Energy research Centre of the Netherlands

EERA Bed Material Workshop

Istanbul , April 18th 2012

www.ecn.nl

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Part 1

Introducing EERA

European Energy Research Alliance

Background on EERA

SET-plan

- The technology pillar of the EU's energy and climate policy
- Aimed at accelerating innovation in cutting edge European low carbon technologies to achieve the EU 2020 targets and 2050 vision (80-95% GHG reduction)

- Two main instruments:
  - EII's: European Industrial Initiatives
  - EERA: European Energy Research Alliance

EERA

Initiative by 10(+5) leading European R&D institutes

Aim: accelerate development of new energy technologies

- Strengthen, expand and optimise research capabilities
- Decrease fragmentation, harmonise national and EC programmes
- Draw on results from fundamental research
- Hand over mature technologies to industry driven research (industry groupings)

Participation in EERA open to all research organisations, but:

- Not just a membership; need to bring in significant R&D capacity

Based on **<u>own</u>** resources (not: additional budgets EC)

Between fundamental and industry driven research

www.eera-set.eu

EERA Membership types

Partners

- Have a seat in the Executive Committee
- Collective responsibility to ensure good overall functioning of EERA
- Fee: 10k€/year

Participants

- Take part with at least 5 py/y in at least one Joint Programme
- Have a seat in the Joint Programme Steering Committee
- Collective responsibility to ensure good functioning of JP
- Fee: determined per JP

Associated Participants

- Take part with less than 5 py/y in at least one Joint Programme
- Contributes to Joint Programme via a Participant
- Fee: determined per JP

Joint Programming

EERA is not a toy of the EC, it should primarily address your interest

- Cooperation you should have done (or wanted) anyway
  - Optimising the use of your scarce resources
- EERA only facilitates
- But: EERA offers the opportunity of to influence EC programmes
- In future joined projects are aimed for

Part 2

The requirements and main themes on bed materials

Requirements on bed materials for fluidized bed systems

In General for Combustion/gasification

- Good fluidization behavior of grains (uniform in size and semi-spherical)
- Sufficiently hard /attrition resistant
- Rel. high melting temperature to avoid agglomeration
- Non-pollutant or hazardous (chemically)

- Cheap in use (considering price/ton and use/GJ produced)

Other possible bed material properties

Functions bed material in indirect gasifier (combined gasification and combustion reactor with circulating bed material):

- Transport of heat to gasifier
- Possible catalytical reduction of tar in gas
- K/S/Cl adsorptie on or in the bed material grains
- Catalytic WGS shift promotion
- CO_2 transport from the gasifier to the combustor
- O_2 transport from combustor to gasifier
- Carbon/tar transport from gasifier to combustor

The choice of the right bed material can help to optimize the gas composition and avoid operational problems.

