Corrosion failure of stainless-steel in caustic soda lines

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The paper deals with the case studies of stainless steel piping corrosion in caustic soda transfer lines at a hydrocarbon processing plant, in the Asian region. The lines were in service of transferring the caustic soda solution from the storage tank farm to different process units, for subsequent use in reaction vessels. To maintain a minimum temperature of the fluid to avoid its precipitation, the lines were accompanied by a steam heat-tracer, throughout the line route. The material of construction (MOC) of the line was stainless steel type 316. After a period of about 3.5 years, 2" caustic line suffered fluid leakage, which was noticed through significant salt accumulation over insulation at one location. A valve was also noticed to leak through a weld at a 1.5" distribution line. The affected components were removed from service and subjected to detailed inspection and laboratory investigation, using advanced tools of metallurgical analysis and characterization. It was found that leakage in 2" line had occurred due to poor workmanship used during the repair of a manufacturing defect at the affected location and leakage of the valve had taken place due to the use of improper welding practice (in the case of subjected weld). In addition, the significant role of metallurgical defects in the parent metal was also disclosed to result in the observed failures. In addition, the contribution of process excursions can't be completely ruled out. Finally, remedial measures are given to avoid the recurrence of such failure.

INTRODUCTION

Sodium hydroxide (NaOH), commonly known as caustic soda, finds diversified applications in various industries and public operations. A few of these include chemical manufacturing; pulp and paper mills; soaps and detergents; cleaning and bleaching agents; oil and gas industry; petroleum refinery; cellulose and textile plants; alumina production; water and waste-water treatment (at a municipal or industrial facility); food and pharmaceutical products; etc. It is preferred over other alkalies due to its strong basicity and relatively ease of handling and storage particularly when used for pH control, neutralization of waste acids, scrubbing of off-gases, catalysis, alkaline extraction, etc. Sodium hydroxide is categorized as a highly toxic (strong irritant to the eyes, skin, and mucous membranes) and corrosive agent. The word 'corrosive' herein considers physiological harms to the living being as well as degradation to the construction materials.

Basic engineering materials used to handle caustic soda generally include black iron, carbon steel, stainless steels, nickel and nickel alloys, certain types of plastics and composites (polyethylene, polyvinyl chloride, fiber reinforced plastic, etc.), etc. with the domination of mild steel at low-to-moderate temperatures [1,2,3]. At elevated temperatures; however, steels are prone to corrosion attacks typically noticeable above 79 °C in concentrated caustic solution [4]. In addition, stress corrosion cracking (known as caustic embrittlement) may encounter with these materials in stress containing components such as weldments if used without stress-relieving treatment (called 'post weld heat treatment' or PWHT), even at 50-100 ppm salt content [5, 6]. Hence, material selection for caustic soda service is driven by many factors such as solution concentration, operating temperature and pressure, presence of other corrosion species in fluid, contamination tolerance, type of equipment or component, location criticality, design life, construction facility limitations, cost and safety considerations, etc.

Since the present study pertains to the corrosion failure of piping items in caustic soda transfer service at a hydrocarbon processing plant, further discussion will focus mainly on the material and corrosion aspects of the respective components. The most common material of construction for piping, used by different industries, is generally limited to black iron and carbon steel (bare or coated or lined with non-metallic materials), austenitic stainless steels and a few polymerics, because of their ease of availability, low-to-moderate cost, established construction method and maintainability, etc. However, no material is found to be completely safe and trouble-free as each one is reported elsewhere [3, 7-13] to face a unique type of damage or failure in the real service. At the facility of current concern, austenitic stainless steel was used for constructing the caustic piping system and; hence, the same material will only be dealt in the forward discussion.

PROBLEM BACKGROUND

The line under the subject was in service of transferring hot caustic soda from the utility tank farm to different process units of the plant, for subsequent applications such as chemical treatment. The details of failed components are outlined below:

The primary line was of 2” size which ran over 600-700 m in length of the plant area; while the secondary lines were of 1.5” size with about 10-15 m in length. The latter ones are used to distribute caustic soda to different equipment in a particular process unit. The construction material of piping was SS316 (austenitic stainless steel type 316) for both size. The primary line is always filled with caustic soda solution of about 50% concentration and kept warm (@about ~50 °C temperature) with the help of a steam-tracing line, installed in-parallel throughout the line route, to avoid inside salt precipitation as the solution is in mostly in “no-flow” condition (operates periodically). The occurrence of corrosion leakage started within about 3.5 years of service installation of the line, against the intended life of 25 years. A few damaged pipe sections as well as a 45° elbow, were cut/ removed from the line and subjected to detailed investigation in a well-equipped laboratory, to explore the cause of trouble as well as to recommend appropriate remedial measures.

