The Clean Energy Transition Partnership

IMPACT OF OXY-COMBUSTION CONDITIONS ON ALKALI RELEASE AND DEPOSIT FORMATION IN RECOVERY BOILERS

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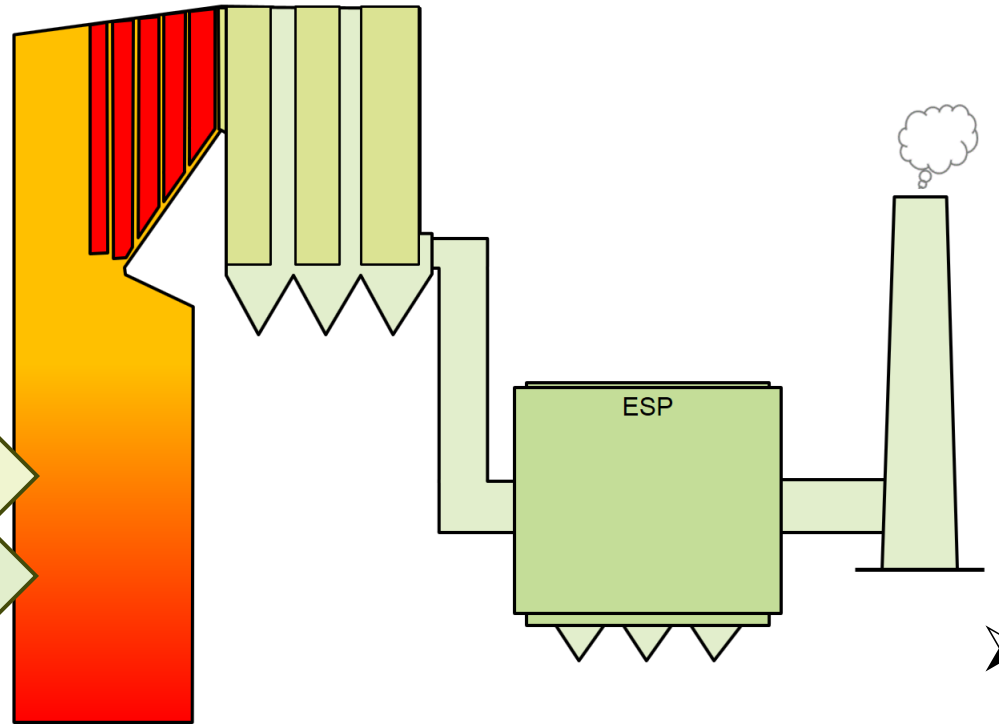
Oxy-Kraft

Oxy-fired black liquor recovery boiler

Traditional Air-combustion



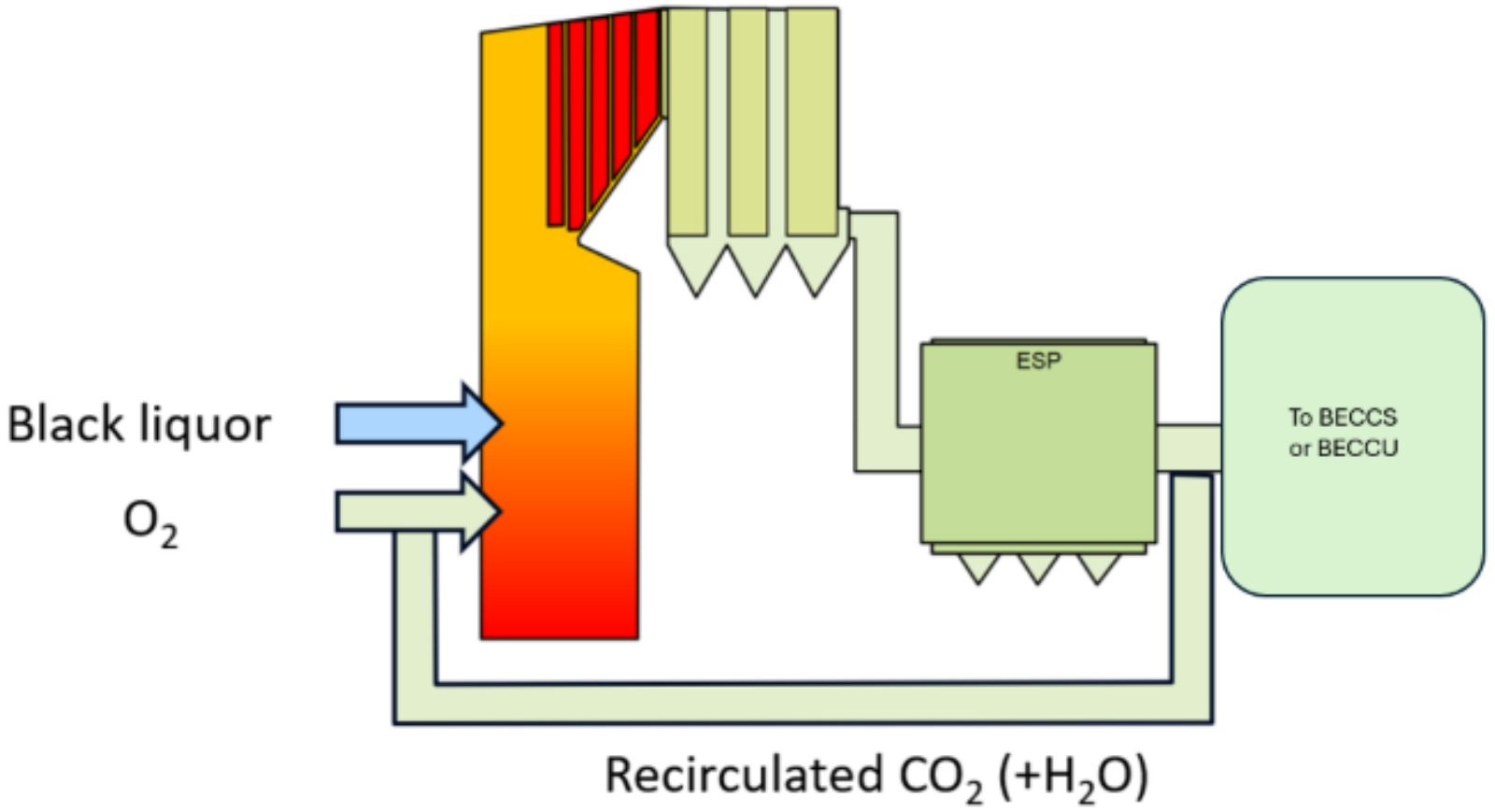
Black liquor

Air (O_2 + N_2)

13 vol-% CO_2
17 vol-% H_2O
3 vol-% O_2
67 vol-% N_2

- For CO_2-capture, beneficial if there is no N_2 in flue gas

Oxy-combustion



Objective

- Impact of oxy-combustion on black liquor droplet burning and implications
    - Burning rate
    - Fume and emission formation
    - Elemental release
    - Impact on deposit formation

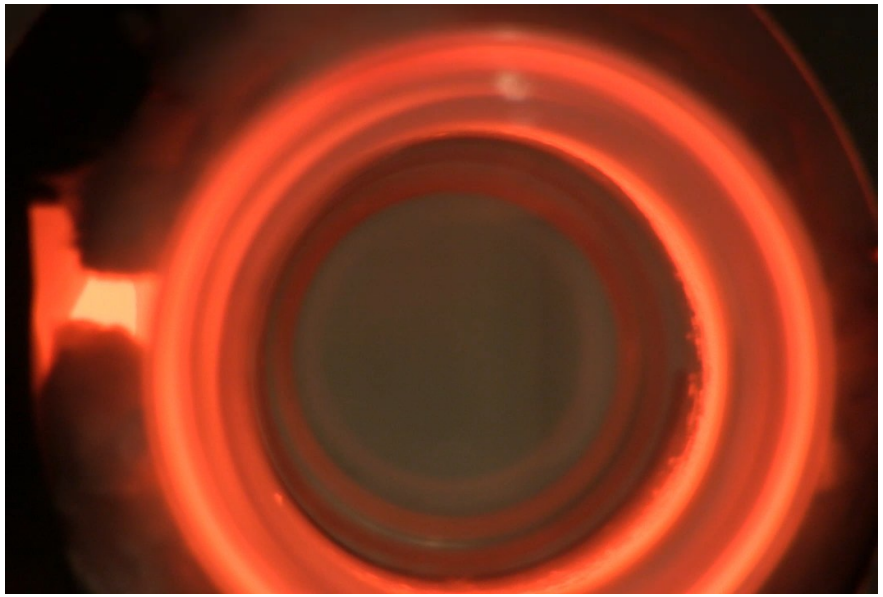
Materials & Methods

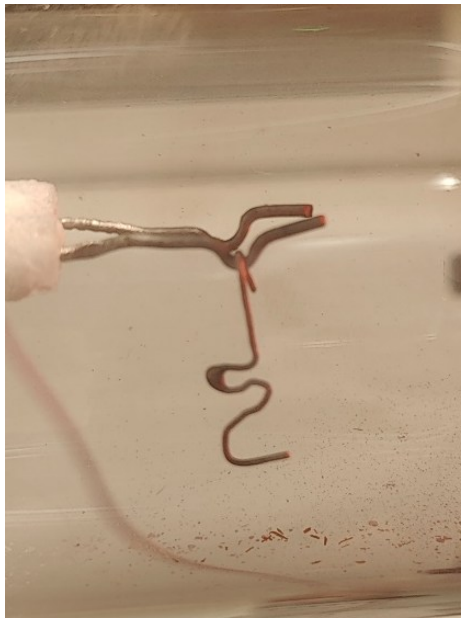
- Three different liquors (~80 %DS)
  - Spain, hardwood (BL623)
  - Nordic, softwood (BL624)
  - USA, softwood (BL626)
- Video recorded combustion experiments in the single particle reactor (SPR) with gas analyzers
  - Droplets á 10-11 mg
  - Reactor temperature 800, 900, 1000 °C
  - Two different gas compositions
    - Air/N_2 and O_2/CO_2

Gases	O_2	N_2	CO_2
"Air"	3 vol-%	97 vol-%	
"Oxy"	3 vol-%		97 vol-%

Materials & Methods

- "Interrupted" tests for residue analysis (ion chromatography)
  - Droplets removed at the point of smelt formation
  - Residues dissolved in ultrapure water and analyzed by ion chromatography for Na^+, K^+, SO_4^{2-} and Cl^-



