

STUDY OF LIMESTONE BEHAVIOUR IN FLUIDISED BED AT AIR AND OXYGEN COMBUSTION CONDITIONS

TCCS-6, 15-16 June 2011, Trondheim, Norway

Toni Pikkarainen¹, Sirpa Takkinen², Ari Kettunen³

¹ VTT Technical Research Centre of Finland,

² Lappeenranta University of Technology,

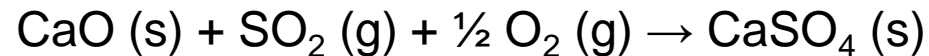
³ Foster Wheeler Energia Oy

CONTENT

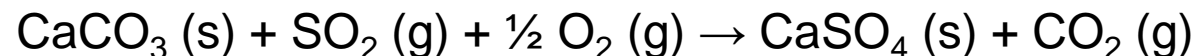
- Background for the study
- Experimental work
- Results and conclusions
- Summary

Sulphur capture in fluidised bed combustors

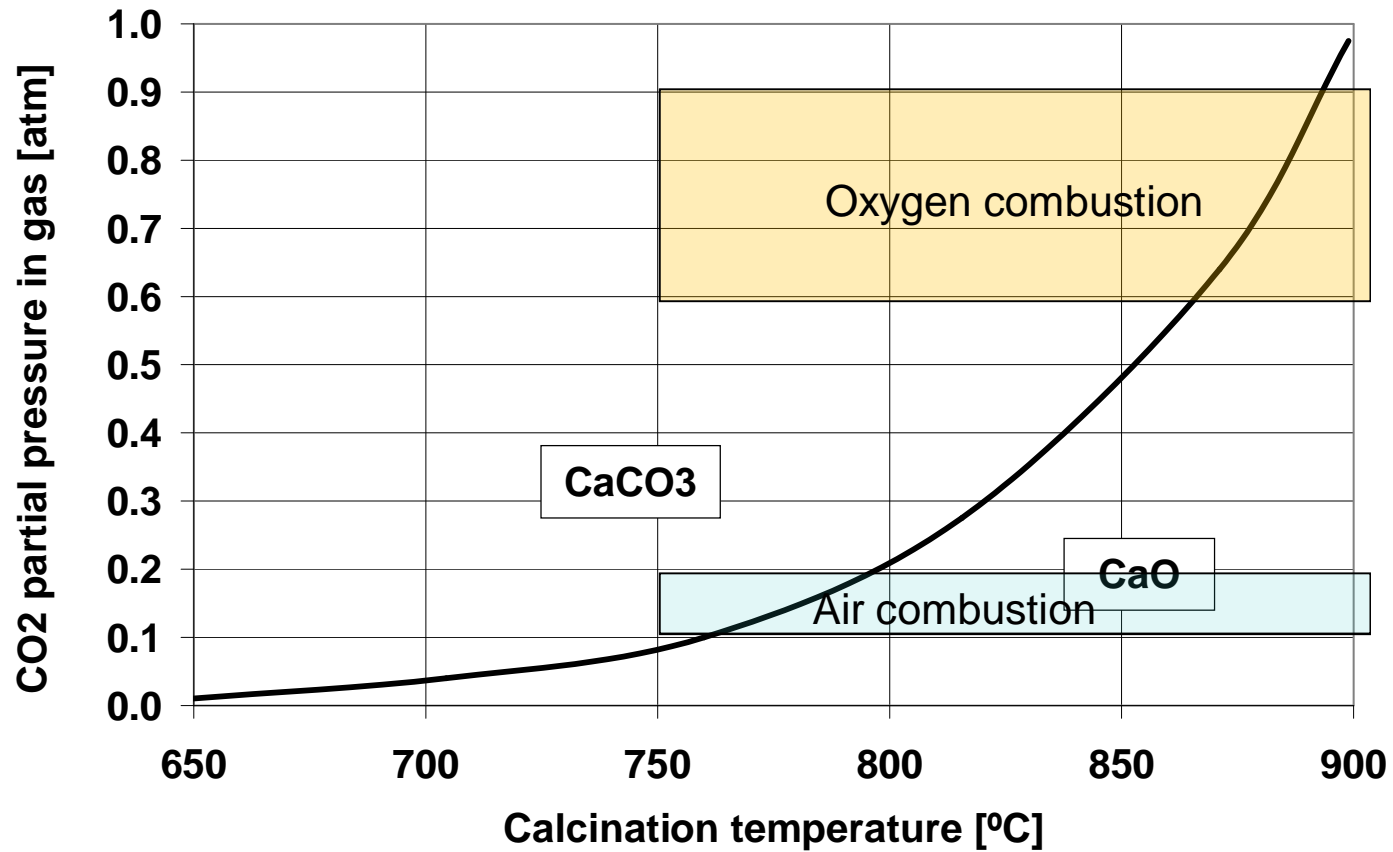
- In fluidised bed boilers sulphur capture is typically carried out in situ by limestone injection into furnace. In air combustion conditions sulphur capture reactions are following:



- In oxygen combustion conditions, the CO_2 partial pressure can be higher than the equilibrium CO_2 pressure over limestone, and the sulphation can occur by direct sulphation without the calcination step:



Sulphur capture in fluidised bed combustors



Sulphur capture in fluidised bed combustors

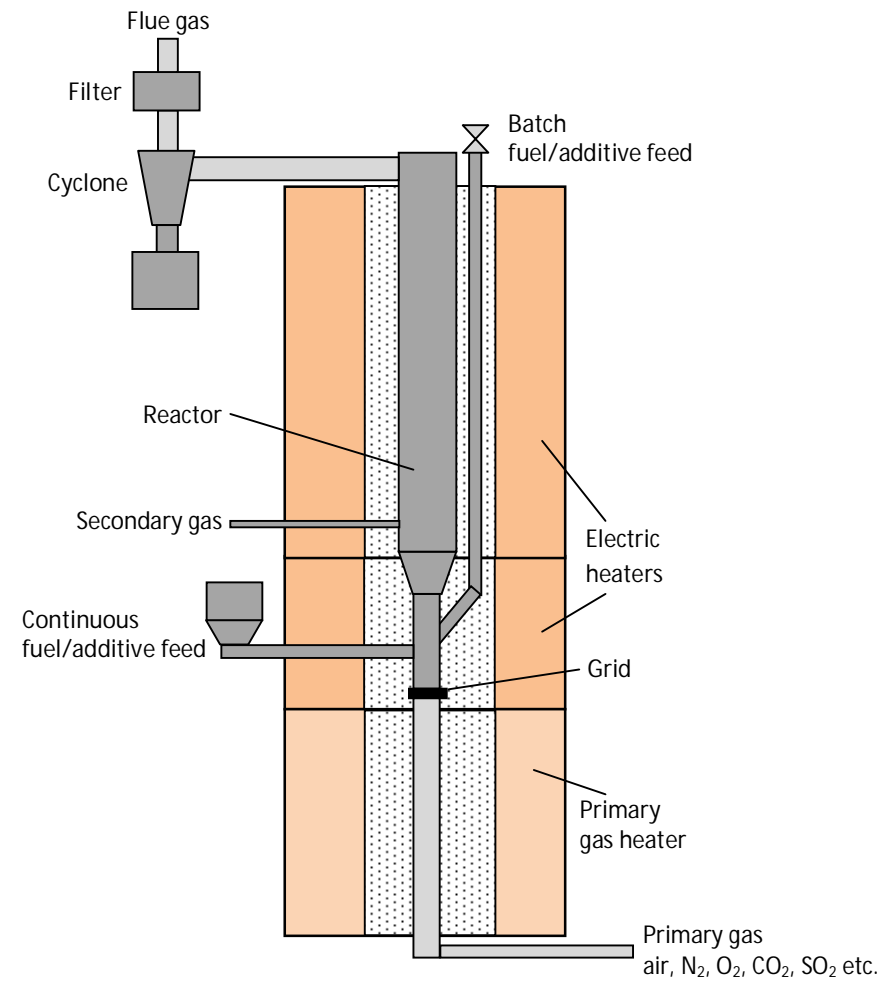
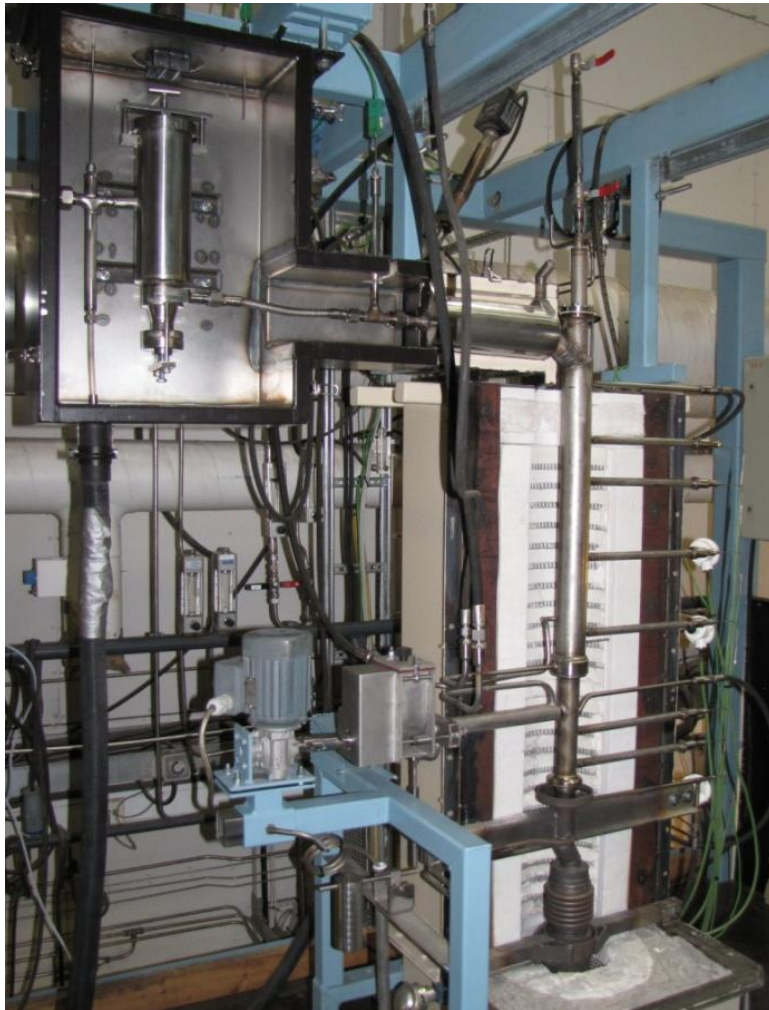
- In normal air combustion limestone behaviour has effect on needed dosage to reach SO_2 concentration in flue gas below the emission limit. Limestone dosage has effect on costs and formed amount of ash needed to be disposed.
- In addition to those in oxygen combustion with carbon capture, flue gas SO_2 concentration has effect on design and operation of flue gas compression and purification unit, and corrosion potential of heat transfer surfaces.
- In air fired atmospheric units, the calcium conversion of limestone seldom exceeds 30–40%. This low conversion is due to the development of a sulphated shell that leads to high diffusion resistance and that drastically inhibits utilization of the sorbent material in the particle core.
- The development of oxy-fuel circulating fluidized bed (CFB) boilers can offer enhanced sulphur capture efficiency because of differences in the gas composition and the temperature profiles, and the possibility to control the conditions inside the combustor.

