
# Furnace injection of dolomitic sorbent as retrotting option for HCl and $SO_2$ removal in waste-to-energy plants

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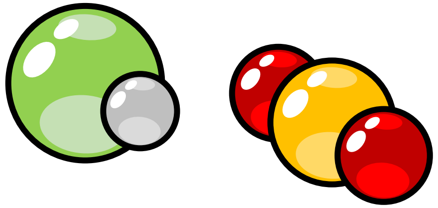
# Acid pollutants and waste-to-energy



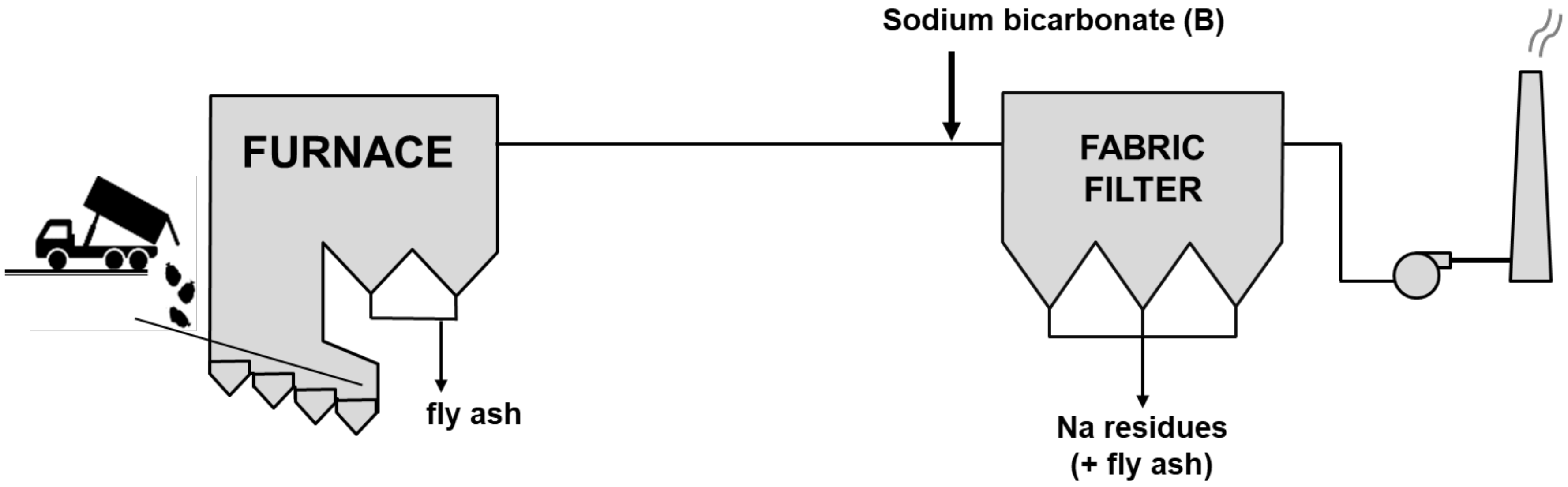
**Acid gases** **(HCl, $SO_2$)** are typical pollutants released by waste combustion, stemming from the Cl and S content in the waste.

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




**Thermal activation**

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

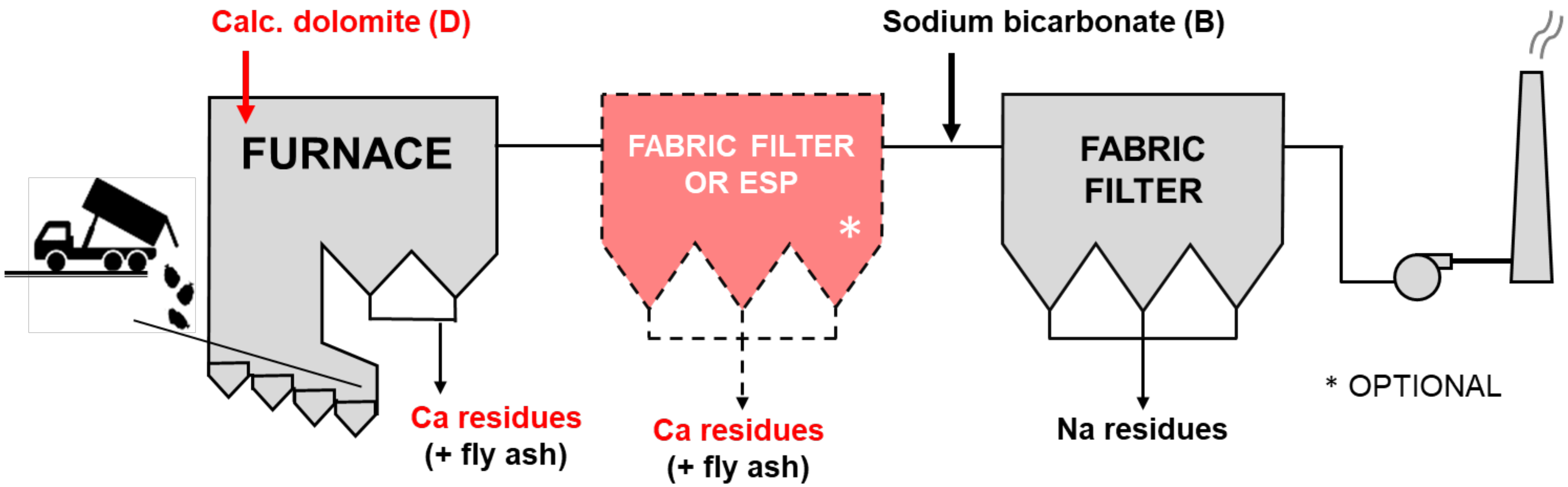
**Acid gas neutralization**

$$Na_2CO_3 + 2\ HCl \rightarrow NaCl + H_2O + CO_2$$

$$Na_2CO_3 + 2\ SO_2 + 1/2\ O_2 \rightarrow Na_2SO_4 + 2\ CO_2$$

# A simple retrofitting option: furnace sorbent injection

Installation of an additional pre-treatment stage directly in the combustion chamber
**Reactant:** calcined dolomite

