Improving the SO₂ and HCl Removal Efficiency by 30 % in Existing Dry FGC without any Capital Investment – On-Site Observations and Results on Latest Developments –

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Dry sorbent injection (DSI) techniques are well known and have been used for a long time in flue gas cleaning systems to control emissions in combustion boilers, coal boilers, biomass firing and energy from waste plants. In this type of systems, a powdered sorbent is injected pneumatically directly in the upper part of the furnace or in the flue gas ducts before a dedusting unit. Several pollutants can be removed using this simple technique but the DSI's removal efficiency is a function of many parameters, like flue gas composition, flue gas temperature, type of equipment and type of sorbent used.

This paper presents the latest product improvement and process optimization that Carmeuse has achieved and the associated Flue Gas Cleaning results obtained with different hydrated lime qualities for flue gas cleaning. We will show how some of the process parameters will influence the flue gas cleaning process and how efficiency improvements of more than 30 % can be achieved by optimizing the sorbent and the operation of the flue gas cleaning unit.

1. Evolution of waste-to-energy plants

In order for the energy recovery from waste installations to prevent the acidic pollutants to disseminate in the environment, they require advanced technology solutions (referred as the Best Available Techniques) and chemical reagents to neutralize acid pollutants and comply with the increasingly restrictive permitted emission limits.
The process of incineration of municipal and commercial waste generates flue gases containing pollutants such as nitrogen oxides, particulate matter, acid gases (mainly hydrochloric acid, sulphur oxides and hydrofluoric acid) and numerous micro-pollutants, such as volatile heavy metals (Cd, Pb, Hg…) and organic compounds (e.g. dioxins and furans) [5, 19, 20]. The acid gases [17] are one of the main components which require cleaning treatments, but as well as removal efficiencies so high that almost a complete elimination of these pollutants from the flue gases is required in order to respect regulatory limits to stack emissions fixed by competent authorities under the Industrial Emission Directive frame for European Union [10]. The evolution of the limits underlines for operators a need to increase the removal efficiencies of those pollutants at each revision of the legislation. This can be visible in Table 1 when comparing the IED document [10] with the newest emission limit values included in the recently released Final Draft of the Waste Incineration BREF document [11].

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<tbody>
<tr>
<td></td>
<td>mg/Nm³ dry corrected at 11% O₂</td>
<td>Annex VI part 3</td>
<td>Chapter 5.1.5. for new plants</td>
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<tr>
<td>SO₂ daily average</td>
<td>50</td>
<td>5 to 30</td>
<td></td>
</tr>
<tr>
<td>HCl daily average</td>
<td>10</td>
<td>&lt; 2 to 6</td>
<td></td>
</tr>
<tr>
<td>HF daily average</td>
<td>1</td>
<td>&lt; 1</td>
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Recently, due to the reducing waste volume and the increasing of separate waste collection [14, 21], several WtE plants have suffered a decrease of available residual municipal waste. The operators substituted their missing urban waste with an increased ratio of commercial wastes, frequently more contaminated by chlorine (Cl), sulphur (S), and/or fluorine (F) [1, 13, 18]. These elements originate more hydrochloric acid (HCl), sulphur dioxide (SO₂) and hydrofluoric acid (HF) during thermal oxidation, increasing the flue gas cleaning needs (in removal efficiency but as well in process flexibility).

Meeting emission limit value thanks to dry sorbent injection

Dry Sorbent Injection is a post-combustion flue gas cleaning technology where a reactive sorbent is injected into the upper part of the furnace (high temperature) or in the duct downstream the boiler (low temperature) to react directly with the products of combustion. The technology effectively and economically mitigates potential emission problems in the flue gases. Dry Sorbent Injection advantages include lower equipment costs (first cost) as well as decreases in operations and maintenance costs – and have a lower life-cycle cost than other technologies [9, 16]. Commonly used sorbents in Dry Sorbent Injection systems include:

- Calcium hydroxide to mitigate HCl, HF, SO₂, SO₃ and Se,
- Sodium bicarbonate to capture HCl, SO₂, SO₃ and to some extent HF,
- powdered activated carbon to adsorb heavy metals and organics compounds.
Reaction products are collected in a downstream particulate control device together with the fly ashes and unreacted sorbent. In function of the sorbent used, these products can be used as feedstock to cement plants or for stabilization of earthen structures. Because a separate scrubber vessel is not needed and no water is involved, capital costs are minimized. Low Capex and operational costs may be partially offset by higher reagent consumption rates due to lower pollutant removal efficiencies when compared to other flue gas cleaning processes, because historically the DSI processes used to show lower removal efficiencies. This higher reagent consumption rate pushed both engineering companies that supply the installations as well as companies supplying the reagents to develop systems and products that increase the effectiveness of the reaction by optimizing the reaction conditions (engineering companies) and designing dedicated sorbents (reagent suppliers).

Among the systems used to improve the efficiency we can find by-product recirculation, by-product reactivation, reaction towers, flue gas conditioning, etc. all of which look towards improving the conditions of the flue gases and improving the contact time between the sorbent and the pollutants in order to increase the speed of the reaction, and overall to improve the utilization rate.

The reagent suppliers are also trying to increase the speed of the reaction and the utilization rate by designing and producing engineered products, which at the same time can also bring more flexibility in regards to the process conditions required for the reaction.

Overall, all the developments done towards improving this type of systems have managed to increase the removal efficiencies that can be obtained, from an initial historical 50 to 70 % up to more than 90 % with the latest technologies.

2. Description of the tests and results collected

2.1. Description of the sorbent used for this evaluation – Evolution of the lime-based sorbent

Over the last decade, hydrated lime manufacturers have developed more efficient sorbents to meet the increased removal efficiencies needed on the market. One of them, Carmeuse developed the CleanCalco product range that will be used for this comparison. The product range, together with the on-site support given by their expert team, brings flexibility to the end-user by enabling him to optimize the flue gas cleaning process with minimal or, in some cases, without any required CAPEX.

The products available in this product range include standard calcium hydroxide sorbents (Ca(OH)₂) and optimized sorbents. This dedicated calcium hydroxide offer different physical properties regarding specific surface area and porous volume, which fit to every need encountered in the dry flue gas cleaning process. Several papers [8, 15] already documented the influence of these parameters under some flue gas conditions. Such porosimetric examination is done by means of a gas sorption analyser using nitrogen
physiosorption and desorption isotherms at -196 °C in order to measure the specific surface area according to the multipoint BET method [6] and the pore volume according to the BJH method [2].

The product range also included specially engineered sorbents like the CleanCalco Depurcal, initially developed and tested in 2011 in several Italian waste-to-energy plants. Its particularity is to be injected directly in the boiler at temperatures above 900 °C. The product underwent several stages of improvement that increased its efficiency, and more importantly, its efficiency in SOx absorption rates, improvements that were proven with the help of several on-site trials in 2013 and 2014.

These improvement processes brought the following advantages [3, 4, 7, 12]:

- neutralizes the acid gases (SO2, SO3, HF and HCl) directly in the furnace/boiler;
- optimizes the performance of the flue gas cleaning process, with less reagent injected and less by-product generation;
- raises the melting point of the ash, making them porous, light and friable; and
- reduces the fouling of the tube and facilitates cleaning.

On top of that, as the product is used in combination with a downstream flue gas cleaning installation, it reduces the amount of sorbent used and the variability of the acid pollutants needed to be treated downstream. Flue gas cleaning overall efficiency and compliance cost for operators can thus be reached by:

- the direct injection in the boiler of the CleanCalco Depurcal that can offer the full advantages presented above, combined with
- the downstream effectiveness of an optimized sorbent like CleanCalco HPV.

