IMPROVED COMBUSTION IN FLUIDIZED BED WITH MANGANESE ORE AS BED MATERIAL

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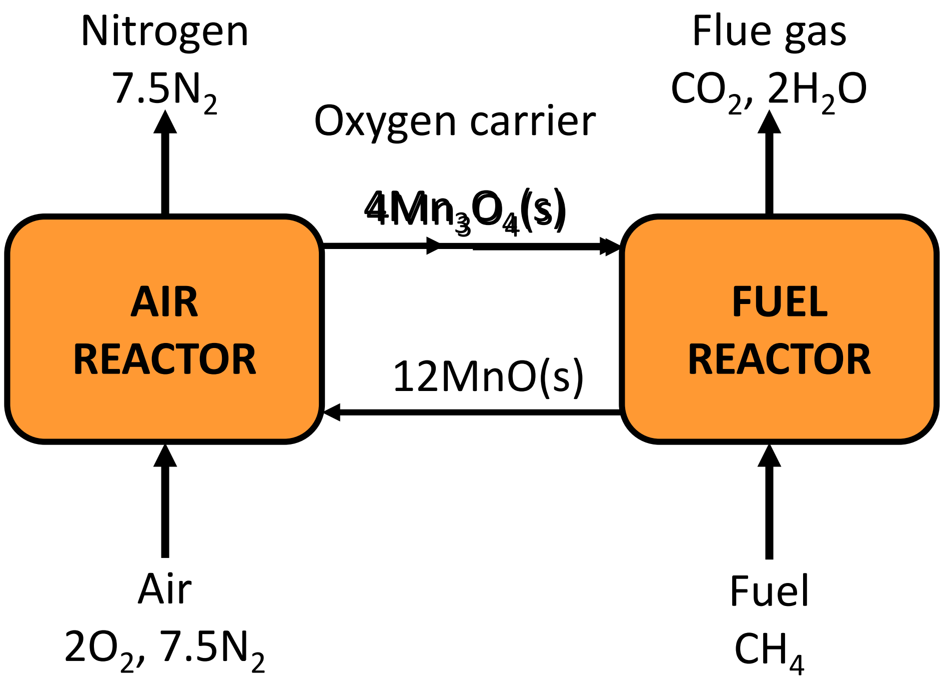
Background: Chemical-Looping Combustion (CLC)

- Oxygen is delivered to the fuel by a solid Oxygen Carrier (OC).
- Flameless reactions at moderate temperatures.
- Produced CO_2 is not diluted with N_2 from the air.
- No energy penalty for CO_2 capture.
- Reactor similar to Circulating Fluidized Bed (CFB) boiler.
- Chalmers have been the leading institution in the development of CLC for more than a decade.



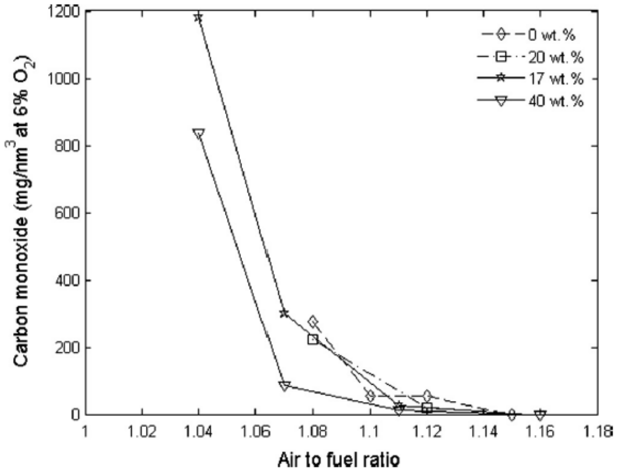
Fuel reactor:	$CH_4 + 4Mn_3O_4O(s) \rightarrow CO_2 + 2H_2O + 12MnO(s)$
Air reactor:	$2O_2 + 12MnO(s) \rightarrow 4Mn_3O_4(s)$
Total reaction:	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

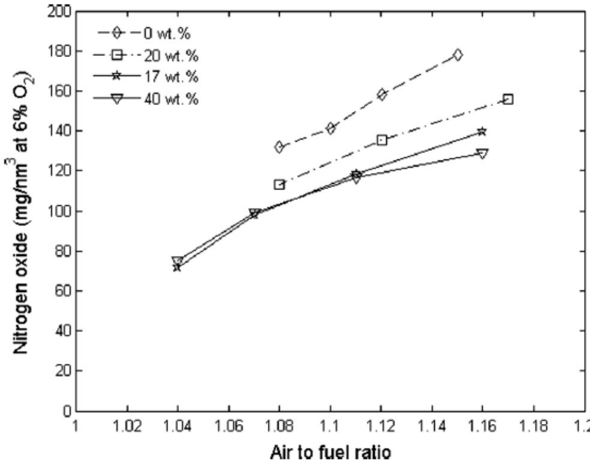
Background: Oxygen carriers in conventional boiler

Experiments at Chalmers Power Central with 40% ilmenite:
(H. Thunman, et al. Using an oxygen-carrier as bed material for combustion of biomass in a 12-MW_{th} circulating fluidized-bed boiler. Fuel 2013;113:300-309)

