# Volatile Organic Compounds

## John Cockerill Europe Environnement


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John Cockerill

# Our technologies to treat them…

**Evolution and Description of the Technologies to treat VOC's since 1980**

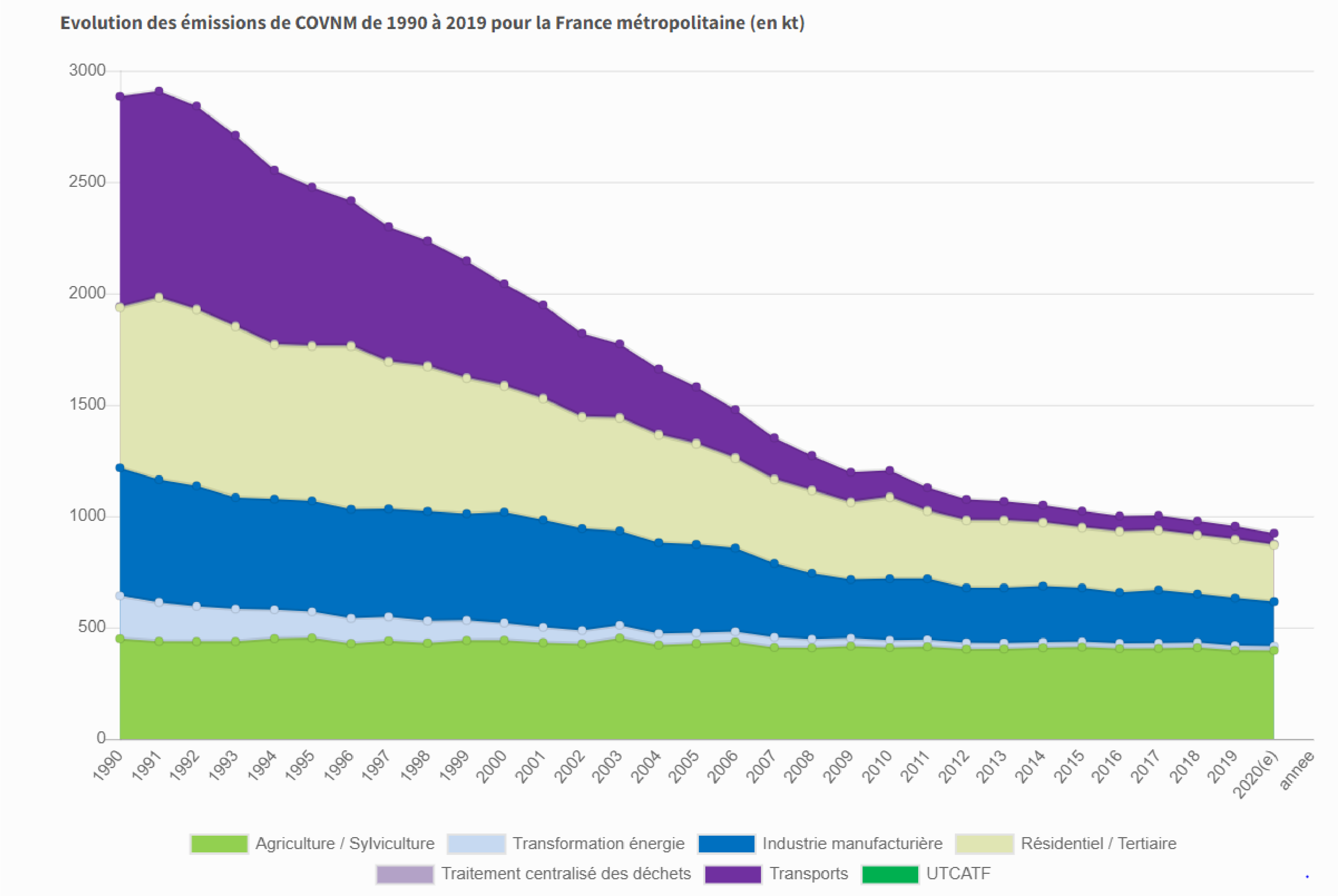
Legislation → La loi du 19 juillet 1976 → Arrêté du 02/02/1998 → Technologies → Thermal Oxidation → Absorption → Adsorption → Biofiltration → Others

**Actual requests from authorities and customers and John Cockerill's solutions To get lower emissions and to minimize CAPEX & OPEX costs**

**Case 1**. NMP recovery in Li-ion battery

**Case 2**. Elimination of hydrocarbons and odours from a waste water treatment plant in Gas industry

# Emissions de COV en France




CITEPA

# Global presence in the environmental technologies sector

**JOHN COCKERILL ENVIRONMENT AND ITS RICH BRAND LEGACY**

AMCEC | BALTEAU | EUROPE ENVIRONNEMENT
PROSERPOL | THE NESA SOLUTION | VENTACID

**JOHN COCKERILL EUROPE ENVIRONMENT OFFICES**


"Supported by the strong financial background & John Cockerill's 5500 employees present on all 5 continents and over 80 worldwide locations, the Group's Environment Sector counts over 350 specialized employees, engineers, technicians & workers.

