Impact of sorbent injection on ash behavior in the small and pilot scale

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Economic low carbon power Production and Emissions Control for Future and Flexible Biomass Co-fired Power Stations

Outline

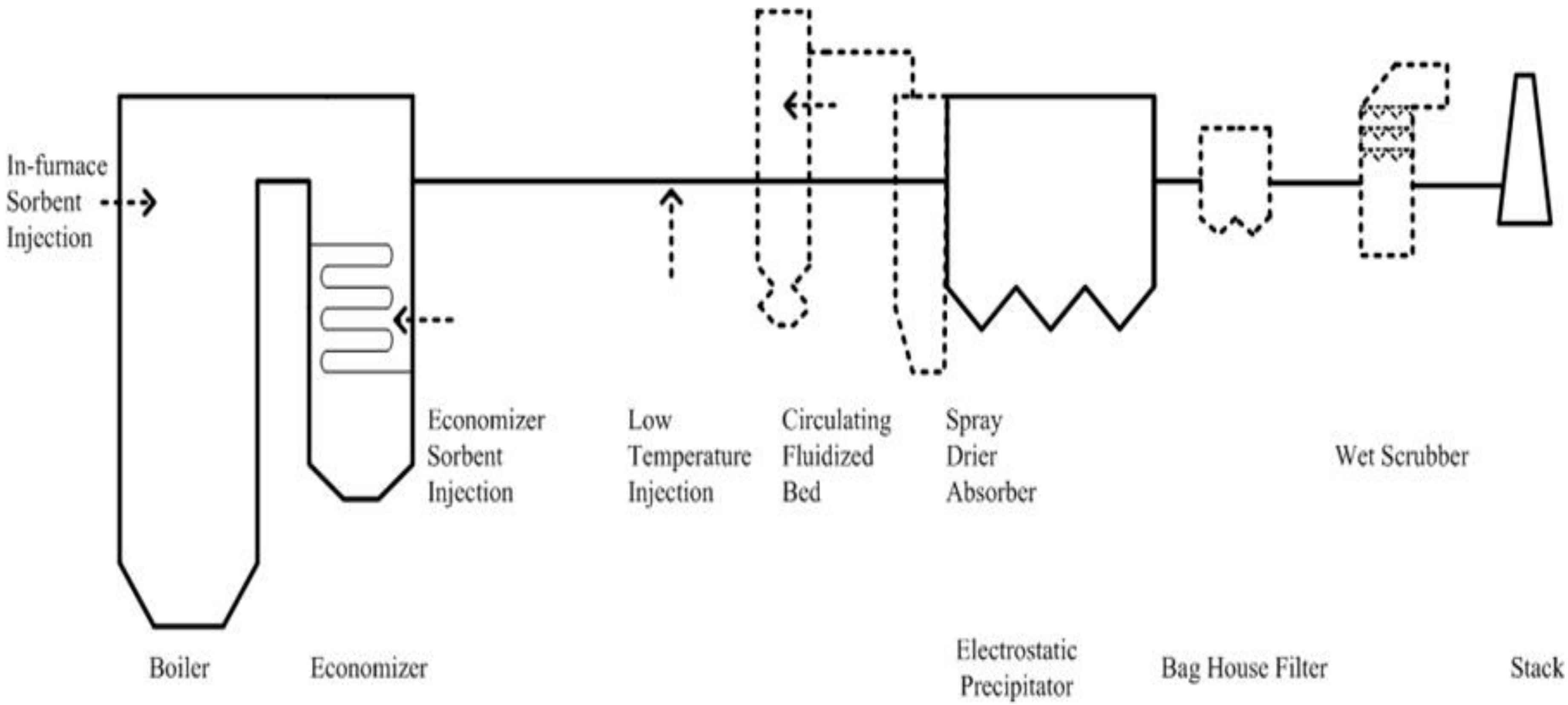
- Objective
- Background
- Motivation
- Methodology
- Results
- Conclusion

Objective: Acid gas removal

- Why limit acid gas (SOx and HCl) emissions
  - Cause harmful impacts to the environment and human health
  - High and low temperature corrosion

- Approaches to limiting acid gases
  - Limiting the input of S and Cl with the fuel input
  - Using different scrubbing technologies for acid gas removal
    - **Dry sorbent injection (DSI) systems**
    - Spray drying absorption (SDA) processes (semi-dry flue gas cleaning process)
    - Wet flue gas desulfurization processes
    - Circulating fluidized bed (CFB) scrubbers

Incorporation in combustion process



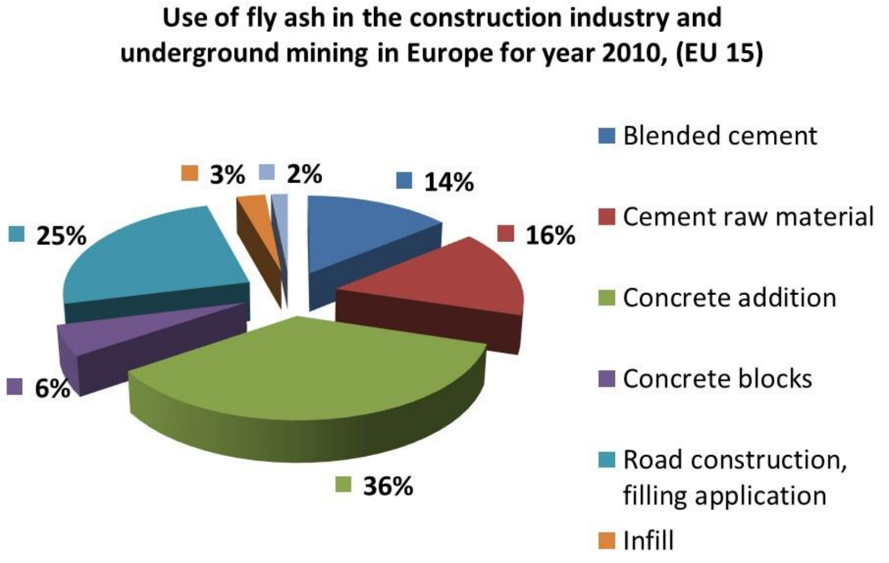
DSI options
-with the fuel
-into the furnace
-in the flue gas duct

