Investigation of Performance of Different Sorbents in a Two-stage Flue Gas Dry Treatment of a MSWI

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One of the most widely used processes for municipal solid waste disposal in several industrialized countries is the thermal treatment with energy recovery, but an important issue related to Municipal Solid Waste Incinerators (MSWI) is the emission into the atmosphere of airborne pollutants. Among these, acid gases (hydrochloric acid, sulphur dioxide and hydrofluoric acid) are of particular concern due to their high potential impact on humans and on the environment (effects due to long term exposure, acid rains, etc. are documented). In the present study, a previously developed operational model was used to perform an economic optimization of operating conditions of an existing waste-to-energy plant, using measured process data. The analysed system consists of a two-stage treatment, where dry powder of calcium hydroxide and sodium bicarbonate are used in the first and in the second stage respectively. Since the composition of the flue gas can vary significantly in a MSWI, a set of simulations was carried out considering the operating conditions of some representative operational periods. The model was then adapted to simulate the performance of the reference plant when using the same reactant in both stages. The considered alternatives were a double stage with calcium hydroxide and a system with bicarbonate in both stages. Finally, a comparison between these systems is presented, analysing reactant costs, disposal costs and overall operational costs.

1. Introduction

The two-stage dry treatment is among the Best Available Techniques for an enhanced removal efficiency of acid gases. This technology is increasingly applied because it allows complying with the restrictive limits of current European legislation on pollutants emissions (Directive 2010/75/EU, 2010). A further advantage of this technology is that it avoids complications and costs due to the need of managing wastewater streams. However, solid residues are generated from the gas removal process. These residual streams should be minimised considering both their amount and harmfulness.

In several Italian MSWIs, granulated calcium hydroxide is used in the first stage of the process, while in the second stage sodium bicarbonate is injected. On one hand bicarbonate has higher removal efficiency with respect to calcium hydroxide, but on the other hand it is more expensive. Due to the relatively scarce industrial experience present on this two-stage technology, there is still a lack of knowledge about the efficiency and yields of flue gas treatment stages.

In the present study, the reaction systems that take place in the two reactors at operating conditions were described by means of an operational model. The implementation in a simulation software allowed to describe the flue gas two-stage treatment, taking also into account the recycle rate of solid products in the first stage.

Simulations were carried out for different process conditions and configurations with the aim of optimizing both reactant feed rates and wastes formed by flue gas treatment without affecting the acid gas removal efficiency.

2. Plant description

2.1 The flue gas treatment section
The analysed flue gas section of the waste-to-energy plant consists in a single line for the incineration of municipal solid wastes and non-hazardous industrial wastes (details of the plant under study are reported in Antonioni et al., 2013).
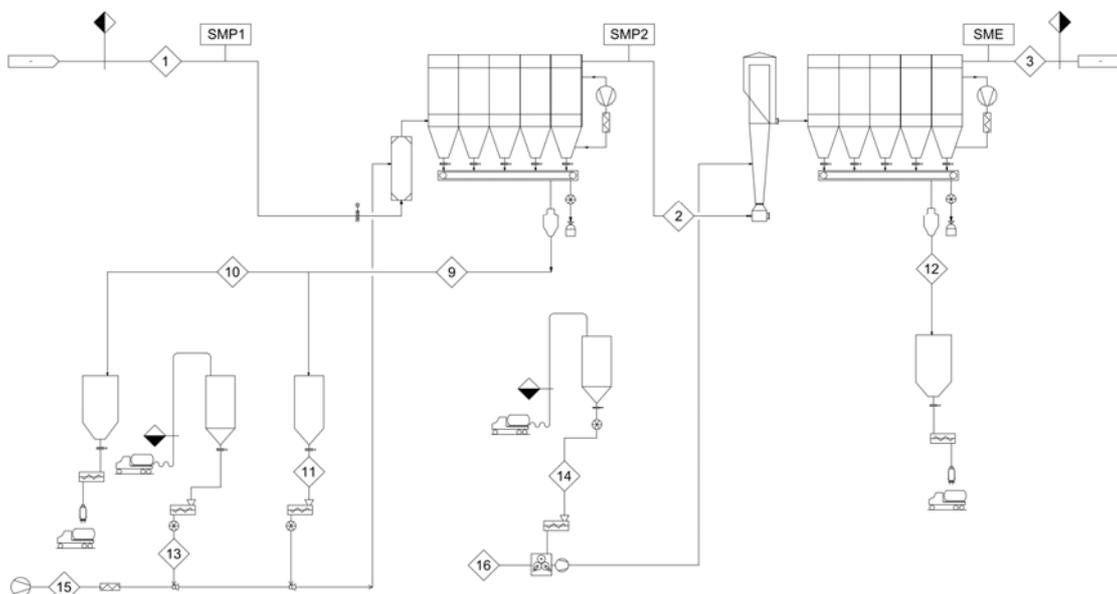

