

# **An Optimized Concept for Flue Gas Cleaning Downstream of MWCs Using Sodium Tetrasulfide for Mercury Removal**

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## **ABSTRACT**

In Germany and other central European countries, new emission standards for refuse incineration plants became effective in 1989/90. In recent years the operators of incinerating plants in Germany demanded higher removal emission efficiencies than required by law in order to obtain local permits. In the course of the procurement process, complex flue gas cleaning systems were approved and built. As a result, the costs for air pollution control systems exceeded the costs of the refuse combustion system (stoker plus boiler) which has been reflected in the constantly climbing disposal costs. Not all of the increased disposal costs have been able to be passed along to the market. Economic pressure has led to a search for simple solutions and low-cost flue gas cleaning systems which correspond to the legal and contractual limits.

A new processes was developed by L. & C. Steinmüller GmbH (Steinmüller) using sodium tetrasulfide ( $\text{Na}_2\text{S}_4$ ) as a additive for the emission control of mercury. This paper will present an overview of the general application of this new technology in the waste-to-energy field. The efficiency of the reduction of mercury, and serviceability and the simple handling of this new technology will be shown by results of plants which are in operating. For a conclusion, an outlook is provided into future applications of this technology over the waste-to-energy field.

## **INTRODUCTION**

When designing Municipal Waste Combustors (MWCs) not only ecological but also economical criteria are decisive in restricting waste processing costs to a justifiable rate. The use of additives provides a significant potential especially for plants equipped with a spray dryer bag house system for achieving compliance at a relatively low cost.

The use of sodium tetrasulfide ( $\text{Na}_2\text{S}_4$ ) as an additive for the inexpensive control of mercury emissions is presented as a possibility to combine both ecology and economy. Particularly with the new requirements in the U.S., this technology offers the opportunity to bring most MWC's in compliance with respect to their Hg-emissions.

Steinmüller developed this patented process technology especially for use in MWCs. Numerous plants employing this technology are already in operation. The high success also led to the use of the  $\text{Na}_2\text{S}_4$  process in hazardous waste incinerators and sewage sludge combustors. Key to this success is

the fact that not only ionic mercury but also elemental mercury is being removed very effectively. The simplicity of operations as well as the low cost for equipment installation and operation, add to the attractiveness of this newly developed technology.

## MERCURY IN MWC'S

At higher temperatures, mercury compounds are thermally unstable. The mercury is gaseous at a temperature of 850°C in the combustion chamber, independent of the compound that is taken into the MWC. The minimal retention of mercury in the bottom ash is due to its high vapor pressure and is less than 5% of the total mercury input as shown in various investigations.<sup>1</sup> Other metals such as copper, chromium, or nickel have a retention rate of more than 90% in the bottom ash.

The mercury vapor in the combustion chamber is mixed with the flue gas and enters the convective section of the boiler. In this section, the flue gas cools down, producing hot water and steam. Due to the decreasing gas temperature, the elemental mercury is able to react with other flue gas components.

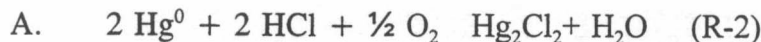
The main reaction of the mercury vapor is the formation of mercury(II)chloride ( $\text{HgCl}_2$ ) out of the gaseous hydrogen chloride ( $\text{HCl}$ ) and elemental mercury ( $\text{Hg}^0$ ) under oxidizing conditions in the flue gas. The exact mechanism of this reduction reaction has not yet been completely understood, but is usually described as:  $\text{Hg}^0 + 2 \text{HCl} + 1/2 \text{O}_2 \rightarrow \text{HgCl}_2 + \text{H}_2\text{O}$ . (R-1)

In case of decreasing temperature, the equilibrium of this reaction shifts more and more to the right side. However, the reaction is not only dependent on temperature. Other flue gas components such as  $\text{O}_2$  and sulfur compounds, as well as the residence time in a certain temperature range, influences the reaction equilibrium.

The thermodynamic balance of the above mentioned reaction is blocked kinetically, therefore, a complete transformation of the  $\text{Hg}^0$  into  $\text{HgCl}_2$  cannot be expected. The mercury chloride formed has a high volatility and is found in the gas phase in the flue gas at the boiler outlet (Table 1).

Beside the formation of mercury (II) chloride other reduction reactions of mercury in the gaseous phase are possible:

**elemental mercury can be oxidized to mercury(I) chloride ( $\text{Hg}_2\text{Cl}_2$ ):**



**elemental mercury can be oxidized to mercury oxide ( $\text{HgO}$ ):**



However, the above described reaction possibilities (R-2 and R-3) are of little importance as  $\text{Hg}_2\text{Cl}_2$ , and  $\text{Hg}^0$  are not stable at temperatures above 400°C.  $\text{Hg}_2\text{Cl}_2$  decomposes into  $\text{Hg}^0$  and  $\text{HgCl}_2$  respectively and  $\text{Hg}^0$  into  $\text{Hg}^0$  and  $1/2 \text{O}_2$ .

A higher amount of mercury(I)chloride can be formed out of  $\text{HgCl}_2$  in the presence of fly ashing which creates a reducing atmosphere.

At the boiler's outlet temperature the  $\text{Hg}_2\text{Cl}_2$  is solid and will be separated together with the fly ash (sublimation temperature 383°C, [Table 1]). Consequently, about 5-10% of the total mercury amount

can be removed with the fly ash in a system equipped with an ESP operated at around 230°C and 20-30% in a spray dryer/baghouse system operated at around 150°C.

Typically, the mercury at the boiler outlet consists mainly of up to 15% Hg<sup>0</sup> and more than 85% HgCl<sub>2</sub>. Characteristic for both species is their high vapor pressure even at temperatures of about 200°C. Thus, the particulate removal equipment usually arranged downstream of the boiler is unable to act as an effective mercury sink.

## MEASURES FOR MERCURY CONTROL

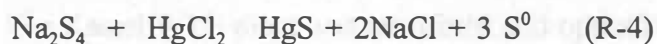
Beside the Hg-separation via Na<sub>2</sub>S<sub>4</sub> as presented in this paper, there are many other processes for the Hg minimization in flue gas that have already been described earlier<sup>4,5,6,7,8,9,10</sup>. Of course HgCl<sub>2</sub> can be effectively removed in wet scrubbers and, to a considerable lesser extent, in spray absorbers. The disadvantage is that both systems are ineffective in trapping elemental mercury.

Metallic and ionic mercury can both be captured in special filters. The activated carbon reactor (ACR) described earlier<sup>4</sup> is proven to be the safest possibility to separate all forms of mercury to levels below the detection limit. Furthermore, activated carbon can also be injected into the flue gas duct upstream of a baghouse. Usually in these so-called carbon injection processes, spent activated carbon is again removed by means of a downstream arranged fabric filter. Recently, alternative processes especially for the separation of elemental mercury have been proposed, e.g. the application of zeolite in the so-called medisorbon process<sup>8</sup> or the amalgamation on precious metals.<sup>7,9</sup>

However, all such filtration processes share the fundamental disadvantage of involving a separate apparatus in the flue gas path. In addition, the disposal of the spent, heavily contaminated sorbent frequently presents severe problems. The high investment and operating costs for these filters make such systems uneconomical.

## THE Na<sub>2</sub>S<sub>4</sub> PROCESS FOR MERCURY SEPARATION

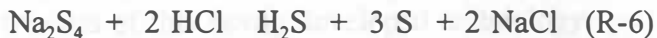
The disadvantages of the various conventional processes as described above sparked Steinmüller to develop its own technology. Mercury removal using Na<sub>2</sub>S<sub>4</sub> can capture both ionic HgCl<sub>2</sub> and elemental Hg<sup>0</sup> in accordance with the following simplified reactions:



It is sufficient to inject the aqueous Na<sub>2</sub>S<sub>4</sub> solution into the flue gas duct, therefore, such a system can be easily retrofitted to an existing flue gas cleaning plant. The Na<sub>2</sub>S<sub>4</sub> reacts with the mercury to form mercury sulphide (HgS) whose red allotrope is known as cinnabar. This is a non-poisonous insoluble salt which is thermally stable up to 400°C (Table 1) and thus effectively immobilizes the mercury. The black allotrope meta-cinnabarite can also be found in MWCs but in the course of several years changes into the stable red allotrope.

