Dry powdered lime for acidic gas removal in coal fired power plant

Impact on the fly ash behavior and valorization

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

Who is Lhoist ?

Lime based dry sorbent injection at 20MW pilot unit in CIUDEN

Dry sorbents delivered to CIUDEN

SO_2 removal performance in CIUDEN

Fly ash analysis & valorization

Conclusions

The Lhoist Philosophy

Who are we ? What are we?

- **Our Philosophy**

Quarry in Belgium
Lhoist Group Collection

WE ARE PROUD INDUSTRIALISTS

The Soldier's Tree, 1993
Rodney Graham
Lhoist Group Collection

WE ARE A FAMILY-OWNED COMPANY

Green Ball, 1995
Gabriel Orozco
Lhoist Group Collection

WE ARE DRIVEN BY OUR CUSTOMERS AND MARKETS

Untitled (Cowboys), 1990
Richard Prince
Lhoist Group Collection

WE ARE PIONEERS

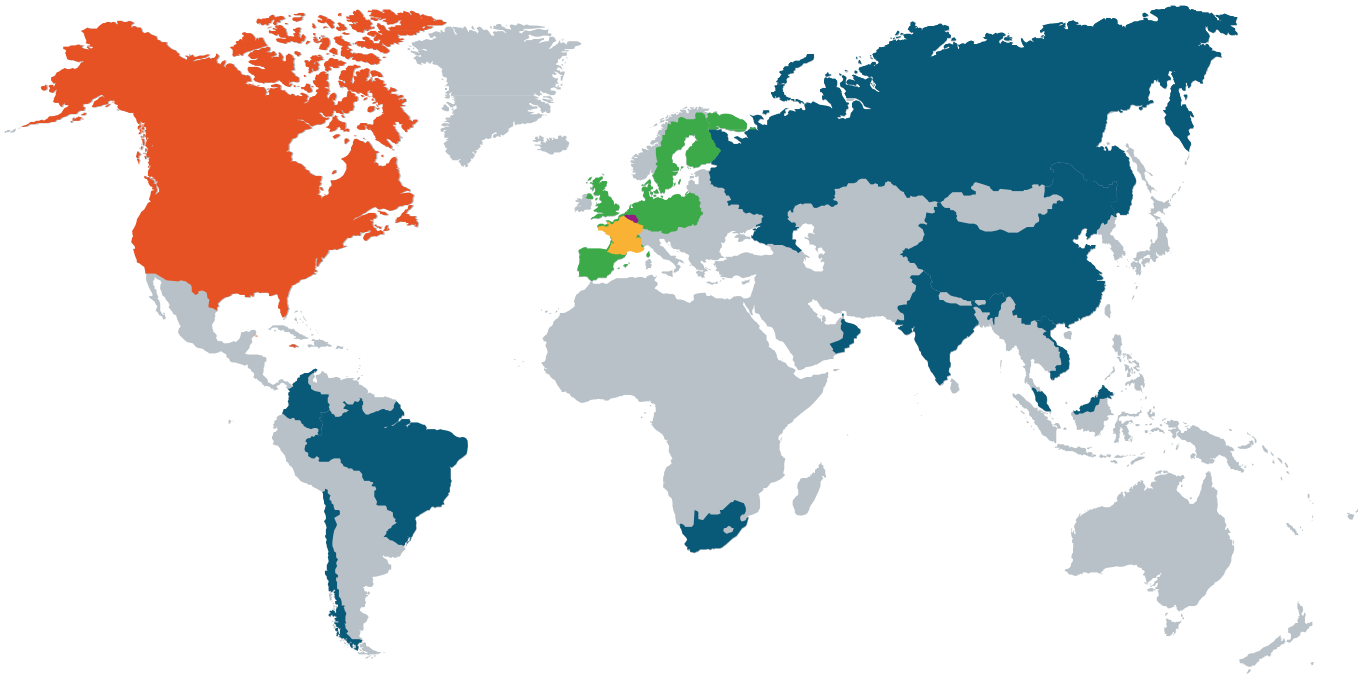
Les joueurs, 1991
Michel François
Lhoist Group Collection

OUR PEOPLE MAKE IT ALL HAPPEN

Lhoist Worldwide Presence

Where are we?

- **Lhoist Group in the world**



OVER 125 YEARS OF EXPERTISE & INNOVATION

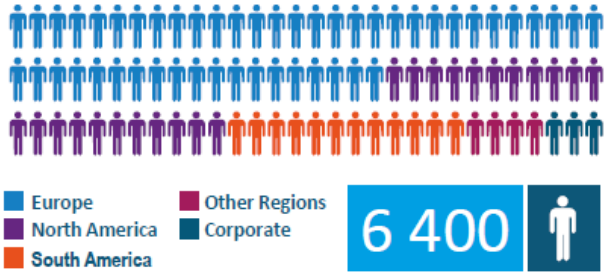
1889	1926	The 80's	The 90's	New millennium
Foundation of the Group in Belgium	First expansion to France	Crossing the Atlantic (US, Canada)	Further development to Western & Eastern Europe	South America, Africa, Asia & Russia

Lhoist Group Key Numbers

What is our size?

- **Lhoist Group**

TURNOVER



>40 NATIONALITIES

- 1 R&D CENTER
- 4 CUSTOMER TECHNICAL SERVICE CENTERS
- > 25 COUNTRIES
- 100 PLANTS
- 800 FGT CUSTOMERS in EU and > 250 in the USA

Lhoist Group Main Products

What do we manufacture?





