Cause Analysis and Suggestion on Corrosion Leakage of Pipe in Atmospheric and Vacuum Pressure Unit

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Abstract. An 800,000 tons/year atmospheric and vacuum distillation unit suffered from corrosion and leakage of the atmospheric top volatile pipeline, which resulted in unplanned shutdown, seriously affecting the safe and stable operation of the unit. In this paper, the corrosion mechanism, raw materials, anti-corrosion measures and operation management are analyzed. The causes of corrosion leakage accidents are given and the relevant suggestions for corrosion control and protection are put forward.

1. Introduction
Atmospheric and vacuum distillation unit, as the leader of petrochemical industry, takes advantage of the different physical characteristics of each component of crude oil, carries out pre-treatment, component separation, extraction and other technological processes, and finally obtains representative units of petroleum products such as gasoline, kerosene, diesel oil, lubricating oil and raw materials of downstream units. As an important process of oil refining, the safety status of the device plays a vital role in the long-term safe operation of the refinery. Because crude oil contains a lot of corrosive substances such as water, salt, sulphide and acid, corrosion is the most common problem in atmospheric and vacuum distillation units, especially in low temperature parts, which has always been the focus of equipment managers. Once corrosion leakage occurs, equipment will pose a major threat to the safety of personnel and equipment [1-3].

Based on a case of leakage of normal pipe in atmospheric and vacuum distillation unit, the direct causes of corrosion leakage at the top of the tower are proposed from the aspects of medium composition, corrosion mechanism, process parameters and process flow, the subsequent measures and suggestions for corrosion prevention and control are given for specific reasons.

2. Unit Overview
A 800,000-ton/year atmospheric and vacuum distillation unit has been in operation since 1997. It is mainly used to process Venezuelan MEREY16, BOSCAN heavy oil and a small amount of Liaohe crude oil. The acid value and sulfur content of heavy oil in MEREY16 and BOSCAN are shown in Table 1. The main equipment of the device includes primary distillation column, distillation column, atmospheric column, heating furnace and related process pipelines. The technical parameters of atmospheric column with serious corrosion and volatile pipeline at the top of corrosion leak tower are shown in Table 2.
Table 1. Ingredient content of raw oil

| Name of raw oil | Acid value of heavy oil (mg KOH/g) | Sulphur content(%) |
|-----------------|-----------------------------------|-------------------|
| MEREY16         | 1.24                              | 2.60              |
| BOSCAN          | 1.39                              | 4.9               |

Table 2. Main technical parameters of corrosion leakage pipeline and equipment

| Name of device | Atmospheric tower | Top volatile line |
|----------------|-------------------|-------------------|
| Date of service | November 1997    | January 2010      |
| Design pressure (MPa) | 0.4              | 0.24             |
| Design temperature(℃) | 250              | 131              |
| Operating pressure (MPa) | 0.3              | 0.06             |
| Operating temperature(℃) | 250              | 111              |
| Main body material | Head: 16MnR+316L  | Cylinder: 16MnR+316L |
|                  |                   | Diameter:1800          |
| Equipment specification | Head: (12mm+3mm)  | Cylinder: (10mm+3mm) |
|                  |                   | Φ273×9               |
| Operating medium | Crude oil          | Naphtha             |

In April 2018, the atmospheric and vacuum distillation unit was repaired and started. In October 2018, inspectors found that the leakage occurred at the three-way position 400 mm downward from the injection point of the atmospheric roof volatilization line. The leakage location is shown in Figure 1. The preliminary analysis shows that the reason is the leakage of the pipe wall caused by the corrosion thinning, and it continues to operate after the temporary pipe card treatment[4]. Fifteen days later, the leakage occurred again and the atmospheric and vacuum distillation unit temporarily stopped. Macroscopic inspection showed that the top of the tower was corroded and perforated seriously, as shown in Figure 2. Through manhole inspection, it is found that the inner parts of atmospheric tower are seriously corroded, the valve is corroded and cracked, and the inner wall of the top head of tower is densely covered with surface cracks, as shown in Figure 3 and 4.

![Figure 1. Diagram of corrosion perforation site](image1)

![Figure 2. Evaporative line corrosion perforation](image2)
3. Equipment Damage Pattern Recognition

Based on the comprehensive analysis of the medium characteristics, process parameters and equipment materials, it can be seen that internal corrosion thinning (including uniform corrosion thinning and local corrosion thinning), wet hydrogen sulfide damage and external corrosion are the main failure mechanisms of the atmospheric and vacuum distillation unit[5]. Figure 5 shows the distribution chart of main failure mechanism of atmospheric pressure unit using risk-based inspection technology. From the distribution chart, it can be seen that the proportion of corrosion thinning of equipment is higher, followed by stress corrosion cracking. For the atmospheric tower and pipe jacking in this analysis, internal corrosion is dominant.

4. Cause analysis of corrosion leakage

After the leakage accident, based on the potential damage mode of the equipment, technicians start with the possible causes of the corrosion intensification, such as the change of medium composition, the fluctuation of process parameters and the rationality of process flow. The reasons for the corrosion leakage of the pipeline on the top of atmospheric tower are summarized as follows.