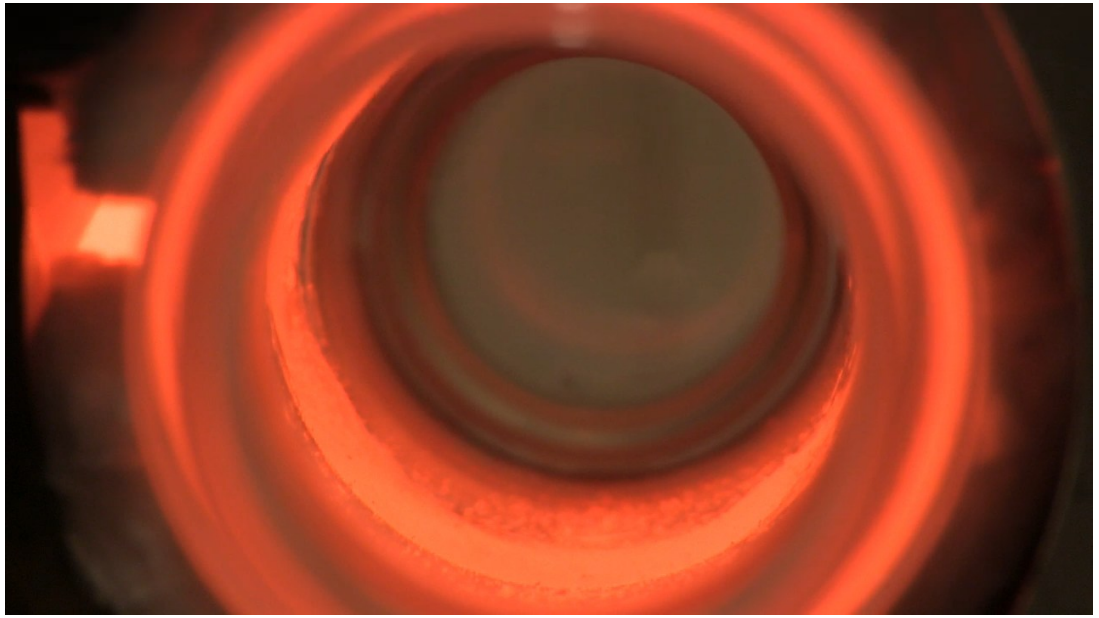


Results

Droplet burning at 900 °C

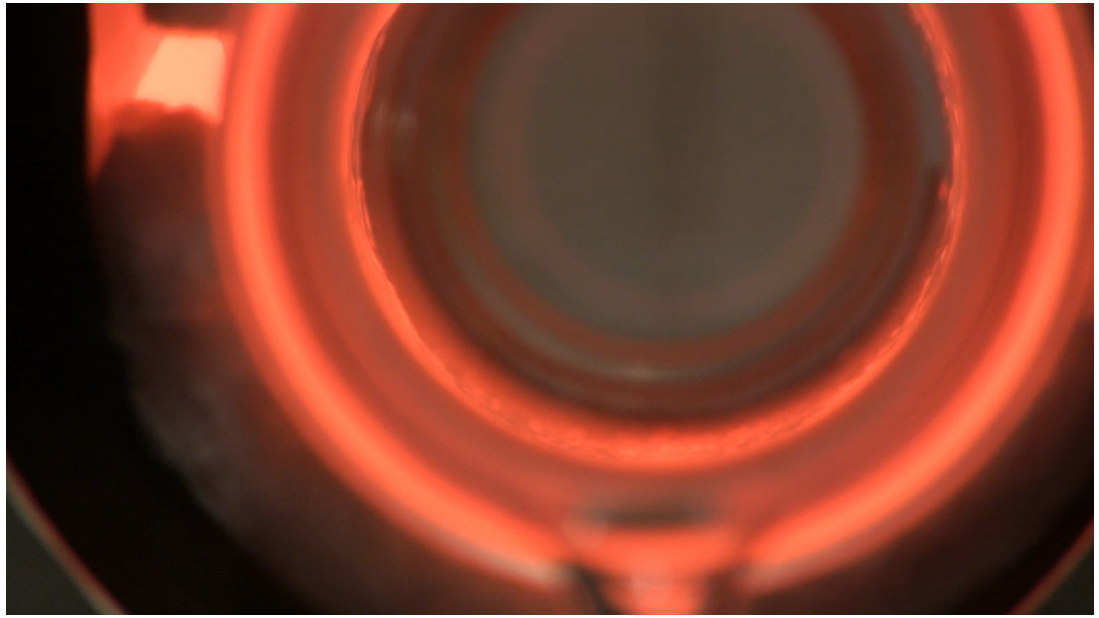
Air

3 % O_2 / 97 % N_2

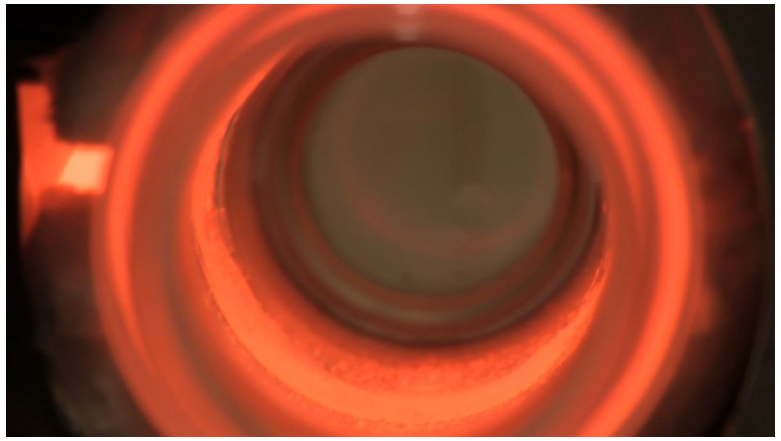
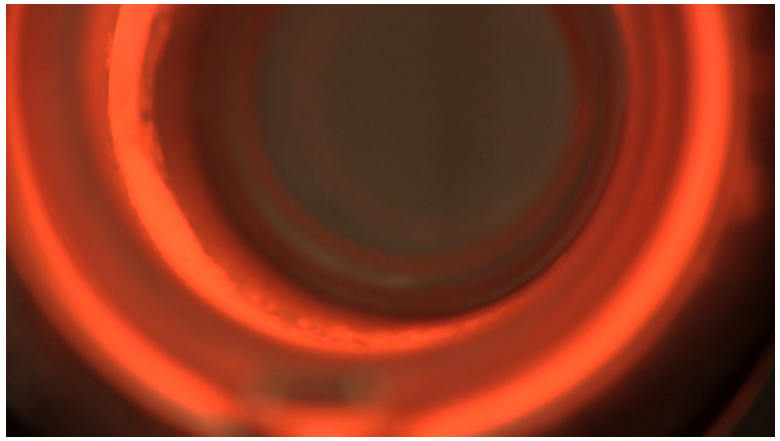
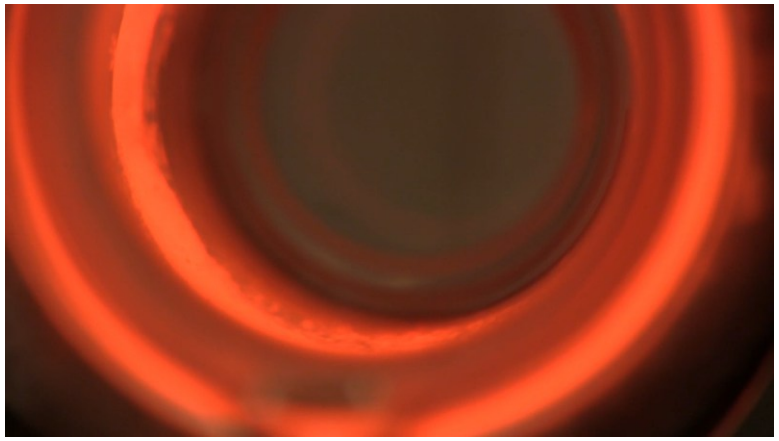
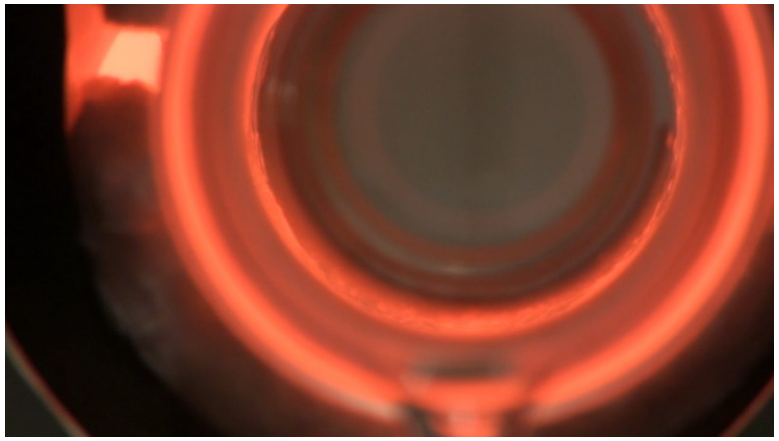
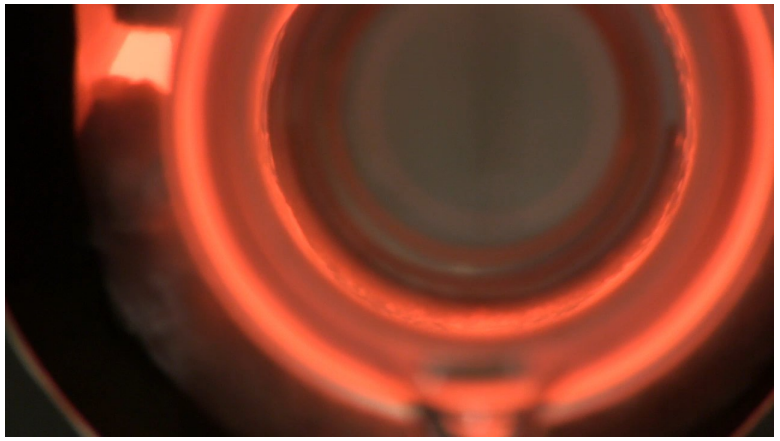
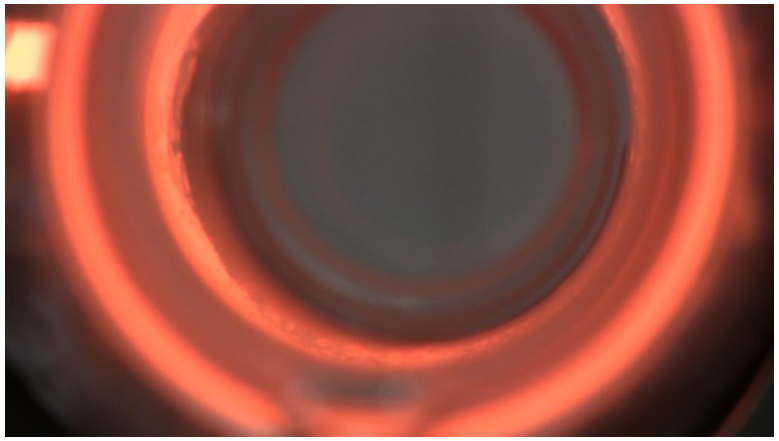


