Alkali Emissions Measurements in Continuous CLC Operation

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Project: Biomass Combustion Chemistry with Oxygen Carriers

Project Leader: Prof. Anders Lyngfelt

Funding: Vetenskapsrådet

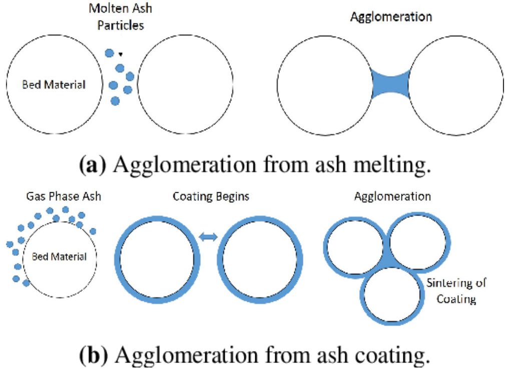
Alkali Related Issues

Gas-Phase Alkali Release

Fouling and corrosion of heat exchange equipment

Alkalis in the bed material

Alkali silicates form sticky melts



Prominent modes of agglomeration (Zimmerman et al. 2016)

Alkalis in CLC of biomass

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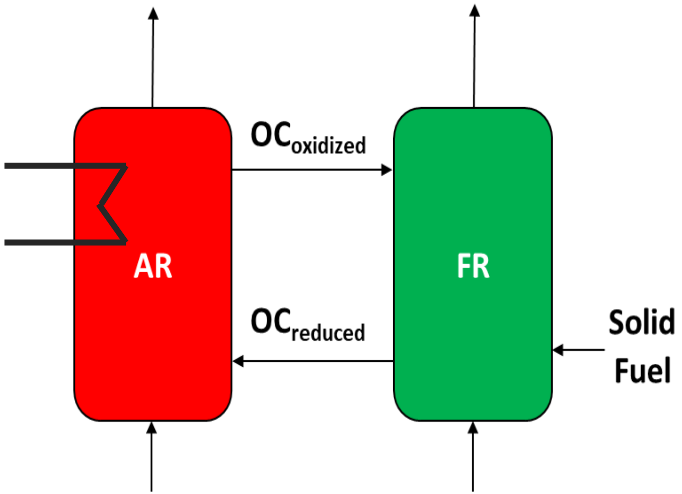

Main Hypotheses:

1. Most alkalis will be released to the gas phase in the FR
   - AR alkali release should be minimum
   - Less issues for HX surfaces (most process heat is recovered in the AR)
   - FR flue gas alkali will be easier to handle: lower flow rate, can operate FR HX at lower temp.
2. Overall gas-phase alkali release should be comparable to combustion of biomass

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Alkali emissions measurement in 3 pilot systems

