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Environmental Control and Emission Reduction for Coking Plants

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Additional information is available at the end of the chapter

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1. Introduction

Coke is a necessary component for the production of iron and steel. Nearly 65 % of the worldwide steel production takes place via so-called pig iron (hot-metal route), which is produced in the blast furnace from iron ore by use of coke.

The importance of coke as raw material for the steel production has been approved during the last years while the worldwide need for steel has strongly increased. Since 1990 the steel production has nearly doubled and reached 1.417 mio. t in 2010 (Worldsteel, 2012). Coke production from hard coals was increased by 70 % in the same period resulting in approx. 593 mio. t in 2010 (Re-Net, 2011)(Fig. 1).

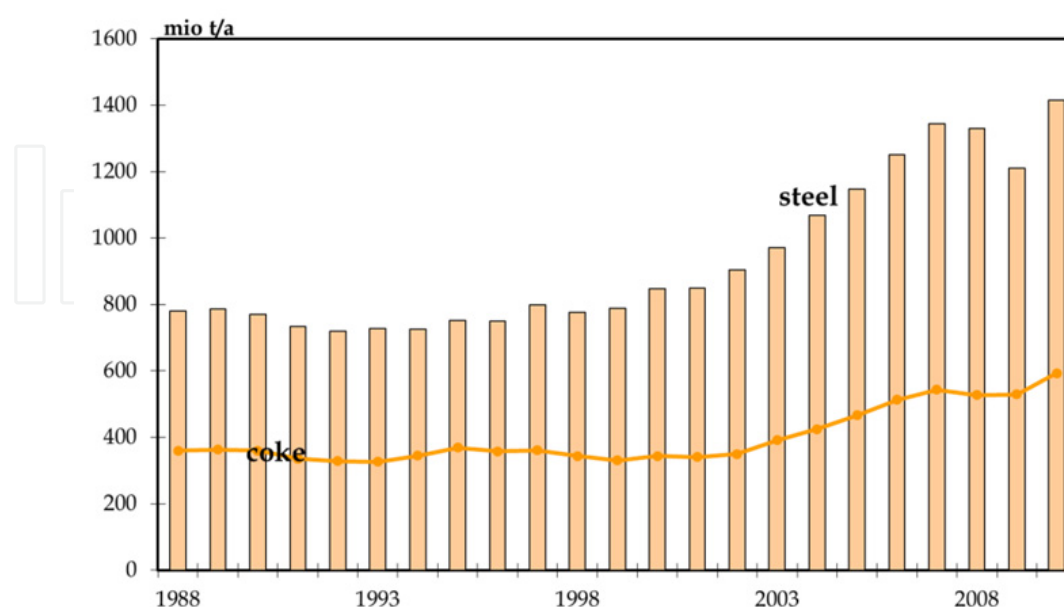


Figure 1. Worldwide crude steel and coke production (Re-Net, 2011, Worldsteel, 2012)

One can assume that this trend will continue in the next future, too. That means, that similar than in the recent years, new coke making capacities will be built and older and smaller plants will be replaced by high performance coke plants, in the future. This will be the case in China, India, Southeast-Asia and South America in particular. Already today approx. 65 % of the coke worldwide is produced in China.

There is a lack of an official statistic from which one can derive the total number of coking plants worldwide. However, it is to assume that this will be in the range of 500 plants, not including so-called primitive ovens, that means smaller coking plants without any technical equipment for operation.

Three principles will still characterize prospective projects for new coking plants: improvement of economics of coke production as well as optimization of the coke quality. A third principle has prevailed during the last four decades because of more stringent becoming legislation: reduction of the impact of the coking process on the environmental, and on the ambient air in particular. Due to the legal demands, coke plant operators were obliged to improve techniques for emissions control, to revamp batteries, or, in some cases, to shut down a battery and built a new one if the new standards could not be fulfilled under economic and technical reasons.

Progress made in emission control at coking plants can be read from an improvement of air quality in the Rhine-Ruhr area in Germany, which is the center of the German cokemaking industry till today (LANUV, 2012). Besides the shrinking importance of coal use in homefiring the reduction of coke plants' emissions is the reason for the continuous decline of Benzo(a)pyrene (BaP) as a highly carcinogenic aromatic hydrocarbon in the ambient air of this area during the last 20 years (Fig. 2).

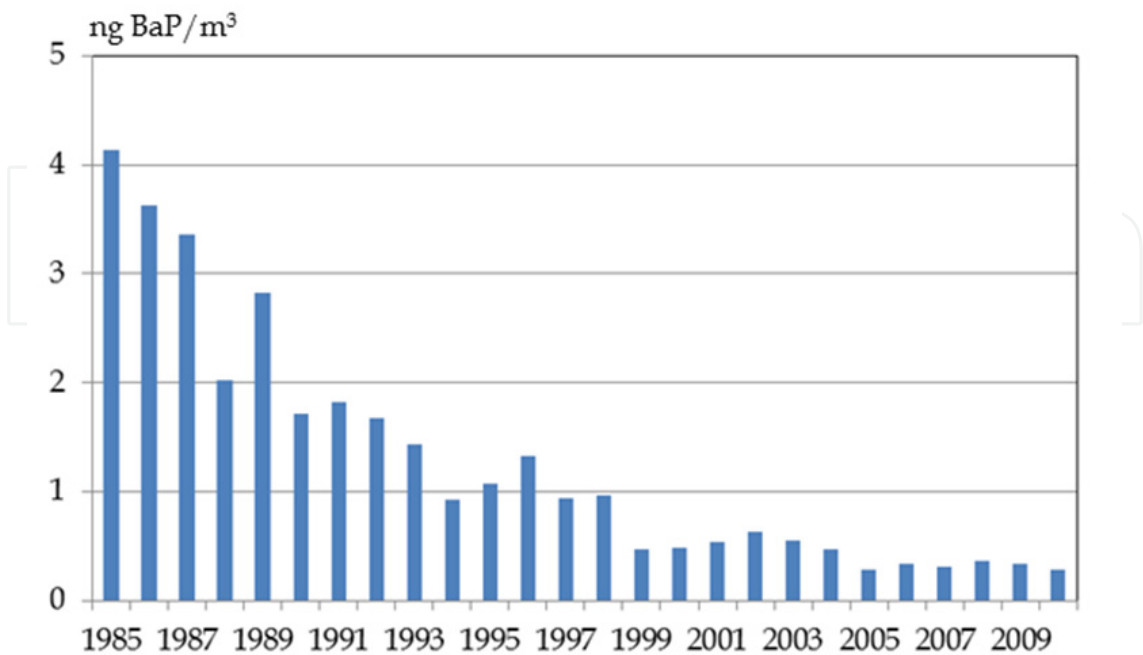


Figure 2. Benzo(a)pyrene (BaP) in ambient air of the Rhine-Ruhr area (LANUV, 2012)

Benzo(a)pyrene plays an important role with regard to the environmental assessment of the coking process. Very often it is used as a guide substance for polycyclic aromatic hydrocarbons (PAH) which can be emitted from leaks at the coking chambers. In order to reduce these fugitive emissions, measuring methods are necessary by which the made progress can be quantified. Reliable statements on the amount of emitted BaP are indispensable, too, for making a forecast on the BaP burden in ambient air of the surrounding.

2. Modern cokemaking technology

2.1. Generals

The bulk of the worldwide coke production in 2011 was effected in conventional coking plants including a recovery of gas and coal chemicals. These plants are very often called by-product coking plants, too. Approx. 5 % of the total coke production originate from the non-recovery technology, which does not recover gas and coal chemicals. Both technologies display a quasi continuous process with charge-wise coke production in several ovens connected in a battery.

A scheme of the total process of conventional coking is shown on Fig. 3. The process can be divided in the two steps: battery operation (left side of Fig. 3), and coke oven gas (COG) cleaning and by-product plant, respectively (right side of Fig. 3).

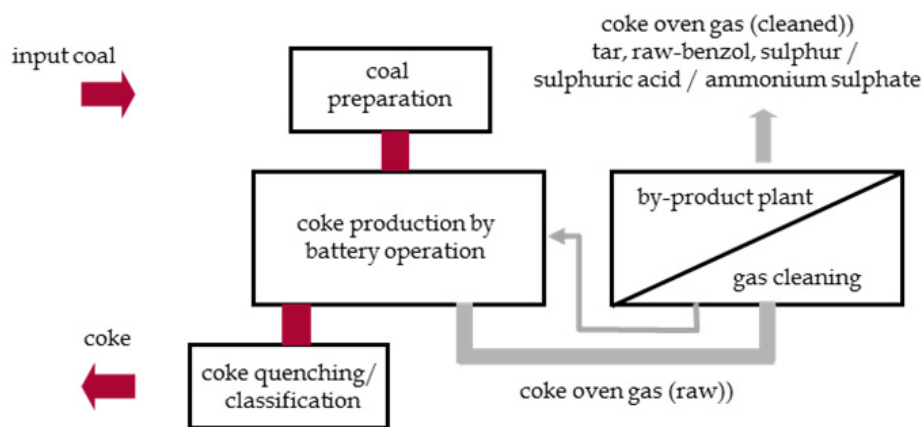


Figure 3. Scheme of conventional cokemaking

2.2. Conventional coking plant – by-product plant

By-product coking plants are comprised of single oven chambers, being 12 to 20 m long, 3 to 8 m tall, and 0.4 to 0.6 m wide, in which the input coal is heated up indirectly. Several chambers are grouped to form one battery (multi-chamber-system; Fig. 4). A single battery may consist of up to 85 ovens. The front-end sides of the individual ovens are sealed with doors. The ovens are charged through charging holes in the oven top. As an alternative, the oven can also be charged from the side via one opened door after the input coal was stamped before in order to build a formed cake (stamp charging). Subsequently to a 15 to 25

hours coking time the doors are opened and the built coke is pushed by the coke pusher machine out of the oven into a coke quench car. Then the coke is quenched in a dry or wet quenching facility. The oven chamber is sealed again, initiating a new carbonization cycle. The gas evolving on coal carbonization leaves the oven chamber through a standpipe (offtake) and is passed on via a common gas collecting main to the gas treatment facilities and to the by-product recovery plant. The ovens are run at a slightly positive pressure of 10 to 15 mm water column.

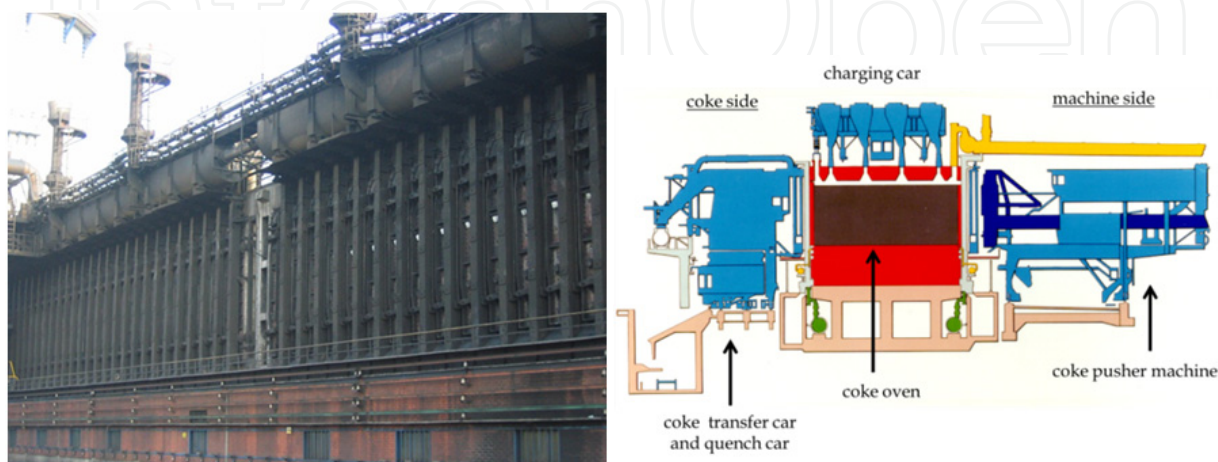


Figure 4. View on the doors of a coke oven battery of the coking plant Zdzieszowice, Poland (left side); schematic drawing of the machines for battery operation (right side)

As outlined in Fig. 7, the oven chambers are heated through heating flues, located between the chambers, in which cleaned coke oven gas or blast furnace gas is combusted. The temperature in the heating flues lies between 1150 and 1350 °C usually.

Battery operation, i.e. charging and pushing is carried out by large machines (Fig. 5) which very often are running automatically.

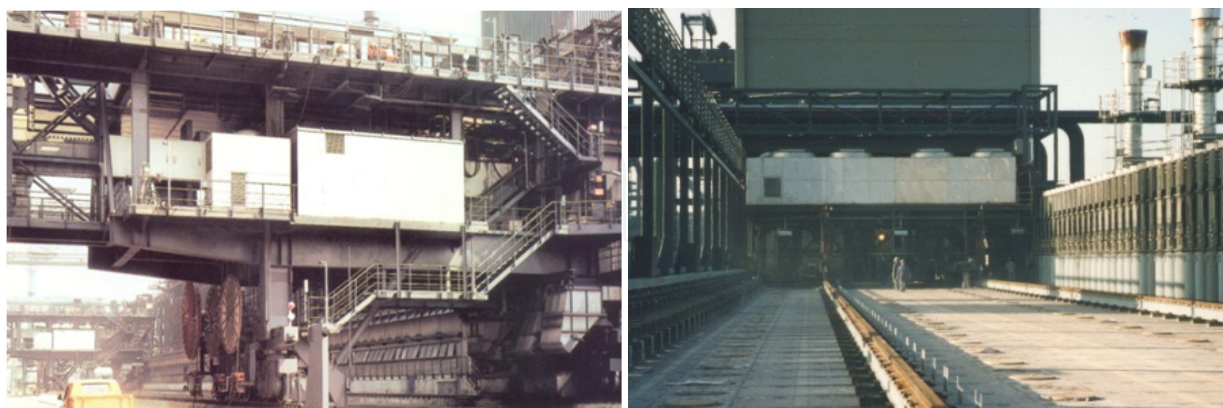


Figure 5. Pusher machine of the coke plant Huckingen (left) and charging car of the former coking plant Kaiserstuhl III (right)

Coke oven gas (COG) as built during the coking process is unsuited for use as underfiring gas for the coke oven batteries and for other applications, because of technical, and of environmental related reasons in particular. The necessary cleaning is made in the so-called

by-product plant which comprises a complex chemical plant. For a coking plant with an annual coke production of 1 mio. t, the design capacity for the by-product plant is about 61,000 Nm³ COG/h.

