Société Tunisienne de l'Electricité et du Gaz

الشركة التونسية للكهرباء والغاز

Sulfur deposition in Gas Transmission Pipelines

WOC 3 Meeting

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STEG, TUNISIA

SUMMARY

- Introduction
- Sulfur deposition phenomena in Tunisian gas installations
- Theoretical review
- Understanding the phenomena
- Recommendations
- Conclusion

TUNISIA


9 300 Km
CANADA
UNITED STATES
RUSSIA
CHINA
INDIA
BRAZIL
AUSTRALIA
Greenland
ALGERIA
LIBYA
EGYPT
SUDAN
NIGERIA
MALI
NIGER
CHAD
ETHIOPIA
SOMALIA
SAUDI ARABIA
IRAN
KAZAKHSTAN
MONGOLIA
INDONESIA
PERU
BOLIVIA
CHILE
ARGENTINA
COLOMBIA
VENEZUELA
ANGOLA
SOUTH AFRICA
NORTH PACIFIC OCEAN
SOUTH PACIFIC OCEAN
NORTH ATLANTIC OCEAN
SOUTH ATLANTIC OCEAN
INDIAN OCEAN
SOUTHERN OCEAN
Antarctica
September 2008

TUNISIA:

Population: 11 millions habitants

Area: 164,000 Km2

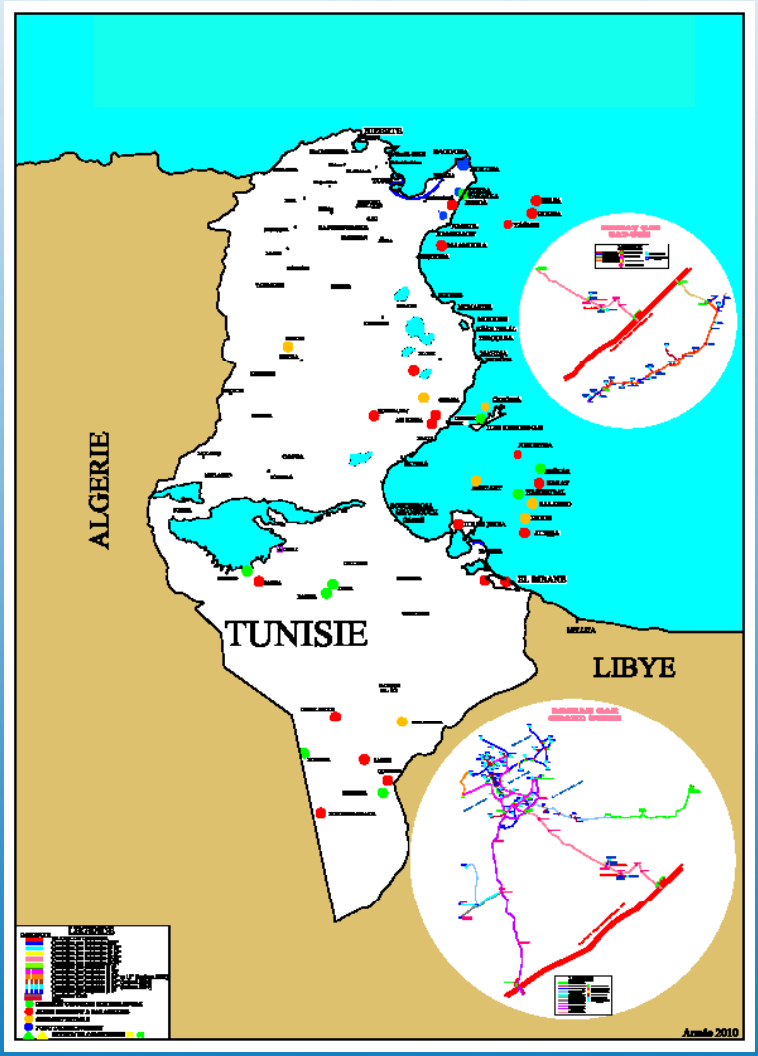
Economy :

* Tourismes
* Phosphate & Chemical industries
* Oil and Gas

STEG

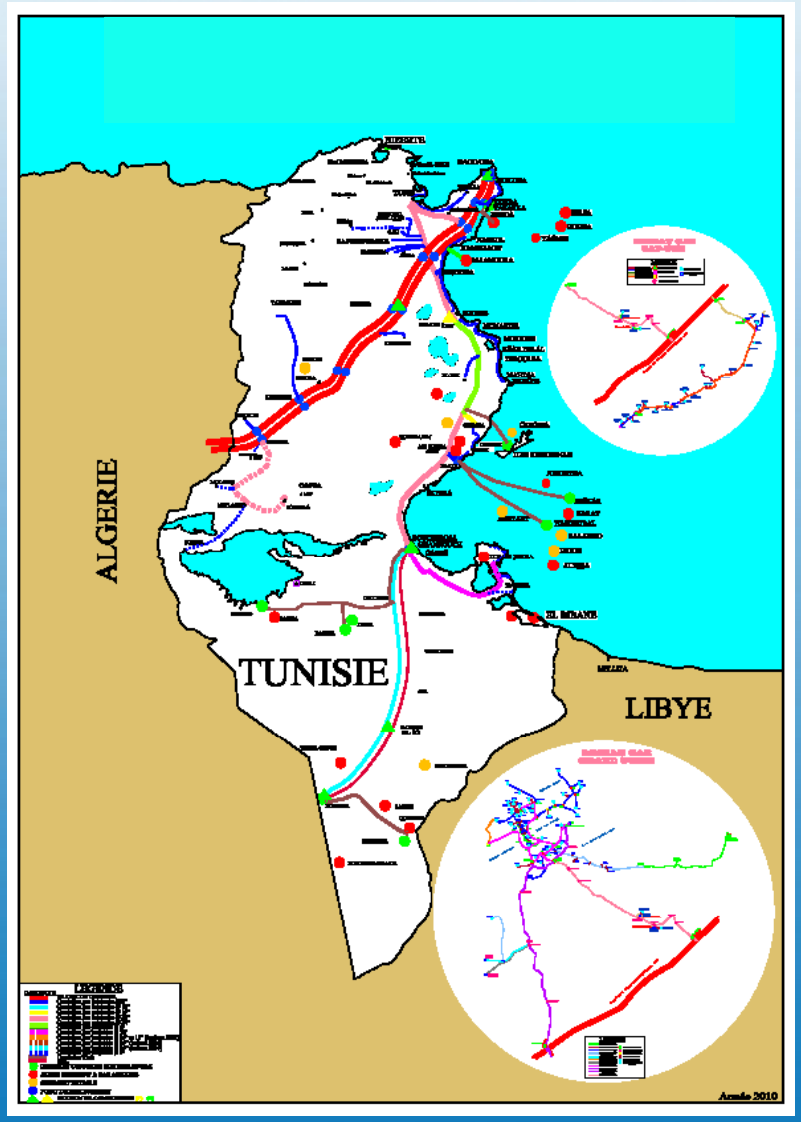
STEG was founded in 1962 as an industrial public utility. Its main activities are gas and electricity Production, Transmission and Distribution.