Figure 1: process flow diagram of the considered flue gas treatment section

Removal of fly ash and acid gases (HCl, HF, SO_2) takes place in the considered section of the flue gas treatment system (Figure 1) according to the reactions listed in Table 1, while other typical pollutants produced in a MSWI (i.e. heavy metals, dioxins and furans, nitrogen oxides) are not considered in the present work.

Table 1: reactions in the first and second stages of the acid gas removal process

1st stage reactions		2nd stage reactions	
$Ca(OH)_2 + 2\,HCl \rightarrow CaCl_2 + 2\,H_2O$	(R1)	$2\,NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$	(R5)
$Ca(OH)_2 + 2\,HF \rightarrow CaF_2 + 2\,H_2O$	(R2)	$Na_2CO_3 + 2\,HCl \rightarrow 2\,NaCl + CO_2 + H_2O$	(R6)
$Ca(OH)_2 + SO_2 + \frac{1}{2}\,O_2 \rightarrow CaSO_4 + H_2O$	(R3)	$Na_2CO_3 + 2\,HF \rightarrow 2\,NaF + CO_2 + H_2O$	(R7)
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$	(R4)	$Na_2CO_3 + SO_2 + \frac{1}{2}\,O_2 \rightarrow Na_2SO_4 + CO_2$	(R8)

2.2 Operating conditions
During normal operations, the conditions of the flue gas are continuously varying due to heterogeneous composition of waste and to steam requirement for energy generation.
On the basis of the monitoring system of the plant under study, operating variables are measured before the first stage at the sampling point 1 (SMP1 in Figure 1), then in the intermediate stream between the two stages (SMP2) and finally, according to the requirements of Italian law (D.Lgs. 11-5-2005 n. 133), the emissions are monitored at the stack (SME), through which flue gas is released into the atmosphere. In Table 2, the measured conditions of the flue gas entering the treatment system (stream 1) are reported for some selected days representative of the typical range of inlet HCl concentrations, with the corresponding calcium hydroxide and recycled solids feed rates (1st stage) and bicarbonate feed rate (2nd stage).

Table 2: daily averaged conditions of streams 1, 13, 11 and 14 (with reference to Figure 1) in three days

Day	Flow rate	HCl	SO_2	HF	CO_2	O_2	H_2O	$Ca(OH)_2$	Recycle	$NaHCO_3$
-	SMP1	SMP1	SMP1	SMP1	SMP1	SMP1	SMP1	Stream 13	Stream 11	Stream 14
-	Nm^3/h	mg/m^{3*}	mg/m^{3*}	mg/m^{3*}	%	%	%	kg/h	kg/h	kg/h
1	90,805	688	24.9	4.3	7.8	8.1	16.4	144.8	142.8	55.7
2	100,367	1,266	50.6	8.9	8.7	7.6	14.8	327.6	220.1	158.5
3	105,044	1,905	89.4	14.3	8.6	7.8	13.6	450.6	235.2	212.2