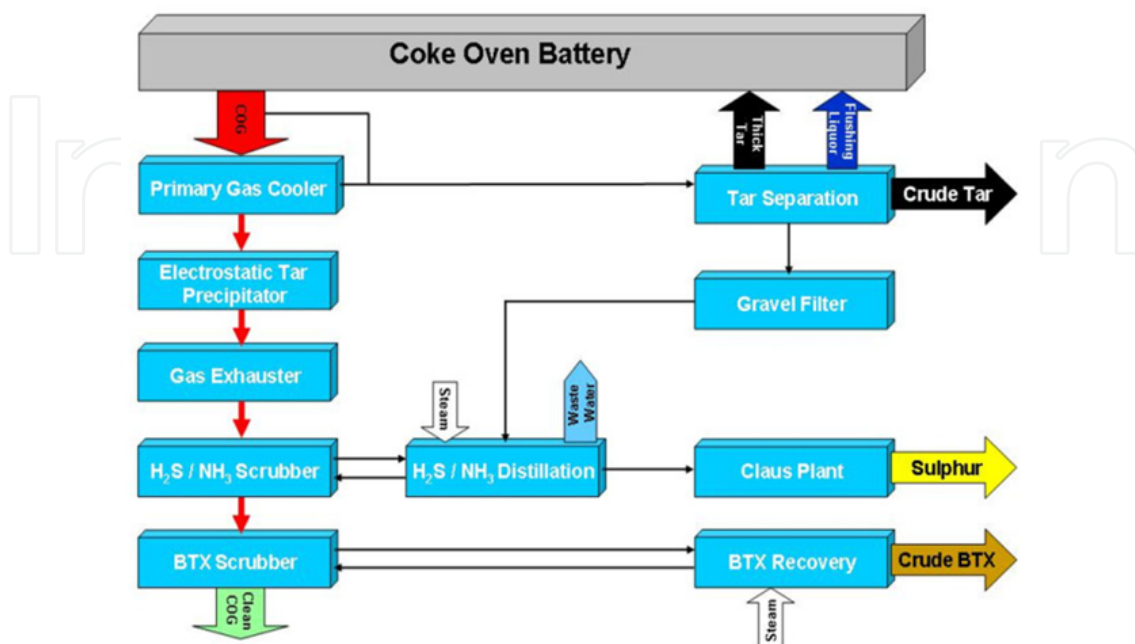


Figure 6. Scheme for a modern by-product plant

A general simplified process diagram is shown in Fig. 6. Coke oven gas leaving the battery ovens has a temperature of 800 to 1000 °C, and just before entering the collecting main it is sprayed with flushing liquor (ammonia water) coming from tar separation. After spraying the gas comes down to temperatures in the range of 80 °C. At this temperature most of the raw tar is condensed, therefore a separation into gas and liquid phase is possible in a downcomer. The liquid phase flows from here to the tar separation unit to separate water and crude tar; crude tar is one by-product.

The raw gas is directed to the primary gas cooler where it is cooled down to 21 °C by indirect cooling. The next step is the electrostatic tar precipitators, where the residual amounts of tar fog are almost completely removed, down to maximum 20 mg/Nm³. After this step COG is sucked off by exhausters keeping the necessary pressure for exhausting the gas from battery and is led to the subsequent gas treatment. There exist two techniques for H₂S removal from COG, in principle (see section 5.2). In Fig. 6 only the ASK process (Ammonium-Sulphur cycle process, ASK), combined with a subsequent Claus plant for sulphur production, as a high value by-product, is shown as the most common desulphurization process in Europe. In section 5.2 this technique is described more in detail.

The last optional gas treatment step is BTX and naphthalene removal in a scrubber using washing oil. The crude BTX is a further by-product.

Most of the water used in the by-product plant is recycled in the process. Only a small amount of waste water, which mainly represents the water content of the input coal, is

produced as effluent of the ammonia still and has to be treated in biological waster water treatment plant.

Typical figures for the quality of coke oven gas before and after gas cleaning are shown on Table 1. The Figures can be varied due to the coal quality and the coking process itself.

| | crude coke oven gas | cleaned coke oven gas | unit |
|------------------|---------------------|-----------------------|------------------|
| Tar | 60- 110 | 0.1 | g/m ³ |
| BTX | 28 - 35 | < 5 | g/m ³ |
| NH ₃ | 7- 9 | < 0.1 | g/m ³ |
| H ₂ S | 4 - 8 | < 0.5 | g/m ³ |

Table 1. Quality of coke oven gas before and after cleaning

2.3. Non-recovery plant – heat-recovery plant

The most essential features by which the non-recovery technology differs from the conventional cokemaking technology with by-product recovery are given in Fig. 7. In contrast to conventional coking by which the coke is heated indirectly by combustion of gas within the heating flues outside the oven chamber, exclusively, during non-recovery coking the necessary heat is transferred both directly and indirectly into the oven chamber as described in the following.

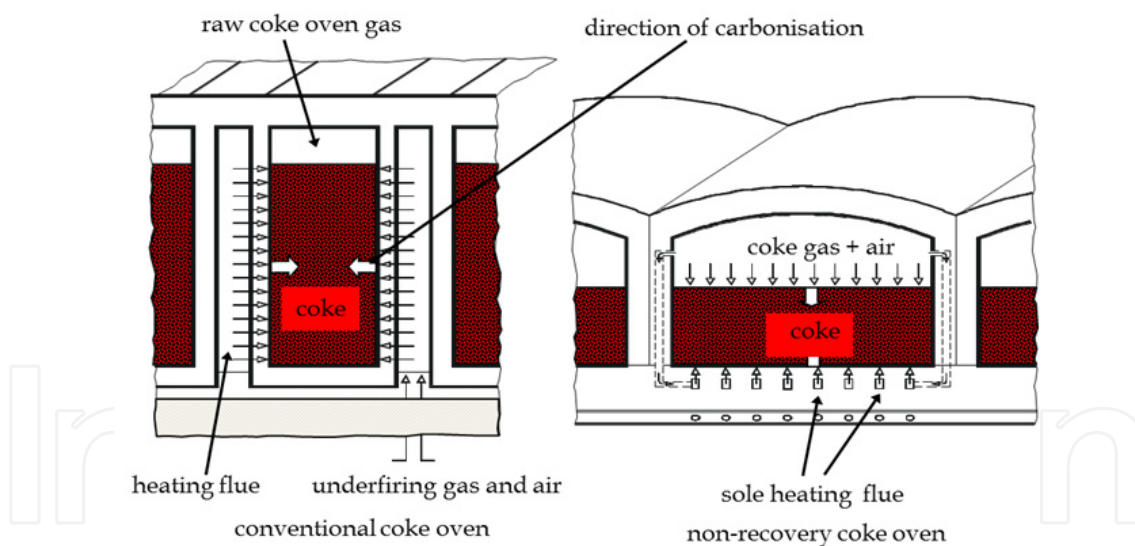


Figure 7. Principle drawings of conventional and non-recovery cokemaking (Hein, 2002).

The basis for modern non-recovery plants is the so-called Jewell-Thomson oven, several ovens of which are grouped together to form one battery (Fig. 8). The ovens are characterized by a tunnel-like shape with a rectangular ground area and an arched top. The dimensions of the chambers of modern plants run up to 14 x 3.6 x 2.8 m (L x W x H). Coal charging (up to 50 t) of the ovens is accomplished through the open pusher side door. Very often the coal is stamped before, and then the coal is charged into the hot oven chamber. Typical charging levels lie at 1000 mm. The carbonization process is started by the heat still

existing from the preceding carbonization cycle. The released coke oven gas is partly burnt by addition of ambient air through the doors and passed through so-called down comers into the heating flues situated in the oven sole. By way of a further supply of air, the complete combustion of raw gas is effected here at temperatures between 1200 and 1400 °C. With plants according to the state of the art, the hot waste gas is utilized to generate energy, and subsequently is subjected to desulphurization before exiting into the atmosphere. The coking time in Jewell-Thomson ovens amounts to approx. 48 hours. After that time, the coke is pushed out and quenched in wet mode, normally.

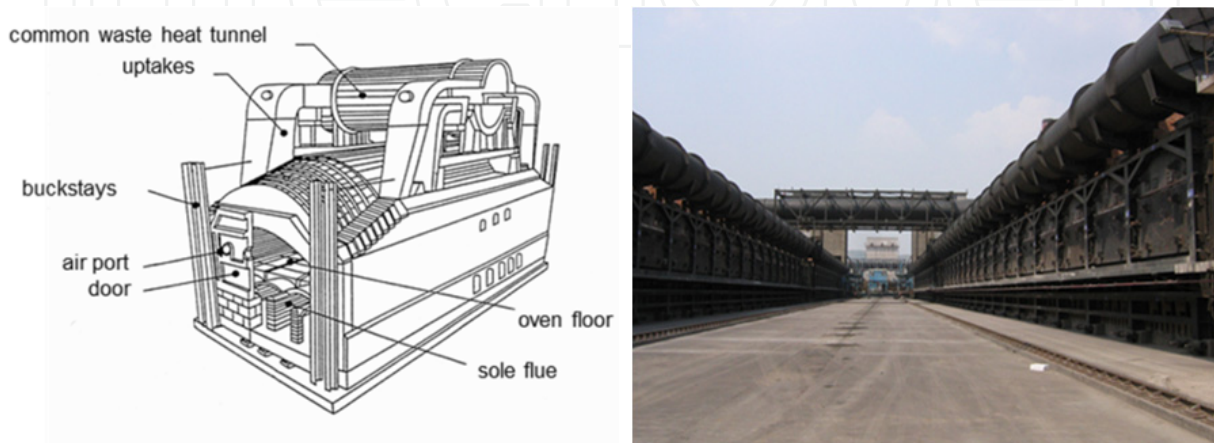


Figure 8. Schematic drawing of the Jewell-Thomson oven (Hein, 2002) (left) and view on the ovens of the heat-recovery cokung plant of the Shanxi Xishan Coal Gasification Co. Ltd., Gujiao, China (right)

Due to the negative pressure, under which the coking process is running, emissions from leaks at the doors are avoided in principle. Dust emissions occurring during coke pushing are exhausted via a coke side shed. Very often suction devices are installed at the pusher side, too, in order to capture emissions caused during charging.

As the techniques for emission control during charging, pushing and quenching are similar to those applied at conventional coking, and fugitive emissions at the ovens are excluded by principle reasons, it is resigned to address emission related issues regarding non-recovery cokemaking in a separate section.

3. Emission sources on conventional coking plants

Typical emission sources with regard to battery operation are shown on Fig. 9. These are directed and fugitive emission sources. Fugitive emissions mainly occur from leaks at the closed openings of the coke oven batteries (doors, charging hole lids and offtakes) or are caused by non-captured emissions during coke pushing and coal charging. These emissions can not be avoided completely, also when considering closure facilities according to state of the art in technology and being under best state of maintenance, and contain dust, polycyclic aromatic hydrocarbon compounds (PAH) and Benzene as most relevant components. Carcinogenic Benzo(a)pyrene is very often used as guide substance for the group of PAHs.

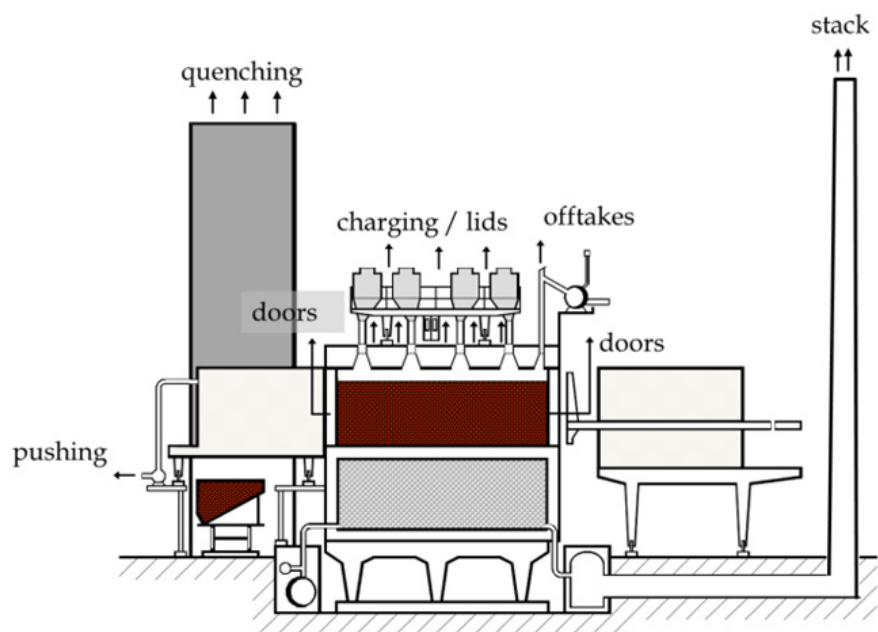


Figure 9. Schematic drawing of typical emission sources at a conventional coking plant

Emissions from directed sources are created at the stack for the off-gas from battery underfiring. The most important compounds which are emitted here are dust, NO_x, SO_x and CO₂. Dust is emitted also by the offgas of the pushing emission control as well as during coke quenching. Emissions caused at preparation of charging coals, and at classification of coke, respectively, are not addressed here because well-proven dust removal systems are available to cope with them.

Emissions from the by-product plant are bearing secondary importance in contrast to emission from battery operation. This is valid for emissions from open tanks, leaks in the piping system and at flanges, pressure valves, pumps, etc., as well as for the off-gas from the technical facilities for sulphur-removal (sulphuric acid plant, Claus plant). On the other hand, more relevance is to be attached to the efficiency of the devices for H₂S removal from the coke oven gas (see section 5.2). Remaining H₂S will influence the amount of SO₂ in the off-gas at the stack of the battery in case of using cleaned coke oven gas for battery heating.

4. Legislation on emission control

4.1. Germany

4.1.1. Generals

Starting, it should be emphasized that legal rules given by the European Union (EU) have a significant impact on the national legislations of the member states. While regulations of the EU become immediately enforceable as law in all member states, directives are only binding for member states with regard to the achievable target, while they leave it up to the member states to decide on the form and means needed to realize the commonly set targets within the framework of their national legal system.

In Germany, the most important legal rule with regard to industrial emission control represents the Technical Instruction for Air Quality Control – Technische Anleitung zur Reinhaltung der Luft – the so-called TA Luft. The first issue of TA Luft was enacted in 1964 and was amended for several times in the following years. The TA Luft is the most essential guide for implementation the demands of the German Federal Immission Control Act - Bundes-Immissionsschutzgesetzes (BImSchG) – which was released in 1974.

The Federal Immission Control Act, amongst others, is based upon the two fundamental principles of "risk defense" and "precaution". The precautionary principle is expressed in the approval of new plants and flows into the demand for compliance with what is called the state of the art in technology in the construction and operation of industrial plants with special regard to environmental control.

The state of the art is basically stipulated in the TA Luft which at the same time generally prescribes ambient air quality standards that must not be exceeded in the vicinity of a new plant after its commissioning. To this effect it is required to calculate the additional burden of the pollutants, which are to be expected upon commissioning of the planned plant, by dispersion calculations (see also section 8.2). Furthermore for precaution, the TA Luft prescribes emission limit standards, especially for directed sources, which shall be examined for compliance within regular intervals.

In view of the "risk defense" principle of the Federal Immission Control Act its 22nd Decree stipulates air quality standards for various hazardous substances, the compliance of which shall be achieved, for example, by implementing so-called air pollution control plans. This area-related rule concerns all plants, that means also those for which a permission has already been granted, and may necessitate an obligation for retrofitting the plant.

The TA Luft amendments which came into force in 1986 gained special importance for the coking plants which were built in the 1980th in Germany. Although the permits for the new constructions of the coke plants Prosper, Huckingen, Salzgitter and Dillingen are dated before the enactment of TA Luft 1986, its demands have to be fulfilled by the new plants to the greatest possible extent.

Compliance with the TA Luft 1986 without any extension, that means including the demand for operation of a coke dry quenching unit, was necessary for the new construction of the coke plant Kaiserstuhl III which was operated in Dortmund between 1992 and 2000.

Due to the progresses reached in emission control in Germany since 1986, an emendment of the TA Luft came into force in the year 2002 (TA Luft, 2002). The permits of the coke plants Schwelgern and of battery no.3 of the Saar central coking plant (Dillingen) were affected from this amendment, which disclaims on dry quenching as the only mode for coke cooling. More informations on the coking plants mentioned before will be given in section 6. The most important features of the current TA Luft with regard to emission control on coking plants will be described in the following sections.