MINERALS

- Limestone
- Dolomite
- Clay and others

CALCINED PRODUCTS

- Quicklime (pebble, ground, milled)
- Burnt dolomite (soft-/hard-/overburnt)
- Hydrated lime

SPECIALTY PRODUCTS

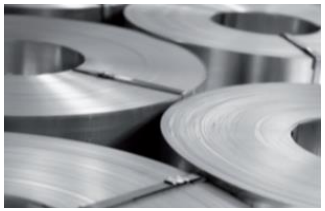
- Milk of lime
- Fluidized lime
- Low dust emission lime
- High porosity hydrated lime
- Formulated products

$CaCO_3$ $MgCO_3.CaCO_3$ $Ca_xMg_yAl_zSi_pO_q(OH)_r$	CaO $MgO.CaCO_3$ $MgO.CaO$	$Ca(OH)_2$, $Mg(OH)_2.CaCO_3$ $Mg(OH)_2.Ca(OH)_2$ Formulated hydrates, clays, minerals & calcined products

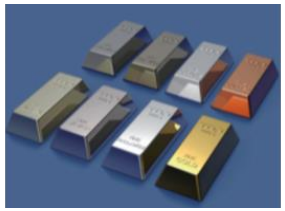
Lhoist Group Main Markets

Who are our customers?