4.1. The salt content of crude oil is abnormal and the chloride ion concentration exceeds the standard seriously.

After the corrosion leakage accident, the technicians analyzed the Liaohe oil and water samples of the raw material tank, and the analysis results are shown in Table 3. According to the data in the table, the inorganic salt content in crude oil increased from 10 mg/L to 100 mg/L, and the chloride ion concentration was abnormal. Because the current electric desalination efficiency can not adapt to the abnormal increase of crude oil salt content, the crude oil salt content entering the downstream process exceeds the standard, which causes the rapid decrease of the PH value of condensate at the top of the tower and greatly aggravates the hydrochloric acid corrosion of the pipeline.
Table 3. Analysis results of Liaohe oil and water samples in raw material tank

| Sample source       | Sample    | pH | Chloride ion concentration (mg/L) | Inorganic salt content (mg/L) | Organochlorine content (mg/L) |
|---------------------|-----------|----|----------------------------------|------------------------------|-------------------------------|
| Oil tank of Liaohe  | Crude Oil | 2~3| 7000                            | 100                          | 5                             |

4.2. The existing electric desalting unit can not remove the organic chlorine in crude oil, which makes the total chlorine content of crude oil exceed the standard.

From the data in Table 1, it can be seen that crude oil from Liaohe Oilfield contains 5 mg/L of organic chlorine, which is higher than the process control value of 1-3 mg/L. The main sources of organic chlorine in crude oil are natural existence, oil recovery and transportation aids. Demulsifiers and desalting agents are also the main sources of organochlorine in the process of electric desalting. The electro-desalination process adopted in this unit is only effective for inorganic chlorine in crude oil, and the removal rate of organic chlorine is relatively low or even ineffective. A large amount of organochlorine is hydrolyzed into HCl in the process, which leads to the increase of HCl concentration, thus aggravating the corrosion of hydrochloric acid and acidic water on top equipment and pipelines.

After the pipeline leakage accident, the technicians sampled and analyzed the naphtha distillation outlet tank. The composition and content of organic chlorine chloromethane and 3-chloropropylene in naphtha samples were analyzed by GC-MS. The test results were shown in Figures 6 and 7.

4.3. Dew point corrosion environment formed, which aggravated the degree of local corrosion.

In the process of production and operation, in order to control the final distillation point (> 175 ℃) and density of naphtha (between 650 kg/m³ and 750 kg/m³), the top temperature of naphtha is usually controlled at about 100 ℃, which is very easy to form dew point corrosion environment of hydrochloric acid. The local corrosion environment is more destructive than uniform corrosion, which accelerates the occurrence of corrosion leakage. Macroscopic inspection showed that the serious corrosion occurred mainly in the lower part of the top reflux, the nozzle of the top volatile line safety valve and the tray float valve, and the above positions were in the dew point.
4.4. The design of process flow is unreasonable.
The typical corrosion environment of hydrochloric acid liquid phase zone is formed in the three-way area after the injection point shown in Figure. 1. Irrational setting of water injection point and mode, no sprinkler at water injection point, incomplete atomization of water injection, dissolving HCL directly in liquid form, forming a hydrochloric acid corrosion environment. The design distance between the injection point and the safety valve nozzle is too small (400mm). It is easier to accumulate fluid in the three-way section after the injection point, resulting in corrosion leakage in this section. In summary, the abnormal medium composition and unreasonable process design caused the serious corrosion of atmospheric tower and the leakage of pipeline at the top of the tower.

5. Corrosion Countermeasures
Internal corrosion of atmospheric and vacuum distillation unit, especially the corrosion at low temperature on the top of tower, is an important problem that perplexes the long-term operation of the unit. It can not be completely avoided by relying solely on material upgrading. In order to prevent corrosion leakage accidents to the greatest extent, it is necessary to coordinate management from process flow, equipment management, corrosion monitoring and other aspects [8-10].

- Strengthen the inspection and evaluation of crude oil quality. Regular inspection and evaluation of crude oil composition, timely understanding of changes in raw material properties, focusing on prevention and control of the impact of organic chlorine concentration changes on the corrosion damage of the unit.
- Strict technological discipline. Strictly control according to the process parameters of the device, strictly observe the device's defensive value and operation boundary, avoid condensation of atmospheric roof oil and gas in non-corrosion-resistant parts to form a corrosive environment.
- Optimize the process flow, rationally select injection points, add special injection nozzles, and pay attention to the blockage of nozzles in actual operation.
- Strengthen the management of electric desalination of crude oil and strictly control the salt content after desalination. Because the raw material is super heavy oil, inorganic salt can not be effectively removed by conventional electric desalting process. Better desalting effect can be achieved by three-stage combination process of vertical-horizontal electric desalting tank, optimization of heat exchange process and improvement of electric desalting temperature.
- Strengthen the management of top injection agent and do a good job of process anticorrosion. Optimizing the top injection agent and strengthening the injection management to ensure that the acid-base value and iron ion concentration of the top condensate are within the reasonable index range.
- Strengthen the quality control of naphtha products. Strengthening the monitoring of side-line products can detect corrosion leakage accidents in time, so as to make timely decisions to avoid unplanned shutdown and other problems, and at the same time to avoid the impact of corrosion on the follow-up units in the combined plant.
- Material upgrading. Because the raw material of the unit is high sulphur and high acid crude oil, the low temperature corrosion on the top of the tower is particularly serious. The practical engineering case shows that the corrosion problem at the top of the tower can be largely solved by replacing the water cooler material with Ti plate wet air cooling and controlling the condensation area in the air-cooled place.
- Strengthen corrosion monitoring and implement fixed-point thickness measurement of pipelines. Fixed-point thickness measurement of pipeline before and after injection point is carried out, and comprehensive inspection is carried out during each overhaul period to ensure timely detection of corrosion phenomena and avoid the occurrence of corrosion accidents.

6. Conclusion
Aiming at a pipeline corrosion leakage accident, the possible failure mechanism of pipeline is given based on the analysis such as medium composition, process temperature, pH value and equipment
material, The effect of failure mechanism on pipeline leakage was verified by means of analysis. The causes of corrosion perforation and leakage of the atmospheric top volatile pipeline are given. Finally, reasonable suggestions for subsequent corrosion protection and control are put forward.

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