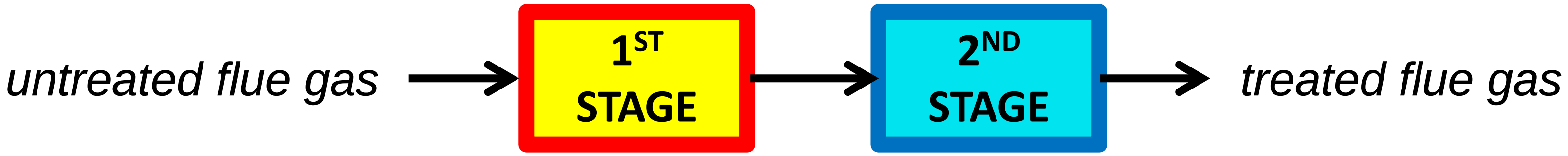


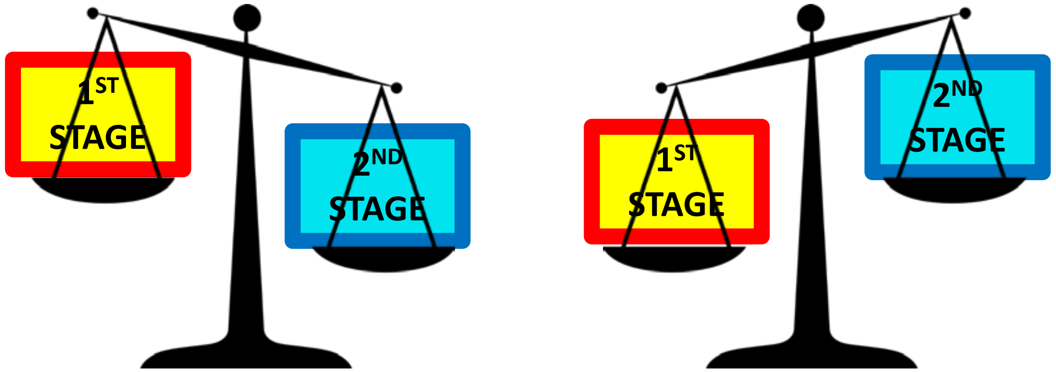

| Thermal activation | Acid gas neutralization |
|---|---|
| $Ca(OH)_2 \cdot MgO \rightarrow CaO \cdot MgO + H_2O$ | $CaO \cdot MgO + 2\,HCl \rightarrow CaCl_2 + H_2O + MgO$ |
| | $CaO \cdot MgO + SO_2 + 1/2\,O_2 \rightarrow CaSO_4 + MgO$ |

# 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 $SO_2$ at stack.

# Aim of the study

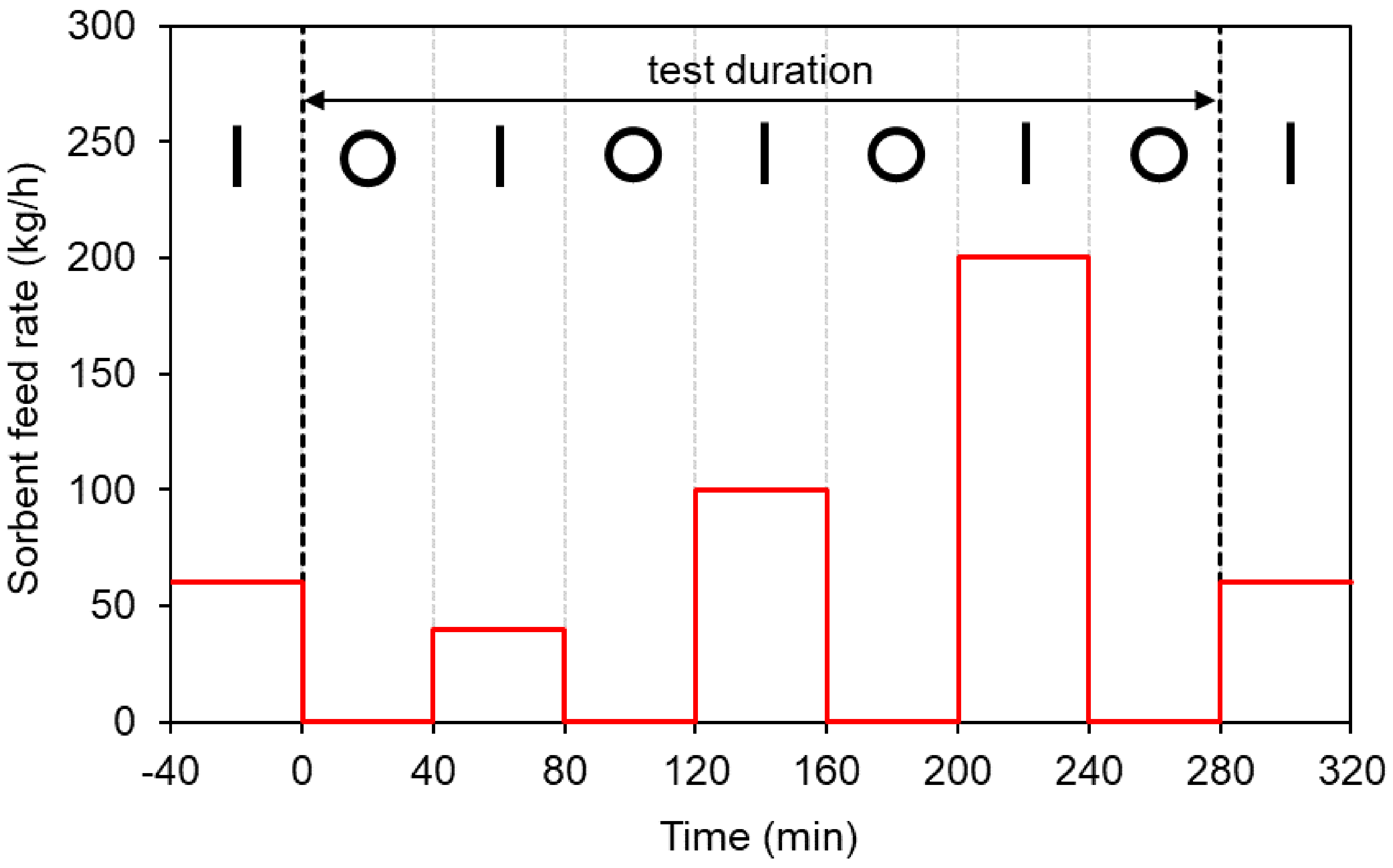
**Which is the optimal feed rate of dolomite that minimizes the operating costs in a two-stage acid gas removal system?**

