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HIGH PERFORMANCE OF "EOLIOS" PITCH FUME TREATMENT SYSTEM

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Abstract

Since the introduction of paste cooling in the fabrication process of anodes, the generation of pitch fume volatile compounds has drastically increased. In parallel, standards of emissions and operational exposure became more stringent. Consequently, technologies to treat such emissions have evolved to comply with those new requirements.

Fives has developed Eolios, a system that optimizes the combination of a dry scrubber based on the adsorption of PAH on coke fines, and a RTO using oxidation technology, which minimizes the energy consumption and the carbon footprint while maximizing the pitch fume treatment efficiency.

The first system was installed at an anode plant in Norway in 2007 to treat the higher concentration streams with very high destruction efficiency on PAH.

Early 2013, outstanding emission levels were also achieved thanks to Eolios, at a paste plant in Qatar, which sets this new technology as a standard in the industry.

Figure 1: Eolios at Qatalum paste plant

Introduction

Green anode plant activities for aluminum smelters generate noxious vapors containing CTPV (Coal Tar Pitch Volatiles) – especially PAHs (Polycyclic Aromatic Hydrocarbons). Some of them have a carcinogenic effect. Fumes collection and treatment prevent from releasing these pollutants into the working environment and atmosphere. Traditional pitch volatile capture has been performed with coke injection followed by filtration (conventional dry scrubbers). This system has proved its efficiency for global CTPV. In recent years, regenerative thermal oxidizers (RTO) have been used at some plants to improve PAHs destruction particularly on the lighter fractions characterized by their low boiling point. However, the high operating cost of the RTO, mainly generated by fuel consumption, makes it inadequate to take in charge a complete treatment unit, especially for the larger gas volume often required to maintain efficient capture at source.

In order to increase destruction efficiency at lower operating costs, Fives Solios provides a dual approach based on the combination of a conventional dry scrubber and a RTO. In such approach, the RTO is dedicated to hot pitch fumes (higher light PAH fraction emissions) while the dry scrubber is dedicated to cold pitch fumes (lower light PAH fraction emissions).

This combined solution is named Eolios and has been successfully installed in Mosjøen, Norway and in Qatalum, Qatar, allowing the use of a RTO of limited size while maintaining optimal level of performance. These two references had have slightly different approaches:

Indeed, the Norwegian facility being located outside the paste plant, required in-line coke injection in order to avoid pitch condensation in the connecting duct. Therefore a pre-filter was also required to capture pitch-loaded coke prior to the RTO.

On the opposite, the plant in Qatar did not require in-line coke injection and collected fumes are therefore directly conveyed to RTO without any pre-filter. Fumes are consequently heated with hot air through insulated duct work.

This paper summarizes the performance achieved with the Eolios technology on both configurations.

Coal Tar Pitch: The Source of PAH Emissions

Nature of PAHs

PAHs are the main components of coal tar pitch, used as a binder for the fabrication of anodes. Coal tar pitch is a solid material at ambient temperature. To be used into the process fabrication of anodes, it is heated to become liquid and is mixed with pre-heated aggregates (Calcined Petroleum Coke) to obtain a homogeneous hot paste (160-200°C).

At such range of temperature, the coal tar pitch releases high amount of CTPVs which are mainly composed of PAHs. PAHs count more than several hundreds of different compounds. Figure 2 hereafter presents a list of the main PAHs known and measured. PAHs can be divided into two groups: light and heavy fractions. This classification depends on the number of aromatic rings in the molecule. When the molecule is composed of at least three aromatic rings, it is qualified as a heavy PAH. Depending on their

molecular weight and temperature, PAHs exist either under solid state (particulate PAHs) or gaseous state (gaseous PAHs).
Among PAHs, naphthalene is the component with the lowest number of aromatic rings (two rings) and the lowest molecular weight.

