

# Monitoring Greenhouse Gases and Their Pollutions in Sarakhs Region Influenced by the Sourest Natural Gas Resource in the Middle East

Nader Nabhani<sup>1</sup>, Mojtaba Mirdrikvand<sup>2</sup>, Saeedeh Imani Moqadam<sup>2</sup>, Amirali Rezazadeh<sup>3</sup> & Seyed Alireza Sakaki<sup>2</sup>

<sup>1</sup> Faculty Member of Petroleum University of Technology

<sup>2</sup> Researcher at Research Center of Petroleum University of Technology

Correspondence: Saeedeh Imani Moqadam, Petroleum University of Technology, Abadan, Iran. Tel: 98-935-728-0659. E-mail: Saeedeh.imani@gmail.com

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## Abstract

Shahid Hashemi-Nezhad Gas Processing Company (S.G.P.C.), located in Sarakhs region of Iran, processes wells that consist of the sourest gases in Middle East. The gas entering the company from gas wells includes 3.5 percent H<sub>2</sub>S and 6.5 percent CO<sub>2</sub> that is quite rare among similar wells for sweetening such large quantities as it does. As a result, greenhouse gases and their possible harmful results are sometimes unavoidable in the area. In this study, greenhouse gases in Sarakhs region, the atmosphere of the company and also the output metering of S.G.P.C. were monitored and analyzed in a three-month period, considering elimination of preliminary contaminants in the sweetening process. Later, sources, fluctuations and deviations of greenhouse gases from global standards were observed and analyzed.

**Keywords:** greenhouse gases, S.G.P.C., Overhaul, standard

## 1. Introduction

Iran produces 2.1% of global greenhouse gases and as a result is ranked 30th in the world. It has been estimated that burnt gases in oil and gas production companies in Iran spread about 35% of the whole greenhouse gases in the country (Iranian Official Report, 2009). Diverse pollutant sources exist in oil and gas production regions, some of which enter atmosphere through flaring. Although the amount of contamination from flares depends of the type of materials, mixtures and combustion efficiency of the flares, most of the combustion processes in the flares result in entering gas contaminations majorly including NO<sub>x</sub> and SO<sub>x</sub> and CO<sub>x</sub> mixtures into the atmosphere (Pereira et al., 1998; Shuman, 1998).

Gas turbines of the motors spread huge amounts of pollution since they are not equipped well with air pollution control systems (Bureau of Resource Sciences, 1998). The gathering of these gases in the atmosphere results in the atmosphere to keep more energy and warmth in itself and damage agriculture, underground waters, and some animals. These gases are mixed with water in appropriate conditions in the atmosphere and would result in acid rains and soil erosion and construction damages consequently (Environmental Protection Agency, 2000).

Investigation and prevention of increasing greenhouse gas sources have been mentioned and followed in lots of pioneer industrial countries due to global warming and other harmful effects of these gases (Bureau of Resource Sciences, 1998; Environmental Protection Agency, 2000). Release of Carbon dioxide and greenhouse gases is a great concern for environmentalists all over the world. Main pollutants influencing human health which are majorly caused by fossil fuels consumption include: Carbon monoxide, Sulfur dioxide, Nitrogen oxides, ozone, particulates, hydrocarbons, and volatile organic compounds (VOCs).

The pollutants SO<sub>2</sub>, CO, and HC directly contaminate the atmosphere and enter the air from their source individually; however, secondary pollutants like photochemical smog, NO<sub>2</sub> and Ozone are commonly produced from preliminary ones under sun wave effects (Glenn, 2011; Mor et al., 2006; Hellebrand, 1998).

Precise analysis of pollutants produced from an oil processing company could warn officials and environmentalists of the conditions. In this study, greenhouse gas sources of Khangiran Gas Refinery are analyzed in detail. Flares, gas turbines, and combustion process of gases of flares are the major sources that must

be investigated to detect and eliminate oil condensate and extra gases and get rid of gases containing sulfur compounds such as H<sub>2</sub>S.

