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Environmental Assessment of Combined Acid Gas Emission Control with Alternative Dry Sorbent Injection Systems

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In a holistic approach to environmental protection, the optimisation of end-of-pipe technologies for air pollution control has to take into account not only process performance but also indirect impacts related to the production of reactants and the disposal of by-products. In this perspective, a thorough environmental assessment of the life cycle impacts associated with the adoption of alternative technologies is a useful tool for the selection of an all-round environmentally sound solution.

In the present study, a comparative analysis is carried out to evaluate the overall environmental footprint of two alternative dry sorbent injection configurations for acid gas removal in waste-to-energy plants, adopting a life cycle viewpoint to consider the related supply and disposal chains. A previously developed operational model is employed to quantify the streams of reactants and residues associated with acid gas emission control for the two alternatives, which are functions of the reactivity of the different sorbents towards three acid pollutants (HCl, SO_2, HF). In particular, HF, which is usually present in considerably lower concentrations than HCl and SO_2 in flue gases, is generally neglected in process optimisation studies, but it is particularly harmful for both human health and ecological integrity. Here its removal is taken into account in order to include the related impacts in the environmental assessment.

1. Introduction

Acid gases like HCl, SO_2 and HF are typical pollutants in flue gases generated by waste incinerators, ceramic factories or glass manufacturing plants. Control of their emissions below the limit values set by the Industrial Emissions Directive in Europe (Directive 2010/75/EU) can be achieved with different treatment systems, among which dry sorbent injection approaches are valued for their cost-effectiveness and ease of operation (Vehlow, 2015). These systems, typically fed with calcium hydroxide or sodium bicarbonate, neutralise acid compounds according to the reactions in Table 1.

However, a complete assessment of the environmental performance of a treatment system is not limited to the mere acid gas removal efficiency, but it has to encompass the indirect environmental burdens related to supply of the reactants and disposal of the by-products generated by the treatment process (Ca-based or Na-based residues), as well. Furthermore, even if the treatment system guarantees the compliance to emission limit values, the impact of the residual emissions of acid gases might not be negligible. In particular, the human toxicity potential of HF is considered to be three orders of magnitude higher than the ones of HCl and SO_2 (Huijbregts et al., 2000), but its emission limit value is only a order of magnitude lower (Directive 2010/75/EU) and therefore an environmental assessment has to give proper attention to this compound, which is often overlooked in process optimisation studies since a set point targeted on HCl emissions is usually enough to guarantee HF emissions below the limit value (Guglielmi et al., 2014).

Here, an approach to the evaluation of the environmental impact associated with the operation of acid gas emission control systems – including the extraction and processing of the reactants and the disposal or reuse of the residues – is proposed. Its application to a case study allowed to identify the environmental consequences of upgrading a single stage Na-based dry treatment system by adding a preliminary Ca-based treatment stage and their relationship with the inlet flue gas composition.

Table 1: Reactions occurring in the acid gas removal process.

Ca-based stage reactions		Na-based stage reactions	
$Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O$	(R1)	$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$	(R4)
$Ca(OH)_2 + SO_2 + ½\ O_2 \rightarrow CaSO_4 + H_2O$	(R2)	$NaHCO_3 + HF \rightarrow NaF + CO_2 + H_2O$	(R5)
$Ca(OH)_2 + 2\ HF \rightarrow CaF_2 + 2\ H_2O$	(R3)	$2\ NaHCO_3 + SO_2 + ½\ O_2 \rightarrow Na_2SO_4 + 2\ CO_2 + H_2O$	(R6)

2. Methodology

The following procedure was followed to carry out the environmental assessment.

Step 1: process simulation. The quantification of the reactant feed rate required to obtain a given acid gas removal efficiency and the related generation rate of solid residues is the starting point. For this purpose, a conversion model for the description of the acid gas abatement process was adopted.

The removal efficiency $X_{i,j}$, expressed as the conversion of the pollutant i when reacting with the sorbent j, is calculated according to the formula:

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

where $rs_{i,j}$ is the ratio between the actual feed rate of the solid reactant j and the stoichiometric rate theoretically required for the total conversion of all the acid gases (see reactions in Table 1) and $n_{i,j}$ are empirical parameters, tuned on the basis of test runs or other available operating data of the acid gas removal system. Details about the formulation of the model and its implementation are reported elsewhere (Antonioni et al., 2012; Guglielmi et al., 2014).