Motivation: Fly ash major applications

Table : energy demand for production

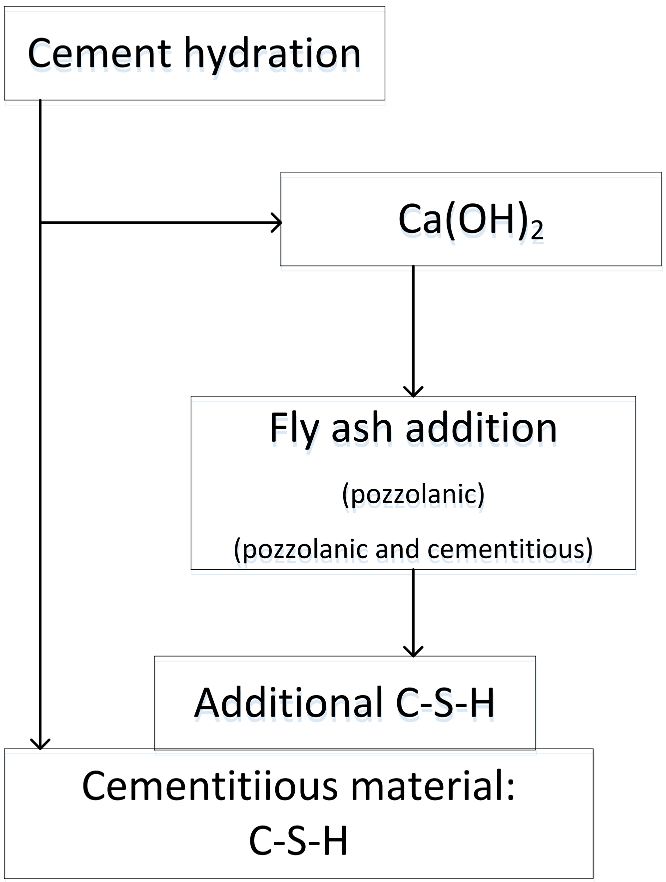
Material	Total Energy Required kJ/kg of Material
Cement	372
Lime	173
Fly ash	0

(Source: (Lohtia 1995))



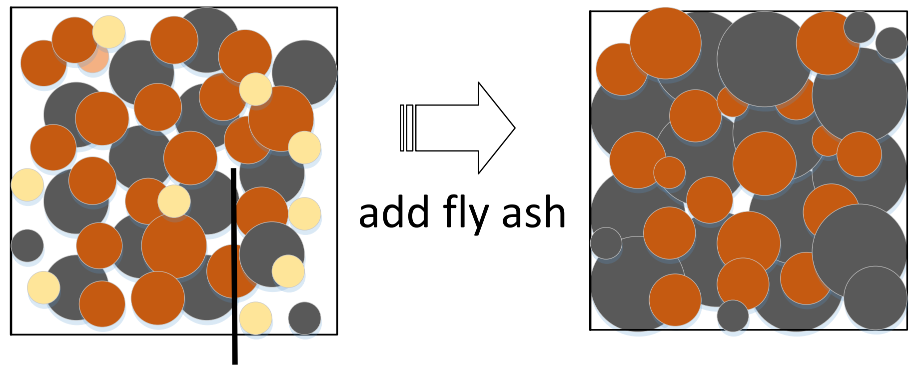
Source: (Feuerborn 2015)

Motivation: Fly ash use benefits

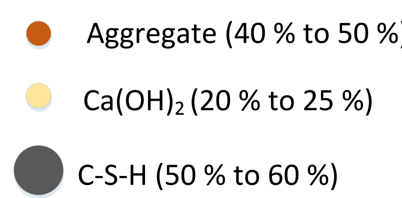


Source: (modified from Sankaralingam 2012)

$$3Ca(OH)_2 + 2SiO_2(amorphous) \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O$$



void space
(porosity)



- Enhanced mechanical properties (e.g. strength)
- Low porosity (more dense)
- Higher resistance to chemical attack
- Lower construction cost
- Resource conservation

Motivation: Concerns of dry sorbent injection

- Potential fly ash concerns in normal concrete from calcium based sorbent injections

1. Increased sulfur content in fly ash

   Sulfate reactions create compounds occupying a greater volume, causing expansion and failure of concrete

2. Increased free calcium content in fly ash

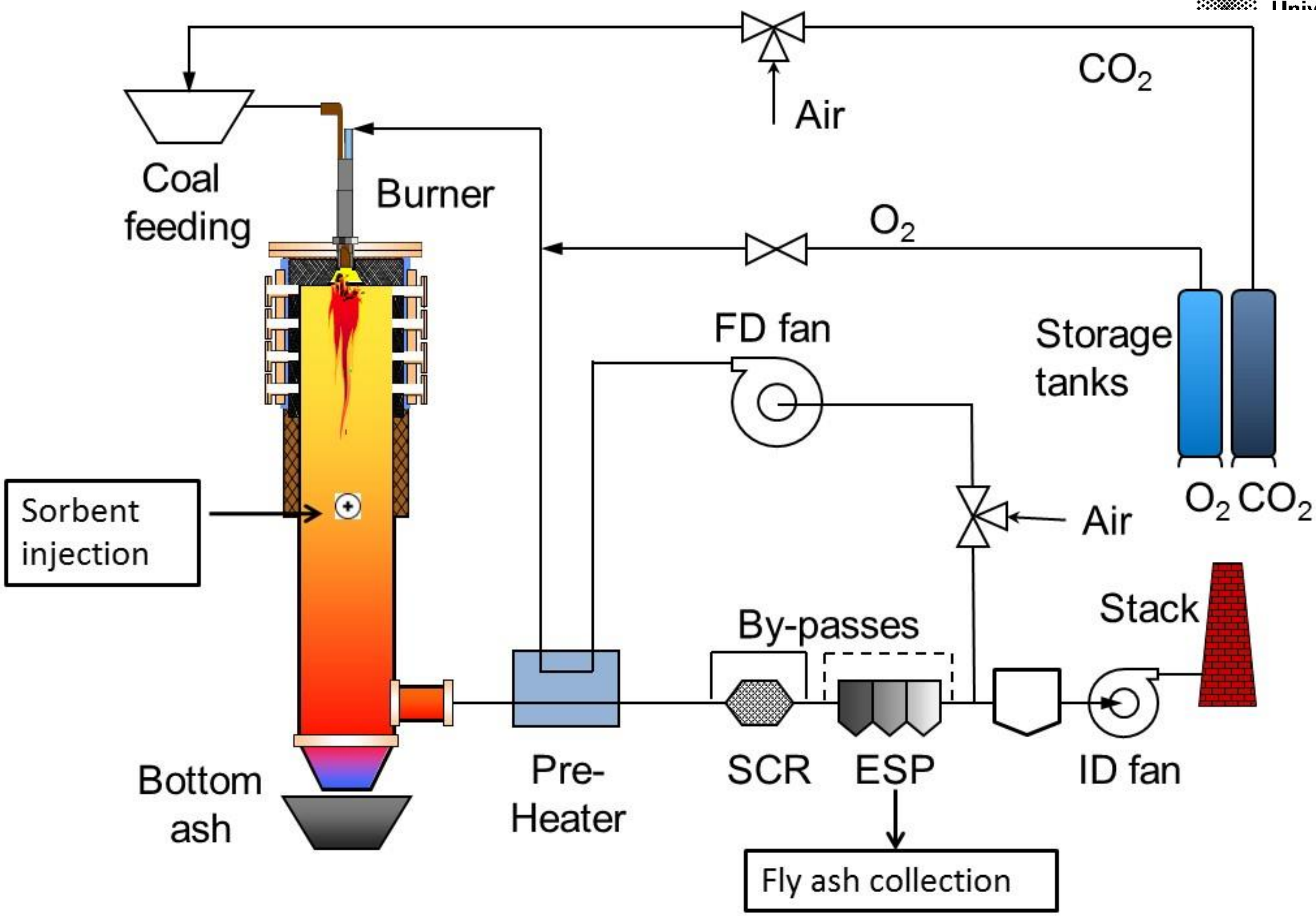
   Excess amounts react with water forming $Ca(OH)_2$, undesirable volume changes in concrete