Apart from the heat exchange with the flue gas, there is also a mass transfer between the droplet of the additive and the flue gas. The most likely mass transfer process between the liquid and the gaseous phase is the dissolving of HCl in the droplets of the Na<sub>2</sub>S<sub>4</sub>, as aqueous alkaline liquids show a strong affinity towards the gaseous HCl.

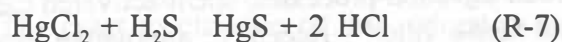
The dissolved HCl will decompose the existing Na<sub>2</sub>S<sub>4</sub> in the droplets as follows:



After evaporation of the droplet, the H<sub>2</sub>S in the flue gas is gaseous. The formed elemental sulphur (melting point of sulphur = 119°C, boiling point = 445°C [Table 1]) exists in liquid form as an aerosol with a diameter of < 1µm. However, it is most unlikely that all Na<sub>2</sub>S<sub>4</sub> molecules will be decomposed by the HCl. Because Na<sub>2</sub>S<sub>4</sub> (melting point = 275°C) is stable at the existing temperatures, it is most probable that Na<sub>2</sub>S<sub>4</sub> particles can still be found in the flue gas after evaporation of the droplet.

In the entrained-flow phase, the mercury reacts with H<sub>2</sub>S<sup>(g)</sup>, S<sup>0(1)</sup>, and Na<sub>2</sub>S<sub>4</sub>. According to the predominant opinion in literature and also according to the vapor pressure curve for pure components, Hg<sup>0</sup> and HgCl<sub>2</sub> can be found in the gaseous phase due to their high volatility. However, the existence of aerosols cannot be denied. Therefore, a different reaction mechanism is assumed to be responsible for the formation of HgS within the entrained-flow phase.

It is most probable that Hg<sup>0</sup> and HgCl<sub>2</sub> are dissolved in the droplet of the additive where they react as:



These reactions are not only dependent on the distribution of educts, but also on the time limited existence of a liquid phase.

Other reaction schemes exist (melting temperature Hg<sup>0</sup> and HgCl<sub>2</sub> - 40°C and 280°C, boiling temperature 360°C and 303°C) [Table 1]) to account for the presence of Hg<sup>0</sup> and HgCl<sub>2</sub> as aerosols.

Hg<sup>0</sup> and HgCl<sub>2</sub> aerosols respectively, can be combined with Na<sub>2</sub>S<sub>4</sub> particles, and can be absorbed and react as :



According to R-7 H<sub>2</sub>S<sup>(g)</sup> can react to form HgS in the gaseous phase as well as in the liquid phase with the HgCl<sub>2</sub> aerosols. S<sup>0(1)</sup> can also be combined with Hg<sup>0(g)</sup> and Hg<sup>0</sup> aerosols and react to form HgS as mentioned in R-8.

Competitive reactions such as the oxidation of Na<sub>2</sub>S<sub>4</sub>, H<sub>2</sub>S or S into Na<sub>2</sub>SO<sub>3</sub>, SO<sub>2</sub>, SO<sub>3</sub>, or S<sub>2</sub>O<sub>3</sub> cannot be excluded. Such competitive reactions would prevent the sulfur from further reactions with mercury. Moreover, sulfide formation of other heavy metals can cause competitive reactions as well. However, in case of the injection of Na<sub>2</sub>S<sub>4</sub> after upstream dust removal, such reactions are of no consequence regarding the sulfur balance. Even if all heavy metals in the flue gas flow react to sulphides, only 4-10% of the fed sulfur could be used up via the Na<sub>2</sub>S<sub>4</sub> injection.

Hence, the equations R-4 and R-5 must be assumed as the basic reaction equations responsible for the transformation of Hg<sup>0</sup> and HgCl<sub>2</sub> during the entrained-flow phase which is started by the reaction of Na<sub>2</sub>S<sub>4</sub> with the dissolved HCl.

## **OPERATIONAL EXPERIENCE WITH MERCURY SEPARATION USING $\text{Na}_2\text{S}_4$**

In addition to extensive laboratory investigations, operational experience with the patented Steinmüller process for mercury separation has been obtained for over three years in the Kassel Waste-to-Energy (WTE) plant and the Ebenhausen hazardous waste incineration plant.

### **Kassel**

#### **Combustion and Steam Generator**

Two combustion units processing a mixture of approximately 2/3 household waste and 1/3 industrial solid waste are installed in the Kassel WTE plant (MHKW Kassel). The boilers were designed in 1968/1969 and replaced in 1997/99. Each boiler has a full load capacity of 250 tpd of waste and at 100% load produces 30 tph of steam (37 bar, 430°C). The steam is delivered to a neighboring district heating and power station.

In the boiler, the flue gas is cooled to approximately 235°C before entering the air pollution control system. Depending on the load, the flue gas volumetric flow rate varies between 50,000 and 55,000 dscm/hr.

#### **Air Pollution Control (APC) System (Figure 1)**

The particulates in the flue gas leaving the boiler are almost completely removed in an electrostatic precipitator (ESP). Upon exiting the ESP, the flue gas is directed to a spray absorber. The spray absorber utilizes a semidry process to inject and intensively mix a lime slurry ( $\text{Ca}(\text{OH})_2$  in aqueous solution and recirculate) into the flue gas thus absorbing most of the  $\text{SO}_2$ , HCl, HF and  $\text{SO}_3$ . These pollutants react with the lime slurry to form calcium salts. After evaporation of the liquid the dry reaction products are removed from the flue gas by means of a fabric filter. The clean flue gas from both units is transported to a common stack via I.D. fans. This system represented the state-of-the art technology over 15 years ago when it was purchased. It became inadequate when new emission legislation was introduced in late 1990.

#### **Expansion of the Existing APC System**

The Kassel WTE plant was retrofitted and optimized by Steinmüller in order to meet the limits of the 17<sup>th</sup> BImSchV. For this purpose, the existing semi-dry flue gas cleaning plant was upgraded with a new lime slaking system and optimized with the help of new control equipment. An ACR and a LTSCR-plant for  $\text{NO}_x$  removal were retrofitted. The retrofit also includes a catalyst for the reduction of CO emissions.

The function of the ACR is to separate heavy metals, dioxins/furans, particulate matter and other residual pollutants such as HCl and  $\text{SO}_2$ . The spent activated char is fed back to the furnace for disposal. In order to prevent the quantitative accumulation of the high volatile heavy metals especially mercury in the APC system, a sink must be provided upstream of the ACR.

In 1994, a Steinmüller  $\text{Na}_2\text{S}_4$  injection system was installed as a mercury sink. The diluted  $\text{Na}_2\text{S}_4$  is injected into the flue gas duct directly downstream of the ESP at a temperature of 220-240°C. The  $\text{HgS}$  produced is almost completely removed by means of the fabric filter. The location of the  $\text{Na}_2\text{S}_4$ -nozzle (approximately 25m upstream of the spray absorber) leads to a minimum residence time of 1.3 s. Dependent on their size, the droplets are evaporated after at most 0.5 s, thus, the droplets do not touch the ducts.

## Trial Run and First Operational Results

As a result of measurements made in 1994, the  $\text{Na}_2\text{S}_4$  concentration was adjusted to approximately 30 mg/dscm in order to achieve a total mercury reduction of approximately 50%. Even though removal efficiencies of over 90% could be achieved, this removal efficiency seemed to be sufficient for the character of a pure Hg sink. Now the installed ACR ensures mercury emissions far below the mercury limit of the 17<sup>th</sup> BImSchV.