* dry gas, normal conditions,11% oxygen

3. Simulation model

3.1 Model description

The model is based on a correlation proposed in a previous work (Antonioni et al., 2011), shortly described in the following in order to show the involved parameters. This empirical function (Eq. 1) relates the conversion of the *i*-th acid gas ($\chi_{i,j}$) to $rs_{i,j}$, which is defined as the ratio between the actual feed rate of solid reactant *j* and the theoretical stoichiometric rate of *j* required to complete the reactions (see Table 1) with acid gas *i*:

$$\chi_{i,j} = \frac{rs_{i,j}^{n_{i,j}} - rs_{i,j}}{rs_{i,j}^{n_{i,j}} - 1} \tag{1}$$

where n_{ij} is an adjustable parameter that can be determined for each reaction of Table 2 (Antonioni et al., 2013).

To calculate the feed rate of solid reactant available for the neutralization of the *i*-th acid gas, competitive reactions have to be considered. With regard to the first stage, it is important to evaluate carbonation (R4 in Table 1), which consumes a significant amount of calcium hydroxide. However, as reported by several authors (e.g. Mura and Lallai, 1994), the calcium carbonate produced through reaction R4, can neutralize in turn HCl (Chin et al., 2005):

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \tag{2}$$

In order to consider its effect, the overall conversion of CO_2 in the first stage has been calculated through the amount of $CaCO_3$ in the solid residues separated in the fabric filter. According to the design data (Antonioni et al., 2012), $CaCO_3$ in residues is about 30 %, corresponding to an overall CO_2 conversion of 0.4 %. It should be noticed that reaction represented by Eq. 2 can be obtained through a linear combination of reactions R1 and R4, so it was implicitly taken into account in the previous implementation of the model (Antonioni et al., 2012). However, in order to estimate CO_2 conversion in different conditions, a first-order reaction with respect to $Ca(OH)_2$ and CO_2 concentrations was assumed. This correlation, considering that CO_2 concentration does not vary significantly in flue gas, leads to the correlation reported in Eq. (3) for the CO_2 conversion as function of calcium hydroxide on the filter cake and of flue gas volume flow rate:

$$\chi_{CO_2} = K \cdot \frac{m_{Ca(OH)_2}}{Q} \tag{3}$$

K represents an overall kinetic constant that depends on reaction kinetics, stoichiometric coefficients and equipment volume. As reported in Table 2, both calcium hydroxide and flue gas rates show significant variations and the conversion of CO_2 changes accordingly.

Another adjustment of the correlation was made with the aim of applying the model to a wider range of conditions (i.e. low *rs*). With reference to the conversion of HCl with calcium hydroxide, the experiments performed by Weinell et al. (1992) and Chisholm and Rochelle (1999) showed that a maximum conversion of the sorbent is present. To take into account this phenomenon, $rs_{i,j}$ has been replaced by an effective $rs_{i,j}$ * in the correlation (1), which has been obtained multiplying $rs_{i,j}$ by the maximum conversion of the sorbent $\chi_{j,max}$:

$$rs_{i,j}^{*} = rs_{i,j} \cdot \chi_{j,max} \tag{4}$$

With this correction, when the solid reactant is in defect, the maximum acid gas conversion expressed by Eq. (1) is limited to the corresponding sorbent conversion. For calcium hydroxide, $\chi_{j,max}$ strongly depends on process conditions (e.g. relative humidity, CO_2 and SO_2 concentrations, initial fraction of voids of the calcium hydroxide particles). On the basis of literature (Chin et al., 2005) and process data, this limit was set to 80% and the parameters $n_{i,j}$ were calculated accordingly.

For sodium bicarbonate, the value of $\chi_{j,max}$ can be assumed equal to 100% due to the high fraction of voids produced during the thermal activation (reaction R5) compared to the increase of volume given by the formation of solid products according to reactions R6 ÷ R8 (Verdone and De Filippis, 2004). This assumption is confirmed by the data showed by Brivio (2007), where the conversion of bicarbonate is almost complete when fed in stoichiometric defect. Thus no correction was required to Eq. (1).

