Dry sorption stabilization of flue gases in biological waste incinerating facility with heating power under 5 MW

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Abstract. Biological and medical waste is always classified as hazardous material such as it must be treated according to its hazardous characteristics. One of the best methods for disposal seems to be a thermal degradation. This research examines the effect of finely crushed sorbent $Ca(OH)_2$ and NaHCO₃ to eliminate these hazardous substances in a small incinerating facility with heating power under 5 MW. The experiment took place in an existing incinerating plant with capacity 250 kg h⁻¹. Sorbents were injected into a flue gas flow at two different places. It was observed that the temperature of flue gas and the residence time significantly influence the sorbent refining effect that is caused by quantity of collision in flue gas stream. Sorbents were dosed into a system with a theoretical consumption excess to serve sufficient refining effect. At dosing rate of 7 kg h⁻¹ $Ca(OH)_2$ the concentration of SO₂ decreased by 34.5% and HCl by 59.0% referring to the initial concentration. At dosing rate of 5 kg h⁻¹ NaHCO₃ the concentration of SO₂ decreased by 32% and HCl by 44.8% referring to an initial concentration. Tested sorbents react with acidic compounds with different efficiency and preferably react with different acid compounds.

Key words: hospital waste, Calcium hydroxide, Sodium bicarbonate, HCl, SO₂.

INTRODUCTION

Hazardous particles and compounds form while waste incineration occurs. According to an enacted legislation, particular substances in a stream of flue gas have to be eliminated according to emission limit (Act No. 201/2012, Czech Republic). It includes sulphur oxides (SO_x), nitrogen oxides (NO_x), halogen hydrogens and persistent organic pollutants (POP) such as polychlorinated dibenzodioxins and dibenzofurans compounds (PCDD/F) that are resistant to environmental degradation (Wey et al., 2001).

Elimination of sulphur oxides and halogen hydrogens in flue gas can be done by several methods. They are classified as the wet process, semi-dry process and dry process. In the wet flue gas cleaning process the flue gas is stabilized by circulating water in a scrubber, the water is enhanced by lime milk. In semi-dry flue gas cleaning process an alkaline sorbent agent is injected to a flue gas flow in a liquid form as a suspension or a solution. The water part is vaporized and dry powdered sorbent captures heavy metals, sulphur oxides and halogen hydrogens then on its surface (Brna, 1990).

Dry refining technology is based on injection of sorbents in a form of a dry powder. The agent is sprayed directly into the flue gas flow (Allen et al., 2001) or mixed with waste going into the reactor (Cunill et al., 1991). Neutral compounds are formed by sorbent reaction with acid components. Solid particles are captured on mechanical separators. Sorbents can be calcium or sodium based, calcium hydroxide (Ca(OH)₂) or sodium bicarbonate (NaHCO₃). There are other synthesized sorbents at the market that can reach higher efficiency in flue gases stabilization under specific condition such as calcium-magnesium-aluminum (Ca-Mg-Al) mixed oxide sorbent or hydrogarnet (Cao et al., 2014).

Calcium oxide can stabilize hydrogen chloride with 54% efficiency at the temperature of 800 °C. However with 80% efficiency at 600 °C (Shemwell et al., 2001). The efficiency is highly dependent on sorbent faction and porosity (Daoudi & Walters, 1991) as well as on ambient temperature (Partanen et al., 2005). Conversion rate of hydrogen chloride grows with increasing size of calcium oxide. However, conversion rate of sulphur oxide increases with decreasing size of calcium oxide. Sulphation greatly accelerates in the presence of hydrogen chloride (Matsukata et al., 1996). Some researchers suggest that calcium carbonate under certain conditions is able to stabilize PCDD/F (Lu et al., 2007). Higher concentration of sulphur oxide in flue gases significantly reduces the formation of these compounds (Van Caneghem et al., 2012).