Steinmüller conducted two series of measurements (Figure 2). Gaseous samples were taken from the raw gas upstream of the  $\text{Na}_2\text{S}_4$  injection, the intermediate gas from the spray absorber and the clean gas upstream of the stack. Furthermore, salt samples from the spray absorber, as well as samples of the residues, were examined. The total mercury concentration of the raw gas varied between 57 and 212 g/dscm @ 11%  $\text{O}_2$  (Figure 3) and, thus, is in the typical concentration range of WTE plants (30 - 700 g/dscm @ 11%  $\text{O}_2$  or even more in case of mercury peaks) as mentioned in the literature. At a rate of 48 to 83% the removal of total mercury is variable at a constant  $\text{Na}_2\text{S}_4$  dosage of 30 mg/dscm.

The behavior of the individual mercury species in the flue gas cleaning plant differs. The separation efficiencies in the entrained-flow phase and the fabric filter for ionic and elemental mercury differ from one another. The average  $\text{Hg}^0$ -portion of 7.3 to 5.8% in the clean gas is significantly below the average portion of 27.5 to 14% in the raw gas. Consequently, far better removal rates can be expected for elemental mercury. The total removal of elemental mercury is more than 80% with an average of 89.4%.

Recent experience shows that if the quantity of  $\text{Na}_2\text{S}_4$  is increased to 45 g/dscm, mercury capture can be increased up to 87-97% (Figure 4). The mercury leaves the plant in form of non-poisonous  $\text{HgS}$  as the analysis of residue samples confirmed.

### **Ebenhausen**

In December 1996, the hazardous waste incineration plant Ebenhausen (SAVA Ebenhausen) was retrofitted with a  $\text{Na}_2\text{S}_4$  injection system to comply with the Hg emission limits set forth in the 17<sup>th</sup> BImSchV.

The APC system of the SAVA (Figure 5) consists of an ESP for dust collection and a multi-stage scrubber with acidic and alkaline circuits suitable for the separation of HCl, HF,  $\text{SO}_3$ ,  $\text{SO}_2$ , as well as mercury and residual dust. Downstream of the scrubber the flue gas is cooled down by approximately 10K in the cooler, thus it is lower than the saturation temperature. Next, the gas goes to a wet ESP. This stage has been primarily designed in order to remove aerosols and to avoid  $\text{SO}_2$  peaks. Before leading the flue gas into the stack, it is mixed with hot air i.e. its temperature is raised by approximately 15K, and consequently, the plume is minimized. Activated carbon is added to the flue gas in the acidic circuit as well as upstream of the flue gas cooler to separate the dioxins/furans.

However, if hazardous waste containing mercury is applied in an amount being most desirable for hazardous waste incineration plants and resulting in a raw gas concentration of approximately 2 mg/dscm, a value of 0.2 mg/dscm can barely be maintained. Due to this fact, the operator asked for the support of Steinmüller to additionally inject  $\text{Na}_2\text{S}_4$  in order to achieve a Hg limit value during continuous operation that complies at least with the required limit value of 0.05 g/dscm of the 17<sup>th</sup> BImSchV.

The injection of  $\text{Na}_2\text{S}_4$  in an aqueous solution resulted in a Hg reduction that was approximately 83% on the average. The achieved mercury concentration was far below the 50 g/dscm required in the 17<sup>th</sup> BImSchV. The average of the mercury clean gas concentration was approx. 0.02 g/dscm. Waste

water analysis showed an increase of the mercury concentration by a factor of approx. 10. This separated mercury reaches the waste water plant, where it is precipitated and is found as non-poisonous HgS in the heavy metal sludge. The readout of the continuous Hg emission monitoring system shows a spontaneous change in the Hg outlet concentration depending on the injection of Na<sub>2</sub>S<sub>4</sub> (Figure 5).

Due to the positive results the owner placed an order with Steinmüller for the installation of a Na<sub>2</sub>S<sub>4</sub> injection system including its own supply station. This plant consists of the injection system as well as a container installed in a drain vat. In the container the Na<sub>2</sub>S<sub>4</sub>-drums, a mixing vessel, pumps, the control and the necessary safety equipment are located. Within eight weeks after confirmation of the order an Na<sub>2</sub>S<sub>4</sub> injection and supply station had been delivered, installed and started.

### **Additional Plants with Na<sub>2</sub>S<sub>4</sub> Application for Mercury Reduction**

As a result of the convincing removal efficiency of mercury, other WTE plants (apart from Kassel and the SAVA Ebenhausen) were also equipped with Na<sub>2</sub>S<sub>4</sub> injection (Figure 7). In case of the Dutch plant GEVUDO Dordrecht (Figure 8), which consists of four combustion units with two APC lines, the Na<sub>2</sub>S<sub>4</sub> is injected prior to a fabric filter after the flue gas has been quenched down to approx. 170°C. In addition, activated char powder is added upstream of the fabric filter, as a result dioxins and furans are already separated at this stage. A multi-stage wet scrubbing system as well as a high-temperature SCR plant with integrated oxidation catalyst for the destruction of dioxins and furans completes the APC system.

Na<sub>2</sub>S<sub>4</sub> as an additive was chosen because the flue gas of two incineration units is not led to a boiler but is suddenly quenched down to approximately 170°C. As a result of the very short residence time the elemental mercury will increase and, therefore, cannot be removed in the downstream wet scrubbing system. Due to the Na<sub>2</sub>S<sub>4</sub> dosing, the amount of carbon required for the separation of dioxins can be minimized. Also, the oxidation catalyst functions as a dioxin sink. Then the Na<sub>2</sub>S<sub>4</sub> (as an additional reactant), supports the separation of mercury at reduced amounts of activated carbon.

In case of the sewage sludge incineration plant VERA Hamburg (Figure 9), Na<sub>2</sub>S<sub>4</sub> is injected at a temperature of approximately 145°C upstream of a two-stage wet scrubbing system to improve the mercury separation efficiency of the first scrubber. The main purpose of this first scrubber is to remove HCl. Therefore, less mercury is to be found in the neutral SO<sub>2</sub>-scrubber, resulting in gypsum containing a minimum of mercury. As, moreover, the spent adsorbent of the downstream arranged entrained-flow reactor is to be returned into the furnace to thermally destroy the dioxins and minimize residues, Hg-separation of the HCl-scrubber is improved and supports its efficiency as a Hg-sink.

Another example of a hazardous waste incineration plant is RVA Böhlen (Figure 10) where mercury raw gas values of up to 6 mg/dscm are to be expected. The emission limit permitted for this plant is 0.01 g/dscm. The required high removal efficiency of about 99.9% is achieved by means of three process steps: first the Na<sub>2</sub>S<sub>4</sub> injection upstream the spray dryer and fabric filter, second low pH wet scrubbing and last, fine polishing within an ACR.

As the spent activated char of the ACR is returned into the rotary kiln, the removal of mercury supported by Na<sub>2</sub>S<sub>4</sub> is the predominant mercury sink. Moreover, accumulation processes of heavy metals are minimized. Such processes can occur due to the mercury release in the spray dryer during the evaporation of the neutralized effluent of the HCl scrubber. Another advantage of the Na<sub>2</sub>S<sub>4</sub> injection is the small amount of mercury in the gypsum, thus wallboard quality gypsum is produced. This is achieved due to a high removal of mercury of up to 98% by means of a combination of the Na<sub>2</sub>S<sub>4</sub> injection system and the HCl scrubber. In this plant the mercury is also found in the residue of the fabric filter as immobile and non-poisonous mercury sulphide.

## DESCRIPTION OF THE MOBILE $\text{Na}_2\text{S}_4$ INJECTION UNIT

In addition to the above mentioned full scale applications, Steinmüller has also designed a mobile  $\text{Na}_2\text{S}_4$  dosing unit including injection equipment to prove the efficiency of the new process on site. This mobile unit is a particularly important innovation since the influence of essential boundary parameters on mercury separation, such as temperature, residence time, flue gas composition, etc., are optimized on site and the most favorable injection point can be selected.

