation and stabilization of under-deposit corrosion cells.
 - Assess the feasibility of vessel repairs by removal and replacement of the affected wall sections, or by covering the affected areas with compatible stainless steel sheet and seal-welding the formed patch to the intact metal.

SUMMARY of TEST RESULTS

Visual and Stereoscopic Examination

1. Visual and stereoscopic examination of the submitted vessel sample revealed an isle of pitting on the ID surface, with the pits measuring up to 1/4" wide and up to 1/8" deep (see Photos 1 – 2). The area contained evidence of grinding and dye-penetrant testing.



Photo 1: The vessel sample, as received. The pitted area is encircled by the red line.

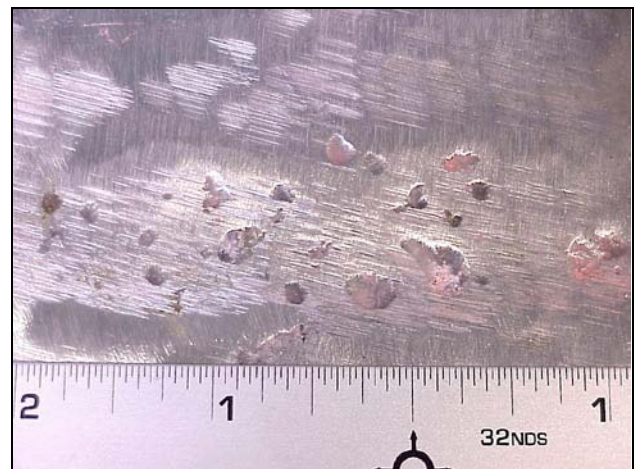


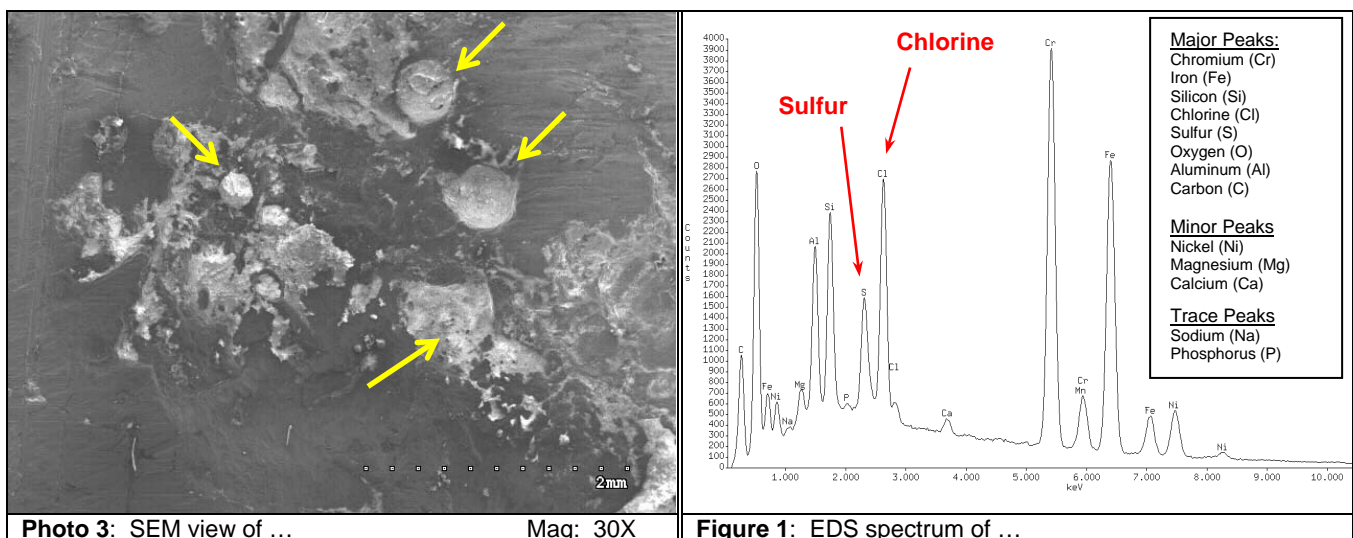
Photo 2: A close-up view of the pitted area.

Visual and Stereoscopic Examination

2. A metal section containing the pits was removed for further examinations described in the following sections of this report.