4.1.2. *Techniques to apply on coking plants with regard to emission control*

As a measure for precaution the TA Luft sets standards for the technical equipment for emission control on industrial plants, and specifies how to operate the plant in a most environment-friendly way. Table 2 contains the most important techniques and work practice standards to apply on the coke oven batteries with regard to the TA Luft-amendments of the year 2002 (TA-Luft, 2002). Most of the standards of the German TA Luft were adopted by the BREF-document of the European Union (EU, 2012) nearly complete. Most of them are described in section 5 more in detail.

| techniques | |
|-------------------------|--|
| - | gravity charging: emission free charging by transfer of charging gases to the main and into the neighbour oven, as an option |
| - | stamp charging: combustion of not transferred gases |
| - | doors with technical gas-proof sealings |
| - | water-sealed lids at offtakes |
| - | single chamber pressure control should be applied |
| - | coke side emission control including a mobile hood and a stationary control device |
| - | coke quenching by dry or wet quenching mode |
| | |
| work practice standards | |
| - | additional sealing of lids of charging holes |
| - | regular, and preferential automatic, cleaning of closure facilities |

Table 2. Techniques for emission control and work practice standards as demanded by (TA Luft, 2002)

4.1.3. *Limit values for emissions at directed sources*

In order to reduce atmospheric emissions from industrial plants as far as possible TA Luft sets limit values which have to be checked regularly. Table 3 contains limit values for emissions at the outlets of directed sources of coking plants. In contrast to the US Clean Air Act (section 4.3) TA Luft contains no legal demands for fugitive emissions by setting standards for the allowed number of visible emissions.

| process | emission | limit value | |
|---|-----------------|-------------|---------------------|
| stamp charging | dust: | 10 | mg/Nm ³ |
| battery underfiring | dust | 10 | mg/Nm ³ |
| | NO _x | 0.50 | g/Nm ³ |
| | sulfur* | 0.8 | g/Nm ³ |
| pushing or | dust | 5 | mg/Nm ³ |
| | dust | 5 | g/t _{coke} |
| quenching dry wet (new plants) wet (existing plants) | | | |
| | dust | 15 | mg/Nm ³ |
| | dust | 10 | g/t _{coke} |
| | dust | 25 | g/t _{coke} |

Table 3. Emission limit values for battery operation according (TA Luft, 2002); *: sulfur content of the heating gas before combustion

Special emission limits are set for the off-gas of a sulfuric acid-plant and of a Claus-plant for sulfur recovery, if exist as part of the by-product plant.

4.2. European union

In the European Union, there are in principle two directives that influence coke plant operation:

- „IED Directive“ (EU, 2010) on industrial emissions (integrated pollution prevention and control)
- „Air Quality Directive“ (EU, 2008)

As mentioned in section 4.1.1. Directives of the EU are only binding for member states with regard to the target to be achieved; they have to be transformed to the national legislation of the member state.

The IED-Directive addresses the conditions for plant operation and sets standards for emission control. This directive stipulates that the "best available technique BAT" which has to be applied is to be described in a so-called BREF document („Best available technique Reference“ document) for certain industrial plants. For coking plants, the set-up of such a BREF document was finalized in the year 2000. An amendment was promulgated in 2012 (EU, 2012), and it assigns “Associated Emission Levels AEL” to the BATs. BAT-AELs give ranges for emission levels which can be achieved by application of emission control techniques according BAT. AELs which are relevant for cokemaking operation are described on Table 4. A more detailed description of the BATs is given in section 5.

The Air Quality Directive (EU, 2008) and its so-called 4. Daughter Directive (EU, 2004) describe the targets and principles of the air quality policy pursued by the European Union. Ambient air standards which are important for cokemaking operation are given on Table 5.

| process | emission | AEL/BAT | unit of measurement | remark |
|---------------------------------|------------------|-----------------------------------|---|--|
| charging | dust | <5 or <50 | g/t _{coke} or mg/Nm ³ | |
| | visible emission | < 30 | sec | duration of visible emissions per charge |
| offgas from battery underfiring | | | | |
| | SO _x | <200 to 500 (as SO ₂) | mg/Nm ³ | depending on the type of gas for underfiring |
| | NO _x | <350 to 500 (as NO ₂) | mg/Nm ³ | for new plants |
| | NO _x | 500 to 650 (as NO ₂) | mg/Nm ³ | for existing plants which are equipped by primary measures for NO _x reduction |
| | dust | < 1 to 20 | mg/Nm ³ | |
| pushing | dust | < 10 to < 20 | mg/Nm ³ | depending on filter type |
| quenching | | | | |
| wet | dust | < 25 | g/t _{coke} | existing plants |
| wet | dust | < 10 | g/t _{coke} | new plants |
| dry | dust | 20 | mg/Nm ³ | |
| battery operation | | | | |
| | visible emission | < 5 to 10 | % | from leaks at doors |
| | | adequate oven pressure regulation | | |
| | | work practice standards | | |
| desulphurization of COG | | | | |
| | H ₂ S | < 300 to 1000 | mg/Nm ³ | applying absorption processes |
| | H ₂ S | < 10 | mg/Nm ³ | applying wet oxidation processes |

Table 4. BAT associated emission levels (AEL) as described in the BREF document (EU, 2012)

| emission | Limit value | | remark |
|--------------------------|-------------|--------------------------|----------------------------------|
| Benzene | 5 | $\mu\text{g}/\text{m}^3$ | |
| Particulate Matter PM10 | 40 | $\mu\text{g}/\text{m}^3$ | |
| | 50 | $\mu\text{g}/\text{m}^3$ | daily average for max. 35 days/a |
| Particulate Matter PM2.5 | 25 | $\mu\text{g}/\text{m}^3$ | from 2015 |
| Benzo(a)pyrene * | 1 | ng/m^3 | from 2012 |

Table 5. Ambient air quality standards (limit values) of the EU (EU, 2008) as an annual average with reference to coking plant operation; *: (EU, 2004)

4.3. USA

4.3.1. Clean Air Act

The Clean Air Act (CAA) of the United States of America was passed in the year 1990. This act of law describes standards for air quality, which exert a very strong influence on the requirements which have to be fulfilled for obtaining the permit to run an industrial plant. The so-called Residual Risk Standard (RRS) should provide an ample margin of safety to protect public health and to reduce the risk to cause cancer to a minimum.

In case of coking plants, amongst others, standards are set for the allowed number of visible emissions (leaking rates as %) from battery operation to reach this goal, as described by the US EPA (US-EPA, 1993a, 2005). For the construction of new coke plants at the green site, the CAA calls for zero visible emissions from battery operation. That means in practise, that in the USA, the non-covery technology is the only one, which is allowed by the US EPA for new green field plants because of the prevailing negative pressure and consequently of the prevention of leaks at the ovens.

For existing conventional coking plants the Residual Risk Standard, which is still open, has to be reached from 2020. It is to assume that the relevant legal demands will be very ambitious. During the recent 20 years the US coke oven plant operators had the chance to approach this target on different tracks, which specify different compliance timetables (Fig. 10) (Ailor, 2003; US-EPA, 1993a). While the MACT-track (Maximum Achievable Control Technology) allows less stringent standards for a long period to fulfill the highest level of emission standards already in 2005, operators who have chosen the LAER-track (Lowest Achievable Emissions Rate) got an extension to reach this standard only in the year 2010.

The relevant standards for the allowed visible emissions are shown on Table 6. Estimates of visible emissions should be based on the results of daily visible emission inspections using EPA Method 303 (US-EPA, 1993b).

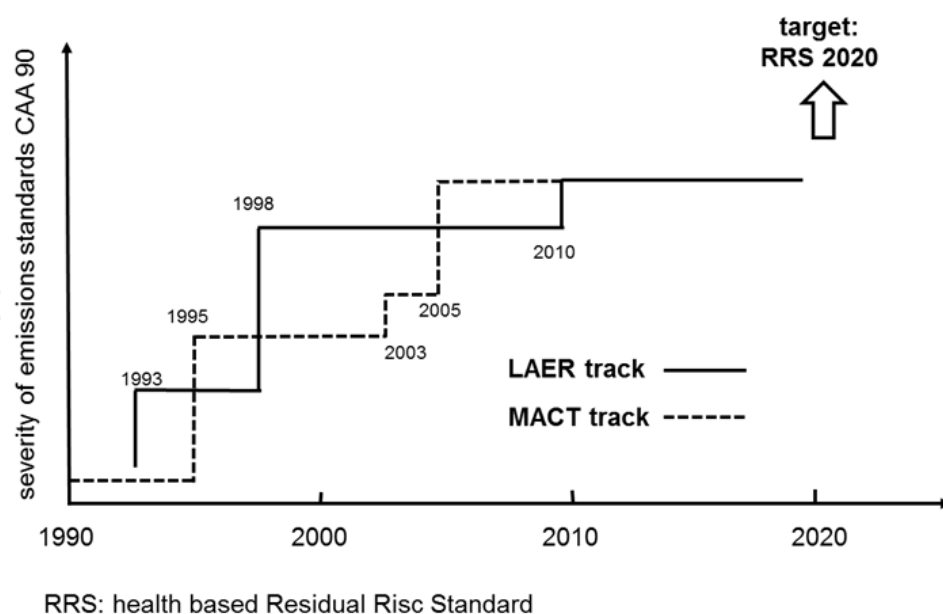


Figure 10. Timetable to comply with the legal demands of the US Clean Air Act

| source | MACT | LAER | remark |
|--------------------------|-----------------|-----------------|--------------|
| | from 01.01.2003 | from 01.01.2010 | |
| doors | 5.5 % | 4 % | ≥ 6 m |
| doors | 5.0 % | 4 % | foundry coke |
| doors | 5.0 % | 3.3 % | < 6 m |
| lids | 0.6 % | 0.4 % | all plants |
| offtakes | 3.0 % | 2.5 % | all plants |
| charging secs per charge | 12 | 12 | all plants |

Table 6. Standards for visible emissions according MACT- and LAER-track respectively for conventional coking plants

It is easily to understand that operators of older plants would have preferentially followed the MACT track as their coking plants will be no longer in operation in the year 2010, probably. After all there were only 5 conventional batteries which have to comply with emission standards equivalent to the 2010-LAER-standard in 2005. On the other hand, operators of new plants, which were equipped with modern techniques for emission control on the date of their track choice, or for which a modernisation was planned, would have preferred the LAER-track supposably. Based on informations given in the year 2003 (Ailor, 2003) the LAER-track was chosen for 40 conventional batteries.

Emissions from pushing, quenching, and combustion stacks are addressed in (US-EPA, 2003a). The most relevant figures of this rule are given on Table 7. The local authority can make an order on more stringent limits than given on Table 7 on special reason, and can set emission standards for other emitted compounds than given on Table 7 with regard to the allowed annual mass flow, additionally.

| process | emission | limit value | unit of measurement | remark |
|-----------------------------------|------------------|-----------------------|--|-------------------------------------|
| pushing | | | | |
| fugitive (not captured) emissions | opacity* | < 30/35 | % | depending on oven height * |
| outlet of dedusting device | dust | 0.01 – 0.04 (5 – 20) | lb/t _{short} coke (g/t _{coke}), | depending on type of control device |
| battery underfiring | | | | |
| stack for offgas | opacity* | < 15/20 % | % | depending on coking time |
| quenching | | | | |
| outlet of quench tower | dissolved solids | < 1.1 | mg/l | quench water |

Table 7. Emission standards for coking plants according (US-EPA, 2003a); *: determination of opacity is made by Method 9 given by US EPA (US-EPA, 1996)

German and European legal regulations set no standards for opacity. Therefore, only the 0.02 lb/t_{short} (10 g/t) limit for pushing emissions from the stack when applying a moveable hood with a stationary control device can be compared with the relevant figure of 5 g/t coke set by German TA Luft for this technique.

In addition to the limit values as described before, the US environmental legislation sets work practice standards. These standards, for example, describe techniques which have to apply with regard to emission control and to emission monitoring, or how to operate the coking plant in a most environmental friendly way.

4.3.2. Quantification of visible emissions

The philosophy of EPA's rules for visible emissions caused from coke oven operation is based on a chain of causalities between:

- number of visible emissions, and
- mass flow of the emitted hazardous compound, and
- concentration of the emitted hazardous compound in ambient air, and
- ambient air quality and cancer risk

due to the usual practice when rating the health risk caused by air pollutants by dose/effect relations. This means, that, amongst others, there must be a quantitative correlation between the set standards for visible emissions and the emission mass flow (mass per time) of the hazardous compound.

The latter can be calculated on base of the frequency of the visible emissions (leaking rate) and of the source strength (emission mass flow) of the visible emission (US-EPA, 2008a, 2008b). Typical source strengths given as kg BSO/h/leak as derived from from page 4-30 of (US-EPA, 2008b) are listed on Table 8. BSO means the so-called Benzene soluble (BSO) portion of the emission. By using a conversion factor for BaP/BSO of 0,00836 (US-EPA, 2008b) the relevant BaP emissions can be calculated. They are given on Table 8 too.

| type of leak | kg BSO/h/leak | mg BaP/h/leak |
|--|---------------|---------------|
| leaks observed according EPA 303 from the yard | 0.019 | 159 |
| leaks observed from the bench* | 0.011 | 92 |
| without visible emissions | 0.002 | 17 |

Table 8. Emission mass flows of door leaks as given by US EPA (US-EPA, 2008b); *: for calculations according equ. 1 smaller leaks which cannot be observed from the yard but only from the bench are additionally taken into account; US EPA estimates the leaking rate of these emissions to 6 % as an average.

Applying a 4 % leaking rate (according EPA method 303) at the doors (post-NESHAP control standard according (US-EPA, 2008b)) the total BSO emissions of a model battery with 62 ovens (124 doors) can be calculated as follows:

$$\begin{aligned}
 & [(124 \times 0.04) \text{ method 303 leaks} \times 0.019 \text{ kg/h/leak} + \\
 & (124 \times 0.06) \text{ bench leaks} \times 0.011 \text{ kg BSO/h/leak} + \\
 & (124 \times 0.90) \text{ no visible leaks} \times 0.002 \text{ kg/h/leak}] \times 8760 \text{ h/a} = 3\,498 \text{ kg BSO/a.} \quad (1)
 \end{aligned}$$

Considering a coke plant with a coal input of 492 000 t/a (344 000 t coke/a) a specific emission factor of 0.0071 kg BSO/t(coal) results for door emissions. By using a conversion factor for BaP/BSO of 0.00836 (US-EPA, 2008b) the specific BaP emissions from the doors amounts to 59.4 mg/t_{coal} and 84.8 mg BaP/t_{coke}, respectively. By comparable evolutions

emission factors for leaks at lids and offtakes as well as for charging can be received (Table 9; compare with Table 4-11 of (US-EPA, 2008b)). It is obvious that the doors are the dominant emission source out of all leaks at the battery.

| US-EPA standard | BSO | | | |
|-----------------|----------------------------------|-------------------------------|------------------------------|----------------------------------|
| | charging kg/t _{coal} | doors kg/t _{coal} | lids kg/t _{coal} | offtakes kg/t _{coal} |
| POST-NESHAP | 0.00025 | 0.0071 | 0.000044 | 0.00015 |
| | | | | |
| | BaP | | | |
| | charging mg/t _{coal} | doors mg/t _{coal} | lids mg/t _{coal} | offtakes mg/t _{coal} |
| POST-NESHAP | 2.09 | 59.36 | 0.37 | 1.25 |
| | | | | |
| | BaP | | | |
| | charging mg/t _{coke} | doors mg/t _{coke} | lids mg/t _{coke} | offtakes mg/t _{coke} |
| POST-NESHAP | 2.99 | 84.79 | 0.53 | 1.79 |

Table 9. Specific emissions at doors according (US-EPA, 2008b)

Emission factors as given in (US-EPA, 2008b) are based on measurements carried out before the year 1980 on coking plants, which could not meet the emissions control standards of current plants. Thereby the coke-side dedusting facilities were used for capturing the emissions from the doors. The US EPA by itself designates the results of these measurements as highly uncertain.