Oxy

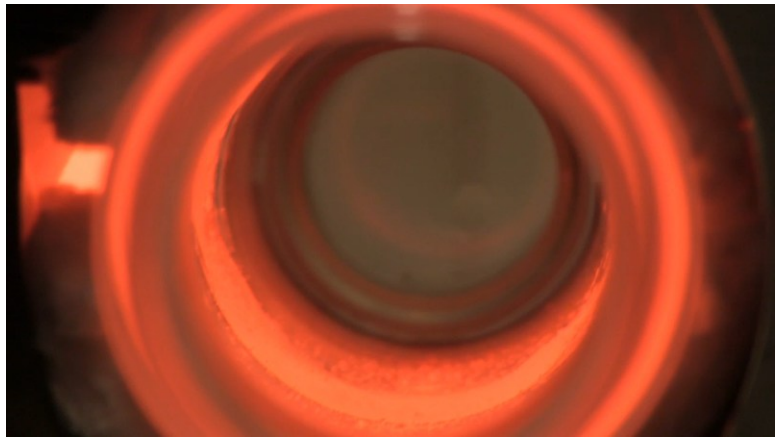
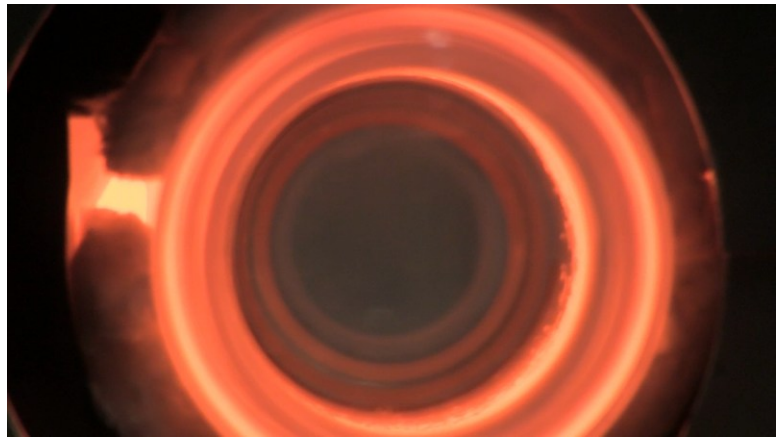
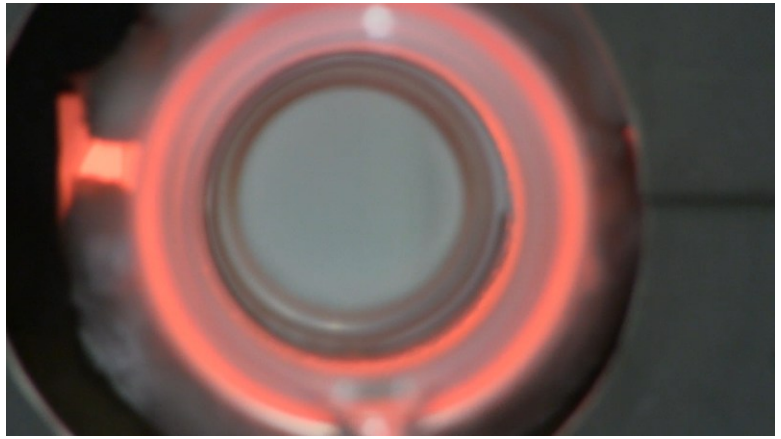
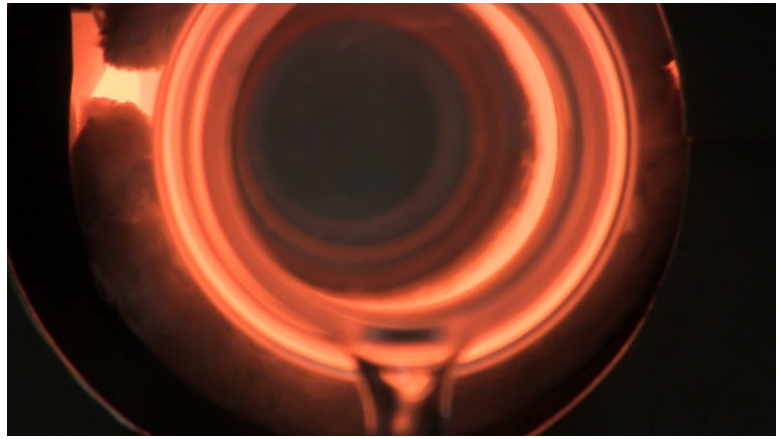
3 % O_2 / 97 % CO_2



"Oxy-combustion": shorter burning time due to CO_2 gasification

	Spain (BL 623)	Nordic (BL 624)	USA (BL 626)
Air			
Oxy			

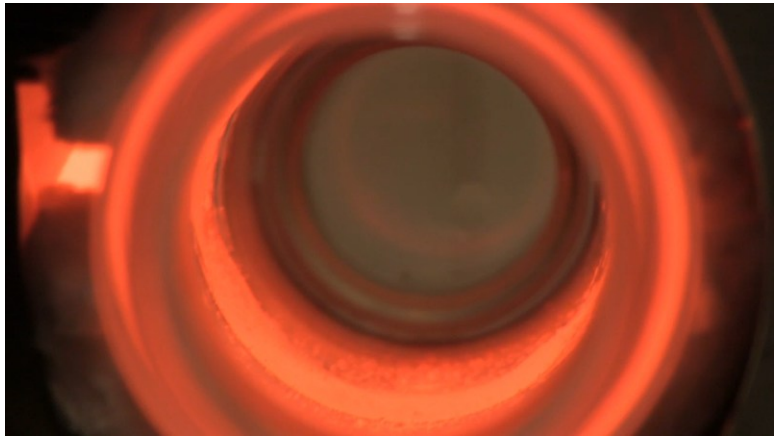
Droplet burning at different temperatures

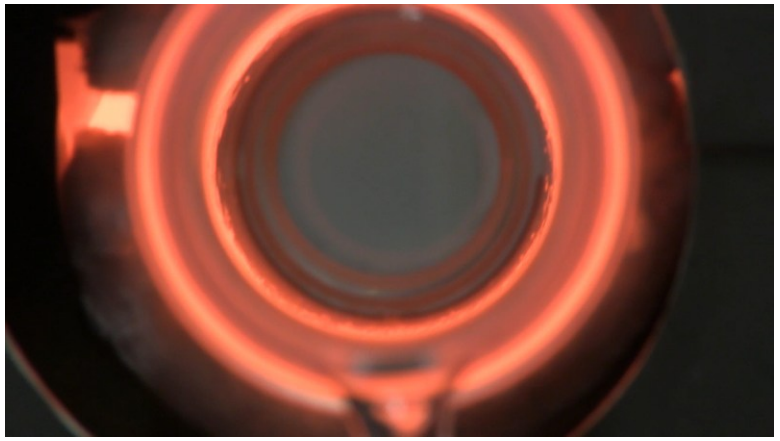
	800 °C, 3 % O_2	900 °C, 3 % O_2	1000 °C, 3 % O_2
Air			
Oxy			

