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STATE OF THE ART IN COKE OVEN GAS TREATMENT A PRACTICAL EXAMPLE [1]

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Abstract

Paul Wurth Italia S.p.A. is realizing a new coke oven plant for BHUSHAN Steel, LTD. at Meramandali – Dhenkanak & Angul District, Orissa, India. The plant will represent the state of the art in coke making incorporating all the most modern technologies in order to have important energy savings, to achieve the best coke quality and to respect environmental issues. Regarding the Coke oven gas treatment plant, which will have a capacity of 70000 Nm3/h, the plant will apply the most advanced technical solutions in this area. The project is carried out with the cooperation of DMT GmbH, Germany, the strategical partner of Paul Wurth in the by product area.
Key words: Coke oven gas treatment; Environment; Technology.

ESTADO DA ARTE EM TRATAMENTO DE GÁS DE COQUERIA – UM EXEMPLO PRÁTICO

Resumo

Paul Wurth Italia SpA está construindo uma nova planta de coque para BHUSHAN Steel,LTD. em Meramandali - Distrito Dhenkanak & Angul, Orissa, na Índia. A planta representa o estado da arte em coqueria incorporando as mais modernas tecnologias, a fim de obter importante economia de energia, alcançar a melhor qualidade de coque e respeitar as exigências ambientais. Quanto à estação de tratamento de gás de coqueria, que terá uma capacidade de 70.000 Nm3 / h, a planta irá aplicar as soluções técnicas mais avançadas nesta área. O projeto está sendo realizado com a colaboração de DMT GmbH, Alemanha, parceria estratégica da Paul Wurth para a área de carboquímicos.
Palavras-chave: Tratamento de gás de coqueria; Meio ambiente; Tecnologia.

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1 INTRODUCTION

Paul Wurth Italia and DMT are two partner companies with a wide experience in the field of coke oven gas treatment plants.
Paul Wurth Italia activity in this field began in the 1980s, when the specific technical PWIT department was belonging to former Italimpianti SpA and was involved in the design and development of the largest Italian coke plants (Taranto, Bagnoli, Piombino, Cornigliano, Trieste). Now PWIT has several references that range from process studies to large turn-key projects relating to complete plants or to specific process units (like primary cooling, either indirect and direct type; ammonia, hydrogen sulphide and naphthalene removal; tar separation etc.).
DMT has an important experience in the coke oven gas treatment as well, it also comes from operating experience in Prosper coke plant. Among DMT references you find important coke oven gas desulphurization units, using normally ammonia for hydrogen sulphide removal and claus plants to produce high purity commercial sulphur. DMT has also the know-how for alternative solutions, including ammonium sulphate or sulphuric acid production.
Our two companies have been working in strict cooperation for approx 5 years and have already developed some projects together.
The most important project under execution is presently the realization of the By-Products plant for **Bhushan Steel Limited**, in Meramandali, Orissa State, India.

2 THE GAS TREATMENT PLANT FOR BHUSHAN STEEL LIMITED

The project started in the middle of 2008. The By-Products plant will be designed for a gas treatment capacity of **70000 Nm^3/h (1st step)**, with provisions for possible future 2nd step which would double the plant capacity up to 140000 Nm^3/h.
A by-products plant has the scope to recover and make valuable the approx 25% of coal material that isn't transformed into coke : this means that every ton of loaded coal generates approx 250 kg of coke oven gas (rich gas with a lower heating value of approx 4300 kcal/Nm^3), tar, BTX, sulphur, etc.
The new Bhushan Steel coke plant has the following design parameters:

- coke production 1,34 Mt/y
- design capacity of coke oven gas: 70000 Nm/h (dry)
- H_2S content in the treated gas: ≤ 0,5 g/Nm^3
- NH_3 content in the treated gas: ≤ 0,03 g/Nm^3
- BTX content in the treated gas: ≤ 3,0 g/Nm^3
- $C_{10}H_8$ content in the treated gas: ≤ 0,05 g/Nm^3
- Tar for content in the treated gas: ≤ 0,02 g/Nm^3
- crude tar production, centrifuged, ~ 200 t/d
- commercial solid sulphur, purity ≥ 99, 5% ; ~ 9 t/d
- crude BTX (benzene + toluene + xylenes) : ~ 40÷45 t/d

