Possible Removal of Mercury in Dry Flue Gas Cleaning Lines of Solid Waste Incineration Units

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2014

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1. Introduction

Sulfur dioxide, HCl , NOx, dust, heavy metals inclusive mercury belong to the most usual pollutants in flue gas from solid waste incineration units [1,2]. The main sources of mercury in municipal solid waste (MSW) are [3]: dry cell batteries, fluorescent lamps, amalgams, old mercury thermometers and relays. The general trend shows clear decrease of mercury content in MSW, however, still at least temporarily the content of mercury in MSW can be significant from the point of view of emissions from incineration.

The main gaseous pollutants from MSW incineration (SO_2, HCl) can be removed by wet, semi-dry or dry absorption/sorption processes [4], NOx emissions are reduced by selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) by addition of ammonia or urea to flue gas. Here we will focus on dry flue gas cleaning methods applied for MSW incineration [5]. Majority of dust from the incineration is usually removed in electrostatic filters or fabric (bag) filters. Dry method of flue gas cleaning are advantageous particularly in smaller solid waste incineration units [5,6], they have usually lower capital costs and simpler operation. The dry gas cleaning methods are based on an alkali sorbent injection and fabric filters for removal of dust and solid products from cleaning (gas-solid reactions).

Amount and form of mercury emissions from MSW incineration depend on waste (fuel) composition, content of mercury and chlorine in waste and on whole process of flue gas cleaning [7-9]. Generally three forms of mercury in flue gas can be distinguished: vapors of elemental Hg, vapors of chemical compounds of mercury and mercury (mainly Hg-compounds) adsorbed on small fly ash particles [8]. In the case of higher HCl/total mercury molar ratio in flue gas (usual case in MSW incineration) prevailing part (majority) of mercury is present in form of $HgCl_2$ and the smaller part in form of elemental mercury vapors [4,8,10].

Removal of both forms from flue gas is dependent on reactions and sorption processes at temperatures approx. below 330 °C [10-14]. Part of $HgCl_2$ and small part of elemental Hg vapors can be adsorbed on particles of solid sorbents for removal of SO_2 and HCl (e.g. active soda, calcium hydroxide etc.). The non-impregnated active carbons, impregnated carbons [10,12,15] or activated lignite cokes [16] are able to remove mainly the mercury compounds ("oxidized forms" like $HgCl_2$, HgO etc.). Generally vapors of metallic (elemental) Hg are adsorbed only weakly on active carbon. Much better chemisorption of elemental Hg is achieved by active carbon based sorbents impregnated by sulfur, alkali poly-sulfides, ferric chloride, $CuCl_2$ etc.[3,17]. Also inorganic sorbents (e.g. porous mineral rocks) with similar

chemical impregnation are applicable [13,18]. Presence of ammonia in flue gas [19,20] (e.g. due to application of SNCR for de-NO$_x$) or ammonia and de-NO$_x$ catalyst (SCR) affects generally forms of mercury in flue gas (Hg/HgCl$_2$/HgO ratio). If flue gas de-NO$_x$ by SCR is applied, substantial part of mercury can be oxidized and changed [20-22] into compounds (HgO, HgCl$_2$, etc.).

In dry flue gas cleaning methods in MSW incineration sorbents based either on soda or calcium hydroxide can be used [5,23,24]. The minimum temperature for dry sorption of acidic gases is about 130 °C and the maximum practically acceptable temperature for dry removal of HCl and SO$_2$ is about 330 °C. The temperatures over approx. 200 °C and 240 °C are not convenient for powdered active carbon based sorbents of Hg and for sulfur vapors and drops because of possible dust explosion and auto-ignition. The mineral (inorganic) sorbents of Hg without impregnation are suitable rather at temperature below approx. 180 °C. The inorganic impregnated sorbents with FeCl$_3$ can be used for max. temperature about 280 °C (melting and decomposition of FeCl$_3$). Above 280 °C only inorganic sorbents impregnated with CuCl$_2$ are probably suitable, but due to catalytic effects of Cu-compounds in de-novo formation of PCDD/PCDF their application is questionable under such conditions [25]. Therefore dry sorption process for simultaneous removal of acidic gas components and mercury is difficult/doubtful at temperatures over approx. 280 °C.

2. Thermodynamics and equilibria in removal of mercury from flue gas

Basic properties (melting point, boiling point) of mercury, mercuric chloride (HgCl$_2$), mercury(I) chloride (Hg$_2$Cl$_2$), potential sulfur based sorbents (sulfur, H$_2$SO$_4$, Na$_2$S$_4$),relevant impregnation chlorides (FeCl$_3$, FeCl$_2$, CuCl$_2$) together with chlorides of selected toxic metals (As, Cd, Pb, Zn) are summarized in **Table I**.

Table I: Melting points and boiling points of mercury, selected mercury compounds, sulfur, H$_2$SO$_4$ and other selected compounds relevant in mercury and heavy metal removal reactions.

Species	Melting point (°C)	Boiling point (°C)	Notice
Hg-elemental	-38.8	356.6	
Hg$_2$Cl$_2$	525 (at P > 2 bar)	383 (sublimat.)	Part. decomp. (Hg$_2$Cl$_2$→ HgCl$_2$ + Hg°)
HgCl$_2$	277	304	
HgO			> 450 °C decomposition
HgS	580		> 450 °C decomposition
Sulfur	115.2	446.6	Auto-ignition: 230 – 245 °C
H$_2$SO$_4$	10	337	> 300 °C decomposition
FeCl$_3$	306	315	> 280 °C decomposition
FeCl$_2$	677	1023	
CuCl$_2$	498	993	> 800 °C decomposition
AsCl$_3$	-16.2	130.2	Volatile, vapours in flue gas
CdCl$_2$	564	967	
PbCl$_2$	501	950	
ZnCl$_2$	292	756	

Mercury vapors can react in flue gas with HCl, sulfur vapors, alkali poly-sulfides , vapors of H$_2$SO$_4$ and chlorides of transition metals (Fe, Cu, etc.).
Thermodynamics of relevant "capture reactions" of elemental Hg and oxidized form of mercury (HgCl$_2$) in terms of Gibbs free energies of corresponding reactions is given in **Tables**

II and **III.** The ΔG_r values have been computed from ΔG_f values of compounds or elements (in non-standard states) [26] by application of usual relationship:.

$$\Delta G_r = \Sigma(\Delta G_f)_{final} - \Sigma(\Delta G_f)_{initial} \qquad (1.1)$$

Where $\Sigma(\Delta G_f)_{final}$ is the sum of the Gibbs free energies of formation for the final (produced) compounds and $\Sigma(\Delta G_f)_{initial}$ is the sum for the input compounds.