The parameters $n_{i,j}$ used in the present application are the one obtained by Antonioni et al. (2012) and reflect the different affinity of the sorbents (calcium hydroxide or sodium bicarbonate) towards the acid pollutants. In absolute terms, $Ca(OH)_2$ is less reactive than $NaHCO_3$, its reactivity being hindered by diffusional limitations (Antonioni et al., 2016). In relative terms, $Ca(OH)_2$ reacts preferentially with the hydrogen halides than with SO_2, while $NaHCO_3$ shows high affinity with both HCl and SO_2 and performs worse towards HF.

Step 2: inventory. Once applied the model to describe the main foreground process (i.e. the operation of the treatment system), data and inventories for the other processes to be considered in the analysis (supply chain of reactants, road transport, utilities, disposal of residues: see the case study for details) were retrieved from databases, like the European Life Cycle Database (ELCD, 2016). A comprehensive inventory of inputs and outputs associated with the acid gas removal process was thus formed.

Step 3: characterisation. On the basis of a literature review of life cycle assessments in the air pollution control sector (Scipioni et al., 2009; Møller et al., 2011; Stasiulaitiene et al., 2016), a set of 6 problem-oriented impact categories – namely: resource depletion, global warming, rain acidification, photochemical oxidation, toxicity in air, waste generation – was adopted to characterise the environmental impacts. Characterisation factors for all categories but waste generation were retrieved from the CML-IA database (CML, 2016) and were expressed in terms of equivalent mass of a relevant reference substance. Impact in the waste generation category was simply accounted by quantifying the mass of unrecyclable residues to be disposed.

Step 4: normalisation and weighting. The indicators calculated at step 3 were normalised and weighted to complete the environmental assessment. Normalisation is needed in order to allow comparison between the impact categories (Tugnoli et al., 2008). Weighted summation (ISO, 2006) is required to aggregate the indicators in a single-score environmental index (I_{ENV}), which gives a concise but representative evaluation of the environmental profile of a technology, allowing easy ranking among alternatives. The chosen normalisation and weighting factors are discussed in Dal Pozzo et al. (2017). A greater weight (0.3) was assigned to the rain acidification and the waste generation categories, being the former the actual environmental issue acid gas removal systems are meant to control and the latter the acknowledged main drawback of any dry treatment system (BREF WI, 2006; Vehlow, 2015), while a weight of 0.1 was given to each remaining category.

3. Reference technologies and case study

The outlined methodology was applied to assess the environmental impacts associated with the upgrade of a single stage (SS) dry treatment technology typically adopted in WtE plants. The SS system, represented in black in Figure 1 along with its supply and disposal chains, removes acid pollutants by injecting sodium bicarbonate in the flue gas, triggering the gas-solid neutralisation reactions R4-6 in Table 1 and capturing the solid residues with a fabric filter. Another fabric filter upstream of the system allows to collect the residues separately from the fly ash generated in the combustion chamber, thus enabling the possibility to send the Na-based residues to a dedicated plant for the regeneration of fresh bicarbonate, which can recycle ~85 % of the incoming residues (Brivio, 2005).

The analysed upgrade is the injection of calcium hydroxide before the first fabric filter, which creates a two stage (TS) system with respect to acid gas removal. Elements related to the upgrade are depicted in red in Figure 1. Calcium hydroxide, although less reactive than sodium bicarbonate, can neutralise the target pollutants according to reactions R1-3 in Table 1. This Ca-based stage can significantly reduce the load of pollutants entering the Na-based stage and the required feed rate of $NaHCO_3$. Thus, the TS configuration generally results more cost-effective than the SS approach, since the low purchase cost of $Ca(OH)_2$ more than compensates its lower reactivity compared to $NaHCO_3$ (Dal Pozzo et al., 2016). The drawback is the non-recyclability of the generated Ca-based residues, which to date are to be sent to appropriate disposal, despite several valorization routes are currently under study on lab or pilot-plant scale (Margallo et al., 2015).

