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MSWI Flue Gas Two-Stage Dry Treatment: Modeling and Simulation

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Power generation from Municipal Solid Waste incineration is widespread used as a technology for solid waste treatment and energy recovery. One of the main impacts of these plants is the continuous emission of pollutants into the atmosphere. Another issue to be addressed is the generation of solid or liquid residues from flue-gas cleaning, depending on the flue-gas treatment process.

Among the substances produced during thermal incineration, acid gases are of particular interest because of their environmental impact. One of the most promising combination of Best Available Technologies for an enhanced removal efficiency of acid gases is the two-stage dry treatment. In the analysed process, solid powder of calcium hydroxide (slaked lime) is used in the first stage while in the second one sodium bicarbonate (more effective) is injected, allowing the decrease of pollutants concentration until the design values.

In the present study an operational model (based on the ratio of reactant rate to stoichiometric rate) is proposed to fit literature data concerning the performance of the process considered. The implementation of the model in a simulation software has allowed describing the design conditions of a typical Municipal Solid Waste Incinerator (MSWI). Other simulations were carried out with the aim of reducing solid products formed by flue gas treatment without decreasing the removal efficiency. The model was also used to assess the possible cost optimization by the identification of optimal reactant feed rates.

1. Introduction

Nowadays the waste management has to deal with several issues, and one of the possible solutions is the thermal treatment with energy recovery. Waste incineration is a proven technology for energy recovery, while other emerging solutions (gasification, plasma, pyrolysis) represent an operational challenge, since they require a significant pre-treatment of the waste and have higher total cost and less energy output, causing technical and economic problems.

Energy recovery from municipal solid waste (MSW) is an expanding technology due to its advantages. The thermal treatment allows reducing the volume and harmfulness of solid wastes to landfill and enables the energy recovery instead of using fossil fuels (with a reduction of CO_2 emission). Other environmental benefits are the reduction of transport distances and the proximity of energy consumers.

One of the main problems related to this technology is the emission of airborne pollutants into the atmosphere. Acid gases are particularly important because of their environmental impact (long term exposure, acid rains, etc.), and a feasible solution is to remove them by means of dry processes. The two-stage dry treatment of flue gas with calcium hydroxide (slaked lime) and sodium hydrogen carbonate (bicarbonate) is an emerging combination of two among the Best Available Technologies for

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acid gas cleaning which provides elevated performance (European Commission, 2006). This technology is widespread used because it permits to respect the restrictive limits of current emissions regulation (Directive 2010/75/EU, 2010) and does not produce wastewater streams. However, an issue related to this system is the generation of solid residues.

Although bottom ashes are generated in larger quantities, the main pollution potential is found in the residues originated from the products of the gas-solid reactions. According to the Directive on IPPC (Directive 2010/75/EU, 2010) the residues shall be minimised considering both their amount and harmfulness.

Even if there are some plants that have already implemented this process, there is still a lack of knowledge about reaction efficiency (Yassin et al., 2007). Thus, solid reactants are fed in high excess and they can be found as un-reacted solids in the generated wastes. In a previous study (Antonioni et al., 2011) it was shown that a two-stage process requires a lower amount of reactants than a single-stage one (Jannelli and Minutillo, 2007). This is due to the lowest lime cost and the highest bicarbonate removal efficiency. In the present study an operational model has been developed in order to optimize the use of solid reactants in a two-stage dry process.

2. Model

2.1 Two-stage process description

The removal of acid gases by dry adsorption is analysed. The alkaline sorbents considered are slaked lime - $Ca(OH)_2$ - and sodium bicarbonate - $NaHCO_3$ - that react with hydrochloric acid (HCl), hydrogen fluoride (HF) and sulfur dioxide (SO_2).

The two-stage dry treatment is one of the Best Available Technologies which uses solid sorbents. Each stage is composed of a reactor followed by a filter. The reactants, lime in the first stage and bicarbonate in the second one, are injected into the reactor as solid powder. The resulting flue-gas cleaning residues are composed of calcium-based and sodium-based salts respectively. If the separation is performed by a fabric filter, the reactions take place in the cake formed on the bags (European Commission, 2006).

The reactions involved in acid gas capture using lime are listed in Table 1 (Reaction 2, 3 and 4). In the first stage carbonatation also takes place (Reaction 1). It removes only a minor part of CO_2 but it is important for the lime consumption (Chin et al., 2005). Bicarbonate decomposes to carbonate with an almost instantaneous and complete process at temperatures above 130 °C (Brivio, 2007). Subsequently, carbonate reacts with the acid gases. The overall reactions that occur in the second stage (at 180 °C) are schematized in Table 1 as Reaction 5, 6 and 7.