Experimental work at the ECN Milena gasifiers

Choose 1 fuel and vary the bed material

Lab scale:
- Sand
- Dolimites/sand
- Olivines

•Effects on gas
•Tar
•WGS
•Attrition

Pilot plant:
- Sand
- Olivines
- Dolomites/sand

•Use in practise
•Scale-effects

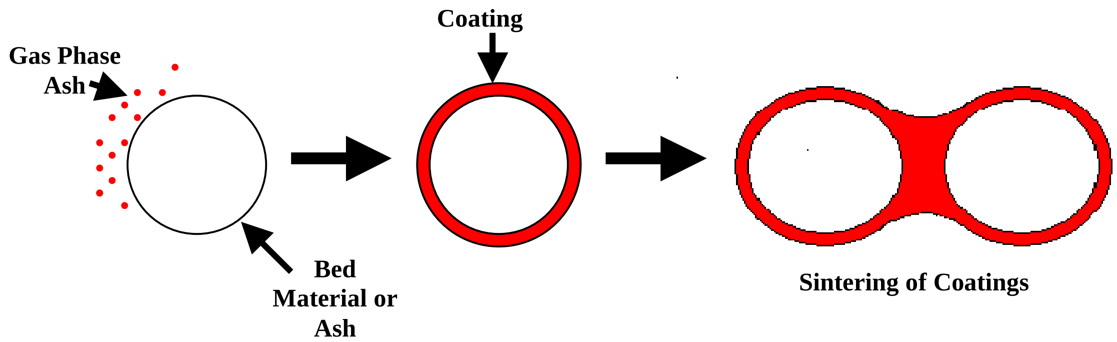
Part 4

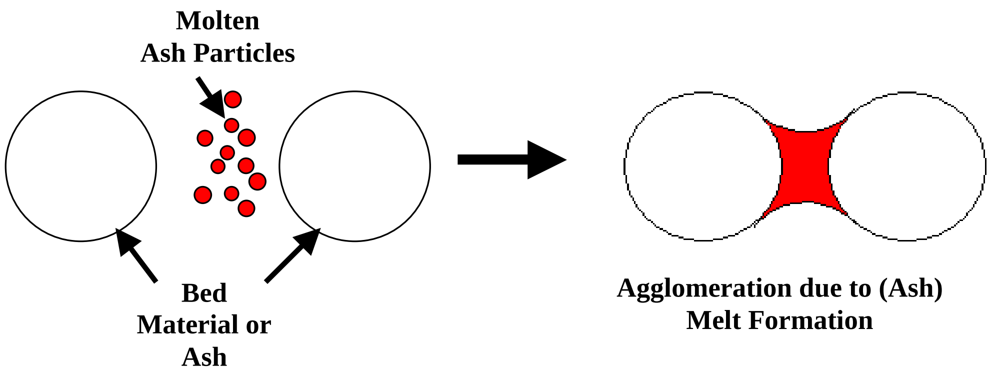
Coating build-up on bed material grains

Agglomeration and the possible effect for catalytic processes

Dr. Rianne Visser, ECN, The netherlands

Knowledge on agglomeration in FB combustion and gasification : Two extreme mechanisms





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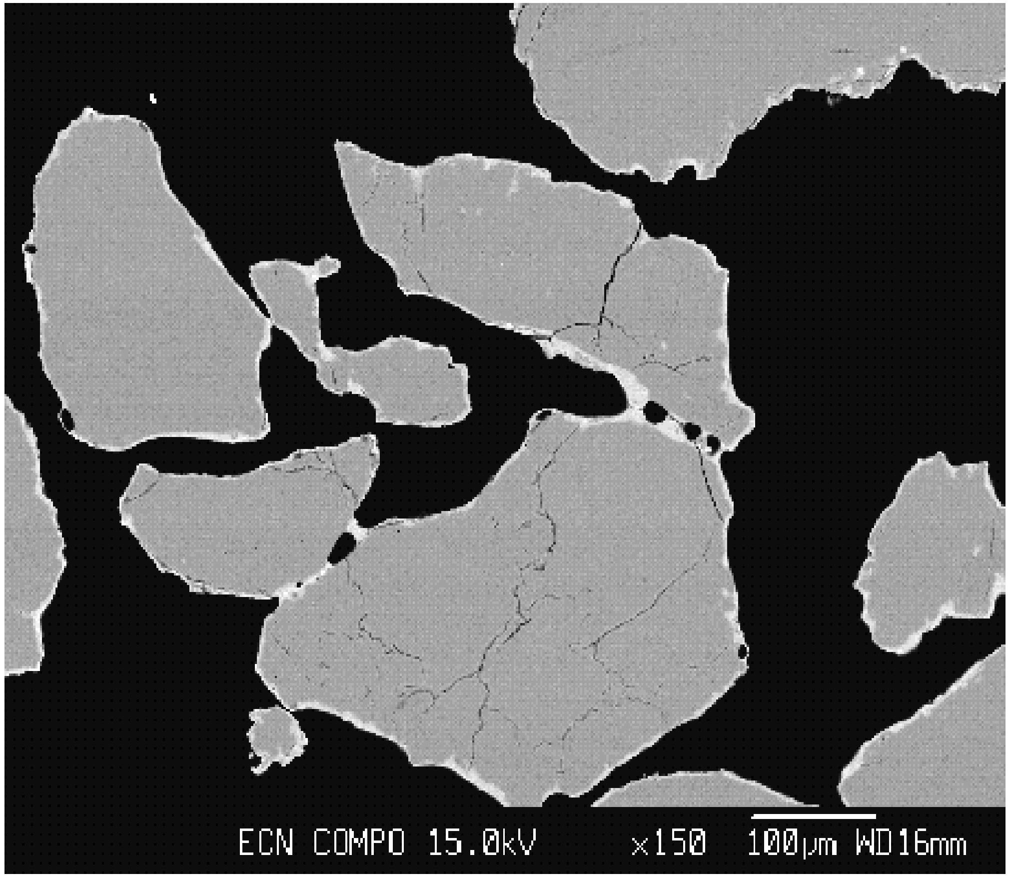
Focus on "Coating induced agglomeration"



SEM-image of
bed material section.