3. Increased chloride content in fly ash

   Cl ions negatively impact the protective film covering steel reinforcement in concrete (corrosion risk)

Methodology

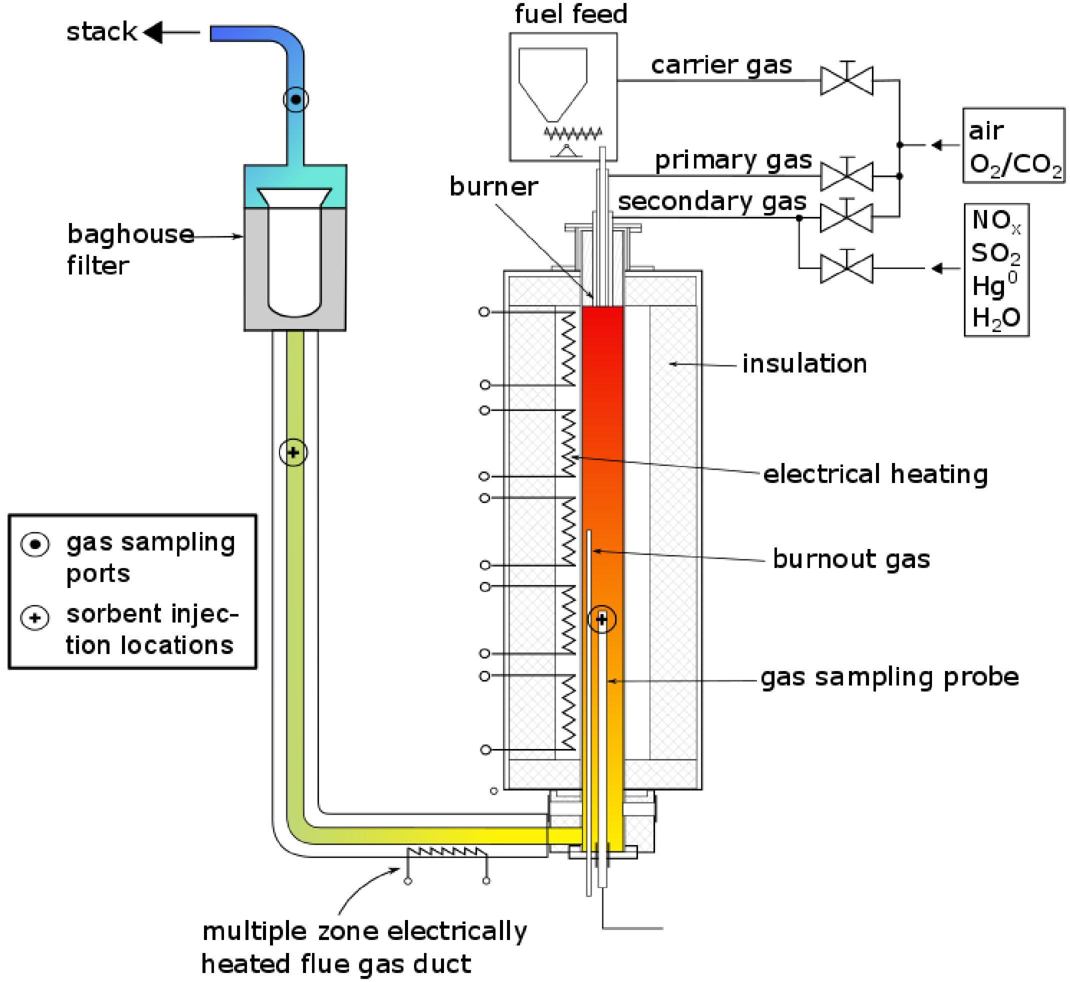
Test facility: 500kW pilot-scale



- Oxy-fuel condition with sorbent in-furnace injection

Test facility: 20kW lab-scale

- Air and oxy-fuel conditions
- In-furnace and before filter sorbent injection under air combustion



Fuel and sorbent characteristics

➢ Coal analysis

Fuel	NCV [MJ/kg, raw]	H_2O [%, raw]	Ash [%, wf]	V [%, waf]	C_{fix} [%, waf]	C [%, waf]	S [%, waf]	H [%, waf]	N [%, waf]	O [%, waf]
US2.5 coal	30.5	1.6	9.43	38.72	61.28	81.91	2.67	5.20	1.59	8.63

Fuel	Al2O3	CaO	Fe2O3	K2O	MgO	Na2O	P2O5	SO3	SiO2	TiO2
US2.5 coal	20.3	3.7	14.4	2.4	0.9	0.7	0.2	3.0	52	1.1

➢ Sorbent analysis

Sorbacal®SPS mainly $Ca(OH)_{2,}$

Methodology: Fly ash characterizations

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- **Chemical composition**
  - Oxides analysis by ICP-OES
  - Reactive SiO_2
  - Reactive CaO

- **Mineralogical classification**
  - X-ray powder diffraction (XRD)

Classification	Mineral phases
Active	Anhydrate, Lime
Semi-active	Carbonates, Calcite, Hematite
Inert	Quartz, Mulite
Pozzolanic	Glass (amorphous material)

