Practical aspects & limitations of doing FGT-trials with Lime in lab- and pilot- scale units

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BiOxySorb

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

Why this presentation with this strange title ??

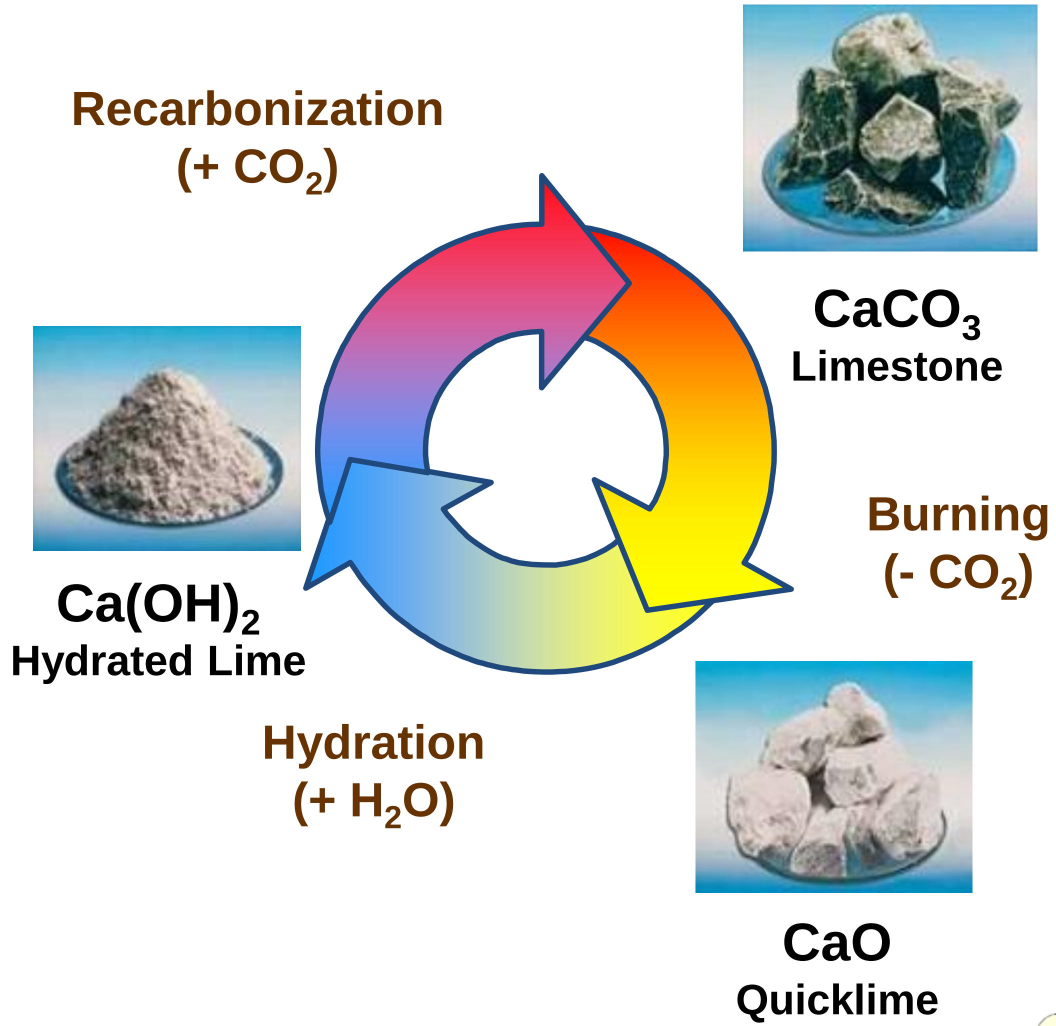
What we (LGE/Rheinkalk) usually do:

- Sell ‚Lime‘ to FGT-customers
- Selcetion of best suitable adsorbens
- Optimization of customers FGT-process
- Run full-scale trials
- Support to Engineering companies
- Feed-back to R&D about ‚market-trends‘

➔Reflections of a partner that was envolved at the beginning (2013) & the end of the Bioxysorb-project (2016)

What we usually sell:

Lime Cycle - FGT Product Examples



used as milled Limestone in wet scrubbers

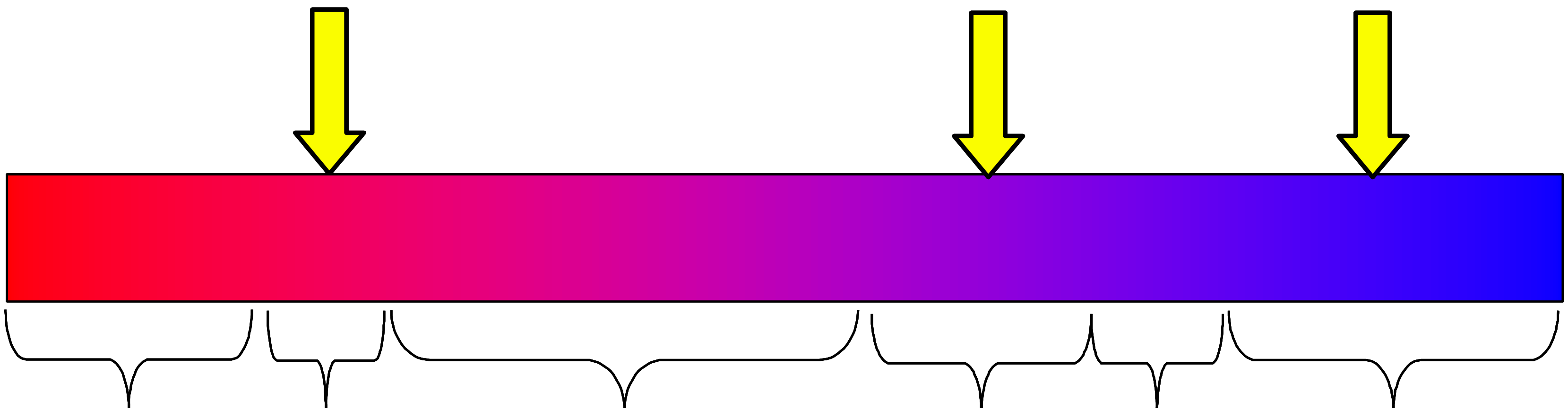
used as Hydrated Lime in dry sorption processes

used as milled Quicklime in Spray Absorbers (Semi-dry)

How the products are used in Dry FGT-processes:

Optimized: Sorbacal® SPS / A — Sorbacal® SPS / SP / A — Sorbacal® SP / SPS

Standard: Hydrated Lime / Limestone — Hydrated Lime — Hydrated Lime



~ 1200 - 1000 °C

~ 1000 - 850 °C

SO_2

~ 850 - 450 °C

~ 450 - 300 °C

SO_2 + HCl
HF

~ 300 - 220 °C

~ 200 – 40°C

SO_2 + HCl
HF

Max. 180°C:

SO_3 is also removed over the whole temperature range

‚Blends' → PCDD/DF + Hg

‚Lime' & AC, HOK
Minsorb®, Dioxsorb®

How much adsorbens is necessary: Theory .....

Neutralization Reactions & theoretical Additive-Demand for $Ca(OH)_2$

Chemical Reaction [g/mol]:	Theoretical Additive-Demand for the Neutralization of
$Ca(OH)_2 + SO_3 \rightarrow CaSO_4 + H_2O$ 74 + 80 → 136 + 18	**1 kg SO_3 : 0,9255 kg $Ca(OH)_2$**
$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$ 74 + 64 → 120 + 18	**1 kg SO_2 : 1,156 kg $Ca(OH)_2$**
$Ca(OH)_2 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + H_2O$ 74 + 64 + 16 → 136 + 18	
$Ca(OH)_2 + 2\ HCL \rightarrow CaCl_2 + 2\ H_2O$ 74 + 2 * 36,5 → 111 + 2 * 18	**1 kg HCl : 1,016 kg $Ca(OH)_2$**
$Ca(OH)_2 + 2\ HF \rightarrow CaF_2 + 2\ H_2O$ 74 + 2 * 20 → 78 + 2 * 18	**1 kg HF : 1,851 kg $Ca(OH)_2$**

In practice, these theoretical values cannot be achieved; difference between ‚Theory‘ and ‚Practice‘ is often expressed through ‚Stoichiometrical Factor‘

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How much adsorbens is necessary: … and Practice

Factors influencing removal performance / adsorbens-consumption:

- **Raw gas concentration & required removal rate:** (‚Contact probability‘)
  1000 → 100 mg/Nm³: 90 %, ‚easy‘ / 10 → 1 mg/Nm³: 90%, ‚difficult‘
- **Affinitiv towards components to be removed:** (‚reaction sequence‘)
  for $Ca(OH)_2$: SO_3 > HF > HCl >> SO_2 (>>> CO_2)
  ➔ Multi-purpose Additive, affinity perfectly fits with the different emission limits (BREF: HF: 5 / HCl: 30 / SO_2: 800 – 1500 [mg/Nm³])
- **Reaction conditions** (mainly temperature & humidity)
  for $Ca(OH)_2$: 2 favorable temperature zones:
  ● 350 – 400°C: ‚thermal activation‘ of $Ca(OH)_2$ (classical ESP temperature zone)
  ● < 180°C: Activation through humidity (fabric filter temperature range)
- **Process Parameter** (contact additive / gas components)
  contact time, additive dispersion, reactor, type of filter, ..
- **Additive-Properties:**
  Hydrated Limes: $Ca(OH)_2$-content, particle size distribution, surface area & porosity

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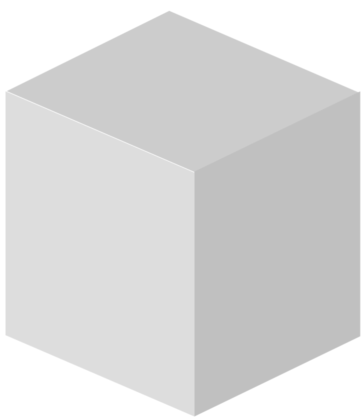
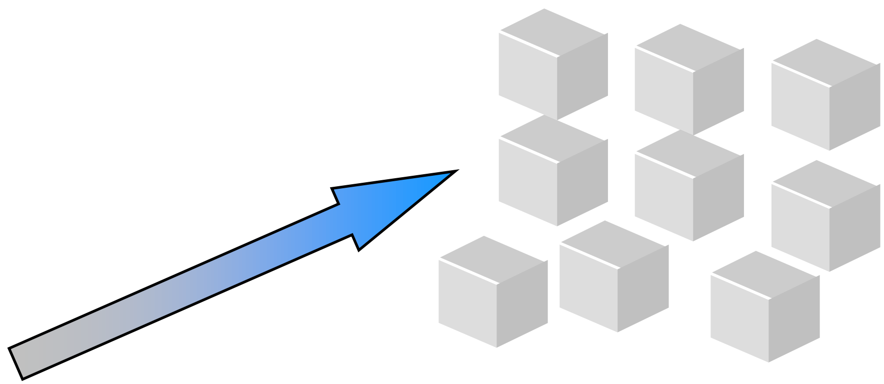
Product Development ‚optimized' Hydrated Limes:

- **Reaction of $Ca(OH)_2$ with acidic gas components**:

  Acid – Base Reaction via Gas – Solid contact

  => decisive: ‚available' Surface Area of Solid

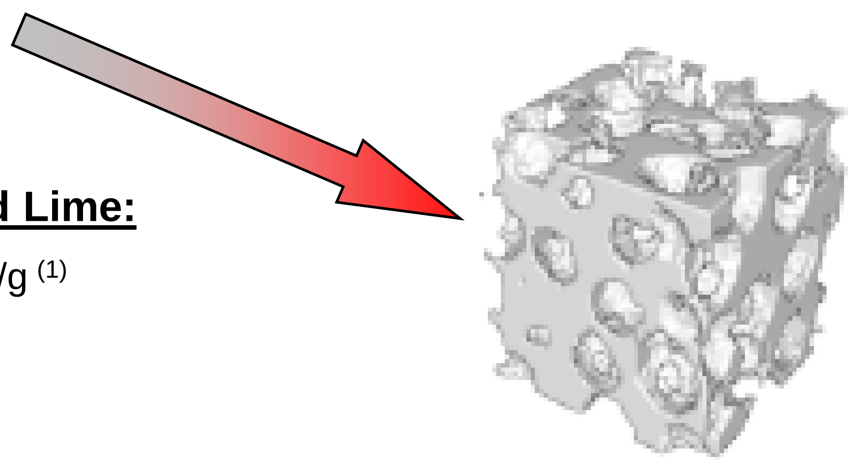




Sorbacal® A:

35 - 38 m^2/g; 0,13 cm^3/g

d_{50}: **2 - 3 µm**



Sorbacal® SP:

42 - 45 m^2/g; 0,25 cm^3/g

d_{50}: 6 - 8 µm

Further development:

→ **Sorbacal® SPS**

Standard Hydrated Lime:

15 - 18 m^2/g; 0,08 cm^3/g (1)

d_{50}: 6 - 8 µm

(1): specific Surface Area/ Pore Volume

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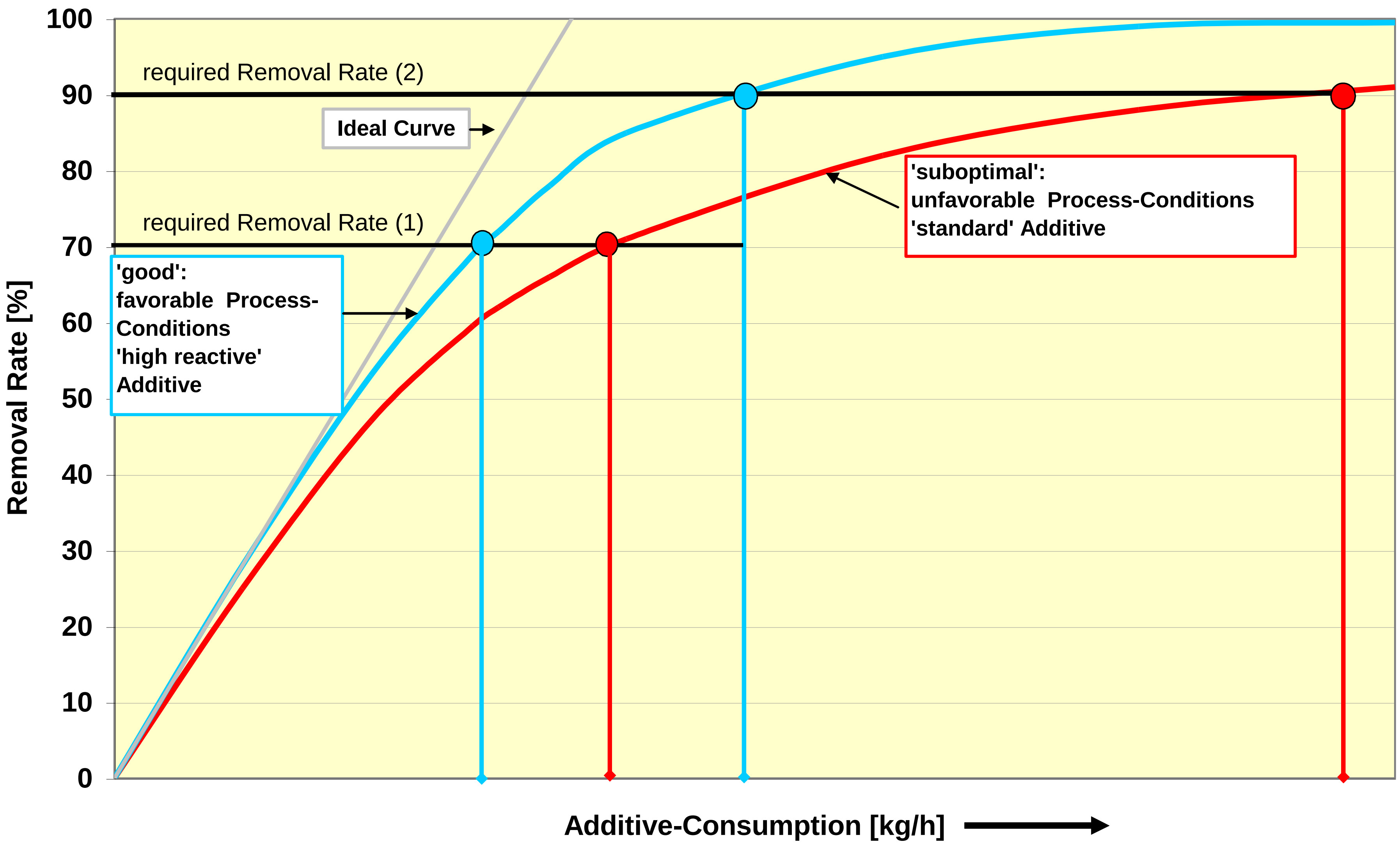
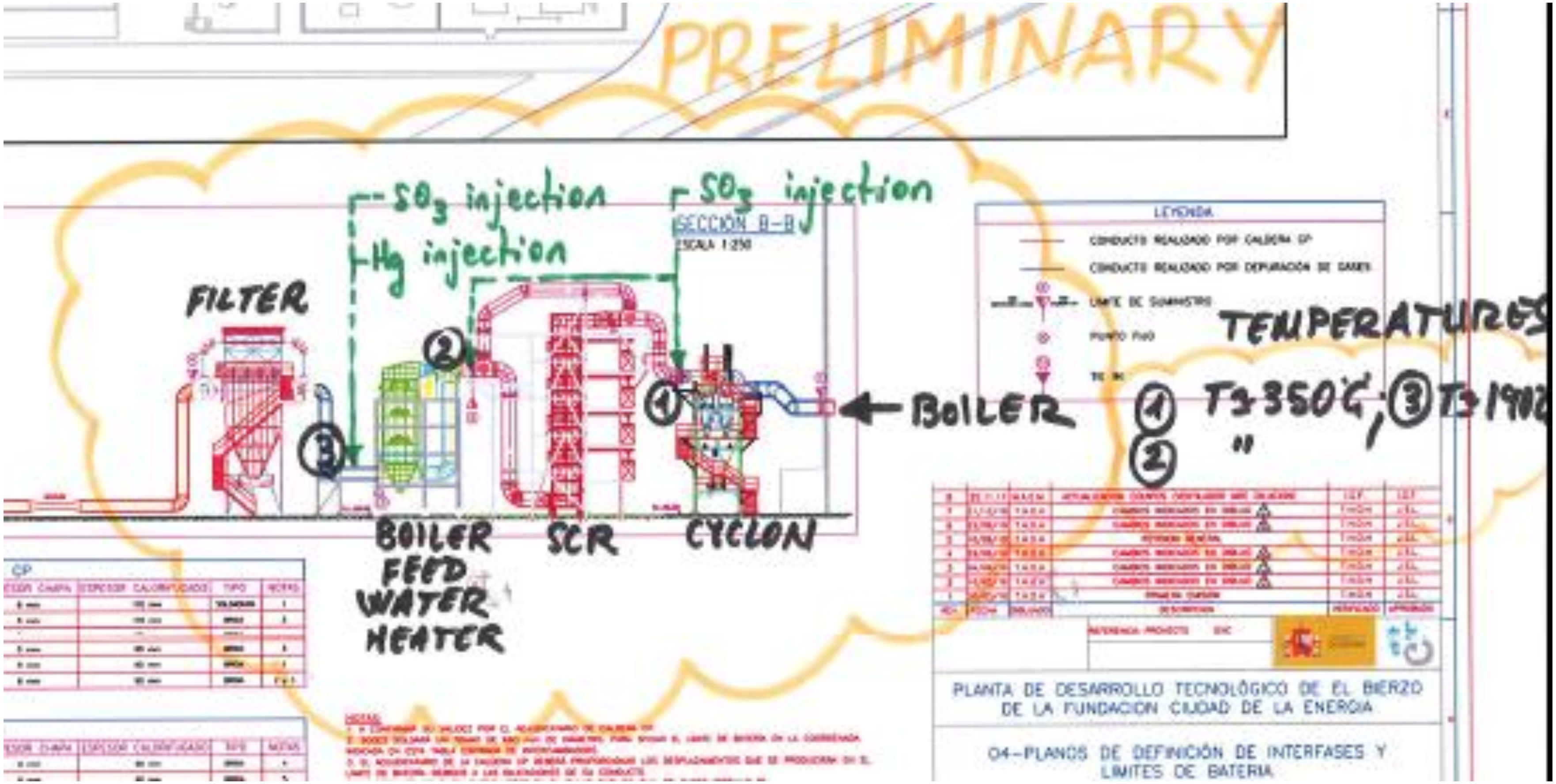
Typical Removal Curve in Practice:



Initial Planning for Pilot Testing at CIUDEN (2013):