Table 1: Carbonatation reaction (1) and acid gas removal reactions (2-7) assumed in the model

Reaction 1	$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
Reaction 2	$Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O$
Reaction 3	$Ca(OH)_2 + 2\ HF \rightarrow CaF_2 + 2\ H_2O$
Reaction 4	$Ca(OH)_2 + SO_2 + \frac{1}{2}\ O_2 \rightarrow CaSO_4 + H_2O$
Reaction 5	$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$
Reaction 6	$NaHCO_3 + HF \rightarrow NaF + CO_2 + H_2O$
Reaction 7	$2\ NaHCO_3 + SO_2 + \frac{1}{2}\ O_2 \rightarrow Na_2SO_4 + 2\ CO_2 + H_2O$

2.2 The conversion model

The model used to simulate the removal of acid gases is based on a correlation developed between the acid gas conversion and the ratio of solid reactant rate to the stoichiometric rate. An empirical function (equation 1) was defined to describe the removal efficiency for each reaction:

$$\chi = \frac{rs^n - rs}{rs^n - 1} \tag{1}$$

where χ is the pollutant conversion, *rs* is the ratio of the actual reactant rate (i.e. sodium bicarbonate and lime) over the stoichiometric rate and *n* is a fitting parameter. This parameter has to be calculated for each reaction from literature or process data. It can be observed that the higher is *n*, for a given stoichiometric ratio *rs*, the higher is the removal efficiency.

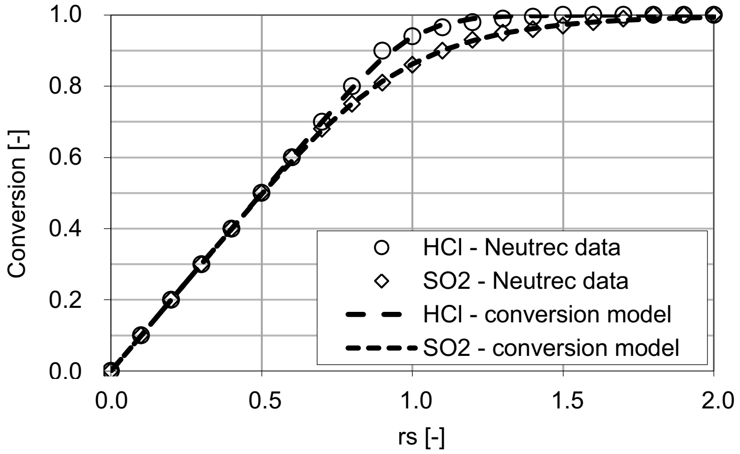

Figure 1: HCl and SO_2 conversions versus the ratio of reactant rate (i.e. sodium bicarbonate) to its stoichiometric rate. Dots correspond to the conversion values of Neutrec process reported by Brivio (2007) while the best fitting curves (obtained from Eq. 1) are represented by dashed lines.

The model was verified through its comparison with the data reported by Brivio (2007) for the reactions between bicarbonate and HCl or SO_2 (Figure 1). It was observed that the empirical correlation has a good agreement with the experimental data. A best-fit regression allowed the calculation of the *n* parameter, that was found to be equal to 16.6 with a mean absolute error of 0.3 % for HCl, while for SO_2 reaction the *n* parameter was equal to 7.3 with an error of 0.4 %.

Equation 1 was applied also to lime reactions and the corresponding adjustable parameters have been calculated.

3. Case study

3.1 MSWI plant examined

The model was applied to a flue-gas cleaning unit of a modern municipal solid waste incinerator (MSWI). The removal of acid gases takes place in a two-stage dry treatment section, where lime and bicarbonate are injected in the reactors and the solid products are separated by means of fabric filters.

In the analysed process the solid products formed in the first stage are recycled to the reactor. This allows the increase of the lime conversion and the decrease of the amount of unconverted reactant sent to disposal. The pollutants considered in this analysis are HCl, HF and SO_2. Other pollutants, such as NO_x or dioxins, were not studied, because their concentrations do not decrease in the acid gas removal process. The main design data are listed in Table 2, where the molar flow rates reported correspond to normalized concentrations (dry gas and 11 % of oxygen) at the exit of the second stage equal to 2 mg/Nm^3 for HCl, 0.5 mg/Nm^3 for HF and 5 mg/Nm^3 for SO_2 (design concentrations are set to half of the emission limits at most).