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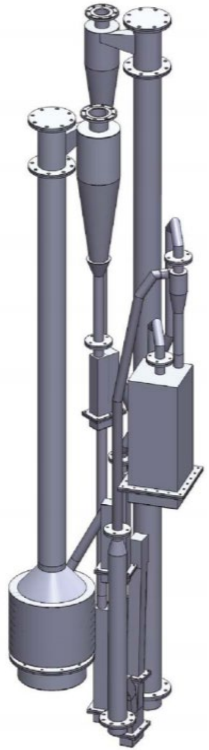
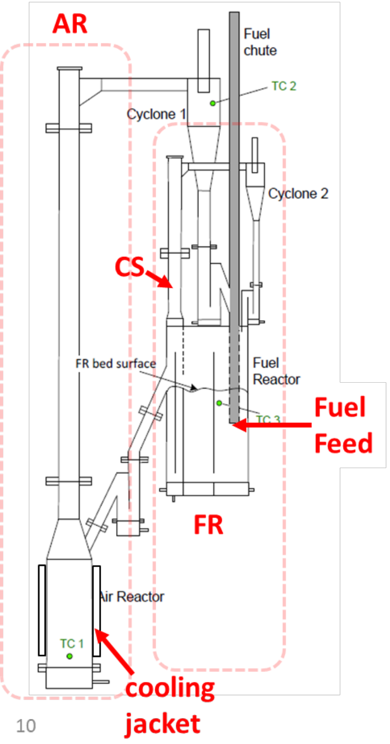
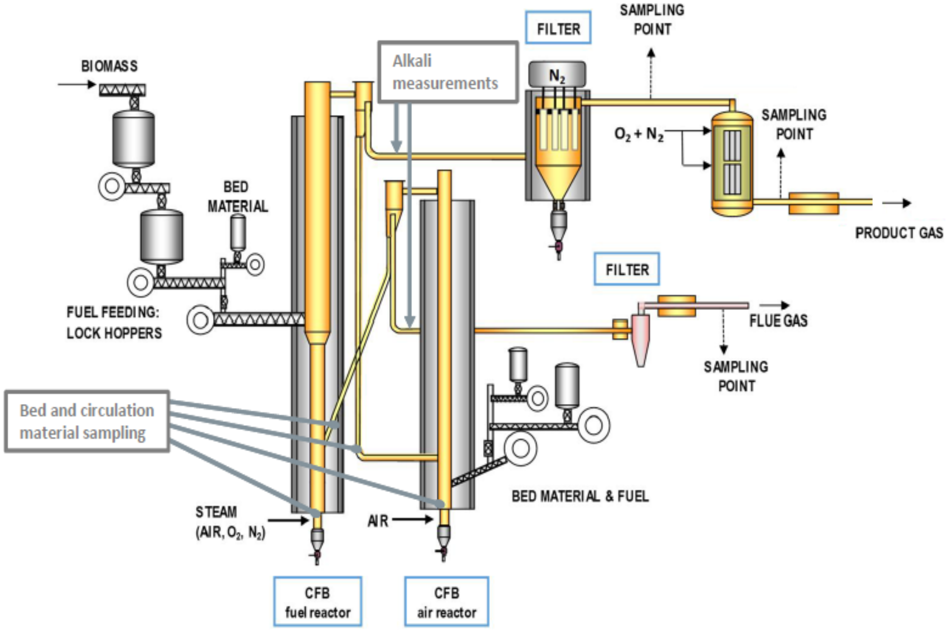
Chalmers 100 kW CLC
Ilmenite & CaMn



Chalmers 10 kW CLC
Ilmenite



VTT 60 kW D-CFB CLC
Ilmenite, Braunite



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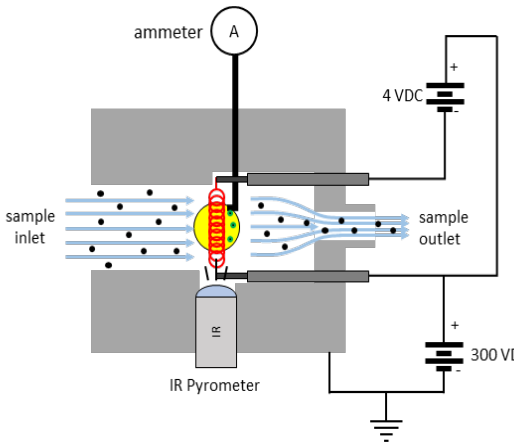
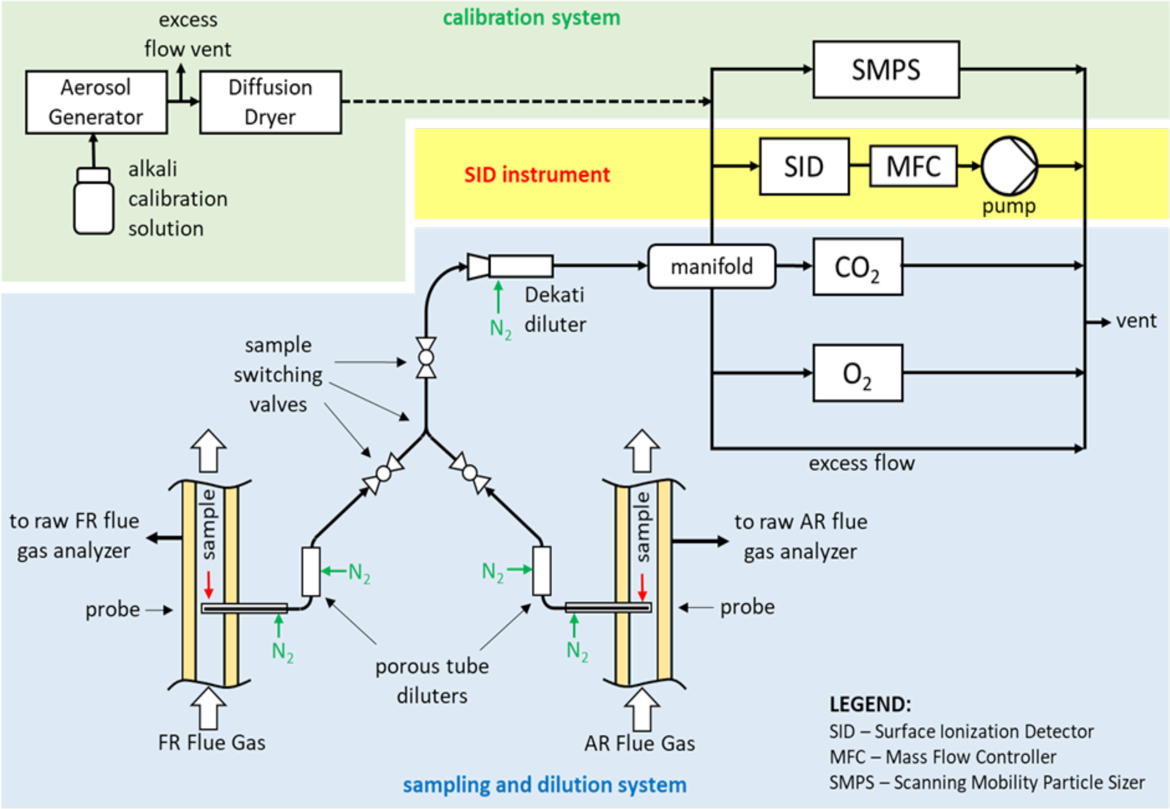
SID-based Alkali Measurement System