Number of employees	13 000
Installed electric power capacity	3 700 MW
Natural Gas availability	5 700 KTOE
Liquefied Petroleum Gas Production	110 K Metric Tons
Number of electricity customers	3 500 000
Number of gas customers	650 000



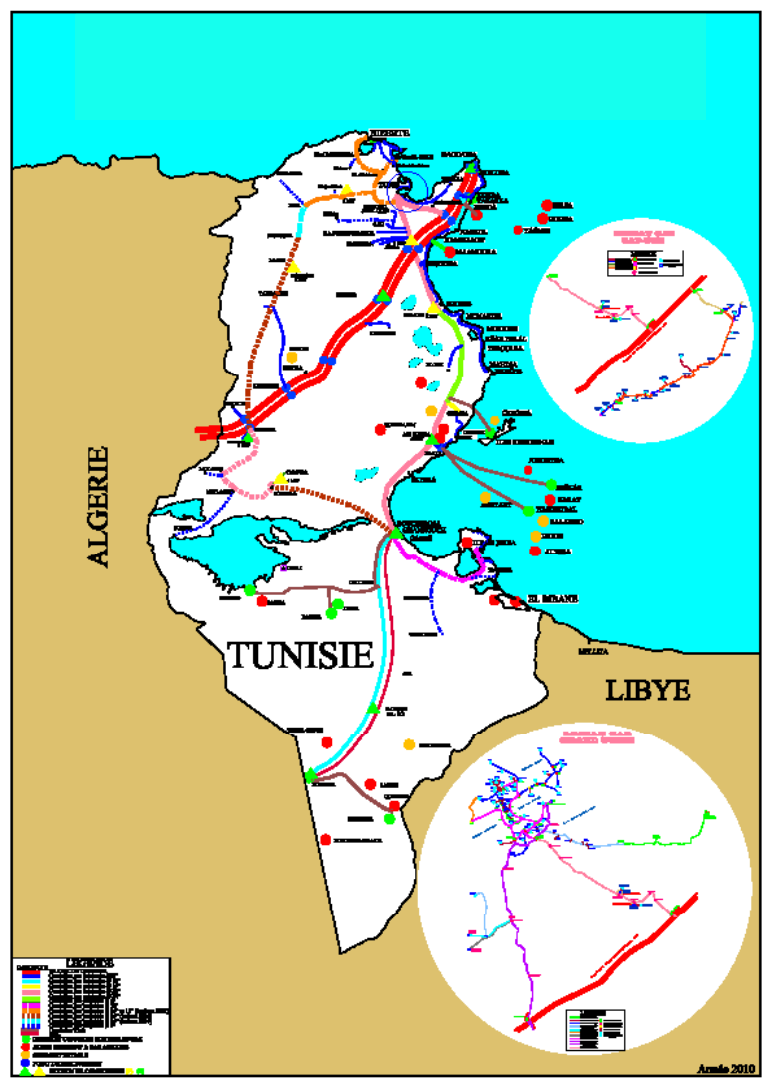
GAS NETWORK (1962)

- **Pressure : 40 bar**
- **Total length : 55 Km**
- **Total length Gas distribution Network : 300 Km (manufatered Gas)**
- **Number of gas customers : 30 000**



GAS NETWORK (2012)

- **Pressure : 76 bar**
- **Total length : 2 300 Km**
- **Total length Gas distribution Network : 12 000 Km**
- **Number of gas customers : 750 000**
- **Number of new gas customers /year 65 000**



GAS NETWORK (2020)

- **Pressure : 76 bar**
- **Total length : 3 200 Km**
- **Number of gas customers : 1 000 000**
- **Number of new gas customers/year : 85 000**

1- INTRODUCTION

Natural gas has became one of the most important energy, with its ecological properties it offers many advantages and is now more and more requested.

Natural gas is a complex mixture of hydrocarbons with a small amount of some other gases, although it is a gas it may contain some particles at gas, liquid or even solid state.

The affect of these small quantities of impurities could be important which is the case of sulfur deposition.

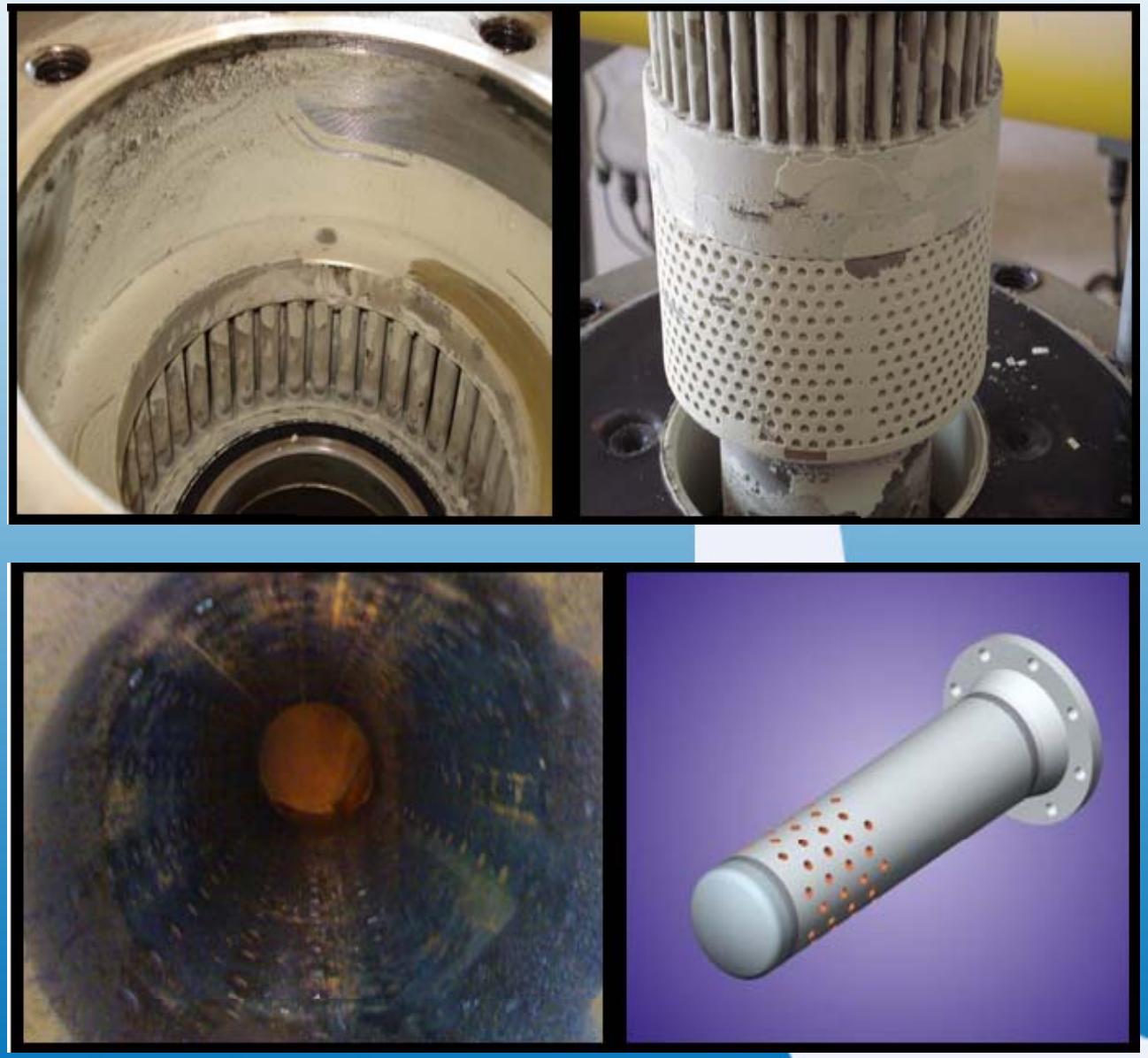
Sulfur deposition is one of the effect that caused a lot of damages and has to be studied seriously

2 - SULFUR DEPOSITION IN TUNISIAN GAS INSTALLATIONS

Sulfur deposition phenomena has been identified in the early 2000’s and was discovered in three different type of gas installations

