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Gas-phase Alkali Interactions with Reactor Walls and OC in a Laboratory Reactor

Biomass combustion chemistry with oxygen carriers

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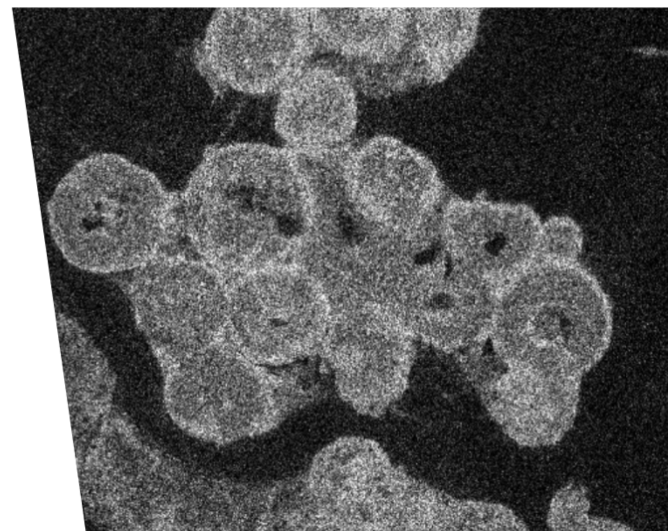
Alkali in CLC

- Biofuel contains high amounts of alkali metals
- Fouling and corrosion of superheater tubes
  - Poor heat transfer → efficiency loss


[Khan et al., 2009]

- Bed agglomeration
  - K, Na + Si forms glassy melts that bind bed material toghether



Alkali in CLC

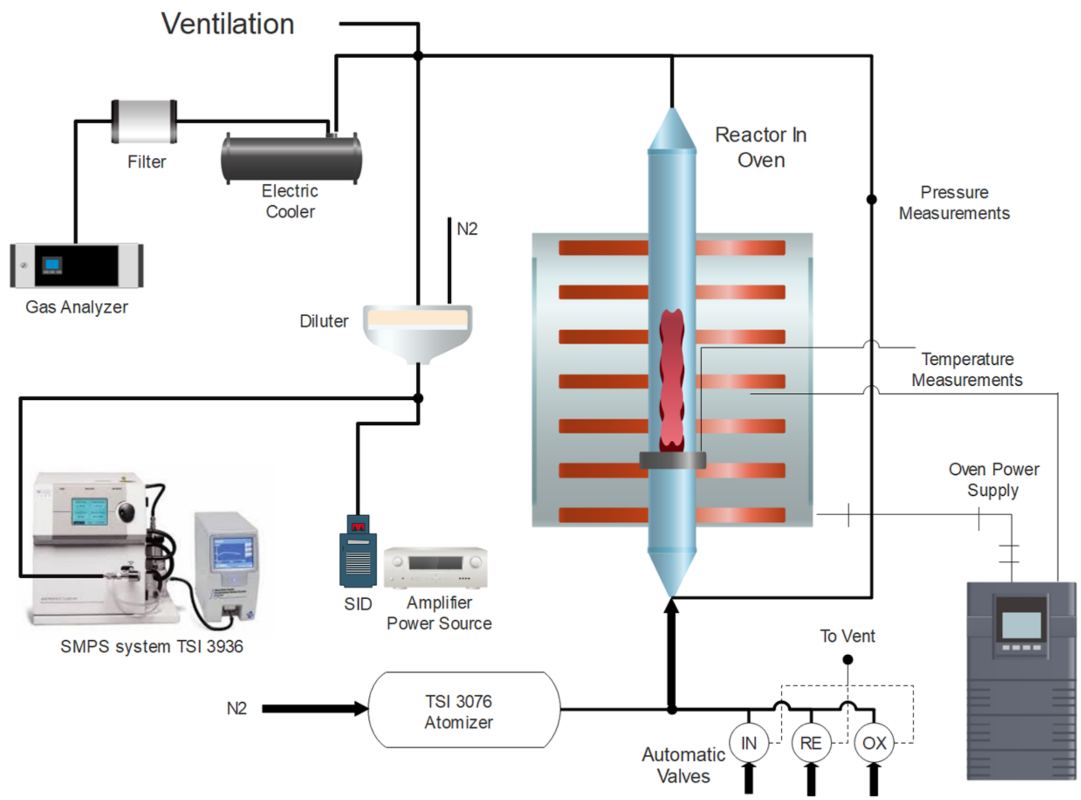
- Fuel converted in fuel reactor (FR), reducing conditions
  - Alkali chemistry in reducing atmosphere
- Main heat extraction in air reactor (AR), oxidizing conditions
  - Alkali chemistry in oxidizing atmosphere
  - Alkali release in AR
    - Desorption from OC
    - Can we ”clean” OC material from alkali by switching environments?

