

## Simulation of a Two-Stage Dry Process for the Removal of Acid Gases in a MSWI

Giacomo Antonioni, Ferdinando Sarno, Daniele Guglielmi, Pamela Morra, Valerio Cozzani\*

Dipartimento di Ingegneria Chimica, Mineraria e delle Tecnologie Ambientali  
Alma Mater Studiorum - Università di Bologna  
Via Terracini 28, 40131 Bologna, Italy  
valerio.cozzani@unibo.it

Power generation from municipal solid wastes is an attractive technology in the area of renewable energy utilization. Because of the restrictive pollutant emission limits dictated by European Union Directives, it is very important to optimize the flue gas cleaning system to reduce the environmental impact caused by incineration, also taking into account economic aspect. In the present study a simplified conversion model for the assessment of removal efficiency of acid gases from flue gas was developed. The model is based on the ratio between the rate of solid reactants and the rate of incoming acid gases with respect to the stoichiometric ratio. The model was implemented with the Aspen Hysys code to simulate a two-stage flue gas cleaning system. Simulations were based on design data of an existing RDF incineration plant and can be easily adjusted to fit other design data. The optimal feed rate of reactants for a fixed removal efficiency was estimated through the proposed model.

### 1. Introduction

Power generation from municipal solid waste incineration is widespread used as a technology for solid waste treatment and energy recovery. However one of the main sources of environment impact for these plants is the continuous emission of pollutants to the atmosphere. Emissions of airborne pollutants are regulated by European Union Directive 2000/76/EC, and concentration thresholds are becoming more and more restrictive, as established by Directive 2008/1/EC on IPPC.

Among substances produced during incineration, acid gases can be effectively removed by means of several technologies such as dry (or semi-dry) processes using solid reactants. The two-stage dry treatment of flue gas with calcium hydroxide (lime) and sodium bicarbonate is a combination of two emerging Best Available Technologies for acid gas cleaning, which have a promising cleaning performance (European Commission, 2006). However, even if there are some plants that are already running this process, showing high levels of effectiveness in terms of exhaust gas concentrations, there is still lack of knowledge about reaction efficiency and reactant consumption. Thus a great amount of solid products and unreacted lime and sodium bicarbonate, which are used in great excess, are produced by Municipal Solid Waste Incinerators (MSWI) and should be disposed of, usually by landfilling.

In the present study, a model for the estimation of the optimal operating conditions for acid gas removal in a two-stage flue gas cleaning system is proposed, aiming at the optimization of reactant feed and at the reduction of solid residues.

## 2. Model

### 2.1 Schematization of acid gas removal process

Acid gases, e.g. hydrochloric acid (HCl) and sulphur dioxide (SO<sub>2</sub>), can be cleaned from the flue-gas by the injection of chemical or physical sorption agents, which are brought into contact with the flue-gas (European Commission, 2006). In dry sorption processes the alkaline sorbent (usually lime or sodium bicarbonate) is fed into the reactor as a dry powder. The resulting flue-gas cleaning residues are composed of Ca-based salts and Na-based salts respectively. It is possible to improve the efficiency of the acid gas removal process by adding a second stage.

In the case-study, the process layout consists of two stages, each one composed of a reactor followed by a fabric filter. In the first stage the reactant is lime, whereas in the second sodium bicarbonate is used. In the model developed it was assumed that the removal of HCl and SO<sub>2</sub> takes place only in the reactors, not in the filter cake. The acid gas capturing reactions are listed in Table 1 (Reaction 1 and 2) for lime. At temperatures above 100°C, bicarbonate decomposes to carbonate with an almost instantaneous and complete process. Subsequently, carbonate reacts with the acid gases. The overall reactions are schematized in Table 1 as Reaction 3 and 4.

Table 1: Set of reactions assumed in the model

Reaction 1	$\text{Ca(OH)}_2 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + 2 \text{H}_2\text{O}$
Reaction 2	$\text{Ca(OH)}_2 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
Reaction 3	$\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$
Reaction 4	$2 \text{NaHCO}_3 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{CO}_2 + \text{H}_2\text{O}$

### 2.2 The conversion model

The model simulates a two-stage treatment section for acid gas removal. It is based on a conversion model in which the removal of acid gases is expressed as a function of the ratio of rate of solid reactant over the stoichiometric rate.

An empirical function was defined to fit the removal efficiency data of the Neutrec process discussed by Brivio, 2007. The correlation proposed is the following:

$$\chi = \frac{rs^n - rs}{rs^n - 1} \quad (1)$$

where  $\chi$  is the pollutant conversion,  $rs$  is the ratio of the actual rate of reactant (i.e. sodium bicarbonate) over the stoichiometric rate and  $n$  is an adjustable parameter.

Equation 1 was applied also to model the lime gas treatment, calculating a specific value for the adjustable parameter.

