# A Case Study on Caustic Corrosion in Refinery Piping

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*Abstract*— **Caustic soda is received from supplier with concentration about 48% and stored at main storage tank and transferred intermittently to the refinery process unit's neutralization tanks at same concentration. Dilution is taking place at these tanks. In order to prevent caustic soda from freezing and /or crystallization (winterization) in intermittent transferring piping, it was kept warm by means of steam tracing and insulation together.**

**Failure of carbon steel piping by caustic stress corrosion cracking (embrittlement) and caustic gouging has been a recurring problem, several repairs attempts were made without success using patch plates and/or temporary clamps. Some parts were totally replaced with schedule 80 piping but suffer failures within 12 months.**

**Close observation of the corroded locations reveals severe grooving along the length of pipe at 3 & 9 o'clock positions where steam tracing line is touching the pipes due to braking of fixation clamps.**

**Several measures were recommended, these include avoidance of hot spots by steam tracing; avoidance of temperature increase during idle condition and redesigning the distribution piping in order to transfer caustic solution with concentration not more than (33%).**

*Index Terms:* **Caustic soda, gouging, embrittlement, steam tracing, Umm Alnar Refinery**

## I. INTRODUCTION

Some process units utilize caustic solutions for neutralizing or removal of sulfur compounds. The liquid sodium hydroxide freezing point varies depending on the concentration. A 50% by weight solution of sodium hydroxide begins to congeal and crystalize at temperatures as high as 10 – 12°C, so it should be stored above 15.5°C [1]. Stagnant diluted caustic solution may become highly concentrated if water is allowed to evaporate, especially near hot surfaces, and in dead legs. This is particularly true when using heat traced piping, and if handling system is only used intermittently. Steam tracing and insulation were used together to keep the transfer piping in a warm condition and prevent caustic soda from freezing. Steam traced piping prevented from touching the caustic piping by applying ceramic spacers. When the spacers fall down /slip out during assembly and by means of expansion and contraction during operation the bare tracer will gets pressed against the pipe causing direct wall-to-wall contact and hot spots with steam tracing.

Carbon steel finds extensive application primarily because of its low cost, reasonably good mechanical properties, and ease of fabrication [2]. Despite its limited corrosion resistance; it is routinely used for most organic chemicals and neutral or basic aqueous solutions at moderate temperatures and frequently used in services with added thickness to assure the achievement of desired service life [3].

Exposure to high solution strength caustic can result in general corrosion of carbon steel above 79$^{o}$C and very high corrosion rates above 93$^{o}$C [4]. Caustic corrosion can occur when the pH is raised excessively on a localized scale, where the protective oxides are no longer stable. Such undesirable pH excursions tend to occur in high temperature zones, where boiling has led to a localized caustic concentration [5]. The gouging is a type of corrosion that occurs on a metallic surface in which a hole, groove or indentation is created and results in irregular wall thinning, the corrosion can proceed to failure in a very short time. It is found under deposits in heat exchangers, results from concentrated caustic left behind after boiler water permeates the deposits and evaporates [6].

Additionally, caustic can cause caustic embrittlement of non-post weld heat treated carbon steel and of austenitic alloys including stainless steels and nickel alloys [7]. It is a form of stress corrosion cracking characterized by surface-initiated cracks that propagate dramatically. Cracking can occur even at low caustic levels if a concentrating mechanism is present. In such cases, caustic concentrations of 50 to 100 ppm are sufficient to cause cracking [4].

Early cases of CSCC in CS were associated with riveted steam boilers, where cracks started in metal that was highly stressed in tension. The majority of more recent industry cases are associated with non-stress-relieved welds, typically in the heat-affected zone (HAZ) and adjacent base metal. Although rare, cracking can also occur away from welds if high tensile stresses are present [8]. Austenitic stainless steels may resist CSCC up to 93°C whereas at higher temperatures Nickel base alloys will be recommended.

The so-called NACE caustic soda service chart explained corrosion resistance of carbon steel, stainless steel and nickel alloys in caustic solutions with respect to

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CSCC, based on temperature and concentration caustic [9].

