1 Introduction

Safety and economic concerns are not the only issues facing the global energy supply, environmental compatibility must also be ensured. There is ever increasing importance on the source of power in the creation of energy. Even though the use of coal is predicted to fall in different scenarios [1], it is still an important source of global electricity generation. In the year 2021 for example, there was a large rebound in coal and oil use [1]. An increasing input of renewables in power generation [1] leads to new requirements of the flue-gas cleaning with regard to load flexibility. Furthermore, flue-gas cleaning is of importance in the context of biomass firing. The firing of coal or biomass leads to the emission of mercury (Hg) and its compounds, which are toxic pollutants. Mercury emissions are a global problem due to their distribution and the bioaccumulation of mercury. For example, coal burning in power generation resulted in the emission of about $292\ t$ of mercury worldwide in 2015 [2]. Although the effects of emission reduction will only become apparent in the future, the emission of mercury has to be reduced in order to cope with the issue. Recent developments in the energy sector show that flue-gas cleaning is becoming an ever more important issue.

In dual-loop flue-gas desulphurization systems, water-soluble components can be absorbed and mercury emissions from thermal power plants can be reduced. Although the technology is well-known and highly developed in real scale, there are very few studies available regarding the behaviour of mercury in dual-loop systems. Theoretically, it believed that the more complex process of the dual-loop process offers increased opportunities of settings and should be able to absorb mercury equally well or even better than in the standard single-loop process.

In this thesis, the absorption process is described by the term "removal of mercury". Due to absorbed mercury being partially reemitted, the term "retention of mercury" is used for the description of the mercury reemissions: high mercury retention is equal to low mercury reemission. Mercury reemission ratios are calculated as percentages of the removed mercury compounds. In summary, the total removal efficiency of mercury in FGDs is characterized by both the removal, and by the retention of mercury. Based on the state of art and science, experiments were performed in a laboratory scale and technical scale dual-loop FGD to investigate the parameters which play a key role in Hg removal and retention of the dual-loop FGD system. Furthermore, investigations will be made to understand how flue-gas composition contributes to the removal and reemission of mercury and how the FGD process could be modified in order to optimize the total mercury removal by adaption to the flue-gas composition and the scrubber chemistry.

Parts of the results presented in this thesis were previously published, including the influence of the pH-value (pH) in single-loop FGD on SO_2 and Hg emissions [78]. Major results from this thesis, on mercury removal and retention in dual-loop FGD including the influence of sulphite and halides, were presented in [3]. Furthermore, results were published in the following articles as second author, including [99], the experimental results in pH, SO_2 and $HgCl_2$ absorption and reemission of mercury in a dual-loop FGD. In [8], the author's contribution was the mass balance of mercury in the FGD while co-firing biomass at a laboratory scale firing system. Regarding other scientific publications, the author's contribution was mercury sorption in an overview article on mercury in thermal power plants [6].

In the context of this work, the following theses were successfully written under the supervision of the author at the University of Stuttgart, Institute of Combustion and Power Plant Technology – IFK: Staiger, Fabian: Experimental Investigations on the Solubility of Limestone and Gypsum in Slurries of Dual-Loop Flue Gas Desulfurization Systems [35]; Ötzel, Thomas: Investigation on mercury removal of flue gas desulfurization in a laboratory-scale firing [93], Heinemeyer, Philipp: Investigation on mercury removal of double-loop flue gas desulfurization in a laboratory-scale firing [94]; Dörr, Christian: Study Of The Behaviour of the Trace Element Mercury In The Flue Gas Cleaning Pathway Of A Laboratory Scale Firing Consisting Of SCR DeNOx Catalyst, Electrostatic Precipitator And Dual Loop Desulphurization System [95]; Fluhr, Johannes: Increasing efficiency of dual-loop wet flue-gas desulphurization by the use of additives [96]; Hezel, Fabian: Experimental Investigations at a Flue Gas Desulphurization Pilot Plant [97].

2 State of the science

In this section, a scientific understanding to the behaviour of mercury in dual-loop flue-gas desulphurization systems is described. Focus is given to the qualification of the dual-loop desulphurization process in the context of mercury removal and retention.