Scanning Electron Microscopy / Energy Dispersive Spectroscopy

1. The surface grinding and the dye-penetrant testing performed by vessel maintenance personnel on the submitted sample caused removal of some corrosion attack evidence. However, SEM examination revealed remnants of nodular and flat deposit formations at the bottom of the pits (see Photos 3, arrows).
2. An EDS spectrum typical of the deposit formations is shown in Figure 1. Major, minor and trace spectral peaks are identified in the Figure inset. The observed elemental composition identified the deposits as a mix of iron, chromium and nickel oxides with sand and clay dust, some organic substances, and with appreciable amounts of chlorine and sulfur compounds (see arrows on Figure 1).
3. The observed heavy presence of sulfur in the analyzed deposits and the nodular deposit morphology implied that the primary factor responsible for the metal pitting was a MIC attack caused by the metabolic activity of either sulfur-oxidizing or sulfate-reducing bacteria.
4. The presence of chlorine peak implied an advanced stage of MIC and/or heavy extraneous contamination with chlorides.



Metallographic Examination

1. A section across a randomly-selected pit revealed a multitude of branching cracks emanating from the pit bottom into the base metal (see Photo 4).
2. At a higher magnification the cracking exhibited transgranular propagation (see Photo 5). The base metal in the underlying areas showed a uniform equiaxed austenitic microstructure with some twinning, typical of a 300-series stainless steel (see Photo 6).
3. The observed microstructural features are characteristic of a chloride-induced stress-corrosion cracking attack in 300-series stainless steel, and support the results of the preceding visual, stereoscopic and SEM/EDS examinations.

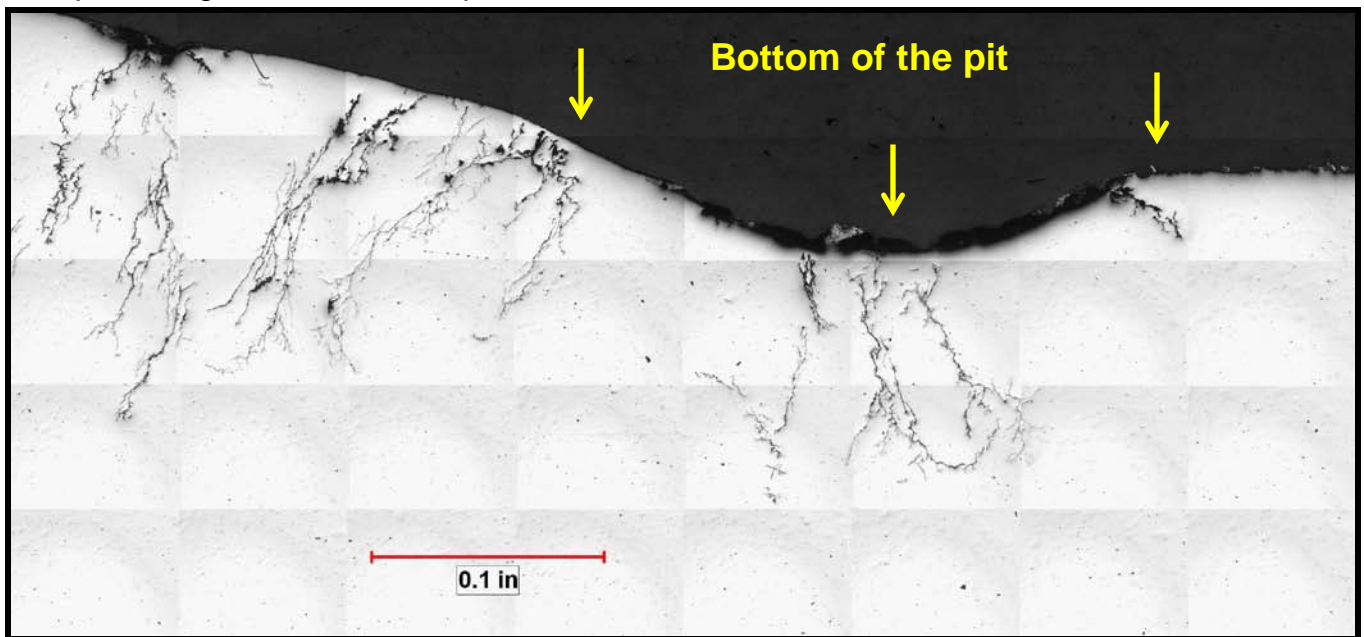


Photo 4: A stitched mosaic image of the pit profile, showing extensive cracking emanating from the bottom.