- Reduced CO emissions with up to 80%
- Reduced NO emissions with up to 30%

→ *Possible to operate the process at lower air to fuel ratios?*





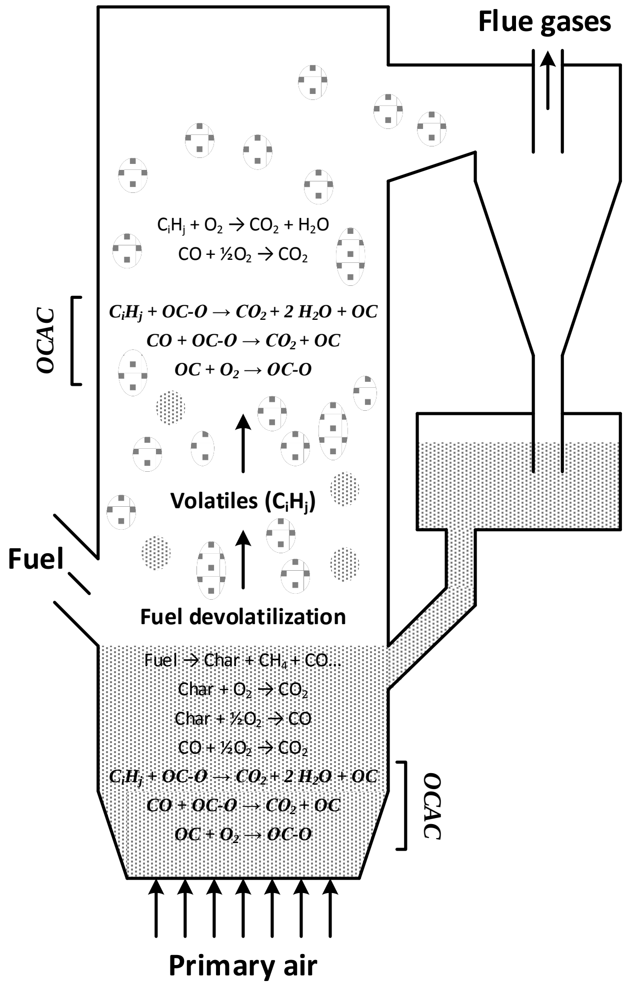
Oxygen Carrier Aided Combustion (OCAC)

What happens when we replace silica sand in a fluidized bed boiler with oxygen carrier particles (OC)?

- The OC is oxidized in sections with excess oxygen.
- The OC is reduced in sections with excess fuel.
- The bed material becomes an oxygen buffer.

→ New mechanisms for oxygen transport in space and time.
→ New mechanisms for fuel oxidation becomes available.
→ Improved fuel conversion in dense bed.
→ Evening out of oxygen potential in combustion chamber.

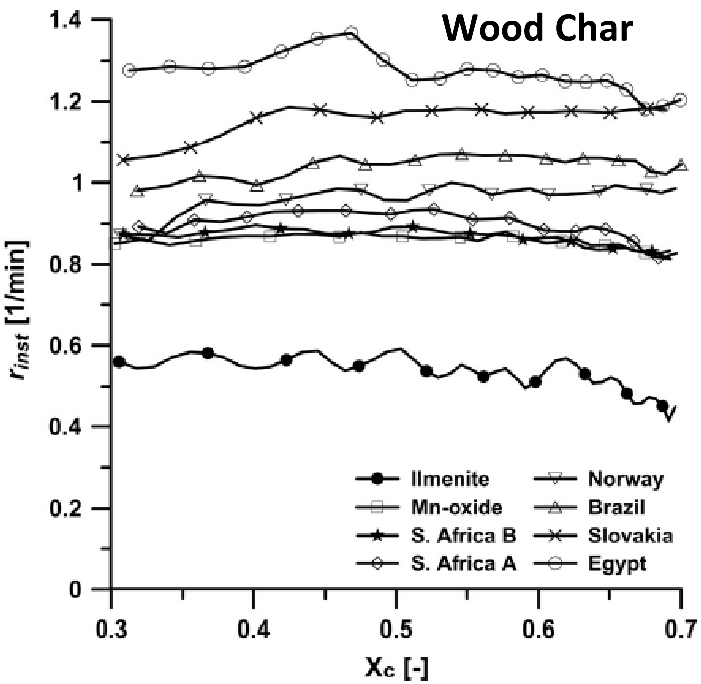
☺ Problems related to poor mixing of air and fuel decrease.
☺ Problems related to irregular fuel feeding decrease.
☺ Problems related to hot spots decreases.
☺ Emissions could be reduced.
☺ Operation at reduced air-to-fuel-ratio could be possible.

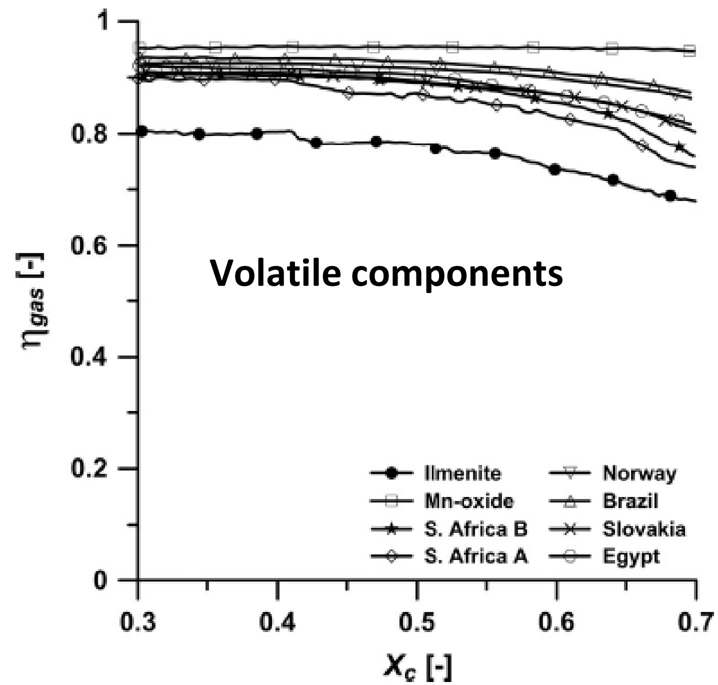


Why manganese ore?