Compound	Formula	MW g/mole	I-Teq	IARC 2010, Carcinogenic
Naphtalene	C10H8	128.2	0.001	-
Acenapthylene	C12H8	152.2	0.001	-
Acenapthene	C12H10	154.2	0.001	-
Fluorene	C13H10	166.2	0.001	3
Anthracene	C14H10	178.2	0.01	3
Phenantrene	C14H10	178.2	0.001	3
Fluoranthene	C16H10	202.3	0.001	3
Pyrene	C16H10	202.3	0.001	3
Benzo(a)fluorene	C17H12	216.3		-
Benzo(b)fluorene	C17H12	216.3		-
Benz(a) Anthracene	C18H12	228.3	0.1	2A
Chrysene	C18H12	228.3	0.01	3
Triiphenylene	C18H12	228.3		-
Benzo(b) Fluorantene	C18H10	226.3	0.1	2B
Benzo(j)fluoranthene	C20H12	252.3		2B
Benzo(k) Fluorantene	C20H12	252.3	0.1	2B
Benzo(a) Pyrene	C20H12	252.3	1	2A
Benzo(e) Pyrene	C20H12	252.3		-
Benzo(g,h,i) Perylene	C22H12	276.3	0.01	3
Indeno(1,2,3-cd)pyrène	C22H12	276.3	0.1	2B
Dibenzo(a,h) Antracene	C22H14	278.4	1.4	2A
Coronene	C24H14	300.4		-
Dibenzo(a,e)pyrene	C24H14	302.4		2B
Dibenzo[a,h]pyrene	C24H14	302.4		2B
Dibenzo[a,i]pyrene	C24H14	302.4		2B
Benzo(b) naphto (2,1-d)thiophene	C16H10 S	234.3		-

Group 1: Carcinogenic
Group 2A: Likely Carcinogenic
Group 2B: Possibly Carcinogenic
Group 3: Not Carcinogenic

Figure 2: List of PAHs with carcinogenic index [2], [4]

Some PAHs which contain five to seven benzene rings are known to be likely or possibly carcinogenic.

However, light PAHs have significant toxicity to aquatic organisms because of their higher solubility in water. So, for both human health and environmental concerns, these PAHs should be destroyed when they are emitted by industrial processes. The benzo(a)pyrene (also named B(a)P), is classified as likely carcinogenic to humans by the International Agency for Research on Cancer (IARC 2010 in Figure 2). It is the most studied PAH and has been often used as a marker.

The EPA regulation has identified 16 PAH molecules as priority pollutants to monitor, based on their carcinogenicity and occurrence, including the naphthalene whose carcinogenicity for human is today contested by some studies [5]. The OSPAR regulation only monitors 11 PAH molecules, which are mainly the heaviest PAHs, the most carcinogenic.

PAH Emissions in the Fabrication Process of Anodes

In paste plants, PAH emissions occur in all areas where coal tar pitch is used or stored at high temperature. The main areas affected by emissions are the paste mixer, the paste cooler and the anode forming area. Obviously, liquid pitch storage tanks are also source of high emissions.

The proportion of light PAHs appears to be 70% of total emissions, against some 30% for heavy PAHs (Figure 3).

The anode paste cooler equipment has been introduced in the anode fabrication process to improve anodes density. In the paste cooler, the anode paste is mixed and sprayed with water (approximately 15 liters of water per ton of paste).

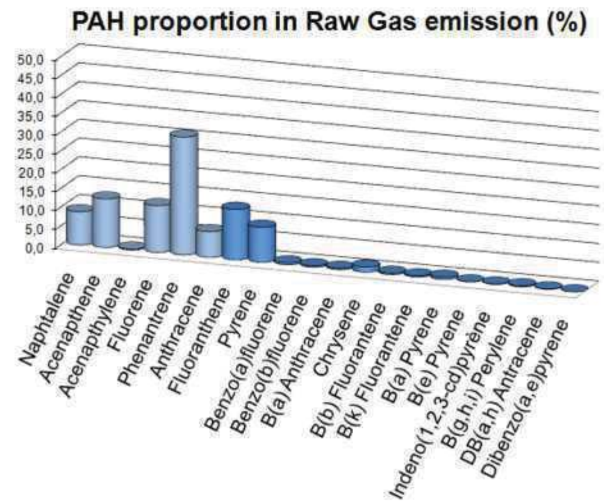

Figure 3: Typical PAH distribution of pitch fumes in paste plant

Using water to cool down anode paste lowers the partial pressure of PAH vapors generated by the paste, thus displacing the equilibrium towards production of light PAH fractions.