900 °C, 3 % O_2

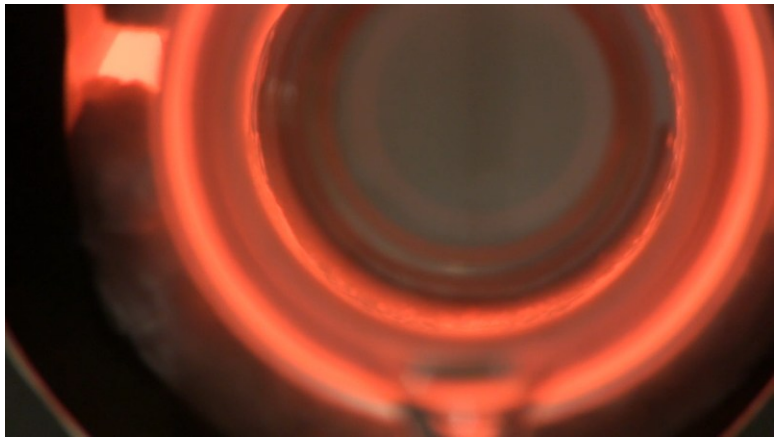
900 °C, 10 % O_2

Air

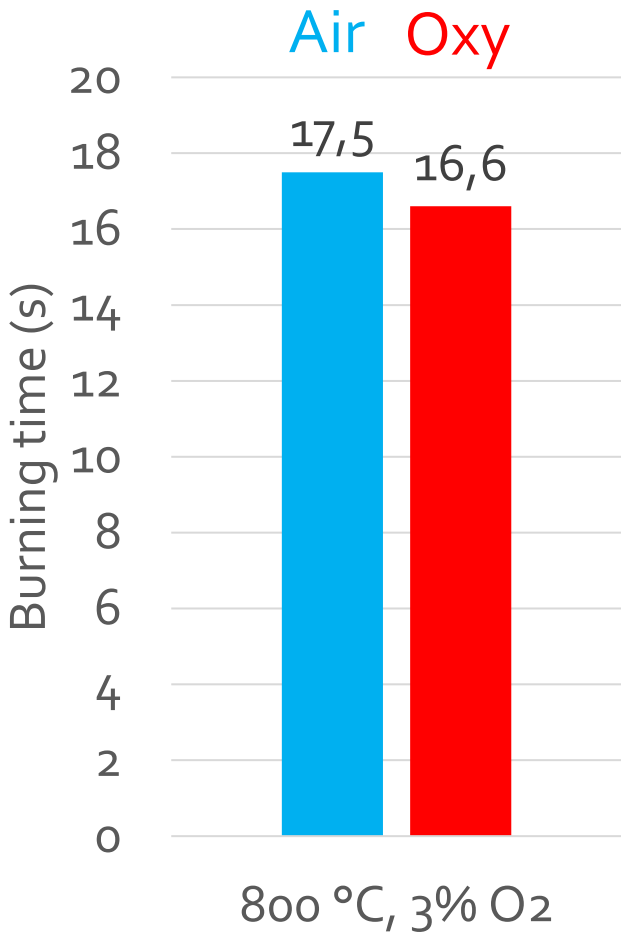




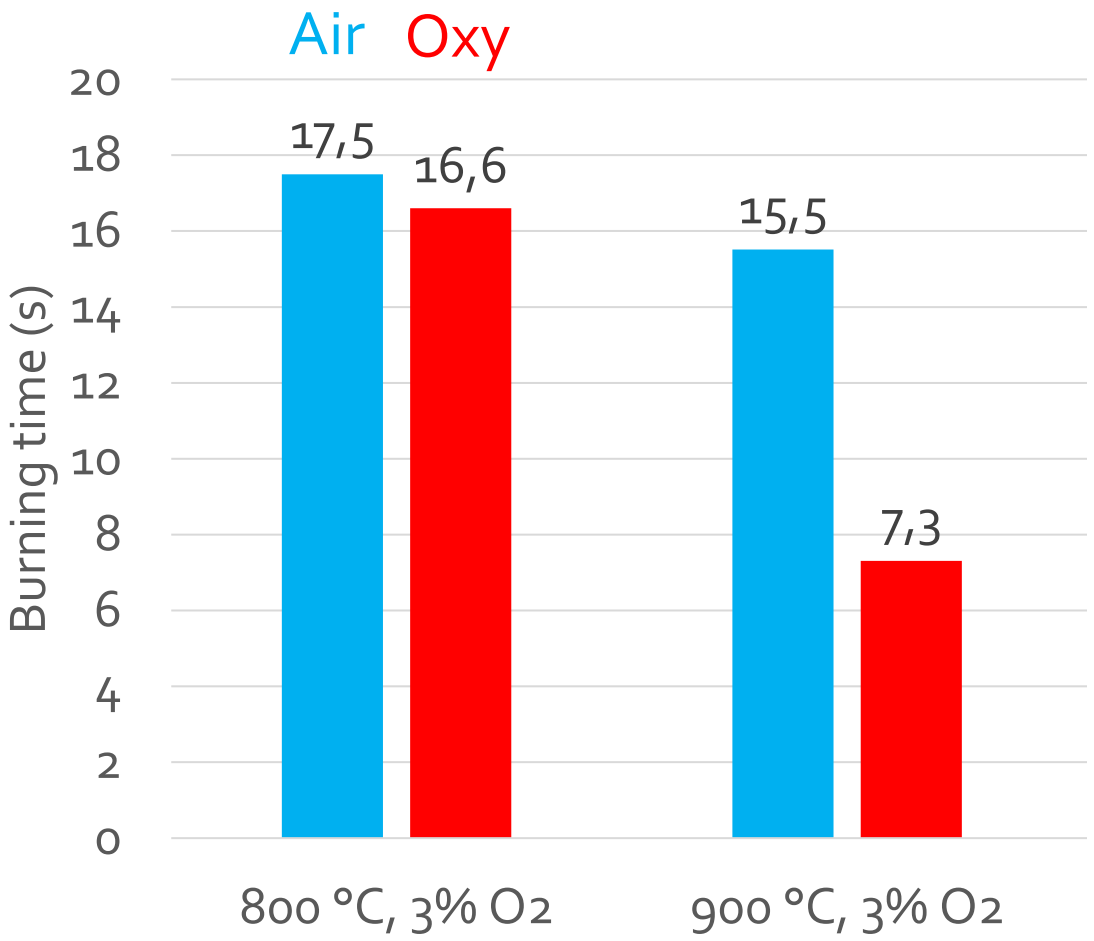
Oxy



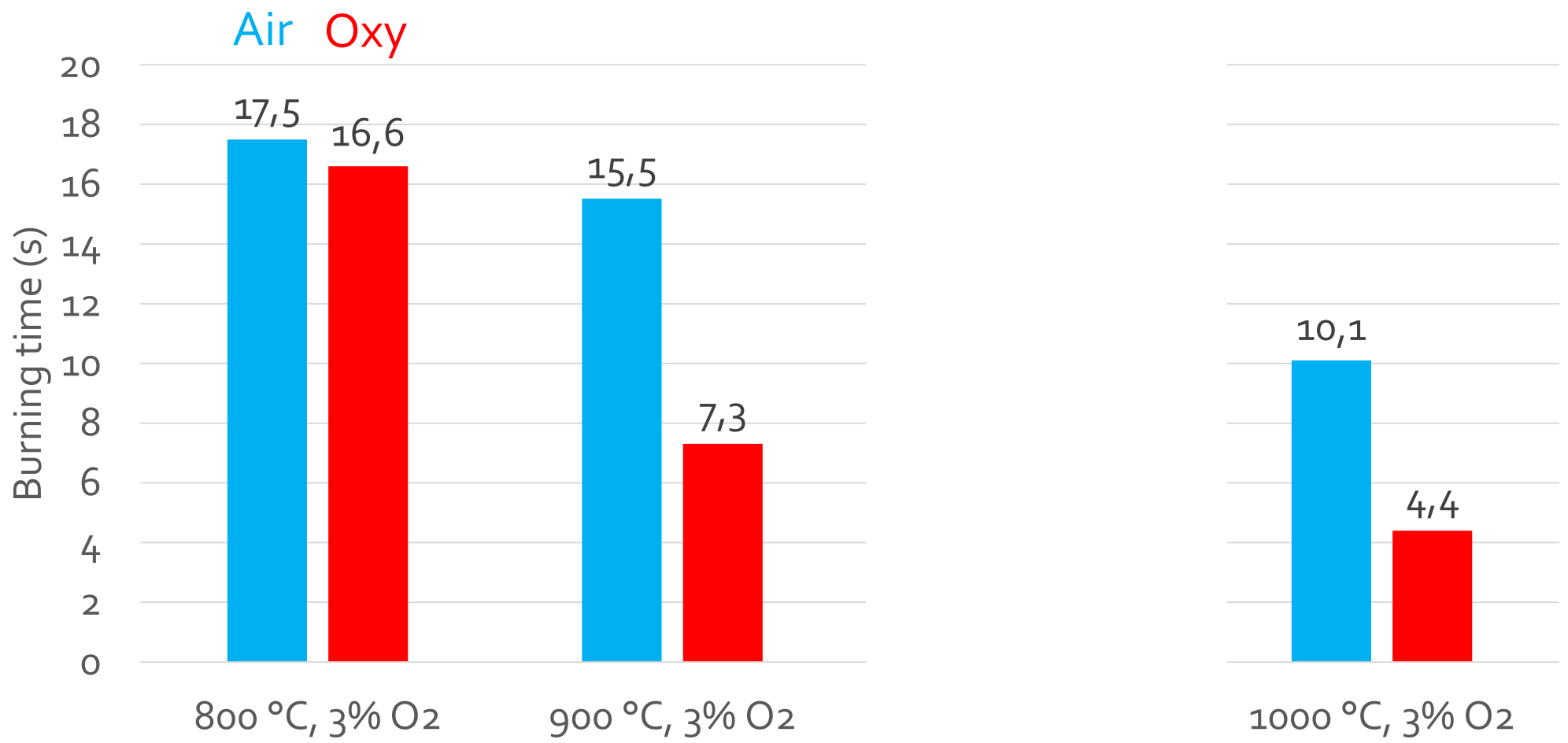
Burning times



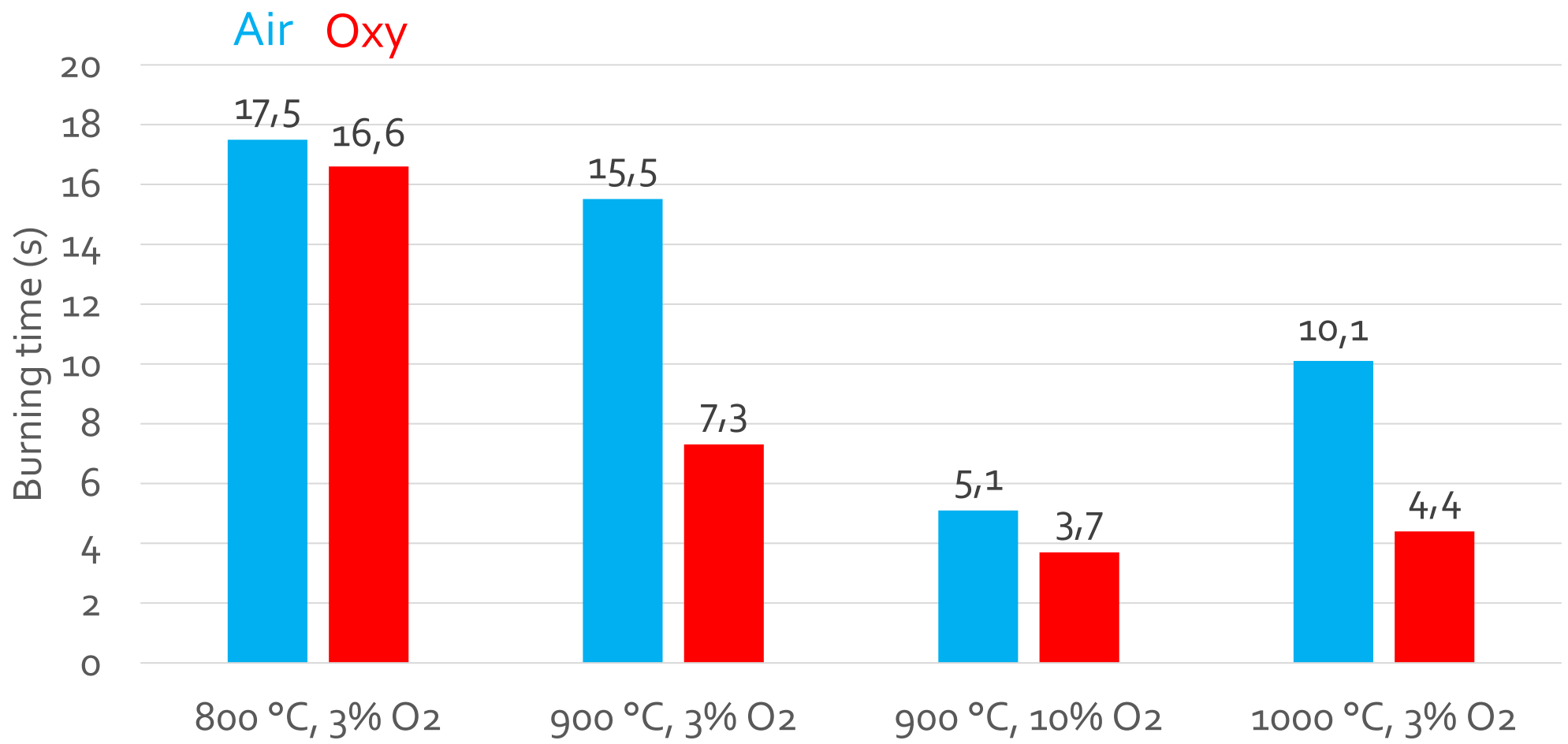
Burning times



Burning times



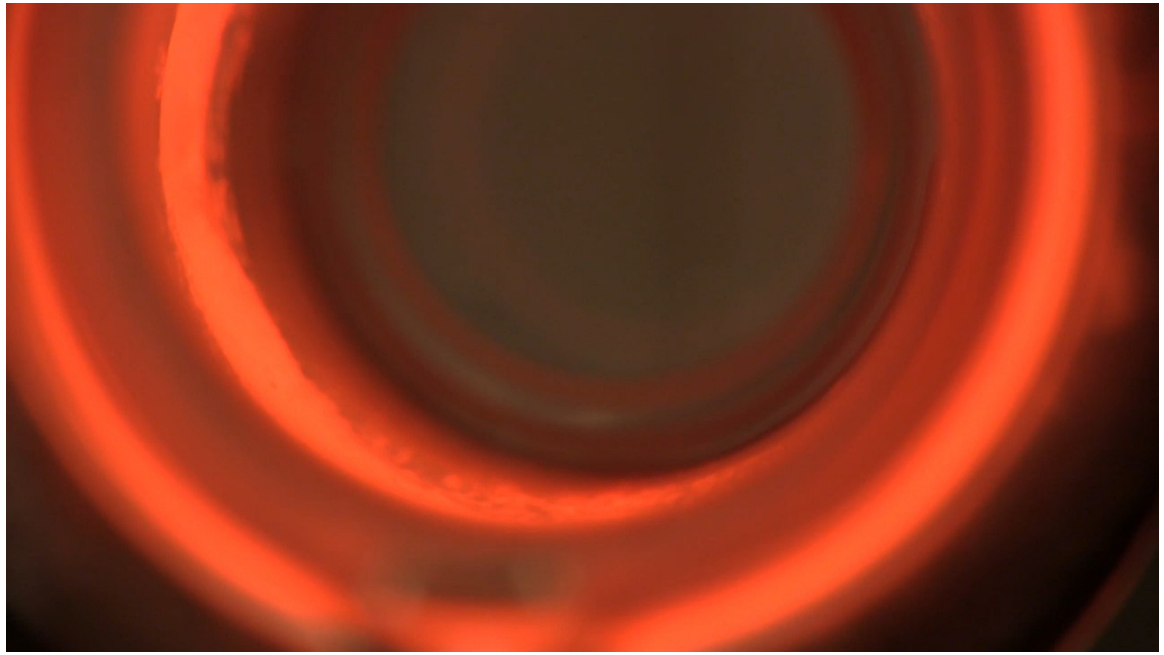
Burning times



Alkali release and fume formation