Table II: Gibbs free energies of reactions relevant to removal of elemental Hg from flue gas at temperature 500 K.

Reaction	ΔG_r (kJ/mol)	Notice
$(1/6)S_6(g) + Hg(g) = HgS(s)$	-56.46	Gaseous sulfur in form of S_6
$Na_2S_4(s) + Hg(g) = HgS(s) + Na_2S_3(s)$	-57.08	Na_2S_x supposed in solid form
$2HCl + 0,5O_2 + Hg(g) = HgCl_2(g) + H_2O(g)$	-181.08	$HgCl_2$ supposed in vapors
$2FeCl_3(s) + Hg(g) = HgCl_2(g) + 2FeCl_2(s)$	-127.54	
$H_2SO_4(l) + Hg(g) + 0,5O_2 = HgSO_4(s) + H_2O(g)$	-141.82	
$H_2SO_4(g) + Hg(g) + 0,5O_2 = HgSO_4(s) + H_2O(g)$	-152.97	
$2CuCl_2(s) + Hg(g) = HgCl_2(g) + 2CuCl(s)$	-132.02	

Sulfur vapors normally present at temperature 500 K (227 °C) in three molecular form (S_8, S_6 and S_4) was supposed for simplicity only in form of S_6 molecules. Sulfuric acid will be in form of vapors (in flue gas), but within sorbents it can be also in liquid form. $HgCl_2$ (due to very small concentrations in flue gas) is supposed in vapor form. As it is obvious from **Table II** the reactions of elemental mercury with HCl, $FeCl_3$, $CuCl_2$ and sulfuric acid are thermodynamically more favorable than the reactions of Hg with sulfur and polysulfide (Na_2S_4).
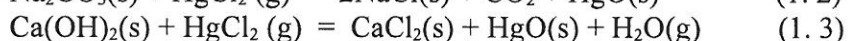
Table III: Selected possible reactions for removal of $HgCl_2$ vapors from gas and selected reactions for removal of volatile heavy and toxic metal chlorides ($ZnCl_2$, $CdCl_2$, $PbCl_2$, $AsCl_3$) by means of Na_2S_4 (or CaS) and thermodynamics in terms of Gibbs free energies of corresponding reactions at 500 K (probability of chloride forms of heavy metals in flue gas is generally dependent on HCl, H_2O and oxygen concentrations in flue gas).

| Reaction	ΔG_r (kJ/mol)	Notice
$Na_2S_4(s) + HgCl_2(g) = 2NaCl(s) + HgS(s) +(3/6)S_6(g)$	-237.65	Gaseous sulfur in form of S_6
$CaS(s) + HgCl_2(g) = CaCl_2(s) + HgS(s)$	-148.35	
$ZnCl_2(g) + Na_2S_4(s) = 2NaCl + ZnS(s) + (3/6)S_6(g)$	-266.73	$ZnCl_2$ supposed in vapours
$ZnCl_2(s) + Na_2S_4(s) = 2NaCl + ZnS(s) + (3/6)S_6(g)$	-199.11	
$2/3AsCl_3(g) + Na_2S_4(s) = 1/3As_2S_3(s) + 2NaCl(s) + (3/6)S_6(g)$	-236.32	Na_2S_x supposed in solid phase form
$CdCl_2(s) + Na_2S_4 = 2NaCl(s) + CdS(s) + (3/6)S_6(g)$	-168.53	$CdCl_2$ supp. in solid state – missing data for $CdCl_2(g)$
$PbCl_2(g) + Na_2S_4 = 2NaCl(s) + PbS(s) + (3/6)S_6$	-248.68	
$PbCl_2(s) + Na_2S_4 = 2NaCl(s) + PbS(s) + (3/6)S_6(g)$	-152.64	For solid form of $PbCl_2$

ΔG_r of reactions of $HgCl_2$ (oxidized form of mercury) with sulfides (poly-sulfides) and comparison with reactions of selected toxic heavy metals with Na_2S_4 is shown in **Table III**.

The direct reactions of e.g. Na_2S_4 with $HgCl_2$ and HCl in flue gas lead to formation of small (sub-micron) droplets and vapors of elemental sulfur. These S-droplets/vapors can react directly in gas phase or after sorption on solid surfaces with vapors of elemental Hg. The reactions of metal chlorides with Na_2S_4 (forming NaCl) are thermodynamically more favorable then the reactions of elemental mercury. Mercury (and similarly other heavy metals) captured in the form of water insoluble HgS has advantage in solidification/stabilization processes for waste dumping (practically no leaching).

In the case of surplus of basic sorbents (Na_2CO_3, calcium hydroxide) in presence of oxygen $HgCl_2$ can react (at least partly) with them to form HgO. At low concentrations of $HgCl_2$ this compound is supposed to be present in vapor form ($HgCl_2(g)$):

$$Na_2CO_3(s) + HgCl_2\,(g)\ =\ 2NaCl(s) + CO_2 + HgO(s) \qquad (1.\,2)$$
$$Ca(OH)_2(s) + HgCl_2\,(g)\ =\ CaCl_2(s) + HgO(s) + H_2O(g) \qquad (1.\,3)$$

In presence of ammonia in gas (e.g. from de-NO_x by SNCR) $HgCl_2$ is (at least partly) decomposed (reduced) to elemental mercury at temperatures over approx. 300 °C according to equation:

$$3HgCl_2\,(g,s) + 2NH_3\ =\ N_2 + 3Hg°(g) + 6\,HCl(g) \qquad (1.\,4)$$
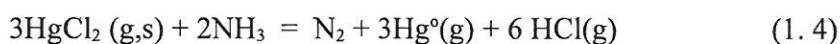
Elemental Hg° is subjected (partly) to oxidation :

$$Hg°(g) + 0.5\,O_2\ =\ HgO(s) \qquad (1.\,5)$$

Thermodynamics in terms of ΔG_r values for these reactions of $HgCl_2$ with alkalis and ammonia at 400 K, 500 K, 600 K and 700 K are given in **Table IV**.