CleanCalco HPV is a premium hydrated lime sorbent, optimized for the use in end-of-pipe Dry Sorbent Injection processes. It presents a higher SO3 specific capture thanks to the higher porosity and higher specific surface. The result is illustrated in Figure 2: a similar dosage increases the capture, or a similar capture is reached with a lower injection.
Air Pollutant Emissions and their Control
– with the focus on waste incineration facilities –

This comprehensive text and practical handbook thoroughly presents the control of air pollutant emissions from combustion processes focusing on waste incinerators. Special characteristics are emphasised and the differences to emission control from combustion processes with other fuels are explained.

The author illustrates the origin and effects of air pollutants from incineration processes, the mechanics of their appearance in the incineration process, primary and secondary measures for their reduction, processes of measuring the emissions as well as the methods of disposing the residues. In particular, the pros and cons of procedural steps and their appropriate combination under various conditions are emphasised.

Moreover, the book contains information and analyses of the emissions situation, the consumption of operating materials and of backlog quantities as well as of the cost structure of waste incinerators with regard to their applied control system. Furthermore, the author explicates the contemporary legal, scientific and technological developments and their influence on air pollutant emission control. An evaluation of the status quo of air pollutant control at waste incinerators in Germany, practical examples about possible combinations and typical performance data complete the content.

Accordingly, this book is a guideline for planning a reasonable overall concept of an air pollutant control that takes the location and the segregation tasks into consideration. This book is addressed to students, decision makers, planners and the operating practitioners if for example the construction of a new system or the implementation of improvement measures have to be conducted.

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2.2. Trial procedure

Each on-site trial is preceded by a preliminary study done by a team of experts. It aims at understanding the fundamental characteristics of the installations from each plant, which in turn enables them to find, together with the operator of the plant, the best hydrated lime product to be injected, the optimum injection point, and the KPI’s that will be followed during the trial itself.

After this first preliminary study, it is also decided together with the operator if a dedicated trial equipment will be used or not. If it is used, the injection flange is installed at the decided injection point and a dosing equipment is installed on-site, as seen in Figure 3.

With the help of the installed equipment, the trial can start. The team is present on site in order to handle the process optimization by using several fixed or variable dosing rates in order to see which is the optimum consumption required in each particular case.

The sorbent has a higher porosity and a higher specific surface (as mentioned in the Table 2 below), that offer an increased contact area between the flue gases containing SO₂ and the neutralizing agent, Ca(OH)₂.

Table 2: Ca(OH)₂ specifications for standard hydrated lime and CleanCalco HPV

<table>
<thead>
<tr>
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<th>CleanCalco HPV</th>
<th>Standard Calcium hydroxide</th>
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<tbody>
<tr>
<td>Ca(OH)₂ available</td>
<td>above 92 %</td>
<td>70 to 90 %</td>
</tr>
<tr>
<td>specific surface (BET)</td>
<td>above 40 m²/g</td>
<td>15 to 18 m²/g</td>
</tr>
<tr>
<td>porous volume (BJH)</td>
<td>about 0,20 cm³/g</td>
<td>below 0,10 cm³/g</td>
</tr>
</tbody>
</table>
2.3. Trial results

2.3.1. Modification of hydrated lime specification in dry flue gas cleaning

Case: Municipal solid waste incineration plant with a total 63,000 t waste/year capacity on two lines

The specification of the sorbent used in dry systems has a big impact over the efficiency of the system itself. In this case, the FGC system consists of a silo, a dosing screw and a pneumatic transport of the sorbent to the injection point located before a bag filter. The pollutants measured at the stack were HCl and SO$_2$, and the system was automatically controlling the dosing rate of the sorbent based on the emission level at the stack. In order to identify quickly the benefit of using CleanCalco HPV in the installation it was decided together with the operator to use a trial equipment and to try to inject a similar amount of sorbent as they are normally using. The reference product was as well a premium hydrate with high specific surface (BET = 40 m$^2$/g) and porosity (0.20 cm$^3$/g) but with a different pore size distribution.

