SORBENT(S) INJECTION

Dry Sorbent(s) Injection - DSI
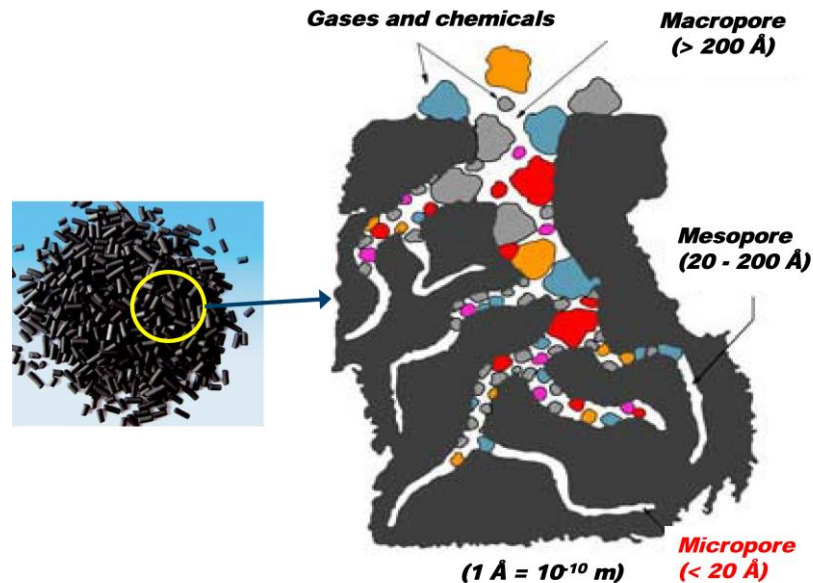**Spray Dry Absorption - SDA**

Process principles

Adsorption of pollutant gases means the selectively retention on the surface/ pores/ interstices of prepared solids. The process may be:
- **Physical adsorption**: it involves a **weak** bonding of gas molecules to the solid. The adsorption process is **exothermic**..
- **Chemisorption**. A combination of surface phenomenon with a chemical reaction.

Mass transfer of compound from bulk gas to gas/solid interface
- penetration into the internal solid surface (pores)
- adsorption (retention) inside the pores
   - physical
    - chemical

Gases and chemicals

Macropore (> 200 Å)

Mesopore (20 - 200 Å)

Micropore (< 20 Å)

(1 Å = 10⁻¹⁰ m)

Process principles

○ **Dry and spray dry systems**: chemisorption
- alternative process option to conventional wet systems
- pollutants removal by **chemical conversion** through reactions with solid and/or semisolid (concentrated aqueous solutions) reactants
- reactant addition in a dedicated reactor or directly in duct for optimum phase contact (mixing with flue gas, reaction time)
- The most important difference between DSI and SDA is the **exit temperature**

Reactor
(spray dry or dry)

In duct
(dry)
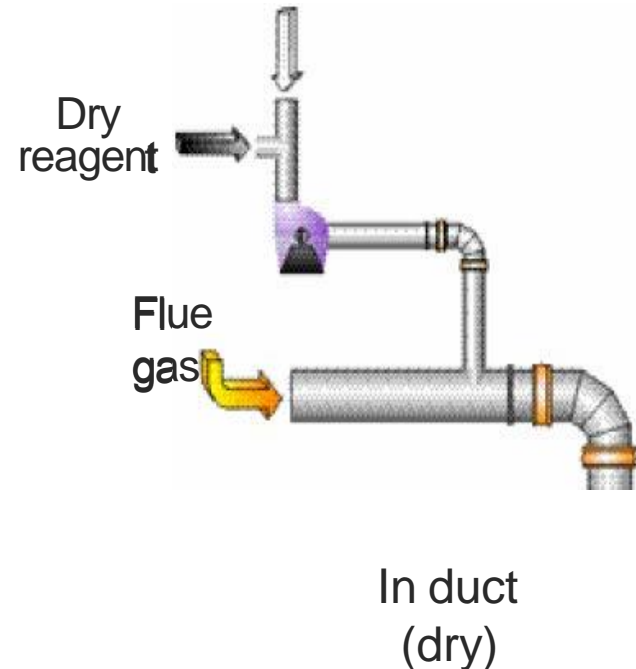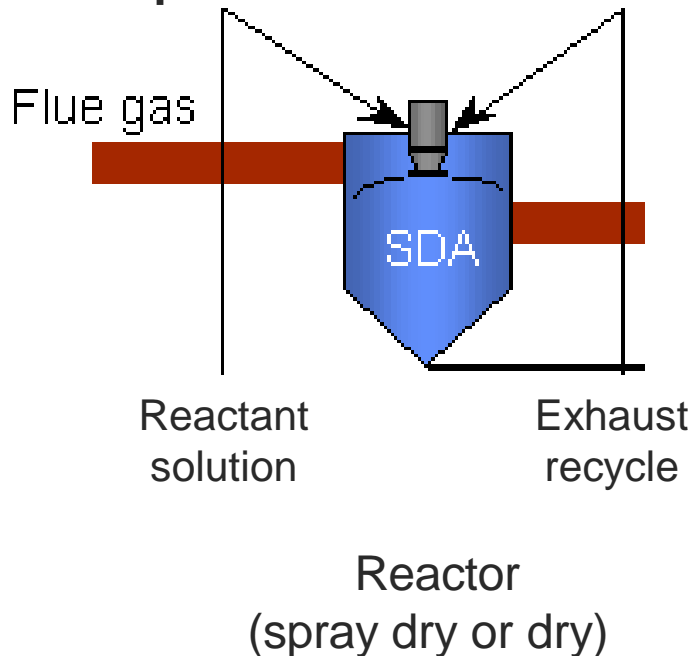
Process principles

○ Dry and spray dry systems: chemisorption

- treated flue gas containing dry reaction products and excess reagent conveyed to a particulate removal device for solids separation, generally a fabric filter where chemical conversion process is completed through **additional contact time** provided by dust layer accumulation on the bags surface

Dust cake

Filter surface

Layer of dry reaction products and available excess reagent
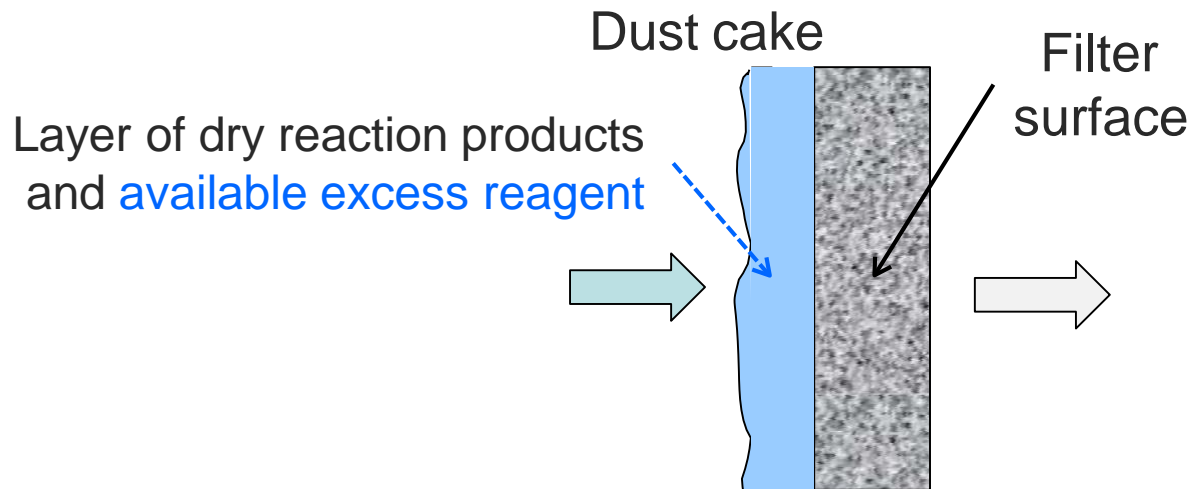
Process principles

○ **Process schematics**
- dry systems: two stages
  - ➢ gaseous pollutant adsorption on solid reactant surface
  - ➢ chemical absorption reaction
- spray dry systems
  - ➢ preliminary conventional liquid chemical absorption
  - ➢ dry adsorption + reaction when all water of reactant solution has been evaporated

○ **Removal efficiency**: complex dependence with:
- reaction equilibrium and kinetics
- specific surface of solid reactant
- pollutant concentration
- flue gas temperature and moisture
- size distribution, concentration and dispersion of solid reagent particles

○ Typical applications
- acid gases neutralization (**HCl, HF, SO$_2$**) with lime (spray dry or dry) or sodium bicarbonate (dry)
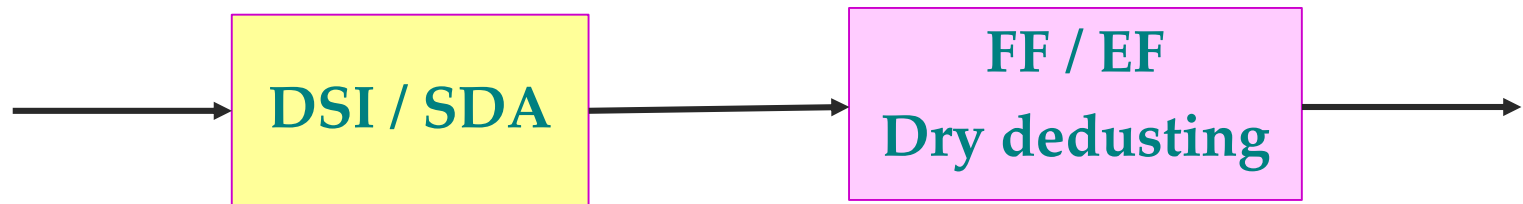
Process principles

DRY TECHNIQUES: ADVANTAGES OVER WET TECHNIQUES

- LOWER H_2O VAPOUR ---> LOWER STEAM CONDENSATION (LESS VISIBLE WHITE PLUME); CONDENSATION AT LOWER TEMPERATURES

- NO REHEATING OF THE FLUE GAS

- HIGHER EXIT GAS TEMPERATURE

- NO LIQUOR TO MANAGE (see example prevention VS control in flue gas neutralization)

Dry and semidry systems

❑ **DSI - Dry Sorbent(s) Injection**
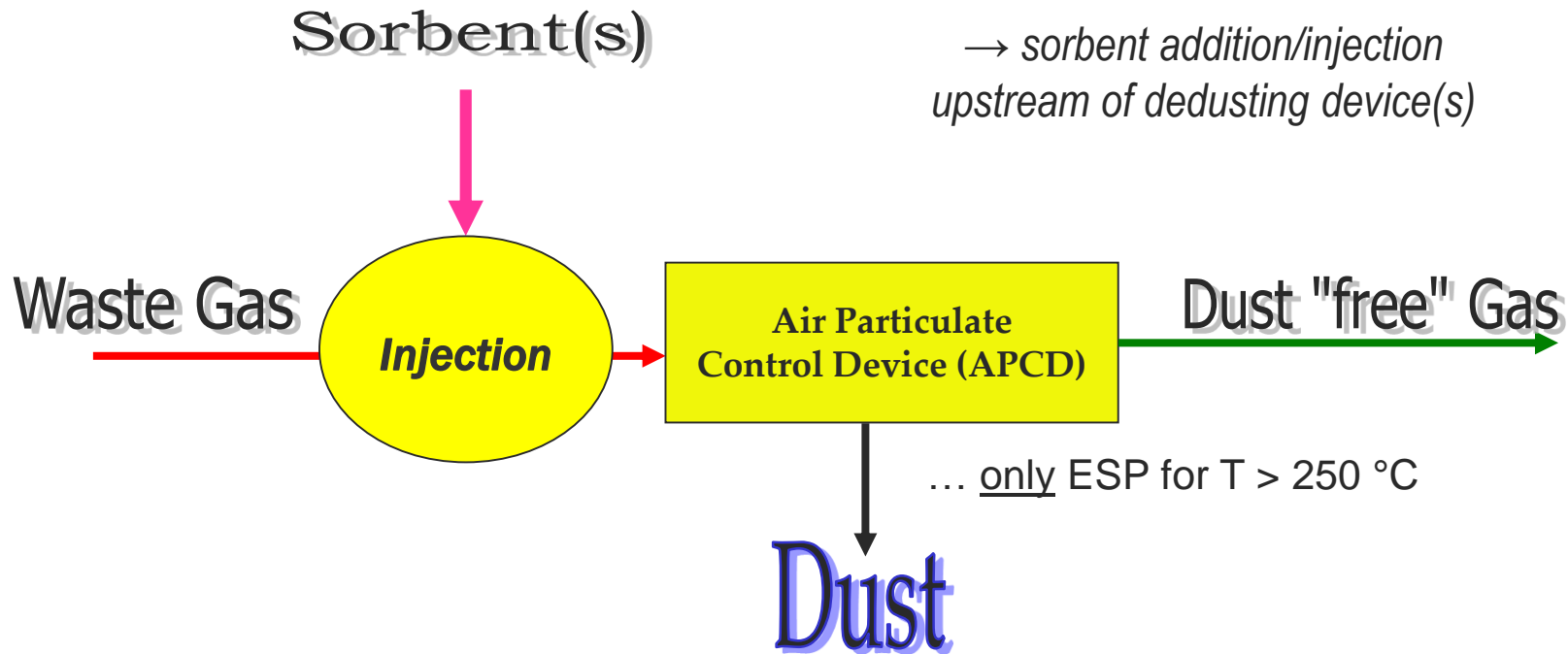❑ **SDA - Spray Dry Absorption (i.e. Semi-dry)**

ARE <u>DRY</u> TECHNIQUES.

```
──────▶  ┌─────────────┐  ──────▶  ┌──────────────┐  ──────▶
         │  DSI / SDA  │           │   FF / EF    │
         │             │           │ Dry dedusting│
         └─────────────┘           └──────────────┘
```

*(*) **SDA** exit temperature: 10 – 20 °C > $T_{DEW\text{-}POINT}$*

(T_{DP} ~ 60–80 °C)

Compared to DSI, the cleaned gas temperature is lower.

