Furnace injection of dolomitic sorbent as retrotting option for HCl and SO₂ removal in waste-to-energy plants

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Acid pollutants and waste-to-energy

Acid gases (HCl, SO$_2$) are typical pollutants released by waste combustion, stemming from the Cl and S content in the waste.

The recent revision of the *Best Available Techniques* for waste incineration issued at the end of 2019 has imposed ambitious targets of acid gas removal efficiency and the environmental permitting will soon adopt the new prescriptions.

As a consequence, existing WtE plants are increasingly retrofitting their flue gas cleaning lines introducing multi-stage treatment processes for the removal of acid pollutants.
State-of-the-art single system for acid gas removal

Currently, the most common method for acid gas removal is their neutralization by in-duct injection of dry powdered sodium bicarbonate and the subsequent filtration of solid reaction products.

\[
2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

Thermal activation

Acid gas neutralization

\[
\text{Na}_2\text{CO}_3 + 2 \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{Na}_2\text{CO}_3 + 2 \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{CO}_2
\]
A simple retrofitting option: furnace sorbent injection

Installation of an additional pre-treatment stage directly in the combustion chamber

**Reactant:** calcined dolomite

\[
\text{Calc. dolomite (D)} \
\text{FURNACE} \
\text{Ca residues (± fly ash)} \
\text{FABRIC FILTER OR ESP} \
\text{Ca residues (± fly ash)} \
\text{Sodium bicarbonate (B)} \
\text{FABRIC FILTER} \
\text{Na residues} \
\text{* OPTIONAL}
\]

**Thermal activation**

\[
\text{Ca(OH)}_2 \cdot \text{MgO} \rightarrow \text{CaO} \cdot \text{MgO} + \text{H}_2\text{O}
\]

**Acid gas neutralization**

\[
\text{CaO} \cdot \text{MgO} + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{MgO}
\]

\[
\text{CaO} \cdot \text{MgO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 + \text{MgO}
\]
Advantage of the two-stage configuration

The two-stage treatment configuration offers a degree of freedom in process control.

The same overall pollutant removal efficiency can be achieved with different repartitions of removal between stages.

A proper selection of the repartiton of removal between stages can minimize the costs (and the indirect environmental impacts) of treatment, while keeping the same emission level of HCl and SO₂ at stack.
Aim of the study

Which is the optimal feed rate of dolomite that minimizes the operating costs in a two-stage acid gas removal system?

Tasks

- conducting an experimental campaign of dolomite acid gas removal efficiency at plant scale
- modelling the performance of both dolomite and bicarbonate to identify the optimal feed rate
- verifying in the real plant if the identified optimal feed rate does achieve the expected benefits
Test run protocol for the assessment of dolomite performance

- **Constraint**: single measurement of gas composition downstream of the furnace
- **On-off test**: incremental steps of constant feed rate, alternated with stop periods
- The acid gas concentration measured during the stop period is considered representative of the raw flue gas composition
Extracting data from test runs

\[ X_{SO2} = \frac{C_{SO2,stop} - C_{SO2, injection}}{C_{SO2, stop}} \]

\[ S\text{R} = \frac{\text{actual feed rate of reactant}}{\text{stoichiometric demand of reactant}} \]
Modelling data from test runs

A semi-empirical model is adopted for the interpretation of the acid gas removal data obtained with test runs:

\[ X_{HCl} = \frac{SR^n - SR}{SR^n - 1} \]

- \( SR \) = stoichiometric ratio
- \( n \) = empirical parameter
- needs plant-specific tuning

Modelling bicarbonate performance

The same approach can be also used to model bicarbonate performance:

- Upstream and downstream measurement of gas composition (P1 + sampling at P2)
- **Protocol**: stepwise variation of bicarbonate feed and measurement of removal efficiency

**Example of Test Run**

**Model Calibration**

- Model
- Process data

**Bicarbonate stage** (reaction tower + baghouse)
Use of the model to identify the optimal operating point

Once the acid gas removal performance of the calcined dolomite is characterized quantitatively, we can answer the question: which is the optimal feed rate of dolomite in a two-stage dolomite + bicarbonate system?

Case study plant

### Cost entries

<table>
<thead>
<tr>
<th>Cost entries</th>
<th>Unit cost (€/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>100</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>250</td>
</tr>
<tr>
<td>Process residues</td>
<td>200</td>
</tr>
</tbody>
</table>

- **Q_{\text{flue gas}} = 60,000 \text{ Nm}^3/\text{h}**
- **C_{\text{HCl,in}} = \{ 600 \text{ mg/Nm}^3, 1000 \text{ mg/Nm}^3, 1400 \text{ mg/Nm}^3 \}**
- **C_{\text{HCl,at stack}} = 2 \text{ mg/Nm}^3**

- the real plant adopts a fixed feed rate of 80 kg/h of dolomite (typical operating point of the plant)
- simulations with the model suggest that a small cost reduction (up to 10% for \( C_{\text{HCl,in}} = 600 \text{ mg/Nm}^3 \)) can be obtained by lowering the amount of dolomite fed to the system
**Test at the real plant to verify model prediction**

- The case study plant typically adopts a fixed dolomite feed rate equal to 80 kg/h.
- The model recommends to use a lower feed rate to minimise costs (e.g. 40 kg/h for a typical inlet HCl conc. of 1000 mg/Nm³).

An experimental campaign was set up to verify the advantage of the lower feed rate suggested by the model:

- Varying the imposed feed rate of dolomite in furnace sorbent injection, by **alternating** 2 days at 40 kg/h with 2 days at 80 kg/h.
- The HCl emission setpoint at stack was always kept at 2 mg/Nm³.

12 days of tests in both the waste incineration lines (A and B) of the case study plant.
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6 days of operation at 80 kg/h
1.42 €/kg HCl

6 days of operation at 40 kg/h
1.25 €/kg HCl (-13%)
Conclusions

• the present study proposed a simple methodology for the optimization of dolomite-based furnace sorbent injection, which is an interesting technique for the retrofitting of waste-to-energy plants

• the methodology, based on the calibration of an operational model with test runs, pinpointed the importance of identifying the optimal operating point for the reduction of acid gas treatment cost

• the validation of the methodology in a real plant demonstrated that a properly optimized dolomite-based furnace sorbent injection can achieve significant cost savings (higher than 10%) compared to a non-optimized system or a single-stage bicarbonate system
THANKS FOR YOUR ATTENTION

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MAIN PAPERS ON ACID GAS REMOVAL


Dal Pozzo, Armutlulu, Rekthina, Muller, Cozzani, CO2 Uptake Potential of Ca-Based Air Pollution Control Residues over Repeated Carbonation-Calcination Cycles, Energy & Fuels 2018, 32, 5386–5395.