- Flue gas sampled at 900-1000° C
- 3 stages of sample dilution
- dilution tracking with CO_2/O_2



Surface Ionization Detector (SID)



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Results: SID-Based Alkali Measurement System

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- Modular and transportable
- Sampling from AR <u>and</u> FR
- Dilution tracking for FR <u>and</u> AR
- Optimized for CLC conditions

- First measurement of gas phase alkalis in CLC
- Now tested at 5 different units

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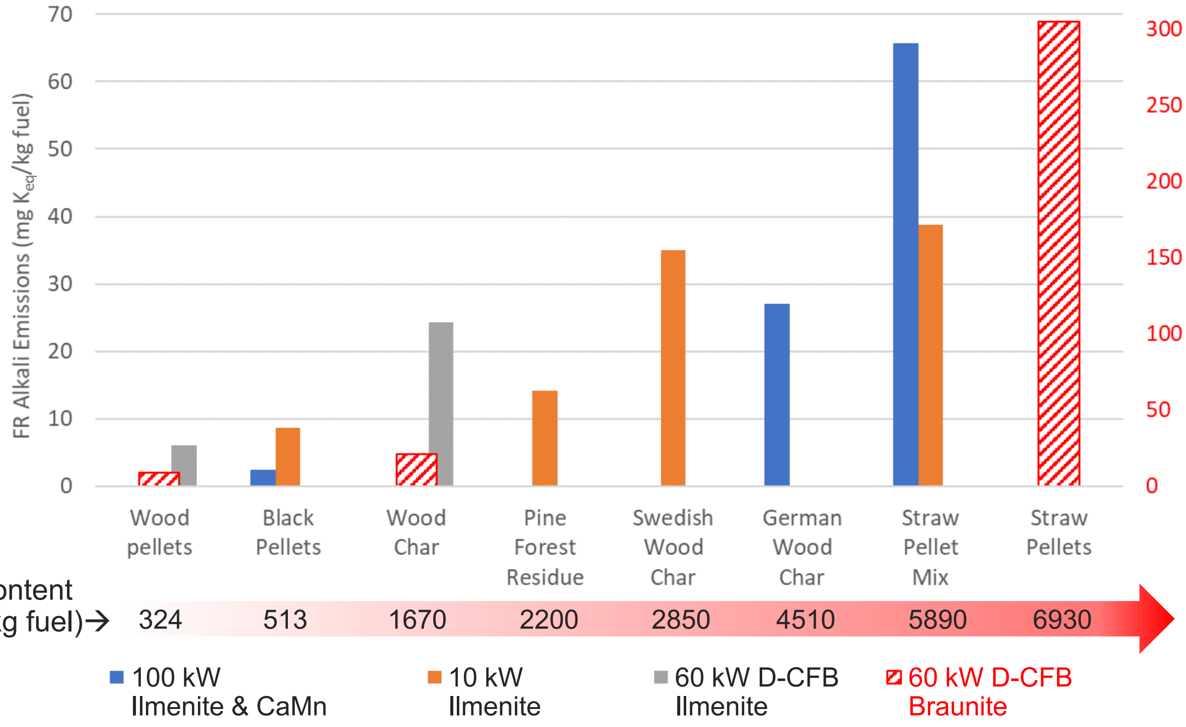
Results: Alkali Emissions vs. Fuel Alkali Content