- **Large diversity of applications**



Iron and steel



Non-ferrous metals

Pulp and paper

Flucal® Calexor®

Britelim®

Drinking water

Water and sludge

Flue gas treatment

Akdolit®

Neutralac®

Sorbacal® Minsorb®

Glass

Civil engineering

Building

Visucal®

Proviacal® Asphacal®

Tradical®

Agriculture

Chemicals

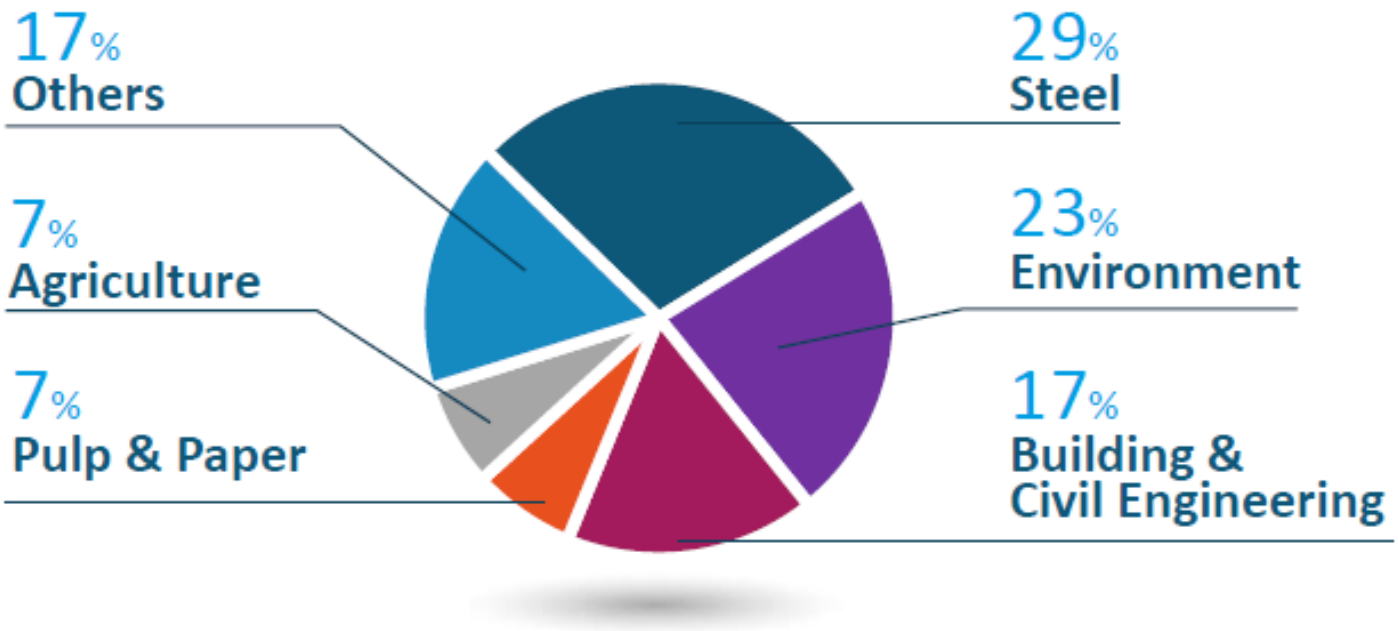
Biofuels

Oxyfertil® Saniblanc®

Lhoist Group Key Numbers

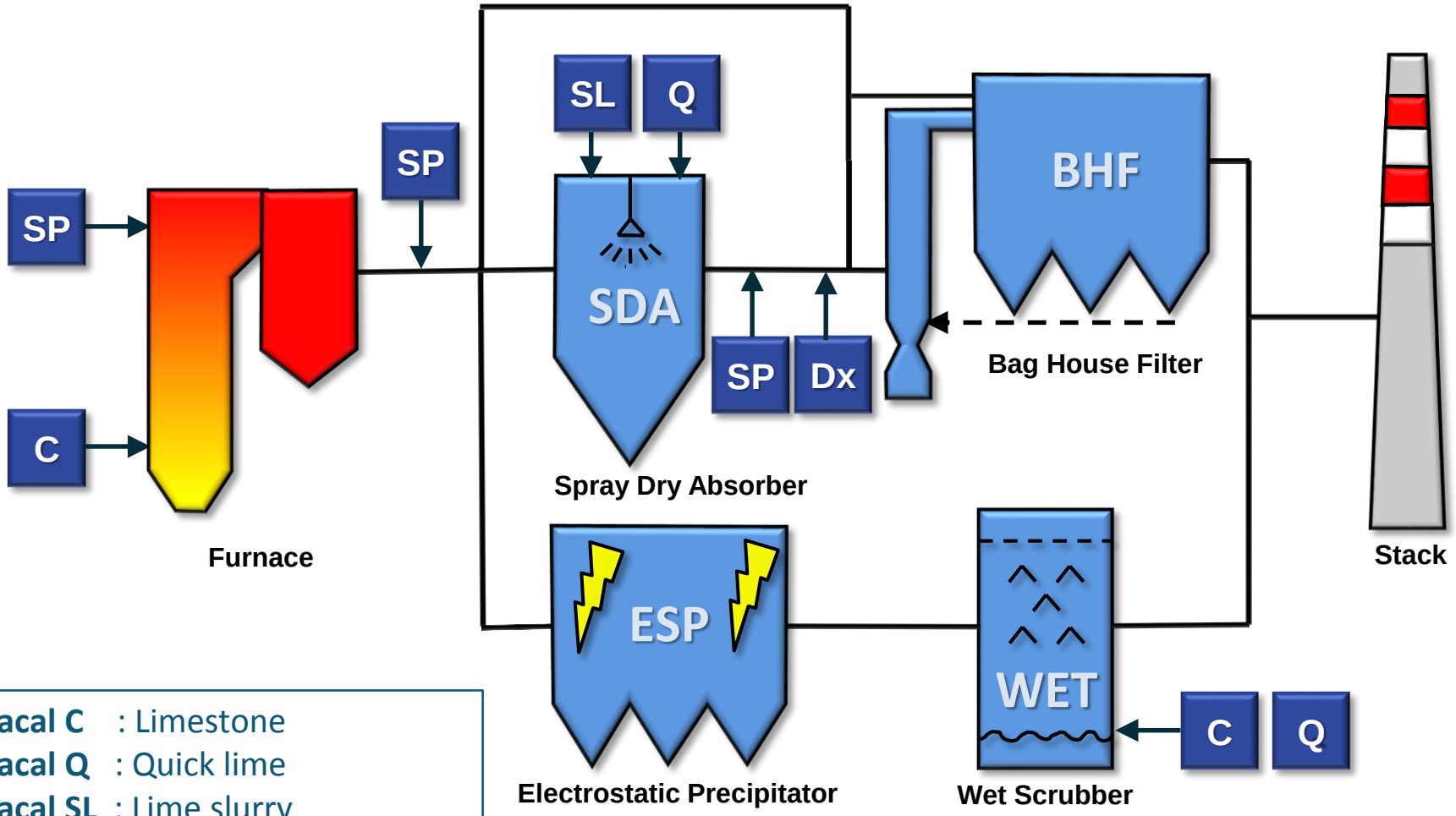
What is our market?

- **Turnover by Market**
  - Environmental applications are important and growing



Flue Gas Treatment with Calcium

The diversity of lime reagents

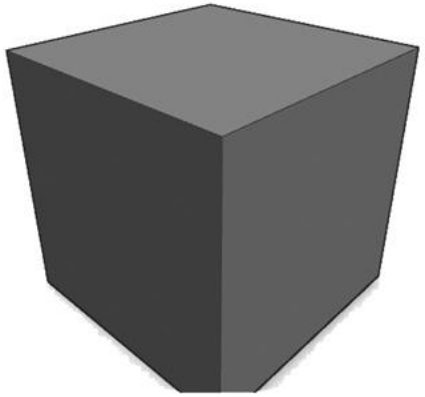


Sorbacal C : Limestone
Sorbacal Q : Quick lime
Sorbacal SL : Lime slurry
Sorbacal SP : Special Hydrated Lime
Minsorb Dx : Mineral sorbent