PHYSICO-CHEMICAL DEDUSTING

Sorbent(s)

→ *sorbent addition/injection upstream of dedusting device(s)*

Waste Gas → **Injection** → Air Particulate Control Device (APCD) → Dust "free" Gas

… <u>only</u> ESP for T > 250 °C
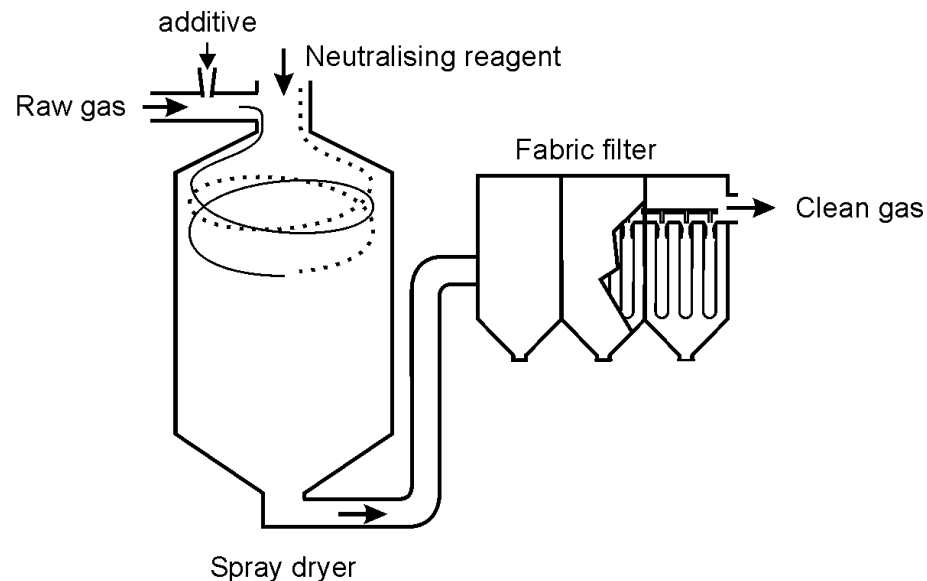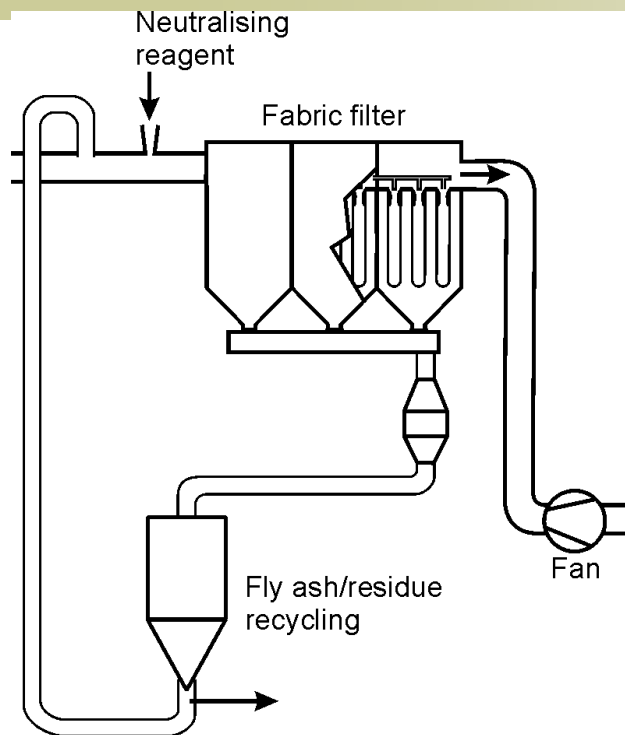
Dust

DSI: DRY REACTANTS/SORBENTS INJECTION

- GAS → completely mixed with Waste Gas (few applications due to lack of gas reactants)

- SOLID (heterogeneous process)→ to mix well with WG, <u>long contact time</u> and <u>very</u> <u>small particles</u> – finely ground particles → large surface areas - required)

SDA: SPRAY DRY ABSORPTION (liquid)/SLURRY OF REACTANTS / SORBENTS: SEMI-DRY

- LIQUID → large surface areas required to mix well with WG →<u>long contact time</u> and <u>small droplets</u> – "atomization")

- SLURRY (partially soluble reactants (e.g. $Ca(OH)_2$ "*milk of lime*" colloidal suspension - latte di calce -)

Dry and semidry systems

Neutralising reagent · Fabric filter · Fly ash/residue recycling · Fan

additive · Raw gas · Neutralising reagent · Fabric filter · Clean gas · Spray dryer

- Simple technology
- Increase mass flows by 25-50% compared with wet systems
- Semidry systems have better stoichiometry than dry

PHYSICO-CHEMICAL DEDUSTING

Two steps*: (common path for both DRY and SEMI-DRY/-WET treatments)*

1ˢᵗ - ADDITION OF WASTE GAS WITH SOLID (LIQUID / GAS) SORBENTS TO FORM SOLID COMPOUNDS / AGGREGATES:

- *Chemical reaction (hot Waste Gas are required! kinetics reasons!)*
  ex. Neutralisation of acid gases: $HCl(g) + NaHCO_3(s) \rightarrow NaCl(s) + H_2O(g) + CO_2(g)$

- *Adsorption (e.g. Flue gas treatment):*
ex. Removal of μ-pollutants : addition of powdered activated carbon (PAC)

A device to introduce the sorbent(s) into the gas stream – a reactor, or simply a duct (the latter only for Dry SS) is required.

2ⁿᵈ - REMOVAL OF SOLID PARTICULATE BY FILTRATION (or by ESP)

DSI: Dry Sorbent Injection

DSI involves the addition of chemicals as a dry solid particulate to form a solid particulate material that can be removed in the downstream particulate collection device such as an ESP or fabric filter*.*

(*sorbents size*: *very small diameter particles that remain suspended in the waste gas, better: ø < 50 μm*); $NaHCO_3$ -sodium bicarbonate - must always be milled on-site just before use, whether it is milled by the a supplier (d_{90} < 40 μm) or milled on-site to a finer particle size (d_{90} < 17 μm).
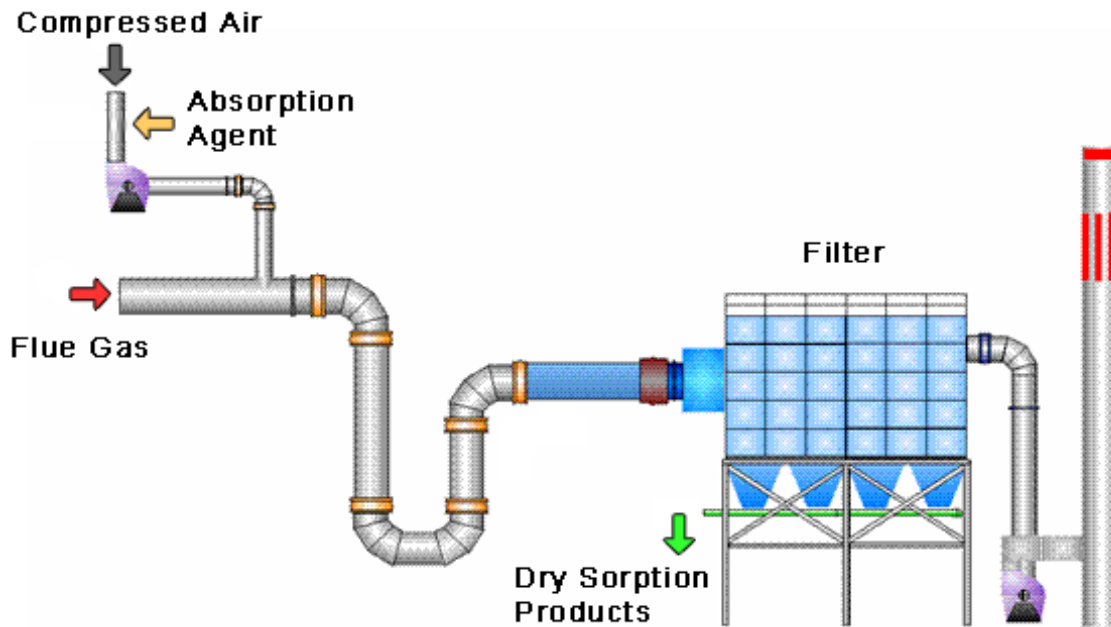
SORBENTS ARE INJECTED:

❑ directly into the flue gas duct (IN DUCT INJECTION), *and/or*

❑ into a REACTION CHAMBER.

▪ Dry Sorbents usually are:

1. Alkaline chemicals *(typically, calcium hydroxide or hydrated lime ($Ca(OH)_2$) or sodium bicarbonate ($NaHCO_3$))* to react with acid gases (SO_2/SO_3, HX (X=F, Cl, Br, I), giving powdery solid salts which are removed in the downstream particulate control device. This technique is effective only for hot gases (t > 140 °C); **at lower temperatures, reactions are too slow**!

2. PAC *(often mixed with the alkaline reagents, for safety reasons, that is to prevent fire and explosion).* Operating temperatures: ≈ < 200°C (adsorption capacity decreases with temperature, also risks of fires!). Exhausted PAC is never regenerated!

DSI - SORBENT ADDITION IN-DUCT

Recirculation of injected sorbents not represented in this scheme!
Partial recirculation of the products is a common industrial practice to:
a) **Increase the efficiency of the process** (due to: higher Sorbent/Pollutants ratio),
b) **Make better use of the sorbents** (decrease the consume!) (sorbents not previously fully exhausted!)
c) **decrease the amount of waste products.**

In-duct DSI is the lowest cost solution. Easy to install in all existing plants. DSI systems take up much less physical space, which is especially important when considering retrofit or upgrades to existing units.
These systems involve the injection of a dry sorbent into the ductwork, and the dry product is collected in a downstream particulate control device. Because a separate absorber vessel is not needed, capital costs are minimized.
Low capital costs may partially be offset by lower reagent utilization, which results in higher operating costs for high removal rates. In-duct DSI are generally applied when lower removal efficiencies are required, or on small plants where the capital cost for other reactors/scrubber types may not be justified.

RECYCLE IN WASTE GAS TREATMENTS

RECYCLE: When a part of a process stream is fed back into an earlier stage of the process, the stream is said to be "recycled." Recycle is often used to increase the rate of conversion of a reactant.

By passing a reactant molecule through the process several times, its chances to react and convert to product are increased. Other reasons to recycle part of a stream include recovery of valuable materials, such as catalysts, improved temperature control over a process, and decreased waste of working (carrier) fluid.

RECYCLE RATIO, R = (mass of recycle) / (mass of fresh feed).

RECYCLING OF REACTANT: If a process stream is recycled in order to increase the conversion of a reactant, we can define single-pass conversion and overall conversion as follows:

❑ **SINGLE-PASS CONVERSION = (reactant input to reactor – reactant output from reactor) / reactant input to reactor**

❑ **OVERALL CONVERSION = (reactant input to process - reactant output from process) / reactant input to process**

Single-pass conversion gives the fraction of reactant converted on a single pass through the reactor. In contrast, overall conversion gives the fraction of reactant converted by the process, which may involve recycling reactant molecules many times through the reactor in order to increase their conversion.

PURGE STREAMS: Purge streams are used to rid a process of an undesirable material or waste. Purge streams are often encountered together with recycle streams, since recycling makes a process particularly susceptible to accumulation of undesired species.

Setting the purge streams is of a fundamental importance for most APCD (air pollution control devices)**! E.g. dry scrubbing (DSI/SDA), Wet scrubbing, …..**

A very interesting APCD scheme is the use of double cleaning system in series: the material discharged from the 2nd, can be conveniently fully recycled in the 1st APCD.

# DSI - SORBENT ADDITION IN A REACTOR (WITH RECIRCULATION)
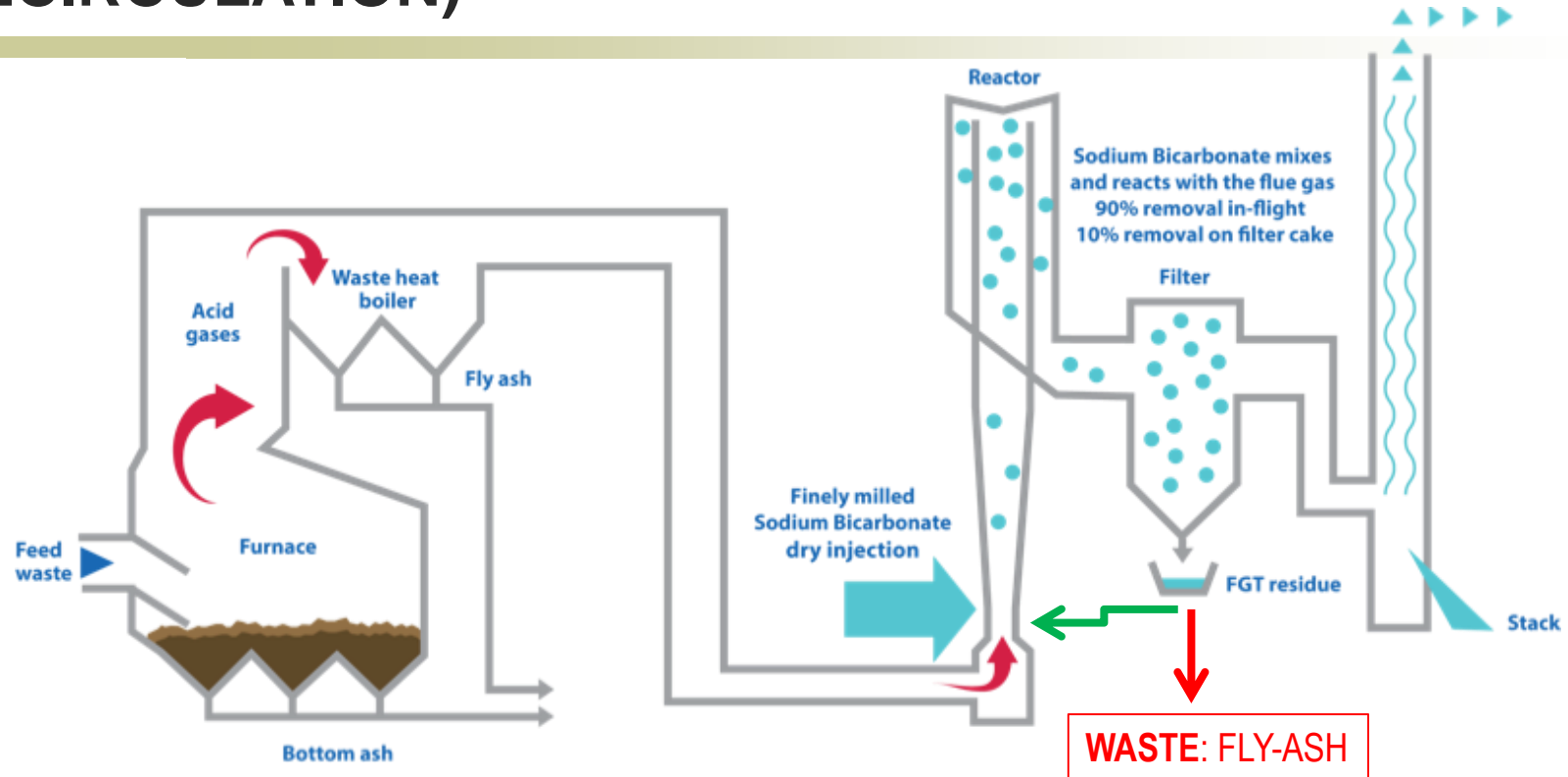
FGT residue is splitted: recycled flow and waste discharged flow.