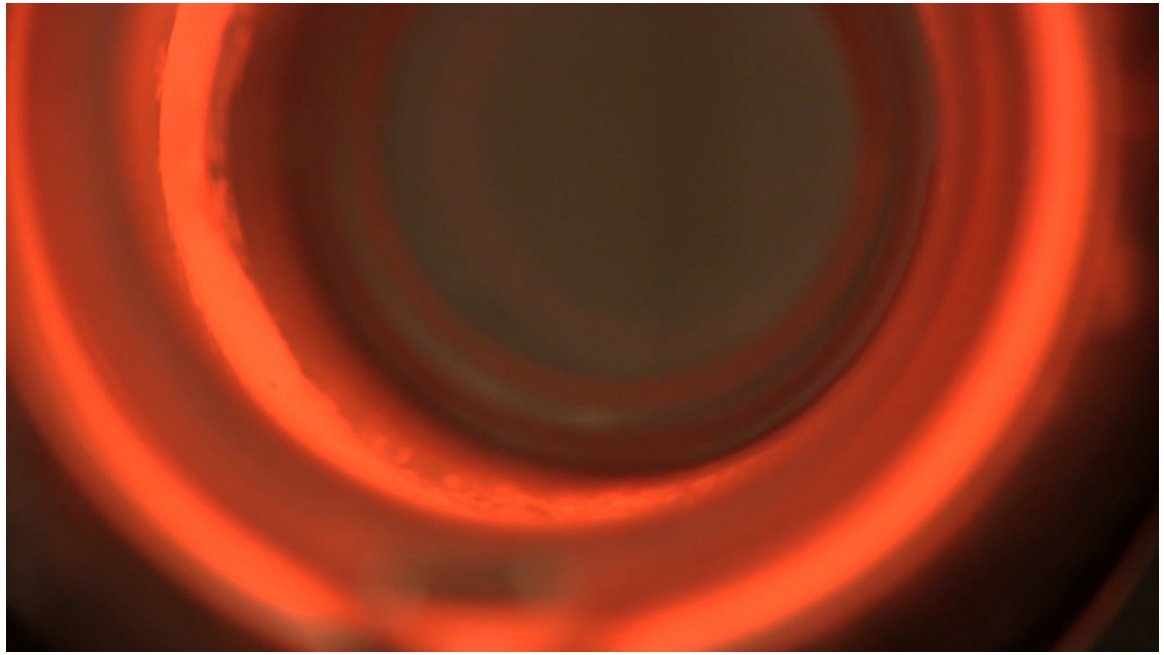
Alkali release and fume formation

Air

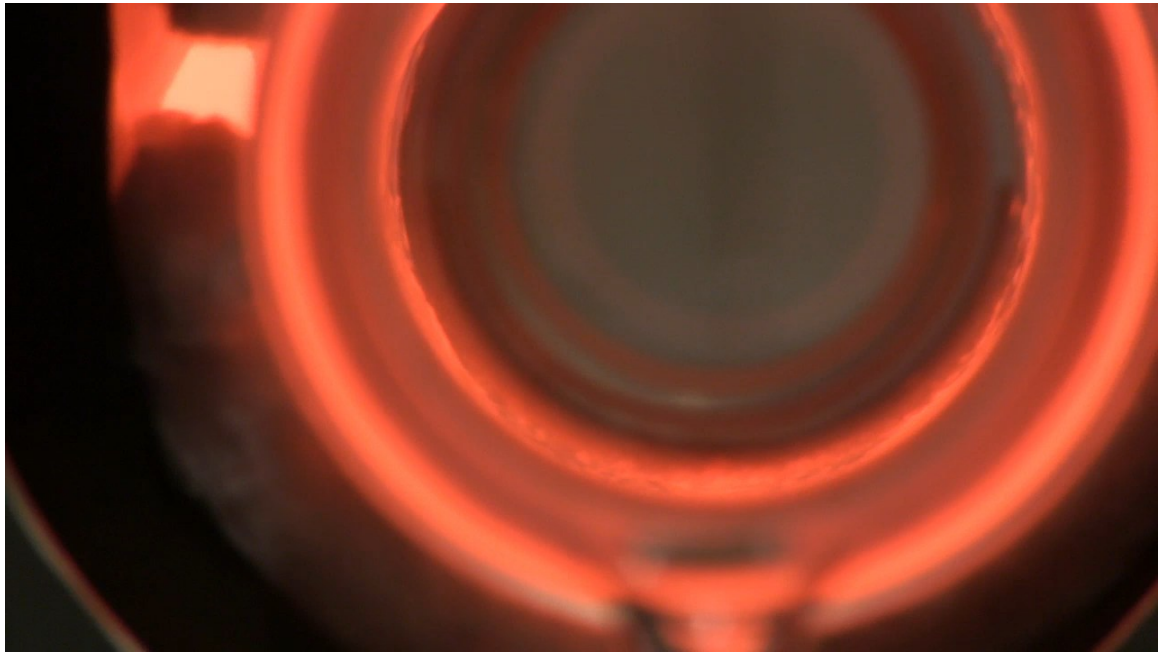


Alkali release and fume formation

Air



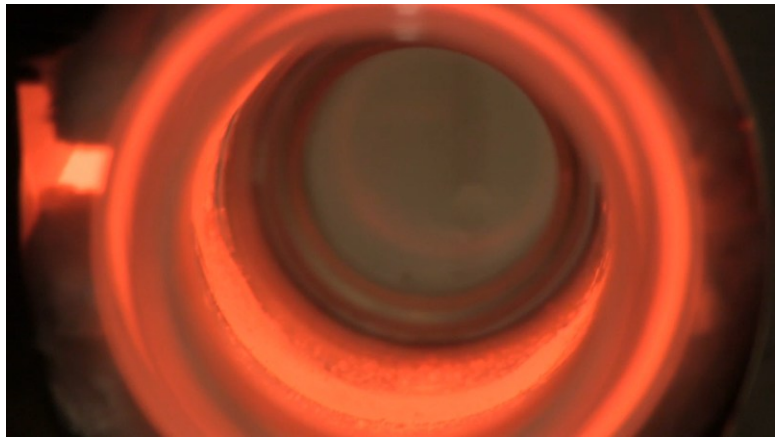
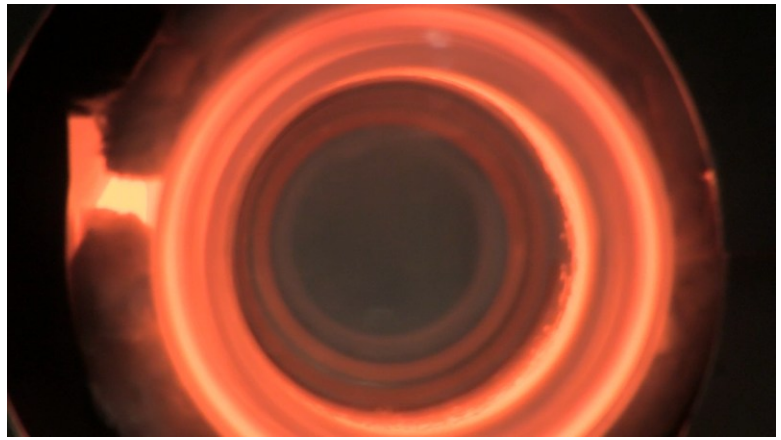
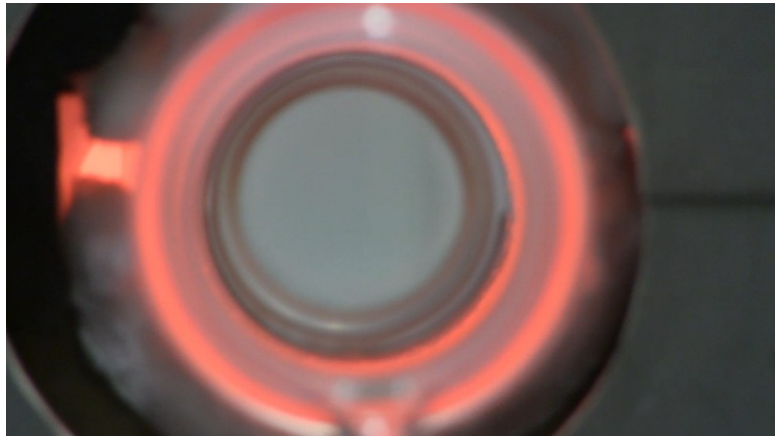
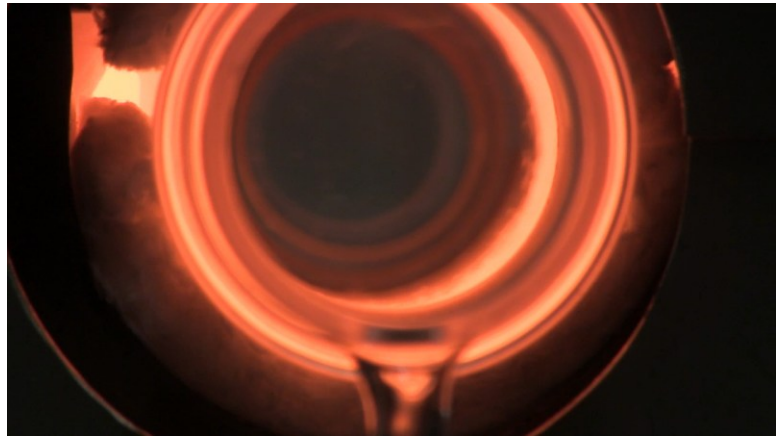
Oxy



”Oxy-combustion”: no visible fume formation

Fume and Temperature

Spain (BL 623)