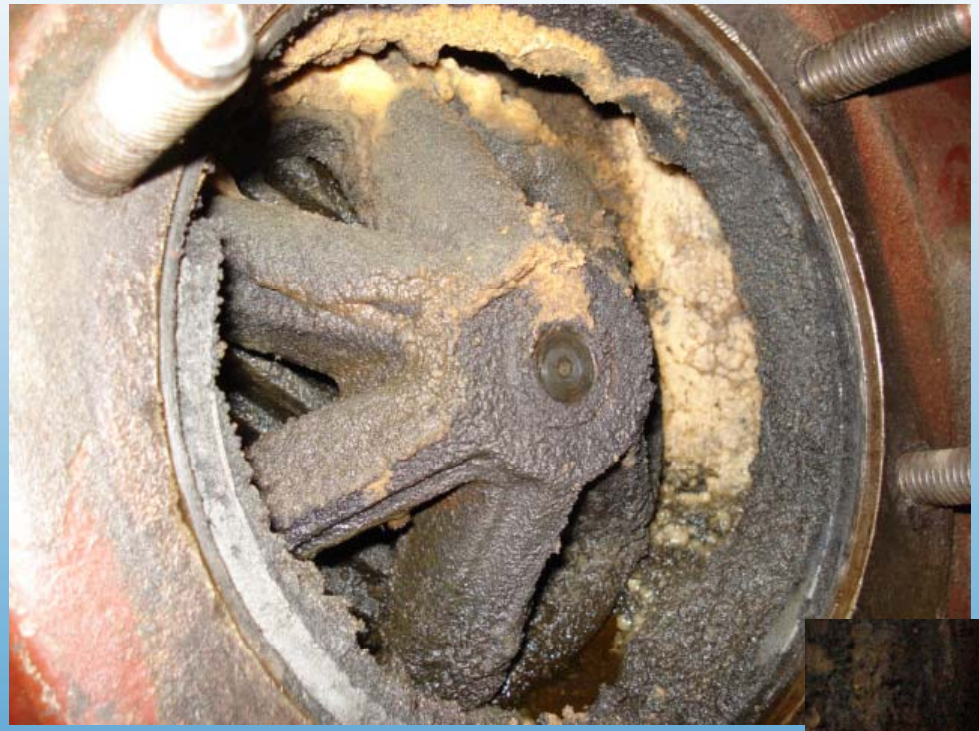
A - GAS REGULATORS (PRESSURE REDUCERS)

A yellow powder discovered in the regulator cages and noise reducers in pressure reduction stations (76/20/4 bar)



B - PROCESS GAS UNIT

The most important was in Feb 2009 in the pistons of a reciprocating gas driven compressor

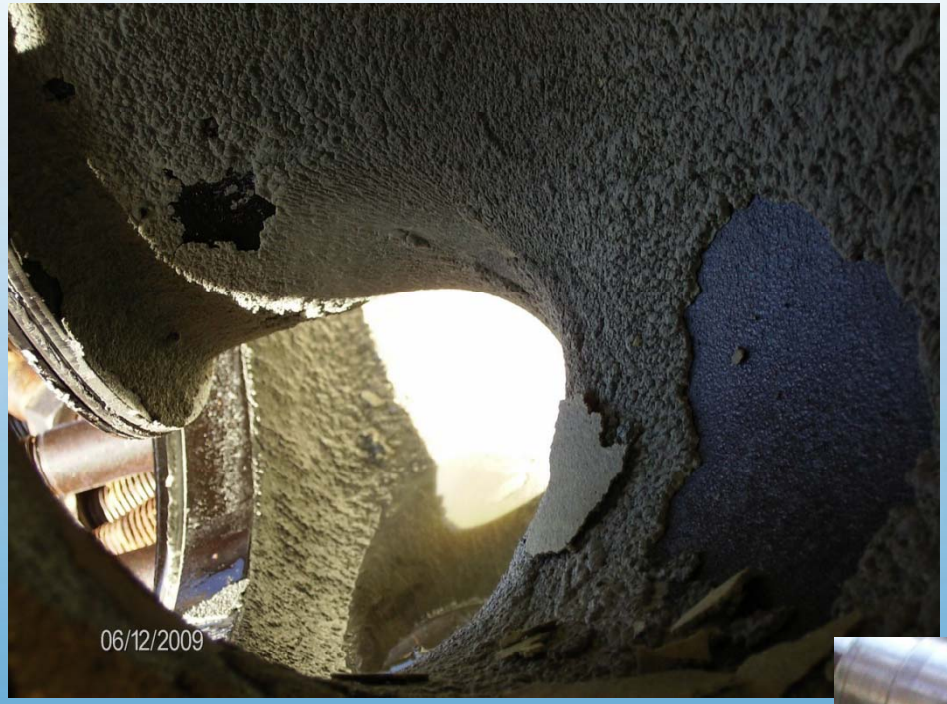


C - GAS TRANSMISSION SYSTEM

In December 2009 a big quantities of sulfur has been discovered in a compression station and caused a lot of damages to the compressors and gas turbines


05/12/2009


05/12/2009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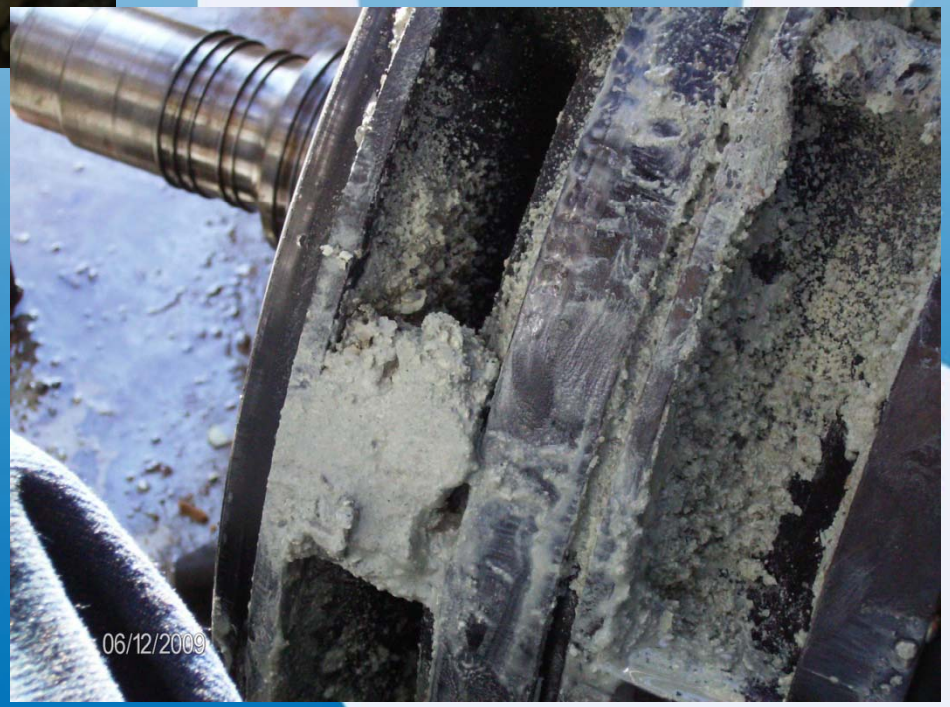
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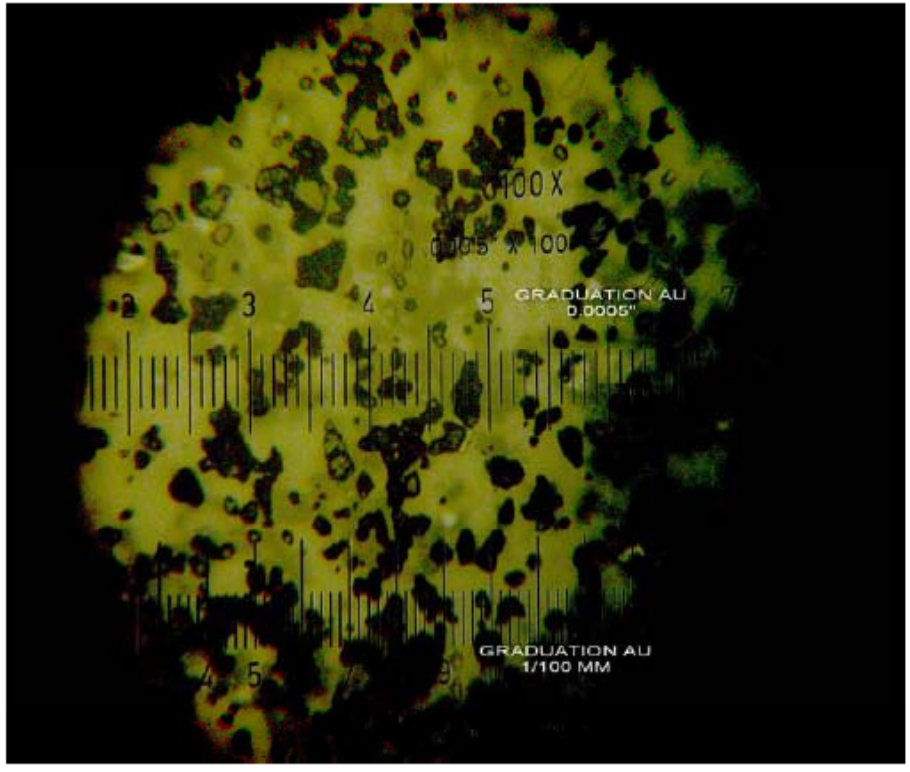
Powder analysis



