A study into the impact of chloride ions on the make-up hydrogen compressors

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Abstract. The presence of unwanted chemicals in process lines and downstream equipment causes defects and failures, which sometimes have significant impacts on systems and imposes extra costs for the production process. In this study, one pair of four-stage make-up hydrogen compressors is investigated. These reciprocating compressors which serve as a part of the hydrogen treating unit have failed approximately simultaneously. The feed of these compressors is net hydrogen-rich gas from the Pacol process. Both dry compressors have shown similar problems in the first and second stages. The simultaneous rise in the cylinder temperature and decrease in the flow has forced shut-down of the compressors for the next actions in the process. Initial inspections have revealed some kind of deposits covered the cylinder and its components. The valves, liquid tested and results have shown significant leakage of all the suction and discharge valves of the cylinders. Moreover, the thickness of all piston rings have decreased up to 50 percent which is more than allowable values. The compositions of deposits, tested by X-ray fluorescence (XRF) and X-ray diffraction (XRD), result from the analysis shown that it contains 35.2 percent (mass fractions) of Chlorine and 27.5 percent of Iron, and noticeable amount of Sulfur or Phosphor. XRD analysis has reported that the Iron Chloride Hydrate is the main part of the fouling sample. In this paper, the impact of the aforementioned chemicals on the compressor components are investigated, and some approaches are proposed to absorb or inhibit these chemicals.

1. Introduction
The most widely used type of compressors found in industrial applications are reciprocating compressors(1, 2), which are crucial elements of the process due to their high-pressure ratio. Maintenance costs of reciprocating compressors are approximately three and half times greater than those for centrifugal compressors (3). An increase in the compressor life for one week could mean a cost saving of a quarter to three-quarters of a million dollars for a refinery (4). So, reducing maintenance costs and downtime is of paramount importance for these machines.

A number of factors have a direct influence on the operating conditions and efficiency of the reciprocating compressors, for which dozens of experimental and theoretical studies have been done in the literatures. In some of these studies, compressor failure mechanism have been categorized. Leonard et al. (4) states 8.8 % of unscheduled compressor shut-downs is because of process problems. Process problems affect the mechanical parts of the reciprocating compressors, such as valves, packings, and piston rings, which cause the rest of unscheduled shut-downs.
Compressor valves can also be damaged by unwanted chemicals. It is a common problem for the reciprocating compressor’s unscheduled shut-downs. According to some studies, compressor valve failure is divided into environmental and mechanical categories. Environmental causes are those elements in the valve environment that can lead to valve failures, such as corrosive contaminants, foreign material, liquid slugs, or improper lubrication.

Unwanted chemicals and contaminated process gas can harm the internal components of the compressors and would impose the process-stop beside the higher repair costs. The presence of corrosive agents, including trace quantities in the process fluids which can cause corrosion cracking, should be specified, and some precautions must be taken. (5)

For instance, the Continuous Catalyst Regeneration (CCR) reformer process inherently creates viscous liquid called green oil, which causes problems for the compressors of this unit. CCR reformer is one of the essential units in refinery plants. The polymerized long-chain hydrocarbons, generally called green oil, are the end-products of undesirable polymerization reactions taking place over the catalyst surface area. The reaction of Hydrogen chloride with hydrocarbons leads to chlorinated hydrocarbons molecules which are green or red and contain mainly C6-C18 hydrocarbons, with a potential tail above C40. These hydrocarbons are believed to be oligomers of light olefinic hydrocarbons, with some aromatic nuclei included in the structures (6).

Green oil forms quickly at high pressure and temperature. In some case studies which have been done on the CCR unit of a refinery plant, observations have shown consistent problems with the presence of downstream equipment’s plugging or fouling with the existence of this green sludge. After removing Chloride from the process gas, the aforementioned problems have not been observed anymore.

Another example of compressor failure due to the process issues has been studied experimentally by Lee et al. (7). In this study, three compressors have faced the problems such as damaged valves and cracked pistons after revamping. The process and mechanical design to decrease the compressor’s failure have been also reviewed the process and mechanical design to decrease the compressor’s failure. The operating conditions was adjusted to reduce the light olefin. As a result, the green oil and chloride formation in process lines have been lowered. Moreover, this study has proposed the valve type alternation and the piston design improvement to withstand the large stresses.

