Technical University of Denmark

Performance of a wet Flue Gas Desulphurisation Pilot Plant under Oxy-fuel Conditions

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Performance of a wet Flue Gas Desulphurisation Pilot Plant under Oxy-fuel Conditions

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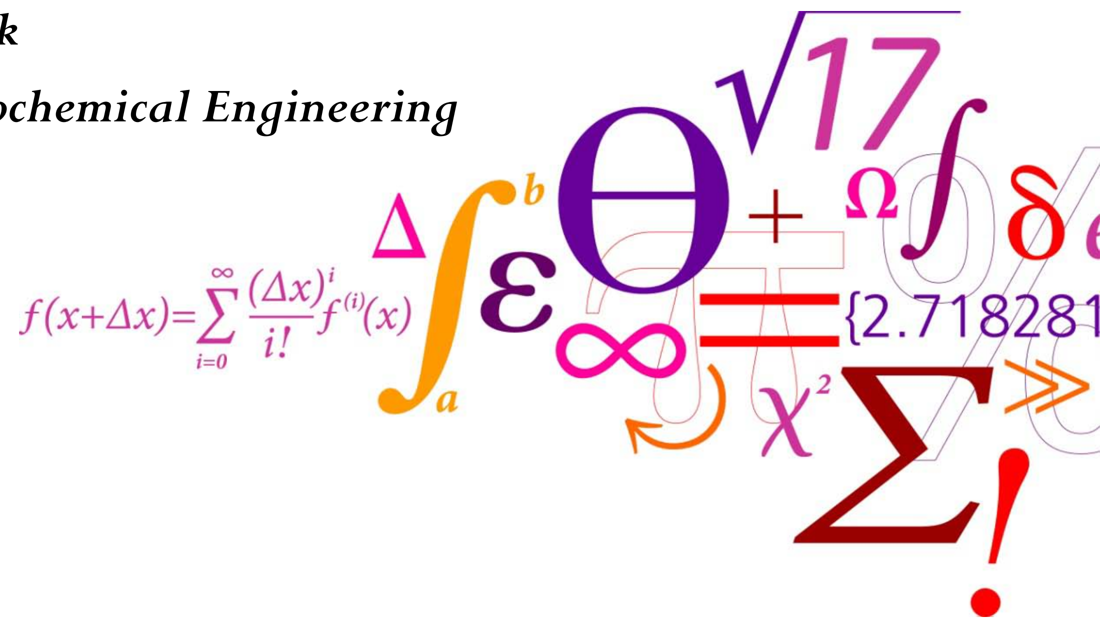

Outline

- Introduction
  - *Technical University of Denmark*
  - *Objective*
  - *Wet FGD and Oxy-fuel combustion*
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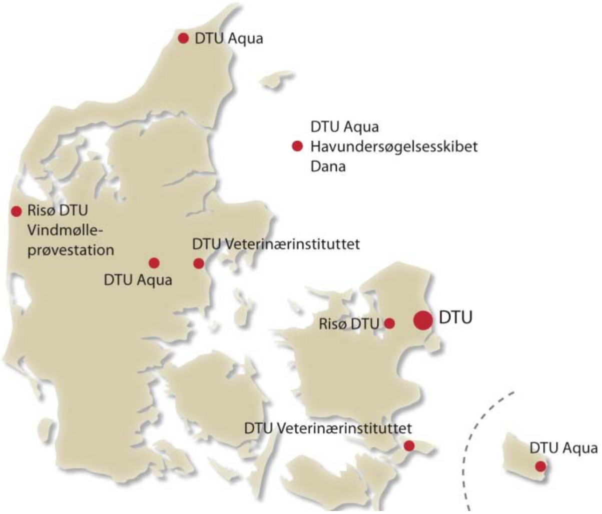
    - *Desulphurisation degree*
    - *Content of residual limestone*
- Conclusions and future work

Technical University of Denmark (DTU)

- Founded in 1829

  - Hans Christian Ørsted (Danish Physicist)
- Engineering education and research
- About DTU
  - *19 departements (Lyngby)*
  - *4500 employes (1050 Ph.D. Students)*
  - *6500 bachelor and master students*