The boundaries of the analysed system are shown in Figure 1: supply of reactants and management of residues are considered, as well as operation of the dry treatment systems, modelled as described in section 2. As mentioned in section 2, inventory data for the processes were retrieved from the ELCD database or direct process information (Na-based residue recycling plant: Brivio, 2005). Impacts associated with construction and installation of the systems were neglected, since very little layout modifications are required in order to convert a SS system with two fabric filters to a TS system.

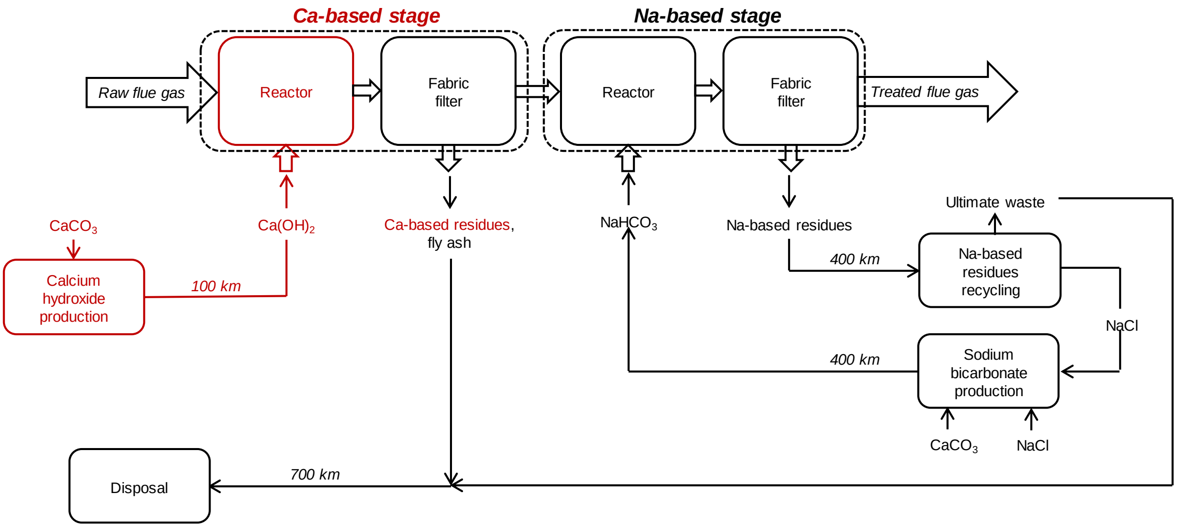

Figure 1: Unit processes considered in the sustainability analysis for the reference technologies.

In order to evaluate the environmental profile of both SS and TS solutions, a case study was designed by considering the operation of these systems on a medium-sized air pollution control line, treating 110,000 Nm^3/h of flue gas from a WtE plant. The functional unit is 1 hour of operation and the process specification is to guarantee that the concentration at stack – target emission value in Table 2 – of each acid gas (HCl, SO_2 and HF) is no more than half of its emission limit value as for Directive 2010/75/EU).

Two different flue gas compositions entering the treatment system are assumed, in order to assess the environmental profile of the systems in broadly different conditions. The first one is representative of the combustion of urban waste. Although being a highly variable fuel, the average European urban waste contains Cl, S and F in the respective mass percentage of 0.4 %, 0.1 % and 0.005 % in dry waste (CEWEP, 2008). Taking into account that approximately 10 % of Cl, 50 % of S and 85 % of F remain in bottom ash after waste combustion (BREF WI, 2006) and the rest generates the respective acid gases, a simple mass balance approach allowed to determine the concentrations of HCl, SO_2 and HF in the raw gas reported in Table 2, which are in line with typical WtE plant data (Guglielmi et al., 2014; Biganzoli et al., 2015). The second one is a flue gas generated by the combustion of a waste specifically rich in fluorine. Certain industrial waste can exhibit high fluorine content and, in particular, automotive shredder residues show F mass fractions up to 0.5-0.75 % in dry waste, generally coupled with a high Cl content (Viganò et al., 2010).

Table 2: Flue gas composition for the two considered waste scenarios and target emission values.

