

MODERN COKE OVEN GAS TREATMENT TECHNOLOGY AT A NEW COKE MAKING PLANT IN BRAZIL*

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Abstract

The implementation of the Gas Treatment Plant (GTP) for CSPECEM, Ceara-Brazil is a result of the closed partnership between Paul Wurth Italia S.p.A. and DMT, the German leading company in Coke Oven Gas Treatment Plants. In addition to technical issues reducing emissions, avoiding of waste and saving environment and energy were technical challenges during the engineering phase. Below mentioned three descriptions of technical solutions represents examples of a number other innovations based on DMT's know-how and experience in the field of by-product plants. Generally the design of the complete GTP is based on the consideration of modern features and design upgrading, with the aim of a safe operation with stable conditions and a long-living cycle of the whole of the plant.

Keywords: By-product plant; Coke oven gas treatment plant.

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1 INTRODUCTION

Paul Wurth Italia S.p.A. in cooperation with DMT, the German leading company in Coke Oven Gas Treatment Plants worked out the design, supplies of special equipment and provides supervisors for erection and commissioning of the new Gas Treatment Plant (GTP) for CSPECEM, Ceara-Brazil.

The plant as described will treat the crude coke oven gas of 87,500 Nm³/h for 1st phase from the new coke oven batteries COB 1&2. The arrangement for 2nd phase (COB 3&4) is also considered. The complete planned GTP (1st and 2nd phase) with all units is designed for a max. quantity of 175,000 Nm³/h coke oven gas (COG) incl. charging gas, respiration gas and tail gas.

The design of the gas handling and by-product facilities is utilising well proven technologies, based on DMT's know-how and experience in the field of by-product plants and in addition on DMT's long-term operational experience from various coke plants, which were owned and operated by RAG AG.

The basic engineering has been started in February 2012. Currently the plant is being built.

2 DESCRIPTION OF THE COKE OVEN GAS TREATMENT PLANT

2.1 General Overview

An overview of the entire by-product plant is given in the following scheme (**figure 1**). The crude gas of the coke oven batteries (COB) of 1st phase (and later 2nd phase) including the loaded flushing ammonia liquor, is taken over from the crude gas mains at defined points.

Leaving the downcomer the gas is directed to the primary gas coolers (PGC). In the PGC's the coke oven gas (COG) is cooled down within two indirect cooling stages using both cooling water and chilled water. Using a continuously operated flushing system inside the PGC's for cleaning purposes the operation time is optimised.

The tar-/ammonia water mixture leaving the down-comer is directed to the static tar separation plant. From the tar separation plant the flushing liquor is returned to the collecting main for flushing the COG coming from coke oven batteries, while coal water is discharged via a tank to the gravel filter plant for final tar removal. Leaving the tar separation plant the crude tar, as product, is led via the storage- and loading station to further disposal. After collecting and preparing within the tar separation plant, by tar solid decanters, solid particles are finally discharged into the battery feed coal.

Coming from the primary gas coolers the cooled COG flows through the electrostatic tar precipitators (ETP) for reducing the tar content upstream the gas exhausters. The cooled and tar reduced COG passes the gas exhausters driven by electric motors. The required performance and suction pressure of the gas exhausters have to be considered for the pressure difference of the entire gas treatment plant, beginning from coke oven batteries down to the inlet of the COG network.