### 2.3 RDF power plant examined

The model was applied to a case-study. The flue-gas treatment section of the refuse derived fuel (RDF) power plant examined by Jannelli and Minutillo (2007) was selected. The plant consists of a SNCR system, a semi-dry reactor and a fabric filter. The removal of acid gases is obtained by the semi-dry absorption process that offers an efficient HCl and SO<sub>2</sub> removal into a finely atomized aqueous mist of Ca(OH)<sub>2</sub>. The water solution evaporates and the reaction products are dry and can be separated by means of the fabric filter.

The pollutants considered in this analysis are HCl and SO<sub>2</sub>. Other pollutants, such as NO<sub>x</sub> 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.

Table 2: Design data of the Lurgi Energie und Umwelt GmbH plant: flows are in kg/h.

	HCl	SO <sub>2</sub>	Ca(OH) <sub>2</sub>	CaCl <sub>2</sub>	CaSO <sub>3</sub>	CaSO <sub>4</sub>
In	81	30	266	-	-	-
Out	0.97	4.83	148	123	39	19
Conversion	98.8%	83.9%	44.4%			

### 2.4 Calculation of model parameters

The  $n$  parameters of Eq. 1 for bicarbonate and lime were calculated from available data both in the case of HCl and SO<sub>2</sub>. For bicarbonate reactions, they were evaluated fitting the data reported by Brivio (2007), obtaining the parameter  $n$  equal to 16.6 for HCl and equal to 7.3 for SO<sub>2</sub>. It was possible to compute the relative errors among the values calculated with the empirical formula and the experimental data: for HCl the mean absolute error was 0.3% and for SO<sub>2</sub> it was 0.4%. In the case of lime, the  $n$  parameters were based on the design data of the incineration plant described by Jannelli and Minutillo (2007) and reported in Table 2, obtaining  $n$  equal to 5.7 for HCl and  $n$  equal to 2.7 for SO<sub>2</sub>.

Figure 1 shows the experimental data corresponding to the conversion values of Neutrec process as well as the values calculated using Eq. 1 with the aforementioned parameters.

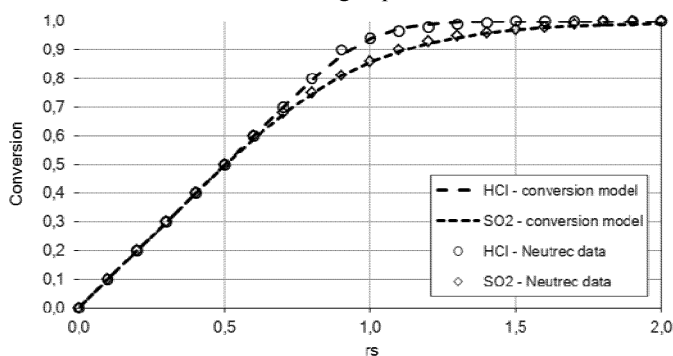


Figure 1: HCl and SO<sub>2</sub> conversions as function of the ratio of the actual rate of reactant (i.e. sodium bicarbonate) over its stoichiometric rate.

### 2.5 HYSYS model for the calculation of conversions and reactant consumption

The Aspen Hysys simulator, a software by AspenTech, was used to implement the model. The software allows representing a process by means of a Process Flow Diagram based on blocks corresponding to unit operations (Aspen HYSYS 7.1, 2009).

Within the simulator, unit operations with reactions can be modeled by means of several types of reactors, among which a conversion reactor. Two of these reactors were selected for the simulation, each followed by a filter. The gas-solid separation were assumed as complete. The reactant was lime for the first reactor and sodium bicarbonate for the second. This type of reactor requires the definition of the correlation parameters ( $C_0$ ,  $C_1$  and  $C_2$ ) which describe the conversions of the removal reactions showed in Table 1. The correlation that relates the conversion with temperature  $T$  is the following:

$$\text{Conversion} = C_0 + C_1 \cdot T + C_2 \cdot T^2 \quad (2)$$

The reactions do not produce significant thermal effects since the amount of reactive substances is considerably lower than the total flow. Thus, the temperature is approximately constant. For this reason,  $C_1$  and  $C_2$  were set to zero.  $C_0$  was expressed as a function of  $rs$  according to Eq. 1 with the  $n$  parameters shown in paragraph 2.4 and using another tool available in Hysys, which allows to describe user defined functions.

The data of all the solid compounds were introduced in Hysys database.

### 2.6 Approach to cost assessment and optimization

The model allowed us to find the optimal operating condition by means of an economic balance based on the reactant costs. Equipment and other operational costs were not taken into account at this stage of the work.

The inlet concentration of HCl is higher than that of  $\text{SO}_2$ , as shown in Table 2. Moreover, the HCl emission limit is lower (Directive 2000/76/EC, 2000). Therefore the most critical acid gas compound is HCl. For this reason the simulations were carried out considering the same HCl emission.

In the economic balance the ratio between the cost of bicarbonate and the cost of lime was set to 3:1 in order to calculate relative money saving compared to single stage case.

## 3. Results and Discussion

The model was used to evaluate the reduction of acid gases in nominal operating conditions considered for design. All the simulations were carried out setting the HCl concentration in the outlet flue-gas to  $9 \text{ mg/Nm}^3$ , which represents the design value of the examined plant. The first simulation carried out models the power plant described in section 2.3. This result, which refers to a lime single stage process, was used as reference point for the other simulations and it is reported in Table 3 as Simulation 1.