Figure 11 shows the principal scheme of the mobile experimental unit which also contains all the main components found in permanent installations. The unit for the  $\text{Na}_2\text{S}_4$ -injection consists mainly of lances including supplying pipes and pumps, a mixing vessel, and components to supply the unit with make-up water and compressed air. Permanent installations are also provided with a control unit.  $\text{Na}_2\text{S}_4$  as a concentrate (40%) which is mixed off site, is either delivered in 55 gal. drums or by tanktruck.

The concentrate is diluted with make-up water to a 5-10% solution in a mixing vessel and the mixing is carried out by an agitator. The diluted solution is pumped from the mixing vessel to the injection point via insulated and heated pipes and then cocurrently injected into the flue gas duct via a dual fluid nozzle.

The  $\text{Na}_2\text{S}_4$ -injection of the mobile unit has been designed for a constant flow rate. This is sufficient for most of the applications. Variations of the flow rate can only be carried out manually. As required the  $\text{Na}_2\text{S}_4$ -dosing plant can also be equipped with a controlled flow rate, e.g. using the steam flow rate or the Hg CEMS as a signal.

The initial investment cost of a full-scale, i.e. permanent  $\text{Na}_2\text{S}_4$ -Plant add up to about U.S. \$250,000 dependent on capacity and local conditions. The additive cost vary largely with the mercury amount which has to be removed, the flow rate of the flue gas and its composition, the injection temperature and the residence time as well. Most commonly additive cost are in the range of 40¢ to 70¢ per ton of waste.

Due to the special difficulties associated with the sampling and the analysis for the various species of mercury,<sup>12</sup> Steinmüller also offers this service using our own sampling equipment, Hg-analyzers and other laboratory equipment and specially trained staff.

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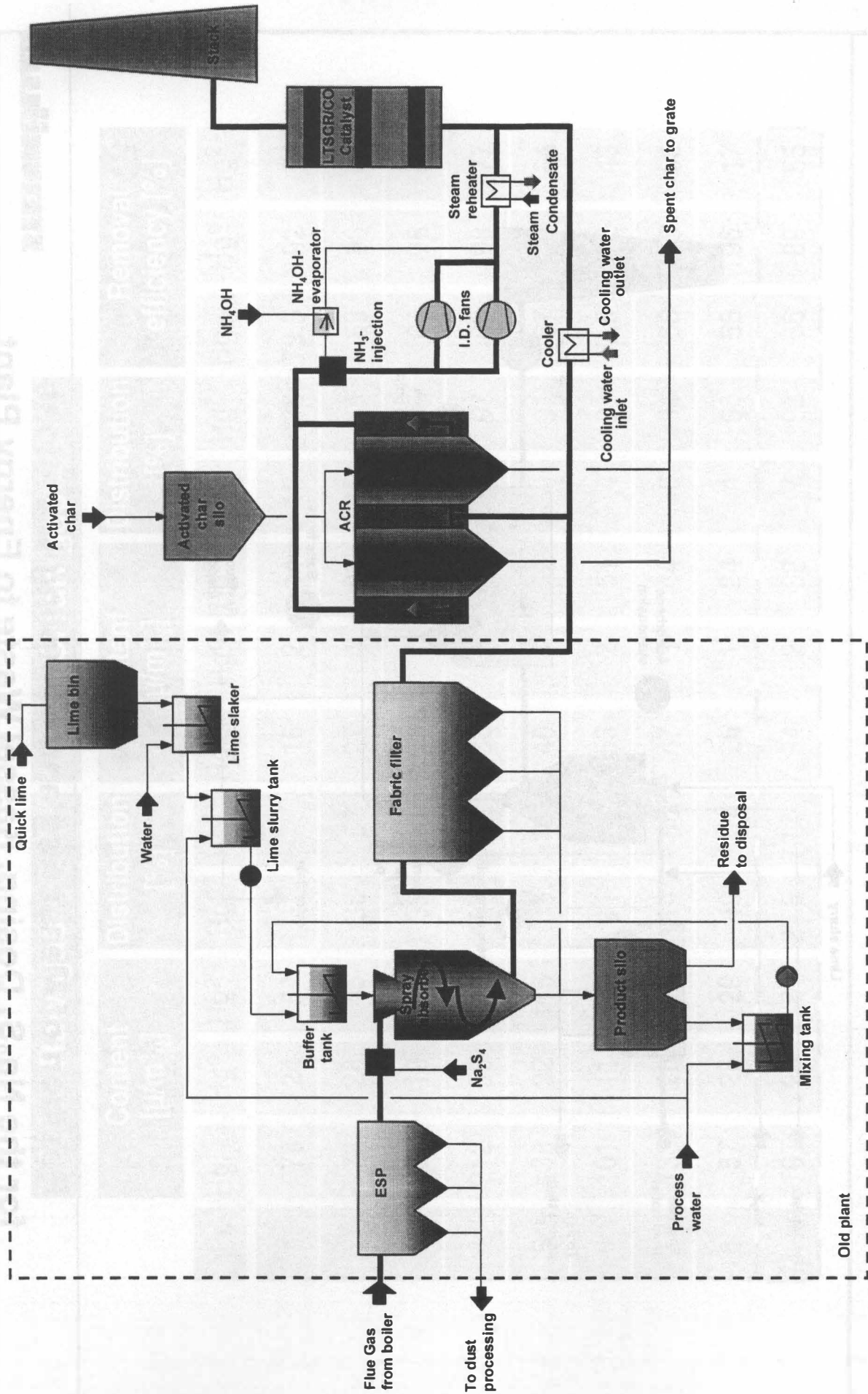
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- <sup>13</sup> Klein, M.R.; Kubisa, R.; Schüttenhelm, W.: Emissionen von Lachgas (N<sub>2</sub>O) und Quecksilber (Hg) bei der Klärschlammverbrennung, VDI-Seminar "Klärschlammverbrennung II", 5./6. December 1996, Bamberg.
- <sup>14</sup> Hartenstein, H.-U.; Licata, A.; Klein, M.: Comparison of Mercury Test Methods, ASME, 05.-08.06.1994, Boston.