Reactivity of ilmenite and manganese ores during fuel oxidation:

(M. Arjmand, et al. Investigation of different manganese ores as oxygen carriers in chemical looping combustion (CLC) for solid fuels. Applied Energy 2014;113:1883–1894)





Why manganese ore?

Ilmenite concentrate

$2Fe_2TiO_5 + 2TiO_2 \rightarrow 4FeTiO_3 + O_2$

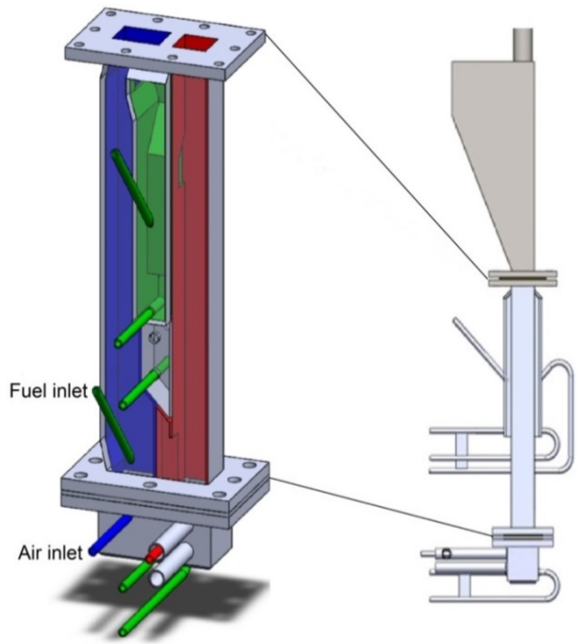
- Slow reaction rate with volatiles
- Reactions with char very unlikely
- Endothermic reaction with fuel
- Oxygen transfer capacity 3.3-5.0 wt%
- 150-200 euro/ton

Manganese ore

$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2 \rightarrow 12MnO + 2O_2$

- Faster reaction rate with volatiles
- Can release gaseous O_2 for char oxidation
- Thermo-neutral reaction with fuel
- Oxygen transfer capacity 3.3-10.0 wt%
- 100-250 euro/ton

The Project



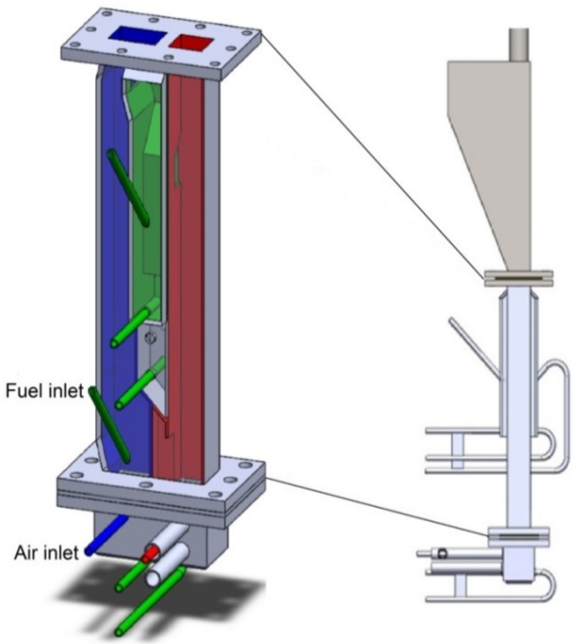
Phase #1

Examination of 5 oxygen carrier particles produced directly from different manganese ores in laboratory reactor.

Phase #2

Experimental campaign with manganese ore as bed material in Chalmers research boiler.

Phase #1 – Laboratory Reactor



Cross section: *25 mm times 40 mm*
Bed height: *130 mm*
Fuel flow: *0.3-0.5 l/min*
Air flow: *4.1 l/min*
Temperature: *800-950°C*
Pressure: *Atmospheric*
Solids inventory: *140-200 g in combustion chamber*
Fuel : *CH_4 with or without 3% NH_3 as NO precursor*

Aim

Characterize Mn-based oxygen carriers with respect to:

- Reactivity and emissions
- Attrition
- Agglomeration
- Physical properties

Expected output

- Verification of key concept
- Input about upscaling
- Improved understanding of manganese ores as OC

Preparation of oxygen carriers

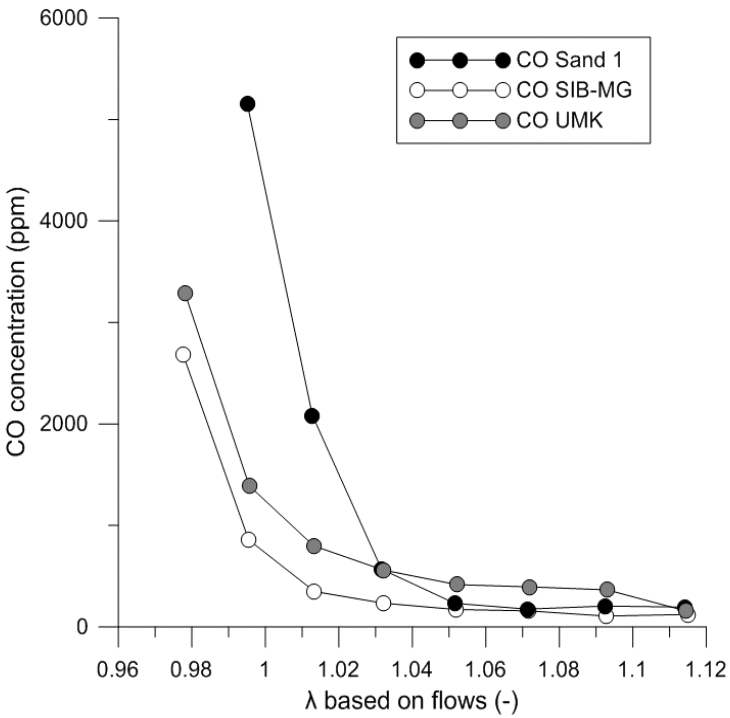
Material	Mn	Fe	Al	Si	K	Ba	Ca	Mg	P	Ti	Mean particle size (µm)	Bulk density (kg/m^3)
NCH	42.6	12.0	0.2	1.6	<0.1	1.5	6.2	0.6	<0.1	<0.1	139	1130
SF-AUS	51.3	10.0	2.3	3.6	1.2	<0.1	0.9	0.2	0.1	0.1	158	1990
SIB-MG	66.4	3.0	3.1	1.4	0.7	0.3	0.1	0.1	0.1	0.1	142	1880
SIB-SF	46.2	5.2	3.4	3.7	1.0	0.2	1.9	0.3	0.1	0.2	234*	1840
UMK	62.0	3.8	2.0	0.9	0.6	1.8	0.2	0.3	0.1	0.1	139	1370