The research work focuses on the dry sorption refining technology in a small biological and medical waste incinerating plant. According to the Air protection Act, heating power of the small incinerating plant is lower than 5 MW (Act No. 201/2012, Czech Republic). The dry sorption refining technology seems to be very efficient for such application. However, it is not commonly used in a waste utilization plants with heating power higher than 5 MW, because there is a very high volume of flue gas transfer in the system. It is difficult to stabilize flue gases sufficiently under such conditions. Wet or semi-dry sorption technologies are usually used for plants with greater thermal output.

The aim of the study is to determine the refining effect of calcium hydroxide and sodium bicarbonate on HCl and SO_2 in relation with process conditions in the dry sorption refining system.

MATERIALS AND METHODS

The experiment took place in the incinerating facility for biological and hospital waste complex Johnson Controls Fabrics Strakonice a.s., Czech Republic. The incinerating plant consists of a pyrolysis-incinerating furnace Hoval – Schiestl GG 24, thermoreactor TR 24 and a steam boiler THD IV 0580 with heating power 1,508 kW. The capacity of the plant was 250 kg h^{-1} and the burned material was injected discontinuously 60–65 kg per every 15 minutes.

The input material was biological and hospital waste. Waste code according to waste catalogue (European Waste Catalogue): 180102, 180103, 180104, 200301, 150202, 150110. The elemental characteristic of incinerated waste in Table 1.

	Share of component	H ₂ O	Ash	Cl	F	S	Heating value
	[%]	[%]	[%]	[%]	[%]	[%]	[MJ kg ⁻¹]
Paper	24	5.8	5	0.5	-	4.2	15.4
Plastic	23	0.1	0.5	18	3	6.7	24.8
Textile	29	6.6	14.2	13.2	1.8	9.5	15.1
Biological component	14	32.1	18.6	5.3	2.1	12	11.4
Solvent, oil	10	0.6	0.8	16.1	1.3	21.3	39.6
Weighted average		7.9	8.1	10.4	1.6	9.1	19.3

Table 1. Biological waste characteristics

Temperature in the furnace chamber was 900 to 950 °C. Two burners for natural gas automatically control the heat to the required temperature. The waste was carbonized and formed gas was mixed with the air and burned in thermoreactor at the temperature 1,100 to 1,150 °C. Formed flue gases flowed to the boiler where the temperature was reduced to 200 to 250 °C. First device for dosing a tested sorbent was placed after the boiler, position A. Flowingly the flue gas passed through the pipe labyrinth_1 which was 8 m long and a heat exchanger where the temperature was reduced to 130 to 135 °C. The second sorbent dosing device was placed after the cooler, position B. Flue gas went through the pipe labyrinth_2 which was 17 m long. All solid particles involving hazardous compounds and sorbents injected into the system previously were captured on a tied filter subsequently. The block diagram of the incinerating facility is given on the Fig. 1.

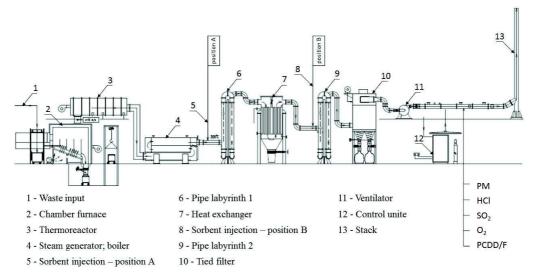


Figure 1. Incinerating facility block diagram.

The measurement of emissions in flue gas was taken according to appropriate legislative (Act No. 201/2012, Czech Republic). The measuring point was placed at the horizontal flue pipe with diameter 355 mm after a ventilator according to ISO 9096 and EN 13284-1.