Consequently, adding water into the paste cooler drastically increases the amount of light PAHs. This phenomenon was first confirmed at the Alcoa Deschambault paste plant, (Canada) where PAH emissions were multiplied by six after paste cooler installation [1]. It was also observed that pitch volatiles concentration is doubled when the temperature of liquid pitch increases by 20°C. Consequently, increasing mixing temperatures have also contributed to higher PAH emissions.

Conventional Coke Dry Scrubbing System

The dry scrubbing system is derived from the potline alumina dry injection scrubbing technology. This treatment system was developed by Solios in 1977 and has been installed up since then in more than 70 plants in the world. It consists in injecting coke fines in a gas stream loaded by pitch fumes. An adsorption phenomenon occurs between coke and pitch fumes, as the large specific area (6,000 to 7,000 Blaine) and opposite electrical charge of the coke fines allow adsorption of pitch fumes pollutants. Then, the fines fraction of coke readily available for the preparation of the anode paste is injected counter-currently to the fume-laden stream. Turbulence and highly efficient contact between the pitch fumes and aerosols are promoted inside a Venturi reactor. Pitch loaded fines are then collected through the dust collector (pulse jet bag filter) and are reintroduced into the anode paste recipe with their condensed hydrocarbons. Finally, clean gases are then released to the atmosphere through a discharge stack (Figure 4). As pitch-loaded fines are recycled into the anode manufacturing process, the process does not imply any waste stream or product loss. As mentioned above, suction points for pitch fumes collection are installed on pieces of equipment that generate pitch vapors in ambient air.

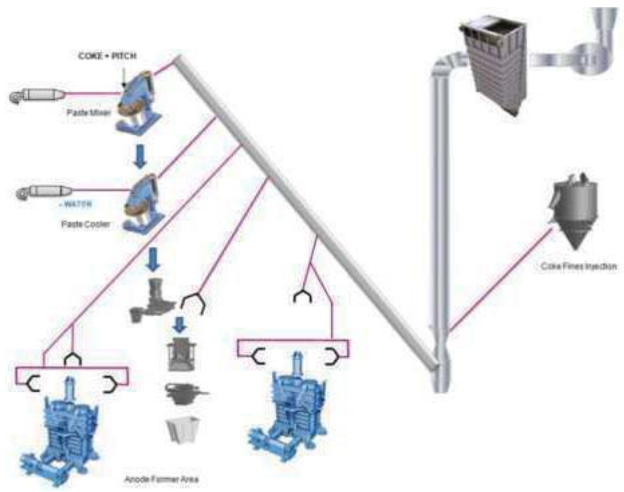

Figure 4: Typical Dry-Scrubbing - schema

Respective suction flow is determined at each point depending of the expected load and temperature of fumes. In some critical areas, an electrical heater is systematically installed to maintain pitch fumes temperature above dew point to avoid pitch and water condensation in the ductwork. For this reason, temperature of fumes released by cooler is carefully controlled to avoid condensation. Water vapor from cooler has always been successfully mixed with hot fumes and participates in diluting fumes load.

Another solution to prevent clogging the ductwork is a configuration with in-line coke injection in multiple points upstream from the Venturi reactor.

Such configuration allows catching tars straight at the equipment fumes pick-up point. Respective suction points with in-line injection are determined in regards to their pollutant load, temperature, moisture content, etc. No matter the chosen configuration (single or multiple coke injection), the ductwork is designed to provide an easy cleaning.

The global PAH capture efficiency of dry scrubbing varies between 90% and 98%, depending on the treatment temperature and the list of PAHs considered (EPA, OSPAR, others).