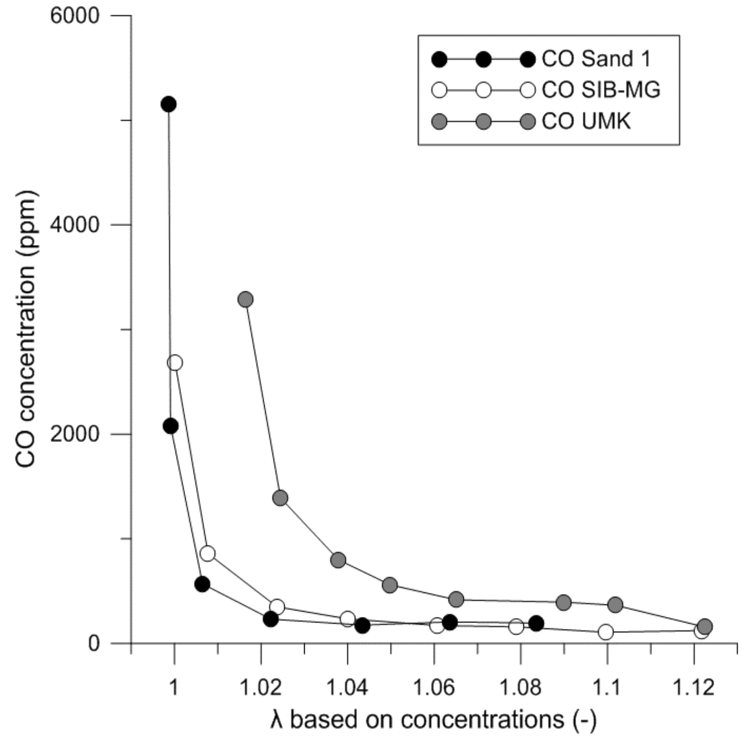
Elemental composition in wt% after heat treatment at 950°C, balance is oxygen.
Mean particle size and bulk density after crushing, heat treatment and sieving.

Examined materials included: i) high grade ore (UMK), ii) medium grade ore (NCH), iii) pre-calcined medium-grade ore (SIB-SF), iv) high-grade manganese product (SIB-MG), v) ore sintered with slag (SF-AUS).

Noticeable difference in density between the samples, which has practical implications with resect to fluidization and fluid properties.

Phase #1 – Laboratory Reactor





CO emissions as function of air-to-fuel-ratio (λ) calculated in two ways at 850°C.

- The bed is capable of providing oxygen, but we were not operating at steady state.
- Experiments with NH_3 indicated increased propensity for NO formation.

Output from phase #1

Conclusions:

- Feasible oxygen carriers could successfully be prepared directly from a range of manganese ores.
- Key characteristics such as density and resistant to attrition was adequate for operation in fluidized bed reactor.
- OCAC tests suggested that the concept worked as intended.

However:

- Existing reactor system was difficult to adapt for OCAC.
- Notably, being a system with two outlets made it difficult to close the species balance when using an oxygen carrier.
- Operation at steady state conditions was hard to achieve.
- Solid fuel system would have resulted in more relevant results.

