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FLUE GAS CLEANING IN MUNICIPAL WASTE-TO-ENERGY PLANTS – PART II

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Abstract

This article is a continuation of the first part of the article flue gas cleaning in municipal Waste-to-Energy plants – part I. The first part contains an extensive introduction to the subject of flue gas cleaning and cover subjects: reduction of dust and particle-bounded heavy metals as well as NO_x reduction. The second part focuses on reduction of acid gases, organic pollutants and heavy metals. One chapter is devoted to examples of working plants: Spittelau (AT), Issy les Moulineaux (FR), Mainz (DE), Zabalgarbi (ES) where used technology and pollutants emissions are shown along with comparison to WTERT 2006 top ten plants and EU limits. Six new Polish Waste-to-Energy plants are shortly describe according to flue gas treatment methods. Some topics, as costs and residual handling, are only briefly mentioned and for more information the reader is advised to use literature which will allow them to learn more about technology, processes and problems presented in the text. The aim of the study is to present the current state of flue gas cleaning in Waste-to-Energy plants.

Key words: Waste incineration, Gas cleaning, Environmental protection, Solid residues from APC, polish plants

INTRODUCTION

With the development of technology, people have become more aware of the of environmental threats created by themselves. Although due to its specific activity (type of fuel incinerated) Waste-to-Energy (WtE) plants are under constant observation of both the authorities and society which causes development in flue gas treatment systems. The upcoming revision is already an old document: Best Available Techniques for Waste Incineration (IPPC Waste Incineration, 2006) may force changes or technology updates of already working plants and set a very high bar for new projects. Investors should pay attention to this fact specially investors who in the near future are planning to start construction of new plants. A good example is the planned second WtE plant in Warsaw which now (not knowing the new guidelines of the European Commission) has to prepare tender which includes parameters which should meet new (unknown) limits to avoid modernisation after a few years of working.

Reduction of acid gases, organic pollutants and heavy metals plays an important role according to effects that could have on the environment and human life. It is well known the effect of acid gases inside WtE plant and it connection with corrosion problems. The first section of the article covers problem of SOx, HCl and HF reduction using three basic methods: dry, semidry and wet. Advantages and disadvantages of each method are mentioned along with the main reaction equations. The section about organic pollutants and heavy metals may be treated as a short summery of the problem. The next section shown chooses examples of working plants.

ACID GASES REDUCTION

Cleaning flue gas from the acid gases can be done using three main methods: dry, semi-dry and wet (which are shown on Fig. 1 in a more developed form). Dry methods are carried out using calcium hydroxide (Ca(OH)₂), calcium carbonate (CaCO₂) or sodium bicarbonate (NaHCO₂). The injection can be done directly to the furnace, duct, hybrid (furnace and duct), or using a fluidised bed reactor (Pajak et al. 2015). Conditioned-dry sorption with hydrated lime, shown in Fig. 2, is carried out using a cooling tower or economizer in order to lower the flue gas temperature (130-160°C), and obtain approximately 6 percent relative humidity, and then the hydrate is injected into a duct (most often with an active carbon). Flue gas conditioning is necessary to capillary condensation, and the formation of the hydrate shell on the surface. The process depends on HCl/SO, ratio, as well as on fabric filters temperature which influences SO, removal efficiency. Dry sorption with sodium hydrogen carbonate method is not as sensitive to humidity and HCL/SO, but has poor reactivity with HF and is more expensive compared to hydrated lime (Ca(OH)₂: 100-130 €/t and NaHCO₃: 190-250 €/t). In the case of soda-sorbents, the products can be deposited in some underground mines (e.g. salt mines), or, if in a small quantity, they can be liquidated in the sea.

