MODERN TECHNOLOGIES TO REDUCE EMISSIONS OF DIOXINS AND FURANS FROM WASTE INCINERATION

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ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are formed unintentionally as byproducts of waste combustion and many other thermal industrial processes. Today PCDD/PCDF is known as one of the most toxic groups of organic substances. Furthermore, they are perceived to be carcinogenic. Although many questions about the toxicological effects of PCDD/PCDF are still unanswered, all possible reduction measures should be investigated to minimize their release into the environment. Consequently, reduction technologies for dioxins and furans are not only needed for densely populated urban areas, but also in rural regions where the population's food is produced. The uptake of PCDD/PCDF via food must considered to be the major pathway of exposure for humans as well as for animals.

After a brief presentation of the regulatory and technical background, this paper gives an overview of the formation routes of PCDD/PCDF in combustion and other industrial thermal processes. The most important sources for PCDD/PCDDF emissions are also described. Secondly, the most commonly applied PCDD/PCDF control technologies will be presented using various types of waste incinerators to demonstrate today's state-of-the-art flue gas cleaning technology. Various modern municipal solid waste (MSW) combustors and a hazardous waste incinerator, as well as an iron ore sintering facility provide actual examples of full-scale systems in commercial operation. The final part of the presentation will give an outlook towards new developments in PCDD/PCDF abatement technologies for more economical PCDD/PCDF reduction.

1. LEGISLATIVE ACTIVITIES

Due to a highly developed environmental sensitivity of the public in Germany and other Central European countries, more and more regulations regarding air and water quality are being implemented. Air emission regulations for power generation, waste incineration, crematories and numerous other thermal industrial processes have created a new market for air pollution control equipment particularly for the effective control of PCDD/PCDF.

Around 1990 the governments of Austria, Germany, the Netherlands, Sweden, Switzerland and other European countries drastically tightened the emission guidelines for many pollutants through implementation of respective legislation. The German 17. BImSchV (17th Implementation Directive to the Federal German Emission Protection Act) [1], which formed the basis for the current legislation within the European Union (EU), is used as an example to outline the implications of such legislation for all kinds of waste incineration plants. Among other things, the minimum acceptable combustion operating conditions were fixed in terms of incineration temperature and flue gas residence time as well as maximum permissible emission concentrations for many air pollutants. One of the most significant achievements of this new directive was the first time introduction of an emission limit for PCDD/PCDF of 0.1 ng I-TEF/Nm^3 (also sometimes referred to as ng I-TEQ/Nm^3). Since the group of PCDD/PCDF consists of 210 individual compounds (75 PCDD congeners and 135 PCDF congeners) with different levels of toxicity, the group is commonly referred to in concentration numbers of toxic equivalents. Several different methods for determining

toxic equivalents were defined. **Table 1** compares the three most commonly used factors for the calculation of toxic equivalents, namely the International Toxicity Equivalency Factors – I-TEF, the World Health Organization's Toxicity Equivalent Factors – WHO-TEF, and the German Umweltbundesamt/ Bundesgesundsheitsamt (Federal Environment Agency/Federal Health Agency) Toxicity Equivalency Factors – UBA/BGA-TEF.

Today, the most commonly used nomenclature is based on I-TEF and expressed in units of ng/m^3. However, there are numerous different standards for the term STP – standard temperature and pressure, and other parameters such as the O_2-content, and the moisture content for the definition of a m^3. Often seen are the terms Nm^3 (Normal m^3 – most commonly used in Europe), Sm^3 (Standard m^3 – most commonly used in the United States and some Asian countries), and Rm^3 (Reference m^3 – commonly used in Canada). All standards are based on dry conditions, thus, the moisture content of the flue gas and the resulting dilution is eliminated, which leads to an increase in the reported over the measured I-TEF concentration. Further, each standard corrects the measured I-TEF concentration to a particular oxygen value. As a result, a Nm^3 is based on 1013 mbar and 0 °C at STP and in Europe is typically further corrected to 11 vol.% O_2; a Sm^3 is based on 1 atm. and 77 F (25 °C) at STP and in the U.S. is typically further corrected to 7 vol.% O_2; and a Rm^3 is based on 1 atm. and 20 °C at STP and in Canada is typically further corrected to 11 vol.% O_2. Consequently, the results reported can only be compared in any meaningful way as long as the definition used for m^3 is also reported and all the numbers to be compared are converted to this same standard [2]. The same numerical values of 0.100 ng I-TEF/Nm^3 and 0.100 ng I-TEF/Sm^3 are in reality two greatly different concentrations. In order to allow a comparison of both values, both need to be brought to the same basis, i.e. ng I-TEF/Nm^3.

Thus, the following steps are necessary to convert the numbers to the same basis:

1. Oxygen Correction: [(21 vol.%O_2 – 7 vol.% O_2)/(21 vol% O_2 – 11 vol.% O_2)] = 1.4
2. Temperature Correction: (298 K/273 K) = 1.1
3. Pressure Correction: not necessary, since 1 atm. = 1013 mbar
4. Overall Correction: 0.100 ng ITEF/Sm^3 * (1.4 * 1.1 Sm^3/Nm^3) = 0.154 ng ITEF/Nm^3

The example shows that the real difference of the two numerically identical values amounts to more than 50%! Thus, it is of crucial importance for data quality management to ensure the same basis when comparing any data. It is equally important to fully understand which basis was chosen as a standard for a respective piece of legislation. Without this information, no valid knowledge of the technological challenge to achieve compliance of a facility can be developed. Also rounding and truncation of emission limits allows for differences. In some countries, the value of 0.1 ng I-TEQ/Nm^3 is rounded to the extent that even a measured value of 0.149 ng I-TEQ/Nm^3 is still acceptable for compliance. In other countries the number is truncated after the first digit after the decimal point leading to the fact that even a measured value of 0.199 ng I-TEQ/Nm^3 meets compliance. Consequently, no correct evaluation of the applicable process technology solution is possible.

The 17th BImSchV also requires certain combustion conditions to be maintained, namely a minimum temperature of 850 °C after the last combustion air injection combined with a flue gas residence time at or above said temperature for at least 2 seconds. An oxygen concentration of at least 6 vol.% must be maintained at all times. These requirements for insuring good combustion practice are mandatory for the incineration of MSW, sewage sludge and other such waste, which does not contain significant quantities of halogenated hydrocarbons. In case of other waste containing chlorinated hydrocarbons, the minimum combustion temperature must be raised to at least 1200 °C with the other 2 requirements remaining unchanged. The reason for these requirements is the significant thermal stability of many halogenated hydrocarbons such as PCDD/PCDF. In order to effectively destroy these compounds, the flue gas must be exposed to sufficiently high temperatures over a long enough period of time while the availability of excess oxygen for the thermal oxidation is ensured at all times.

However, the 17th BImSchV also allows for combustion conditions different from the ones required by the directive as long as individual measurements at the individual facility claiming an exception provide proof that the emission concentrations, especially of PCDD/PCDF, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), are not higher than at the operating conditions specified in the directive. This provision allows the operator to optimize the actual operation of the individual facility based on economical and other considerations without

compromising on environmental compliance. Most hazardous waste incineration facilities in Germany, which burn large quantities of halogenated hydrocarbons and other Persistent Organic Pollutants (POPs) as defined by the United Nations, take full advantage of this flexibility given by the 17th BImSchV in order to lower their operating costs.

2. DIOXIN AND FURAN FORMATION ROUTES

Since the early PCDD/PCDF measurements at MSW combustors revealed rather high PCDD/PCDF emissions at the stack, it was believed that these toxic substances are formed in the furnace. Today, much more about the formation mechanisms of PCDD/PCDF is known. Indeed, a well designed and operated combustion furnace has been fully recognized as the only means of almost complete destruction of the incoming dioxins/furans. **Figure 1** details the PCDD/PCDF destruction efficiency of an efficient combustion process, which ensures thorough mixing, adequate temperature and sufficient residence time. Nevertheless, the remaining PCDD/PCDF emissions from waste incinerators were still not considered acceptable to protect public health and the environment. Since it was unclear where and how the PCDD/PCDF formation occurred, a lot of measurements and intensive research was performed and sophisticated emission inventories were developed.

After nearly two decades of intense research and testing the answer is clear, although several details still have to be investigated. The reformation of relevant dioxin/furan concentrations in waste incineration plants takes place downstream of the furnace/combustion chamber in the boiler and during dust removal. **Figure 2** reveals the two basic mechanisms of reformation of PCDD/PCDF occuring after the combustion process and during cooling of the flue gas. This phenomenon is virtually independent of the actual destruction efficiency of the combustion process and is responsible for significant dioxin/furan concentrations in flue gases downstream of the furnace.

The first mechanism occurs between 300-800° C and is a homogenous gas phase reaction. PCDD/PCDF are formed through so called "precursors" or "pre-dioxins" (**Figure 3**). Such precursors are, for example, polychlorinated benzenes, phenols and biphenyls.

The second mechanism of reformation is the so called De-Novo-Synthesis of dioxin and furans. It is reasonable to assume that De-Novo-Synthesis contributes the predominant portion to the total PCDD/PCDF emissions from modern MSW incineration plants. For older MSW incineration plants or special incinerators (i.e. hospital waste incinerators or crematories) the individual share of the two formation mechanisms can widely differ. Due to very poor combustion operating conditions, extremely high emission values of PCDD/PCDF have been observed.

Two main theories are commonly accepted concerning the De-Novo-Synthesis reaction process. Both theories assume dioxin/furan reformation as a heterogeneous gas-solid phase reaction on the surface of fly ash particles. Inorganic chlorides such as NaCl or HCl in conjunction with catalytic active metallic chlorides like $CuCl_2$ or $FeCl_3$ will form elemental chlorine (Cl_2) in the presence of oxygen according to the well known Deacon reaction, shown in **Figure 4**. Subsequently, Cl_2 reacts with aromatic components in the flue gas or fractions from the carbon in the fly ash to form chlorinated organic compounds and fragments, which combine to become PCDD/PCDF in the next reaction step.

The first theory postulated by Hagenmaier [3] assumes a dualistic principle of catalytic PCDD/PCDF destruction depending on temperature and oxygen concentration (dechlorination/hydrogenation) and catalytic PCDD/PCF reformation by means of chlorine. The destruction of PCDD/PCDF by dechlorination increases exponentially with temperature; whereas the formation is limited with increasing temperature with the reaction velocity of chlorine formation becoming the rate determining step. Due to the mentioned influencing factors such as chlorine concentration and carbon catalytic surface activities, a temperature range results, where the PCDD/PCDF destruction velocity is substantially higher than the formation velocity (**Figure 5**). Thus, a well designed, operated and maintained waste incinerator acts as an overall sink for PCDD/PCDF due to an overall destruction efficiency of over 99.99%.

The second theory formulated by Griffin [4] assumes a limiting control-mechanism for the chlorination reaction of organic compounds. The in situ formation of chlorine (Cl_2) gas, according to the copper catalyzed Deacon reaction, increases with decreasing temperature, increasing oxygen concentration and decreasing water vapor concentration. The kinetics of both reactions, i.e. the formation of Cl_2 and the chlorination of aromatics, are enhanced with an increase in temperature. These reactions indicate that

aromatic ring structures and Cl_2 present in the flue gas are the potential ingredients for the reformation and subsequent emissions of PCDD/PCDF. However, chlorination of aromatics is limited when sulfur is present in the flue gas. If SO_2 exists in excess relative to Cl_2, the competitive oxidation reaction of SO_2 to SO_3 predominates. Chlorine is intercepted by SO_2 and consequently it would not be present in sufficient quantities for the formation of chlorinated aromatics as detailed in **Figure 6**. Following this theory, a chlorine to sulfur ratio of less than approximately 0.1 would be sufficient to prevent the reformation of PCDD/PCDF, because the chlorine interception reaction should predominate (**Figure 7**).

Both theories of the De-Novo-Synthesis have been supported by measurements and examples. However, it cannot be definitely decided which one is right. The De-Novo-Synthesis is most active in a temperature range of 200 – 500 °C with a maximum at approximately 350 °C.

From the theoretical knowledge about PCDD/PCDF destruction during waste combustion and subsequent reformation in the heat recovery boiler, several equipment design and combustion operation principles have been derived as primary measures to minimize PCDD/PCDF emissions from the incinerator before entering the flue gas cleaning plant. Today, such primary measures are consequently applied for the design and construction of new plants. It has also been suggested that these measures should be combined with the addition of inhibitor substances into the boiler to suppress the Deacon reaction. Nevertheless, an emission limit of 0.1 ng $I\text{-}TEQ/Nm^3$ cannot be ensured without additional gas cleaning equipment for the removal of PCDD/PCDF from the flue gas.

3. SOURCES OF DIOXINS AND FURANS

According to the above mentioned facts it can be concluded that not only waste combustion plants, but virtually all combustion and thermal industrial process categories in which chlorine occurs in combination with a carbon source at a temperature above 180 °C, are potential sources of dioxin and furan formation and emissions. Therefore, in some European countries such as Germany, the Netherlands, Sweden, and Great Britain as well as in North America (Canada and the U.S.) all processes with such conditions precedent were examined. National PCDD/PCDF inventories were established [5] based on very extensive testing campaigns of all potential industrial sources to determine their individual contribution to the total national emissions of PCDD/PCDF.

Among these process categories were:

- waste incinerators of all kinds;
- coal, oil, and wood combustors;
- vehicle traffic;
- most metallurgical industries, especially sintering processes;
- high-temperature processes;
- accidental fires;
- chemical production processes;
- and numerous others.

Some results of intensive measurements as well as information from the literature are presented in **Tables 2** and **3**. Some 10 years ago, municipal solid waste and its subsequent combustion were among the most important sources of dioxin and furan emissions. The introduction of new, strict emission limits in the early 1990´s led to a dramatic change in this situation. Today, waste incineration has become a rather insignificant source of PCDD/PCDF emissions. Up to then, measured dioxin/furan concentrations in the flue gas stack of MSWI plants varied between 1 and 92 ng $I\text{-}TEQ/Nm^3$ (@ 11% O_2) [6]. Starting with the introduction of the new legislation, most of the existing facilities were retrofitted with extensive flue gas cleaning systems. The remaining facilities were either closed down or rebuilt completely. Also additional new waste incineration plants were built. Interestingly, separate studies of the PCDD/PCDF content in the raw waste conducted in the U.S., Canada, and in Germany have indicated that MSWI plants reduce this PCDD/PCDF component by at about 90%. That is for every nanogram of PCDD/PCDF in the waste 0.1 nanogram is emitted from the stack making incinerators net reducers of PCDD/PCDF to the environment when compared to landfill which does not reduce the PCDD/PCDF component of the MSW. Of course, all plants now fully comply with the new stringent standards. Actually, most of the MSWI plants have PCDD/PCDF emissions significantly below the European Union emission limit of 0.1 ng $ITEF/Nm^3$.

It is worthwhile to note that the German 17th BImSchV does not differentiate between the various types of waste regarding their emissions from incineration. Thus, the emission limits for municipal waste, industrial waste, hospital waste, sewage sludge, hazardous waste and other types of waste are identical. Consequently, the dioxin/furan emissions from all

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types of waste combustion were lowered significantly as well. In the European Union an emission regulation similar to the 17th BImSchV was introduced for hazardous waste incinerators in 1994, and for municipal waste combustors in 1999. As expected, the dioxin/furan emission limit within the European Union is now 0.1 ng I-TEF/Nm^3 (@ 11% O_2, 1013 mbar, 0 °C, dry basis) for all types of waste incineration. The corresponding regulation for MSWI will have to be complied with by 2001.

Today, the most important dioxin/furan source in Germany is the metallurgical industry, especially the iron ore sintering processes in the primary steel industry and similar processes in the secondary non-ferrous industry and the metal recycling industry. Within the sintering processes, a mixture of various substances is combined and baked at high temperatures (1000-1200 °C). The material is mixed with coke and transported on a moving chain grate, the sintering belt. Burners above the belt heat the top of the material to the required temperature and cause the coke to eventually ignite. By drawing combustion air through the mixture of coke and iron ore, the flame front is moved through the sinter bed. The liberated heat causes the iron ore to agglomerate and sinter to larger particles suitable for the blast furnace process. The flue gas drawn from the sinter bed contains large amounts of particulate matter. Since it consists largely of iron ore particles, it is recovered and put back onto the sintering grate. Iron ore sintering plants are normally only equipped with ESPs as gas cleaning equipment for the recovery of the iron ore dust drawn from the bed with the flue gas flow. Stack testing for PCDD/PCDF at such plants revealed emissions of up to 47 ng I-TEF/Nm^3. Combined with volumetric dry flow rates typically ranging from 250,000 to more than 1,000,000 Nm^3/h, the mass flow of emitted PCDD/PCDF is significant [7,8]. Although the current regulations do not yet require dioxin/furan control for these processes, such emission limits can be expected to be implemented within the near future in Austria, Germany and the Netherlands. Subsequently, the European Union is also expected to implement such limits.