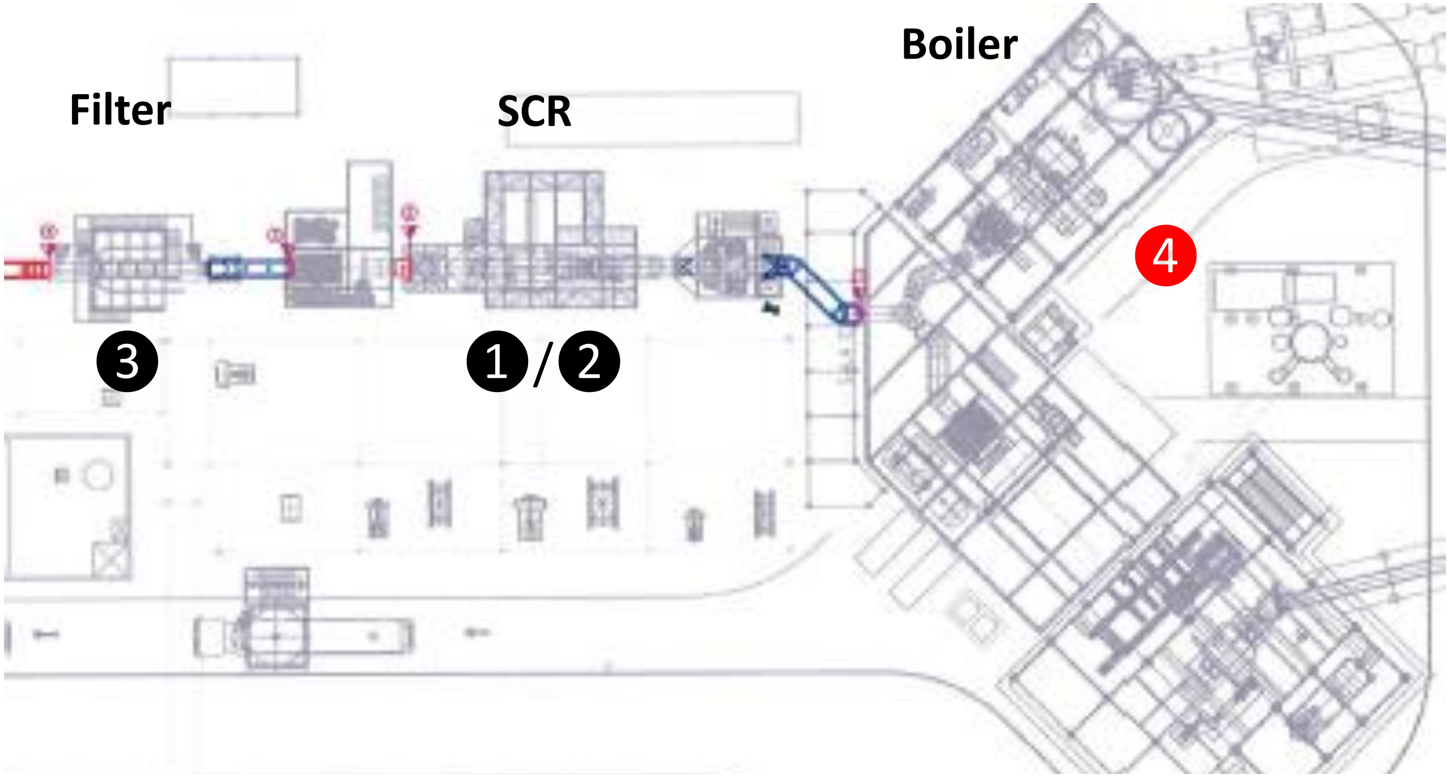
SO_3 – Removal @ 350°C ❶ or ❷ & 190°C ❸: Sorbacal® SPS

Hg – Removal @ 190°C ❸: Limestone-Activated Carbon Blend (ATEX)

in ‚Air Mode' and ‚Oxyfuel mode'

Lhoist: Delivery of 2 Adsorbens

Programm for Pilot Testing at CIUDEN (2016):



SO_3 – Removal @ 350°C ❶/ ❷ & 190°C ❸: Sorbacal® SPS

Hg – Removal @ 190°C ❸: Limestone-Activated Carbon Blend (ATEX)

