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FUME TREATMENT SYSTEMS BASED ON RTO TECHNOLOGY FOR CARBON BAKING FURNACES

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Abstract

Increasing environmental demands, especially for emissions of the carcinogenic PAH (Polycyclic Aromatic Hydrocarbons) require new technologies for the treatment of fumes from carbon anode production plants. Thermal systems have been supplied to several paste plants as well as baking furnaces for the production of anodes, electrodes and cathodes. Due to the specific pollutants such as HF and the behaviour of the sticky condensates, the systems have to be designed properly to ensure a high availability. Pre-filters and preheating avoid clogging of the heat exchanger material of regenerative thermal oxidizers (RTO's). In addition, stringent health and safety issues as well as a specific fire protection system have to be considered during the design, construction and operation of a new plant. The paper shows the required process steps and the technical solution on the basis of plants for several baking furnaces in Poland and France.

Situation of Emissions

Independent of the technical systems used for the production of carbon products, such as electrodes, special graphite products or anodes, Polycyclic Aromatic Hydrocarbons (PAH's) are an important issue for the production manager. As PAH's are classified as carcinogenic, a major target is to reduce emissions and the impact on people as well as on the environment.

Sources of emissions occur across the whole manufacturing plant for processes where pitch is used. The following areas can be identified in carbon plants:

- Liquid pitch storage and melting
- Paste plant or green carbon production
- Baking furnace

As the baking furnace represents the majority of the emissions of a carbon manufacturing plant, this paper will only investigate the emissions from baking furnaces.

The U.S. Environmental Protection Agency (EPA) has classified seven PAH compounds as probable human carcinogens: benz(a)pyrene, benz(b)fluoranthene, benz(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene [1].

In order to compare emissions and to have a common basis, 16 PAH compounds which can be found in all emissions are grouped together and referred to as PAH16. The distribution within this group has been measured by LTB and Figure 1 shows the distribution for four different emission sources. Most important is that different emission sources show a very similar distribution of the different PAH's. Hence, this could be seen as a strong basis for future selection of a fume treatment system.

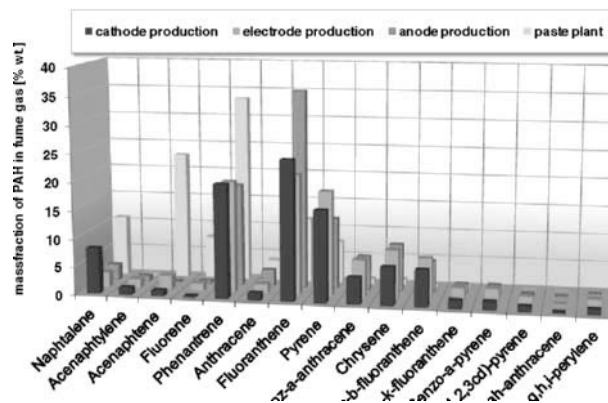


Figure 1: Distribution of PAH from Different Sources (LTB measurement data)

In many countries, benz(a)pyrene, B(a)P is used to monitor PAH's instead of measuring all PAH16 compounds and it is currently listed separately in the draft for the IPPC non-ferrous metals from July 2009. So the critical pollutants of PAH16 (or B(a)P) and Benzene are important considerations for carbon manufacturing plants and have to be considered during the design of the fume treatment systems (FTS).

In the past, conventional dust collecting systems like electrostatic precipitators or bag house filters have been used. To enable a proper efficiency, these systems have to be equipped with a cooling system in order to condense some of the gaseous compounds. Figure 2 shows that not all PAH's can be condensed, and for example, naphthalene is more than 90% gaseous. Consequently, purification with conventional filter systems as a stand-alone solution is no longer possible in order to meet current emission limits.

Based on the above, a new method for the treatment of emissions is required. Thermal treatment has been recognized already as an efficient method to reduce volatile organic compound (VOC) emissions. Several Regenerative Thermal Oxidizers (RTO's) have been installed for liquid pitch storage and green paste plant emissions. The solution at EMAL has already been reported [2].

To avoid the need to replace existing fume treatment plants of baking furnaces, some efforts have been made to improve the overall efficiency by optimizing the combustion inside the furnace. It has been reported that firing systems could be improved in order to reduce the PAH emissions [3], but a further thermal treatment is mandatory [4].