Experimental – Test matrix

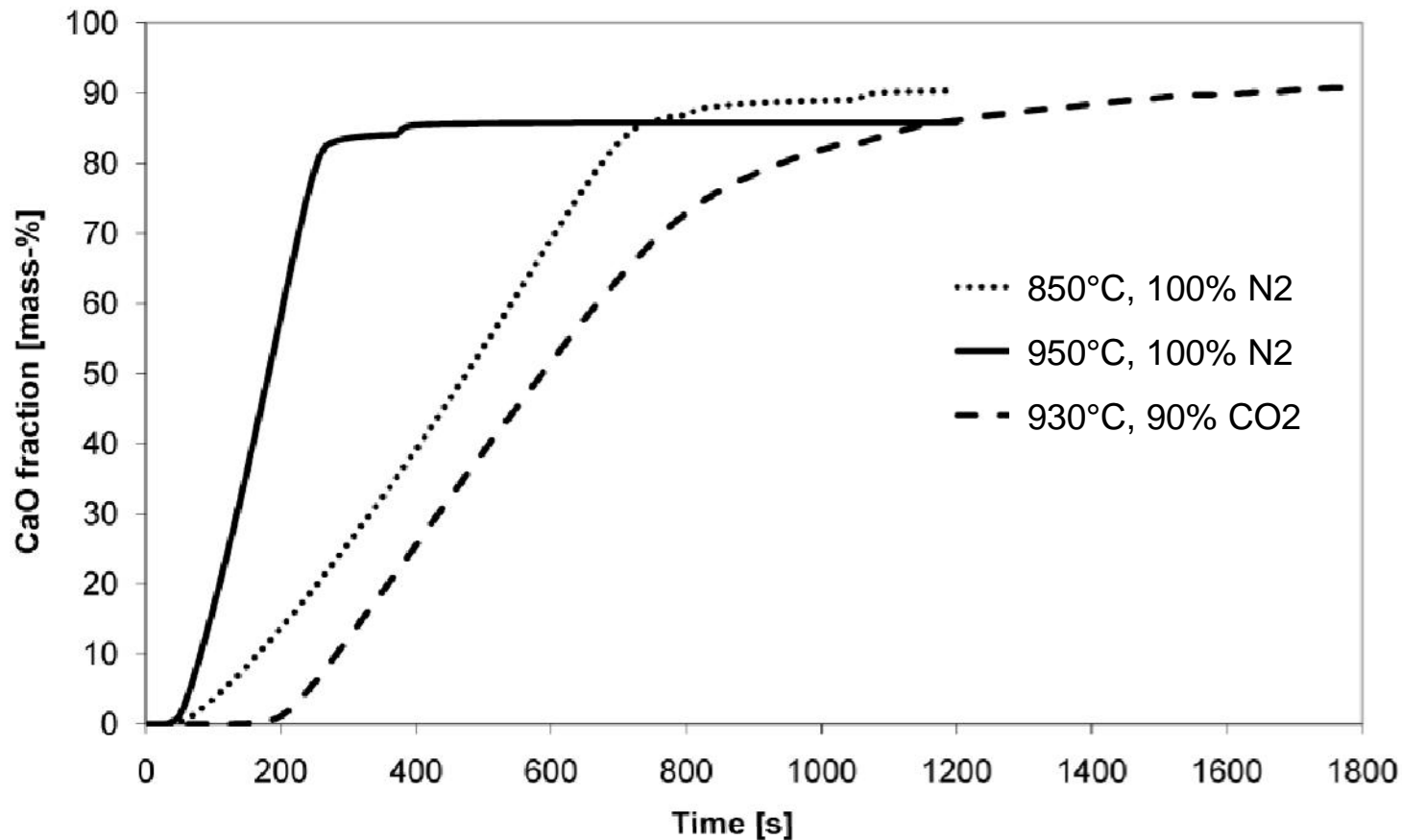
Test	Description	Gas atmosphere				Time [min]	Temp. [°C]
		N2 [vol-%]	CO2 [vol-%]	O2 [vol-%]	SO2 [ppm]		
1	Calcination in N2	100	0	0	0	20	850
2						20	950
3	Pre-calcination+sulphation	90	0	10	2200	20+30	850
4						20+30	950
5	Calcination, effect of CO2	44	46	10	0	30	860
6		36	54	10	0	30	860
7		0	90	10	0	30	930
8	Sulphation in N2, medium temperature	90	0	10	2200	5	850
9						30	
10						180	
11						360	
12	Sulphation in N2, high temperature	90	0	10	2200	5	950
13						30	
14						180	
15						360	915
16	Sulphation in CO2, medium temperature	0	90	10	2200	5	850
17						30	
18						180	
19						360	
20	Sulphation in CO2, high temperature	0	90	10	2200	5	950
21						30	
22						180	
23						360	915
24	Cyclic changing atmosphere	~35.5-43.5	~45-55	~9.5-11.5	2200	30	870
25		~35.5-43.5	~45-55	~9.5-11.5		360	870
26		~35.5-43.5	~45-55	~9.5-11.5		360	925

- Batch feed of sieved limestone sample
- Shares of different calcium species – CaCO₃, CaO and CaSO₄ – were analysed after each test.
- Shape of particles, porosity and a rough distribution of components were analysed by optical microscopy.
- Cross-sections of particles were analysed by SEM-EDS to study distribution of different species inside the particles and different sulphation patterns in different conditions.