Alkali interactions with stainless steel and calcium manganite OC and the effect of:
- Different atmospheres
- Operating temperatures

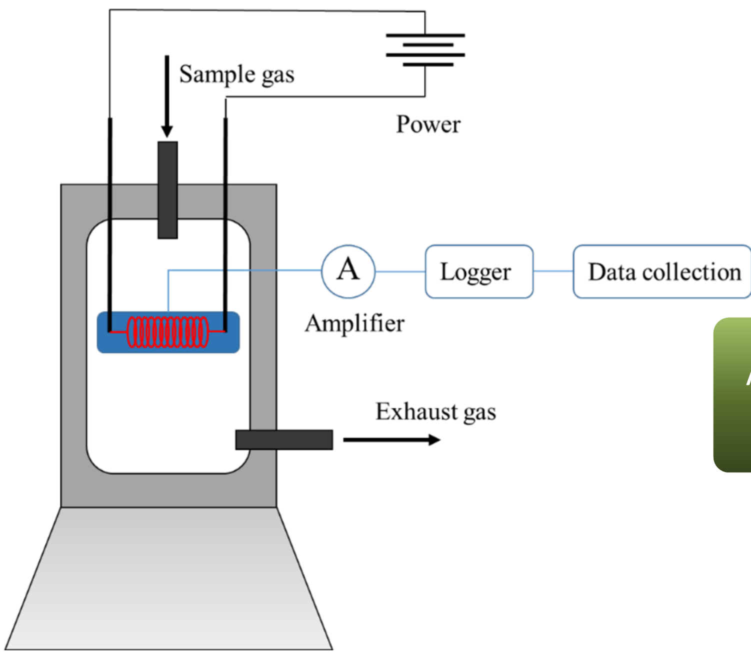
Fluidized bed - Laboratory reactor system

- Stainless steel reactor
  - Easy to change operating conditions
- Alkali aerosol atomizer
  - Injecting a continous flow of KCl

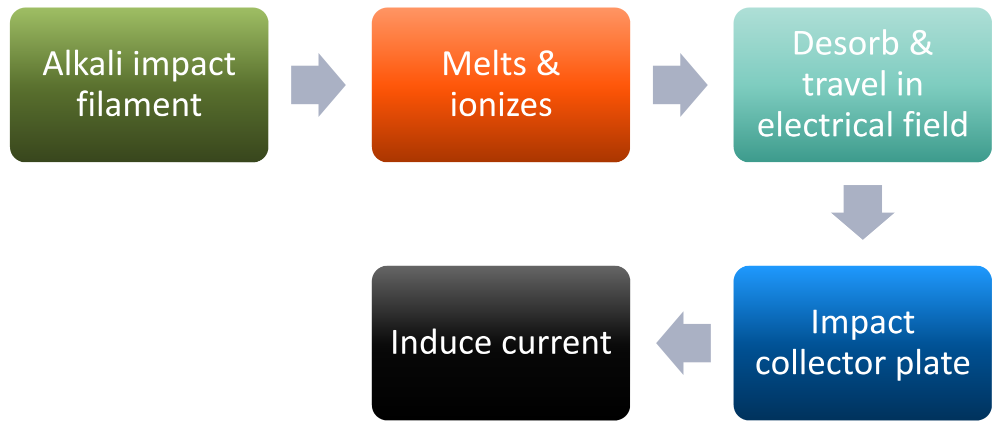
- Gas analyzer
- SMPS
  - Particle measurements
- SID
  - Alkali measurements



Surface ionization detector (SID)



- SID current ∝ alkali concentation
- Measure total alkali (K + Na)



Empty reactor system – establish background

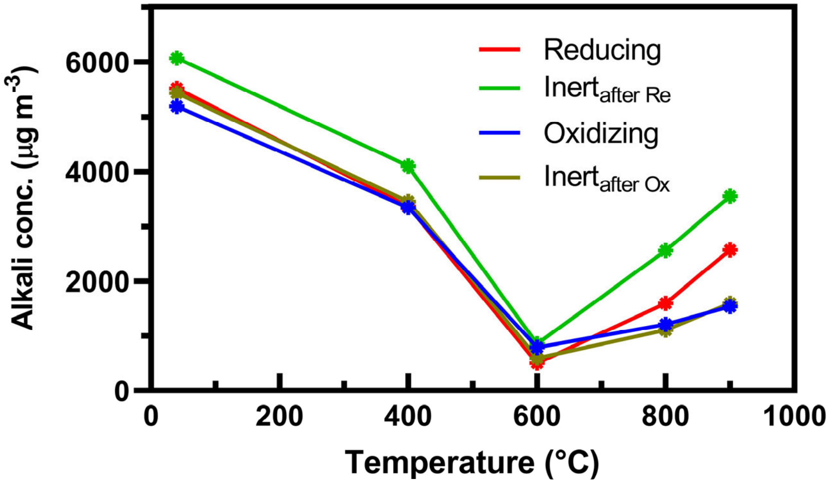
The alkali-wall interactions are large in an empty reactor system.