The parameters of the model have been calculated on the basis of a complete set of plant data (reported in Antonioni et al., 2013) taking into account the carbonation reaction (R4), the maximum conversion of $Ca(OH)_2$ and fly ash in the recycle. The resulting conversion curves are plotted in Figure 2, where the comparison between the acid gas conversions measured in the reference plant and the empirical correlation shows a general sufficient agreement. Differences are due to extremely scattered data points that are usually measured in a real plants under normal operating conditions.
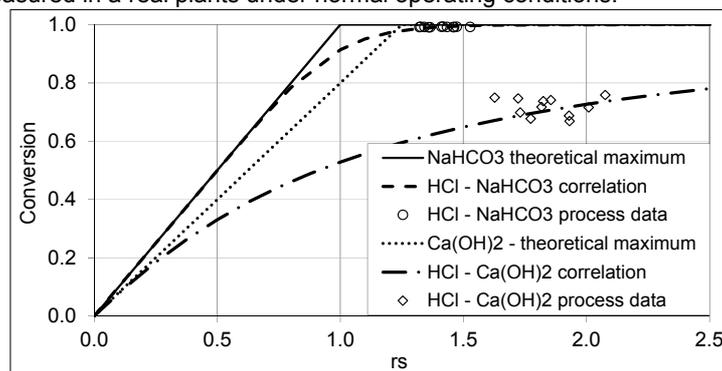

Figure 2: daily averaged HCl conversion in the first and second stages of the reference plant and corresponding correlations

3.2 Model implementation

Model validation for its application to describe operational conditions is shown elsewhere (Antonioni et al., 2013) and its verification was made through the comparison between measured concentration at the stack (SME) and the values calculated with the model. With reference to the average over the entire period (13 days), a good agreement was observed, particularly with regard to the HCl concentration (2.72 mg/Nm^3 measured vs 2.94 mg/Nm^3 calculated).

Since the composition of the incoming flue gas can vary significantly in a MSWI, in the present work a series of simulations was carried out to evaluate the sorbent feed rates that optimize the operation for different conditions of the incoming flue gas (corresponding to the average conditions measured in some representative days, reported in Table 2) and with different configuration of the plant (i.e. using the same sorbent in both stages).

Simulations were carried out setting the conditions of incoming flue gas (stream 1) equal to the average measured values during the analysed day. The calcium hydroxide feed rate (stream 13) was varied (thus varying the conversions at the first stage), while the total recycle rate was kept constant at its daily average value. However, the recycle stream composition changes according to the stoichiometry of the reactions and to the amount of fly ash (whose concentration in flue gas was fixed to the typical value of 3000 mg/Nm^3). The bicarbonate rate was adjusted in order to obtain a HCl concentration at the stack equal to 2 mg/Nm^3, which is 1/5 of its emission limit (Directive 2010/75/EU, 2010). This choice also ensures that emission concentrations of all acid gases are below the emission limits because hydrogen chloride has typically a higher inlet concentration and a lower emission limit with respect to other acid gases.

In order to perform an economic optimization of operational costs, the unit costs of the solid streams were set to typical values provided by a multi-utility company: 80 €/t for $Ca(OH)_2$, 240 €/t for $NaHCO_3$ and 200 €/t for the disposal of the produced solids. Other cost variations are not taken into account, since they do not significantly depend on reactants' feed rates.

4. Results and discussion

4.1 Optimization of operating conditions

The overall operating costs for the acid gas removal, calculated as the sum of reactant and disposal costs, shows a minimum when plotted against the HCl conversion in the first stage ($\chi_{HCl,Ca(OH)2}$, the controlled variable in the control system) as shown in Figure 3 (solid lines) and clearly the higher is the HCl inlet concentration the higher is the cost. However, for each considered day, a minimum in overall costs (black dots) is always present for a first stage conversion of about 60%. Actual costs (white dots) can be estimated to have been between 3% and 8% higher with respect to the calculated optimal conditions.