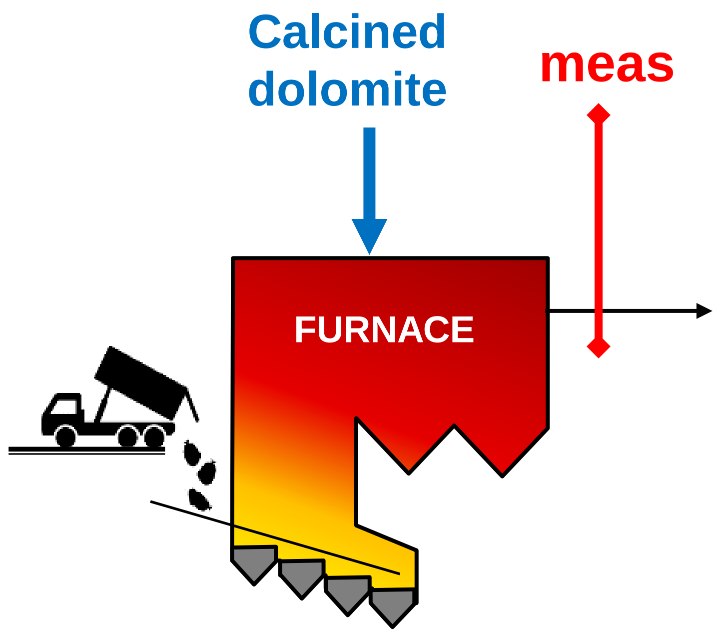
## Tasks

- 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

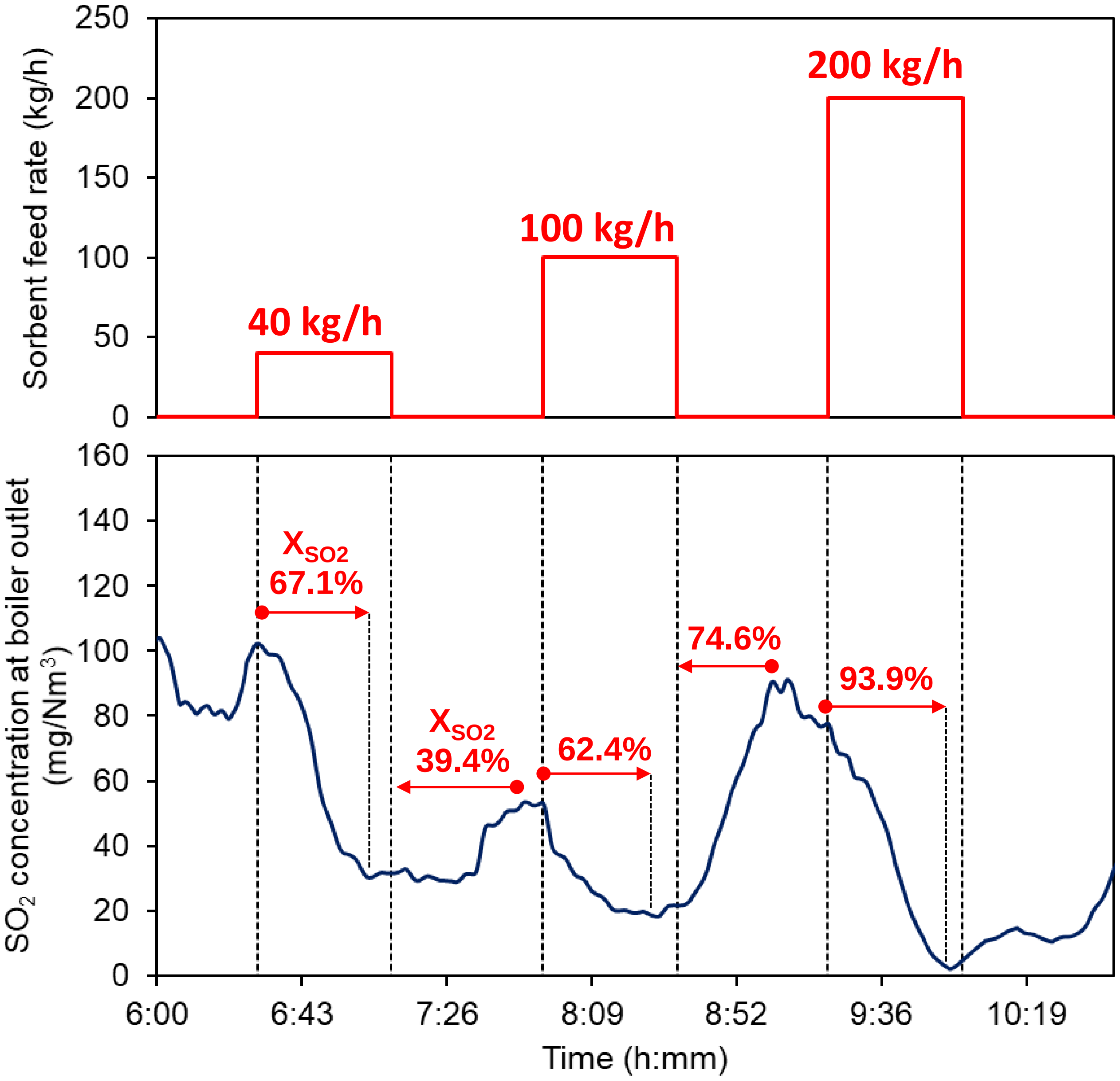
# Test run protocol for the assessment of dolomite performance