INVESTIGATION

Diagnostic investigation methodology involved a review of design, construction, operation and maintenance records of the caustic soda handling circuit; visual and aided inspection of failed parts at both surfaces (inner as well as outer); wall-thickness check including near leakage points; characterization and analysis of the damaged material, surfaces and deposits using optical and scanning electron microscope (SEM) with EDS tool; etc., and outcomes are described in the following paragraphs.

Case-1: 2” Primary line

The photograph in Figure 1 shows the affected portion of 2” primary line after the removal of the insulation. It is clear from the picture that corrosion occurred at one location in the straight section of the line resulting in a big hole. The latter facilitated leakage of fluid during running plant and was primarily discovered through the salt accumulated over insulated line, at the affected location. For internal inspection, the damaged spool was longitudinally cut into two pieces (bifurcated). Consequently, the whole inner surface of the pipe was found to be suffered from general caustic corrosion to a measurable extent, including the hole bearing site as shown in the photograph (Fig. 2). In order to identify the probable causes of the problem, many relevant aspects (suspected to contribute to the resultant corrosion) will now be reviewed and evaluated in the following paragraphs.

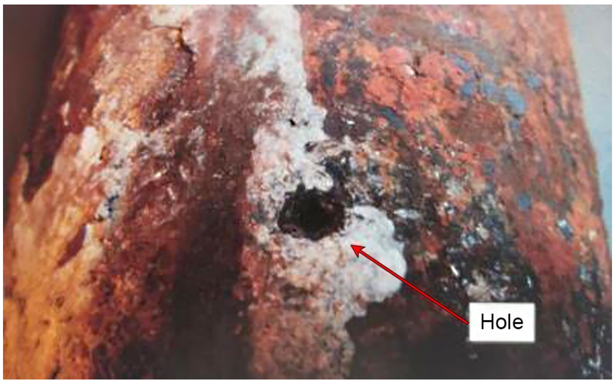


Fig. 1. Outer surface of the line with perforation and salt accumulated at leakage point

Firstly, the pipe’s material of construction was checked for metallurgical conformance. The primary SEM (with EDS) analysis indicated compliance of bulk material to SS316 requirements with respect to constituent elements, thus in line with the designed material and shown in Table 1. Product-wise, the pipe is manufactured with the seamless extrusion process which is confirmed by the absence of any seam weld, noticed during visual and aided inspection of the test spool. However, microscopic analysis made at the cross-section of the hole location revealed the existence of a certain spot weld as shown in the photograph (Figs. 3 and 4). To ensure the source of the spot weld, maintenance and inspection record of the line were thoroughly checked, and found that no any repair activity was performed on it during the service period. Hence, it is anticipated that an attempt was made during either manufacturing or construction to plug a hole (at a defective site) on

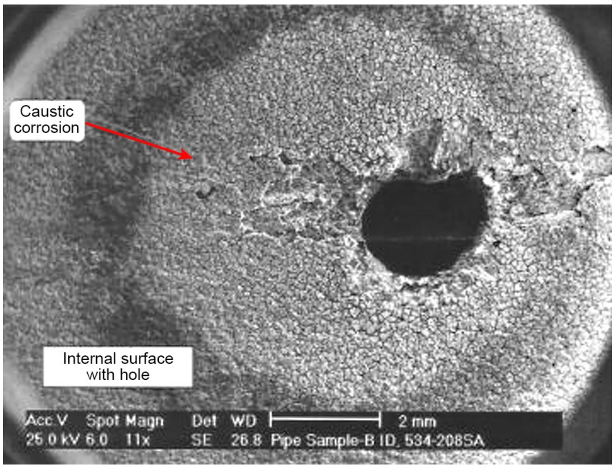


Fig. 2. Caustic corrosion throughout the inner surface of the line including the perforation site