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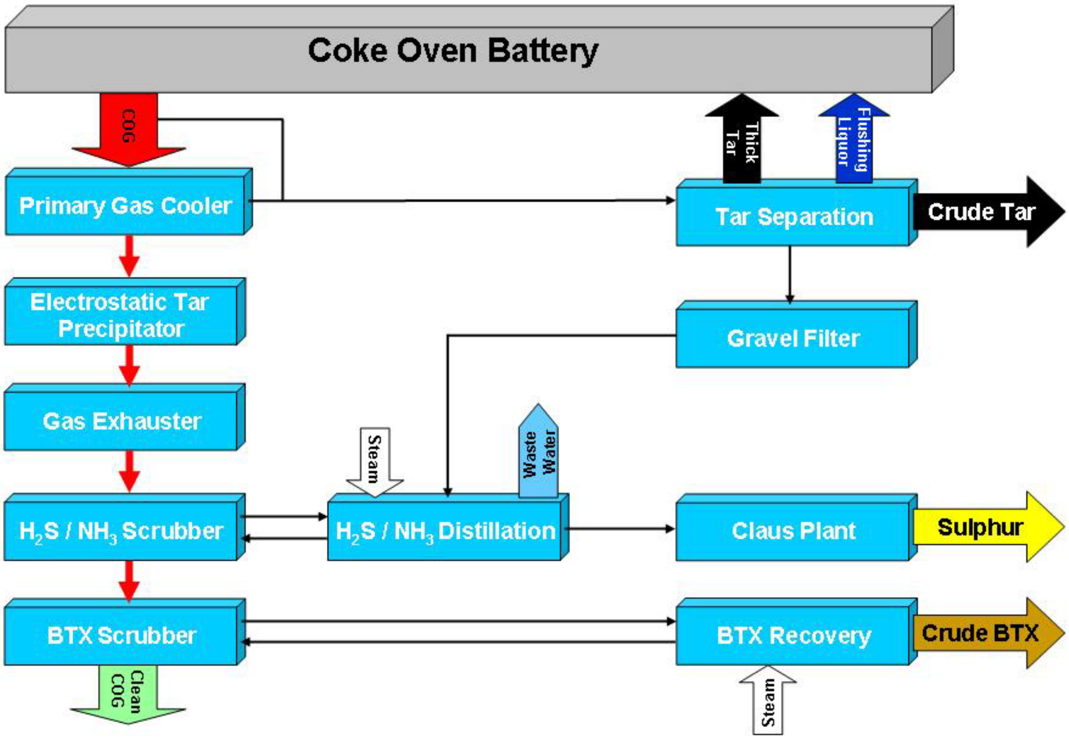

Figure 1. General simplified process diagram.

3 ENVIRONMENTAL AND SAFETY ASPECTS

Safety and environment protection are key items in our design

As known, a By-Products plant is a particularly complex chemical plant. The chemical compounds involved into its processes (H_2, CH_4, CO, BTX, NH_3, H_2S, HCN, $C_{10}H_8$, tar components, etc.) have physical and chemical characteristics that can be particularly hazardous if they aren't handled carefully and with strong attention to safety.

The risks of explosions, releases of gas and liquid noxious substances to the environment, etc. have been deeply checked during the design development of the project and brought to the most advanced provisions for safety.