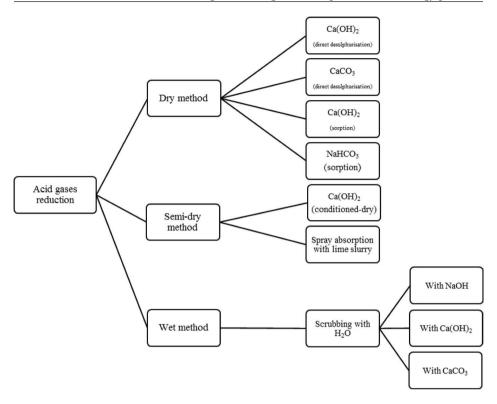


Figure 1. Acid gases reduction methods

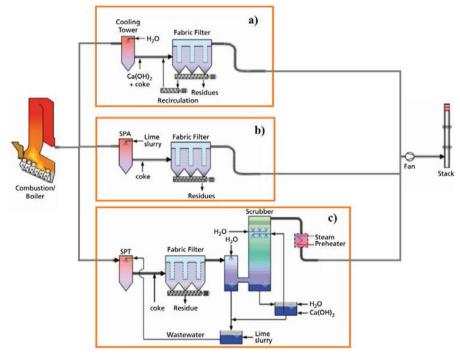
Semi-dry method uses agent in a liquid form (usually aqueous solution of calcium hydroxide and activated carbon), which, after evaporation of water and reaction with acid gases in dry form, is removed from the reactor. This method involves the conditioning of flue gas to a lower temperature, which should be kept above 120°C in order to prevent the formation of the hygroscopic calcium chloride (CaCl₂) (Mokrosz, 2010), which can occur when flue gas is rich in HCL. Semi-dry method is often used in association with the fabrics filters, where most of reactions take place (Piecuch, 1998), and sometimes a recirculation of absorbent is applied in order to trigger a more efficient use.

In a wet flue gas treatment, the agent is added in a liquid form, and the product is also in a liquid form. This method is common in traditional power plants (87% of plants use this method (Benkő and Mizsey, 2007)), according to a high removal efficiency (above 90%), but it is not so popular in WtE plants. For more information on the types of installations, please go to the Europe REACH for ISWA (2012). Wet method is applied in two stages: first, it involves cooling

the flue gas separate hydrogen chloride (HCl), hydrogen fluoride (HF) and dust, as well as particle-bound and gaseous heavy metals. Second stage intents to reduce sulphur dioxide (SO₂).

In acid removal stage the most popular reacting agents are: limestone (CaCO₃), dolomite (CaCO₃·MgCO₃) – used mainly in coal fired power plants, burned lime (CaO) – after converted in contact with water to Ca(OH)₂, hydrated lime (Ca(OH)₂) and sodium hydroxide (NaOH). Thus, cleaning flue gas from acid gases can be divided into two groups due to the added agent:

- lime based processes,
- sodium based processes.



Source: Löschau and Karpf, 2015, edited

Figure 2. Acid gases reduction a) conditioned dry process with hydrated lime, b) spray absorption process with lime slurry (SPA=Spray Absorber), c) wet flue gas cleaning system with lime slurry and spray absorber

Lime based processes are done through particles, which in contact with flue gas, react and on the surface of them adsorption takes place. Cases where liquid phase is used are known. Lime agents react with acid pollutants, like: sulphur dioxide (SO₂), sulphur trioxide (SO₃), hydrogen fluoride (HF) and hy-

drogen chloride (HCl). Lime should be added in an amount of 2 or 3 times bigger then the stoichiometric amount of the reactant (IPPC Waste Incineration 2006) (UBA, 2001), which in some cases can cause higher production of residuals.

Below are listed main reactions which take place after adding lime agent into flue gas in a different form:

$$CaCO_3$$
 temp $CaO + CO_2$ (1)

reaction (5) can only occur with temperature higher than 800°C,

$$Ca(OH)_2 \to CaO + H_2O \tag{2}$$

$$CaO + SO_2 \rightarrow CaSO_3 \tag{3}$$

$$CaO + SO_2 + 0,5O_2 \rightarrow CaSO_4$$
 (4)

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \tag{5}$$

$$CaO + 2HF \rightarrow CaF_2 + H_2O \tag{6}$$

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O \tag{7}$$

$$Ca(OH)_2 + SO_2 + H_2O + 1/2 O_2 \rightarrow CaSO_4 + 2H_2O$$
 (8)

Sodium bicarbonate (NaHCO₃) after injection, is calcining to a form of a porous structure sodium carbonate (Na₂CO₃), and reacts according to the following equations:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$
 (9)

$$Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$$
 (10)

$$Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2$$
 (11)

$$Na_2CO_3 + 2HCL \rightarrow Na_2Cl + H_2O + CO_2 \tag{12}$$

$$Na_2CO_3 + 2HF \rightarrow 2NaF + H_2O + CO_2$$
 (13)

The process using sodium bicarbonate is very sensitive to temperature which should be kept above 135°C (Kong and Davidson, 2010), but there are well known cases where reactions occur below this temperature (Keener and Davis, 1984).