the pipe using spot welding. However, this plug weld is found at and adjacent to the outer dia of the pipe only, without through thickness penetration (up to the inner dia), thereby leaving a cavity at the inner pipe surface. The same defect could also have become a hot spot for fast propagation of the localized corrosion (and complete wall perforation) originated by the general caustic attack occurring at the whole pipe (inner diameter). Besides, the rate of general corrosion noticed in the present case is around 1 mpy which is also higher side of the values indicated in isocorrosion chart [14] for SS316 in caustic soda solutions. The measured depth of attack varies from 0.06 mm to about 0.1 mm at the inner diameter of the pipe. Thus, it became essential to find out the source of enhanced general corrosion as well, in the current material environment system. To start with, confirmation of the metallurgical integrity of the construction material, using a detailed micro-analytical characterization technique, was carried out on a pipe sample. Cross-sectional analysis of the corroded surface disclosed a number of inclusion defects in the body of bulk material as shown in a typical photograph (Fig. 4) containing oxygen, magnesium, aluminium, silicon, sulfur, calcium, etc. Here, one should note that the reaction of hydroxyl ions (the main ingredient of caustic soda) with aluminium, magnesium and silicon (present in the inclusions) could have accelerated the corrosion at the inner dia of the pipe. Moreover, the temperature of fluid was also recorded to exceed by about 30 °C then the allowable operating limit which could also have contributed to the obtained high value of corrosion-rate (like many other cases) but only to a small extent (as per referred isocorrosion chart) as a significant increase in corrosion is expected around 100 °C temperature in 50% caustic solution. Still, some refereed literature [15] has indicated that there is a real possibility that type 300 series SS may undergo rapid general corrosion in hot 40% to 50% caustic than indicated in isocorrosion diagrams.

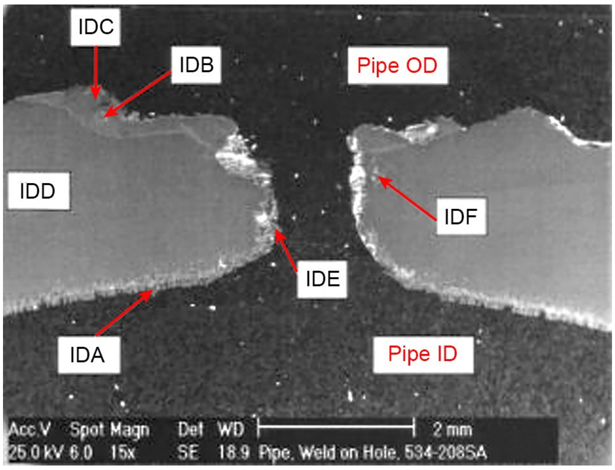
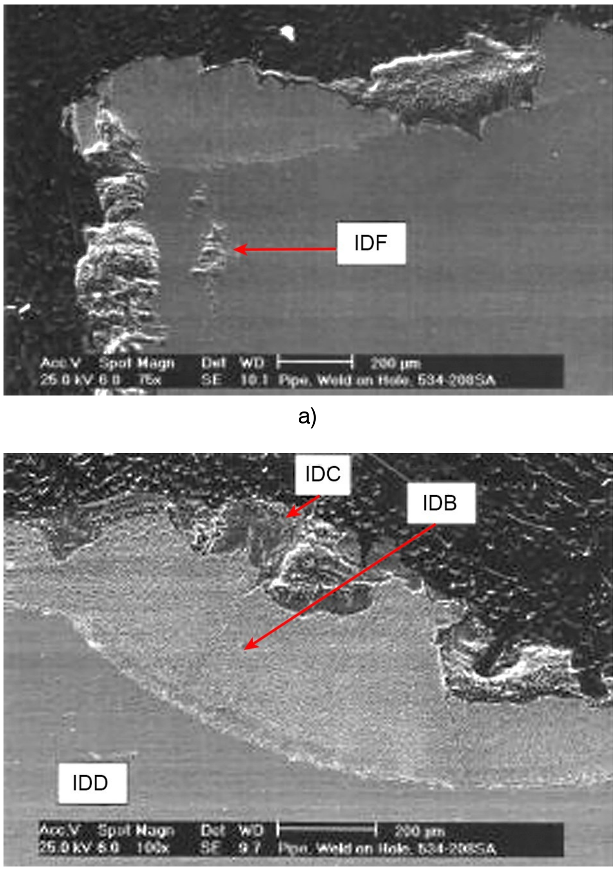


Fig. 3. Microscopic analysis made at the cross section of the hole location revealing the existence of certain spot-weld at and near the outer surface



b)

Fig. 4. Cross-sectional magnified view of the perforated location showing: a) inclusions in the body, b) spot weld at the outer surface