Among them:

- protection of process areas using explosion proof electric components wherever necessary
- up-to-date waste water treatment plant to meet local regulations for discharge water quality
- closed venting system for tanks and equipment containing aromatic hydrocarbons, to collect and recycle any gaseous effluent to coke oven gas treatment avoiding its release to atmosphere
- selection of materials resisting to corrosion wherever necessary (anti-acid bricks, stainless steels of various type, titanium, etc.)
- wide use of instrumentation and analyzers to monitor continuously plant operation
- selection of pumps and piping suitable to prevent leakages
- inertization with nitrogen of sulphur solidification equipment
- firefighting network with pressure water and foams where necessary
- safety showers and eye-washers wherever necessary

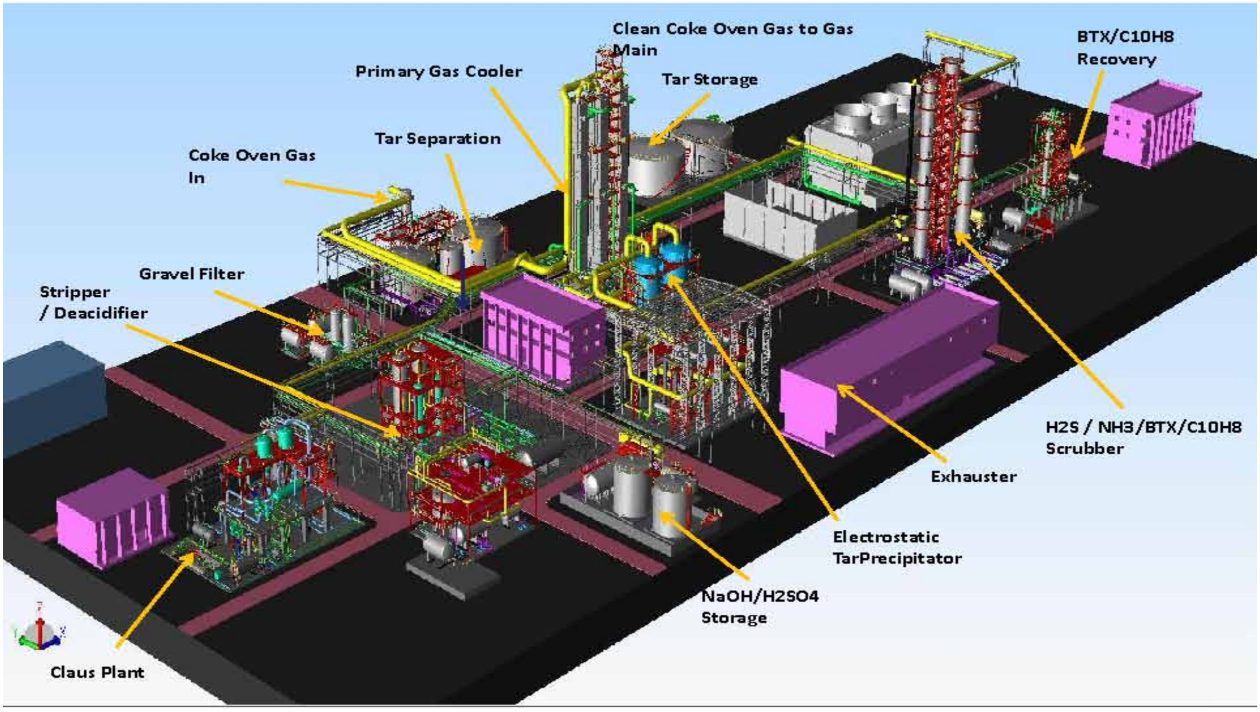

Figure 2. Indicative 3D view of a by-product plant.