The yellow powder was analyzed and showed:

- 90% of Sulfur 10% (Fe+Si)
- 64% of particles have a size 5-20 µm and 34% higher than 20.

3 - THEORETICAL REVIEW

A - Sulfur (S)

- bright yellow crystalline solid S_8
- Atomic Number 16 Atomic Mass 32
- Used to be produced from salt domes, now it is produced as a byproduct of removing sulfur-containing contaminants from oil and gas
- Used as fertilizers and chemical industry (Sulfuric acid)

- sulfur can react as either an oxidant or reducing agent.
- It oxidizes most metals and several non metals, including carbon
- It reduces several strong oxidants, such as oxygen and fluorine.
- Sulfur forms polyatomic molecules with different chemical formulas

- Oxidation state 6, 5, 4 , 3, 2, 1, -1, -2.
- Melting pt 115°C(*)
- Boiling pt 444°C (*)
- 4 triple points
- Great variety of possible molecular structures, it can react with organic and inorganic substances and then can exit in a large number of different molecular forms

(*) depending on the molecular structure

B - Some Chemical reactions

$H_2S + Fe = FeS + H_2$

$3H_2S + Fe_2O_3 = 2FeS + 3H_2O + S$

$4H_2S + Fe_3O_4 + = 3FeS + 4H_2O + S$

$FeS + 1/2\ MnO_2 + 3H = Fe(OH)_3 + S$

$2H_2S + SO_2 = 3S + 2\ H_2O$

$2H_2S + O_2 = 2S + 2H_2O$