Quartz sand after gasification of wood

Agglomeration due to coating formation

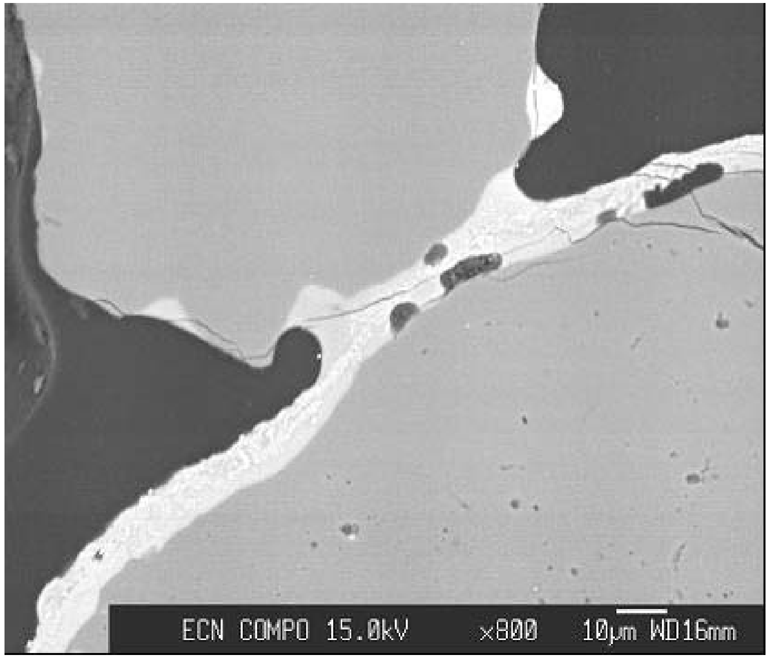
Coatings are white rims

Predominant composition
Coatings (K,Ca)-silicates

Samples commercial scale installation:
Good comparison of lab-scale and commercial scale samples

Quartz bed material and waste wood

Bed material is replaced continuously



Thick coatings and sintering of coatings

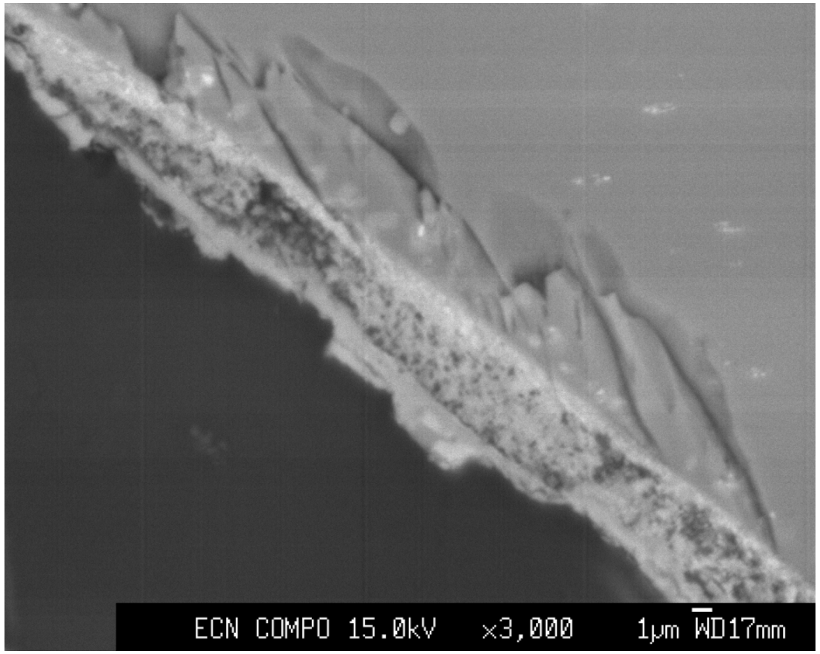
Coatings on bed material and catalytic activity

To be considered:

- Interaction of bed material with fuel ash components, both agglomeration and coating formation possible resulting in “poisoning catalytic activity” ?

- Composition of a porous coating could have a positive effect on water gas shift reaction and gas composition

- Activation/deactivation catalytic bed material due to alternating oxidizing/ reducing gas conditions?
  Are the residence times sufficient?