Figure 2 shows three different methods which are used worldwide to reduce acid pollutants. Option (a) is a conditioned dry process with a hydrated lime, (b) spray absorption process with lime slurry and (c) wet flue gas cleaning system with lime slurry and spray absorber. Apart from the process temperature, another essential factor for a cleaning process is ratio between hydrogen chloride (HCl) and sulphur dioxide (SO₂) (Saanilahti, 2008), which depends on fuel.

Table 1. Advantages and disadvantages of acid removal methods

Dry m	ethod	Semi-dry	y method	Wet method		
Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages	
Simple technology	Efficiency 30-40%	Efficiency 60-80%	More expensive absorbent in comp. to wet method	Efficiency above 90%	High automation of installation	
Minimal amount of auxiliary equipment	Residuals	Automa-tion	Worse use of absorbent in comp. to wet method	Low consump. of absorbent	High corrosiveness	
Lack of wastewater after process	Major consumption of absorbent	Simple technology	Higher demand for compressed air	Residuals in the form of gypsum	Large area needed	
Low cost of absorbent	Pollution of the heat exchange surface	Lack of waste wa-ter after process	Higher investment costs comp. to dry method	Leaching of the compounds of chlorine and fluorine	Drop in flue gas temperature	
No need for flue gas conditioning	The high cost of disposal of residuals	About the 50% lower water consump-tion in comp. with the wet method	The high cost of disposal of residuals	Low sensitivity to fluctuations in flow	The possibility of crystallization in the system	
Low operating costs	Lifting dust before filters	Dry residuals	Additional devices	Common in traditional power plants	A large number of devices	

Source: Pajak et al., 2015

ORGANIC POLLUTANTS AND HEAVY METALS REDUCTION

Heavy metals occur most frequently in the form of non-volatile oxides, so they can be removed during dust reduction process except for mercury (Hg), which is highly volatile and therefore very difficult to reduce on emission limits level. The directive on industrial emissions (Directive 2010/75/EU), limits average emission value for Hg over a sampling period of a minimum 30 minutes, and a maximum of 8 hours to 0,05 mg/Nm³ (dry, 11% O₂). Primary techniques for mercury reduction are focused on preparing and separating the fuel in that way, so it eliminates materials rich in Hg. Secondary techniques are intended to transform mercury into ionic mercury by adding oxidants, and then deposited

in the scrubber or direct deposition using active carbon, hearth furnace coke or zeolites. Adsorbent is added into a flue gas duct, or it is located in a moving bed absorber for example. Most often, an active carbon is added as a based sorbent in the temperature between 130-190°C, or as a mixture with lime hydrate. In some cases, to achieve a needed level of mercury, the impregnating of AC is used what results in the residuals which may be included in the category of hazardous waste. Organic pollutants, which are represented by most popular PCDD/F, are removed from flue gas using the same absorbers like in the case of mercury mentioned above. De-novo mechanism of formation has to be consider (particularly unstable regimes of waste incineration with fluctuating oxygen concentration can contribute to higher PCDD/F emissions).

MUNICIPAL WASTE-TO-ENERGY PLANTS

According to Wilts and Gries (2014), 448 incineration plants were operating in 2010 with a total incineration capacity of 76 875 128 tonnes in Europe. These numbers are still rising in relation to the increasing number of Municipal Waste-to-Energy facilities. New plants can use very rich experience provided not only by contractors, but also individual countries or cities. Table 2 provides basic information on selected cases of reduction methods used in flue gas cleaning system, as well as shows emission values of four plants: Spittelau (AT), Issy les Moulineaux (FR), Mainz (DE), Zabalgarbi (ES). They are compared to the EU limits and to the Waste-to-Energy Research and Technology Council's (WTERT) ten WtE plants that were nominated for the WTERT 2006 Award (WTERT, 2016).

Spittelau Municipal Waste Incinerator (build in 1969) was in the nominated group, but finally lost to the winner from Italy Brescia Termoutilizzatore. Despite the failure, the Vienna incinerator has many reasons to be proud of. Apart from the fact of having a very low pollutants emission, Spittelau used the first in Europe SCR deNOx system. Plant constantly renews the different sectors in order to keep up, the last renovation of two lines has finished in 2015 (Jonas et al., 2015).