As already shown in Table 3, in Great Britain the emission situation is slightly different. Various municipal solid waste combustion plants were responsible for the highest dioxin/furan emissions until the mid 90's. For MSW combustors the regulation IRP 5/3 has been valid since December 1996, lowering dioxin/furan emissions of each plant to 1.0 ng I-TEF/Nm^3. In the meantime, new plants are also designed to meet the new European Union emission limit of 0.1 ng I-TEF/Nm^3.

4. DIOXIN REMOVAL TECHNOLOGIES

German engineering companies were among the first ones in the world to develop suitable PCDD/PCDF reduction techniques. Depending on the client's individual requirements, stack measurements consistently indicate that the installed dioxin/furan emission control equipment is capable of lowering the emissions far below the legal emission limit of 0.1 ng I-TEQ/Nm^3.

In Germany and also in other Central European countries there is a great lack of space for landfilling. Consequently, it became economically feasible to consider the reutilization of the byproducts and residues from flue gas cleaning. Although most of the commonly known byproducts are considered hazardous waste by law, German companies developed and built recovery processes for HCl (production of marketable hydrochloric acid, NaCl or $CaCl_2$), SO_2 (production of marketable gypsum) as well as bottom ash and fly ash treatment processes [9].

Today the German environmental engineering industry is fully capable of supplying a wide variety of PCDD/PCDF reduction processes individually tailored to the client's needs and the legal requirements. These technologies are based mainly on physical adsorption e.g. onto activated carbon, coke, or char; or on PCDD/PCDF destruction by means of catalytic oxidation.

Table 4 provides an overview of the most widely applied PCDD/PCDF control technologies and lists their various operating temperatures as well as the main equipment features. However, these PCDD/PCDF control technologies differ with respect to their control efficiency for dioxins, furans and other organic pollutants as well as acid gases and heavy metals. They also vary with respect to investment and operating cost. The task of the environmental control engineers is to prudently choose among these processes in order to supply the client with the most cost-effective solution for each individual application. Consequently, almost each waste incinerator which was retrofitted to comply with the tightened legislation in the last decade has a different process flow scheme for the flue gas treatment system.

4.1 Adsorbent Injection

The lowest cost approach for dioxin/furan reduction in order to achieve regulatory compliance is usually the injection of an activated carbon, Sorbalit, coke, or char based adsorbent upstream of a particulate matter collection device, typically a fabric filter as shown in **Figure 8**. In many cases, compliance with a limit of 0.1 ng I-TEF/Nm³ (dry basis, 11 % O_2) can be achieved. The adsorbent adsorbs the dioxins and furans on their way to the filter and in the filter itself. Here it is separated from the flue gas together with other particulate matter such as fly ash or reaction products of a preceding dry or semi-dry acid gas removal system.

The dioxin/furan removal efficiency depends largely on the quality of the adsorbent injection, the adsorbent – flue gas mixing system, the kind and operation of the filter as well as the mass flow rate of the adsorbent. For applying this technology most effectively, preferably a fabric filter (FF) should be used as a particle collector because of the additional contact time of the adsorbent with the flue gas in the gas stream and in the filter cake on the bags. Lower adsorbent consumption will result from applying a baghouse rather than an ESP. A critically limiting condition, especially for retrofits, is the boiler outlet temperature, which often significantly exceeds 200 °C. This, however, must be considered the absolute maximum permissible temperature for this technology, due to the loss of adsorption capabilities coupled with the increased PCDD/PCDF formation at higher temperatures. Also due to safety reasons associated with the use of a ignitable material such as activated carbon, a temperature range of 130 – 170 °C is strongly recommended.

Adsorbent injection is particularly advantageous if subsequent flue gas cleaning components are installed for high quality byproduct recovery (e. g. wall board quality gypsum from SO_2-absorption). The most common adsorbents are powdered activated carbon or powdered hearth oven coke, made from lignite. The use of special mixtures and minerals such as aluminum oxides providing a very high specific surface area has been developed more recently.

4.2 Entrained Flow Reactor
The entrained flow reaction process is a typical tail-end process for flue gas polishing. Upstream of the entrained flow reactor is a flue gas pre-cleaning system, which is mainly required for removing the bulk of the fly ash and the acid gases. Such a pre-cleaning system may be a dry, semi-dry or wet scrubbing system. With this technology, most commonly regulated air pollutants (SO_x, HCl, HF, Hg and other heavy metals, as well as dioxins and furans) except NOx can be removed to values below most legal emission limits (see **Figure 9**). Dioxin/furan testing at full scale waste incineration facilities revealed values as low as 0.01 ng I-TEQ/Nm³ (dry basis, 11 % O_2). Within this process the same adsorbents as mentioned above are applied. However, the adsorbent is usually applied in a mixture with hydrated lime and/or other inert materials such as limestone.

The process consists of 1) a fresh adsorbent supply and injection, 2) a fabric filter for the removal of the used adsorbent, 3) an adsorbent recirculation system, and 4) a storage system for spent adsorbents. Depending on the overall configuration of the air pollution control (APC) system, a reheating system, a bypass, and a start-up heating system might be required. The spent adsorbent is commonly injected back into the combustion zone of the furnace in order to destroy the adsorbed PCDD/PCDF thermally. The adsorbent recirculation system enhances the utilization of the active surface area of the adsorbent to a maximum possible extent. It also minimizes the use of fresh adsorbent while still ensuring the required high concentration of adsorbent in the entrained flow reactor. A minimum concentration of adsorbent particulates in the reactor is important due to the required adsorbent distribution in the flue gas duct and due to cleaning intervals of the filter bags. The pressure drop across a fabric filter operated as an entrained flow reactor is usually slightly higher than in a conventional fabric filter for the purpose of particulate removal only. An additional sink, such as the injection of Na_2S_4 [10], for mercury collected on the adsorbent might also be needed when reinjecting the spent adsorbent back into the furnace.

4.3 Activated Carbon Reactor
Another extraordinarily effective tail-end solution for the control of dioxins and furans is the activated carbon reactor (ACR). In an ACR granular hearth oven coke (HOC) is commonly used as adsorbent. The particle size of HOC is approximately twenty times larger than the powdered adsorbent used in the entrained flow processes. An ACR can be arranged similarly to the above described entrained flow reactor at the tail end of the APC system. With an ACR most pollutants can be reduced to extremely low levels, sometimes below the detection limits. Among these pollutants are all higher molecular weight organics such as PCDD/PCDF, PCBs and PAHs. An ACR is also capable of completely buffering even extreme

peaks of the inlet concentration of all pollutants. Even NO_x can be reduced if special activated carbon derivatives are used [11, 12]. Extensive test measurements of dioxins, furans and other organic pollutants at numerous full scale facilities showed PCDD/PCDF emission values below 0.001 ng I-TEF/Nm^3 (dry basis, 11 % O_2).

Figure 10 shows the design principle of a two-bed, cross-flow ACR. Typically, an ACR is a modular counter current or cross-flow reactor extendable to 2, 4, 6, or 8 beds depending on the flue gas volume flow rate to be treated. The raw gas enters the reactor from the bottom through the raw gas distribution chamber. Due to the same pressure drop across each HOC bed, the flue gas distributes evenly and flows horizontally through each bed The residence time of the flue gas in the HOC bed is typically in the range of 5 – 10 seconds. During this time the adsorption process takes place. The adsorbent enters the reactor from the top and flows down vertically to the bottom. Each bed is equipped with several discharge units and a screw conveyor to collect the discharged adsorbent. The ultimately polished flue gas is collected in the clean gas chambers. Subsequently, the clean gas ducts are recombined. Dampers are required in the clean gas ducts in order to briefly take an individual bed off line while discharging the spent adsorbent from the first layer. A special discharge program depending on time, pressure drop, and pollutant load controls the adsorbent removal procedure.

Figure 11 details the design of one individual adsorbent bed. Each bed consists of a inlet gas distribution system, three independent HOC layers, which are separated by perforated shrouds, and a adsorbent retention system in the gas outlet. The first layer serves for the filtration of particulates and the adsorption of dioxins, furans, other organics, and heavy metals as well as SO_2. In the second layer the remaining SO_2, and the lighter HCl is adsorbed. The third layer is a spare layer, which doesn't contribute to the adsorption process during normal operation. Due to the very long residence time of the adsorbent within the ACR, a very low adsorbent consumption rate is achieved. The spent adsorbent is commonly fed into the combustion zone of the furnace or combusted externally in order to destroy adsorbed organics thermally. Specially developed combustion systems for HOC are also in commercial operation.

As mentioned earlier, a reheating system and a bypass might be required. However, a separate heating system for start-up and also an inert gas supply for

safety reasons are mandatory. Many full-scale ACRs have been in commercial operation for more than 5 years, treating volumetric flow rates between 5,000 and 250,000 Nm^3/h and containing up to 8 modules. These systems are in commercial operation in coal fired power plants as well as in municipal, hospital, industrial, and hazardous waste combustion plants.

4.4 Tail-End Selective Catalytic Reaction (SCR)
Besides adsorption processes, the catalytic destruction of dioxins and furans provides another control option which has been widely applied. **Figure 12** shows the oxidation reactions for two tetra-chlorinated dioxin and furan species which occur on the catalyst surface in the presence of oxygen. Mainly CO_2 and HCl will result as destruction products. Honeycomb catalysts similar to those familiar from the well known SCR (selective catalytic reduction) DeNOx process are commonly employed for this residue free PCDD/PCDF control technology. The dioxin/furan reduction rate depends mainly on the installed catalyst volume, the reaction temperature, and the space velocity in the SCR reactor. Therefore, the process can be designed to meet almost any specific requirements. Dioxin/furan testing at commercially operating full-scale facilities showed that emission values lower than 0.01 ng I-TEF/Nm^3 (dry basis, 11 % O_2) can be easily achieved. The major advantages of this process are simple operation and no residues, apart from a very small amount of spent catalyst (after several years), which can also be recycled. At low operating temperatures (< 200 °C) safety precautions are not required. For higher operating temperatures a security bypass is recommended in order to protect the catalyst from potential destruction caused by temperature excursions. Such temperature excesses have been observed in isolated incidents due to VOC and CO emissions from the furnace during upset combustion conditions.

Typically, in MSW incinerators a tail end catalytic dioxin/furan removal system is combined with a SCR DeNO$_x$ system. The concentration of SO_2 and SO_3 remaining in the flue gas downstream of the flue gas pre-cleaning components determine the minimum required operation temperature of the SCR system. As shown in **Figure 13**, such a system typically consists of a regenerative or recuperative heat exchanger, a natural gas or light oil fired duct burner or a steam reheater, an ammonia supply and injection system (in case of combination with a SCR-DeNO$_x$) and a reactor containing the catalyst. A bypass and start-up system is also necessary for most applications. The higher the operation temperature the lower is the required catalyst

volume. However, the overall cost of the system depends on the sum of the operating cost for reheating and overcoming the additional pressure drop and the investment cost for the heat exchanger, the duct burner or steam reheater, the catalyst, and the SCR reactor.

PCDD/PCDF control by means of an oxidation reactor is usually not applied downstream of a MSW incinerator unless combined with a SCR-DeNO$_x$ system. Normally, either NO$_x$ or heavy metals such as mercury have to be removed in the flue gas cleaning plant as well. Therefore, combined processes are preferred. In other industries such as the steel industry, the situation is different. Here combined processes are not required. Consequently, the first order for a PCDD/PCDF oxidation reactor after an iron ore sintering plant was placed in 1997. The system, which will be described in section 5.6, has been in commercial operation since November 1998 [13]. Upstream of the SCR reactor only an ESP and an I.D. fan are arranged. This tail-end solution was chosen due to its low overall pressure drop and the lack of additional residue treatment.

5. EXAMPLES OF FULL SCALE PLANTS

5.1 MVB Hamburg

The municipal waste incineration plant Müllverbrennungsanlage Borsigstraße (MVB) in Hamburg consists of 2 identical 520 ton per day combustion lines and was designed for a total capacity of 320,000 t/a. Each line includes a combustion system including the heat recovery boiler as well as an entire flue gas cleaning plant. The recovery systems for hydrochloric acid and gypsum are common to both lines. The plant has been in commercial operation since 1994. Unconditional continuous compliance, cost-effectiveness and high availability have been demonstrated during year round operation. **Figure 14** shows the generalized process flow scheme for the flue gas cleaning plant. In order to reduce NO$_x$ by means of the SNCR (selective non-catalytic reduction) process, aqueous ammonia is injected into the furnace. This primary NO$_x$ control technology allows the federal emission limit of 200 mg/Nm^3 (dry basis, 11% O$_2$) to be met. The secondary air pollution control equipment starts after the waste heat boiler.

The flue gas exiting the boiler with a temperature between 200-230 °C is quenched down to approximately 170 °C in an evaporative cooling tower with process water. Upstream of the quench cooler powdered HOC is injected as an adsorbent for the removal of the bulk of the heavy metals as well as

PCDD/PCDF. The next stage comprises of a fabric filter, which is not only used for the collection of particulate matter, but also for an almost complete removal of PCDD/PCDF and heavy metals, including mercury, all adsorbed on the HOC. A two-stage co-current acid gas scrubber, which uses water at a pH-value of 0 or less as a scrubbing liquor, serves for the removal of HCl and HF. No neutralizing agent is added to the scrubbing liquor. Make-up water is continuously added in order to replace the evaporative losses from cooling the flue gas down to near saturation. Raw hydrochloric acid of approximately 10 wt.% concentration is discharged from the scrubber to the HCl recovery plant. The next stage consists of a counter current scrubber for SO$_2$-removal. In order to enhance absorption and provide a reaction partner for the absorbed SO$_2$, quick lime (CaO) is constantly added to the scrubbing liquor. This allows the scrubber to be operated at a constant pH-value of approximately 6. Due to the SO$_2$ absorption and sulfite oxidation process in the scrubber, gypsum is formed. The scrubbing liquor containing the suspended gypsum crystals is fed to the gypsum dewatering system for the recovery of wall board quality gypsum. The last stage of the APC train is a wet ESP for the additional removal of fine particulate matter and also to avoid the discharge of aerosols to the atmosphere.

The excellent PCDD/PCDF control efficiency has been demonstrated over the last 5 years of operation. The actual PCDD/PCDF emissions downstream of the fabric filter are far below the plant's permit limit of 0.05 ng I-TEF/Nm^3 (dry basis, 11 % O$_2$). Originally, the HOC-injection system for PCDD/PCDF and heavy metal control upstream of the wet scrubbers was primarily considered for the enhanced quality and purity requirements of the end products, the 30 wt.% hydrochloric acid and the wall board quality gypsum. The gypsum quality is similar to gypsum from FGDs in power stations and used for the production of wall board and other building and civil construction materials made from gypsum.

5.2 MHKW Leverkusen

The MHKW Leverkusen was originally designed for an annual incineration capacity of 256,000 t/a of municipal waste. Between 1994 and 1996, the facility was retrofitted with a new flue gas cleaning system to meet the highest standards. Before the extensive retrofit, each of the three units (furnace and waste heat boiler) was only equipped with a spray dryer absorber and an ESP for flue gas cleaning. This existing APC plant was not acceptably suited for insuring

compliance with the newly introduced German legislation, the 17th BImSchV. Especially the lack of effective process steps for the control of PCDD/PCDF, mercury and NOx required substantial upgrading of the existing APC system. However, the existing system remained in place and was incorporated into the new flue gas cleaning plant, as detailed in the chosen process flow scheme in **Figure 15**.

The retrofitted flue gas cleaning system starts after the existing ESP and consists of a cross-flow tubular heat exchanger, a dual stage co-current HCl-scrubber, a single stage counter-current SO_2-scubber, an entrained flow reactor and a low temperature SCR for NO_x removal. The old spray absorber was converted to operate as a quench cooler. Only in the case of upset conditions in the sodium chloride salt or the gypsum recovery systems, can it be used as a spray dryer as well. The existing ESP remained for the removal of the bulk of the particulate matter. The HCl-scrubber is operated at a pH-value of approximately 1. This level is maintained by the continuous addition of NaOH for partial neutralization of the absorbed HCl. The resulting NaCl, containing raw acid of approximately 60 g Cl-/l, is extracted from the scrubber and fed to a multi-stage NaCl recovery plant for the production of marketable NaCl salt. Wall board quality gypsum is also produced by the same process as described for the MVB facility.

The entrained flow reactor serves as a sink for PCDD/PCDF and also reduces mercury and the other heavy metals as well as the residual acid gases and particulate matter. A mixture of powdered HOC and hydrated lime or limestone is used as an adsorbent. The spent adsorbent is charged back into the furnace in order to avoid another residue for disposal. PCDD/PCDF emission tests confirmed PCDD/PCDF concentrations emitted to be significantly lower than the permit limit. As a result of the elaborate 6-stage APC process, all actual emission concentrations of all regulated air pollutants are well below those required by the 17th BImSchV and also substantially lower than those required by the plant's permit.