5. Progress in emission control technologies – Best Available Techniques (BAT)

Environmental legislations for industrial plants, like the German TA Luft (TA-Luft, 2002) or IED of the EU (EU, 2010), demand very often for application of the so-called Best Available Techniques (BAT) for emission control according the state of the art in technology, (section

4.1/4.2). The following section will give a brief description of the most important techniques. Additional informations on the emission levels which can be achieved by the relevant technique are given on Table 4 (section 4.2).

5.1. Battery operation

5.1.1. Charging

BAT is an emission free charging by transfer of charging gases to the collecting main and into the neighbour oven, as an option (Fig. 11)

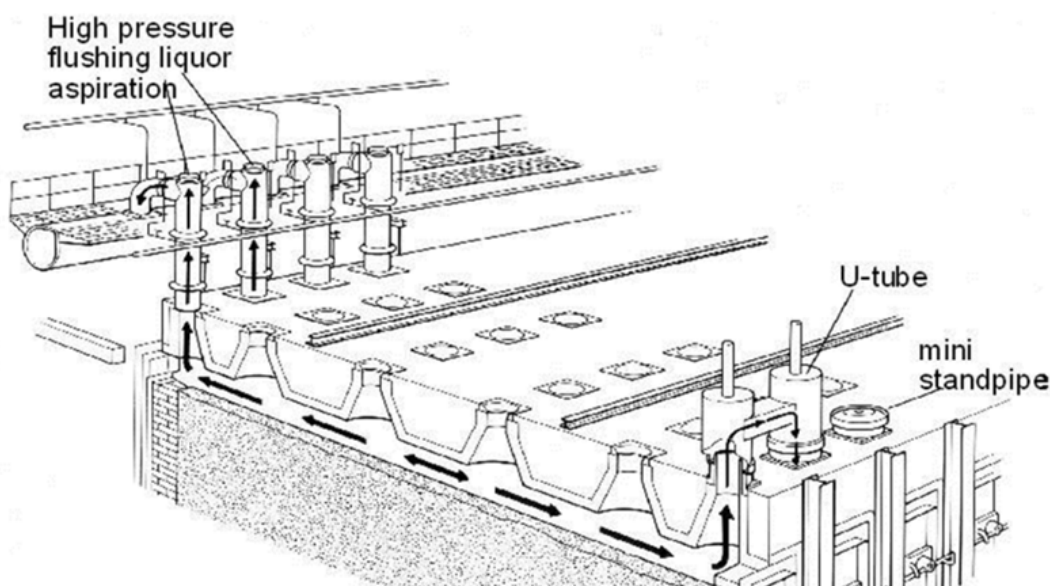


Figure 11. Principles of emission free charging of coke ovens

5.1.2. Larger oven chambers

A reduction of total fugitive emissions from battery operation can be achieved by lessening the sealing surfaces as well as the number of oven cycles. Naturally, such measures can be achieved only when building a new battery equipped with larger chambers as they were built by 7 to 8 meter ovens in the 1980th in Germany (section 6). Larger oven chambers provide less openings per t of produced coke due a reduction of the specific sealing surface. Fig. 12 shows (top side) the reduction of the number of closure facilities (openings) which was reached by a replacement of two smaller and older plants by the new coke plant Kaiserstuhl III, while the total capacity of both variants kept constant at 2 million tonnes coke per year. The drastic reduction of fugitive emissions of Benzo(a)pyrene and Benzene, caused by less openings but also by improved techniques, can be read from Fig. 12 (bottom side).

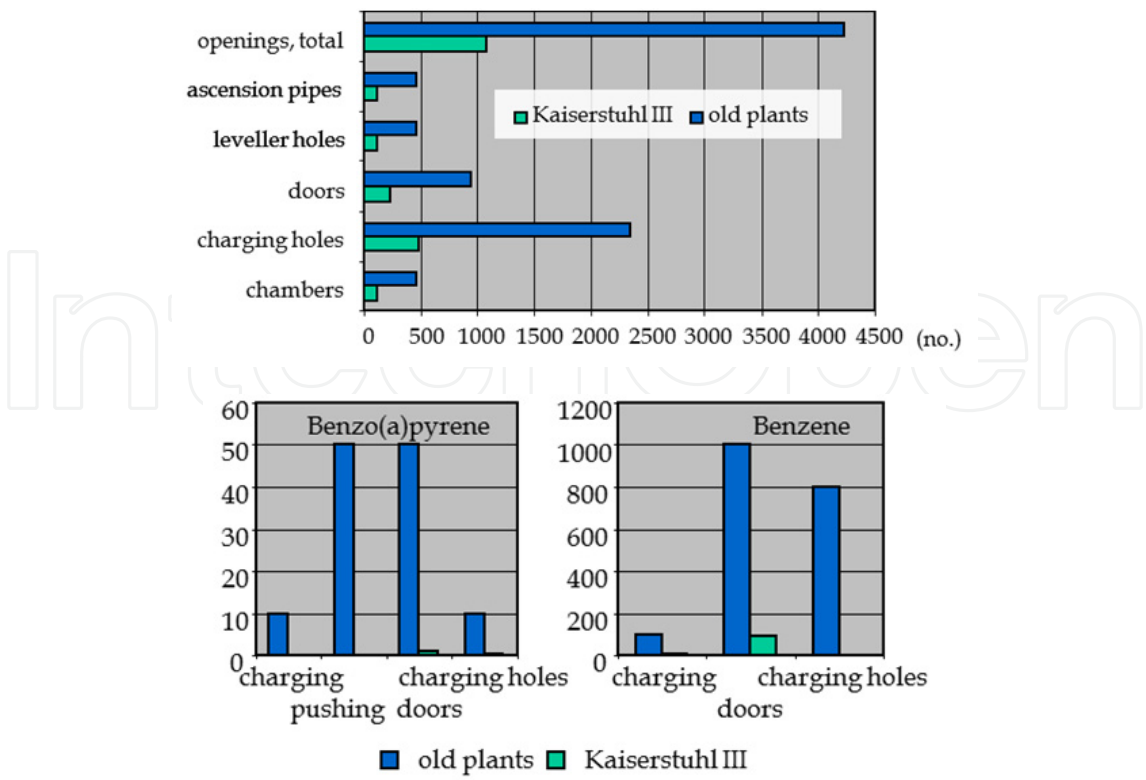


Figure 12. Emission reduction by lessening the sealing surface; top side: reduction of openings; bottom side: reduction of fugitive emissions by Benzo(a)pyrene and Benzene respectively (Hein, 2010)

Construction of larger oven chambers do not favour the intention of environmental control only, but also the economics of cokemaking. Desing data of the modern high capacity batteries as running in Germany today, can be received from Table 10 in section 6.

The development of chamber heights during the last 100 years is shown very arrestingly in Fig. 13.

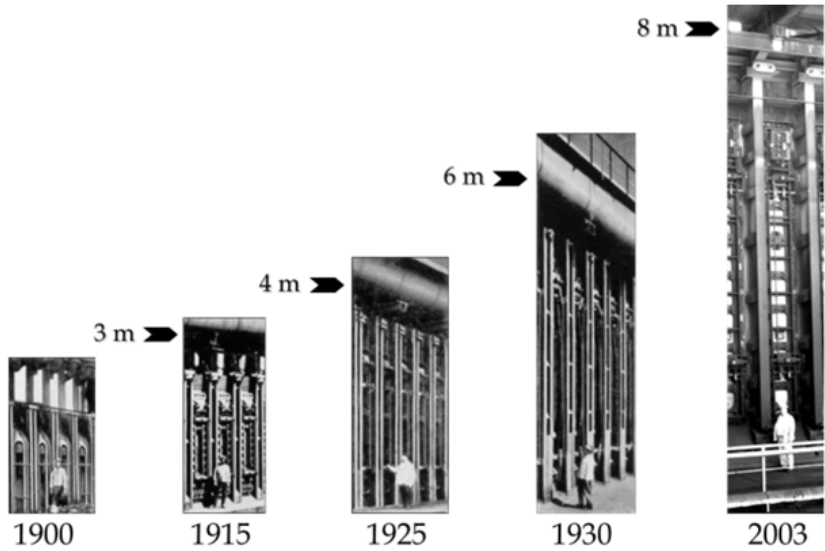


Figure 13. Development of typical heights of coke oven chambers (Hein, 2009)

5.1.3. Closure facilities

In order to improve the control of fugitive emissions from leaks at the battery, optimized closure facilities at doors, charging hole and offtakes have to be applied, and a good maintenance of them is demanded. BAT are flexible doors with springloaded sealings (Fig. 14, left side), for batteries higher than 6 m especially. An additional improvement is attainable if the pressure gradient at the sealing that constitutes the driving force for emissions could be lowered. This was done by the coke oven builders by means of gas channels in the door through which the escaping gas can flow into the direction of the gas space without greater flow resistance. All modern coke oven doors meanwhile have such gas channels as can be seen from Fig. 14, right side).

At the offtakes water sealed lids are BAT in order to reduce emissions.

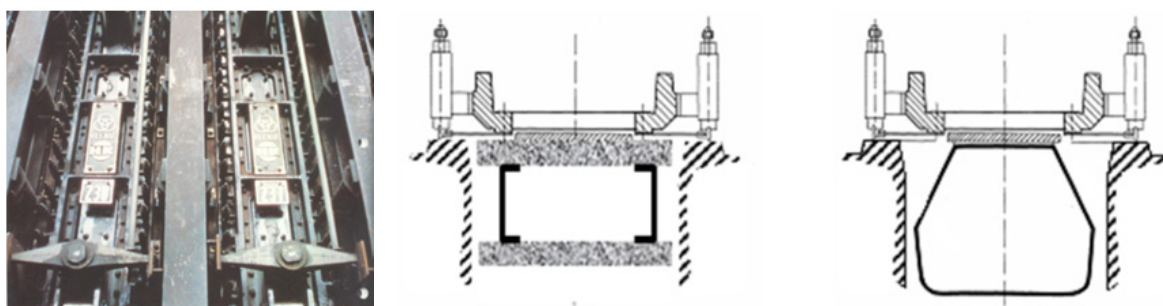


Figure 14. Modern door systems; left side: flexible doors (Krupp-Koppers, n.d.); right side: principle drawings of gas channels behind the door (Arendt et al., 2009)

5.1.4. Oven chamber pressure regulation

A reduction of fugitive emissions can be achieved by measures to regulate the chamber pressure within the coke ovens as function of progress in carbonization. BAT, e.g. is the PROven system (Pressure Regulated Oven), which was invented by DMT (Huhn, 1995). PROven regulates the pressure within each oven chamber at a constant and slight positive pressure during coking in order to eliminate fugitive emissions as much as possible. Fig. 15 shows on the left side principles of this system, and on the right side the reduction of PAH emissions by use of PROven in contrast to a non pressure regulated oven chamber (100 % PAH) (Spitz, 2005). In the year 2011 the PROven system was installed at 15 coking plants worldwide with more than 2100 ovens (Kaiser, 2011) including the new coking plant Schwelgern.

An alternative system has been developed by Paul Wurth and is called SOPRECO (Single Oven Pressure Control System). In 2011 the SOPRECO system was installed at the coking plant Dillingen, Germany, in 50 ovens, a second battery with 50 ovens is under construction (Faust, 2010).

5.1.5. Battery heating

Emissions from battery underfiring are limited by application of the following techniques: improved desulfurization of the used coke oven gas in order to reach a remaining

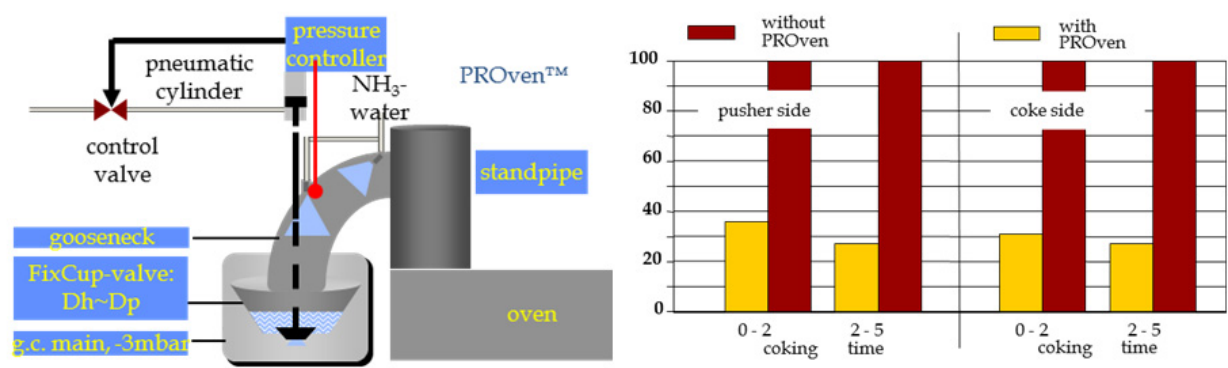


Figure 15. Left side: Principle of the ROven-system; right side: achievable emission reduction for PAH compounds

sulphur content of less than $< 0.8 \text{ g /Nm}^3$ and by special heating relevant technical measures in order to comply with a NO_x standard of 500 mg/Nm^3 . While the desulphurization is achieved by absorption or by wet oxidation of H₂S (see section 5.2.1.), the NO_x reduction is reached by waste gas recirculation and stage wise heating, in particular (Fig. 16). The latter was necessary anyway because of the taller becoming chamber heights.

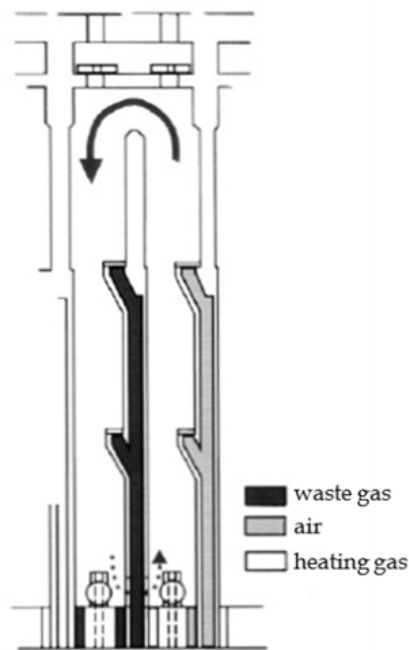


Figure 16. Principle scheme of stage wise heating

5.1.6. Coke pushing

In order to minimize emissions during coke pushing, an installation of a dedusting system is required, disposing of a hood, a suction device and of a filter system. The so-called “Bandschleifenwagen” (Fig. 17) with a subsequent stationary dedusting achieved acceptance.

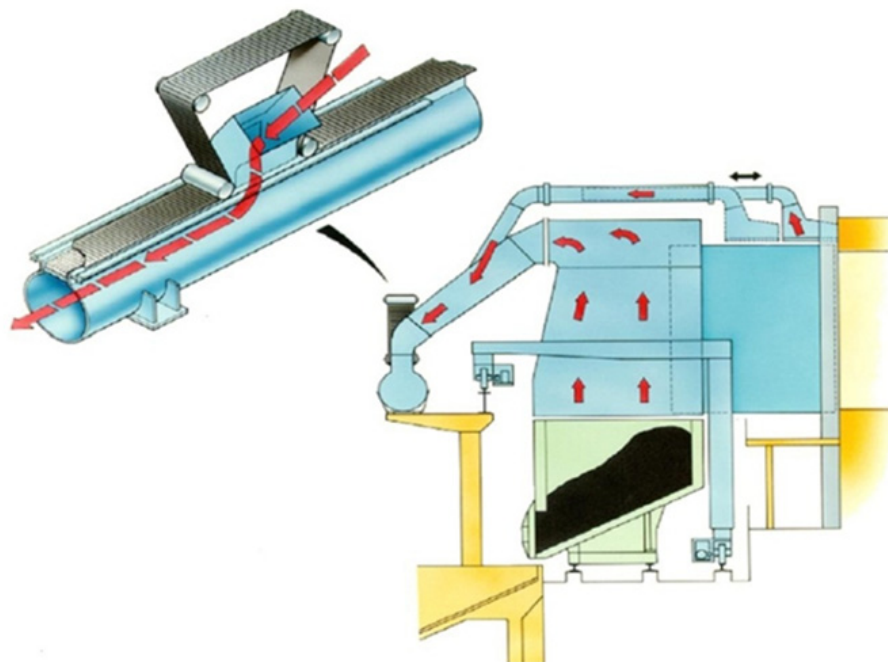


Figure 17. Drawing of the “Bandschleifenwagen” as part of the coke side dedusting device (Stoppa, 2003)

The efficiency of a modern coke side dedusting system is illustrated from Fig. 18.



without



with de-dedusting

Figure 18. Coke pushing without (left side) and with coke side dedusting (Coking Plant Prosper, Germany - right side)

5.1.7. Quenching

BATs are wet quenching as well as dry quenching.