Experimental – Test rig

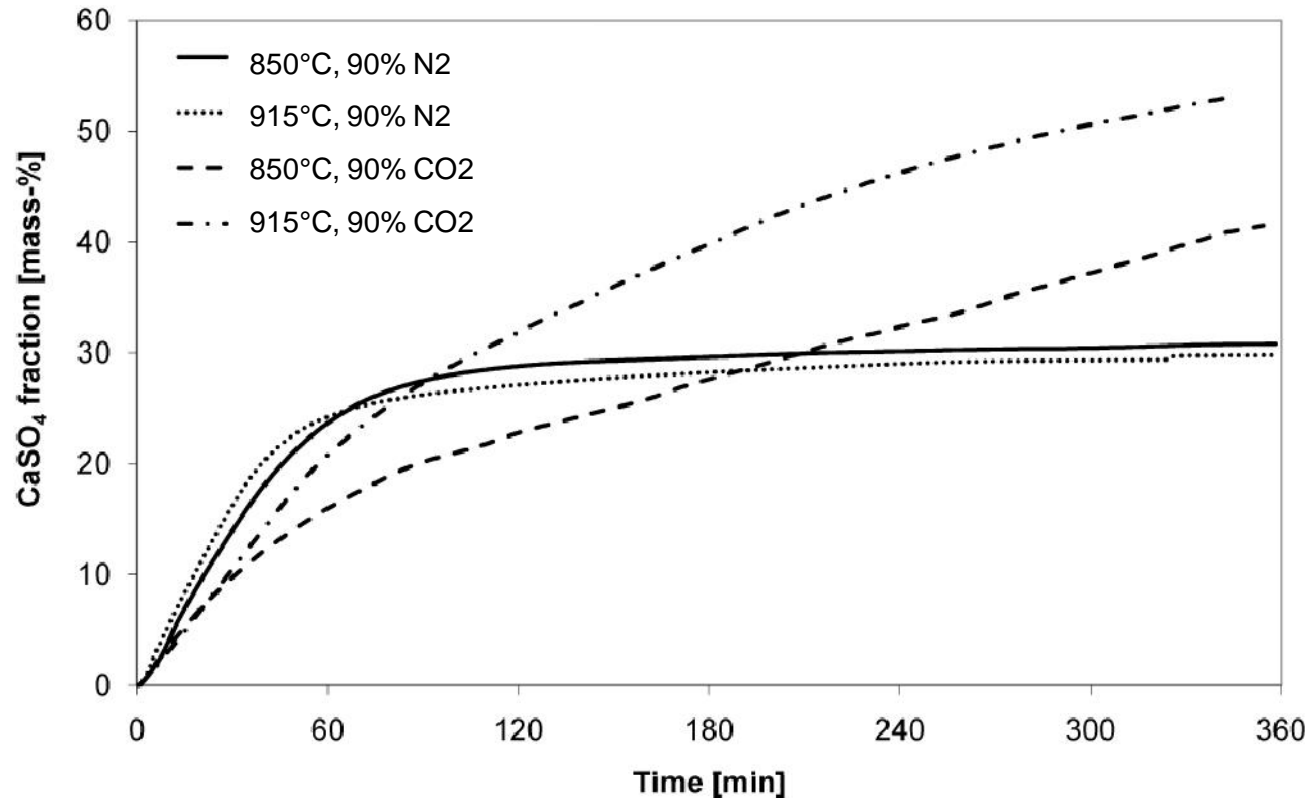


Results – Calcination



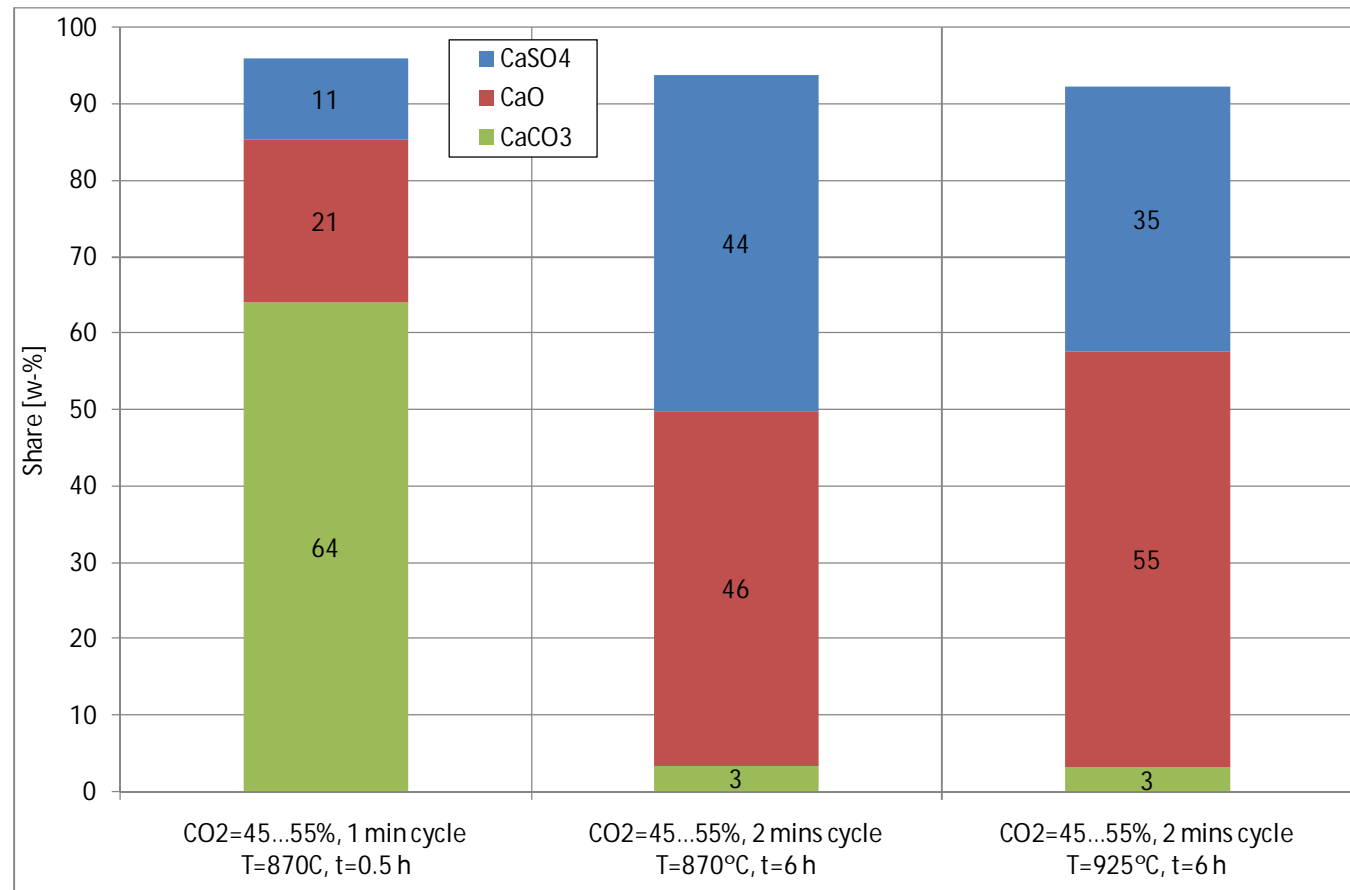
- At N₂-based atmosphere calcination was completed in 5...15 minutes depending on temperature.
- At high temperature (~930°C) and at CO₂ atmosphere (90 vol-%) calcination time was prolonged to about 30 minutes, even if conditions were in CaO side of the equilibrium curve.
- At lower temperature level (~860°C) and at CO₂ concentrations 46 and 54 vol-% calcination was hindered or prevented (CaO fraction after 30 min tests 36 w-% and 21 w-%, respectively).

