"LIMITS AND CHANCES IN FLUE-GAS CLEANING
- INTERNATIONAL PERSPECTIVE"

DIETER O. REIMANN, DIRECTOR DR.-ING.
MHKW BAMBERG, FRG

General

Every thermal conversion of gaseous, liquid, and solid fuels or refuse-derived fuels creates emissions. The amount of these emissions depends on the pollutants in the fuel, on its homogeneity and its breakability down, as well as on the chemical, physical, and mechanical conditions during the combustion process. Combustion-dependent emissions like carbon monoxide or organic carbon can be kept at very low levels by using optimized combustion technique [1]. Other organic or inorganic pollutants, which are released during the combustion process, must be detained by appropriate flue-gas cleaning systems to the greatest possible extent.

These emissions, which are reduced by secondary measures, depend mainly on the content of the pollutants in the fuel. Solid fuels cause higher emission freights than gaseous or liquid fuels, due to their higher demand on oxygen in the combustion air.

TABLE 1
Comparison of Refuse Pollutants and Heavy Metals
from Various Plants and Range of Results [2]

Element	German UBA (FRG1990)	Mean values German Babcock (Horch 1987)	Mean values (Brunner & Mönch 1987)	EAWAG (CH 1982)	Mean values Bamberg (Reimann 1987)	Range of results g/Mg
Chlorine (Cl)	3000-8000	7000	6900	7000	7500	6900-8000
Fluorine (F)	10-50	200	140	-	100	100-200
Sulphur (S)	650-5000	5000	2700	5000	-	2700-5000
Zinc (Zn)	5000	1000	2000	1200-2000	1900	1000-2000
Cadmium (Cd)	2,0-50	10	8,7	3,0-15	10	3,0-15
Lead (Pb)	-	800	430	500-1200	450	430-1200
Copper (Cu)	-	400	200	240-600	500	200-600
Chromium (Cr)	-	-	-	-	250	/250/
Mercury (Hg)	0,3-14	4	2	5	4	2,0-5,0
Nickel (Ni)	-	-	-	-	80	/80/
Arsenic (As)	-	-	-	-	4	/4/

All data in g/Mg refuse

Current Situation

The thermal treatment of household waste, household-like trade refuse, sewage sludge, and hazardous waste in Germany currently amounts to 10.5 million metric tons per year tantamount to 30% of these kinds of refuse. In 1992, about 9.5 million tons of refuse-derived fuel have been thermally converted in the existing 49 municipal waste incinerators and in one pyrolysis plant, 0.7 million tons in 27 hazardous waste incinerators, and 0.3 million tons sewage sludge with 30% dry solid (DS) content in 15 sewage sludge incinerators [3].

The number of landfills is dropping drastically because of consumption of space. New landfills can hardly be opened because people do not accept them [3], and the new "TA-Siedlungsabfall" (Technical Guideline for Municipal Waste) will exclude the deposition of untreated waste to a large degree [4]. Therefore, after avoidance of waste and recycling [5], the thermal treatment of the remaining waste will strongly gain importance. The existing incineration capacity will be insufficient and must be increased by 7-10 million metric tons per year, according to cautious estimates and in view of the additional annual 10-15 million tons from the new German states [6].

In the public opinion there exist reservations and disapproval not only against any kind of waste treatment facilities, particularly against thermal waste treatment, but also against combustion plants for solid primary fuels like brown coal.

The opposition is based mainly on the potential release of gaseous substances or microparticals in untreated raw gas. These pollutants are partly highly toxic organic compounds which are released during the thermal treatment or whose formation is just suspected, respectively. Among these substances are chlorinated and brominated dioxins and furanes as organic prime pollutant substance as well as heavy metals like mercury, thallium, and cadmium which also show highly toxic effects.

Therefore, the ultimate goal of advanced flue-gas cleaning technologies can be seen as to realize ecologically necessary minimizations of emissions in the best possible way which is oriented towards the toxicology of the released pollutants. The translation of this ecological challenge has to be guided by the technical feasibility and must stay within the bounds of the economically justifiable.

Assessment and evaluation of forward-looking flue-gas cleaning technologies is not only limited to the process technology, but must also consider the type of generated residues and used additives. So far as technologically possible for the chemical absorption of essential pollutants, precedence should be given to naturally occurring compounds like limestone in contrast to artificially generated chemicals like caustic soda and ammonia.

Mercury, which evaporates completely during combustion and enters the gas phase, can hardly be removed by conventional treatment and therefore must be adsorbed on particulates or activated carbon or coke, respectively. Better results are obtained by natural condensation with scrubber liquids and subsequent precipitation with environmentally neutral precipitating agents like trimercapto-s-triazine (TMT 15) [7].

Mercury can be considered as the prime agent amougst heavy metals. If its concentration in the flue-gas can be lowered to less than the threshold limit of 0.05 mg/m^3 flue-gas, as a rule all other heavy metal limits are usually met.

Emission Limits

In order to improve the acceptance of thermal combustion plants for solid fuels and refuse, permitted emission limits are continuously suited to the state, often even to an anticipated state of the art.

emission	dimension	max. daily meanvalues		max. half-hour meanvalues		separate measurement		anticipated state of the art
		coal 13. BlmSchV >50 MW	refuse 17. BlmSchV	coal 13. BlmSchV >50 MW	refuse 17. BlmSchV	coal 13. BlmSchV >50 MW	refuse 17. BlmSchV	refuse daily value repect. sep. measur.
O2-reference	Vol.-%	7* (6,5)**	11° (3)°°	7 (6,5)	11 (3)	7 (6,5)	11 (3)	11 (3)
dust	mg/m3	50	10	100	30			<3
CO	mg/m3	250	50	500	100			<20
SO2	mg/m3	2000	50	4000	200			<20
NOx	mg/m3	800 * / 1800 ***	200	1600 * / 3600 ***	400			<70
HCl	mg/m3	200 (<300 MW)	10	400	30			<3
HF	mg/m3	30 (<300 MW)	1	60 (<300 MW)	4			<0,3
Org. C	mg/m3	-	10	-	20			<4
Hg	mg/m3					-	0,05	<0,02
Cd+Tl	mg/m3					-	0,05	<0,01
heavy metals	mg/m3					-	0,5	<0,1
dioxin-TE	ng/m3					-	0,1	<0,1

* grate and fluidized bed firing   ° grate firing
** pulverized coal firing with dry ash removal   °° pyrolyses
*** pulverized coal firing with liquid ash removal
all statements refer to standard conditions (273 K, 1013 mbar, corresponding O2 reference)
formula for oxygen reference:

Em: measured emission
EB: emission, referred to the oxygen reference
Om: measured oxygen content
OB: corresponding O2 reference

EB = ((21 - OB) / (21-Om)) . Em   mit

Beside the emission limits of the Decree for Large Combustion Plants with capacities over 50 Megawatts [8] which dates back to 1983, table 2 shows the permissible emission limits for the combustion of waste according to the latest update of the German Federal Air Quality Control Act [9]. The maximum allowable daily mean values as well as the average half-hour values are given. These values have to be established through continuous monitoring.

Emission limits for the decisive heavy metals and the dioxin-TE value are stated as one-time readings.

Some emission limits, which have already been established for the combustion of waste, do not exist for the combustion of coal in plants greater than 50 Megawatts. This includes heavy metals, organic carbon, and the dioxin-TE value, although some of these compounds are among the emitted substances from these plants. As a rule, all coal-fired power plants in Germany, which are equipped with up-to-date wet desulfurization systems, are also set up for the removal of mercury. In order to be actually able to lower the mercury concentration from an initial level of 0.2-0.25 mg/l [10] to the required level of 0.05 mg/l wastewater (sometimes 0.01), TMT 15 (trimercapto-s-triazine) is used [11].

The last column of table 2 shows the expected, technically feasible minimum emission or threshold limits, according to the anticipated state of the art.

The figures in table 2 cannot be compared directly, because they are based on different oxygen levels. In addition, the specific combustion air demand for the treatment of refuse-derived fuel is 1.5-2 times higher than the demand for the combustion of coal.

At the moment, this results in a 3-10 times higher specific emission rate from coal-fired plants compared with the incineration of refuse.

On this examination, the annual total fuel quantity, which is added during combustion or incineration, has to be taken into consideration. This amounts to 220-270 million metric tons per year with hard coal and brown coal and is about 20-25 times higher than for the treatment of refuse which is 10.5 million tons per year.

TABLE 3
Comparison of Permissible Emissions According to Some International Regulations for Waste-to-Energy Plants [12]

	EEC		EEC	GERMANY		NETHERLANDS	AUSTRIA	SWITZERLAND
Kind of regulation	Directive Proposal		Directives 89/369 89/429	17. Decree to BlmSchG		Directive "Incineration"	Decree LRV.K	Decree LRV
Kind of refuse	Hazardous waste		Mun. waste	All waste incinerations		Haz./Mun. waste	Haz./Mun. waste (Incineration with boiler)	Haz./Mun. waste
Kind of plants	New and existing Proposal 92		New and existing 1. Dec. 1990	New and existing 1. Dec. 1990		New and existing 15. Aug 1989	New 13. Januray 1989	New and existing 1. Feb 1992
Realisation up to			1996	(1994-1996)		(1993-1997)		(1997-2002)
N° Pollutant								
1 Total dust	5	10	30	10	30	5	15	10
2 TOC	5	10	20	10	20	10	50	20
3 HCl	5	10	50	10	60	10	10	20
4 HF	1	2	2	1	4	1	0,7	2
5 SO2	25	50	300	50	200	40	50	50
6 NOx				200	400	70	100	80
7 Mercury		0,05	0,2		0,05	0,05	0,05 (0,1)	0,1
8 Cadmium	(Incl.Tl)	0,05	0,2	(Incl.Tl)	0,05	0,05	0,05	0,1
9 Other heavy	Sum	0,5	Pb+Cr+Cu+Mn 5	Sum	0,5	Sum 1	Pb + Zn + Cr 2	Pb + Zn 1
			NI + As 2				As + Co + NI 0,5	
10 PCDD/F dioxin-Te ng/m3	0,1 (target)			0,1		0,1	0,1	
Cont. measure. #1-6	24 h	0,5 h	1 h	24 h	0,5 h	1 h	0,5 h	1 h
Measurement #7-9		0,5 - 4 h	(with adaptation)		0,5-2 h	(with exceptions)	generally	(with adaptations)
Duration #10			6-16 h		6-16 h		3-10 h	-

Probably in the future, the emission limits for coal-fired power plants and those for thermal refuse treatment will be at the same low level, simply because of environmental reasons and the principle of equality.