In complement of previous studies on observed problems of the compressors due to the process issues, this research has been done on the dehydrogenation and hydrotreating process. For better understanding, a brief description of the process has been explained in the next section.

1.1. Process description

The dehydrogenation process is a fixed bed catalytic process designed to selectively dehydrogenate a high purity, normal paraffin feed to the corresponding mono-olefin product. The feed to the dehydrogenation unit is supplied from a normal paraffin separation process (such as Molex Process). The feed must be appropriately hydrotreated to be free of potential dehydrogenation catalyst poisons, such as sulfur and nitrogen compounds. (8)

The desired product from the dehydrogenation unit, founded based on Pacol license, is generally a mixture of normal mono-olefins in C10-C13 or C11-C14 carbon range. These olefins are then used with a detergent alkylation process unit to produce linear alkylbenzene (LAB) by reacting the olefins with benzene. The linear alkylbenzene is usually sulfonated to produce a biodegradable detergent in a downstream unit.

As shown in Figure 1, the dehydrogenation reactor is filled with fixed bed platinum-containing catalyst. Selective dehydrogenation of normal paraffin feed to the corresponding mono-olefin product takes place in this reactor. The flow scheme and process equipment of dehydrogenation unit are very similar to many other hydrogen recycle reaction systems; such as platingforming, isomer, tatoray, etc. The net rich hydrogen gas produced is sent to the hydrotreating unit.

Potential acidic catalyst poisons such as chloride and fluoride-containing compounds must not enter the dehydrogenation reactor. These compounds could decompose on the catalyst and deposit the
chloride or fluoride ions on the catalyst surface. This would produce acidic catalyst sites that would significantly increase cracking reactions, light end production, and n-paraffin isomerization. Therefore, the fluoride, chloride, and other unwanted chemicals such as Sulfur and heavy metal levels should be less than one ppmwt (Parts Per Million by weight) in the dehydrogenation feed. Separation of these undesirable compounds is done in the hydrotreating process using the hydrogen produced in the dehydrogenation unit.

![Figure 1. Paraffin Dehydrogenation Unit (8).](image)

The hydrotreating unit is founded based on the “Unionfining license”. Figure 2 provides a generic view of the flow scheme of a “Kerosene hydrotreating unit”. The feed is exchanged with reactor effluent, mixed with recycle hydrogen, and then heated to reaction temperature in a fired heater. Afterwards, the combined feed flows through the reactor, which contains the catalyst that accelerates the reaction. The reactor effluent is cooled in exchange with the feed and then within a series of coolers before being separated in a vapor-liquid separator. The vapor portion is recompressed, combined with fresh hydrogen, and returned to the reactor feed. The liquid portion is fed to a fractionator, stripped of light ends, H2S, and NH3 (8).

![Figure 2. Kerosene Hydrotreating Unit (KHT)(8).](image)
The hydrotreating process reduces the sulfur and nitrogen to less than 0.5 wt ppm and the metals to undetectable levels (6). Makeup hydrogen is added to the reactor effluent stream before it enters the reactor product's condenser. The makeup hydrogen is obtained from the hydrogen plant and the dehydrogenation unit. Since, kerosene hydrotreater operates at a pressure of 59 kg/cm², the make-up hydrogen must be boosted to unit pressure by makeup compressor. The makeup compressor for the hydrogen from the dehydrogenation unit is a four-stage reciprocating compressor. Hydrogen from the dehydrogenation unit recycle gas stream is available at a pressure of about 2 kg/cm² and enters the suction at the first stage of the four-stage compressor, and stripped gas from the low-pressure flash drum enters the 3rd stage suction.

The four-stages reciprocating compressor increases the make-up gas pressure from about 2kg/cm², to the reactor product separator pressure of about 59 Kg/cm².