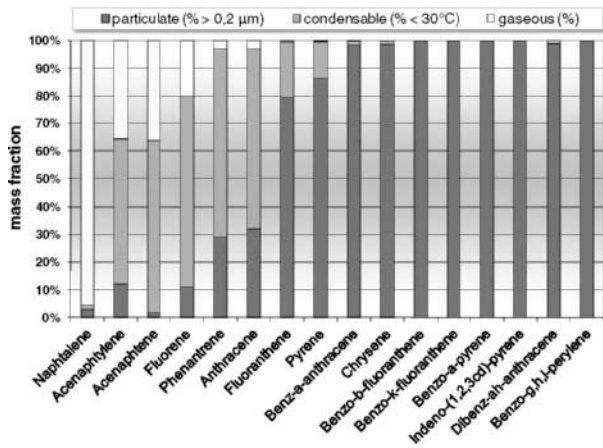


Figure 2: Physical State of PAH16 at Common Fume Conditions (temperature 120°C, humidity 5 % vol.; LTB measurement data)

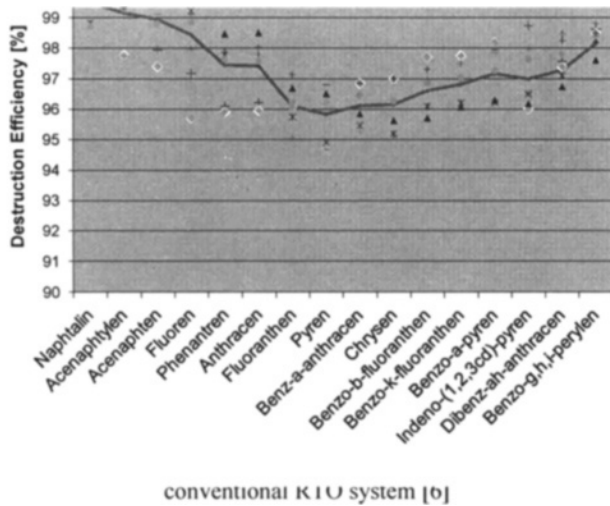
Concept of a Thermal Fume Treatment

Based on the results of several ROxiTHERM™ plants [5], it has become apparent that normal RTO systems would fail due to the relatively high amount of condensed particles, i.e. tar. When considering the use and performance of an RTO system, the following items have to be considered:

- Particulate matter and pre-filtering
- Design of the RTO (condensates & redundancy)
- Hydrogen Fluoride (HF) emission due to butts recycling
- SOx emissions

Pre-Filter

Currently, several baking furnaces for the production of electrodes and anodes are equipped with RTO systems. On all these applications, the focus is on PAH control. The achievable efficiency measured at various single RTO systems and the average numbers (red line) are shown in Figure 3.



These measurements have shown that the achievable destruction efficiency of a single RTO system is limited due to adsorption and desorption effects which are a result of the

different vapor pressure behavior of each single PAH compound.

If the requirements are more stringent (typically the case in Europe) and the efficiency has to be higher or soot occurs, a second step of treatment has to be considered. For baking furnaces already equipped with an electrostatic precipitator (ESP), this could be used or a specific pre-filter can be installed instead. The pre-filter is filled with ceramic media which are specially chosen to provide a higher turbulence and impact surface compared to those used in an RTO. This enables the collection and storage of particles in the pre-filter instead of the RTO heat exchanger. Figure 4 shows a pre-filter which was in operation for two days and which is already loaded with particles and condensates.



Figure 4: Packing in a Pre-filter



Figure 5: Pre-filter System of a FTS (during installation)

As the storage volume for particles is limited, the pre-filter has to be cleaned regularly. The purification has to be done “off-line”, i.e. without normal use of the filter. For the design of a system, a second pre-filter needs to be considered. Figure 5 shows a pre-filter system with four filter units for a flow rate of 135,000 Nm³/h (80,000 scfm) where three units are always in operation in parallel, allowing one to be cleaned.

The purification works similar to the so-called “burn-out” of a RTO, where hydrocarbon deposits are gasified via injection of hot air, which leads to an increase of temperature up to more than 400°C (750°F).

Condensates in RTO

In spite of the installation of pre-filters, a considerable amount of condensates can still reach the RTO which is a big challenge for standard RTO systems. Due to an accumulation, especially at the bottom inlet of the ceramic heat exchanger media, the free area for the fumes is clogged and the heat transfer is reduced. The clogged channels of the ceramic media can be seen in Figure 6 as well as the cleaned ceramic media after a burn-out. Another important factor is the increased fire risk due to flammable deposits in the RTO. This risk can be reduced by operating a special cleaning mode, the burn-out.

