Research on the Monitoring Methods of VOCs Leak of Open Circulating Water System in Refineries

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Abstract. Open circulating water heat exchangers are widely used in refineries. According to the current emission standards, whether a circulating water system is leaking is determined by total organic carbon (TOC) concentration at the inlets and outlets of circulating water heat exchangers. However, this method is rough with low compatibility, making it hard to judge the actual leak of a circulating water heat exchanger. Taking a typical refinery with a yearly output of five million tons of oil as an example, we established a ledger of an open circulating water system and optimized the method to judge whether the system is leaking in this paper. The results show that there are 63% of the circulating water heat exchangers can be decided by monitoring the quality of circulating water. Among all, the leak of only 18.81% of the circulating water heat exchangers can be decided by monitoring the amount of TOC.

1. Introduction

VOCs emission of circulating water refers to the process that VOCs volatilize to the atmosphere by steam stripping of cooling towers or wind due to the leak of circulating water heat exchangers [1-4]. The existing environmental management policies of the United States [5-9], EU [10-11], and China have made the emission of VOCs from circulating water a job within regulation. The research shows that the emission of VOCs from circulating water accounts for 2.4% of the total emission of the refinery, reaching about 200 t/a [12]. According to The discharge standard and measurement methods of pollutants from paint manufacturing (GB 37822-2019) [13], the concentration of TOC in circulating water through the inlet and outlet of heat exchangers of an open circulating water system needs to be measured every 6 months. If the concentration of TOC through the outlet is 10% greater than that through the inlet, then a leak is considered to have occurred. However, the requirement has the following problems:

(1) Not all the circulating water heat exchangers need to be tested.

For example, some of the circulating water will transfer heat with materials without VOCs such as hot water and electro-desalting water. As for some of the circulating water heat exchangers, the pressure of the circulating waterside is higher than that of the material side. Therefore, even though the heat exchanger leaks, VOCs materials will not flow into circulating water.

(2) It is not reasonable to judge whether there is a leak by analyzing the concentration of TOC.
For example, the components of some gas phase pipelines (mainly composed of C2–C4 hydrocarbons) have already escaped before sampling, sample transport, and sample into the analytical instrument, and it is meaningless to analyze TOC. Therefore, how to scientifically establish a list of controlled circulating water heat exchangers and accurately identify a leak of VOCs has become the daily focus and difficulty for refineries. However, there are few reports on these researches. Under this circumstance, taking a typical refinery with a yearly output of five million tons of oil as an example, we established a ledger of controlled circulating water heat exchangers and optimized the leak detection method, aiming to provide management suggestions on VOCs emission of circulating water for refineries.

2. Research on the establishment method of a ledger

2.1 Applicability Analysis of Circulating Water Heat Exchangers

According to the applicability analysis of a ledger of dynamic and static sealing points mentioned in *Leak Detection and Repair Work Guidelines for Petrochemical Enterprises*[^15], the concept of controlled and exempted circulating water heat exchangers is proposed based on the material category and the operation state of circulating water heat exchangers to take the leaking heat exchangers into regulation.

**Controlled circulating water heat exchangers**: They refer to the ones which need to be brought into routine management and control where the leak of the materials involved may cause the change of quality of circulating water. All the circulating water heat exchangers with VOCs involved are included. For example, the excess heat from the products of the coolers of oil refining units are always taken away by circulating heat exchangers, but VOC materials may volatilize into the circulating water system when there is a leak of a heat exchanger, leading to the increase of the amount of VOCs in the water system. So, this kind of circulating water heat exchangers need to be regulated.

**Exempted circulating water heat exchangers** refer to the ones which should not be taken into account based on their operating state. Since even when there is a leak of VOCs of a heat exchanger of this kind, the quality of the circulating water will not be affected, or the impact is negligible. There are mainly two situations:

1. The pressure of the circulating water side is higher than that of the side of materials when the heat exchanger is working;
2. Exposure to VOCs only during start, downtime, breakdown, emergency response, or temporary operation.