Table IV: Gibbs free energies (ΔG_r) in kJ/mol for the above mentioned reactions of $HgCl_2(g)$ in a temperature range 400 – 700 K

Reaction	ΔG_r at 400 K	ΔG_r at 500 K	ΔG_r at 600 K	ΔG_r at 700 K
(1. 2)	-27.558	-27.46	-27.387	-27.111
(1. 3)	9.665	11.049	12.441	13.833
(1. 4)	-66.35	-123.683	-181.047	-238.355
(1. 5)	-69.441	-49.178	-29.221	-9.552

Thermodynamic analysis suggests that at higher temperature (over 200 – 250 °C) $HgCl_2$ is reduced to metallic mercury be free ammonia (present as ammonia slip a.g. after application of SNCR of NO_x). In the case of active soda based dry system of gas cleaning $HgCl_2$ tends to be changed into HgO (de-halogenation effect), on the other hand in dry system with $Ca(OH)_2$ sorbent and in presence of calcium chloride HgO tends rather to be changed into $HgCl_2$ (halogenation effect on mercury).

At temperatures below approx. 200 °C , in presence of oxygen and absence of reducing species, Hg-vapors are partly oxidized in flue gas to HgO.

3. Requirements on emissions (flue gas cleaning) from MSW incineration

General trend in all EU countries is shifting the limits for emissions from MSW incineration to lower values (more stringent air pollution control legislation). As an example of requirements on flue gas cleaning lines in MSW incineration units, **Table** V compares raw flue gas concentrations of pollutants with prescribed day average emission limits in Germany [1,26].

In near future even more stringent limits for pollutants are expected (e.g. 100 mg NO_2/m^3, lower limits for SO_2 and HCl emissions, further reduction of limits for heavy metal emissions inclusive mercury). Flue gas cleaning in waste incineration is therefore a complex problem, where mercury emissions are only part of overall emission figure and reduction of Hg-emissions is necessary to consider in relations with emissions of other pollutants.

Table V: Requirements on flue gas cleaning in waste (MSW) incineration and comparison with raw flue gas concentrations of pollutants [1,26]

Category of pollutant	Raw flue gas concentrations (mg/m³)	Permitted day average value [26] of emissions (mg/m³)	Required degree of separation (%)
Dust particles	2000 - 10000	10	99 – 99.9
HCl	300 – 1500	10	98 – 99
HF	2 – 20	1	~ 95
SO₂	200 - 800	50	85 - 95
NOₓ as NO₂	200 – 400	200 (100 exp.)	~ 50 (70)
Hg	0.2 – 0.7	0.03	85 - 95
Σ (Cd and Tl compounds)	1 - 10	0.05	95 - 99
Σ (As, Co, Cr, Cu, Mn, Ni, Pb, Sb, V, Zn compounds)	10 - 80	0.5	> 95
Σ(As, Cd, Co, Cr compounds+Benzo(a)pyren)	2 - 20	0.05	> 95
Σ (PCDD/PCDF)	1 – 4 ng/m³	0.1 ng TEQ/m³	> 90

Another very significant matter is character and properties of solid residues from waste incineration (bottom ash, fly ash, residues from air pollution control, etc.), how to cope with such categories of solid residues (handling, dumping, landfilling, solidification/stabilization, utilization, etc.).

In this sense solid residues with very low solubility (or insoluble) in water within a range of pH values between approx. 4 and 10 are more advantageous. In the case of mercury and mercury compounds, one of the very stable and safe forms for the environment is mercury sulfide (HgS), stable on air and insoluble in water.

As it follows from the **Table V**, the requirements on flue gas cleaning procedures (inclusive Hg-removal processes) in MSW incineration are generally high.

4. Selected dry methods for flue gas cleaning and conditions for mercury removal

For smaller MSW incineration units dry methods or semi-dry (wet-dry) method of gas cleaning are usually preferred [1-5,23,24]. These methods are based on removal of acidic gas components (HCl, HF and SO_x) by either calcium hydroxide or soda (Na_2CO_3, $NaHCO_3$) based sorbents. We have chosen four typical examples of dry methods of flue gas cleaning schemes:

a) Combination of SNCR with soda based flue gas cleaning at temperature 140 – 180 °C, fabric filters for removal/separation of dust, reaction of solid sorbent with gases, sorption of heavy metals (e.g. Hg) and PCDD/PCDF and for simultaneous separation of air pollution control (APC) residues.

b) Combination of SNCR with conditioned $Ca(OH)_2$ based sorbent at 120 – 170 °C, fabric filter for removal of dust, reaction of the sorbent with acidic gases, sorption of heavy metals, PCDD/PCDF and separation of APC residues.

c) Combination of SNCR with $Ca(OH)_2$ sorbent at higher temperatures (210 -250 °C) with catalytic teflon or ceramic filter for destruction of dioxins, additional de-NO_x by SCR and with simultaneous dust removal, reaction of solid sorbent with acidic gases, removal/sorption of heavy metal compounds and separation of APC residues.

4.1 Combination of SNCR and dry sodium bicarbonate for gas cleaning

We consider here combination of cheaper de-NOx by SNCR (NH_3 or urea based method) at 850 – 900 °C, rough removal of dust by cyclones and/or electrostatic precipitator (ESP) and removal of acidic flue gas components (SO_x, HCl, HF) by dry active soda (Na_2CO_3) with large specific surface produced by in-situ decomposition of $NaHCO_3$ at temperatures over approx. 130 °C and bag filters operated at temperatures 140 – 180 °C. Soda sorbents are less effective in deep removal of HF than in HCl or SO_2 removal (also thermodynamic reasons). Flue gas from MSW incineration will contain heavy metal compounds, where Zn, Cd, partly As, Pb compounds will be adsorbed mainly on fly ash. Only very small part of mercury in flue gas (mainly in form of $HgCl_2$, Hg_2Cl_2, $HgSO_4$ and HgO) will be bound with fly ash (usually < 5 – 10 %) and will occur in separated fly ash from cyclones and ESP (depending on flue gas composition and operation temperature of fly ash separators). Cu, Cr, Ni, Mn will be present mainly in bottom ash.