Tab. 1 Data of EDS analysis at different points on wall cross-section at the leakage location

wt.%	Area	C	O	Si	Cr	Fe	Ni	Mo	Ca
Parent metal	IDD	–	–	–	17.37	69.59	11.01	2.02	–
Weld	IDB	–	–	0.89	17.88	67.38	11.26	2.59	–
Zones	IDA	11.73	13.81	0.94	3.17	17.45	52.10	–	0.80
	IDE	16.26	14.42	0.79	4.37	26.05	38.11	–	–
	IDF	4.91	20.05	0.50	5.23	36.87	32.45	–	–
	IDC	11.91	17.63	–	0.73	48.73	21.01	–	–

The safe limits indicated are 70 °C for 50% caustic and 80 °C for 40% solution. Thus, numerous inclusion defects in the parent material as well as periodic excursions in the process and operating condition of the fluid (than the permitted limits), could have jointly promoted the overall corrosion of the caustic line, with domination of the former aspect over the latter ones. For the leakage; however, poor workmanship adopted during plugging (by spot welding) of a hole in the pipe wall (attributed to a manufacturing defect) might be considered as the main culprit though metallurgy of the weld-electrode was noticed sound.

Case-2: 1.5" Elbow in secondary line

The picture of the damaged elbow is shown in Figure 5. In this case, leakage took place at one side weld of the elbow (made to join it with the upstream pipe) while the other one (downstream side weld) was found okay. On axial cutting of the elbow with the intent of internal inspection, the entire root of the affected (circumferential) weld was found to be eaten-away to a measurable extent, though the weld cap was noticed still intact (except wall perforated sites) as shown in Figures 6 and 7. Also, whole inner surface of the elbow is found to be attacked by general caustic corrosion causing a loss of about 3% in wall-thickness (amounting to 0.09 mm) within a short period of about 3 years. Corrosion sectional microscopy of the affected (inner) thickness evidently revealed corrosion stringers scattered even into the depth of the metal wall, as shown in Figure 8. Moreover, stress corrosion cracking (SCC) is also noticed on the inner dia of the elbow (as well as attached pipes) as shown in Figures 9 and 10 with a crack-depth of about 1 mm. The cracks are noticed to be of transgranular type. The occurrence of SCC in the current material environment system has become a matter of serious concern. The intensity of cracking was most severe in high stress portion (bend) of the elbow. From Figure 9, it may further be noticed that a few long stringer-like corrosion zones cross the stress corrosion cracks. Forthcoming paragraph will deal with the probable causes of experienced corrosion damages as well as associated mechanisms, based on the results of different evaluations, analyses and characterization.

The degree of general corrosion attack (on the elbow's whole inner surface) is considered to be higher than the values indicated in the literature for the current

Fig. 5. Failed elbow showing poor welding at one side (left) weld joint

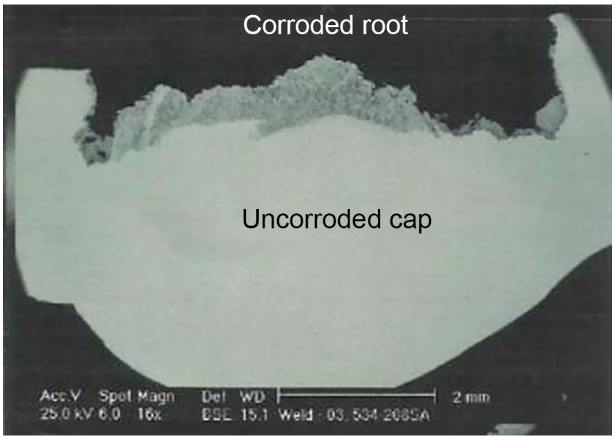


Fig. 7. Cross sectional microphotograph of the corroded weld route in case of one side (MMA) weld of the elbow

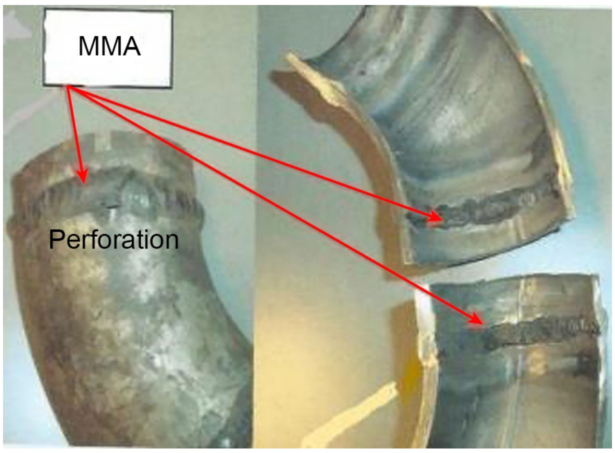


Fig. 6. Poor welding resulted in dissolution/corrosion of weld-root at one side (MMA) weld of the elbow