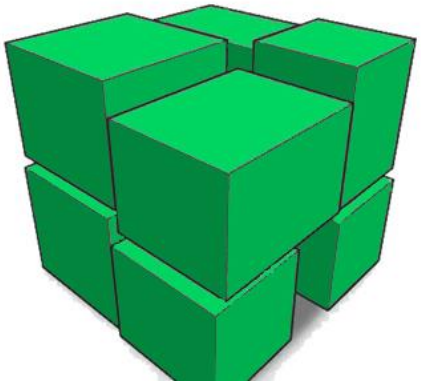
Advanced Gas Treatment Reagents

Lhoist engineered sorbents

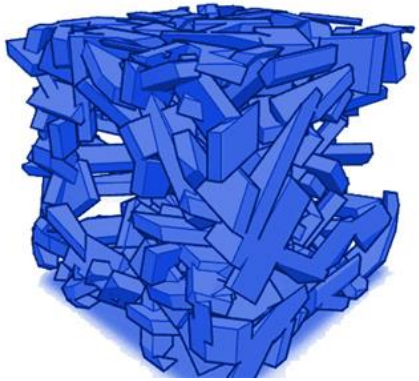
- **Advanced Dry Sorbent Properties**



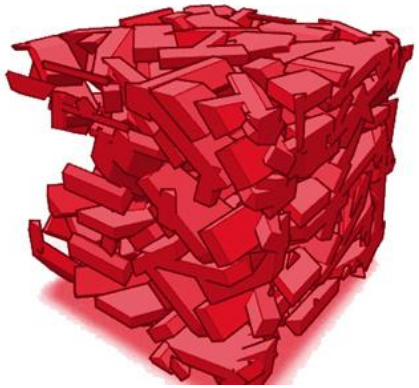
Local Hydrate



Sorbacal® H



Sorbacal® SP



Sorbacal® SPS

Parameter	Local Hydrate	Sorbacal® H	Sorbacal® SP	Sorbacal® SPS	
Available Lime (EN-459)	70 - 90	>90	>90	>90	(wt%)
Surface Area (BET)	5 - 15	>20	>40	>40	(m^2/g)
Pore Volume (BJH)	0.02 - 0.08	0.1	> 0.2	> 0.2	(ml/g)
Particle Size (d_{50})	4 - 25	5 - 14	5 - 14	5 - 14	(µm)
SO_2 removal performance	20 - 50	100	200	220 - 300	(%)

The table shows typical values

Lime based dry sorbent injection at 20 MW pilot unit in CIUDEN

Lime based dry sorbent injection at 20 MW pilot unit in CIUDEN

In furnace injection

Upstream baghouse injection

BiOxySorb

Dry sorbents delivered to CIUDEN

- Sorbacal® SPS
  - High performance high porosity hydrated lime


- Finely milled natural limestone



- Activated carbon (35%) + milled limestone (65%)

Sample type	Finely milled limestone	Sorbacal® SPS	Activated Carbon GL 50 (Norit)
Humidity (%)	0,1	1,8	-
C total (%)	11,8	0,8	80,4
$CaCO_3$ (%)	98,3	6,4	-
$Ca(OH)_2$ (%)	0	93,3	-
Particle size distribution (Laser) - d50 (µm)	6,4	7,5	12,5
Particle size distribution (Laser) - d90 (µm)	24,2	39,3	88,7
Specific Surface Area BET (m^2/g)	1,6	31,6	680
Total Porous Volume BJH (17-1000A°) (cm^3/g)	0,005	0,186	0,397
Partial Porous Volume BJH (100-300A°) (cm^3/g)	0,001	0,098	-
Bulk density (unpacked) (g/cm^3)	0,83	0,49	0,26
Packed density (packed) (g/cm^3)	1,22	0,61	0,38


+

A little dose of chemistry..

❑ Hydrated lime

- $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$
- $CaSO_3 + ½\ O_2 \rightarrow CaSO_4$

- $Ca(OH)_2 + SO_3 \rightarrow CaSO_4 + H_2O$

- $Ca(OH)_2 + HCl \rightarrow CaClOH + H_2O$
- $CaClOH + HCl \rightarrow CaCl_2 + H_2O$

In furnace injection (above 900°C):

- $Ca(OH)_2 \rightarrow CaO + H_2O$ **(very fast)**
- $CaO + SO_2 + ½\ O_2 \rightarrow CaSO_4$
- $CaO + SO_3 \rightarrow CaSO_4$

But: $CaO + CO_2 \rightarrow CaCO_3$ (below 850°C)

❑ Limestone

- $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$
- $CaSO_3 + ½\ O_2 \rightarrow CaSO_4$

Very slow, Limited to surface reaction (no porosity)

- $CaCO_3 + SO_3 \rightarrow CaSO_4 + CO_2$

- $CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2$

In furnace injection (above 900°C):

- $CaCO_3 \rightarrow CaO + CO_2$ **(rather slow)**
- $CaO + SO_2 + ½\ O_2 \rightarrow CaSO_4$
- $CaO + SO_3 \rightarrow CaSO_4$

But: $CaO + CO_2 \rightarrow CaCO_3$ (below 850°C)

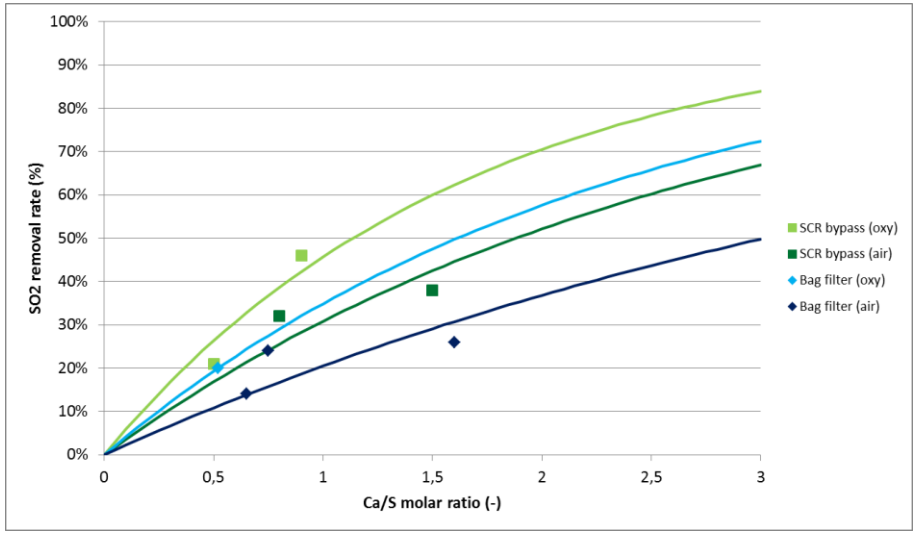
SO_2 removal performance in CIUDEN

AIR mode flue gas composition :
SO_2 = 550ppm; HCl = 3ppm; CO_2=15%; H2O = 6%; O_2 = 3%