	800 °C, 3 % O_2	900 °C, 3 % O_2	1000 °C, 3 % O_2
Air			
Oxy			

Sodium and potassium release at 1000°C

	% of BL-Na released	% of BL-K released
Air	15-30%	30-40%
Oxy	1-3%	13-15%

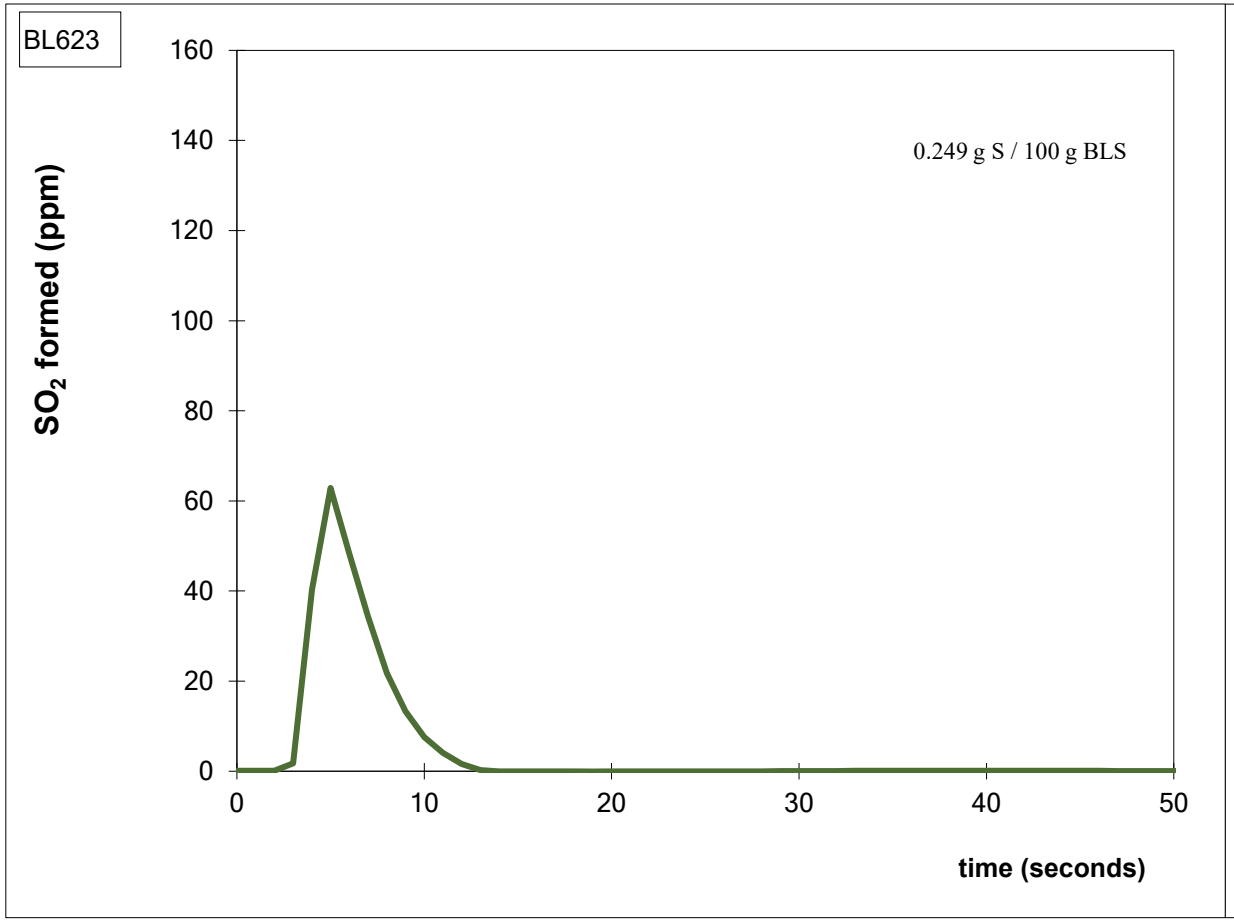
CO_2 inhibiting Na release

- Lower temperature of the particle in oxy-combustion conditions due to gasification reactions?
- CO_2 suppressing Na release
  - CO_2 in the gas inhibiting reduction of $Na_2CO_3(l)$

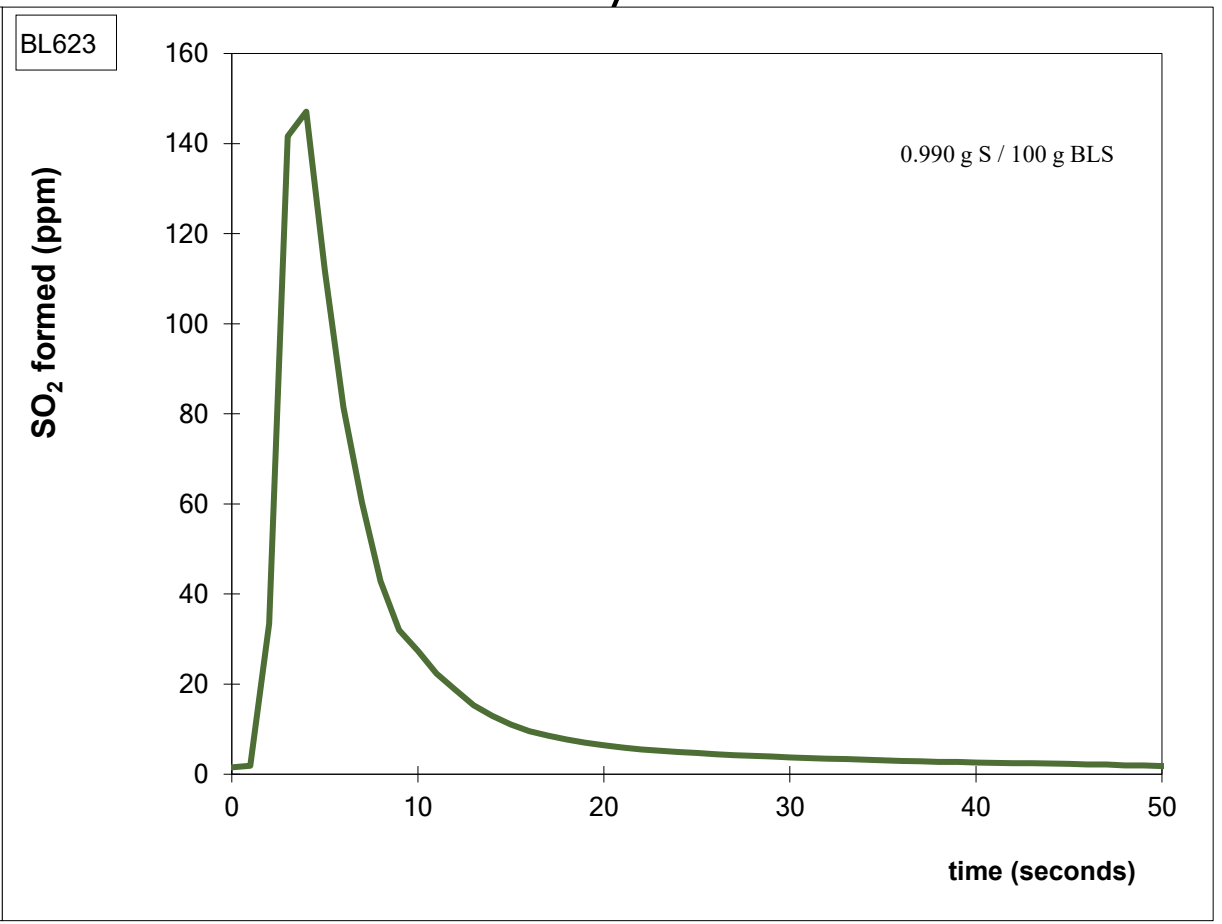
$$Na_2CO_3(l) \xrightarrow{C(s)} Na(g), CO, CO_2$$

SO_2 formation at 900 °C

Air



Oxy



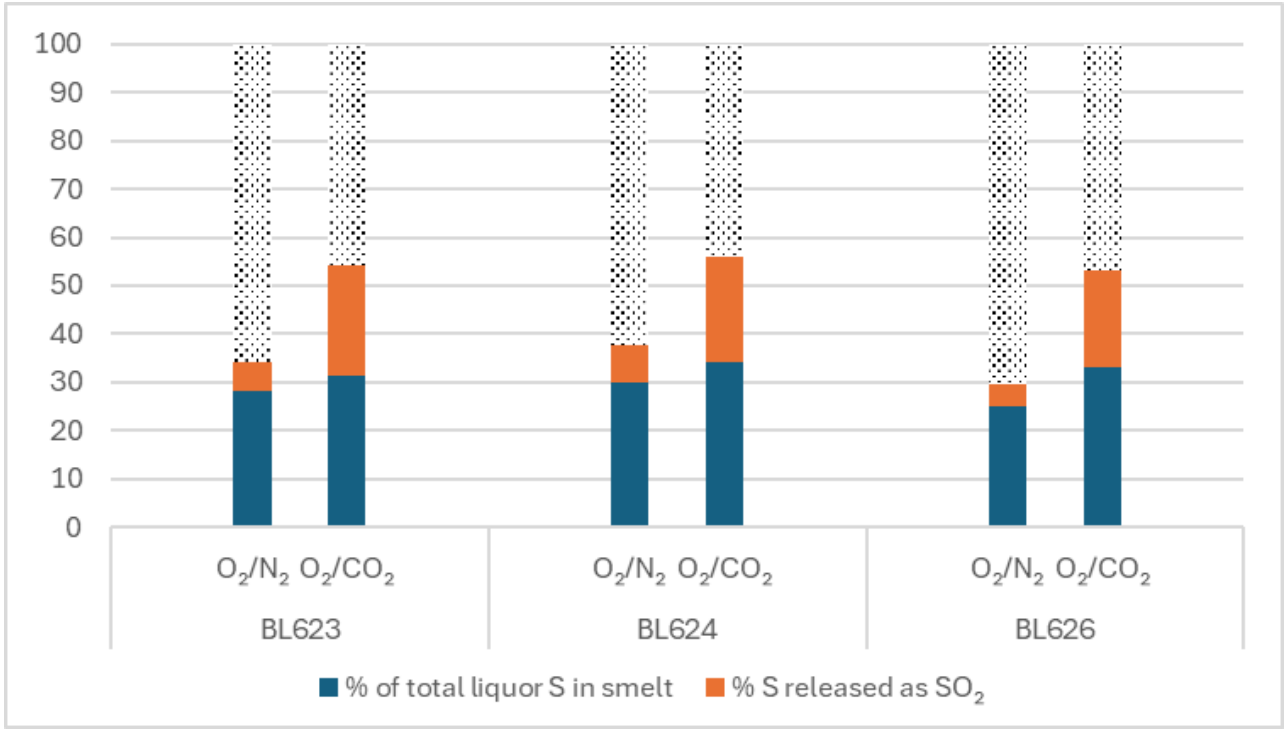
SO_2 formation during droplet burning (900 °C)

% of BL-S	Spain (BL623)	Nordic (BL624)	USA (BL626)
Air	6 %	8 %	5 %
Oxy	23 %	22 %	20 %

SO_2 formation during droplet burning (900 °C)

% of BL-S as SO_2	Spain (BL623)	Nordic (BL624)	USA (BL626)
Air	6 %	8 %	5 %
Oxy	23 %	22 %	20 %

Note, SO_2 captured by fume in air conditions. Similar sulfur release expected, as can be seen from S retained in smelt.