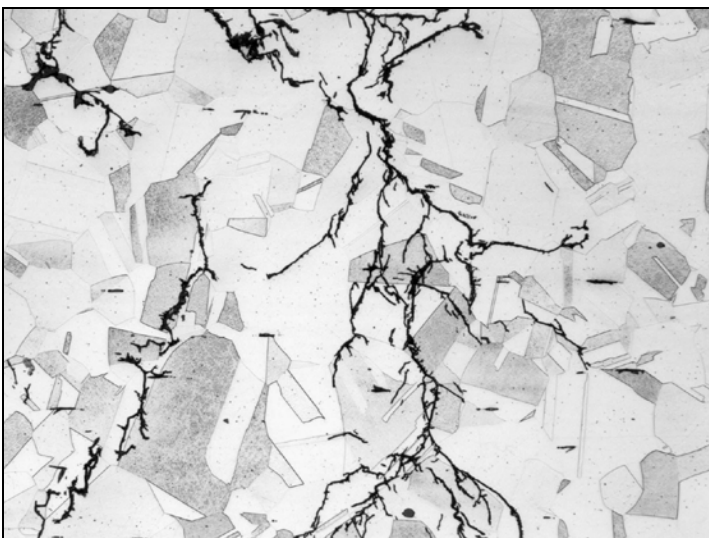


Photo 5: Mag: 100X; Etchant: 10% oxalic acid, electrolytic
Transgranular cracking at the bottom of the pit, viewed at a higher magnification.

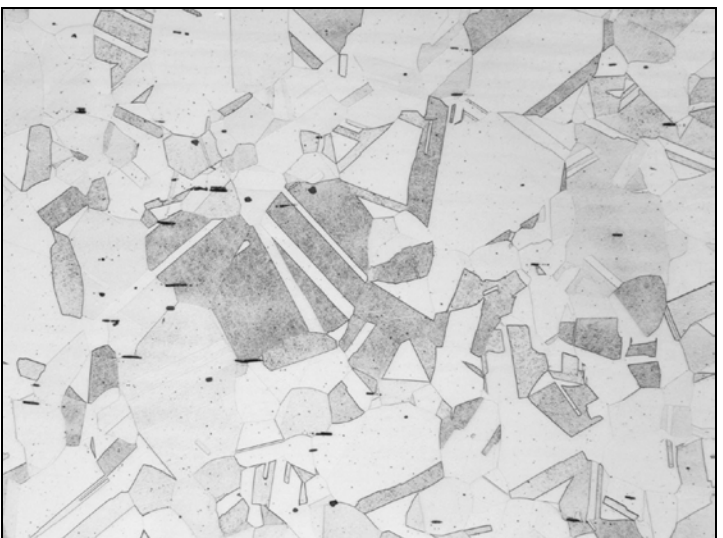


Photo 6: Mag: 100X; Etchant: 10% oxalic acid, electrolytic
A normal austenitic microstructure typical of the base metal.

Report No. [REDACTED]

Chemical Testing

1. Chemical testing identified the material of the submitted sample as a 300-series austenitic stainless steel similar to Type 316L, but with a slightly lower level of molybdenum (.10% Mo below the specified 2.00% Mo min.).
2. The results are shown in Table 1 attached.

Hardness Testing

1. Hardness testing revealed an average value of ~77 HRB, indicative of an annealed condition.
2. The results are shown in Table 2 attached.

Table 1 – Hardness Testing*

Hardness, HRB
77 77 78

* Testing performed in accordance with ASTM E18.

Table 2 – Chemical Testing*

Element	Sample Material
Carbon	.028%
Manganese	1.50
Phosphorus	.020
Sulfur	.016
Silicon	.42
Nickel	12.92
Chromium	17.24
Molybdenum	1.90
Copper	.17
Nitrogen	.03

Report No. [REDACTED]

* Testing performed in accordance with ASTM E1086.