Flue gas properties and the concentration of particulate matter (PM), hydrogen chloride (HCl), sulfur dioxide (SO₂), oxygen (O₂) were determined according to technical standards:

- Gravimetric determination of the mass concentration of particulate matter (ISO 9096 EN 13284-1);
- Determining flow velocity and volume flow (ISO 10780);
- Determination of moisture in the gas pipeline (EN 14790);
- Paramagnetic determination of oxygen (EN 14789);
- Photometric determination of the mass concentrations in inorganic chloride compounds (EN 1911);
- Determination of sulphur dioxide mass concentration, automated system UVF fluorescence NDUV (ISO 7935, EN 14212);
- Determination of carbon oxide mass concentration, automated system NDIR (ISO 10396, EN 15058).

All volumes, weights of combustion air and emission concentration are given for normal conditions, i.e., at t = 0 °C, p = 101.325 kPa and the reference oxygen content in the flue gases $O_r = 11\%$.

Some results (Figs 3, 4) are given as a value of conversion. The conversion is expressed by following equation:

$$x_i = \frac{(c_{i,0} - c_i)}{c_{i,0}} \tag{1}$$

It is a volume of substance eliminated by tested sorbent given as a share of initial concentration.

For the experimental measurement, two different sorbents were tested on efficiency to eliminate hazardous particles in flue gases.

- Calcium hydroxide: Ca(OH)₂;
- Sodium Bicarbonate: NaHCO₃.

Sorbents react with acidic components of flue gas according to following chemical equations:

$$SO_2 + Ca(OH)_2 = CaSO_4 + H_2O$$
 (2)

$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O \tag{3}$$

$$SO_2 + 2NaHCO_3 + 1/2 O_2 = Na_2SO_4 + 2CO_2 + H_2O$$
(4)

$$HCl + NaHCO_3 = NaCl + CO_2 + H_2O$$
⁽⁵⁾

The theoretical consumption of the sorbent was calculated for every experiment according to stoichiometric relation expressed in following equations:

$$G_{Ca(OH)_{2}}^{T} = M_{Ca(OH)_{2}} \times V \times (\frac{c_{SO_{2}}}{M_{SO_{2}}} + \frac{c_{HCl}}{\frac{1}{2}M_{HCl}})$$
(6)

$$G_{NaHCO_{3}}^{T} = M_{NaHCO_{3}} \times V \times \left(\frac{c_{SO_{2}}}{\frac{1}{2}M_{SO_{2}}} + \frac{c_{HCl}}{M_{HCl}}\right)$$
(7)

where: $M(SO_2) = 64.066 \text{ g mol}^{-1}$; $M(HCl) = 36.461 \text{ g mol}^{-1}$; $M(Ca(OH)_2) = 74.093 \text{ g mol}^{-1}$; $M(NaHCO_3) = 84.007 \text{ g mol}^{-1}$; V =flue gas flow $[Nm^3 h^{-1}]$; C_{SO2} , $C_{HCl} =$ concentration $[mg m^{-3}]$.

RESULTS AND DISCUSSION

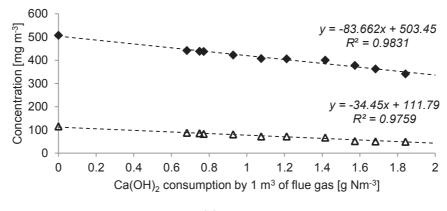
Elimination of HCl and SO₂ by Calcium Hydroxide

Calcium hydroxide was injected into a flue gas pipe after the heat exchanger (position A). Concentration of hydrogen chloride and sulphur dioxide was measured in relation to various volume of calcium oxide that was added into a system.

The flue gas went through the pipe labyrinth_1 where the mean residence time was 0.6 s. Then it went through the cooler with the mean residence time of 1.1 s. The flue gas went through pipe labyrinth_2 with the mean residence time of 1.3 s. The sorbent was captured on a mechanical filter then. The total time of possible reaction between the injected sorbent and acid flue gas elements in the system was approximately 3 s.