5.3 MVA Stapelfeld
The MVA Stapelfeld consists of 2 identical 550 t/d units and went into full operation in 1981. Each furnace and boiler was originally designed for a capacity of only 19 metric tons of waste per hour and was recently upgraded to its current capacity. The design of the furnace ensures that the flue gases from the combustion furnace remains at all times at a temperature of above 850 °C for more than 2 seconds

after the last injection of the secondary combustion air. In the heat recovery boiler they are cooled down to approximately 190 °C before entering the flue gas cleaning plant. Upstream of the second economizer of the boiler an ESP is installed for the removal of particulate matter. After the second economizer the flue gas is led through a multi-stage wet scrubbing system which removes most of the SO_2, HCl and HF. Prior to that, a cross-flow tubular glass heat exchanger uses the enthalpy of the raw gas downstream of the second economizer to reheat the saturated flue gas discharged from the scrubber system to approximately 130 °C. Subsequently, an I.D. fan is installed, which originally discharged the flue gas through the stack. Even though this APC system was absolutely state-of-the-art at its time, the newly introduced standards for PCDD/PCDF, heavy metals and NO_x could not be met without a retrofit.

In 1996, the plant's APC retrofit and upgrade was completed to meet the new requirements of the German 17th BImSchV. The additional gas cleaning equipment for flue gas polishing is shown in **Figure 16.** The newly designed volumetric flow rates are now 140,000 Nm³/h (wet basis, 11% O_2) for each line. This additional flue gas polishing system represents a typical example of an upgrade chosen for numerous facilities in Europe in order to meet the new legislation, especially with respect to the extremely stringent requirements for the effective control of PCDD/PCDF.

An activated carbon reactor (ACR) and a low temperature SCR-plant were added. The ACR removes heavy metals, PCDD/PCDF, particulate matter and other pollutants such as remaining HCl and SO_x to levels around or even below the detection limits. The ACR of each APC train consists of two independent reactors with four beds each to ensure maximum flexibility and a certain redundancy. Additionally installed booster fans overcome the pressure drop of the ACR and SCR and discharge the flue gas through the existing stack. During start-up and shut-down, these fans are also used to preheat and cool the ACR and SCR, respectively. The one SCR reactor per APC train is operated at a relatively low temperature of 200 °C. Such a low temperature can be used due to the virtually complete removal of SO_2 and SO_3 from the flue gas by the ACR. Thus, the risk of the formation and deposits of ammonia sulfate (($NH_4)_2SO_4$) and ammonia bisulfate (NH_4HSO_4) is avoided. Otherwise such formation and deposit could shorten the lifetime of the catalyst dramatically. For heat recovery and reheating purposes a regenerative

heat exchanger and a steam reheater are installed respectively. Ammonia, which is needed as a reducing agent for NO_x, is mixed into an extracted flue gas slip stream to ensure complete evaporation of the injected aqueous ammonia solution and an optimal NH_3/NO_x distribution after being reintroduced into and mixed with the main flue gas stream.

To avoid the loss of municipal waste incineration capacity through the replacement by the high calorific value of the spent activated carbon in the main furnace, the spent HOC is incinerated separately in a specially developed external combustion chamber. The adsorbed organic pollutants are completely decomposed at a temperature of approximately 800 °C. The flue gas of the external combustion chamber is mixed with the flue gas of the main furnaces and treated in the existing gas cleaning system. Like in other plants, where the spent activated carbon is fed back onto the grate, a sink for highly volatile heavy metals such as mercury is needed upstream of the activated carbon filter. In the MVA Stapelfeld the sink for mercury is the wet scrubbing system. It absorbs more than 70 % of the total incoming mercury. In cases of dry or semi-dry processes a separate sink for mercury must be installed. This problem can be solved very cost effectively using the newly developed sodium tetra sulfide (Na_2S_4) injection technology. This proprietary technology utilizes Na_2S_4 to react with elemental as well as ionic mercury (mostly present as $HgCl_2$) to form HgS (cinnabar) [10,14].

The results obtained during extensive PCDD/PCDF testing demonstrated very impressively the enormous potential of the ACR technology for the virtually complete removal of PCDD/PCDF, PAHs, PCBs and other POPs as well as heavy metals, acid gases and particulate matter. As such, this technology represents the most effective way to simultaneously control all pollutants to levels around or below their detection limit. Numerous European incineration facilities for hazardous waste, municipal waste, medical waste, sewage sludge and even coal fired utility boilers have been retrofitted with the ACR technology.

5.4 Gevudo Dordrecht
The MSW incineration plant Gevudo in Dordrecht, Holland consists of four 310 ton per day incineration lines connected to two identical flue gas cleaning trains. The retrofit of the existing system focused on the adsorbent injection systems for powdered HOC and sodium tetra sulfide (Na_2S_4) downstream of the evaporative cooling towers, in which the flue gas is quenched down to approximately 170 °C. The

subsequent flue gas cleaning plant consists of a fabric filter, a 2-stage wet scrubbing system and a wet ESP. The tail-end of the retrofitted system presents a high temperature SCR plant for combined NO_x reduction and integrated oxidation catalyst for the simultaneous removal of PCDD/PCDF (**Figure 17**). This technology is commonly referred to as SCR-DeNOx/DeDiox technology, which is also widely applied in Europe.

As a peculiarity, the APC train is equipped with two mercury reduction systems (HOC and Na_2S_4) and two dioxin reduction systems (HOC and oxidation catalyst). This results from the fact that very high emissions of elemental mercury and dioxins/furans were expected, because the flue gases treated by each APC train originate from one incinerator with a waste heat recovery boiler and one without a heat recovery system. The new flue gas treatment plant was commissioned in 1997. The results of PCDD/PCDF tests proved that the European emission limit of 0.1 ng I-TEF/Nm^3 (dry basis, 11 % O_2) can met at all times.

At the chosen operating temperature of 320 °C the described SCR-DeNOx/DeDiox process also reduces polychlorinated biphenyls (PCB), chlorobenzenes and polycyclic aromatic hydrocarbons (PAH) as well. Therefore, just by applying the ACR technology the emissions of these persistent toxic organic pollutants will also be minimized significantly. Removal efficiencies of more than 99% have been achieved, depending on the control process and inlet concentrations.

5.5 RVA Böhlen
The RVA Böhlen is a classical rotary kiln type hazardous waste incinerator with an annual throughput capacity of about 30,000 metric tons of solid, sludge, and liquid hazardous waste with an average heating value of 14 MJ/kg. The plant went into operation in 1998 and thus represents a new facility rather than a retrofitted plant. The plant was permitted to meet emission limits which are about a factor of 10 below the 17th BImSchV. As a result of the highly concentrated hazardous waste burned, the raw gas concentrations of the pollutants are an order of magnitude higher than in typical MSW combustors. Consequently, the chosen flue gas cleaning process has to ensure extremely high removal efficiencies for all pollutants. The result is an elaborate 7-stage flue gas cleaning process as shown in **Figure 18** [15]. The first stage consists of a 2-field ESP for the removal of the bulk of the particulate matter, followed by a Na_2S_4 injection system which acts as the main sink for the

mercury. The next stage is a spray dryer for the effluent treatment from the first scrubber. Between the first scrubber and the spray dryer is a baghouse for the removal of the spray dried reaction salts. The first scrubber is almost identical to the one at the MHKW Leverkusen presented earlier. The only difference is that quick lime is used as a neutralizing agent instead of NaOH. The resulting calcium chloride solution is fed to the spray dryer for cooling the flue gas to an acceptable temperature for the baghouse by evaporating the water. Simultaneously, the reaction salts dissolved in the solution are converted to a dry powder. The dried reaction salts are combined with the fly ash from the ESP and used as a stabilizing mortar in underground salt caverns. The second scrubber and the gypsum recovery system are identical with the system presented at the MHKW Leverkusen and the recovered gypsum is also recycled. However, this effective pre-cleaning process is still not sufficient to meet the extremely stringent permitted emission limits imposed by the local permitting authority.

Thus, an ACR and a low temperature SCR-DeNO$_x$ system are used for flue gas polishing, similar to the system retrofitted at the MVA Stapelfeld. The flue gas coming from the second scrubber is reheated by means of a cross-flow tubular glass heat exchanger to a temperature of around 130 °C before entering the ACR. After the ACR, all emission limits except NO$_x$ are already achieved. In order to reduce the NO$_x$ emissions, the flue gas passes through the I.D. fan and a steam reheater, where it is further heated to about 170 °C, before it enters the SCR-DeNO$_x$ plant. Anhydrous ammonia is injected before the I.D. fan for the NO$_x$ reduction. The flue gas exiting the SCR DeNO$_x$ plant enters the cross-flow heat exchanger again to reheat the flue gas coming from the second scrubber, before it is discharged through the stack. The spent HOC from the ACR is fed back into the rotary kiln, thus destroying all the adsorbed organics, including PCDD/PCDF.

Extensive testing of the facility revealed that the emission limits for PCDD/PCDF were far below the stringent permit value of 0.05 ng I-TEF/Nm^3. Emission concentrations of all the other regulated air pollutants were also significantly below the permitted values, even though most of the permitted values are about one order of magnitude below the 17th BImSchV. This system fully proves that today's state-of-the-art flue gas treatment technology can effectively control even the highest concentrations of pollutants to levels at or below their detection limits.

5.6 Thyssen – Sinter Belt 2

As mentioned in section 4.4, the world's first catalytic oxidation reactor went into operation at the Thyssen steel plant in Duisburg, Germany in late 1998 [13]. The advantages of such an arrangement compared to a typical tail-end SCR at a MSW incinerator are: cost savings resulting mainly from the avoidance of flue gas reheating (gas-gas heat exchanger, burner, etc.) and a lower pressure drop. **Figure 19** shows the simplicity of such a DeDiox reactor. Due to the novelty of this application in the steel industry, the system is equipped with additional soot blowers for possible catalyst cleaning. This type of reactor arrangement is well known from high dust SCR DeNO$_x$ plants in fossil fuel fired power generating plants.

The SCR DeDiox system was built as a demonstration plant by a consortium of steel producers from Belgium, France, Germany and the Netherlands. This was done in order to test various technologies in terms of their suitability to achieve an PCDD/PCDF emission limit of 0.1 ng ITEF/Nm^3 from sintering operations. **Figure 20** details the overall process flow scheme of the sinter belt No. 2 at the Thyssen-Krupp AG in Duisburg, Germany, where the demonstration plant is in operation. After thorough investigation of the various potentially viable PCDD/PCDF control technologies, the consortium decided to test 2 types of PCDD/PCDF removal systems. Consequently, sinter belt No. 2 was equipped with an adsorbent injection system and a SCR DeDiox reactor.

As can be seen from the overall process flow scheme of the facility, the adsorbent injection system is located upstream of the ESP. Powdered activated HOC and other adsorbents are being tested extensively. However, it would be very surprising if a PCDD/PCDF concentration below 0.1 ng I-TEF/Nm^3 could be maintained at all times. The SCR DeDiox reactor is located at the tail-end of the APC system, right before the flue gas enters the stack. A gas burner is located directly upstream of the reactor to insure proper pre-heating before start-up and also to maintain the minimum operating temperature of 130 °C.

Figure 21 provides a typical general arrangement of such a system. At temperatures as low as 130 °C a SCR DeDiox reactor is usually equipped with up to 6 layers of catalyst. Higher operating temperatures allow the required catalyst volume to be reduced substantially. Thus, this technology is best suited for applications at temperatures above 200 °C, even though the achieved removal efficiency even at temperatures as low as 130 °C clearly indicates that the

technology is fully capable of meeting an emission limit of 0.1 ng I-TEF/Nm³ at all times.

6. NEW DEVELOPMENTS IN PCDD/PCDF CONTROL

Several new developments in the field of PCDD/PCDF control are currently under way. Most of the effort is put into developing new adsorbents, mainly aiming to solve the two most pressing disadvantages associated with activated carbon, HOC, and activated char. All these carbon based adsorbents are not only expensive, but also flammable, which requires additional safety equipment as well as close process control. This later feature also limits the application of carbon based adsorbents to a temperature range well above the acid dew point of the flue gas (usually above 130 °C) and, to avoid temperature excursions, below the critical value of about 200 °C.

Such a low cost technology is the so-called Aktinert technology [16], which tries to avoid both disadvantages. It is based on a new adsorbent consisting of an inert limestone center coated with activated carbon dust (**Figure 22**). Aktinert refers to the sorbents <u>act</u>ive surface on an <u>inert</u> center. The activated carbon fraction is only 0.5 to 3 wt.%. The first measurements with the new process were carried out at iron ore sintering plants. The PCDD/PCDF adsorption efficiency was about 99.98 % and reduced the emissions from 20 to 0.005 ng I-TEF/Nm³ (dry basis, actual O_2). Most of the advantages of the ACR process remain, while the investment and operating costs, as well as safety requirements, are significantly lower.

The principle design of the Aktinert process is shown in **Figure 23** [17]. It consists of a fresh adsorbent supply system, a fixed bed reactor similar to the ACR and an adsorbent preparation system. Here a very small amount of spent adsorbent is removed and the inert center is recoated with fresh adsorbent. Due to the lower total carbon content inside of the reactor the operating temperature range is widened to 110-200 °C. Since the main application of this technology is the removal of PCDD/PCDF and heavy metals, the bed depth can be significantly reduced. Where as the typical bed depth of an ACR is between 0.7 and 1.0 meters, the Aktinert reactor allows bed depths as low as 0.3 meters. This reduces the pressure drop and the required footprint of the Aktinert reactor without compromising on the removal efficiency for PCDD/PCDF and heavy metals. These pollutants will be caught in the first layer of a bed. Estimates quantify a total cost savings potential of approximately 25 % compared to an entrained flow reactor and at least 30 % compared to a conventional ACR. Yet the well proven design principles of the ACR technology can also be fully benefited from.

7. CONCLUSIONS

Today, the effective control of PCDD/PCDF emissions from all industrial thermal processes is not a question of available air pollution control technology. It is rather a question of the political will of an economy and/or a country to burden its industry/economy with the cost associated with installing such control measures.

Numerous PCDD/PCDF removal technologies have been proven to be effective over many years in full scale installations. Thus, these PCDD/PCDF abatement technologies are commercially available on the world market. Their PCDD/PCDF removal efficiency varies almost directly in proportion to their investment and operating cost. Consequently, it is only a matter of political decision making to what degree a country is willing to invest in PCDD/PCDF emission control. Most Central European and Scandinavian Countries have decided to reduce their PCDD/PCDF emissions drastically. This led to the development and installation of extremely efficient APC equipment such as ACRs and catalytic DeDiox reactors. Other countries such as the United States take a somewhat less stringent approach and define adsorbent injection as the best available control technology. However, almost all industrialized countries in the world have acknowledged the need for the highly effective control of PCDD/PCDF in order to protect the public health as well as the environment. Even the developing countries and the countries in transition are already taking steps towards the regulation and control of PCDD/PCDF emissions. Finally, PCDD/PCDF are also included in the United Nation's International Treaty on POPs, which will require all nations to adequately address this international problem. Today's technology provides the solutions, it is up to politics to mandate their implementation.