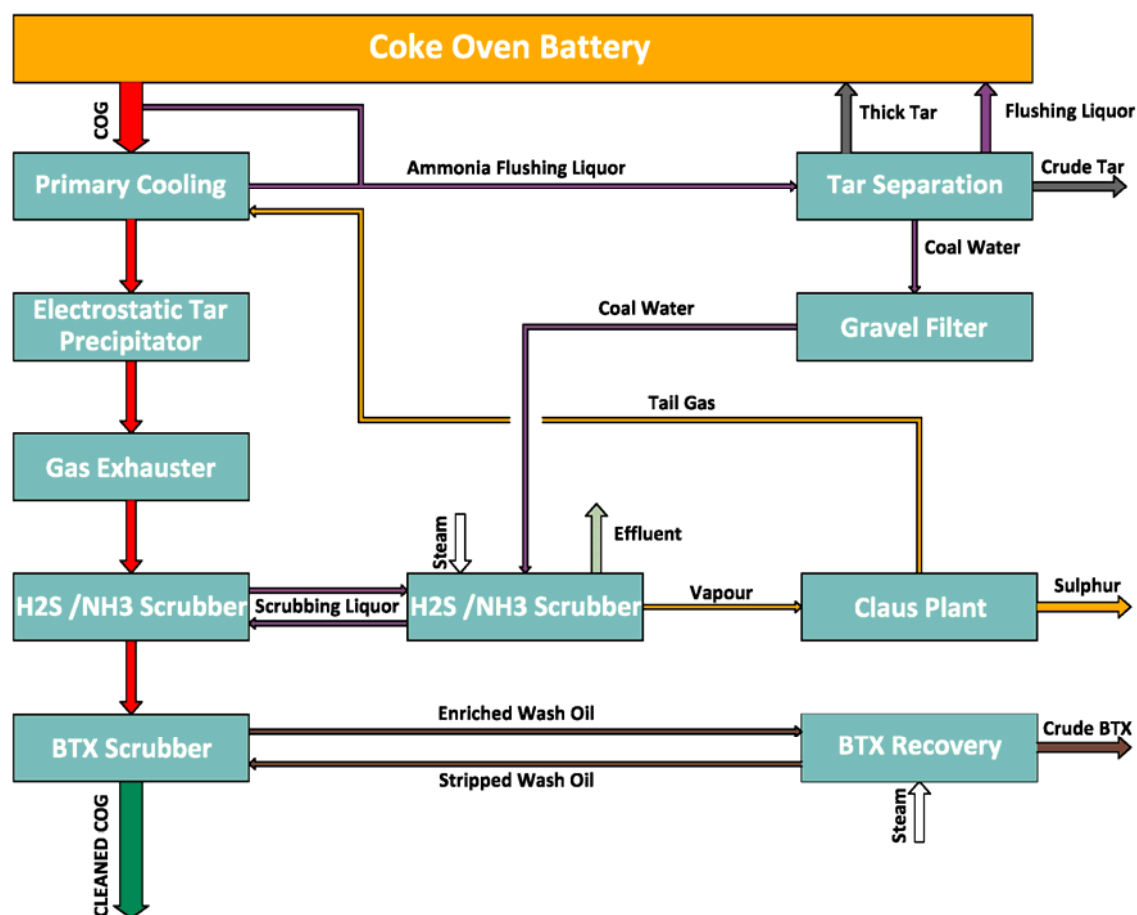


Figure 1: Overview Flow Diagram of the By-product Plant

After leaving the gas exhausters the COG passes a scrubber system with integrated final and internal cooling stages for reducing the H₂S-/NH₃-components. By these cooling stages, operated indirectly with chilled water, the reached temperature level secures the required performance values of the scrubber system. The scrubbing liquor for the H₂S/NH₃ removal consists of stripped and deacidified water supplied by the distillation plant.

As final gas cleaning stage a BTX-/Naphthalene scrubber is applied. In order to reduce the BTX- and Naphthalene content the COG coming from H₂S-/NH₃-scrubbers is scrubbed by special tar based wash oil. For the regeneration of the wash oil and the production of crude BTX as product a stripping system is provided.

In order to strip the H₂S- and free ammonia-compounds from the enriched scrubbing liquor coming from the H₂S and NH₃-scrubbers, a distillation plant consisting of deacidifiers (DS) and ammonia strippers (AS) is provided with the capability to handle the entire scrubbing liquor. The excess coal water, leaving the gravel filter plant, is stripped under the presence of caustic soda (NaOH) in a fixed ammonia still column section to remove the fixed ammonia compounds. The surplus outlet stream is led to the biological effluent treatment plant (BETP).

The vapours leaving the distillation plant, mainly consisting of H₂S, NH₃, HCN, CO₂ and hydrocarbons, will be treated in a combined NH₃ cracking-/elementary sulphur plant (Claus Plant). In this process the NH₃-/HCN components are cracked while the H₂S content is converted to liquid sulphur. The tail gas flow of the Claus Plants is returned to the crude gas mains upstream the primary gas coolers.

