MERCURY REMOVAL IN COAL-FIRED POWER PLANTS, POSSIBILITIES HOW TO ATTAIN VERY LOW EMISSIONS AND MINIMIZATION OF HAZARDOUS WASTE STREAMS

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Emissions of toxic heavy metals (HMs), as Hg, As, Cd, Pb, etc., and some harmful compounds of F, Se, and B are related to waste streams from coal-fired power plants (CFPP). Coal/lignite combustion, due to relatively high content of ash, sulfur, and chlorine, generates in flue gas cleaning processes tremendous amount of fly ash, $CaSO_4$ and $CaCl_2$. Measures for minimization of Hg- and NOx-emissions (e.g. addition of bromides and NH_3) change properties of fly ash, wastewater and speciation/partition of HMs. Wet flue gas desulfurization (FGD) consumes high amount of fresh water and generates harmful wastewater with water soluble salts. The planned, more stringent limits on emissions of dust, Hg, HCl, HF, SO_2, etc. in CFPP will increase contents of polluting compounds in solid and liquid waste streams. We critically assess possibilities, measures and obstacles for higher efficiency of Hg and HMs removal from flue gas in CFPP, together with efficient removal of other pollutants including mutual influences and interrelations. The fates of mercury, selected harmful HMs, and some other pollutants in waste streams from wet FGD are critically analyzed and discussed. Non-toxic, stable forms of mercury (e.g. HgS) and other HMs in solid waste should be preferred. Schemes and measures for minimization of emissions and hazardous waste streams from air pollution control (APC) are compared and discussed for three selected technologies of coal combustion with different methods of gas cleaning.

Keywords: Coal combustion, Mercury removal, Hazardous waste, Heavy metals, Zero liquid discharge, Water recovery

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1. Introduction

Mercury (Hg) is a naturally occurring element present in the Earth's crust mainly in the form of HgS. Natural sources of mercury in the environment include elemental mercury vapor from volcanoes and forest fires and the release of inorganic mercury by weathering, movement of water and transformation in atmosphere [1]. More recent anthropogenic sources include burning of coal and fossil fuels [2], mining of mercury, precious metal refinement [3], electrical and automotive part manufacture, and chemical processing, and release through waste incineration [4], landfills [5] and industrial contamination of water systems. In spite of advances in understanding the pathology associated with mercury exposure [6] plenty of relations, toxic effects and bio-availabilities of various complexes of mercury and heavy metal (HM) compounds is still not fully or even in some cases very insufficiently known and understood [7].

Nowadays, one of the decisive sources of Hg emissions is combustion of coal due to mainly huge amount of combusted coal/year worldwide. According to estimates [3], about 70 % of mercury is emitted directly to the atmosphere (as elemental mercury Hg^0 and Hg^{2+} compounds) and the rest is coupled with solid and liquid waste streams (fly ash, wet FGD related waste, waste liquids, etc.) from coal combustion, flue gas cleaning and some industrial processes (cement production, non-ferrous metallurgy, etc.). Emissions of toxic metals like arsenic, cadmium, lead, zinc, etc. are related mainly with emissions of fly ash (particularly micron and sub-micron particles) and with wet FGD, where significant part of the remaining arsenic and lead compounds on very small dust particles is captured [8-10]. Coals contain, however, relatively very significant amounts of sulfur, usually relatively lower chlorine concentration and, sometimes, also not negligible concentrations of fluorine, bromine and sometimes even iodine. In a combustion process [2] the stated elements are converted into SO_X, HCl, Cl_2, HF, HBr and Br_2. Presence of particularly HCl, HBr (Br_2) and SO_X in flue gas has impacts on mercury speciation and on volatility and capturing of some other HMs in flue gas cleaning lines.

In flue gas desulfurization facilities (FGD), the presence of particularly HCl may increase alkali sorbent consumption and HCl, HF and HBr/Br_2 have the influence on wastewater treatment [11]. Content of bromine in coals is variable and is only partly related with chlorine content [12]. Fate, partitioning and forms of mercury, arsenic, selenium, chlorine, fluorine and bromine depends on coal combustion technology, flue gas cleaning line arrangement and conditions [8,9,13]. Particularly chlorine and bromine are found in liquid waste as water soluble chlorides and bromides (waste water, waste slurry) from wet flue gas cleaning methods. Coal combustion and waste incineration waste ash materials and flue gas cleaning residues present huge amount of waste material with content of heavy metals, rare earth elements [14,15], $CaSO_4$ and other (e.g. $MgSO_4$, $FeSO_4$) sulfates, sulfites, chlorides, fluorides, bromides (e.g. $CaCl_2$, CaF_2, $CaBr_2$), nitrates, etc. Generally, only a part of the combustion residues (some part of fly ash, and of residues from wet FGD processes) is utilized in building industry, in cement production, etc. [16], but a substantial part of the waste from APC is still disposed/landfilled.

The Ca-salts (sulfates/sulfites, chlorides, fluorides, bromides) in wet FGD [17-20] have different solubilities in water. Solubility of CaF_2 in water is only around 150 mg/l at 20 °C. Solubility of $CaSO_4 \cdot 2H_2O$ in water is about 2.4 g/l. Solubilities of $CaCl_2$ and $CaBr_2$ in water are high (more than 200 g/liter). Moreover, particularly $CaCl_2$ forms hygroscopic hydrates (e.g. $CaCl_2 \cdot 2H_2O$ and $CaCl_2 \cdot 6H_2O$) causing sticky nature of solid waste containing $CaCl_2$.

Fate of mercury in a flue gas cleaning process with SCR de-NOx, dust filtration (electrostatic precipitator (ESP) or fabric filters) and wet FGD depends highly on Hg-speciation (ratio of Hg^{2+}/Hg^0), temperature of APC steps and on presence of unburnt carbon residues in fly ash [2,9,21-26]. The oxidized form of mercury (mainly $HgCl_2$) is absorbed either in the quencher or in the absorber (wet FGD) utilizing limestone slurry for SO_2 absorption/removal. Efficiency of oxidized mercury (Hg^{2+}) removal in wet FGD depends on the re-emission of mercury caused by reduction of a part of $HgCl_2$ captured [27-29]. Reduction of $HgCl_2$ to elemental mercury is dependent on conditions in wet FGD process, pH, ORP, temperature, presence of complexing anions (chlorides, bromides, etc.) and on precipitation removal of mercury in form of HgS or organic compounds or their salts containing sulfur (e.g. TMT, DTCR, etc.) [20,27,30-36]. Addition of organic acids and water soluble Mg-salts for more efficient absorption of SO_2 has some impact (side effects) also on mercury re-emissions [37-39].

In the case of full retention of $HgCl_2$ and mercury related complexes in absorption slurry, partition of Hg generally occurs in the process of gypsum production and separation. Usually majority of water soluble Hg-compounds is related with slurry waste and waste water containing water soluble chlorides[27,40-42]. Separation of bigger crystals of gypsum leads to enrichment of the remaining waste slurry containing also Fe, Mn, Ca and As containing impurities [43,44]. The waste water contains majority of alkali chlorides, bromides and a part of less soluble CaF_2 [19,45]. A part of remaining water soluble calcium sulfate, $CaCl_2$, CaF_2 and aluminates can be removed by precipitation - e.g. by magnesium–aluminum oxide [46,47], by aluminum sulfate [48] or by a co-precipitation with calcium hydroxide and sodium aluminate [49].

Generally, there is a problem with removal of massive concentrations of chlorides, smaller concentrations of bromides, selenium compounds (selenites and selenates) and boron, and small concentrations of Hg from wastewater after wet FGD [50,51]. Challenge in the wastewater treatment and management is attaining the status near zero (waste) liquid discharge (near ZLD), which implies production of solid salts and recycling (reuse) of the relatively clean resulting water in the wet FGD [52-54]. The concept of zero liquid discharge means wastewater treatment process reducing wastewater amount and producing clean water suitable for reuse. The ZLD technologies consist from brine concentrators and crystallizers that use thermal evaporation to turn the brine into highly purified water and solid dry product, ready either for landfill disposal (solidified/stabilized) or for salt recovery. Besides traditional processes based on evaporator/crystallization systems there are also other promising technologies: electro-dialysis/electro-dialysis reversal (ED/EDR), forward osmosis (FO), membrane distillation (MO) and other similar processes [19,54-57].

Environmentally acceptable solutions of solid waste from FGD processes mean that the solid waste materials from wet (or dry) FGD with contents of HMs, selenium, etc. are in water insoluble or very sparingly soluble forms, fixed in a water insoluble form in mineral or other matrix (stabilized and solidified) or at least encapsulated by solidified materials eliminating solubility [52,58,59]. The solidified and stabilized solid waste should involve heavy metals in form of non-toxic (non-hazardous) compounds: mercury as HgS, arsenic, mostly captured on fly ash and partly in wet FGD systems, is stabilized by presence of oxidized form of arsenic (As^{5+}) and by interaction with mainly Fe_2O_3 and CaO [9,60-62]. Moreover, nonmetallic pollutants (e.g. selenium and boron) should be in water insoluble or sparingly soluble forms. In enhancement of mercury oxidation in flue gas by HCl and/or $HBr/CaBr_2$ addition (for better sorption of mercury on fly ash particles and efficient absorption of oxidized mercury in wet FGD systems), the side effects of bromine and chlorine on formation of brominated/chlorinated organic persistent compounds [63,64] boiler corrosion should be carefully taken into account [64-66].

The ultimate goals of the environmentally sound and acceptable flue gas cleaning in combustion and incineration processes should be limitation of emissions of NO_x, SO_x, HCl, HBr, HMs, with simultaneous applicability of ash based waste, possible recovery of REE and other valuable elements from coal/lignite ash (bottom ash, fly ash), minimization of production of hazardous waste, water consumption saving (adherence to near ZLD concept) and, if possible, production of re-usable products from water soluble salts ($CaCl_2$, $MgCl_2$, etc.). The complex problematics of deep flue gas cleaning, growing attention paid to reduction of hazardous solid/liquid waste generation and future strategies/possibilities of minimization of discharge of solid and liquid waste is assessed in newer review articles [16,67-70]. The new more stringent emission limits for coal/lignite combustion plants (see **Tab. 1**) are valid since August 2021 (Commission Implementing Decision (EU) 2017) [71]. At the same quality of fuels, the more efficient flue gas cleaning means higher amount of separated fly ash and higher amounts of Hg, sulfur compounds, chlorides fluorides and other pollutants in wastewater and solid waste from such facilities..

Tab. 1: BAT associated emission levels (yearly average) for dust, Hg, SO_2, and HCl emissions for existing plants and for new plants in combustion of coal and lignite

Characteristics of fuel, combustion and thermal input	Dust emissions (mg/Nm^3)		Hg emissions ($\mu g/Nm^3$)		SO_2 emissions (mg/Nm^3)		HCl emissions (mg/Nm^3)	
Lignite combustion	Exist. plant	New plant	Exist. plant	New plant	Exist. plant	New plant	Exist. plant	New plant
Thermal input > 100 MW_{th}	-	-	-	-	-	-	1–5	1–3
Thermal input 100–300 MW_{th}	2–14	2–5	<1–10	<1–5	95–200	80–150	-	-
Thermal input > 300 MW_{th}	-	-	<1–7	<1–4	10–130[1] 20–180[2]	10–75[1] 20–75[2]	-	-
Thermal input 300–1000 MW_{th}	2–10	2–5	-	-	-	-	-	-
Bituminuous coal comb.								
Thermal input > 100 MW_{th}	-	-	-	-	-	-	1–5	1–3
Thermal input 100–300 MW_{th}	2–14	2–5	<1–9	<1–3	95–200	80–150	-	-
Thermal input > 300 MW_{th}	-	-	<1–4	<1–2	10–130[1] 20–180[2]	10–75[1] 20–75[2]	-	-
Thermal input 300–1000 MW_{th}	2–10	2–5	-	-	-	-	-	-

[1]PCC boilers [2]CFB boilers

Complex effects of combustion of various fuels (coals/lignites), fuel composition (Hg, Cl, S and HM contents), combustion methods (PCC, CFB combustion) and the kinds of flue gas cleaning line composition/methods (line with wet FGD, CFB combustion with FF, CFB combustion with wet-dry calcium hydrate based method) on emissions of mercury in Czech Republic were studied lately [72]. The results on mercury emission without special measures (AC injection, bromine compounds addition/dosing, without optimization of wet FGD, etc.) have shown that fabric filters are more efficient for reduction of mercury emissions than ESP. Significant roles are played by temperature of gas filtration and by chlorine content in fuels. The most efficient flue gas cleaning method for Hg emission mitigation was found to be the wet-dry method with fabric filters (mainly due to lower temperature of final flue gas filtration)

The solid waste landfill of non-utilizable waste should be minimized, it should be quite safe, without release of gaseous emissions, without generation of hazardous waste, without water pollution and without dangerous soil transformations of pollutants [73,74].

Undoubtedly, this is a very complex and huge task, particularly in the sector of coal-based power generation, but also in waste incineration and cement production. This review tries to assess the possibilities and problems on ways leading to such a desirable status in overall emissions and waste generation in CFPP with accent on mercury (and some other selected HMs) pollution minimization.

This our review does not analyze emissions and environmental impacts of oxy-fuel combustion of coals and CFPPs with post-combustion separation technologies for CO_2 from flue gas.

2. Fate of mercury and selected elements in flue gas filtration and NOx reduction (SCR and particulate emission control) and utilization of fly ash

Behavior, removal processes for mercury and volatile HM compounds (e.g. arsenic compounds) and various interactions of pollutants in flue gas are influenced by flue gas composition (particularly concentrations of HCl, SO_2, NOx, HF, HBr, etc.) and by parameters/arrangement of dust filters and selective catalytic reduction (SCR) for de-NOx. HBr (due to easier formation of elemental bromine) is a stronger oxidizing agent for mercury and As_2O_3 in flue gas [75-77] than HCl.

Effects of SCR on oxidation of mercury and behavior of some other HMs depend on position of SCR in flue gas cleaning line, catalysts [78-80] and on presence of oxidants in flue gas (elemental bromine, chlorine, peroxides, selective catalysts, etc.).

According to Alcove Clave et al. 2019 [81], effects of SCR catalyst on Hg-oxidation and SO_2 oxidation depend on V_2O_5 content in the catalyst, temperature, NH_3/NO_x molar ratio, As_2O_3 content, presence of small dust particles/aerosols, etc.

Generally, three positions of SCR de-NOx can be distinguished in a typical air pollution cleaning (APC) line in coal combustion technologies:

1. hot, high dust SCR position upstream dust filters (most frequently ESP) with operating typically between 300 and 400 °C [82]
2. medium temperature, low dust SCR position downstream particulate filters with typical operating temperature 200–260 °C [82,83]
3. tail end clean flue gas position downstream the wet flue gas desulfurization (FGD) with operating temperature approx. 180–260 °C and upstream flue gas

heat exchanger for heating of flue gas to the required de-NOx temperature [4,84].

All combinations of SCR/ESP/wet FGD in flue gas cleaning and their operating conditions have their advantages and disadvantages, various impacts on mercury and HMs removal efficiency, and interactions with other pollutants. Flue gas cleaning set-up and operation parameters are guided by emission limits, possible utilization/handling of waste from APC, economy, reliability, etc. [9,82,85-87].