This paper intends to review process parameters, inspection findings and failure histories experienced in caustic piping of Um Al-Nar refinery in Abu Dhabi, and find possible causes of the failure and recommend remedial measures to avoid reoccurrences in future.

## II. BACKGROUND

Caustic soda is received from supplier with concentration about 48% & Chloride content of 125 PPM and stored at main storage tank (4008F) in unit 40 and transferred intermittently to refinery process units neutralization tanks (1103-L, 1358L, 1501L &2011F) at same concentration. Refer to figure 1 and table 1, dilution is taking place at these tanks as per end user requirement.

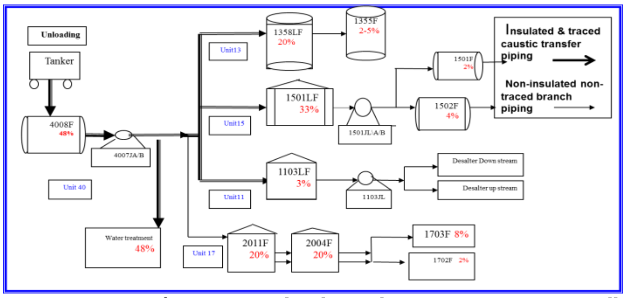


Figure1. Layout of Existing Feed and Distribution Caustic Piping to All Refinery Units

Table 1. Refinery UNIT'S Daily Caustic Consumption

| Unit | Concentration level | Design consumption L/D | Periods of caustic transfer |
|---|---|---|---|
| Unit11 | 3% | 3600 | Once in 15 days |
| Unit 13 | 20% | 240 | Once per shift |
| Unit 15 | 30% | 1200 | Once in 15 days |
| Unit 17 | 3% | 1754 | Once in 5 days |
| Unit 17 | 10% | 3571 | Once in 5 days |
| Unit 40 | 48% | 434 | Once in 3 days |

Caustic leakage due to failure of carbon steel piping by caustic corrosion has been a recurring problem in refinery caustic transfer and distribution piping with different sizes (¾"- 4"). Several repairs attempts were made without success using batch plates and/or temporary clamps. Some parts were totally replaced with schedule 80 piping but suffer failures within 12 months.

Subsequent detailed visual inspection revealed that failures of caustic piping took the form of caustic gouging and caustic stress corrosion cracking CSCC (caustic embrittlement), as illustrated in figures 2a&b. The affected area were mainly elbows, weld joints and heat affected zones (HAZ). The severe corrosion concentrates at 3 & 9 o'clock positions, it is more severe at 3 o clock position where steam tracing line is touching compared with 9 o'clock position, particularly where fixation clamps (spacers) were broken. Non-frequent failures were also noticed in non-insulated and none traced pipes.

Pipe skin temperature is measured at some locations and found approx. = 55 °C on 2" caustic pipe and 87°C on 1/2" steam tracing piping. Steam tracing was found online even without caustic transfer (intermittent).

Figure 2a. Caustic Gouging

Figure 2b. Caustic Embrittlement (CSCC)

## III. DISCUSSION

As per caustic service chart in Figure 3, Caustic solutions can be handled and stored safely with carbon steel equipment at temperature approximately 65$^{o}$C However, for caustic service above 65°C, carbon steel must be post weld heat treated to avoid CSCC at welds and properly fitted none metallic spacers or better using pre-insulated tracer, that will eliminate hot spots since tubing is continually isolated along its length.

During summer days metallic piping temperature can sometimes exceed 70°C, due to solar energy, particularly if the system is stagnant with steam tracing, the temperature will go higher and caustic corrosion/cracking can be expected. In order to prevent increasing caustic concentration by higher temperature, it has been warned against leaving even lower concentrations of caustic solutions in heat traced piping during intermittent injection. This can be achieved by water flushing the system after every use using preferably steam condensate water. As per proposed new dilution skid at unit 40, figure 4, the transfer of high concentrated caustic for long distance will be eliminated and this in turn will avoid material degradation and personnel injury.