Fuel Reactor Emissions

- Emission increase with fuel alkali content
- Trend is consistent in all campaigns



Results: Alkali Emissions vs. Fuel Alkali Content

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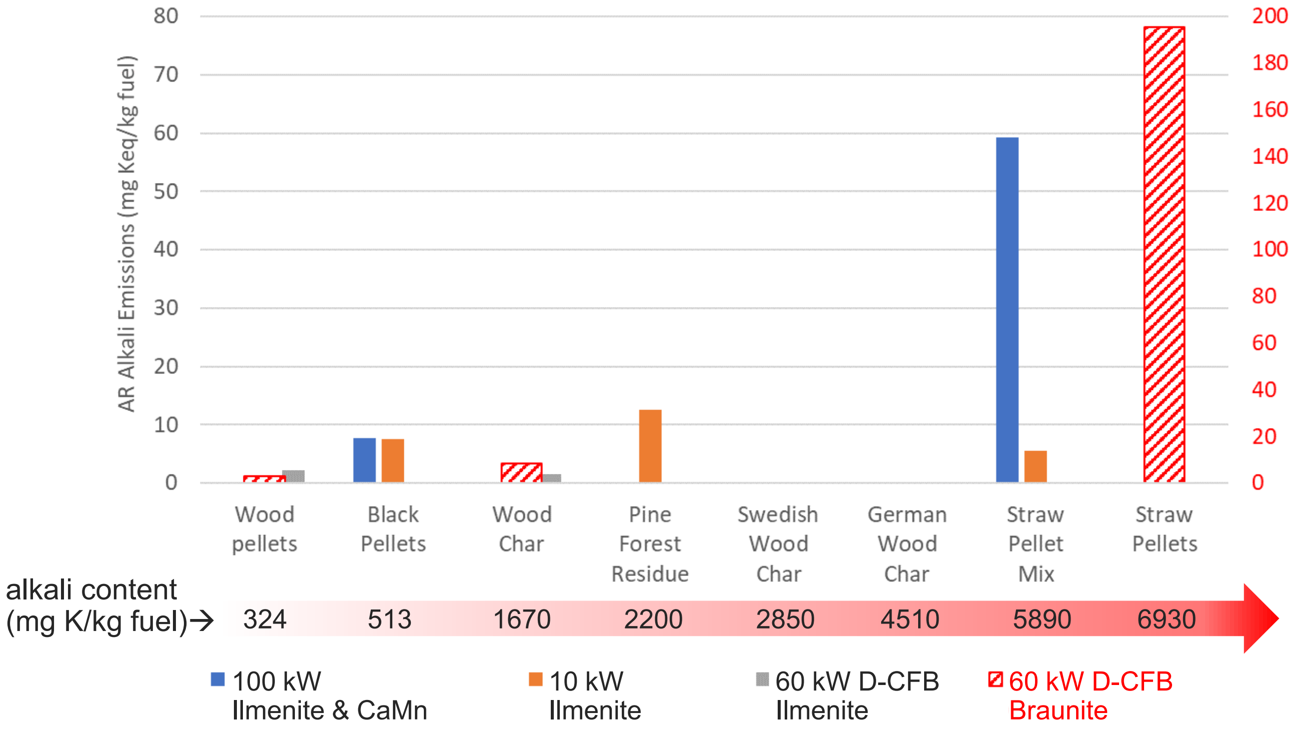
Air Reactor Emissions

- No consistent trend



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Results: Alkali Release Distribution