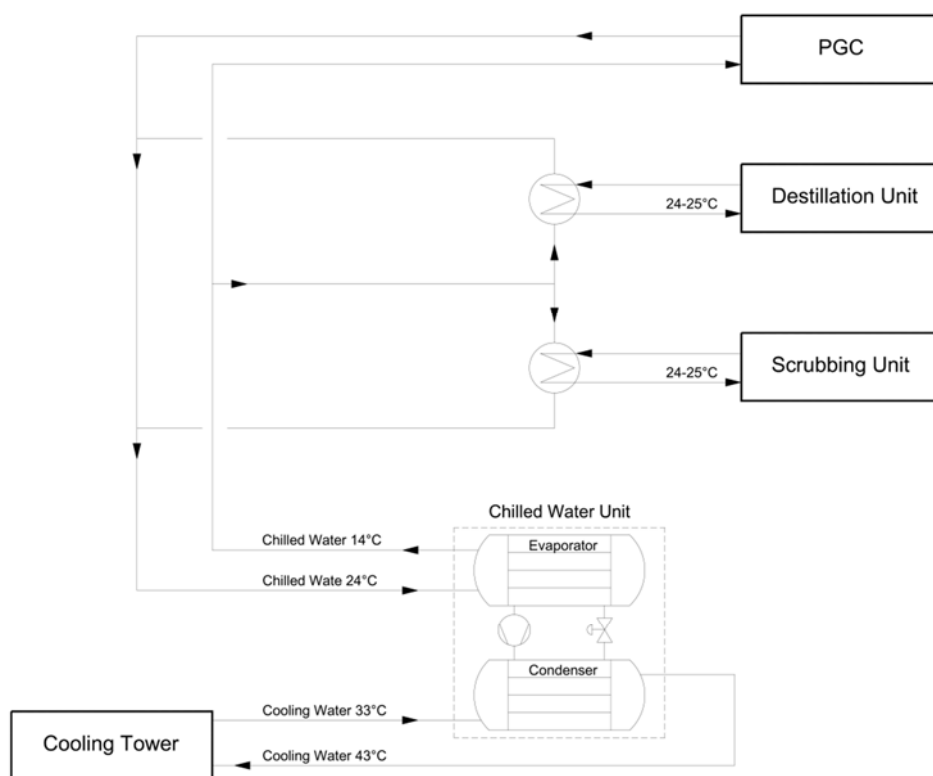
Below the following three technical descriptions of different units are given as examples for implementation.

2.2 Chilled Water Plant

Corresponding state of the art high performance scrubbing system needs for the absorption process a temperature decrease. Therefore a chilled water system is designed (see figure below). This chilled water system allows keeping optimum COG and process water temperatures even during hot periods.

The technical standard and the structure of the chilled water plant, comprising of absorption type (e.g. lithium bromide system) or compressor type refrigerating units. The type which should have been considered depends on the availability of steam and electrical power as well as the required technical specifications. The chilled water plant has to be designed with respect to naphthalene precipitation risks in the primary cooling area and regarding the minimisation of heat exchanger areas. Feed temperature of the chilled water is about 14 °C and return temperature amounts to 24°.

More detailed information and the structure of the chilled water plant are shown in the attached scheme (figure 2).



CHILLED WATER SYSTEM

Figure 2: Overview Chilled Water System

2.3 BTX - Scrubbing System and Recovery Unit

After leaving the NH₃ scrubber the COG is directed to the BTX scrubbing system for removal the BTX compounds. A schematic flow diagram is given below (figure 3). The COG enters the scrubber at the bottom and moves upwards through the

scrubbing sections before it leaves the scrubber at the top. The COG, reduced by BTX components, is directed to the COG distribution network.

The scrubbing procedure is carried out by wash oil, coming from the stripped oil buffer tank, which enters at the top of the scrubber flowing downwards in counter flow to the rising COG. The scrubbing sections consist of expanded metal or structured packings and distribution trays.

The enriched wash oil leaves the scrubber at the bottom via a sealing pot by gravity and is collected in a buffer tank before it is fed to the wash oil regeneration plant.