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TABLE 1: COMMONLY USED TOXICITY EQUIVALENT FACTORS

Congener	I-TEF	WHO-TEF	UBA/BGA
2,3,7,8-Cl$_4$DD	1	1	1
1,2,3,7,8-Cl$_5$DD	0.5	1	0.1
1,2,3,4,7,8-Cl$_6$DD	0.1	0.1	0.1
1,2,3,7,8,9-Cl$_6$DD	0.1	0.1	0.1
1,2,3,6,7,8-Cl$_6$DD	0.1	0.1	0.01
1,2,3,4,6,7,8-Cl$_7$DD	0.01	0.01	0.01
Cl$_8$DD	0.001	0.001	0.001
2,3,7,8-Cl$_4$DF	0.1	0.1	0.1
1,2,3,7,8-Cl$_5$DF	0.05	0.05	0.1
2,3,4,7,8-Cl$_5$DF	0.5	0.5	0.1
1,2,3,4,7,8-Cl$_6$DF	0.1	0.1	0.1
1,2,3,7,8,9-Cl$_6$DF	0.1	0.1	0.1
1,2,3,6,7,8-Cl$_6$DF	0.1	0.1	0.1
2,3,4,6,7,8-Cl$_6$DF	0.1	0.1	0.1
1,2,3,4,6,7,8-Cl$_7$DF	0.01	0.01	0.01
1,2,3,4,7,8,9-Cl$_7$DF	0.01	0.01	0.01
Cl$_8$DF	0.001	0.0001	0.001

TABLE 2: SOURCES OF DIOXIN AND FURAN EMISSIONS IN GERMANY [7]

	1989/90	1994/95	Estimate 1999/2000
	g I-TEQ/a	g I-TEQ/a	g I-TEQ/a
Waste Incineration (all types)	400	30	< 1
Metal Industry	740	240	< 40
Power Stations (all fossil fuel)	5	3	< 3
Industrial Combustions	20	15	< 15
Other Thermal Industrial Processes	1	< 1	< 1
Domestic Coal and Wood Combustion	20	15	10
Crematories	4	2	< 1
Vehicle Traffic	10	4	< 1

TABLE 3: EMISSION SOURCES OF DIOXINS AND FURANS IN GREAT BRITAIN [8]

	Present Estimate (1995)	Future Projected Estimate	Estimate Quality
	g I-TEQ/a	g I-TEQ/a	(H = high, M = medium, L = low)
MSW Combustion	460-580	15 [1] – 1.5 [2]	H/M
Chemical Waste Combustion	1.5-8.7	0.3 [2]	M/M
Hospital Waste Combustion	18-88	5	H/M
Iron Ore Sintering Plants	29-54	29-47	M/L
Iron and Steel Production	3-41	14	M/L
Non Ferrous Metal Industry	5-35	10	M/L
Industrial Coal Combustions	5-67	5-67	H/M
Domestic Wood Combustion	2-18	2-18 [3]	L/L
Domestic Coal Combustion	20-34	20-34 [3]	L/L
Crematories	1-35	1-35 [3]	H/L
Vehicle Traffic	1-45	1-45 [3]	H/L

(1) Since December 1996, IRP 5/3 with 1 ng I-TEQ/Nm^3 has been valid

(2) Assumed to comply with EU Draft Directive COM (92), Final-SYN 406 (0.1 ng I-TEQ Nm^3)

(3) No reduction has been assumed. This is not necessarily valid (for example with Crematoria and Traffic)

TABLE 4: DIOXIN/FURAN CONTROL TECHNOLOGIES

Process (*)	Adsorbent	normal operating temperature (°C)	main equipment
Adsorbent injection upstream particulate matter removal devices	Activated carbon, hearth oven coke, special minerals	135-200	Fresh adsorbent supply, injection system, FF or ESP for new installations
Entrained flow reactor	Activated carbon, hearth oven coke, activated char, special minerals, and mixtures of these substances with $Ca(OH)_2$ or inerts	110-150	fresh adsorbent supply, FF, recirculation system, spent adsorbent system
Activated carbon reactor (ACR)	Hearth oven coke, activated carbon	110-150	Fresh adsorbent supply, fixed bed reactor, spent adsorbent system
tail-end catalytic oxidation	None (ammonia only for NOx removal)	130 (260)-350	reactor with catalyst, (ammonia supply)

(*) various combinations of these processes are also possible and are in full scale operation (e.g. entrained flow reactor with adsorbent injection, adsorbent injection with tail end catalytic oxidation, or tail end catalytic oxidation with ACR).
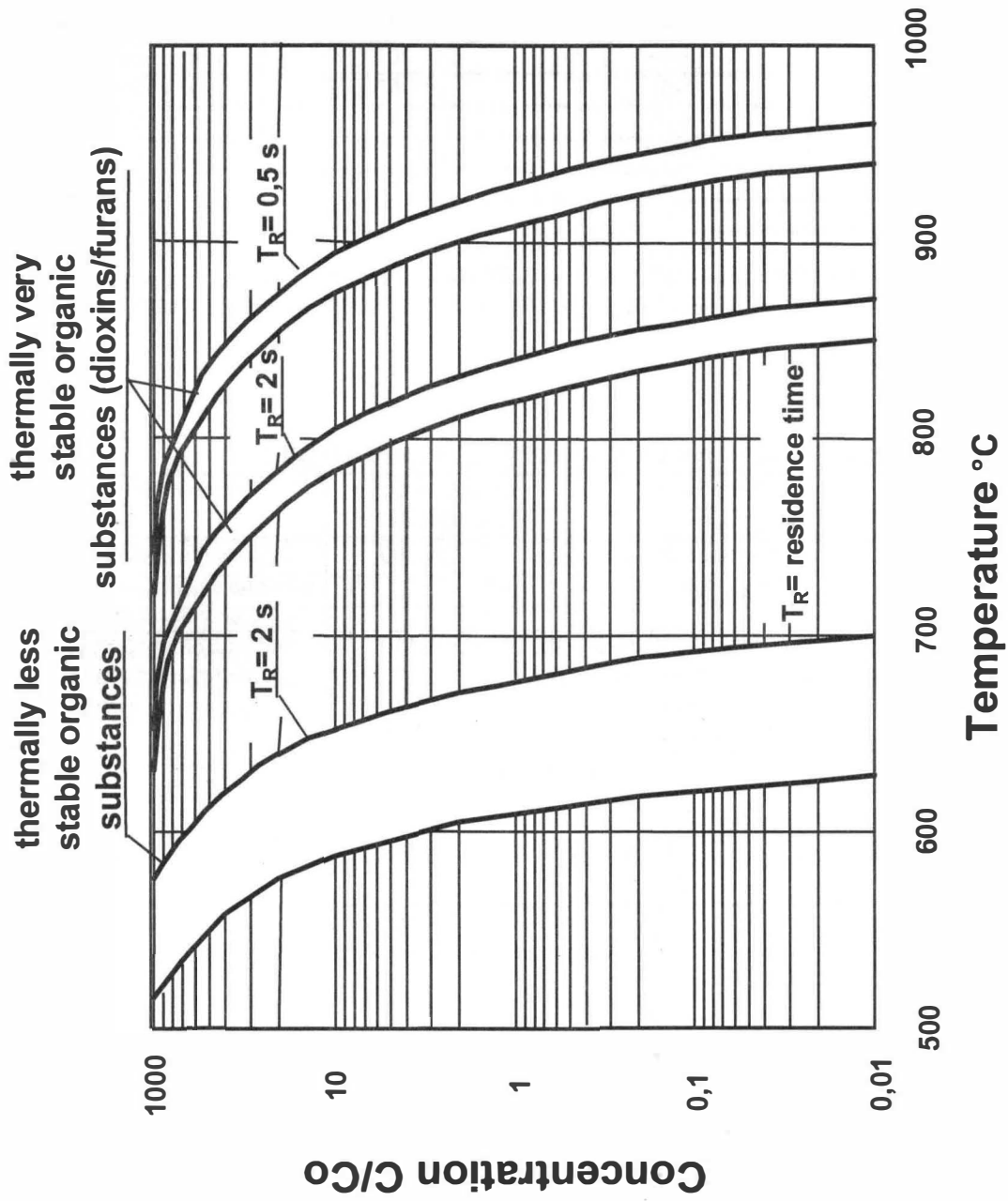
Figure 1: Thermal Destruction of Organic Substances in Air
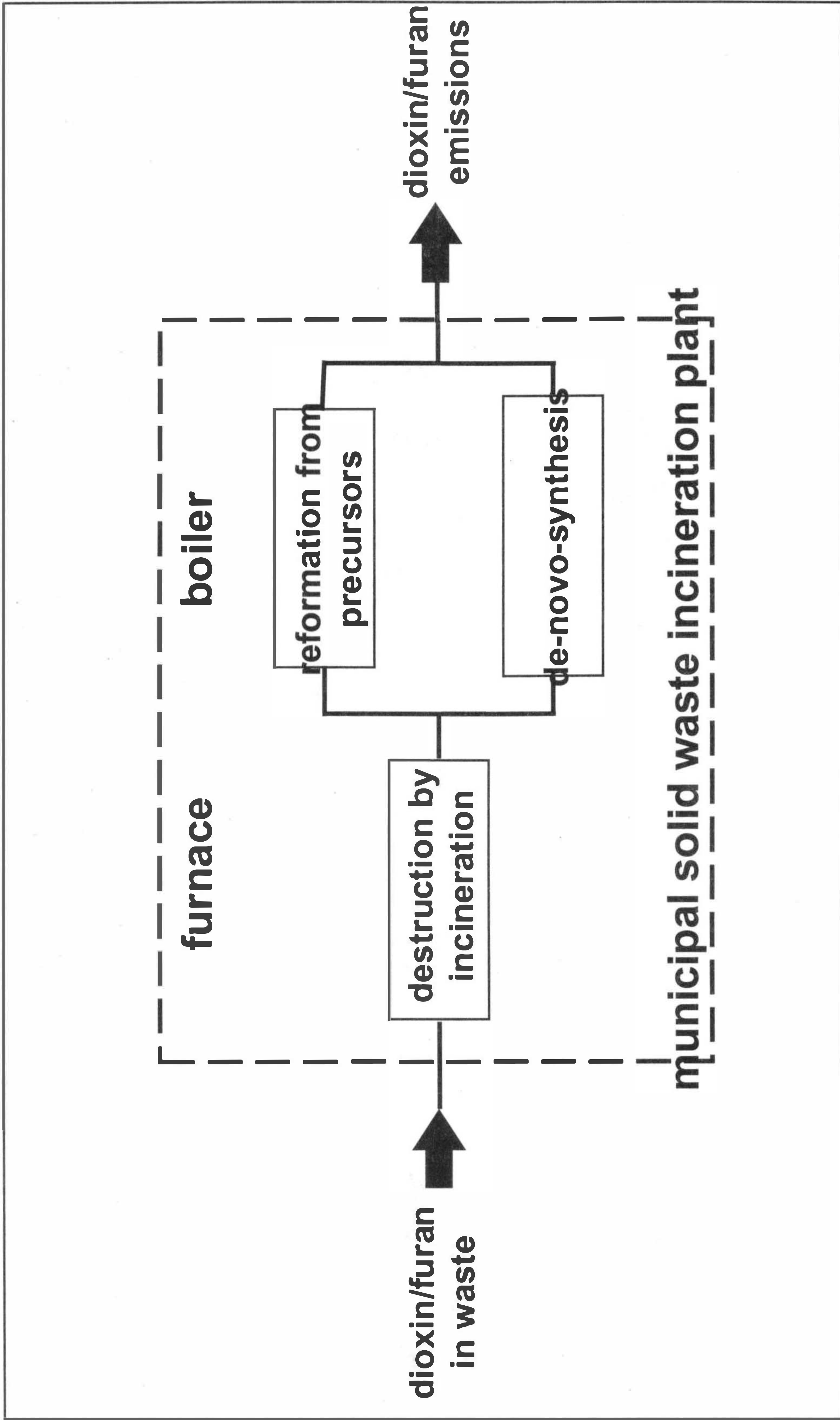
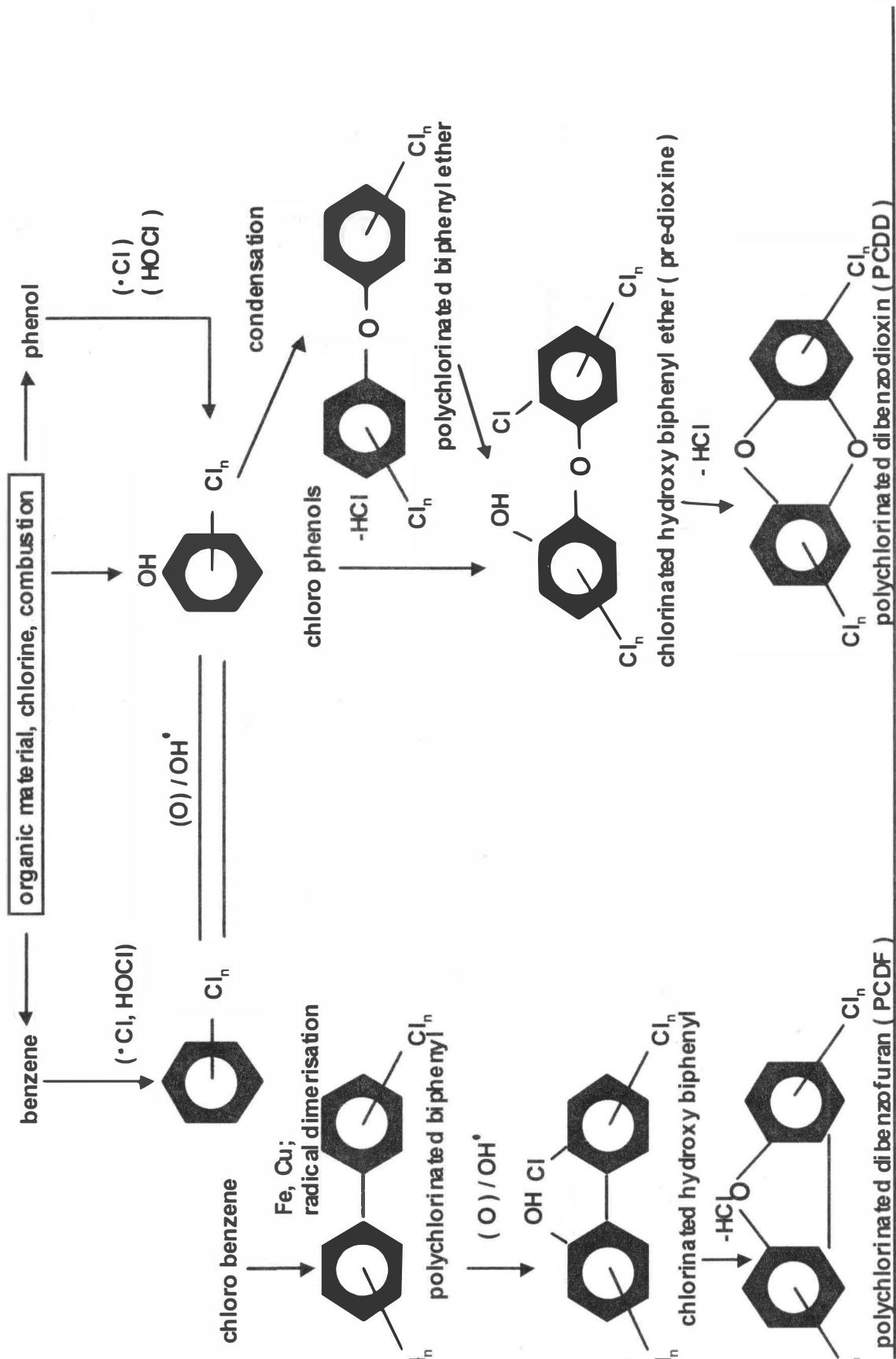**Figure 2: PCDD/PCDF Destruction and Formation in an Incineration Plant**

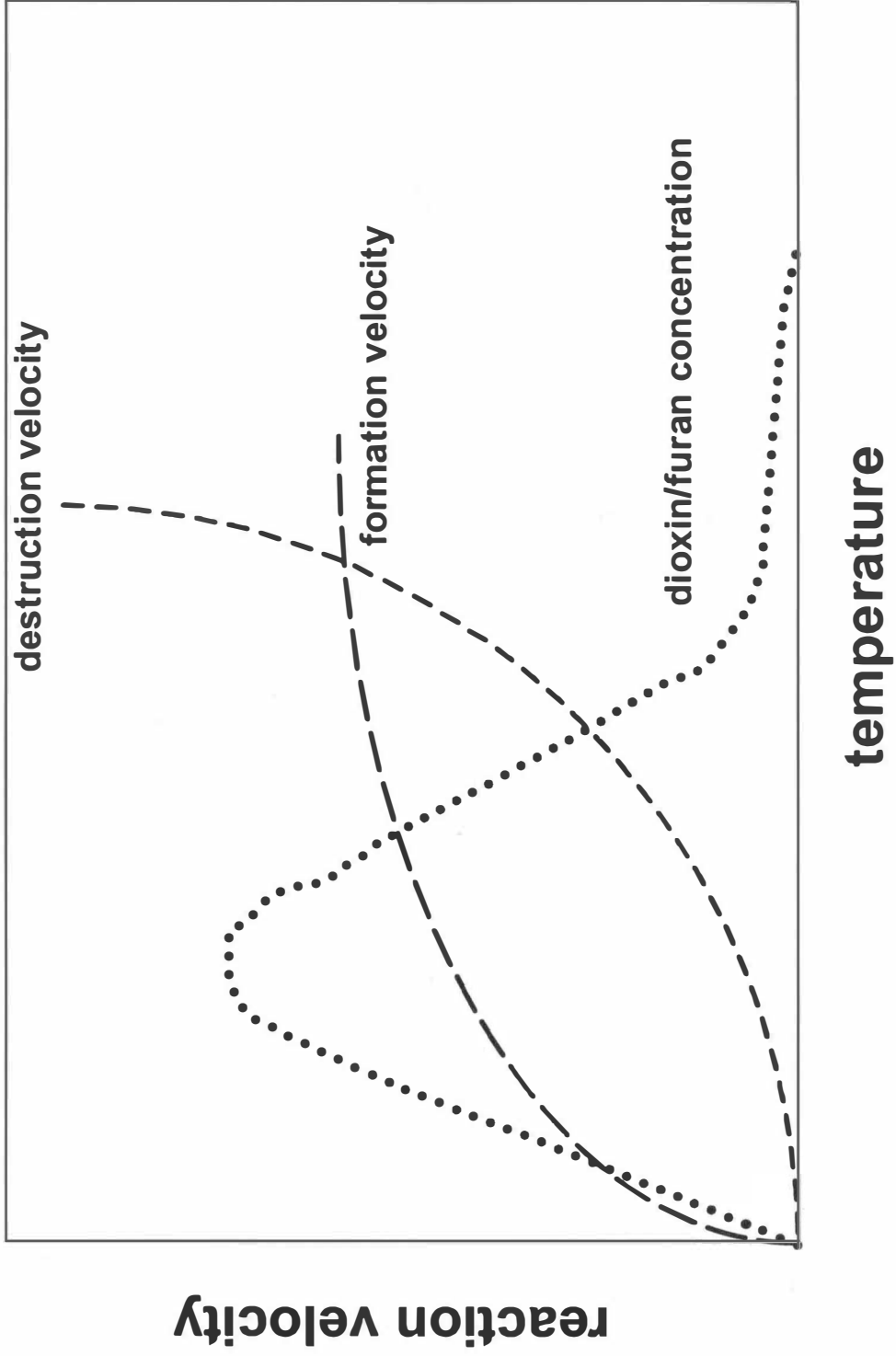**Figure 3: Possible Formation Routes for Dioxins/Furans**