The removal efficiencies corresponding to the values reported in Table 2 are referred to a lime rate of 313 kg/h in the first stage and a bicarbonate rate of 142 kg/h in the second stage. The ratio of recycled product to disposal product is equal to 3.6 with a mass fraction of lime of 0.15. The CO_2 concentration in the inlet flue gas is equal to 8.5 % and its conversion, with respect to Reaction 1 of Table 1, is equal to 0.4 %.

Table 2: Incoming and outgoing rates of acid gases in the two stages expressed in mol/h with respect to a 110,000 Nm^3/h basis of flue gas

	HCl	HF	SO_2
1st stage feed	2758.1	62.9	392.6
1st stage exit / 2nd stage feed	829.4	18.9	275.5
2nd stage exit	6.93	3.16	9.86

3.2 Calculation of model parameters

The model parameters *n* were determined for each reaction of lime and bicarbonate applying Eq. 1. The values of χ and *rs* were obtained from the design data reported in Table 2.

The conversion of the generic acid gas *i* was calculated with the following expression:

$$\chi_i = \frac{\dot{n}_{i,in} - \dot{n}_{i,out}}{\dot{n}_{i,in}} \tag{2}$$

The *rs* ratio was evaluated by dividing the actual rate of reactant by its stoichiometric rate according to the reactions in Table 1.

In the case of lime (first stage), the *n* parameter is 1.64 for HCl and HF, and equal to 1.78 for SO_2. For bicarbonate reactions, the *n* parameters obtained from the data of Table 2 are equal to 17.21 for HCl, 4.28 for HF and 10.15 for SO_2. These values are slightly different from the parameters calculated fitting the literature data (paragraph 2.2), which were obtained in laboratory conditions considering only a single reaction. The differences are due to fabric filters, where reactions continue, increasing the removal efficiency.

3.3 Implementation within HYSYS to simulate and optimize the acid gases removal

The correlations proposed in paragraph 2.2 have been implemented within the software Aspen Hysys to simulate the two-stage process described above. The software allows representing a process by means of a Process Flow Diagram based on blocks corresponding to unit operations (Aspen HYSYS, 2009).

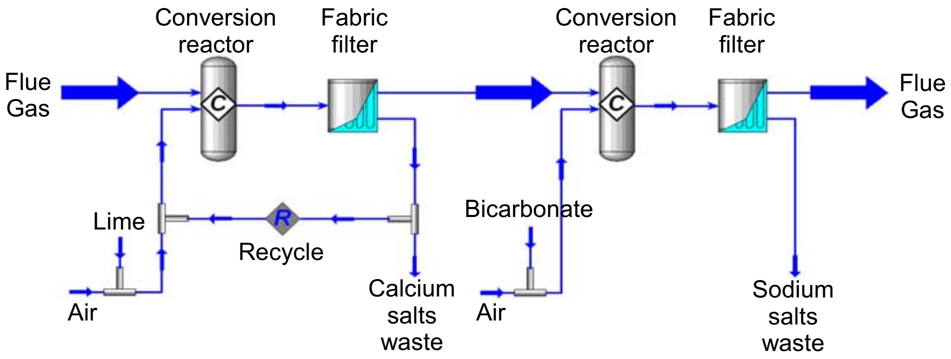

Figure 2: Representation of the two-stage process implemented within Aspen Hysys.

In the implementation it was assumed that the removal of acid gases does not take place in the filter cake, but only in two conversion reactors. This type of reactor requires the definition of the conversion for each reaction showed in Table 1. Eq. (3) reports the default correlation available in Aspen HYSYS, that relates the conversion with temperature T:

$$Conversion = C_0 + C_1 \cdot T + C_2 \cdot T^2 \tag{3}$$

Since the reactions do not produce significant thermal effects because the amount of reactive substances is considerably lower than the total flow, the temperature is approximately constant and C_1 and C_2 were set to zero. C_0 was expressed as a function of *rs* according to Eq. 1 by means of user defined functions, making use of the *n* parameters reported in paragraph 3.2.

Both reactors are followed by a filter, where gas-solid separation was assumed to be complete. The software allowed also the simulation of the recycle of the solid products in the first stage. The flue gas treatment section implemented within Hysys is shown in Figure 2.

3.4 Cost assessment and optimization

The model allowed us to calculate both reactant rates necessary to achieve the required emission concentrations and solid wastes produced in each stage. In the simulation software, the costs of every stream can be specified, allowing the identification of the optimal operating condition by means of an economic balance. Equipment and other operational costs were not taken into account at this stage of the work.

In the implemented model, the ratio of bicarbonate cost to lime cost was set to 3:1, while the disposal cost was set at 2.5 times the lime cost. These values allowed the calculation of relative money saving compared to design conditions.