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		100 kW Ilmenite & CaMn		10 kW Ilmenite		60 kW D-CFB Ilmenite		60 kW D-CFB Braunite	
Fuel	**mg alkali/kg fuel**	**FR**	**AR**	**FR**	**AR**	**FR**	**AR**	**FR**	**AR**
Wood Pellets	324					1.9%	0.7%	2.9%	1.0%
Black Pellets	513	0.7%	1.8%	1.7%	1.5%				
Wood Char	1670					1.3%	0.1%	1.3%	0.5%
Pine Forest Residue	2200			0.7%	0.6%				
Swedish Wood Char	2850			1.2%					
German Wood Char	4510								
Straw Pellet Mix	5890	1.1%	1.1%	0.7%	0.1%				
Straw Pellets	6930							4.4%	2.8%

Alkali Emissions Distribution:

- 0.8 – 7.2 wt% of fuel alkalis are released to the gas phase
- AR emissions can be significant
- Several cases where AR emissions = or > FR emissions

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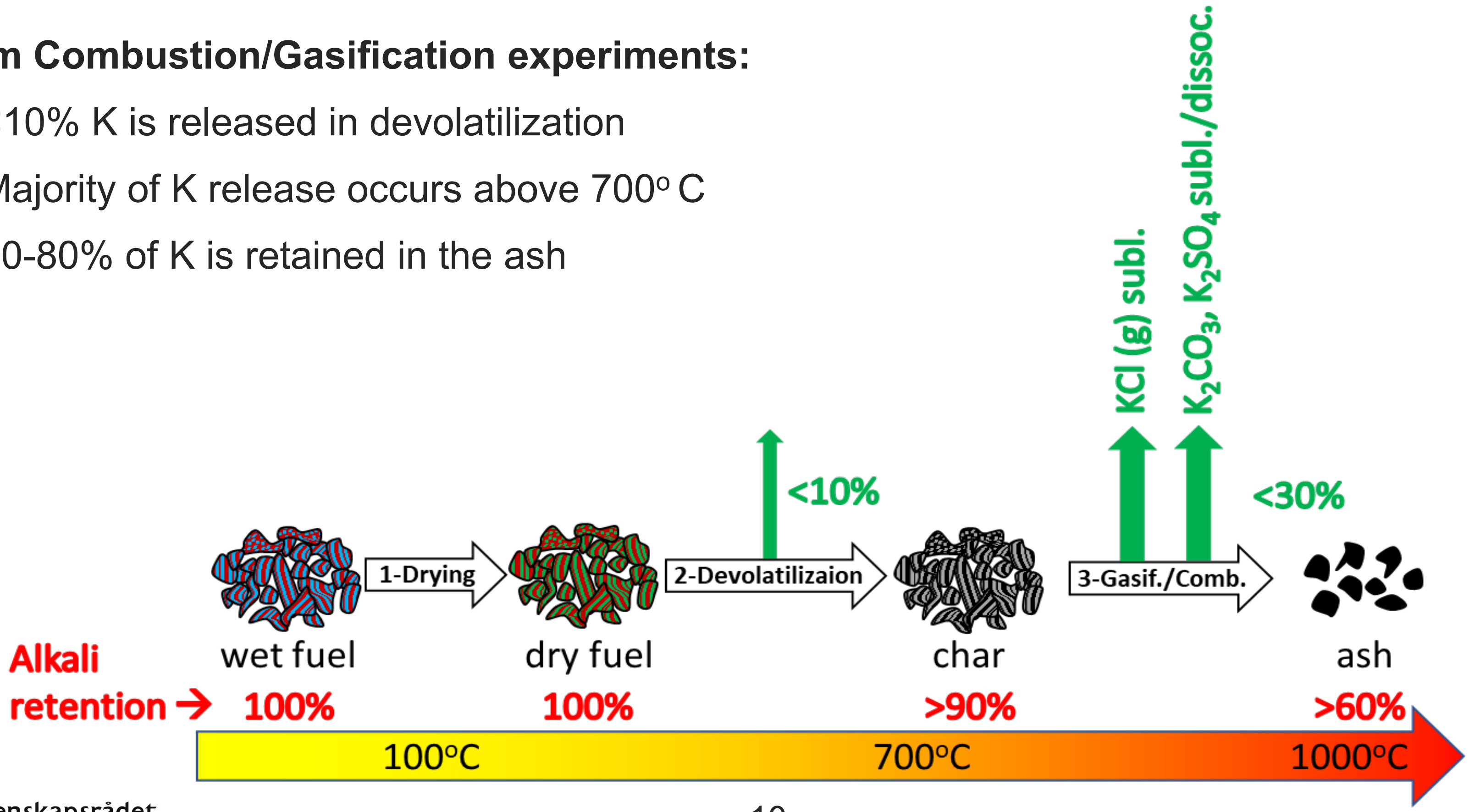
Results: Origin of AR emissions