Table 1. Selected physical properties of Hg and Hg-compounds

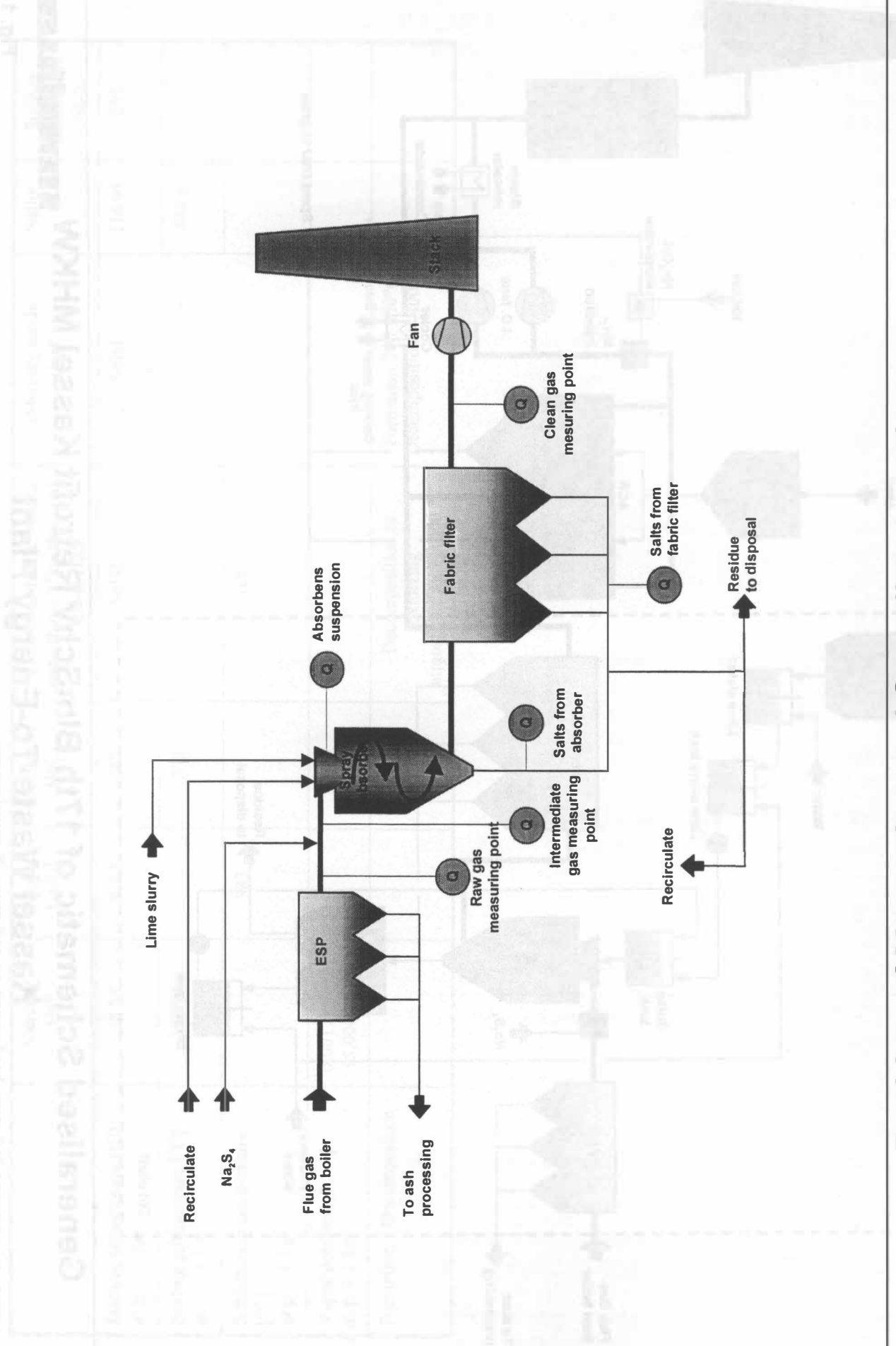
	Mercury Hg <sup>0</sup>	Calomel Hg <sub>2</sub> Cl <sub>2</sub>	Sublimate HgCl <sub>2</sub>	'Meta-cinnabarite' black, meta-stable 'Cinnabar' red, stable HgS	Mercury oxide HgO	Sulfur S	Sodium tetrasulfide Na <sub>2</sub> S <sub>4</sub>
Melting temperature [°C] at p = 1 bar	-38.84	Solid	280	Solid	Solid	118.95	275
Boiling temperature [°C] at p = 1 bar	356.95		303			444.6	
Sublimation temperature [°C] at p = 1 bar		383		580			
Vapor pressure [20°C] at p = 1 bar	0.0017 mbar = 15,000 µg/m <sup>3</sup>						
Formation / Decomposition				Decomposition in oxidizing atmosphere and ≥ 400 °C	Formation 300-350°C Decomposition > 400°C		



**Generalised Schematic of 17th BImSchv Retrofit Kassel MHKW Kassel Waste-To-Energy Plant**

**Fig. 1**

Table 1. Selected physical properties of the acid by-product



**Position of Measuring and Sampling Locations  
for the Na<sub>2</sub>S<sub>4</sub> Dosing, Kassel Waste to Energy Plant**

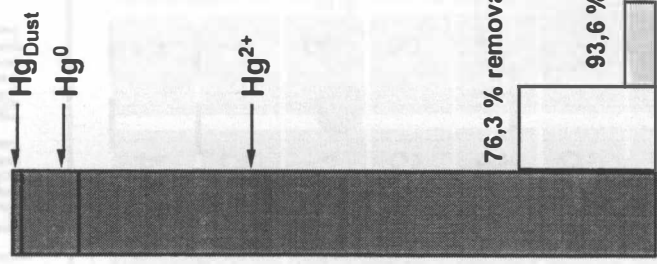
No.	Raw gas						Clean gas							
	Content [ $\mu\text{m}^3\text{N}$ ]			Distribution [%]			Content [ $\mu\text{m}^3\text{N}$ ]			Distribution [%]			Removal efficiency [%]	
	Hg <sub>ges</sub>	Hg <sup>o</sup>	Hg <sup>2+</sup>	Hg <sup>o</sup>	Hg <sup>2+</sup>	Hg <sup>2+</sup>	Hg <sub>ges</sub>	Hg <sup>o</sup>	Hg <sup>2+</sup>	Hg <sup>o</sup>	Hg <sup>2+</sup>	Hg <sub>ges</sub>	Hg <sup>o</sup>	Hg <sup>2+</sup>
1	78	24	54	31	79	16	2	14	12	88	79.5	92	74	
2	73	28	45	38	62	27	4	23	15	85	63	86	49	
3	57	19	38	33	67	20	1	19	5	95	65	95	50	
4	212	58	154	27	73	36	1	35	3	97	83	98	77	
5	138	22	116	16	84	46	4	42	9	91	67	82	64	
6	101	11	90	11	89	53	2	51	4	96	47.5	82	43	
7	138	20	118	14	86	47	3	44	6	94	66	85	63	
8	57	28	29	49	51	25	1	24	4	96	56	96	17	
Mean	107	29	81	27.5	72.5	34	2	32	7	93	66	89	55	

Results of Trial Run with Na<sub>2</sub>S<sub>4</sub> Injection  
Kassel Waste-To-Energy Plant, November 1995

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Fig. 3

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$Hg_{ges}$  [mg/m<sup>3</sup>]