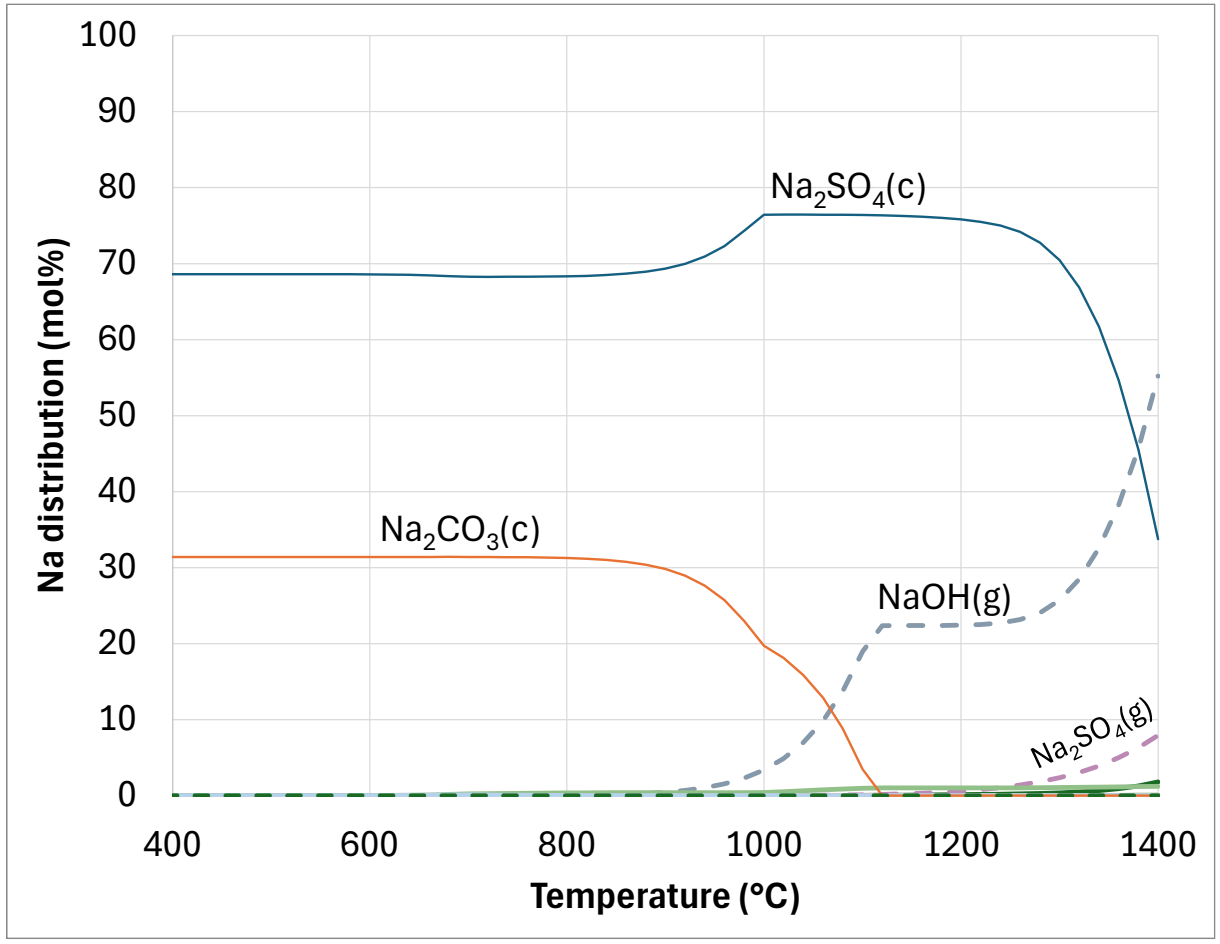


Fume formation in oxy-combustion

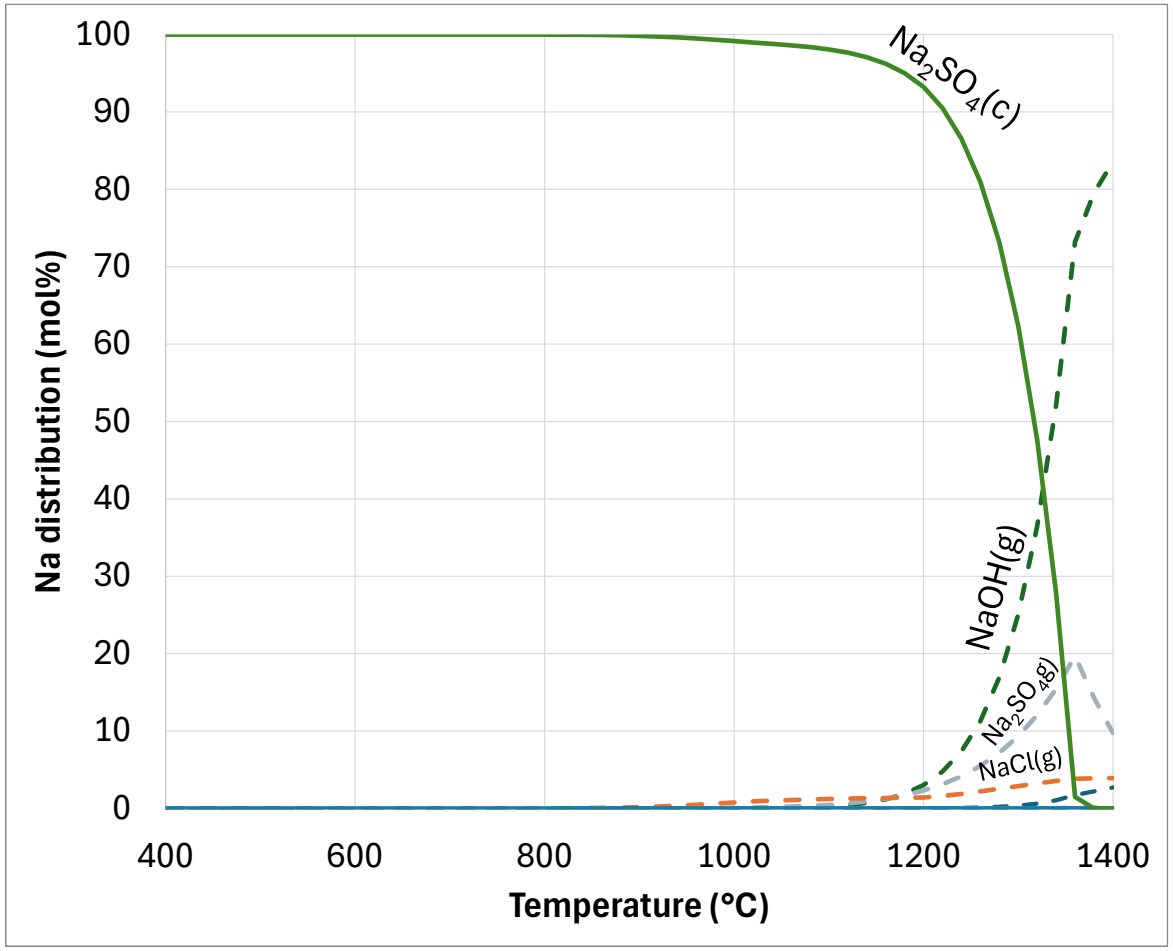
- Sulfur release about the same as in air-fired conditions
- Alkali release significantly lower, especially sodium