- **Physical charateristics**
  - Particle size ditribution (PSD), Malvern 2600

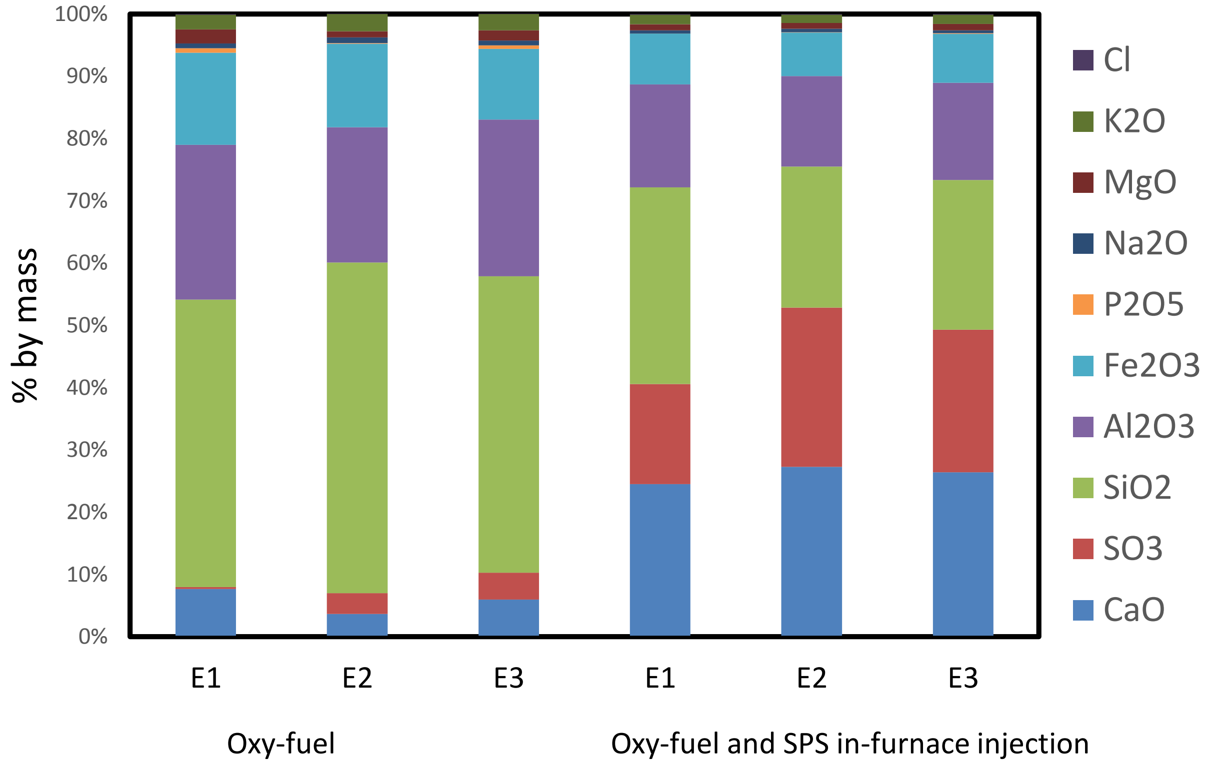
Methodology: Fly ash utilization

European Union standards

- Fly ash for concrete – Part 1: Definition, specifications, and conformity criteria (EN 450-1) ***(high technical application)***
- Hydraulic road binders- Part 1: Rapid hardening hydraulic road binders- composition, specifications, and conformity criteria (EN 13282-1)
- Hydraulic road binders- Part 2: Normal hardening hydraulic road binders- composition, specifications, and conformity criteria (EN 13282-2)
- Cement- Composition, specifications and conformity criteria for common cements (EN 197-1)

Results: Fly ash characteristics

Chemical composition (500 kW)



- Increased S content of the ash with sorbent injection
- Capture of sulfur with finer particles finding in ESP2 and ESP3

Fly ash enrichment of elements (500 kW)

	Dilution factor
Al_2O_3	1.5
Fe_2O_3	2.2
MnO_2	1.3
SiO_2	2.3
Average	1.9

$$\text{Dilution factor} = D_A = \frac{X_{(i,A)}}{X_{(i,A+S)}}$$

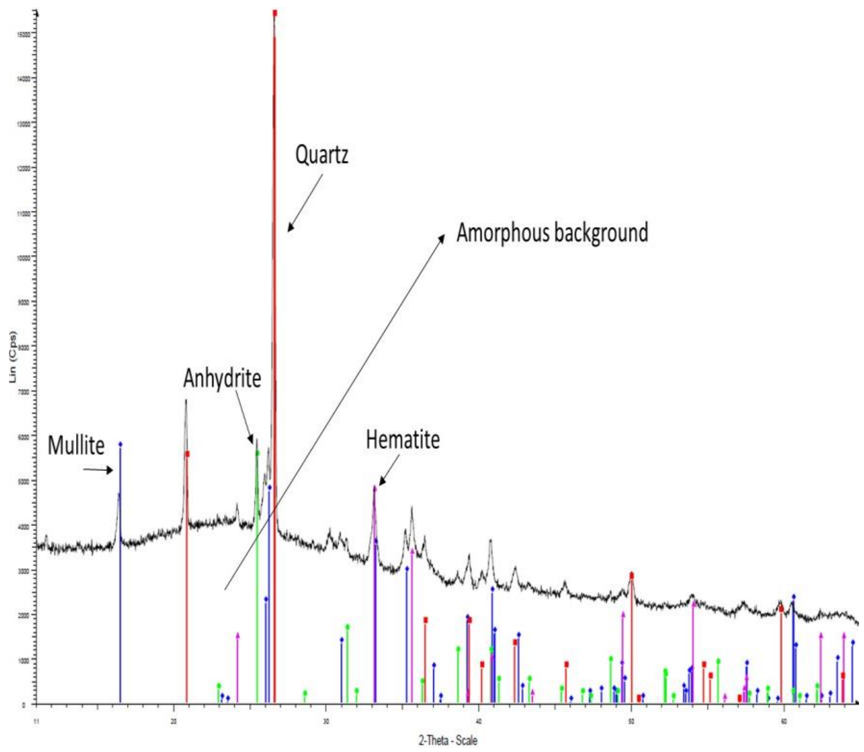
$X_{(i,A)}$: Oxide concentration in the fuel ash
$X_{(i,A+S)}$: Oxide concentraion in the fly ash

Ca and S mass based enrichment factor	
Ca	12
S	14

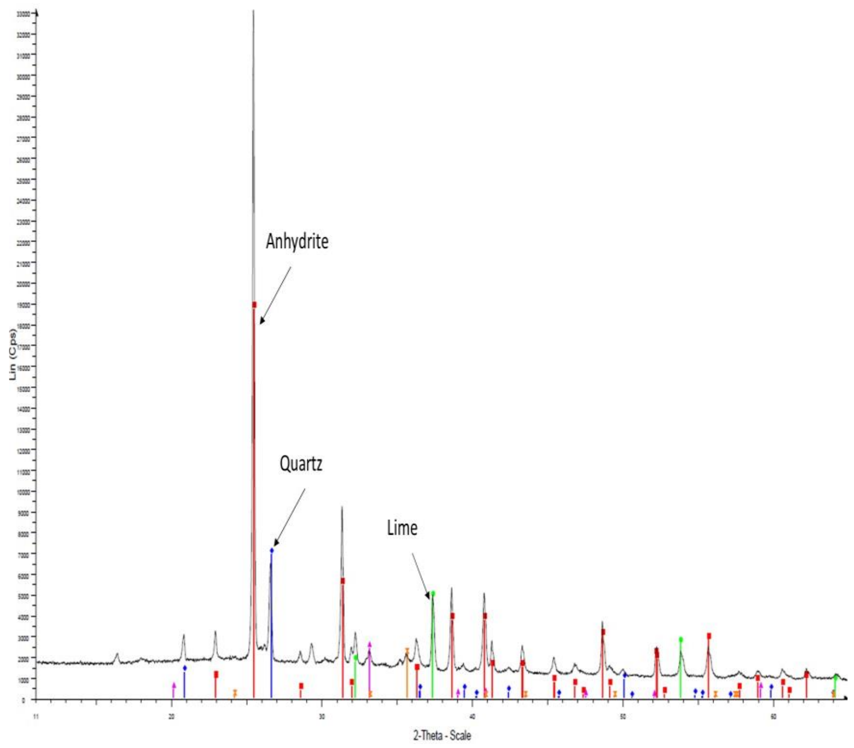
$$\text{Enrichment factor} = \frac{X_{(i,A+S)}}{X_{(i,A)}} \times D_A$$

XRD analysis (500 kW)