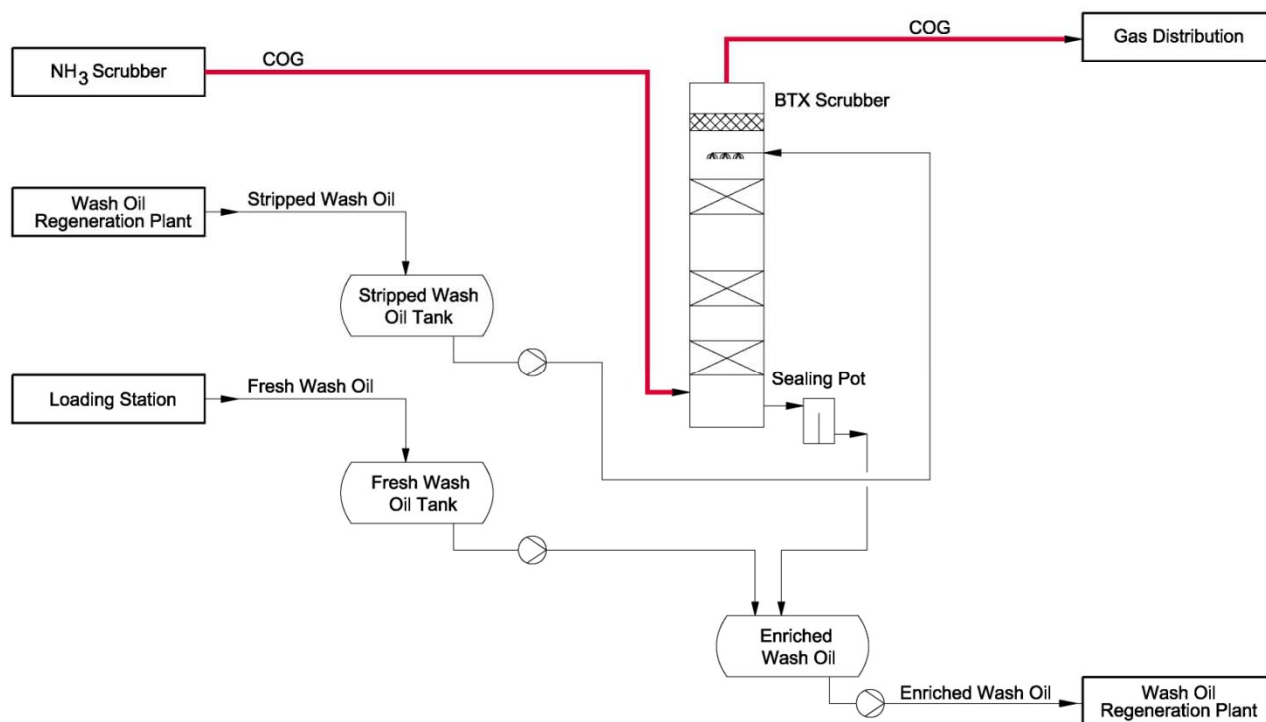


Figure 3: BTX Scrubbing System

Wash oil losses are to be compensated by adding fresh wash oil into the enriched wash oil buffer tank. The fresh wash oil is supplied from fresh wash oil tank.

The enriched wash oil, leaving the BTX scrubbing system, is fed to the wash oil regeneration plant to reuse it for further wash processes in the BTX scrubber. Thereby, a saleable BTX fraction is produced.

Enriched wash oil from the BTX-scrubber (see figure 4), intermediately stored in a buffer tank, is pumped to the BTX stripper, passing 2 heat exchanger groups for indirect heating with hot stripped oil and steam, respectively. The BTX fraction is stripped by adding steam in the bottom area of the distillation column. The BTX fraction loaded with water vapour, leaves at the top of the BTX stripper and passes a condenser / cooler, sequentially, before entering a separation tank.

The separation tank is equipped with special packings to reach an excellent separation between water/crude benzene. The crude benzene is fed to the storage tank by means of pumps while the separation water is discharged to the distillation plant. As a site fraction of the BTX stripper, the naphthalene oil fraction is drawn, collected in a drain tank and mixed to crude tar coming from tar storage tanks.