SO_3 – Removal @ 900°C ❹: Sorbacal® SPS & Limestone

in ‚Air Mode' and ‚Oxyfuel mode'

Lhoist: Delivery of 3 Adsorbens and Dosing equipment

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Equipment for Pilot Testing at CIUDEN (2016):

1m³-Silo & Dosing (5 – 50 kg/h) unit for:

- $CaCO_3$/AC-Blend (no ATEX)
- $CaCO_3$

18m³-Silo & Dosing (10 – 100 kg/h) unit for:

- Sorbacal® SPS

Both Silos equipped with

- blow through rotary valve
- load cells & Dosing (5 – 50 kg/h) unit for:
- Side-Channel Blower (200 Nm³/h Air)

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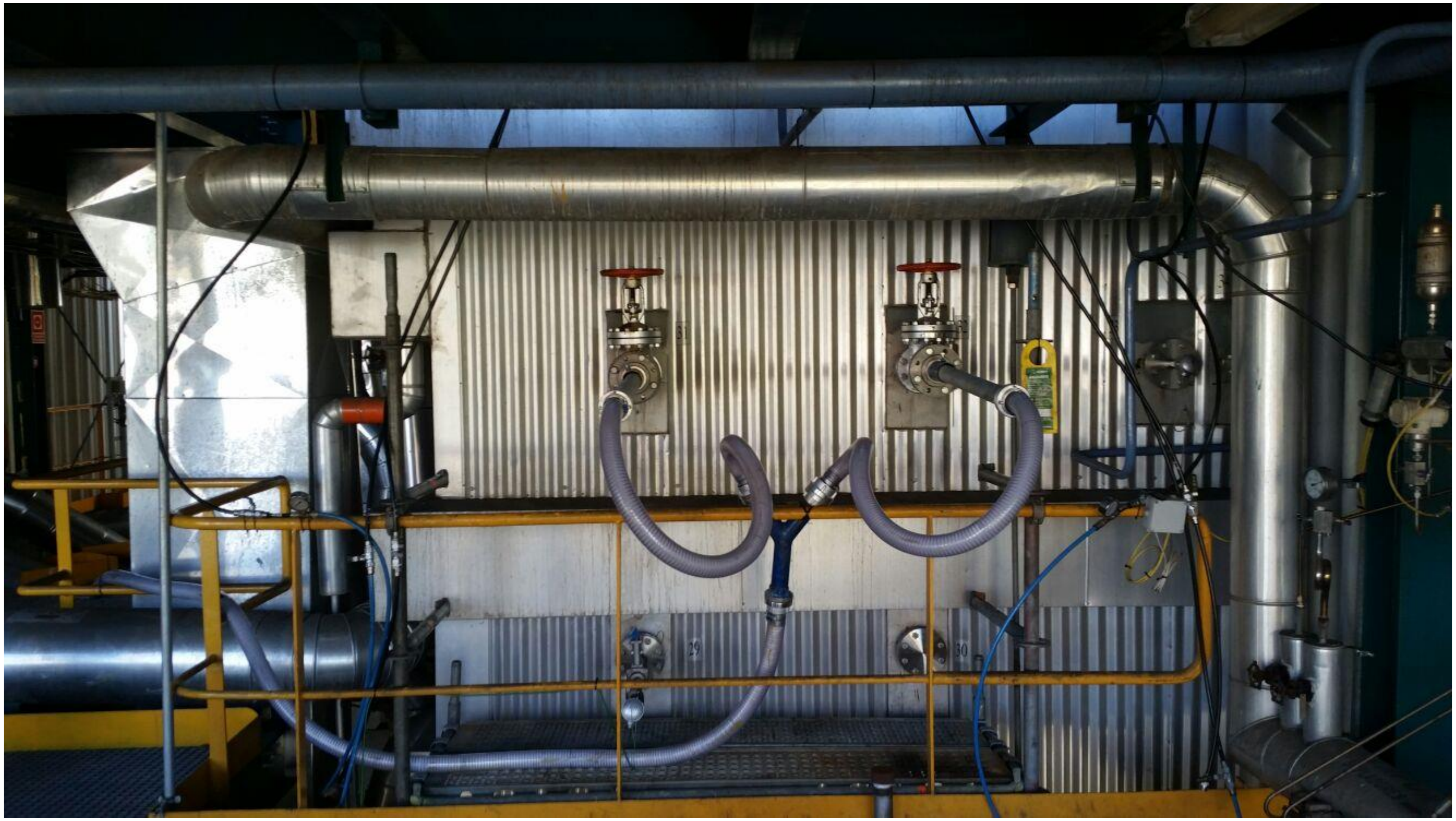
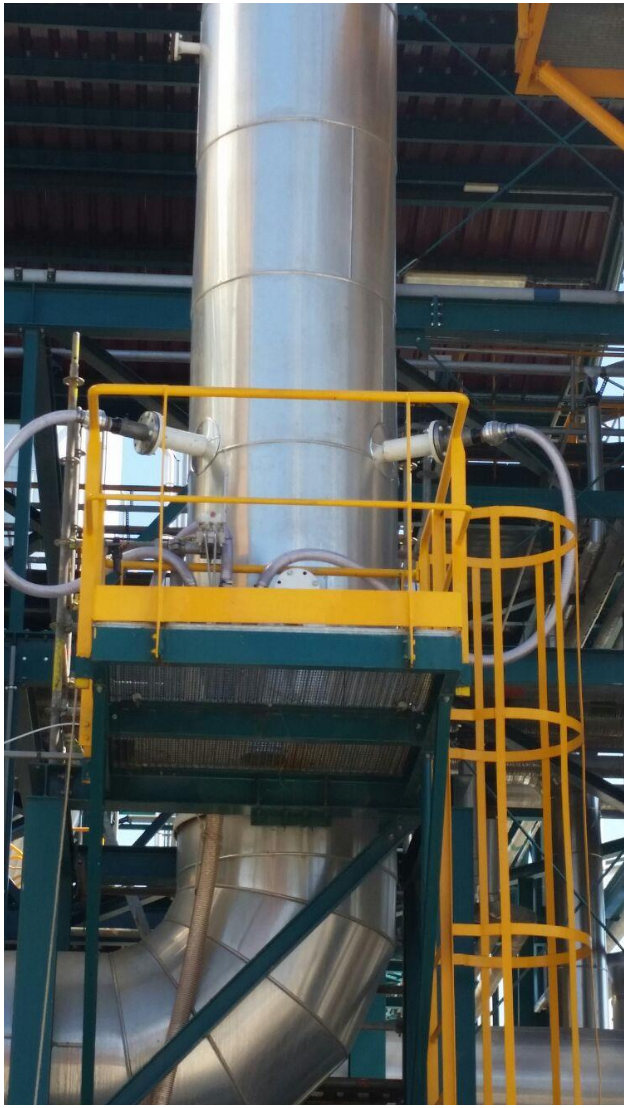
Equipment for Pilot Testing at CIUDEN (2016):