The tail-end position of SCR has, of course, relatively low impact on mercury fate in flue gas and emissions of other pollutants. Oxidation of SO_2 to SO_3 and oxidation of ammonia (for the de-NOx) in flue gas are negligible under such conditions. The main interaction is sorption of a part of remaining Hg and As-based pollutants on the catalyst (depending also on HCl concentration in flue gas). The advantage of such position of SCR is relatively slow poisoning of the catalyst, because the substances harmful for the catalysts are removed upstream the SCR de-NOx. Under such conditions, adsorption of mercury decreases with increasing SCR temperature and increases with Hg concentration in flue gas. Effect of Hg-speciation: higher sorption is observed for oxidized mercury. Sorption of mercury slightly decreases with increasing NH_3 concentration [84]. The sorption of mercury is dependent on catalyst composition, particularly on V_2O_5 content and its properties. The adsorbed mercury can be washed out (approx. 50–80 %) from the catalyst by diluted water solutions of HCl and acetic acid. The amount of arsenic oxides in flue gas for interaction with SCR catalyst depends on efficiency of arsenic removal in filters (ESP, fabric filters, hot, dusty SCR) and in wet FGD [61]. A small part of the remaining As-oxides (if present in flue gas) can be deposited on the SCR catalyst. The interactions depend on SCR catalyst composition.

The medium temperature, low dust SCR (position downstream dust filters) contributes, according to catalyst composition, to oxidation of mercury by HCl and HBr/Br_2 in flue gas. HBr/Br_2 is more effective in Hg-catalytic oxidation than HCl [88]. Particularly SCR catalyst containing CeO_2, Mn-oxides and MoO_3 are efficient for mercury oxidation. Presence of high concentrations of SO_2 in flue gas inhibits oxidation of Hg, but simultaneous presence of NO_x in concentrations comparable to SO_2 supports also Hg-sorption and oxidation on SCR catalysts. Higher concentrations of SO_2 together with NH_3 for catalytic de-NO_x can contribute to undesirable formation and deposition of ammonium salts (sulfite, sulfate, hydrogen-sulfate and chloride) on the catalyst [4], particularly at lower operating temperatures (below 240 °C). Arsenic compounds deposition/removal on SCR catalyst downstream dust filters is not important, particularly in the case of colder flue gas filtration with modern efficient methods (combined filters) for removal of submicron dust particles enriched with arsenic compounds [60,80]. The oxidation of Hg in flue gas caused by low dust SCR has positive impact on efficiency of Hg-removal in wet FGD placed downstream. The low dust SCR is used particularly (but not only) for CFB combustion of high ash lignite and subbituminous coals.

Hot (operating temperature 300–400 °C), high dust SCR de-NO_x (position upstream dust filters) suffers from dust caused abrasion (requires special construction, wider channels in the catalyst and periodic gas blows), significant catalytic oxidation of SO_2 (esp. by V_2O_5 based catalysts) and possible poisoning by deposition and interaction with arsenic and partly volatile heavy metals compounds. On the other hand, mercury and oxidized Hg^{2+} compounds are not adsorbed on the catalyst under such higher temperature conditions. Therefore, deposition of mercury compounds is not a problem in such SCR. The dust particles with oxidized mercury compounds, sulfates and possible ammonium salts are removed in downstream filters (ESP). It seems that ammonia slip from SCR can contribute to more efficient mercury removal in downstream, consecutive ESP [89].

During the period of the past 10 years, various new and modified SCR catalysts have been developed with the target to reduce undesirable SO_2 and NH_3 oxidation, to increase conversion of Hg to oxidized Hg-compounds and to increase resistance of high temperature SCR catalysts to abrasion and poisoning by arsenic and HM compounds [22,82].

Combination of high temperature SCR with a special catalyst for efficient Hg-oxidation together with colder conditions for ESP filters (below 150 °C) or with a gas cooler between SCR and ESP can remove substantial part of mercury and arsenic bound with fly ash particles [22] . Special gas cooler can selectively remove condensed vapors of sulfuric acid (if necessary), but material of the cooler has to withstand conditions with hot, concentrated H_2SO_4. Under such conditions of flue gas cleaning, the heavy metals (particularly Hg, As, Pb and Zn) are very concentrated on fly ash particles. It means, however, also more problematic utilization of such fly ash and more difficult stabilization/solidification for dumping/landfilling. Mercury is present in fly ash mainly in the water soluble form of $HgCl_2$ or $HgBr_2$ (under conditions of adding HBr, S_2Br_2 or $CaBr_2$ intentionally to flue gas) [64,75,90,91].

Fly ash enrichment with Hg, As and generally with heavy metals in flue gas cleaning is dependent on conditions of fly ash removal: temperature, efficient removal of submicron particles, presence of HCl/HBr in gas, unburnt carbon content in fly ash [92,93] and upstream presence of SCR de-NOx. Modern combined filters (particularly combinations of ESP with electrostatically enhanced fabric filters with surface membranes) are very efficient in removal of arsenic, particularly at temperatures below 170 °C [24,40,61]. Presence of unburnt carbon in fly ash particles and HCl/HBr in flue gas together with lower temperature conditions of ESP or other fly ash filters cause more efficient capture of Hg in dust filters [9,94]. Fabric filters are usually more efficient [95] in removal of mercury (Hg_p and Hg^{2+}) and capturing of submicron dust particles than ESP based filters. Significant factors in this improved efficiency are longer residence time of particles and higher efficiency of removal of submicron dust particles.

New measurements on lignite-fired power stations in Poland [96] with dosing of bromides (mixture of $CaBr_2$, NH_4Br, NaBr) to inlet coal (0.08 to 0.1 kg Br/ton of coal), for lignite coals containing about 0.5 ppm Hg, have shown that the effect of bromides dosing is dependent on Ca, S, and Cl content in fuels. Ca- and S-compounds present in coal\lignite have negative influence on the method (higher Br/Hg mass ratio is required). The Br/Hg mass ratio should be higher than 100. Bromine (as HBr) is about 100 times more efficient for Hg oxidation than chlorine (as HCl) in flue gas. Consequence of bromines application: about 75–80 % of Hg was retained in fly ash in modern, efficient ESP - of course with impacts on properties/utilization of the fly ash. The price of such bromine addition method is estimated to be 3–5 times cheaper in comparison with AC addition upstream or downstream the ESP (fly ash filters).

Higher content of Hg- and As-compounds in filter dust means higher potential for leaching of those heavy metals in landfilling/disposal. Possibilities of removal of mercury from flue gas by various measures (addition of $CaBr_2/CaCl_2$, solid sorbents for Hg, selective oxidation catalysts for $Hg^0(g)$ and wet FGD with special additives for enhanced mercury sorption) are schematically shown in **Fig. 1**. Additional FF is suitable for both further decrease of dust emissions and minimization of amount of Hg-containing waste.

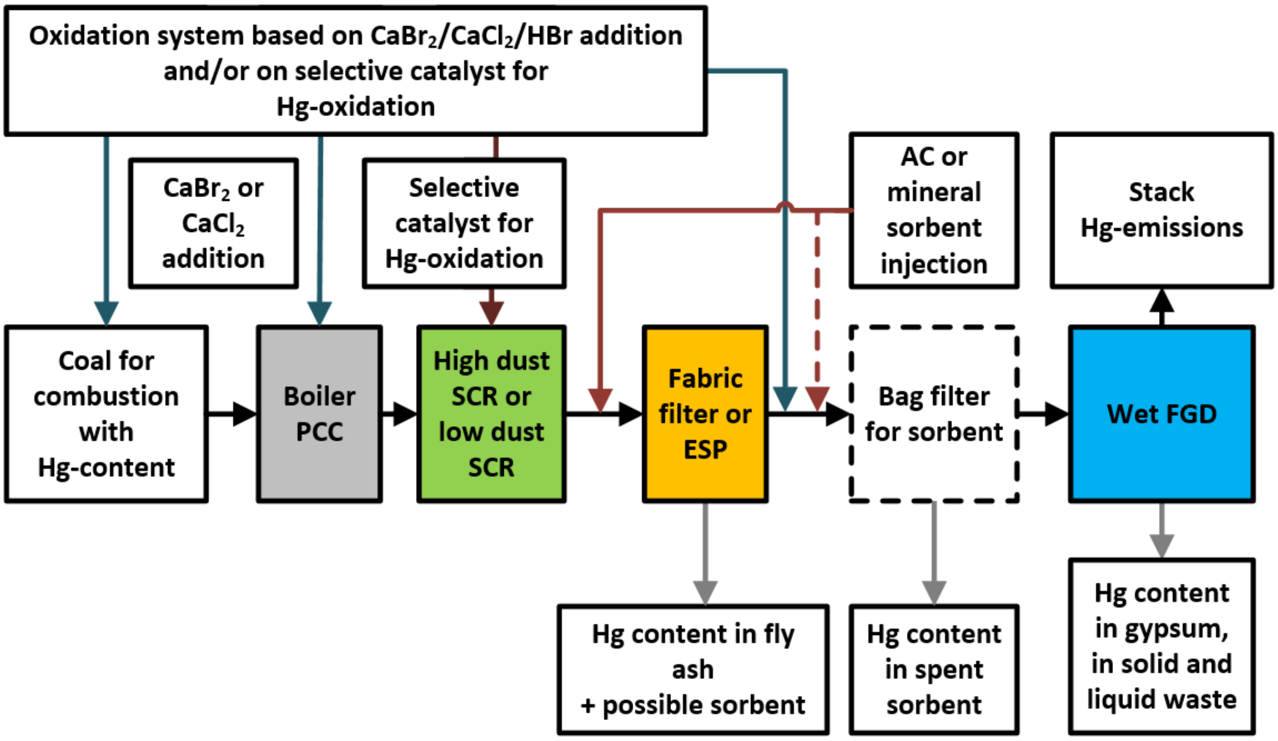

Fig. 1: Scheme of possible mercury emission control options in PCC flue gas cleaning and ways of mercury outputs from the flue gas cleaning system. Dashed lines indicate measures for higher efficiency of Hg-removal

Simplified situation in speciation of Hg in flue gas and in idealized, optimized effects of the important parts of flue gas cleaning line in coal combustion on mercury emissions, their speciation and effects of $CaBr_2$ addition on the Hg-fate in flue gas cleaning is illustrated in **Fig. 2**.

If the concentrations of mercury or mercury and SO_2 behind the wet FGD are still high, another method for reduction of Hg and SO_2 emissions can be used: catalytic sorbent polymer modules (SPM, developed by Gore & Associates). The operation conditions for the sorbent modules are typically downstream wet FGD, at temperatures between 60 and 80 °C. The catalyst in the polymer membrane oxidizes elemental mercury and, simultaneously due to presence of reactive sulfur, Hg is converted to HgS [97]. SO_2 is oxidized to SO_3 and converted in presence of water vapors to sulfuric acid forming droplets on the hydrophobic surface of the polymer modules (30 cm height).

A new approach in better mercury oxidation and removal is based also on the low-dust and low-temperature oxidation of mercury right downstream the electrostatic precipitator (or another dust filter) and upstream of the wet FGD [87,98]. The SCR catalyst requires also optimization in composition [99,100]. In needed/specific cases even combination of high dust SCR, ESP, flue gas temperature adjustment and catalytic oxidation of Hg by selective catalysts can be considered [101] for more efficient absorption of mercury in wet FGD.

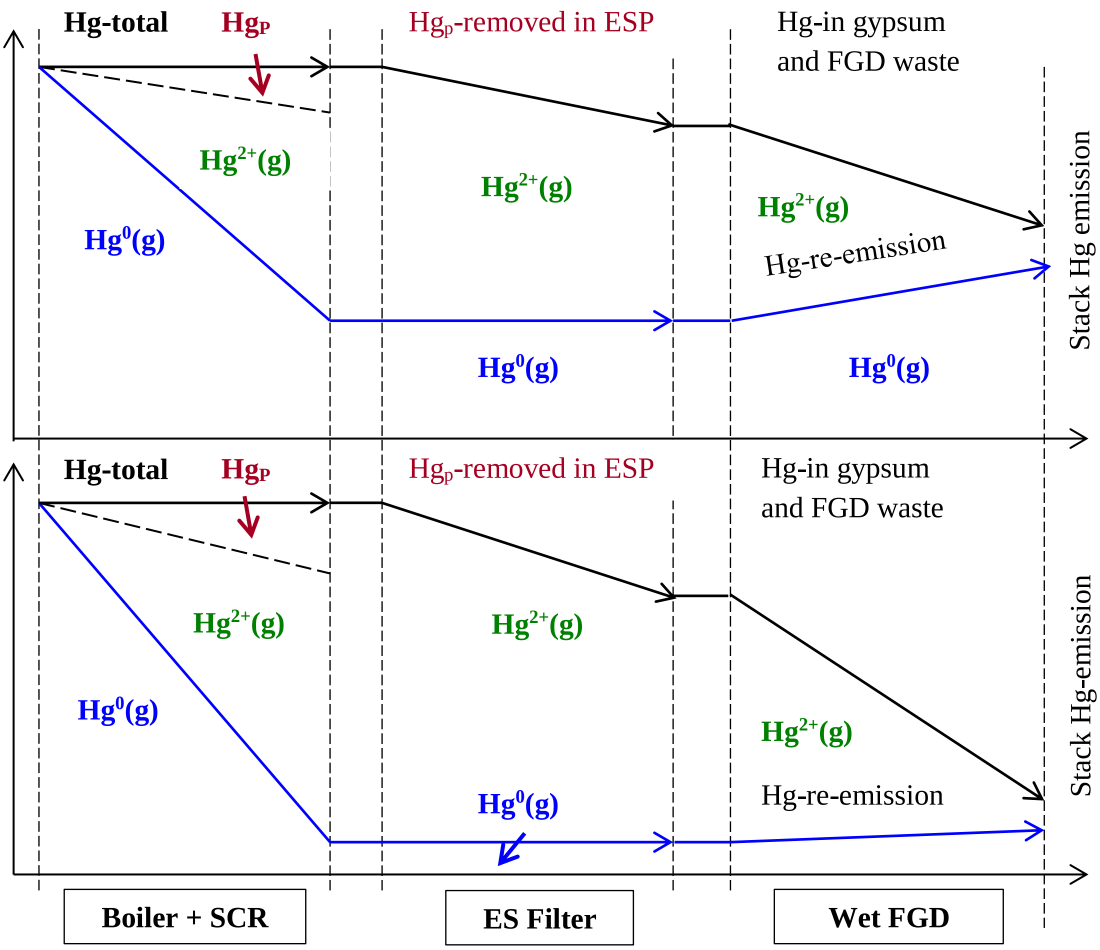

Fig. 2: Simplified scheme of mercury speciation, relative Hg-concentration in flue gas and resulting emissions in usual flue gas cleaning with ESP and wet FGD (upper part) and comparison with optimized flue gas cleaning with Ca-bromide addition together with measures for minimization of Hg^0 re-emission in wet FGD [27] (lower part)

Comparison of distribution of mercury, arsenic and some selected HMs between fly ash and bottom ash in powder coal combustion and in circulating fluidized bed (CFB) is shown in article by Zheng et al. 2017 [8]. In the case of CFB combustion relatively higher concentration of arsenic compounds was found in bottom ash mainly due to lower temperature of combustion in comparison with powder coal combustion. Typical flue gas cleaning line for CFB combustion of coals/lignites (without application of wet methods of gas cleaning) and possibilities of improved mercury removal are shown in **Fig. 3**.

Fly ash from coal combustion is a material of growing application possibilities and interests [16].The existing and future estimated utilizations of fly ash (geo-polymers, catalysts, aerogels, raw material for REE recovery, etc.) are shown in **Fig. 4**. Nowadays, the recovery of REE and some other valuable metals from fly ash particles is discussed and experimentally studied [14,15,102]. The total content of REE elements in coal fly ash can be between approx. 300 and 500 ppm, where light REE elements are prevailing [14].

All thermal processes applied to coal fly ash cause desorption of elemental mercury and mercury compounds adsorbed onto fly ash ($HgCl_2$, $HgBr_2$, HgO, HgS, etc.) [103-105].