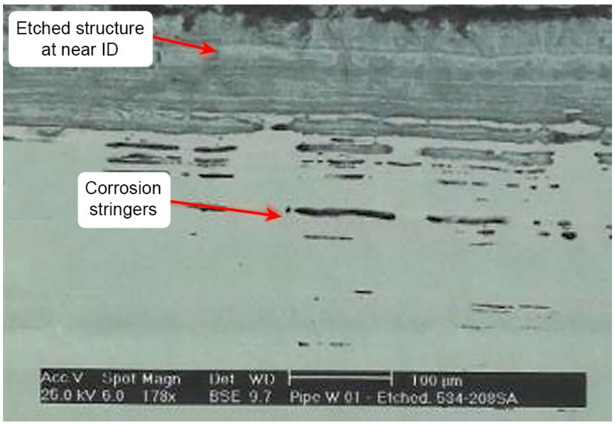


Fig. 8. Corrosion sectional microphotograph of the codded surface and bulk material of elbow, showing corrosion stringers

material-environment combination. Since this observation is the same as experienced in the previous case study, there is no need for further discussion on this mode of corrosion damage as its occurrence and mechanism can be understood in the same way as explained earlier. To explore the cause of preferential corrosion at the root of one side weld, the engineering and construction of the piping were re-visited. As per the approved WPS (weld procedure specification), tungsten inert gas (TIG) welding should have been employed in the current job. However, the use of manual metal arc (MMA) welding is suspected in the case of the corroded weld. While, the other side weld (root) appears to be done by a standard (approved) process and, therefore, its root is found in sound condition. Besides, TIG welding activities appear to be carried out in the shop, while MMA one at the site without proper precautions of contamination and control of weld processes. Further, chemical analysis of the damaged weld showed only 8% chromium and 5% nickel which are below the SS316 weldment requirement. This creates doubt on the use of proper weld consumables as it doesn't conform to the specifications of TIG or MMA weld electrodes for the subjected material. The low content of principal alloying elements could have reduced the overall corrosion resistance of weldment thus making it susceptible to general caustic corrosion. Also, the chemistry of weldment would have facilitated its anodic dissolution and cathodic protection of adjoining elbow and piping material. Besides, the area ratio of small anode to large cathode would have further accelerated the corrosion attack of the weld root than it would have naturally corroded in the caustic solution. Moreover, high carbon peeks were additionally noticed in the SEM (EDS) analysis of corroded weld which is a clear indication of the presence of certain carbonaceous material (such as grease) during the execution of the welding operation at the site. In short, poor workmanship adopted during welding work may be attributed to result in the failure of this weldment. In the case of sound weld; however, weldment composition conformed to the requirement of SS316 consumables (AWS 5.9 Class ER316). Here, it is worth clarifying that the chemical composition of parent (elbow) material also met the standard requirement of SS316 with respect to constituent elements. Now, some light will be thrown on the third mode of corrosion damage experienced by the elbow, i. e., the SCC. From cross sectional microscopy (shown in Fig. 8), it may be noticed that the cracks are dominantly of transgranular type, thus might be caused by caustic stress corrosion cracking (CSCC). Though chloride SCC (Cl-SCC) can also result in similar cracks, but chlorides contamination is not detected during caustic's chemical analysis. Besides, chloride cracks normally have the appearance of more branches and secondary cracks than those seen in the microphotographs of the affected section. Some of the literature [15] indicates that chlorides, a common contaminant in concentrated caustic, do not aggravate SCC and may even play an inhibitive role. Hence, the role of Cl-SCC may be eliminated in the occurrence of current cracking failure. Further, dissolved oxygen may also promote the degree of SCC in some cases but fluid in lines under the subject is mostly in a stagnant state with minimal turbulence. Besides, the solubility of oxygen will be questionable at prevailing temperatures and caustic concentrations. Thus, a possible contribution of oxygen in the initiation and propagation of SCC in the present case may also be ruled out. Now, certain impurities elements like aluminium and magnesium present in elbow material (found as inclusion in the elbow material) may react with caustic at the prevalent service conditions to form