Flue gas, after leaving the boiler at a temperature of 180 °C, is cleaned from dust in three stage ESP (operating voltage 60kV and efficiency >95%), and then enters a two stage wet scrubbing. First stage involves cooling flue gas up to 60-65°C with fresh water and scrubbing in a cross-flow scrubber with water/ lime slurry (pH 1), which separates hydrogen chloride (HCl), hydrogen fluoride (HF) and dust, as well as particle-bound and gaseous heavy metals. Second stage intents to reduce sulphur dioxide (SO₂) in a counter-current scrubber with NaOH solution (pH 7), after which the flue gas goes to the electrodynamic Venturi to reduce dust content to values < 1 mg/dscm. After reheating up to 105°C, partially

cleaned flue gas goes to deNOx and dioxin destruction system where vaporised ammonia water (NH₂) is added and temperature rises up to 280°C.

Table 2. Pollutants reduction methods and emission values for selected cases with comparison to EU limits

WtE Plant Reduction		Spittelau, Vienna (AT) ³	Issy les Moulineaux, Paris (FR) ⁴	Mainz (DE) ⁵	Zabalgarbi, Bilbao (ES) ⁶	WTERT top ten plants ⁷	EU limits ⁸
Dust and particle		ESP ¹ and electrodynamic Venturi	ESP, BF ²	BF	BF	-	-
NO _x		SCR	SCR	SNCR	Flue gas recirculation and SNCR	-	-
Acid gases		Wet method	Dry method	Semi-dry and wet method	Semi-dry method	-	-
Dioxins		Catalytic conversion with ammonia	Active carbon	Active carbon	Active carbon	-	-
NO _x	mg/Nm³	28 (86%*)	28.33 (86%*)	125 (37.5%*)	140 (30%*)	129 (35.5%*)	200
SO ₂		0.8 (98%*)	1.75 (96.5%*)	4.22 (91.5%*)	10.6 (79%*)	6.8 (86%*)	50
Particles		<0.2 (98%*)	-	1.06 (89%*)	1.5 (85%*)	3.09 (69%*)	10
HCl	-	0.8 (92%*)	3.28 (67%*)	0.42 (96%*)	3.8 (62%*)	7.88 (21%*)	10
HF	-	<0.1 (90%*)	0.05 (95%*)	-	0.19 (81%*)	-	1
Dioxins and furans	ng TEQ/m³	0.02 (80%*)	0.003 (97%*)	0.003 (97%*)	0.006 (94%*)	0.02**	0.1

^{*}percent under EU limits

^{**} Dioxins emission

¹ Electrostatic precipitator

² Bag filters (fabric filters)

³(Spittelau, 2008) – emission values from 2006

⁴Reduction method information from (WSP, 2013), Emissions data based on (Syctom, 2014)

⁵ Reduction method information from (WSP, 2013), Emissions data based on (MHKW-Mainz, 2016)

⁶ Reduction method information from (WSP, 2013), Emissions data based on (Zabalgarbi, 2016)

⁷ WtE plants that were nominated for the WTERT 2006 Award for "one of the best WTEs in the world" (WTERT, 2016)

⁸ (Directive 2010/75/EU)

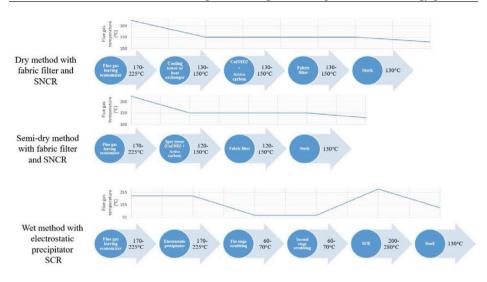


Figure 3. Examples of temperature profiles for typical flue gas treatment stage

Three catalytic converter plants reduce the nitrous gases (NOx) to harmless nitrogen and steam. This stage destroys dioxins and furans with the efficiency above 95%. During incineration of 1tone of waste, 746 l of Fresh water is demanded, 2,6 kg lime, 2,4 kg sodium hydroxide solution 30 %, 3 kg ammonia 25% and 205 kg slag and gypsum, 17 kg fly ashes, 1 kg filter cake, and 4,400 dscm purified flue gas (dry) is produced.

Issy les Moulineaux, Paris WtE plant would probably be in a group of those nominated to 2006 WTERT award, but it has started operating in 2007. As shown in Table 2 the emission values are at good – low level comparable with the previously described incinerator in Vienna. The plant was built for 600 million Euro with the intention of meeting future (restrictive) EU emission limits. In this case, after electrostatic precipitator, a dry sorption sodium bicarbonate system is used to remove acid gases in particular SO_2 and active carbon to deal with dioxins and furans. To reduce $NO_{\rm X,a}$ low temperature SCR system with ammonia is used. The plant operates with an unusual combination of ESP and fabric filters in order to achieve strict limits of particles emission.