Mercury in fly ash can be converted to HgS (non-toxic Hg-compound) by reaction with sulfur, sulfur cement, alkali-sulfides, organic and inorganic polysulfides or by mixing/reaction with wet FGD waste brine [106-109]. In addition, conversion of mercury to HgSe stabilizes mercury into water insoluble and stable compound. Reactive forms of FeS_2, FeS and some other sulfides are also suitable for stabilization of mercury in waste fly ash and in similar waste materials for disposal [110,111]. Sulfides (ZnS, FeS, FeS_2 in nano-size of particles) are very reactive and they can stabilize Hg and Hg-compounds in a form of complex stable compounds containing reactive sulfur [112,113]. Under conditions of higher pH values ($pH > 8$) and presence of water soluble sulfides and poly-sulfides, HgS can form water soluble complexes resulting in increase of total dissolved mercury in leaching [114].

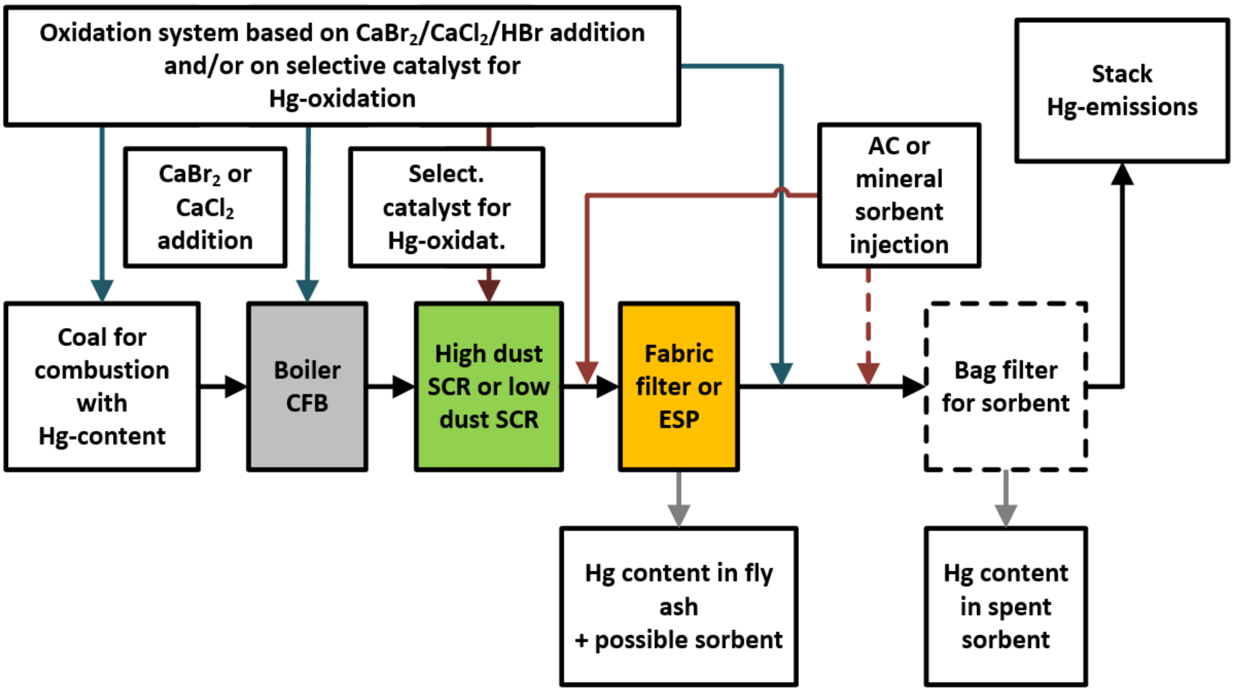

Fig. 3: Scheme of Hg emission control in CFB combustion of coal/lignite with possible high dust or low dust SCR (downstream the filters) positions and with two possible places of sorbent application

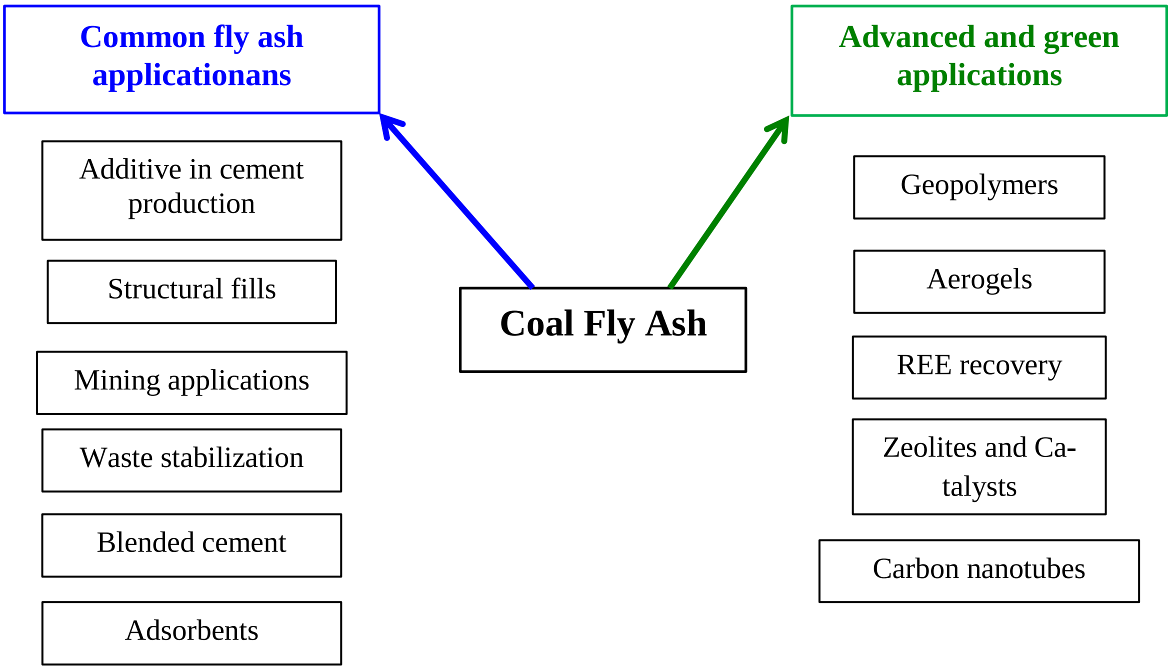

Fig. 4: Scheme of existing and future possible utilizations of coal fly ash [16]

More efficient removal of mercury from flue gas by added solid sorbents is generally possible by two arrangements of sorbent injection: upstream and downstream the ESP or fabric filter. In the case of upstream ESP addition of either carbonaceous or mineral sorbents [115,116] to flue gas, the sorbents with captured mercury are in a mixture with filter fly ash. In the case of downstream ESP removal of mercury from flue gas by sorbent injection, the sorbent (and also mercury content) in mixture with some small part of remaining fly ash particles will be far more concentrated. A novel technology for mercury removal considers combination of fabric filter with Hg-sorbent involved in felt/fibers and optional oxidation catalyst [117].The fly ash in ESP will be substantially cleaner under conditions of higher operating temperature, with only very small content of mercury and some other difficult elements. Chemical stabilization of such fly ash (for suppressing of As, Se and B leaching) is easier [118]. Such arrangement of flue gas cleaning line is, however more expensive (double flue gas filtration needed). Up to now, carbonaceous sorbents are prevailing for purpose of mercury removal from flue gas [116]. However, at present also impregnated or chemically adjusted mineral sorbents are utilized [115]. The advantage of mineral sorbents can be higher compatibility with stabilization/solidification procedures utilizing cement and lime - based solidification materials.

3. Oxidation of mercury in flue gas upstream wet FGD by additives (HBr, HCl, bromides, chlorides, etc.) side effects (corrosion, formation of organic brominated/chlorinated compounds)

Efficient removal of mercury from flue gas by wet absorption process (flue gas desulfurization, de-HCl, etc.) requires transformation of elemental mercury in flue gas into water soluble, oxidized mercury compounds [75, 119], most often $HgCl_2$ or $HgBr_2$.

Formation of $HgCl_2$ in gas phase requires rather lower temperature (below approx. 400 °C) and presence of sufficient amount of HCl in gas phase. HCl is partly oxidized into elemental chlorine, but in the presence of higher SO_2 concentration, chlorine is consumed by the SO_2 oxidation reaction:

$$SO_2 + Cl_2 + 2H_2O \rightarrow 2\ HCl + H_2SO_4 \quad (3.\ 1)$$

HBr (when present in gas) is more easily then HCl oxidized to Br_2:

$$2HBr + 0.5\ O_2 \rightarrow H_2O + Br_2 \qquad (3.\ 2)$$

Br_2 (and similarly I_2 when present) is not consumed by the reaction with SO_2. It is substantial difference between behavior of chlorine and bromine (or iodine) in flue gas. Also $CaBr_2$ at lower temperatures (below approx. 300 °C) is more suitable than $CaCl_2$ for conversion of elemental mercury vapors (Hg^0) to mercury bromide [120]. The thermodynamic data for the relevant reactions in form of Gibbs reaction energies are given in **Tab. 2.** Data of Gibbs energies of formation (ΔG_f) have been taken from thermodynamic tables for chemical compounds [120].

Tab. 2: Gibbs reaction energies (ΔG_r) for important reactions of HCl, HBr, HI, Cl_2, Br_2, I_2, $CaCl_2$ and $CaBr_2$ with mercury at 500 K (227 °C)

Chemical reaction	ΔG_r (kJ/mol)	Notice
$2HCl + 0.5O_2 \rightarrow Cl_2(g) + H_2O(g)$	-24.78	-
$2HBr + 0.5O_2 \rightarrow Br_2(g) + H_2O(g)$	-105.19	**Oxidation of HBr is easier than HCl oxid.**
$2\ HI + 0.5O_2 \rightarrow I_2(g) + H_2O(g)$	-198.94	Oxidation of HI is easier than HBr oxidation
$SO_2 + Cl_2(g) + 2H_2O(g) \rightarrow 2HCl)g) + H_2SO_4(g)$	-51.3	Cl_2 is consumed by reaction with SO_2
$SO_2 + Br_2(g) + 2H_2O(g) \rightarrow 2HBr(g) + H_2SO_4(g)$	+29.1	**Br_2 is not consumed by reaction with SO_2**
$SO_2 + I_2(g) + 2H_2O(g) \rightarrow 2HI(g) + H_2SO_4(g)$	+122.8	**I_2 is not consumed by SO_2**
$CaBr_2+Hg^0(g)+H_2O(g)+0.5O_2 \rightarrow HgBr_2(g) + Ca(OH)_2$	-112.1	**Preferred reaction to $HgBr_2$**
$CaCl_2+Hg^0(g)+H_2O(g)+0.5O_2 \rightarrow HgCl_2(g) + Ca(OH)_2$	-60.2	-
$CaBr_2 +Hg^0(g) + CO_2 + 0.5O_2 \rightarrow CaCO_3 + HgBr_2(g)$	-160.86	Prefer. reaction to $HgBr_2$ at higher CO_2 conc.
$CaCl_2 + Hg^0(g) + CO_2 + 0.5O_2 \rightarrow CaCO_3 + HgCl_2(g)$	-109.02	**-**

For efficient mercury oxidation small concentration of HBr (or Br_2) in flue gas are sufficient, usually approx. two orders of magnitude lower than HCl concentration for similar Hg-oxidation effects [19,76,121]. In the case of insufficient concentration of HCl in flue gas, $CaBr_2$ addition to combusted coal is suggested for support of conversion of Hg^0 to oxidized Hg^{2+} form [27,75,77]. Bromine addition to flue gas (in various initial form) can, on the other hand, enhance boiler tubes corrosion [64,65] and is suspected from formation of brominated organic POP compounds (like brominated dioxins, phenols etc.) particularly in presence of unburnt carbon or addition of active carbon to flue gas [63].

Dry methods for flue gas cleaning and behavior of mercury, HCl, SO_2 and HBr in systems with soda and $Ca(OH)_2$-based sorbents within a temperature range 130–300°C were analyzed and compared in literature [4,122]. Mercury and HBr have different fate in systems with soda and $Ca(OH)_2$ dry sorbents. Higher concentrations of elemental bromine vapors can be expected in systems with calcium hydroxide and simultaneous presence of HCl. Na_2CO_3 is a much better sorbent for both HCl and HBr than $Ca(OH)_2$.

Another option for Hg-oxidation, used rather for flue gas with lower concentrations of SO_2, is absorption of mercury vapors into water solution with hydrogen peroxide [123,124]. Mercury vapors and SO_2 are oxidized and according to prevailing anions either $HgCl_2$ or $HgSO_4$ are formed. The water soluble inorganic compounds of Hg are precipitated by alkali sulfides, inorganic and organic poly-sulfides into water insoluble, non-toxic HgS, which can be selectively separated under assumption that the anions remain after neutralization in water soluble form (e.g. Mg-salts, Na-salts, etc.). Gypsum ($CaSO_4{\cdot}2H_2O$) is, unfortunately, only slightly soluble in water. For precipitation of mercury from aqueous solutions also Na-salt of sym. Tri-mercapto-triazin (TMT), Dithiocarbamates (DTCR) or similar compounds soluble in water can be used [125]. Precipitation of mercury by such organic agent is not selective, because simultaneously some other HMs (e.g. cadmium, silver, etc.) are removed. Such precipitates containing mercury are usually sparingly soluble or practically insoluble in water and their filtration is feasible.

On the other hand, controversial opinions remain on their long-term stability in dumping/landfilling and their environmental stability/toxicity.

4. Staged absorption (scrubbing) with selective removal of HCl and possibilities for selective removal of mercury in wet processes

Removal of acidic gases (HCl, SO_2, HF, HBr, etc.) by absorption can be done simultaneously in one absorber/scrubber in one stage, but usually within two stages, [27] or , particularly for higher concentrations of HCl in flue gas, in two steps, with selective removal of HCl in the first absorption/quench step [126]. The schemes of one stage wet FGD process without and with HCl pre-washing are shown in **Fig. 5**. Scheme of a two stage wet FGD process with two stages with different pH is shown in **Fig. 6**

Absorption of HCl into hot water or to water solutions of $CaCl_2$ is relatively efficient at temperatures around 60–70 °C [126]. On the other hand, absorption of SO_2 (at inlet SO_2 concentration above 1000 ppm$_v$) is, under such conditions (60 °C, pH values below 2), inefficient, very low. SO_2 co-absorption with HCl at 60 °C and in presence of HCl in solutions of $CaCl_2$ requires pH above 3 and rather lower $CaCl_2$ concentrations (with concentrations of HCl below approx. 0.02 %) [126].

The equilibrium concentration of HCl in water (water solution) is decreasing with increasing temperature of absorption.. Equilibrium concentration of HCl in gas phase increases with increasing concentration of HCl in liquid phase.