Boiler Injection ($CaCO_3$ & Sorbacal® SPS

Equipment for Pilot Testing at CIUDEN (2016):



Injection at fabric filter (Sorbacal® SPS & AC-Blend)

Equipment for Pilot Testing at CIUDEN (2016):

Test Matrix:

Injection location	Additive	Main target
Before fabric filter at ~ 190°C	Sorbacal® SPS ($Ca(OH)_2$)	SO_3-removal
Before fabric filter at ~ 190°C	AC – blend ($CaCO_3$ + 35% AC)	Hg-removal
SNCR-Bypass at ~ 350°C	Sorbacal® SPS ($Ca(OH)_2$)	SO_3-removal
Boiler at ~ 850°C	Sorbacal® SPS ($Ca(OH)_2$)	SO_3-removal
Boiler at ~ 850°C	Limestone ($CaCO_3$)	SO_3-removal

In total, ‚only' 5 different trial set up's;

But:

- Different adsorbens-quantities
- ‚Air Mode' and ‚Oxy Mode'
- Time to reach stable ‚Baseline' before each trial
- Minimum time to reach stable trial conditions (especially for Hg)
- Extras (If possible, use CO_2 as transport medium for adsorbens)

Main Reflections:

● Very Interesting results on behaviour of our adsorbens in Oxy-Mode

● Don‘t underestimate the time to reach stable ‚Baseline‘

● Limit yourself on number of adsorbens & species to be removed

And last but not least:

● Trials close to home are less time consuming

"We've had a few problems going from lab scale up to full-scale commercial."