From Combustion/Gasification experiments:

- <10% K is released in devolatilization
- Majority of K release occurs above 700^{o} C
- 60-80% of K is retained in the ash



Results: Origin of AR emissions

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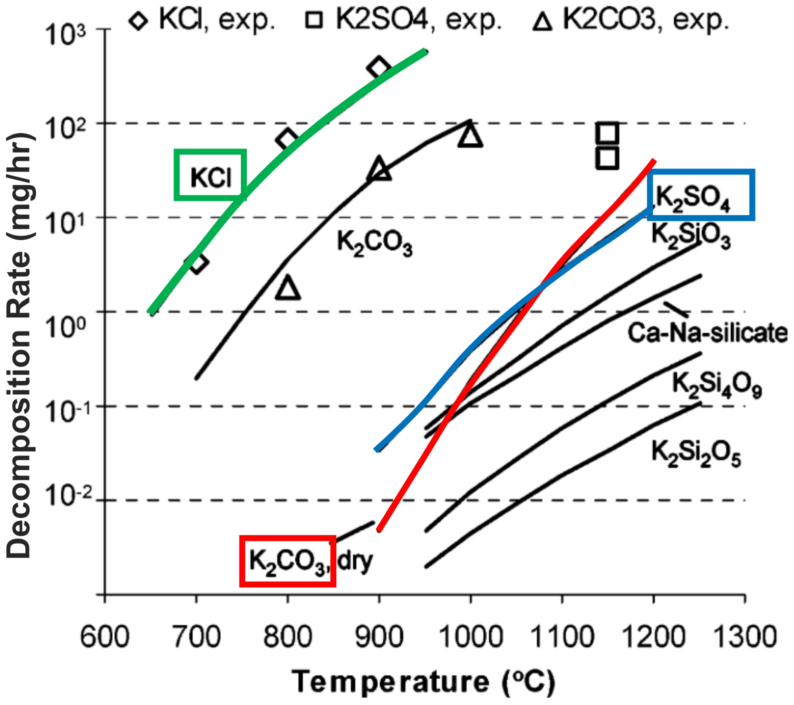
Carryover of condensed alkalis to AR can occur via carryover of:

1. Unconverted char
2. Ash

- Both can contain undecomposed K compounds
- Continue gas phase release of alkali in the AR
- AR temperature is up to 100^o C higher than the FR



Potassium compound release rates vs. Temperature (Knudsen et al. 2004)

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Results: Alkali Retention

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Fuel	mg alkali/kg fuel	100 kW Ilmenite & CaMn	10 kW Ilmenite	60 kW D-CFB Ilmenite	60 kW D-CFB Braunite
Wood Pellets	324			97.5%	96.9%
Black Pellets	513	97.5%	96.8%		
Wood Char	2200		98.7%		
Pine Forest Residue	1670			98.6%	98.2%
Swedish Wood Char	2850				
German Wood Char	4510				
Straw Pellet Mix	5890	97.8%	99.2%		
Straw Pellets	6930				92.8%

Alkali Retention:

- Retention is >92% for all oxygen carriers, fuels, and tests
- Retention was confirmed by bed material and filter material analysis

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Results: Alkali Retention

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Retention can be divided into

1. Retention by fuel ash formation process → estimated at 60-80 wt%
2. Effect of OC material → 10-30 wt%

Both Ilmenite and Braunite can form the following stable compounds at CLC temperatures:

- K-silicates
- K-aluminosilicates
- K-manganates
- Ilmenite can also form K-titanates