Partial recirculation of FGT (flue gas treatment) residue added in this scheme.
A steady-state is maintained after few hours/days: **mass of fly-ash discharged ≈ mass of injected reactants. The value of R** (*R, recycle ratio = mass of recycled residue/mass of fresh reactants*) *depends on specific technique and on the technical director.*

PREVENTION VS CONTROL

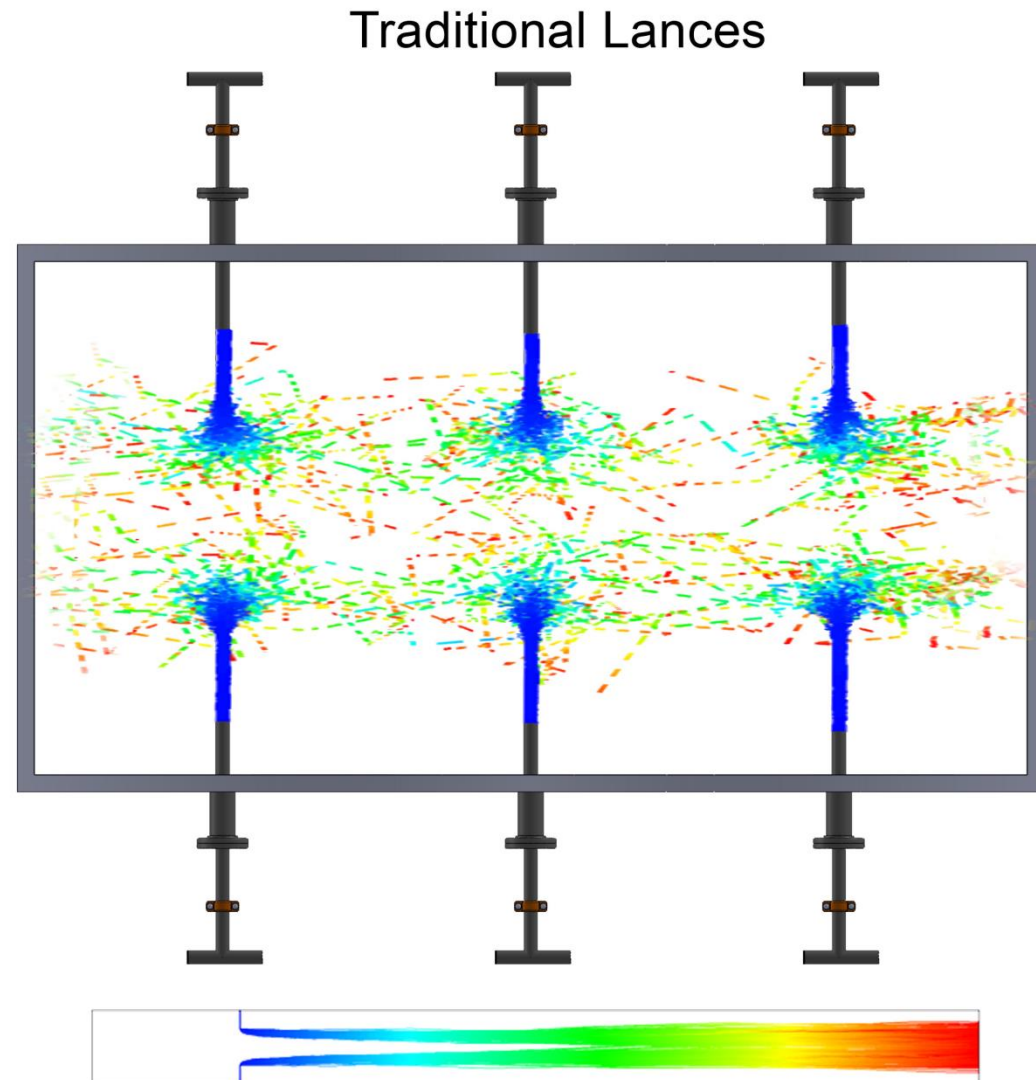## Dry reactor (DSI Technique: in-duct DRY SORBENT INJECTION)
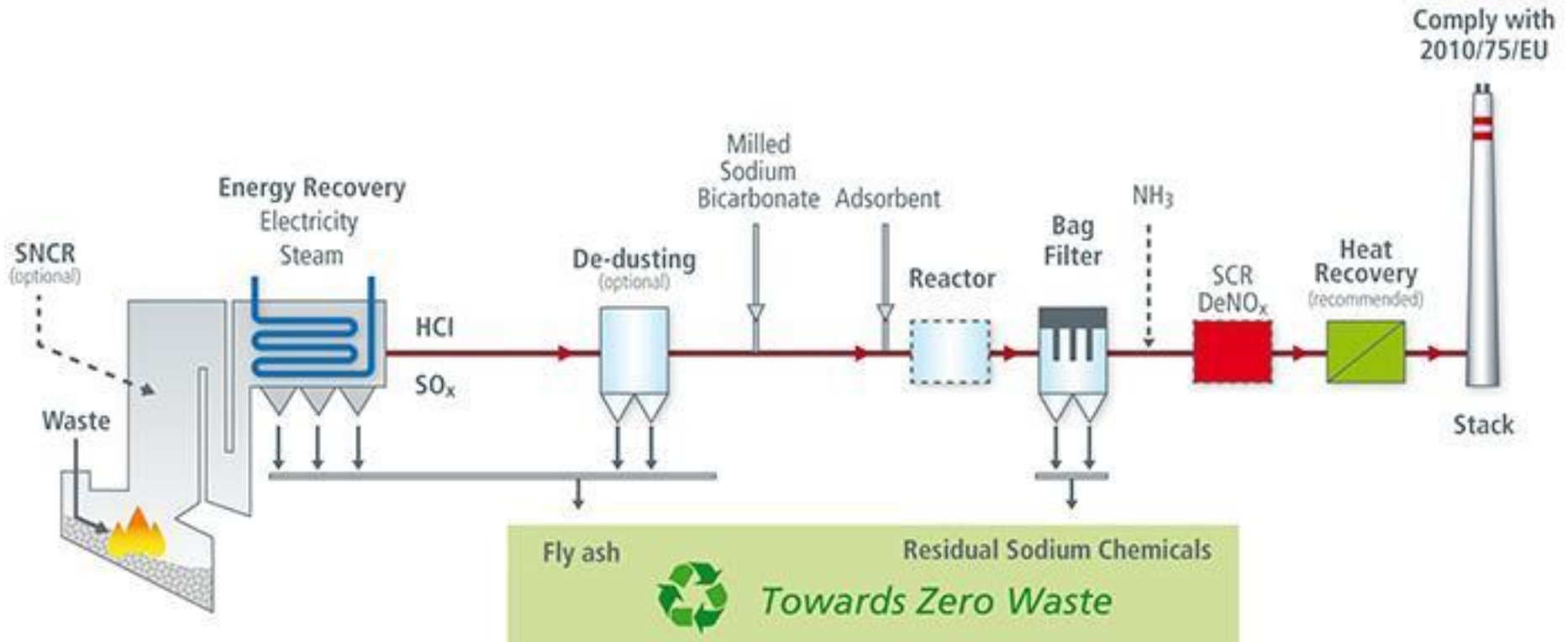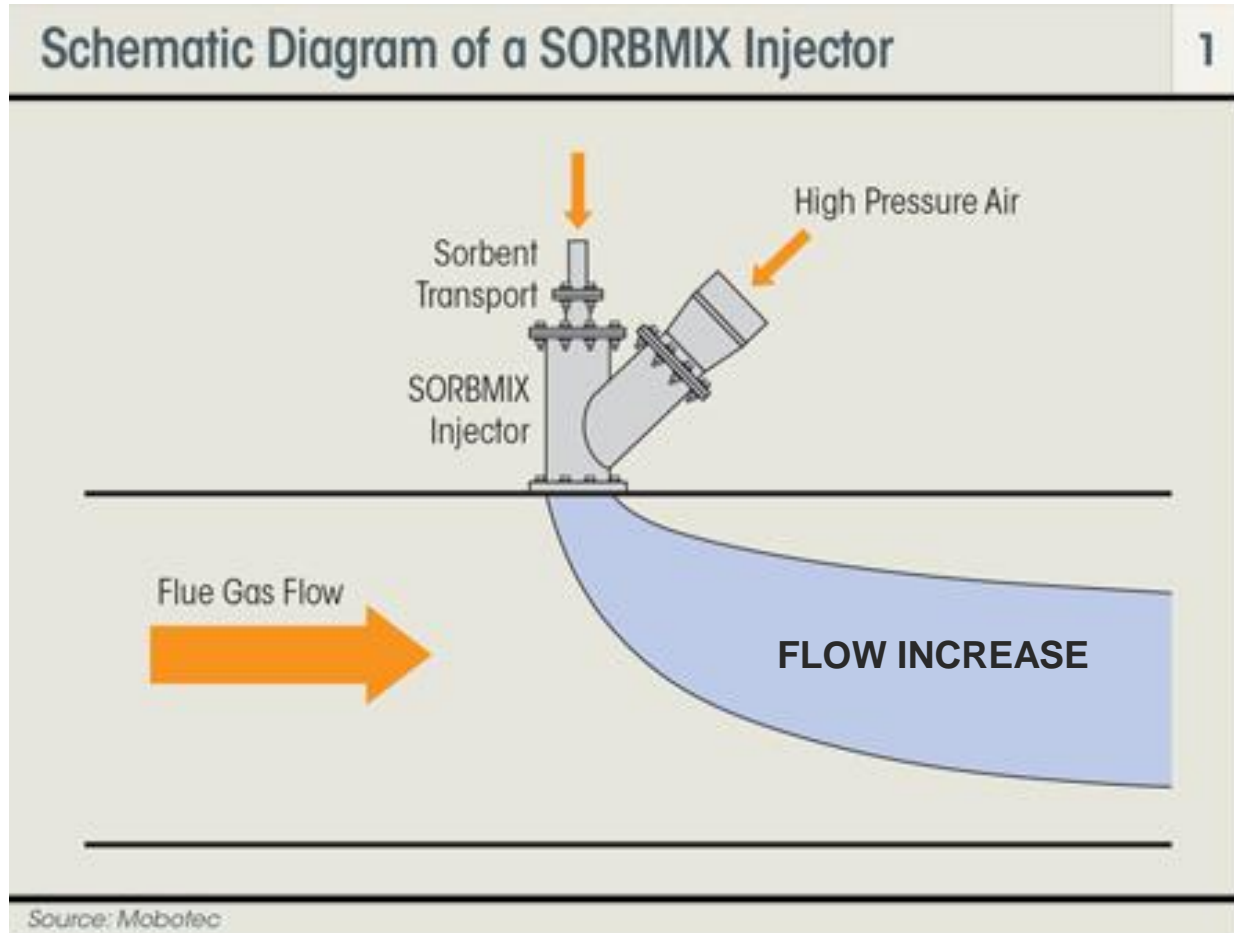

SCHEME TO GET "CLEAN RECYCLABLE SOLID RESIDUE"

Dry reactor (DSI Technique: DRY SORBENT INJECTION)

SCHEME.
"IN-DUCT INJECTION",
THAT IS WITHOUT
**REACTORS!! The duct**
operate as a reactor!

Traditional Lances

Residence time profile

Dry reactor (DSI Technique: DRY SORBENT INJECTION)

Schematic Diagram of a SORBMIX Injector — 1

- High Pressure Air
- Sorbent Transport
- SORBMIX Injector
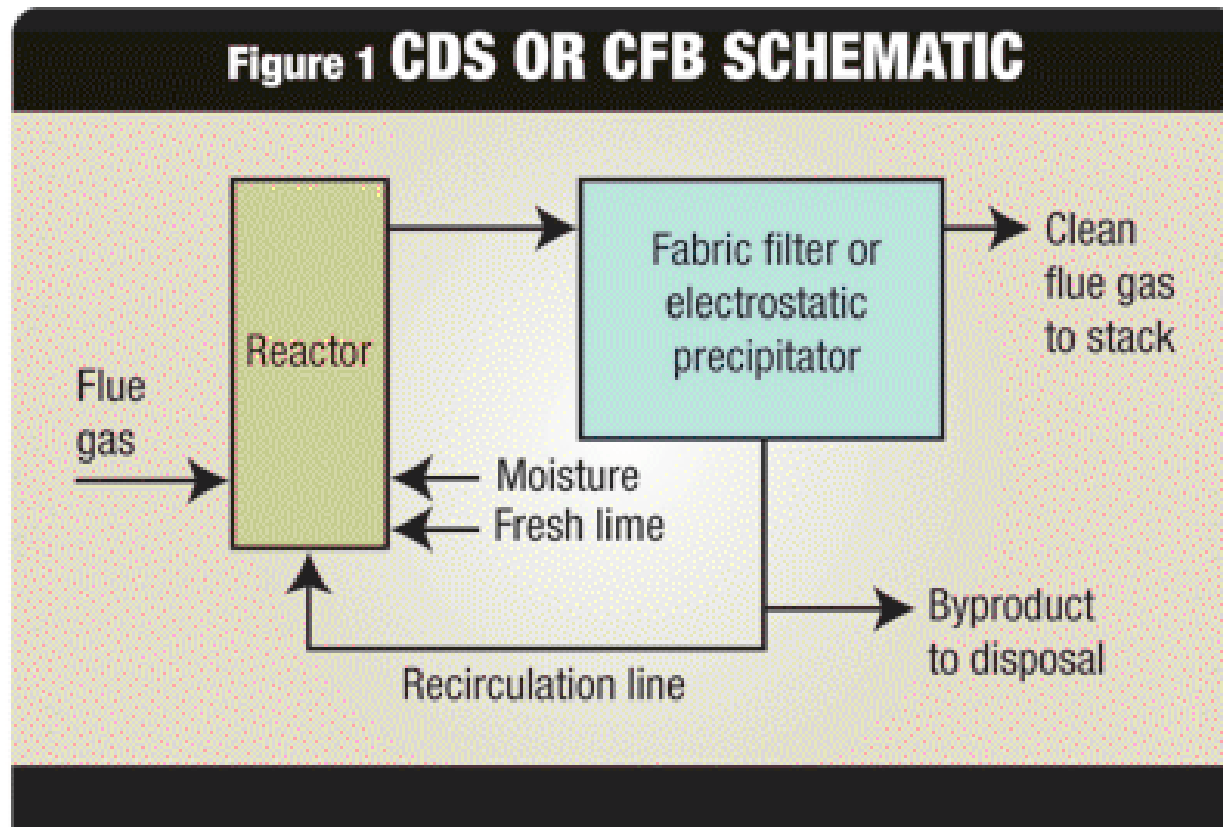- Flue Gas Flow
- **FLOW INCREASE**

Source: Mobotec

SCHEME "IN DUCT INJECTION". WITHOUT REACTORS!!

DSI - SORBENT ADDITION IN A REACTOR (WITH RECIRCULATION)
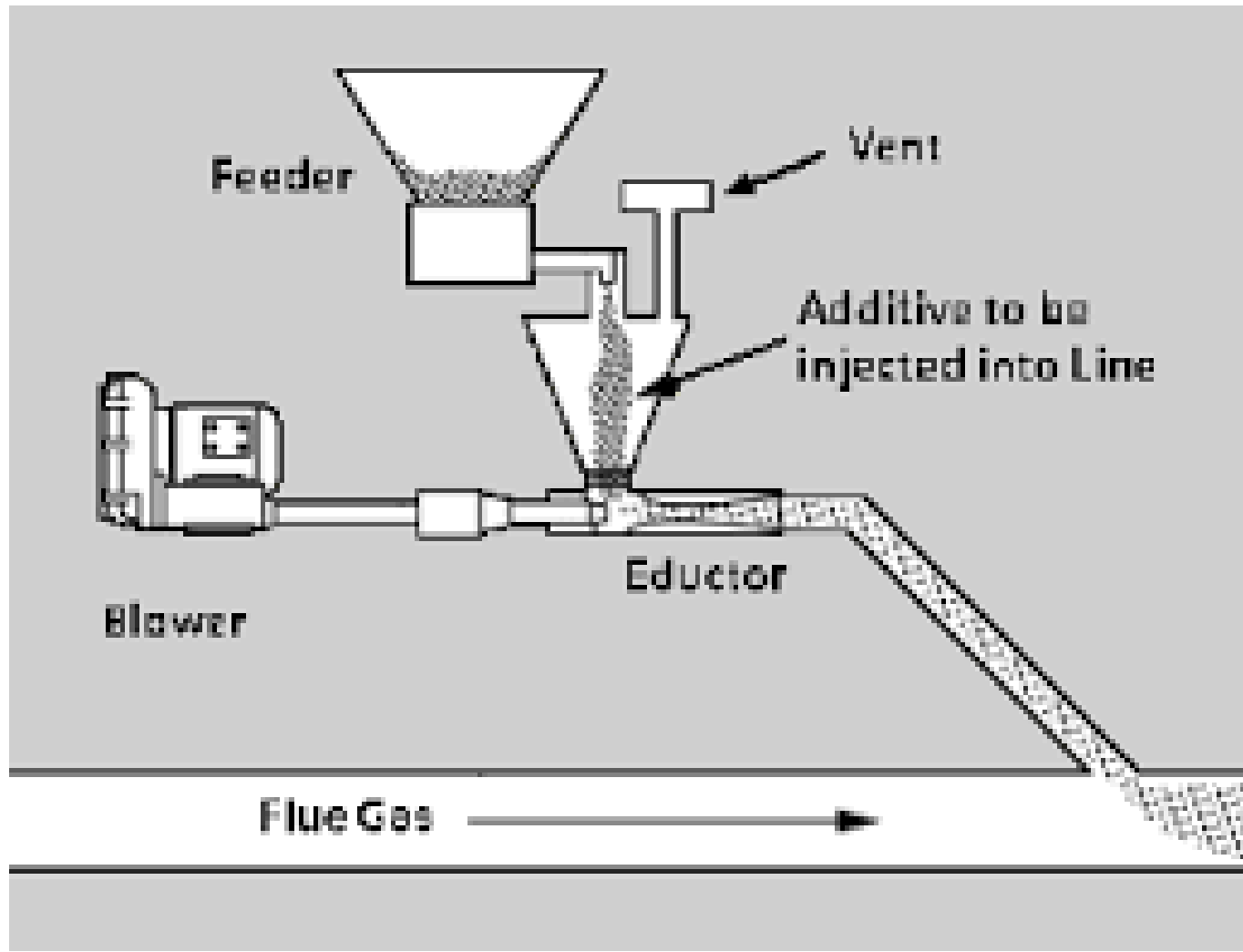
SCHEME "IN DUCT INJECTION". WITHOUT REACTORS!!

