Source detection and removal of organic chloride component in crude oil

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Abstract

Organic chloride or undesaltable chloride contamination in crude oil can cause HCl to be formed during hydrotreating process, which can corrode equipment through accumulation; therefore, piping and vessels can wear dangerously thin and become susceptible to leaks and explosions in both upstream and downstream units. For this reason, the acceptable concentration of organic chloride should ideally be kept below 1ppm. Our research was carried out in accordance with ASTM D 4929, section 11 procedure for collecting the naphtha cut at 204°C (400°F) and the distillation method was adapted from ASTM D 86 for the distillation of petroleum products.

The results of this investigation showed the followings:

1. Controlling of excessive organic chloride in crude oil is highly important and must be taken seriously as a corrosive component,
2. However there are methods available and applicable for the management of this component during hydrotreating process or even before formation of organic chloride,
3. The organic chloride content of crude oil can be controlled by detecting its sources, such as:
    a. Chlorinated solvents and additives used in crude oil production, transportation and storage tanks,
    b. Chemicals used in enhanced oil recovery processes,
    c. Unmonitored disposal of various chlorinated compounds in crude oil storage tanks.

Keywords: organic chloride; crude oil; corrosive; source detection; removal.

Introduction:

A significant factor that contributes to corrosion exerted by crude oil is through formation and accumulation of chlorides. A typical distribution for salts in crude oils is 70-75% NaCl, 10% $CaCl_2$ and 10-15% $MgCl_2$. The chlorides can contribute to the corrosivity of crude oil by the accumulation of salts in processing units that, in turn, will lead into the formation of hydrogen chloride. The Hydrogen chloride thus generated will serve to enhance the corrosion rates of the equipment whose immediate result will be increasing the risk marine or running equipment and low efficacy of operation as well as diversely affecting the production. The importance of removing organic chloride from crude oil is so high that, in addition to affecting the technicality of dealing with crude oil, it can also affect the quality of the crude. The latter factor will be a death-life matter for oil producing countries because if the concentration of organic chloride in crude oil goes above 1 ppm, it will adversely affect the export of the oil and this will add yet another dimension to the disaster scenarios thus produced.

In this paper, we will briefly touch the methods and techniques currently in use to detect and remove organic chlorides in crude oil. The main service of this paper, in our opinion, will be that it will serve as a reference that in a precise, easy-to-follow language will briefly touch the sign cant issues related to this matter.

1. The root cause of the problem

Introduction of chlorides in water used in oil refining processes through various strategies such as addition of (oxidising) biocides such as chlorine [1] or water injection to the reservoir for enhanced recovery [2] is possible. In the literature, one can find a good number of research that mainly focus on separating the salt-containing water from the crude to control the possible source of chlorides [345], However in this paper we will mainly focus on chlorides that can be found in crude oil. Obviously, these chlorides can also come from the formation water which is entrained with the oil.

In crude oil, chlorides can exist in two forms, organic chloro-hydrocarbon and inorganic chloride (e.g. sodium chloride). The removal of the inorganic chlorides is not that difficult to achieve as conventional desalination processes would do it. Therefore, it will be the organic chlorides that will promote the danger of corrosion. In fact, the organic chloride can exist as the compounds shown in Table 1 in a typical crude oil:

Table 1: Various organic chloride compounds that may exist in a typical crude oil

Chemical compound's name	Formulation
Chloroform	CH_3-Cl
Carbon Tetra-chloride	C-Cl_4
Ethylene Tetra-chloro	C-Cl_2=C-Cl_2
Vinyl Chloride	C_2H_3-Cl
Chloro-Benzene	C_6-H_5-Cl
Fereon 113	C_2Cl_3
Chloro-perrine	CH_2=CClCH=CH_2
Di-chloride Propylene	$C_3H_6Cl_2$
Methane Di-chloro	CH_2Cl_2
Ethylene Tri-chloro	CHCl=CCl_2

In a typical refining plant, problems with crude oil organic chloride can be seen at hot-spots as shown in Figure 1:

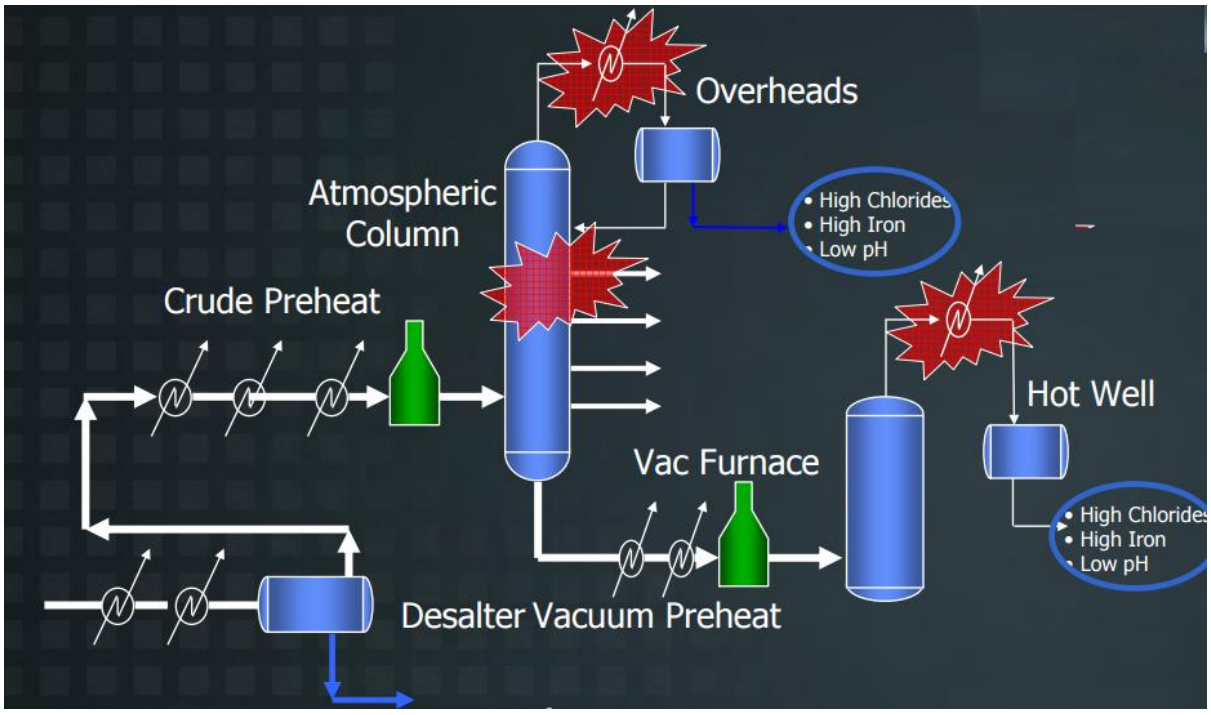

Figure 1. Hot-posts in a crude oil refining plan where organic chloride can be a problem (red starts)

Based on the salts found in crude oil, it is NaCl that mainly controls the content of chlorides. However, to maximize the amount of raw crude extracted from the wax, an organic chloride de-waxer must be added to the crude. It is this chloride that is hard to be removed using conventional desalting methods and it is also this chloride that makes the source of the problem. In fact, if one wants to classify the problems arising from the existence of organic chlorides in crude oil, it can be categories into the following two interrelated problems:

a) Its content measurement
b) Chloride build-up

As organic chloride is not in free form but the amount of free chlorine ions that are soluble in water, This is a very important drawback as without knowing the amount of organic chlorides, it is too hard (if not impossible) to determine the counter-measures necessary to be taken not to let it go down 1 ppm.

Chloride build-up is not a single mechanism but in fact two hydrating processes. These hydration processes are shown below:

Hydration process 1: hydration of organic chlorides (the main process that results in increasing chloride content in crude oil)

Hydration process 2: hydration of inorganic Chlorides

While during conventional electrical desalting, it may be difficult to remove inorganic chlorides, with increasing the process temperature, the hydration process (process 2) increases and the inorganic chlorides hydrate into free chlorine ions.