$$2C_2H_6O_2 + 3Fe = 2C_2H_6 + Fe_3O_4$$

$$C_6H_{14}O_4 + 3Fe = C_6H_{14} + Fe_3O_4$$

$$C_6H_{14}O_4 + H_2S = C_6H_{14} + H_2O + SO_3$$

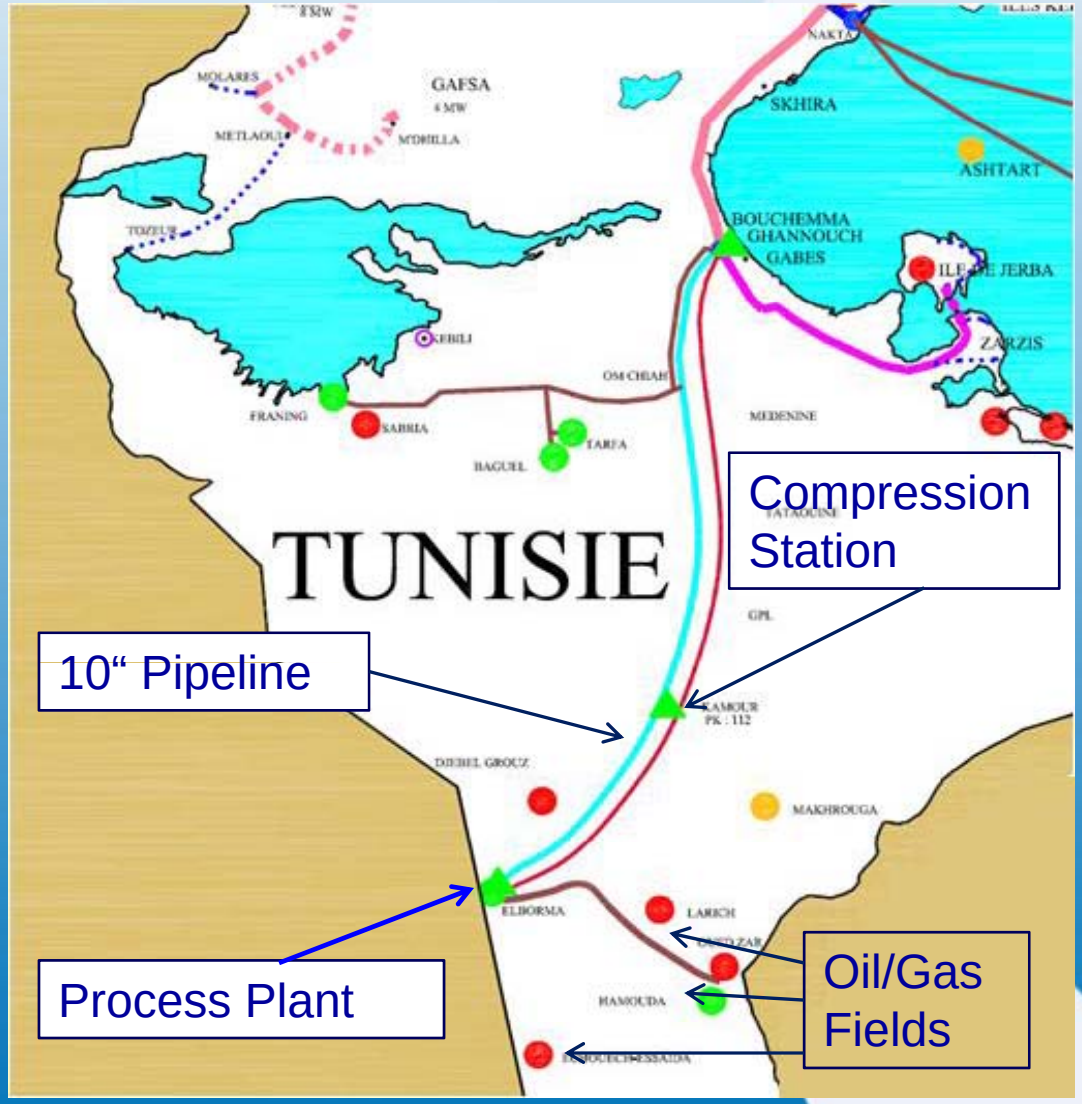
$$CH_3OH + H_2S = CH_4 + S + H_2O$$

$$CH_3OH + Fe = CH_4 + FeO$$

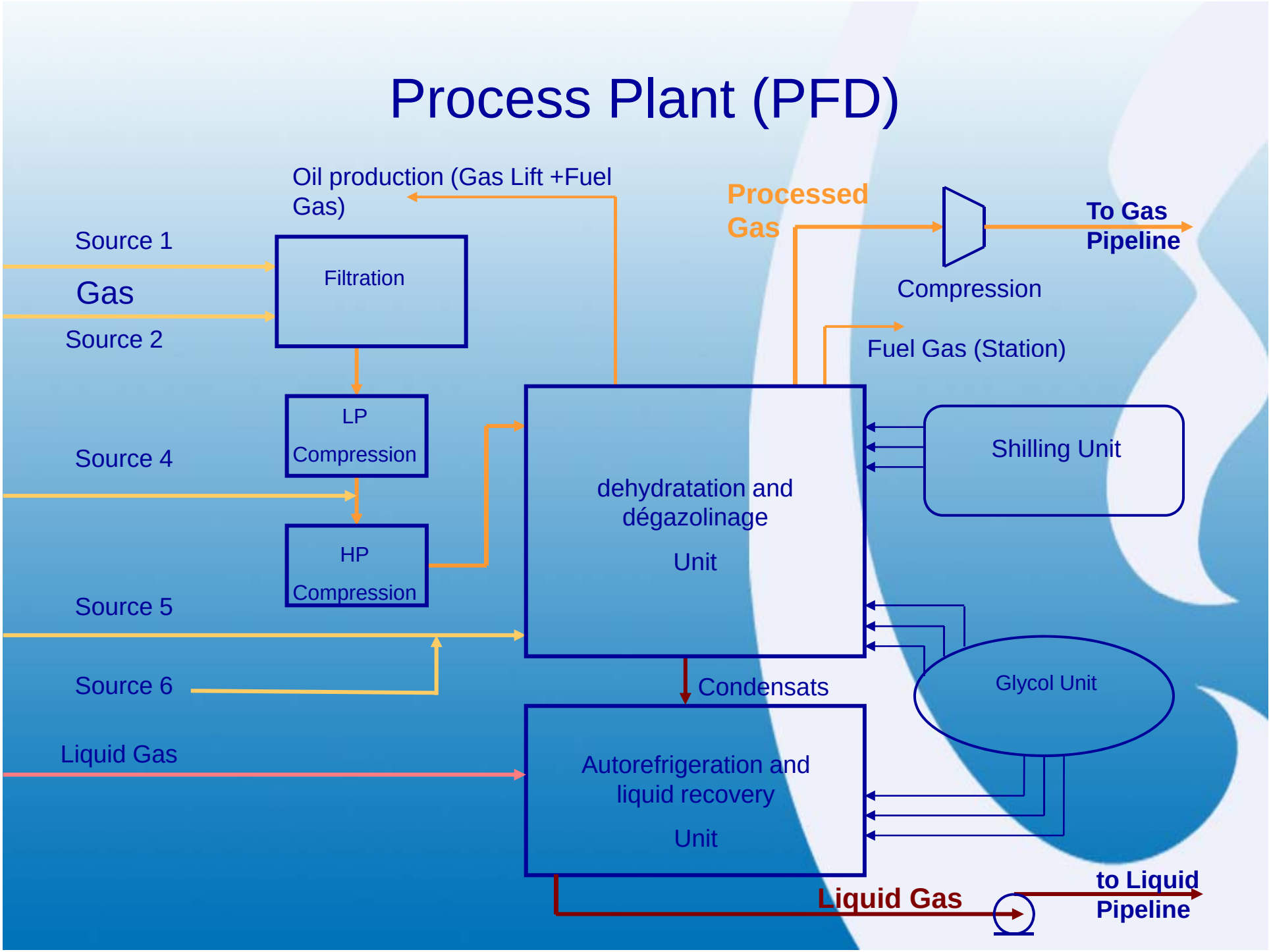
4 - UNDERSTANDING THE PROBLEM

- Different analysis have been made to the gas feeding the system in order to determine the sulfur content of each gas, no particular values have been recorded, all the gas samples showed a normal concentration of H_2S and total sulfur
- in order to understand more this phenomenon, many technical documents have been studied and also the pipeline and the gas composition have been deeply analyzed.

Gas Process Description



Process Plant (PFD)

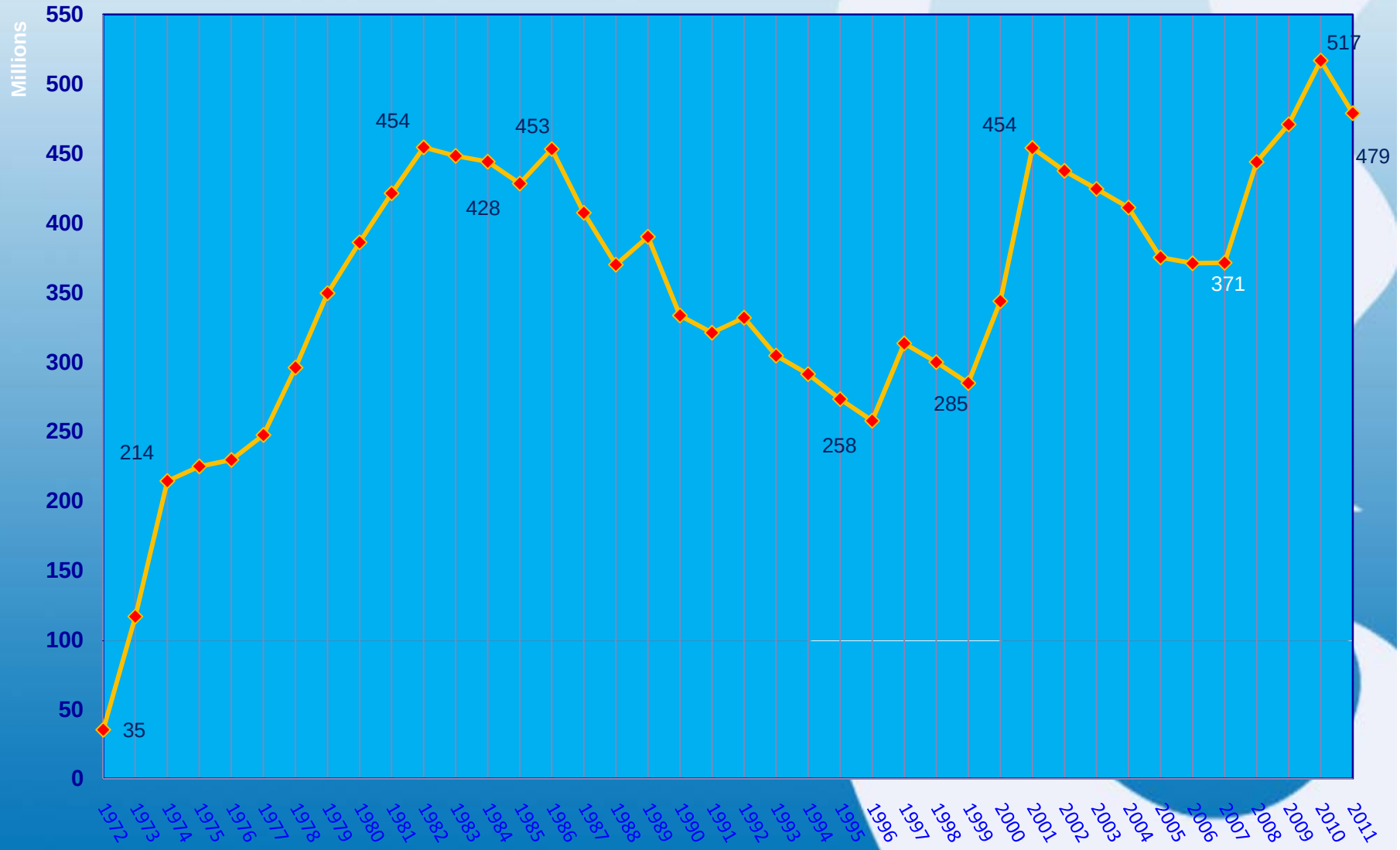


- The gas process plant is feed by six different gas sources, all the analyses done to those sources showed a normal amount of sulfur contents and in some cases the sulfur was much below the normal values.
- The processed gas is with a low concentration of heavy hydrocarbons, the experience has showed that in case of problem in the shilling unit, the concentration of heavy hydrocarbon increase which may yield to sulfur formation