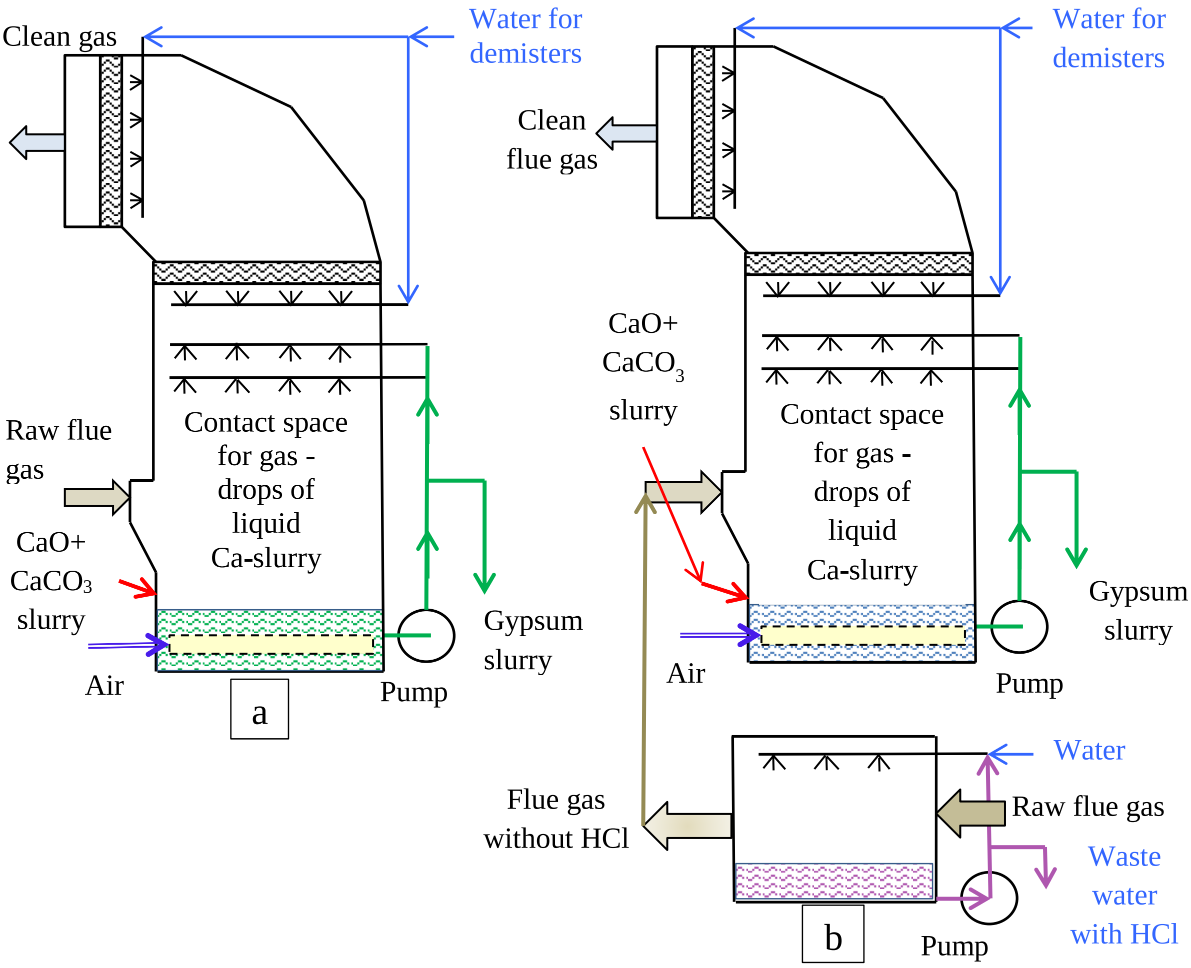

Fig. 5: Comparison of the scheme of one stage wet FGD process (a) with the scheme of one stage FGD process with pre-washing (preliminary removal) of HCl (b)

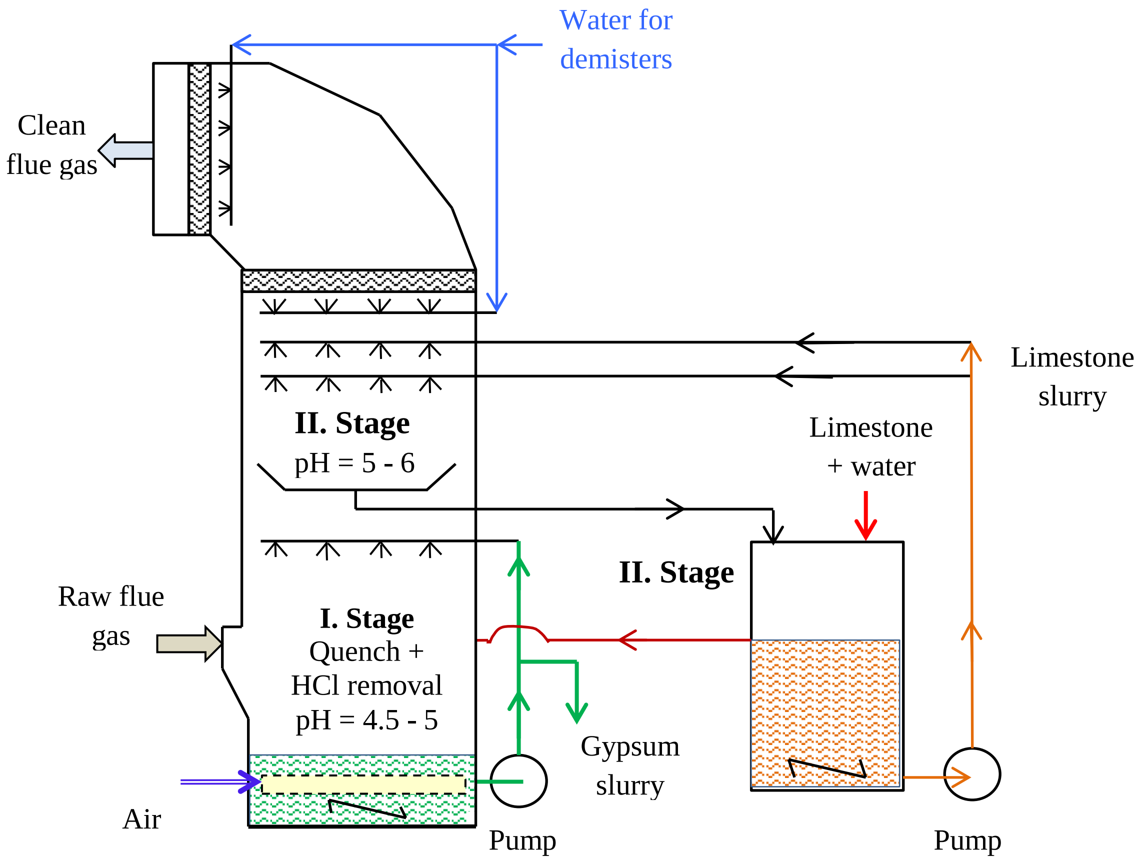

Fig. 6: Scheme of two stage wet FGD process for HCl and SO_2 removal

Under conditions of selective HCl absorption into hot water solution of $CaCl_2$+HCl, vapors of $HgCl_2$(g) and partly Hg^0(g) will be absorbed into the solution. It means that the preliminary selective washing (pre-washing) of HCl from flue gas will simultaneously remove substantial part of $HgCl_2$(g) and only a smaller part of Hg^0(g). Presence of relatively strong, stable complex of $(HgCl_4)^{2-}$ in the solution will suppress reduction of Hg^{2+} by SO_2 and Fe^{2+} and therefore will decrease the re-emissions of Hg^0(g).

Under conditions of presence of fly ash particles in flue gas a part of them will be captured in hot water absorption together with HCl. Similarly mercury in the form of $HgCl_2$(g) will be also captured in hot water solution. $HgCl_2$ in water with excess of HCl will form complexes containing anions $(HgCl_3)^-$ and $(HgCl_4)^{2-}$ which can mediate absorption of Hg^0 vapors [127]. The absorption efficiency of Hg^0(g) is, however, strongly dependent on $HgCl_2$ concentration in water (which will be rather low). It means that significant part of oxidized mercury, and only a smaller part of Hg^0 will be captured in the hot, quenching water with HCl content. In the case of gases with very high concentrations of SO_2, very low concentrations of HCl and significant concentrations of mercury in Hg^0(g) and Hg^{2+}(g) forms, a two stage absorption method was proposed and developed [128]. Absorption of a substantial part of SO_2 takes place in the first stage (with simultaneous reduction of Hg^{2+} to Hg^0(g) form) and relatively selective absorption of mercury into solutions of H_2SO_4+$HgSO_4$ is offered in the second stage.

According to investigations of acid gases removal by partial condensation of water vapor from flue gas and composition of water condensate, HF, HCl and SO_2 were removed from flue gas in a pilot plant heat exchanger [129]. At inlet flue gas concentrations of HF, HCl and SO_2 approx. 50, 60 and 6000 mg/m^3 respectively, and outlet temperature of flue gas from the heat exchanger about 40 °C, approx. 84 % HF, 50 % HCl and only 12.6 % SO_2 has been removed. However, sulfates and sulfites attained relatively highest concentrations (about 2/3 of all anions) in liquid phase [129]. Due to presence of fly ash in condensed water also Fe^{3+} (and often Ca^{2+} and Al^{3+}) can be detected in liquid phase. With increasing temperature of water condensation (quenching) the efficiency of removal of acid gases and Hg (mostly in the form of Hg^{2+}) decreases[130], but the relative percentage of chlorides and fluorides dissolved in liquid phases (related to SO_4^{2-} and SO_3^{2-}) increases [129].

If the quencher is a part of dual-loop FGD process (in the first step contact of flue gas with more acidic washing medium, in the second step absorption of main part of SO_2 into limestone slurry and there is overflow connection of the slurry with quencher part), the quencher has lower pH, higher overall chlorides concentration ($CaCl_2$ + $FeCl_3$ + $AlCl_3$ + HCl) and is more suitable for sulfite oxidation by air to gypsum and for mercury absorption [30,131]. Dual-loop arrangement is more efficient for SO_2, HCl and mercury removal than the single loop. Higher chloride and bromine concentrations in liquid phase support complexing of mercury and prevent Hg-reemissions caused by reduction of Hg^{2+} by sulfites [31].

Operational care, regular cleaning, suppressing of foaming effects in limestone suspensions during absorption [132,133] and proper function of demister in wet FGD is very substantial for attaining high efficiencies of SO_2 absorption, low emissions of dust, some HMs and for prevention of fouling of heat exchanger (re-heater) of flue gas.

5. Wet FGD for removal of SO_2 and HM and factors affecting sorption of oxidized mercury and re-emission of elemental mercury

Wet FGD is widely accepted method for efficient removal of SO_2, HCl and HF from flue gas [20,134,135]. Simultaneously significant reductions of small dust particles emissions [44,136], emissions of some heavy metals (e.g. mercury, arsenic, cadmium, zinc, lead) [8,61] and emissions of some non-metallic elements and their compounds (Se, B etc.) [9] take place in wet FGD. Efficient removal of small fly ash particles (enriched in content of volatile HM compounds) can be optimized by FGD arrangement, residence time, liquid to gas ratio in the scrubber and by application of chemical agglomeration of dust particles in the limestone slurry [136,137]. Wet flue gas desulfurization contributes to reduction of Hg^{2+} concentrations in flue gas by absorption of oxidized mercury compounds, mainly $HgCl_2(g)$ [21,27,31,32, 138].

Re-emissions of mercury from absorption solutions and slurries (caused by reduction of Hg^{2+} to Hg^0) are dependent on protecting complexing reactions of mercury [34,35,139] caused mainly by presence of chlorides and bromides in solution [33,75,140], on oxidation-reduction potential (ORP) [30,124], concentration of SO_2 in flue gas, activities of water soluble sulfites, precipitation of mercury by inorganic sulfides, poly-sulfides and organic compounds containing sulfur [33,40,141-143], on pH, temperature and addition of Hg-adsorbents (e.g. active carbon, etc.) [28,31,139]. Presence of reducing cations (e.g. Fe^{2+} and Mn^{2+}) in absorbing slurry also contributes to reduction of Hg^{2+} and reemissions of mercury [144]. As it was proved experimentally, mercury is also slightly absorbed by rubber and some plastic materials under conditions of wet FGD [28].

The chemistry of complexing reactions (formation of stable mercury complexes in scrubbing liquor and stability of various Hg-complexes were studies and described e.g. in Ph.D. theses by Bittig and Heidel [35,139]. Stable complexes of mercury can be formed besides halides (Cl^-, Br^-, I^-) also (depending on pH) with (OH^-)-ions, SCN^-, SO_3^{2-}, $S_2O_3^{2-}$, etc. Generally, the formation of stable mercury complexes (particularly with bromides, iodides or with some organic compounds) prevents reduction of Hg^{2+} to Hg^0 by SO_2 (+sulfites) and reemissions. On the other hand, presence of higher concentrations of HgI_2 in slurries in wet FGD can cause higher emissions of mercury from FGD in a form of $HgI_2(g)$, as it was found by Krzyzyńska et al. 2020 [144]. An example of comparison of dependence of Hg^0 and HgX_2 reemissions from model slurries at 60 °C on concentrations of chlorides, bromides and iodides in the slurry for SO_2 absorption at pH = 5.1 and Hg^{2+} concentration 0.25 mg/l is shown in **Fig. 7**. As it is obvious from the figure, particularly bromides are very strong agents for suppression Hg-reemissions (both Hg^0 and HgX_2 reemissions). It is interesting that the lowest reemissions of Hg^0 and HgX_2 (where X = Cl, Br, I) were achieved with a mixture of bromide and chloride.

On the other hand, at pH > 6 and higher SO_3^{2-} concentrations in absorption slurry Hg^{2+} forms stable complex anion $Hg(SO_3)_2^{2-}$ and ORP decreases. Under such conditions Hg-reemissions (depending also on other conditions) increase. At acidic conditions, however, the oxidation of sulfites by oxygen is easier[28,139].

Foaming and flotation effects in limestone-water suspensions [133] cause reduction of desulfurization degree and loss of smaller particles from the suspension for efficient desulfurization. Effects of foaming on mercury reemission are probably complex and not quite clear.

Presence of ammonia in flue gas (e.g. from SCR or SNCR for de-NOx) entering wet FGD causes elevation of pH of the absorbing slurry, better absorption of SO_2, but slowdown of $CaCO_3$ dissolution/reaction and significantly higher entrainment of aerosols/droplets containing ammonium salts [145,146]. Mercury reemission increases with increasing concentration of ammonia in flue gas entering wet FGD [89].

Measures for more intensive reactive absorption of SO_2 with limestone slurry particles (addition of Mg-compounds or poly-carboxylic organic acid) have also impacts on behavior of mercury in absorption slurry. Basic Mg-compounds (MgO, $Mg(OH)_2$) contribute directly to higher pH values in absorbing slurry and in the second stage through formation of ion-pair $MgSO_3^o$ [39,147]. The water soluble salts of Mg ($MgSO_4$, $MgCl_2$) tend to form un-dissociated ion-pair $MgSO_3^o$ contributing to better dissolution and recrystallization of $CaSO_3$, to more efficient formation of bigger crystals of $CaSO_4*2H_2O$ [38, 43] and to binding of some part of SO_3^{2-} anion (increasing pH). The main influence of increasing Mg^{2+} ion concentration in limestone slurry on Hg^{2+} behavior is decreasing available SO_3^{2-} concentration for other reactions and for reduction of Hg^{2+} and reemission of Hg^0 [39,147].

The effects of di-carboxylic and tri-carboxylic organic acids (e.g. adipic acid, succinic acid, etc.) on SO_2 sorption lies in buffer action (stabilization of pH at higher values) [37,139,148].

Under conditions of real wet FGD (higher temperatures, oxidation of sulfites, presence of catalytically active metals in the slurry, some possible bacterial attack) a part of such acids can be degraded/chemically changed [149,150] in a relatively short time. Adding poly-carboxylic organic acids into absorbing slurry leads to moderate increase in mercury reduction (Hg-reemission) [37,139].