Some of the emissions, e.g. those of heavy metals and the dioxin-TE value, can probably be kept without any additional flue-gas cleaning, as long as monofuels are combusted. This doesn't apply to mercury, which can be detected in critical concentrations in the scrubber water of coal fired power plants, coming out of the raw gas [10].

The chemical and physical processes during the combustion of coal or the incineration of refuse are very similar, and the generated emissions mainly depend on the content of the fuel. Therefore, similar techniques can be used for flue-gas cleaning. However, the combustion of high sulfur coal (sulfur dioxide emissions) or coal dust burning with liquid slag removal with its high NO_x-levels can make it difficult to stay within the emission limits.

FIGURE 1

Schematic of Refuse Incineration MWC Bamberg (FRG) with Specific Loads per Mg of Refuse

cleaned gas

0,9 m3 H2O

0,3 m3 sewage plant

reheating

NaOH

sewage sludge 15 kg sludge (3 kg DS)

gypsum sludge 15 kg sludge (3 kg DS)

0,9 m3 H2O

H2O-stage 1   NaOH-stage 2

wet scrubber

scrubber wastewater

lime

TMT 15

hydroxide sludge 12 kg sludge(1 kg DS)

Bamberg Model

35,2 kg/24 kg DS wet mixed residues special landfill

saturated steam 26 bar 226°C

ESP

raw gas with 0,3 m3 H2O

dust 20 kg DS

3,7 Mg steam/Mg refuse

boiler ash 3-4,8 kg

bottom ash 296 kg

0,35 m3 H2O

340 kg

25 kg 50%Fe

scrap iron

building material rubble 295 kg 0-64 mm

boiler water

boiler

combustion temperature 850-1.100°C

mixed refuse 1.000 kg

incinerator combustion air 4-5.000 m3

n=1,6 - 2,0

0,30 m3 H2O

wet scrubber

20 kg >64 mm

building material

partial burned

All data g/Mg refuse; Mg = metric ton; DS = dry solids

sewage sludge 1,3 m3 (3%DS)

130 kg (30%DS) or 39 kg DS/Mg refuse

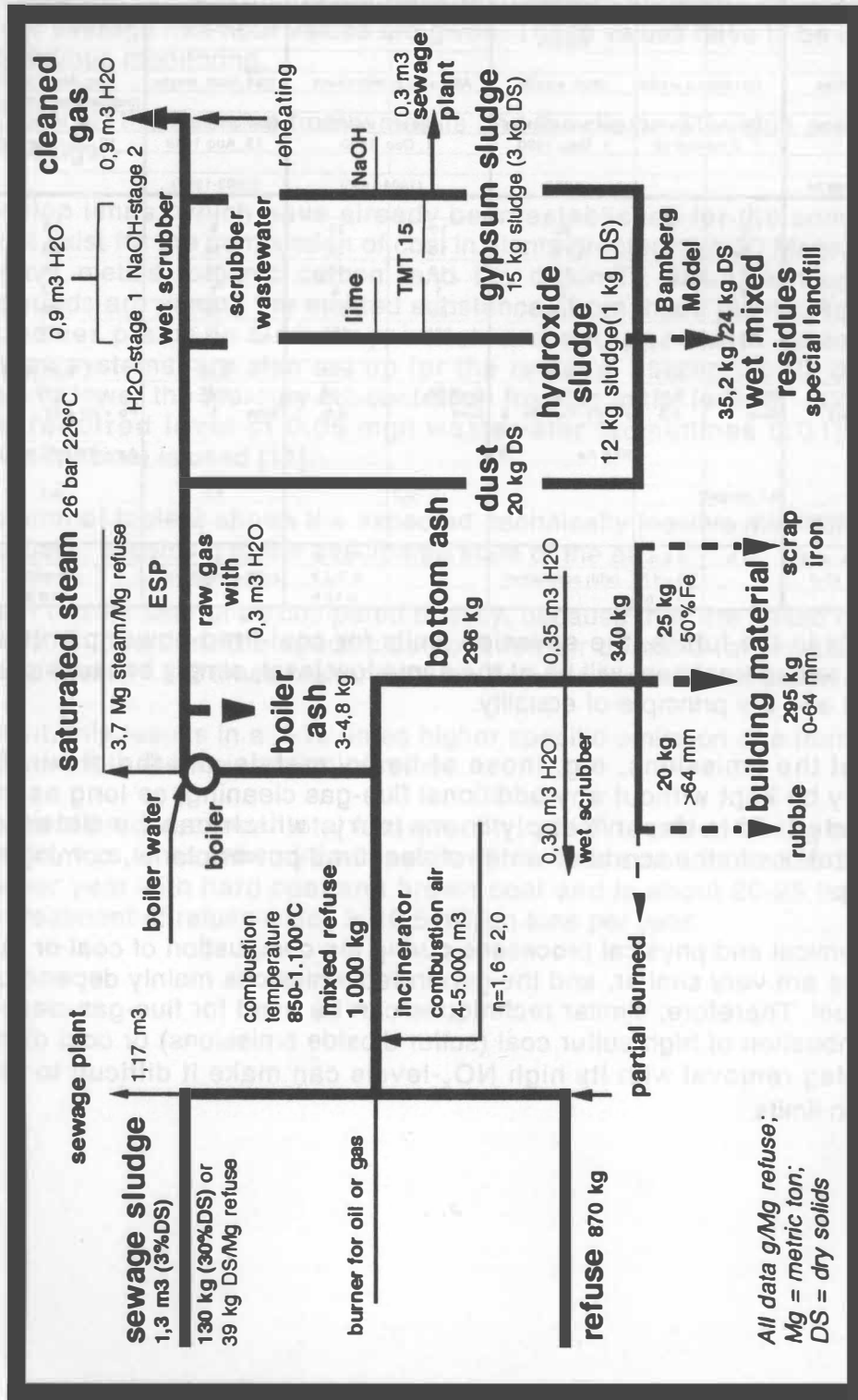1,17 m3

sewage plant

burner for oil or gas

refuse 870 kg

Figure 1 shows an up-to-date thermal refuse treatment including the mass-balances.

FIGURE 2
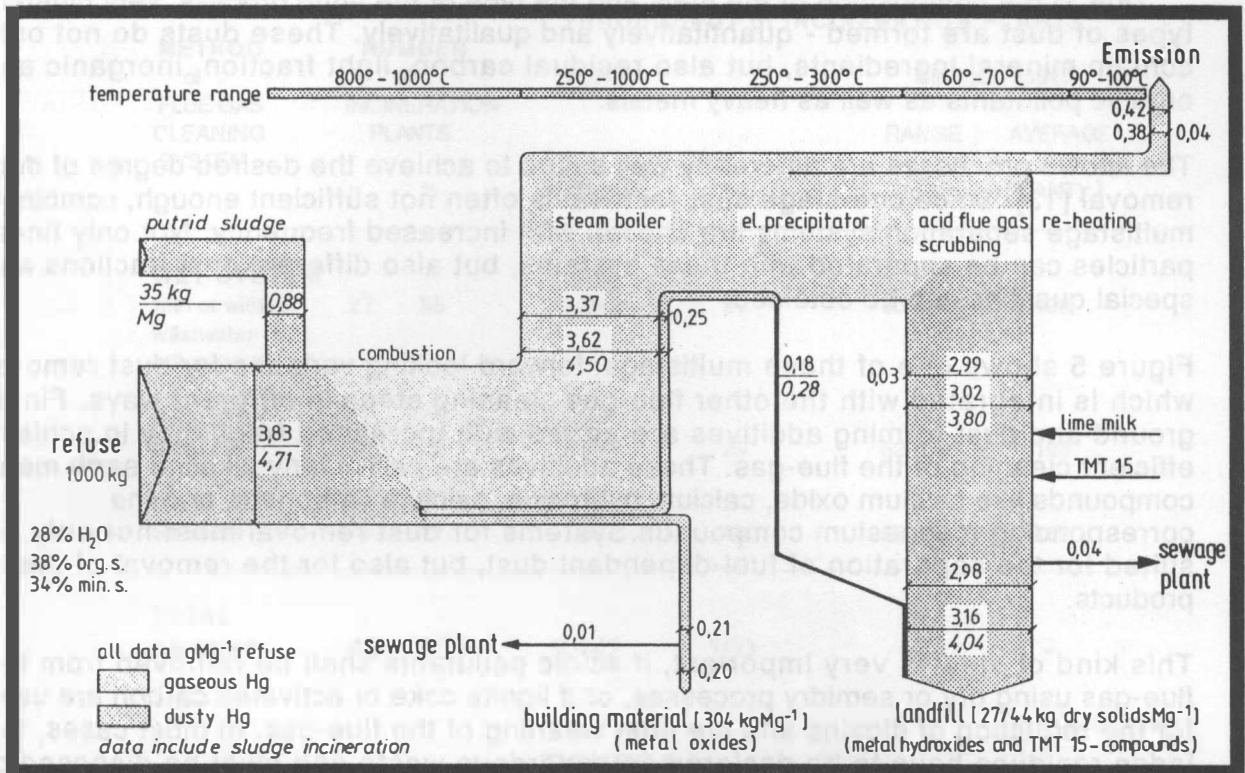**Distribution of Mercury Depending on Temperature and Flue-gas Cleaning Process**

Figure 2 shows the distribution of mercury depending on the temperature of the flue-gas and the chosen single steps in the flue-gas cleaning process with dust removal and wet scrubbing. The distribution is similar for hydrogen chloride and sulfur dioxide.