Operating conditions for empty reactor study:

- Temperatures: 25, 400, 600, 800 and 900 ºC
- Atmospheres:
  - Oxidizing: 3 % O_2 in N_2 – to mimic air reactor
  - Reducing: 6.5 % H_2 + 6.5 % CO in N_2 – to mimic fuel reactor
- Alkali aerosol concentrations: **0, 6 or 12 mg KCl m^{-3}**

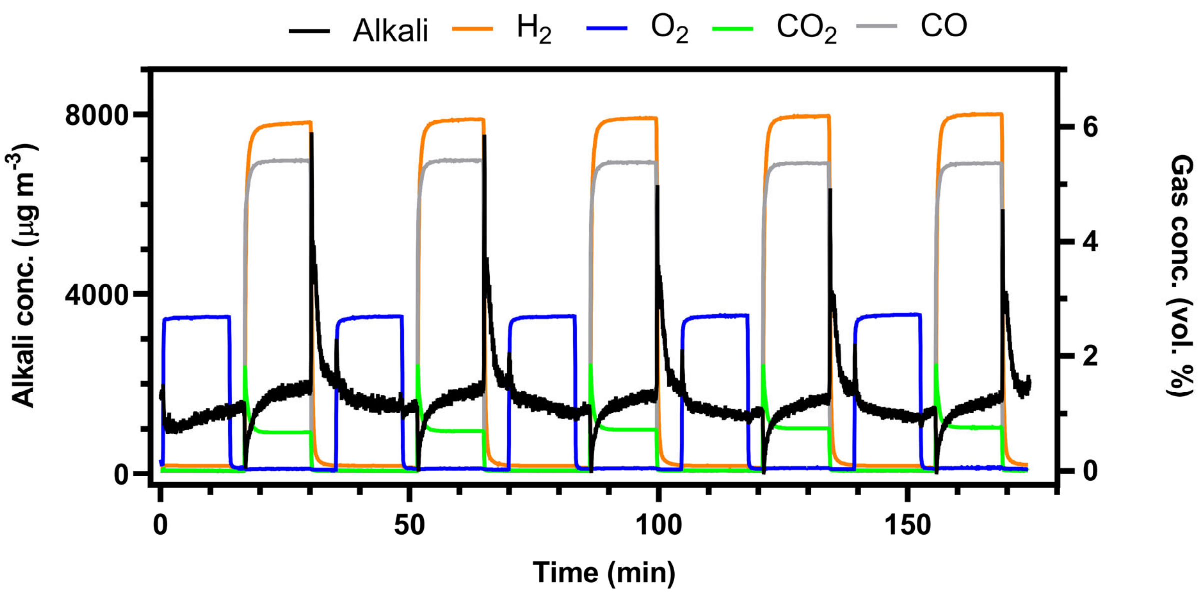
Empty reactor system – large wall effects

- Low alkali losses at 25-400 ºC
- Highest alkali losses at 600 ºC
- Alkali concentration recover at 800-900 ºC
- Alkali **particles** for T < 500 ºC
- Alkali in **gas-phase** for T > 500 ºC



Empty reactor system – consequtive redox cycles

- Large transient effects when changing gas atmosphere
- High losses when switching to reducing atmosphere
- Sharp release when switching from reducing to inert atmosphere