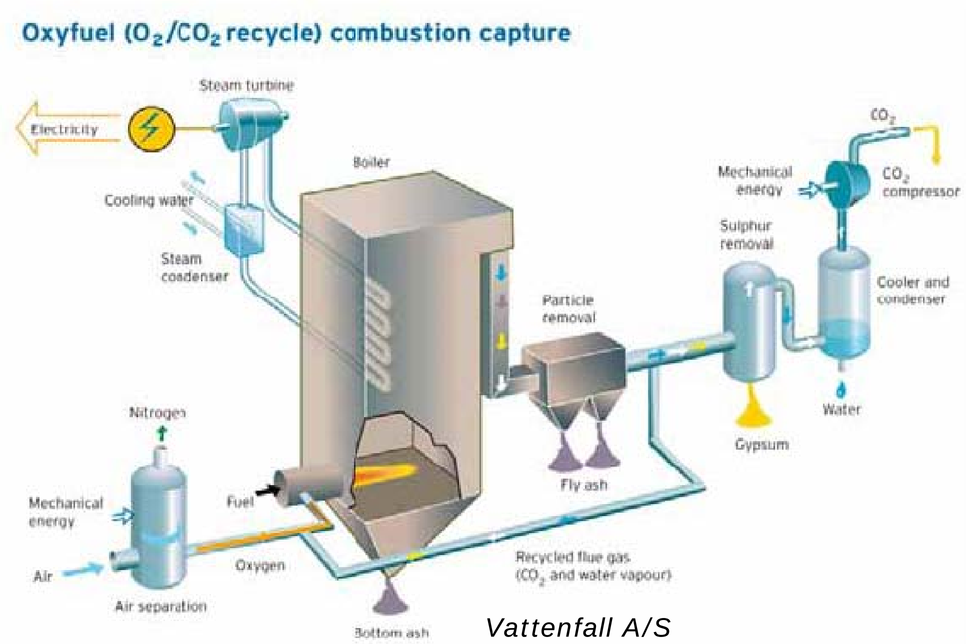


Project objective

Objective

- To investigate the effect of oxy-fuel combustion on wet FGD operation
  Parameters studied:
  - *CO_2 atmosphere*
  - *Higher flue gas temperature (H_2O content)*
  - *Higher SO_2 concentration*
  - *Reduced flue gas flow rate*

Oxy-fuel and wet FGD



Vattenfall A/S

Flue gas desulphurisation

- Ensuring a clean CO_2 stream or recycle stream
- Wet FGD – widespread, traditional and highly efficient

$$CaCO_3(s) + SO_2(g) + 2H_2O + \frac{1}{2}O_2 \rightarrow CaSO_4 \cdot 2H_2O(s) + CO_2$$

- Potential process conditions dependent on recycle location

Potential wet FGD process changes

- **CO_2 atmosphere**
  - *CO_2 absorption (absorber) and a decreased limestone dissolution rate*

    $CaCO_3 + 2\ H^+ \leftrightarrows Ca^{2+} + CO_2 + H_2O$

- **Higher saturation temperature**
  - *Wet recycle yields higher gas phase water content*
  - *Decreased SO_2 solubility*