Na distribution in fume

Air-firing

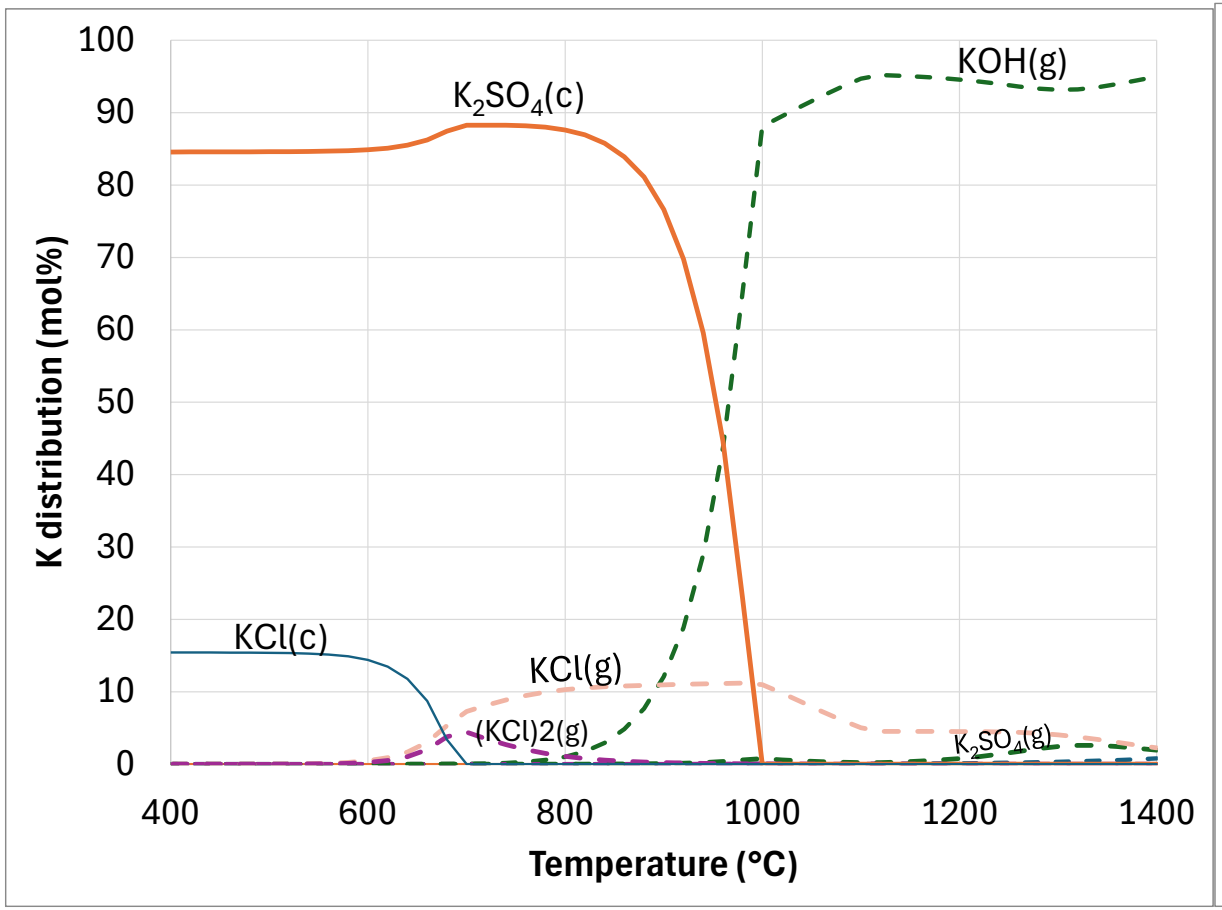


Oxy-firing

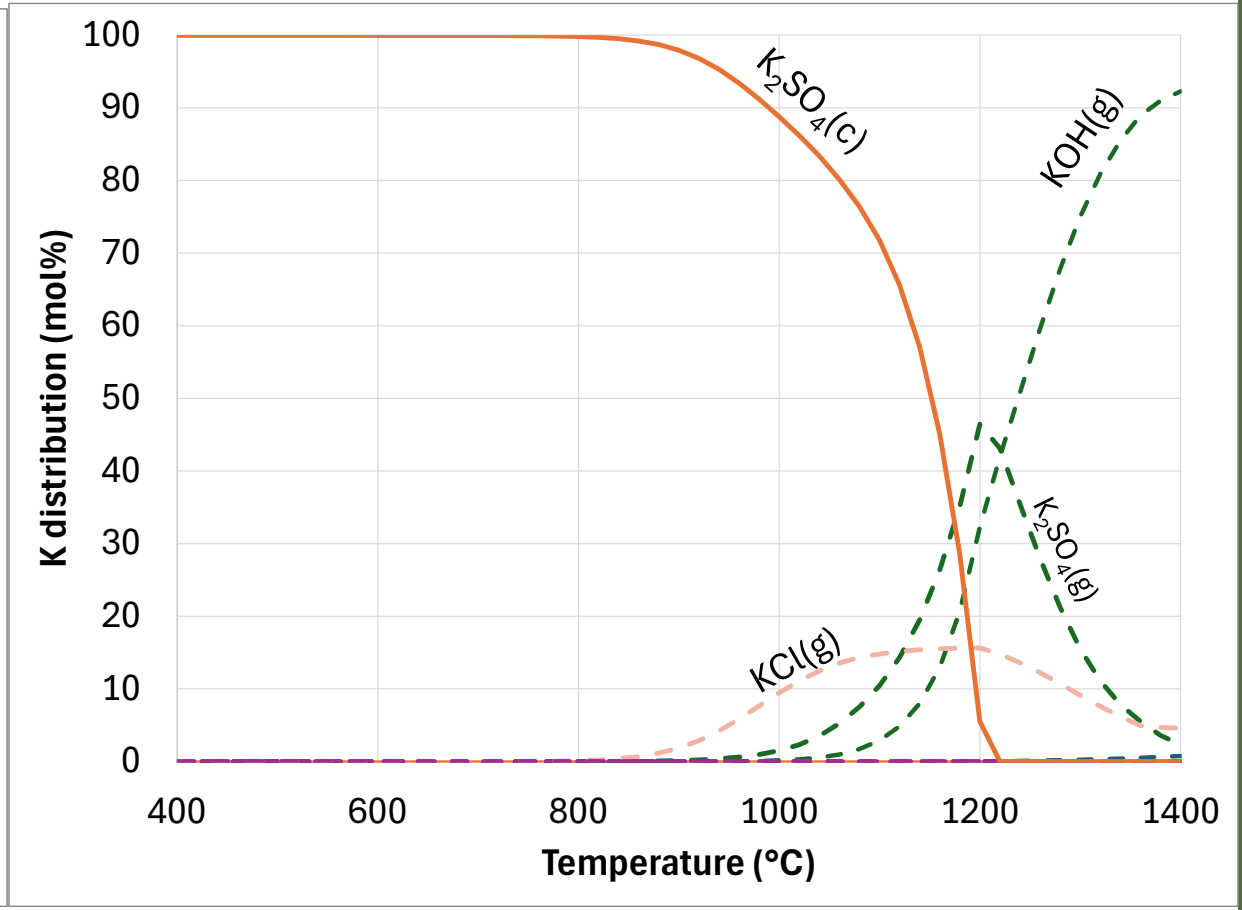


K distribution in fume

Air-firing

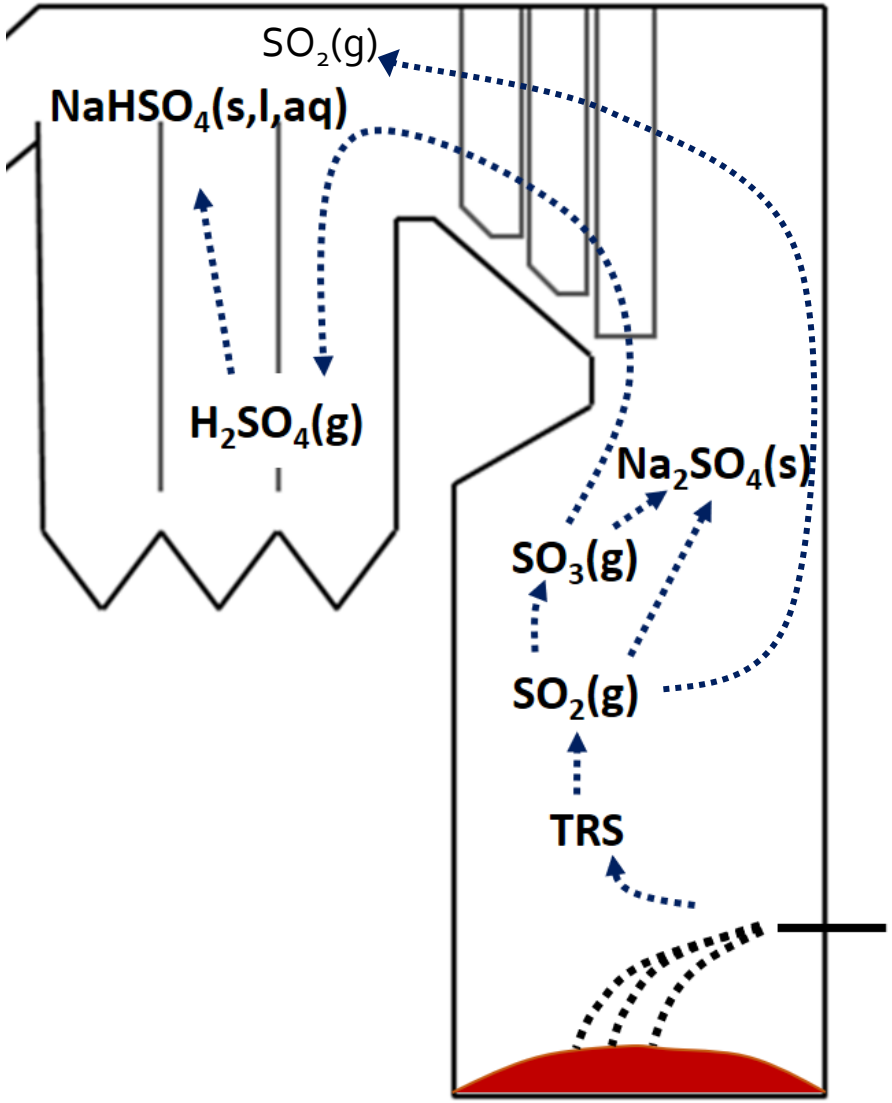


Oxy-firing



- In air-conditions virtually all sulfur in the form of sulfate in the fume
- In oxy-conditions excess SO_2 in the flue gas
- SO_3 formation (max 2% of SO_2) (10-15 ppm_v SO3)
- <500 °C SO_3 start to form $H_2SO_4(g)$

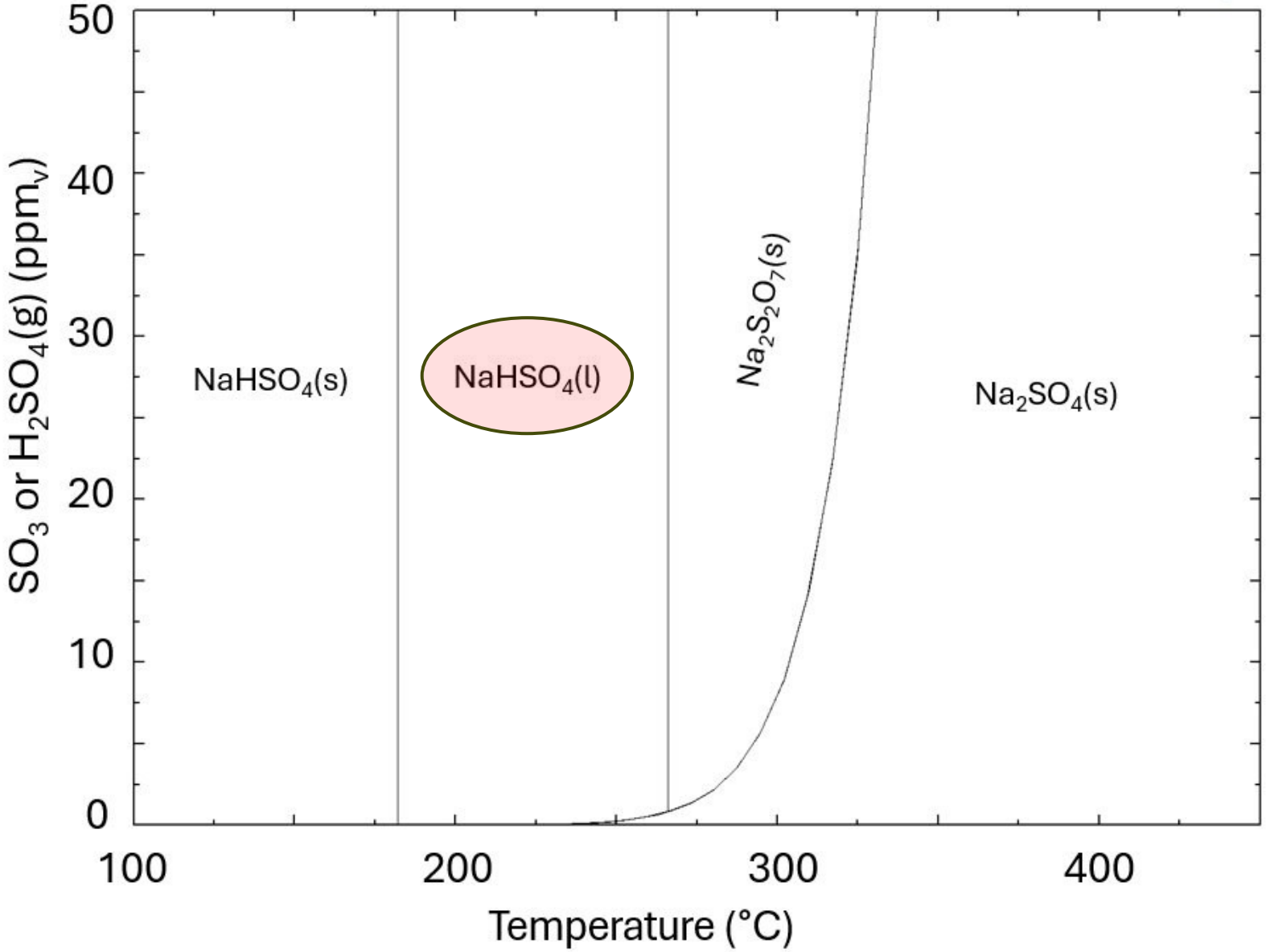
→ Possible formation of acidic sulfates (pyrosulfate and bisulfate)



Formation of acidic sulfates

$Na_2SO_4(s) + SO_3(g) \rightarrow Na_2S_2O_7(s)$

$Na_2SO_4(s) + H_2SO_4(g) \rightarrow 2NaHSO_4(s,l)$



Summary

- Based on these laboratory results, oxy-combustion leads to:
  - Shorter burning times (possible changes in black liquor spraying)
  - Significantly less dust formation
  - Mainly sulfate-rich fume
  - Formation of acidic sulfates, attention in economizer area
  - Scrubbing of excess SO_2 needed

Acknowledgements

- The EU CETpartnership programme
- Project partners:
  - Åbo Akademi University (coordinator), Finland
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