## 2. Monitoring the Greenhouse Gases in S.G.P.C.

Investigations in Khangiran gas refinery was done over greenhouse gases through daily sampling in monitoring stations located over control room, and safety and fire fighting units. The results are classified and shown based on the measurements of gases (Hayhoe et al., 2010). Characterization of air pollutant in a natural gas processing plant are shown in Table 1.

Table 1. Characterization of air pollutant in a natural gas processing plant (Carson & Mumford, 2002)

Process	Air Pollutant
Catalytic Cracking	Particulates
	Carbon Monoxide
	Sulfur Dioxide
	Nitrogen Oxides
	Hydrocarbons
	Aldehydes
	Ammonia
Catalytic Reforming	Hydrocarbons
	Inorganic Chlorine
Sulfur Recovery Plant	Sulfur Dioxide
	Reduced Sulfur (H <sub>2</sub> S, CS <sub>2</sub> , COS)
	Hydrocarbons
Storage Vessels	Hydrocarbons
Fluid Coking	Particulates
Wastewater Streams	Hydrocarbons
Cooling Towers	Hydrocarbons
Equipment Leaks	Hydrocarbons
Blowdown System	Hydrocarbons
Distillation	Hydrocarbons
Steam Boiler, Process Furnace or Process Heater	Particulates
	Nitrogen Oxides
	Carbon Monoxide
	Sulfur Oxides
	Hydrocarbons
Compressor Engine	Carbon Monoxide
	Nitrogen Oxides
	Sulfur Oxides
	Hydrocarbons
Vessel Loading (Barge)	Hydrocarbons
Gasoline Rack Loading	Hydrocarbons

### 2.1 Volatile Organic Compounds (VOCs)

Over 26 percent of the pollution caused by VOCs is from oil and gas industry. The major part of this pollution in gas industry is released through transferring gases (Bylin, 2011). The main sources of VOCs spread in Khangiran are:

- Blow down and leakages of operating units (Gholishahi & Jafarzade, 2010).
- Venting pumps or other equipments that require venting (GAO, 2010).
- Automation systems that use gas pressure for operating.
- Compressors leakages (spinning and reciprocating compressors).
- Gas wells completion (Tamura, 2011; EIA-National, 2007).

The amount of released VOCs in Khangiran refinery was measured in a three month period and the results are illustrated in Figure 1. Thered line shows the global standard for VOC amount that should not exceed 0.24 ppm per three hours. However, once during the test period, it passed the standard limits. Decisions should be made to prevent such happening since even a small amount can sometimes cause irrecoverable damages to both human health and environment.

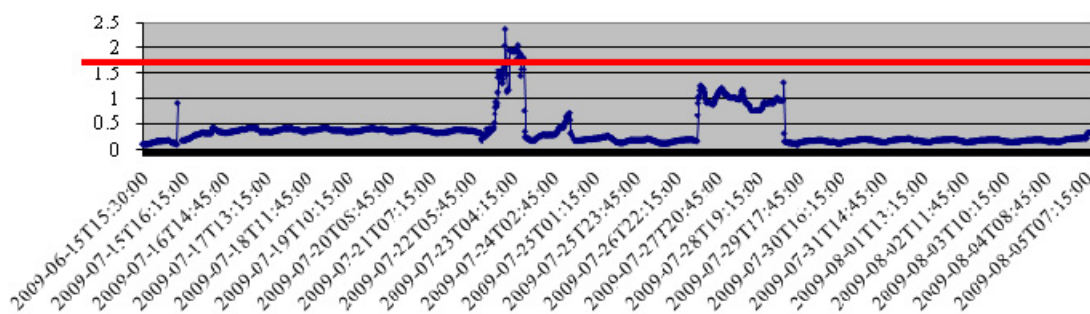


Figure 1. Released VOCs in a three month period

## 2.2 Nitrogen Oxides

$\text{NO}_2$  gases launch a cycle that would cause more than 2.5 times of the global standard of ozone production per hour in the environment of the company. Figure 2 illustrates the amount of  $\text{NO}_2$  released in a three month period of our study. The red line in the diagram exhibits the amount of standard  $\text{NO}_2$  in a year that should not exceed 0.053 ppm based on NIOSH standard. In addition, the standard of  $\text{NO}_2$  release in an hour is about 0.21 ppm.