- **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

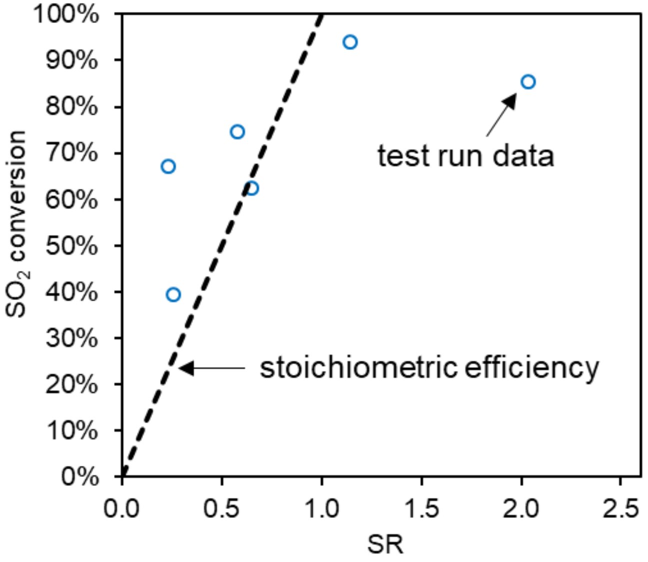


# Extracting data from test runs




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




$$SR = \frac{actual\ feed\ rate\ of\ reactant}{stoichiometric\ demand\ of\ reactant}$$

# Modelling data from test runs

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

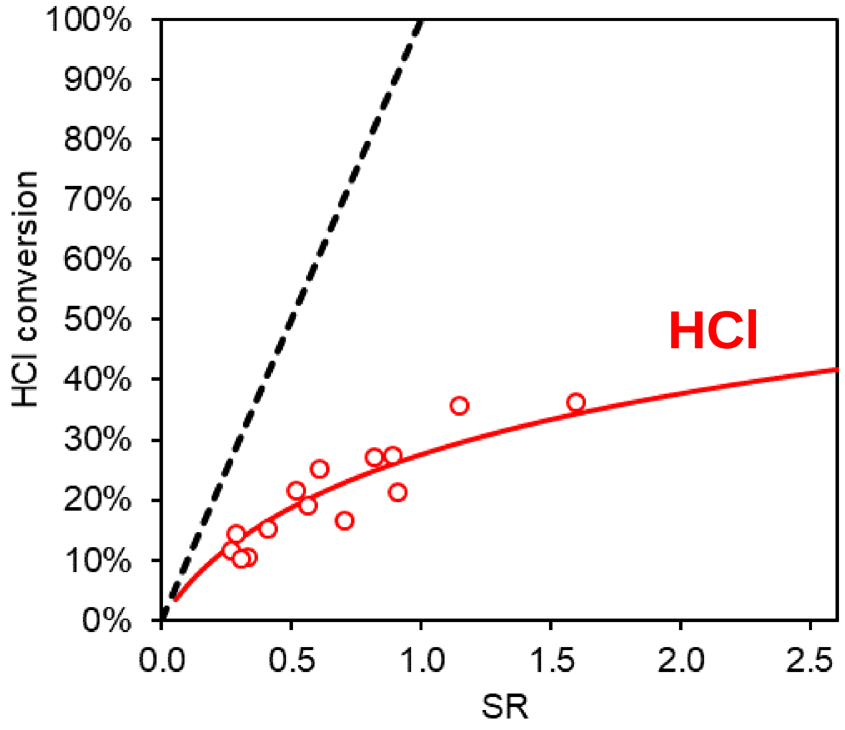
$$X_{HCl} = \frac{SR^n - SR}{SR^n - 1}$$