During the combustion process in fossil-fired thermal power plants, pollutants like hydrogen halides and mercury, carbon dioxide, nitrogen oxide, sulphur dioxide and dust, are released and dependent upon variations in fuel composition. For instance, nitrogen monoxide is formed in thermal-, fuel- and prompt-mechanism. Sulphur dioxide (SO_2) is formed from the combustion of sulphur-containing fuels, according to eq.2-1 [4]. The standard enthalpy of formation ΔH_f^0 is given in eq.2-1.

$$S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)} \qquad \Delta H_f^0 = -297\,\frac{\mathrm{kJ}}{\mathrm{mol}} \qquad \text{(eq.2-1)}$$

Typical sulphur contents in hard coal are lower than one per cent. Typical mercury contents vary within the range of 0.02 to $10\ mg/kg_{\ (daf)}$ [6], depending on the fuel. Secondary fuels like sewage sludge can contain up to $10\ mg/kg_{\ (daf)}$ [5]. A correlation of the mercury content and the grade of coalification, to separate the mercury content from organic and inorganic parts, has not been sufficiently clarified [7]. Due to its vapour pressure, mercury is released in its elemental form (Hg^0) at combustion temperatures higher than $1273\,K$. At this temperature, mercury compounds decompose, and release elemental mercury. This means that the emission behaviour of mercury cannot be influenced by firing conditions, only by flue-gas cleaning.

2.1 Flue-gas desulphurization processes

In this section, in relation to the qualification of the processes for mercury removal, common desulphurization processes are described. The processes are separated into wet, quasi-dry, dry and other processes. The section concludes with a short overview on the importance of wet limestone FGD.

In wet scrubbing processes, the flue-gas is in contact with a liquid. This is realized in a scrubber in order to achieve a large contact area of the liquid and gas phases.

Spray absorbers are the dominating technology, as venturi scrubbers come along with a higher pressure drop [16]. In wet limestone desulphurization systems, limestone or burnt lime products are used for the neutralization of the absorbed sulphur dioxide. Besides limestone, other neutralization media are used, for instance sodium sulphite. The latter is used in the Wellman-Lord process [17]. This process is regenerative, which means that the absorbent is recirculated. Sulphur dioxide is absorbed with sodium sulphite, which reacts to sodium bisulphite with one oxonium ion. The heating of the solution during regeneration leads to the release of sulphur dioxide, which can be reduced to either hydrogen sulphide or to sulphur in the Claus process. The Wellman-Lord-process has the advantage of being a regenerative process which produces elemental sulphur, but it is also complex and requires a lot of energy for the regeneration and the production of sulphur. So far, the behaviour of mercury in this process has not been examined within technical literature.

The Walther process is a combined process for desulphurization and denitrification of flue-gas with ammonia. The product is ammonia sulphate, which can be further used as a fertiliser [16]. But if mercury is absorbed, it has to be removed to avoid it becoming part of the fertiliser and possibly entering the food chain.

Quasi-dry processes benefit from a wet sorbent, which absorbs SO_2 due to its water solubility. The water evaporates and the dry sorbent is later removed by a particle filter. Sodium or calcium-based compounds are used. The final product for calcium-based processes is a mixture of gypsum, calcium sulphite and calcium oxide, which can be further treated thermally in order to obtain a higher gypsum concentration [16] [122]. It is advantageous that no wastewater is generated [16]. On the other hand, no pure gypsum is produced and fly ash contamination of the gypsum, as well as significant mercury contents are possible. It can be assumed that mercury is absorbed and then reemitted by evaporation while the absorbent is dried. The subsequent deposition of mercury containing particles is another aspect which is disadvantageous within this process.

Dry desulphurization processes can underlie the principle of physical adsorption, by using, for example, activated coal. Another possibility is chemical absorption by additives like calcium oxide or magnesium oxide [16]. The dosage of the additive can be realized at various points of the flue-gas path or in the firing system, for instance, in a spray dryer absorber. Fluidized bed firings, for example, achieve good desulphurization results by the addition of additives to the fuel [18]. The removal of SO_2 is significantly influenced by the temperature. Furthermore, calcium-based additives have a stronger capacity to absorb SO_2 than magnesium-based additives and they have a larger temperature range [16]. The range is set by the activation energy for the chemical reaction on the lower limit and the equilibrium on the gaseous phase on the upper limit [16]. Dry desulphurization processes achieve sufficient high removal efficiencies only at superstoichiometric dosing rates [16]. The mercury removal is reported between 24 and $98\,\%$ in dependency on the used fuel [114].