Results – Sulphation



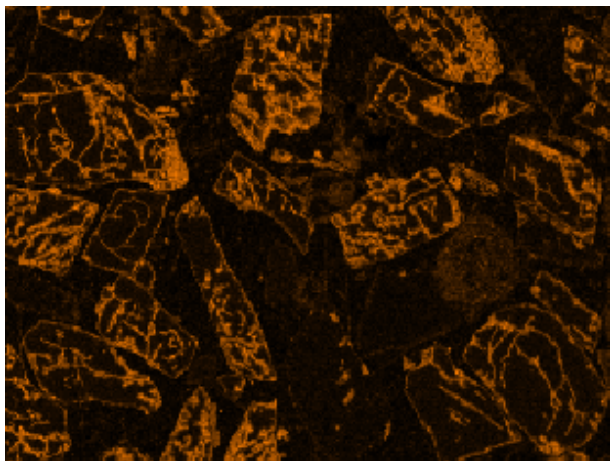
- At N₂-based atmosphere sulphation was completed after about 30...60 minutes.
- At CO₂-based atmosphere sulphation reaction is slower suggesting that the calcined limestone has a higher global reaction rate than the uncalcined one
- At CO₂-based atmosphere sulphation continues much longer and higher CaSO₄ shares were measured after longer exposure
- The highest sulphur capture was measured at high temperature tests at CO₂ atmosphere. In these conditions sulphation occurs by calcination–sulphation route, but where calcination was slowed down by high CO₂ partial pressure.

Results – Sulphation in cyclic conditions

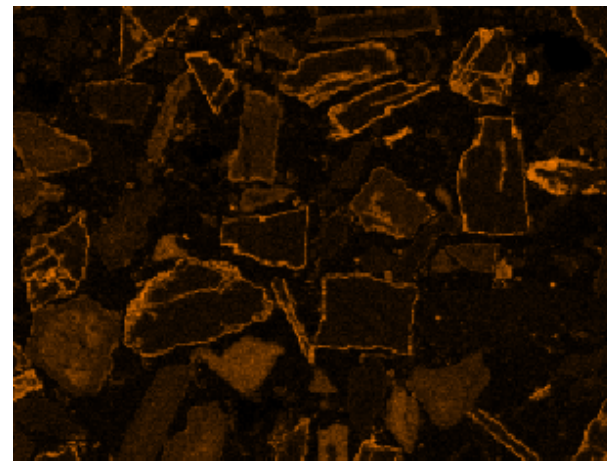


- During cyclic tests at 870°C temperature CO₂ concentration was varied so, that conditions were on both sides of the calcination curve. Conditions in test at 925°C were favourable for calcination.
- Sulphation at 870°C temperature continues long after 30 minutes: share of CaSO₄ was four times higher after 6 hour test compared to share after 30 minutes test.
- At 870°C share of CaSO₄ was a bit higher compared to test at 925°C.