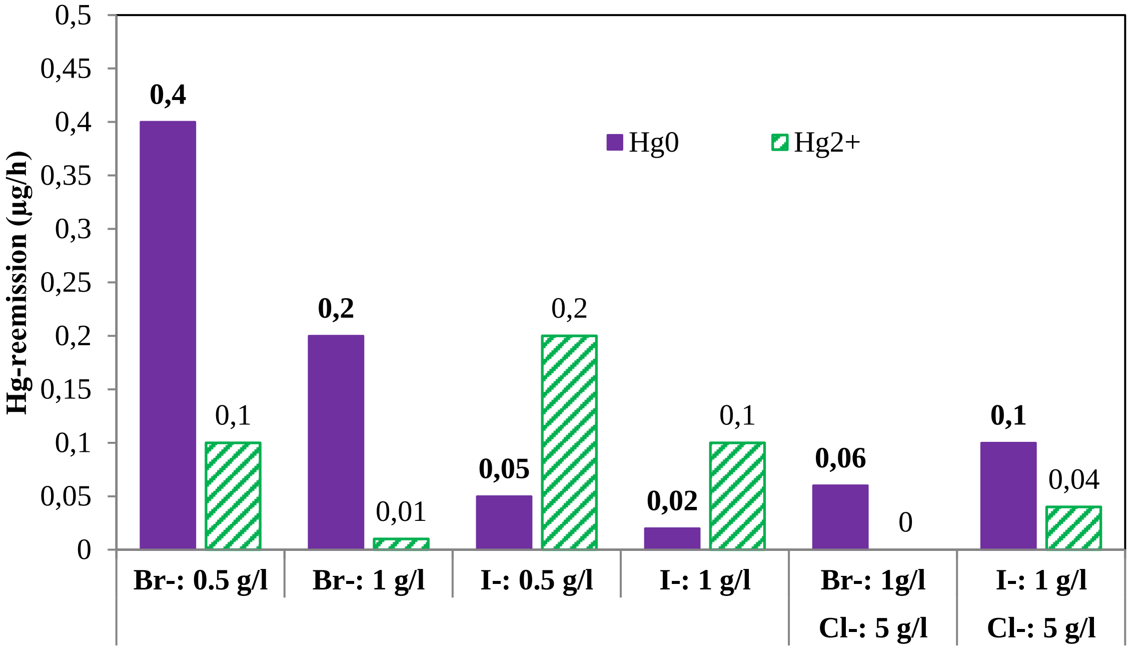

Fig. 7: Effects of concentrations of bromides, chlorides and iodides in water-limestone slurry in absorption of model gas with SO_2 (2g/m^3) in the slurry at 60 °C, (pH = 5.1 and [Hg^{2+}] = 250 μg/l) on Hg-reemissions [139]. The basic Hg^0 reemissions in slurry with concentration of chlorides 5 g/l was more than 0.5 μg/h.

Thus, their utilization for more efficient sorption of SO_2 should be optimized, depending on presence of complexing anions, temperature of the absorption and liquid/gas ratio in the scrubbing process.

6. Optional catalytic oxidation and sorption of mercury as HgS downstream wet FGD

Under conditions of insufficient sorption of mercury (or Hg + SO_2) in wet FGD, additional method for mitigation of particularly mercury emissions can be offered: the catalytic SPM methods at temperatures 60–80 °C, utilizing modules with height about 30 cm [97]. The catalyst in the polymer membrane oxidizes elemental mercury from flue gas and simultaneously, due to presence of reactive sulfur, mercury vapors are converted into HgS. SO_2 is oxidized to SO_3 and converted in presence of H_2O vapors to H_2SO_4, forming droplets on the hydrophobic surface of the polymer modules. The droplets of liquid H_2SO_4 on the polymer modules surface together with settled aerosol (mist particles) of gypsum from wet FGD have to be removed from the surface by regular water flushing (at least 1 time per day) to avoid fouling and the waste water from flushing is recycled to wet FGD. Practical capacity of the modules for Hg (due to presence of other HMs and gaseous pollutant) attains 3 to 5 mass %. The modules in series are able to reduce the Hg-emissions to 20–25 % of the input values.

The life time of the catalytic modules is between 1 and 5 years [97] according to Hg content in flue gas, composition of flue gas (HMs, SO_2, HCl, HF, etc.). The spent sorbent polymer catalytic modules have character of non-hazardous waste due to presence of mercury only in the form of HgS. The position of SPM is typically downstream wet FGD, however, the modules can be placed also downstream efficient ESP or FF after cooling the gas to the temperature suitable for the catalytic process.

Unlike systems injecting oxidizing chemicals, such as calcium bromide, this system presents no risk of air preheater corrosion, and does not impact the wastewater treatment system on the scrubber effluent stream. The system is unaffected by SO_2/SO_3 concentrations (suitable for high sulfur coals). In addition, the system can provide protection against scrubber re-emissions in a way that doesn't impact gypsum quality or the waste water treatment system. The modules also carry a co-benefit of additional SO_2 removal, which can help to meet the tighter SO_2 emissions limits and possibly to avoid upgrade/retrofit of existing FGD scrubbers.

7. Partition of mercury and Hg-precipitates among gypsum, wastewater and slurry waste (influence of particle size, inert particles, iron compounds, etc.)

Efficiency of mercury removal from a CFPP flue gas is a complex function of set-up of the flue gas cleaning line, flue gas composition, conditions for operation of ESP (filters), SCR de-NOx and desulfurization (wet FGD). Efficiency of Hg removal in dust filters increases with decreasing temperature of dust removal (very significantly at working temperatures below 110 °C), on presence of HCl/HBr in flue gas and on upstream SCR ability to oxidize mercury [8,27]. It is clear, that simultaneously with increasing efficiency of mercury removal from flue gas, increasing amount of mercury in FGD gypsum and waste products has to be expected.

Relative amount of mercury captured in wet FGD depends mainly on degree of oxidation of mercury upstream the FGD, and on conditions suitable for minimization of Hg-reemission [8,9,21]. Substantial part of Hg^{2+} compounds present in absorbing slurry ($HgCl_2$, $HgBr_2$, Hg_2SO_4, $HgSO_3$) and complex compounds of mercury (e.g. $HgCl_4^{2-}$, $HgBr_4^{2-}$, $Hg(SO_3)^{2-}$) are water soluble. Hg^0(l) is practically insoluble in water-limestone slurry and under thermal conditions prevailing in wet FGD is evaporated into flue gas. HgO(s), if present in absorbing water slurry, is very sparingly soluble in water, but under conditions of pH below approx. 6 can react with the present anions. Solubilities of selected Hg-compounds and of elemental Hg^0 are given in **Tab. 3.**

Tab. 3: Solubility of Hg^0 and selected Hg-compounds in water at 20-25 °C [139]

Compound	Hg^0	HgO	HgS	Hg_2SO_4
Solubility [g/l]	6.1·10-5	$5 \cdot 10^{-2}$	$2.5 \cdot 10^{-24}$	$2 \cdot 10^{-5}$
Compounds	Hg_2Cl_2	Hg_2Br_2	Hg_2I_2	
Solubility [g/l]	$4 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	
Compound	$HgCl_2$	$HgBr_2$	HgI_2	
Solubility [g/l]	68.1	6.1	$5.5 \cdot 10^{-2}$	

Partition of mercury in products of wet desulfurization [2,8,20,27,41,151] is dependent on concentration of chlorides in absorbing solution, addition of precipitating agent for mercury (inorganic sulfides/polysulfides, organic sulfur containing compounds, adsorbents, etc.), on presence of iron, manganese and aluminum compounds forming dregs (sludge) with adsorbing surfaces at pH > 5.5, on particle size distribution of gypsum slurry, etc. Usually, the content of adsorbed mercury decreases with increasing size of gypsum and sludge particles (with decreasing specific surface). Bigger gypsum crystals, lower content of Fe-compounds in sludge and Ca-sulfites in FGD slurry, smaller crystals of precipitated Hg-sulfide compounds by addition of inorganic sulfides or organic sulfur containing additives lead to lower content of mercury in produced gypsum [8,151-153]. Despite of wet FGD-gypsum production processes respecting such factors, content of mercury is one or two orders higher than content of Hg in natural gypsum (above 0.3 mass ppm). Content of mercury in gypsum particles with diameter (characteristic size) over 15 μm can be, however, relatively low. Mercury in FGD-gypsum is present in various forms: volatile Hg^0 (often correlated with content of sulfites in gypsum), water soluble Hg-compounds ($HgBr_2$, $HgCl_2$), water insoluble/sparingly soluble compounds (HgS, HgO, Hg_2Cl_2, $HgSO_4$, etc.).

Precipitation of mercury in wet FGD sludge by sulfides, poly-sulfides of organic compounds with sulfur (TMT salt, DTCR-salt etc.) transforms Hg into water practically insoluble Hg-salts, but excess of such precipitation additives can cause partial or total dissolution of the precipitated salts due to formation of water soluble complexes [142]. Therefore, the doses of such additives must be appropriate, proportional to mercury concentration and simultaneously with respect to possible side reactions with other HMs present.

Contents of individual forms of mercury in gypsum can be determined by thermal fractionation of Hg-compounds in gypsum [154,155] and by leaching procedures (e.g. by specific sequential chemical extraction tests) [154,155]. Only very small part of mercury (usually less than 4 %) present in FGD gypsum from real wet FGD facilities is soluble in water and a mixture of 0.1mol/l CH_3COOH and 0.01 mol/l HCl in sequential 18 hour leaching tests with liquid/solid ratio = 10 [155]. It confirms (together with results of temperature fractionation of Hg-compounds) prevailing presence of HgS modification, and Hg_2SO_4/$HgSO_4$ in wet FGD gypsum. Nevertheless, the emissions of Hg^0(g) and volatile Hg-compounds in production of calcium sulfate demi-hydrate by thermal decomposition of FGD gypsum ($CaSO_4 \cdot 2H_2O$) and in production of gypsum based wall boards are not negligible [142].

A decisive part of mercury in products from modern wet FGD plants is in waste sludge and wastewater [8,27, 42]. With application of mercury precipitation (inorganic and organic sulfides), the wastewater (after filtration/centrifugation of the waste sludge) is practically mercury-free. Majority of waste chlorides (mainly in the form of $CaCl_2$) is in the wastewater from wet FGD [19].

The main part of arsenic is bound, however, with gypsum particles, similarly as Pb (due to formation of water insoluble $PbSO_4$ in wet FGD). The main part of cadmium is usually found in wastewater or waste sludge. The usual partitions of selected toxic metals (Hg, Cd, As, Pb) in wet FGD facilities of modern coal-fired power stations are given in **Tab. 4**. The characteristics of flue gas cleaning lines and fuel utilized are in **Tab. 5** [8].

As it is obvious from **Tab. 4**, arsenic and lead are concentrated practically in all cases mainly in gypsum. On the other hand, cadmium and mercury are more distributed among all outputs streams from wet FGD. However, a substantial part of those elements and their compounds can be coupled with gypsum. A significant part of cadmium is commonly found in wastewater from wet FGD.

Concentrations of HMs in output streams from wet FGD and partition among gypsum, sludge and wastewater are dependent on fuel, ash composition, flue gas cleaning line arrangement, temperature of fly ash removal, contents of sulfur and chlorine (+ bromine) in coal and on contents of impurities (Fe, Al compounds) in limestone, on particle size distribution of the slurry from wet FGD and separation method for sludge.

Tab. 4: Partitions of selected heavy metals among output streams (gypsum, sludge of fines and wastewater) from wet FGD in five coal-fired plants [8]

Relat. partition of selected elements in output streams from wet FGD (mass %)	Plant No 1 PCC, bitumen. coal	Plant No 2 PCC, bitumen. coal	Plant No 3 PCC, bitumen. coal	Plant No 4 PCC, bitumen. coal	Plant No 5 CFB, bitumen. coal + sew. sludge
As - gypsum	98.5	92	99	96	98
As - sludge	1.5	8	1	3	2
As - wastewater	~0	~0	~0	1	~0
Cd - gypsum	55	20	84	91	18
Cd - sludge	13	18	4	3	2
Cd - wastewater	32	62	12	6	80
Hg - gypsum	27	67	97	73	45
Hg - sludge	30	22	3	24	28
Hg - wastewater	43	11	~ 0	3	27
Pb - gypsum	97.5	92	94.5	90	89
Pb - sludge	2.5	7	3.5	10	10
Pb - wastewater	~0	1	2	~0	1

Tab. 5: Characteristics of coal fired plants, flue gas cleaning lines, fuels used and consumption of limestone and process water [8]

Plant and fuel characteristics	Plant No 1	Plant No 2	Plant No 3	Plant No 4	Plant No 5
Flue gas cleaning line	SCR+ESP+ wet FGD+wet ESP	SCR+ESP+ wet FGD+wet ESP	SCR+ESP+ wet FGD+wet ESP	SCR+ESP+ wet FGD+wet ESP	SNCR+SCR+ FF+wet FGD +wet ESP
Inlet gas temperature in ESP or FF	88 °C	90 °C	125 °C	94 °C	120 °C
Fuel feed, t/h	268	175	179	246	49.2
Content of ash in fuel, mass %	12	18.11	22.26	16.89	31.05
Fly ash flux, t/h	27.5	27.6	35.0	35.3	11.9
Content of S in fuel, mass %	0.83	0.8	0.7	0.45	1.35
Content of Cl in fuel, mg/kg	145	285	103	465	468
Limestone for wet FGD, t/h	12.4	6.1	5	4.8	0.97
Process water to wet FGD, m^3/h	79.8	72	83	65	16.5

It is necessary to realize, that higher efficiency of mercury removal from flue gas means simultaneously higher content of mercury in fly ash and in slurry from wet FGD (the main output streams of captured mercury).One of the main problems is how to attain lower content of mercury (particularly as Hg^0 and in a form of water soluble compounds) and how to fully convert mercury and other heavy metals in sludge and wastewater from wet FGD process into non-toxic, stable and water insoluble form. The main procedures for attaining such state are adjustment of pH, precipitation of hydroxides, precipitation of Hg and some other HMs as sulfides, dithiocarbamates, TMT-derived salts, etc. [156] and wastewater cleaning with coagulants (Fe^{3+} or Al^{3+} salts). Nova days, emerging electrochemical processes as for example electrocoagulation [157-159], electrodialysis and electrochemical precipitation/adsorption [160,161] are tested for attaining higher efficiencies in wastewater cleaning, mercury sorption/removal and for minimization of amount of sludge with content of heavy metals and efficient desalination. Advantages and disadvantages of electrochemical methods for HMs removal from wastewaters, sludges and suspensions are discussed/assessed e.g. in two reviews [68,162]. Anodic oxidations for enhancement of sulfite oxidation and mercury absorption (as well as for suppression of Hg-re-emissions) are also investigated [50,163].

Leaching of HMs from wet FGD gypsum is a matter of occupational hygiene and in the case of waste gypsum for disposal it is also a matter of environmental (particularly water related) protection. Experience with gypsum and leaching measurement in USA indicated [164] that Hg-leaching from FGD gypsum was below concentration limits for drinking water and that variability of leaching in relation with pH was relatively low. On the other hand, Se, Sb, B, Cd and Mo exerted leaching values from gypsum over limits for drinking water - as shown in **Tab. 6**:

As it follows from the table, the more problematic elements from the point of view of leaching from gypsum into water are rather selenium, antimony, cadmium, boron and molybdenum. Cadmium has high sensitivity to pH in leaching solution. Arsenic can be extracted from gypsum mainly under lower pH values. In the case of boron the measures for limitation of leaching and appropriate guidelines for limit values are investigated. Nowadays, by applying various measures in improved removal of fly ash, stabilization of HMs in wet FGD and production of gypsum ("modern FGD gypsum process") Mo, Cd and Sb related leaching problems are solved [165]. However, selenium and boron related leaching problems (in less severe form) still persist [67].

Tab. 6: Leaching data for selected elements from wet FGD gypsum [163] with violet color area indicating potentials for exceeding tresholds for maximum concentration limit (MCL) for drinking water or toxicity characteristic threshold (TC)

	As	Hg	Se	Sb	B	Cd	Pb	Mo
Total content in gypsum (mg/kg)	2–4	0.01–0.5	2–30	2–6	NA	0.3–0.5	1–12	2–12
Leach results (µg/l)	0.5–10	0.01–0.6	4–3000	0.2–10	40–70000	0.1–50	0.1–10	1–600
MCL (µg/l)	10	2	50	6	7000 DWEL	5	15	200 DWEL
TC (µg/l)	5000	200	1000	-	-	1000	5000	-
Variability with pH	Low to medium	Low to medium	Low to medium	Low	Low to medium	High	Low	-

DWEL – Drinking water equivalent level: Low variability with pH: less than one order of magnitude difference
Medium variability with pH: 1–2 orders of magnitude difference
High variability with pH: more than two orders of magnitude difference

8. Separation of toxic elements and compounds from wastewater and waste sludge in wet FGD with gypsum production

Separation, minimization and stabilization of waste materials containing mercury and other toxic heavy metals (As, Cd, Pb, etc.) and elements (F, Se, etc.) is a very complex task [62,67,166-168].