Phase #2 – Chalmers research boiler

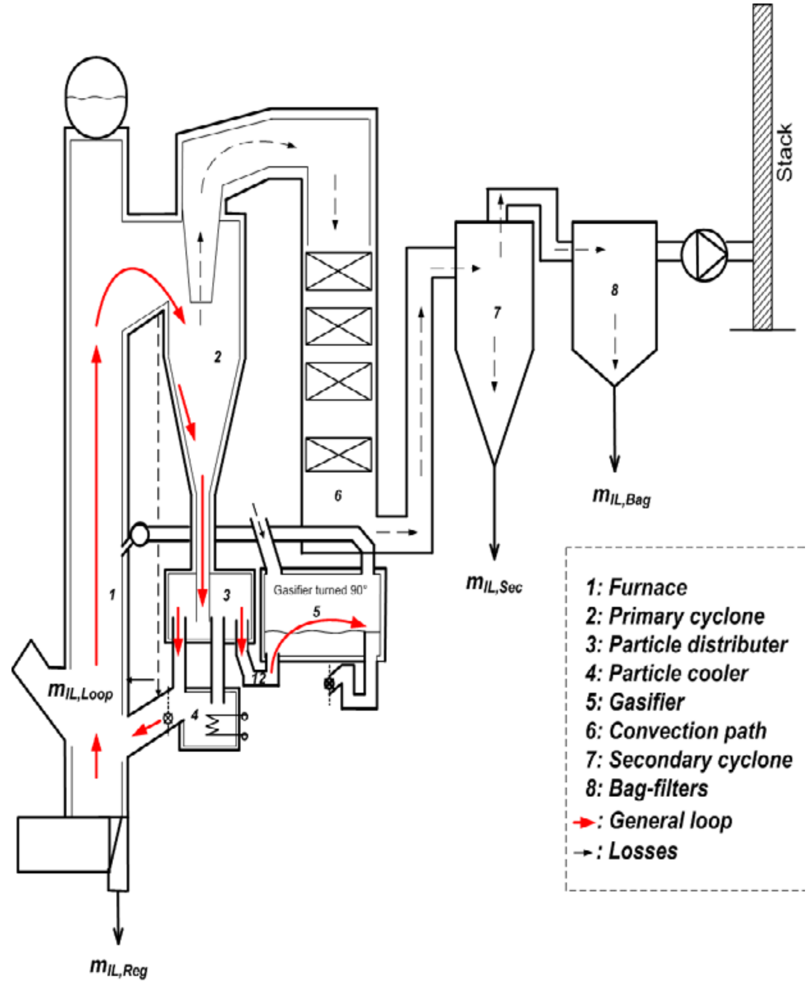
- Perform an experimental campaign with manganese ore as bed material in Chalmers research boiler.
- Provide real operational data from a real boiler.
- Provide a good indication about issues such as agglomeration and attrition.
- Examine and demonstrate large scale logistics of oxygen carrier particles.

Phase #2

Experimental campaign with manganese ore as bed material in Chalmers research boiler.

About Chalmers research boiler

- Semi-commercial plant operated by Akademiska Hus AB and excess heat sold to Göteborg Energi.
- Circulating Fuidized Bed (CFB) boiler.
- 12 MW_{th} with coal or 8 MW_{th} with biomass.
- Intergraded with an indirect gasifier (2-4 MW_{th}).
- Solids inventory ≈2500 kg plus ≈2000 kg in the gasifier.
- Roughly 100 measuring holes in boiler.
- Sampling of ash and bed material possible.
- Analysis equipment for gas concentrations, temperature, pressure etc.



Large batch of oxygen carrier

Characteristics of the large batch of oxygen carrier for Chalmers Research Boiler.

Material	SIB-SF
Chemical composition	46.2% Mn, 5.2% Fe, 3.7% Si, 3.4% Al, 1.9% Ca, 1.0% K, 0.3% Mg, 0.2% Ba, 0.2% Ti, 0.1% P, balance O
Provided as	Sintered lumps, a few cm in diameter
Treatment	Crushing, multi-step grinding, sieving, dedusting
Product sieved to size	100-400 µm
Mean particle size	200 µm
Bulk density	1840 kg/m^3
Batch size	12.1 tonnes
Yield in production process	≈ 50%

SIB-SF was chosen for the large batch. This ore had the advantage that it was available directly in calcined form via a cooperation partner (Sibelco Nordic AB). It was grinded into particles by UVR-FIA, a German mining research institute.

The campaign

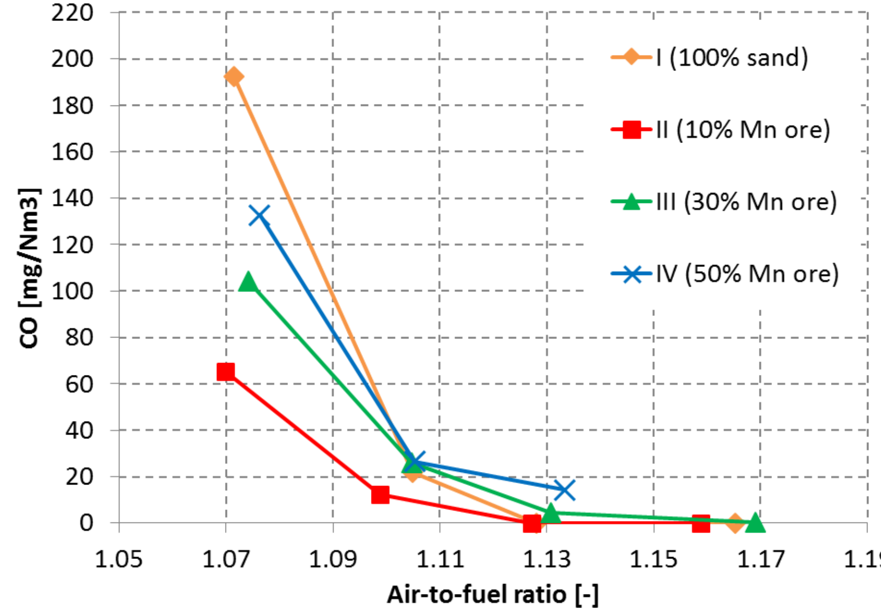
- Fuel was wood chips corresponding to 5-6 MW_{th}.
- Bottom bed temperature was set to 870ºC.
- Amount of bed material regulated to achieve 5.5 kPa pressure drop.
- Startup with clean boiler at the beginning of the firing season.
- Start with partial substitution, followed by operation with 100% manganese ore.