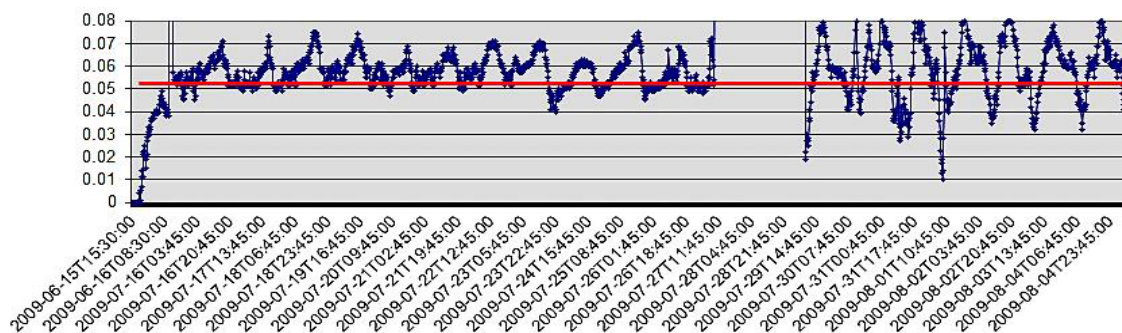


Figure 2. The amount of  $\text{NO}_2$  in a three month period

At critical conditions, the pollutant ozone (tropospheric ozone) is over three times of its global standard amount in SPGC. Tropospheric ozone is the molecule of ozone that absorbs dangerous waves of the sun in stratosphere layer of the atmosphere. When it is produced in lower layers of the atmosphere near the surface of the earth, it is recognized as a severe pollutant for the environment. It has extremely harmful impacts on both human health and agricultural industry (Seinfeld & Pandis, 1998).

$\text{NO}_x$  formation in S.G.P.C. is a result of three main causes:

- In addition to methane, ethane, water, and hydrogen sulfide in gas wells that feed the company, there is Nitrogen. Existence of Nitrogen was quite disregarded in the processes of the company. Molecules of Nitrogen leave the well and spring up the process without being much noticed. Through high pressure and temperature of

sulfur recovery unit (SRU), proper condition of oxygen and nitrogen reaction is created and then produced NO<sub>x</sub> enters the cycle of pollution.

b. Stacks and boilers of water and steam unit are a major source of NO<sub>x</sub> production due to two main reasons: the possibility of increasing excess air to more than the design amounts and high temperature of the flame; the first of which produces much Nitrogen for the process rather than what has been transmitted from gas treatment unit (GTU), and the latter is the activation energy from the Nitrogen (McInnes & Wormer, 1990; Zeldovich, 1946; Ozone formation in the troposphere, 2005). Figure 3 shows this effect in detail.

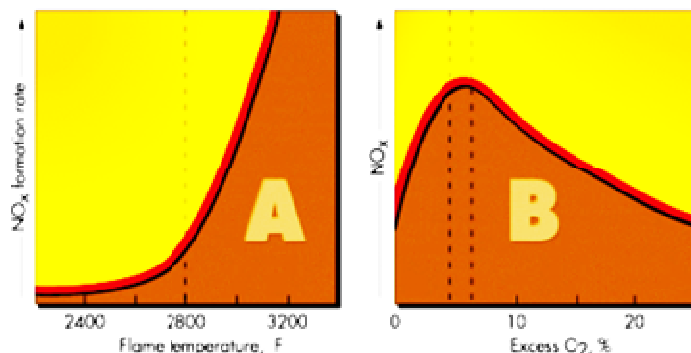


Figure 3. the amount of released NO<sub>x</sub> spread based on the flame temperature and injected excess air (Tamura et al, 2011)

c. In total shut down or overhaul of the units, the equipments are filled with Nitrogen. At the start up, assuming that Nitrogen is an innocuous gas, it is released to the environment through flaring or other ways. Monitoring the surrounding environment of the refinery and the region illustrates that the amount of NO<sub>x</sub> increases noticeably after the startup. Table 2 and Figure 4 demonstrate increased amount of NO<sub>x</sub> during overhaul.