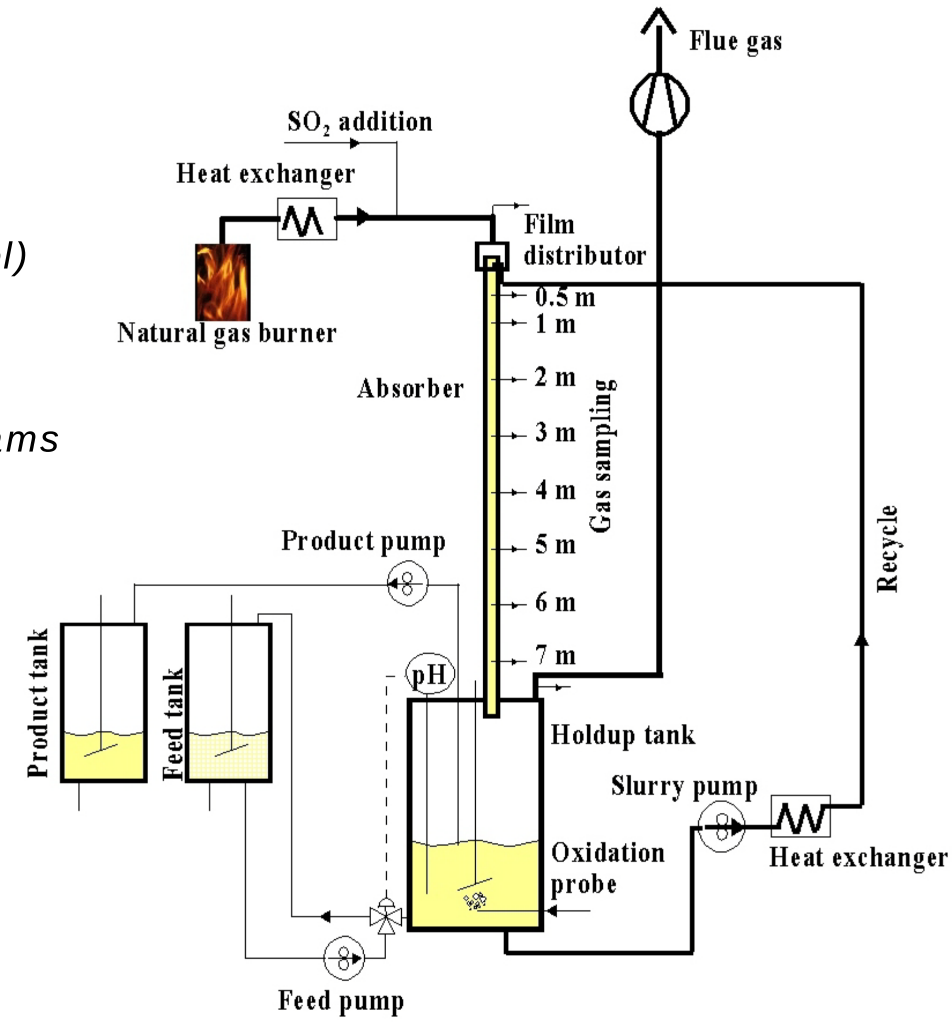
- **SO_2 concentration / flue gas flow rate**
  - *Recycle location or changing modes of operation (air-firing/oxy-fuel)*
  - *Prolonged gas phase residence time*
  - *Increased importance of liquid phase transport resistance*

- **External oxidation**

Pilot plant outline

Overview

- Packed tower absorber
  - *- Downscaled (single vertical channel)*
  - *- Co-current flow*
  - *- Multiple sampling sites*
  - *- Well controlled gas and liquid streams*



Experimental overview

Air-firing - pH 5.4

- Base-case

Oxy-fuel - pH 5.4

- Oxy-fuel (~ 90 % CO_2)
- Oxy-fuel and 10 mM adipic acid

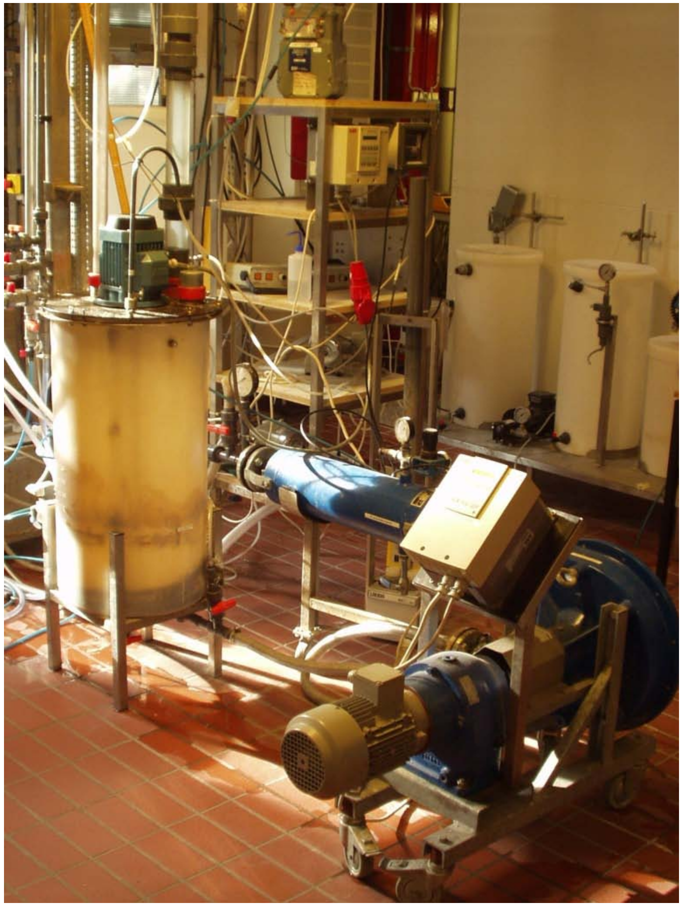
Oxy-fuel - pH 5.0

- Oxy-fuel
- Oxy-fuel and low gas flow rate
- Oxy-fuel, low flow and T (~ 53 ^oC)