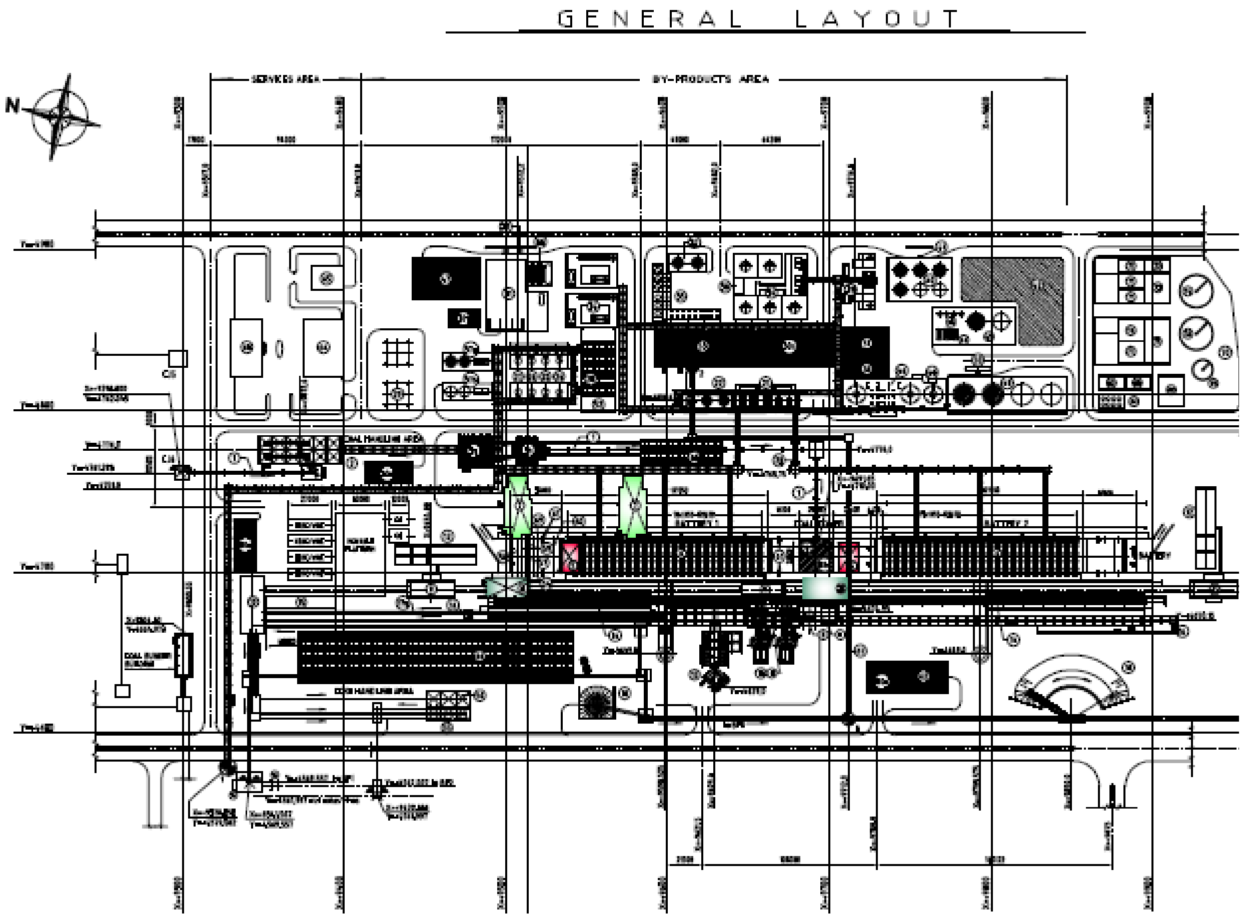

Figure 3. General layout of BSL complete coke oven plant (including space provisions for future doubling)