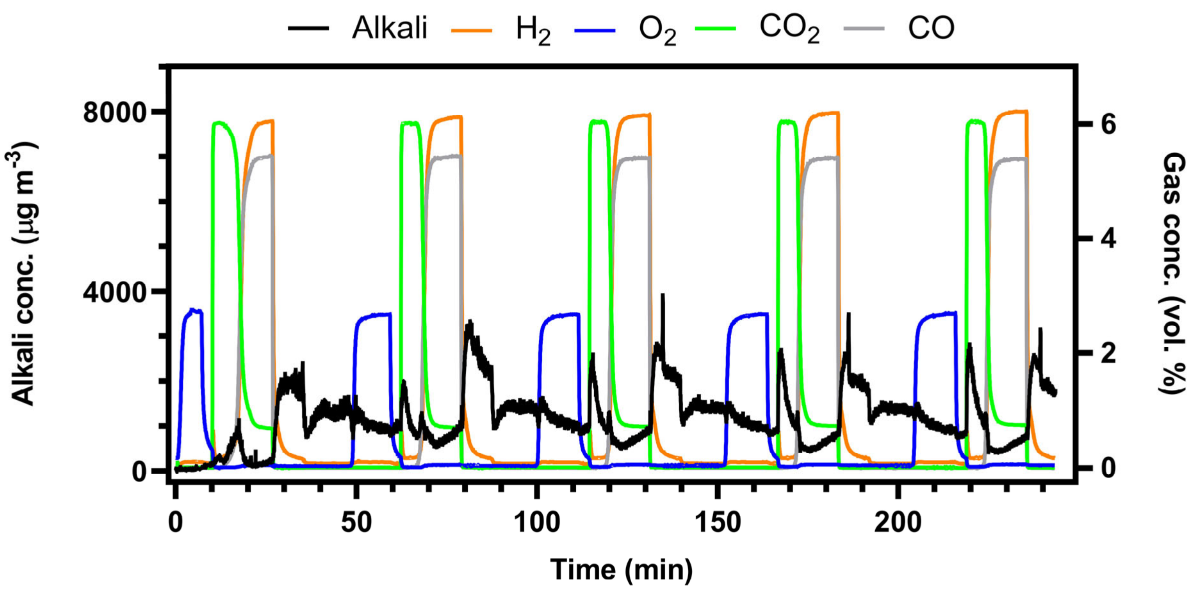


Fluidized bed – OC experiments

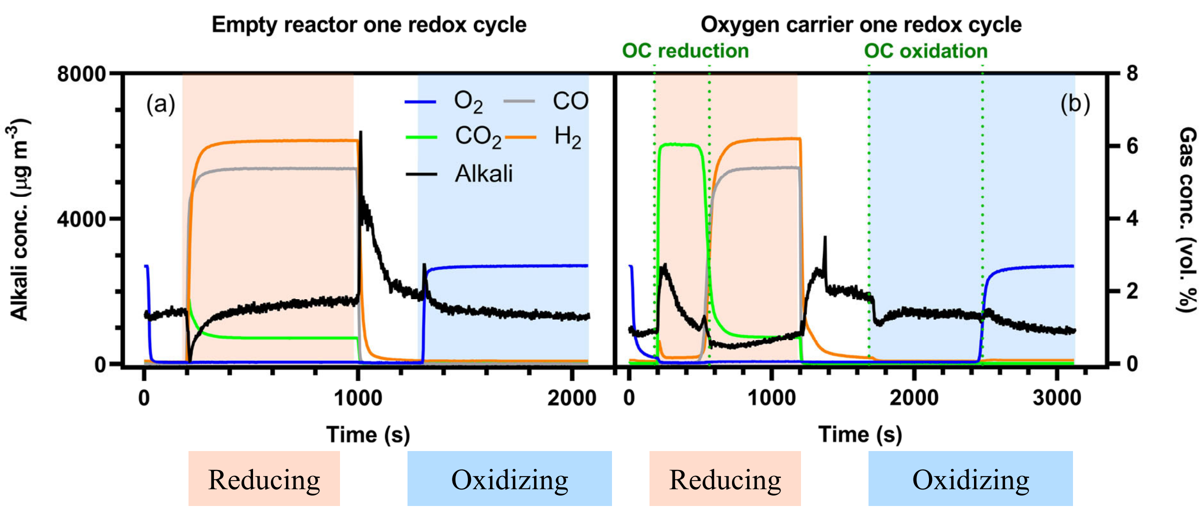
- OC bed material: $CaMn_{0.775}Ti_{0.125}Mg_{0.1}O_3$
  - Perovskite with CLOU properties
- Operating temperatures 800, 850 and 900 ºC
- Atmospheres:
  - Oxidizing: 3 % O_2 in N_2 – to mimic air reactor
  - Reducing: 6.5 % H_2 + 6.5 % CO in N_2 – to mimic fuel reactor
- Atmosphere durations:
  180 s inert → 1000 s reducing → 500 s inert → 1450 s oxidizing
- Alkali aerosol concentrations: **0, 6 or 12 mg KCl m^{-3}**

Oxygen Carriers – consequtive redox cycles

- Large transient effects when changing gas atmosphere
- High concentrations when switching to reducing and inert atmospheres