Purpose and Function of Flue-gas Cleaning

Up-to-date flue-gas cleaning systems usually consist of several procedural steps which have to be assigned differently. The functions of flue-gas cleaning can be classified as follows:

* dust removal (e.g. cyclon, ESP, fabric filter)
* separation of acidic pollutants like HCl, HF, HJ, SO_2 with simultaneous separation of volatile heavy metals like Hg, Tl, Cd and semi-metals (wet-scrubber, semidry or dry systems
* NO_x reduction (DeNO$_x$) (e.g. SNCR, SCR)
* minimization of organic pollutants like C_{org}, dioxins, furanes, PAH, PCB (e.g. catalyst, activated coke/carbon injection or filter, oxidation methods)

In order to stay within emission limits during the combustion of fuels or refuse, the systems are used in various combinations due to their different capabilities.

139

Dust Removal

Due to the composition of the fuels and the type of the firing process, very different types of dust are formed - quantitatively and qualitatively. These dusts do not only contain mineral ingredients, but also residual carbon, light fraction, inorganic and organic pollutants as well as heavy metals.

The known processes are differently well suited to achieve the desired degree of dust removal [13]. Since one-stage dust removal is often not sufficient enough, combined multistage separation systems are chosen with increased frequency. Not only finest particles can be separated with these systems, but also different dust fractions and special qualities can be obtained.

Figure 5 shows one of these multistage, forward-looking varieties for dust removal which is integrated with the other flue-gas cleaning steps in different ways. Finely ground and dust-forming additives are added with increased frequency to achieve efficient cleaning of the flue-gas. These additives are particularly alkaline earth metal compounds like calcium oxide, calcium hydroxide, calcium carbonate, and the corresponding magnesium compounds. Systems for dust removal must not only be suited for the separation of fuel-dependent dust, but also for the removal of these products.

This kind of view is very important, if acidic pollutants shall be removed from the flue-gas using dry or semidry processes, or if lignite coke or activated carbon are used for the reduction of dioxins and the final cleaning of the flue-gas. In most cases, the laden residues have to be declared as hazardous waste and must be disposed of accordingly.

If equipment has to be chosen which utilizes the activated carbon/lime injection in front of a fabric filter for dust removal, these mixtures which are based on lime are of great importance.

Separation of Acidic Pollutants and Volatile Heavy Metals with Different Processes

In principle, the processes which are used for the removal of acidic pollutants like HCl, HF and SO_2, can be divided into wet, semidry, and dry processes.

TABLE 4
Number and Distribution of the Prime Flue-gas Cleaning Systems
- Wet, Semidry, Dry - at the Waste Incineration Plants in the FRG

METHOD of FLUE GAS CLEANING SYSTEM	NUMBER of INCINERATION PLANTS		THROUGHPUT of INCINERATION PLANTS			
			TOTAL		SINGLE PLANT	
					RANGE	AVERAGE
	n	%	$10^3 Mgxa^{-1}$	%	$10^3 Mgx(axPLANT)^{-1}$	
WET SYSTEM with or without wastwater effluent	27	55	5.342	57	60 - 592	198
SEMIDRY SYSTEM	14	28	2.748	29	62 - 386	196
DRY SYSTEM	8	17	1.352	14	25 - 400	169
TOTAL AMOUNT	49	100	9.442	100	-	-

(STATUS 1992)

FIGURE 3
Scheme of the Different Flue-gas Cleaning Processes
for the Removal of Acidic Pollutants

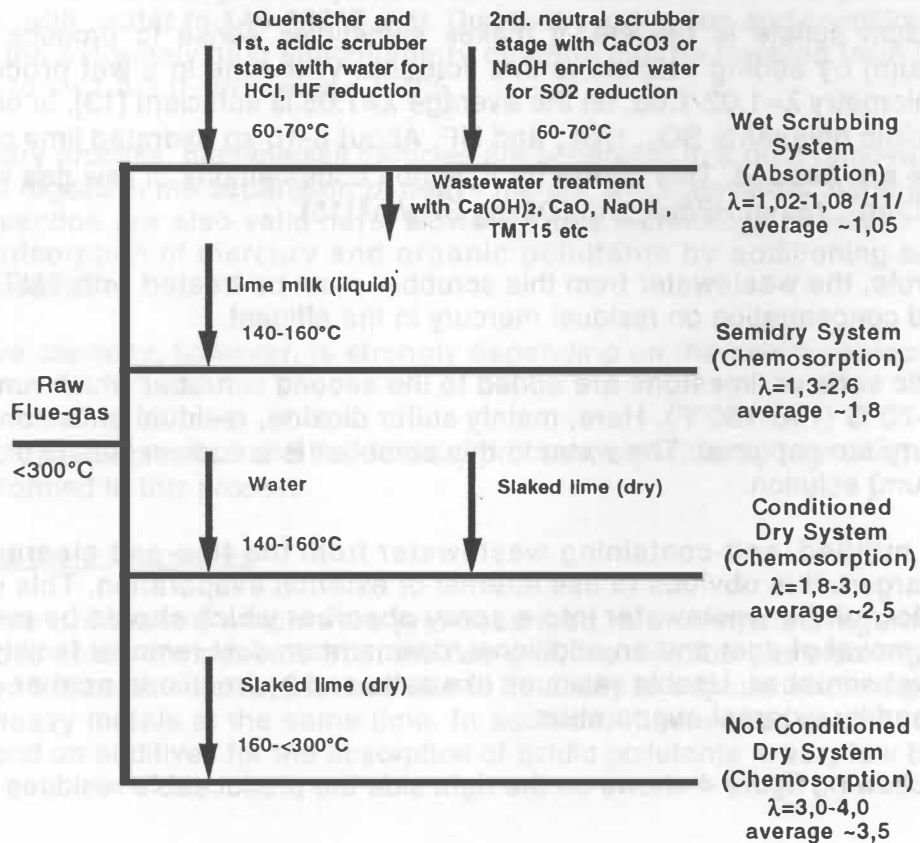Figure 3 shows the different technologies which are used for the removal of acidic pollutants.

Wet Processes

The flue-gases which have usually been freed of dust and have a temperature of <300°C (<570°F), are quenched with water and cooled down below the dewpoint temperature, which is, depending on the acid content, between 60°C and 70°C (140-160°F). The quencher precedes the first wet scrubber which is operated with water at low pH. It removes mainly HCl, HF, HJ, fine particals, and volatile heavy metals, especially mercury.

The effluent is drained from the scrubber loop and neutralized, e.g. with slaked lime or quicklime, which precipitates most of the heavy metals as hydroxides with the exception of mercury.

Mercury is dissolved in the scrubber water as a chlorocomplex which can be removed only with sulfur containing agents [11,14].

Only those precipitating agents will be used in the future which are ecologically neutral during production, easy in application, not critical in case of overdosage, and which do not show detrimental effects in the long run. This set of requirements is only met by the sodium salt of Trimercapto-s-triazine (TMT). None of the other mercury precipitating agents like sodium sulfide, thioacetamide, dithiocarbamates, and polythiocarbonates, which are nevertheless in use today, is a patch on TMT. The TMT 15 demand is about 100-200 ml/m^3 treated wastewater due to the concentration of mercury [7].

If sodium sulfate is present, it makes sometimes sense to produce calcium sulfate (gypsum) by adding calcium to this solution. With lime in a wet process a very low stoichiometry λ=1.02-1.08, on the average λ=1.05 is sufficient [13], in order to separate the acidic pollutants SO_2, HCL, and HF. About 8-10 kg hydrated lime per metric ton of refuse are needed. This is true for common compositions of raw gas with about 1000 mg HCl/m^3, 15 mg HF/m^3, and 500 mg SO_2/m^3 [15].

As a rule, the wastewater from this scrubber must be treated with TMT 15 to meet the limited concentration on residual mercury in the effluent.

Caustic soda or limestone are added to the second scrubber which runs at neutral pH at 60-70°C (140-160°F). Here, mainly sulfur dioxide, residual emissions, and residual mercury are captured. The water in this scrubber is a sodium sulfate or calcium sulfate (gypsum) solution.

If the purified, salt-containing wastewater from the flue-gas cleaning may not be discharged, it is obvious to use internal or external evaporation. This is done best by backflow of the wastewater into a spray absorber which should be installed between pre-removal of dust and an additional, downstream dust removal facility in front of the first wet scrubber. Usable residues like salts and hydrochloric acid or gypsum can be obtained by external evaporation.

The following figure 4 shows on the right side the produceable residues of wet flue-gas

cleaning with the corresponding procedural steps. Wet flue-gas cleaning generates the smallest, undiluted, specific residue quantities.