OXY mode flue gas composition :
SO_2 = 2550ppm; HCl = 5ppm; CO_2=70%; H2O = 7%; O_2 = 3%

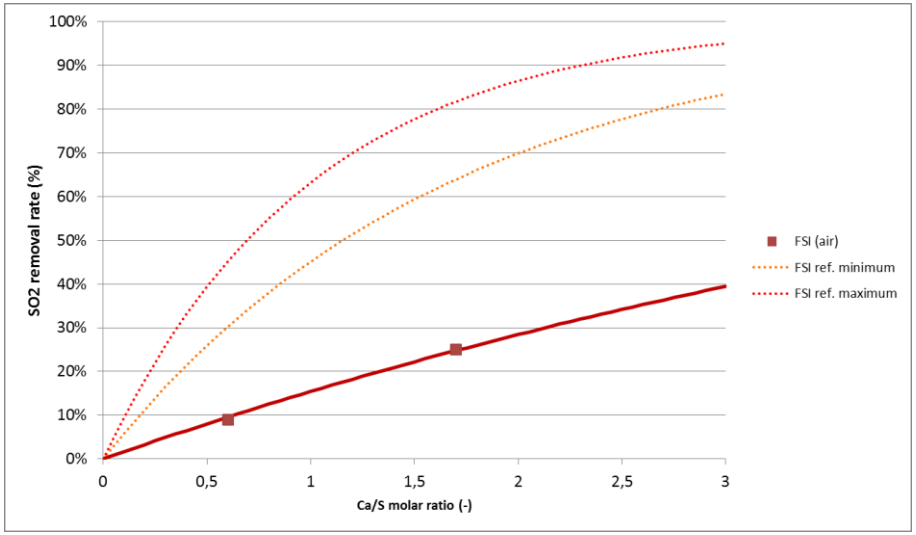
- Coal only : AIR mode vs. OXY mode

Fuel = 100% Coal
AIR mode vs. OXY mode
Sorbent = Sorbacal®SPS
Injection location: SCR bypass (350°C); baghouse filter (200°C)



- Order of magnitude in-line with expectations
- Better performance for **OXY** mode compared to Air mode
  - No detrimental effect of CO_2 despite high concentration (70%)
  - Due to 4-5x higher SO_2 concentrations

Fuel = 100% coal
AIR mode (OXY mode not available)
Sorbent = Sorbacal®SPS
Injection location: Furnace sorbent injection (FSI) (850°C)

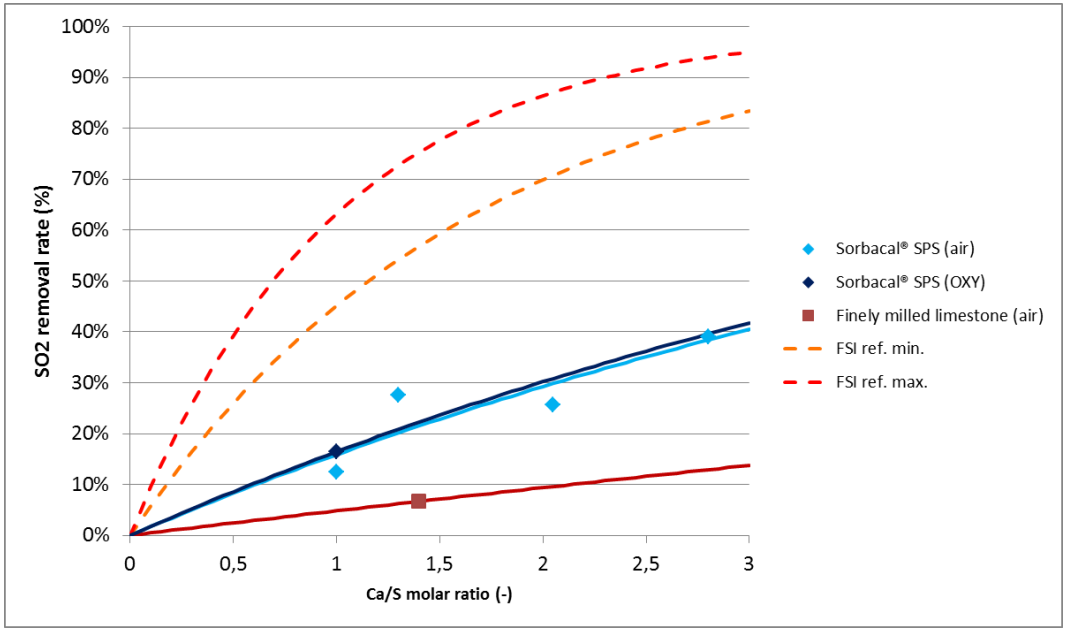


- FSI: performance significantly below expectations
  - Too low temperature, short residence time, lack of dispersion quality

SO_2 removal performance in CIUDEN

- Coal + Biomass : AIR mode vs. OXY mode

Fuel = Coal + Biomass (saw dust)
AIR mode vs. OXY mode
Sorbent = Sorbacal®SPS, finely milled limestone
Injection location: Furnace Sorbent Injection (FSI)



! Only FSI mode tested !

- Sorbacal® SPS :
  - performance significantly below expectations (Too low temperature, short residence time, lack of dispersion quality)
  - Similar performance in AIR and OXY mode

- Finely milled limestone: Much lower performance than Sorbacal® SPS in comparable test conditions
  - Much slower reaction with limestone

No suitable conclusion for SO_3, HCl and Hg removal

Fly ash analysis & valorization

- Valorization in cement: EN-450 standard
  - Sulphate (SO_3): < 3%
  - Free CaO: < 1,5%
  - Active CaO: < 10%
  - Alcali (Na_2O eq.): < 5%
  - Chlorides (Cl-): < 0,1%
  - MgO: < 4%
  - Reactive SiO_2: > 25%
  - $SiO_2+Al_2O_3+Fe_2O_3$: > 70%

EUROPEAN STANDARDS

CE

Compliant with European Community standards.