Separation of mercury and selected HMs: for separation (precipitation) of mercury and some other heavy metals present, usually inorganic sulfides [28,33,169], poly-sulfides [28,107], organic compounds containing sulfur and polysulfides [27,28,33,34,169] are used. At acidic conditions the precipitation of mercury by inorganic sulfides is interfered by decomposition and partly by possible oxidation of sulfides [28], therefore the precipitation is only partial. At higher pH levels (above approx. 7) the precipitation of heavy metals (inclusive Hg) by sulfides is more effective. The size and nature of precipitated Hg-sulfides depends on operating conditions (concentration, temperature, composition of wastewater, etc.). In the case of excess of alkali sulfides and polysulfides in precipitation of mercury in solutions at conditions of pH > 8 the concentration of total dissolution mercury increase with pH value (2 and more orders of magnitude in the pH range 8–14) due to formation of water soluble complexes (e.g. HgS_2^{2-}, HgS_x^{2-}, etc.) [114].

In the case of organic sulfur compounds (TMT, DMTC, etc.) used for precipitation of mercury, the Hg-removal efficiency typically increases with increasing pH values (pH > 7). Nowadays, products of inverse sulfur vulcanization with unsaturated vegetable oils/chemicals with double bonds are suggested for removal of mercury and some other HMs from acidic solutions [109,170, 171]. Removal of Hg^{2+} mercury ions from acidic water solutions by sorbents produced by inverse vulcanization of unsaturated oils or some chemicals is relatively highly selective for mercury [171] in comparison with other metals (Fe, Zn, Cd, etc.).

Another possibility for Hg-removal from waste water/sludge is adsorption on active carbon (AC), zeolites, functionalized sorbents, immobilized metal organic frame-works, etc. [27,28,138,172-175]. Recently, the immobilized ionic liquids have been tested for selective removal of Hg or other heavy metals from flue gas and waste streams of gypsum production [174]. Functionalized metal-organic framework (e.g. with selenium) are investigated for permanent sequestration of mercury in

FGD gypsum, sludge and wastewater [175]. There are also powdered AC and supported ionic liquids suitable for removal of mercury in wet FGD with application of bromine compounds for better oxidation of Hg [176].

Separation of Se compounds: selenium is a metalloid element, its content in coals is typically between 0.5 and 7 ppm(mass). SeO_2 is the prevailing Se oxide in flue gas. According to conditions of dust filtration and position of SCR a part of selenium is captured in fly ash [8, 13]. Selenates (SeO_4^{2-}) and selenites (SeO_3^{2-}) are the most common Se-compounds in absorbing slurries in wet FGD [8,19]. Selenate is the less toxic of the two forms. In the frame of partitioning of Se in wet FGD products and waste streams, Ca-selenate is prevailing in FGD gypsum. Lower part of Se is present in wastewater and waste sludge from wet FGD. Selenite is more bound in wastewater and sludge than selenate with coagulated particles containing Fe, Al, Mn , oxides, etc. Under strongly reducing conditions and lower pH values (below approx. 4.5) formation of elemental Se is probable with possible reaction with Hg to HgSe [28]. Possible applicable technologies for removal of selenium from FGD wastewater [42] are summarized in **Tab. 7**. Selenites and selenates can be immobilized by means of ettringite [177]. Se- and B-compounds in fly ash from coal combustion can by stabilized (suppression of leaching to water) by Ca-compounds [118]. For chemical stabilization of selenites calcium sulfoaluminate-belite cement is suggested [178].

Tab. 7: Selected technologies for selenium removal from FGD wastewater [42]

Process	Description	Advantages	Disadvantages
Biological treatment	Se(IV) and Se(VI) are reduced to Se(0) by microbial action (similar to S(VI) reduction)	Demonstrated technology for Se removal (polishing of chem. precipitation effluent)	Some system with lower chloride concentrations, performance erratic, difficult control
Oxide sorption system	Selenium adsorbs on the surface of GFO, GFH or GTO sorbents. Se(VI) is better than Se(IV)	Novel sorbents can achieve levels of Se in effluent streams below 2 μg/l	No studies of performance in FGD wastewater. Sorption media require replacement, competition from V, P and Si comp.
Ion exchange	Se adsorbs to ligands on ion exchange resin beads, releasing a weakly attached co-ion	Resins for selenium removal of Se(IV) and Se(VI) already exist	Not suitable for high TDS waters. Requires pretreatment for SO_4^{2-} and suspended solids removal
Zero-valent iron (ZVI)	Selenium ions are converted to elemental Se by ZVI . Se(IV) is better than Se(VI) for reduction	ZVI is already used for pretreatment of constructed wetland. Suitable for ELGs compliance	No commercial experience with ZVI. Narrow pH range, requires pretreatment to remove NO_3^- and NO_2^- ions

Separation of fluorides: fluorine is bound in wet FGD mainly with calcium (CaF_2). Solubility of calcium fluoride is relatively low (about 5–10 mg/l) and depends on pH and concentration of $CaCl_2$. Fluoride concentration decreases as both, pH and $CaCl_2$ concentration increase. If a part of fly ash with content of active Al_2O_3 enters the wet FGD, complex insoluble compounds containing fluorine, aluminum and alkali metals (e.g. anion AlF_6^{3-}) are formed. Attainable concentrations of fluorine in water solutions are in such a case below 1 mg/l. Addition of aluminum sulfate to sludge from wet FGD containing waste gypsum and fluorides (molar ratio F/Al approx. 0.1–1.5) at pH ≈ 6.5 can substantially decrease fluorine concentration in solution (50–80 % decrease). Fluorine leachable concentration for such a case are comparable with guidelines for non-hazardous waste [48]. Simultaneous removal of sulfate and fluorine from wet FGD wastewater by co-precipitation with calcium hydroxide and sodium aluminate ($NaAlO_2$) is able to reduce soluble sulfate concentration in wastewater to values about 0.8 g/l and to contribute to precipitation of fluorides. The precipitated particles contain gypsum, ettringite, aluminum hydroxide and fluorine-aluminum containing complex compounds. Moreover, treatment of wastewater by electrocoagulation [44,179] is recommended for reduction of fluorine and heavy metals (Hg, Mn, Pb, Ni, Cu, etc.). Such electrocoagulation methods are, however, very rarely used [69,159] in large units.

European emission limits for gaseous pollutants (NO_x, SO_2, HCl, HF) dust and heavy metals emissions inclusive mercury are given in Commission Implementing Decision from July 2017. Strict requirement on effluent streams of water from flue gas cleaning are also there.

EPA in USA [42] identified four main problems/challenges and research needs to attain low limits for pollutants in wastewater and solid waste from wet FGD in coal combustion:

a) removal of selenium species from FGD wastewater: mainly in the forms of selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}, $HSeO_3^-$) [19],

b) zero liquid discharge with pollutants from FGD wastewater enabling water reuse in coal fired power plants [180,181],

c) developing water treatment systems, which can cope with short term fluctuations in electricity and wastewater production/composition,

d) optimization of balance for capital and operating costs for overall wet FGD treatment under situation when the power plant lifespan is uncertain.

9. Stabilization/detoxification of Hg and minimization of solid hazardous waste containing mercury and HMs

Fly ash from flue gas cleaning in coal combustion contains (depending on filtration conditions and upstream SCR) mercury and other HMs, which are subjected to potential leaching. Therefore, their stabilization (conversion to less soluble compounds) is needed [52, 58]. In the case of dewatered waste sludge from wet FGD process or in the case of lower quality gypsum production, the material is usually intended for damping/landfilling. In such a case all toxic components of the waste material should be solidified and stabilized for minimization of leaching of toxic compounds [45,58,59,182,183]. Toxicity Characteristic Leaching Procedure (TCLP) [184] defined in Environmental, Health and Safety Online Guidelines [185] present characteristic limits for leaching (TCLP) procedure. E.g. for Hg: 0.2 mg/l, Se: 1 mg/l, As: 5 mg/l, Cd: 1 mg/l, Pb: 5 mg/l. Heavy metals compounds in waste materials are stabilized by addition of sulfides or polysulfides [36], colloidal elemental sulfur from thiosulfate or polysulfide decomposition, etc. Some organic poly-sulfides are also suitable for such purpose [109,186]. Particularly mercury can be stabilized by addition of products of inverse vulcanization of vegetable oils/organic unsaturated compounds [171].

Another possibility for stabilization/solidification of mercury contaminated waste is by means of zeolites and chemically bonded phosphate ceramics or by addition of calcium sodium phosphate and magnesium potassium phosphate [187,188].

The sludge and wastewater after separation of gypsum in wet FGD contains majority of mercury present in slurry from FGD. Thickening of gypsum-suspension from wet FGD, separated in hydro-cyclones, requires dewatering in spin-driers and vacuum band-filters and two stage washing process to reduce contents of water soluble salts in gypsum. Requirements on high quality final gypsum are summarized in **Tab. 8.**

Maximization of gypsum yield (over 60–70 mass %) requires formation of developed bigger crystals of gypsum, special construction and washing function of hydrocyclones [91,189,190]. The washing water is usually mixed with smaller particles of slurry fraction from hydro-cyclones and the wastewater/sludge is processed to thickened sludge and cleaned wastewater. The classical cleaning process for sludge/waste water with production of sedimented/filtered sludge containing precipitated heavy metals and process design for reduction of the amount of sludge with higher Hg-content is shown in **Fig. 8**.

Tab. 8: Criteria for quality of power station-gypsum from wet FGD [28]

Parameter	Unit	Value
Rest moisture	Mass %	<10
$CaSO_4 \cdot 2H_2O$ content	Mass %	>95
Water soluble Mg salts	Expressed as Mass % of MgO	<0.1
Water soluble Na-salts	Mass % of Na_2O	<0.06
Content of chlorides	Mass % Cl	<0.01
$CaSO_3 \cdot 0.5\ H_2O$ content	Mass %	<0.5
pH		5–9
Color		white

For comparison, the process with two output streams of sludge is shown there. Such process can be optimized up to a level when only about 2 % of sludge with higher content of stabilized mercury [28] is produced. The classic scheme of wastewater/sludge cleaning (with only one output concentrated sludge stream) has disadvantage in higher Hg-reemissions due to pH adjustment before sulfide addition for Hg stabilization [29].

Because contents of toxic elements (Hg, Cd, As, Se) in purging water from gypsum production and sludge filtration can be high in wet FGD processes, the ecological opinion was rather against the wet FGD process [191] in the past. The methods and costs of FGD wastewater cleaning are variable and depends on coal composition and upstream methods of flue gas cleaning applied [192]. Typical FGD wastewater composition and ranges of typical pollutant concentrations are given in **Tab. 9**. The chlorides and sulfates of Ca^2+, Mg^{2+}, Al^{3+}, Fe^{3+}, etc. are water soluble and their concentrations can fluctuate in broad ranges. The cleaning methods are dependent on adherence to ZLD and on possible utilization/cost of recovered chemical compounds or clean, re-usable water [193]. Laboratory experiments on the removal of heavy metals by aged ZVI in concentrated FGD brines have shown that high temperature and Mg^{2+} are the dominant factors for enhancement of ZVI's reactivity for the removal of Se, As, Cd and Cr in brine matrices [194].

The amount of sludge with low Hg concentration is more than one order of magnitude higher than the amount of sludge with high Hg-content.

As it is obvious, aluminum, arsenic, copper, mercury and partly selenium compounds, can be at least partly separated/removed by filtration of the waste suspension of fines. On the other hand, boron compounds and chlorides are on the same level of concentrations after sedimentation and filtration of the wastewater/sludge. For repeated utilization of the water, however, particularly concentrations of aluminum, arsenic, copper, mercury, arsenic, magnesium and sulfate have to be reduced.

Effluent limitations for wastewater from wet FGD are given in **Tab. 10**.

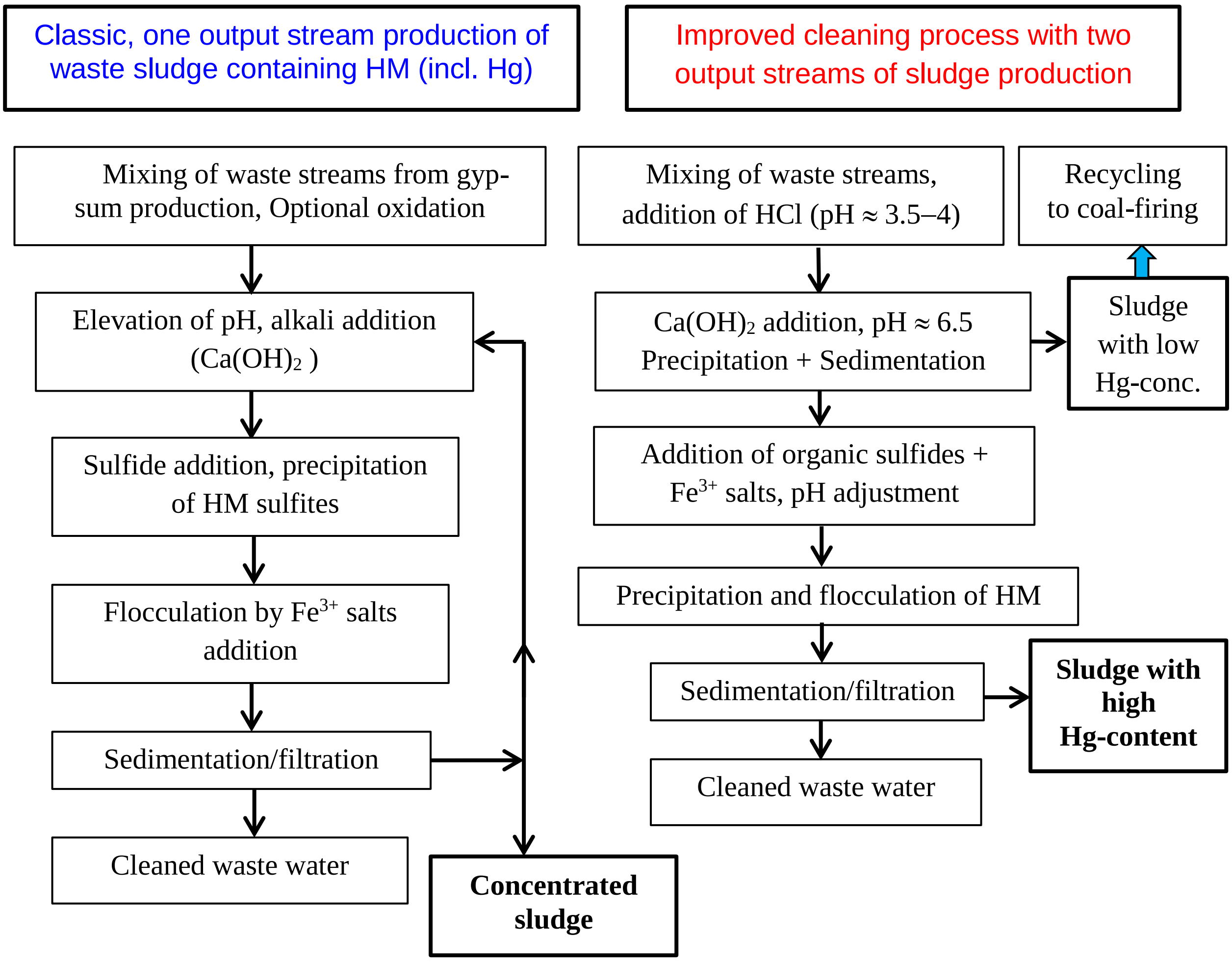

Fig. 8: Comparison of two methods for sludge/wastewater treatment. Production of one output stream (left) and two output streams of sludge with higher and lower Hg-content [27,28].