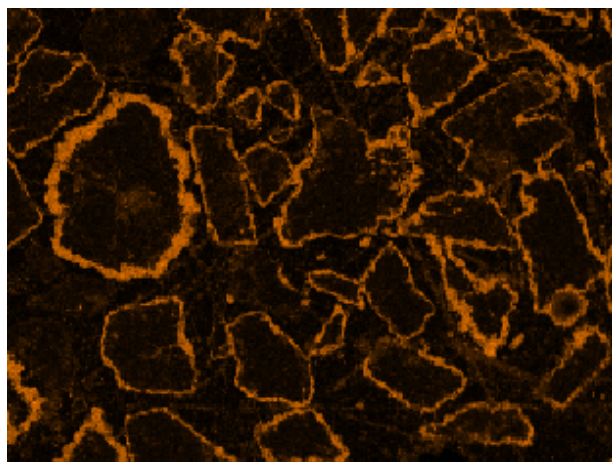
SEM-EDS – distribution of sulphur after 3 hours



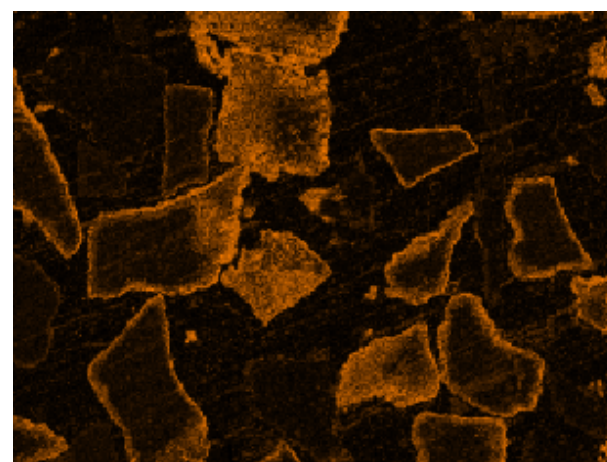
N₂-based sulphation 180 min at 850°C
Network sulfation structure



N₂-based sulphation 180 min at 950°C
Core-shell structure

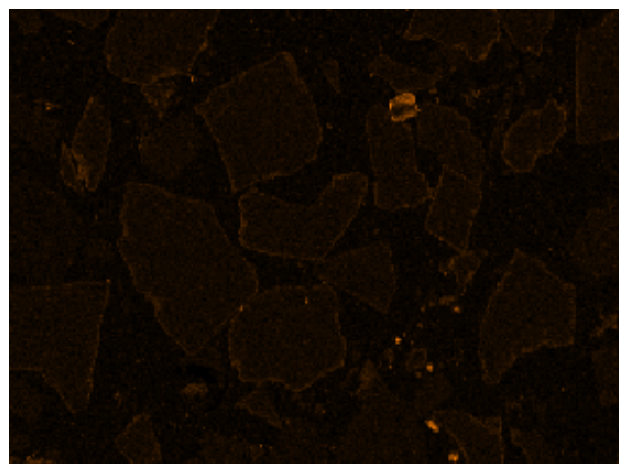


CO₂-based sulphation 180 min at 850°C
Core-shell structure

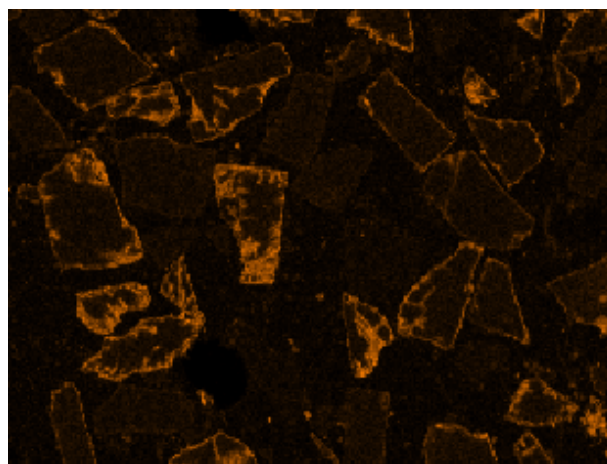
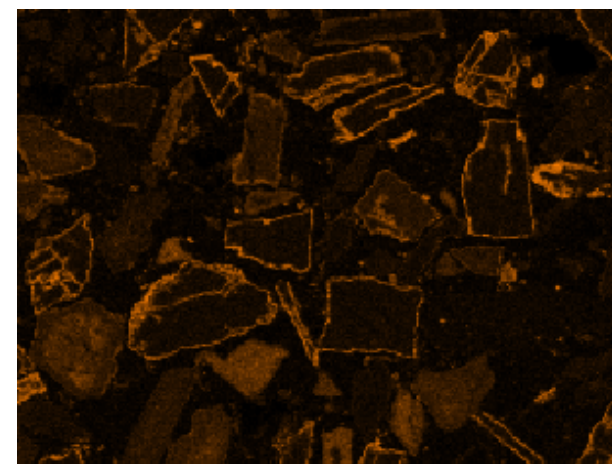