Semidry Processes

The usually dedusted flue-gas with a temperature of 300°C is cooled down to 140-160°C through the injection of a lime suspension. Since the contact and the transition of the alkaline reagent to the pollutant is inhomogeneous and incomplete, the reagent must be provided in relatively high excess. In this case, the reactions in this technology need a stoichiometry of $\lambda=1.3-2.6$, on the average $\lambda=1.8$.

The temperature of the flue-gas must not be lowered under 140°C in order to be able to separate the salt/lime mixture in the form of dust and without encrustations in the subsequent dust removal facility.

Often, the semidry process is operated without preseparation of dust, which means that dust and acidic pollutants are separated at the same time and therefore as a mixture. The capture of heavy metals, especially mercury, is limited because the flue-gas temperature >140°C only allows partial condensation. The specific residual quantities are up to 50% higher than with the wet process.

Encrustations and sediments in the spray absorber can have a negative effect on this process which is why in some places the dry process is used.

Dry Process

The dry process differs from the semidry process in the way that dry alkaline products are added instead of alkaline suspensions. In order to improve the reaction rate between the acidic flue-gas components and the additives, the flue-gas is usually cooled down with water to 140-160°C first. Due to the saturation and conditioning with water vapor, the extremely high stoichiometry demand can be lowered from in some places $\lambda= 3-4$ to $\lambda= 1.8-3.0$, on average $\lambda=2.5$.

Like the semidry process, the lime/salt particles are separated in a dust removal unit by filtration. With regard to the separation of heavy metals, the statements made earlier in the semidry section are also valid here. However, this technology allows to achieve remarkable adsorption of mercury and organic pollutants by additioning activated carbon/lignite coke.

The adsorptive capacity, however, is strongly depending on the acidic components in the flue-gas.

Compared to the wet process and the semidry process, significantly higher amounts of residues are formed in this process.

Comparison of the 3 Processes

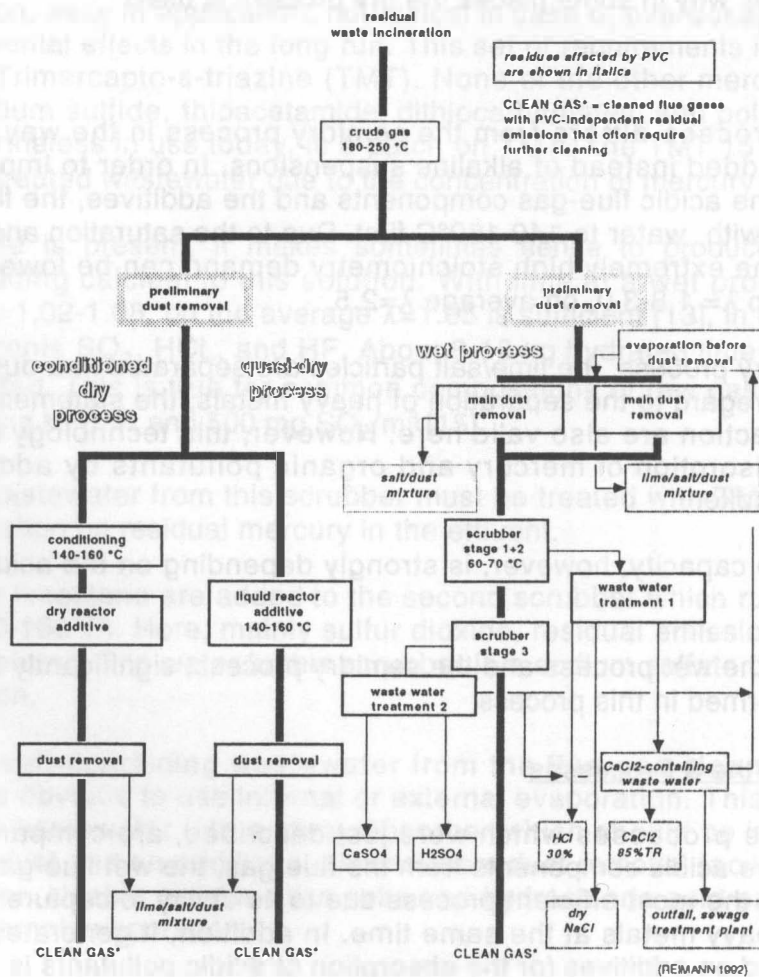If the three processes which were just described, are compared regarding their ability to remove acidic components from the flue-gas, the wet flue-gas cleaning system turns out to be the most efficient process due to its ability to capture acidic ingredients and volatile heavy metals at the same time. In addition, it generates usable residues, and the demand on additives for the absorption of acidic pollutants is very low because

of its required stoichiometry of λ=1.05.

Since capital investment, demand on space, and the complexity of the process are lower for the dry process and to some extent also for the semidry process, these technologies are also in use. The simpler technology, however, generates hardly usable products and demands more of the additives. In order to achieve sufficient removal of the acidic pollutants, the necessary high excess of stoichiometry requires 80% to 150% more additives like lime, and the separated products are pollutid mixtures and by lime diluted residues whitch can hardly be used.

The more the threshold limit for acidic gases are lowered, the more difficult it gets to meet these limits, even with drastic overdosage of additives. Whether the dry and the semidry process can meet future threshold limits for heavy metals, even combined with activated carbon injection or lignite coke addition, is uncertain. The specifically high quantities of residual products cannot be recycled so far. This is in contradiction with recycling efforts.

FIGURE 4
Table of Dry / Semidry / Wet Processes for the Removal
of Acidic Pollutants as well as Potential Residues

(REIMANN 1992)

There are some efforts under way in the Federal Republic of Germany to retrofit some of the existing plants, which are operated with dry flue-gas cleaning systems, with wet scrubbers. Switzerland, for example, has recently retrofitted the Johann-Stausser Facility in Zurich. Today, most of the 33 Swiss MWC are equipped with wet scrubbers.

NO_x Reduction

NO_x emissions can be diminished below the current German threshold limit of 200 mg/m^3 with various processes. Through optimized firing process and recirculation of the flue gases into the combustion chamber, an average NO_x level of 300-500 mg/m^3 can already be kept.

Should lower values, e.g. <200 mg/m^3 be required, wet-oxidation are ruled out due to the high expenditure on the means of chemical auxiliaries and the hardly sufficient separation efficiency.

The non-catalytic NO_x process (SNCR process) with NH_3 injection into a temperature window of 800-950°C presents itself as inexpensive solution. With this simple technology, NO_x reduction of 40-80%, 50% on average, can be achieved. If very low emission levels (<100 mg/m^3) shall be attained, this can be done with excessive dosage of NH_3, but this is accompanied by a very high slip of ammonia. This can lead to a change in color of the flue-gas, and the smell of the residues can be a real nuisance. In addition, corrosion cannot be excluded.

If a wet scrubber is used after the SNCR process, the NH_3 can be stripped from the wastewater and fed back into the system. In this simple way, these problems by NH_3 overdosage can be solved. This technology guarantees the lowest demand on ammonia, too.

Alternatively, urea or liquid manure from animal farms can be used, but the liquid manure first requires preparation. Through the addition of other chemicals, e.g. methanol, the window of reaction temperature, which is required for efficient NO_x control can be expanded to 600-1100°C.

The catalytic process (SCR process), which uses catalysts and the addition of NH_3 at a temperature range of 250-350°C, has been proven to be very worth while. It is possible to surely reach a degree of NO_x removal of 70-80% which means that NO_x limits below 70 mg/m^3 can be obtained. Up to date types of catalysts have proven their efficiency not only in coal-fired power plants, but also in refuse incineration in the longer term.

Processes, which use activated carbon or lignite coke in place of catalysts, are also suited. In this case, the catalysts are replaced by filters made of activated carbon or lignite coke, respectively. As with all other technologies mentioned before, NO_x is reduced through the addition of ammonia. The degree of removal is greater than 70%.

Activated carbon/lignite coke filters have the big advantage of removing traces of acidic pollutants, organic components, and traces of heavy metals like mercury all at the same time.

Compared with the catalytic process, the use of activated carbon/lignite coke offers the advantage of significantly lower reaction temperatures, which must be kept below 100°C as a rule. The superficial gas velocity of the flue-gas in the filter is limited to 0.1-0.2 m/s m², which calls for disadvantageously large filter areas. Extensive safety criteria have to be observed to avoid hot spots and self-ignition of the activated carbon/lignite coke.

Disposal of the laden coke-filter can be a problem. If activated carbon/lignite coke, which is laden with volatile heavy metals (Hg), shall be incinerated in the same plant, a wet scrubber with the corresponding wastewater treatment must be installed as a mercury trap.

Other technologies, e.g. the addition of soda ash for simultaneous removal of SO_2 and NO_x, or wet scrubbers with electrolytic conversion are under development.

The SNCR process is usually efficient enough to achieve residual NO_x levels below 200 mg/m. If regulations require threshold limits below 100 or even below 70 mg/m³, only the catalytic (SCR) process or the activated carbon/lignite coke technology will be taken into consideration. Ammonia or similar additives are used as reagents.

Minimization of Organic Pollutants (Particularly Halogenated Dioxins and Furanes)

Table 5 shows the technologies for the minimization of the dioxin-TE-content which are in use today.