Further processes include the DESONOX process, where the flue-gas passes a hot ESP and then after sufficient heating, enters a reactor containing two types of catalyst, with a temperature (T) between 703 and $743\,K$ [17]. The first catalyst is a SCR DeNOx system containing titanium dioxide, which promotes the reaction of ammonia and NO_x to nitrogen and water. The second catalyst contains vanadium pentoxide and promotes the conversion of SO_2 to SO_3, which is condensed as sulphuric acid. Two scrubbers follow which remove hydrogen halides and the remaining sulphuric acid, as well as a bag house filter for sulphuric acid aerosols [17]. In this process, the degree of sulphuric acid and the slurry of the second washing step, have to be monitored to measure any containment of mercury.

Another process is the use of activated carbon [17]. This is a regenerative process with the principle of physical adsorption. SO_2 adsorbs onto activated coal and is desorbed as rich gas at $T = 673\,K$. The rich gas is cleaned by wet scrubbing in order to absorb heavy metals like mercury [17]. As a result, sulphuric acid is produced. Due to the additional scrubbing, high mercury removal efficiencies are assumed to be achieved. In total, the process is very complex and it is rather used in thermal waste utilization.

Seawater FGDs make use of the alkalinity of the seawater ($pH\,8$) as a scrubbing solution [17]. To avoid endangering aquatic life, aeration is realised in another sump, where sulphite is oxidized to sulphate [17]. This leads to a pH higher than 6.5 before the water is led into the ocean [17]. Due to the missing recirculation, the large amount of wastewater is disadvantageous. Mercury is fed into the ocean and this can negatively enter the food chain.

The importance of wet limestone scrubbing is based on the advantages of the process and its widespread usage. In Germany, the share of limestone or lime based wet FGD related to the maximum effect of the power plant, amounted to $86\ \%$ in 1990 [17]. It was followed by quasi-dry processes ($7.6\ \%$), dry additive processes ($3.7\ \%$) and the Wellman-Lord process ($1.8\ \%$) [17]. In 2004, the share of limestone, or lime-based wet FGD in Germany, already amounted to $95\ \%$, which means that the other processes shared $5\ \%$ [17]. In the same year, the worldwide share amounted to approximately $86\ \%$ of the world capacity [19]. Considering newer power plants in Germany, the share of limestone, or lime-based wet FGD is assumed to be even higher today. The large share of limestone, or lime-based wet FGD, shows the relevance of the process. Its simplicity, in contrast to the alternatives and high removal efficiencies, may be the reason. Other advantages concern mercury behaviour. In the wet FGD process, water soluble substances can be absorbed, providing a high removal efficiency of oxidized mercury compounds Hg^{2+}. The mercury sink wastewater treatment leads to a safe solution for mercury removal.

2.2 The removal of sulphur dioxide in wet flue-gas desulphurization systems

Flue-gas desulphurization systems based on the principle of wet limestone scrubbing are highly developed, both in single and dual-loop systems. In the field of mercury behaviour in dual-loop flue-gas desulphurization, experimental investigations and research have to date been insufficiently covered. A theoretical account is instead considered and suggestions are given concerning demands on further research. As a first step, sulphur dioxide removal is described both in general terms and in the dual-loop process. The removal of hydrogen halides is of high relevance, as these influence both the removal and retention of Hg in the dual-loop FGD. The main part of the section deals with a detailed description of the state of the science related to the dual-loop process. The questions emerging from the current scientific understandings, and the goal of the investigations, are set-out at the end of the section.

In the wet FGD, the flue-gas is in contact with a liquid in a scrubber, mostly in a spray absorber. Desulphurization in wet FGD, is a process which consists of multiple steps, see eq.2-6 to eq.2-14. At first, sulphur dioxide is physically absorbed in droplets. Then it is dissolved in the form of sulphuric acid and is present mainly as hydrogen sulphite in aqueous solution at pH around $4-5$, which are typical in wet FGD. The dissociation of sulphur dioxide leads to a decrease of the pH in the suspension sump by the release of oxonium ions. In wet limestone desulphurization systems, the suspension is neutralized by limestone or burnt lime products. By the aeration of the suspension in the sump, hydrogen sulphite is oxidized to sulphate. The final step is the formation of gypsum, where calcium and sulphate crystallise to calcium sulphate dihydrate together with water, resulting in the so-called FGD-gypsum. The overall reaction is formulated in eq.2-2.

$$2\,SO_{2\,(g)} + 2\,CaCO_{3\,(s)} + O_{2(g)} + 4\ H_2O_{\,(l)}$$
$$\rightarrow 2\,CO_{2\,(g)} +\ 2\,CaSO_4 \cdot 2\,H_2O_{\,(s)} \qquad \text{(eq.2-2)}$$

The desulphurization process depends on the pH of the suspension. The SO_2 absorption is promoted by high pH, as it goes along with the release of oxonium ions. In contrast, a low pH leads to an improved limestone solubility through the consumption of oxonium ions.