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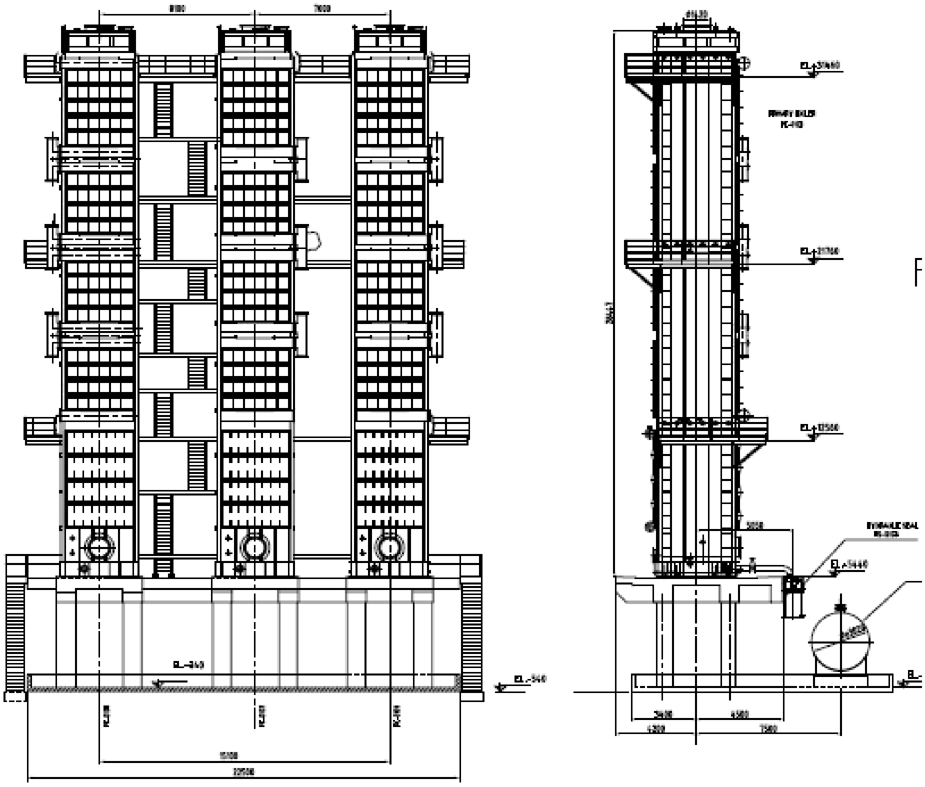

Figure 4. Basic view of coke oven gas primary coolers.

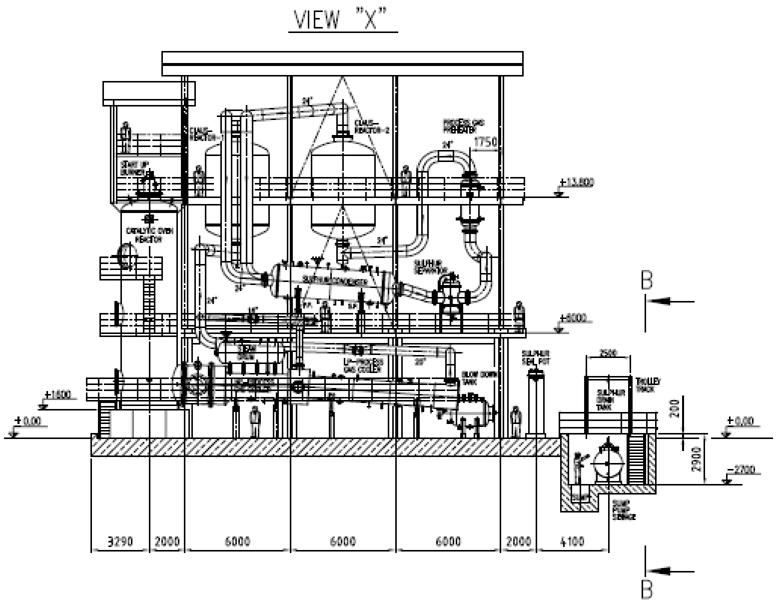

Figure 5. Basic view of claus plant.

4 PLANT COMPOSITION

The By-Products plant is mainly composed of the following equipment:

- 3 gas primary coolers, 2 operating, 1 stand-by
- 2 electrostatic detarrers, 1 operating, 1 stand-by

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- 2 gas exhausters, 1 operating, 1 stand-by
- 1 hydrogen sulphide scrubber
- 1 combi scrubber (stand-by for ammonia or hydrogen sulphide scrubbing)
- 1 ammonia scrubber
- 1 BTX/Naphthalene scrubber
- 2 tar preseparators, 2 tar decanters, 2 tar centrifuges, 2 tar storage tanks
- coal water filtration and storage unit
- NH_3/ H_2S stripping unit
- NH_3-cracking/elementary sulphur unit ("claus" plant)
- sulphur solidification ("pastillation") and storage unit
- BTX recovery and storage unit
- cooling water and chilled water units
- waste water treatment plant with sludge drying and recovery
- utilities distribution and steam condensate recovery system
- ecological venting collection system
- firefighting systems
- storage units for soda solution, water chemicals, etc.
- loading bays for produced and purchased chemicals
- pumps and piping for all process and utility fluids
- steel structures for supporting and access to process equipment
- electric power distribution systems, earthing, lighting, lightning protection, etc.
- process analyzers and control instrumentation and automation
- chemical laboratory
- etc.