[ ] = upstream of

[ ] = downstream

of fabric filter

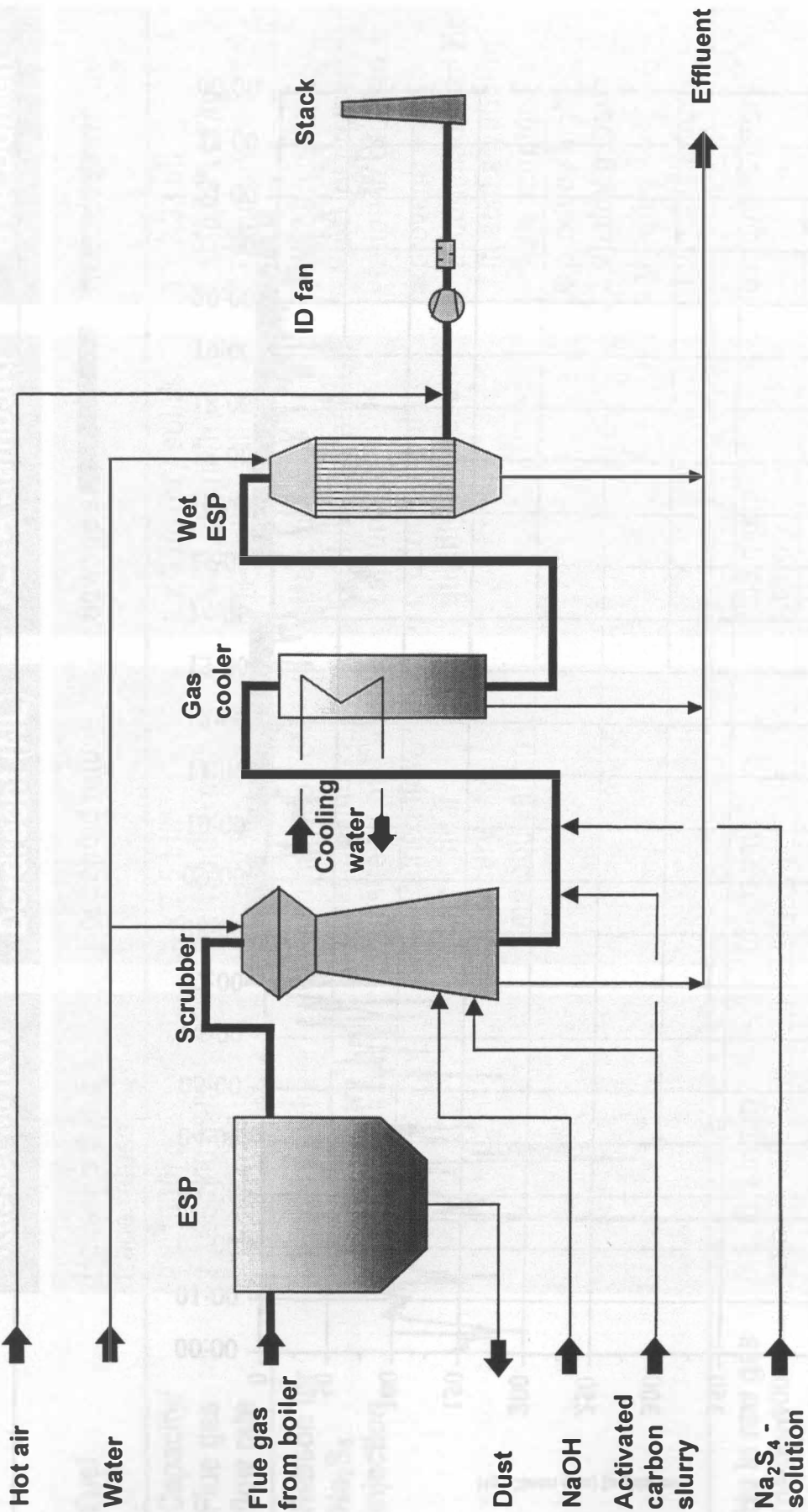
= 17. BlmschV

$Na_2S_4$  - Injection

# Mercury Removal by Injection of $Na_2S_4$

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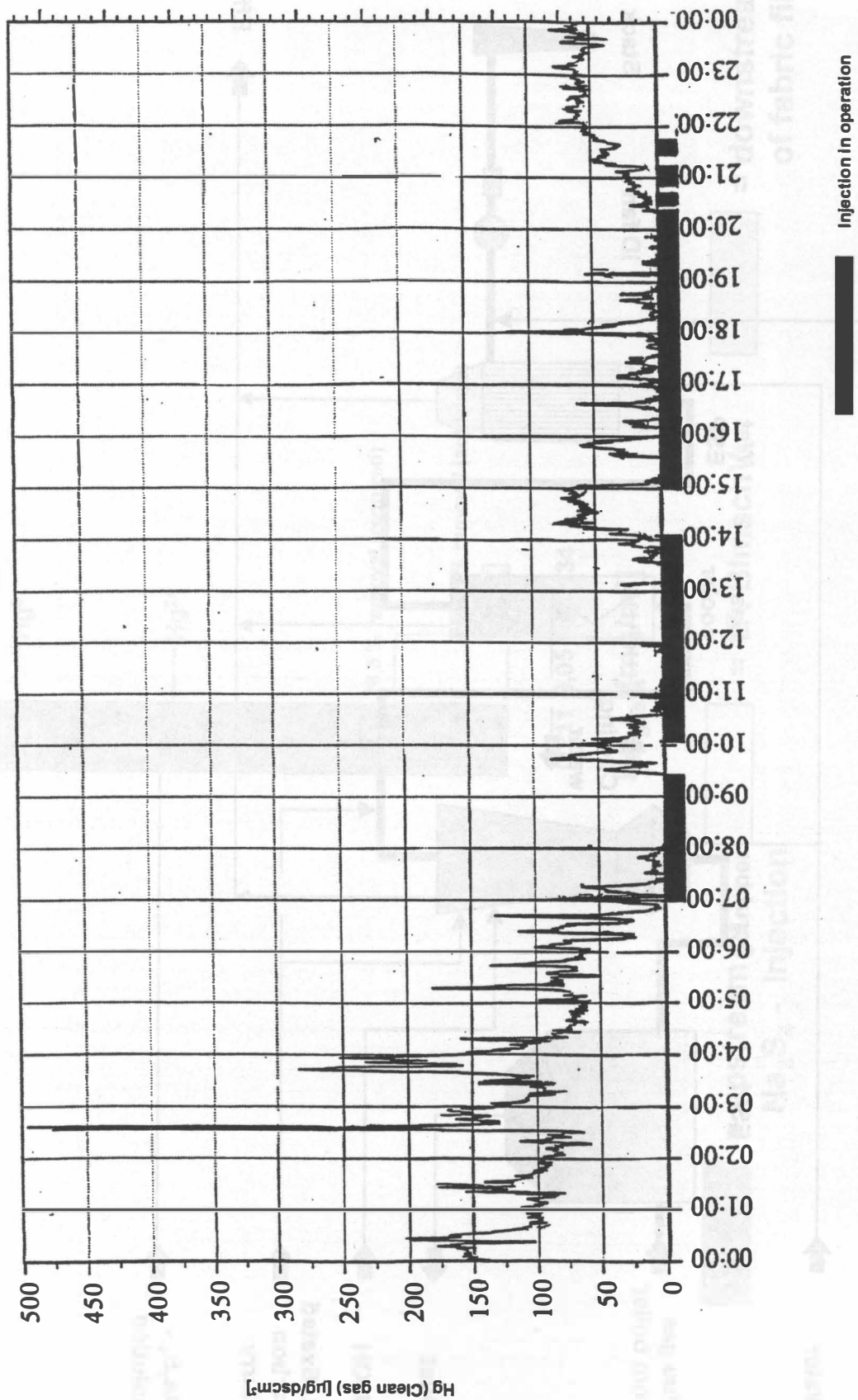
Fig. 4



**Generalised Schematic of Flue Gas Cleaning Plant**  
**SAVA Ebenhausen**

**STEINMÜLLER**

Fig. 5



**Clean Gas Concentration of  $Hg_{total}$  at SAVA Ebenhausen  
with Discontinuous  $Na_2S_4$  - Injection (1996-09-05)**