Decisive part of Hg in flue gas will be in vapor form (elemental mercury Hg°, and mercury (II) chloride $HgCl_2$), at lower temperatures (below approx. 150 °C) part of mercury can be present in form of aerosol (submicron drops of Hg° and submicron solid particles of $HgCl_2$). There are several possibilities how to remove mercury from flue gas at such conditions (140 – 180 °C): active carbon (AC) based sorbents (non-impregnated or impregnated), mineral sorbents [18] and combination of sodium polysulfide [28] with downstream sorbent application (e.g. AC or a mineral sorbent). Adsorptive removal of PCDD/PCDF requires presence of AC. The mineral (inorganic) sorbents are less efficient in dioxine removal than the AC-based sorbents. The interactions of impregnation compounds (sulfur based, H_2SO_4, $FeCl_3$ and other) with adsorbed dioxins are not completely known.

The non-impregnated AC sorbents are more active at lower temperatures, i.e. rather at 140 °C than at 180 °C - see **Fig. 1**. The non-impregnated AC adsorbs SO_2 and H_2O vapors from flue gas forming H_2SO_4 in AC pores. $HgCl_2$ vapors are better adsorbed by AC than vapors of elemental mercury (Hg°). Sorption of Hg° is improved by elevated concentrations of HCl in flue gas (**Fig. 2**). Simultaneously also volatile inorganic and organic species will be adsorbed from flue gas. Impregnation of AC with sulfur or $FeCl_3$ facilitates sorption of Hg° (conversion

of Hg to HgS and HgCl$_2$). Another possibility for better removal of elemental mercury vapors and simultaneous conversion of HgCl$_2$ to environmentally acceptable, inert HgS is reaction with sodium poly-sulfides (e.g. Na$_2$S$_4$). The main reactions of Na$_2$S$_4$ in flue gas are:
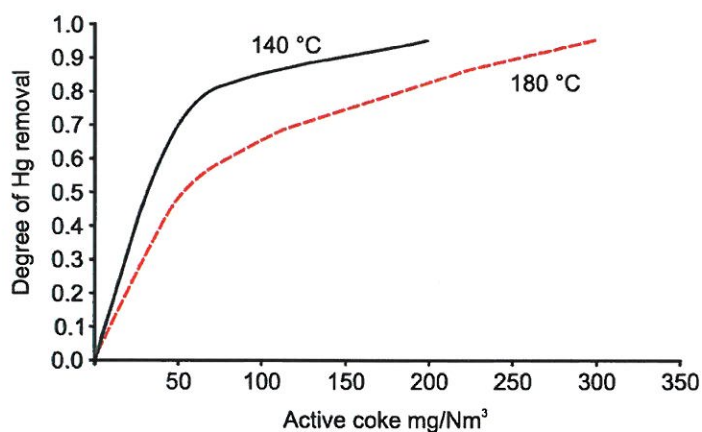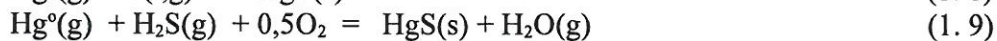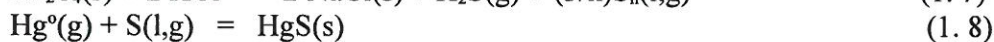
$$Na_2S_4(s) + HgCl_2(g) = 2NaCl(s) + HgS(s) + (3/n)S_n(l,g) \qquad (1.6)$$
$$Na_2S_4(s) + 2\ HCl = 2\ NaCl(s) + H_2S(g) + (3/n)S_n(l,g) \qquad (1.7)$$
$$Hg^o(g) + S(l,g) = HgS(s) \qquad (1.8)$$
$$Hg^o(g) + H_2S(g) + 0,5O_2 = HgS(s) + H_2O(g) \qquad (1.9)$$
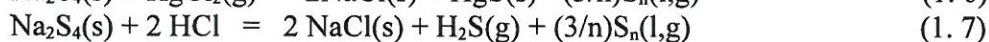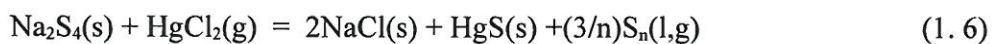
Fig. 1: Example of dependence of Hg-removal efficiency by adsorption of Hg from flue gas on active coke concentration in flue gas and temperature [5], concentration of Hg (all forms, Hg^o, HgCl$_2$, etc.) in flue gas is 1 mg/m^3.
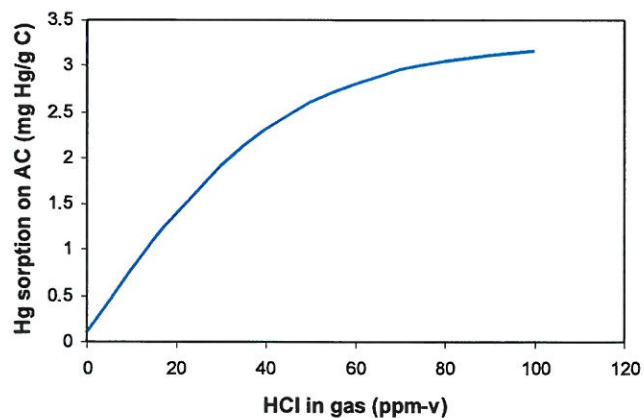

Fig. 2: An example of effect of HCl concentration in flue gas on Hg^o sorption on non-impregnated carbon sorbent (AC) at 135 °C [10].