The measuring point was after a heat exchanger where the temperature of flue gas was 225 °C. The mean volume of flue gas was 3,629 Nm³ h⁻¹ and mean volume of O_2 was 10.1 ± 0.98%. Theoretical consumption of Ca(OH)₂ was calculated according to Eq. (6). The theoretical sorbent consumption was determined at level 2.553 kg h⁻¹ for stated conditions. During the test 2.5 to 7 kg h⁻¹ of Ca(OH)₂ was dosed into the system and the concentration of HCl and SO₂ was measured based on injected sorbent volume.

The first value represents the reference point for evaluation when no sorbent was injected into the system. The dependence of HCl and SO₂ concentration in flue gas on volume of $Ca(OH)_2$ consumed by 1 m³ of flue gas in the system is shown on the graph (Fig. 2).



 \bullet SO₂ Δ HCI

Figure 2. Reduction of HCl and SO₂ concentration in flue gas based on dosing Ca(OH)₂.

The results show that calcium hydroxide reacts with both hydrogen chloride and sulphur dioxide. The concentration of acid flue gas elements linearly decreases based on surplus of injected calcium hydroxide. At dosing rate of $7 \text{ kg h}^{-1} \text{ Ca}(\text{OH})_2$ the concentration of SO₂ decreased by 34.5% and HCl decreased by 59.0% referring to the initial concentration. The analysis of ash captured on a filter showed the conversion of

injected calcium oxide in the system was 30%. The volume of sulphur in the ash was 5.8% and volume of chlorides was 4.1%. It means that calcium hydroxide reacts preferably with sulphur oxides rather than chlorides.

Next experiment is focused on determining an influence of injected point on sorbent refining effectivity. The measurement was conducted under the same condition as the previous one. However, the place of sorbent injection was changed. It was placed after the cooler, before pipe labyrinth_2 (position B). The temperature at this point was 135 °C.

Graphs (Figs 3, 4) display the conversion of SO_2 and HCl that is caused by dosing $Ca(OH)_2$ into the system on different places. The conversion is calculated according to Eq. (1).

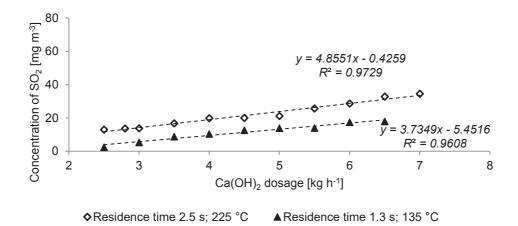


Figure 3. The effect of doosing place on Ca(OH)₂ efficiency to reduce SO₂ concetration.

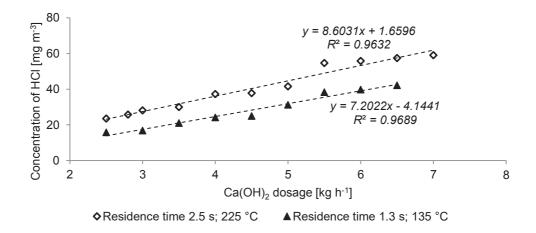


Figure 4. The effect of doosing place on Ca(OH)₂ efficiency to reduce HCl concetration.

The conversion rate of HCl is higher for dosing place at position A. The maximum conversion of HCl was 59.0% when 7 kg h^{-1} was dosed.

The dosing place highly influences the sorbent ability to react with acidic flue gas elements. There are mainly two parameters that influence number of collisions and reactions in flue gas flow, residence time in the system and the temperature (Bradna et al., 2016). In the first case, when the sorbent was injected in front of pipe labyrinth_1 (position A), the residence time was 3 s. However, in second case (position B) was the residence time 1. s. The experiment proves that sorbent effectiveness is dependent of kinetic conditions in the flue gas. With decreasing temperature and shorter residence time, the number of collusions reduce and subsequently decreases the sorbent effectiveness.

The conversion rate of SO_2 is higher for dosing place at position A. The maximum conversion of SO_2 was 34.5% when 7 kg h⁻¹ was dosed.