- Other valorization ways: Soil stabilization,waste or sludge treatment & sanitization, ...
  - Site specific (chemical compatibility, legal aspects, commercial opportunities)
  - Much smaller market

Fly ash analysis & valorization

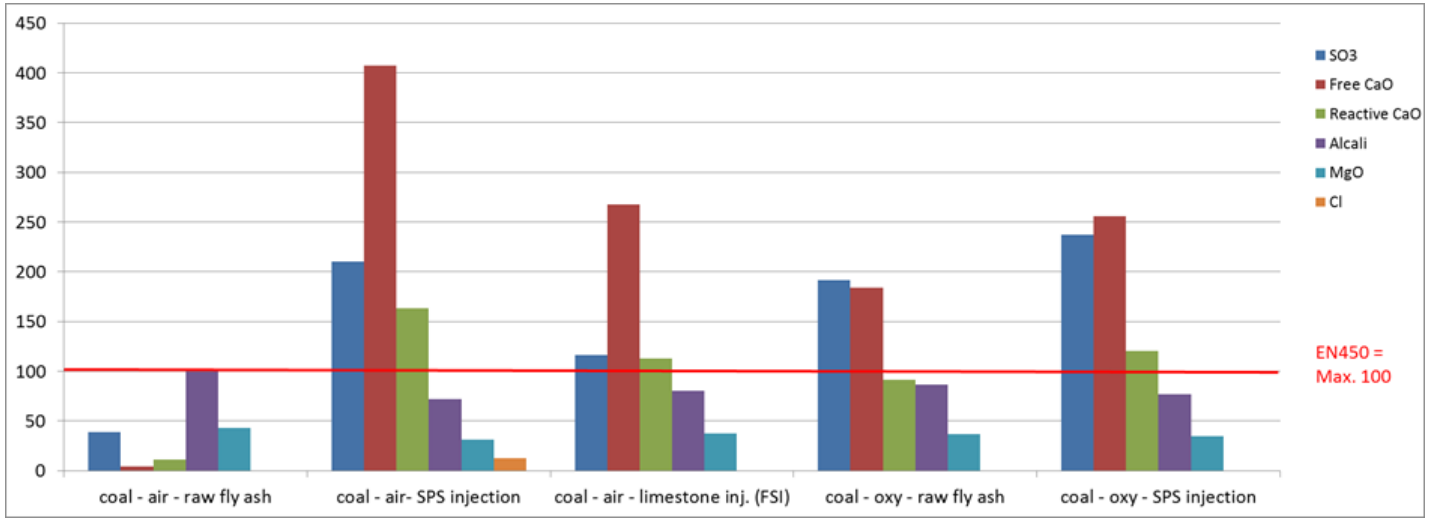
Fly ash analysis: Example

	Analysis Method	BE1116.269.2	BE1116.269.1	BE1116.269.3	BE1116.269.4	BE1116.269.6	BE1116.269.8	BE1116.269.7
Client reference		Biox S1-T1-A2	Biox S1-T1-A3	Biox S1-T1-A4	Biox S1-T2 -A2	Biox S1-T2 -A3	Biox S1-T3 -A2	Biox S1-T3 -A3
Sample date		22/05/2016	22/05/2016	23/05/2016	23/05/2016	23/05/2016	24/05/2016	24/05/2016
sample description		air-coal-raw fly ash-base case AIR mode	air-coal-raw fly ash-higher O2 excess	air-coal-raw fly ash, Air mode OFAS level 3	air-coal-furnace-SPS-low	air-coal-furnace-SPS-high	Air-coal-SCR-SPS-low	Air-coal-SCR-SPS-high
DSI Sorbent type		-	-	-	SPS	SPS	SPS	SPS
Humidity (%)	LoI 150°C	0,4	0,2	0,2	0,3	0,4	1,3	0,4
Volumetric CO2 (%)	EN196-2	0,0	0,4	0,0	0,0	2,0	1,8	1,7
Available CaO (%)	EN196-2	0,3	0,0	0,0	1,5	13,2	13,2	11,8
eq. Ca(OH)2	calc.	0,4	0,0	0,0	2,0	17,4	17,4	15,6
Ca as CaO (%)	SQ XRF	3,5	3,2	3,1	5,8	24,5	22,1	23,4
Mg as MgO (%)	SQ XRF	1,8	1,7	1,7	1,7	1,4	1,4	1,3
S as SO3 (%)	SQ XRF	1,3	1,3	1,0	1,5	6,3	9,0	7,5
Cl (%)	SQ XRF	0,0	0,0	0,0	0,0	0,0	0,1	0,0
Na as Na2O (%)	SQ XRF	2,8	2,8	2,9	2,8	2,1	2,1	2,2
K as K2O (%)	SQ XRF	3,5	3,2	3,1	3,1	2,3	2,3	2,3
Si as SiO2 (%)	SQ XRF	49,7	50,9	51,4	48,8	34,5	34,8	34,2
Al as Al2O3 (%)	SQ XRF	24,5	24,4	24,3	23,4	16,6	16,9	16,8
Fe as Fe2O3 (%)	SQ XRF	10,6	10,0	10,4	10,7	8,5	8,2	8,7
P as P2O5 (%)	SQ XRF	1,1	0,9	1,0	1,0	0,9	0,8	0,9
Ti as TiO2 (%)	SQ XRF	1,6	1,6	1,6	1,6	1,6	1,6	1,6
Others (Mn, Sr, As, Cr, V, Zn…) (%)	SQ XRF	0,3	0,3	0,3	0,3	0,3	0,2	0,3