Tab. 9: Typical FGD wastewater characteristics – total sample concentrations and characteristics of filtered wastewater samples in USA [42]

Parameter	Total (liquid + suspended solids) sample concentrations			Filtered (after filtration)
Species and pH	Minimum	Maximum	Median	Median
Aluminum (mg/l)	0.95	174	87.48	12.6
Arsenic (mg/l)	0.006	0.415	0.211	0.078
Boron (mg/l)	15.1	510	262	262
Copper (mg/l)	0.076	4.2	2.15	0.184
Mercury (mg/l)	0.008	0.103	0.056	0.005
Selenium (mg/l)	0.04	2.93	1.48	0.92
Total dissolved solids (g/l)	4.35	57.7	31.0	27.4
Total suspended solids (g/l)	-	>90	-	-
Fluorides mainly CaF_2	-	>18	-	-
Chlorides-mainly $CaCl_2$ (g/l)	0.384	28.8	14.6	14.9
Sulfates (depending on supersaturation and suspended gypsum)	-	>30	-	-
pH	5.9	7.3	6.6	6.7

Tab. 10: Effluent limitations for wet FGD wastewater [42,195]

	Existing source regulation		New source regulation	
Constituent	30-day Avg.	Daily Max.	30-day Avg.	Daily Max.
Arsenic (µg/l)	8	11	-	4
Mercury (µg/l)	0.356	0.788	0.024	0.039
NO_3^-/NO_2^- as N (mg/l)	4.4	17	-	-
Selenium (µg/l)	12	23	-	5
TDS (mg/l)	-	-	24	50

Removal of $Ca^{2+}$and Cl^- ions from FGD wastewater by precipitation is rather difficult, requiring a two stage process and addition of $NaAlO_2$ [196] for precipitation of Friedel´s salt with bound chlorine. Another possibility is application of electrochemical methods like electrodialysis or combination of ED with electrolysis and electrocoagulation [69,160].

10. Comparison of emission reduction, adherence to ZLD principles, waste generation and composition of waste streams for three selected cases of CFPPs

In this chapter we compare three typical cases of CFPPs with different methods of flue gas cleaning, management of waste streams and possibilities how to attain low water consumption and status of near ZLD. In our analyses various effects are considered and compared: e.g. coal composition (moisture, ash content, contents of S, Cl, HMs, Se, B, REE), possible addition of bromine/$CaBr_2$ for enhancement of mercury oxidation, consumption of limestone, properties and possible utilization of solid waste from given combustion technology with supposed flue gas cleaning and management of waste streams.

10.1. PCC with combination of high-dust SCR, ESP and wet FGD with wastewater processing and formation of APC waste streams

A scheme of power plant with coal combustion, flue gas cleaning containing high dust SCR, ESP and wet FGD with gypsum production and wastewater processing is shown in **Fig. 9**.

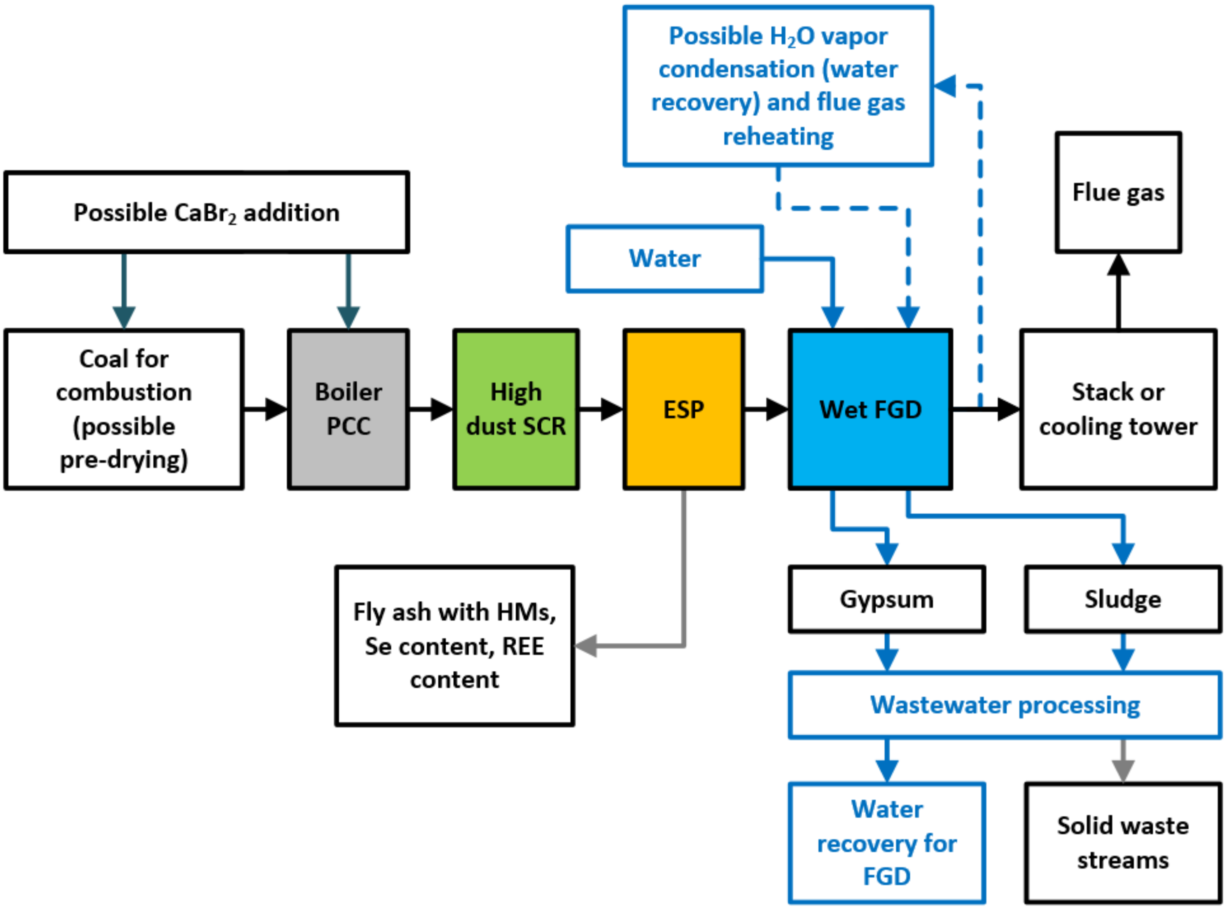

Fig. 9: Scheme of CFPP with flue gas cleaning containing high dust SCR, ESP and wet FGD with gypsum production and wastewater processing generating recovered water stream and solid waste stream

Adherence to principles of ZLD requires recovery of relatively clean water for return to FGD, production of solid waste output streams and minimization of generation of hazardous waste containing water soluble HMs, Se- and B-compounds. Water recovery is possible not only from FGD wastewater, but also from flue gas saturated with water vapor downstream wet FGD by partial condensation of water vapor and utilization of the recovered heat e.g. for district heating [197].

Another option for water recovery is offered for wet coals/lignites, where pre-drying with water vapor condensation from drying recirculated gases can contribute to water recovery/saving [193,198].

In the case of low content of chlorine in coal, oxidation of mercury in flue gas (conversion to $HgCl_2$) will be insufficient for efficient removal of Hg^{2+} in wet FGD. In such a case, addition of $CaBr_2$ to coal or addition of HBr/Br_2 into flue gas is recommended [190]. The undesired side effects of such improvement for Hg-removal are, however, higher corrosion of heat exchangers, metallic surfaces, possible formation of brominated compounds in ESP and some content of water soluble bromides in wastewater from wet FGD process.

If ZLD and formation of concentrated solid waste streams are considered, bromides (e.g. $CaBr_2$, NaBr etc.) will be contained in a mixture with $CaCl_2$, $MgSO_4$, and other water soluble salts in a solid waste stream. Selective removal of bromides is relatively difficult and requires e.g. electrochemical desalination [199]. Removal of $CaCl_2$ from wastewater by means of Friedel´s salt precipitation [10,200] is possible, but it requires high surplus of $Ca(OH)_2$ and aluminate salts. Therefore, effectivity of chlorides removal is low.

Water saving strategy requires recovery of water from flue gas (partial condensation of water vapor) downstream the wet FGD. According to temperature of saturated flue gas (usually 50–65 °C) and resulting final temperature of flue gas after condensation (approx. 40–50 °C), about half of the water vapor content of flue gas could be condensed for water recovery and return to the FGD by direct or indirect cooling of flue gas and successive water cleaning [197,201]. The cooled, saturated flue gas is released either into atmosphere through cooling tower (without heating) or through a chimney after sufficient heating (for reduction of relative humidity of the flue gas). Recuperative heating (heat exchangers) is usually applied utilizing sensible heat of flue gas upstream of the wet FGD. Such heat exchangers suffer from corrosion and fouling by aerosols/droplets containing gypsum and chlorides [202,203], and they need, at least in a part of them, to be covered by special corrosion resistant materials (e.g. PTFE layers). Flue gas outlet of water vapor saturated gas with aerosols/droplets [202,204,205], through cooling tower causes both increasing atmospheric emissions of aerosol/droplets containing gypsum/chlorides by drift and pollution of the cooling water by falling droplets with inorganic salts.

Therefore, in such a case, the cooling water needs more often regeneration or wastewater blowdown together with higher consumption of fresh water. It means higher requirement on water consumption/wastewater cleaning.

Improved efficiency of mercury removal by addition of $CaBr_2$ to coal and precipitation/removal of mercury from wet FGD wastewater/sludge by a special inorganic additive containing polysulfides (generating polysulfane H_2S_x) is described in relevant literature [77,190].

Generation of mercury and HMs containing hazardous waste can be minimized according to scheme of wastewater processing illustrated in **Fig. 8**.

In the case of reasonable content of REE or other valuable elements (e.g. Ge) in coal, conditions for fly ash separation are adjusted to recover efficiently the compounds of selected valuable elements. This scheme for flue gas cleaning and waste management/disposal is probably suitable for coals with relatively higher content of sulfur, lower to medium content of chlorine, higher content of mercury and some HMs, Se-compounds and significant content of recoverable REE, Ge, Ga, etc.

10.2. PCC with combination of high-dust SCR, ESP and wet FGD with wastewater adjustment and flash evaporation utilizing flue gas heat – formation of mixed waste stream from fly ash and FGD waste

The scheme of power plant with coal combustion, flue gas cleaning containing high dust SCR, ESP/FF, wet FGD with gypsum production and flash evaporation of moderately concentrated wastewater upstream of the filters is shown in **Fig. 10**. Such arrangement of flue gas cleaning and waste disposal from FGD [206,207] generates only one mixed stream of solid waste (fly ash and dried waste from FGD). Water recovery is feasible again from flue gas downstream the wet FGD. The status of near ZLD is realized relatively simply in this way. Solidification/stabilization of the mixed material (fly ash + FGD waste) captured in filters requires special treatment, addition of special additives, iron compounds, sulfur compounds, cement or lime [178,208] for chemical stabilization and solidification.

Recovery of REE or other valuable elements from mixtures of fly ash with waste from wet FGD is unsuitable and more difficult than in the foregoing case. Stabilization/solidification of the mixture (fly ash + solid waste from FGD) is complicated by presence of water soluble salts ($CaCl_2$, $MgSO_4$, bromides, etc.). From the point of view of economy [192,209,210] this method can be relatively cheap under assumption that contents of sulfur, chlorine, mercury and some other selected HMs are relatively low and the S/S procedure for the mixed waste is not excessively complicated and expensive.

The problems with aerosols/droplets in flue gas exiting FGD and with pollution of cooling water in cooling tower are similar as in the foregoing case.

Ammonium presence in flue gas (caused by e.g. ammonia slip from SNCR) has an impact on fly ash composition captured in filters, on changed pH and ORP conditions in FGD and on aerosol composition in flue gas at the outlet from wet FGD.

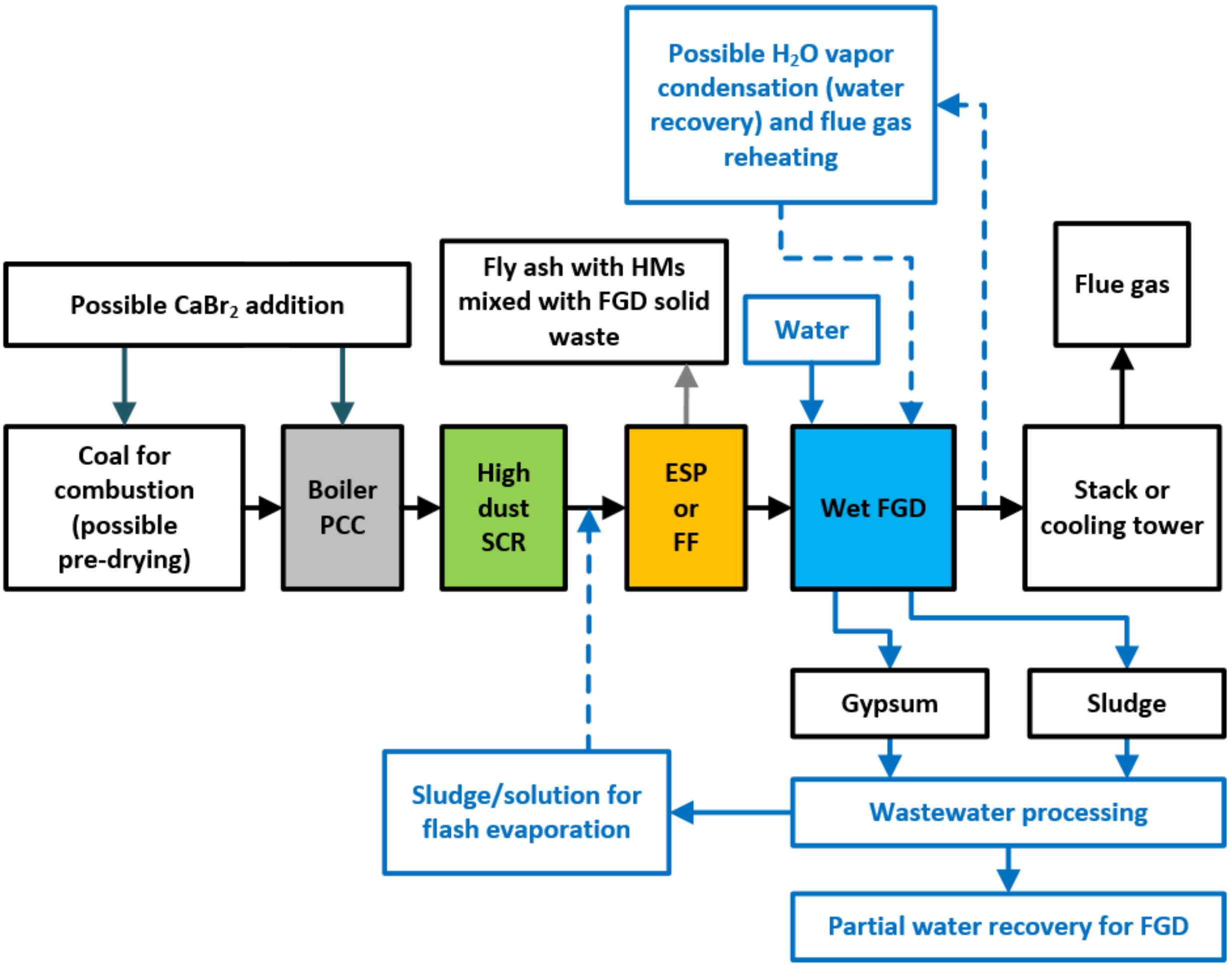

Fig. 10: Scheme of CFPP with flue gas cleaning containing high dust SCR, ESP or FF, wet FGD with gypsum production and flash evaporation of moderately concentrated wastewater upstream of the filters

10.3. CFB combustion with in-situ desulfurization by limestone, FF for fly ash removal, AC injection and possible additional FF for AC+Hg capture

The usual scheme of power plant with CFB coal/lignite combustion, flue gas cleaning containing rather low dust SCR, fabric filter (FF) for fly ash and desulfurization products removal, injection of AC based mercury sorbent or impregnated AC/mineral sorbent, possible additional FF for deep removal of dust and mercury sorbent (without any wastewater discharge) is shown in **Fig. 11.**

Circulating fluidized bed combustion with in-situ desulfurization by limestone addition has operating temperature typically around 850 °C (substantially lower than PCC). CFB combustion is suitable particularly for coals/lignites with lower calorific value, high ash coals, mixed fuels and fluctuating quality of fuels. For high ash lignite and subbituminous coals, low dust position of SCR is usually preferred due to slower deactivation of catalyst. A smaller part of ash with $CaSO_4$ and remaining non-reacted CaO is removed as bottom ash.