5 PROCESS DESCRIPTION - GAS TREATMENT

Plant operation is based, as can be seen on the attached simplified diagram, on a series of treatments that begins with the separation between raw gas and liquors (ammonia water and tar) in a downcomer.

Raw gas is directed to the primary coolers, where it is cooled in two stages (the upper one using cooling tower water, the lower one using chilled water) to a final temperature of 21-22°C. Primary coolers tubes are continuously washed with a light tar-ammonia water emulsion coming from tar decanters, with the results of keeping each primary cooler in operation for months without intensive washing.

The Primary cooling step reduces not only the gas temperature (and therefore its water content and its density) but also because it removes most of naphthalene, tar fog and important amounts of ammonia, hydrogen sulphide and other chemicals.

Gas leaving the primary coolers is directed to electrostatic detarrers, where the residual amounts of tar fog are almost completely removed (down to maximum 20 mg/Nm_3) by an electric field produced by a high voltage gap between emitting electrodes and capturing electrodes (bee hive type) where small tar particles are attracted and then removed.

After this step gas is sucked by exhausters (one operating, one stand-by), which remove continuously gas produced by the battery, keeping the right pressure, and convey it to the following treatments and to the several gas users with sufficient pressure. Gas exhausters are driven by electric motors (in other plants steam turbines are used as alternative, when steam cost is particularly convenient) and for

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safety reasons, two separate power feeds are foreseen. Inlet pressure to exhausters is about -300/-400 mmH_2O, while delivery pressure is about +1600/+1700 mmH_2O. Pressurized gas is then conveyed to scrubbing section.
The first scrubber removes H_2S, using deacidified water (enriched ammonia solution) provided from the stripping/deacidification unit and pre-enriched water coming from the NH_3-scrubber.
The second scrubber, called “combined” or “combi” scubber is a stand-by column that can be used to replace H_2S scrubber or NH_3scrubber in case of their maintenance.
NH_3 is removed in the third scrubber using stripped water coming from stripping/deacidification unit.
Removal of H_2S is foreseen after the H_2S/NH_3-scrubbing unit down to 0,5 g/Nm^3, a value more than sufficient to meet local regulations for SOx emissions. It is very important to note that this desulphurization process doesn’t require the use of purchased chemicals (like many alternative processes do) but only the same NH_3 removed from coke oven gas.
All H_2S and NH_3 (plus amounts of CO_2 and HCN) removed from coke oven gas in the scrubbers, are absorbed in the process enriched water, that from the H_2S scrubber bottom is sent to stripping/deacidification unit.
Here the stripping tray columns (made in titanium and stainless steel) remove the absorbed gases from the enriched solution, which is mostly recirculated to the gas scrubbing.
The H_2S/NH_3 vapours leaving the deacidifiers top are partly condensed, to reduce their water content, and sent to a combined ammonia cracking/elementary sulphur plant..
The H_2S/NH_3-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 H_2S is burned to SO_2. 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 H_2S/SO_2 for the reaction in the following Claus reactor.
The main reactions are:

$$H_2S + 1{,}5\ O_2 === SO_2 + H_2O \text{ (oxidation of one } H_2S \text{ mole every three)}$$

$$2\ H_2S + SO_2 === 2\ H_2O + 3/x\ S_x \text{ (production of elemental sulphur)}$$

$$NH_3 === 0{,}5\ N_2 + 1{,}5\ H_2 \text{ (ammonia cracking)}$$

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. 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.
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 (Sx) plus H_2O.