Wet quenching

The hot coke is treated by water spraying under the quench tower to cool it down. The caused dust is hindered to leave the tower by special baffle constructions which are installed in the tower. The so-called Coke Stabilisation Quenching (CSQ) represents an advanced quenching technology comprising a combination of spray quenching and submerging in water. The CSQ tower contains a two set of baffles and comprises a height of 70 m, in contrast to approx. 40 m which was the maximum height of conventional quenching towers up to now (Fig. 19).

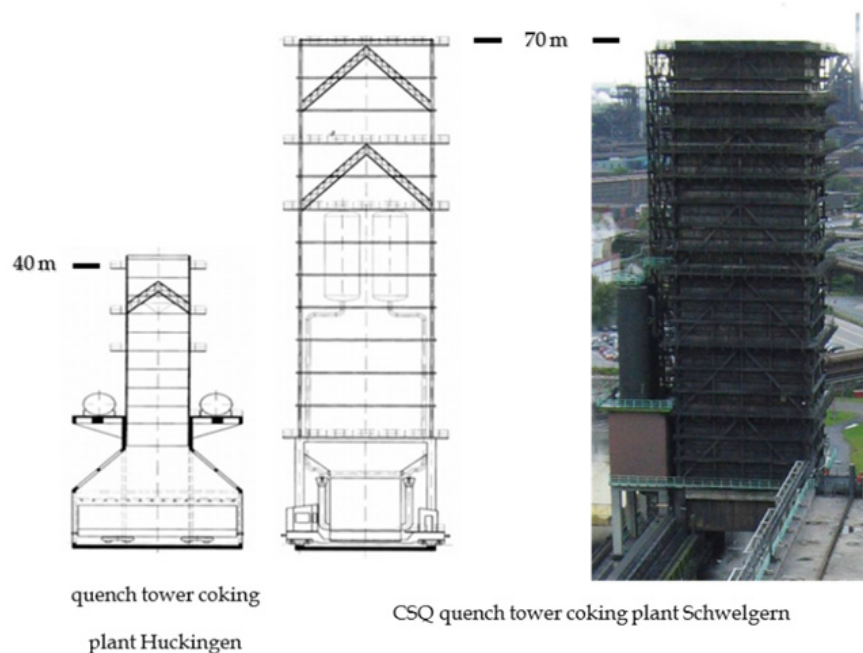


Figure 19. CSQ quench tower of the coking plant Schwelgern in contrast to the quench tower of the coking plant Huckingen (top side); bottom side: baffles (Nathaus, n.d.) for dust emission control before installation in a quench tower

Dry quenching

During dry quenching the hot coke is cooled down in a closed cooling chamber by use of an inert gas which is circulated and cooled down thereby within a heat exchanger. The produced steam can be used for electricity production. A scheme of a dry quenching plant is shown in Fig. 20.

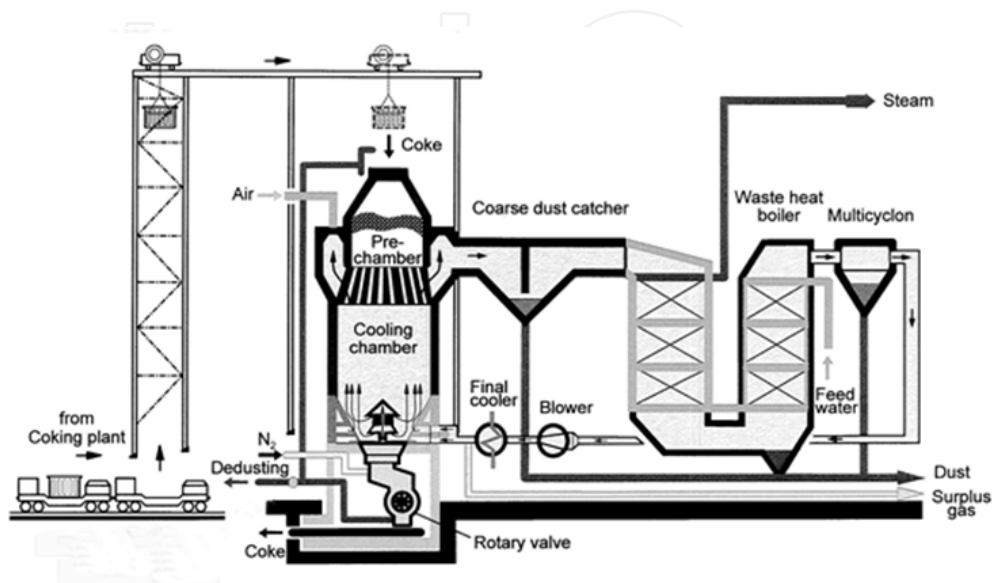


Figure 20. Schema of the dry quenching plant of the former coking plant Kaiserstuhl III (Stoppa et al., 1999)

Dry quenching is extended for application in countries, in which a water operated wet quenching is not possible because of meteorological reason, or which are characterized by water shortage. On the other hand, the use of dry quenching techniques is advantageously to operate in countries with high prizes for electricity.

5.2. By-product plant

5.2.1. Desulphurisation of coke oven gas

Because of its hydrogen sulphide (H₂S) content (up to 8 g/Nm³) unpurified coke oven gas (COG) is unsuited for use in many industrial applications. Typical desulphurisation processes according BAT to clean COG are (Sowa et al., 2011):

- absorption/stripping processes with subsequent conversion to sulphur containing compounds,
- wet oxidation processes with subsequent production of sulphur.

In Europe, the most commonly applied process is the absorptive process using a so-called ASK process (Ammonia-Sulphur cycle process, ASK; see Fig. 6 in section 2.2., too). It is a combination of H₂S and NH₃ removal. A first scrubber removes H₂S, using deacidified water providing from the distillation. A second scrubber is in combination with the first one for the removal of NH₃. The washer fluid which is loaded with H₂S and NH₃, respectively, is sent to a

distillation unit (stripping/deacidification). This unit removes the adsorbed gases from the enriched solution; the water is mostly recirculated to the gas scrubbing. The $\text{H}_2\text{S}/\text{NH}_3$ -vapours are led to the desulphurization unit, which is mostly a catalytic ammonia cracking combined with a sulphur recovery plant (Claus plant). A photo of a modern Claus plant can be seen in Fig. 21. Other options for desulphurization are the production of sulphuric acid or ammonia sulphate. In all cases the produced chemicals are further by-products.



Figure 21. View on a modern Claus plant

The second absorptive process variant is the Vacuum Carbonate process commonly operated with potassium carbonate which has some tradition at West European and Asian coke plants.

The most commonly applied wet oxidative process (outside Europe) is the Stretford process. Wet oxidative processes possess a higher efficiency for H_2S removal than adsorption processes (see Table 4). However, they need the addition of specific chemicals, like vanadium compounds, quinone and hydroquinone compounds as catalysts, the wastes of which have to be discharged. Usually this waste water is treated separately owing to the presence of compounds that have a detrimental effect on the biological wastewater treatment plant.

5.2.2. Gas tight operation of the by-product plant

In modern by-product plants fugitive gaseous emissions are minimized by gas-tight operation of the gas treatment plant. The measures are, minimize the number of flanges, using of gas-tight flanges, or closed venting system for tanks and equipment containing aromatic hydrocarbons. By use of pumps and piping suitable to prevent leakages, a release of any effluent to the environment can be avoided.

5.2.3. *Biological waste water treatment plant*

BAT is a wastewater treatment by using efficient tar and PAH removal, using efficient ammonia stripping and biological waste water treatment with integrated nitrification and denitrification to fulfill the common local regulations for discharge water quality. Limiting values are existing for free ammonia, $\text{NH}_3\text{-N}$, BOD, COD, cyanides, hydrocarbons and phenol.

6. **Situation of the German cokemaking industry**

Today five modern coking plants comprising with high capacity batteries are in operation in Germany. These plants, the fotos of which are given on Figures 22 and 23, fulfill the highest standards for emission control techniques with regard to the state of the art. They are equipped with modern wet quenching systems in order to comply with the legal demands of the actual TA Luft (TA-Luft, 2002) while the former coking plants August Thyssen and Kaiserstuhl III have been provided with modern dry quenching facilities.

In 2011 battery no. 1 of the coking plant Dillingen is under construction; this is a replacement of an old battery. At Huckingen a second battery is under construction as an extension.



1983: Dillingen



1984: Huckingen

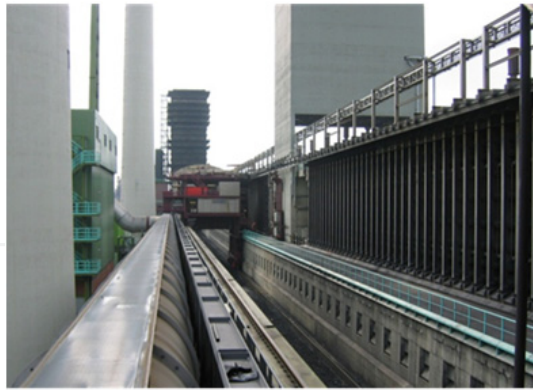


1985: Salzgitter



1985: Prosper

Figure 22. Coking plants currently in operation in Germany which were build in the 1980th, including date of commissioning



2003: Schwelgern

2010: Dillingen
(battery no. 3)

Figure 23. Coking plants currently in operation in Germany which were commissioned under the influence of the TA Luft 2002, including date of commissioning

The most essential design data of the five coke plants operating today are summarized on Table 10.

| | | oven chamber dimensions | | | | production rate | |
|------------------------------|--------------------|-------------------------|--------|-------|----------------|------------------------|----------|
| | | hight | length | width | volume | | per oven |
| | commis- sioning | m | m | mm | m ³ | 10 ⁶ t/a | t/a |
| Central Coking Plant Saar | 1983/2010 | 6.25 | 16.4 | 490 | 44 | 2.4 | 13300 |
| Huckingen | 1984 | 7.8 | 18 | 550 | 70 | 1.08 | 15430 |
| Salzgitter | 1985 | 6,2 | 16.6 | 465 | 43 | 1.42 | 13150 |
| Prosper | 1985 | 7 | 16.3 | 590 | 61 | 2 | 13700 |
| Schwelgern | 2003 | 8.4 | 20 | 590 | 93 | 2.64 | 18860 |

Table 10. Design data of the five German coke plants currently in operation (Hein, 2009)

The chamber height of 8.4 m of the new Schwelgern plant marked a new record for coke constructions. Now, the coke plant with the tallest chamber heights and the highest chamber volume worldwide is operating at the coking plant Schwelgern in Duisburg, Germany. The coking plant Saar in Dillingen is operated as stamp charging plant, and with 6.25 m hight the tallest for this technique.

The total production of the five plants was 8.15 mio. t coke in 2010. This is a sharp decrease when looking back to the year 1957 when approx. 50 mio. t coke were produced (Fig. 24).

The main cause for this change in Germany was the decline of coke sale for home firing and other applications than for pig iron making. On the other hand the coke need of the German iron and steel industry has fallen due to the reduction of the specific coke demand for the blast furnace as well as to the buying of coke from abroad, while the total hot metal production kept nearly constant since this time. The necessary adjustments in capacity were carried out in such way, that preferable older plants were shut down, which could not meet

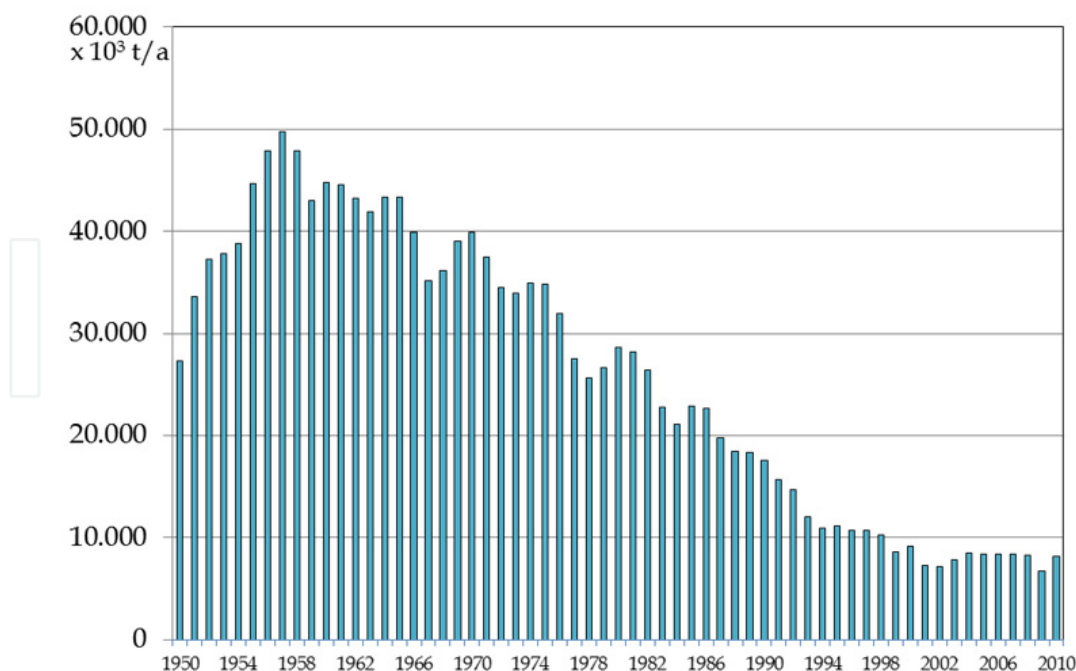


Figure 24. Annual coke production in Germany since the year 1950 (Kohlenstatistik, 2012)

the more stringent environmental standards, and which were not able to reach the economics which were typical for this time. This change has faced the mining industry, in particular, as this branch was the owner of nearly 75 % of the coking plants in Germany 50 years ago.

Due to the former dominance of the mining coking plants for the coke production the most sustainable impetus for new developments in cokemaking technology came from the German mining industry till the early 1990th years. Thereby, in particular, the basics were set for the construction of high capacity batteries as realized in the five coking plants running today, by research and development carried out in technical and semi-technical testing facilities for coking trials owned by the mining industry. The research in cokemaking technologies was centralized at the Bergbau-Forschung in Essen, the nucleus of the today's DMT GmbH & Co. KG.

Progress made in further development of cokemaking technology and its implementation in practice, in particular, would not have been successful without the innovative legacy of the German coke oven constructor companies. Out of the four prosperous German companies Dr. C. Otto, Carl Still, Heinrich Koppers and Didier Kogag Hinselmann, today only one exists, the Uhde GmbH which took over their business activities during the last 30 years step by step. German cokemaking technique is accepted worldwide, and according to this it is not surprising that more than 100 000 coke ovens all over the world have been constructed by German companies.

Progress reached in emissions control on German coking plants can be described by a drastic reduction of production specific emissions caused by battery operation due to the more stringent becoming legal rules for environmental control (Fig. 25).