Sorbent addition in a reactor (with PARTIAL recirculation)

Figure 1 CDS OR CFB SCHEMATIC

The word "lime" is a generic term used to describe many calcium based chemical:

a. CaO (quick lime)
b. $Ca(OH)_2$ (Hydrated Lime; slaked lime)
c. $Ca(OH)_2$ slurry.

OPERATIVE PARAMETERS: GENERAL OVERVIEW

- <u>lower</u> removal efficiencies attainable with respect to wet systems
- optimum efficiencies in restricted T ranges
  - ➢ lime: 120°C - 150°C
  - ➢ bicarbonate: 170°C - 190°C
- excess reagent required with respect to stoichiometry
  - ➢ bicarbonate: dosage ratios = 1.2-1.5
  - ➢ lime: dosage ratios = 1.5-2 (lower values for spray dry system)
- requirements for optimum reactant atomization in spray dry systems
- requirements of specific size distribution of solid reagent in dry systems
- separated solid products recycle for lime systems, with high values for dry process
- final residues in dry form
- absence of spent liquid effluents (spray dry) and of any liquid stream (dry)

OPERATIVE PARAMETERS: REACTANTS (lime, Ca(OH)$_2$)

Lime process principles
- reactions involved
  - $Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2H_2O$
  - $Ca(OH)_2 + 2\ HF \rightarrow CaF_2 + 2H_2O$
  - $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$

APPLICATIONS

Spray dry systems   Dry lime systems
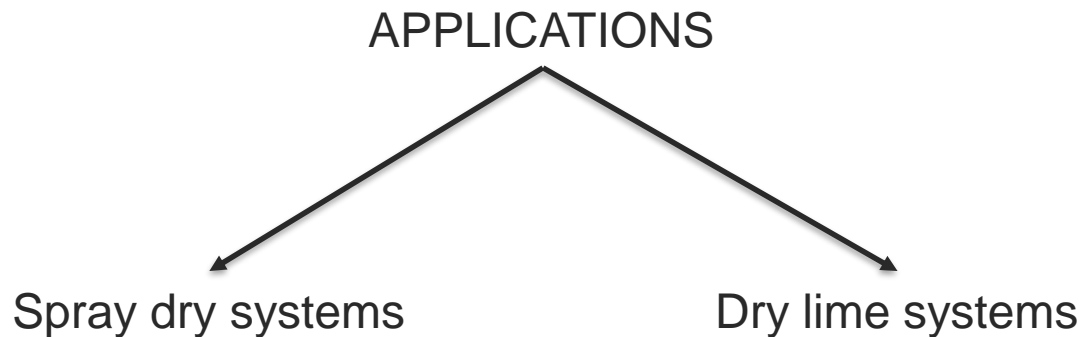
OPERATIVE PARAMETERS: REACTANTS (lime, Ca(OH)$_2$)

Spray dry systems

- concentrated slaked lime solutions addition in a contact reactor
  - ➤ conventional chemical liquid absorption
  - ➤ simultaneous water evaporation by flue gas heat content
  - ➤ dry reaction completion

- general characteristics
  - ➤ preliminary partial absorption in aqueous phase: good efficiency, lowers excess reagent requirements
  - ➤ raw flue gas cooling and saturation with moisture: positive effects on efficiency, negative drawbacks for fabric filter cleaning
  - ➤ operational needs of atomizing concentrated lime solutions (scaling, erosion, plugging, …)

OPERATIVE PARAMETERS: REACTANTS (lime, Ca(OH)$_2$)

Dry lime systems
- granular dry slaked lime addition
  - ➤ no liquid absorption intervention
  - ➤ need to utilize finely grounded lime for increase efficiency
- general characteristics
  - ➤ possibilities of direct in duct injection
  - ➤ <u>absence of liquids</u> (no simultaneous liquid phase reaction), no gas cooling nor moisture increase
    - – reduced efficiency, higher excess reagent, significant recycle of products
    - – less effects on fabric filter dust cake quality and plume visibility
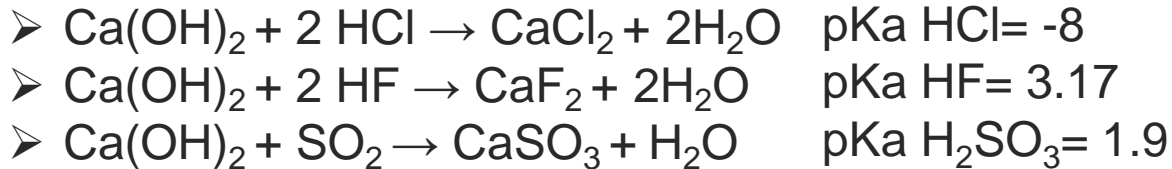 - ➤ no lime aqueous solutions to be prepared nor sprayed/atomized
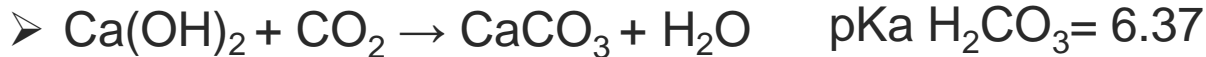
Grounding for increasing
specific surficial area

SO$_2$

HF

HCl

Ca(OH)$_2$

CaF$_2$

CaCl$_2$

CaSO$_3$
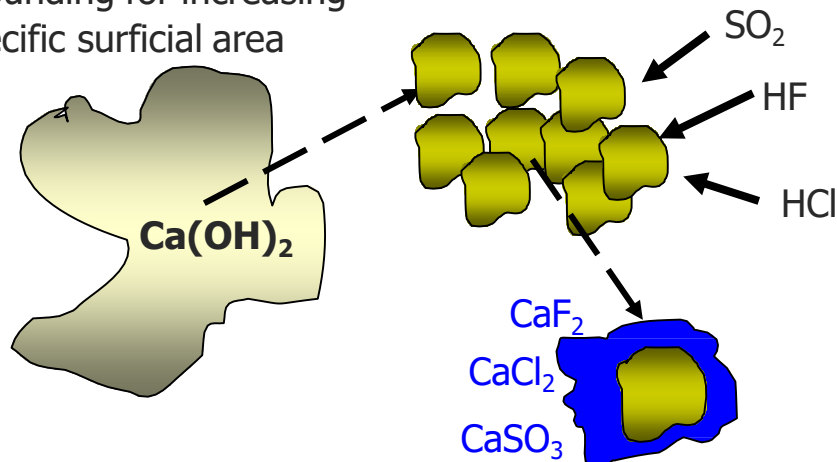
Temperature 120 - 150°C

OPERATIVE PARAMETERS: REACTANTS (lime, Ca(OH)$_2$)

- reactions involved
  - $Ca(OH)_2 + 2\,HCl \rightarrow CaCl_2 + 2H_2O$ pKa HCl= -8
  - $Ca(OH)_2 + 2\,HF \rightarrow CaF_2 + 2H_2O$ pKa HF= 3.17
  - $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$ pKa H$_2$SO$_3$= 1.9

- reactions to avoid (competitive process)
  - $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ pKa H$_2$CO$_3$= 6.37

In order to avoid the formation of calcium carbonate we have to work on acidity property. Lime is a strong base and react better with a strong acid (HCl).
However, you have to consider that the concentration of HCl is very low in the flue gas.

EXAMPLE:

Concentration CO$_2$ in air = 400 ppm

Flue gas flow= 100000 Nm^3/h

Flow CO$_2$ = 400 cm^3/m^3 * 100000 Nm^3/h = 40 Nm^3 CO$_2$/h ≈ 2kmol CO$_2$/h= 88 kgCO$_2$/h
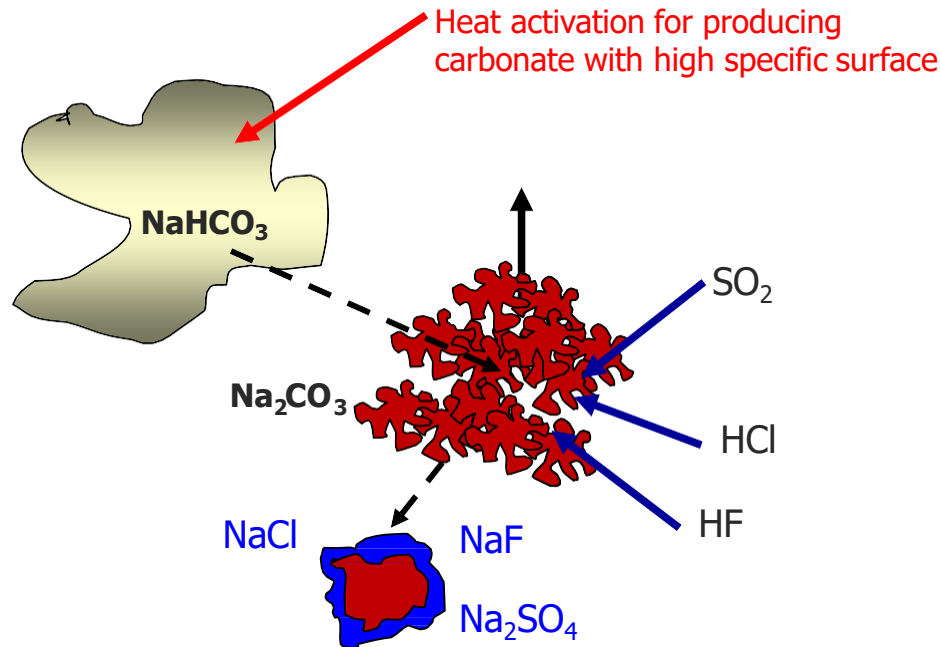
I have to expect a large quantity of solid waste

OPERATIVE PARAMETERS: REACTANTS (dry bicarbonate)

Dry bicarbonate systems
- reactions involved
  - $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$ (heat activation)
  - $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$
  - $Na_2CO_3 + 2HF \rightarrow 2NaF + CO_2 + H_2O$
  - $Na_2CO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow Na_2SO_4 + CO_2$

Heat activation for producing carbonate with high specific surface

$NaHCO_3$

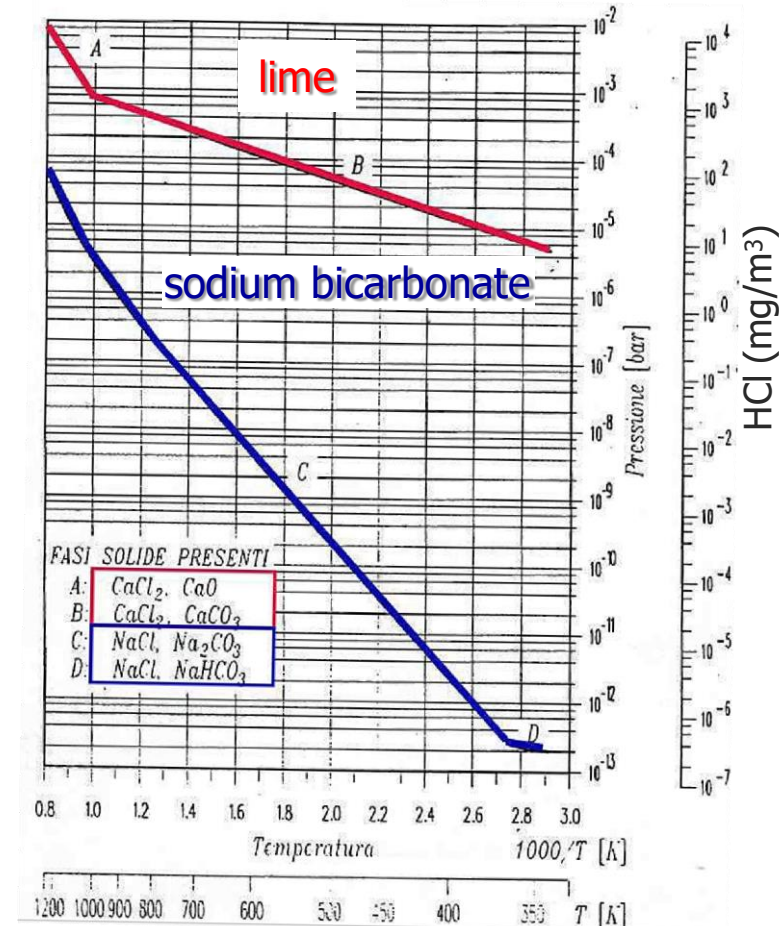Na_2CO_3

SO_2

HCl

HF

$NaCl$ NaF

Na_2SO_4

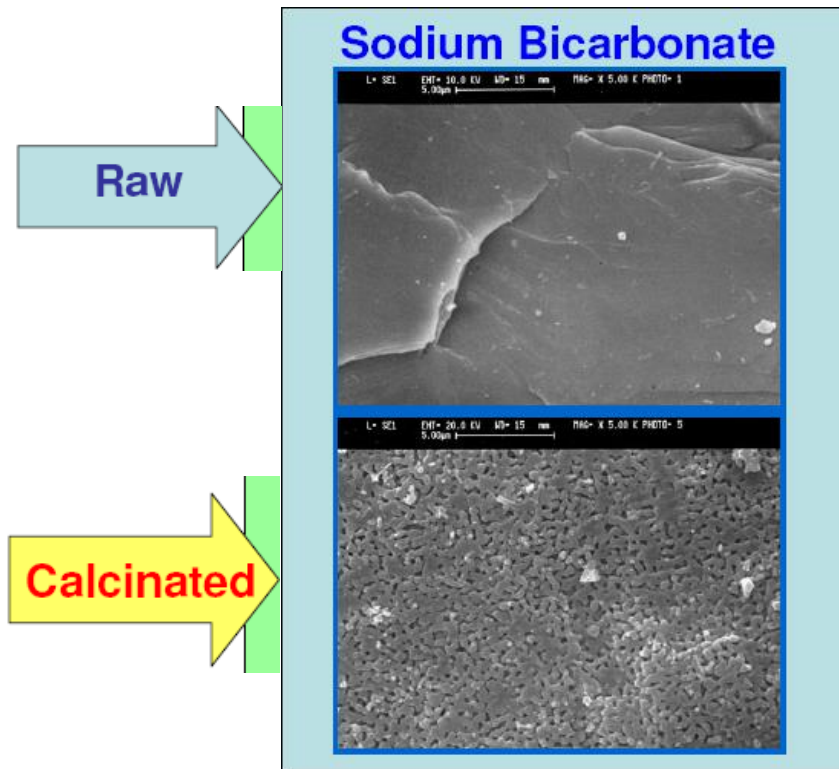**Temperature 170 - 190°C**

OPERATIVE PARAMETERS: REACTANTS (dry bicarbonate)

Dry bicarbonate systems
- general characteristics
  - reaction equilibrium more favorable with respect to lime: higher efficiencies, less required excess reagent
  - easier operation with respect to lime
    - less difficulties of bicarbonate transport, movement and addition
    - no requirements of recycling separated product
  - potential for reagent regeneration/recycle
  - higher cost of reagent
  - higher operating temperature required for reagent activation (170-190°C)
  - reduction of moisture effects due to higher temperatures at fabric filter inlet

HCl equilibrium concentration

HCl equilibrium concentration diagram showing lime and sodium bicarbonate curves. Pressure [bar] and HCl (mg/m³) on vertical axes; Temperatura and 1000/T [K], T [K] on horizontal axes.