The two-stage process case was then simulated, setting the lime rate to half of the value used in the first simulation (Simulation 2 of Table 3). The rate of bicarbonate in the second stage was calculated in order to obtain the same HCl emission. It can be observed that the two-stage process requires a lower amount of reactants than the single-stage one. This is due to the higher bicarbonate removal efficiency.

In order to find out if a minimum required amount of the reactants exists, simulations were carried out decreasing the amount of lime used in the single stage case and by adding the necessary bicarbonate to reach  $9 \text{ mg/Nm}^3$  of HCl in outlet. The results are shown in Figure 2, where it can be observed that a minimum is present. This is because bicarbonate is more effective than lime, but it has a higher molecular weight. The corresponding lime and carbonate rates are reported in Table 3, Simulation 3.

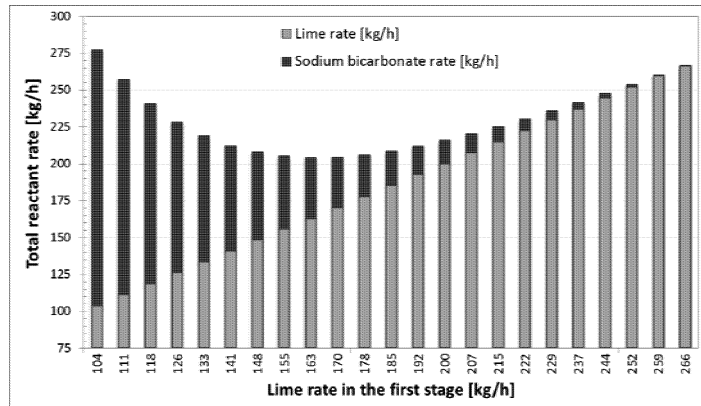


Figure 2: Total rates of solid reactants, obtained setting HCl in the outlet to  $9 \text{ mg/Nm}^3$ .

As mentioned in paragraph 2.6, bicarbonate is more expensive than lime, therefore a cost-based optimization is possible. The plot in Figure 3 indicates the cost variation due to the one-stage process (the point on the right side). The lime rate corresponding to the minimum cost (reported as Simulation 4 in Table 3) is higher when compared to the one calculated for the minimum consumption of reactants, because of the higher cost of bicarbonate.

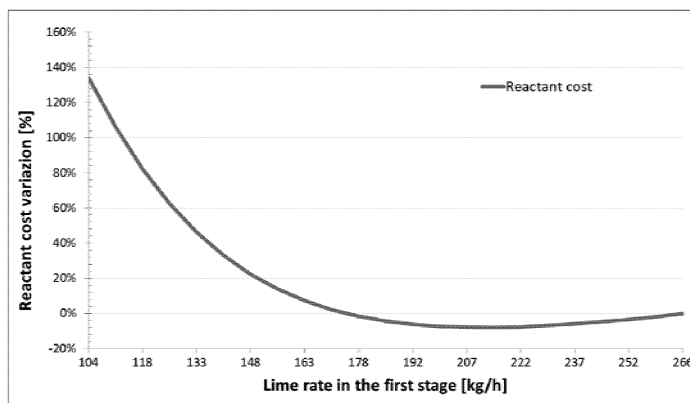


Figure 3: Variation of the total reactant cost relatively to the single stage process, referring to a bicarbonate-lime cost ratio of 3:1.

All the results of the previously described simulations are listed in Table 3. For each simulation the table reports the rate of solid reactants and the estimated saving.

Table 3: Simulations results carried out setting HCl in the outlet to 9 mg/Nm<sup>3</sup>.

	Ca(OH) <sub>2</sub>	NaHCO <sub>3</sub>	Total	Cost difference
Simulation 1	266 kg/h	-	266 kg/h	-
Simulation 2	133 kg/h	86 kg/h	219 kg/h	+46%
Simulation 3	163 kg/h	41 kg/h	204 kg/h	+7%
Simulation 4	215 kg/h	10 kg/h	225 kg/h	-8%

Setting the economic optimization to obtain an outlet HCl concentration equal to 1 mg/Nm<sup>3</sup> (more realistic, according to the BAT values reported in European Commission, 2006, and concentration limit value of Directive 2000/76/EC, 2000) the saving compared to the single-stage increases to 40%.

#### 4. Conclusion

A conversion model was proposed for the simulation of the flue-gas cleaning system of an RDF incineration power plant. The model can be a useful tool in evaluating the HCl and SO<sub>2</sub> removal efficiencies and the estimation of the economic optimal operating conditions. The model was applied to simulate the design data of an existing MSWI, but may be easily adjusted to fit other data.

The economical optimization applied to reactors for acid gases capturing (with lime and sodium bicarbonate injections) provided a minimum of the total cost of solid reactants. This is a function of the pollutant conversion, the rates and the unit cost of the reactants. The results also evidence that the model allows an economic optimization of operating conditions, indicating optimal balancing among first and second stage flue-gas removal efficiencies.

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