TABLE 5
Overview of Dioxin-TE Minimization Methods (as of 1992/93)

Method	Treatment point	Temp. range °C	TE dioxin ng/m3	Advantages	Disadvantages	Comments
Preventative measures	Exclusion, during collection of waste ingredients which lead to dioxin formation	-	?	Theoretically no additional process required	None	Practically impossible to realize with residual waste since no absolute exclusion of dioxin components possible
Primary measures	Furnance and after-burning zone	>850	<0.1	Thermal destruction of org. pollutants; scarcely any dioxin-containing residues; side effect with good insulation	Consequent stack gas cooling - resynthesis, further removal of dioxin required	Reliable method for destroy- org. pollutants even in re- sidues from stack gas treat- ment
Stack gas treatment >400 °C	Upstream of inside or downstream of the boiler with high temp. dust re- moval or inhibitors	>400	<1	Low-dioxin residues; residue recycling to furnace for detoxification	Side effects of inhibi- tors have to be studied, material aspects, incrus- tation, costs, safety risks	Adequate only in combina- tions of further downstream dioxindegrading measures
Stack gas treatment <400 - >200 °C	Between boiler and stack gas treatment quenching process; catalystic oxi- dation after the stack gas treatment	<400	<1	Low-dioxin residues in the case of down- stream dust removal; dioxin-free residues	Reduced energy removal risk of incrustation/ corrosion, large space requirement, reheating of stack gas	Uniform abrupt quenching difficult; useful only in combination with SCR NOx
		>200	>0.1			
Stack gas treatment <200 °C	Substantial dust removal <5 mg/m3, stack gas scrub- bing, possibly downstream active coke filter in fixed bed or flight process; dry/semidry process; A-coke injection+ fabric filter	<100	0.1	Ideal final tre tment as control filter, hardly any residues and low active coke requirement; can be used with fabric filter with little expense	Active coke problems, such as spontaneous ignition, costs, re- sidues and disposal, high space requirement with fixed bed filter, unreliable process	Combination of multistage scrubber with additive or downstream fabric filter and active coke flight stream process suitable for minimum total emissions
		>140	0.1			
						(D. O. Reimann)

In comparison to coal firing, higher dioxin values are detected in the emissions of refuse incinerators. The threshold limit for the Toxic Equivalent (TE) of dioxin is laid down at 0.1 ng/m^3. As one can see from table 5, combustion technology or dust removal from the hot gas as well as quenching are not efficient enough. Though the application of these processes results in a reduction of today's dioxin emissions of 1-5 ng/m^3, the limitation on 0.1ng TE/m^3 by far cannot be achieved [16].

At the moment, only the catalytic oxidation process, the process using activated carbon/ lignite coke filter, and the activated carbon injection with lignite coke or with a mixture of lime and activated carbon/lignite coke are suitable systems for the dioxin-TE-reduction. First trials are carried out with the application of hydrogen peroxide in oxidative processes.

Organic pollutants can be oxidized on a catalyst which is particularly true for halogenated dioxins and furanes. Traces of heavy metals and acidic pollutants as well as SO_3 can poison the catalyst and shorten its lifetime.

Very good results can be obtained with activated carbon/lignite coke filter, because they do not only capture organic ingredients through adsorption, but also other final emissions. Problems can arise, in spite of extensive self-control, through hot spots in the filter. In addition, the disposal of the bulky filters which are laden with hazardous materials might not be easy.

It seems that the activated carbon injection, which is simpler, therefore less expensive than other processes and safe to operate, will gain acceptance. In front of a fabric filter, additives are injected into the flue-gas, which consist either of pure activated carbon or a mixture of activated carbon or lignite coke. Organic pollutants and final emissions are captured "during flight" or in the formed precoat layer on the filter surface. The dust is recirculated several times, and only small amounts of dust, laden with pollutants, are removed. The big advantage of this process is that the share of activated carbon/lignite coke in this mixture can be reduced to less than 3% without adverse effects on its capability to remove pollutants from the flue-gas. The main part of the mixture usually consists of lime, which reduces the risk of spontaneous combustion of the precoat layer due to its content of activated carbon/lignite coke to almost zero. The use of fabric filters guarantees final dust removal and cleaning of the total flue gases and takes on the function of a so called emergency or police filter.

Summary / Potential Scheme of Future Flue-gas Cleaning

The scheme of a potential future flue-gas cleaning system is shown in the following figure 5. All elements of flue-gas cleaning, which were described earlier, have been taken into consideration, especially under the point of view that reusable or environmentally neutral products have to be generated.

As it can be seen in figure 5, the products which will be incinerated, enter appropriate combustion systems, and the flue gases pass related heat exchangers. The gases enter the flue-gas cleaning system, where the dust is mainly obtained as boiler ash, but also from the dust precipitator, from the spray dryer, and from the fabric filter. The collected dust either goes into a general dust treatment with potential dust smelting, or is deposited in an appropriate disposal site, e.g. underground or in a hazardous waste landfill. Slag can be disposed of at a disposal site for inert products or be utilized. The spray dryer in front of the cloth filter serves mainly as evaporator for the cleaned

wastewater from the scrubber stages 1 and 2. After scrubbing, the flue gas is reheated from 60-70°C to 100-120°C and may pass a lignite coke stage where organic compounds and other pollutants are removed. Eventually, NO$_x$ reduction takes place on a catalyst. For safety reasons, a fabric filter can be installed at the very end which is coated using the activated carbon injection down stream fabric filter and which acts as a police filter.

FIGURE 5
Scheme of a Potential, Advanced, Future Refuse Treatment Facility

(Reimann1993)
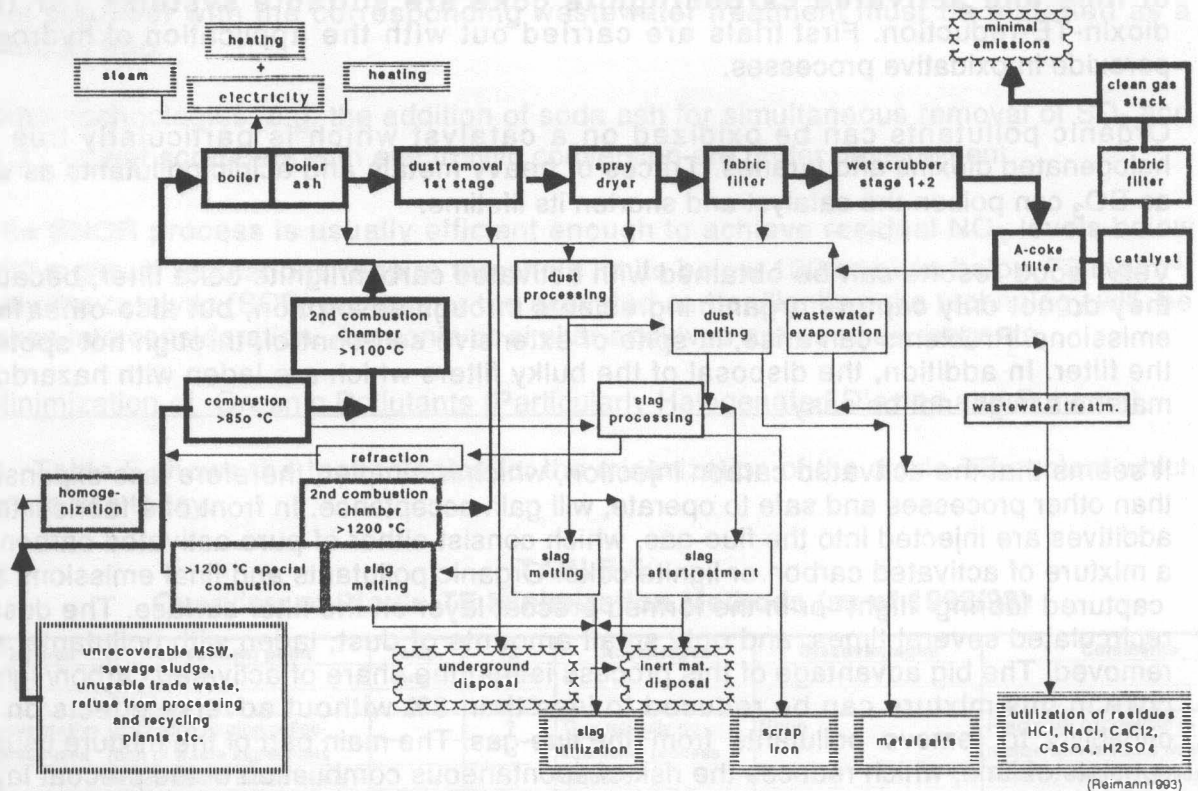
Compared with refuse, hard coal and brown coal usually contain less pollutants making it easier to re-use the products which are generated by flue-gas cleaning. For the same reason, simpler flue-gas cleaning systems are sufficient for coal combustion.