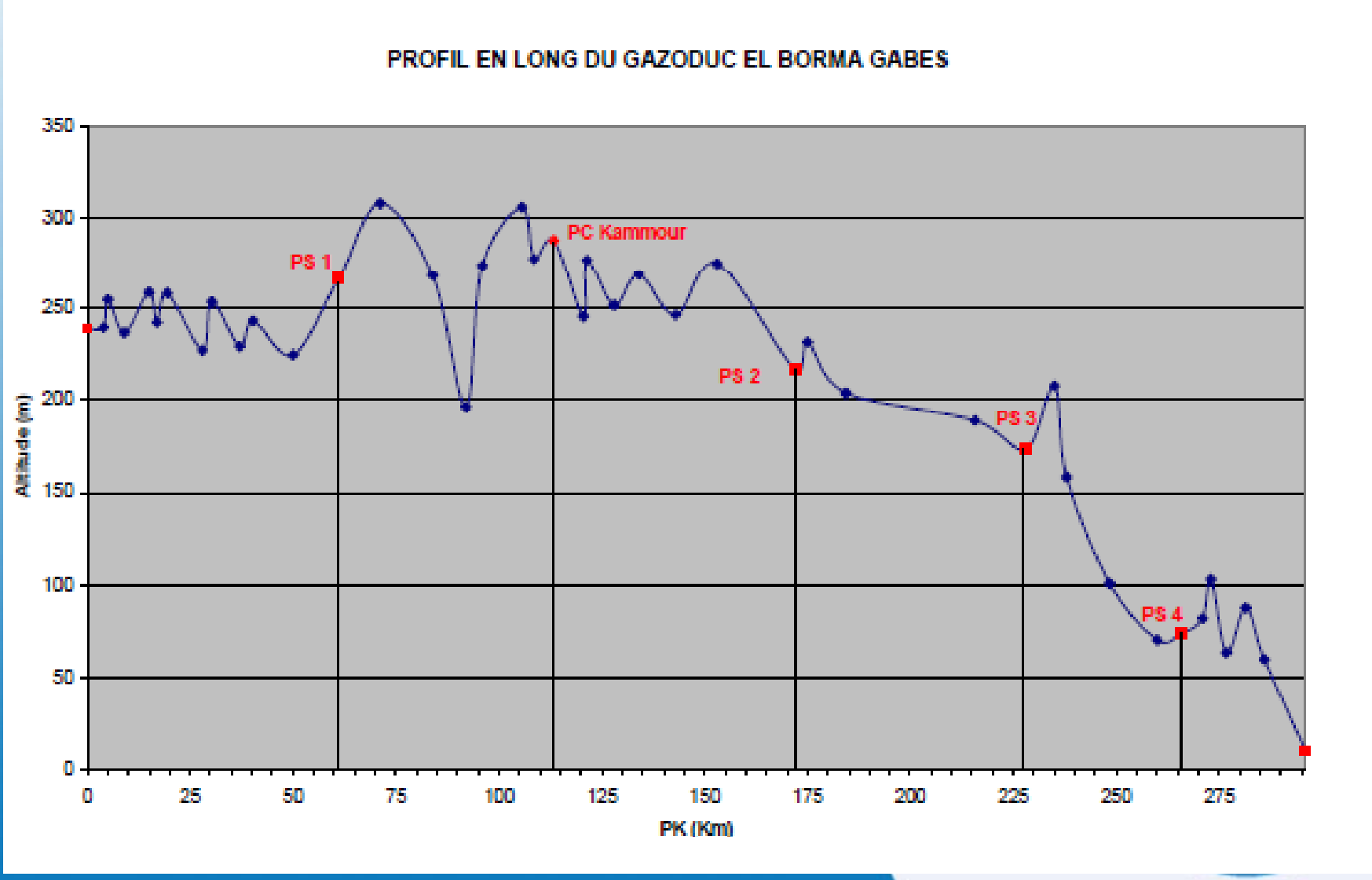
Pipeline description

- Treated gas from the processing plant is compressed to 76 bar and transmitted into a 10” 300km pipeline commissioned in 1972.
- The pipeline is X42 with a nominal wall thickness of 5.56 mm.
- The pipeline is cathodically protected, inspected by an intelligent pig in 2002 and 15% of the pipeline was changed and recommissioned in October 2009.