CO₂-based sulphation 180 min at 950°C
Uniformly sulfated and core-shell structure

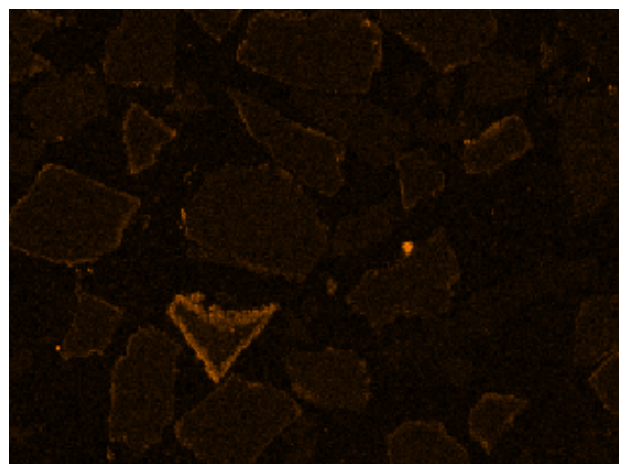
SEM-EDS – distribution of sulphur as a function of time



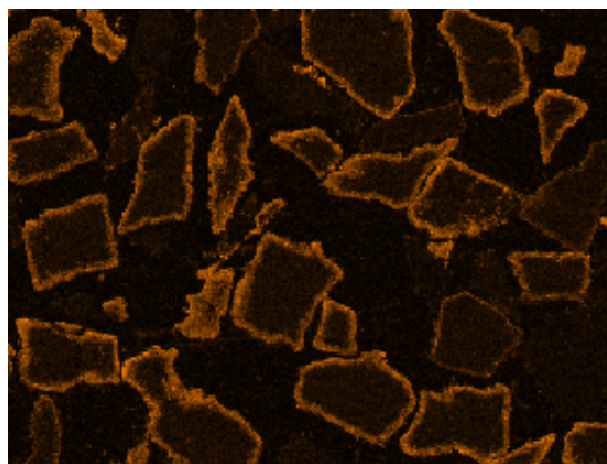
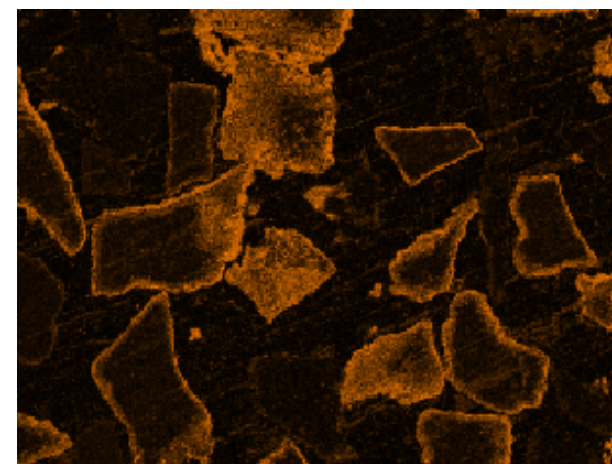
5 minutes

30 minutes
N₂-based sulphation at 950°C

180 minutes



5 minutes

30 minutes
CO₂-based sulphation at 950°C

180 minutes

Summary

- The influence of different conditions on sulphur capture efficiency during fluidized bed desulphurisation was studied by experiments
- In calcination tests at 850...950°C temperatures at N₂-atmosphere calcination was completed after ~20 minutes and temperature had no effect on share of CaO at the end of tests.
- At 850°C temperature CO₂-atmosphere decreased the rate of calcination and main part of the calcium remains as CaCO₃ after 30 minutes test.
- At 930°C temperature calcination occurs at CO₂-atmosphere and after 30 minutes test calcination was complete.
- Initial sulphur capture rate was higher at N₂-atmosphere, but at CO₂-atmosphere sulphation continues for hours leading to better sulphur capture if residence time of limestone is sufficient
- The best sulphur capture performance was measured in conditions where calcination rate was hindered but not prevented by CO₂
- Different sulphation patterns inside the particles were obtained:
 - Network structure at N₂-based atmosphere at 850°C
 - Core-shell structure at N₂-based atmosphere at 950°C and at CO₂-based atmosphere at 850°C
 - Uniformly sulphated and core-shell structure at CO₂-based atmosphere at 950°C

Acknowledgements

The experiments described in this presentation have been performed for Foster Wheeler with support from Tekes (the Finnish Funding Agency for Technology and Innovation).

**Thank you
for your attention!**

Toni.Pikkarainen@vtt.fi



**VTT creates business from
technology**