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Ion Chromatography for Determining Chloride Contents in Gas, Water and Condensate Samples from Gas-Condensate Reservoir

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Abstract: The minor and trace amounts of chloride content in nine samples of natural gas, water and condensate were quantitatively determined via ion chromatography(IC). The selected samples were collected from Egyptian Western Desert gas-condensate reservoir with the aim of studying the field analysis procedure and the performance of the gas plant. IC gives an accurate determination of chloride content in the gas production process in order to contribute in the knowledge of technologies used for chloride removal to produce high-quality natural gas and hydrocarbon liquids. This study is based on the analysis and evaluation of chloride ions present in gas and liquid samples obtained from different stages of field-processing operations.

Keywords:- Chloride content, Natural gas, Water, Condensate, Ion Chromatography, Egyptian gas plants and Chloride content

Introduction

Contamination of petroleum with inorganic anions, such as chloride, may lead to reduced petroleum quality due to the formation of plugging deposits and cause corrosion in components of gas-condensate plant [1] that is in contact with the petroleum fractions. Ion chromatography (IC) with suppressed conductivity detection is the simplest approach for determining inorganic anions in the product of petroleum fractions such as natural gas, condensate, oil and separated water , enabling the detection of the target anions with a single injection, reasonable analysis times, and minimal or no sample preparation.

The processing of natural gas consists of the separation of some of the components present at the well exit, such as water, acid gases and heavy hydrocarbons, to adjust the gas to transport or commercials specifications [2]. In simple terms, the gas processing industry gathers, conditions and refines raw natural gas from the earth into saleable, useful energy forms for use in a wide variety of applications [3].

All natural gases contain water vapor to some extent [4-7], which comes from the water phase in the reservoir. Concentration of such water vapor range from trace amounts to saturation [8]. This water vapor is the main source of the chloride ion in natural gas and its concentration depends on the concentration of the chloride ions in the reservoir water phase. The vapor cause operational problems such as hydrate formation, corrosion, high pressure drop, and consequently slugging flow and reduction in gas transmission efficiency [9]. In particular, moisture level in natural gas must be maintained below a certain threshold so as to prevent hydrate formation and minimize corrosion in transmission pipelines [10-13].

Experimental

As the natural gas stream flows from the well it passes through two main separators Tr-1 and Tr-2 where gas, condensate and water streams are separated and subjected to processing. The sample analysis will require the following information from each sample.

Location, operating conditions of pressure and temperature recorded in addition to Chloride content. The descriptions of the collected samples are presented in Tables 1.

A – For natural gases

There is no standard method to analyze the chloride ions in gas stream. Since the source of the chloride in the gas is that the dissolved water, therefore we extract such water and analyze the chloride in such extracted water by ion chromatograph.

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Table 1: List of Samples from Egyptian Western Desert Gas-Condensate Plant

Sample No	Type of Fluid	Sample Name	Description	Conditions	
				P, bar	T, °C
1	Water	W1 (V-2011)	Water Outlet from Inlet Sep V-2011	70.0	79.0
2	Water	W2 (V-2021)	Water Outlet from Inlet Sep V-2021	70.5	81.0
3	Gas	G1 (V-2011)	Natural Gas Outlet from Inlet Sep V-2011	70.0	79.0
4	Gas	G2 (V-2021)	Natural Gas Outlet from Inlet Sep V-2021	70.5	81.0
5	Cond.	C1 (V-2011)	Condensate Outlet from Inlet Sep V-2011	70.0	79.0
6	Cond.	C2 (V-2021)	Condensate Outlet from Inlet Sep V-2021	70.5	81.0
7	Gas	G3 (V-2002)	Natural Gas Outlet from V-2002	22.7	59.0
8	Cond.	C3 (V-2002)	Condensate Outlet from V-2002	22.7	59.0
9	Water	W3 (V-2002)	Water Outlet from V-2002	22.7	59.0