As previously mentioned, even the presence of a small amount of hydrogen chloride in the net hydrogen gas can cause problems with process and equipment, such as corrosion in equipment such as pipes, valves, and compressors. Classically, a chlorination agent is injected during catalyst production and regeneration in the oxychlorination process to restore the optimal metallic phase dispersion of the platinum-based catalyst and restore a typical chlorine content of 0.9-1.1 weight percent on the catalyst. This typically leads to hydrotreating make-up gas chlorine content of about one ppmw (Parts Per Million by weight). Since the hydrogen gas from dehydrogenation unit contains chlorine, entering the make-up compressor suction, the main chlorine contributor is hydrotreating make-up gas, which leads to exacerbated issues of green oil formation, corrosion, and fouling.

1.2. Previous reviews

Similar problems have been observed in some industries. The same kind of liquid was found in a Korean refinery complex. The problem was solved by installing a chloride absorber at the outlet line of the reduction chamber. Special absorbent in a fixed-bed vessel can remove small quantities of chloride as a trapping material in liquid or gas streams (6).

A non-regenerative promoted alumina is the right choice for the removal of hydrogen chloride in the gas phase. A promoted activated alumina is designed to trap both inorganic and organic chloride impurities in a process stream. Some companies have also recommended their adsorbents which achieves up to 99% chlorine removal efficiency and reduces the operating cost of a CCR Platforming unit.

Karimi and Mohamadmoradi (9) have also done a feasibility study to investigate ways to reduce green oil production using a hierarchical analysis with the help of Expert Choice software. They have selected three activated alumina adsorbents, enhanced alumina, and the combination of carbon fiber and activated carbon. They have also indicated that the hybrid of carbon fiber and activated carbon alternative was selected as the best adsorbent with 35.3% priority over other adsorbents.

2. Observations and Discussion

According to the process mentioned earlier, hydrogen gas from the dehydrogenation unit enters the make-up compressors to enter the hydrogen cycle of the hydrotreating unit. The hydrogen-gas pressure must be increased to 59 kg/cm² and injected into the hydrotreating reaction loop. The make-up compressors are four-stage reciprocating types, where the pressure ratio for each stage is approximately 2.5. The first stage suction pressure is 2.58 kg/cm². Typically, due to the low working pressure for the first and second stages of these compressors, observations at the maintenance program did not show serious problems.

The most common problems which lead to unscheduled maintenance of these compressors, according to the maintenance history, are the increase in discharge gas temperature and a decrease in the overall flow of the compressors. In some cases, where the compressors are forced to stop operation, investigations of the components have revealed some kind of chemicals covering the valves and inside of the cylinders of first and second stages. Fouling formed in these stages is shown in Figures 3 to 5.
The second stage’s rider ring band measurement by using feeler gauge has shown that the wear rate was high, and piston rings must have been changed. The chemicals which covered the first stage were powder likes, and the second stage components were covered with some kind of sludge. In this investigation, liquid oil was found in the third stage cylinder too, and the valve plate was covered with coked hydrocarbon. The valves have been liquid tested at the workshop, and all of the valves have been rejected. The valve components observations have shown that part of the valve ring was damaged. Also, the springs were broken or were not found in the valve assembly. Moreover, all the packing rings were covered by previously-mentioned deposits.

In this case, analysis of fouling sample, taken from compressor’s components, was an excellent method to diagnose and analyse these problems. This problem was repeated several times, but often, the amount of sample was not enough for laboratory tests. In one case in which enough sample was available for analysis purposes, the deposit samples were sent to an accredited laboratory for X-ray fluorescence (XRF) based on ASTM E 1621-13 standard and X-ray diffraction (XRD) based on BS EN 13925-1 standard analysis. The fouling sample of the compressor contained 35.2 weight percent of chlorine and 27.5 weight percent of iron. Also, sulfur, calcium and phosphor is detected. The test results are shown in Table 1 and Table 2.
Figure 4. Fouling formation in second stage of make-up compressor, a) on the valve b) in the cylinder c) on the valve cover.

Figure 5. a) Fouling on the gas packing rings b) defected valve.