2.2 Establishment of Circulating Water Heat Exchanger Ledger in a Refinery Enterprise

Taking a typical refinery with a yearly output of five million tons of oil as an example, a ledger of the circulating water heat exchangers of each unit of the refinery is established after the exempted and controlled circulating water heat exchangers are summed up by data collation and on-site investigation. The ledger of the circulating water heat exchangers of the main units of the enterprise is seen in Table 1 and Figure 1.

| Unit                                | Subtotal | Number of circulating water heat exchangers (sets) | Number of non-controlled circulating water heat exchangers | Number of controlled circulating water heat exchangers | Obligated | Exempted |
|-------------------------------------|----------|--------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|-----------|----------|
| Crude unit (5 million tons/year)    | 18       | 10                                                | 6                                                        | 2                                                        |           |          |
| Hydrocracker (1.2 million tons/year)| 15       | 0                                                 | 14                                                       | 1                                                        |           |          |
| Hydrogen production plant (40,000 normal cubic meter/hour)| 5       | 1                                                 | 2                                                        | 2                                                        |           |          |
| Catalytic cracking unit (1.4 million tons/year) | 36       | 3                                                 | 24                                                       | 9                                                        |           |          |
| Gas separation unit (200,          | 14       | 0                                                 | 13                                                       | 1                                                        |           |          |
| Product refining unit | Sulfur recovery unit (4000/3000 tons) | Solvent reclamation | Sour water stripping | Continuous catalytic reforming unit (600, 000 tons/year) | Benzene extraction unit (150, 000 tons/year) | Gasoline hydrogenation plant (600, 000 tons/year) | Kerosene hydrogenation plant (600, 000 tons/year) | Diesel hydrogenation plant (1, 400, 000 tons/year) | Isomerization unit (200, 000 tons/year) | Total |
|-----------------------|--------------------------------------|---------------------|---------------------|--------------------------------------------------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------|
| 2                     | 2                                    | 0                   | 0                   | 13                                                     | 9                                             | 12                                             | 4                                             | 6                                              | 6                                             | 162         |
| 2                     | 6                                    | 0                   | 0                   | 9                                                      | 1                                             | 0                                              | 0                                             | 0                                              | 0                                             | 39          |
| 0                     | 6                                    | 3                   | 0                   | 1                                                      | 3                                             | 0                                              | 0                                             | 5                                              | 0                                             | 102         |
| 0                     | 0                                    | 0                   | 0                   | 0                                                      | 0                                             | 0                                              | 0                                             | 0                                              | 0                                             | 21          |

Figure 1 Proportion of Controlled Circulating Water Heat Exchangers of the Main Units in the Enterprise
As can be seen from Table 2-1 and Figure 2-1, there are 162 circulating water heat exchangers in the whole refinery, of which 123 are controlled, accounting for 75.9%. Among them, 102 exchangers are not exempted, accounting for 63% of the total number of circulating water heat exchangers, while 21 units are exempted, accounting for 12.9%. 39 heat exchangers are not controlled, accounting for 24.1%.

The result shows that the emission of VOCs can be effectively controlled by merely the regular management and control of the 63% obligated circulating water heat exchangers.

3 Optimization of Leak Detection method for Obligated Circulating Water Heat Exchangers

3.1 Leak Analysis Obligated Circulating Water Heat Exchangers

According to the classification of volatile organic compounds (VOCs) materials in Leak Detection and Repair Work Guidelines for Petrochemical Enterprises, the change of circulating water quality where a leak occurs will be discussed based on the state of the materials involved in the heat exchange of the obligated circulating water heat exchangers.

(1) Heat transferring between circulating water and volatile organic gas

When the material side of a circulating water heat exchanger is a volatile organic gas, the gas will involve in the circulating water system when the heat exchanger leaks. However, due to the state of the material, the gas will dissipate into the air quickly when the sampling and testing process is in progress, leading to no significant impact on the value of TOC of circulating water. Thus, the test for TOC detection is also meaningless.

(2) Heat transferring between circulating water and volatile organic liquids

When the material side of the circulating water heat exchanger is a volatile organic liquid, the liquid will involve in the circulating water system when the heat exchanger leaks. However, the target liquid is light, and it will dissipate into the air when the sampling and testing process is in progress. So there are actually few residues in the circulating water, and it is of less significance to test the amount of TOC.

(3) Heat transferring between circulating water and volatile organic heavy liquids

When the material side of the circulating water heat exchanger is a volatile organic heavy liquid, the liquid will involve in the circulating water system and almost all of it will remain in the circulating water due to its heavy mass when the heat exchanger leaks. So, how a heat exchanger leaks can be decided by the concentration of TOC at the inlet and outlet of a circulating water heat exchanger.