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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 liquid sulphur system, 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 H_2S/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 SO_2 and H_2S, is directed to the crude gas collection main in front of the PGC.
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. Optionally, the liquid sulphur may also be discharged to a solidification unit to produce sulphur pellets: Liquid sulphur is distributed in form of small drops on a stainless steel belt, cooled from the bottom with water, and solidified on it. The small sulphur "pastilles" of few millimetres size are conveyed by a bucket elevator to a storage silo, and periodically loaded on closed trucks.
The 2-stage claus plant guarantees a plant efficiency of elementary sulphur with an overall conversion higher than 90-92%.
Sulphur produced with this process configuration has a very high purity (more than 99,5%) and it is bright yellow and commercially saleable.
Alternative desulphurization processes require the purchase of chemicals and most of the produced sulphur is unsaleable in due to the reachable bad quality of produced sulphur. The dispose of the produced bad quality sulphur implies additional cost.

Figure 6. Stretford low quality Sulphur (Solidified Product after Autoclave).

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Figure 7. Claus Sulphur of very high purity (Solidified Sample after S-Separator).

Gas almost free of H_2S and NH_3 is now removed, as last stage, by BTX and naphthalene in a scrubber using washing oil of mineral type (called "solar oil").
The removal of BTX is an economical choice, wherever raw BTX (mixture of benzene, toluene and xylenes) has an appreciable market value.
Also BTX/naphthalene removal, as well as H_2S / NH_3 removal, is a closed loop absorbtion/deabsorbtion process.
Enriched wash oil, containing BTX and $C_{10}H_8$ removed from coke oven gas, is heated in a heat high recovery system and sent to BTX stripping column. A side stream is sent to $C_{10}H_8$ stripping column and top vapours from both strippers are completely condensed together with stripping steam leaving the columns.
Raw BTX and water are separated in a decanter and raw BTX is stored and sold.
A small fraction of oil enriched with naphthalene is cooled and naphthalene is separated by crystallization and recycled to coal or to alternative treatment.

6 PROCESS DESCRIPTION – TAR AND WATER TREATMENT

Coming back to the separation between gas and liquor in the downcomer, we have first described gas treatment and recovery of sulphur and BTX.
But another important job of a by-products plant is the treatment of tar and coal water. Coke oven gas leaving battery ovens has a temperature of 800-1000°C and just before entering the battery collecting mains it is sprayed with ammonia water coming from tar separation.
Due to gas temperature part of this water spray evaporates and evaporation heat is removed from hot gas, that is cooled. Of course, there is a physical equilibrium where water cannot be more evaporated because saturation value in the gas is joined. This value depends on water content in the raw gas coming out from the oven (partly physical water contained in the coal, partly chemical formation water produced by reaction between coal hydrogen and oxygen).
Normally raw gas temperature after spraying is approx 80-82°C. At this temperature most of raw tar chemicals are condensed (even if the most volatile remain still in the gas and will be removed in the primary coolers and in the electrostatic detarrers).

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The condensed tar and the sprayed water flow in the lower part of the pipes together with raw gas till the downcomer, and from here flow by gravity to the tar separation unit.
The first step is the solid tar particles removal, occurring in the tar preseparators. A rotating drum with holes of few millimetres holds coarser solids, that otherwise could block downstream equipment.
These matters fall in the bottom, are removed by a sludge scraper and collected to a bin, from where are periodically carried to coal loaded to the battery.
Water and liquid tar flow across the separation drum and flow to the tar decanters, vertical cylindrical tanks with conical bottom.
The difference of density between tar and ammonia water, makes the former to settle in the bottom of the separator, carrying also smaller solids (coal particles mainly).
Raw tar is removed from here and pumped to tar centrifugation. This operation is required to remove solids (normally up to 6-8%) from raw tar before sending it to storage and sale. Leaving solids in the tar would reduce its economical value, for the problems that solids would arise in the storage, in the transport and in the final utilization.
Water removed from tar is pumped to the battery collecting main to cool, as already said, raw coke oven gas to 80-82°C.
But in this closed circuit there is a continuous water increase (water from coal) that must be removed.
A stream of decanted water, corresponding to the H_2O coming from coal (therefore called “coal water”) is continuously removed and sent to further treatments before being discharged.
The first treatment is filtration, to remove its solid content to approx 20 mg/lt, in order to avoid clogging of heat exchangers, trays, etc.
Filtered coal water contains NH_3, H_2S, HCN, etc. and needs to be stripped from these components. In this plant, as in many others, stripping is carried on together with water coming from NH_3 / H_2S scrubbing.
The ammonia stripping is performed, as usual, in two columns: free NH_3 stripping column, where steam is sufficient to remove NH_3 from water, and fixed NH_3 stripping column. In this case, being part of NH_3 chemically bond to strong anions (like SO_4^{--} , Cl-, etc.), a previous reaction with a strong alkali (NaOH in this case) is used to remove them from ammonia salts and allow its separation as free NH_3 (NH_4OH === $NH_3 + H_2O$).
In the water balance of the plant coal water is the main stream to be treated before discharge. Another important stream is due to the amounts of steam used for stripping (NH_3/H_2S stripping and deacidification, BTX stripping, $C_{10}H_8$ stripping), that condensates and is mixed with coal water.
The waste water treatment plant, is suitable to reduced the residual water composition to the acceptable limits foreseen for this plant location:

- pH: 5,5 ÷ 9
- BOD_5 : ≤ 30 mg/l
- COD: ≤ 50 mg/l
- Phenols content (as C_6H_5OH): ≤ 5 mg/l
- Cyanides (as CN^-) : ≤ 0,2 mg/l
- Tar and oils: ≤ 10 mg/l
- Total ammoniacal nitrogen (as N): ≤ 50 mg/l
- Suspended solids: ≤ 100 mg/l
- Transparence to colour: ≥ 30 cm

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7 TECHNOLOGICAL EXPERIENCE IN BY-PRODUCTS

The project includes the most advanced technologies of this field, coming from experience and know-how that Paul Wurth Italia SpA and DMT have collected in many years of activity all around the world.
Among the process equipment we mention:

- **Primary coolers** of indirect type, with capacity of 37500 Nm^3/h each (our experience includes also primary coolers of 42500 Nm^3/h each, among the largest ever built in the world), with design provisions to cool gas without intensive cleaning for several months.

Figure 8. Primary coolers for 42500 Nm^3/h coke oven gas each.

- **Gas scrubbers** of well experienced and reliable design, suitable to clean coke oven gas to the required values, with low pressure drop (and therefore reduced power consumption) and a very high degree of reliability
-

Figure 9. Gas scrubbers for 100000 Nm^3/h to remove NH_3, H_2S, $C_{10}H_8$.

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- **NH_3/ H_2S Stripping** made with highly corrosion resistant materials

Figure 10. Titanium made NH_3/ H_2S stripper for high efficiency removal

- **Sulphur recovery unit (claus plant)** based on similar experience for the largest claus plants ever built in the coke plant sector

Figure 11. A claus plant for high purity sulphur recovery

- **Tar separation** sized to produce good quality tar (with low content of water and almost negligible content of dust), with closed venting system for environmental protection

Figure 12. Tar decanters

8 PROJECT STATUS

The project development is in compliance with the time schedule agreed with the Client, taking into account the whole coke plant development that Bhushan Steel Ltd is carrying on.
The process and detail calculations, the emission of drawings, like process diagrams, P & Is, layouts, equipment construction drawings as well as steel structures, civil works, etc. is almost complete; technical specifications have been completely issued and most of the important equipment have already been ordered or are just being selected.
Start up is foreseen in March 2012.

9 CONCLUSIONS

The main scope of this short description is to give main information about PWIT and DMT technological capacity and experience to design and develop a modern coke oven gas treatment plant with important quality requirements and, very important too, high attention to safety and environment.
In conclusion the main aims of our activity can be summarized as follows:

- priority attention and care to safety and environmental aspects, due to the chemical and physical characteristics of the handled materials
- design aimed to fulfil all process performances and guaranteed values, minimizing operation costs (for example using the same ammonia in the gas to remove H_2S) and maximizing plant reliability (for example using well proven technological solutions as above described)
- attention to energy savings, maximizing internal heat exchanges (in the stripping units for example) and steam condensate recovery (mainly from chillers units)
- time schedule respect in close cooperation with the client requirements