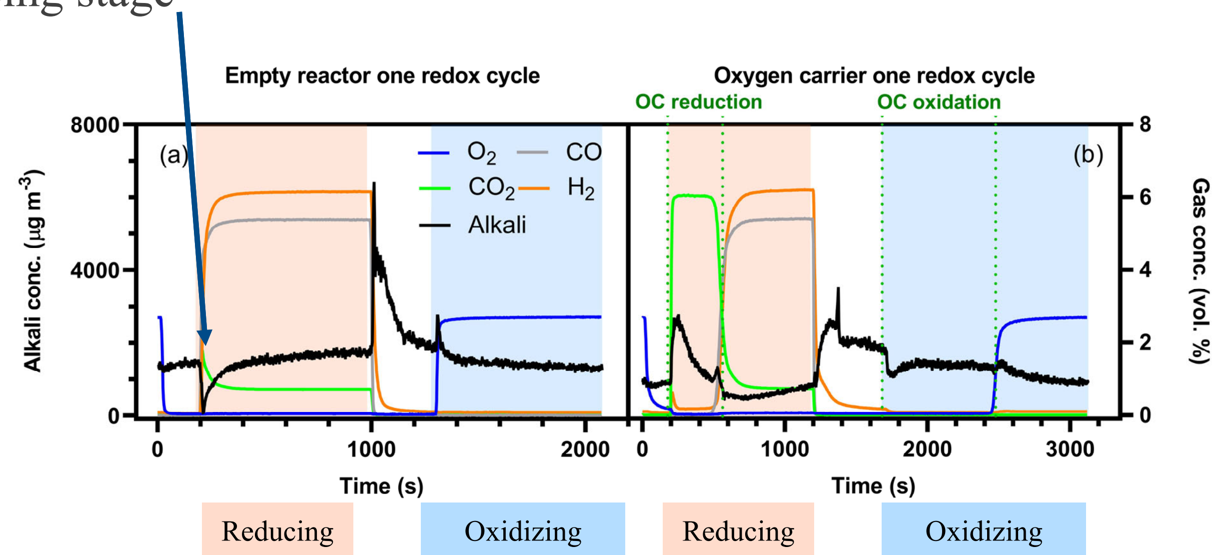


Comparison of empty reactor and OC fluidized bed



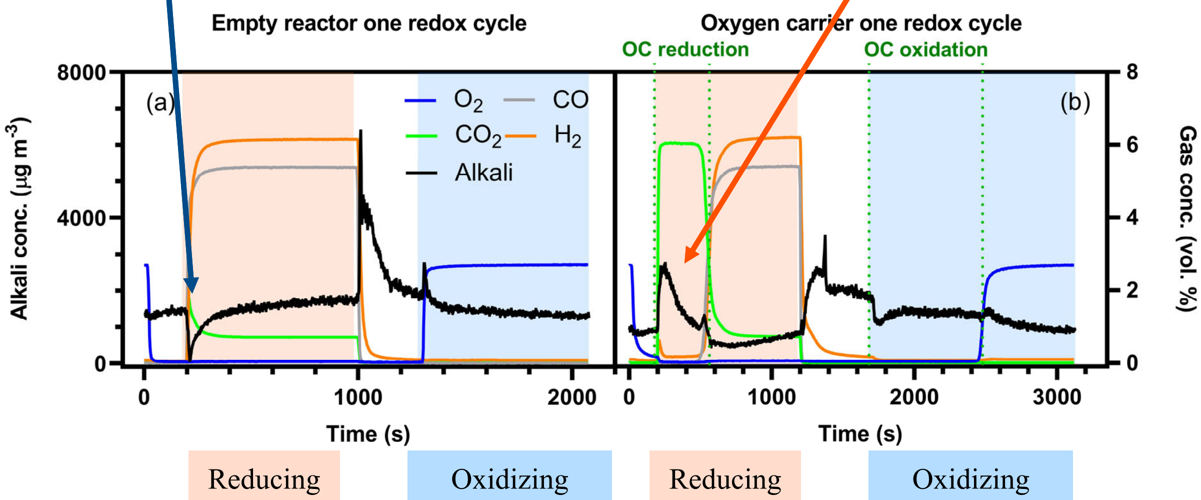
Comparison of empty reactor and OC fluidized bed

- High losses in the beginning of the reducing stage



Comparison of empty reactor and OC fluidized bed

- High losses in the beginning of the reducing stage
- OC release alkali in the beginning of the reducing stage



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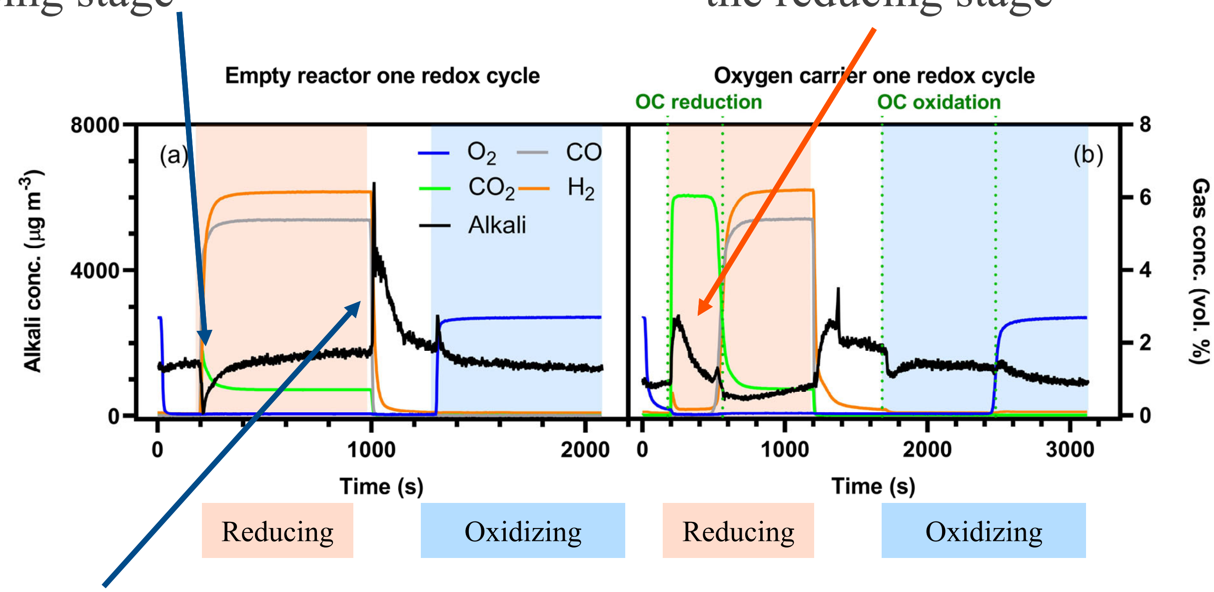
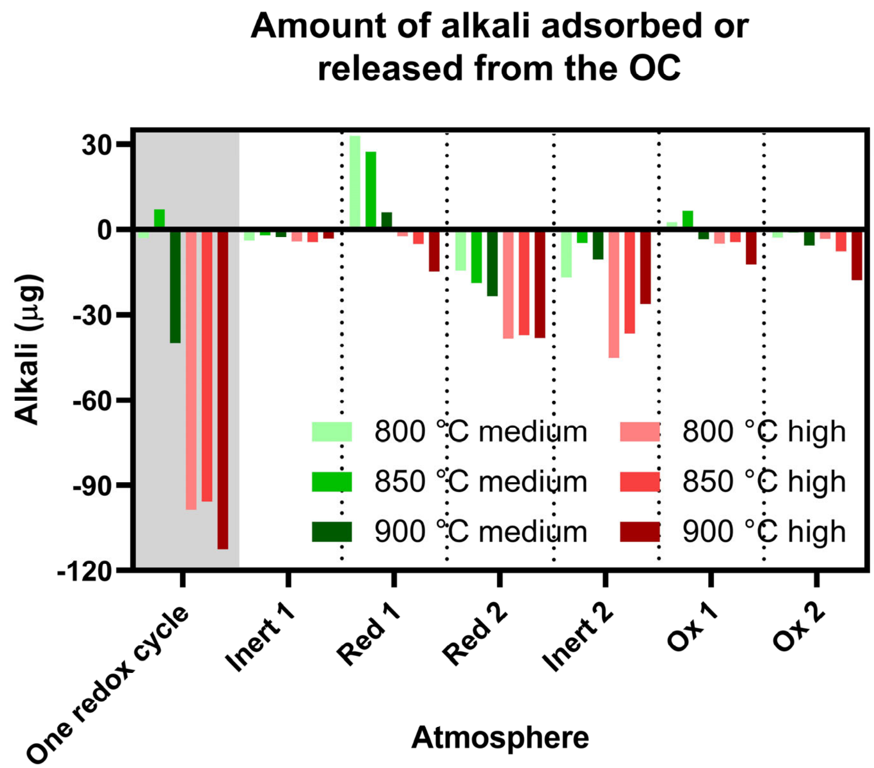