Aerosol (drops, solids) of sodium poly-sulfide is generated by spraying (atomization) of 4 – 8 % water solution of Na_2S_4 into flue gas. Sulfur (in reactions 1.6 - 1.8) is in both forms, submicron liquid drops and vapors. Aerosol of solid particles of HgS (generated in the reactions) is separated together with solid products of APC reactions on fabric filters and/or partly captured by added AC dust (primarily present for adsorption of dioxines).

Therefore combination of non-impregnated AC or sulfur impregnated AC (feeding rate about 100 mg/m^3) together with upstream spraying of Na_2S_4 water solution into flue gas (about 100 mg of Na_2S_4/m^3) seems to be the optimum choice for removal of mercury in dry process of flue gas cleaning based on soda (or $NaHCO_3$). Prevailing part of mercury will be in form of HgS.

Problem is, however, with APC residues [5,29], containing about 30 – 35 mass % of fly ash, about 30 % NaCl, about 15 % Na_2SO_3 + Na_2SO_4, AC (2 – 4 %) and toxic NaF (about 0,4 %) [5].

Moreover some small concentrations of heavy metal chlorides, ammonium salts (due to SNCR and ammonia slip) and traces of organics are commonly also present. Ammonium salts are decomposed in water solution by reaction with Na_2CO_3 and water soluble chlorides of heavy metals are converted by soda to (usually insoluble) carbonates. Such APC residue material with high amount of soluble salts is impossible to utilize as a building material or addition to cement based mixtures for solidification/stabilization. The only simple possibility of handling is removal/conversion of heavy metal compounds +organics by addition of AC, filtration and discharge of water solution of mixed sodium salts (with majority of NaCl) to the sea. Recycling technology converting (by application of four cleaning steps) the APC residues to raw material applicable in soda production technology [30] is relatively complicated and expensive. However, it is possible to reduce the amount of dangerous residues (waste) to only 4-7 % of the original amount of APC waste by proper separation procedures/treatments.

4.2 Combination of SNCR and dry calcium hydroxide for gas cleaning

We consider here de-NO_x by SNCR at 850 – 900 °C, rough removal of dust by cyclones and/or electrostatic precipitator (ESP) and removal of acidic flue gas components (SO_x, HCl, HF) by dry calcium hydroxide with large specific surface at temperatures approx. between 120 and 170 °C and bag filters (for separation of APC residues). Removal of acidic gases from flue gas by dry calcium hydroxide is dependent on reactivity of $Ca(OH)_2$, temperature and content of water vapor in gas (proximity of dew point of water vapors in gas and condensation of water vapors in pores). The reactivity of $Ca(OH)_2$ depends on structure, particle size, specific surface and pore size/total volume. Reactivity of pollutants towards dry calcium hydroxide [19] is in the order: SO_3 > HF > HCl > > SO_2 > CO_2 . Reactivity of $Ca(OH)_2$ decreases with increasing temperature between 120 and 170 °C (at given content of water vapor in gas). This is confirmed also by thermodynamics [31] (decreasing equilibrium constants of halogenation reactions of $Ca(OH)_2$ and CaOHCl with increasing temperature as shown in **Fig. 3**). Temperature of sorption below approx. 130 °C at higher concentrations of HCl in gas can be operationally difficult because of possible formation of viscous solutions and hygroscopic particles containing salt hydrates ($CaCl_2*2H_2O$ and $CaCl_2*H_2O$) - as it indicates a part of phase diagram of the system with water and $CaCl_2$ (**Fig. 4**).
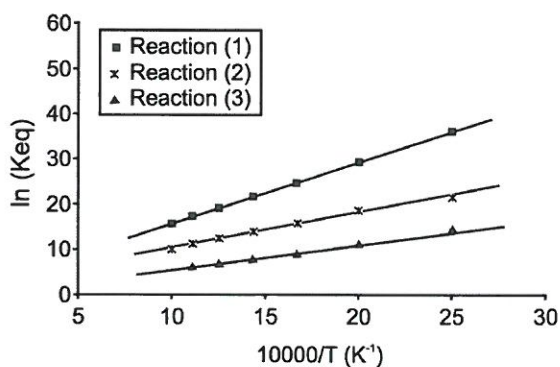
Fig. 3: Dependence of equilibrium constants (K_{eq}) for reactions of HCl sorption by $Ca(OH)_2$ based sorbents [31] . Reaction 1: $Ca(OH)_2 + 2HCl = CaCl_2*2H_2O$, Reaction 2: $Ca(OH)_2 + HCl = Ca(OH)Cl*H_2O$, Reaction 3: $Ca(OH)Cl*H_2O + HCl = CaCl_2*2H_2O$
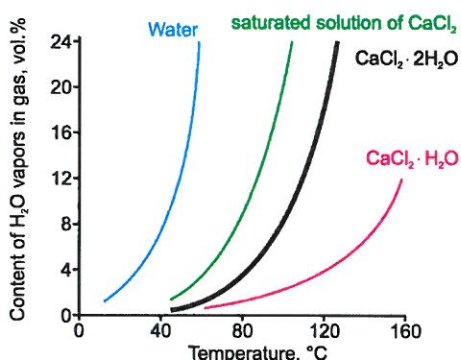

Fig. 4: A part of phase-diagram for the system calcium chloride-water between 20 and 160 °C and water vapor content in flue gas between 0 and 24 vol. % [5].