**350** SPECIALISTS

**5** OFFICES

**3** MANUFACTURING SITES

OVER **15,000** WORLDWIDE REFERENCES

IN OVER **+50** COUNTRIES

ON **5** CONTINENTS

# In figures

**21 600**
fans

**1 735**
activated carbon filters

**1 600**
scrubbers

**300**
biofilters

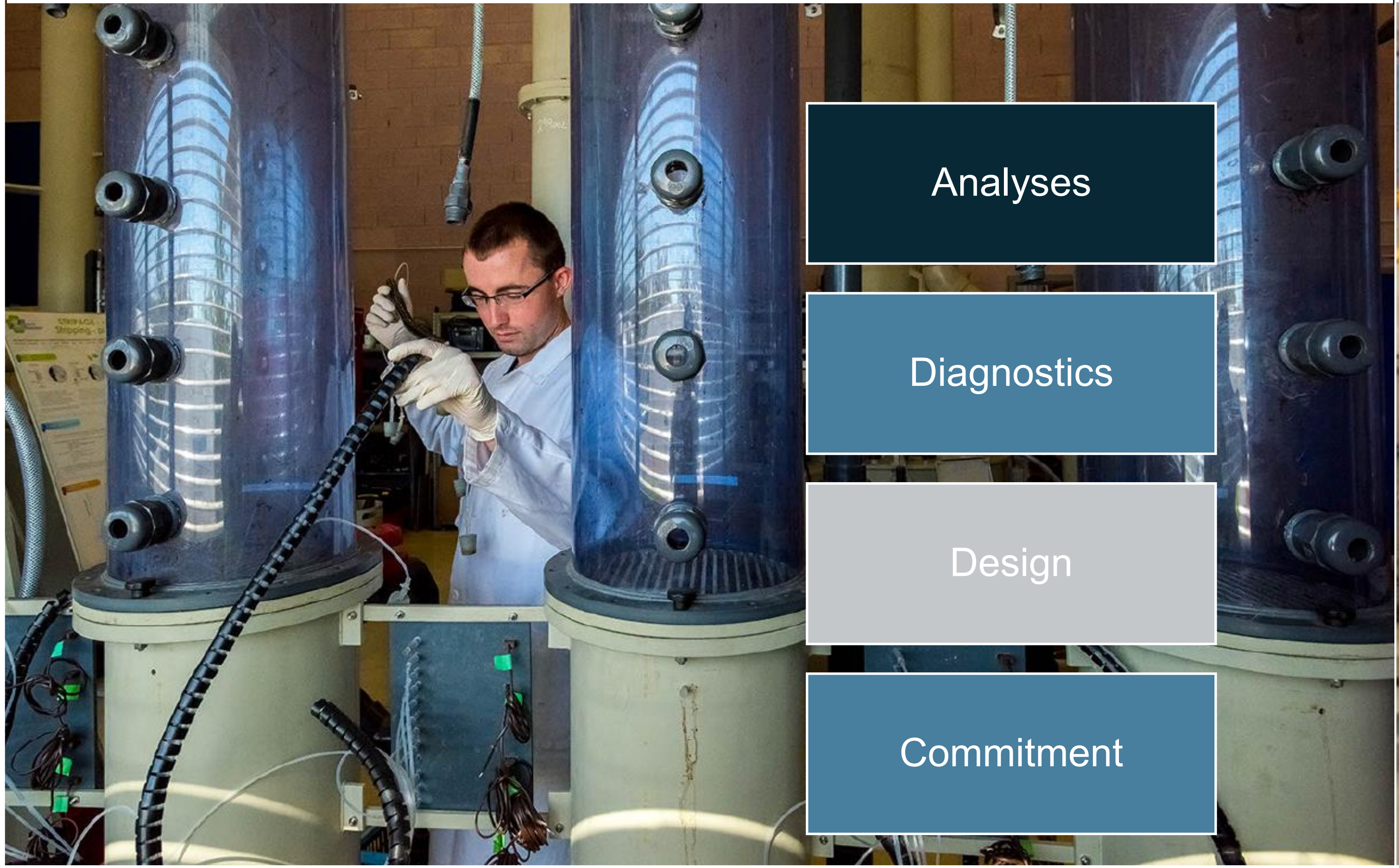
**1000**
customers

**45**
countries

**30**
partners