The inorganic salts can also contribute to corrosion: Magnesium chloride and a part of calcium chloride through hydration at around 50°C and each mole of them will produce two moles of hydrochloric acid (HCl). If this HCl is in the form of “dry” gas, it will not be corrosive but water; it will form hydrochloric acid with a pH of 2 or lower. This will in turn create a very aggressive environment.

2. An outlook in to Standards and Patents related to organic chlorides

Being of such paramount importance, one can imagine that a number of standards, methods and patents have been proposed to deal with the problem of organic chloride in crude oil. Table 2 lists some related standards and patents.

Table 2. A selection of standards and patents related to studying organic chloride in crude oil

Standard/ Patent Code	Title Description
ASTM D4929-04	Standard test method for determination of organic chloride content in Crude Oil
ASTM D7536M	Standard test method for Chlorine in Aromatics by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
Patent US 4721824A	Guard bed catalyst for organic chloride removal from hydrocarbon feed
Patent USCN102127464A	Method for removing organochlorine from hydrocarbon oil

Needless to say that in addition to these standards and methods, each country has developed its own way of dealing with this issue, which while within the framework of the standards; it has some modifications based on the local working conditions. An example of such is the methods developed by Iranian oil and gas industry. We will not disclose all the details of such techniques here for obvious reasons but we would like to emphasize on the fact that organic chlorides is indeed a hot topic for research and many researchers both in academia and industry are currently working hard to maintain the levels within required internationally accepted limits.

3. Root cause investigation method (Suggested)

Due to the complexity of the problem, it is always useful to treat the case of organic chlorides from two perspectives: a research perspective and an industrial perspective. The research perspective must be focused on finding more precise ways to find out the source of contamination, the best way to isolate the problem (for example developing de-waxing stuff that would not contain chlorides), more effective separation methods to separate formation water chemistry of the entrained water from the crude oil and the like. On the other hand, an industrial perspective-based on the experience of the authors-may be suggested as below:

1. Try to find out the source of organic chloride: it can come from the seawater, the entrained water in the crude, Naphtanic acid and/or Asphaltine hydrolyses in the well, addition of chlorine as an oxidising biocide, addition of some corrosion inhibitors, malfunction of Marine Growth Protection System and the like. One has to bear in mind that correct recognition of the problem source will be a key factor in controlling the problem. If, for example, it is the biocide that causes the problem, then it can be decide to replace it with either a non-chloride-containing agent or a non-oxidising biocide. This will have a huge impact on controlling the issue,
2. After the source of the problem is determined, then its proper treatment can be simulated under carefully designed conditions. The main point is that like all simulations, the principle of similarity between the field conditions and the laboratory conditions must be observed. This way, the obtained results will ensure having a smooth operation schedule,
3. After confirmation of the problem being related to organic chloride existence, two strategies must be designed: one strategy must focus on corrosion management of these chlorides in the plant (CM strategy) and another strategy must focus on controlling the chlorides level in the crude (Quality strategy). With a CM strategy, safe operation and production will be maintained. This is a very important issue because without safe equipment, there will be no guaranteed high quality production. However when it comes to Quality strategy, then whole scenario will change: if the quality of the exported crude oil is below a certain threshold, chances are that it will have an economic as well as political impact on that country. Therefore, it is of high priority to always run inspections on time to watch for corroding areas that would match those shown in Figure 1 and also keep an eye on the quality of the crude oil produced.

Conclusions:

- Chlorides in crude oil can cause serious issues, both technical (corrosion of the equipment) and economical-political (low quality of the exported crude oil),
- These chlorides can be both organic and inorganic chlorides. The main source of the problem is through organic chlorides especially because neither can they be separated as easy as inorganic ones nor can their amount be measured precisely,
- There are standards as well as patents related to the issue of organic chlorides but each country can also develop its own local standards and practical guides based on scientific as well as field facts and figures,
- Based on our experience, we proposed a three stage root cause investigation plan that focuses on finding the source of contamination, simulating its treatment and then apply and realising that organic chlorides problem is a two-folded issue that must be treated by both a CM as well as a crude oil quality strategies.

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