Elimination of HCl and SO₂ by Sodium Bicarbonate

Powdered sodium bicarbonate (NaHCO₃) was injected into a flue gas pipe after the heat exchanger (position A). Concentration of hydrogen chloride and sulphur dioxide was measured based on various volume of sodium bicarbonate that was added into the system. The mean volume of glue gas flow was 3,380 Nm³ h⁻¹ and mean volume of O₂ was 10.5 ± 1.13%. Theoretical consumption of NaHCO₃ was calculated according to Eq. (7). The theoretical sorbent consumption was determined at level 2.341 kg h⁻¹ for stated conditions. During the test 1.8 to 5 kg h⁻¹ of NaHCO₃ was dosed into the system and the concentration of HCl and SO₂ was measured based on injected sorbent volume.

The first value represents the reference point for evaluation. It was measured when no sorbent was injected into a system. The dependence of HCl and SO_2 concentration in flue gas on volume of NaHCO₃ injected to a system is shown on following graph (Fig. 5).

The dependence of HCl and SO₂ concentration in flue gas on volume of NaHCO₃ consumed by 1 m^3 of flue gas in the system is shown on the graph (Fig. 5).

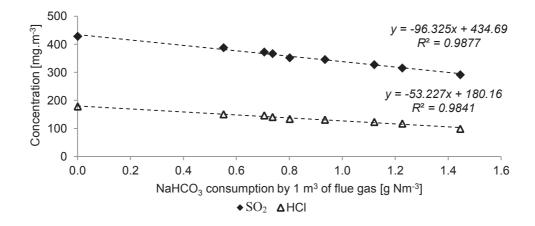


Figure 5. Reduction of HCl and SO₂ concentration in flue gas based on dosing NaHCO₃.

The results show that sodium bicarbonate reacts with both hydrogen chloride and sulphur dioxide. The concentration of acid flue gas elements linearly decreases based on surplus of injected NaHCO₃. At dosing rate of 5 kg h⁻¹ NaHCO₃ the concentration of SO₂ decreased by 32% and HCl by 44.8% referring to an initial concentration. The analysis of ash captured on the filter showed the conversion of injected sodium bicarbonate in the system was 53%. The volume of sulphur in the ash was 3.2% and volume of chlorides was 5.1%. It means that sodium bicarbonate reacts preferably with chlorides rather than sulphur oxides. It also shows that NaHCO₃ can eliminate the content of HCl in flue gas better that calcium oxide. The development of these new technologies is the subject of further research, not only on this solved issue (Hart & Hartova, 2016).

CONCLUSIONS

The research focuses on the dry sorption refining technology in a small biological and hospital waste incinerating plant with heating power under 5 MW. Two different sorbents calcium hydroxide and sodium bicarbonate were tested on ability to eliminate concentration of HCl and SO₂ in flue gases. Theoretical consumption of tested sorbent was calculated for stated condition. It was obvious that theoretical amount of injected sorbent wasn't enough to reduce the concentration of measured acidic compounds to sufficient level. It was caused by low quantity of collisions in flue gas flow between sorbent and eliminated compounds. During experiments, the excess of theoretical amount for each sorbent was injected into the system and the refining effect was observed. Both sorbents react with acidic compounds with different efficiency. Calcium hydroxide reacts preferably with sulphur oxides rather than chlorides. At dosing rate of 7 kg h⁻¹ Ca(OH)₂ the concentration of SO₂ decreased by 34.5% and HCl by 59.0% referring to the initial concentration. Sodium bicarbonate reacts preferably with chlorides rather than sulphur oxides. It can eliminate the content of HCl in flue gas better that calcium oxide. At dosing rate of 5 kg h⁻¹ NaHCO₃ the concentration of SO₂ decreased by 32% and HCl by 44.8% referring to an initial concentration. The most suitable arrangement would be probably a combination of both sorbents at different dosing places.

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