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Thank you for your attention

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What did we learn from the ECN Milena tests

- Different ratios of quartz sand/dolomite
- Comparison of dolomite versus olivine (general)

- Comparison of the various olivines
  - Why are the effects of one olivine so different from another?
    - Origin of the mined material
    - Pretreatment of the mined materials?
    - Is there anything we can say about the relevant (catalytic) processes.

Comparison between dolomite and olivine

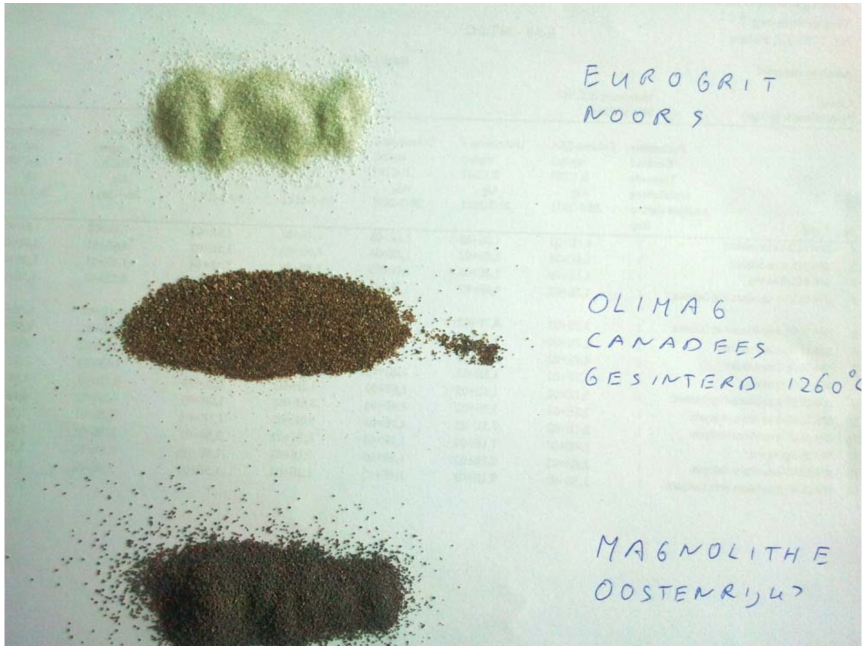
Olivine	Dolomite
Hardness OK	Too soft as FB bed material
Volume refreshment rate small	Refreshment rate high
Price rel. high (especially with pre-treatment)	Low price
Price/ton x volume/time determines the cost of use	
Chlorine/sulphur capture low	Cl and S capture high
Tar reduction depends on type of olivine and pre-treatment	Tar reduction high
No fines problem downstream/ no fouling of bed material	High quantity of fines downstream/fouling

Different olivines used in lab scale (30 kWth)

Three types of olivine tested:

- Pretreated olivine from Austria and Canada
- Untreated olivine from Norway

Different results suggest that the one olivine is unlike the others.