# Process engineering – R&D
# Innovation dedicated to our clients

## A highly qualified team



- Analyses
- Diagnostics
- Design
- Commitment

## A state-of-the-art equipment

# R&D

Olfactomètre

Chromato - FID

Hall pilote avec colonnes

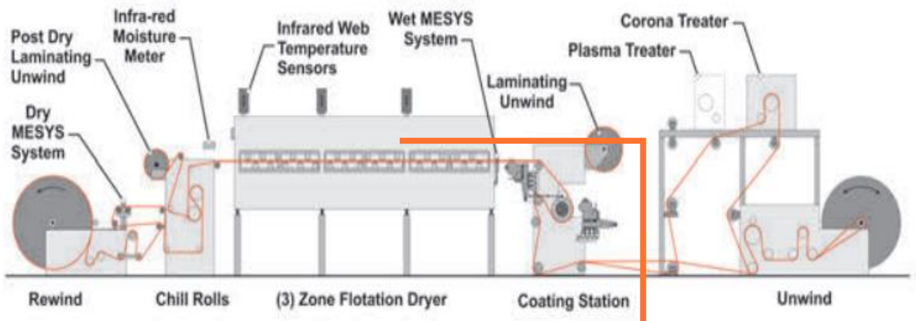
# Workshop : 10 000 sqm

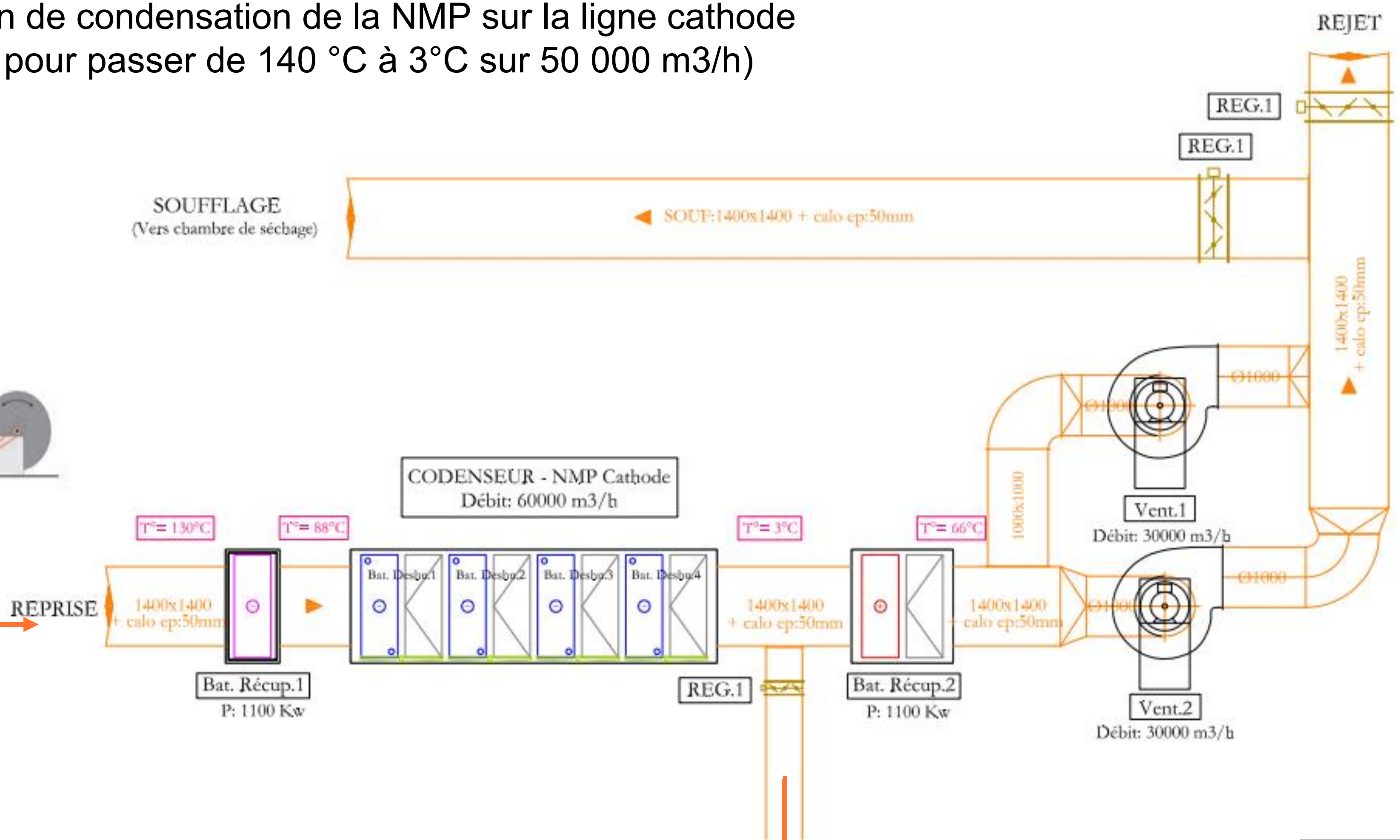
- 2 production sites (France & Hungary)