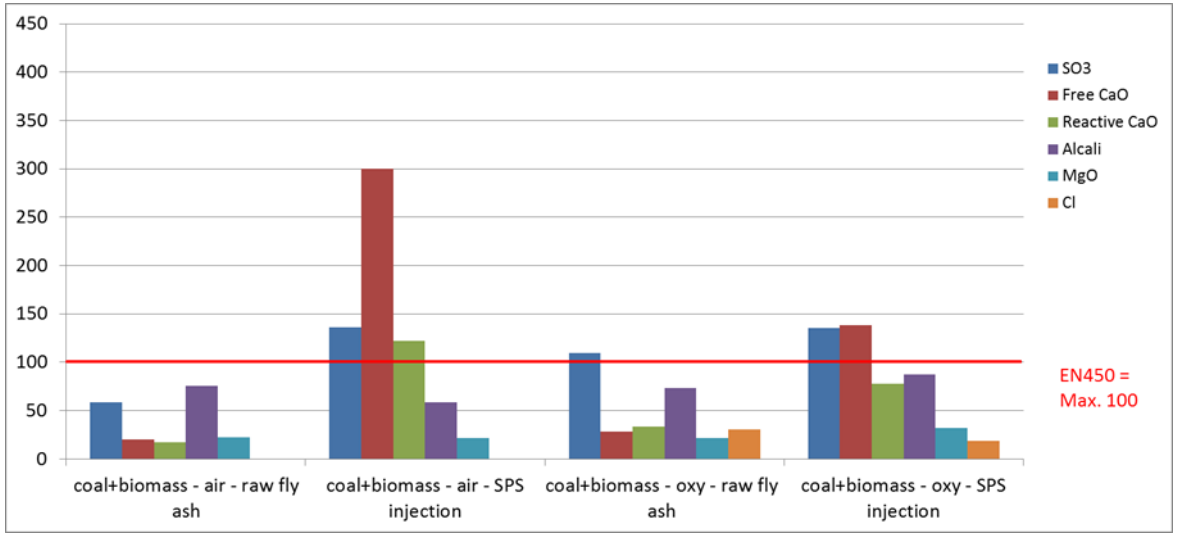
Fly ash analysis & valorization

Valorization in cement: analysis vs. EN-450 standard

(BELOW 100 for compliance)



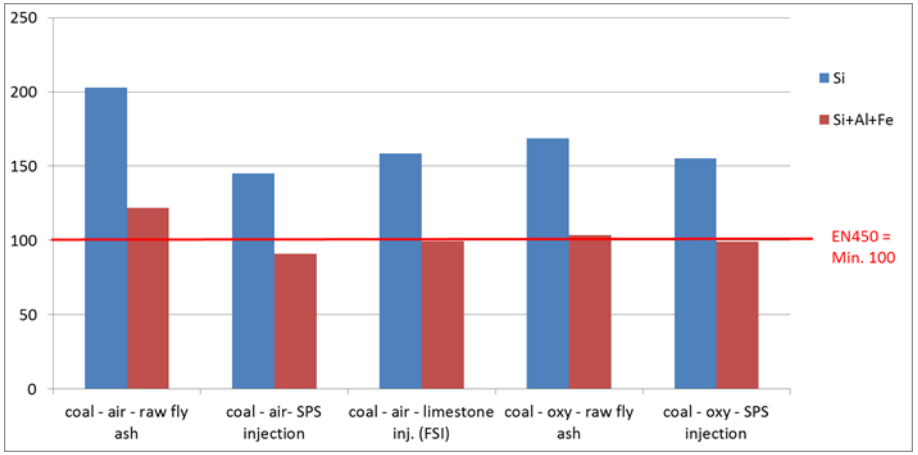
Coal only



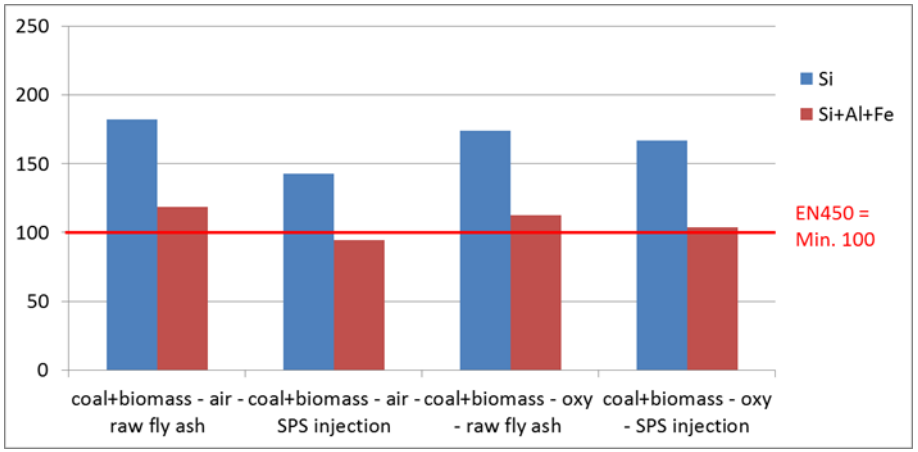
Coal + Biomass

Fly ash analysis & valorization

Valorization in cement: analysis vs. EN-450 standard (ABOVE 100 for compliance)