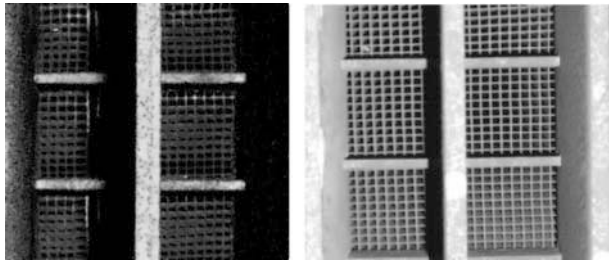


Figure 6: Ceramic Media Before and After Burn-out

During this burn-out, hot gas is drawn from the RTO combustion chamber down to the inlet of the ceramic media and all organic deposits, such as sticky hydrocarbons, are gasified. As the gasified deposits have a high calorific value, they will be used as fuel for the system, and will be directed into the oxidation chamber. For this, LTB has developed a special annular gap burner, Figure 7, through which the gases are injected directly into the combustion chamber and completely oxidized. This allows the burn-out to work without increased emissions.

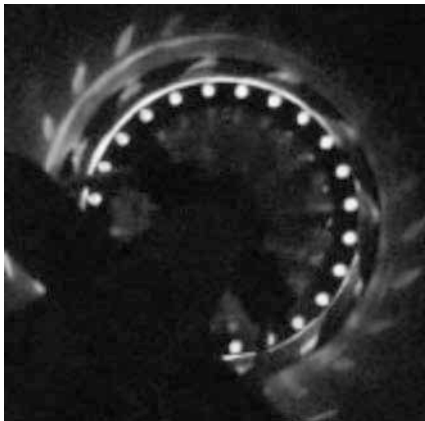


Figure 7: LTB Annular Gap Burner

A normal 3-chamber RTO can only run as a 2-chamber RTO during burn-out mode which leads to a reduced cleaning efficiency due to the missing purging cycle. LTB therefore uses a fourth chamber in order to ensure a continuous 3-chamber mode even when one chamber is operated in burn-out mode (emission-free burn-out mode). Measurements at a plant in Germany showed that the B(a)P-emissions of an optimized 4-chamber RTO do not increase significantly even during the burn-out mode of one chamber, Table 1.

Table 1: B(a)P Efficiency of an Optimized 4-chamber RTO during Normal Operation and Burn-out mode

Operation mode	BaP Input mg/m ³	BaP Output mg/m ³	BaP Efficiency %
normal	4.68	0.13	97.3
normal	4.18	0.19	95.6
normal	2.95	0.08	97.3
Burn-out	6.24	0.24	96.3
Burn-out	8.21	0.18	97.9
Burn-out	7.96	0.22	97.3

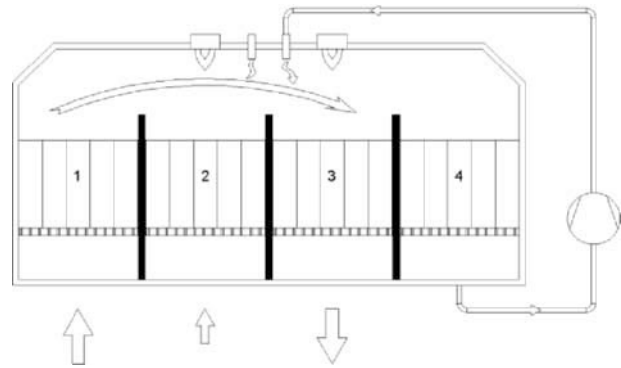


Figure 8: 4-chamber RTO with Emission-Free Burn-out Mode

The 4-chamber RTO shown in Figure 8 operates according to the following functions, which change during normal operation:

- Chamber 1: fumes inlet
- Chamber 2: purging to avoid peaks
- Chamber 3: clean gas outlet
- Chamber 4: burn-out/ purification

Furthermore, the 4-chamber RTO shows another benefit: Since most fume treatment plants have to be run with a very high availability, several installations are operated in parallel to enable maintenance and regular inspections without any reduction of fume treatment capabilities. For example, a baking furnace usually runs for several years without a shut-down, and a bypass is allowed only for a short time. Therefore, one would have to install three conventional 3-chamber RTO units in order to keep full redundancy. For these applications, LTB developed a method to run the fume treatment system with two RTO systems only, even during maintenance of one RTO. These RTOs can be operated in a special mode, which allows one unit to run with double the volume flow for a limited time, the so-called TWIN MODE™ shown in Figure 9.

During this new mode of operation, the purging and burn-out will be avoided and two pairs of the four chambers will operate in parallel. As shown in Figure 9, two chambers run with the fume inlet and two with the clean gas outlet providing the double fume treatment capacity.