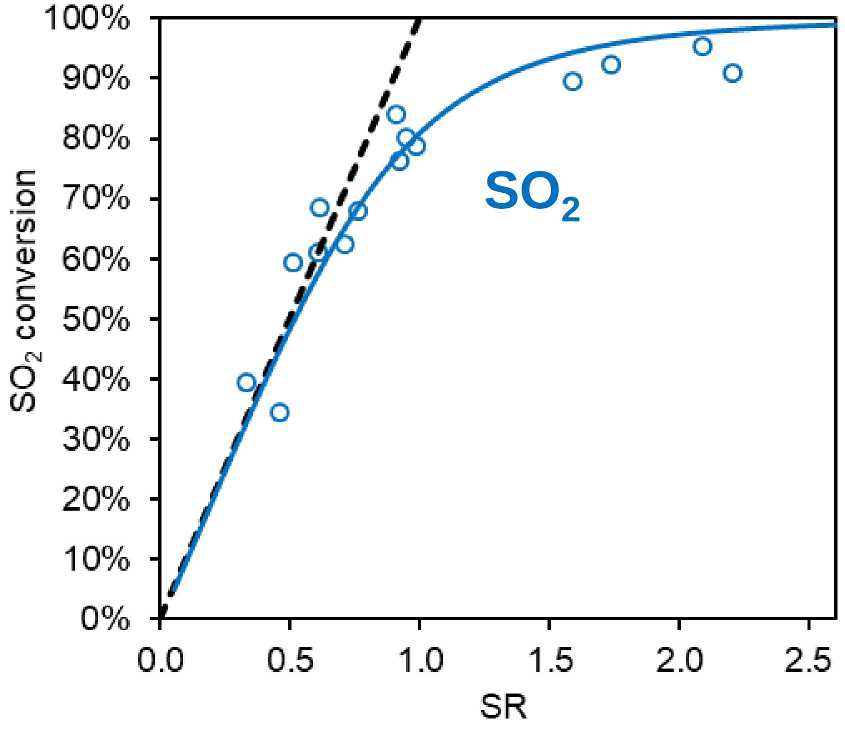
**SR** = *stoichiometric ratio*

***n*** = *empirical parameter*

↑

*needs* ***plant-specific tuning***



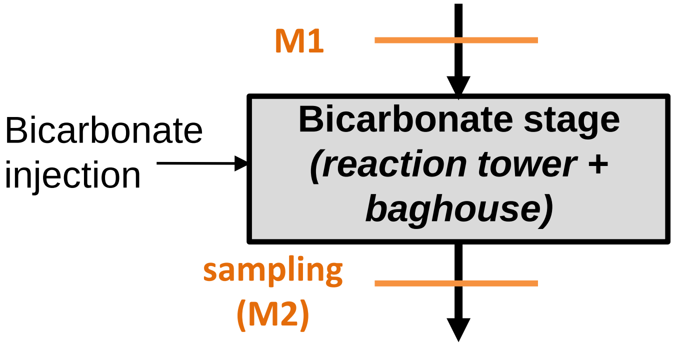




Dal Pozzo et al., *J. Haz. Mater.* **2020**, 394, 122518.

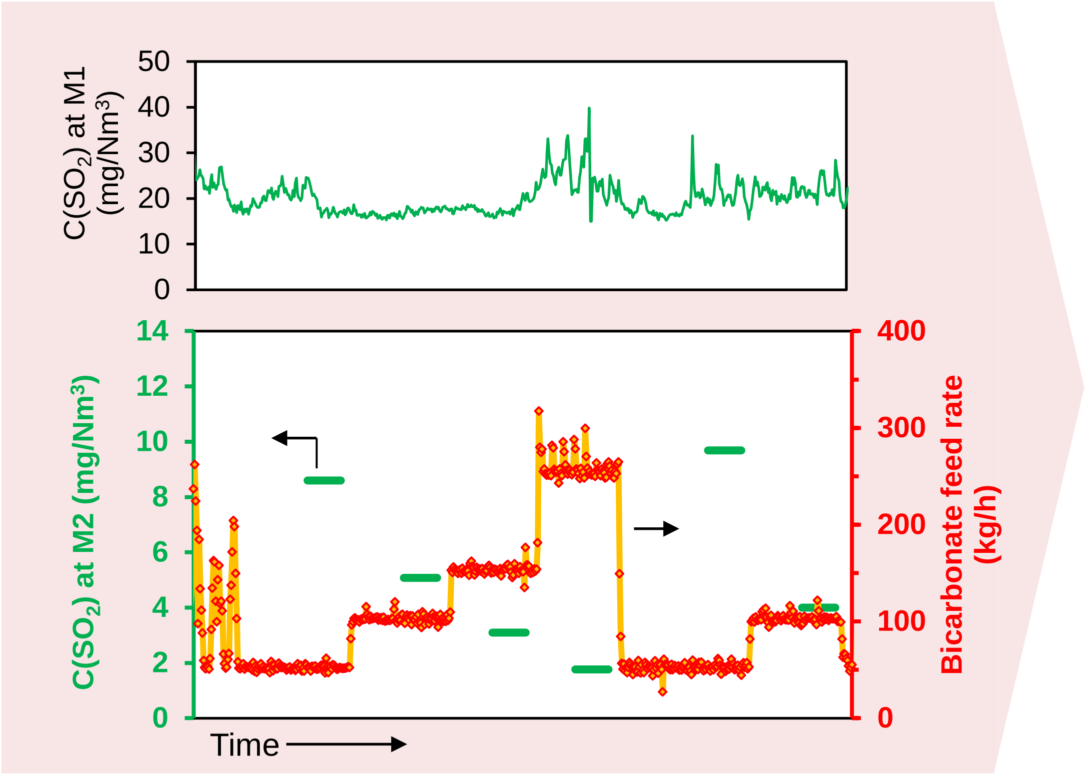
# Modelling bicarbonate performance

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

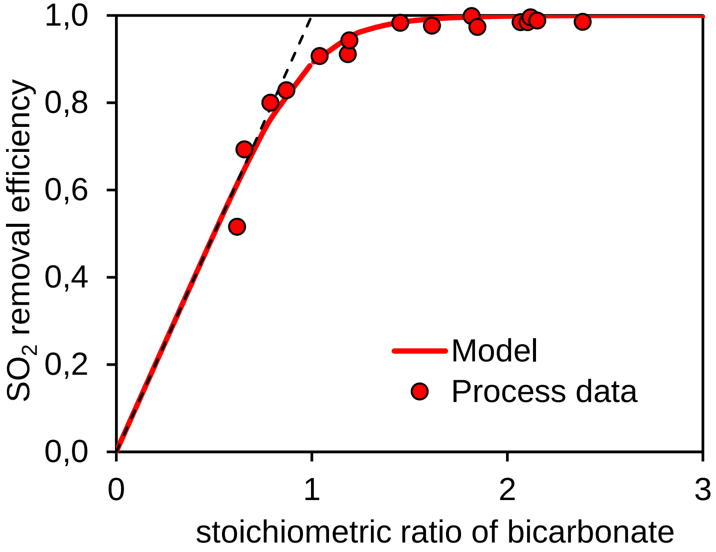
- Upstream and downstream measurement of gas composition (P1 + sampling at P2)
- **Protocol:** stepwise variation of bicarbonate feed and measurement of removal efficiency