Experimental methodology

Experimental procedure

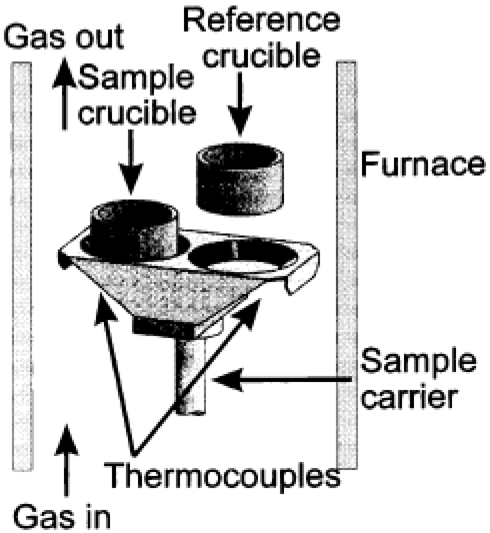
- Steady state
  - *5 days desulphurisation*
  - *1000 ppm SO_2 flue gas (natural gas burner)*
- Oxy-fuel experiments
  - *1000 ppm SO_2 flue gas (gas cylinders)*
  - *Until a steady limestone consumption rate*



Sampling procedure

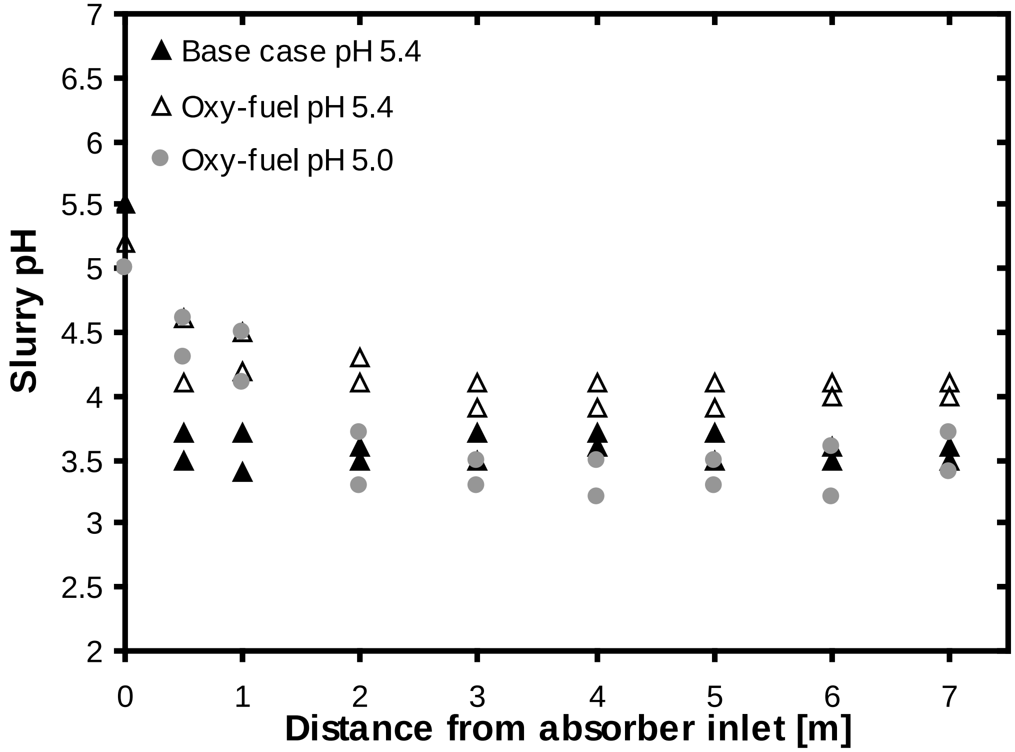
Sampling

- Gas phase composition
  - *- Absorber profile*
  - *- Overall degree of desulphurisation*
- Absorber pH
  - *- Multiple sampling points*
- Residual limestone
  - *- Thermal analysis in STA*