Table 1. XRF Semi-Quantitative fouling analysis results based on ASTM E 1621-13(10)

| Component | L.O.I\(^a\) | Fe  | Cl  | S   | Ca  | P   | Si  | Al  |
|-----------|-------------|-----|-----|-----|-----|-----|-----|-----|
| Mass      | 30          | 27.5| 35.2| 5.3 | 0.26| 0.26| 0.08| 1.4 |

\(^a\) Loss Of Ignition measured by heating the sample for 1.5 hours in 950 °Celsius
Due to the hydrotreating process characteristics, identifying small amounts of sulfur, phosphor, and calcium compounds in fouling samples are predictable. But results of the analysis declared that significant amounts of chlorinated compounds have been identified in the fouling samples. Also, the presence of iron chloride compounds indicated that this chemical has caused corrosion in the compressor components resulting in the creation of aforementioned corrosion product.

Table 2. XRD fouling analysis results based on BS EN 13925-1(11)

| Component | Iron Chloride Hydrate | Iron Chloride Hydrate | Sulfur |
|-----------|-----------------------|-----------------------|--------|
| Chemical  | FeCl₂·2H₂O            | FeCl₂·4H₂O            |        |
| Formula   |                       |                       |        |

The dominant metal in the fouling composition is iron at 27.5 weight percent content. This suggests that the residue of the particulate analysis is mainly iron compounds. XRD analysis reported that the Iron Chloride Hydrate is the main part of the fouling sample. Therefore, the existing of chlorine trace in hydrogen, which was generated in the dehydrogenation unit, can form some deposits with iron compounds. It can also form green oil with hydrocarbon content of recycle gas, and settle in the compressor components.

To accurately detect the amount of chlorine in compressor components, samples of hydrogen gas, and condensates separated in the compressor stages, were analyzed. However, the chlorine content in these samples was less than the detectable level of measurement methods which have been used previously.

Among the analysis methods that have been used in this study, the following can be applicable:
- Make-up hydrogen gas analysis using Dräger method (12) based on ASTM D4490 (No chlorine compounds were detected in this analysis.)
- Analysis of hydrotreating unit feed condensate samples separated in compressor drain paths. (Test results are shown in Table 3)
- Analysis of sour water separated from hydrocarbons in hydrotreating unit separator. (Test results are shown in Table 4)

Table 3. Results of Analysis of hydrotreating unit feed and condensates samples from compressors drain paths based on ASTM D4929(13)

| Test Method       | Sampling Points                          | Hydrotreating Unit Compressor Drain | Dehydrogenation Unit Compressor Drain | Kerosene Feed of Hydrogen unit |
|-------------------|------------------------------------------|-------------------------------------|---------------------------------------|--------------------------------|
| ASTM D4929        |                                          | <1                                  | <1                                    | 2                              |

Table 4. The test result of sour water separated in hydrotreating unit separator based on Standard Method 4500(14)

| Test Method       | Sour Water Chloride Content, mg/l |
|-------------------|----------------------------------|
| Standard Method 4500 | 1                                |

The above analyses results showed that the chlorine detected in compressor fouling was not detectable in any of the other liquid and gas stream samples as mentioned above, so in this case, the
only reliable method for chlorine detection is the analysis of the fouling in compressor components during repair procedures.

For more reliable definition of fouling source, a more accurate analysis of the fouling has been done after 9 month of the compressor service. In this case, the sample X-ray fluorescence (XRF) has been done in two stages: before testing the loss of ignition (L.O.I) and after testing the loss of ignition (L.O.I), for which results are presented in Table 5.

| Component | L.O.I (%) | Fe₂O₃ | Cl | SO₃ | CaO | I₂O₃ | MnO | SiO₂ |
|-----------|-----------|-------|----|-----|-----|------|-----|------|
| Before L.O.I Test | 54.42 | 34.4 | 8.25 | 2.8 | 0.04 | 01 | 0.08 | N.D. |
| After L.O.I Test | 0 | 98.1 | 0.16 | 0.14 | 0.35 | 24 | 0.03 | 0.98 |

* Loss Of Ignition measured by heating the sample for 1.5 hours in 950 °Celsius

As it shown in the table, the chloride content of the samples changes before and after testing the loss of ignition (L.O.I). From this analysis, it is inferred that there are two types of chlorine compounds in the sample:

- Organic chlorinated compounds that have loss during Loss of Ignition (L.O.I) test.
- Inorganic chlorinated compounds, which remains after the Loss of Ignition (L.O.I) test.