1. Deacon reaction

$$2 \, HCl + 0{,}5 \, O_2 \longrightarrow Cl_2 + H_2O$$

2. chlorination reaction

$$Cl_2 + aromatics \longrightarrow chlorinated \ aromatics \ (dioxins/furans)$$

Figure 4: Deacon Reaction and Chlorination of Aromatics

Dualistic Principle of Dioxin Formation and Destruction

1. Deacon reaction

$$2\ HCl + 0{,}5\ O_2 \longrightarrow Cl_2 + H_2O$$

2. chlorination reaction

$$Cl_2 + \text{aromatics} \longrightarrow \text{chlorinated aromatics (dioxins/furans)}$$

3. interception reaction of chlorine

$$SO_2 + Cl_2 + H_2O \longrightarrow SO_3 + HCl$$

Deacon Reaction and Alternative Reaction Routes of Chlorine
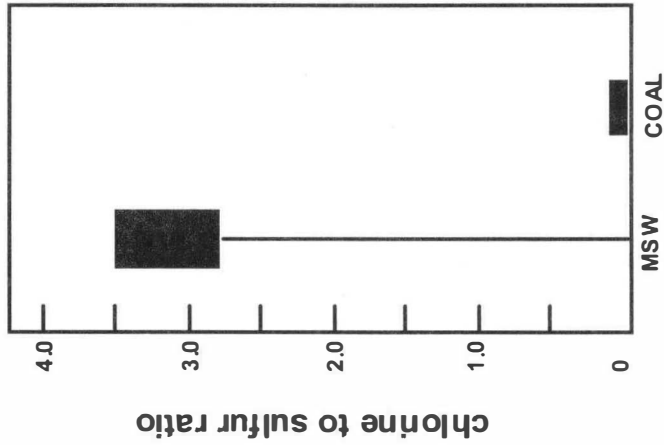
chlorine to sulfur ratio
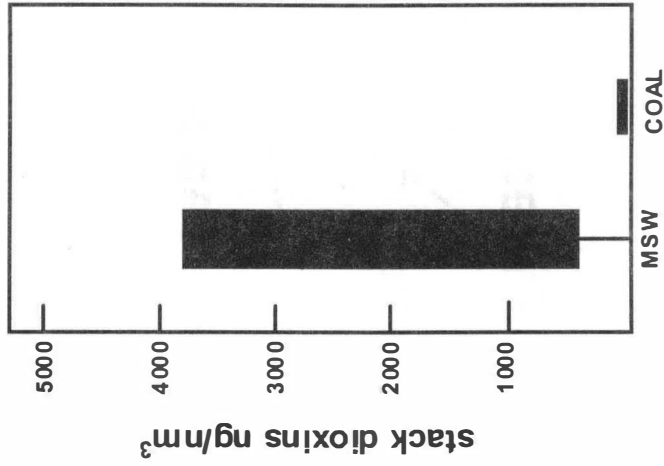
stack dioxin levels
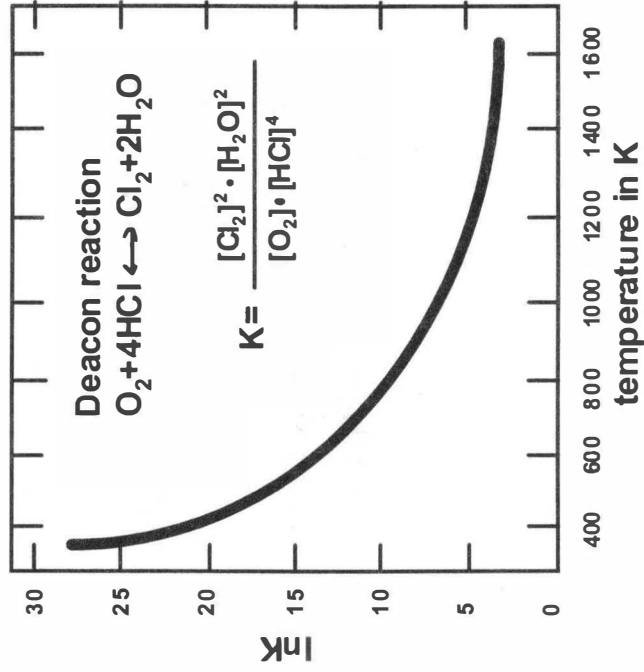
chlorine - HCl equilibrium

Deacon reaction
$O_2 + 4HCl \longleftrightarrow Cl_2 + 2H_2O$

$$K = \frac{[Cl_2]^2 \cdot [H_2O]^2}{[O_2] \cdot [HCl]^4}$$

gure 7: Cl/S Ratio, Dioxin Emission Levels, and Deacon Equilibrium Const
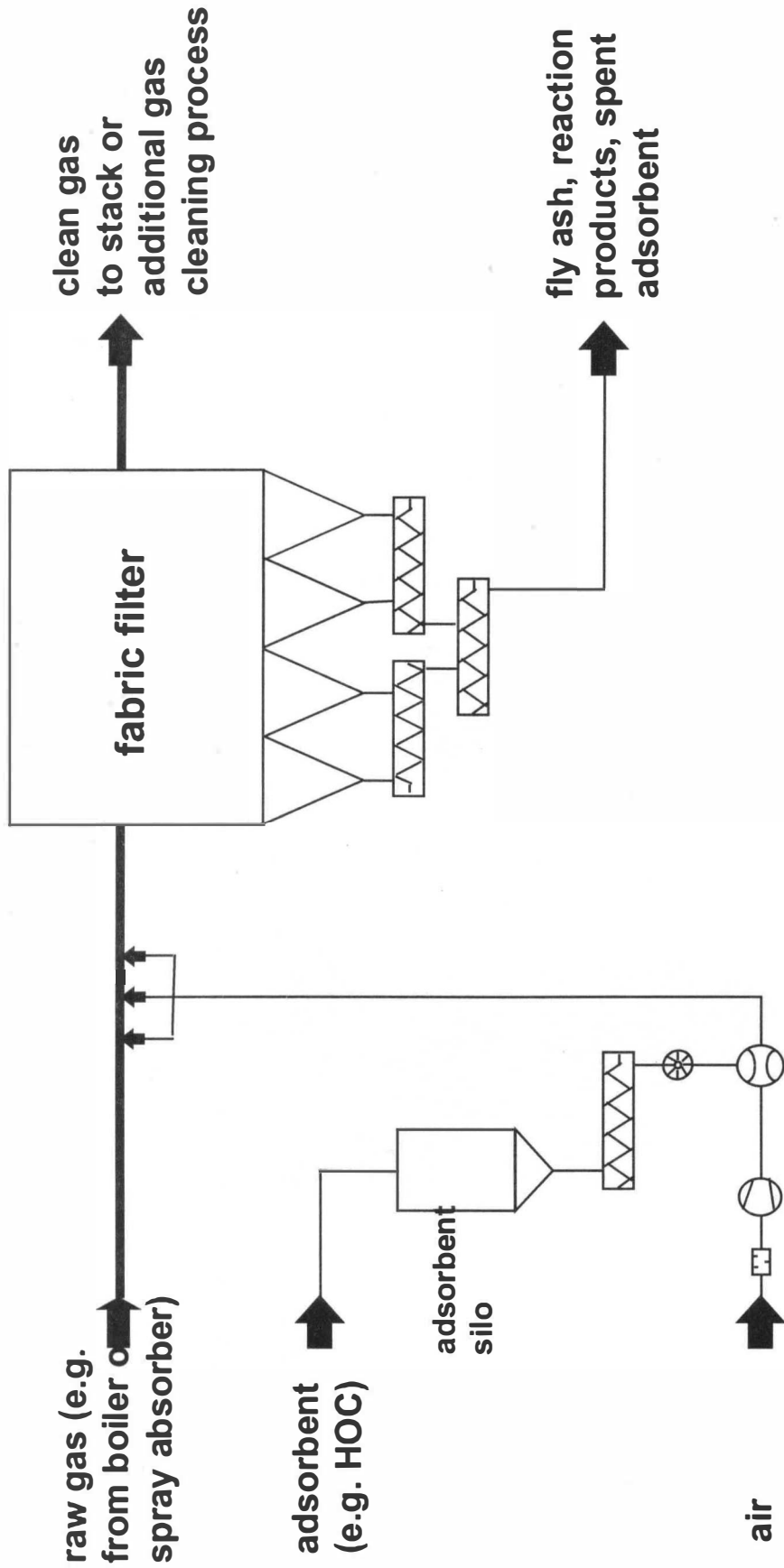
Figure 8: Principle of Adsorbent Injection Upstream a Particulate Filter

clean gas
to stack or
additional gas
cleaning process

fly ash, reaction
products, spent
adsorbent

fabric filter

raw gas (e.g.
from boiler o
spray absorber)

adsorbent
(e.g. HOC)