In the following, desulphurization in the wet FGD is regarded in general, both from the perspective of process engineering and chemistry. This is important for the operation of the FGD, because desulphurization greatly influences the removal and retention of mercury in dual-loop FGD. Following, is a description of the dual-loop desulphurization processes.

2.2.1 General processes

Regarding dimensioning of facilities, the characteristics of the absorption process can be described by a simplified mass transfer approach, [23] [26]. To describe the removal processes of wet FGD systems, the first considerations are the fundamentals of absorption. According to the two-film theory of W. K. Lewis and W. G. Whiteman [25] diffusion layers are formed at the phase boundaries, see Figure 1. These diffusion layers are the main resistance to the heat and mass transfer, while the velocity is limited by the slowest diffusion process.

p, p_{gr} absorptive partial pressures in the gas phase and gas boundary layer

c, c_{gr} absorptive concentrations in the liquid phase and liquid boundary layer

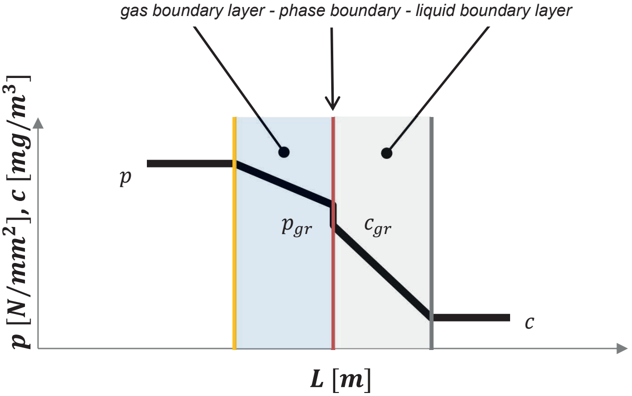

Figure 1: Diffusion layer and concentration course in the two-film theory, adapted from [25]

Diffusion laws based on the kinetic theory of gases, describe the mass transfer process in the phase boundaries. The mass transfer of the gaseous component is essentially determined by the surface of the phase boundary and the mass transfer coefficients in gaseous and liquid phase [27]. The molar flux $\dot{N}$ can be described as a function of mass transfer coefficient β, area A and concentration difference Δc_i, see eq.2-3. The two-film theory implies a dependency of the mass transfer on the phase boundary area A, which should be maximized for promoting mass transfer. Consequently, smaller droplet sizes are beneficial. Furthermore, increasing the ratio of liquid to gas phase L/G leads to decreasing concentrations in the liquid phase and a larger contact area.

$$\dot{N} = \beta\, A\, \Delta c_{\,i} \frac{1}{\tilde{M}} \qquad \text{(eq.2-3)}$$

The mass transfer coefficient on the gaseous side can be described as a function of the Sherwood number [98] [123]. The determination is conducted empirically based on the Sherwood, Reynolds and Schmidt numbers [123] [124] [125]. The mass transfer resistance in the gas phase depends on the relative speed between the gas and liquid phases [23]. In this context, there are several semi-empiric correlation equations concerning spray absorbers [27]. In the spray absorber, the residence times of the liquid and the gaseous phase are connected. The residence time of the liquid phase in the spray-absorber depends on the flue-gas velocity, droplet size and absorber height.

In the investigated laboratory and at technical scale, the main surface comprises a film on the walls of the absorber. Concerning film flows, the mass transfer coefficient on the gaseous side is calculated, amongst others, in reference to the kinematic viscosity [98]. Due to the strong mixing in the liquid film if waves occur, the mass transfer coefficient is increased up to factor three compared to waveless film flows [98].