It is important to note that most of the chlorinated compounds in the samples are organic. These compounds can be made by the polymerisation reaction in which green oil is generated. It seems the best strategy to tackle this issue was to remove chloride from this hydrogen stream utilizing a specific adsorbent. For this reason, an action plan has been defined to implement a chloride guard bed on the hydrogen gas stream from the dehydrogenation reactor.

Some procedures to inhibit chloride in the process gas have been suggested by licensors, which are discussed in the Introduction. However, to get the best result, it is necessary to survey and encounter this problem from different aspects and utilize suitable solutions. For this reason, a closer look at the solutions and their pros and cons is of high importance. To get best approaches, the cost calculation of each proposed solution and the assessment of solution’s reliability is crucial. It is necessary to mention that the fixed capital investment and maintenance costs of these chloride guards must be calculated and compared to the other solutions.

Therefore, other solutions should be considered. The first and the most vulnerable part of the reciprocating compressors due to the history of downtimes are the suction and discharge valves, so alternating the valve type for a more reliable, efficient, and robust type is an option. One of the most comfortable options for the more reliable valve is to upgrade the valve internals using robust material for rings and springs, so that compressors’ internal design does not change with an upgrade in the valve’s internal components. However, for severe unwanted chemical entrance into the compressors, which make more issues, it is suggested to replace ring-type valve by poppet type ones. By this change, valves utilize a high lift area and aerodynamic flow path. The valve lifetime can increase two times due to its design. In this procedure, the design of the compressor valves will be manipulated.

Wearing non-metallic parts like pressure rings, rider rings and sealing rings that can withstand harsh environments, is a solution that can improve components life and reliability. Employing a more suitable material composition such as polytetrafluoroethylene (PTFE) alloy with a high-performance filler or proprietary-blend low-creep PTFE are the preferred materials.

Because of the higher temperature and pressure in the third and fourth stages, as well as the difference in process conditions of these stages due to the addition of stripped off-gas from hydrotreating flash drum to the third stage, the above-mentioned enhanced material has been selected.
for these stages of the compressor. In this way, the upgrade in materials increases the lifespan of the pressure and the rider rings from 1000 hours to 10000 hours on average. Therefore, it is reasonable to use these materials for non-metal components of the first and second stages.

The aforementioned issues would happen in case it is not possible to prevent unwanted chemicals entrance in the process lines. For reducing the maintenance costs, compressor’s monitoring is a priority. By diagnosing the malfunctions of compressors at the right time, unscheduled shut-downs can be prevented. For instance, by using a pressure vs. volume graph plus temperature monitoring, it is possible to identify the exact defected valves or pressure rings. By utilizing rod drop, the decrease in the rider band can be easily detected.

The initial set-up cost for compressors’ condition monitoring is high. However, compared to the other unwanted and imposed maintenance costs, it will be more logical to utilize the monitoring systems. For a long-term solution, it seems that a combination of the solutions mentioned above, is a perfect choice for more reliable process conditions and continuous production. Furthermore, more analytical studies, investigations, and cost calculations are necessary to choose the best procedure to achieve the best process stability and reliability.

3. Conclusion
 Chlorides existing in recycle and make-up hydrogen gas produced in dehydrogenation units causes problems such as corrosion and fouling inside downstream pipes, compressors and reactors, disrupts the process operation, poisons the catalysts, and decreases the reliability of the process. The analysis revealed that the only reliable chlorine detection method is analyzing the foulings in compressor components during repair procedures. The composition of these sediment samples tested by X-ray fluorescence (XRF) and X-ray diffraction (XRD) indicates that they contain significant amounts of chlorine and iron compounds. XRD analysis reported that the iron chloride hydrate is the main part of the fouling samples. More accurate analysis of the fouling highlights the fact that most of the chlorinated compounds in the samples are organic.