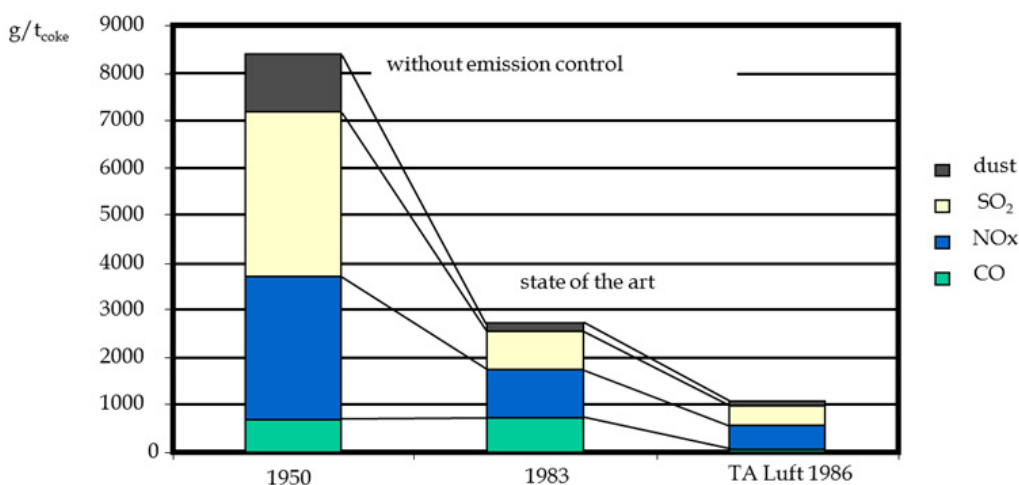


Figure 25. Reduction of specific emissions on German coking plants between 1950 and 1986

7. Determination of fugitive emissions of Benzo(a)pyrene from leaks at the battery

7.1. Measuring method

A quantitative method for measuring fugitive emissions from leakages at the battery was developed by Deutsche Montan Technologie GmbH (DMT) and its predecessor institute Bergbau-Forschung GmbH (BF) respectively. The relevant measurements included particle bound as well as gaseous compounds, and were carried out between 1980 and 2006 at various coking plants of different age in Europe which additionally were different in their design and in the state of maintenance of the closure facilities.

For the measurements a complete encapsulating of the relevant source is necessary as described in the following as an example of measurements at the coke oven doors. For this the outer door zone of the coke oven door is covered (see Fig. 26, left) by a thermo-stable transparent film (foil) in order to detect the strength of visible emissions, simultaneously. Preferentially the foil is fixed on the buck stays. The gas accumulated in the collecting space has to be withdrawn and analysed. For this, the foil at its bottom contains an opening while the top of the collecting space is combined with a vertical arranged tube. Because of thermal buoyancy clean air enters the opening at the bottom while the mixture of air and the emissions looked for leave through the pipe at the top of the collecting space. Typical volume flows are in the range between 50 and 200 Nm³/h depending on the design, the dimension of the door, the magnitude of the opening at the foil's bottom as well as on the meteorological marginal conditions. The relevant gas velocities range between 4 to 10 m/sec. From this main gas flow the sampling gas was sucked off isocinetically with a flow rate of about 2 Nm³/h.

For measurements of leakages at closed lids of the charging holes and of the offtakes, respectively, equipment for encapsulating was used, as shown on Fig. 26, (right). In order to get a constant gas-flow, pressured air as carrier gas was injected into the encapsulated space.



Figure 26. Equipment for measurements of fugitive emissions at doors (left side), lids (right side, top) and offtakes (right side, bottom)

In all cases the sampling gas is led via a dust filter and afterwards through an additional filter containing a synthetic resin for adsorption of still remaining gaseous PAH compounds. Sampling has to be done during the whole coking cycle, which was divided in several steps with separate sampling in some trials.

The taken samples are analysed in the laboratory for PAH-compounds by means of GC/MS and HPLC, respectively, in accordance with a national standard method (VDI, 1996).

7.2. Results from measurements at single leaks

Results from measurements at single leaks are given as emission mass flow m_f (mg BaP/h/closure facility) as an average of the sampling time) in a first step. The relevant figures are derived from the initially measured mass concentration (mg BaP/Nm³) in the sampling gas and the main gas volume flow (Nm³/h). To make the results more comparable the emission mass flows are converted to product specific emissions (mg BaP/t_{coke}) by consideration of the production rate per oven and the coking time. This figure is typical for the closure facility under investigation.

Fig. 27 shows the distribution of BaP in the gaseous and on the particle phase of emissions from oven leaks, as function of total particle concentration and off-gas temperature, respectively. It could be shown, that with increasing temperature of the waste gas, the portion of BaP in the gaseous phase increases, too (Fig. 27, right). And one receives the result, also, that with increasing dust emission the portion of BaP in the gaseous phase decreases (Fig. 27, left).

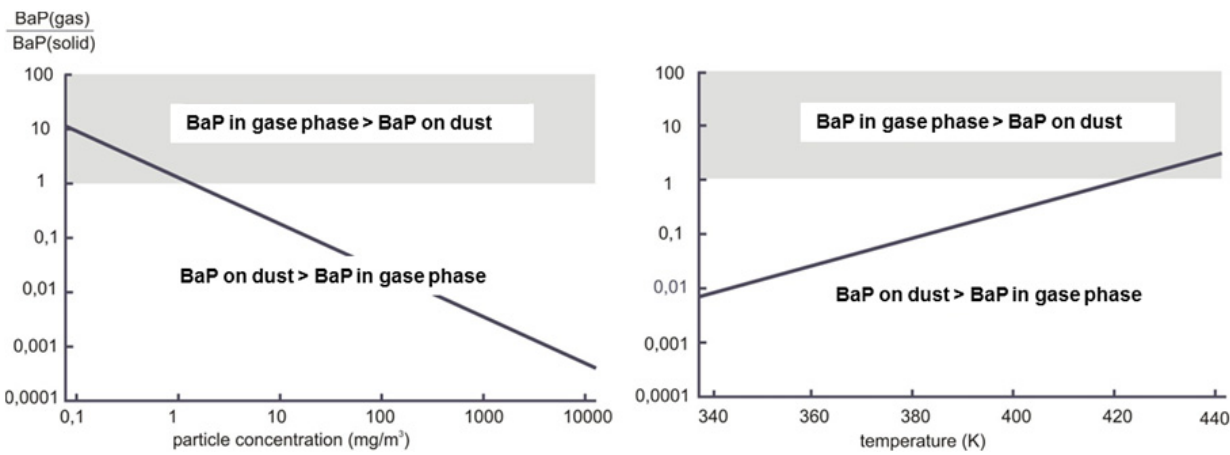


Figure 27. Proportion of BaP in gaseous and dust bound phase in emissions from coke oven leaks

Typical emission ranges for Benzo(a)pyrene as received by the measurements with concern to leaks at coke oven doors and chamber lids, respectively, are listed in Figures 28 and 29 (Eisenhut et al., 1990, 1992).

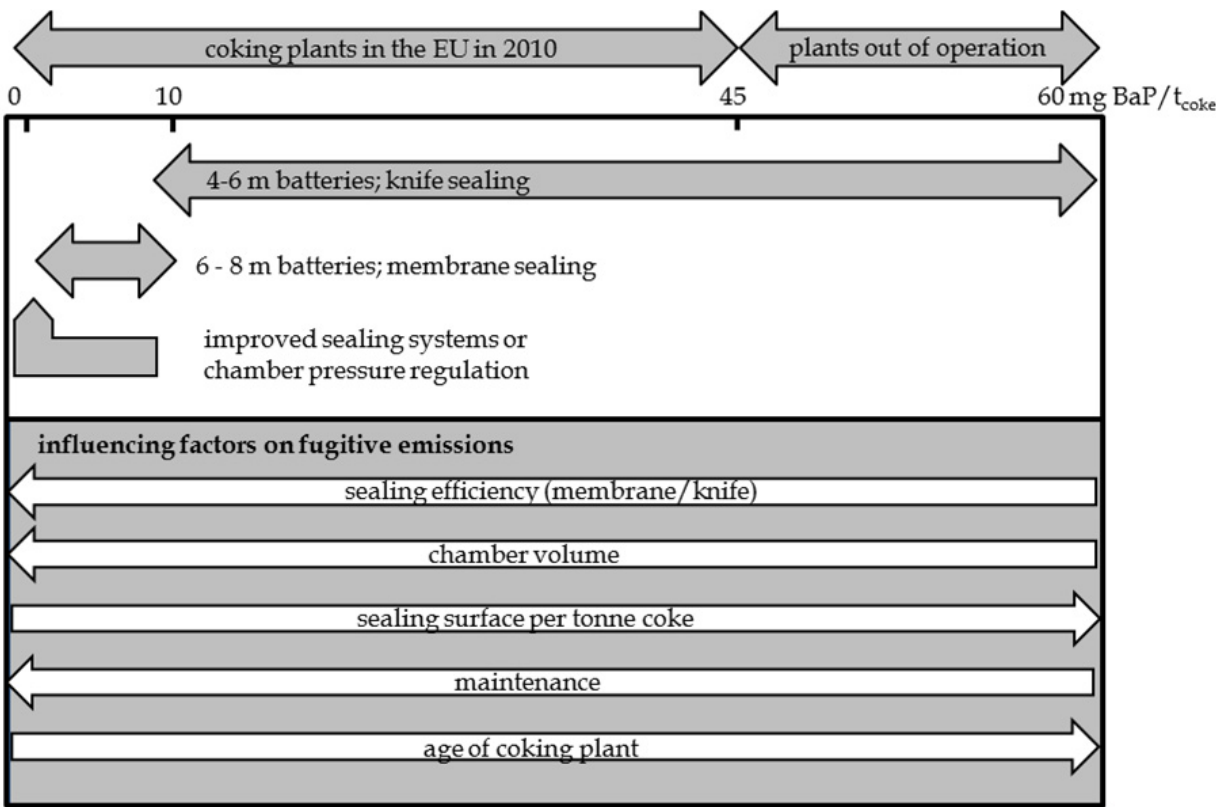


Figure 28. Typical ranges for Benzo(a)pyrene emissions ($\text{mg BaP/t}_{\text{coke}}$) from single leaks at coke oven doors as received from measurements

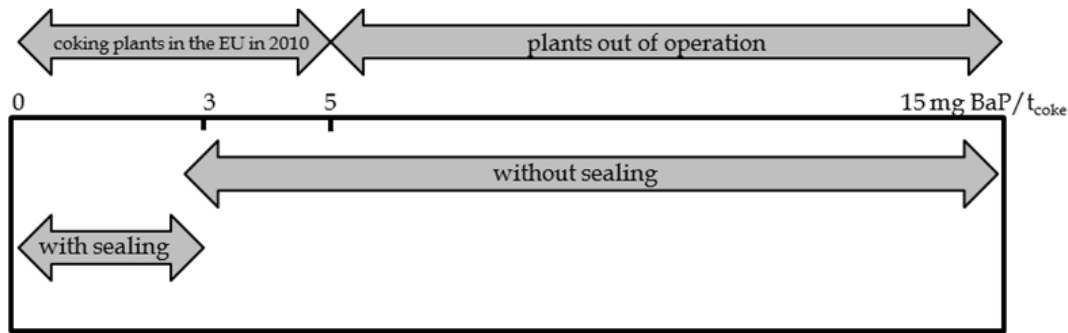


Figure 29. Typical ranges for Benzo(a)pyrene emissions (mg BaP/t_{coke}) from single leaks at charging lids as received from measurements

Fig. 28 shows also factors which have influenced the measurement results. These influence factors are valid for the results of measurements at the closed lids of the charging holes, too (Fig. 29). In both cases the age of the plants, the maintenance of them, the quality of the sealing facilities and the specific sealing surface per tonne of coke, which is in the opposite direction with the oven volume, have an impact on the amount of the emissions. As the measurement have started in early 1980th the shown ranges for emissions also include results from old plants with 4 m ovens in a bad condition and antiquated techniques for emission control. These plants are no longer in operation in Europa. And also in a more generalized view, one has to state that these plants are not typical for worldwide cokemaking operation of today. By consideration of this, Table 11 contains typical emission ranges for Benzo(a)pyren for coking plants caused by single leaks at the batteries which are still running today. Besides emissions from leakages at closed doors and lids, Table 11 contains also emissions from closed offtakes. Consequently it is to state that the lowest BaP emissions can be received at 6 to 8 m high flexible doors which are equipped by membrane sealings. The relevant emissions per door lie in the range between 1 to 10 mg BaP per t of coke. For new plants with an excellent maintenance, emissions at single doors go down to 1 mg/t_{coke}. Under optimal conditions, for example if a chamber pressure regulation system is installed (chapter 5.1.4.), BaP emissions are reduced below 1 mg/t_{coke}. BaP emissions at the chamber lids lie in a range between 0.3 and 5 mg/t_{coke}. The lowest emissions can be achieved at modern and well tended plants if the lids are sealed by special fluids or pastes after closing the relevant opening at the roof of the battery. In this case emission below 1 mg/t_{coke} can be received. Typical BaP emissions from leaks at the offtakes are below 3 mg/t_{coke}. On modern plants with water sealed lids at the offtakes emissions go down below 1 mg/t_{coke}.

| doors | control technique | lids | control technique | offtakes | control technique | unit of measurement |
|---------|----------------------------------|---------|-------------------|----------|-------------------|--------------------------|
| 10 - 45 | knife sealing | 3 - 5 | not sealed | < 3 | metal/metal | mg BaP/t _{coke} |
| 1 - 10 | membrane sealing | 0.3 - 3 | sealed | < 1 | water sealed | mg BaP/t _{coke} |
| < 1 | improved techniques, like PROven | | | | | mg BaP/t _{coke} |

Table 11. Product specific emissions for single leaks at the batteries of current coking plants

From Fig. 30 one can derive that over three-fourth of the fugitive BaP emissions from battery leaks in total is caused by emissions at the doors.



Figure 30. Spread of fugitive emissions from single leaks at the battery

This is in good correlation with the Figures given bei the US EPA (Table 9 of section 4.3.2.), and is the reason why in the following section emissions from coke oven doors are concerned, only, when discussing strength of leakages, as estimated by the US EPA and DMT, respectively.

7.3. Investigations at door leaks of definite strength

Normally, by use of only one emission figure, as received from Table 11, and multiplication with the annual coke production is not possible to estimate the annual BaP emissions of the total coke oven battery. The reason for this is the inequality of the strengths of the emissions at the various sources of one type (door, lid and offtake, respectively).

Analogously to the procedure from the US EPA (see section 4.3.2.) the total emissions of the plant should be calculated on base of the frequency of the visible emissions (leaking rate; section 7.4.) and of their strength (mass/h/leak), in the following. This will be done as an example for door emissions, as these emissions play the dominant role with regard to the total emissions caused by the battery (see Fig. 30 in section 7.2.)

To meet this goal varios door leaks, which strongly differ in their visible strength, were investigated as described in section 7.1., however by applying shorter sampling times (up to 5 h) with a nearly constant source strength over the sampling period. Typical strengths of visible emissions at doors are shown in Fig. 31. The emissions are categorized in:

- strong (st),
- medium (m),
- slight (sl)
- non visible emissions (n.v.e.)

For each category of visible strength typical BaP emission mass-flows (mf) could be determined, the ranges of which are shown on Table 12 (see also Fig. 32 in section 7.6.).

The specific mass-flows which are typical for visible emission strengths can be transfered to other plants where measurements have not been carried out. The assignment has to be done by an expert, on base of comparisons with results of measurements at comparable plants.