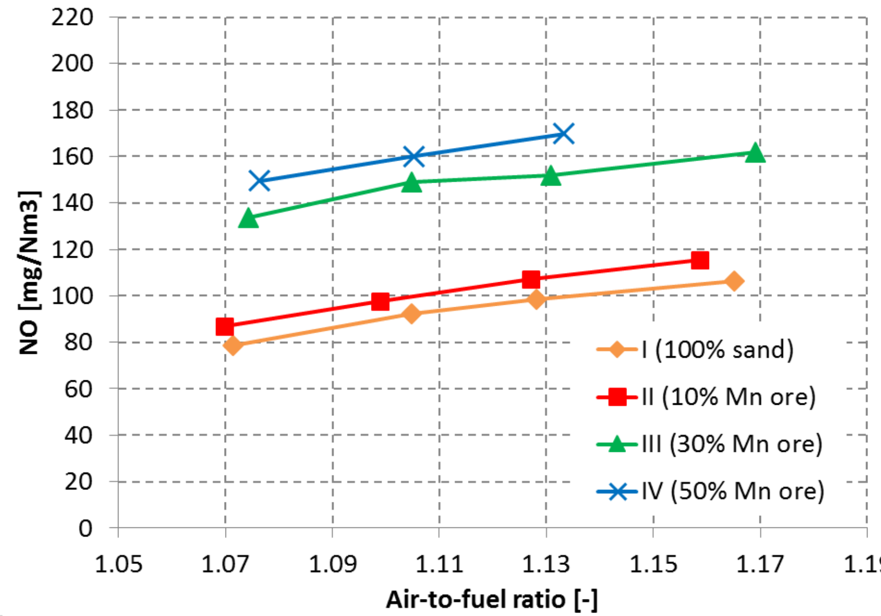
Overview over experiments performed in Chalmers Research Boiler.

Test	Day	Sand [wt%]	Mn ore [wt%]	Comment
I	1	100	0	Reference
II	2	90	10	
III	3	70	30	
	4	70	30	
IV	5	50	50	
Stop during weekend (day 6-7). This was necessary in order to remove material contaminated with sand and allow for operation with 100% manganese ore.				
	8		100	Start-up with Mn ore
V-VI	9		100	Also operation at 800°C
	10		100	
	11		100	
	12		100	
Operation with 100% manganese ore during weekend (day 13-14) by the plant operator (Akademiska Hus AB). No experimental activities.				
VII	15		100	Experiments with sulphur feeding
VIII	16		100	Regenerated bed, sulphur feeding

Partial substitution

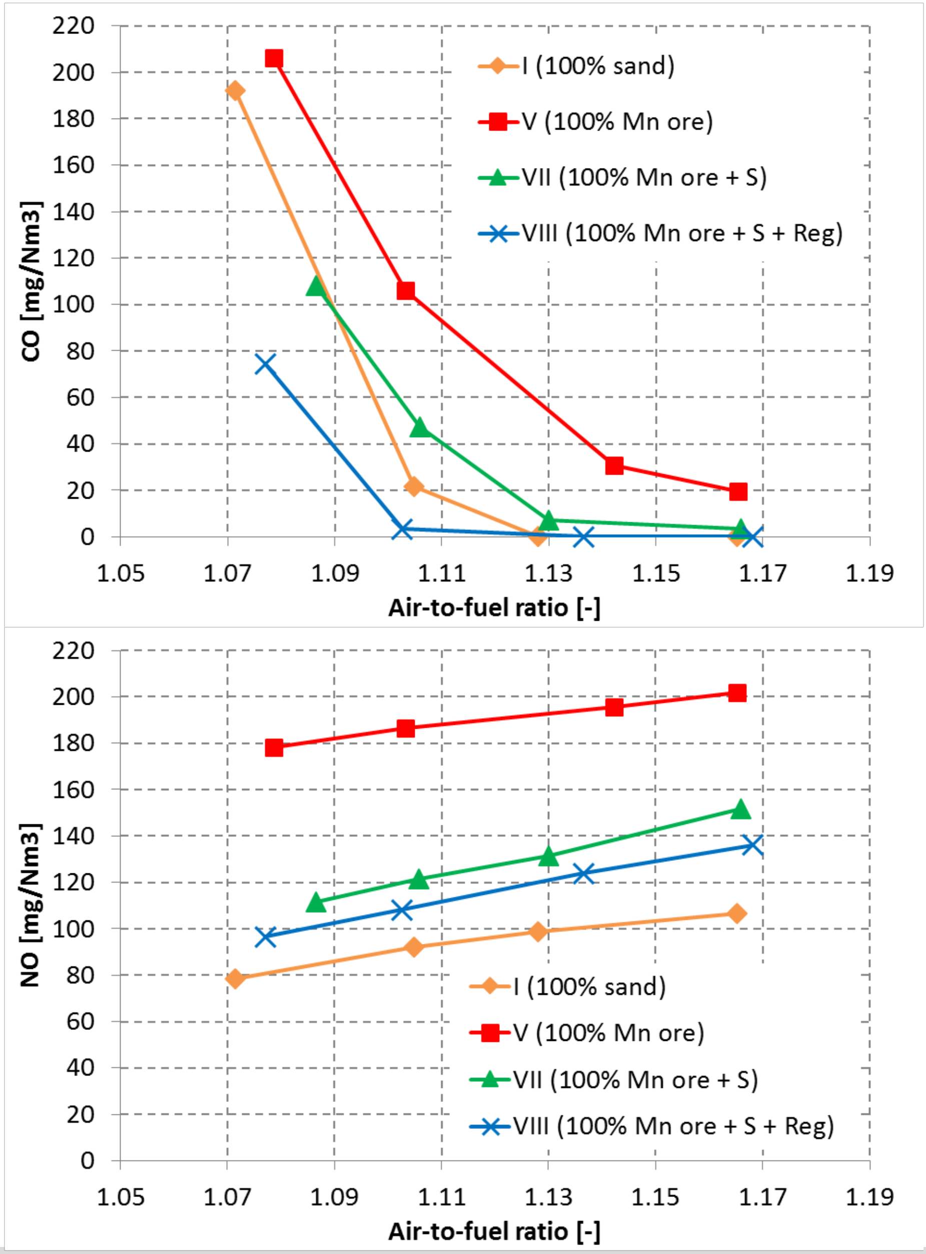
- Considerable effect on CO (≈70% reduction at λ<1.11) with as little as 10% substitution.
- Increased Mn-content did not improve the effect and the NO emissions increased.
- Increased Mn-content was achieved by removing bed material and replacing it with fresh manganese ore.
- Fresh ore had high K-content and sand was not regenerated, which may be the reason for declining combustion results as function of time.