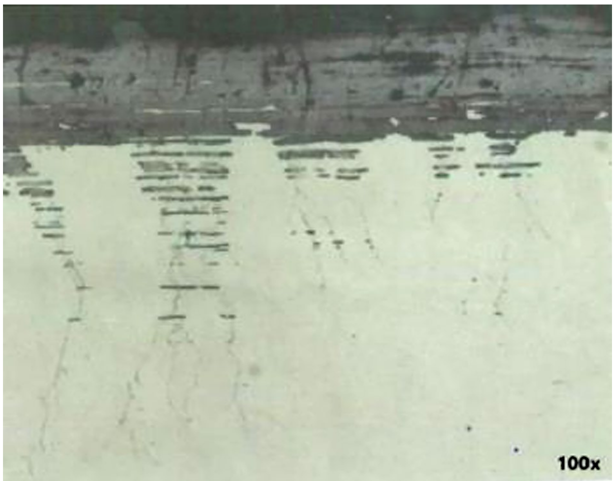


Fig. 9. Light gyliceregia etched structure revealing inclusion's dissolution at the crack-path interface. A few inclusion at cracks/inclusion-intersections were dissolved by hydroxyl ions

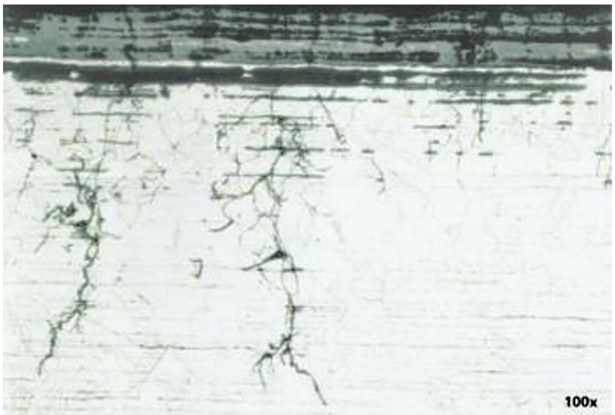


Fig. 10. Corrosion sectional microphotograph of the codded surface andStress corrosion cracking (dominantly transgranular- with a few intergranular cracks). About 1 mm deep cracks are noticed within 2 cm on both sides of the root weld (MMA) and originated at the ID of the elbow. General caustic corrosion is also evident on the inner surface as well as sub-surface metal

metal hydroxides and possibly generate some hydrogen gas. Thus, there is a remote possibility of intergranular corrosion cracks (noticed at a few locations) which might be a result of hydrogen embrittlement; however, SCC cracks are dominantly of transgranular nature. The best explanation for the long stringer-like corrosion zones that cross the stress corrosion cracks is the transport of hydroxyl ions down to crack and followed by their reaction with inclusion elements (Fig. 9). Finally, it may be concluded that observed SCC is dominantly a case of CSCC. Here, it is very important to note that SS316 is not prone to CSCC at the designed conditions and such damage is expected only above 100 °C (even above 120 °C as per certain industry's experiences). Hence, the cause of CSCC in the current scenario may be attributed to poor metallurgy of elbow material as well as periodic excursions in process/operating conditions.

CONCLUSIONS AND RECOMMENDATIONS

- Leakage in 2" primary line has occurred due to poor metallurgy of the construction material as well as improper practice used to repair a manufacturing defect (external plug-welding of a revealed pit/ pinhole without full wall penetration, leaving a cavity at the inner dia. of pipe). The material contained numerous stringer-like bands of inclusions bearing elements of high reactivity to hydroxide (caustic soda). There may be a limited contribution of unfavourable service conditions (encountered periodically) also. To avoid current failure, complete piping should be replaced with a new one having no metallurgical- and manufacturing- defects. There is no need to upgrade the material of construction at this stage.
- Leakage of one side weld at 1.5" elbow is diagnosed to have taken place due to poor workmanship (including method, cleanliness and consumables) adopted during its welding with the adjacent pipes resulting in localized dissolution (corrosion) of the weld root. Other types of corrosion can be attributed to poor metallurgy of the construction material and intermittent excursions in process/ operating conditions. Besides, elbows are the area SCC prone components of piping due to the containment of bending stresses, in the normal course. To get rid of all these problems, the following precautions are recommended:

a) Ensure proper metallurgy of the elbow material.

b) During a welding activity, approved weld procedure specification (WPS) shall be fully complied. Besides, special attention shall be given to using an appropriate weld consumable as well as avoiding any source of contamination.

c) Process and operating conditions shall be closely monitored to avoid chemical and temperature excursions, as these may exponentially aggravate the corrosivity of fluid.

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