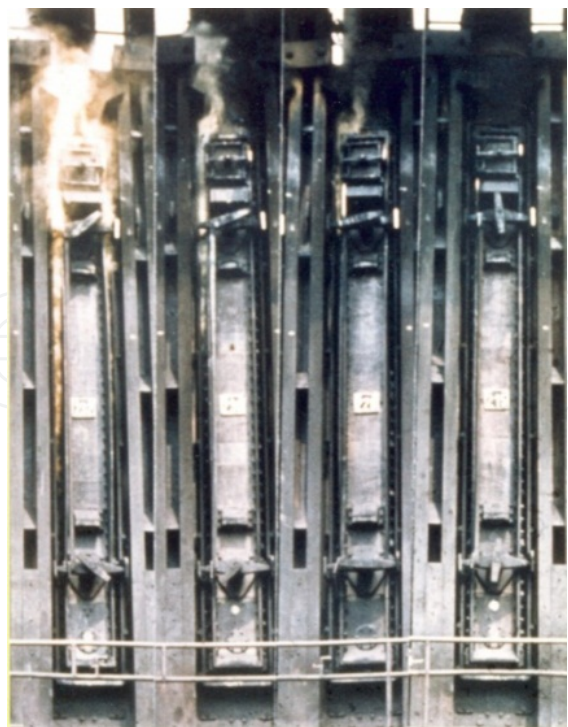


Figure 31. Four categories of visible strengths of door emissions

| strength of visible emissions | strong (mf _{st}) | medium (mf _m) | slight (mf _{sl}) | n.v.e. (mf _n) | unit of measurement |
|--|-------------------------------|------------------------------|-------------------------------|------------------------------|------------------------|
| all plants | 150-600 | 50-150 | 10-40 | < 10 | mg BaP/h/leak |
| plants according state of the art (membrane sealings) | 150-200 | 50-150 | 10-40 | < 10 | mg BaP/h/leak |

Table 12. Typical emissions BaP mass flows mf for leaks of different visible strength at coke oven doors

7.4. Assessment of visible emissions and of leaking rates

The leaking rates at the different sources are determined by an inspection of the battery and counting the visible emissions according tho EPA method 303 (US-EPA, 1993b). A distinction from the EPA method is made with regard to the different strengths of the visible emission, as it is shown for door emissions in Fig. 31, as an example.

Thus, the result of the determination of visible emissions will be, in pinciple:

- no. k of strong emission
- no. l of medium emissions
- no. of slight emissions, and
- n-(k+l+m) no. of none visible emissions,

whereby k,l and m are the numbers of leaks with visible emissions of different strengths, and n ist the number of doors in total.

The DMT-method for inspection of the leaking rates differs from the US-EPA 303 method by its four categories for emission strength while the US EPA method only results in the decision on the existence of a visible emission or not.

7.5. Determination of the total emissions caused by the battery

By mathematical combination of the number of leaks with their relevant emission mass flow the total emission E (mg BaP/h) of the battery (plant) with regard to emissions from door leaks can be determined, according equation 2.

$$E = k \times mf_{st} + l \times mf_m + m \times mf_{sl} + (n-k-l-m) \times mf_n \quad (2)$$

Where mf_{st} , mf_m , mf_{sl} and mf_n are the emission mass flows of different strengths of visible emission (Table 12), k , l and m are the numbers of visible emissions of different strengths at doors, and n is the number of doors in total. Equation no. 2 is comparable to equation no. 1 (section 4.3.2.) by which relevant calculations are made by US EPA (US-EPA, 2008b). Product specific BaP emissions caused by door leaks, which are typical for the emissions of the total plant, can be derived by multiplication of the result of equation no. 2 with the annual operation time and dividing by the annual coke throughput. Results of these calculations, which often are called emission factors, are given in section 7.6., and are compared there with relevant emissions given by the US EPA.

7.6. Comparison of BaP emissions from own measurements with results given by US EPA

On base of equation 2, total BaP emissions caused by all doors of a modern high capacity battery (70 ovens, 7.8m high, 1 mio. t coke per year) are calculated (line 8 and 9 of Table 13) by applying the extreme values of the given ranges for emission mass flows according Table 12 (line 3). Leaking rates (portion of no. of visible emissions (no. v. e.) of the total no. of openings in %) of 4 % (2 % slight and 2 % medium emissions) according the post-NESHAP standard and of 3.3 % (1 % slight and 2.2 % medium emissions) according the LAER standard are applied in order to make the results comparable with calculations of the US EPA (line 1 to 7 of Table 13).

Results given in lines 1 and 2 are derived on base of the model battery, as described in section 4.3.2. (62 4 m ovens per battery with a coke capacity of 344 000 t coke per year), and on leaking rates of 4 % and 3.3 % respectively, analogously to equation no. 1. These emissions will be reduced significantly when considering a high capacity battery with larger oven dimensions (line 3 and 4) due to the lower specific sealing lengths. Lines 5 to 7 contain ranges for BaP emissions caused at doors as given by a Risk Assessment Document of the US EPA (US-EPA, 2003b) for 5 US batteries which comply with the LAER standard (2010) already today (see section 4.3.1. also).

The origin of the applied emission mass-flows for the calculations according equation no. 1 and no. 2 one can read from column 8 of Table 13. To make data from US EPA comparable with own results, a conversion of BSO to BaP and t_{short} to t_{metric} was necessary.

| | | leaking rate | | batt. height | capacity | BaP | ref. of emission mass flow |
|---|--|-----------------|-----------------|-----------------|-------------------------|-------------------------|-------------------------------|
| | | no. v.e. (%) | | (m) | (t/a x10 ³) | (mg/t _{coke}) | |
| 1 | model batt. | 4 | post- NESHAP | 4 | 344 | 84,8 | (US-EPA, 2008b) |
| 2 | model batt | 3.3 | LAER | 4 | 344 | 81,4 | (US-EPA, 2008b) |
| 3 | high capacity oven | 4 | post- NESHAP | 7.8 | 1000 | 30,6 | (US-EPA, 2008b) |
| 4 | high capacity oven | 3.3 | LAER | 7.8 | 1000 | 29,4 | (US-EPA, 2008b) |
| 5 | 5 US batt. | 1.58 - 2.81 | actual | 3.4 - 5 | 65 - 589 | 22 - 57 | (US-EPA, 2003b) |
| 6 | 5 US batt. | 5; (3.8) | MACT | 3.4 - 5 | 65 - 589 | 25 - 88 | (US-EPA, 2003b) |
| 7 | 5 US batt. | 3.3; (3.8) | LAER | 3.4 - 5 | 65 - 589 | 25 - 78 | (US-EPA, 2003b) |
| 8 | high capacity batt. | 4 | 2sl+2m | 7.8 | 1000 | 2.65 - 16.43 | DMT/Table 11 |
| 9 | high capacity batt. | 3.3 | 1ss+2.2m | 7.8 | 1000 | 2.66 - 16.41 | DMT/Table 11 |
| | *: non visible emissions are not considered | | | | | | |

Table 13. Comparison of product specific BaP emissions (emission factors) caused by door leaks from own measurements with figures given by the US EPA (US-EPA, 2008b, 2003b).

From Table 13 one can read that all data given by the US EPA for BaP emissions from door leaks are significantly higher than those calculated by DMT. The reason for this is easily to understand and can be caused back to the higher values for the emission strengths (emission mass-flows of the single leak) as given by the US EPA (see Fig. 32 and Table 8 in section 4.3.2., respectively), and to the extra addition of 6 % emissions which can be observed only from the bench according the procedure of the US EPA. And in addition, it is to remark that the total emissions of plants according the state of the art with visible emissions less than 4 % are predominantly influenced by the strength of the non visible emissions (< 10 against 17 mg BaP/h/leak). The quality of the DMT-values for BaP emission strength could be confirmed by several dispersion calculations, by which the additional load caused by coke plant emissions on the ambient air in the surrounding of the coke plant, where the actual BaP concentration was determined by measurements, could be forecasted sufficiently on base of the above mentioned emission factors. In this context, it is to remark, that emission, as published by the US EPA, will lead to an overestimation of the BaP concentration in the surrounding, if forecasting (section 8.2.) the addition load in ambient air caused by a planned coking plant, e. g. in the process for getting a license for operation.

An explanation for the differences in BaP emission strength as determined by the US EPA and DMT, respectively, can be found in the high uncertainty of the US EPA figures, and in their determination on old coking plants with low standards for emission control, according to the ascertainment of the US EPA by itself (US-EPA, 2008b).

If emissions from charging lids and offtakes are taken into account, one can assert that there are only slight differences in the emissions determined by DMT and the US EPA, respectively.

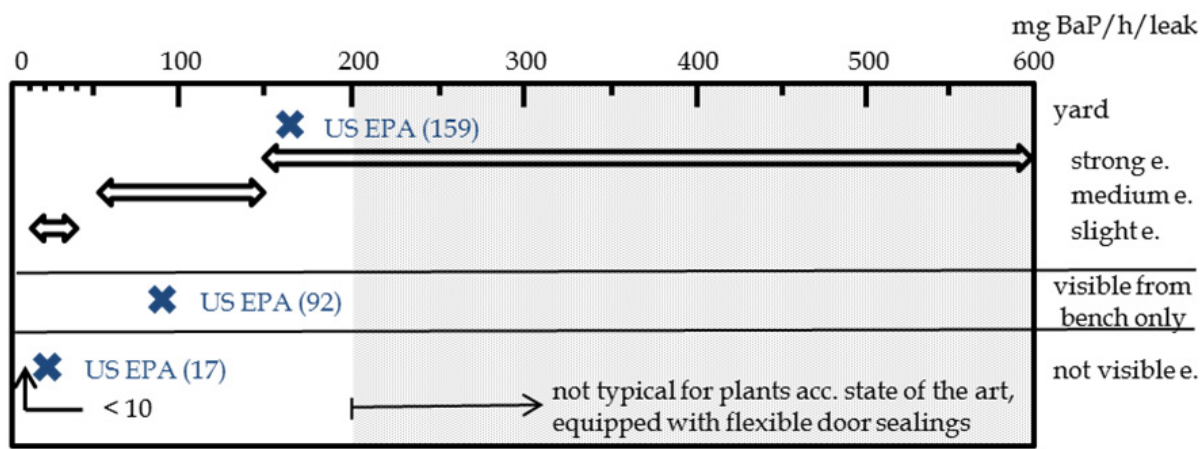


Figure 32. Ranges for emission strength (mg BaP/h/door leak) as determined by DMT and US EPA (cross marks), respectively (US-EPA, 2008b)

8. Benzo(a)pyrene in the vicinity of coking plants

A correlation between the Benzo(a)pyrene (BaP) emissions caused by a coking plant and the BaP concentration in ambient air in the surrounding of the plant could be shown by a lot of measurements. Measurements were made according (DIN-EN, 2008) by analysing the particulate bound portion of the collected dust. Thereby factors could be determined, which influence the amount of concentrations, as given on Table 14, and which will be described in the following.

| | |
|---|--|
| BaP in ambient air near coking plants is caused by: | -applied techniques for emission control on the plant |
| | -status of plant maintenance |
| | -age of the battery and of the closure facilities |
| | -local meteorological influences on spread of emissions |
| | - distance of the impacted area (measuring point) from the battery |

Table 14. Factors influencing BaP concentrations in ambient air caused by coking plant operation

Three coking plants, located in the Rhine-Ruhr area in Germany, were under investigation. In the following they are called coking plant A, B or C.

8.1. Results from measurements

For more than 20 years, ambient air has been examined for BaP in the surrounding of coking plant A (LANUV, 2012). The measuring station is located about 800 m away, in lee-side position to the coke plant. Measurements are taken two times or three times per week over a sampling period of 24 h. The coking plant is a modern plant yielding an annual coke production of approx. 2 million tons. The batteries are aged approx. 25 years, and fulfill the requirements imposed under the 2002 TA Luft for emission control.

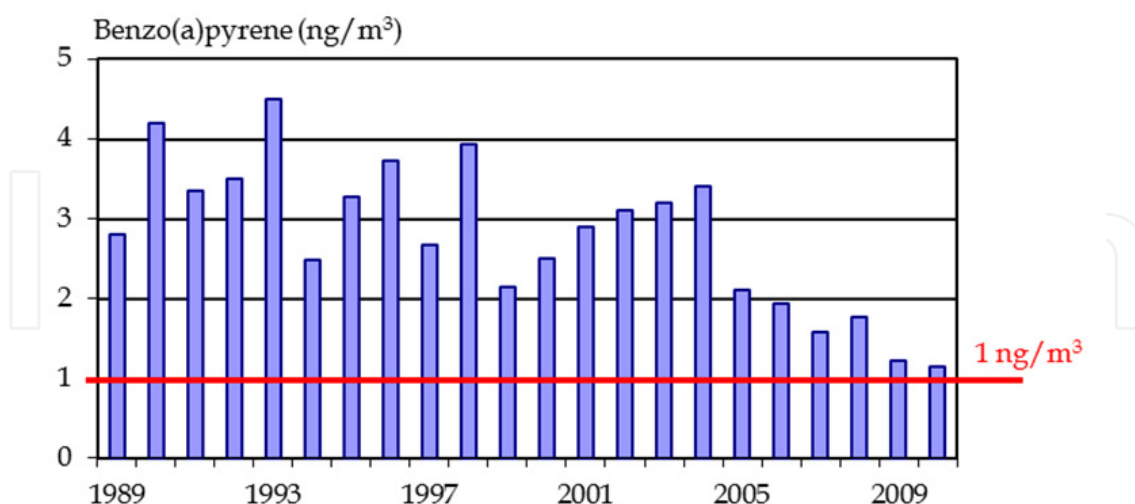


Figure 33. Benzo(a)pyrene in ambient air near (lee-side) coking plant A as annual mean (LANUV, 2012)

Fig. 33 shows the annual average concentration of BaP determined during the past years, that never fell under a BaP concentration of 1 ng/m^3 , which is set by the European Union as ambient air standard (EU, 2008).

The importance of coking plant's emissions on the BaP burden in the vicinity can be proved by an evaluation of the measurements in front of the preferential wind direction at the measuring day within a two years' term (Fig. 34) (Hein et al, 2003; DWD, 2003; LANUV, 2003). The mean annual BaP concentrations for the period under evaluation (1999-2000) lie at 2.2 and 2.5 ng/m^3 , respectively. The highest BaP concentrations occur when the wind blows from the wind direction sector between 135 and 255° , with the maximum occurring during wind directions from approx. 200° . As the measuring station stands in a direct lee-side position to the coking plant in case of a wind direction from 195° , the inevitable conclusion is that the coke plant is mainly responsible for this burden during lee-side weather situations that reaches 3.7 ng/m^3 on average. This conclusion can be confirmed by the absence of any other important BaP emitter in the weather-side of the coking plant. For measurements on days marked by wind directions falling outside the specified sector, it results a mean BaP concentration of 0.6 ng/m^3 . This BaP concentration is mainly congruent with the BaP background load which is typical for the industrial region where the coke plant is located, roughly amounting to 0.5 ng/m^3 .

When discussing the influence of meteorology on measured BaP concentrations, one should not ignore that other influential factors apart from the direction of wind are to be taken into account, for example the vertical exchange of air, which is typical for the season very often. A seasonal influence on the determined BaP concentrations can be clearly seen from measurements (LANUV, 2003) in the surrounding of coking plant B with an annual capacity of approx. 1.0 mio. t coke (Fig. 35). This plant is about 25 years old, and is equipped with techniques for emission control in compliance with the legal demands of the TA Luft 2002.