Extraction Method

1. The cylinders were washed carefully with a proper solvent followed by deionized water and then dry it and evacuated by connecting them to the vacuum pump.
2. Some volume of deionized water was placed in beaker of 500 ml and inserted the bottom cylinder valve into such water and opened it to suck a sufficient amount of this water and then closed the valve, the cylinder was checked for 1hr.
3. The valves of the cylinder were opened and discharged the water into a bottle and analyzed it by ion chromatograph to measure any amount of chloride ions in the used water.
4. Steps 2 and 3 were repeated until the chloride ions in water is nil or as low as possible, 100 ml of deionized water was insert in the cylinder and allowed it to settle down.
5. The upper cylinder valve was connected to the suction pump to evacuate the air inside the cylinder to facilitate the entrance of the gas volume into the cylinder.
6. 300 cc volume of gas sample was put on the gas meter and connected it the upper valve of the cylinder and opened it to suck such volume of gas and closed the valve. The gas water mixture was checked for 1 hr.
7. The water was discharged from the cylinder into a bottle and analyzed by ion chromatography to measure the chloride ion concentration.

Ion Chromatography (IC)

Water containing chloride ions were analyzed using Dionex model DX 600 Ion Chromatograph (IC) connected with Electrochemical detector (Dionex, Ed50) using high capacity column [ASTM D 4327]. The column used is Ion Pac AS9-HC (4X 250nm), the eluent 9.0 mM Na_2CO_3 at flow rate 1 ml min $^{-1}$, the injection volume is 10µl.

B – For condensates

The chloride ions present in condensate samples were determined according to ASTM: D 3230-89 by Electrometric method. This test method is based on the conductivity of a solution of condensate in a polar solvent when subjected to an alternating electrical stress. The sample is dissolved in a mixed solvent and placed in a test cell consisting of a beaker and two parallel stainless steel plates. An alternating voltage is impressed on the plates and the resulting current flow is shown on a milliammeter. The salt content is obtained by reference to a calibration curve of current versus salt content of known mixtures.

C – For water samples

The anions in water sample were determined experimentally according to ASTM: D-4327 using the same method conditions used in the analysis of the water extracted from gas samples. Each water sample was filtered using Whatman No.42 filter paper and diluted with deionized water prior analysis. Total of five and six mixed anion standard solutions were used for instrument calibration.
Aliquots of the water samples were diluted with measured volume to be within the measuring range, and 10µl of the solution was injected into the column.

Results and discussion

The major role of gas-condensate plants is to process both associated and non associated gas to produce high-quality natural gas and hydrocarbon liquids. Sale of liquids provides a significant portion of the income from these plants. Plants optimize profits by adjusting the fraction of liquids recovered while meeting the specifications for the natural gas.

Egyptian Western Desert Gas-Condensate Plant has tow separators at which gas, condensates and water were separated under certain conditions of pressure and temperatures. Field operations may include dehydration, CO_2 and H_2S removal, and compression. Unless the gas is completely free of any liquids, once it enters the plant, the gas and liquids go into inlet receiving, where the initial gas-liquid separation is made. Condensed water, hydrocarbon liquids, and solids are removed. Water and solids are processed for disposal, and the hydrocarbon liquids go on to liquids processing (3).

The studied gas samples were taken from the outlet separators and the collected liquid samples include condensate and water from outlet separators. This study depends on collecting the samples, analysis and evaluation of the inorganic chloride ions in the studied gas plant in order to study its performance of gas plant. Table (1) shows the collected gas and liquid samples under study.

1. Water samples from outlet separators Tr-1 and Tr-2

The chloride content of the water samples from outlet separators Tr-1 and Tr-2 and from vented gas V-2002 are 47947, 55344 and 87.25 mg/l respectively. The data obtained show relatively high concentrations of chloride ions indicating the higher salinity of these water samples.