Oxyfuel scenario



Oxy-fuel with SPS in-furnace injection



- Reduced amorphous material and increased active phase with sorbent addition

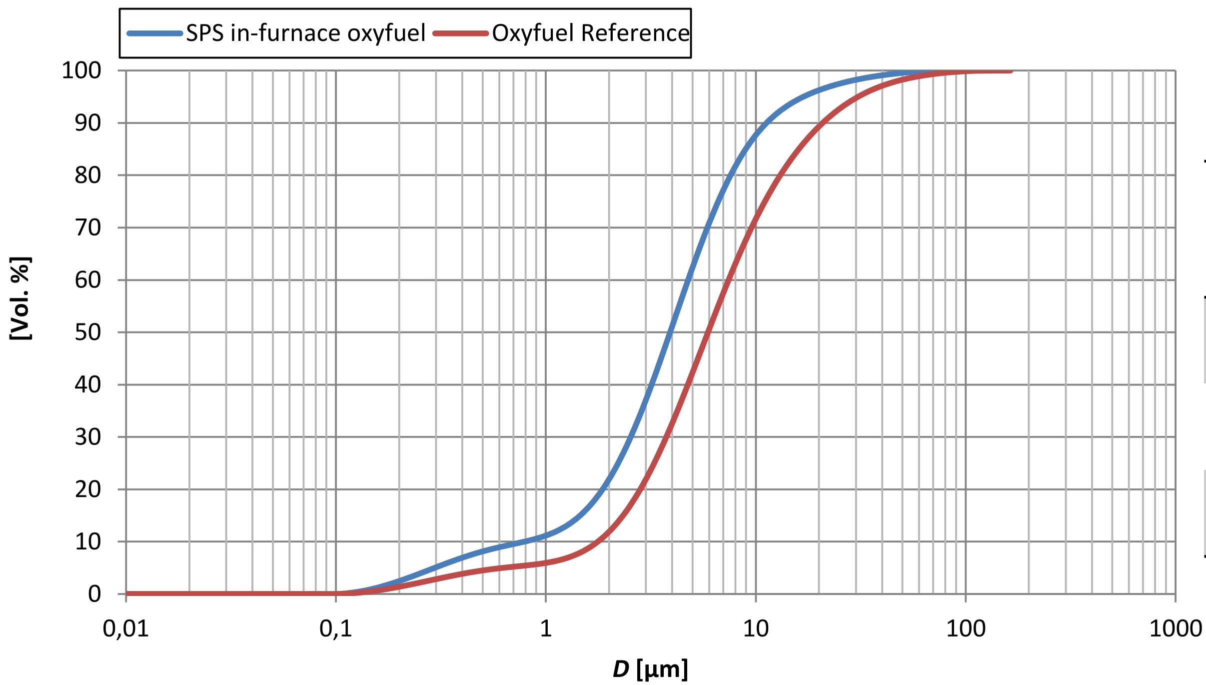
XRD analysis (500 kW)

Scenario	Quartz	Anhydrite	Lime	Hematite	Mullite	Amorphous matter
Oxyfuel	+++	++	-	++	++	+++
Oxyfuel with SPS	++	+++	++	+	+	-

+++ significant; ++ moderate; + insignificant; - none

Scenario	Effect
Oxyfuel	Pozzolanic quality fly ash- react with $Ca(OH)_2$ to produce C-S-H
Oxyfuel with SPS	Shifted to mineral phases that have an active or semi-active quality

Fly ash particle size distribution (500 kW)



Parameter	Oxyfuel reference	SPS in-furnace oxyfuel
D_{10}	2.00	0.89
D_{50}	6.72	4.43
D_{90}	23.7	12.8

- Reduced particle size distribution due to fine sorbent particles
- Smaller particles sizes and higher surface area leading to more reactivity
  → improve fly ash performance in concrete

Chemical composition (Air and oxy-fuel 20 kW)

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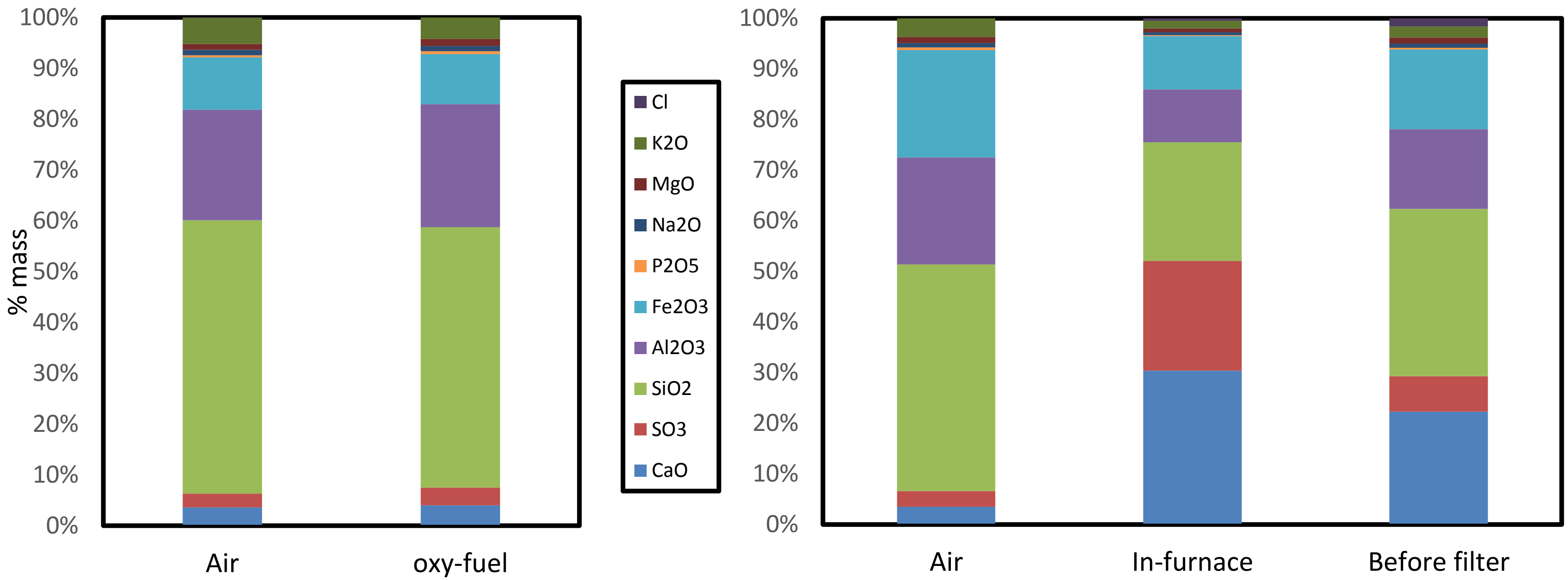
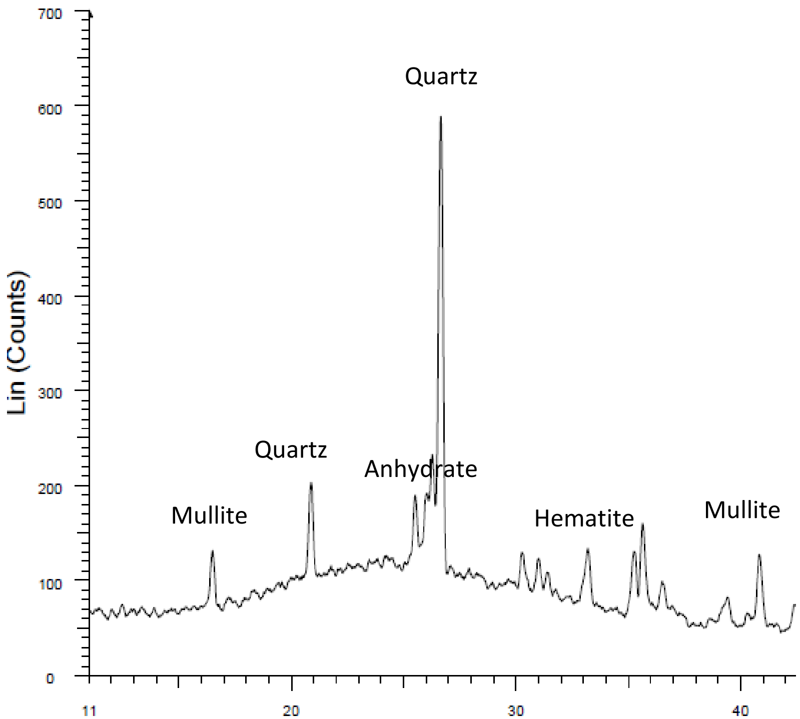