Netzsch-Gerätebau GmbH

Absorber pH



- pH decrease as SO_2 is absorbed

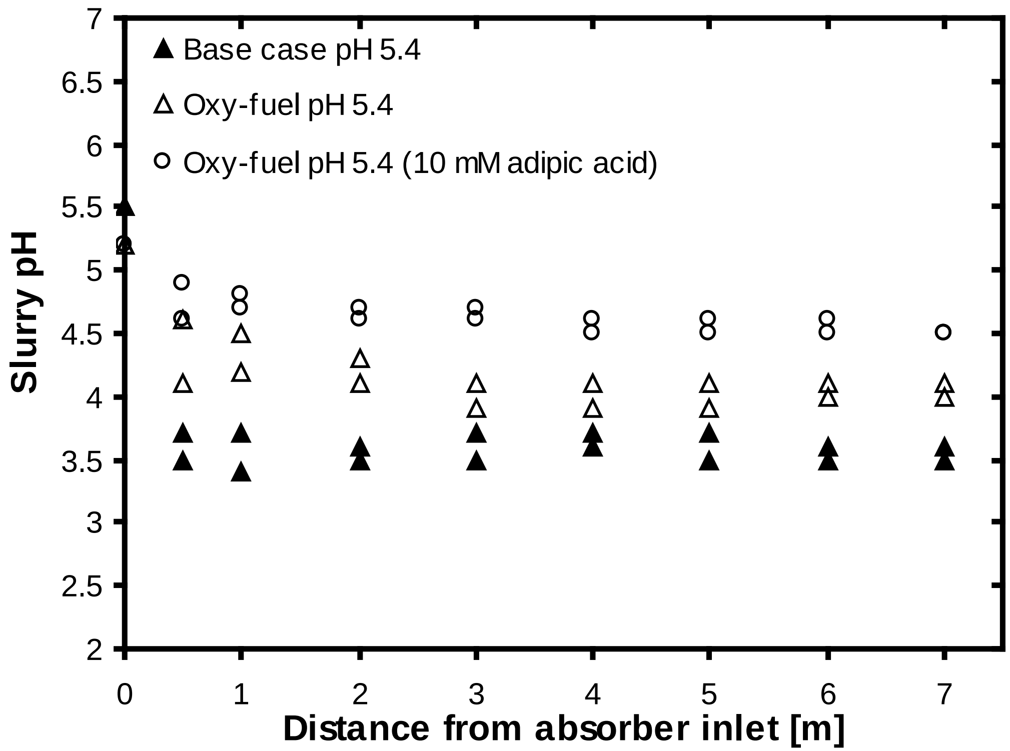
  $SO_2 + H_2O \leftrightarrows H_2SO_3 \leftrightarrows HSO_3^- + H^+$