This efficiency is higher for heavy PAH (fluoranthene, pyrene and heavier). For these components, the common efficiency is about 99,5%. The dry scrubbing system philosophy is based on the ability of PAHs to condensate when entering in contact with coke fines inside the reactor: this allows their adsorption on the surface of coke fines. That explains the higher efficiency of the process on heavy PAH fraction, which condensate easily.

The condensation and, as a consequence, dry-scrubber efficiency, obviously depends on the temperature.

In cold countries where climate conditions are favorable to the condensation of the light PAH fraction, the global coke dry scrubber efficiency can rise up to 98%. As explained above, the most toxic PAHs are the heaviest fractions (B(a)P or equivalent), which are extremely well treated by conventional coke dry scrubbers. In the last 30 years, coke injection dry scrubbers have been recognized as being the most practical solution in green anodes plant. [Ref EPA MACT 1996]

Today, in order to face the increase of PAH emissions in the green anode process production, a new technology based on an oxidation reaction of the hydrocarbons has been developed. This technology will be described here below.

RTO: New Technology for a Better Destruction of light PAHs

The RTO Principle

The RTO is widely used in solvent and painting industries to destroy hazardous air pollutants like VOC (Volatiles Organic Compounds) or odorous emissions.

PAHs, mainly composed of C-H bonds, are easily broken by oxidation as follows.

$$\mathbf{C_aH_{2b} + (a+b/2)\, O_2 \rightarrow aCO_2 + bH_2O + Heat}$$

The oxidation temperature is about 850-900°C, depending on the nature of PAHs. Good combustion practices include management of the “3T”: Temperature, Turbulence and Time.

RTO Description (Figure 6)

The RTO is a compact equipment composed of 3 main elements:

- *The combustion chamber,* where the oxidation reaction takes place;
- *Ceramics beds*, which are used as heat exchangers: they store heat and recover it to preheat the inlet gas flow, allowing for energy savings;
- *The valve box*, which includes two valves for inlet & outlet duct fumes isolation and one purge valve per chamber.

Raw pitch fumes (1) are introduced via the inlet valve box into tower B and pre-heated when passing through the ceramics (5) in order to reach the required temperature for PAH combustion. The residence time in the combustion chamber (6) (about 1-2 seconds) is enough for the destruction of PAHs. The combustion of PAHs is exothermic, therefore reducing the consumption of the burner (7). The clean gas is conveyed from the combustion chamber into the second heat exchanger A then is released through the exhaust stack (9). The third heat exchanger C is in purge mode in order to remove the remaining raw gas residues (Figure 5).

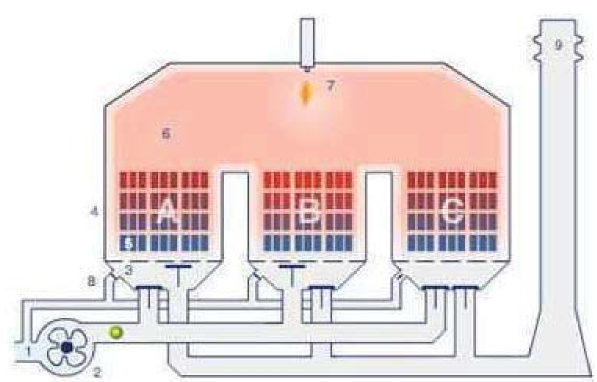

Figure 5: The RTO Principle

A bake-out is necessary to remove all condensates built-up at the grids and at the bottom of the ceramics. A bake-out consists in heating up these residues at 450°C during 5-6 hours. This operation removes all deposits (Figure 6). The control of pressure drop through the ceramics allows quantifying their fouling.

Figure 6: RTO grids before and after a bake-out

As oxidation of pitch fumes is exothermic, when the concentration of pitch fumes in the raw gas is about 1-1.5g/Nm^3, the RTO is in auto-thermal mode, with no any additional gas input [3].

Eolios at Qatalum Paste Plant:
An Innovative Solution for Optimum Emission Performances

Figure 7: RTO at Qatalum paste plant

Process Description

At Qatalum paste plant, stringent emission requirements have led Fives Solios to install the Eolios system to treat coal tar pitch fumes.