## Example of Test Run




## Model calibration



# 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?***

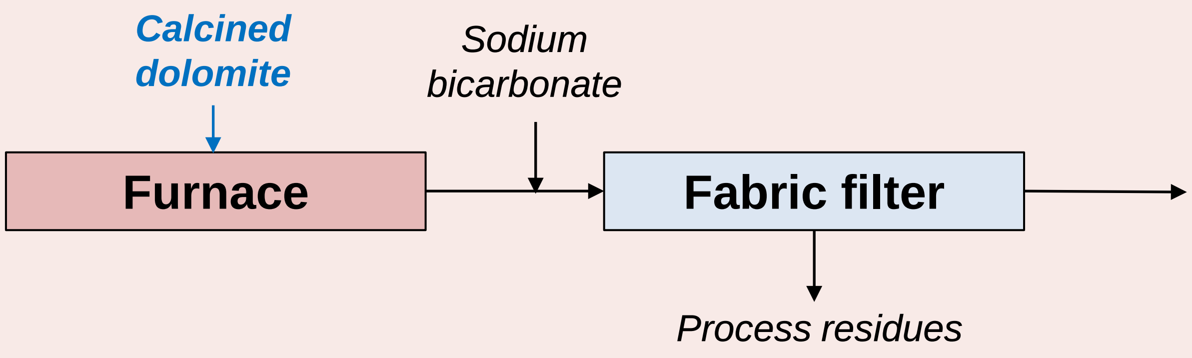
## *Case study plant*

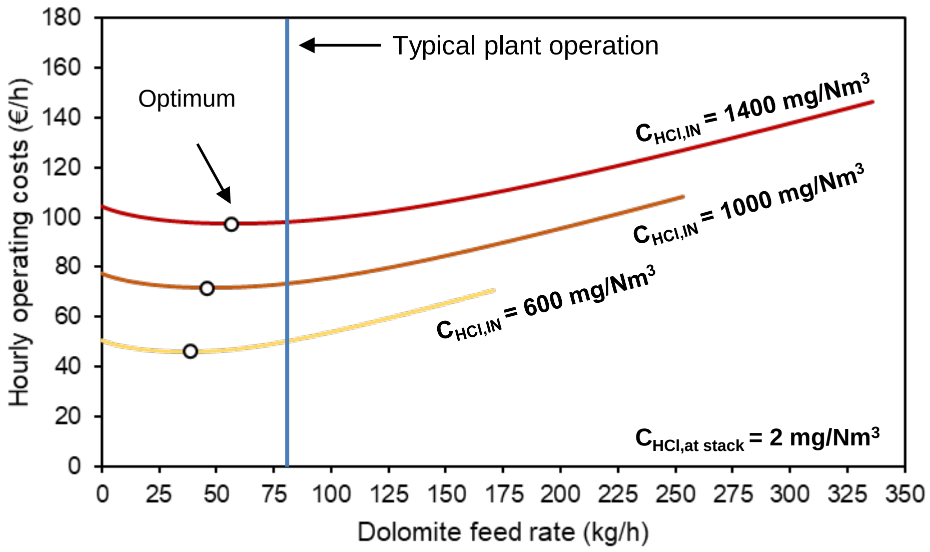
$Q_{flue\ gas} = 60{,}000\ Nm^3/h$

$C_{HCl,in} = \begin{cases} 600\ mg/Nm^3 \\ 1000\ mg/Nm^3 \\ 1400\ mg/Nm^3 \end{cases}$

$C_{HCl,at\ stack} = 2\ mg/Nm^3$

| Cost entries | Unit cost (€/t) |
|---|---|
| Dolomite | 100 |
| Sodium bicarbonate | 250 |
| Process residues | 200 |