At temperatures over approx. 200 °C the sorption of acidic HCl and SO_2 increases with temperature [19,32] due to accelerated kinetics of sorption reaction [32,33]. Systems with dry $Ca(OH)_2$ are less suitable for deeper removal of SO_2 and sorption of SO_2 is enhanced by simultaneous sorption of HCl. For better sorption and efficiency relatively higher stoichiometric surplus of $Ca(OH)_2$ has to be used (> 1.6) together with higher humidity of flue gas and partial recirculation of the partly reacted sorbent. Dry reactive sorbents on Ca-bases with high reactivity and large specific surface (e.g. Sorbacal® SP) are offered commercially. The results of flue gas cleaning parameters attained by Sorbacal SP are shown in **Fig. 5**. More than 50 % removal efficiency for Hg has been commonly achieved with such kinds of sorbents. Only the concentrations of PCDD/PCDF were higher after cleaning with Sorbacal SP than the prescribed limits for air pollution in MSW incineration [18] and therefore other methods for dioxins reduction should be applied (AC and/or catalytic destruction methods). As also visible, the $Ca(OH)_2$ sorbents are very active in HCl removal, but removal of SO_2 from flue gas is less efficient. As mentioned in Chapter 2 (Eq. 1.3 and **Table IV**) $HgCl_2$ is not converted into Hg or HgO by $Ca(OH)_2$ (difference in behavior of $HgCl_2$ on soda and $Ca(OH)_2$ sorbents).
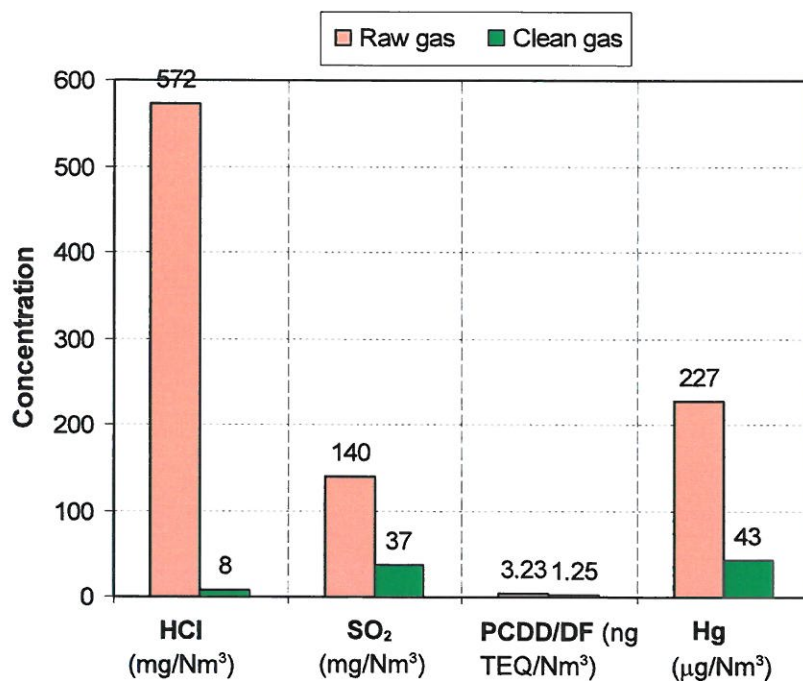
Fig. 5: Removal (separation) of HCl, SO$_2$, Hg and PCDD/PCDF by Ca(OH)$_2$ based sorbent with large specific surface, type Sorbacal® [18] at temperatures 160 – 170 °C.
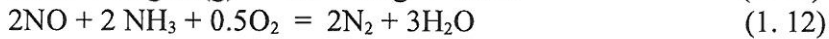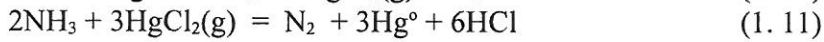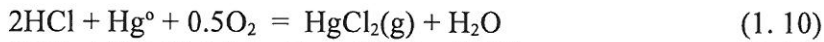
For removal of mercury (Hg° + HgCl$_2$) vapors and aerosols in principle two kinds of sorbents can be used: carbon (AC) related and mineral sorbents [13,18,34] based on bentonite, montmorillonite, expanded perlite, zeolite, etc. and their mixtures with dolomite. The main components of such sorbents are SiO$_2$, Al$_2$O$_3$, CaO and MgO. The sorbents, according to requirements on efficiency of Hg removal, are optionally impregnated [13] by sulfur, Na$_2$S$_4$, FeCl$_3$ etc. The new generation of mineral sorbents (e.g. Minsorb®) can be used in mixture together with Sorbacal or similar dry calcium hydroxide sorbents [34-36]. The common feeding rates of mineral sorbents (e.g. Minsorb®) in flue gas cleaning is 100 – 300 mg/m^3 of flue gas and their efficiency in mercury and dioxins (PCDD/PCDF) removal is claimed to be comparable [35] with AC based sorbents at temperatures between 130 and 180 °C. Mineral matrix is better compatible with cement in solidification/stabilization of the APC residues. The common major components of APC residues in such dry Ca(OH) based flue gas cleaning process are: CaCl$_2$ (its hydrates), calcium hydroxyl-chloride (CaOHCl) calcium carbonate, calcium sulfate and sulfite hemi-hydrates, non-reacted Ca(OH)$_2$ and fly ash (about 20 – 30 %). The main (well) water soluble compound is CaCl$_2$. Moreover formation of CaCl$_2$ hydrates (hygroscopic nature) on air will cause sticking of particles in storing of such residues. Heavy metal compounds will be practically in water insoluble form (hydroxides, sulfates, sulfides etc.). For a better stabilization of heavy metals a small amount of sodium or calcium sulfide could be added.

4.3 Combination of SNCR , SCR and dry calcium hydroxide based cleaning at temperatures between 210 and 250 °C

In relation with new more stringent limits for NO$_x$ emissions in MSW incineration (change from 200 mg NO$_2$/m^3 to 100 mg NO$_2$/m^3) it is expectable that the applied (simpler and cheaper) SNCR method in some cases will be not sufficient for meeting the new limits for NO$_x$ emissions. One of possibilities in such a case is combination of SNCR and SCR for

deeper de-NO$_x$. SCR of NO$_x$ can be operated generally between approx. 180 and 350 °C, depending on dust , HCl, SO$_2$, CO, organics etc. contents in flue gas and on the type of catalyst [18,20-22,37]. Kinetics of the catalytic de-NO$_x$ reactions is usually faster at temperatures over 240 – 250 °C. In the case of dusty flue gas it is advisable to place the catalytic de-NO$_x$ downstream ESP or bag filters. For higher concentrations of HCl and/or SO$_2$ in flue gas the temperatures below approx. 230 °C are operationally difficult, because of formation and deposition of ammonium salts (NH$_4$Cl, (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$) on catalyst. If we consider conditions for the overall process of removal of HCl, SO$_x$, HF, mercury, dioxins and partial reduction of NO$_x$ at temperatures 210 – 250 °C, the de-NO$_x$ catalyst (or de-NO$_x$ + de-dioxine catalyst) should be protected by upstream separation of dust, reduction of HCl (HF), SO$_2$ and separation of volatile heavy metal compounds prior to contact with the catalyst. Various SCR de-NOx catalysts have simultaneously ability to destroy PCDD/PCDF at temperature 210 – 250 °C [38-41].