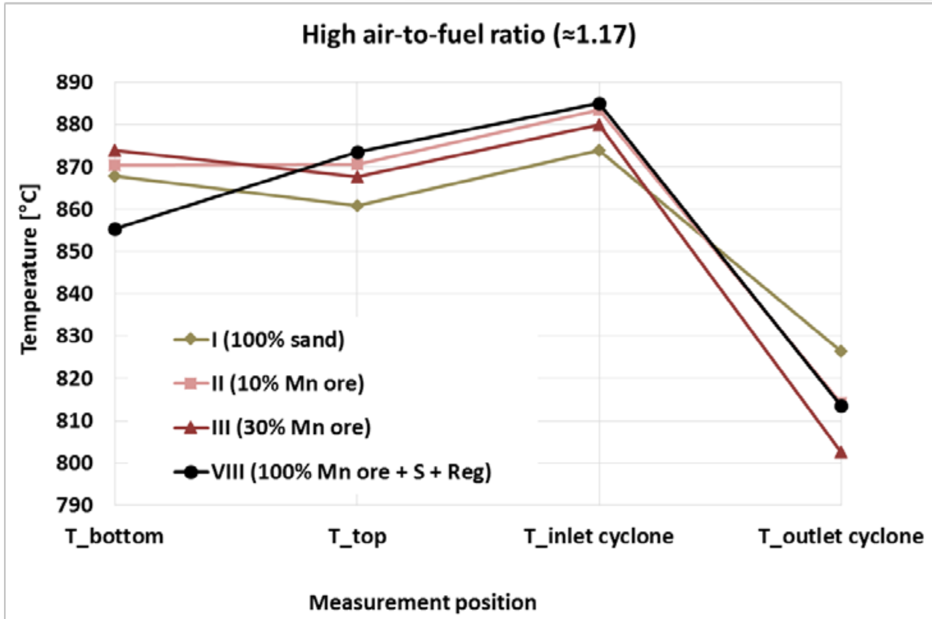
100% substitution

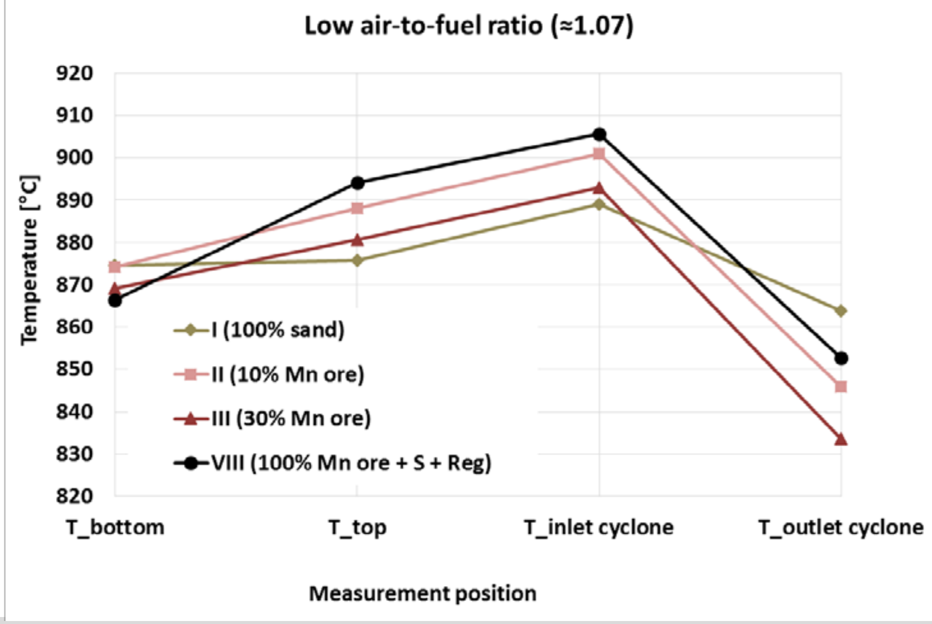
- Higher emissions of CO and NO compared to sand reference.
- But temperature profile still suggested enhanced conversion in the combustion chamber.
- This suggests poor conditions during final combustion stage.
- Sulphur feeding and partial regeneration of the bed resulted in greatly improved results.
- Results subject to interpretation. We link them to poor removal of alkali. The fresh ore has high K content and we had a finite amount of ore available.



Temperature profile

- Temperature drop over cyclone much higher than with sand reference in all cases, independent on emissions.
- This suggests that much less combustion take place in the cyclone.
- This is especially clear for when 100% manganese ore is used.
- Suggests that problems related to emissions are related to the final combustion stage (which is what determines emissions, at least for CO).