adsorbent
silo

air
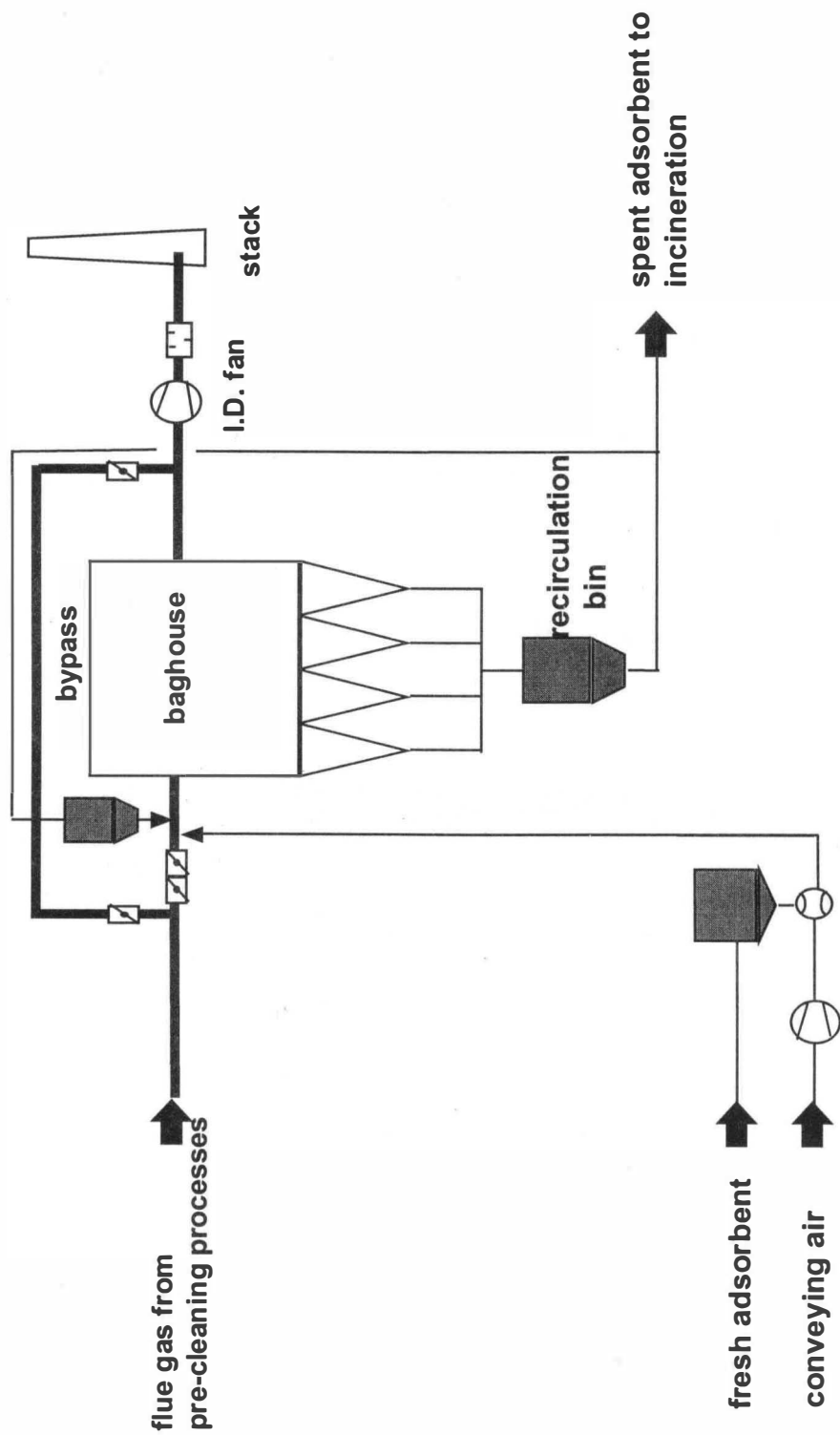
Figure 9: Process Principle of an Entrained Flow Adsorber
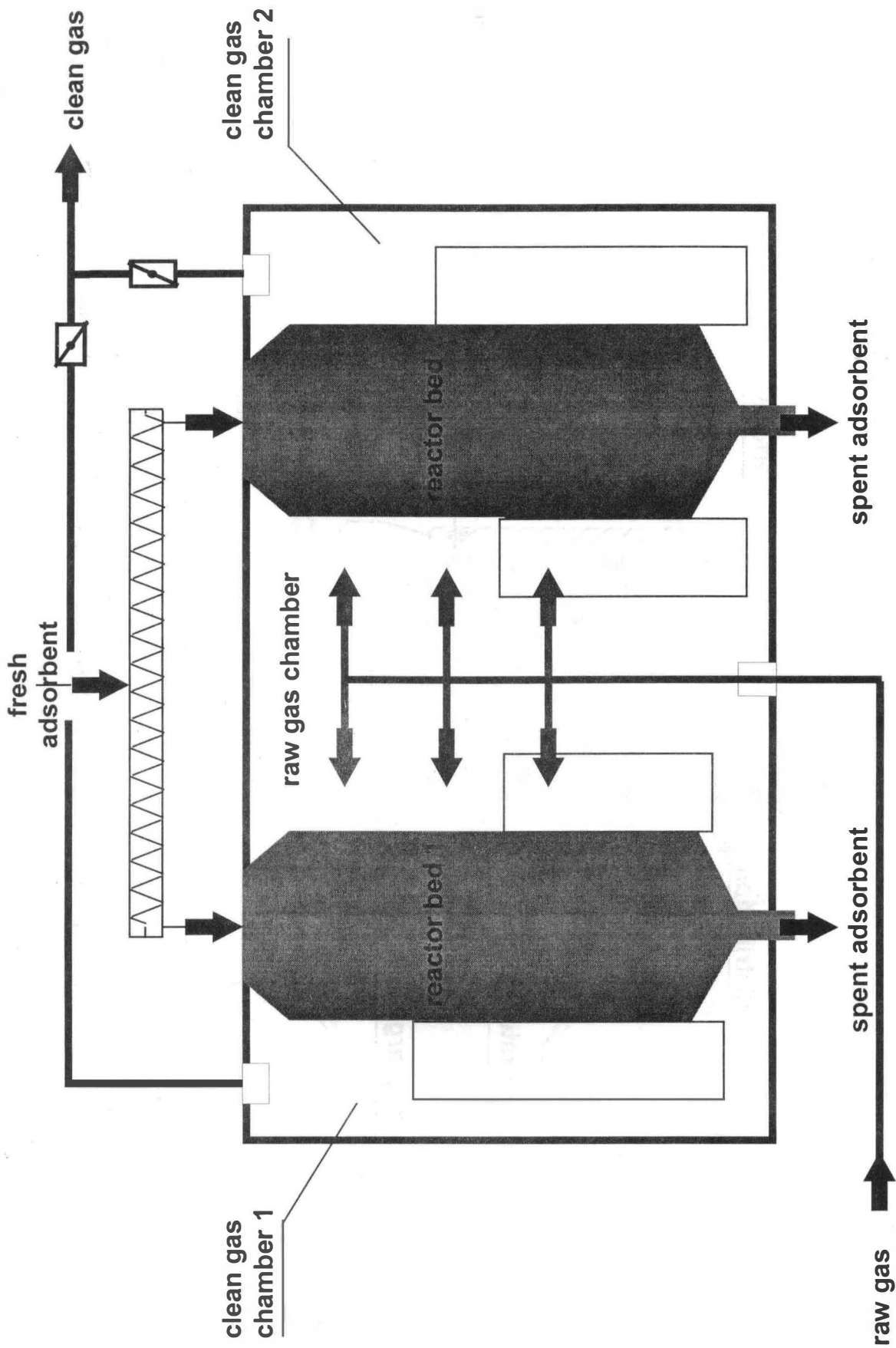
Figure 10: Principle Scheme of a Two-Bed Cross-Flow ACR
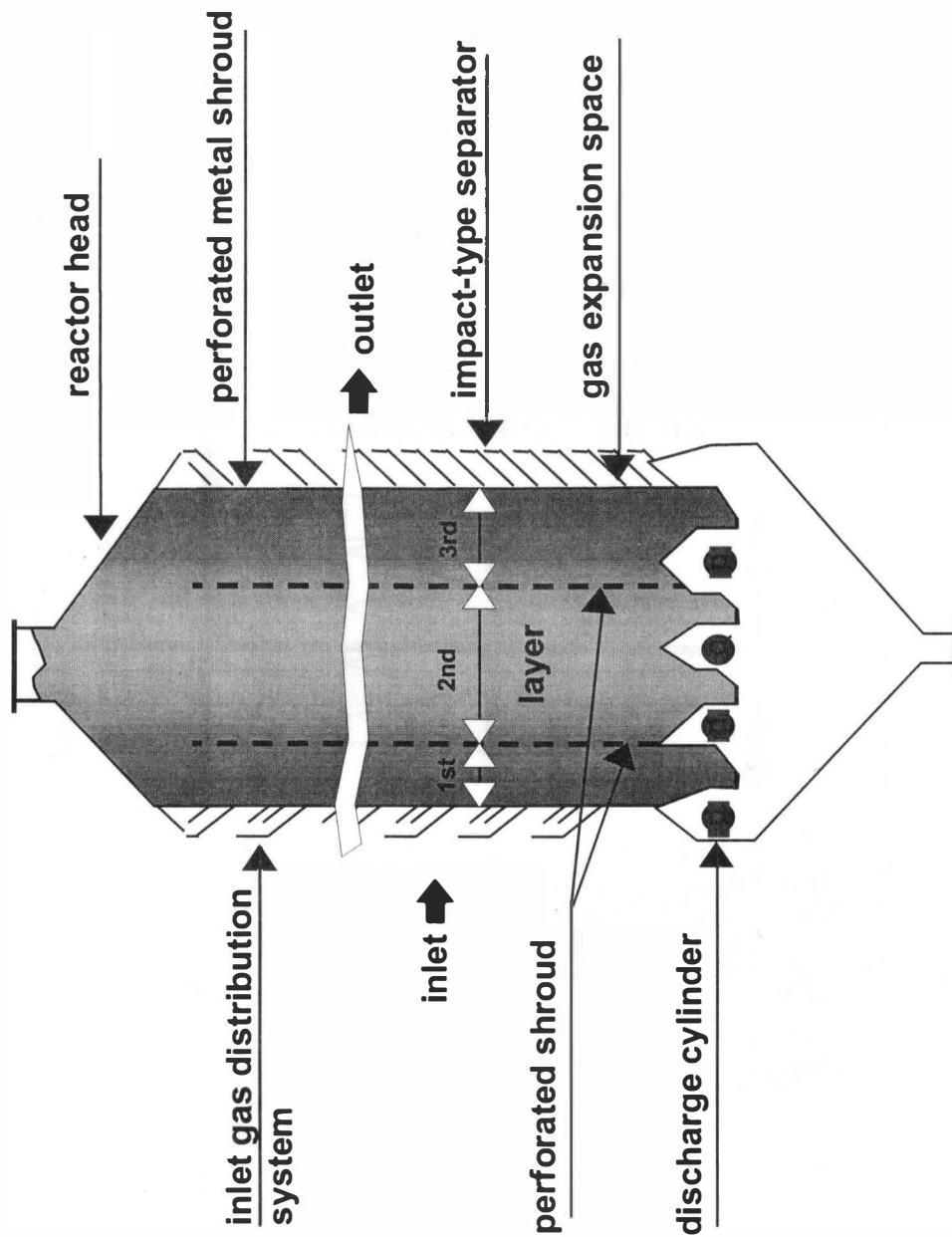
Figure 11: Adsorbent Bed Design Concept of a Cross-Flow ACR
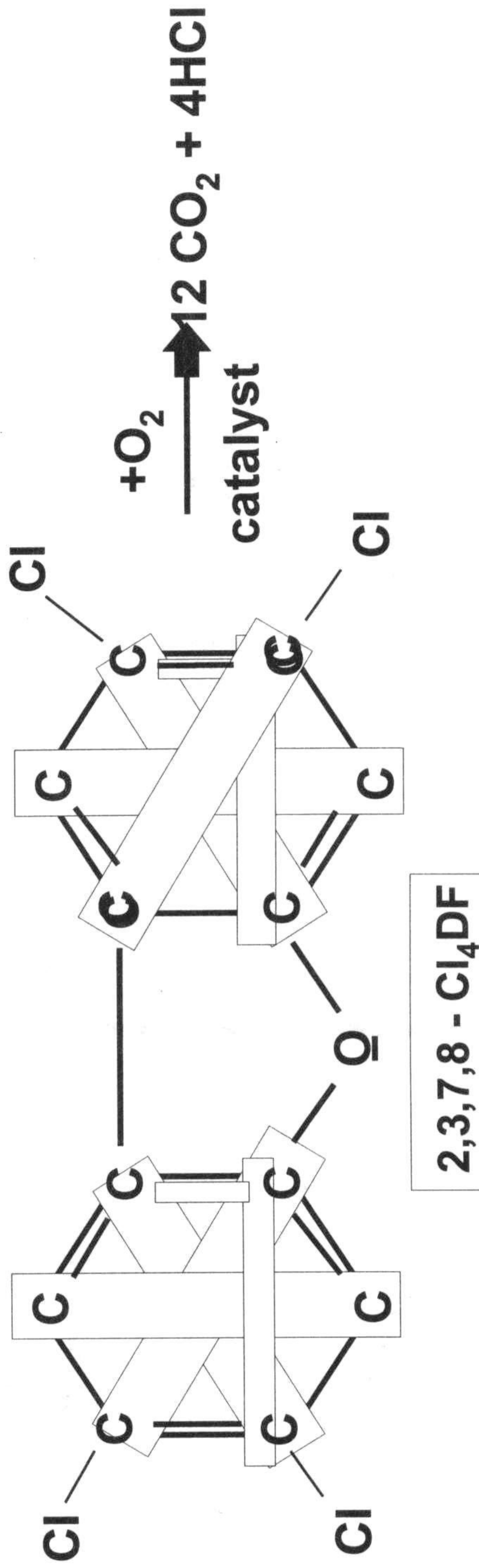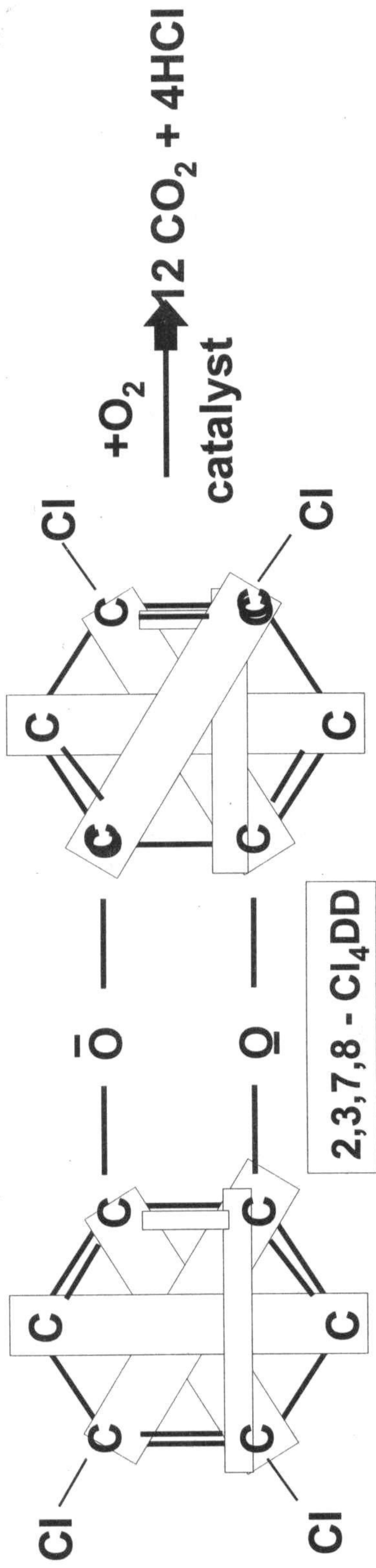
Figure 12: Principle Reaction Mechanisms of the Catalytic PCDD/PCDF Oxidation
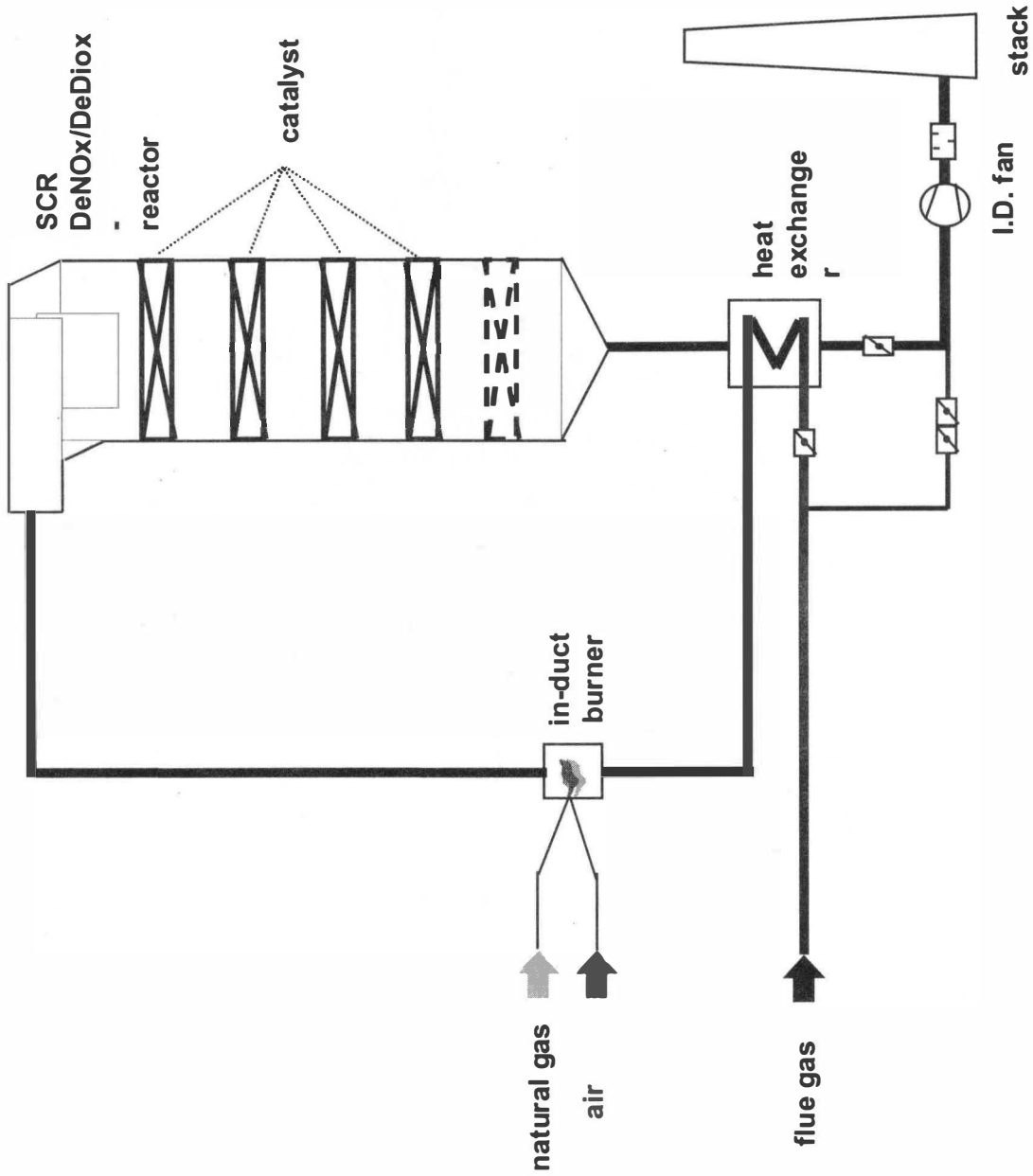
Figure 13: SCR System for Simultaneous NO$_x$ and PCDD/PCDF Removal
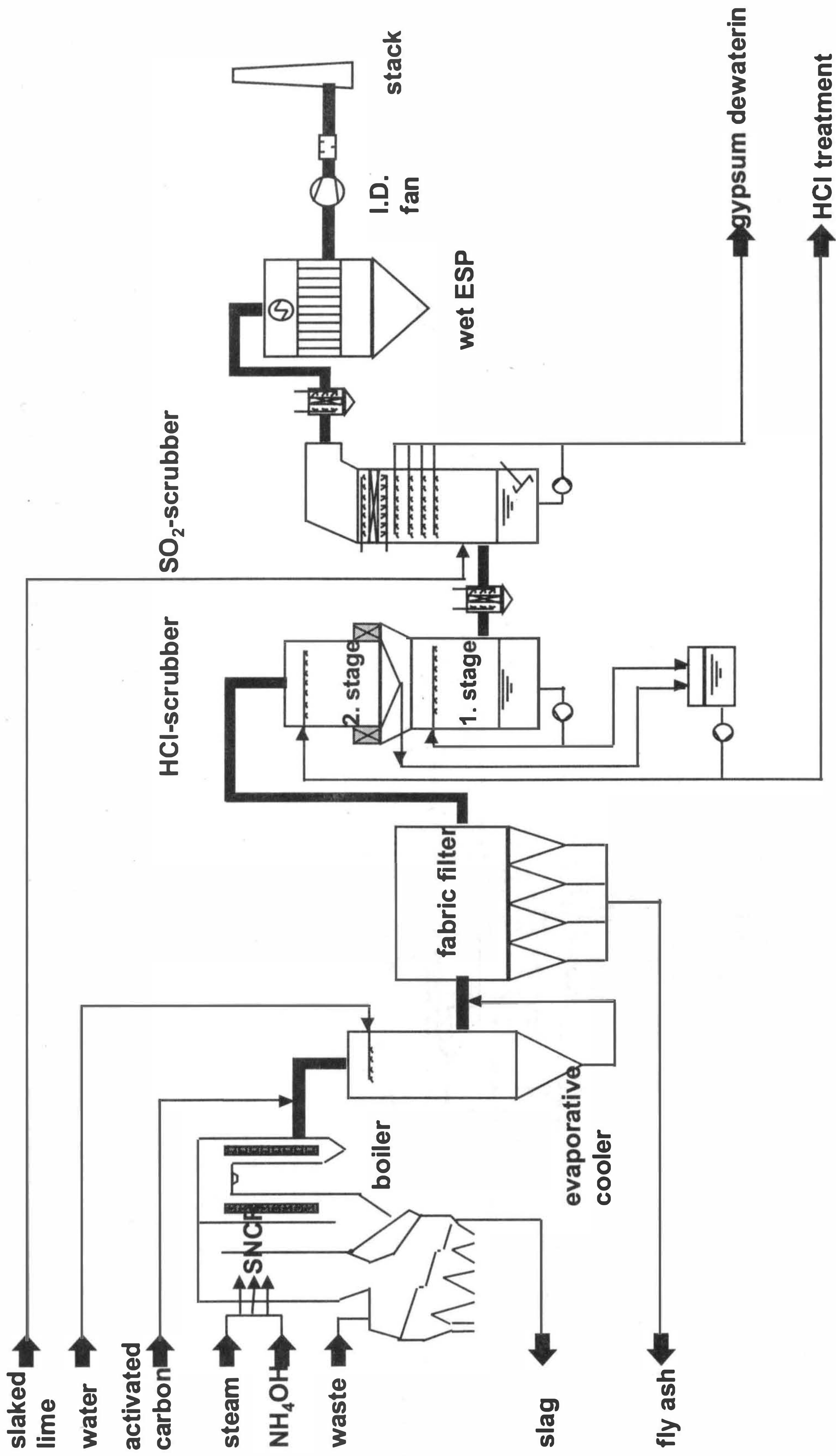
Figure 14: MVB Borsigstraße Process Flow Diagram

Labels in figure:

slaked lime
water
activated carbon
steam
NH₄OH
waste
slag
fly ash

SNCR
boiler
evaporative cooler
fabric filter
HCl-scrubber
2. stage
1. stage
SO₂-scrubber
wet ESP
I.D. fan
stack
gypsum dewaterin
HCl treatment