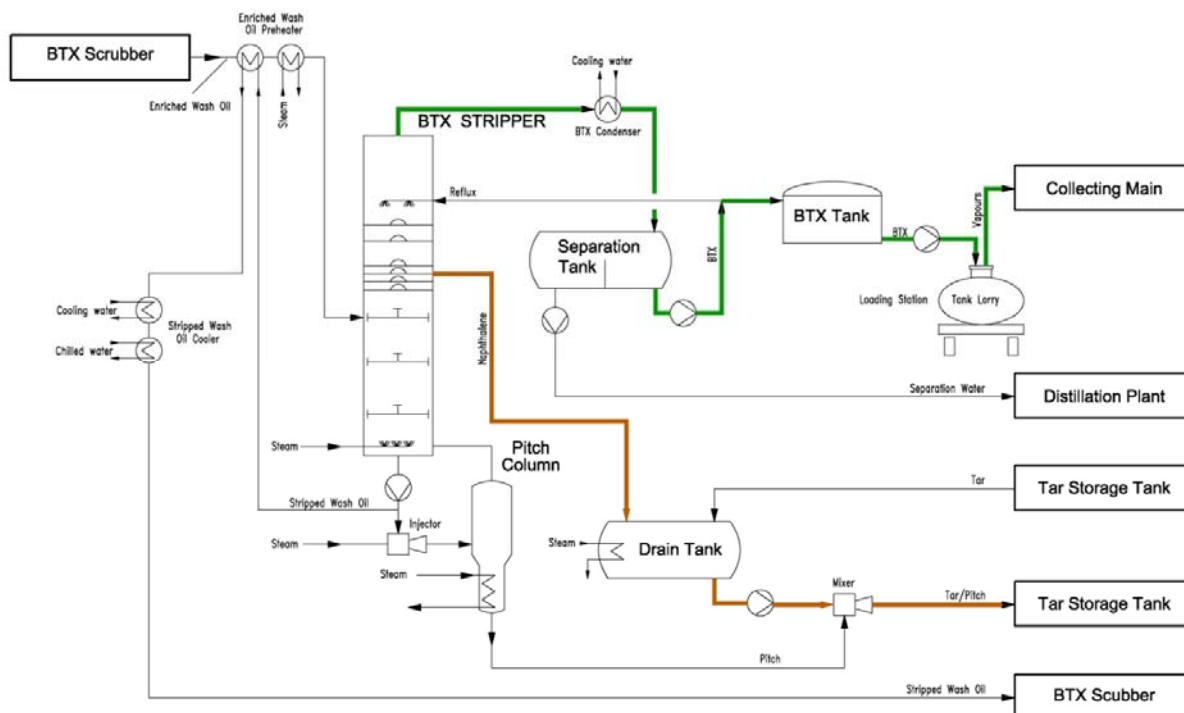


Figure 4: Wash Oil Regeneration Plant

The stripped wash oil leaves the bottom of the stripper and is pumped through 3 groups of heat exchangers. In the first heat exchanger group the heat of the stripped wash oil is used for indirect heating up the cold enriched wash oil, coming from the BTX-scrubber plant. Applying the following 2 heat exchanger groups, the stripped wash oil is indirectly cooled with cooling and chilled water. Then, the stripped wash oil is directed to the buffer tank of the scrubbing system for further use in the BTX scrubber.

Before feeding the hot stripped wash oil to the above mentioned oil-/oil heat exchanger, a small part of hot wash oil is led to the pitch column, supported by injected steam. By removing high viscose pitch components, the wash oil is kept in a feasible range of viscosity.

The used wash oil is generated by a distillation fraction of crude tar from coke plants. The discharged residuals from the pitch column are mixed to the naphthalene oil / crude tar mixture, which is fed to the tar storage tanks. No additional treatment of waste oil/muck is necessary.

2.4 Combined NH₃-Cracking/Elementary Sulphur Plant (Claus Plant)

For processing the H₂S/NH₃ vapours coming from the distillation plant, a combined ammonia cracking/elementary sulphur plant (see schematic flow diagram below, figure 5) is provided. In this project a high efficiency process with a 2-stage Claus reactors is installed.