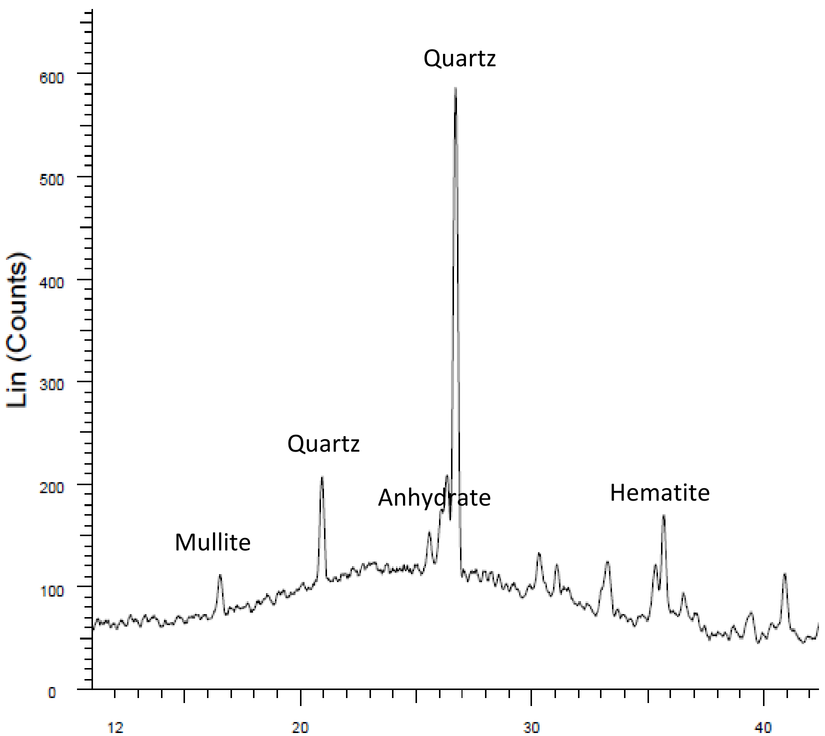
- No difference in chemical composition under air and oxy-fuel conditions
- Increased S content for in-furnace injection
- Increased Cl content for before filter injection

XRD analysis (Air and Oxy-fuel, 20 kW)

Oxy-fuel combustion



Air combustion



- No significant difference between the mineral faces in air and oxy-fuel combustion conditions

XRD analysis (Sorbent injection, 20 kW)

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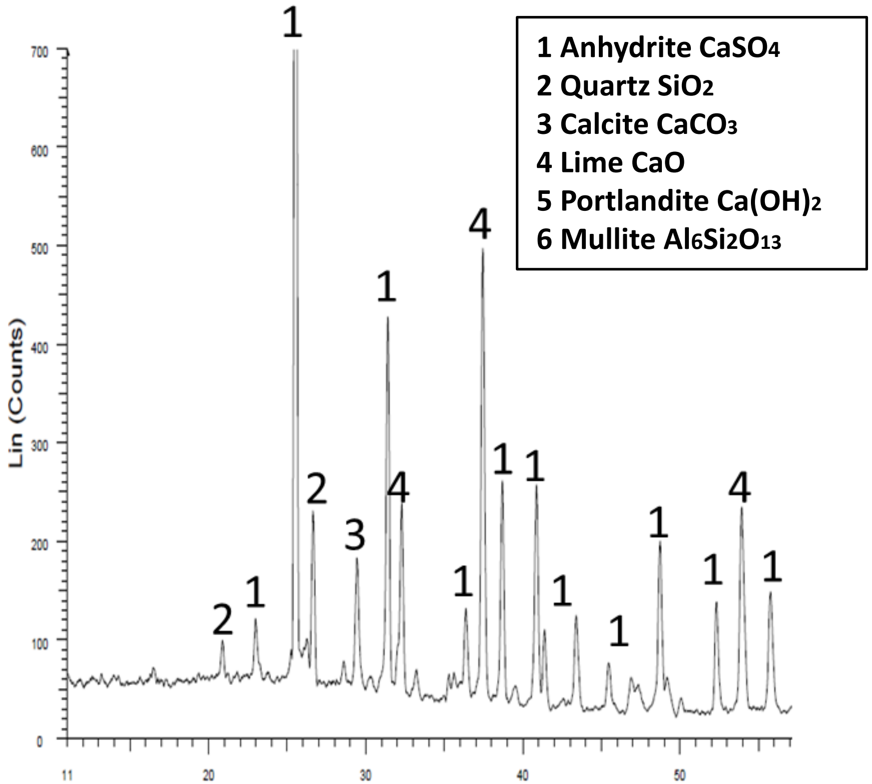
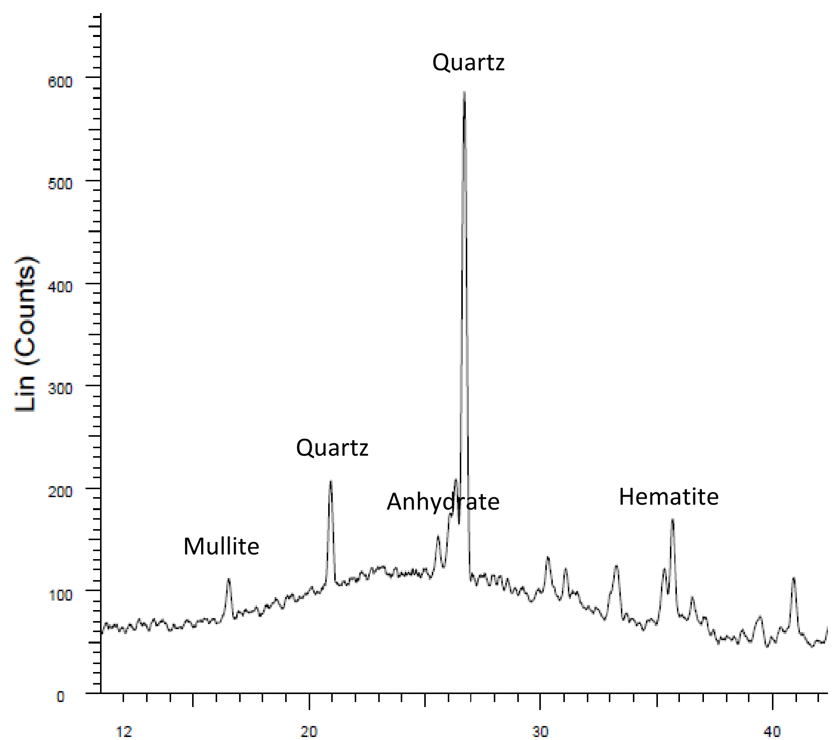
Air comb. with in-furnace injection