By use of appropriate flue-gas cleaning systems which usually consist of dust removal, separation of acidic pollutants, heavy metals removal, NO$_x$ reduction, and minimization of organic pollutants, clean gases can be generated with very low final emissions. These achievable emissions certainly meet the requirements of the Federal Republic of Germany and of the EEC. Alkaline earth metal compounds like quicklime, slaked lime, or limestone are important aids. They are needed for the removal of acidic pollutants, for the minimization of organic pollutants and components from the flue gas, as well as for the neutralization and cleaning of acidic, polluted scrubber water from the recommendable wet flue-gas cleaning process. However, the processes cannot run without the use of chemicals like NaOH, NH$_3$, or TMT 15.
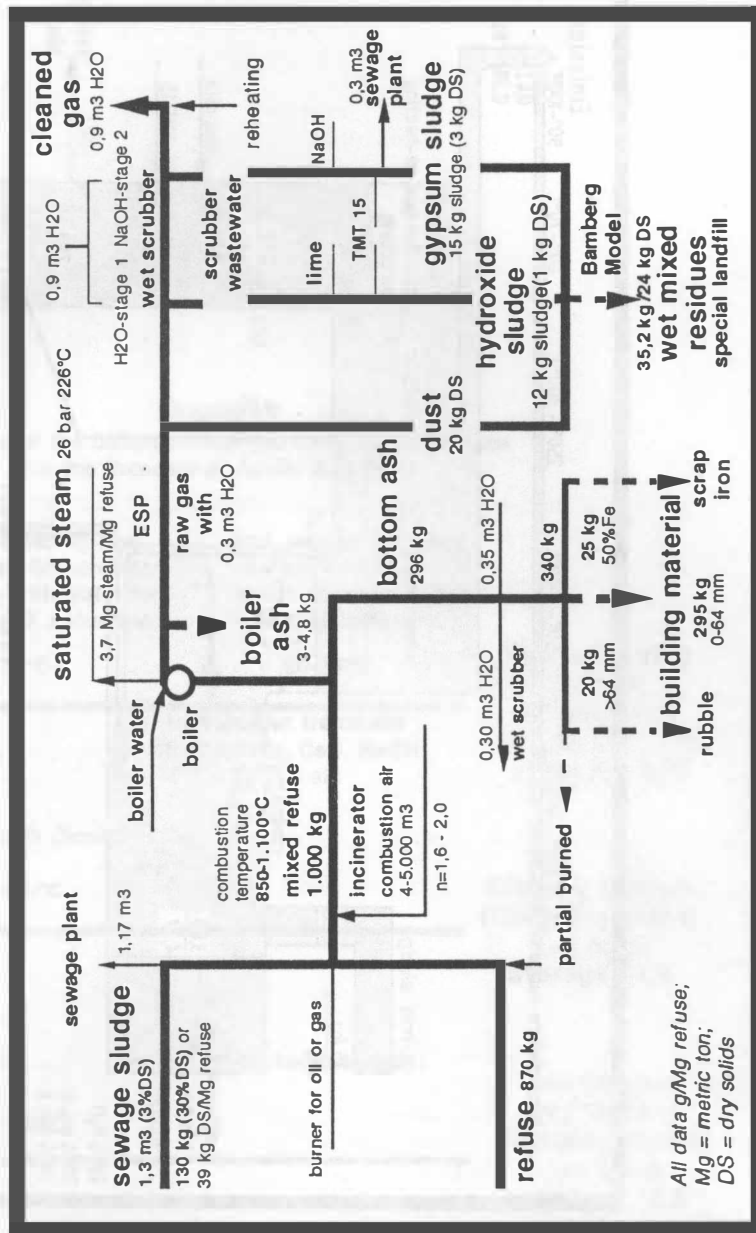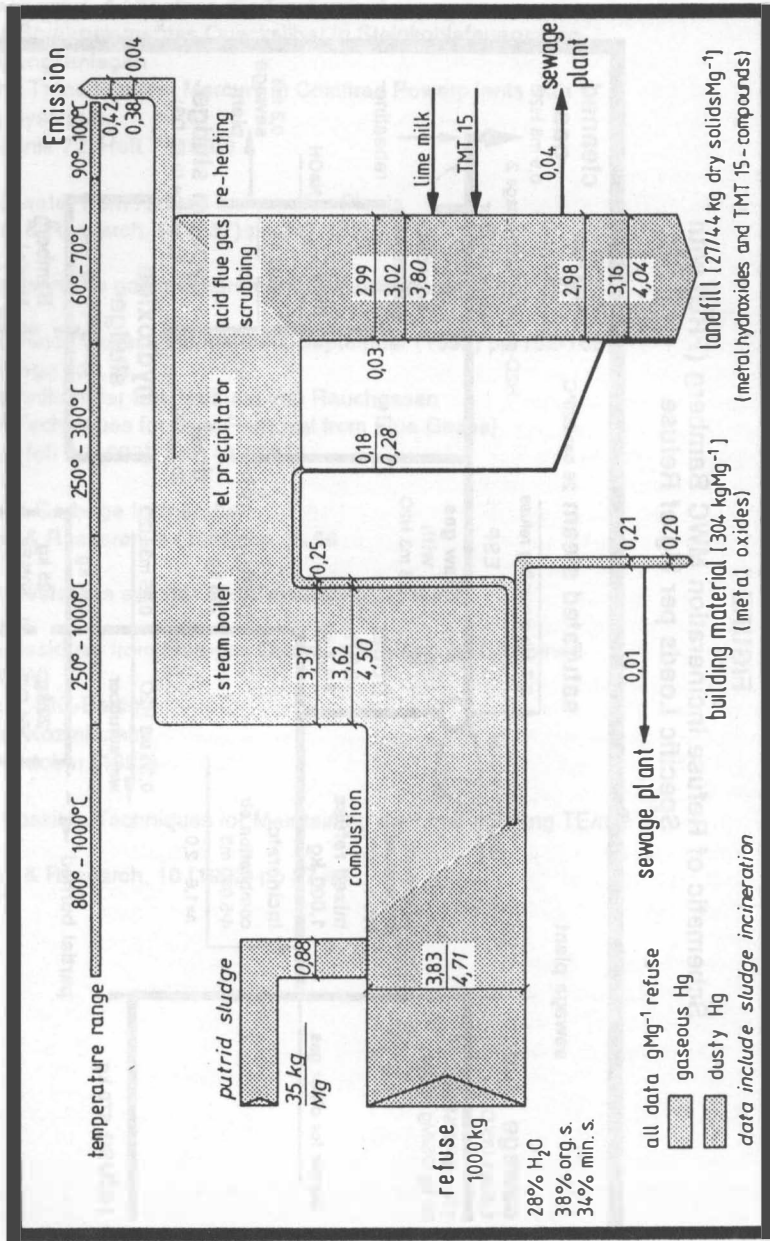
148

BIBLIOGRAPHY

[1]   Reimann, D. O.,
        Rostfeuerungssysteme und Emissionsminderung durch
        Feuerleistungsregelung
        (Grate-firing Systems and Decrease of Emission by Optimized Combustion
        Processes)
        in: Müllverbrennung und Umwelt 5,
        (Hrsg.): K. J. Thomé-Kozmiensky
        EF-Verlag, ISBN 3-924511-56-X (1991)

[2]   Reimann, D. O.; Hämmerli-Wirth, H.,
        Die thermische Restabfallbehandlung in zeitgemäßen
        Abfallwirtschaftskonzepten
        (Thermal Treatment of Refuse in Up-to-date Waste Management Programs)
        AbfallwirtschaftsJournal, Heft 8 "Verbrennung 1" (1992), pp 605-679
        und AbfallwirtschaftsJournal, Heft 12 "Verbrennung 2" (1992) pp 954-983

[3]   Akademie für Raumforschung und Landesplanung,
        Elemente einer integrierten Abfallwirtschaft
        (Elements of ans Integrated Waste Management)
        ARL Hannover, Forschungs- und Sitzungsbericht Nr. 196 (1993)

[4]   Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit,
        Sechste allgemeine Verwaltungsvorschrift zum Abfallgesetz
        (TA Siedlungsabfall)
        (6th General Administrative Rule to Waste Regulation (Technical Instruction for
        Municipal Waste)
        Projektgruppe TA Siedlungsabfall, Bonn, Stand vom 27.08. (1992)

[5]   Bayerischer Landtag,
        Gesetz zur Vermeidung, Verwertung und sonstigen Entsorgung von Abfällen
        und zur Erfassung und Überwachung von Altlasten in Bayern (Bayerisches
        Abfallwirtschafts- und Altlastengesetz - BayAbfG)
        (Rule for Avoidance, Utilization, and Other Management of Waste and for
        Registration and Surveillance of Superfunds[1] in Bavaria (Bavarian Law of
        Waste Management and Superfunds - BayAfG)
        München, Rechtsgültig seit 1. März (1991)

[6]   Fischer, G.,
        Brauchen wir noch Deponien
        (Do We Still Need Landfills?)
        EntsorgungsPraxis, 11, (1992) p 747

[7]   Degussa,
        TMT 15 für die Abtrennung von Schwermetallen aus Abwässern"
        Firmenprospekt "Umwelt und Degussa
        (TMT 15 for the Removal of Heavy Metals from Wastewater)
        CH 312-6-2-1187 Vol. (1987)

[8]   Bundesministerium des Inneren,
        13. Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes
        (Verordnung für Großfeuerungsanlagen - 13. BImSchV)
        (13th Decree to the Implementation of the German Federal Clean Air Act
        (Decree for Large Combustion Plants))
        Bonn, vom 22. Juni (1983)

[9]   Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit,
        17. Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes
        (Verordnung über Verbrennungsanlagen für Abfälle und ähnliche brennbare
        Stoffe - 17. BImSchV-)
        (17th Decree to the Implementation of the German Federal Clean Air Act
        (Decree on Combustion Plants for Waste and Similar Combustible Materials)
        Bonn, vom 01. 12. (1990)

[10] Gutberlet, H.; Spiesberger, A.; Kastner, F.; Tembrink, J.,
      Zum Verhalten des Spurenelementes Quecksilber in Steinkohlefeuerungen
      mit Rauchgasreinigungsanlagen
      (The Behavior of the Trace Element Mercury in Coalfired Powerp lants with
      Flue-gas Cleaning Systems)
      VGB Kraftwerkstechnik 72, Heft 7 (1992)

[11] Reimann, D. O.,
      Treatment of Wastewater from Refuse Incineration Plants
      Waste Management & Research, 5 (1987) pp 147-157