FASI SOLIDE PRESENTI
A: $CaCl_2$, CaO
B: $CaCl_2$, $CaCO_3$
C: $NaCl$, Na_2CO_3
D: $NaCl$, $NaHCO_3$

OPERATIVE PARAMETERS: REACTANTS ($NaHCO_3$)

Sodium Bicarbonate — Raw / Calcinated

Calcination of Sodium Bicarbonate at > 140 °C
("POP-CORN" EFFECT)

$NaHCO_3$ sodium bicarbonate

$$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

Production of gases

Na_2CO_3 sodium carbonate

Strong increase of surface area!

Sodium Bicarbonate (SOLVAir *)
Particle Size: $d_{50} \sim 100\ \mu m$
          In-line milling before injection!
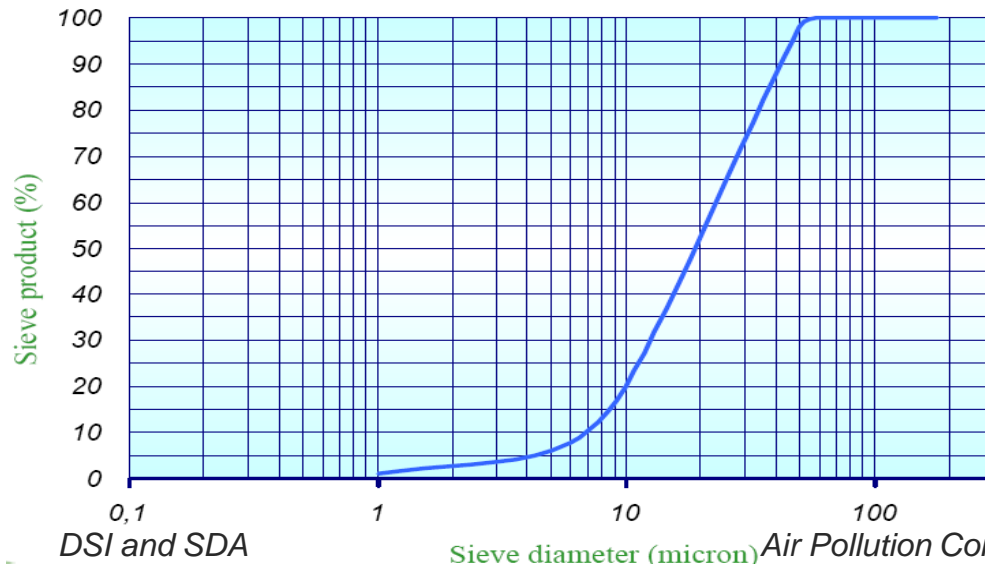
Milled Sodium Bicarbonate particle sizes:
• d_{50}: < 10 μm
• d_{90}: < 25 μm

Granulometry of sodium bicarbonate BICAR® SOLVAY
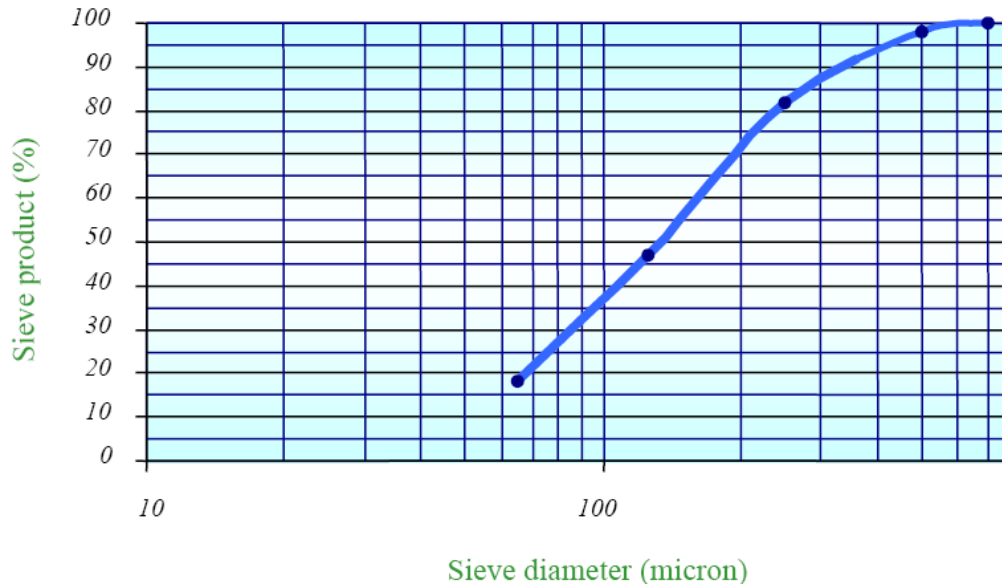
Commercial

d_{50}: 200 μm

Ground (Milled)

d_{50}: 20 μm

Granulometry of sodium bicarbonate BICAR® SOLVAY

A common approach to define the particle size of a solid material is its D_{10}, D_{50}, and D_{90} distribution width, as shown in Figure.
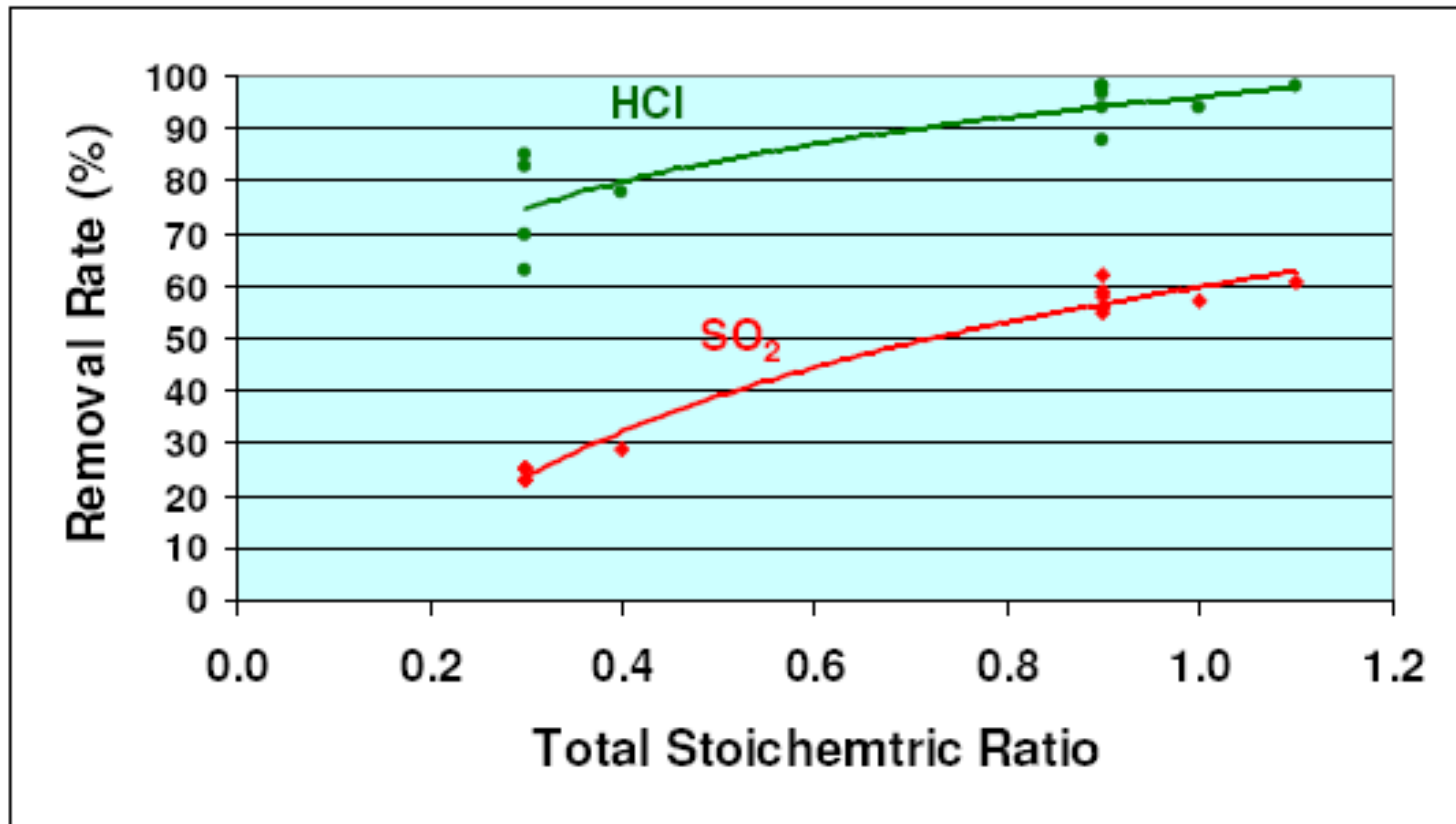
The D_{50}, the median, has been defined as the diameter where half of the population lies below this value.

Similarly, 90 percent of the distribution lies below the D_{90}, and 10 percent of the population lies below the D_{10}
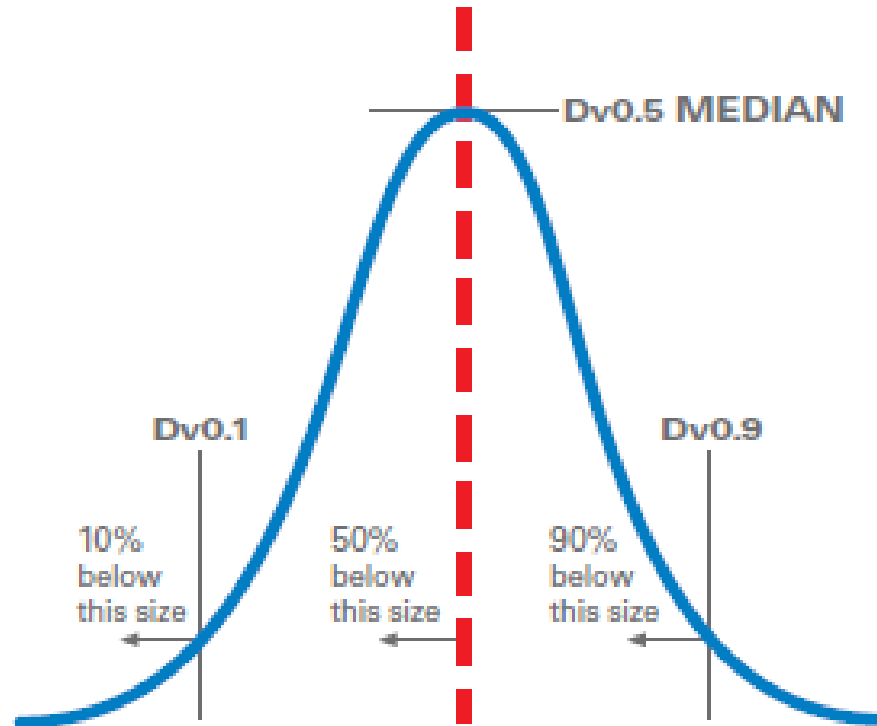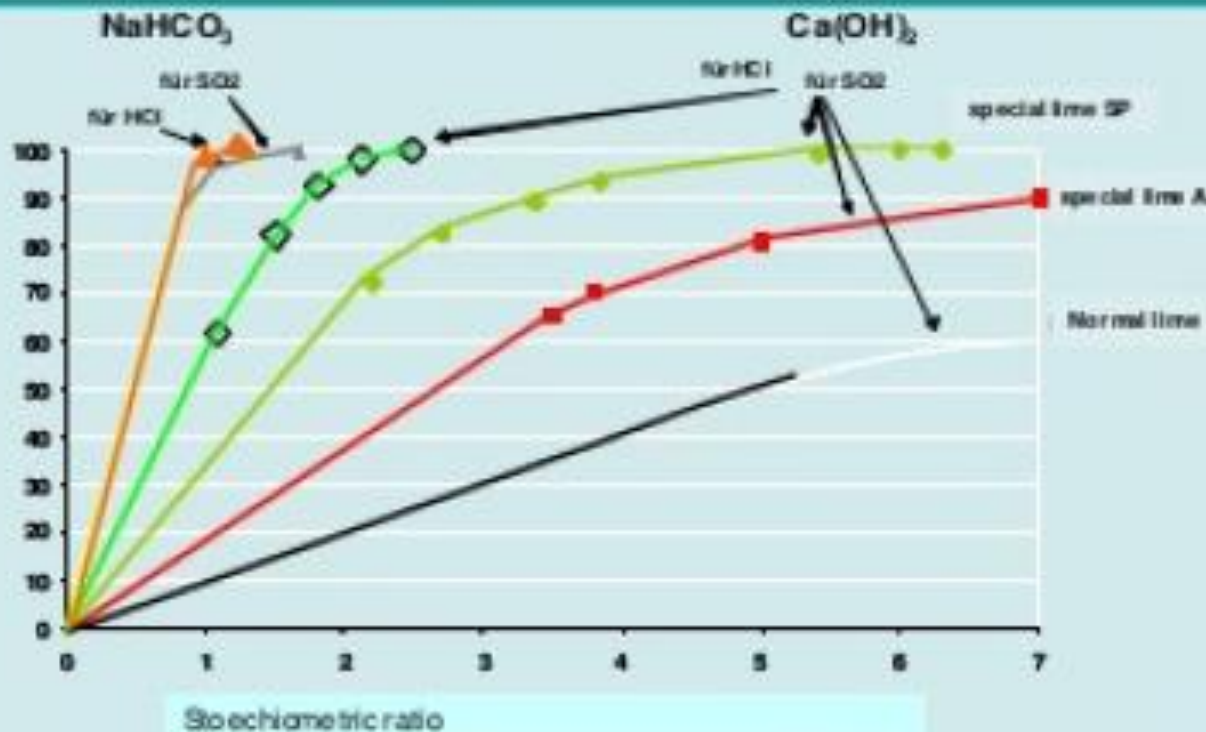
OPERATIVE PARAMETERS: REACTANTS (NaHCO$_3$)

Performance of HCl and SO$_2$ mitigation

OPERATIVE PARAMETERS: REACTANTS (NaHCO$_3$ and Ca(OH)$_2$)

Absorption rate vs. Stöchiometric ratio in comparision of different additives:

DSI-Comparison of HCl and SO$_2$ removal rates with NaHCO$_3$ and Ca(OH)$_2$
HCl > SO$_2$;
NaHCO$_3$ > Ca(OH)$_2$

NaHCO$_3$ is generally more efficient than Ca(OH)$_2$
HCl is more efficiently removed than SO$_2$.
HCl ELVs set by Competent Authorities are generally (much) lower than SO$_2$ ELVs.