The high concentrated fumes collected from the paste cooler, which contain mainly light PAH fractions and water vapor, are specifically treated by a RTO unit. This flow is about 4,000 Nm^3/h (including the hot air). Fumes emitted by the remaining pieces of equipment (mixer, vibrocompactor, etc.) are treated by a dedicated dry scrubber (flow rate of 42, 000 Nm^3/h) (Figure 8).

To avoid tar and water condensation in the duct, it is necessary to heat up the fumes with a hot air generator located before the paste cooler. Upstream the RTO, a drain pot is installed to collect tar condensates and avoid their accumulation inside the RTO ceramics. After mixing with hot air, diluted fumes enter the RTO unit at a temperature of 150°C..

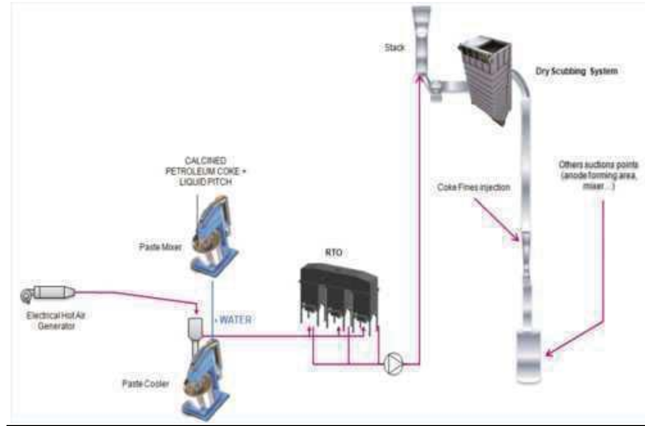

Figure 8: Eolios at Qatalum paste plant

Eolios Performance

A set of FID (Flame Ionization Detector) measurements has been performed in order to estimate the relationship between RTO temperature and destruction efficiency. The FID measures the concentration of Total Volatiles Organic compounds.

FID measurements performed at Qatalum plant show clearly that a higher combustion temperature enhances RTO efficiency due to an increase in organic compounds destruction.

We measured a 91.2% efficiency at 840°C against 96.2% at 870°C.

Once the system was fine-tuned, performance tests have been undertaken at the main stack by a third party. PAH emissions were measured as per ISO 11338-1-1 standard.

Results display a **0.96 mg/Nm^3 concentration for 16 PAH (Norwegian Standard 9815)** corresponding to a global destruction efficiency for the Eolios system of **99%. This value sets a new benchmark for the Eolios designed without pre-filter.**

Eolios at Mosjøen: Good Results after 6 years

Fives Solios supplied its first Eolios at Alcoa Mosjøen Aluminium Smelter in 2007.

On this reference, the ventilation of the green anode plant is split into two separate lines: the wet fumes line, treated with a dry-scrubber followed by the RTO and the dry fumes line, treated with a dry-scrubber only. These two lines are implemented in parallel and join each other at the stack.

On both lines are installed in-line coke injections which allow catching pitch vapors on the coke fines close to the location of emissions. The dry line generates a low concentration of pollutants and is mainly taken in charge by a Venturi reactor with coke injection followed by filter bags. The wet line collects much more gaseous tars and PAHs and is treated by RTO associated to a pre-filter with coke injection (Figure 9).

The dry line is designed to treat 54 000 m^3/h at 35°C (48,700 Nm^3/h) whereas the wet line is designed to treat 19,000 m^3/h at

65°C (15,200 Nm^3/h) Guarantee was given on PAH16 according to the NS 9815 list (light fraction naphtalene, acenaphtene, acenaphtylene, and fluorene excluded) at 0.05 kg/h for both dry and wet lines.

Eolios performance has met the PAH plant requirement of 0.05 kg/h (NS 9815) or **0.8 mg/Nm^3** for the whole plant.