- Walls release alkali when switching to inert atmosphere

Empty reactor system – OC fluidized bed

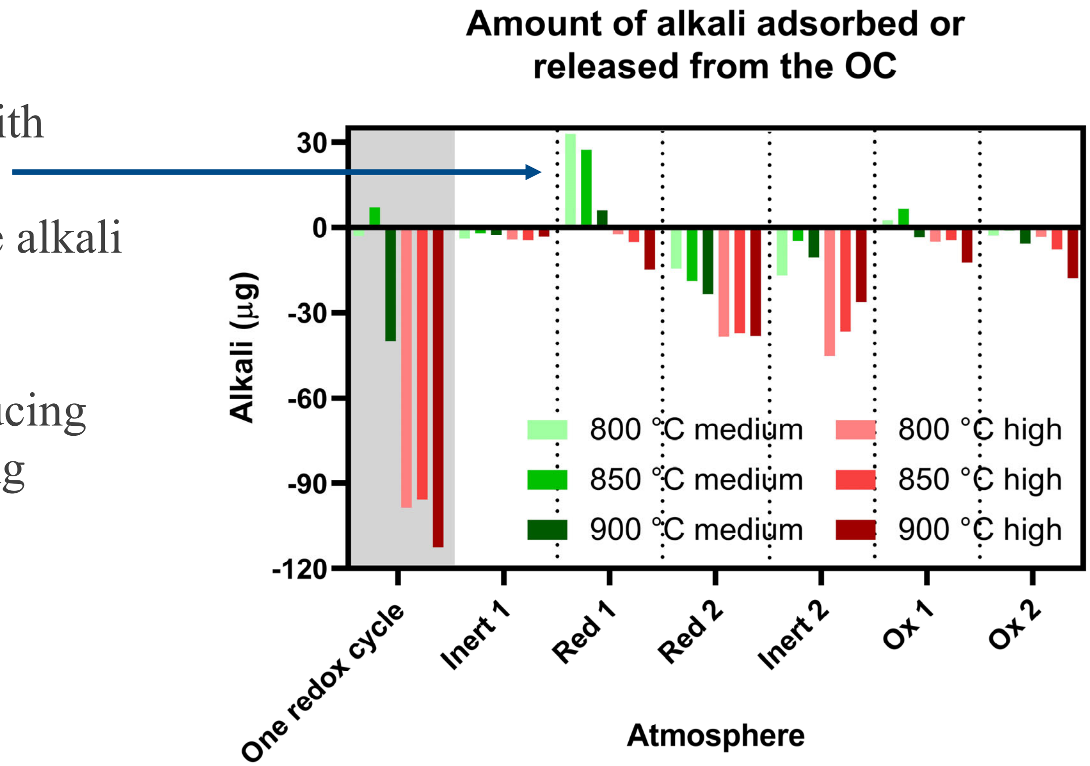
$$OC_{alkali} = OC_{signal} - Empty_{signal}$$

- The OC particles adsorb alkali over a complete redox cycle
- Larger uptake at higher alkali loading



Empty reactor system – OC fluidized bed

- OC release alkali during *red1* with *medium alkali loading*
- OC adsorb or does not affect the alkali during all other stages
- Larger uptake by the OC in reducing conditions compared to oxidizing