3.2 Sampling and Analysis of Obligated Circulating Water Heat Exchangers

According to the analysis above, corresponding sampling and analysis methods for the different states of materials involved in the obligated circulating water heat exchangers when there is a leak that will affect the quality of circulating water are proposed in this section.

(1) Volatile Organic Gases

A. Sampling

Considering the volatility of this kind of materials, it is suggested to adopt the open sampling method. For example, the gases will be sampled at the side of the outlet of a circulating water heat exchanger, and some instruments will be used to detect the volatile organic gases in the water. The “collection” sampling method can also be used, which is conducted at the outlet side of the circulating water heat exchanger (shown in Figure2). There is a special outlet for releasing the escaping gases during the sampling process, and some instrument is used to detect the gases at the outlet.
B. Analysis

The volatile organic compounds in the effluent of circulating water are detected by a hydrogen flame ionization detector (HFID) \[15\]. A hydrogen flame ion detector (FID) can measure organic compounds by the flame produced by the combustion of hydrogen compounds with air. When the hydrocarbons volatilize into the detection zone, the following chemical reactions will occur and there will be the formation of ions:

$$RH + O \rightarrow RHO^+ + e^- \rightarrow H_2O + CO_2$$

An electrode with polarization voltage is also installed in the detection chamber. The formed ions are attracted to the electrode. A current is formed due to the migration to the collector, which is proportional to the concentration of hydrocarbons produced by the oxidization.

The configuration of a typical ionized detector is shown in Figure 3.

Advantages of hydrogen flame ion detection include:

a. a wide linear dynamic range;

b. high sensitivity to hydrocarbons (including methane);

c. very stable and repetitive responses;

d. hardly affected by CO, CO$_2$ and vapor in the normal environment.

Methane is used as the standard gas. After the single-point calibration at 100 ~ 500 ppm, the detection results range from 1.0 ppm to 10,000 ppm, which can meet the needs of the analysis.

(2) Volatile Organic Liquids

A. Sampling

When a volatile organic liquid enters the circulating water, part of it will volatilize into the atmosphere during the sampling process. So a “collection” sampling method should be used instead of an open one. Some pure air should be pumped into the collector during the sampling process, if possible.
In this way, the organic matter in the water will volatilize to the gas collection port and they can be detected by the instrument at the gas outlet.

**B. Analysis**

Its analysis method is the same as that of VOCs, whose core idea is to determine the content of heat transfer medium in circulating water by monitoring the VOCs volatilizing from water to air.

3) **Volatile Organic Heavy Liquids**

**A. Sampling**

On-site sampling and laboratory analysis should be adopted since the materials are relatively heavy and the proportion of the target materials volatilizing from water to air is small. However, it should be noted that a “splash” sampling method is not allowed. The sampling tube should be inserted into the bottom of the sampling bottle, and the flow rate of circulating water should be controlled. When the sample is full, the sampling bottle should be sealed as quickly as possible and there should be no gas-phase space in the sampling bottle in order to avoid the materials from volatilizing during the process of sampling and transportation.

**B. Analysis**

As for volatile organic heavy liquids, they are different from the materials mentioned above that are tested by their concentration from circulating water to air to decide how serious a leak is, which means total organic carbon in water can be measured directly. TOC refers to the carbon content of dissolved or suspended organic matter in water (expressed as mass concentration), and it is an aggregative indicator that can show the total amount of organic by carbon content. And it is based on the Water quality—Determination of total organic carbon—Combustion oxidation nondispersive infrared absorption method (HJ 501-2009) [17].

In summary, the sampling and detection methods for different types of materials are shown in Table 2.

| Categories          | Characteristics | Sampling methods          | Location of analysis | Analytic factors             | Analytical methods                |
|---------------------|-----------------|---------------------------|----------------------|-----------------------------|----------------------------------|
| Gas                 | Extremely volatile | On-site open sampling “Collection” sampling | Sampling point | Non-methane total hydrocarbon | Hydrogen flame ionization detector |
| Light liquid        | Volatile        | “Collection” sampling     | Sampling point | Non-methane total hydrocarbon | Hydrogen flame ionization detector |
| Heavy liquid        | Non-volatile    | Under-liquid non-splash sampling | Laboratory | Total organic carbon | Infrared absorption |