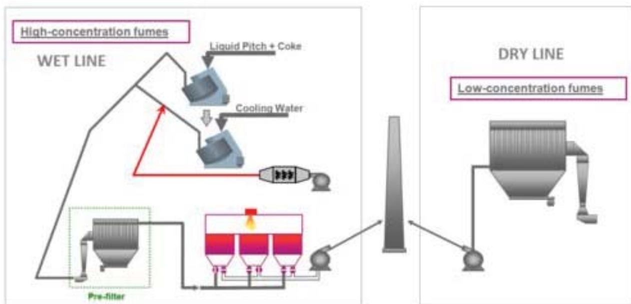

Figure 9: Eolios at Mosjøen Plant

The pre-filter installed on the wet line runs exactly like the one of the dry line.

The first important maintenance intervention on the RTO appeared recently after 6 years operation. Regarding dry-scrubber, the regular preventive maintenance has ensured correct running of the plant over this whole time (Figure 10).
Routine measurements still testify of this global efficiency after six years of operation. As an example, PAH measurements performed from May 2012 to April 2013 were in average 0,014 kg/h and at maximum 0,040 kg/h at stack for both wet & dry lines. Dust measurements at the same period remain inferior at 0,040 kg/h as well with an average of 0,018 kg/h.

Figure 10: Mosjøen Paste Plant RTO

Comparison between Eolios configurations

As detailed earlier, the two Eolios systems supplied by Fives Solios respectively at Mosjøen (2007) and Qatalum (2010) are slightly different: Mosjøen plant is equipped with a pre-filter, which is similar to a conventional coke dry-scrubber of reduced size, installed upstream the RTO. Whereas Qatalum plant is simpler and has no filtration upstream the RTO.

This difference of design is linked to the characteristics of each plant and necessity of pre-filter is evaluated by Fives Solios on a case-by-case basis.

Our experience has led us not to propose a pre-filter, except if one of the following conditions is filled:

- **When dust concentration in fumes at RTO inlet is expected to be high**. Indeed, a RTO is very sensitive to dusts that can build up inside honeycomb and prematurely damage ceramics. Dusts are also responsible of high temperature peaks inside the combustion chamber as they represent an additional energy provision. It has also been observed that dusts favor tars condensation and deposits on the ductwork and at the RTO inlet. Presence of dusts depends on what equipment is included in the RTO line or wet line. Usually, paste mixer is the most important dusts contributor with possible flight of coke fines that will end their way in the pitch fumes network. When the paste mixer is vented by the dry-scrubber as in Qatalum, a pre-filter upstream from the RTO is not necessary.
- **When there is a long distance between the RTO and the Green anode plant**. If the configuration is such that the RTO is far from the emission suction points, a pre-filter will allow proceeding to a coke injection before the RTO. This coke injection is useful to keep the inlet duct clean all along the distance and avoid tars condensation. Indeed, abrasion properties of the coke are used to prevent from clogging inside the duct network and treatment by coke injection serves of duct cleanser.

Whatever the chosen configuration, the Eolios has demonstrated its efficiency.

<u>Eolios vs. Full RTO</u>

The introduction of the RTO in the Eolios configuration to treat part of coal tar pitch fumes emitted by the paste plant can raise a question about the possibility to use it to all paste plant streams.

The advantage of such configuration is to have a diluted stream that is optimal for RTO operation. However, as the RTO is more efficient on light PAHs, the global destruction efficiency for PAHs in a whole (light and heavy) is limited at 95%. This limited efficiency is due to the adsorption/desorption phenomenon of heavy and intermediate PAHs that occurs in heat exchangers during a cycle. This configuration seems totally unable to achieve the 99% observed for the Eolios system at Qatalum and Mosjøen Paste plant.

An alternative to the full RTO is the Hydrid RTO which conveys highly concentrated streams directly to the combustion chamber via a specific burner.

The energy consumption for such configurations (full RTO and full Hybrid RTO) is another parameter to take into account: A more diluted stream decreases pitch fumes concentration, taking away the RTO from autothermal mode. A full RTO of 50,000 Nm^3/h, requires around 100 m^3/h of gas whereas a RTO integrated in the Eolios technology will only consume about 20 m^3/h of gas. The hybrid RTO requires even higher gas consumption, up to 120 m^3/h (hybrid flow rate: 3,000 Nm^3/h & main RTO inlet: 27,000 Nm^3/h), (see figure 11).