Simulations were carried out setting a fixed emission concentration of hydrochloric acid, since under typical process conditions fulfilling the emission limitations for HCl will ensure also that these are fulfilled also for all the other acid gases.

4. Results and discussion

A first simulation was carried out considering the design conditions of the plant described in paragraph 3.1. The results are reported in Table 3 as “Design conditions” and were used as a reference point for the other model runs.

Simulations were performed by varying the rate of lime injected in the first stage in an appropriate range for the plant considered, and, consequently, the removal efficiency at this stage was modified.

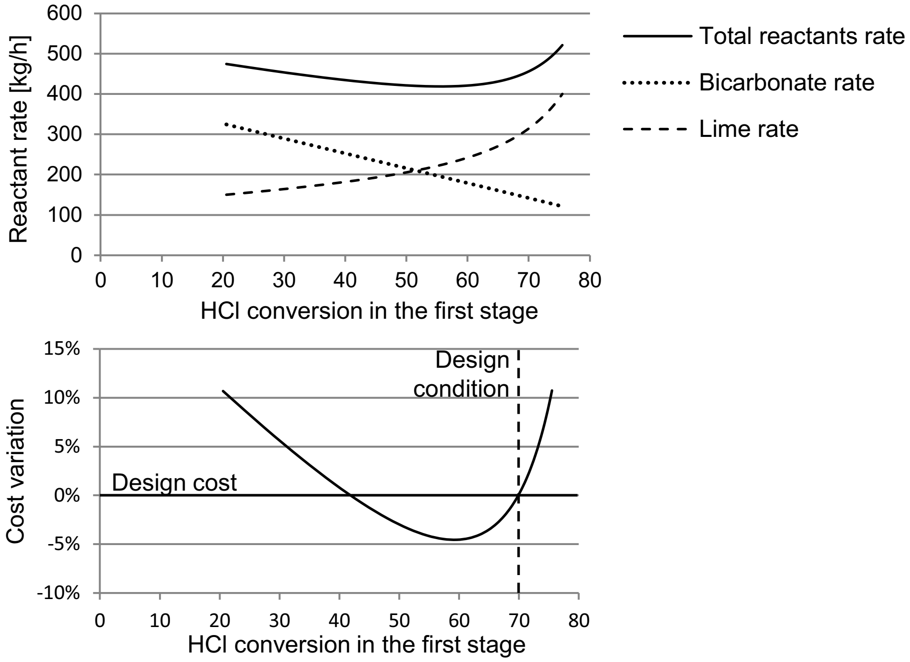

Figure 3: a) Solid reactant rates as a function of HCl conversion in the first stage; b) Variation of reactants and disposal costs with respect to design conditions.

Table 3: Results of simulations for a fixed HCl outlet concentration of 2 mg/Nm^3.

	$Ca(OH)_2$ kg/h	$NaHCO_3$ kg/h	Total kg/h	Solid wastes kg/h	Cost difference %
Design conditions	313.0	142.0	455.0	503.0	-
Reactants optimization	224.0	194.6	418.6	441.2	-4.3
Cost optimization	238.0	182.0	420.0	448.6	-4.6

The bicarbonate rate in the second stage was calculated in order to obtain the design value of HCl emission (2 mg/Nm^3).

The results are shown in Figure 3-a. As shown in the figure, a minimum exists. This is the result of the combination of two factors: on the one hand bicarbonate is more effective than lime and, on the other hand, bicarbonate has a higher molecular weight compared to the lime and requires a double molar rate for the same acid gas being removed. The minimum rates of lime and bicarbonate are reported in Table 3 (“Reactants optimization”). A cost-based optimization was performed considering that bicarbonate is more expensive than lime (as reported in paragraph 3.4). The plot in Figure 3-b represents the cost variation with respect to the design conditions for the considered process (vertical line). The lime rate corresponding to the minimum cost (reported as “Cost optimization” in Table 3) is only slightly higher than the value that provides the minimum consumption of reactants. In fact, in spite of its higher cost, the use of bicarbonate is more effective and produces less solid wastes.

5. Conclusions

An operational model based on literature data was proposed to describe the removal efficiency of acid gases (HCl, HF and SO_2) in an incineration power plant. The model was developed considering the ratio of solid reactants (calcium hydroxide and sodium bicarbonate) to stoichiometric values.

The model parameters were calculated using the design data of an existing MSWI where the acid gas cleaning system is a two-stage dry treatment. The implementation within Aspen Hysys allowed the reproduction of the design conditions of the plant analysed. With respect to these results, an optimization of the reactant rates was performed, providing the operating conditions to obtain the minimum. The economic optimization allowed the calculation of the money saving with respect to the design conditions taking into account both reactant and disposal costs.

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