Air combustion



- Reduced amorphous background and more active material $CaSO_4$ formation

XRD anlysis (Sorbent injection, 20 kW)

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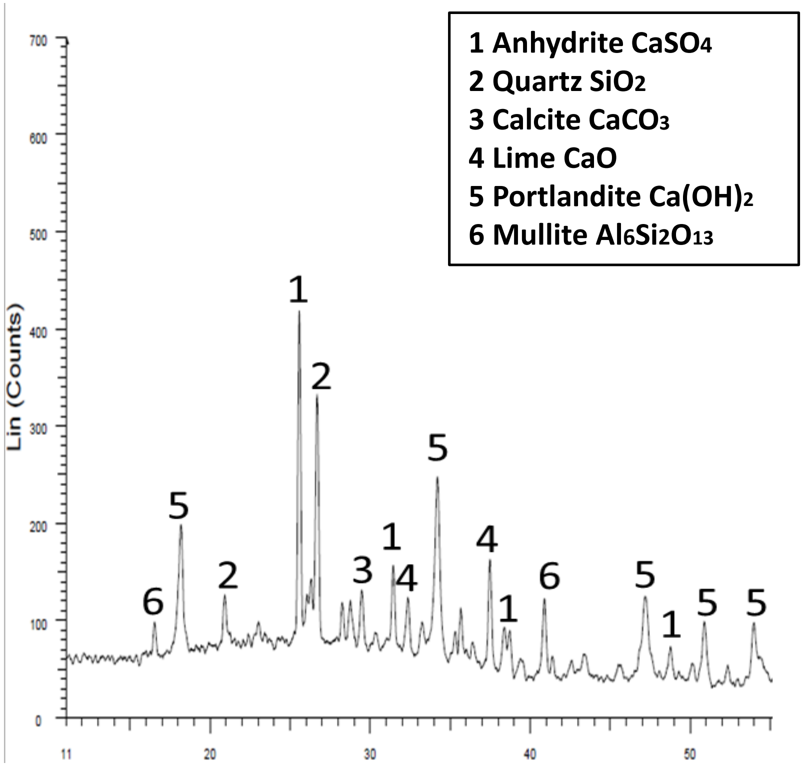
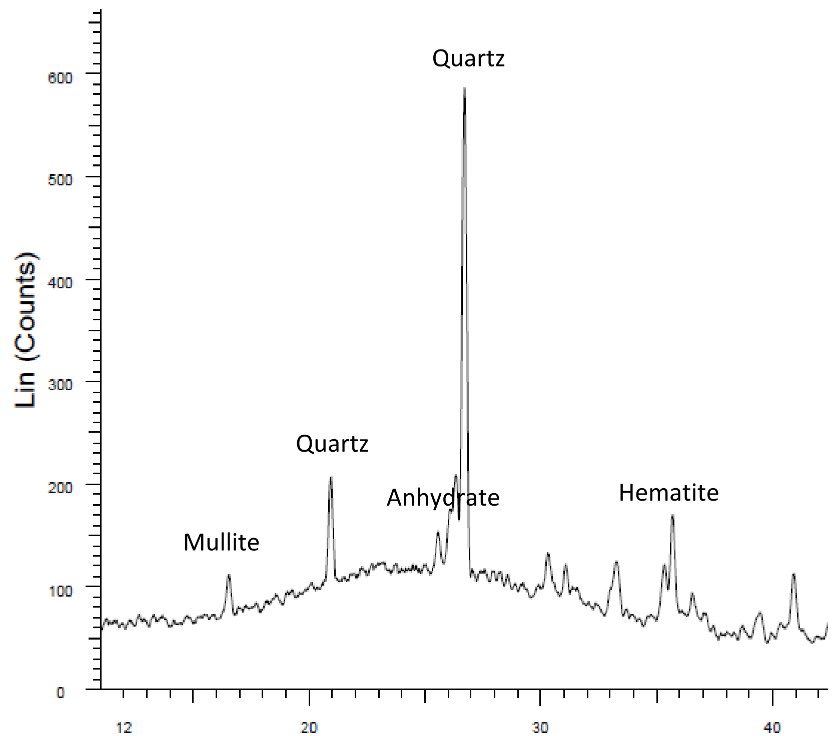
Air comb. with before filter injection



Air combustion



- Reduced amorphous background and more unreacted $Ca(OH)_2$

Results: Fly ash marketability

Fly ash marketability for concrete (EN450-1)

EN450-1 (for concrete) Some parameters	Value [% mass]	Oxyfuel (500kW)	Oxyfuel, SPS in-furnace (500 kW)	Air (20 kW)	Oxy-fuel (20kW)	Air, SPS in-furnace (20 kW)	Air, SPS before filter (20 kW)
Loss on ignition class A class B class C	≤ 5 ≤ 7 ≤ 9	5.4	2.2 (4.18)	4	7	0.8	1.1
SiO_2-Al_2O_3-Fe_2O_3	≥ 70	74.83	42.09	86	85	41.2	61.1
Reactive (CaO)	≤ 10	satisfied	9	10	10	15.9	17.7
Reactive SiO_2	≥ 25	42	8.67	-	-	-	-
SO_3	≤ 3	2.97	23.1	2.7	3.5	23.2	7.7
Chloride (Cl^-)	≤ 0.1	0.016	0.088	0.08	0.06	0.5	1.8

(Source: Feuerborn 2011)

- Oxy-fuel combustion does not have impact on fly ash utilization
- Sorbent injection deteriorates the fly ash characteristic for EN450-1

Fly ash marketability for cement (EN 197-1)

Cement- Composition, specifications (EN 197-1)

EN 197-1	Value [% mass]	Oxyfuel (500kW)	Oxyfuel, SPS in-furnace (500 kW)	Air (20 kW)	Oxy-fuel (20kW)	Air, SPS in-furnace (20 kW)	Air, SPS before filter (20 kW)
Reactive (CaO)	≤ 10 (a) ≤ 10-15 (b)	satisfied	9	10	10	15.9	17.7
Reactive SiO_2	≥ 25	42	8.67	-	-	-	-
SO_3	≤ 4	2.97	23.1	2.7	3.5	23.2	7.7
Chloride (Cl^-)	≤ 0.1	0.016	0.088	0.08	0.06	0.5	1.8