2. Natural gas samples from outlet separators Tr-1 and Tr-2 and from vented gas V-2002

There is some amount of condensate and water dissolved in each gas sample from outlet separators Tr-1 and Tr-2 and from vented gas V-2002, the chloride ions contained only in water, so any chloride contents in gas and condensate are accompanied with the water dissolved in gas and condensate samples. The efficiency of measuring the chloride content in gas samples depends mainly on the method of water extraction from gas sample, because there is no standard method for measuring the chloride contents in gases [14]. The concentration of the chloride ions in natural gas samples from outlet separators was given in Table 2. There is a difference in chloride content in the two gas samples from the two studied separator due to the operating conditions and the dissolved salt which affecting the amount of chloride in natural gas. Solubility of water increases as operating temperature increases and decreases as operating pressure increases [3]. Therefore the higher chloride concentration of the gas from outlet separator Tr-1 due to it contains excess water which may be due to the low separator efficiency.

Table 2. Chloride contents in water and gas samples from separators V-2011 and V-2021 and vented gas V-2002

Analytical Parameters	Results
Chloride content in **W1 (V-2011)**	47947
Chloride content in **W2 (V-2021)**	55344
Chloride content in **G1 (V-2011)**	282.7
Chloride content in **G2 (V-2021)**	266.4
Chloride content in **G3 (V-2002)**	251.5
Chloride content in **G4 (V-2002)**	87.25

3. Condensate samples from outlet separators V-2011 and V-2011

The condensate samples from the three studied points in gas plant contain gas and water dissolved in it but in different ratios, the low percentage of water in the second separator Tr-2 reflects its high performance compared with separator Tr-2. The increase in the percentages of dissolved gas in condensates accompanied with increase in chloride ion in the order V-2002 > Tr-2 >Tr-1. The chloride in stream composition means chloride in the condensate composition including the chloride in water and dissolved gas, the chloride in stream represents the highest value in the first separator V-2011 followed by second separator V-2021 and V-2002. These result due to the decrease in water contents in the same order. The results of the chloride analysis of the condensate stream from the outlet separators Tr-1, Tr-2 and V-2002 are given in Table (3). The condensate samples contain high levels of chloride ion concentrations. In addition, it was found that these condensate streams contain different amounts of free water as given in Table (3), which indicate that there is a carryover in the separators. The chloride content in condensate samples increase from V 2002 to Tr-2 and Tr-1 because of the free water in V 2002, is higher than that in Tr-2 which is higher than that in Tr-1 which explains the higher chloride contents in V 2002 followed by Tr-2 and Tr-1, which matches with the results for the gas and condensate samples since the expected source of chloride in the hydrocarbon gases or liquid is the associated water moisture.

Table 3. Chloride contents in condensate samples from separators V-2011, V-2021 and V-2002

Analytical Parameters	Separator V-2011 (Tr-1)	Separator V-2021(Tr-2)	Outlet from V-2002
Phases:			
Gas, wt%	4.234	4.623	9.590
Condensate, wt%	83.326	90.017	90.134
Free Water, wt%	12.44	5.360	0.276
Chloride content in Dissolved gas, ppm	32.0	37.2	115.07
Chloride in Condensate, ppm	4.5	7.8	0.78
Chloride in Free Water, ppm	26792.3	36783.1	7463
Chloride in Stream, ppm	3332.9	1980.3	32.34

Conclusion

- The accuracy of the method used for measuring the chloride contents ion gas samples depends mainly on the method of water extraction from gas sample, because the water content is the source of chloride in natural gas and condensate.
- The salts dissolved in the liquid water in equilibrium with natural gas reduce the water content of the gas and this reflected on the chloride ion content..
- There is a difference in chloride content in the gas samples from the two studied separator due to the operating conditions and the dissolved salt which affecting the amount of chloride in natural gas. Solubility of water increases as operating temperature increases and decreases as operating pressure increases the chloride content in condensate samples increase in the order V 2002 > Tr-2 > Tr-1 because of the free water in V 2002, is higher than that in Tr-2 which is higher than in Tr-1.
- Ion chromatography is a good analytical tool for accurate quantitative determination of chloride content in the gas production process in order to contribute in the knowledge of technologies used for chloride removal to produce high-quality natural gas and hydrocarbon liquids.

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