OPERATIVE PARAMETERS: effect of particle size
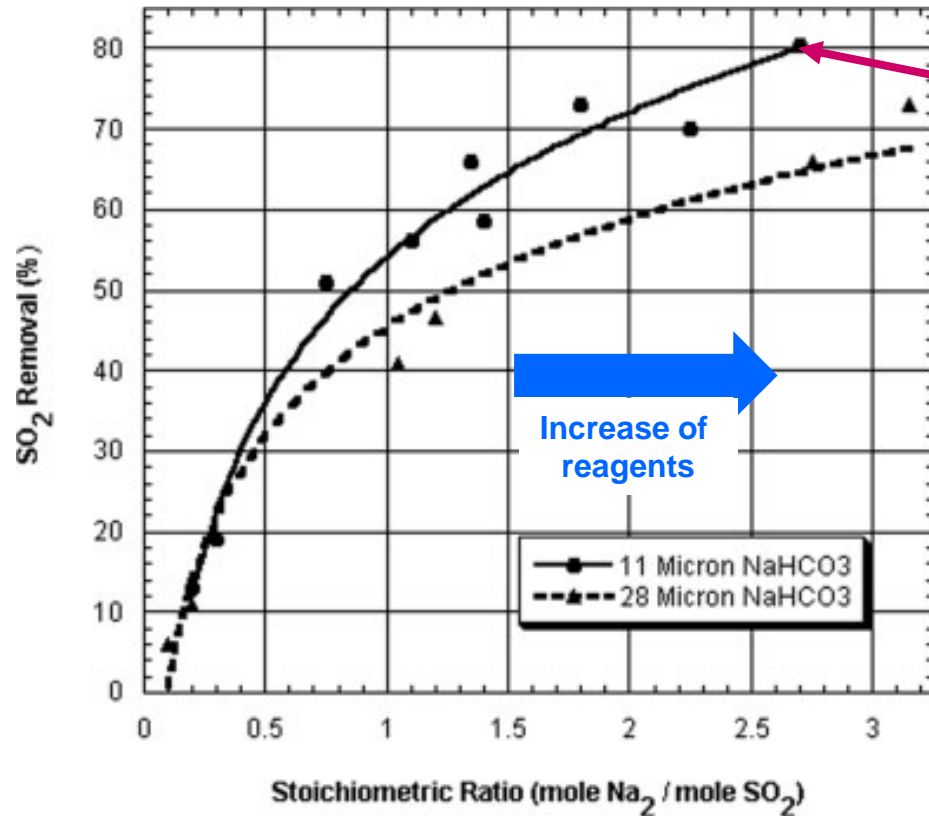
NaHCO$_3$: 11 µm is better than 28 µm!
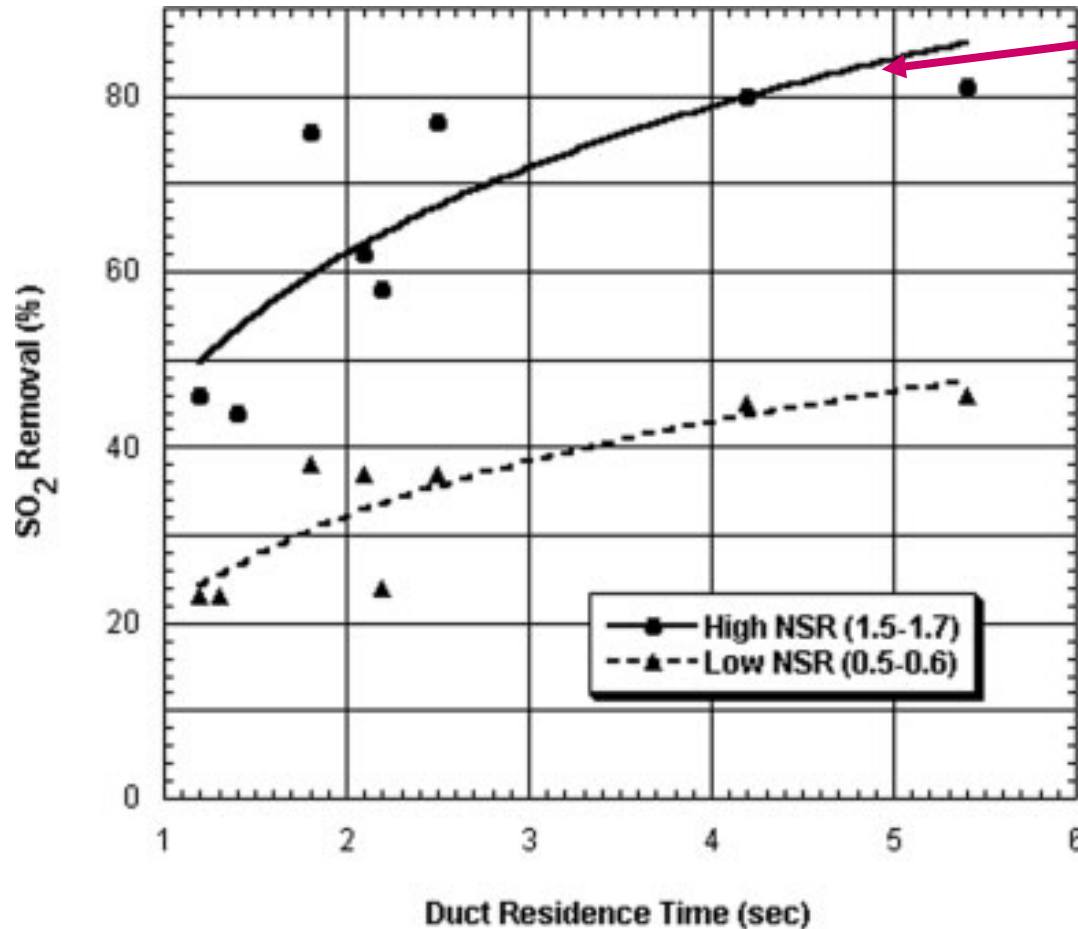
Comparison of removal rates of:

11 µm NaHCO$_3$ vs. 28 µm NaHCO$_3$

- inlet [SO$_2$]: 310-330 ppm;
- in-duct residence time: 5 s.

Sorbents were tested upstream of the ESP.

OPERATIVE PARAMETERS: effect of in duct resident time

Better results with higher NSR!

NaHCO$_3$

Inlet SO$_2$ concentration: 350–380 ppm.

T = 205 - 210 °C

NSR = *normalized stoichiometric ratio*

DRY SORBENT(S) INJECTION - DSI

The sorbent material (dry fine powder) is injected directly into the gas ductwork and/or in the reaction chamber <u>before the particulate control device</u>.

Sometimes:
- the gas is conditioned *(e.g. cooled)* to operate at the most convenient temperature range;
- the solid reagent can be milled to obtain very fine particles.

SOLID REAGENT MILLING

The most dramatic reduction in consumption for sodium-based sorbents is achieved by reducing sorbent particle size through milling, which in turn increases reactivity. The challenge using typical sodium-based sorbents, such as sodium bicarbonate, is that it becomes more difficult to handle as particle size decreases. Additionally, high temperatures experienced during certain milling processes can degrade the performance of milled sodium based sorbents.

MILLING PERFORMANCE REQUIREMENTS

The primary goal of sorbent milling is to get the smallest practical particle size (5-30 µm range).

Temperatures must be < 55 °C to prevent sorbent handling problems and degraded sorbent efficiency related to pre-calcination. Furthermore, <u>milling material and then storing the milled material in a silo or hopper results in re-agglomeration of the previously milled particles</u>.

In-line milling is advantageous as it does not require a downstream silo or hopper to temporarily store milled sorbent. Instead, the mill needs to be compatible with varying air volumes driven by conveying requirements.
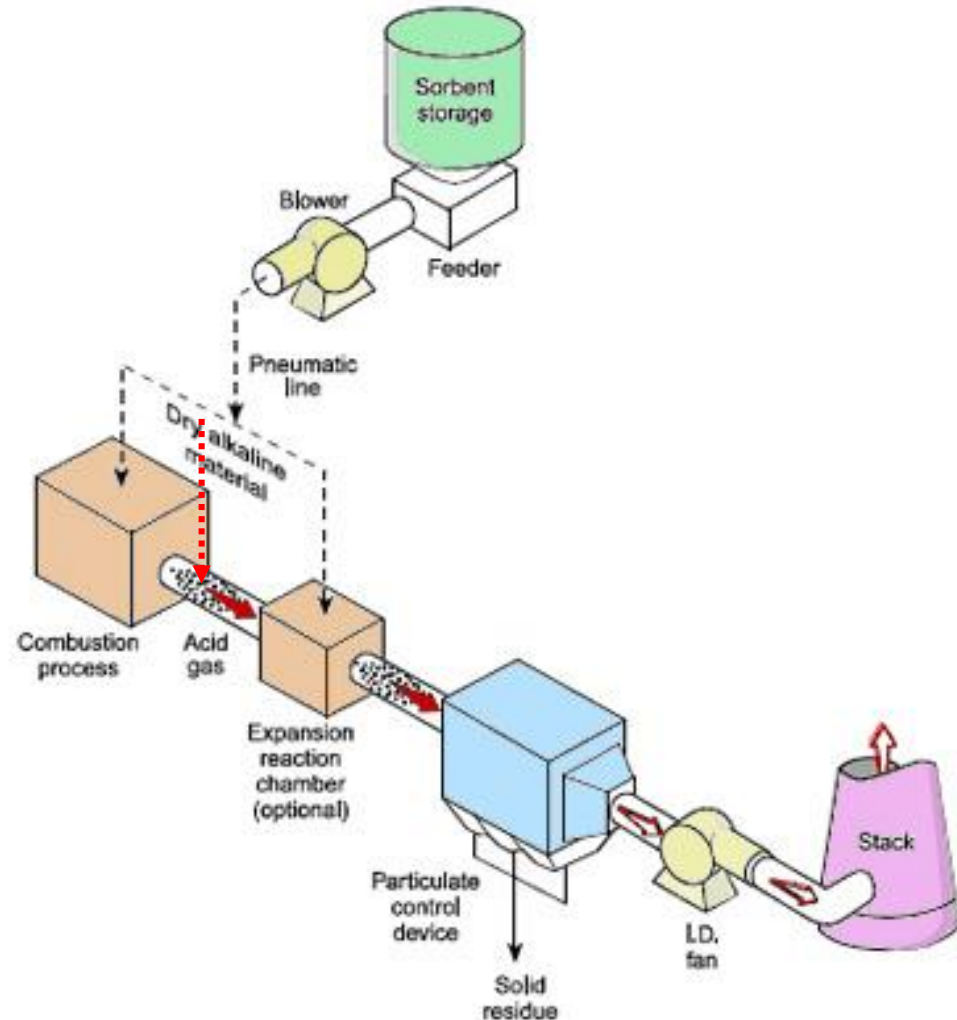
DRY SORBENT(S) INJECTION - DSI

The DSI system components are dry sorbent storage tanks, weight feeders to meter the required amount of sorbents, blowers and transfer lines, and injection devices such as a venturi.

The dry sorbent material is injected through a pneumatic line to the injection area where transfer through the line provides fluidization and turbulence of the sorbent material.

An expansion **/ reaction chamber** may be part of the design to increase the residence time of the sorbent with the acid gases.

Sticky fly-ash *particles* occurs on the *tube* walls of the heat exchangers-

DSI systems are widely used in waste incinerators.

IN-DUCT SORBENT INJECTION

Sorbent

Air

Fabric Filter (FF)
or
Baghouse (BH)

Stack

Fan

Flue Gas

ID-Fan
(Induced Draft Fan)

Typical dry process (solid reagent injection in the pipe)
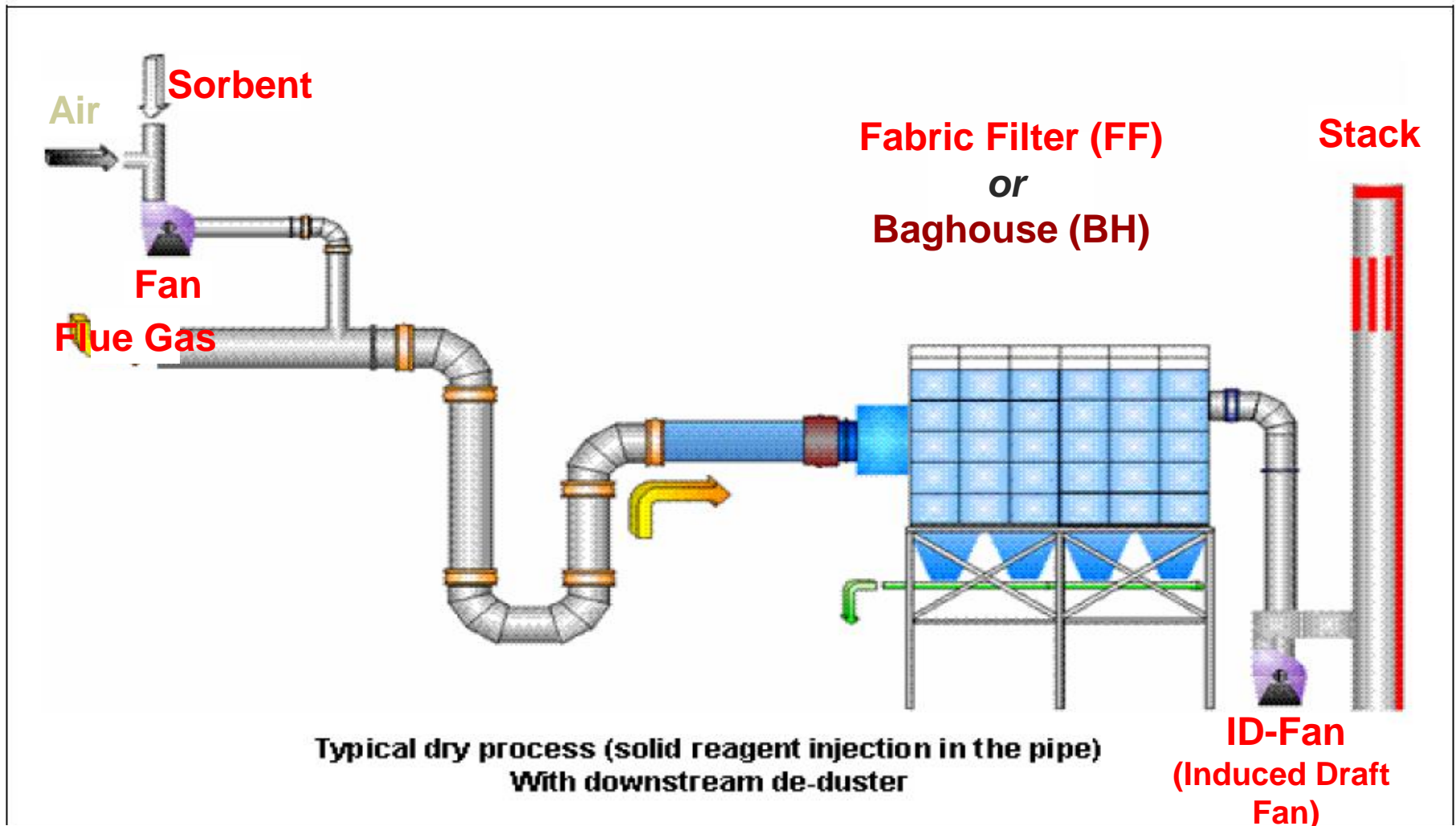With downstream de-duster

Figure 2.44: Schematic diagram of a dry FGT system with reagent injection to the FG pipe and downstream bag filtration

DSI - DOSING UNIT & BLOWER

DSI - DOSING UNIT & BLOWER

Multi-point injection in the WasteGas duct

DSI – COST OF CHEMICALS

Common Name or Mineral	Chemical	Formula	Cost ($/ton)
Limestone	Calcium carbonate	$CaCO_3$	$25[a]
Lime, quicklime	Calcium oxide	CaO	$57[b]
Lime, slaked lime, hydrated lime	Calcium hydroxide	$Ca(OH)_2$	$70[b]
Soda ash	Sodium carbonate	Na_2CO_3	$105[c]
Caustic soda	Sodium hydroxide	$NaOH$	$200[d]
Nahcolite[e]	Sodium bicarbonate	$NaHCO_3$	$260[c]
Trona[f]	Sodium sesquicarbonate	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$	$65[c]

$NaHCO_3$ and Na_2CO_3 can be produced in the Solvay process; for $Ca(OH)_2$ a recovery process can't be used.