(a) Siliceous fly ash : Reactive SiO_2 ≥ 25% and reactive CaO <10%
(b) Calcareous fly ash : Reactive SiO_2 ≥25% and reactive CaO>10-15%

- LOI requirement is already satisfied in EN 450-1
- Fly ash obtained from sorbent injection do not meet the requirements for cement standards (EN 197-1)

Fly ash marketability for road binders (EN 13282)

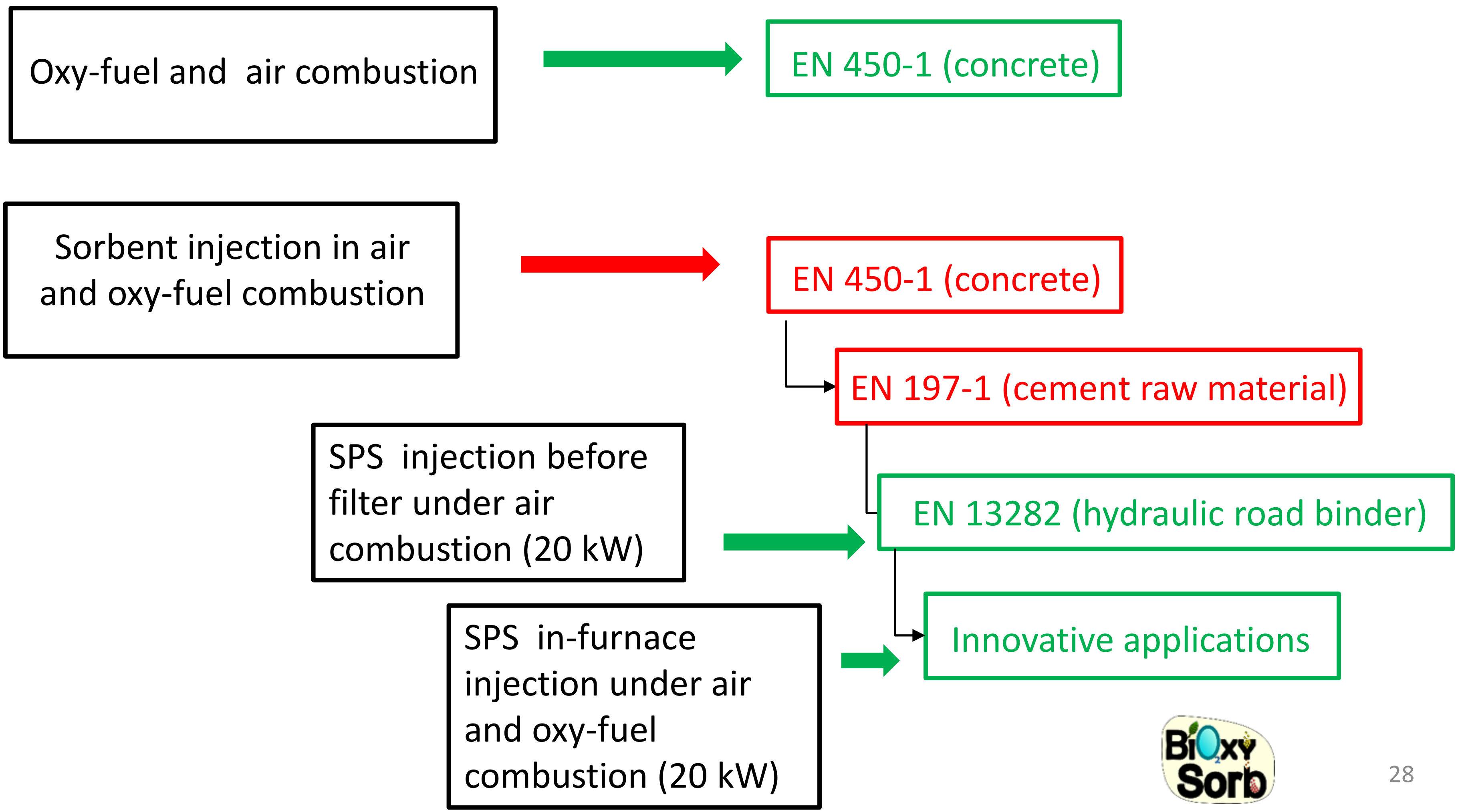
Hydraulic road binders- (EN- 13282-1)

EN 13282-1	Value [% mass]	Oxyfuel (500kW)	Oxyfuel, SPS in-furnace (500 kW)	Air (20 kW)	Oxy-fuel (20kW)	Air, SPS in-furnace (20 kW)	Air, SPS before filter (20 kW)
Reactive SiO_2	≥ 25	42	8.67	-	-	-	-
SO_3	≤ 5 (a) ≤ 10 (b)	2.97	23.1	2.7	3.5	23.2	7.7

(a) Siliceous fly ash : Reactive SiO_2 ≥ 25% and reactive CaO <10%
(b) Calcareous fly ash : Reactive SiO_2 ≥ 25% and reactive caO>10-15%

- Considering calcareous fly ash, SPS injection before the filter under air condition at 20 kW scale meets the requirement for road binders (EN 13282)

Fly ash marketability based on current evaluations and widely used standards



Potential innovative fly ash uses

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- **Innovative soil amendment**
  - Improve soil structure and physical characteristics
  - Acid neutralizing reactions (calcium): releases nutrients; reduces plant toxicity (Al, Mn, Fe) in acidic soils
  - SiO_2, CaO, Al_2O_3, SO_4 react to form secondary minerals: decrease toxic heavy metals leaching; improve water retention, soil strength, and porosity in soils (calcium alumina-silicate hydrates)

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

$$Ca^{2+} + 2OH^- + SiO_2 \text{ (clay silica)} \rightarrow CaO{\cdot}SiO_2{\cdot}H_2O$$

$$Ca^{2+} + 2OH^- + Al_2O_3 \text{ (clay alumina)} \rightarrow CaO{\cdot}Al_2O_3{\cdot}H_2O$$

Source: (Dermatas 2003)

- **Innovative fertilizer**
  - Calcium oxide reaction with acidic components in soil improve plant fertility
  - Ca and S are secondary plant nutrients

- **Masonry constituent**
  - Aerated concrete bricks (principal constituents: quartz sand, pulverized fly ash, anhydrous calcium sulfate ($CaSO_4$)
  - External render base coat component
    - High SO_3 content (acids resist weather and acid rain)
  - Floor screeds

Conclusion

- Oxy-fuel combustion does not affect mineral phases of the fly ash
- Sorbent injection reduces the amourphases background of the fly ash and increases the active and semi active mineral phases
- Oxy-fuel combustion generates a fly ash quality applicable to normal coal ash standards (EN 450-1)
- Before the filter injection of SPS generates a fly ash applicable for hydraulic road binders from chemical analyses of limits
- In-furnace injection of SPS generates a fly ash quality with potential benefits in innovative land use, masonry or mortar, and etc. (i.e. take advantage of the behavior of the calcium minerals phases)

Thank you for your attention!

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