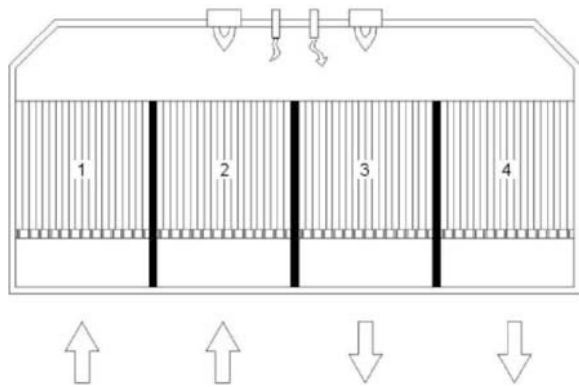


Figure 9: TWIN MODE™ System during double volume flow operation

HF Emissions

Due to the recycling of butts, HF will be emitted during the baking of anodes. For the purification, different solutions can be used. Wet scrubber systems, which are designed to reduce HF only, are not the best choice if a downstream water treatment is required. This increases the investment and operating costs. Alternatively, a dry system which uses the high absorption ability of HF towards alumina or limestone could be used. If alumina is available on site, a dry scrubber with alumina injection would be the preferred solution because the alumina could be re-used in the pot rooms. If this is not the case, a dry scrubber system with limestone could be a solution.

LTB has a patented, one stage packed bed absorber system using granular limestone. The reaction creates fluorspar, which is a natural, non-toxic mineral and can be disposed of easily:

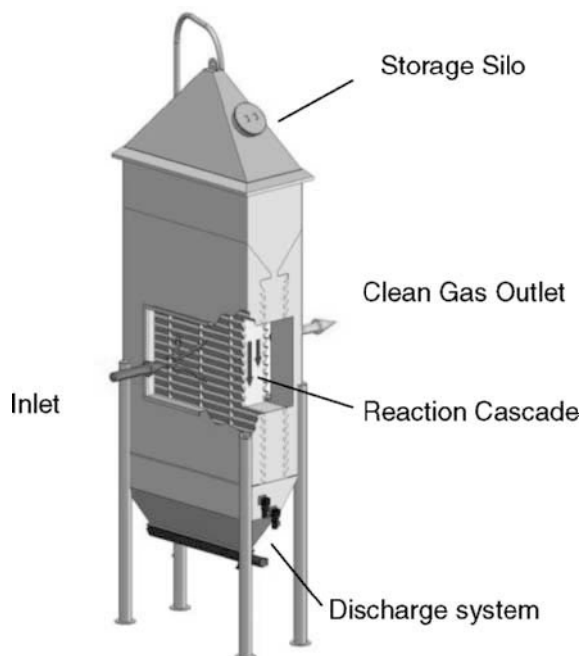


Figure 10: LTB Packed Bed Filter for HF absorption

As shown in Figure 10, the limestone is stored in a silo and led to a cascade, into which the gases pass in a cross flow. After the

reaction takes place, the material is transported downwards in a moving bed and discharged. The gases leave the plant cleaned.

A number of installations in different industries show good HF abatement with reasonable consumption of limestone. Various Measurements have shown an average consumption of limestone of below 10 kg per kg HF, Table 2 (values based on the use of Blaubeuren limestone).

Table 2: Specific Consumption of Limestone for HF Absorption in a LTB packed bed filter

Flowrate m ³ /h S.T.P	HF inlet mg/m ³ S.T.P	HF outlet (measured) mg/m ³ S.T.P	Lime- stone cons. kg/h	Spec. cons. kg lime/kg HF
25,000	35	< 1	8.0	9.1
25,000	35	< 1	8.0	9.1
21,000	30	< 1	4.0	6.3
6,000	70	< 1	4.0	9.5
6,000	70	< 1	4.0	9.5
6,200	50	< 1	3.0	9.7

SO_x Emissions

Sulphur emissions are a result of sulphur in the raw materials like pitch and coke. Even if low sulphur coke with only 1.5% S is used, this will create emissions which can exceed the current European limits of 200mg/m³ as well as limits of 500 mg/m³ elsewhere in the clean gas.

Fuel itself can also be a source of emissions. Rising energy costs have led to the use of alternative fuels such as heavy fuel oil (HFO) or even residue derived fuels (RDF). Since the costs are approximately \$500/t less than any other distillate fuel or natural gas, HFO or RDF seem to be economic fuels. But on the other hand, these fuels contain a significantly higher amount of sulphur.