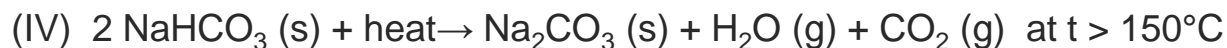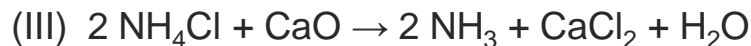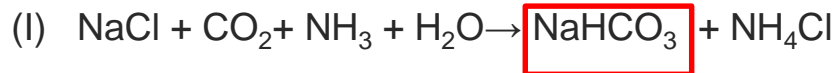|	Price (2019) Euro/ton
$Ca(OH)_2$ (calcium hydroxide)	48.00
$NaHCO_3$	750.00

SOLVAY PROCESS: production of sodium bicarbonate

The Solvay process results in soda ash (predominantly sodium carbonate (Na_2CO_3)) from brine (as a source of sodium chloride (NaCl)) and from limestone (as a source of calcium carbonate ($CaCO_3$)). The overall process is:

$$2\ NaCl + CaCO_3 \rightarrow \boxed{Na_2CO_3} + CaCl_2$$
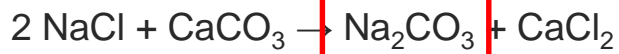
Solvay plant at Rosignano (Tuscany, IT)

The actual implementation of this overall reaction is done IN four steps.

(I) $NaCl + CO_2 + NH_3 + H_2O \rightarrow \boxed{NaHCO_3} + NH_4Cl$

(II) $CaCO_3 + heat \rightarrow CO_2 + CaO$

(III) $2\ NH_4Cl + CaO \rightarrow 2\ NH_3 + CaCl_2 + H_2O$

(IV) $2\ NaHCO_3\ (s) + heat \rightarrow Na_2CO_3\ (s) + H_2O\ (g) + CO_2\ (g)$ at t > 150°C

PERFORMANCE OF BH VS. ESP

SO$_2$ Neutralization by NaHCO$_3$
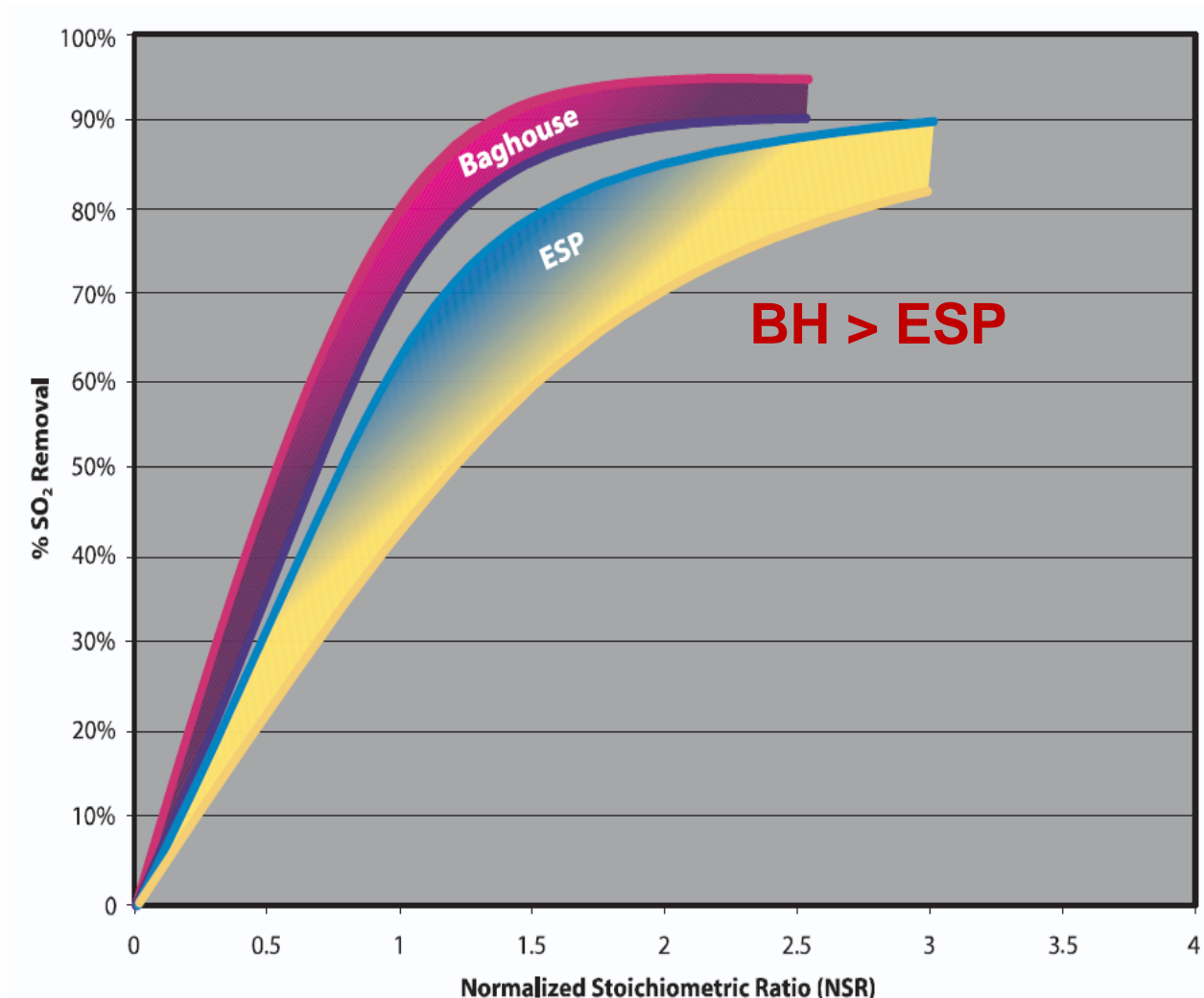
BH is to be preferred to ESP as a final APCD when a very high performance is required.

DRY SORBENT(S) INJECTION - DSI

THE ADDED SORBENTS MUST BE USED EFFICIENTLY:

- appropriate amount of sorbents …
- if too low → difficulties when low emissions limits are required; additional difficulties if the sampling reference period is short (0.5 h for waste incinerators; in all other applications the minimum is 1 h, or higher: e.g. 8 h for dioxins);
- if too high → high reactants costs; high costs for disposal of the resulting waste (hazardous waste – *rifiuto speciale pericoloso*).

→ FORWARD *AND/OR* FEEDBACK AUTOMATIC REACTANTS ADDITION REQUIRED FOR HCl (PLUS HF, SO_2, ..) AND NOx! (Hg: continuous monitoring required for waste incineration plants in Veneto)

WASTE INCINERATION

1. Forward and Feedback <u>c</u>ontinuous <u>e</u>missions <u>m</u>onitoring <u>s</u>ystems (CEMS) allow the process to be continuously adjusted *(that is regulate the flow of the reagent addition)* to control emissions of concerned pollutants.
2. Some gas pollutants *(e.g. dioxins and furans, PAH, PCB and metals*)* cannot be continuously measured: CEMS of other pollutants may often be used as "surrogate controls", <u>together</u> with periodic sampling;
3. *For PCDD/F and other organic micropollutants, <u>continuous sampling</u> systems for periods of 1 or 2-weeks may be installed as additional control. The MSWI incinerator in Padova runs 12 fourteen-days continuous sampling for each line, that is the cont. sampling covers 50% of the annual operating period of the plant. Samples have to be analyzed in laboratories; average concentrations of the set periods are thus obtained.*
<u>*Note*</u>*: * but Hg!*

IN-DUCT SORBENT INJECTION: RESIDENT TIME

$$t_{(residence)} = V \; (m^3) \; / \; G \; (m^3/s) \; [s]$$

V = DUCT + BH (or ESP) empty volume

Total volume is the sum of both duct and APCD

t_r **GENERALLY IS LOW (***a dedicated reactor can strongly increase the resid. time!***)**

DUCT: means volume after inj. point up-to the dedusting device

EMPTY DEDUSTING DEVICE: means the entire volume of cyclones, sedimentation chambers and ESP, but *only* the inlet volume + interstitial volume for jet-pulse FF.

ADDED REACTANTS MUST BE USED EFFICIENTLY:

- right temperature → ($NaHCO_3$/$Ca(OH)_2$, only with hot flue gases; PAC only < 200 °C);

- right dosing. Automatic dosing (*forward/feedback monitoring of pollutants concentrations*) possible for: $NaHCO_3$/$Ca(OH)_2$ and NH_3/urea; PAC possible only for Hg control, but not possible for dioxins and other micropollutants control;

- sufficient reaction time and good mixing;

- high contact surface (atomization/micronisation of reagents)

EXAMPLE: SIZING A DSI INJECTION SYSTEM. Calculate the minimum pipe *(or duct)* volume.
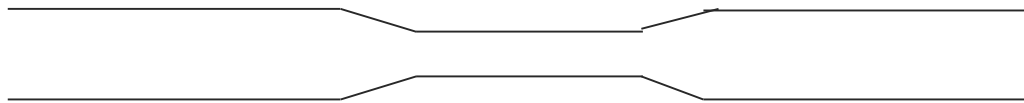
Design a DSI – dry sorbent injection system - of an alkaline base in a flue gas duct.
Are given the following data:
- gas flow at the injection point, G: 108,000 m^3/h,
- circular duct;
- duct residence time,
- t_r: 1.0 seconds;
- flue-gas velocity, v: 20 m/s.
  Problems with high velocity:
  o increase of drop preassure: $\Delta P \rightarrow v^2$
  o problem of noise;
  o erosion due to the dusts.

wooclap

The best point for the injection is the venturi (restriction area):
G= S*v
In venturi the velocity could be 100 m/s

Calculate the duct diameter (D) and the required duct length (L), that is the distance required between the injection point and the downstream particulate control device.

DRY NEUTRALIZATION OF HOT GASES CONTAINING SO$_2$ by NaHCO$_3$

DIMENSION

Bicarbonate typically has to be milled prior to use.

Milling on site to d_{90} < 20 microns with direct injection gives the best results.

Storage and handling issues increase as d_{90} approaches 20 microns

TEMPERATURE

At the operating conditions (140-250 °C):

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2(g) + H_2O(g)$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

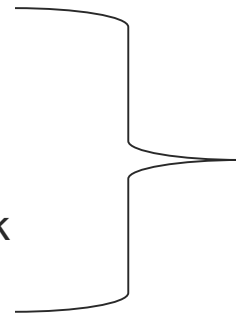*Na$_2$SO$_3$ is further oxidized as follows:*

$$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4$$

Which is the best temperature for neutralization?

Dry neutralization: T >140°C

PAC: T < 220°C

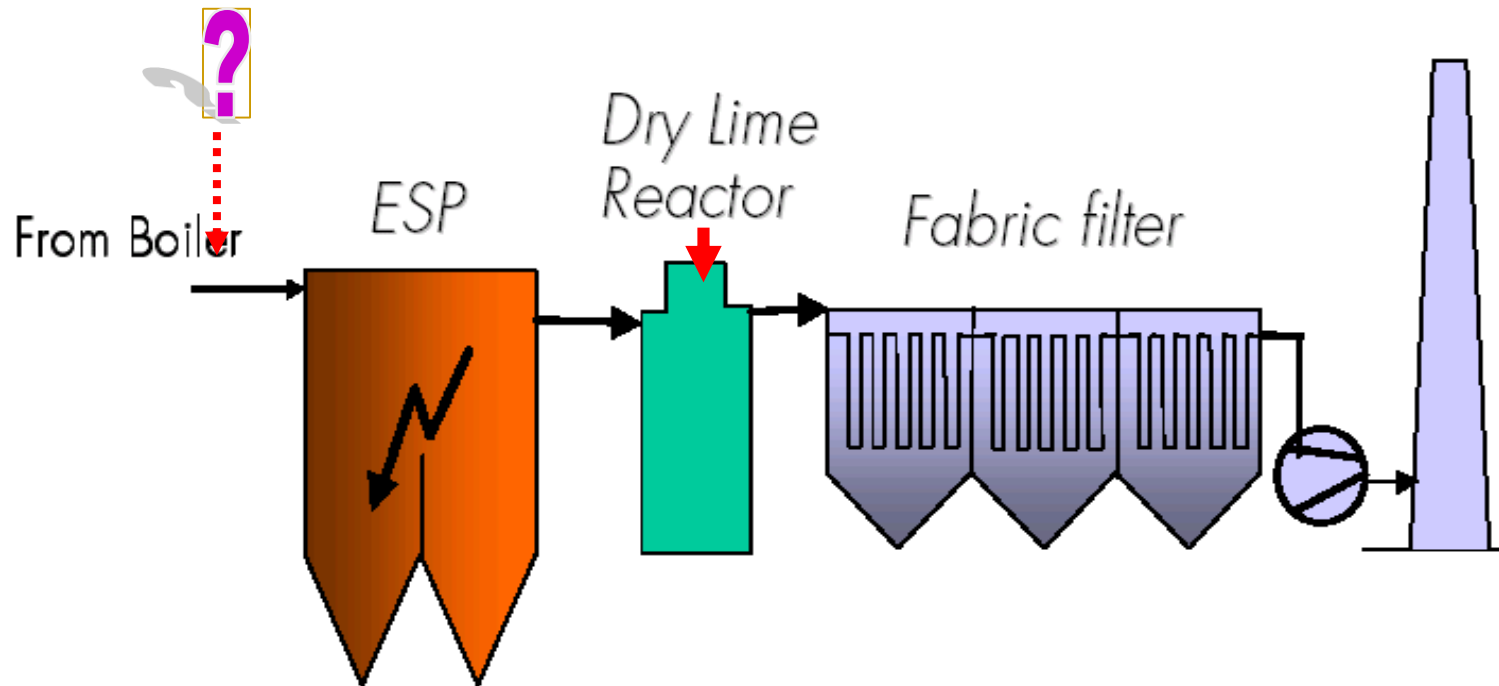The process of PAC is adsorption (weak process)

If both are used, the temperature is a compromised

DEDICATED REACTION CHAMBERS

Higher contact times are achieved if a <u>dedicated reactor</u> is used in addition / <u>instead</u> of in-duct injection!

<u>**Example**</u>**: Two-stage dedusting process plus sorbent injection**

The ESP acts as a dust pre-cleaner. The pollutants content of the dust discharged from the FF, but also, of the dust emitted to the atmosphere, is much lower. ESP acts really as a pre-cleaner; I'd suggest <u>in-duct injection</u> of some reagents upstream of the ESP!