Conclusions Empty Reactor

- Alkali in gas phase above 500 ˚C.
  - Highest losses at 600 ˚C
  - Lower losses above 800 ˚C
- Wall interactions depend on:
  - Atmosphere, alkali loading and temperature
  - Large transient effects when changing gas composition
- Reduction of steel oxides forms a potassium-rich phase
  - Stable in a reducing atmosphere but not under inert conditions

Andersson, V. et al. Alkali-wall interactions in a laboratory-scale reactor for chemical looping combustion studies. Fuel Processing Technology, 217 (2021)

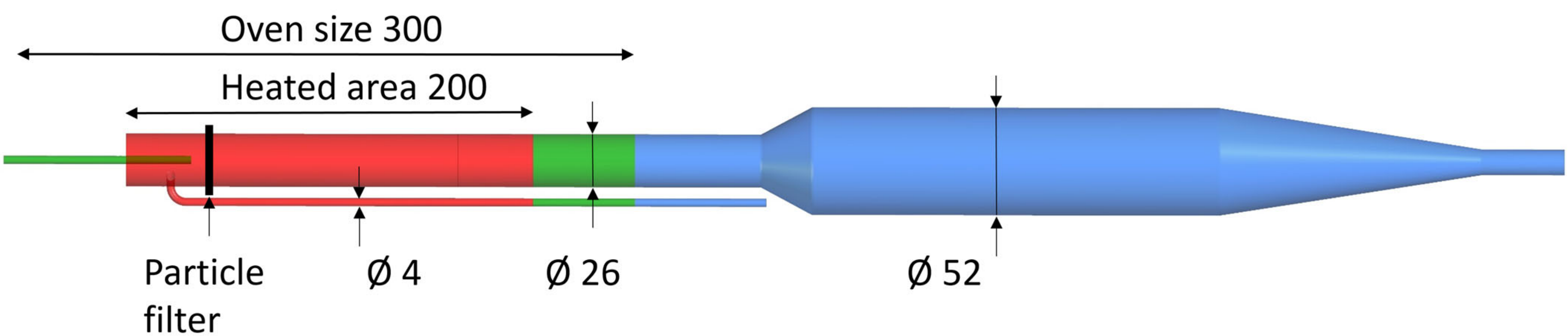
Conclusions OC fluidized bed

- OC adsorb alkali in all atmospheres
  - Except in the **initial** part of the reducing stage
- Larger uptake in reducing conditions compared to oxidizing
- Alkali uptake increases with increasing gas phase alkali concentration
- The uptake is associated with changes in the chemical composition of the OC

Alkali Interactions with an Oxygen Carrier used in Chemical Looping Combustion
Manuscript submitted for publication.

Future work

- New reactor is built with the aim of reduced wall effects
  - Designed with improved alkali aerosol injection
  - FeCrAl stainless steel (extremely good corrosion resistance)
  - Manuscript: *Design of a Laboratory-Scale Fluidized Bed Reactor System used for Alkali studies in Chemical Looping Combustion*