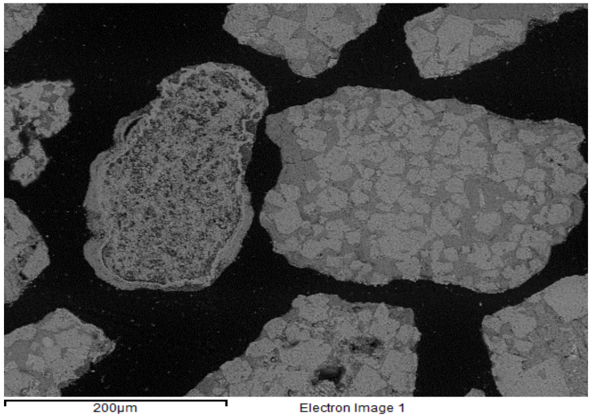


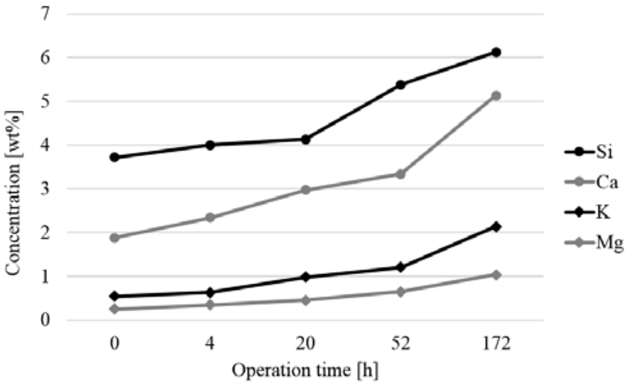
Observations with respect to general operability

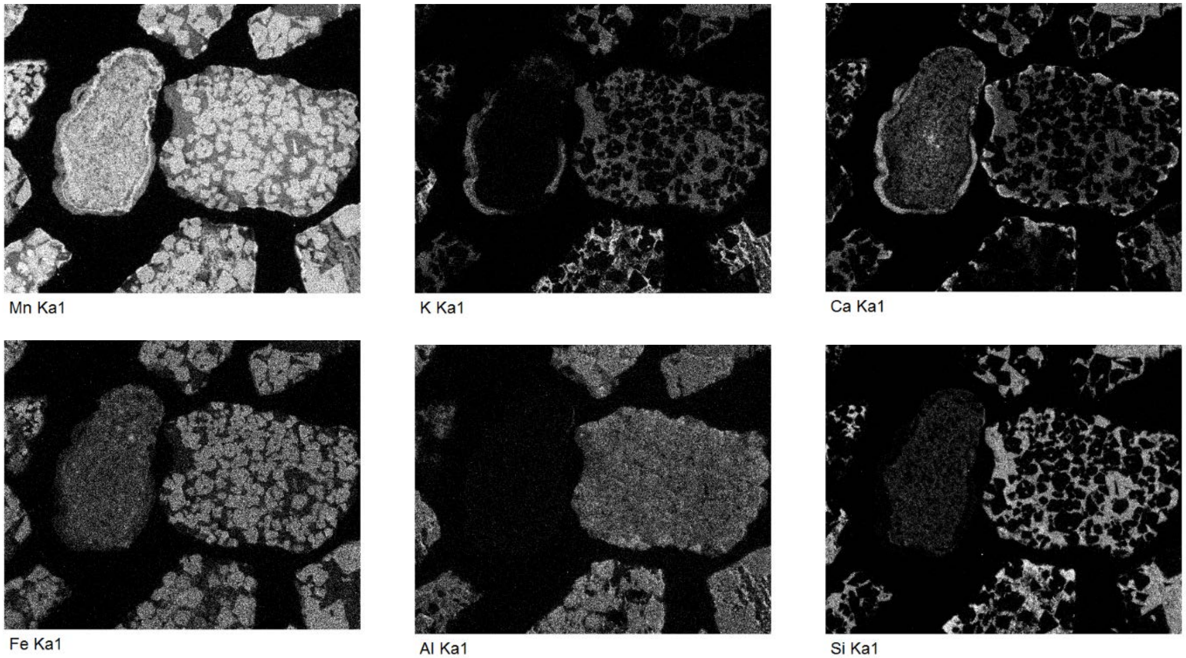
- Plant operated with wood chips for 23 days with >10% manganese ore.
- Bed temperature was 870ºC, near the temperature limit for silica sand.
- No practical problems related to agglomerations were encountered.
- No regeneration between day 8 and day 15, would likely have resulted in agglomeration with silica sand.
- Agglomeration tests at SP suggests that manganese ore could be more resistant to agglomeration than silica sand. Fresh ore did not agglomerate even at the maximal temperature of 1100ºC.
- The 10% mixture operated with biomass showed minor tendencies towards agglomeration at 876ºC, apparent agglomeration at 941ºC.
- The attrition rate was very low (basically too low to measure).

Post-experimental analysis of oxygen carrier

Currently ongoing. Not covered by the project hence the slow progress.







Material not homogeneous with particles containing Al behaving very differently compared to material without Al.

Conclusions

- From a practical point of view manganese ore is a viable bed material for fluidized bed boilers.
- At certain conditions very considerable improvements with respect to reduced CO emissions could be achieved.
- At other conditions emissions of CO and NO was higher compared to reference experiments with sand.
- The temperature profile of the boiler suggests that the manganese ore worked as intended at all occasions. This means that emissions were affected by poor burnout in the cyclone.
- Both low-level substitution and use of 100% manganese ore could be viable.
- Strategies for bed regeneration, removal of ash elements and reuse of bed material needs to be considered and developed.

Current and future plans

Current projects:

- OCAC with ilmenite
  (ongoing project with E.ON, due to NDA I have to refer to 'improbed.com')
- OCAC for heat transfer to tube reactors located inside bubbling fluidized bed
  (ongoing project with Haldor Topsøe, funded by Energimyndigheten)
- CLC of biomass to generate 'negative CO_2 emissions'
  (ongoing project with 6 partners, funded by Nordic Energy Research)

Future direction:

- Dedicated experimental reactor for OCAC with biomass
  (under construction)
- Use of waste streams from steel-making as bed material in OCAC/CLC
  (industrial partner exists but at the moment no major project)
- CLC of biomass as a method to eliminate high temperature corrosion
  (no infrastructure for CO_2 transport and storage needed)

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