As an example, a production plant for 170,000 tons of anodes per year and a baking furnace with an estimated energy demand of 2.5 GJ/t baked anodes, will have a consumption of approximately 70 kg/t. This creates a fume gas of approximately 100,000 m³/h S.T.P.. The energy consumption of this plant would be 1.35t HFO/hr, which contains 60 kg of sulphur. Expressed as sulphur dioxide (SO₂) this will be 120 kg/hr or 1200 mg/m³. Together with the emissions coming from the packing coke, this will lead to an overall SO₂ concentration of more than 1500 mg/m³.

For the abatement of sulphur dioxide emissions, there are several technical solutions which are used in different industries depending on the local situation. In general, the desulfurization processes can be divided into dry and wet scrubber systems.

Dry scrubber systems use high-porosity adsorbents with very high specific surfaces for capture of the sulphur dioxide and reaction to solid sulphur salts which are normally separated in bag filters. In some cases, the fumes have to be conditioned to a certain humidity and temperature and therefore need an additional conditioning stage. So the complete system consists of the injection system for the absorbent into the gas stream, a high-efficient mixing zone and the separation of the reactant

particles out of the clean gas flow. Absorption agents may be calcium hydroxide or mixtures of limestone based products with other reactants such as activated carbon.

On the other hand, wet scrubber systems consist of the wet scrubber with the reaction zone, the dosing of the neutralising agent and the discharging of the neutralised solution.

Most wet scrubbers are of the spray tower type in which the absorption liquid and the neutralising agent are dispersed by spraying nozzles. Due to the high specific surface of the spray droplets, sufficiently high reduction rates of the sulphur dioxide can be achieved. Depending on the type and amount of the neutralizing agent, reduction rates of more than 90% are possible.

When water is used as the absorption agent, the neutralising agent may be caustic soda, limestone/hydrated lime or sodium carbonate. A special kind of wet system is the seawater scrubber. In this system, the hydrogen carbonate which is naturally contained in the seawater is used as the neutralizing agent.

Similar to power stations, where flue gas desulfurization (FGD) is state of the art, the choice of the system is dependent on the required destruction efficiency. For high input concentrations and an expected efficiency of more than 90% (in order to reach future lower limits), only a wet system is applicable. Table 3 compares the operating cost of several wet systems for the above mentioned example in which the following boundary conditions are assumed:

- Temperature of the fumes: 160°C
- Required SO₂ clean gas concentration: 500 mg/m³
- Costs of electricity: 0.06 €/kWh
- Costs of freshwater: 1.00 €/m³
- Costs of caustic soda (25%): 90.00 €/t
- Costs of limestone (95%): 35.00 €/t
- Costs for solid/ sludge disposal: 30.00 €/t
- Costs for water disposal: 1.00 €/m³

Table 3: Operating Expenses of Wet scrubbers for FGD

System	seawater	Caustic soda	limestone
Absorbant	0.00	47.00	6.00
Disposal	0.00	3.00	10.00
Electricity	70.00	8.00	27.00
Freshwater	0.00	12.00	0.00
OPEX €/h	70.00	70.00	43.00

All these systems are able to absorb HF as well, so the use of butts would be possible, but the consumption of reactant will increase. In particular, the seawater scrubber is affected since the required amount of seawater will increase dramatically due to the low natural concentration of the neutralizing agent. Hence, the electrical costs for the seawater pumps may double, if HF concentrations of 150 mg/m³ are present and should be reduced to < 3 mg/m³.

So the choice of the right system depends on the conditions on site and the location. For example, the plant may be located close to the sea or there may be a possibility for a low-cost disposal of the discharged absorbent. These conditions have a strong impact on the costs of operating such a system. Therefore, there is not just one proper solution. Rather a

detailed comparison of each case and the boundary conditions is strongly recommended.

Example

Several plants are currently under construction. Figure 11 shows three RTO systems during installation of a FTS for several baking furnaces. The whole FTS consists of a pre-heating of the fumes in order to avoid corrosion, a set of four pre-filters (see Figure 5) and three four-chamber RTO systems. This technology was chosen by the customer to ensure they reach emission levels of less than 50 µg/m³ benz(a)pyrene.



Figure 11: RTO system of a FTS for Several Baking Furnaces

Conclusions

RTO has developed into an established and proven technology for treating carbon plant emissions. As demonstrated in this paper, RTO designs can be readily adapted to specific plant conditions and emissions targets.

If HF has to be treated in addition to PAH's, a packed bed filter with moving beds is a practical solution due to the low investment and operating costs.

For SO_x treatment, the local emission limits and the costs of utilities have to be checked and the costs of each system have to be compared. This is mandatory especially if use of alternative fuels or coke with high sulphur content is considered.

For each application, the detailed conditions have to be considered in order to find the solution with the lowest capital and operating expenses.

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