For simulations where HCl concentration is higher, it is important to operate near to the optimal condition, as the costs rapidly increase using different set points (Day 3 in Figure 3, solid line). Conversely, when the incoming HCl is low (e.g. Day 1), keeping the conversion of the first stage below 70% is enough to minimize the operating costs.
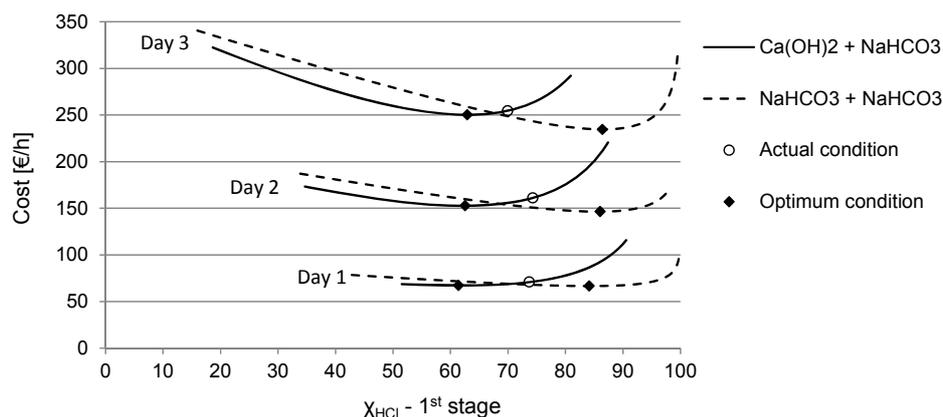

Figure 3: operating costs as a function of first stage HCl conversion

4.2 Simulation of alternative configurations

The model was then applied in order to simulate the performance of the plant when using only one reactant (i.e. only hydrated lime or only bicarbonate). Day 2 was selected as reference condition, since it is representative of the average inlet concentration (see Table 2). The minimum operating cost for this day is reported in the first column of Figure 4. The first simulated alternative was a double stage with calcium hydroxide, obtained by changing the sorbent in the second stage and calibrating its feed rate to reach the same HCl concentration at the stack. Results reported in Figure 4 show that using this configuration, operating costs would be definitely higher. The second case was referred to a bicarbonate - bicarbonate systems (in this case, the recycle rate in the first stage was set to zero, as the unreacted sorbent in solid would be negligible). Simulations (dashed lines in Figure 3) indicate that it would be possible to achieve a slight reduction of operating costs with respect to the actual condition, but the difference is so low that this conclusion could be affected by uncertainties, in particular concerning the assumption that the model parameters are constant outside the calibration range. Moreover, for flue gas with high HCl content, the fraction of $Ca(OH)_2$ that reacts with CO_2 could decrease because of reaction represented by Eq. 2: this effect is not taken into account by the present model and could determine a better performance of the $Ca(OH)_2$. Also the use of calcium hydroxide with high specific surface could be of interest because the expected maximum conversion is higher due to the higher initial void fraction, thus reducing the reactant and disposal cost for the lime stage.

The distribution of reactants and disposal cost (Figure 4) shows that when calcium hydroxide is the only reactant, disposal costs are about 75 % of the total operating costs. In fact, a considerable amount of unreacted calcium hydroxide is present in solid waste. This could be reduced using an higher recycle rate. A higher recycle rate would decrease also operating costs of the existing plant (operating with calcium hydroxide and bicarbonate), possibly lowering costs below the process with bicarbonate at both stages.