Higher concentrations of NH$_3$ in flue gas change the speciation of Hg in flue gas by reduction of HgCl$_2$ to elemental Hg° (as shown in eq. 1. 4). The de-NO$_x$ catalysts in contacts with Hg° commonly cause oxidation of mercury [20-22], according to conditions and composition of flue gas, to HgO and HgCl$_2$. The three main reactions affecting the fate of mercury in SCR in presence of HCl, NH$_3$ and oxygen are [20, 37]:

$$2HCl + Hg° + 0.5O_2 = HgCl_2(g) + H_2O \qquad (1.10)$$
$$2NH_3 + 3HgCl_2(g) = N_2 + 3Hg° + 6HCl \qquad (1.11)$$
$$2NO + 2\,NH_3 + 0.5O_2 = 2N_2 + 3H_2O \qquad (1.12)$$

At higher concentrations of NH$_3$, HCl and SO$_3$ and temperature below approx. 220 – 240 °C formation of ammonium chloride, ammonium sulfate and NH$_4$HSO$_4$ have influence on the available NH$_3$ and can cause deposition of ammonium salts on the SCR catalyst. With increasing amount of mainly SO$_2$ in flue gas (because HCl is removed by Ca(OH)$_2$ preferably) the safe operating temperature of teflon and ceramic catalytic filters [41-43] increases – as schematically shown in **Fig. 6**

Structure of catalytic teflon (PTFE) based multi-filter, i.e. de-NOx and de-dioxins teflon composed bag filter with surface membrane for efficient separation of small dust particles and with a felt layer of expanded Teflon fibers with embedded submicron catalyst particles and the schematic catalytic function is shown [43] in **Fig. 7**.
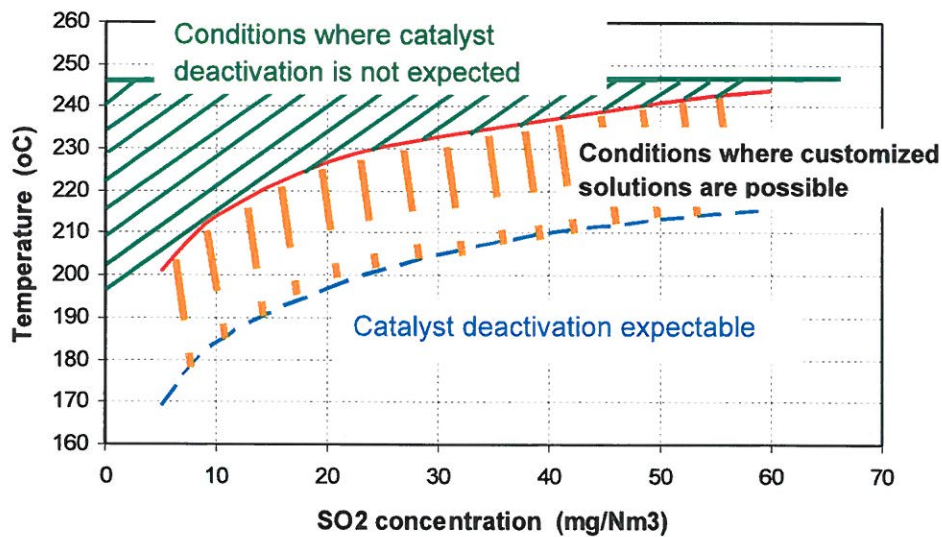
Fig. 6: Effect of SO$_2$ concentration in flue gas (in contact with SCR catalyst in Gore Teflon catalytic multi-filter) on suitable operating temperature of catalytic de-NO$_x$ filters [42].
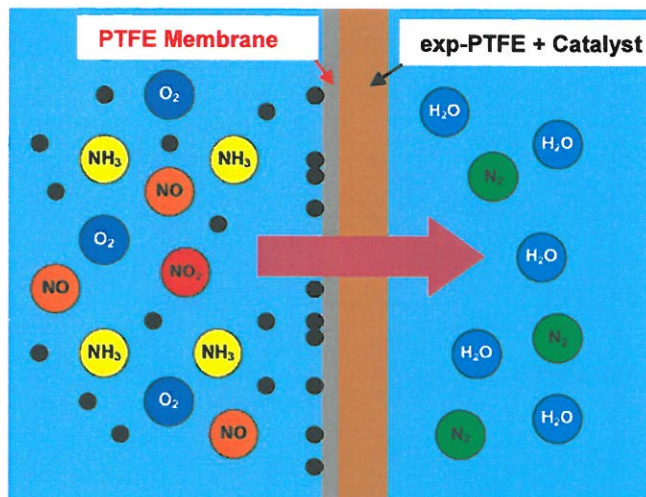

Fig. 7: Schematic picture of Gore Teflon (PTFE) based multi-filter [43] with surface membrane for separation of dust (+ APC residues from dry gas cleaning) and catalytic felt layer (expanded PTFE fibers) for de-NO$_x$ and simultaneous catalytic destruction of PCDD/PCDF.

Presence of reactive Ca(OH)$_2$ upstream the SCR system will cause substantial reduction preferably of HCl, HF and SO$_3$, therefore the deposition of corresponding ammonium salts on SCR will be suppressed and more ammonia will be available for the NH$_3$ reactions (eq. 1. 11 and 1. 12). Removal of HCl and SO$_2$ by dry Ca(OH)$_2$ sorbent is at temperatures 210 – 250 °C less efficient than at temperatures 120 – 160 °C [19,36] (minimum of dry Ca(OH)$_2$ reactivity is at temperatures 190 – 210 °C). Nevertheless the new calcium hydroxide based sorbents [35,36] with large specific surface and suitable (tailored) pore size distribution are believed to

be still able to remove HCl and SO$_2$ at such temperatures to meet the prescribed emission limits.