Component	Urban waste	F-rich waste	Target emission value
	mg/Nm^3	mg/Nm^3	mg/Nm^3
HCl	800	1000	5
SO_2	100	100	25
HF	5	85	0.5

4. Results and discussion

The methodology outlined in section 2 was applied to the case study by simulating different operating points of the TS system with the model of Antonioni et al. (2012). The degree of utilisation of the Ca-based stage was modified by varying the feed rate of $Ca(OH)_2$. No utilisation of the Ca-based stage corresponded to the simulation of the SS system. The feed rate of $NaHCO_3$ was varied accordingly, in order to obtain a concentration at stack for each acid gas that is no more than half the emission limit value as of Directive 2010/75/EU. In the case of urban waste, the controlling compound was found to be HCl, i.e. in order to reach its target emission value of 5 mg/Nm^3, the emissions of SO_2 and HF resulted lower than their target values (e.g. for the SS system, 0.23 mg/Nm^3 for HF and 0.47 mg/Nm^3 for SO_2). Conversely, for the fluorine-rich waste, the controlling compound was HF.

Given the quantification of reactants and residues associated with the required acid gas abatement, the environmental index for the single and two-stage acid gas removal systems was estimated under the assumptions of section 2. Clearly enough, the treatment of the flue gas generated by the waste rich in fluorine implies higher environmental impacts than that of the urban waste. As evident from Figure 2, the environmental profile of the TS system depends on the repartition of the reactant feed between the two stages and therefore it exists an operating point that minimise I_{ENV} (“optimum”). For the urban waste scenario, the TS optimum is only slightly better than the SS solution, while a clear reduction of the environmental impact can be noted for the TS optimum in the F-rich waste scenario.

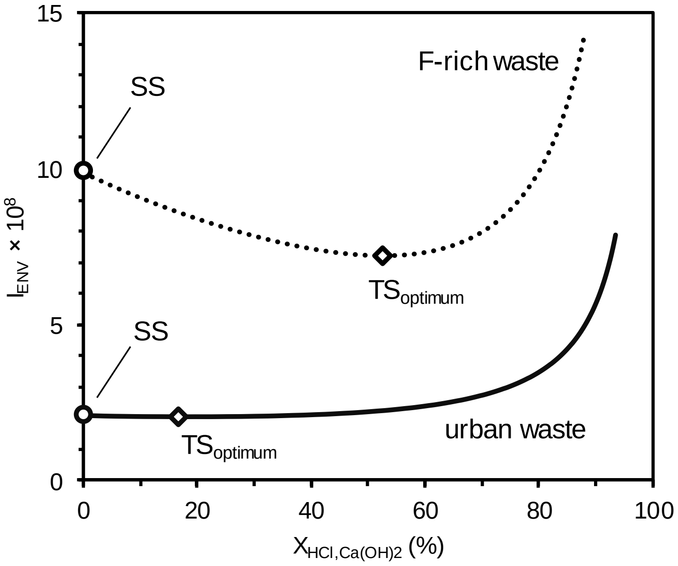

Figure 2: Environmental index I_{ENV} evaluated for the TS system as a function of HCl conversion in the Ca-based stage, $X_{HCl,Ca(OH)2}$, for the two scenarios of Table 2. The SS system corresponds to no utilisation of the Ca-based stage. The optimum of the TS system is the operating point for which I_{ENV} is minimised.

Table 3 reports the contribution of the impact categories to I_{ENV} for the SS system and the TS system at its optimum, allowing to understand the drivers behind these differences. In the case of urban waste, although the I_{ENV} is similar between SS and TS, its composition changes noticeably: the SS system based on the injection of $NaHCO_3$ exhibits lower generation of waste thanks to the recyclability of the Na-based residues, while the TS solution, which substitutes part of the $NaHCO_3$ feed with $Ca(OH)_2$, outperforms the SS system in all the other categories since the production of $Ca(OH)_2$ is less energy-consuming and gives rise to less airborne emissions than that of $NaHCO_3$. The same pattern is confirmed in the F-rich waste scenario, but in this case the I_{ENV} of the TS optimum is noticeably lower than that of the SS system because the high waste generation is outweighed by a noteworthy better performance in the other categories (in particular, rain acidification).

Table 3: Indicators, weights and normalised values x 10^8 for SS and TS at optimum for the two waste cases.