Finally the third bar in Figure 4 shows that a single stage treatment with bicarbonate feed could be an economically favourable alternative since it would lower also investment costs. However, it is out of the scope of the present study to carry out a detailed cost/benefit analysis of this alternative.
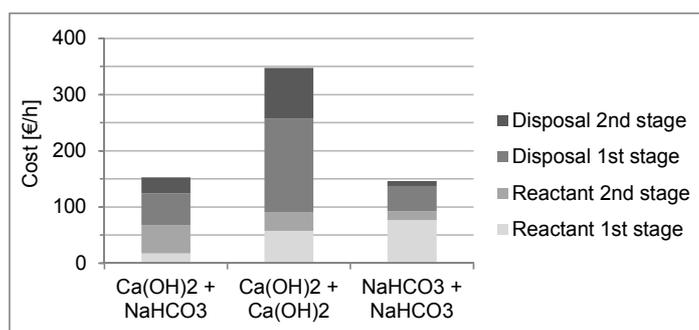
Figure 4: minimum operating costs with current configuration (1st bar), two-stage with calcium hydroxide (2nd bar) and two-stage with sodium bicarbonate (3rd bar)

5. Conclusions

A model derived from the analysis of literature data was implemented and calibrated to describe the removal efficiency of acid gases (HCl, HF and SO_2) in the flue gas treatment section of an existing waste to energy plant. The acid gas cleaning system is constituted by a two-stage dry treatment, where the dry sorbents are calcium hydroxide in the first stage and sodium bicarbonate in the second stage.

The model parameters were calculated using operational data measured in a period of 13 days. The model can be applied to an existing plant, even if further calibration (e.g. on the basis of specific test-runs) could be required since process data were rather scattered. The implementation of the model within the Aspen Hysys software allowed the reproduction of the average conditions of 3 selected days. The analysis of process operating costs based on reactant and solid disposal costs allowed the identification of an economic optimum for each analysed day.

The model was then applied in order to simulate alternative configurations for the flue gas cleaning system. It was found that if calcium hydroxide was used in both stages, operating costs would be higher. Conversely, using a two-stage system with sodium bicarbonate would allow to slightly decrease operating costs.

References

Antonioni G., Sarno F., Guglielmi D., Morra P., Cozzani V., 2011, Simulation of a two-stage dry process for the removal of acid gases in a MSWI, Chemical Engineering Transactions, 24, 1063-1068, DOI: 10.3303/CET1124178

Antonioni G., Guglielmi D., Stramigioli C., Cozzani V., 2012, MSWI Flue Gas Two-Stage Dry Treatment: Modeling and Simulation, Chemical Engineering Transactions, 26, DOI:10.3303/CET1226036

Antonioni G., Guglielmi D., Cozzani V., Stramigioli C., Corrente D., 2013, Modelling and simulation of an existing MSWI flue gas two-stage dry treatment, Process Safety and Environmental Protection, In Press, DOI: 10.1016/j.psep.2013.02.005

Brivio S., 2007, Depurazione dei fumi e valorizzazione dei prodotti (Flue gas cleaning and by-products valorisation, in Italian), Power Technology, 4, 42-44

Chin T., Yan R., Liang D.T., Tay J.H., 2005, Hydrated lime reaction with HCl under simulated flue gas conditions, Industrial and Engineering Chemistry Research, 44 (10), 3742-3748

Chisholm, P.N., Rochelle, G.T., 1999, Dry absorption of HCl and SO_2 with hydrated lime from humidified flue gas, Industrial and Engineering Chemistry Research, 38 (10), 4068-4080

Directive 2010/75/UE of the European Parliament and of the Council of 24 November 2010 on industrial emissions (Integrated Pollution Prevention and Control), OJ L 334, 17.12.2010

D.Lgs. 11-5-2005 n. 133, Attuazione della direttiva 2000/76/CE, in materia di incenerimento dei rifiuti, Gazz. Uff. 15 luglio 2005, n. 163, S.O. (In Italian)

Mura G., Lallai A., 1994, Reaction kinetics of gas hydrogen chloride and limestone, Chemical Engineering Science, 49 (24 A), 4491-4500

Verdone N., De Filippis P., 2004, Thermodynamic behaviour of sodium and calcium based sorbents in the emission control of waste incinerators, Chemosphere, 54 (7), 975-985

Weinell C.E., Jensen P.I., Dam-Johansen K., Livbjerg H., 1992, Hydrogen chloride reaction with lime and limestone: kinetics and sorption capacity, Ind. Eng. Chem. Res., 1992, 31 (1), 164–171