More information about flue gas cleaning stage, as well as the whole plant mentioned in Table 2: Mainz in Germany and Zabalgarbi in Spain, can be found in (WSP, 2013) or (MHKW-Mainz, 2016) and (Zabalgarbi, 2016).

Figure 3 shows basic temperature profiles for typical flue gas treatment stage, where only those devices mentioned in the articles are shown: a dry method of acid gases removal with a fabric filter and SNCR, semi-dry acid gases removal method with a fabric filter and also SNCR, two stage wet method with

ESP and tail-end SCR. With devises mentioned in Figure 3, it can be noticed that profile temperature profiles for dry and semi dry method are similar with a totally different profile for wet method. It must be noticed what was and what was not included in the profiles. Some devices or processes can influence flue gas cleaning stage or the whole system, as well as the temperature ranges for individual equipment can be different depending on the company, flue gas, cooperating technology etc. Dry process shown in Figure 3, is based on lime sorbent in case sodium bicarbonate injection temperature profiles differ. Usually before NaHCO₃ injection, ESP is used and afterwards a bag filter which makes the temperature more constant. And when SCR tail-end is used the temperature increase is not so significant.

According to Grieco and Poggio (2009) and Poggio and Grieco (2010), the research on the influence of flue gas cleaning system on the energetic efficiency of a waste-to-energy plant, methods in which a water injection is required (what causes a drop in the flue gas temperature) lower the electric efficiency. In case of the wet method, an additional reheating is needed what results in additional reduction of the electric efficiency. In four cases simulated by Grieco and Poggio (2009) the following results were obtained: the best efficiency was reached by dry method with NaHCO₃ injection 25.3%, dry method with Ca(OH)₂ reach 24.77%, semi-dry neutralisation with Ca(OH)₂ achieves 24.36 %, and dry scrubber + wet scrubber with steam heater reach 24.29% (using gas/gas heater 24.78% electric efficiency was achieved). In cases where SCR deNOx method was used, the electric efficiency dropped about 0.33-0.75% in order to reheat the flue gas.

NEW WtE PLANTS IN POLAND

Currently in Poland are building six new Waste-to-Energy plants which make Poland the most active in this aspect country in the Europe at the moment (Cyranka, et al., 2016). WtE plants are located in: Bydgoszcz, Krakow, Bialystok, Szczecin, Konin, Poznan and have total design capacity of approx. 1 mlm t/year (Pająk and Jurczyk, 2016). All plants are going to be fully operational in the end of 2016. Flue gas cleaning methods together with throughput for each plant are shown in Table 3.

It can be noticed that the most popular technique use in new Polish projects is semi-dry method as well as Selective Non-Catalytic Reduction (SNCR) for NO_X reduction. It is also worth to mention that all plants are using technically mature and proven moving grate technology (Cyranka and Jurczyk, 2016).

150,000

94 000

210 000

City Description Bydgoszcz Krakow Bialystok Szczecin Konin Poznan Flue gas Wet + Semi-dry, Multistep Semi-dry, Semi-dry, semi-dry, Wet, SNCR cleaning SNCR wet, SNCR **SNCR SNCR** technology **SNCR**

120 000

Table 3. Flue gas cleaning technology in six new Polish plants

Source: based on Pająk and Jurczyk, 2016

180 000

220 000

Throughput

[Mg/year]

CONCLUSIONS

The article is a two part summary of the state of art in flue gas cleaning stage in modern Waste-to-Energy plants aimed at introducing the reader into the topic. Currently, the technology used for the cleaning of flue gases from acidic gases, organic compounds and heavy metals meet with no problem emission limits. However, approaching to the end revision of the BAT document and the associated changes in emission limits can cause the need for FGT stage update in oldest installations. A difficult task stands before investors who already have to decide on the parameters placed in a tender for a new plant taking into account not only the cost but also the forthcoming changes in the emission limits.

The literature used in both parts will help readers understand the complex problems that occur in the paper as well develop information only mentioned in text, for example: the costs associated with the construction and operation (Achternbosch and Richers, 2002; Poggio and Grieco, 2010; Xin-gang et al., 2016).

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