Indicator	Weight	Urban waste		F-rich waste	
		SS	TS, opt.	SS	TS, opt.
Resource depletion (RD)	0.1	0.64	0.55	4.97	2.67
Global warming (GW)	0.1	0.61	0.55	4.79	2.75
Toxicity in air (TA)	0.1	0.57	0.17	6.75	6.10
Rain acidification (RA)	0.3	6.04	5.60	26.20	14.10
Photochemical oxidation (PO)	0.1	0.27	0.23	1.37	0.85
Waste generation (WG)	0.3	0.40	0.77	2.92	7.54
Environmental index (I_{ENV})	**-**	**2.10**	**2.06**	**9.90**	**7.19**

The increased advantage of a two-stage approach when shifting from urban waste to fluorine-rich waste is explained by the decomposition of the I_{ENV} in the shares related to the abatement of each acid gas down to its target emission value (Figure 3). While for urban waste the repartition is similar for both SS and TS, with a slightly higher SO_2-related share in the TS due to the scarce reactivity of $Ca(OH)_2$ towards SO_2, in the case of F-rich waste the combination of high incoming load and strict target emission value for HF severely penalises the Na-based stage, being $NaHCO_3$ less reactive to HF than to HCl or SO_2. Hence, the HF-related share is lower for the TS system, in which the Ca-based stage can significantly contribute to HF removal.

It is worth recalling that, thanks to the increase of selective waste collection in municipalities, several European WtE plants originally designed to burn municipal waste have now to balance the decreasing feed rate of urban waste with increasing shares of industrial waste (Biganzoli et al., 2015). In the light of this scenario, the present analysis comes timely and shows that retrofitting existing Na-based dry treatment systems with the addition of an injection point for calcium hydroxide could be a viable solution to handle the increased load of acid pollutants while decreasing the overall environmental footprint of the process.

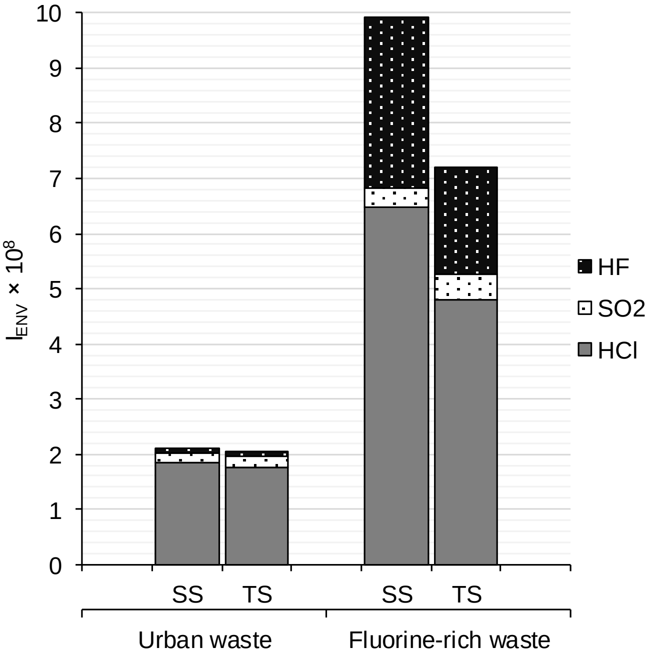

Figure 3: Comparison of the environmental index I_{ENV} for the SS and TS systems in the cases of urban waste and fluorine-rich waste. The contributions to I_{ENV} related to the abatement of each acid pollutant down to its target emission value (Table 2) are specified.

5. Conclusions

Stating the importance of correctly accounting the indirect environmental burdens in pollution control technologies, an environmental assessment was proposed to compare the performance of a state-of-the-art dry treatment system fed with sodium bicarbonate with a proposed upgrade equipping an additional treatment stage fed with calcium hydroxide. The analysis highlighted that, while for a low load of acid pollutants in the flue gas the single stage and two-stage solutions show a similar environmental footprint, the two-stage approach can handle high loads of halides generating less overall environmental impacts. The result is of interest for municipal solid waste incinerators facing increased feed of industrial waste.

References

Antonioni, G., Dal Pozzo, A., Guglielmi D., Tugnoli, A. Cozzani, V., 2016, Enhanced modelling of heterogeneous gas-solid reactions in acid gas removal dry processes, Chemical Engineering Science 148, 140-154.