Table 2. Gradual increase of produced ozone during overhaul

NO <sub>2</sub> (ppm)	SO <sub>2</sub> (ppm)	H <sub>2</sub> S (ppm)	O <sub>3</sub> (ppm)
0.047	0	0.132	0.258
0.049	0	0.113	0.260
0.054	0.124	0.005	0.337
0.053	0.123	0.017	0.333
0.057	0.378	0.041	0.334
0.059	0.378	0.035	0.335
0.057	0.378	0.041	0.334
0.065	0.378	0.001	0.342
0.063	0.277	0.001	0.340
0.071	0.376	0.004	0.342

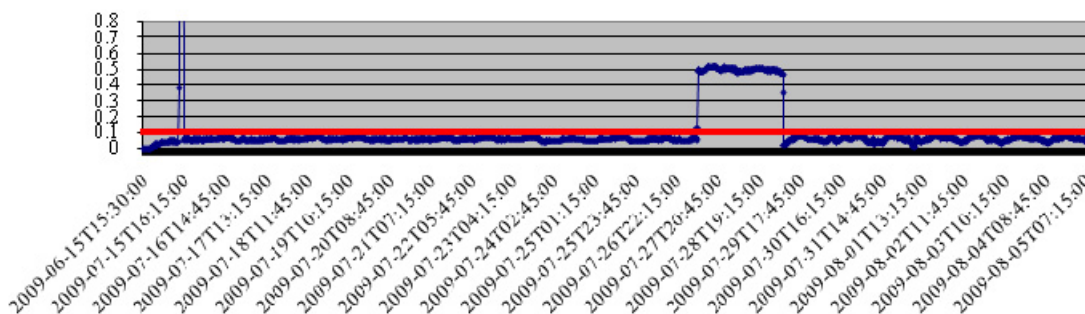


Figure 4. The increased amount of NO<sub>2</sub> during overhaul and its difference with the usual amounts (great scale of Figure 3)

The amount of NO<sub>x</sub> in the surrounding atmosphere of the company was quite little. Ozone quantity however, seems to be noticeable. Concluding from Figures 4 and 5, even a small quantity of NO<sub>x</sub> may cause production of an ozone amount which is over 2.5 times the global standard per hour in the region. As shown in Figure 5, the global NIOSH standard suggests 0.12 per hour ozone release as a harmless amount; however, the amounts in the area exceed the standards.

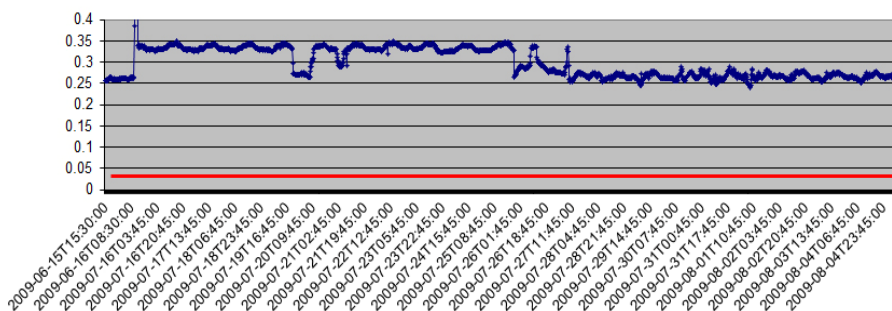


Figure 5. The average amount of produced ozone in the atmosphere of the company and surrounding

A chief portion of released NO<sub>x</sub> is NO that oxidizes in the atmosphere and produces NO<sub>2</sub>. The produced NO<sub>2</sub>, along with hydrocarbons in the presence of sun beams, creates photochemical smog (Staehelin et al., 2000). In addition, NO<sub>2</sub> can be compounded with hydroxyl radicals and form acid rains (Koebel, 2000). Besides, thermal and fuel Nitrogen oxides are other sources of NO<sub>x</sub> spread; the first is the result of Hydrogen and Nitrogen mixing in high temperature, and the latter is produced while combustion as a result of oxidized Nitrogen of the chemical formula of the fuel (Ogriseck, 2010).