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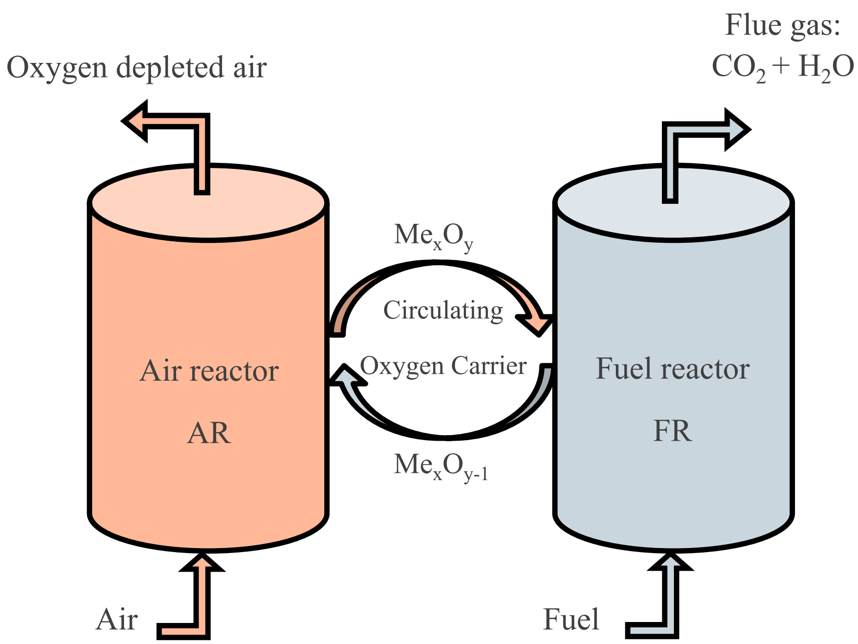
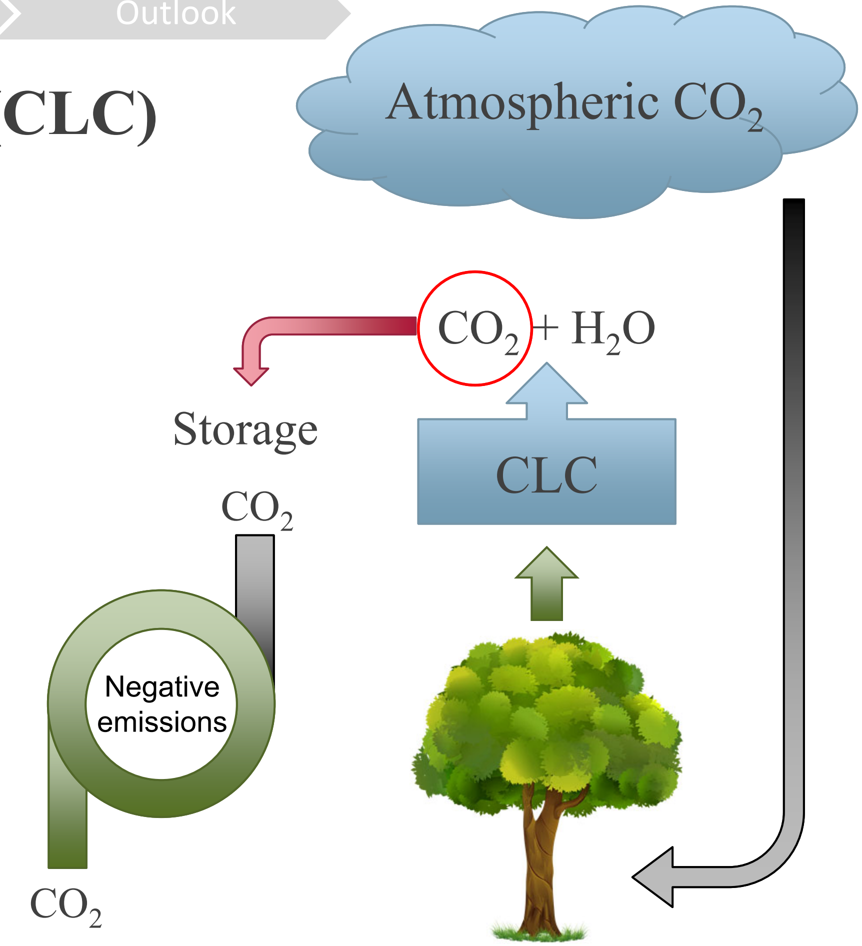
Thanks for your attention

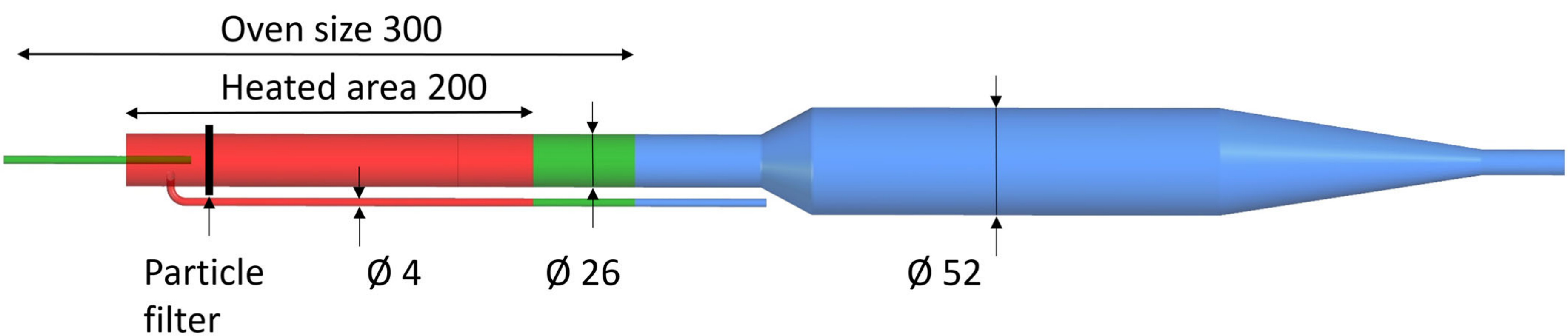
Chemical Looping Combustion (CLC)





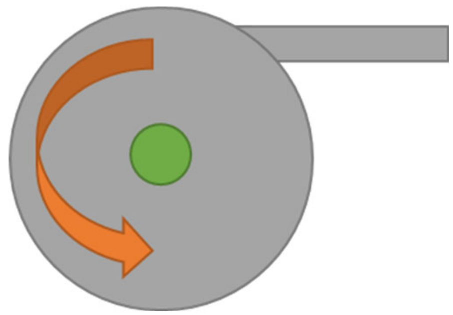
Change reactor geometry – reduce wall effects

- Limit alkali losses below the bed
  - Aerosol temperature below 500 ºC
- Limit alkali losses above the bed
  - Reduce the hot wall area above the bed
- Material, FeCrAl alloy → forms Al_2O_3 oxide
- Improve aerosol formation in the exhaust
  - Increased diameter of ambient section
  → Faster cooling
  → More efficient nucleation/coagulation
  → Lower A/V ratio – less condensation



Change reactor geometry – reduce wall effects

- Aerosol flow in a tube
- Swirling reactor gases
- Preheated reactor gases



Computational fluid dynamics