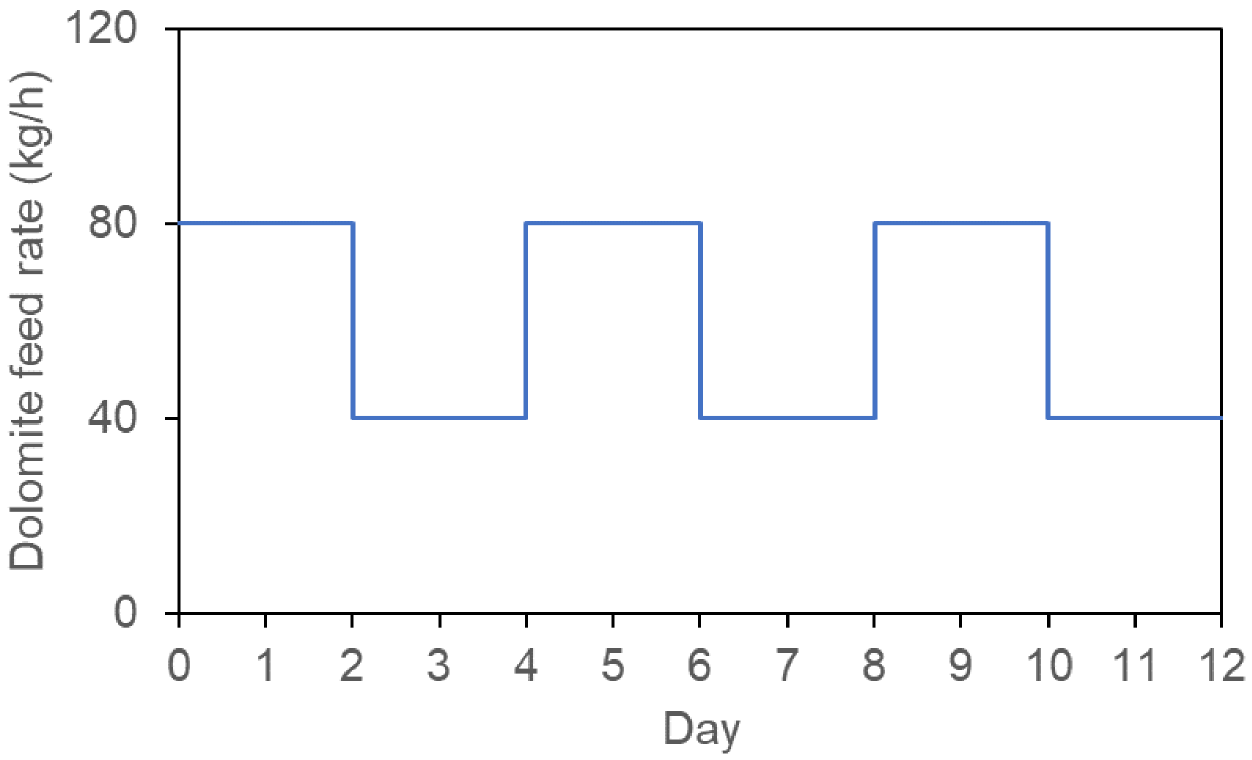




- the real plant adopts a fixed feed rate of 80 kg/h of dolomite (typical operating point of the plant)
- simulations with the model suggest that a small cost reduction (up to 10% for $C_{HCl,in} = 600\ mg/Nm^3$) can be obtained by lowering the amount of dolomite fed to the system

# 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/Nm$^3$)

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




**12 days** of tests in both the waste incineration lines (A and B) of the case study plant

- 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/Nm$^3$**

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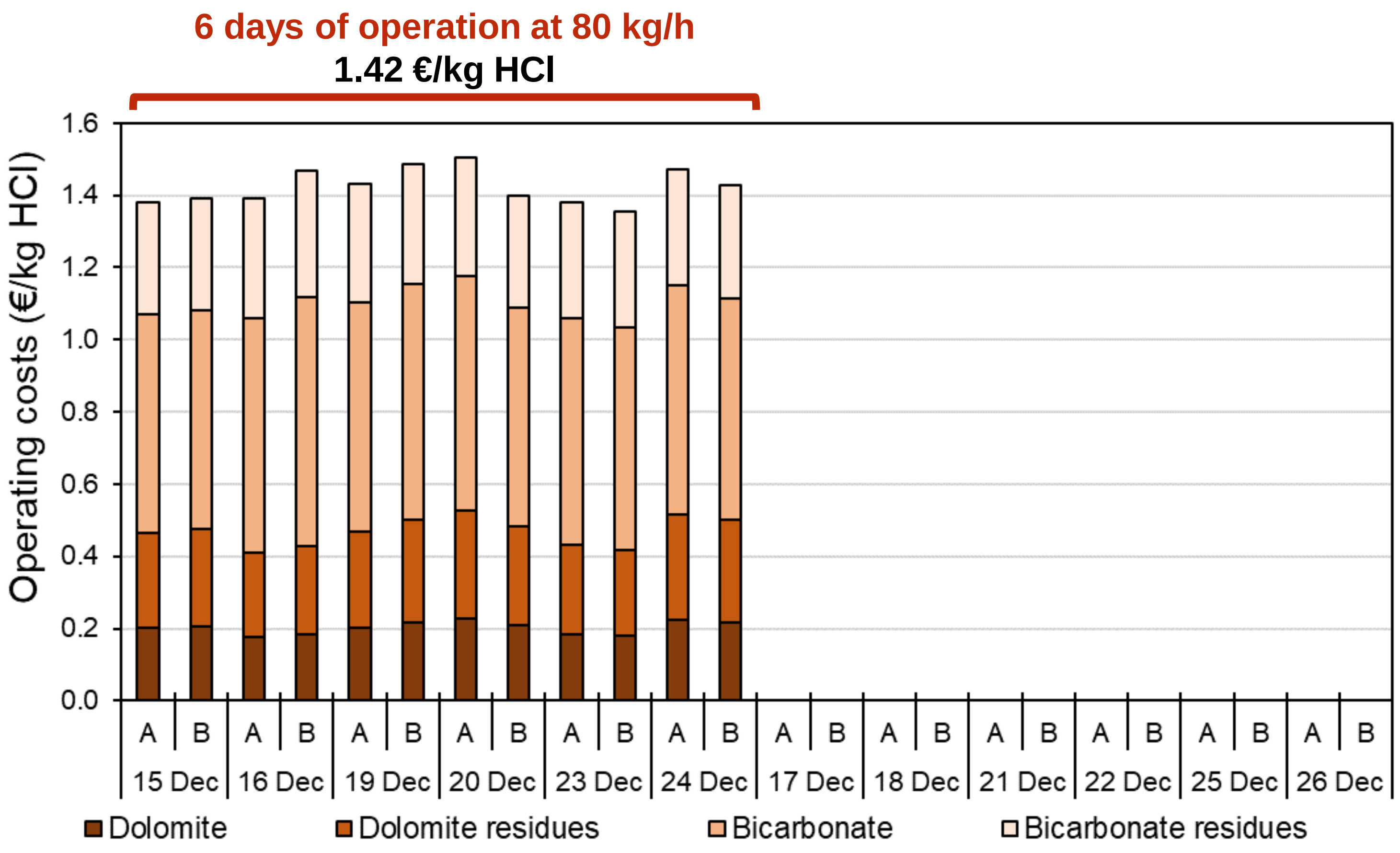