Nowadays, Carbon monoxide removal in industrial processes has become a great concern. This process, if not controlled well, would result in NO<sub>x</sub> intensification. It is worth noting that based on our experiments comparing day and night conditions, sunlight plays a pivotal role in increasing ozone production.

### 2.3 Carbon Monoxide

Through monitoring of atmospheric measurement stations of Khangiran refinery, the amount of released CO was as shown in Figure 6. Based on NIOSH standard, the amount is logical at first; however, it passes the standard (35ppm/hour-9ppm/8hour) in the beginning of August. This increase is due to environmental effects and the maximal production rate of the company and the combustion processes in the company. As a result, the amount of fuel injection and the temperature of the combustions must be under precise supervision and control monthly based on the weather conditions. Through our study result, the rate of CO production was unjustifiable in that month. The observation illustrated that the results were due to inappropriate adjusting of boilers in that period.

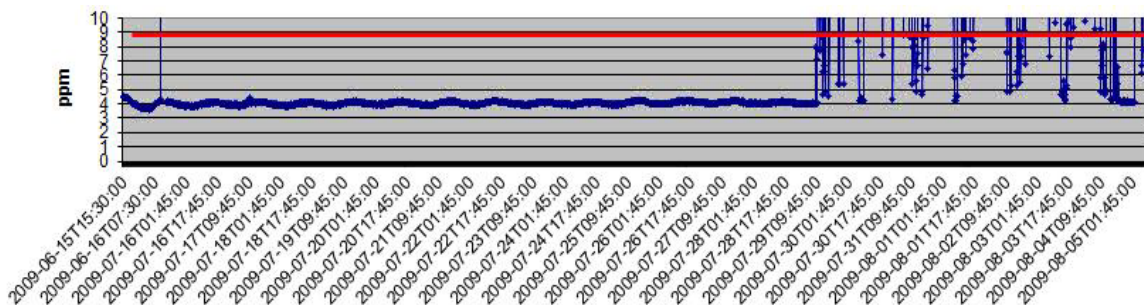


Figure 6. The amount of released CO in the atmosphere of the company

2.4 Hydrogen Sulfide

Concerning the influencing features and specifying proper sampling locations, the existing H<sub>2</sub>S was observed as well as other gases in the atmosphere of the company and the whole region. The feed gas of SGPC is a sour type and contains 10% acidic gases (6.5% CO<sub>2</sub> and 3.5% H<sub>2</sub>S). Therefore, it is well-equipped with complex controllers due to perilous effects of Hydrogen sulfide. Being rare in containing much Sulfur, there are only a few gas wells with the same conditions in the world (Reports of S.G.P.C, 2010); i.e. the wells we focused on were quite unique in the world. Owing to the fact that the sourest gas in the Middle East is extracted in Khangiran region, the Sulfur dioxide production through ‘Claus’ technology is of great significance. As a result, the amount of H<sub>2</sub>S derived compounds is controlled to a large extent. As illustrated in Figure 7, the oscillations will reach 0.15 ppm in amount.

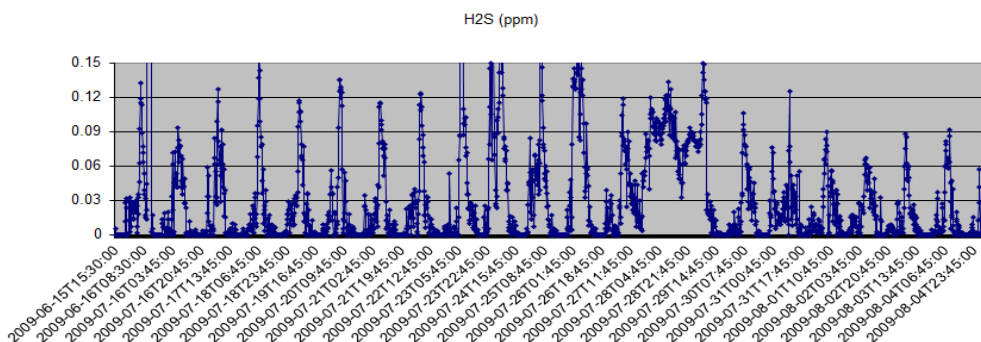


Figure 7. The amount of H<sub>2</sub>S in the atmosphere of the refinery in a three month period

Table 3 illustrates the purity of produced Sulfur from sour gas feed of the company. The derived compounds are sent for aggregation to be used and sold for experimental and industrial purposes. As demonstrated in the table, H<sub>2</sub>S amount will be decreased to none. In recycling Sulfur through ‘Claus’ process, acidic gas—a toxic product that is produced through natural gas refining- is formed to usable Sulfur and innocuous gas which is released to the atmosphere (Seeger, 2005).



