1st International Conference on Structural Integrity

Under-Degposit Caustic Corrosion on Sodium Carbonate Pipeline

Hussain H. Almahamedh*

SABIC, Jubail, 3196, Kingdom of Saudi Arabia

Abstract

Under deposit corrosion (UDC) is defined as a localized corrosion that develop beneath or around deposit on a metal surface. UDC represents an important threat in the integrity matrix of petroleum and petrochemical production and transportation facilities, and has been cited as responsible for high corrosion rates and loss of containment during operations. For a sodium carbonate production process, crude caustic from the caustic plant enters the sodium carbonate storage tanks. When the batch cycle begins, crude caustic is pumped to the top of the carbonation tower. The caustic stream flows down through two packed sections where it contacts boiler’s stack flue gas rising up through the tower. The caustic (sodium hydroxide) reacts with the carbon dioxide in the flue gas to form sodium carbonate. A carbon steel pipeline then transports sodium carbonate. This carbon steel pipeline experiences frequent leaks. An investigation was conducted to identify the types and possible causes of the corrosion on the sodium carbonate pipeline. XRF (X-Ray Fluorescence Spectrometry) and carbon/sulfur analyzer and XRD were used to chemically identify the deposited materials in the pipeline and to study the damage morphology. It was concluded the failure of the pipeline is attributed to caustic corrosion aggravated by deposited of process carry-over materials.

1. Introduction

The Caustic Carbonation System converts crude caustic (Sodium Hydroxide) from the caustic plant to sodium carbonate. The sodium carbonate, in turn, is used to purify raw brine.

Crude caustic (~11% by weight of sodium hydroxide) at ~90°C from the caustic plant enters the sodium carbonate storage tanks. When the batch cycle begins, crude caustic is pumped to the top of the carbonation tower. The caustic stream flows down through two packed sections where it contacts boiler stack flue gas (approximately 9% by volume carbon dioxide) at 3.42 kPa and 165 °C, rising up through the tower. The caustic (sodium hydroxide) react with the carbon dioxide in the flue gas to form sodium carbonate as shown in the chemical reaction:

\[ 2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]

The pipe that is used to transport sodium carbonate and crude caustic from the carbonation tower and to the sodium carbonate tank, respectively, experiences frequent leaks. Many leaks mostly developed in bottom of the line. Detailed investigation showed...
that the failure of the pipeline is most likely attributed to caustic corrosion. Presence of deposit-forming material, such as carry-offer material in the flue gas, accelerate the corrosion process. This carry-offer material was identified as the black powder.

Black powder is corrosion related contaminants found in pipelines that transport gas, hydrocarbon condensates, and liquefied petroleum gas (LPG). It has been reported that black powder in some cases contains iron oxides [1,2] and in other instances a mixture of iron oxides and iron sulfides [3, 4]. Black powder causes fouling of compressors, contamination of instrumentations, blocking of furnace nozzles, plugging of filter systems and corrosion of pipelines. It is estimated that black powder costs the industry millions of dollars per year [5]. In addition to the effects of black powder on the corrosion of their transporting pipelines, it can also make its way from pipelines to downstream processes damaging equipment through corrosion process [6].

This paper presents a failure investigation of the corrosion of sodium carbonate pipeline.

2. Investigation

Sample of the failed pipe was cut for investigation. Two samples of deposits from the pipeline were collected as well. One sample was collected from the pipe and the other one was from upstream of the boiler, Figure 1.

![Fig. 1. (a) pipe sample in as received condition; (b) internal of the pipe; (c) deposit collected from the pipe; (d) deposit collected from flue gas pipe.](image)

2.1. XRF/CS and XRD Analyses

The chemical composition of the flue gas pipeline deposit and the sodium carbonate pipeline internal deposit was analyzed using XRF (X-Ray Fluorescence Spectrometry) and C/S analyzer, Table 1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Internal deposits</td>
</tr>
<tr>
<td>C</td>
<td>5.80</td>
</tr>
<tr>
<td>O</td>
<td>25.6</td>
</tr>
<tr>
<td>Na</td>
<td>13.6</td>
</tr>
<tr>
<td>S</td>
<td>0.10</td>
</tr>
<tr>
<td>Cl</td>
<td>2.70</td>
</tr>
<tr>
<td>Ca</td>
<td>7.40</td>
</tr>
<tr>
<td>Fe</td>
<td>Balance</td>
</tr>
</tbody>
</table>
The XRD patterns of the internal deposits products show the presence of pirssonite (Na₂Ca(CO₃)₂•2(H₂O)), magnetite (Fe₃O₄), hematite (Fe₂O₃), Sodium Chloride (NaCl) and calcium sulphate (Ca(SO₄)). For the boiler upstream deposit, the XRD patterns indicate the presence of magnetite, silicon oxide (SiO₂), calcium magnesium silicate (Ca₃Mn₂Si₃O₁₂) and silicon carbide (SiC).

2.2. SEM/EDS analyses

A sample with the deposits was mounted, Figure 2, for examination under the scanning electron microscope (SEM), and chemically analyzed using the energy dispersive spectroscopy (EDS), Figure 3.
3. Discussion

The aforementioned analyses confirmed that the failure of the pipeline was a localized corrosion. It was observed the leaks of the pipe take place in the bottom of the line between 3&9 O’clock positions. Obviously, the carry-over from the upstream of the boiler, is the main source of the deposits in this system. This type of deposit is known as black powder. Some studies have identified black powder to contain primarily iron oxides and in other instances, a mixture of iron oxides and iron sulphides. The EDS chemical analysis of the collected samples, reveals it mainly consists of iron oxides. It has been reported that, black powder vary in size distribution, quantity and chemical composition [5]. In addition to the effects of black powder on the corrosion of gas pipelines, it can also make its way from pipeline to downstream processes damaging equipment through corrosion process [7].

Based on many literatures and standards, carbon steel is highly resistance to sodium carbonate with < 20 Mils/year corrosion rate up to 49 °C [8,9], without considering the effect of the corrosive species presence in the system.

Depositing of the black powder and/or corrosion product accelerates the caustic corrosion. Under deposit corrosion occurs in variety of environment and can be of a variety of forms. The composition of the deposited material play an important role in the mechanisms of under deposit corrosion and the morphology of the resulting damages. Under the deposited material, NaOH get concentrated to a high pH level. The increase in pH value results in dissolution of the protective magnetite (Fe₃O₄) layer, and consequently accelerate the corrosion process.

4. Conclusion

The results of the conducted analyses suggests that the failure of the pipe attribute to under-deposited caustic corrosion. It can be concluded the deposit was introduce to the pipeline as a carry offer in flu gas. In addition, some particles can also precipitate at low flow velocity or during shutdown. Therefore, caustic concentrate under the deposited to a high pH level. This increase in the pH level causes dissolution of the protective magnetite (Fe₃O₄) layer and consequently accelerate the corrosion process.

References