Antonioni, G., Guglielmi, D., Stramigioli, C., Cozzani, V., 2012, MSWI Flue Gas Two-Stage Dry Treatment: Modeling and Simulation, Chemical Engineering Transactions 26, 213-218.

Biganzoli, L., Racanella, G., Marras, R., Rigamonti, L., 2015, High temperature abatement of acid gases from waste incineration. Part I: Experimental tests in full scale plants, Waste Management 36, 98-105.

BREF WI, 2006, Best Available Technique Reference document on Waste Incineration, <eippcb.jrc.ec.europa.eu/reference/BREF/wi_bref_0806.pdf> accessed 12.12.2016

Brivio, S., 2005, The SOLVAL platform: a sodium sludges valorization, an industrial reality for the environment (in Italian), L'Ambiente 3, 48-49.

CML, 2016, CML-IA Characterisation Factors. Institute of Environmental Sciences (CML), Universiteit Leiden, <www.universiteitleiden.nl/en/research/research-output/science/cml-ia-characterisation-factors> accessed 12.12.2016

Dal Pozzo, A., Antonioni, G., Guglielmi, D., Stramigioli, C., Cozzani, V., 2016, Comparison of alternative flue gas dry treatment technologies in waste-to-energy processes, Waste Management 51, 81-90.

Dal Pozzo, A., Guglielmi, D., Antonioni, G., Tugnoli, A., 2017, Sustainability analysis of dry treatment technologies for acid gas removal in waste-to-energy plants, Journal of Cleaner Production, in press.

Directive, 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (Integrated Pollution Prevention and Control), <eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32010L0075&from=EN> accessed 12.12.2016

ELCD, 2016, European reference Life Cycle Database, <eplca.jrc.ec.europa.eu/ELCD3/index.xhtml> accessed 12.12.2016

Guglielmi, D., Antonioni, G., Stramigioli, C., Cozzani, V., 2014, Investigation of performance of different sorbents in a two-stage flue gas dry treatment of a MSWI, Chemical Engineering Transactions 36, 187-192.

Huijbregts, M.A.J., Thissen, U., Guinée, J.B., Jager, T., van de Meent, D., Ragas, A.M.J., Wegener Sleeswijk, A., Reijnders, L., 2000, Priority assessment of toxic substances in life cycle assessment, I: Calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES-LCA, Chemosphere 41, 541-573.

ISO, 2006, ISO 14040: Environmental Management – Life Cycle Assessment – Principles and Framework, International Organization for Standardization.

Margallo, M., Taddei, M.B.M., Hernández-Pellón, A., Aldaco, R., Irabien, A., 2015, Environmental sustainability assessment of the management of municipal solid waste incineration residues: A review of the current situation, Clean Technology & Environmental Policy 17, 1333-1353.

Møller, J., Munk, B., Crillesen, K., Christensen, T.H., 2011, Life cycle assessment of selective non-catalytic reduction (SNCR) of nitrous oxides in a full-scale municipal solid waste incinerator, Waste Management 31 (6), 1184-1193.

Scipioni, A., Mazzi, A., Niero, M., Boatto, T., 2009, LCA to choose among alternative design solutions: the case study of a new Italian incineration line, Waste Management 29, 2462-2474.

Stasiulaitiene, I., Martuzevicius, D., Abromaitis, V., Tichonovas, M. Baltrusaitis, J., Brandenburg, R., Pawelec, A., Schwock, A., 2016, Comparative life cycle assessment of plasma-based and traditional exhaust gas treatment technologies, Journal of Cleaner Production 112 (2), 1804-1812.

Tugnoli, A., Santarelli, F., Cozzani, V., 2008, An Approach to Quantitative Sustainability Assessment in the Early Stages of Process Design, Environmental Science and Technology 42, 4555-4562.

Vehlow, J., 2015, Air pollution control systems in WtE units: an overview, Waste Management 37, 58-74.

Viganò, F., Consonni, S., Grosso, M., Rigamonti, L., 2010, Material and energy recovery from Automotive Shredded Residues (ASR) via sequential gasification and combustion, Waste Management 30, 145-153.