Table 3. Final purity of the produced Sulfur in Khangiran refinery

Material	Volume percentage	Interval of change in production
ASH	0.0231	0.011-0.0454
Carbon and organic compounds	0.0391	0.040-0.0933
Sulfur	99.9378	99.865-99.945
Humidity and Volatility	0.11082	0.005-0.351
Acidity	0.001	0.0008-0.0012
Chlorine	0.0007	0.0006-0.0008
H <sub>2</sub> S	0	0

Analyzing the metering of the output gas of the company, less than 2.4 ppm of H<sub>2</sub>S was measured which is not a dangerous amount based on global standards. However, regarding the necessity of the company to continue nonstop working, the concentration of H<sub>2</sub>S exceeds 5 ppm in some cases due to Amine scarceness. Amines are the materials that should be used for gas sweetening.

### 2.5 Sulfur Dioxide

Nitrogen oxides and Sulfur dioxide are the most released gases in quantity. The amount of monitored SO<sub>2</sub> in the company's atmosphere in less than NIOSH standard according to Figure 8. As illustrated, it reaches 0.05 ppm as the maximum amount. The standard suggests an amount of 0.14ppm per 24 hours and 0.31 ppm during a year.

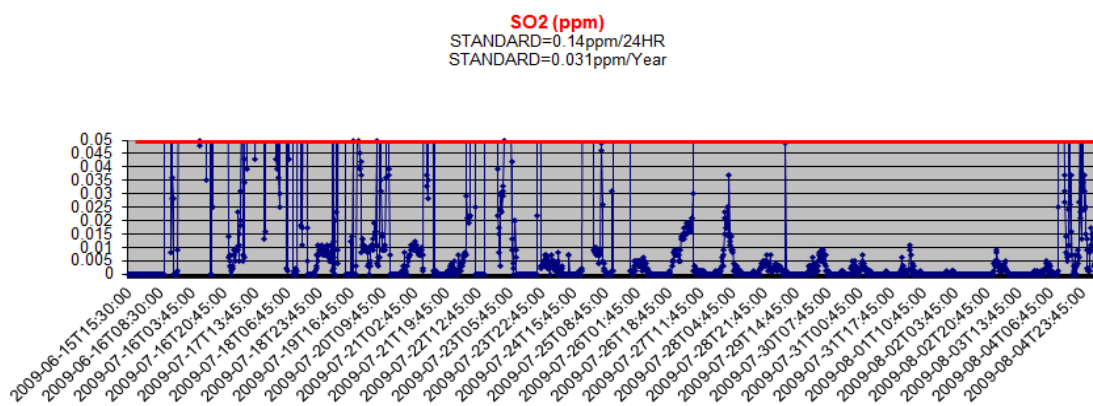


Figure 8. The amount of released SO<sub>2</sub> in the company's atmosphere in a three month period

### 3. Conclusion

Monitoring contaminations in a gas processing company is always of great importance since lots of direct and indirect pollutions might influence environment and human health. This study was conducted to measure amounts of greenhouse gases released in SGPC—which processes the sourest gas wells in the Middle East—and the region of Sarakhs where it is located. What matters the most is discovering the sourest sources of these pollutants and controlling them. Unavoidable gases like Nitrogen for instance, shall be used cautiously for purging processes. Preventing leakages of equipments like compressors will reduce the possibility of releasing VOCs, Carbon monoxide, and Sulfur dioxide to the atmosphere. In addition, formation of tropospheric ozone pollutant which is a result of Nitrogen release is quite dangerous and worrying for the environment. Controlling and minimizing released greenhouse gases are absolutely giant steps that should be taken after monitoring.

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