Under the top pressure of the deacidifier and ammonia stripping system, the H₂S/NH₃-vapours are led to the burner system of the cracking reactor. Operating at sub-stoichiometrical combustion conditions, at a proper temperature for reaction, a certain ratio of H₂S is burned to SO₂. The combustion air is supplied by an air blower. After preheating in a steam operated heater the air is directed into the burner system. Especially, for start-up operation and after process interruptions partly cleaned COG

or natural gas is used for heating up and stabilising the combustion. The COG/natural gas is supplied by a gas blower.

Inside the catalyst bed of the crack reactor the NH_3 and HCN compounds of the vapours are cracked. Downstream of the catalytic bed secondary air is supplied to adjust the stoichiometrical ratio of $\text{H}_2\text{S}/\text{SO}_2$ for the reaction in the following Claus reactors.

The hot process gas leaves the crack reactor and passes the waste heat boiler system. In this boiler system the process gas is indirectly cooled by generating steam via boiler feed water, added by pumps. The parameters of the produced steam can be selected in a certain range. As shown in the flow diagram, it is proposed to generate HP-steam in combination with LP steam. During cooling down of the process gas within the LP boiler, the first sulphur is condensed. After separation it is directed to the sulphur sealing pot.

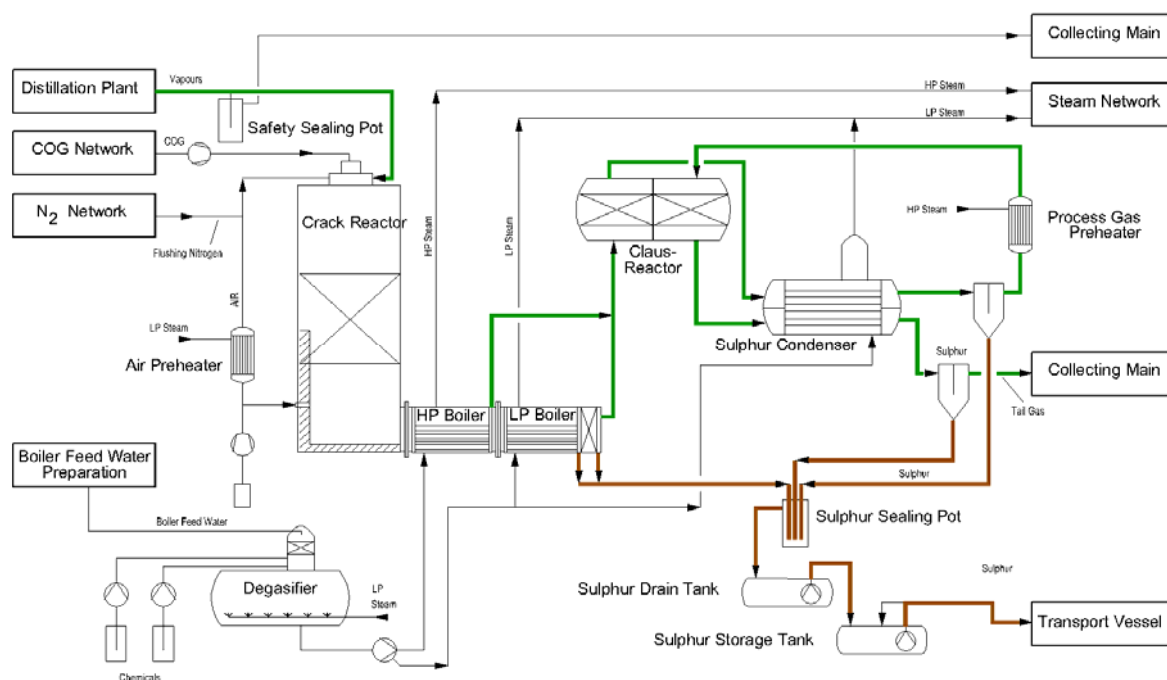


Figure 5: Combined NH_3 -Cracking/Elementary Sulphur Plant

By mixing the outlet gas of the HP boiler with the outlet of the LP boiler the required inlet temperature to the 1st Claus reactor stage is adjusted. Within the first and second stage of Claus reactors, the process gas passes a catalyst bed. By that, the reaction between SO_2 and H_2S takes place to produce liquid elementary sulphur (S_x) plus H_2O .