Considering the two-film theory of W. K. Lewis and W. G. Whiteman, there is, at the boundary, an equilibrium where Henry's law is applicable. The Henry volatility constant H_i is shown in eq.2-4. The partial pressure p of the gas component i is equal to the Henry volatility constant H_i multiplied by the concentration in the liquid phase c of component i divided by the molar mass $\widetilde{M}$. The Henry volatility constant at a specific temperature $H(T)$ can be described by the exponential function shown in eq.2-5. H at the reference temperature θ $(T = 298.15\,K)$ and the constant C_i are described in literature for the specific species, see [30]. This means that the solubility of the gas decreases for increasing temperature.

$$H_i = \frac{p_i}{c_i}\widetilde{M} \qquad \text{(eq.2-4)}$$

$$H(T) = H(\theta)\exp\left[C_i\left(\frac{1}{T(\theta)} - \frac{1}{T}\right)\right] \qquad \text{(eq.2-5)}$$

In a given FGD system with a fixed absorber geometry and fixed raw gas composition and temperature, the concentration difference of the gas component in the liquid phase is highly significant in the mass transfer of the component. Consequently, processes which lower the liquid concentration, like complexation reactions or redox reactions, can increase the removal efficiency of a gaseous component.

2.2.2 Influences on the removal of sulphur dioxide

Sulphur dioxide $SO_{2\,(g)}$, the anhydride of sulphurous acid $H_2SO_{3(aq)}$, is well soluble in water. In the following, it is labelled $S(IV)$ because of its oxidation state IV. $S(IV)$ exists amongst others in the following three species sulphur dioxide SO_2, bisulphite-

${HSO_3}^-$ and sulphite-ion ${SO_3}^{2-}$. The desulphurization process is described in the following four steps. The first is the physical dissolution of sulphur dioxide, which is characterized by the dependency on the partial pressure of SO_2 according to Henry's Law. The Henry constant [28] is dependent on the temperature in the liquid and gas phase [29]. A higher temperature leads to a lower solubility of SO_2 in water. The Henry volatility constant H_{SO2} describing the solubility of SO_2 in water at $T = 298\ K$ is equal to $0.72\ mbar.m^3/mol$ [30]. The solubility of sulphur dioxide in water decreases for higher shares of dissolved chloride ions [31] [32].

The second step is the dissociation of sulphur dioxide**.** Sulphurous acid is a polyacid. The dissociation implies a decrease of the pH by the release of oxonium-ions according to eq.2-6. The equilibria of these dissociation reactions are described by acid dissociation constants, which are calculated from the concentrations of the species at equilibrium.

$$SO_{2\ (g)} + 3\ H_2O_{\ (l)} \rightleftarrows {H_3O^+}_{\ (aq)} + {HSO_3^-}_{\ (aq)} + H_2O_{\ (l)}$$

$$\rightleftarrows 2\ {H_3O^+}_{\ (aq)} + {SO_3^{2-}}_{\ (aq)} \qquad \text{(eq.2-6)}$$

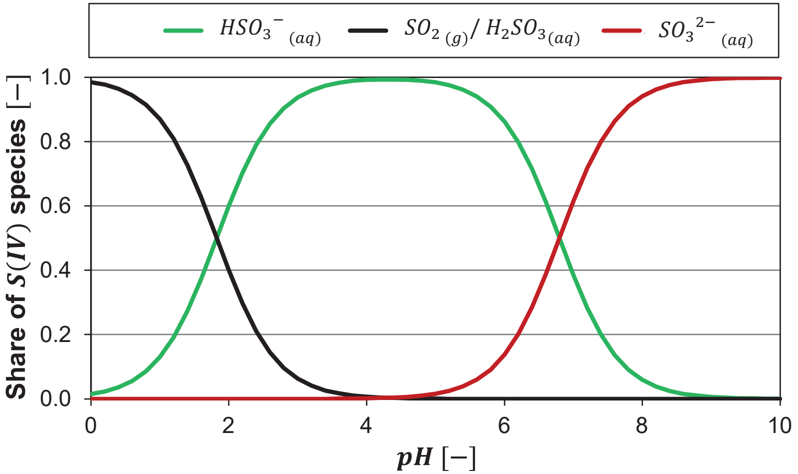

Figure 2: Share of $S(IV)$ species in dependency of pH, adapted from [23]

The logarithmic acid dissociation constants pK_a of sulphurous acid are the negative logarithm of the acid dissociation constants and they amount to 1.96 and 7.20, see