  $HSO_3^- + ½\ O_2 \leftrightarrows H^+ + SO_4^{2-}$

- Oxy-fuel pH 5.4

  - increased absorber pH

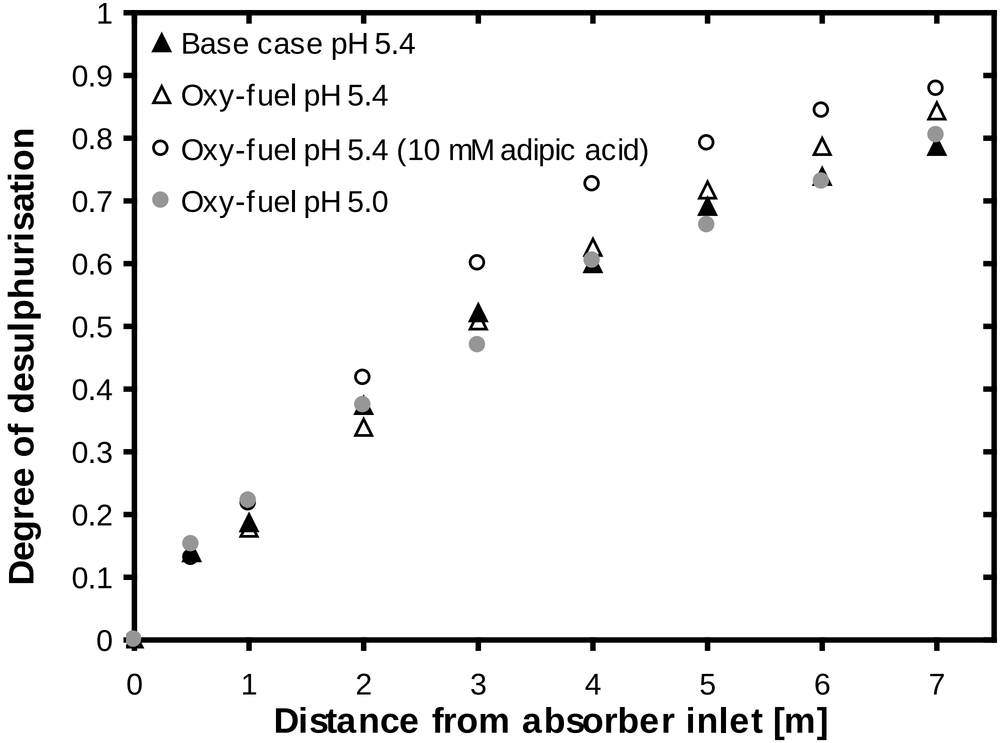
Absorber pH



- Oxy-fuel pH 5.4 (10 mM adipic acid)

  - High and stable absorber pH

Absorber desulphurisation

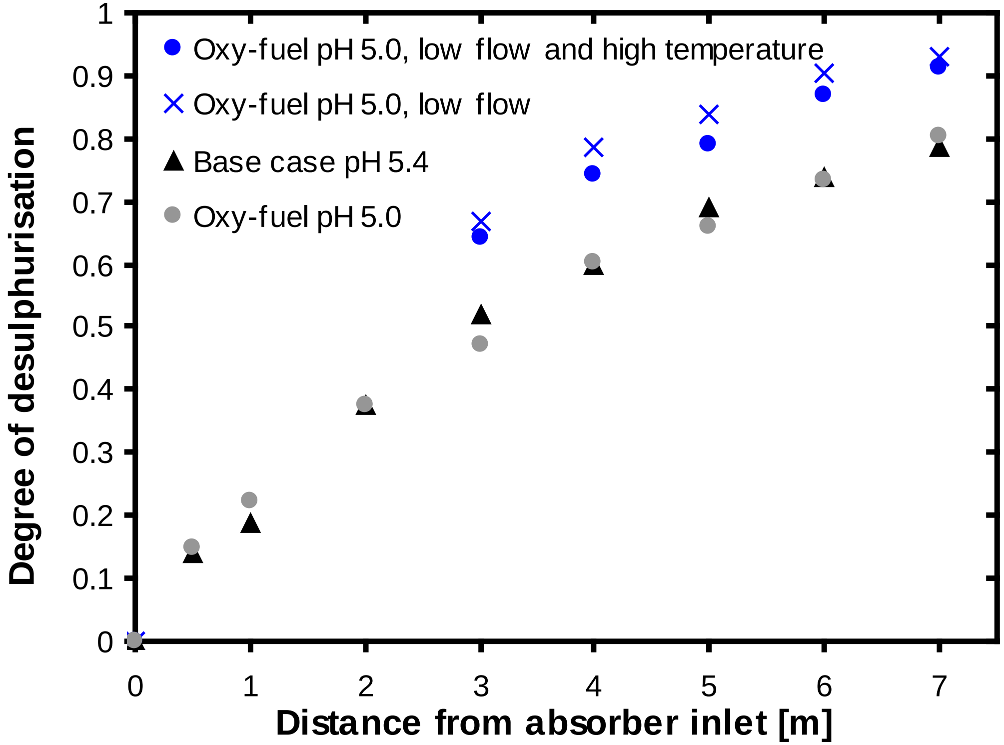


- Increased degree of desulphurisation

  - Oxy-fuel pH 5.4 (10 MM adipic acid)

  - Oxy-fuel pH 5.4

Absorber desulphurisation



- Increased degree of desulphurisation

  - Oxy-fuel experiments with low flow rates

- Base-case 5.4 and Oxy-fuel pH 5.0 very similar

Total degree of desulphurisation

Experiment	**C_{SO2}** *[ppm]*	**C_{CO2}** *[%]*	***pH***	***T*** *[°C]*	**η (±1)** *[%]*
Air-firing	1070	7	5.4	46	91
CO_2 atmosphere (pH 5.4)	1040	90	5.4	44	94
- pH 5.4 (10 mM adipic acid)	1030	90	5.4	44	97
- pH 5.0	1030	91	5.0	43	92
- Reduced flow rate	4940	90	5.0	44	99
- Elevated Temperature	4950	85	5.0	53	99