121
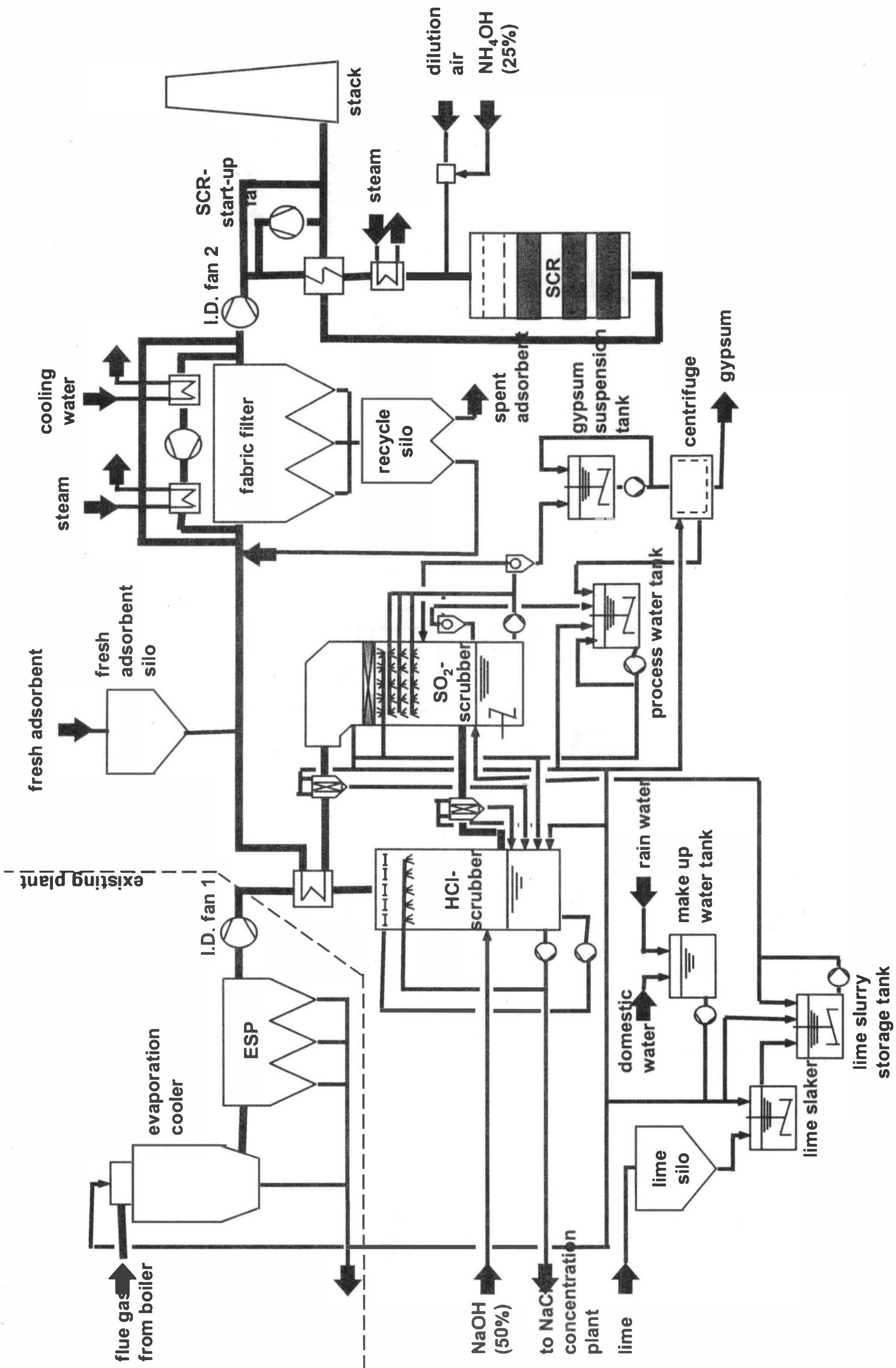
Figure 15: MHKW Leverkusen - Principle Process Flow Scheme of APC Retrofit
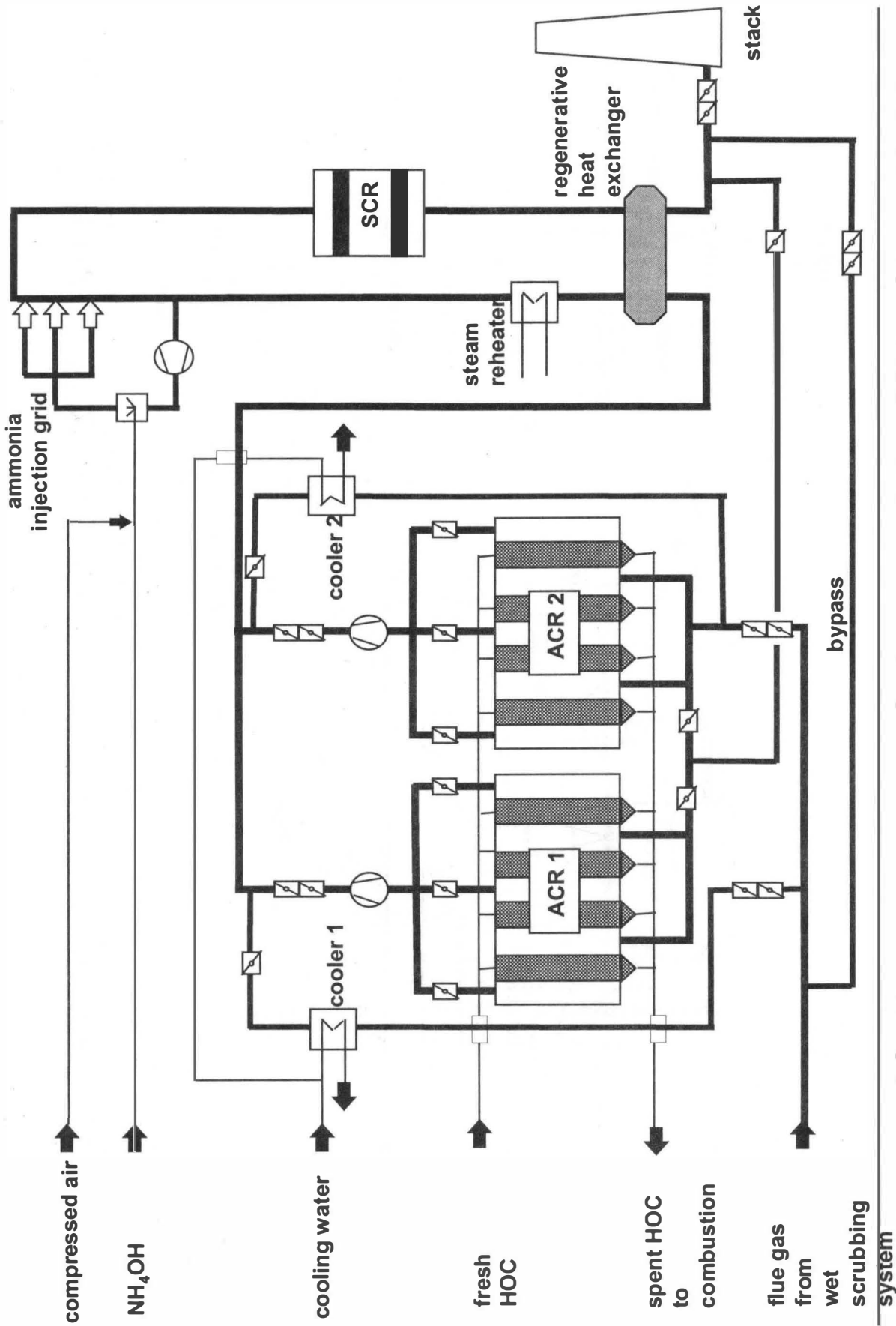
Figure 16: Process Flow Scheme of the MVA Stapelfeld Retrofit

Labels within figure:

- compressed air
- NH₄OH
- cooling water
- fresh HOC
- spent HOC to combustion
- flue gas from wet scrubbing system
- ammonia injection grid
- SCR
- regenerative heat exchanger
- stack
- steam reheater
- cooler 1
- cooler 2
- ACR 1
- ACR 2
- bypass
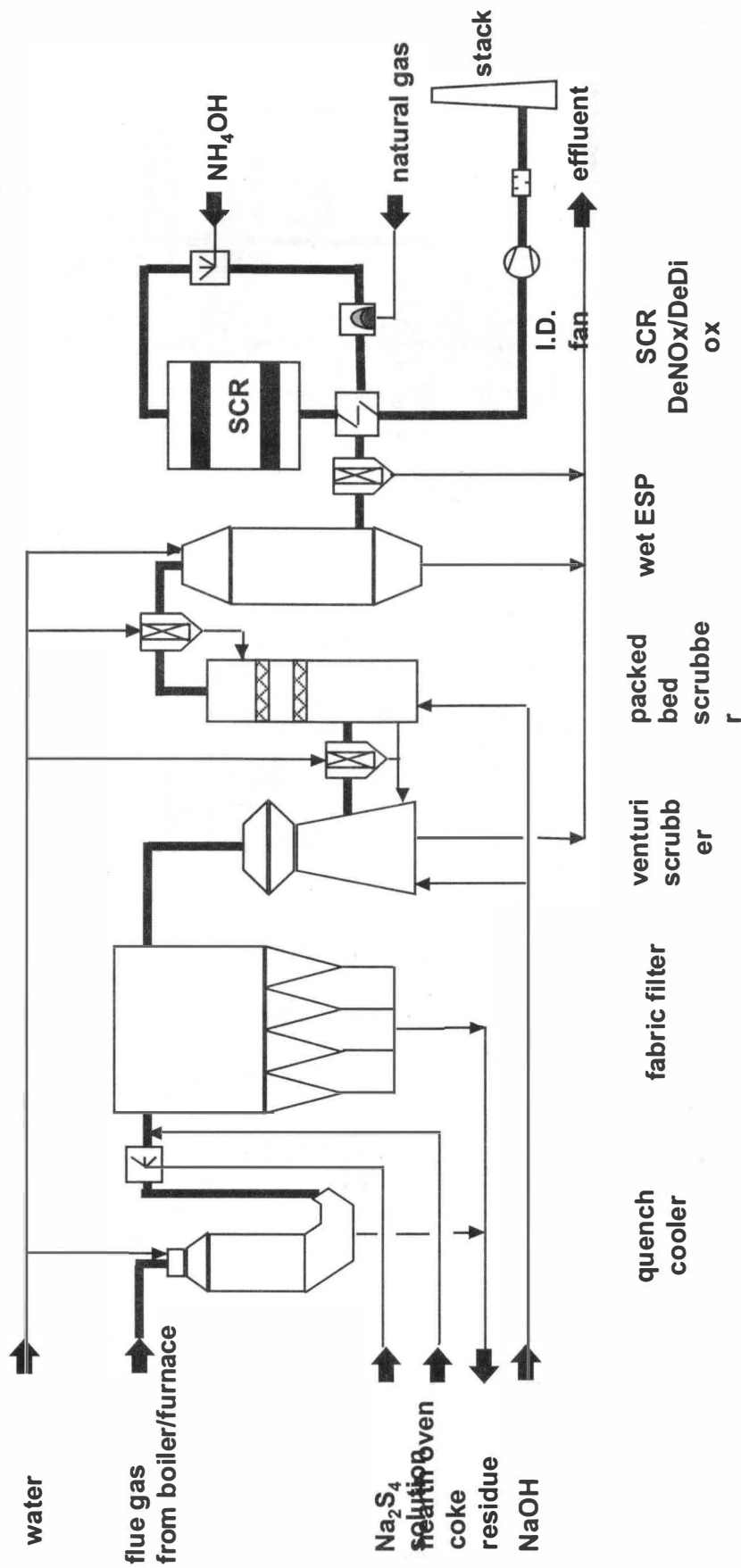
Figure 17: Process Flow Scheme of Flue Gas Cleaning Plant Gevudo
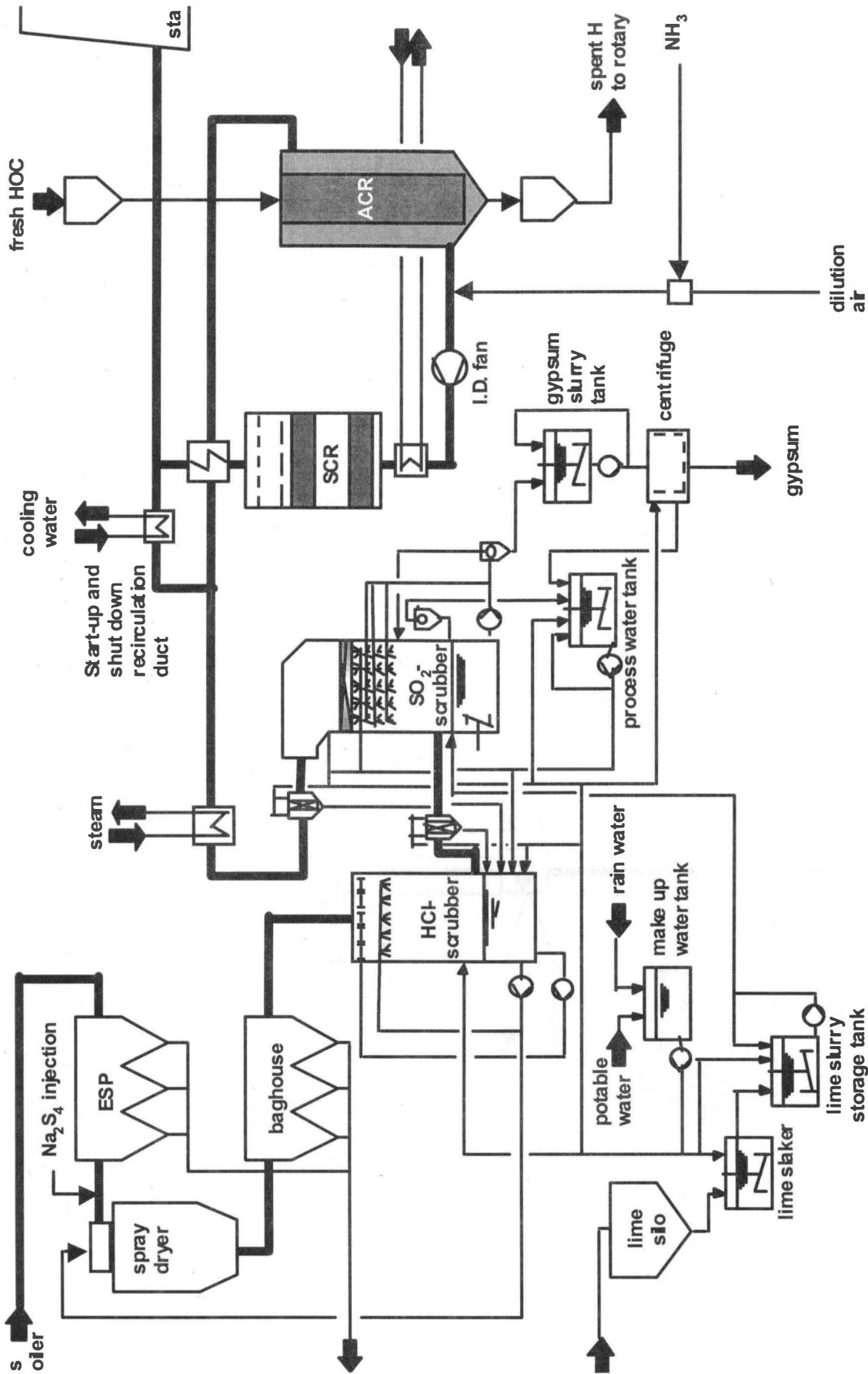
Figure 18: Process Flow Scheme of the RVA Böhlen APC System