A significant part of ash with small particles of $CaSO_4$/CaO/$CaCO_3$ is removed in FF. Depending on operating temperature of FF, content of unburnt carbon and chlorine (in form of chlorides) in fly ash, a substantial part of mercury is captured and removed together with fly ash in FF [211,212]. Similarly, a decisive part of As, Cd, Pb, Zn and some other compounds of HMs are removed on the primary FF. Fly ash from CFB combustion (particularly from lignite combustion) is more efficient for sorption of Hg_p and Hg-compounds than fly ash from high temperature PCC. The rest of mercury is captured by means of sorption on injected activated carbon particles or impregnated AC particles in successive FF. The lower the sorption temperature the more efficient sorption of Hg, particularly on non-impregnated AC, is attained. Suitable temperatures are usually between 100 and 140 °C. The mercury adsorbed on AC can be stabilized by sulfides, polysulfides or organic compounds containing sulfur. Higher concentrations of SO_2 in flue gas deteriorate efficiency of mercury sorption on AC. Higher concentrations of HCl, higher oxygen concentration and presence of oxides of transition metals improve Hg-oxidation and sorption on AC.

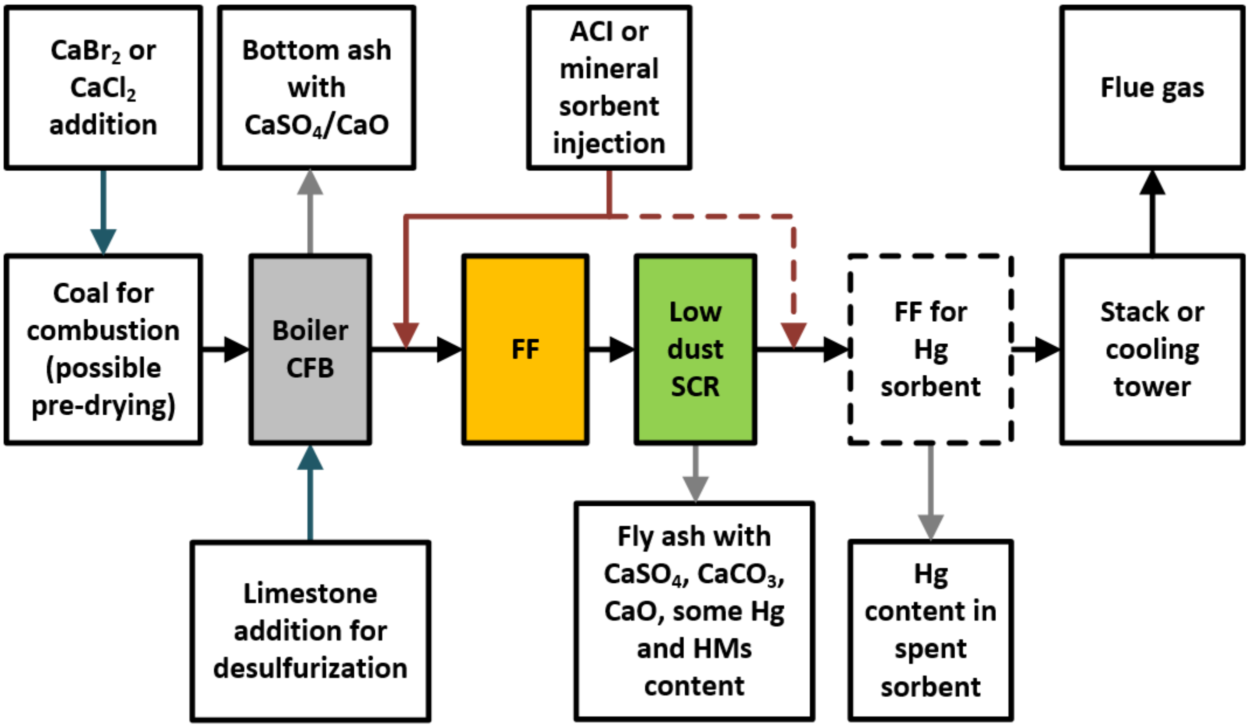

Fig. 11: Scheme of power plant with CFB coal/lignite combustion, flue gas cleaning containing fabric filters (FF), usually low dust SCR, injection of AC/mineral based mercury sorbent, and possible additional FF for removal of the spent sorbent with mercury load (without any wastewater discharge)

Disadvantage of CFB based technology with dry flue gas cleaning is relatively high consumption of limestone (Ca/S molar ratio for 80–90 % desulfurization of flue gas is usually between 1.4 and 2. Utilization of fly ash from CFB combustion for recovery of valuable elements is more difficult due to relatively high content of Ca-compounds in a mixture with fly ash. On the other hand, there is practically no consumption of water and no generation of wastewater in this technology. Flue gas is not saturated by water vapor downstream the second filtration and no reheating of flue gas upstream the stack is needed. However, in retrofitting of older units with CFB combustion with in-situ additive desulfurization (due to more stringent limits for SO_2 emissions), additional wet FGD is often needed for this purpose. Another option for efficient flue gas cleaning in CFB combustion is wet-dry desulfurization by means of $Ca(OH)_2$ slurry with AC addition and downstream application of FF. Under such conditions the final SO_2, HCl and Hg-emissions can be very low.

Mixtures of fly ash with $CaSO_4$/CaO, depending on coal and flue gas composition, can exert the so called puzzolanic properties – it means hardening after addition of water or water with some additives. Such solid product prevents leaching of HMs from fly ash and causes very good chemical stabilization of the mixed waste material.

Presence of ammonia in flue gas (from SNCR or SCR of NO_x) causes mainly presence of ammonium salts in fly ash, partly also in AC with adsorbed mercury.

11. Conclusions

Mercury compounds in coal and other fuels are transformed during combustion processes to elemental mercury and oxidized mercury compounds (HgO, $HgCl_2$, Hg_2SO_4, etc.), depending on flue gas composition, temperature, presence of sorbents and cooling rate.

According to operational parameters and composition of the flue gas cleaning lines, a part of mercury is removed as Hg_p in filters (ESP, FF). According to temperature, presence of HCl in flue gas, chlorides and unburnt carbon in fly ash particles, mercury is adsorbed in various forms on fly ash particles.

Fly ash particles are increasingly valuable raw material for recovery of REE metals and some other useful and scarce elements (e.g. Ge, Ga). Coal combustion related fly ashes are used in cement production, as fillers, additives to concretes, etc. However, any thermal processing of fly ash with temperatures approx. above 200 °C (e.g. cement production, smelting of fly ash with alkalis for REE recovery) is potential source of mercury emissions and according to operating temperature of some other elements (As, Pb, etc.).

The remaining substantial part of mercury in flue gas downstream fly ash filters (usually over 60–80 %) will continue in flue gas to be removed in a dry sorption process by AC or mineral sorbents (better with impregnation) or removed in a wet flue gas cleaning process (FGD) together with SO_2, HCl and other acid gases. In the case of insufficient concentration of chlorine in coal (and consequently in flue gas) a source of bromine (e.g. $CaBr_2$) should be added to coal for combustion. HBr/Br_2 presence in flue gas is substantially more efficient in Hg-oxidation ($HgBr_2$ formation) than HCl/Cl_2 ($HgCl_2$ formation).

Wet FGD systems (mostly a two-stage process based on limestone slurry scrubbing) removes a part of small fly ash particles present in flue gas (together with HMs present on them – like Pb and As compounds) and removes oxidized water soluble Hg-compounds ($HgCl_2$ and $HgBr_2$). Hg^0 is only partly absorbed into acidic solutions containing HCl and $HgCl_2$ (e.g. in pre-washer HCl removal from flue gas upstream the wet FGD removal of SO_2). It means that the efficiency of wet FGD for mercury removal depends primarily on $HgCl_2/Hg^0$ ratio in flue gas. Wet FGD process has, at least in a part, reduction atmosphere contributing to reduction of Hg^{2+} compounds to elemental mercury and its re-emission. The re-emission of Hg is influenced by presence of Hg complexes ($HgCl_4^{2-}$, $HgBr_4^{2-}$, etc.) in absorption slurry, pH, ORP, temperature, SO_2 concentration in flue gas.

In the case of insufficient mitigation of Hg-emissions by wet FGD, the catalytic SPM method can be used downstream for Hg-emission reduction. Advantage of this method is in binding of mercury in the form of non-toxic HgS.

The waste streams from wet FGD comprise gypsum (as useful product), waste sludge and wastewater (as waste streams). Mercury is generally present in all outputs, but content of Hg in gypsum can be minimized (selection of bigger slurry particles, careful washing). The output streams from wet FGD contain also other heavy metals (As, Cd, Pb, etc.), Se-compounds, B-compounds, etc. Arsenic, lead and Se-compounds are often concentrated in gypsum, Cd and Hg rather in waste sludge and wastewater. Boron is present mainly in wastewater. Deep removal of Se- and B-compounds from FGD wastewater is still rather problematic and expensive.

Due to the fact that HgS is the only one recognized non-toxic compound of mercury (organic S-containing salts as TMT and other precipitated compounds of mercury being still discussed and doubted), mercury present in the sludge and wastewater needs transformation into HgS (addition of alkali-sulfides or poly-sulfides, inorganic/organic). Transformation of water soluble Hg-compounds into elemental mercury has no sense, because it presents no sellable product (in fact liquid Hg^0 has now negative price). The overall wastewater cleaning process from wet FGD can be arranged/adapted into two stages, where mercury is precipitated and concentrated in the second stage sludge forming only relatively small part (5–15 mass %) of the sludge. The primary sludge with low content of mercury (containing significant part of precipitated HM compounds from FGD) can be recycled into combustion, together with coal. The secondary sludge with stabilized form of Hg (in the form of HgS) and some other stabilized HM can be solidified.

The increasing lack of natural fresh water in the world together with high consumption of water in wet FGD and generally relatively high water evaporation losses led to trials and development of processes/technologies based on principles of low water consumption FGD technologies. It supposes condensation of water vapor from flue gas and application of technical developments using conception of zero liquid discharge (ZLD) from FGD process (with water recycling/re-use). These concepts can save fresh water sources needed for flue gas cleaning line, but the potential technologies with ZLD conception are still expensive, with substantial energy demands. Moreover, they solve only insufficiently production and utilization (recycling) of water soluble salts produced as solid waste or dense sludge waste from the wastewater. In this respect, CFB combustion technology with "in situ" dry desulfurization by limestone addition and with dry Hg removal by solid sorbents is better, with practically no water consumption in flue gas cleaning. The mixed (ash + $CaSO_4$ + CaO) residues from CFB coal/lignite combustion have puzzolanic activity, but they enable no production of utilizable gypsum. Recovery of REE or some other valuable elements from mixtures of fly ash with Ca-compounds is more difficult than from pure fly ash. Semi-dry method of flue gas desulfurization by $Ca(OH)_2$ slurry has also no production of wastewater (adherence to ZLD), but the technology needs water for the inlet slurry preparation. Removal of mercury and some other HMs from flue gas is more efficient on fabric filters often used in de-dusting of flue gas in CFB combustion. The lower the temperature of flue gas filtration by FFs the lower Hg emissions can be achieved. This is particularly proved by semi-dry desulfurization with low final filtration temperature (below 100 °C).

Pressure on lower consumption of fresh water for substitute of evaporated water and blowdown (polluted) water in cooling towers (in open cycle cooling with water recirculation) leads to implementation of indirect cooling methods and to limitations in water vapor saturated flue gas discharge through cooling towers. The aerosols/droplets from flue gas downstream the wet FGD contribute to cooling water pollution and higher needs/costs for cooling water cleaning and recovery. Direct outlet of water vapor saturated flue gas with aerosols/droplets downstream wet FGD through the cooling tower is cheaper than reheating of the saturated flue gas and its exit through the stack, but such solution leads to higher aerosol emissions of Ca, Fe, ammonium and other salts to the atmosphere and to increased cooling water pollution.

As it is obvious, the complex solution of environmental impacts in coal-fired power generation technologies needs to improve, minimize the waste output streams (particularly hazardous waste containing water soluble HMs), cut down external water consumption, maximize utilization of the coal related ash and air pollution control (APC) waste for recovery of some valuable elements (like REE) and water soluble salts. Such new complex, environmentally friendly solutions require, however, substantially higher energy consumption, new technological schemes, mitigation of problems coupled with membrane and electrochemical methods of wastewater cleaning technologies (fouling, scaling, clogging, high energy consumption) and looking for new ways of utilization of the coal combustion related waste according to principles of circular economy.

The prices of coals and lignites on the market will be more diversified according to content of ash, sulfur, chlorine, bromine, HMs, Se, boron, etc. in fuels. Pressure on minimization of hazardous waste formation and disposal from coal combustion and flue gas cleaning is increasing.

In leaching tests and analytical procedures, more simple, more directed and more practical methods will be required for determination of speciation of mercury in solid waste materials to confirm exclusive content of non-toxic HgS in waste. Similarly a better insight into speciation and toxic properties will be required for other HMs. Last, but not least, new analytical procedures for Se- and B-compounds in wastewater, cheap and reliable methods for solid waste stabilization, minimization of leaching and minimization of hazardous waste streams will be required.

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Abbreviations

AC	Active carbon for sorption
ACI	Active carbon injection
APC	Air pollution control
BAT	Best available techniques
CC	Coal combustion
CFB	Circulating fluidized bed
CFPP	Coal fired power plant
CS-ESP	Cool side electrostatic precipitator
DMTC	Dimethyl-dithiocarbamate
DTCR	Dithiocarbamate
DWEL	Drinking water equivalent level
EC	Electrocoagulation
ED	Electrodialysis
ELGs	Effluent limitation guidelines
ESP	Electrostatic precipitator (for fly ash removal)
FA	Fly ash
FF	Fabric filter (for fly ash removal)
FGD	Flue gas desulfurization
FO	Forward osmosis
GFH	Granular ferric hydroxide
GFO	Granular ferric oxide
GTO	Granular titanium oxide
HM	Heavy metal
MCL	Maximum concentration limit
MD	Membrane distillation
MSWI	Municipal solid waste incineration
NF	Nano-filtration
ORP	Oxidation-reduction potential
PCC	Pulverized coal combustion
PTFE	Polytetrafluorethylene polymer
REE	Rare earth elements
RO	Reverse osmosis
SCR	Selective catalytic reduction of NOx
SNCR	Selective non-catalytic reduction of NOx
SPM	Sorbent polymer modules for Hg removal
S/S	Stabilization and solidification
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total dissolved solids
TMT	2,4,6-trimercaptotriazine
ZLD	Zero liquid discharge
ZVI	Zero valent iron (used for reduction)

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