- CO_2 atmosphere
  - *Increased desulphurisation degree*
  - *Lower pH counters the effect*
  - *High degree of desulphurisation with 10 mM adipic acid or low Q_{flue}*

Residual limestone

Experiment	C_{SO2} [ppm]	C_{CO2} [%]	*pH*	*$CaCO_3$*(±0.6) [g/l]	η (±1) [%]
Air-firing	1070	7	5.4	3.2	91
CO_2 atmosphere (pH 5.4)	1040	90	5.4	5.0	94
- pH 5.4 (10 mM adipic acid)	1030	90	5.4	5.2	97
- pH 5.0	1030	91	5.0	2.3	92
- Reduced flow rate	4940	90	5.0	1.9	99
- Elevated Temperature	4950	85	5.0	1.7	99

- CO_2 atmosphere
  - *- Increased residual limestone content*
  - *- Also with 10 mM adipic acid*
  - *- Lower pH counters this effect*

Discussion

Dissolution of limestone

$CaCO_3\ (s) \leftrightarrows Ca^{2+} + CO_3^{2-}$ (1)

$H^+ + CO_3^{2-} \leftrightarrows HCO_3^-$ (2)

$HCO_3^- + H^+ \leftrightarrows CO_2 + H_2O$ (3)

$CO_2\ (aq) \leftrightarrows CO_2\ (g)$ (4)

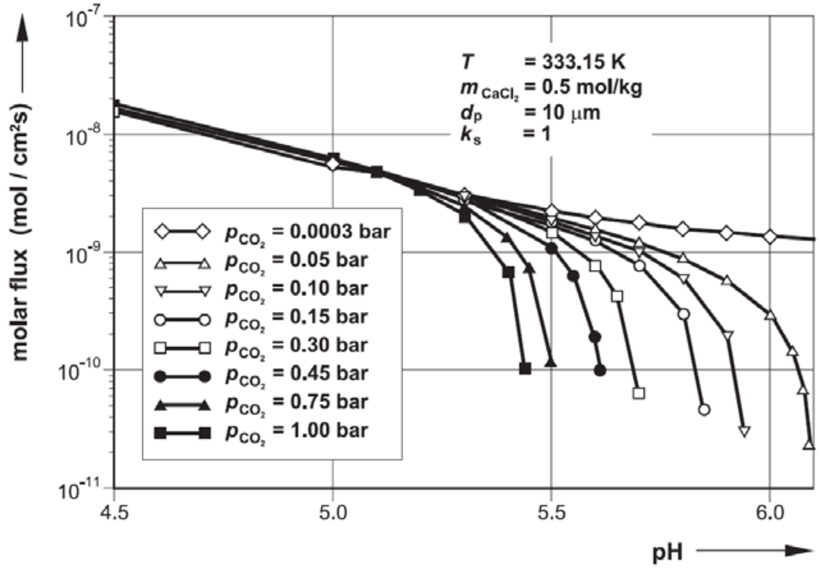


Figure 1. Dissolution rate of limestone particles with a diameter of 10 μm.

Allers et. Al 2003

- Critical pH changes with CO_2
- Above critical pH (5.2-5.5)
  - *- Increased HCO_3^- concentration*
  - *- Increased CO_3^{2-} at the particle surface*
  - *- Lower Ca^{2+} concentration at the particle surface*
  - *- Drastic reduction in limestone dissolution rate (ΔCa^{2+})*
- Verified experimentally by Allers et al. 2003 and Chan et al. 1982

Conclusions

Desulphurisation of an oxy-fuel flue gas stream

- A higher absorber pH
- An increased content of residual limestone
- An increased degree of desulphurisation
- A minor correction of pH (5.0 vs. 5.4) compensate for the changes
- High degrees of desulphurisation obtained for low flow rates
  - *No temperature effect could be distinguished*

Publication

- Manuscript “Performance of a wet flue gas desulphurisation pilot plant under oxy-fuel conditions” accepted by Industrial and Engineering Chemistry Research
- Expected publication in spring 2011

Thank you for the Attention

Further information:

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