	Full-RTO	EOLIOS
Description of solution	→ All pitch fumes are directed to a RTO preferably equipped with a pre-filter.	→ Only high concentrated fumes generated from the paste cooler and other equipment handling hot fuming paste are direction to a RTO. → All other sources are directed toward a conventional Coke Dry Scrubber.
Destruction/capture efficiency of PAHs	→ 95 to 99%	→ 99%+ in cold and moderate climate such as Norway and Canada; → 97%+ in hot climate
Characteristics of a typical 50,000 Nm³/h system		
Typical flow distribution	→ 50,000 Nm³/h treated by a RTO.	→ 5,000 Nm³/h treated by a RTO. → 45,000 Nm³/h by a coke dry scrubber.
→ **Natural gas**	→ 3.9 GJ/h or 103 m³/h → 226,000€/year @ 0.25€/m3	→ 0.8 GJ/h or 20 m³/h → 44,000 €/year @ 0.25€/m3
→ **CO_2 Emissions from natural gas consumption**	→ 850 T/Year	→ 170 T/Year

Figure 11: Full RTO vs Eolios

Moreover, the flow rate passing through the heat exchanger is used to size the RTO. RTO dimensions will increase with flow rate, therefore increasing considerably CAPEX.

In both configurations, the system (full RTO and hybrid RTO) cannot benefit of the biggest asset of the Eolios: flexibility. RTO direct by-pass to the atmosphere does not exist in the Eolios solution, as the RTO by-pass is directed to the dry-scrubber. It means that pitch fumes are at least treated by the coke dry-scrubber in case of unexpected problem that would require stopping the RTO. This offers an attractive possibility to switch on the dry-scrubber by-pass which remains quite “clean” in terms of emissions. This possibility is not available with a full RTO or hybrid RTO configuration.

This advantageous RTO by-pass through dry-scrubber is very comfortable for operation. Whereas a direct by-pass must be used at the strict minimum for environmental worries – that is to say mostly during emergency conditions – Fives Solios by-pass including fumes treatment can also be used for any maintenance or operation issue. It is worth reminding that an RTO has important inertia due to its ceramics and can be protected, using the by-pass, from abrupt and impetuous variations at inlet. Therefore, any of these variations can be absorbed by the coke dry-scrubber and keep the RTO ready to run on dirty fumes without delay when the problem is solved and inlet conditions are back to normal operational ones.

Last but not least, the Eolios offers a higher treatment capacity over full RTO or hybrid RTO configurations. To limit full RTO CAPEX, RTO suppliers tends to reduce as much as possible the treated flow rate, whose temperature shall be high enough for condensation problems. The Eolios does not need to heat fumes on its dry-line, as coke injection of the dry-scrubber adsorbs tars at ambient temperature. It is quite interesting to be able to increase ventilation on the paste plant, as the possibility to treat more air with same inlet data is directly linked to safety issues (ambient air quality in paste plant). The possibility to increase the treated flow is also useful for revamping considerations and much easier to perform on an Eolios that on a full RTO solution.

Conclusion

Environmental emissions are becoming more and more stringent, especially for suspected carcinogenic substances such as PAH’s from pitch vapor. Dry scrubbers remain the most efficient technology to treat heavy PAHs, however the introduction of RTO to treat lighter PAHs is a radical improvement for the whole pitch fumes treatment system.

The Eolios solution, which combines dry scrubbing and RTO, allows operating the green anode plant while maintaining PAH emissions at stack below such stringent requirements. Eolios exhibits a lower operating cost and a smaller carbon footprint than alternative technologies, such as full RTO for instance, while providing very comfortable flexibility of operation thanks to its convenient by-pass to dry-scrubber.

The implementations of Eolios at Mosjøen Paste plant and recently at Qatalum Paste plant confirm the benchmarking performance and benefits associated with this technology.

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