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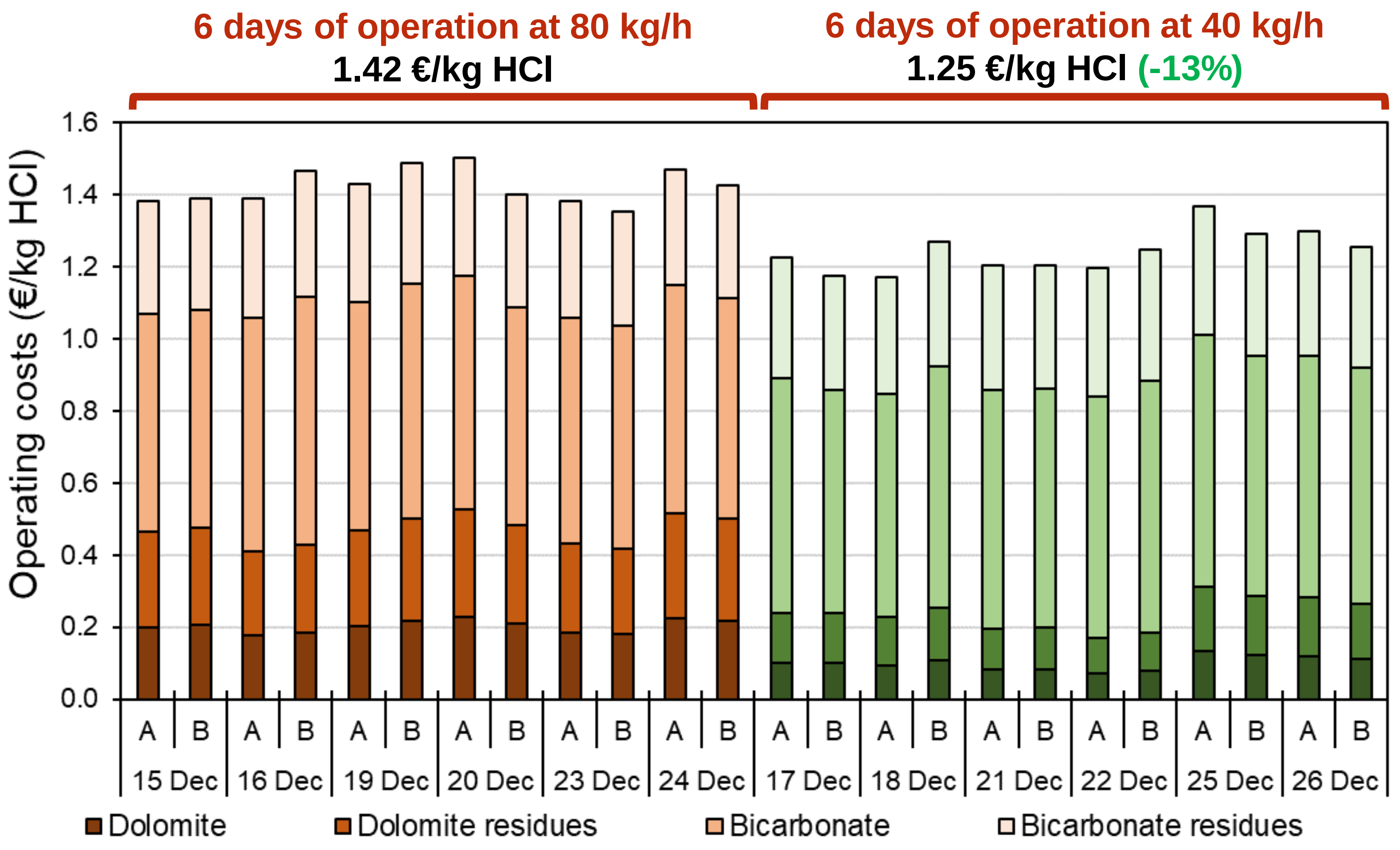

# Conclusions

- 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, Muratori, Antonioni, Cozzani, Economic and environmental benefits by improved process control strategies in HCl removal from waste-to-energy flue gas, *Waste Management* **2021**, 125, 303–315.

Dal Pozzo, Lazazzara, Antonioni, Cozzani, Techno-economic performance of HCl and SO2 removal in waste-to-energy plants by furnace direct sorbent injection, *Journal of Hazardous Materials* **2020**, 394, 122518.

Dal Pozzo, Moricone, Tugnoli, Cozzani, Experimental Investigation of the Reactivity of Sodium Bicarbonate toward Hydrogen Chloride and Sulfur Dioxide at Low Temperatures, *Industrial and Engineering Chemistry Research* **2019**, 58, 6316-6324.

Dal Pozzo, Guglielmi, Antonioni, Tugnoli, Environmental and economic performance assessment of alternative acid gas removal technologies for waste-to-energy plants, *Sustainable Production and Consumption* **2018**, 16, 202-215.

Dal Pozzo, Moricone, Antonioni, Tugnoli, Cozzani, Hydrogen Chloride Removal from Flue Gas by Low-Temperature Reaction with Calcium Hydroxide, *Energy & Fuels* **2018**, 32, 747-756.

Dal Pozzo, Armutlulu, Rekthina, Muller, Cozzani, $CO_2$ Uptake Potential of Ca-Based Air Pollution Control Residues over Repeated Carbonation-Calcination Cycles, *Energy & Fuels* **2018**, 32, 5386–5395.

Dal Pozzo, Guglielmi, Antonioni, Tugnoli, Sustainability analysis of dry treatment technologies for acid gas removal in waste-to-energy plants, *Journal of Cleaner Production* **2017**, 162, 1061-1074.

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

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

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