Pipeline Annual Flow Rate



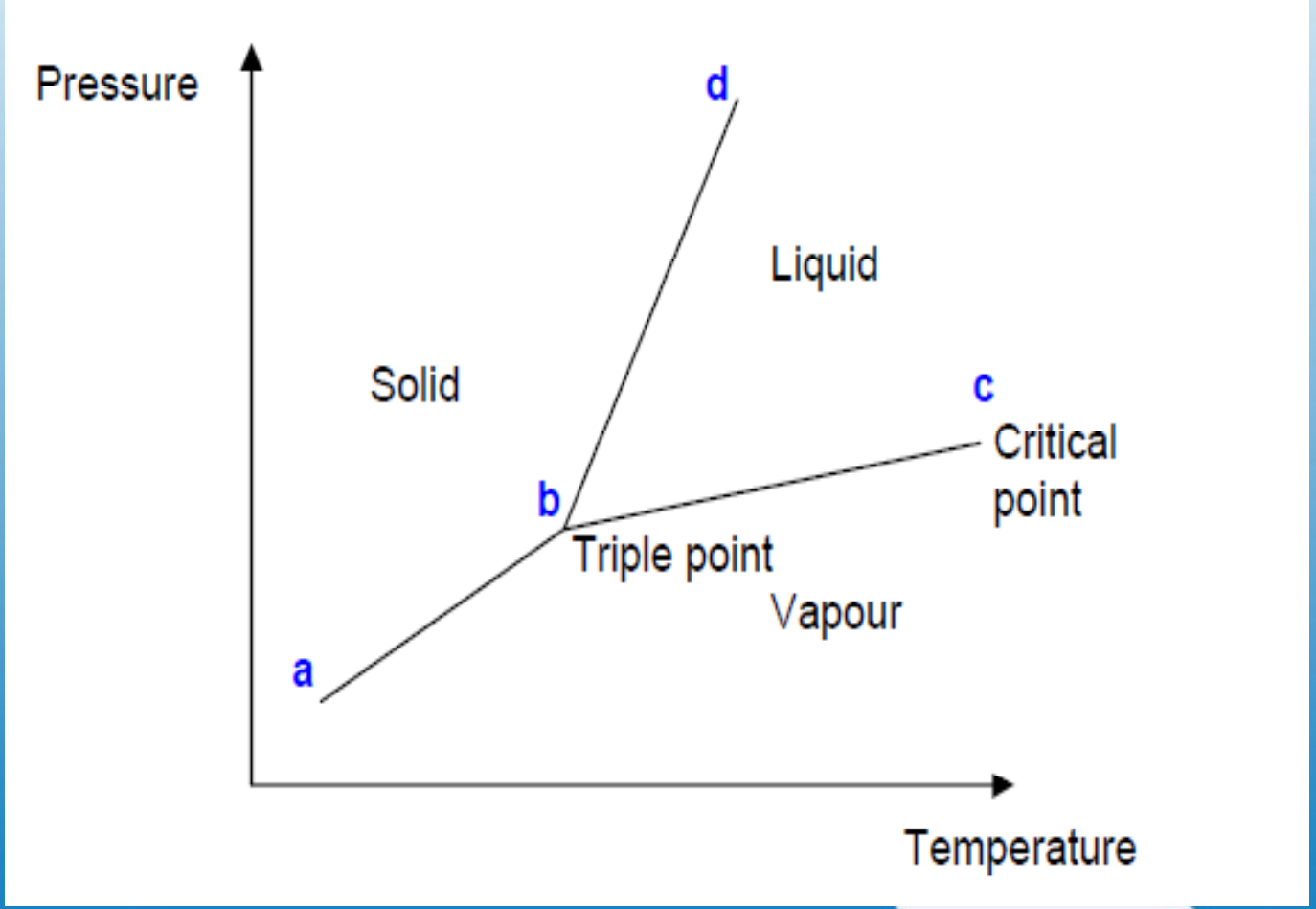
Pipeline longitudinal route



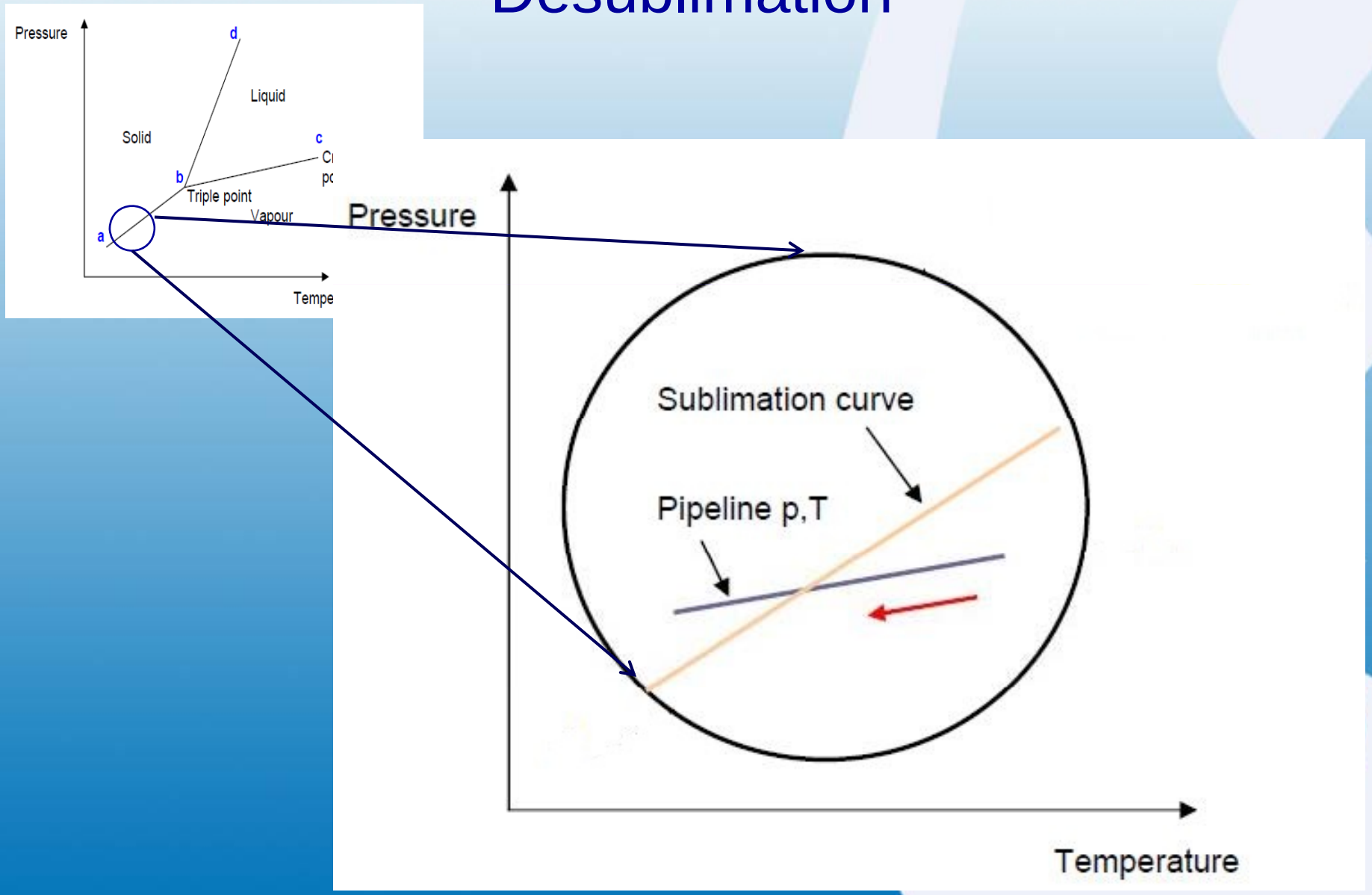
- The sulfur formation in the pipeline happened in December 2009 and during 2010 when the pipeline recorded its maximum full rate.
- The pipeline route represents a lot of level deviations especially before the compression station where a difference of altitude of more than 100m has been recorded, this may have an effect on gas condensation through the pipeline (retrograde condensation).

- After analyzing and studying those phenomena, we conclude that elemental sulfur formation is due to a desublimation effect, i.e. sulfur at vapor state change directly to solid state without passing though the liquid state.

Phase Diagram



Desublimation



Sulfur deposition is caused by desublimation which is related to the temperature and pressure drop but also to some other phenomena such as :

- The retrograde phenomena

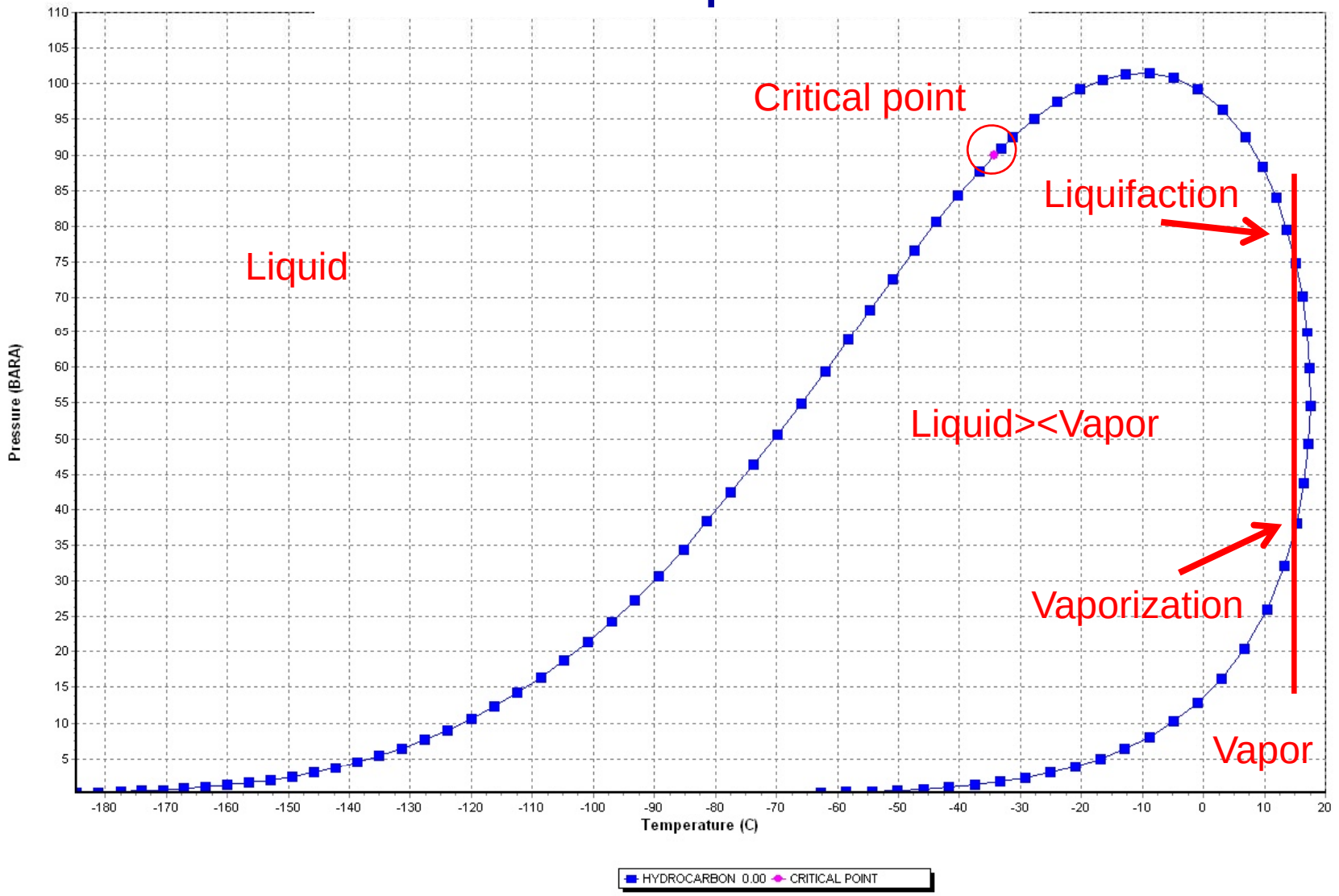
- The particles formation

Retrograde phenomena

Natural gas as multi-component mixture is characterized by an envelope phase which determine at each P, T the state of the mixture.