[12] Vicard J. F.,
      Recent developments in flue gas measurement methods, particularly in the
      field of incineration
      ISWA Annual Conference Papers, Amsterdam, September (1992) pp 162-166

[13] Reimann, D. O.; Turegg von, R.,
      Bedeutung und Techniken der Entstaubung von Rauchgasen
      (Importance of and Techniques for Dust Removal from Flue Gases)
      EntsorgungsPraxis Heft 4 (1990), pp 142-153

[14] Reimann, D. O.,
      Mercury Output from Garbage Incineration
      Waste Management & Research, 4 (1986) pp 45-56

[15] Reimann, D. O.,
      Beeinflussung der Reststoffe aus der Rauchgasreinigung durch
      PVC-Mitverbrennung
      (PVC-Influence on Residues from Flue-gas Cleaning Systems by Combined
      Combustion with MSW)
      Tagungsband zum 7. IRC-Berlin
      (Hrsg): K. J. Thomé-Kozmiensky
      EF-Verlag, Berlin, Oktober (1992)

[16] Reimann, D. O.,
      Dioxin Emissions: Possible Techniques for Maintaining the Limit of 0.1ng TE/m^3
      (as of 1990/91)
      Waste Management & Research, 10 (1992) pp 37-46

FIGURE 1

Schematic of Refuse Incineration MWC Bamberg (FRG) with Specific Loads per Mg of Refuse

All data g/Mg refuse;
Mg = metric ton;
DS = dry solids

Emission

temperature range: 800°–1000°C | 250°–1000°C | 250°–300°C | 60°–70°C | 90°–100°C

combustion — steam boiler — el. precipitator — acid flue gas scrubbing — re-heating

lime milk   TMT 15

0,42 / 0,38   0,04 / 0,04

refuse 1000 kg
28% H₂O
38% org.s.
34% min. s.

putrid sludge
$\frac{35\ kg}{Mg}$

0,88

3,83 / 4,71

0,25

3,37 / 3,62 / 4,50

0,18 / 0,28

0,03

2,99 / 3,02 / 3,80

2,98 / 3,16 / 4,04

0,04

landfill [27/44 kg dry solids Mg⁻¹]
(metal hydroxides and TMT 15- compounds)

sewage plant

0,21 / 0,20

0,01

building material [304 kg Mg⁻¹]
(metal oxides)

sewage plant

all data g Mg⁻¹ refuse
gaseous Hg
dusty Hg
data include sludge incineration

FIGURE 3
Scheme of the Different Flue-gas Cleaning Processes
for the Removal of Acidic Pollutants

FIGURE 4
Table of Dry / Semidry / Wet Processes for the Removal of Acidic Pollutants as well as Potential Residues

residual waste Incineration

crude gas 180-250 °C

residues affected by PVC are shown in italics

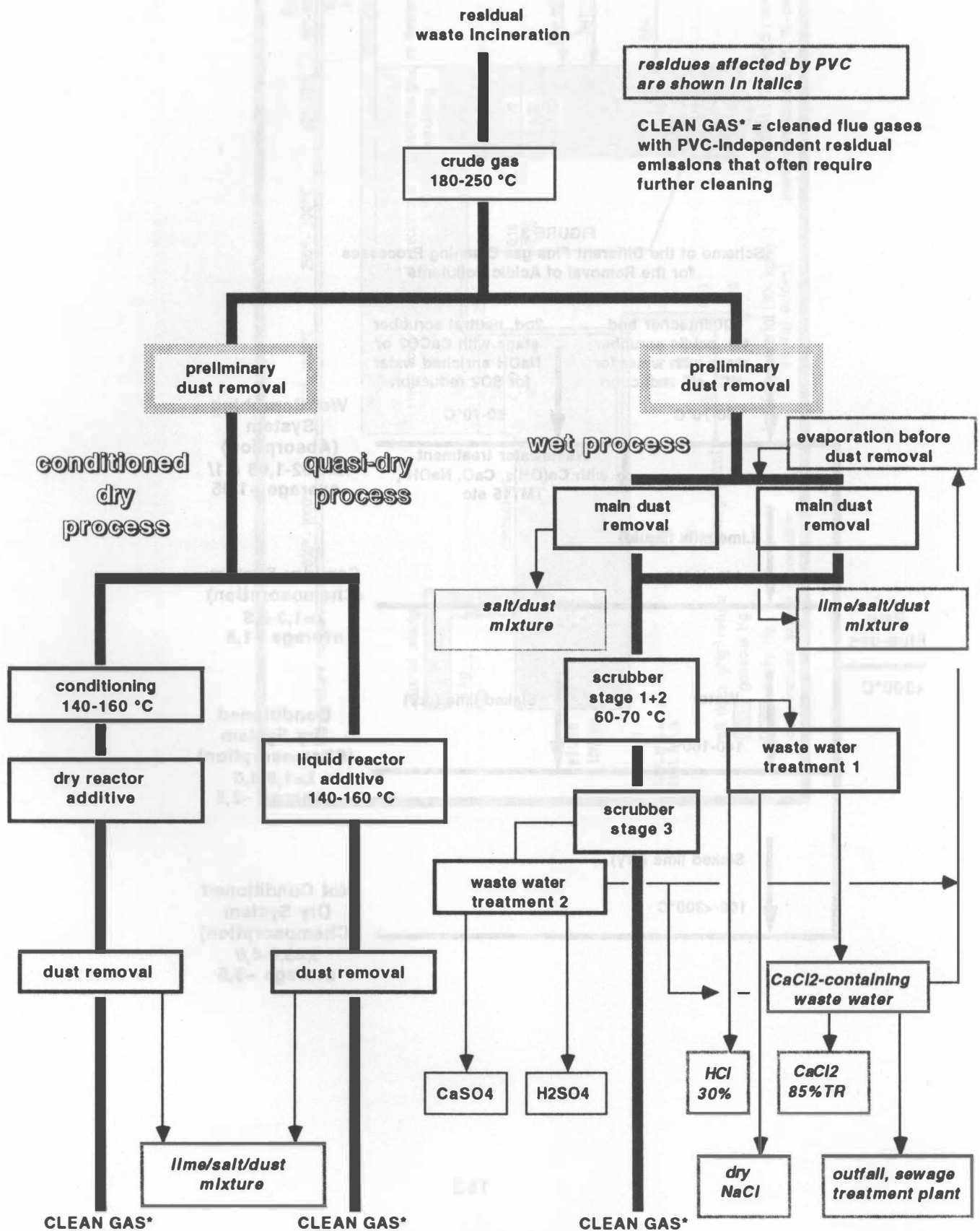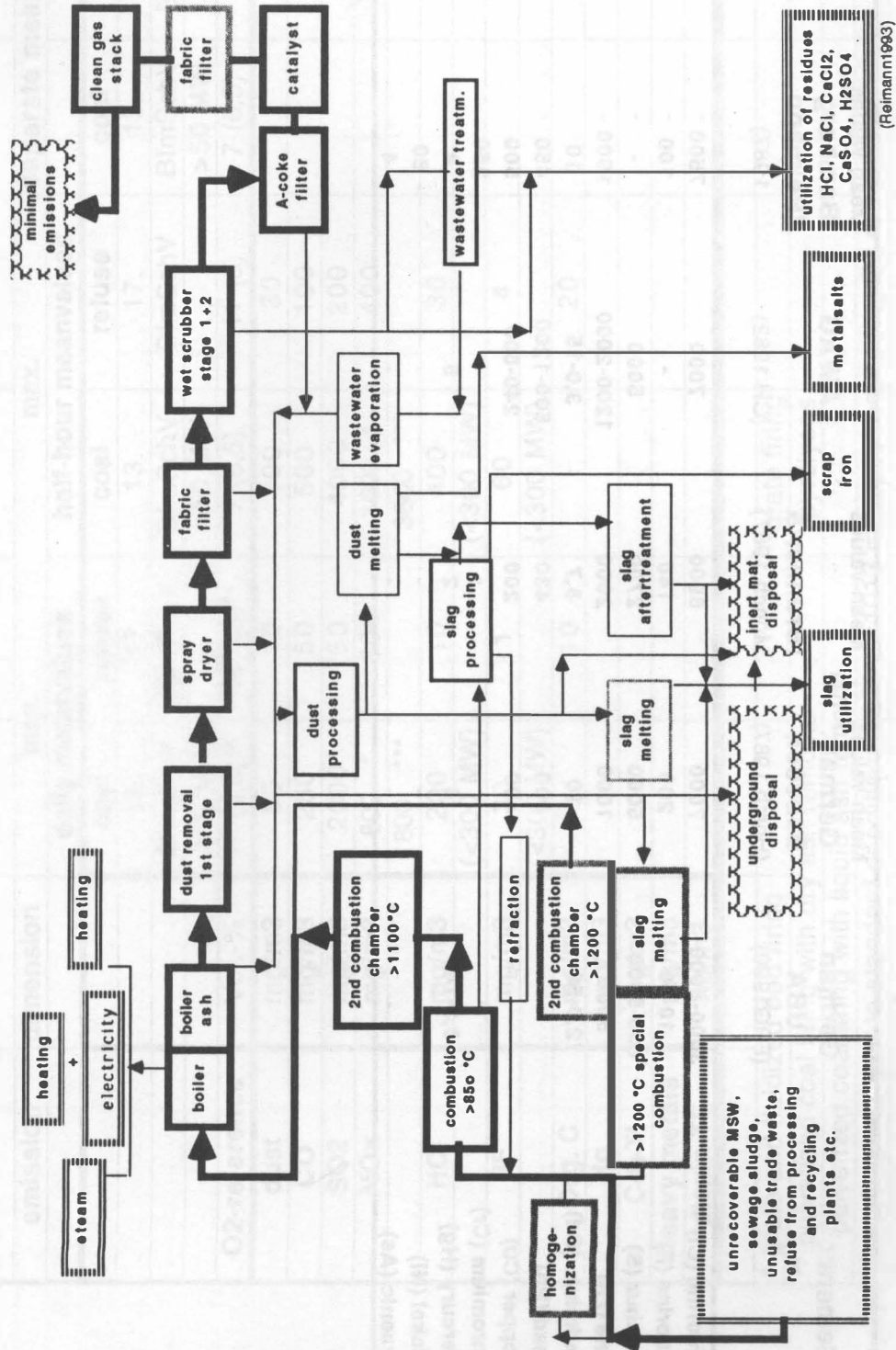CLEAN GAS* = cleaned flue gases with PVC-independent residual emissions that often require further cleaning