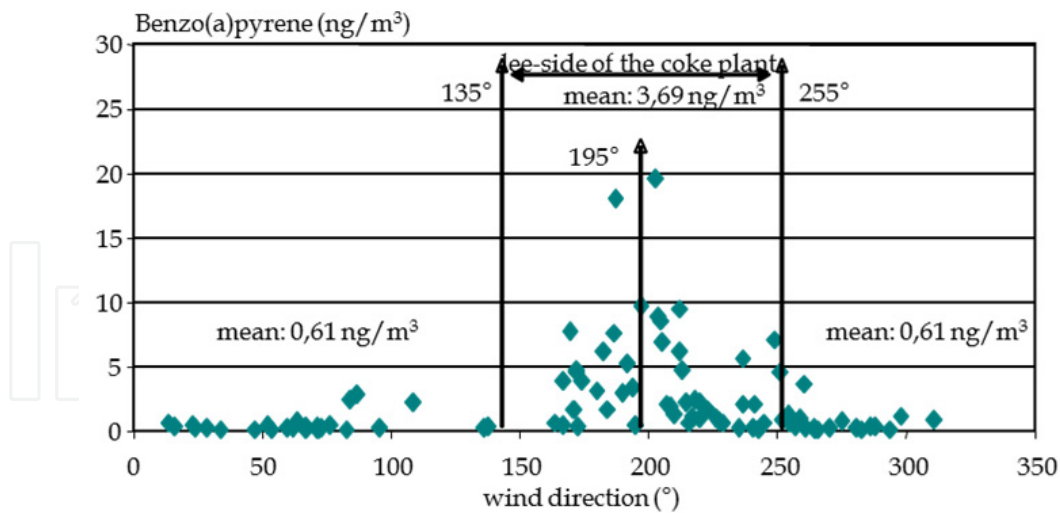


Figure 34. Influence of wind direction on Benzo(a)pyrene concentration in ambient air near coking plant A (DWD, 2003; Hein et al., 2003; LANUV, 2003)

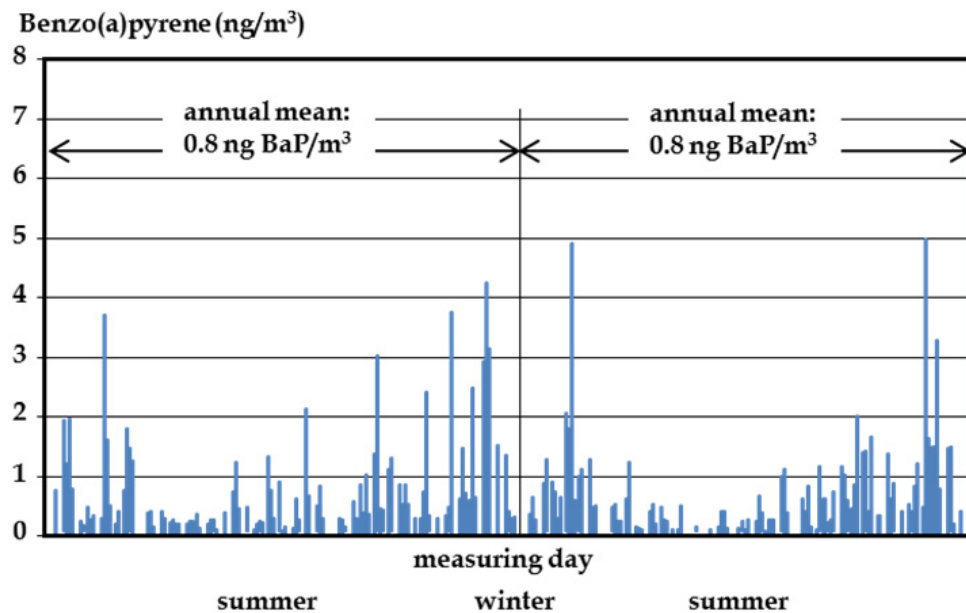


Figure 35. Benzo(a)pyrene in ambient air in lee-side of coking plant B during a two years period (LANUV, 2003)

The measurements were taken lee-side of the plant in a distance of 1000 m. Due to the larger distance of the measuring point from the plant, and to the less coking capacity, the BaP concentrations near coking plant B are lower than those near plant A. The annual BaP concentrations lie at 0.8 ng/m^3 and complies with the relevant ambient air standard of 1 ng BaP/m^3 as given by the EU (EU, 2004).

An influence caused by the seasonal effects, but also by improvements in the applied emission control techniques, can be also clearly seen from a three years measurement campaign in the surrounding of coking plant C, which composed of an annual capacity of approx. 1.5 mio. t coke (Fig. 36). The age of the various batteries of this coking plant, that has

shutdown in 1999, was between 35 and 40 years on date of the measurements. However, the coke oven batteries including the oven machinery have been rehabilitated before the final measuring period such that they fulfilled the most essential demands imposed under the 1986 TA Luft. The measurements were carried out at a distance of approx. 250 m both on the lee-side and weather-side of the batteries. On the lee-side, the annual means for BaP ranges from 23 to 37 ng/m³, while more than 50 % of the measured values were above 10 ng/m³. The rehabilitation work carried-out during the measuring period led to a reduction in the BaP burden at the most strongly burdened measuring station on the lee-side by up to 20 % relative to the annual average. Fig. 36 shows the already known seasonal influence on measuring values which, like for coke plant B, is mainly attributable to the different meteorological conditions prevailing during the summer and winter term. However, a base load of up to 6 ng/m³ was determined for the winter months at both measuring positions. Presumably, coal fires in private households which were quite popular in this region at that time mainly caused this base load.

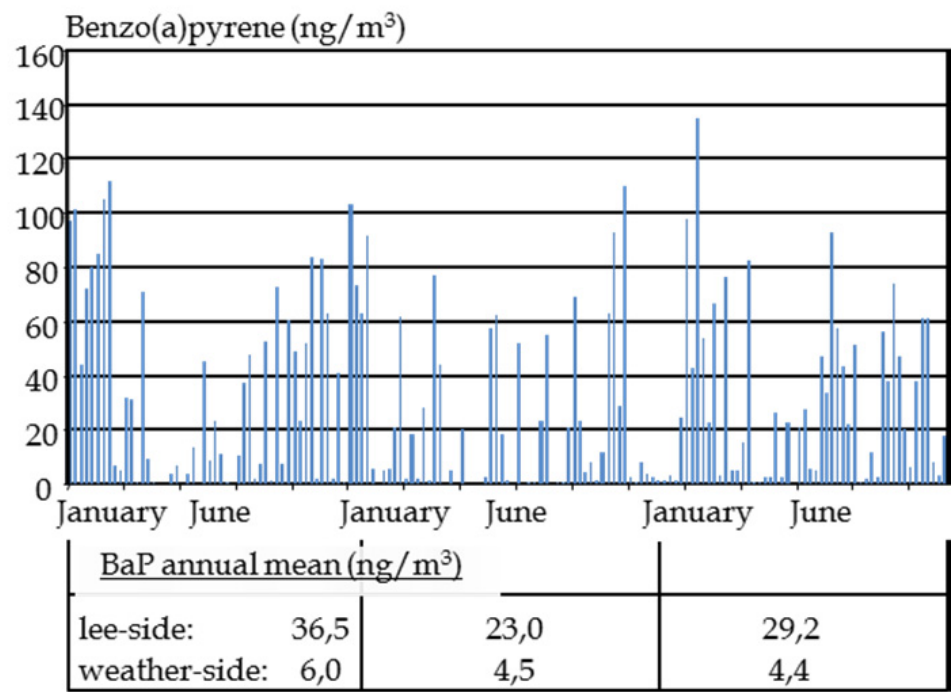


Figure 36. Benzo(a)pyrene in ambient air near coking plant C (shutdown in 1999) during a three years period

8.2. Calculated Benzo(a)pyrene concentrations

The additional burdens of BaP, caused by coke plant’s emissions, in the surrounding of coking plants A and C, respectively, were calculated by applying a spread model as per Gauß, without taking account of the influence exerted by buildings on the wind field (Hein et al., 2003). The wind field was just described by the spread class statistics for the site of the coking plant. The applied emission mass flow rates were based on those ranges given in section 7.

By evaluation of existing measuring data on the overall BaP burden near both coking plants, it was possible to calibrate the mathematical assumptions, and the assumed emission mass-flows in particular, by a factor of 1.18. The corrected results from calculations for the site of coking plant A are reflected in Fig. 37 (top side) in a so-called iso-line representation, which gives the total load of BaP as an annual average (for the year under investigation) near this plant, assuming a base load of 0.5 ng/m^3 which was typical for the Rhine-Ruhr area in the time under investigation.

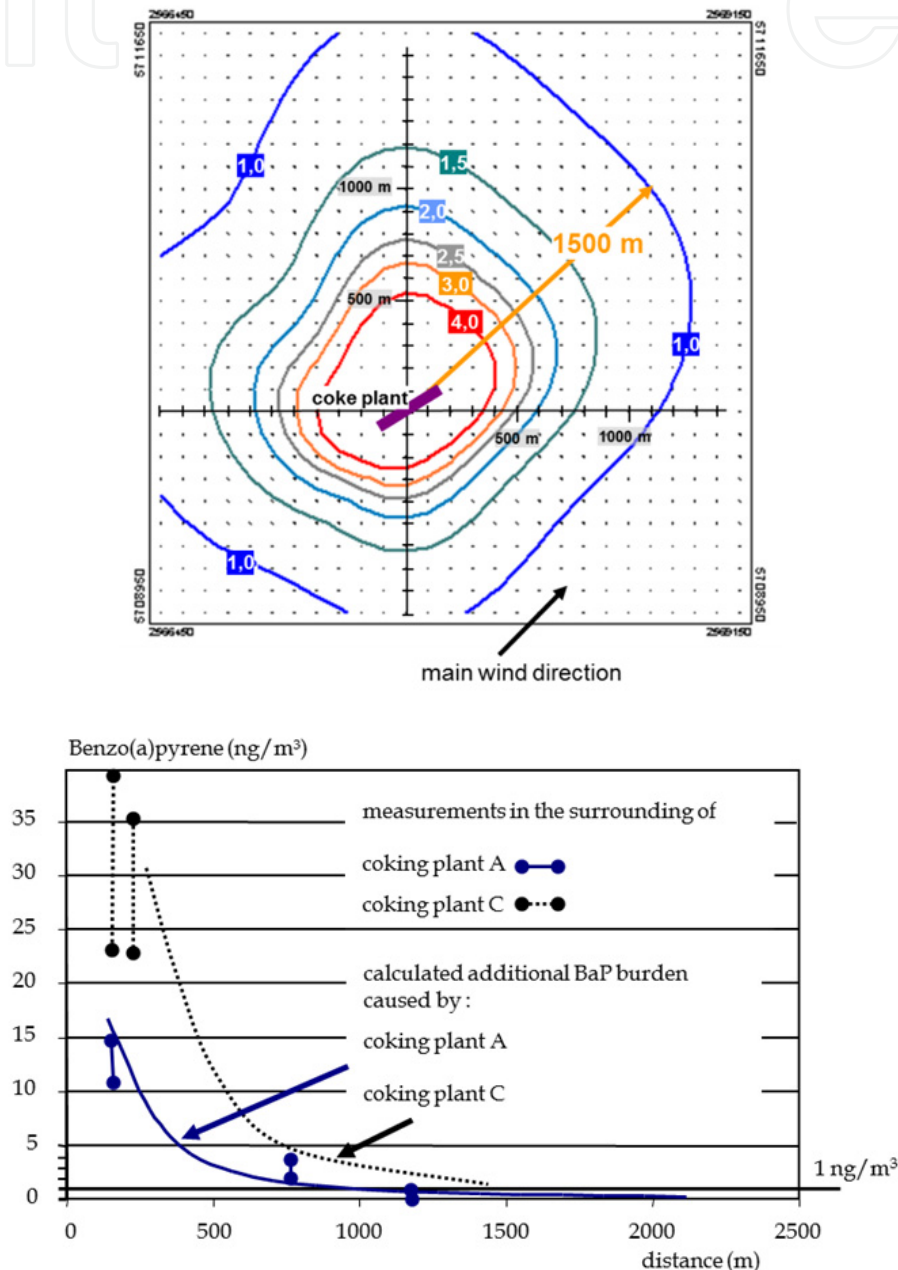


Figure 37. Calculated BaP concentrations (ng/m^3 as an annual mean) in ambient air near German coking plants; top side: total BaP concentrations near coking plant A considering a base load of 0.5 ng BaP/m^3 ; bottom side: calculated additional burden and measured concentrations in the surrounding of plant A and C, respectively

From Fig. 37 (top side) one may conclude that, in the period under investigation, the ambient air standard for BaP of 1 ng/m^3 (as a sum of base load and additional burden) as demanded in (EU, 2008) will be complied with in north-east of the investigated coking plant A only from a distance of approx. 1,500 m onward away from the battery center, assuming a base load of 0.5 ng/m^3 . The graph in the bottom of Fig. 37 shows the nearly asymptotic decline of the additional burdens by BaP, caused by battery operation, in the main direction of wind in progressive distance from both coking plants under investigation. The spread characteristics shown here can be confirmed by BaP measurements (overall load) that were taken in the environment of these plants in the past.

Inasmuch as their meteorology as well as their coke throughput rates is comparable with the two investigated coking plants, a transfer of the outlined spread behaviour to other coking plants with comparable emission control standards should be possible.

9. Summary and conclusions

Coke will be an indispensable precursor for steel production worldwide, also in the future. A further extension of the current cokemaking capacities in the world will depend on the global economics and on the future behaviour of export willing countries to sell coke for reasonable prices, of China in particular. It is to assume, if there is need for building of additional cokemaking capacities, the relevant plants will be built in countries with an increasing steel demand. Besides for China, this will be the case for India, Southeast-Asia and South America. Another trend will be inevitable worldwide, that means the replacement of older and smaller plants by modern high capacities batteries for cokemaking. This will be necessary not only by economic but notably by ecological reasons. Worldwide the legal demands for improvements in emission control on coking plants have been tightened in the last years. Legislation for environmental control as given by the Clean Air Act in the US, by the German TA Luft or by the BREF document of the European Union are accepted as a standard for other countries. Improvements in emission control could be achieved by application of the Best Available Techniques for emission control on coking plants during the last years in Europe, and in Germany in particular. By consequent compliance with future standards, as described in the draft of the revised BREF document, further improvements in air quality in the surrounding of the plants will be achieved. At this, special importance is to be attached to emissions containing carcinogenic compounds, like Benzo(a)pyrene (BaP), which are emitted during conventional cokemaking because of inevitable leaks at the closure facilities of the oven chambers. Similar to the non-recovery technology for cokemaking, which operates under negative pressure, these fugitive emissions can be drastically reduced at conventional cokemaking, too, by application of techniques for control the pressure of the oven chamber.

In order to predict the impact of coke plant's emissions on the ambient air in the surrounding, it is necessary to quantify their amount. The paper describes methods for measuring fugitive emissions containing Benzo(a)pyrene at single closure facilities of the

coke ovens, whereby emissions from doors play a dominant role. Based on these results, an estimation of the BaP emissions of the total plant is possible. It could be shown that so-called emission factors for BaP from doors, as an average of all doors of the battery, as given by the US EPA are higher than those from own measurements. By use of untypical high emission factors for a prognosis of the impact of coke plant's emissions on the ambient air and thus on the health risk for the people living nearby, it can happen that the importance of a coking plant is overestimated. By use of emission factors, which determination is described in this paper, for spread calculations, a sufficient forecast on the additional burden of BaP in ambient air in the surrounding of the coking plant is possible, when comparing with actual results of measurements. Additionally, parameters could be evolved which influence the impact of coke plant's emissions on ambient air. One of them is the location of the coking plant with regard to the relevant residential area where the ambient air measurements are carried out. In case that the coking plants are located mid of spacious industrial areas, the ambient air concentration for BaP of 1 ng/m^3 as set as a standard in Europe can be achieved in most cases, provided the relevant plant doesn't exceed a capacity of maximum 2 to 3 mio. t and is equipped with techniques for emission control according the state of the art.

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