As it can be seen in Figure 4 by switching to this sorbent, the plant managed to achieve 24 % lower SO$_2$ emissions at the stack, while maintaining the same dosing rates and the same HCl emission levels. This means that for the same amount of Ca present in the system, a higher utilization rate was achieved. These lower SO$_2$ emissions also ensure the future compliance of the plant.

2.3.2. Modification of hydrated lime specification in dry flue gas cleaning

Case: Municipal solid waste incineration plant with a total 700,000 t waste/year capacity on four lines

In this case, the flue gas cleaning process consists in a dry process with a conditioning tower but without a recirculation of the material collected in the filter. The trial intended to demonstrate the impact and the improvement brought by the use of a more performing hydrated lime vs. the reference case operating with hydrated lime with high specific surface (BET = 40 m$^2$/g) and high porosity (0.2 cm$^3$/g). CleanCalco HPV hydrated lime offers an improved specific surface area
Improving the SO$_2$ and HCl Removal Efficiency by 30 % in Existing Dry FGC

of above 40 m$^2$/g as well as a porous volume of about 0.20 cm$^3$/g with engineered pore size distribution to improve sulphur capture. In this case, the product was used directly from the installation in the plant.

In Figure 5, the orange column corresponds to the reference case normalized at 100 % dosing rate, while the dark blue column corresponds to the full operation with the optimized sorbent. As it can be seen, there is a decrease of approximately 17 % in the dosing rate of the sorbent when the switch to the optimized product was done. This decrease corresponds to the same emission levels at the stack, as the process automation system of the customer was controlling the dosing rate of the sorbent automatically, based on the removal requirements of the pollutants.

During the trial the technical expert team also noticed that the stability of the sorbent dosing rate as well as the pollutant levels at the stack were very low, and had quite big and unexplained variations. At that moment, they moved together with the customer in making a more in detail root cause analysis in order to see what was causing the issue with the dosing of the sorbent. After identifying the cause as a setting in the operation of the dosing screw, they corrected the fault and managed to decrease further the consumption rates with an extra 14 %, reaching a total decrease of 31 % in the sorbent consumption rates by simple flue gas cleaning process optimization with a correct sorbent and a correct dosing loop.

![Figure 5: Trial results: up to 31 % dosage reduction (for same stack emission) when using CleanCalco HPV in an optimized dosing system instead of alternative Calcium hydroxide offering high porosity and high specific surface area](image)

3. Conclusions

CleanCalco HPV injection at the cold end DSI is an innovative answer to the flue gas cleaning concerns both in waste-to-energy plants as well as in other applications. This solution allows the users to achieve their required emission limit values while at the same time reducing their costs and increasing their installations efficiency while at the same time reducing the quantity of sorbent used by more than 30 %.

The major key implications on operators’ process focus on:

- increasing FGC reliability regarding compliance with emission value limits at the stack,
- generating savings on operational cost linked to flue gas treatment,
- higher flexibility of the FGC process,
• high efficiency on acids removal (HCl, SO₂, SO₃, HF),
• full time compliance to emission standards imposed at the stack, and
• suitable process for a variety of boiler types/manufacturers.

4. Sources


[12] Grosso M., Biganzoli L., Giugliano M.: Improving the environmental performances of WTE plants with high temperature flue gas pre-cleaning and enhanced bottom ash recovery. 8th i-CIPEC conference, 2014, HangZhou, China


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Acronyms used in the document and definitions

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>BAT</td>
<td>Best Available Technique</td>
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<td>BET</td>
<td>Specific surface</td>
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<td>BREF</td>
<td>BAT reference document</td>
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<td>CAPEX</td>
<td>Capital Expenditure</td>
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<td>DSI</td>
<td>Duct Sorbent Injection</td>
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<td>FGC</td>
<td>Flue Gas Cleaning</td>
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<td>Furnace Sorbent Injection</td>
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<td>OPEX</td>
<td>Operating expenditure</td>
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<td>PV</td>
<td>Porous Volume</td>
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<td>Scanning Electron Microscopy</td>
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<td>Waste Incineration</td>
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