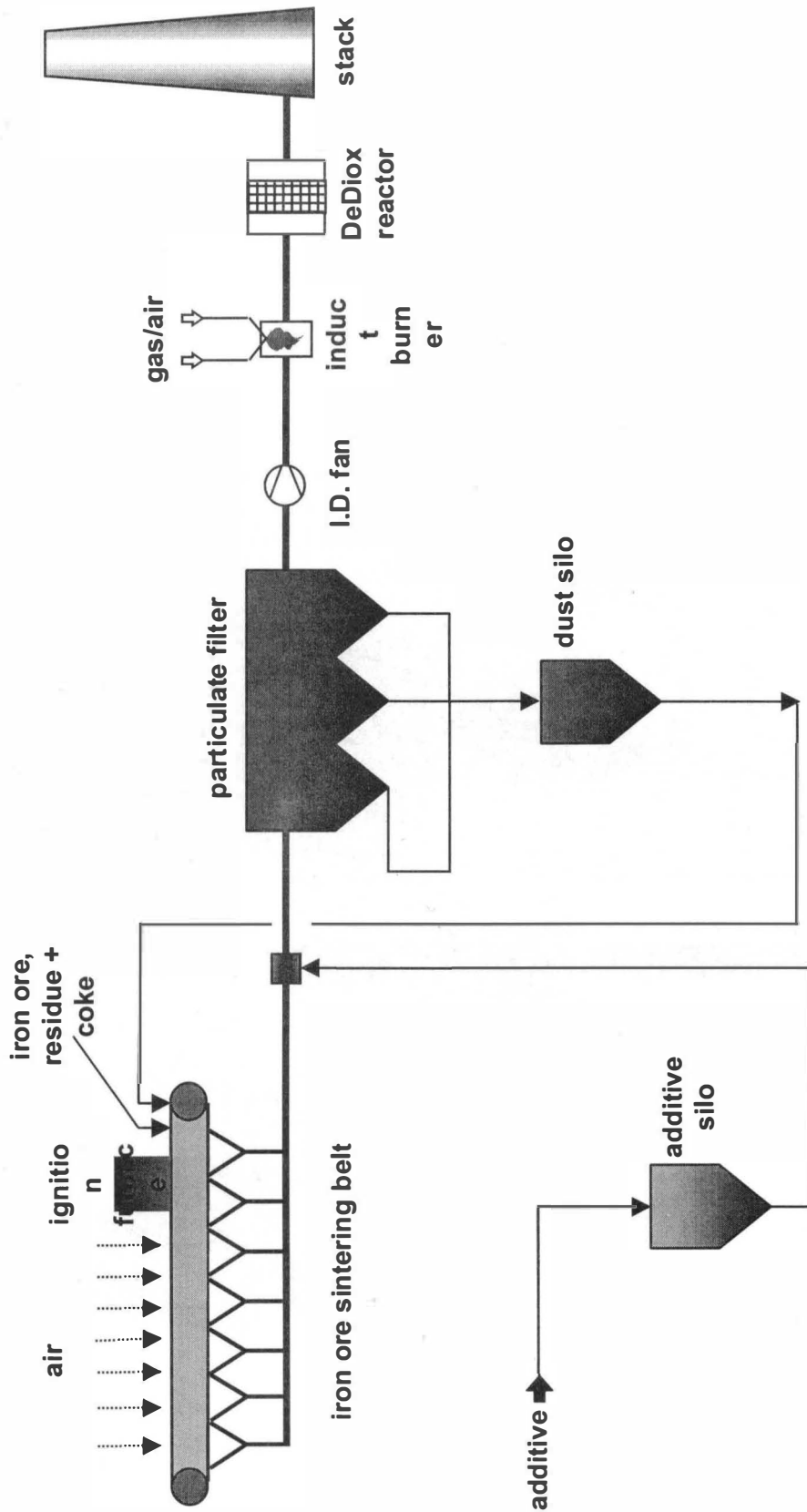125
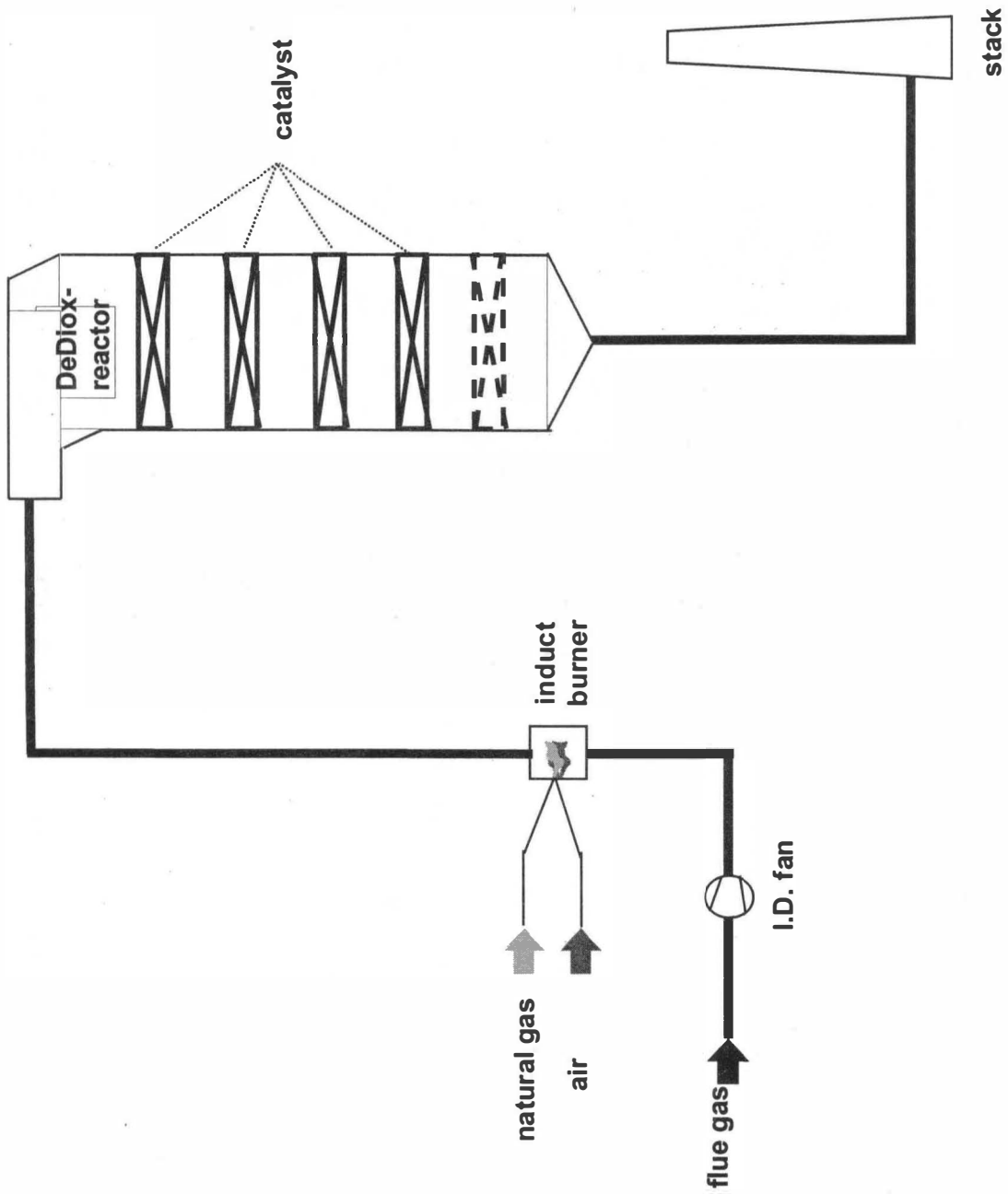
Figure 19: Thyssen SB2 DeDiox Catalyst Reactor

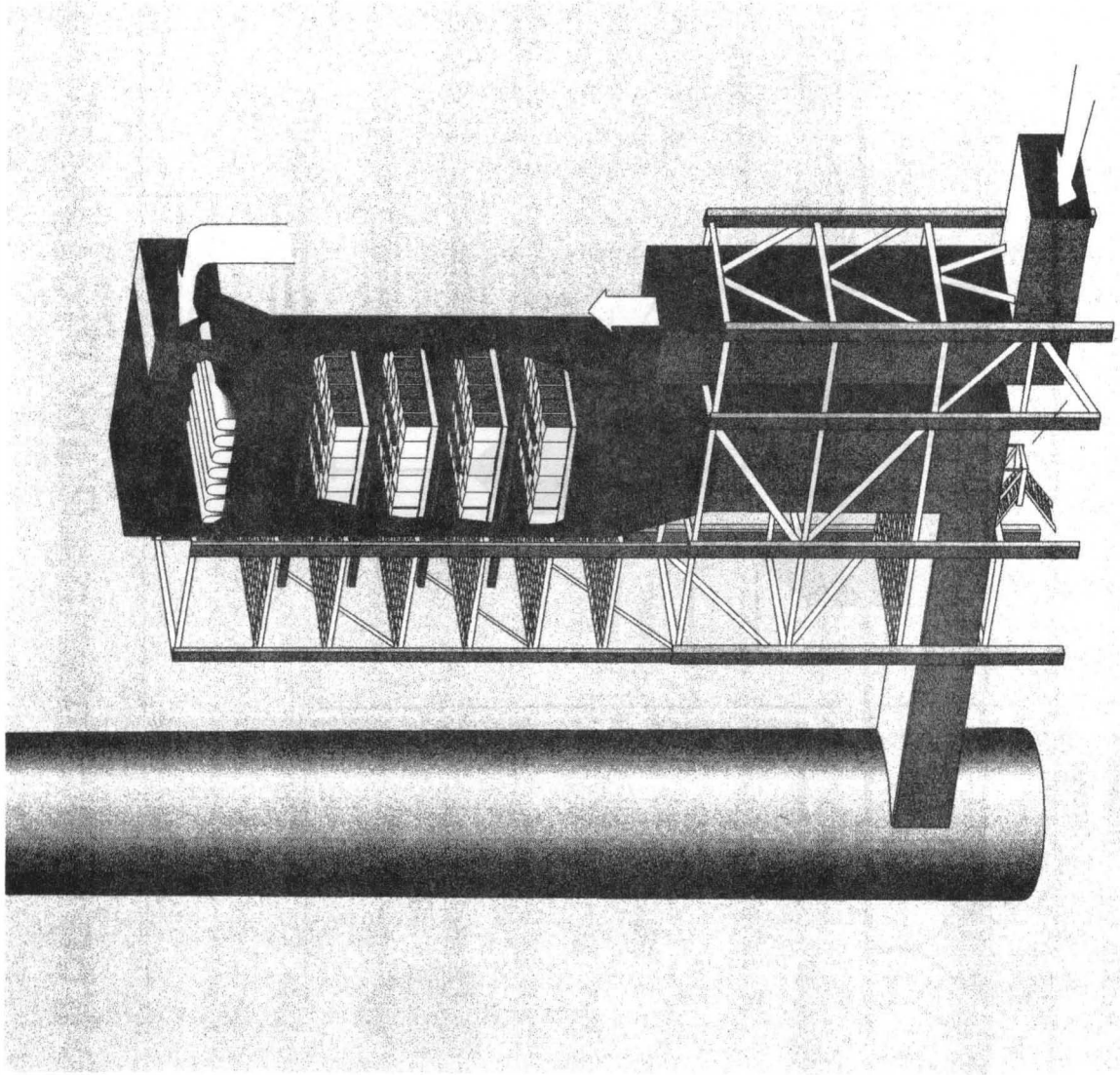**Figure 20: Iron Ore Sintering Plant Process Flow Scheme**

Labels within figure: stack; DeDiox reactor; gas/air; induct burner; I.D. fan; particulate filter; dust silo; iron ore, residue + coke; ignition; air; iron ore sintering belt; additive silo; additive
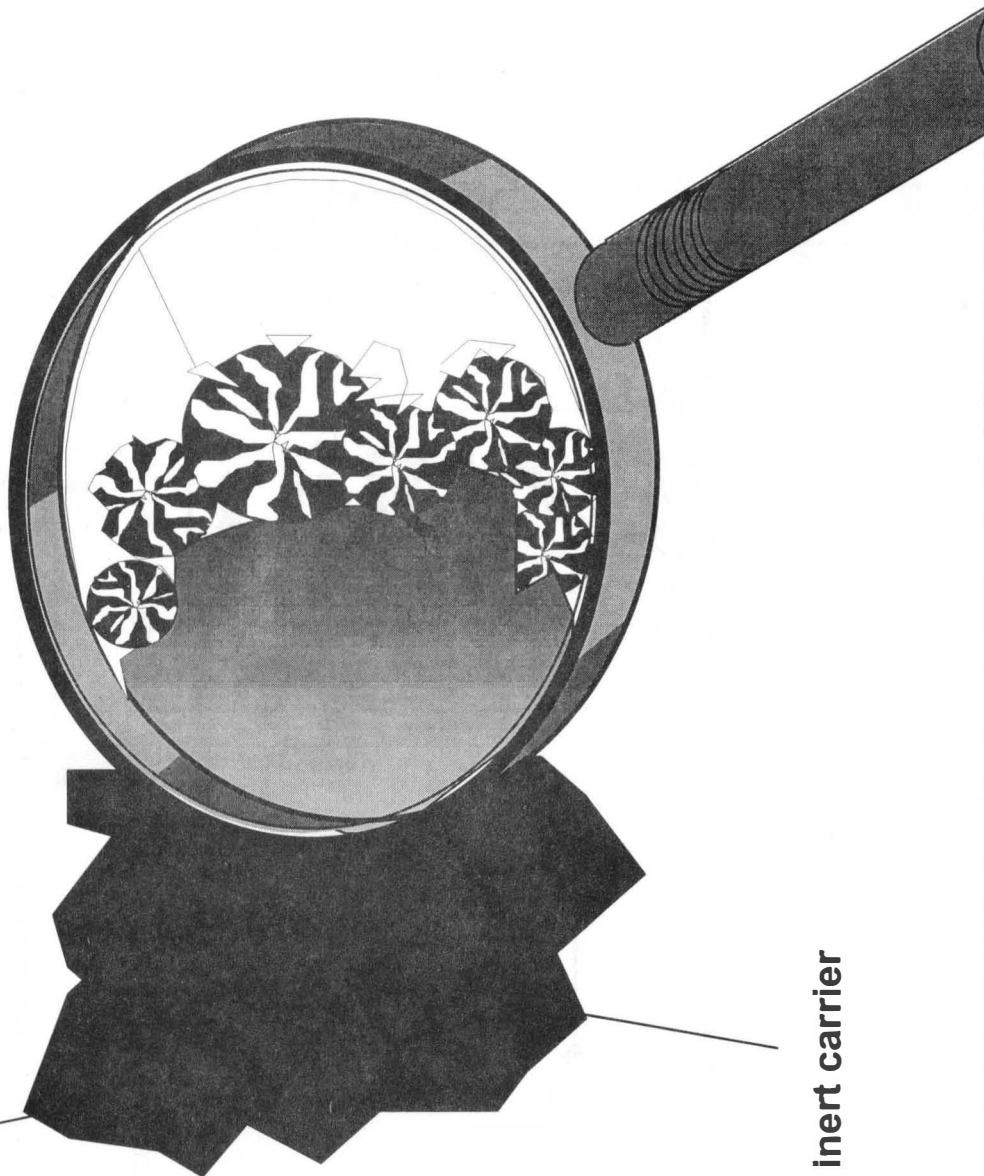
Figure 21: Typical Arrangement of a DeDiox Reactor for PCDD/PCDF Control

hearth oven coke dust or activated carbon dust
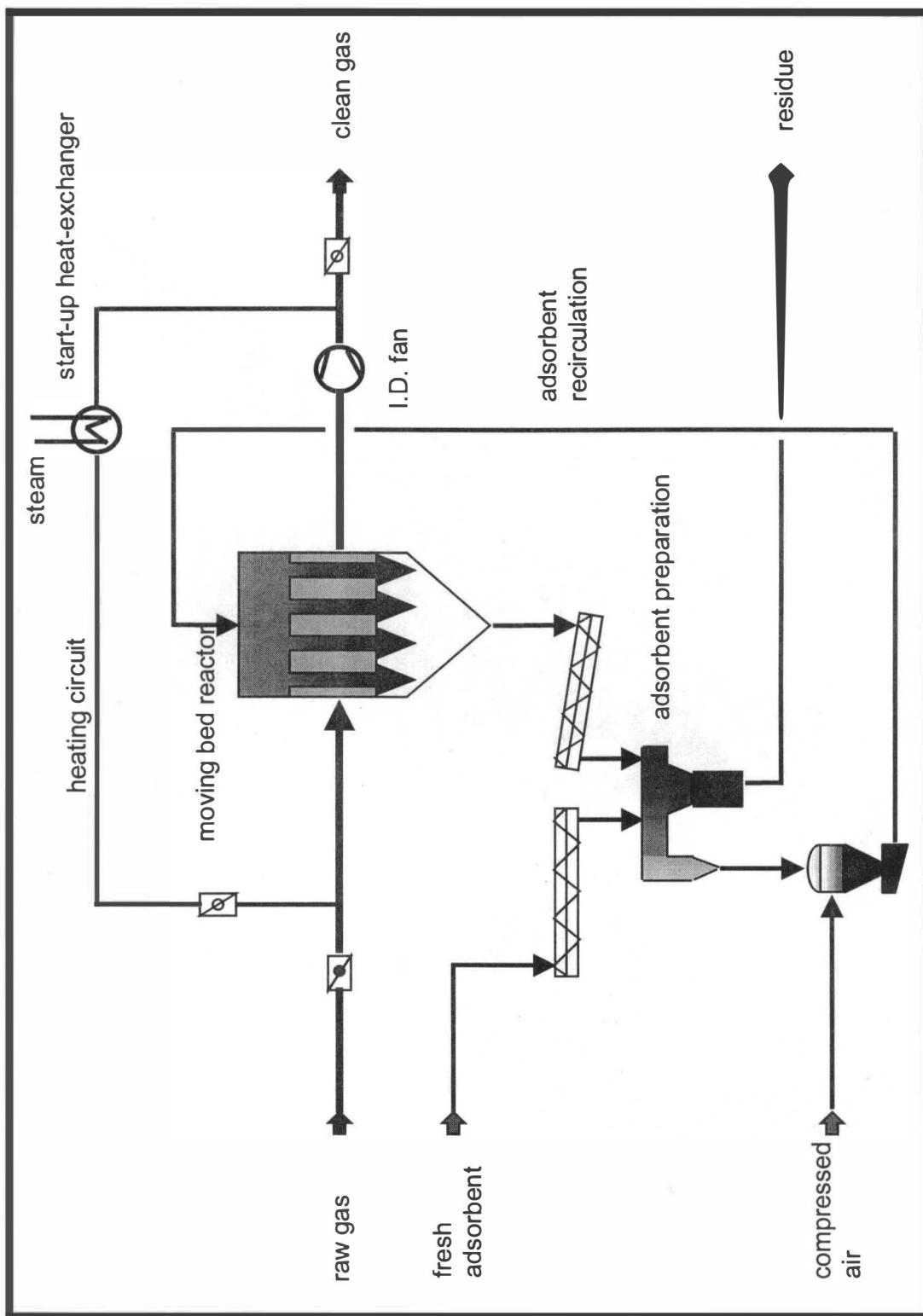
inert carrier

Figure 22: AKTINERT Adsorbent

Figure 23: The AKTINERT Process for PCDD/PCDF Control