For more reliable compressors and process conditions, according to investigations, experiences, and researches, a combination of these solutions can be applied:

- Chloride removal from process streams. It seems that the best way to prevent these problems is to eliminate the source of the problem. Similar experiences show that after removal of chloride from the process, the aforementioned problem was not observed anymore. In this way, an action plan is defined to implement a chloride guard bed on the hydrogen gas. Particular types of adsorbents loaded in a fixed-bed vessel enable removing small quantities of chloride in liquid or gas streams.
- Using a more suitable material for non-metal wearing parts like piston rings, sealing rings, and metal components that can withstand harsh environments, or contaminated process gas, can be a solution to improve components life and reliability.
- Implementing a condition monitoring system to measure rod drop, P-V diagram, and temperature monitoring to diagnose compressors problem before any catastrophic failure happens due to compressors malfunction.
- Valve type alternation from ring-type into poppet type; poppet type valves utilize a high lift area and aerodynamic flow path. The valve lifetime can be increased drastically due to its design.

One of the important points about the solutions is that with the observation of problems in both recycle and make-up hydrogen gas equipment, selecting the optimal location for the chloride guard has a significant impact on the effectiveness of chloride removal system. Because of the high volume of recycled gas in the Pacol and CCR hydrogen recycle loop, installation of chloride guard bed on
hydrogen circulating gas can deteriprate the advantages of this solution. Therefore, to achieve the best solution, more economic investigations are required on this subject.

4. Acknowledgments
We would like to express our special thanks to Iran Chemical Industries Investment Company (ICIIC) executives who provide us with the opportunity to accomplish this project.

5. References
[1] Bloch HP and Godse A 2006 Compressors and modern process applications (John Wiley & Sons) pp 3-20
[2] Bloch HP and Hoenfer JJ 1996 Reciprocating compressors: operation and maintenance (Elsevier)
[3] Griffith WA and Flanagan EB 2001 Int. Conf. on 30th Turbomachinery Symposium Online, Continuous Monitoring Of Mechanical Condition And Performance For Critical Reciprocating Compressors (Texas: Texas A&M University Turbomachinery Laboratories).
[4] Leonard SM 1996 Hydrocarbon processing Increase reliability of reciprocating hydrogen compressors pp 67–74
[5] Api Standard 618 Fifth Edition 2007 Reciprocating Compressors for Petroleum, Chemical and Gas Industry Services (washington DC, USA: American Petroleum Institute) p 69.
[6] Karan OK Ay Ma Kahrman K and Selmen A 2013 Petroleum technology quarterly Combating green oil formation in a CCR reformer p 18.
[7] Kim B Uk Lee S and Lee S 2017 Int. Conf. on 46th Turbomachinery Symposium Reliability Improvement for Booster Reciprocating Compressor In CCR Reformer (Texas: Texas A&M University Engineering Experiment Station Turbomachinery Laboratory).
[8] Meyers RA 2016 Handbook of petroleum refining processes (McGraw-Hill Education) pp 5.13 8.37.
[9] Karimi A and Mohamadmoradi HR 2020 Iranian Chemical Engineering Journal Study of Reducing the Amount of Green Oil in the CCR Plant of Oil Refinery Unit 18(107) pp 6-14.
[10] ASTM E1621-13 2013 Standard guide for elemental analysis by wavelength dispersive x-ray fluorescence spectrometry (West Conshohocken, PA).
[11] BSI. BS EN 13925-1 Standard 2003 Non-destructive testing X-ray diffraction from polycrystalline and amorphous materials General principles. (British Standard Institute)
[12] ASTM D4490-96 2016 Standard Practice for Measuring the Concentration of Toxic Gases or Vapors Using Detector Tubes (West Conshohocken, PA).
[13] ASTM D4929-19 Standard Test Method for Determination of Organic Chloride Content in Crude Oil (West Conshohocken, PA).
[14] 4500 Cl-Chloride standard methods for the examination of water and wastewater 1999 Standard Methods for the Examination of Water and Wastewater (American Water Works Association).