### 3.3 Medium Classification of Circulating Water Heat Exchangers of a Refinery

Taking a typical refinery with a yearly output of five million tons of oil as an example, the obligated circulating water heat exchangers of a refinery will be sorted out according to the state of the medium involved, combined with the above analysis. And the details are shown in Table 3 and Figure 4.

| Unit              | Number of the obligated circulating water heat exchangers (units) |
|-------------------|---------------------------------------------------------------|
| Crude unit (5 million) | Subtotal 6, Gas 0, Light liquid 2, Heavy liquid 4           |
| Process Description                                      | Gas | Light Liquid | Heavy Liquid | Total |
|----------------------------------------------------------|-----|--------------|--------------|-------|
| Hydrocracker (1.2 million tons/year)                     | 14  | 9            | 5            | 0     |
| Hydrogen production plant                                | 2   | 2            | 0            | 0     |
| (40,000 normal cubic meter/hour)                         |     |              |              |       |
| Catalytic cracking unit (1.4 million tons/year)          | 24  | 0            | 10           | 14    |
| Gas separation unit (200,000 tons/year)                  | 13  | 0            | 13           | 0     |
| Solvent reclamation                                     | 3   | 0            | 3            | 0     |
| Sour water stripping                                    | 1   | 1            | 0            | 0     |
| Continuous catalytic reforming unit (600,000 tons/year)  | 9   | 2            | 7            | 0     |
| Benzene extraction unit                                  | 3   | 3            | 0            | 0     |
| (150,000 tons/year)                                     |     |              |              |       |
| Gasoline hydrogenation plant (600,000 tons/year)         | 12  | 7            | 5            | 0     |
| Kerosene hydrogenation plant (600,000 tons/year)         | 4   | 1            | 3            | 0     |
| Diesel hydrogenation plant (1,400,000 tons/year)         | 5   | 3            | 1            | 1     |
| Isomerization unit (200,000 tons/year)                   | 6   | 2            | 4            | 0     |
| Total                                                    | 102 | 27           | 56           | 19    |

Figure 4 Medium Classification Ratio of the Obligated Circulating Water Heat Exchangers of the Main Units of the Enterprise
As can be seen from Table 3 and Figure 4, of the 102 obligated circulating water heat exchangers in the refinery, 27 of them are ones with volatile organic gas, accounting for about 26.7%, and 56 of them are ones with a volatile organic liquid, accounting for about 54.5%. Moreover, there are 19 heat exchangers with volatile organic heavy liquid, accounting for about 18.8%.

The result shows that monitoring TOC in circulating water can detect whether there is a leak of only 18.8% of the obligated circulating water heat exchangers. Therefore, the state of the materials involved in the heat exchangers should be fully understood to choose a proper method to qualitatively analyze whether there is a leak of a heat exchanger in the actual production.

4. Conclusions
This paper mainly discusses the problems existing in the detection of circulating water heat exchangers based on the current standards and regulations. Through the analysis on the operating state of circulating water heat exchangers and the materials involved, more reasonable sampling and detection methods for circulating water heat exchangers are put forward to judge whether the heat exchangers leak more accurately. The details are as follows:

(1) A ledger is established while the concept of “controlled” and “exempted” heat exchangers is introduced. Taking a typical refinery as an example, there are 162 circulating water heat exchangers in total. Among them, there are 39 non-controlled heat exchangers, accounting for about 24.1% while there are 21 exempted ones, accounting for 12.9%. Moreover, there are 102 obligated controlled heat exchangers, accounting for about 63%.

(2) According to Guidelines for VOCs Pollution Source Investigation in Petrochemical Industry, obligated heat exchangers are classified into three types by the materials involved, which are ones with gases, light liquids and heavy liquids. There are 27 ones with volatile organic gases, accounting for about 26.7%; there are 56 ones with volatile organic liquids, accounting for about 54.5%, and 19 ones with volatile organic heavy liquids, accounting for about 18.8%.

(3) In view of the different states of the materials of the obligated heat exchangers, different methods are used to test whether there is a leak. As for gas materials, an open sampling method or a “collection” sampling method should be used before a hydrogen ion flame ionization detector is used to detect the volatile organic compounds in the effluent of circulating water. As for light liquid materials, a “collection” sampling method should be used before a hydrogen ion flame ionization detector is used to detect the volatile organic compounds in the effluent of circulating water. As for heavy liquid materials, the total organic carbon of circulating water can be directly measured by on-site sampling and laboratory analysis.

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