Results: OCAC vs CLC Alkali Emissions

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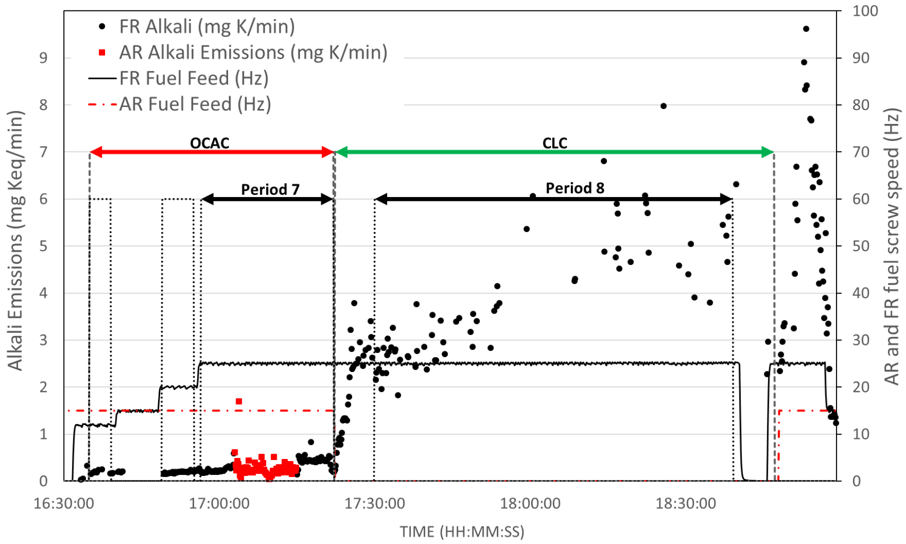
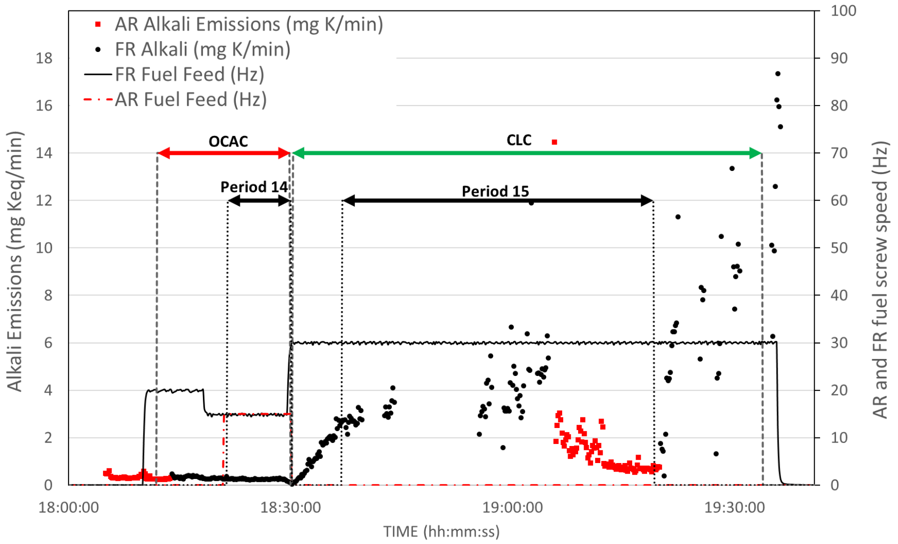


Alkali emissions (Ilmenite & Wood Char)



Alkali emissions (Braunite & Wood Char)

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Results: OCAC vs CLC Alkali Emissions

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OC Material	Fuel	mg alkali/kg fuel	OCAC FR emissions (mg K/kg fuel)	CLC FR emissions (mg K/kg fuel)	% increase with CLC
Ilmenite	Wood Pellets	324	1.9	6.1	217%
	Wood Char	1670	2.3	24.4	983%
Braunite	Wood Pellets	324	9.2	8.7	-5%
	Wood Char	1670	3.2	21.4	564%
	Straw Pellets	6930	19.4	305.3	1470%

Effect of FR atmosphere:

- FR emissions in CLC mode higher than in OCAC mode
- Difference cannot be explained by temperature difference of the two modes