The lowest recorded refinery climate temperature in winter at night time was around 6°C and freezing temperature of liquid 50% caustic is around 10 – 12°C

[1], therefore insulation alone can be fair enough to maintain a minimum of 16°C temperature without crystallization.

## IV. CONCLUSION AND RECOMMENDATIONS

- ✓ The failure of carbon steel piping is most likely to be due to caustic cracking and caustic gouging at weld joints, elbows and supports.
- ✓ Since the caustic is transferred intermittently from utility storage to other units dilution skids, where the piping is left idle with local temperature increase by steam tracing. This may in turn concentrate the left caustic and accelerate attack especially in summer time.
- ✓ Carbon steel can be still used in distribution piping to handle caustic solutions with concentrations below 35% and at temperature up to 75$^o$C with proper stress relieving and properly fixed non-metallic spacers or better using pre-insulated tracer.
- ✓ To avoid caustic stagnation condition during idle times it might be advisable to water flush the transfer lines after every use using preferably steam condensate water and by implementing the modification of proposed dilution pit at unit 40.
- ✓ Steam tracing maybe avoided in concentrated caustic supply piping, since insulation alone can maintain a minimum of 16°C temperature without crystallization.

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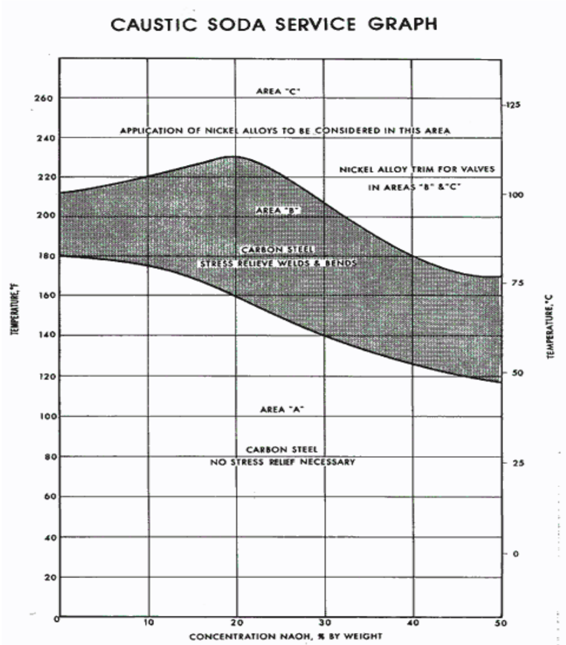


Figure 3. NACE Caustic Soda Service Chart [9].

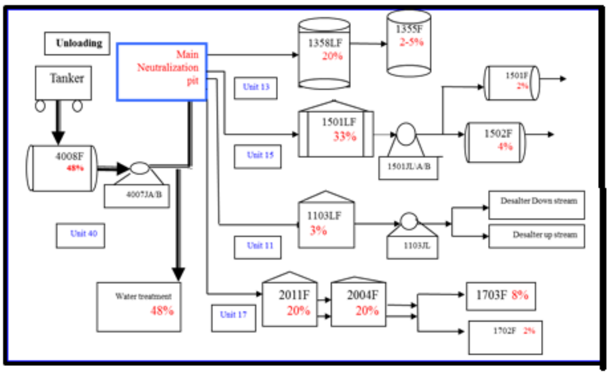


Figure 4. Layout of Modified Feed and Distribution Caustic Piping to All Refinery Units

## BIOGRAPHIES

**Salem Ali Karrab** was born in Misurata. Libya in 1963. He received the BSc degree in Metallurgical engineering from University of Tripoli, in 1987, and the MSc. Degree in corrosion engineering from University of Manchester "UMIST" in 1998 and PhD degree in corrosion engineering from University of Assiut, Egypt in 2013. He also holds International Diploma in Safety Management from British Safety Council in 2000. He has 17 years experience in inspection and corrosion in refinery and petrochemical industries with RASCO and ADNOC. He is currently a lecturer in Materials Science at Misurata University since 2006. His main areas of research interests include failure analysis, corrosion & control, surface engineering and industrial safety and environmental protection.