Leaving the first stage of the Claus reactor, the process gas is directed to the first stage of a sulphur condenser. Similar to the LP boiler, the process gas is indirectly cooled by boiler feed water generating LP steam. Then the process gas passes a separator for precipitation of the condensed sulphur. While the liquid sulphur is led to the sulphur sealing pot, the process gas flows to a downstream gas heater. Using produced HP steam of the HP boiler, the process gas is indirectly reheated up to conversion temperature for the Claus reaction. After reheating the process gas is led to the second stage of the Claus reactor to convert more $\text{H}_2\text{S}/\text{SO}_2$ and to produce further sulphur according to above mentioned reaction. Subsequently, in the second stage of the sulphur condenser the gas is indirectly cooled while LP steam is generated. After cooling the process gas and sulphur precipitation in the downstream

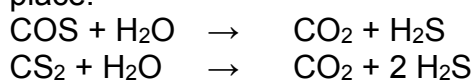
separator, the process gas (tail gas) with residual contents of SO₂ and H₂S, is directed to the crude gas collection main in front of the PGC. Leaving the separator, the sulphur flows into the sulphur sealing pot.

The produced liquid sulphur, firstly collected in the sulphur sealing pot, is discharged into a sulphur drain tank and from there pumped to the sulphur storage tank. Both, the sulphur drain and the storage tanks are steam heated by coils. Periodically, the liquid sulphur is fed into transport vessels for distribution to further disposal by a loading station.

The surplus steam, produced in HP-/LP-boiler and sulphur condenser, is led to the steam distribution network for further utilisation.

Beside on a higher efficiency by using a 2-stage Claus reactor, also the composition of the tail gas should be considered. For avoiding additional organic based Sulphur in effluent, the Claus Plant is designed as described below:

By using of a double stage Claus Plant the cracking of Ammonia and the production of liquid Sulphur from H₂S/NH₃-vapour feed are realized. Furthermore, the Hydrolysis reactions according to the following reactions take place:



Contrary to operating a double stage Claus Plant, during operating a Single Stage Claus Plant above mentioned hydrolysis reactions are not executed. COS and CS₂ is not converted in a Single Stage Claus Plant and is recycled via Tail Gas line to Primary Gas Coolers and downstream plant components. These gas components react in downstream scrubber and distillation columns and cause via Effluent the Thiocyanate problem in the BETP.

3 RESULTS

The impurities of crude COG in front of the gas treatment plant is given in following Table 1.

Table 1. Impurities of crude COG (depending on the coals used)

Components	Unit	Value
Tar	g/Nm ³	15
Hydrogen Sulphide	g/Nm ³	8
Ammonia	g/Nm ³	9
Naphthalene	g/Nm ³	8
BTX	g/Nm ³	33

After leaving the gas treatment plant the design of the impurities is given below (Table 2).

Table 2. Impurities of cleaned COG

Components	Unit	Value
Tar	g/Nm ³	< 0.02
Hydrogen Sulphide	g/Nm ³	< 0.5
Ammonia	g/Nm ³	< 0.04
Naphthalene	g/Nm ³	< 0.1
BTX	g/Nm ³	< 5

3.1 Subtitle – Application Example

- Integrating a new chilled water plant (Pos. 2.2), coke making plant Prosper ArcelorMittal, Germany, 2008
- Installation of BTX - Scrubbing System and Recovery Units (pos. 2.3) in the frame of designing a complete GTP, PT Krakatau POSCO, (Paul Wurth Italia S.p.A.), 2013
- Combined NH₃-Cracking/Elementary Sulphur Plant (Claus Plant, pos. 2.4) installation within existing GTPs at POSCO, Korea, 2007

4 CONCLUSION

The described plant applications can be integrated in gas treatment units of coking plants and similar process applications with the aim

- of reducing pollutant- and impurity emissions into environment,
- to optimize process sequences and economical yields of gas cleaning plants,
- to prevent process disturbances,
- to save energy and material resources.

Above mentioned three descriptions of technical solutions represents examples of a number other innovations based on DMT's know-how and experience in the field of by-product plants and in addition on DMT's long-term operational experience from various coke plants, which were owned and operated by RAG AG.

SOURCE

- 1 All documentation published in this paper are internal documents of DMT GmbH & Co KG.