Results: OCAC vs CLC Alkali Emissions

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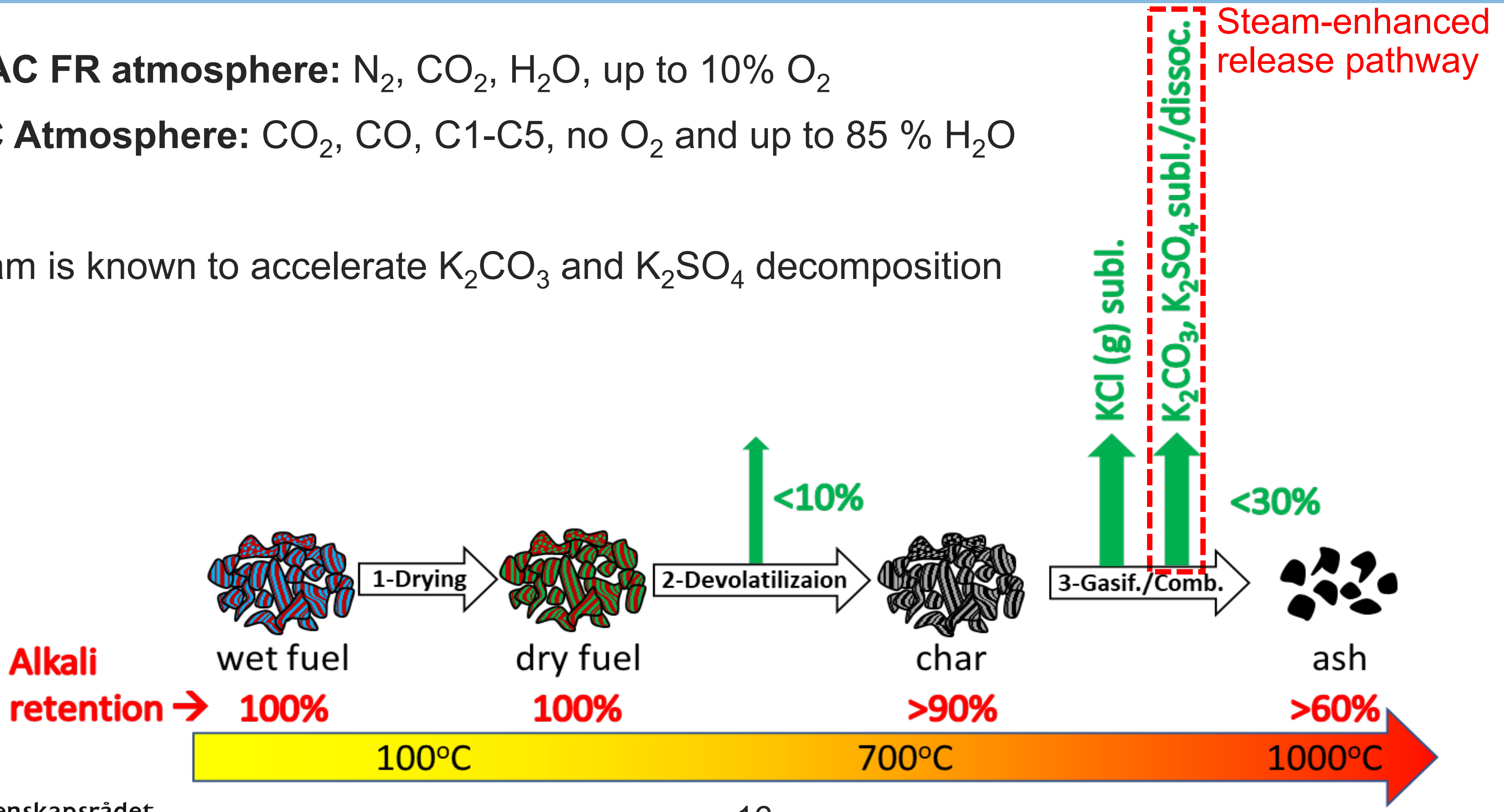
OCAC FR atmosphere: N_2, CO_2, H_2O, up to 10% O_2

CLC Atmosphere: CO_2, CO, C1-C5, no O_2 and up to 85 % H_2O

Steam is known to accelerate K_2CO_3 and K_2SO_4 decomposition



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CONCLUSIONS

Conclusions:

- SID based measurements are well suited for alkali measurement in CLC
- <10% of alkalis are release to the gas phase in CLC
- FR alkali emissions are typically higher than AR, but AR emissions can be significant
- >90% of alkalis are retained in condensed form
- CLC operation releases more gas-phase alkalis vs. OCAC operation
- FR’s steam content is responsible for increased emissions levels

Thank You !