Disadvantage of such temperature range for Ca(OH)$_2$ sorbents is in necessity to use a higher molar surplus of the hydrated lime based sorbents. Soda (or NaHCO$_3$) based sorbents have higher reactivity towards HCl and SO$_2$ at such temperatures (210 – 250 °C) and operation near stoichiometry of cleaning reactions is feasible [19,24].

For removal of volatile heavy metal compounds and dioxins, application of AC sorbents is excluded from safety reasons (possible explosion and self-ignition). Un-impregnated mineral sorbents based on bentonite and generally on phyllo-silicates minerals are insufficiently active at temperatures over approx. 210 °C and therefore their impregnation by sulfur, Na$_2$S$_4$ or by FeCl$_3$ is needed for higher efficiency of mercury removal from flue gas. FeCl$_3$ has disadvantage in possible contribution to de-novo formation of PCDD/PCDF in presence of organics and/or carbon (e.g. in/on fly ash particles). On the other hand, sulfur impregnation of mineral sorbents for mercury is able (at least partly) to suppress de-novo formation of chlorinated dioxins. The catalytic removal of PCDD/PCDF at temperature 210 – 250 °C is very efficient - commonly over 97 % chlorinated dioxins can be destroyed [39,41] on PTFE catalytic multi-filters.

The dry products of APC reactions are separated on a fabric (bag) filter or membrane filter, which has to withstand temperatures about 250 °C. Generally teflon (PTFE) or ceramic materials are suitable for such conditions.

The SCR de-NO$_x$ process (in case of insufficiency of SNCR) can run on a catalyst within the bag filter material (e.g. felt made of expanded PTFE fibers with small (submicron) catalyst particles or in position of "tail-end cleaning" on a monolithic catalytic structures containing TiO$_2$/V$_2$O$_5$ as the main components with MoO$_3$, WO$_3$, MnO$_x$, CeO$_2$ and other minority catalytic components. Comparison of aspects of operation of SNCR, tail-end SCR and Gore® de-NOx multi-filter technology [42] is given in **Table VI**.

Table VI: Comparison of important aspects of operation of SNCR of NO$_x$, tail-end SCR and catalytic multifilter SCR of NO$_x$ [42]

	SNCR	Tail-end SCR de-NO$_x$ (monolithic structure)	Gore® (Remedia™) de-NO$_x$ (multi-filters)	*Notes*
NO$_x$ reduction	50 – 70 %	85 – 95 %	< 90 %	At 160 °C: ~50 % At 230 °C: ~70 %
NH$_3$ slip	< 10 mg/m^3	< 3 mg/m^3	< 5 mg/m^3	
Pressure drop of de-NO$_x$ function	0 – 1 mbar	10 – 30 mbar	0 – 3 mbar	Only static mixer
Demand of space	Pract. 0	Relatively high	0	Standard bag filter
Life time	> 10 years	> 7 years, depending on catalyst and conditions	> 5 years	(Remedia up to 12 years)
NH$_3$/NO$_x$ stoichiometry	1.5 – 3.0	~ 1.05	~ 1.1	
Regeneration of the catalyst	No catalyst	Heat out, external washing	External washing	Possible in operation

The solid APC residues (from the captured dust) will contain relatively smaller concentrations of PCDD/PCDF (less than in processes with application of AC at lower temperatures). The amount of PCDD/PCDF will depend mainly on content of unburnt carbon in fly ash separated in membrane bag filters. According to impregnation species used for mineral sorbents of heavy metals, the prevailing captured form could be either sulfide or chloride form with some small content of metal-oxides.

5. Conclusions

Removal of mercury and other volatile heavy metal compounds from flue gas in MSW incineration has to be considered as an integral part of overall flue gas cleaning scheme (de-dusting, de-HCl+SO$_2$, de-NO$_x$, de-dioxins). Removal of mercury in dry flue gas cleaning is more difficult at temperatures over approx. 250 °C. Choice of sorbents for removal of Hg +HgCl$_2$ vapors is broader (AC, mineral sorbents, impregnated and non-impregnated sorbents) at lower temperatures (130 – 170 °C).

The overall flue gas dry cleaning schemes in MSW incineration should take into account maximum possible utilization of APC residues (it means fly ash, residues from removal of acidic gases containing mercury, heavy metals, PCDD/F , higher PAH etc.) and easy solidification/stabilization of residues with minimum leaching of harmful compounds (heavy metals, organics, PCDD/F etc.). All dry flue gas cleaning methods based on removal of acidic gases by NaHCO$_3$ (soda-based) or Ca(OH)$_2$ sorbents suffer from formation of water soluble components (NaCl, Na$_2$SO$_x$, CaCl$_2$). Treatment, recycling and utilization of such solid residues is still relatively complicated and expensive.

From the point of view of overall efficiency of MSW incineration and R(1) factor, the both dry methods of flue gas cleaning (based on soda or calcium hydroxide) at temperatures 130 – 170 °C seems to be slightly more advantageous than the semi-dry or wet methods of flue gas. From the point of view of stable, insoluble form of mercury in solid residues from flue gas cleaning (APC residues) HgS is the best form – it means that sorbents and methods of mercury removal based on sorbents impregnated with sulfur, Na$_2$S$_4$ and similar have an advantage. Mercury capture methods removing mercury in form of HgCl$_2$ must use further stabilization to prevent mercury leaching.

Catalytic removal of PCDD/F is more advantageous than AC sorbents based methods, because content of such compounds in APC residues behind the catalytic removal (catalytic filters) is lower. On the other hand, catalytic destruction of chlorinated dioxins requires temperatures over approx. 200 °C. The optimum temperatures for catalytic de-dioxins and catalytic de-NOx are usually different. In flue gas de-NO$_x$ (incineration of municipal solid waste) there is clear contemporary tendency to avoid SCR and rather to apply combination of SNCR with dynamic primary measures directly in combustion (incineration) process of waste.

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