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Fig. 6

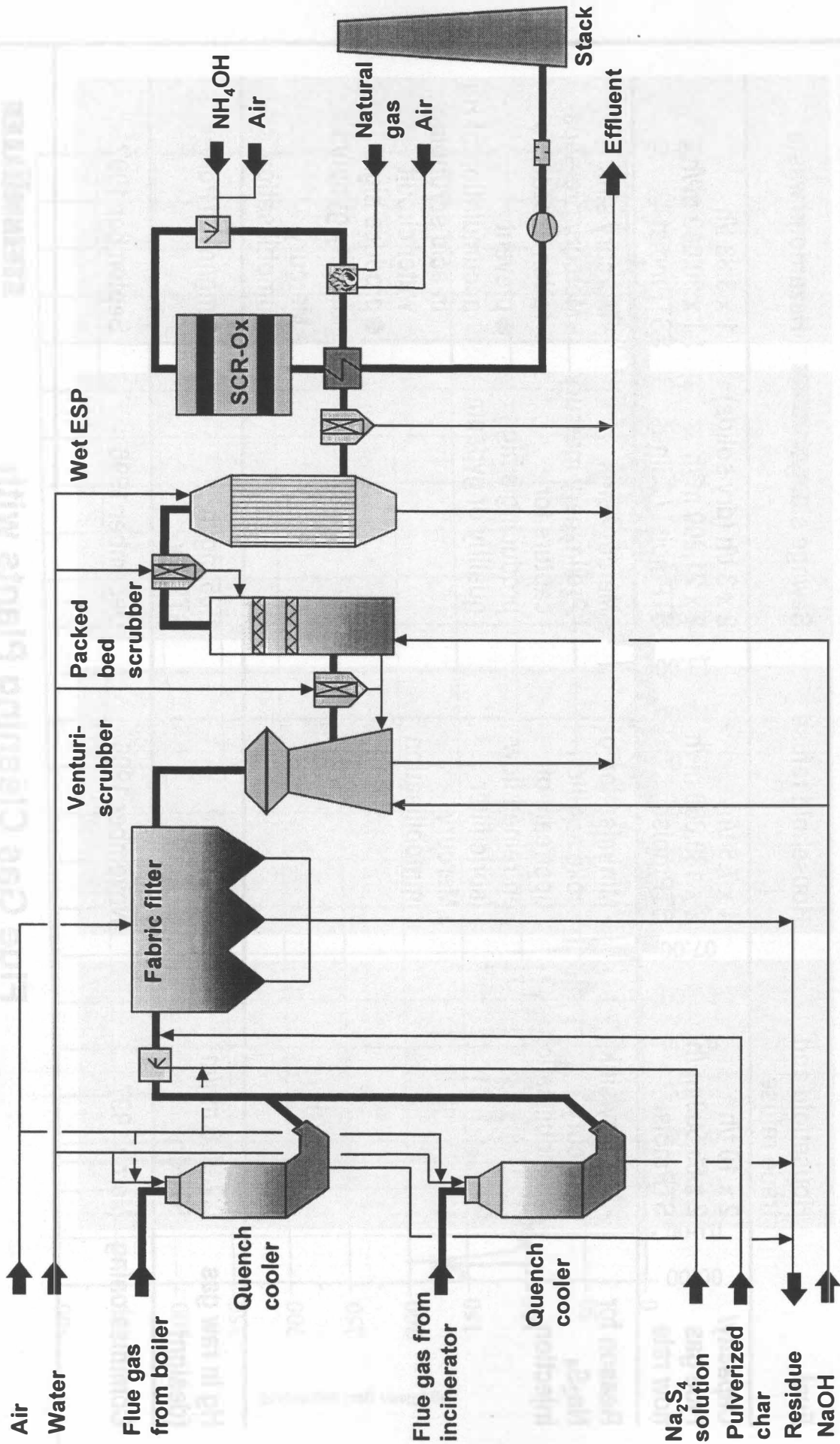


	<b>Kassel MHKW</b>	<b>Gevudo Dordrecht (NL)</b>	<b>VERA Hamburg</b>	<b>RVA Böhlen</b>
<b>Fuel</b>	Household and trade refuse	Household refuse	Sewage sludge	Hazardous waste
<b>Capacity/ Flue gas flow rate</b>	2 x 10 t/h 2 x 65,000 m <sup>3</sup> /h STPmoist	4 x 7.5 t/h 2 x 130,000 m <sup>3</sup> /h STPmoist	2 x 3 t/h (dry solids) 2 x 21,200 m <sup>3</sup> /h STPmoist / 3 lines	1 x 3.33 t/h 1 x 30,000 m <sup>3</sup> /h STPmoist
<b>Reason for Na<sub>2</sub>S<sub>4</sub> injection</b>	- Mercury sink - Mercury immobilisation	- Minimisation of coke addition upstream of entrained flow fabric filter - Mercury immobilisation	- Mercury sink - Preliminary mercury capture for producing a high quality of gypsum	- Mercury sink - Mercury pre-separation in order to prevent accumulation of Hg in acid scrubbing water circuit ● produce high quality gypsum - Mercury immobilisation
<b>Hg in raw gas (design)</b>	0.2 - 0.6 mg/m <sup>3</sup> STPdry	0.7 mg/m <sup>3</sup> STPdry	1.35 mg/m <sup>3</sup> STPdry	6 mg/m <sup>3</sup> STPdry
<b>Commissioning</b>	March 1997	November 1996	December 1996	September 1997

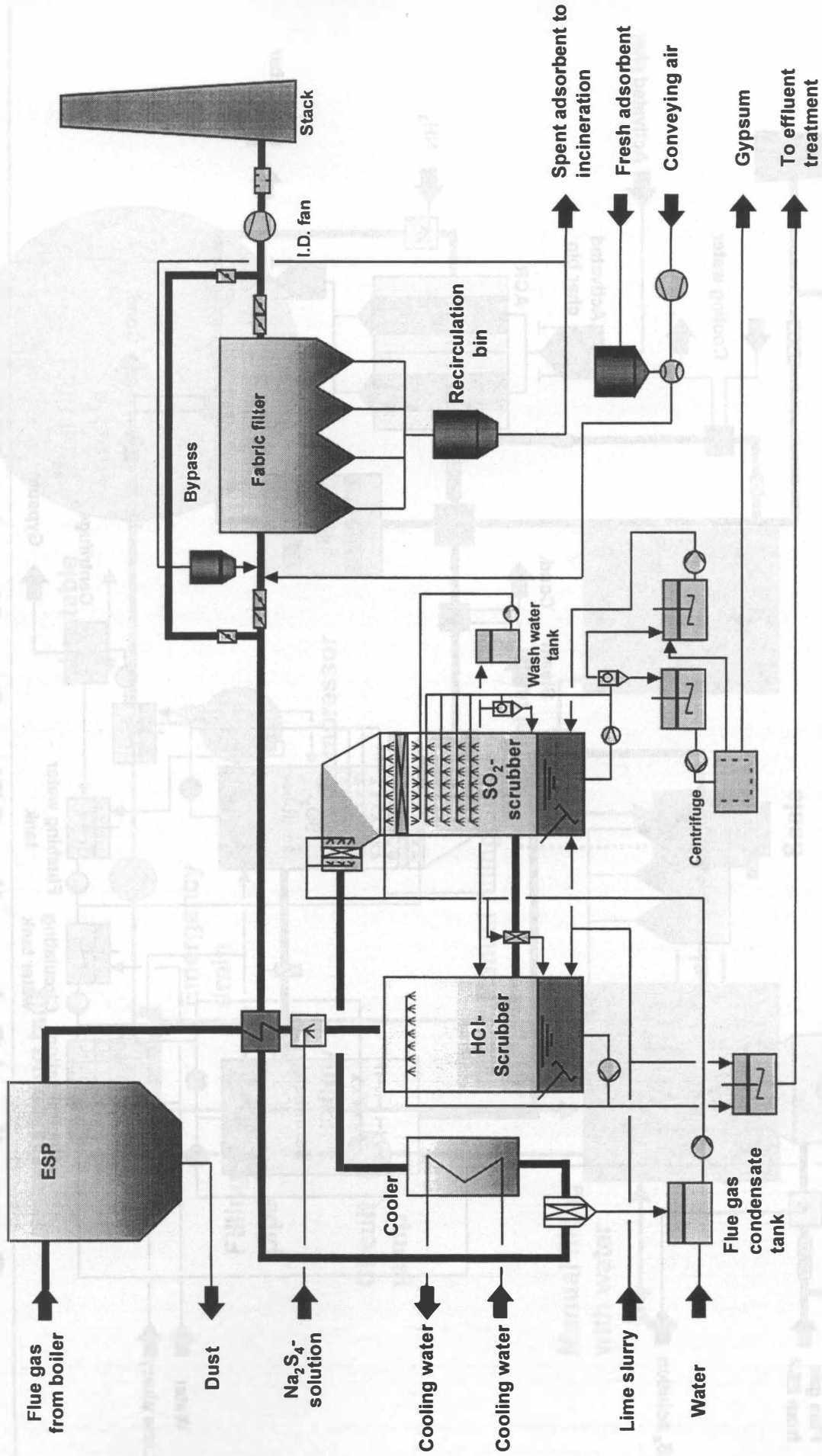
**Flue Gas Cleaning Plants with Na<sub>2</sub>S<sub>4</sub> Injection**