In some situations a pressure drop causes the gas mixture to cross twice the due point line and part of the gas will liquefy and then vaporize again which is the retrograde phenomena

Gas Envelope Phase



By having a retrograde condensation an amount of heavy hydrocarbons will condensate and by this the gas composition will have a change in the components and then a change in the partial pressure.

The H2S partial pressure may become supersatured under a pressure drop and sulfur under gaseous state passes trough the desublimation curve and becomes solid.

Particles formation

The particle formation process assumes that the sulfur vapor becomes supersaturated at a certain pressure and temperature reduction stage.

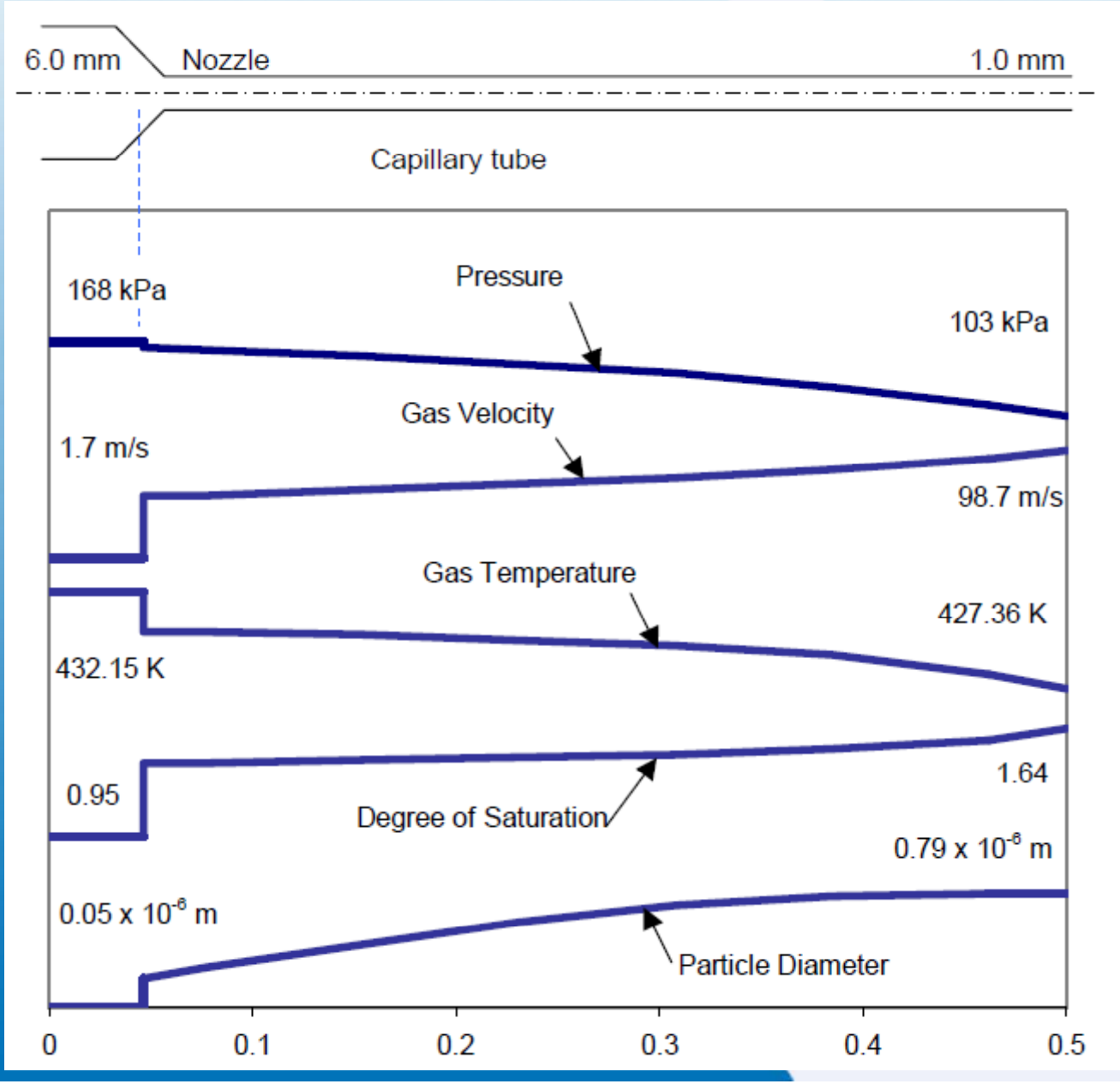
Once the velocity of gas increases heat is transformed to kinetic energy and then a reduction in temperature, as the temperature is reduced a critical supersaturation is reached and a nucleation process occurs, then fine particles will be created and sticked to each other.

Wagner experiement

All the above phenomena were stated in Wagner experiment which consists of sending gas though a nozzle and then the following parameters are recorded at inlet and outlet of the nozzle:

- Pressure
- Gas Velocity
- Gas Temperature
- Degree of Saturation
- Particles size

Wagner experiment



The sulfur deposition is a complex process and the studies are still going on. It can be assumed that the mechanisms associated to this deposition have been identified and are known.

The sulfur at vapor state is the most important element that causes the deposition depending on its pressure and temperature.

The sulfur deposition occurs within a very dynamic environment where a variety of physico-chemical process take place.

Many factors contributing to the deposition have been identified such as:

Many other factors contributing to the deposition have been identified such as:

- Retrograde condensation
- Oxygen
- water
- Glycols/ DEG/ TEG
- COS
- SO2
- Black powder
- Liquid hydrocarbons

For the case of sulfur deposition in transmission pipeline, the causes have been identified and the solution is to avoid those conditions.

For the case of sulfur deposition in the gas regulators, the studies are in progress to find a complete solution although the causes are also known and are the same.

A complete solution could of two types:

-Chemical inhibition:

This can be done by injection inhibitors such as scavengers (oxygen or h2s) which interact with sulfur components and then avoid sulfur deposition

- Mechanical trap

This can be done by designing a trap (a nozzle) which create sulfur deposition then a filter which stops the particles

5 - RECOMMENDATIONS

In order to avoid sulfur deposition some recommendations have been stated:

- Ensure a fully process gas and avoid sending rich gas into the pipeline.

- Ensure an appropriate glycol process and avoid “extra quantity” also avoid methanol injection in the pipeline.

- Maintain transmission gas temperature high.

- Avoid air injection into the pipe by using a reasonable number of pigging operations

- Ensure a fully dehydrated pipeline before commissioning.

- Avoid operating at maximum and full capacity pipeline, you may reach high velocity gas (especially for old pipeline).

- avoid intrusion of liquid or solid particles to the pipeline (e.g after Tie-in).

- When large pressure reduction is needed, proceed by stages (76/20/4 bar).

6 - CONCLUSION

•Sulfur deposition in gas pipeline could be considered as a “new” and not well known phenomenon.

• Unlike sulfur problems in oil and gas fields, sulfur deposition in gas pipeline was not sufficiently treated by researches and studies.

• it appeared especially after operating gas pipelines at full operating capacity (max pressure) and with a gas containing heavy hydrocarbons.

- A phenomenon considered to be harmful, and is to be taken seriously, many damages occurred in a compression station where 2 compressors and 1 gas turbine have been completely damaged.

- Today we know the conditions of avoiding its formation, the challenge now is to develop a complete solution to avoid it.

To be Continued…

THANK YOU FOR YOUR ATTENTION

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