preliminary dust removal

preliminary dust removal

conditioned dry process

quasi-dry process

wet process

evaporation before dust removal

main dust removal

main dust removal

salt/dust mixture

lime/salt/dust mixture

conditioning 140-160 °C

scrubber stage 1+2 60-70 °C

waste water treatment 1

liquid reactor additive 140-160 °C

dry reactor additive

scrubber stage 3

waste water treatment 2

CaCl2-containing waste water

dust removal

dust removal

CaSO4

H2SO4

HCl 30%

CaCl2 85%TR

lime/salt/dust mixture

dry NaCl

outfall, sewage treatment plant

CLEAN GAS*

CLEAN GAS*

CLEAN GAS*

(REIMANN 1992)

154

FIGURE 5

Scheme of a Potential, Advanced, Future Refuse Treatment Facility

(Reimann1993)

TABLE 1

Comparison of Refuse Pollutants and Heavy Metals from Various Plants and Range of Results

Element	German UBA (FRG1990)	Mean values German Babcock (Horch 1987)	Mean values (Brunner & Mönch 1987)	EAWAG (CH 1982)	Mean values Bamberg (Reimann) 1987	Range of results g/Mg
Chlorine (Cl)	3000-8000	7000	6900	7000	7500	6900-8000
Fluorine (F)	.10-50	200	140	-	100	100-200
Sulphur (S)	650-5000	5000	2700	5000	-	2700-5000
Zinc (Zn)	5000	1000	2000	1200-2000	1900	1000-2000
Cadmium (Cd)	2,0-50	10	8,7	3,0-15	10	3,0-15
Lead (Ph)	-	800	430	500-1200	450	430-1200
Copper (Cu)	-	400	200	240-600	500	200-600
Chromium (Cr)	-	-	-	-	250	/250/
Mercury (Hg)	0,3-14	4	2	5	4	2,0-5,0
Nickel (Ni)	-	-	-	-	80	/80/
Arsenic (As)	-	-	-	-	4	/4/

All data in g/Mg refuse

156

TABLE 2 — Comparison of Permitted Emissions Limits for Solid Fuels

emission	dimension	max. daily meanvalues		max. half-hour meanvalues		separate measurement		anticipated state of the art
		coal 13. BImSchV >50 MW	refuse 17. BImSchV	coal 13. BImSchV >50 MW	refuse 17. BImSchV	coal 13. BImSchV >50 MW	refuse 17. BImSchV	refuse daily value repect. sep. measur.
O2-reference	Vol.-%	7* (6,5)**	11° (3)°°	7* (6,5)	11 (3)	7 (6,5)	11 (3)	11 (3)
dust	mg/m3	50	10	100	30			<3
CO	mg/m3	250	50	500	100			<20
SO2	mg/m3	2000	50	4000	200			<20
NOx	mg/m3	800 * / 1800 ***	200	1600 * / 3600 ***	400			<70
HCl	mg/m3	200	10	400	30			<3
HF	mg/m3	30 (<300 MW)	1	60 (<300 MW)	4			<0,3
Org. C	mg/m3	-	10	-	20			<4
Hg	mg/m3					-	0,05	<0,02
Cd+Tl	mg/m3					-	0,05	<0,01
heavy metals	mg/m3					-	0,5	<0,1
dioxin-TE	ng/m3					-	0,1	<0,1

* grate and fluidized bed firing
** pulverized coal firing with dry ash removal
*** pulverized coal firing with liquid ash removal
all statements refer to standard conditions (273 K, 1013 mbar, corresponding O2 reference)
formula for oxygen reference:

° grate firing
°° pyrolyses

Em: measured emission
EB: emission, referred to the oxygen reference
Om: measured oxygen content
OB: corresponding O2 reference

$$EB = ((21 - OB) / (21 - Om)) \cdot Em \quad \text{mit}$$

157

TABLE 3 — Comparison of Permissible Emissions According to Some International Regulations for Waste-to-Energy Plants

	EEC	EEC	GERMANY	NETHERLANDS	AUSTRIA	SWITZERLAND
Kind of regulation	Directive Proposal	Directives 89/369 89/429	17. Decree to BImSchG	Directive "Incineration"	Decree LRV.K	Decree LRV
Kind of refuse	Hazardous waste	Mun. waste	All waste incinerations	Haz./Mun. waste	Haz./Mun. waste (Incineration with boiler)	Haz./Mun. waste
Kind of plants	New and existing	New and existing	New and existing	New and existing	New	New and existing
	Proposal 92	1. Dec. 1990	1. Dec. 1990	15. Aug 1989	13. Januray 1989	1. Feb 1992
Realisation up to		1996	(1994-1996)	(1993-1997)		(1997-2002)
N° Pollutant						
1 Total dust	5	30	10	5	15	10
2 TOC	5	20	10	10	50	20
3 HCl	5	50	10	10	10	20
4 HF	1	2	1	1	0,7	2
5 SO2	25	300	50	40	50	50
6 NOx			200	70	100	80
7 Mercury	0,05 (incl.Tl)	0,2	0,05 (incl.Tl)	0,05	0,05 (0,1)	0,1
8 Cadmium	0,05	0,2	0,05	0,05	0,05	0,1
9 Other heavy	Sum 0,5	Pb+Cr+Cu+Mn 5	Sum 0,5	Sum 1	Pb+Zn+Cr 2	Pb+Zn 1
		NI + As 2			As + Co + Ni 0,5	
10 PCDD/F dioxin-Te ng/m3	0,1 (target)		0,1	0,1	0,1	
Cont. measure. #1-6	24 h	1 h (with adaptation)	0,5 h	1 h (with exceptions)	0,5 h	1 h (with adaptations)
Measurement #7-9	0,5 - 4 h		0,5-2 h		generally	
Duration #10	6-16 h		6-16 h		3-10 h	-

THROUGHPUT of INCINERATION PLANTS

METHOD of FLUE GAS CLEANING SYSTEM	NUMBER of INCINERATION PLANTS		TOTAL		SINGLE PLANT	
	n	%	10^3Mgxa^{-1}	%	RANGE 10^3Mgx(axPLANT)$^{-1}$	AVERAGE
WET SYSTEM with or without wastwater effluent	27	55	5.342	57	60 - 592	198
SEMIDRY SYSTEM	14	28	2.748	29	62 - 386	196
DRY SYSTEM	8	17	1.352	14	25 - 400	169
TOTAL AMOUNT	49	100	9.442	100	-	-

(STATUS 1992)

Table 4: Number and Distribution of the Prime Flue-gas Cleaning Systems
- Wet, Semidry, Dry - at the Waste Incineration Plants in the FRG

TABLE 5
Overview of Dioxin TE Minimization Methods (as of 1992/93)

Method	Treatment point	Temp. range °C	TE dioxin ng/m3	Advantages	Disadvantages	Comments *
Preventative measures	Exclusion, during collection of waste ingredients which lead to dioxin formation	-	?	Theoretically no additional process required	None	Practically impossible to realize with residual waste since no absolute exclusion of dioxin components possible
Primary measures	Furnace and after-burning zone	>850	<0.1	Thermal destruction of org. pollutants; scarcely any dioxin-containing residues; side effect with good insulation	Consequent stack gas cooling - resynthesis, further removal of dioxin required	Reliable method for destroying org. pollutants even in residues from stack gas treatment
Stack gas treatment >400 °C	Upstream of inside or downstream of the boiler with high temp. dust removal or inhibitors	>400	<1	Low-dioxin residues; residue recycling to furnace for detoxification	Side effects of inhibitors have to be studied, material aspects, incrustation, costs, safety risks	Adequate only in combinations of further downstream dioxindegrading measures
Stack gas treatment <400 - >200 °C	Between boiler and stack gas treatment quenching process; catalystic oxidation after the stack gas treatment	<400 >200	<1 >0.1	Low-dioxin residues in the case of downstream dust removal; dioxin-free residues	Reduced energy removal Uniform abrupt quenching risk of incrustation/ corrosion, large space requirement, reheating of stack gas	difficult; useful only in combination with SCR NOx
Stack gas treatment <200 °C	Substantial dust removal <5 mg/m3, stack gas scrubbing, possibly downstream active coke filter in fixed bed or flight stream process; dry/semidry process; A-coke injection+ fabric filter	<100 >140	0.1 0.1	Ideal final treatment as control filter, hardly any residues and low active coke requirement; can be used with fabric filter with little expense	Active coke problems, such as spontaneous ignition, costs, residues and disposal, high space requirement with fixed bed filter, unreliable process	Combination of multistage scrubber with additive or downstream fabric filter and active coke flight stream process suitable for minimum total emissions

(D. O. Reimann)