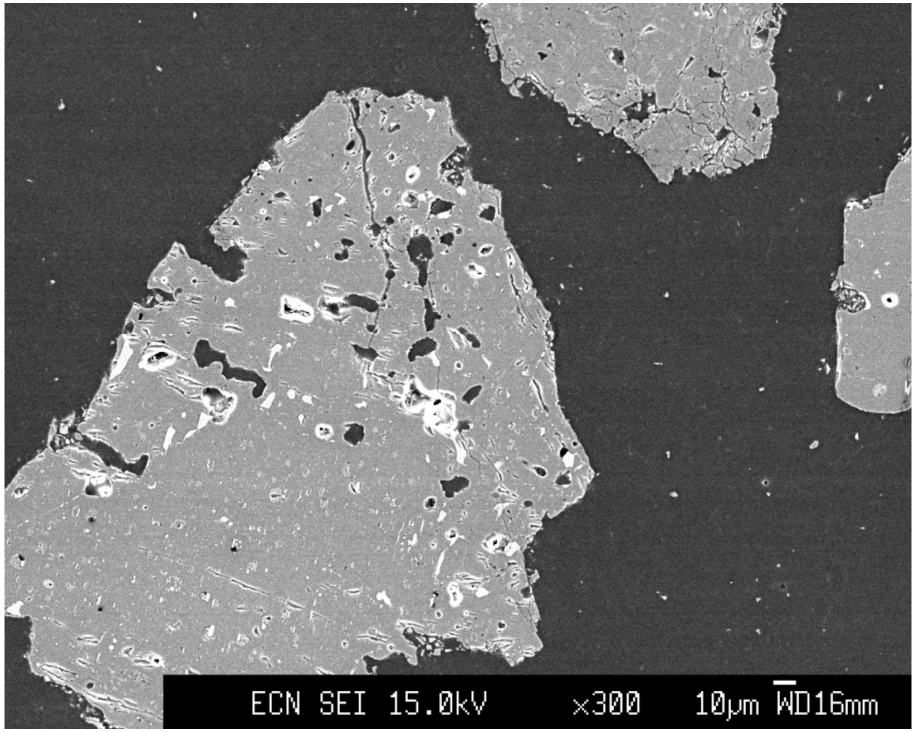
Why the one olivine isn't the other

Three types of olivine	Norwegian	Canadian	Austrian
Origin	Dunite (olivine) Mine, very pure	Residue from asbestos mining. Containing serpentines	Residue from Cr-mining (prob. containing hydrates as well)
Appearance	Solid grains, good hardness Light green	Brownish material, containing some porosity	Brownish material, containing some porosity
Pre-treatment	None	1260 °C/2 hours	1600 °C/4 h
After oxidation /microscopy info	Some iron excluded and some Fe-minerals	Some iron excluded and some Fe-minerals	Some iron excluded and some Fe-minerals

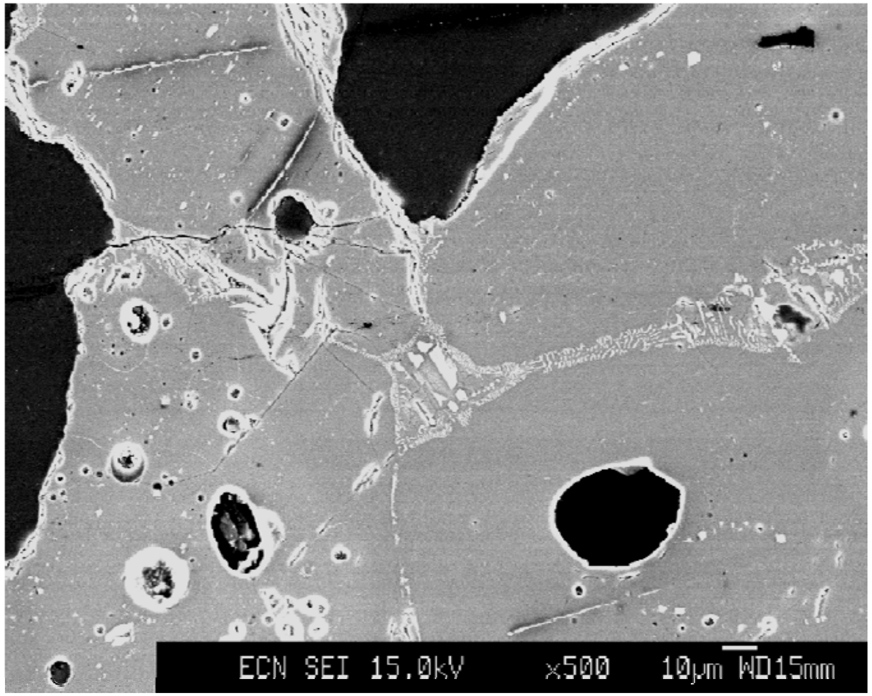
Austrian olivine as received from the supplier

Fairly porous material with partially segregated iron both internally and at the rim.

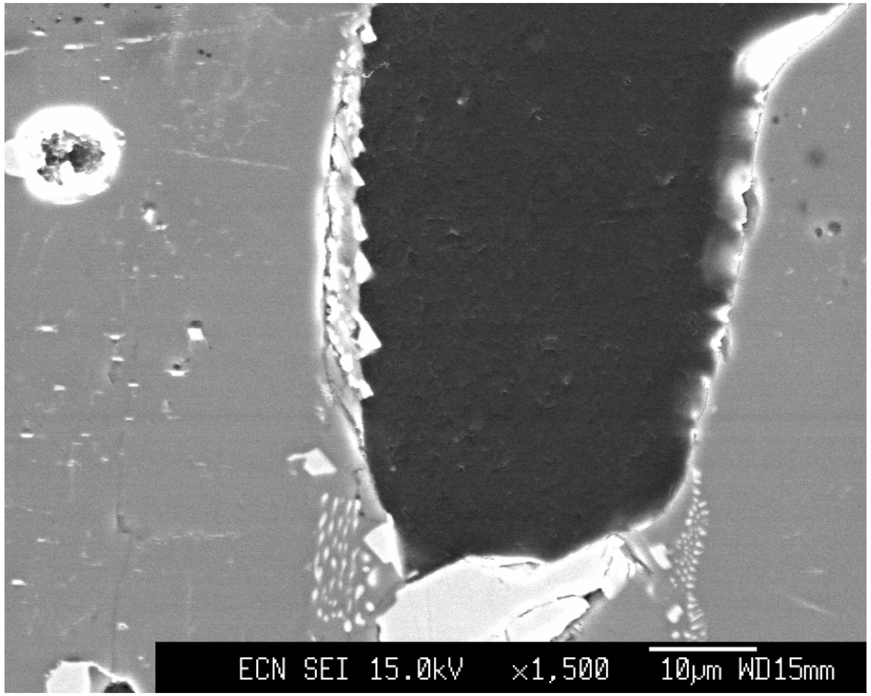
Supplier has sintered material already at 1600 °C for 4 hours and subsequently milled to desired grain size