**STEINMÜLLER**

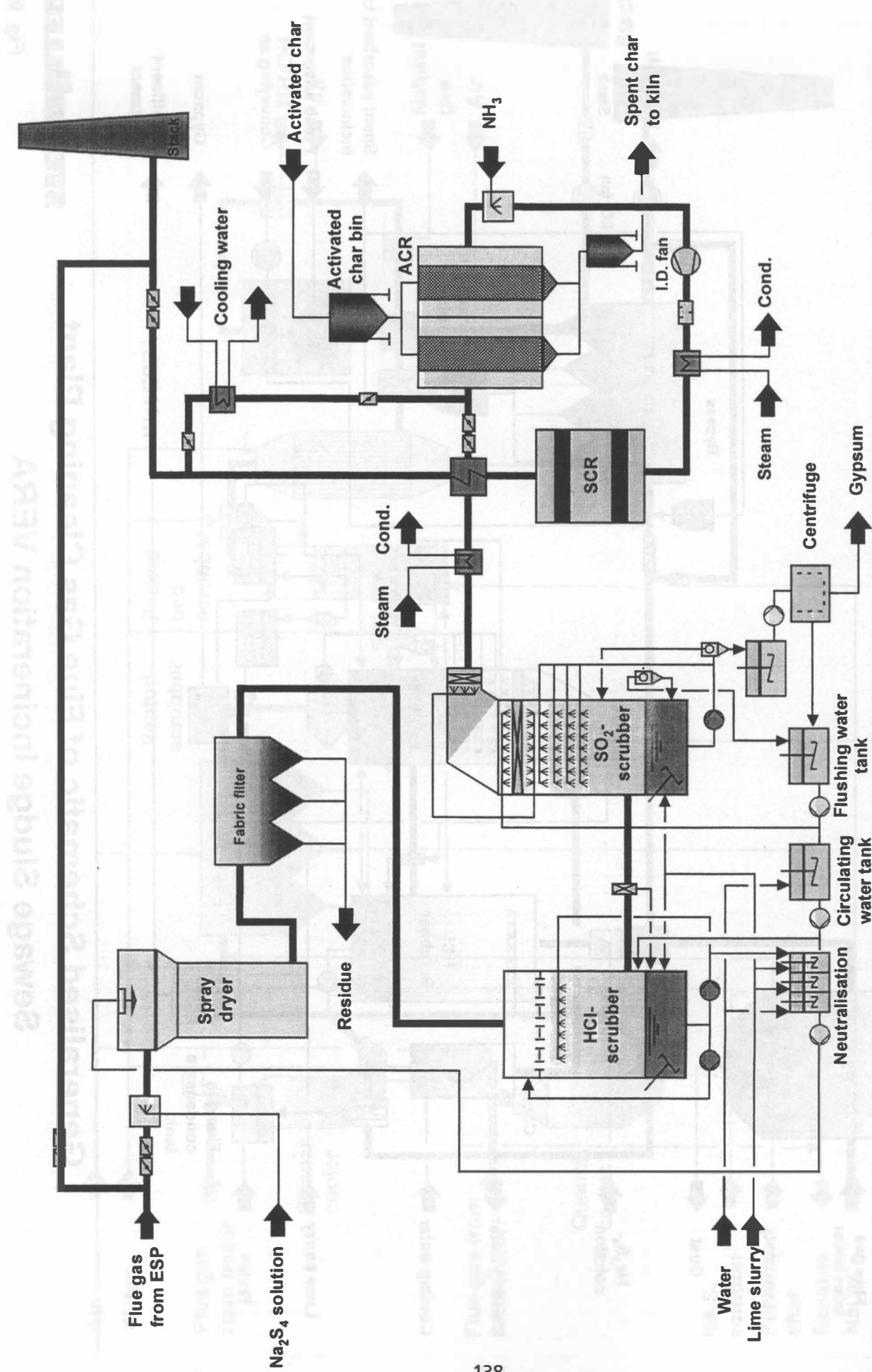
Fig. 7



**Generalised Schematic of  
Flue Gas Cleaning Plant Gevudo**



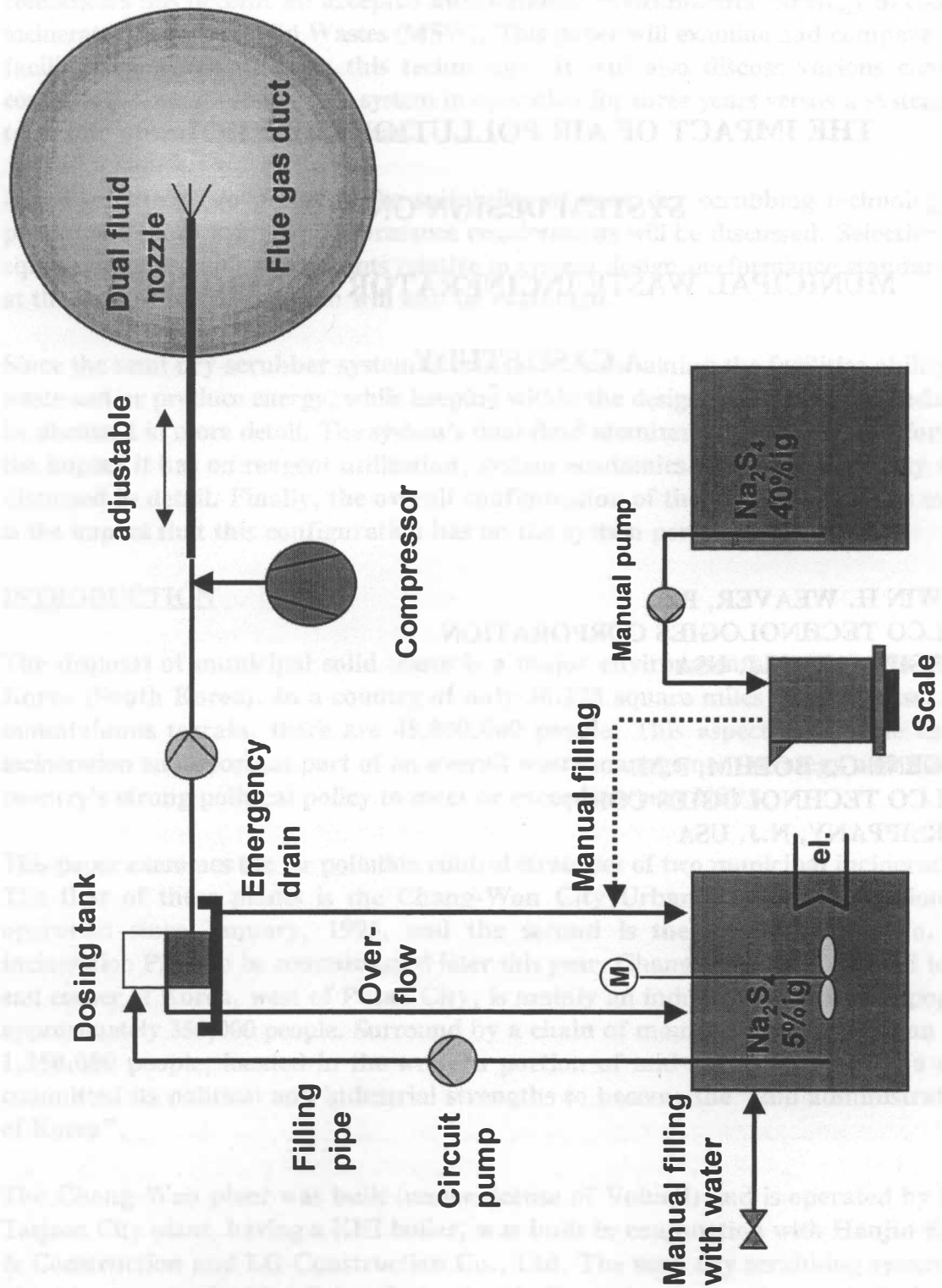
**Generalised Schematic of Flue Gas Cleaning Plant  
Sewage Sludge Incineration VERA**



**Generalised Schematic of Flue Gas Cleaning Plant**  
**RVA Böhlen**

**STENMÜLLER**

Fig. 10



**Schematic Representation of Mobile Test Unit for  $\text{Na}_2\text{S}_4$  injection**