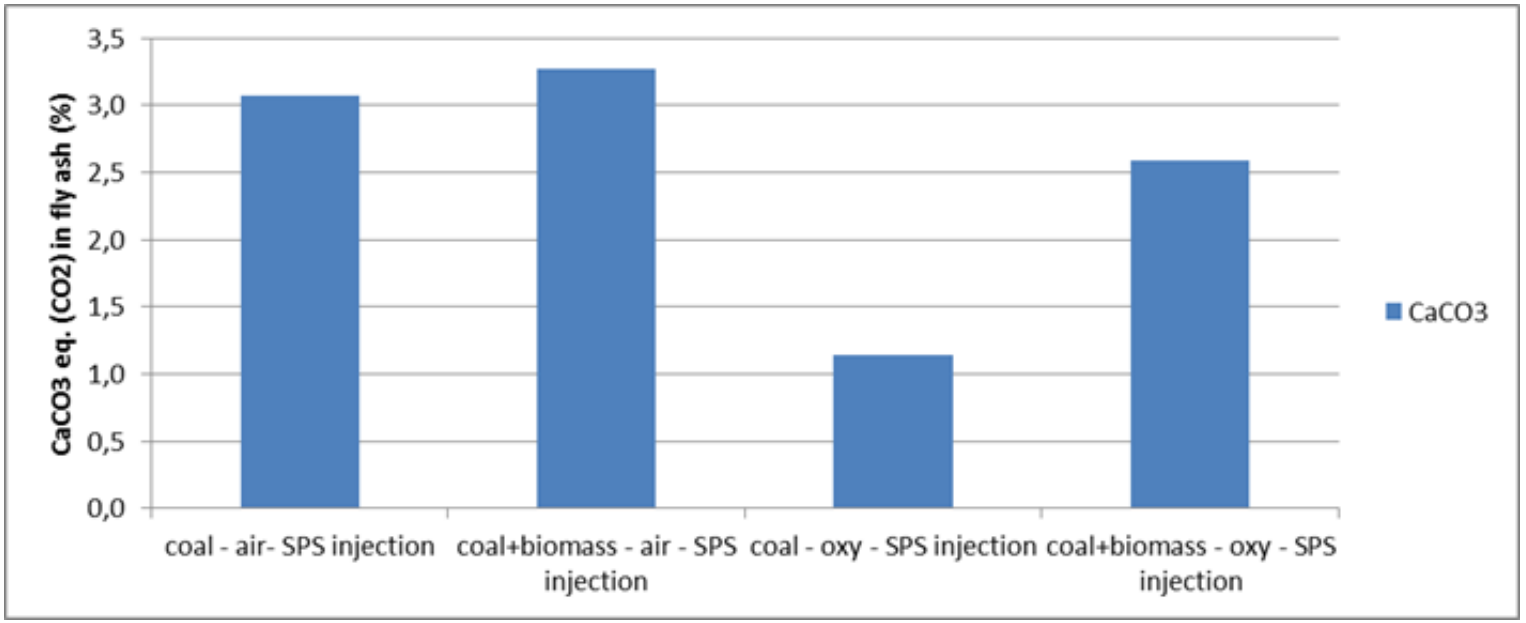
Coal only



Coal + Biomass

Impact of OXY mode on sorbent carbonation

$CaCO_3$ content in fly ash (with sorbent injection)



NO additional detrimental effect of CO_2 in OXY mode compared to AIR mode

(CO_2 concentration = 68-73% in OXY mode)

Conclusions

- Successful delivery and operation of the mobile sorbent dosing units + sorbents in large scale (20 MW) pilot test facility in CIUDEN

- SO_2 removal performance :
  - Performance fair agreement with expectation for 350°C injection (SCR bypass) and 200°C injection (upstream baghouse filter)
  - Much lower performance than expected in Furnace Sorbent Injection (850°C), due to unadequate temperature & residence time.

- Higher SO_2 removal performance in OXY mode compared to AIR mode
  - **No additional detrimental effect of CO_2 in OXY mode** (CO_2 > 68%)
  - SO_2 concentration 4-5x higher in OXY mode

- No suitable conclusion for SO_3 & HCl removal
  - too low concentrations
- No suitable conclusion for Hg removal by activated carbon
  - Too short trial, no filter vaccination

Conclusions

- Fly ash valorization:
  - Fly ash without acidic gas sorbent contamination
    - AIR mode: Fly ash are compliant for valorization in cement (EN 450)
    - OXY mode: Fly ash not always compliant with EN 450 (SO_3 content)
  - Fly ash with lime-based acidic gas sorbent contamination
    - In the conditions of the tests, fly ash not compliant with EN 450 standard, due to following criteria:
      - ✓ Most of the time: SO_3 content, Free CaO.
      - ✓ Sometimes: Reactive CaO; SiO_2+Al_2O_3+Fe_2O_3
  - Fly ash with alcali-based acidic gas sorbent contamination
    - No compliance with EN 450 standards, due to Alcali (Na_2O eq.) and SO_3 content
    - Alkali are highly detrimental to cement applications and strictly regulated
- Potential valorization of fly ash contaminated with lime-based by-product for applications with less stringent constraints, depending on local contingencies
    - Soil stabilization & hardening
    - Waste or sludge stabilization & sanitization
    - Neutralization of acidic streams, ...