Austrian olivine oxidized at 1600 oC/4 h at ECN



Segregation of Fe (as FeO) to outside surface and internal zones (next fractures?)



Detail of Fe-segregation at 1500 x

Iron as oxygen carrier in olivine

Oxidation of iron(II) to iron(III) results in rejection of Fe-oxide from olivine plus formation of amorphous silica (Champness, 1970).

(1) $(Mg,Fe)_2SiO_4$ + ***O_2*** → $Mg_2SiO_4 + Fe_2O_3$ + *$SiO_{2\,amorf}$*

Reduction of iron (depending on pO_2, pH_2 and temperature) Swiercynski et al. 2006, at very low pO_2 or (log pCO_2 / pCO) suggest:

(2) $Fe_2O_3 + MgFe_2O_4$ → Fe0 + Fe(II) + MgO + ***O_2 for gas phase reactions***

However, Milena gas conditions show (log pCO_2 / pCO) that indicates iron is maximally reduced to FeO and not to the metallic state. Eq (1) can be partly reversed.

Iron chemistry in oxidation/reduction

--→ Oxidation ←Reduction --			
Fe°	FeO	Fe3O4	Fe2O3
Metallic iron	Wustite	Magnetite	Hematite
Metallic iron only	Fe^{2+} only	Fe^{2+} and Fe^{3+} sites	Fully Fe^{3+}
--→ oxygen consumption			
----------←oxygen donation---			

In olivine, under reducing conditions, part of the Fe that is reduced retreats into the olivine while part of the separated Fe_2O_3 can be reduced to Fe_3O_4 or FeO and oxygen comes free for gas phase reactions.

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Preliminary conclusions on olivine

•In general olivine as bed material can reduce the amount of tar in the gas compared to quartz sand.

•The main contribution is expected to be from Fe segregated to the surface and on the different oxidation states the Fe can be in.

•Various “olivines”, however, make a difference to the extent of tar reduction. Noticeably the higher the pretreatment temperature the better the tar reduction capabilities. The worst performer is the REAL olivine.

•The possible effects can be due to:

1. Oxygen transport
2. influence on CO-shift reaction
3. Catalytic tar conversion

Lab-scale experiments: summary results

	Sand	Olivine (Norway)	Olivine (Austria)	Olivine (Canada)	12% Dolomite in sand
Tar reduction	_ _	**o**	**+**	**o/+**	**+**
WGS shift	_	**o**	**o/+**	**o**	**+**
O2 transport	_	**o/+**	**+**	**+**	_
Carbon/tar transport	_	_	_	_	**+**
Attrition res.	**+**	**+**	**+**	**+**	_
Price	**++**	**o**	_	_	**+**

What topics could use further attention

The origin of “olivin” material and the pre-treatment make a big difference. Some systematic work on these issues is needed. Is olivine a good bed material or is sintered serpentine better?

Some lab-scale testing on elucidating which effects are occurring (oxygen transport, effect on CO-shift, direct catalytic reduction of tars or indirectly via WGS…..) under which conditions (expressed e.g.on log pCO2/pCO scale) in order to optimize further use.

Do (Ca-containing) coatings have a positive contribution on tar reduction and is this the effect we see coming up after some 2 or 3 days of operation?

Would it be feasible to push the pCO2/pCO to the stability field of metallic Fe?

And what benefits would that have?

Are the optimum conditions for tar reduction bed materials so different from the gasifier/combustor system that a separate reactor would be the wiser option.