DESIGN CONSIDERATION

Main parameters largely empirical

- reaction temperature

- excess reactant ratio

- sorbent granulometry (contact surface)

- separated products recycling ratio

- gas/reactant contact time (injection-reaction chamber or duct-fabric filter)

- gas/reactant mixing (in duct or reaction chamber configuration, liquid dispersion system)

POWDERED ACTIVATED CARBON DRY INJECTION SYSTEM

The Powdered Activated Carbon dry injection system pneumatically conveys a predetermined and adjustable amount of PAC from bulk bags into the flue gas streams of incinerators for mercury and dioxin reduction. The unit is portable, being built of two eight-foot tall sections, which makes set-up and movement easy.
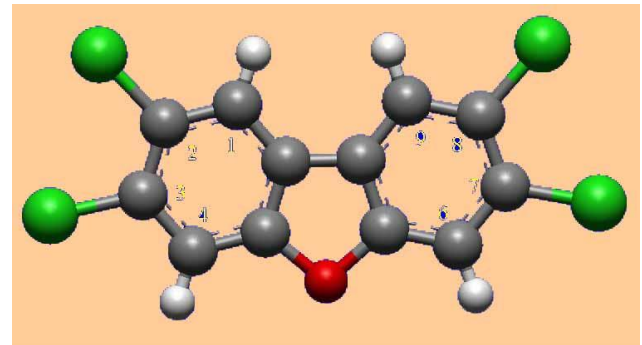
PAC is metered using a volumetric feeder into a pneumatic eductor, where motive air transfers the carbon to the final injection point.

A series of interlocks control the operation of the unit and allow local and/or remote operation/monitoring of the unit.

GAC, Granular Activated Carbon is not common used.

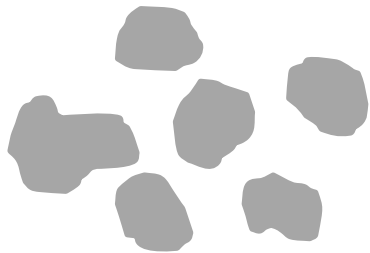**2,3,7,8-TETRACHLORODIBENZO-*p*-DIOXIN**

2,3,7,8-TETRACHLORODIBENZOFURAN

POWDERED ACTIVATED CARBON DRY INJECTION SYSTEM

The adsorption process in PAC depends to the temperature and to the dimension of the chemical to be removed.
At 15°C - 220°C the efficiency is good for high weight organic carbons (as PCB), but it is small for small compounds.

No chemical bond, but intermolecular forces (weak)

PCB

Dose of PAC≈ 100 mg /Nm^3 of flue gas

In MSWI mercury is nowadays present a low concentration because the waste containing mercury (for example medicine and electric waste) has been reduced.

Adsorption processes operate more effectively at low temperatures due to the higher adsorption capacity

SEMI-DRY SCRUBBING SYSTEMS SDA (Spray Dry Absorption)

In spray dryer absorbers, the flue gases are introduced into an **absorbing tower** (dryer) where the gases are contacted <u>with a finely atomized alkaline slurry</u> [a lime slurry, typical; a suspension of water and $Ca(OH)_2$]. This technique is effective for hot gases (t > 100 °C), typically, flue gases.

❑ <u>Products</u>: solid particulate;
❑ <u>Cleaned flue gas</u>: hot gas *(but with a dew point higher than DSI, dry injection)*

Acid gases are absorbed by the slurry mixture, and react to form solid dry salts; e.g.:
$Ca(OH)_2$ (slurry) + 2 HCl(g) = $CaCl_2$(s) + 2 H_2O(g)
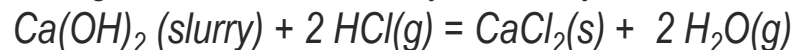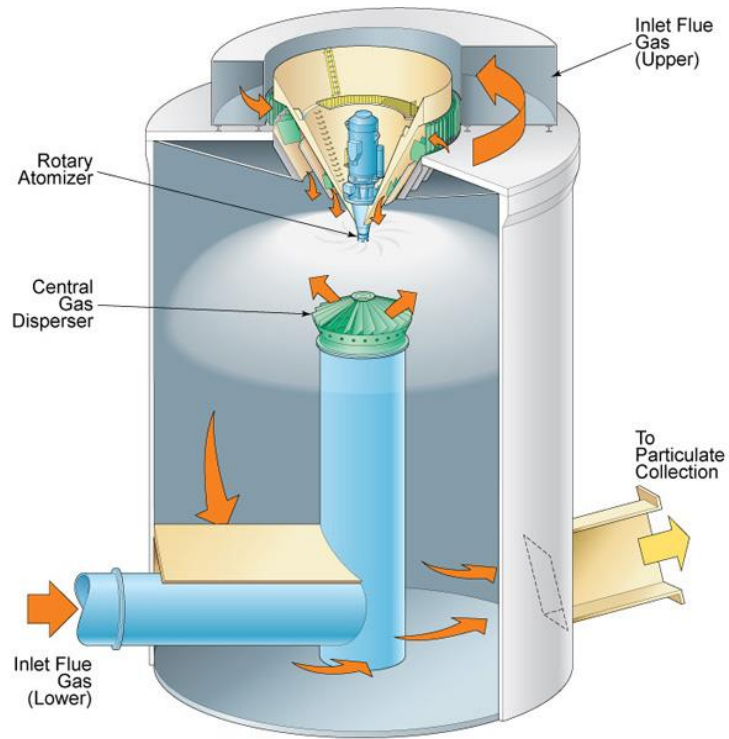
The heat of the flue gas is used to evaporate <u>all</u> the water droplets leaving a non-saturated flue gas exiting the absorber tower.

The effect of cooling and humidifying the hot gas stream can increase the collection efficiency over simple dry injection. As a result of cooling, all pollutants which have a significant vapour pressure at flue gas temperature (*inlet temperature*) tend to be present more in the solid state and are easier to capture in the downstream fabric filter (or ESP).

SDA is also known as a <u>semi-dry</u> or <u>semi-wet</u> <u>technique</u>; I prefer <u>semi-dry</u> to emphasize the fact that the end "products" (the reaction products and the treated gas) are dry. Obviously it remains <u>that the outlet gas increases its relative humidity RH</u>, due both to a decrease in temperature, and the increase of the water content (absolute humidity), as with the slurry water is added!

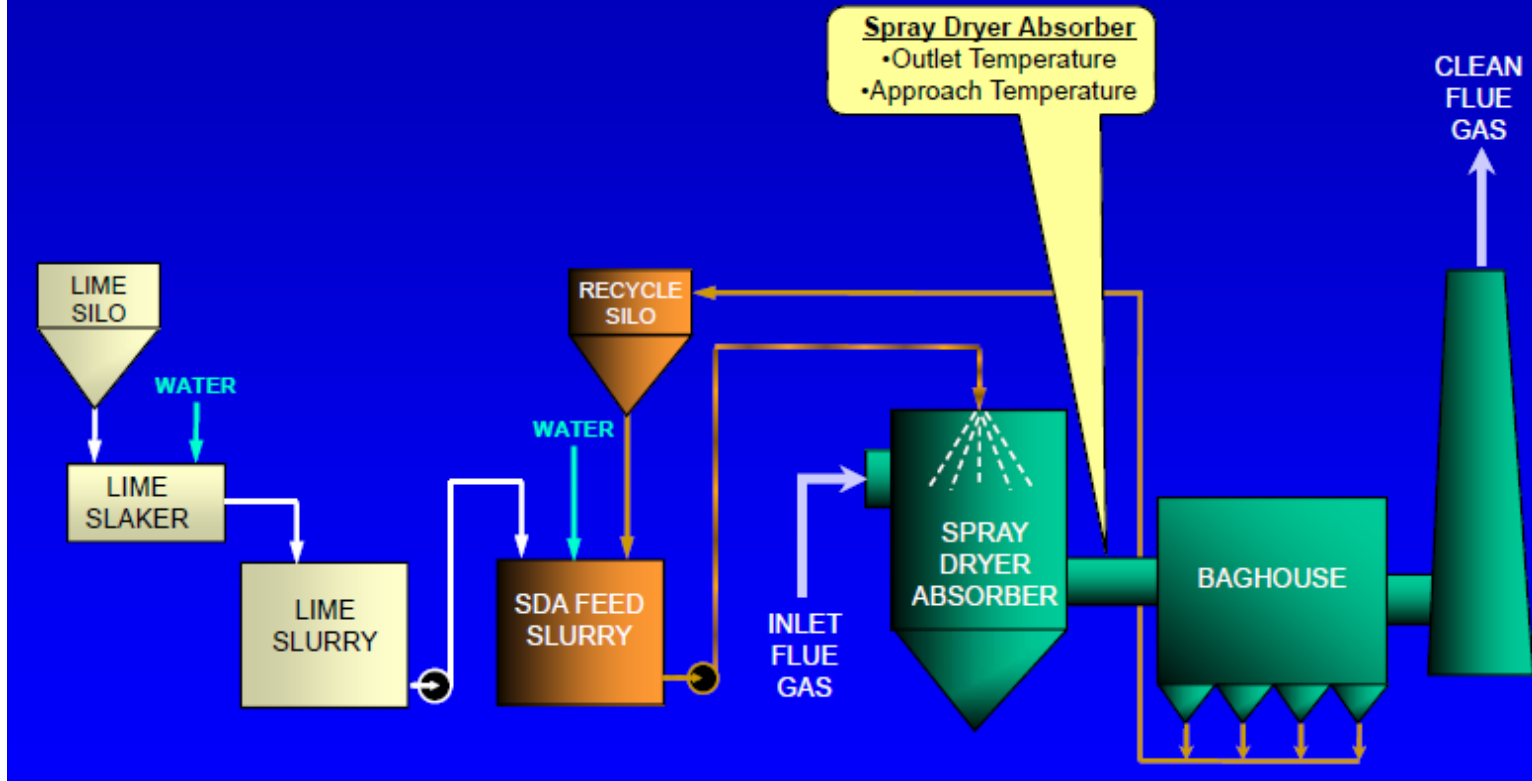# SEMI-DRY SCRUBBING SYSTEMS SDA (Spray Dry Absorption)

Atomization of lime slurry

Inlet Flue Gas (Upper)

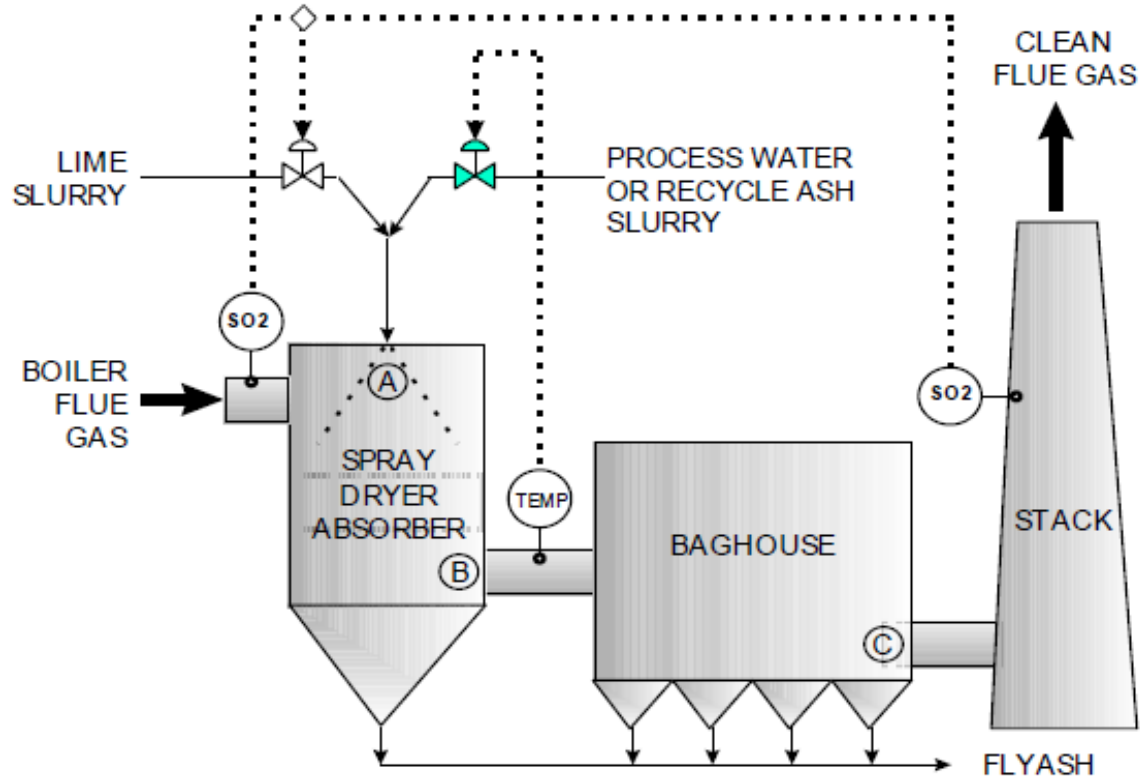Rotary Atomizer

Central Gas Disperser

To Particulate Collection

Inlet Flue Gas (Lower)

Typical <u>dry</u> FGD Spray Dryer Absorber

SDA - SPRAY DRY ABSORPTION

Recircolation of reactants is a very important task

SDA - SPRAY DRY ABSORPTION

Two control systems:
- Feed back system: the concentration of the pollutant is measured at the stack. If the concentration is above the ELV, the intervention can be delayed
- Feed forward: the concentration of the pollutant is measured before the treatment

POSSIBLE PROBLEMS WITH SDA

IF the SDA exit flue gas temperature: 10 − 20 °C > $T_{DEW-POINT}$ *(T_{DP} ~ 60–80 °C)*

$$\rightarrow T_{exit} < 100 °C$$

Temperature is the «force driving»

*...**Problems:***

❑ *not possible a <u>DSI/SDA 2nd stage</u> because: either the temperature is too low (DSI and SDA), or RH is too high (SDA)*

❑ *strong heating is required in case of downstream DeNOx SCR (ΔT > 100 °C !)*

❑ *plume visibility (due to the > H_2O vapour content) and lower plume rise (due to the < T_{exit}).*

EXAMPLE OF SDA: Centrale Lamarmora di A2A

	Ingresso SDA	Uscita FF
Portata (Nm³/h)	295 000	316 000
Temperatura (°C)	140-145	65-70
Pressione (Pa)	- 4 600	- 6 400
H_2O (% vol.)	7	12,1
O_2 (% vol.)	6,7	6,8
SO_2 (mg/Nm³ dry 6% O_2)	1857	150
Particolato (mg/Nm³ dry 6% O_2)	100	2

Emissioni (mg/Nm³ dry 6% O_2)	Limiti di emissione antecedenti	Limiti di emissione dal 2012	Prestazioni del nuovo sistema SDA + FF
SO_2	350	250	150
Particolato	10	10	2

Group 3 revamped:

HD-SCR → EF → SDA → FF → **STACK** (T ≈ 80 °C)

Injection of: NH_3 upstream of SCR ; $Ca(OH)_2$ slurry in SDA

Il sistema di desolforazione del gruppo 3 della Centrale del Teleriscaldamento Lamarmora di Brescia è stato recentemente rimodernato - nuovo assorbitore a semi-secco (SDA) - per ridurre le emissioni di SO2 in atmosfera.

For the injection of $Ca(OH)_2$ a pneumatic system is uses. Therefore the flow increases from 295.000 Nm³/h to 316.000 Nm³/h.
In general the flow increase could be to:
• pneumatic system
• water vapour (in particular this problem is present with wet control devices)
• Calcination of Sodium Bicarbonate
• no completely closed systems (holes, etc.).
If the volume increases the resident time decreases.

GENERAL CONSIDERATION

○ Advantages
- **absence** of residual liquid streams
- **absence** of **drawbacks** from **liquid** solutions
  - ➢ corrosion, scaling
  - ➢ cool and visible plumes
  - ➢ spent liquid treatment
- **final product** available in **solid form**, with no further operation required prior to final treatment and disposal
- **potential** for **reutilization** of products with some dry system configurations

○ Disadvantages
- **lower efficiencies** with respect to conventional wet systems
- even in optimum design and operating conditions, **clean gas concentrations levels** generally **higher** than those achievable with **wet configurations**