# Case 1 : Recovery and treatment of NMP

Usine ACC/Nersac
Gigafactory ACC/Douvrin

Installation de condensation de la NMP sur la ligne cathode
(5 étages pour passer de 140 °C à 3°C sur 50 000 m3/h)

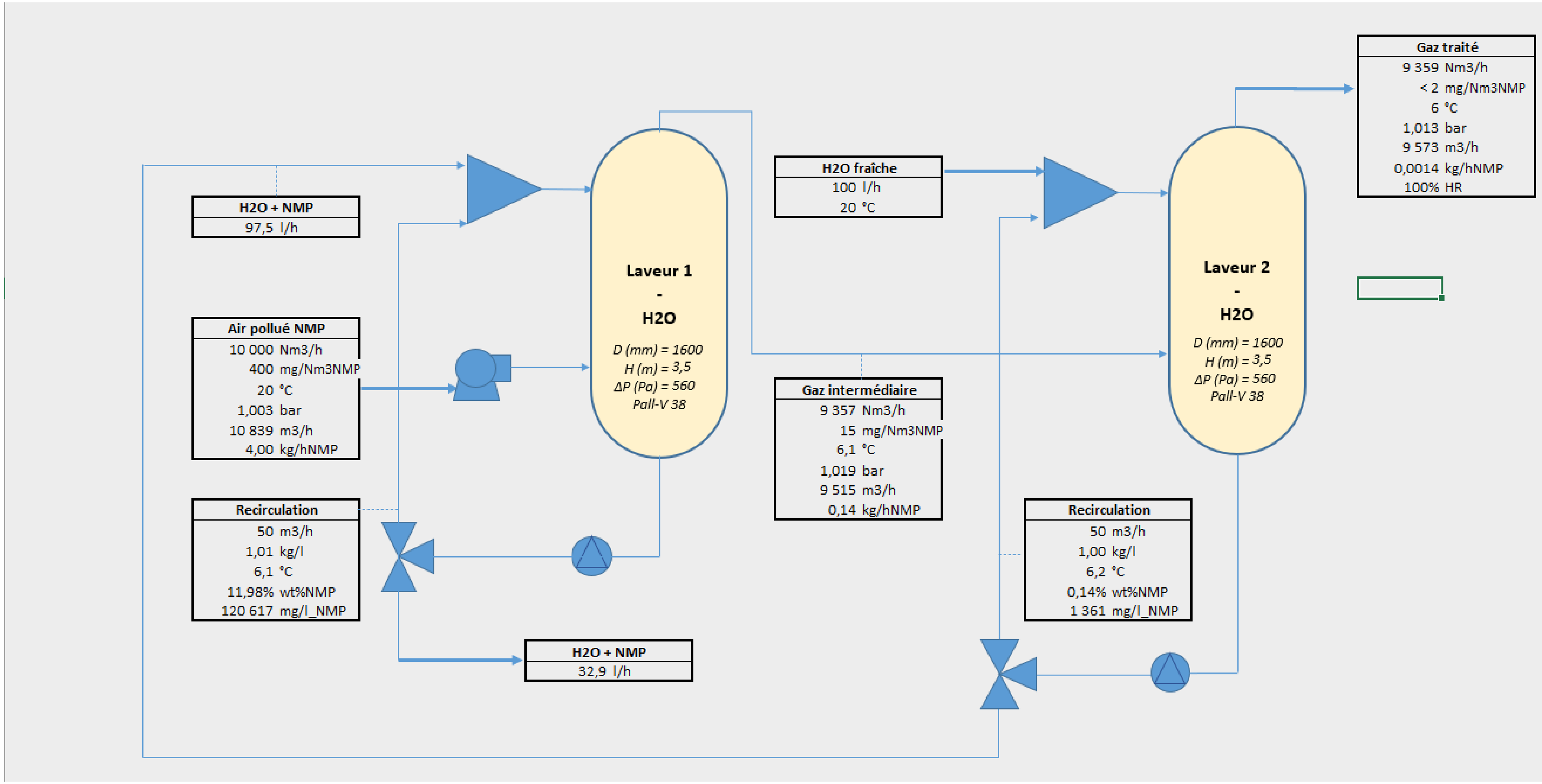



Vers unité de lavage

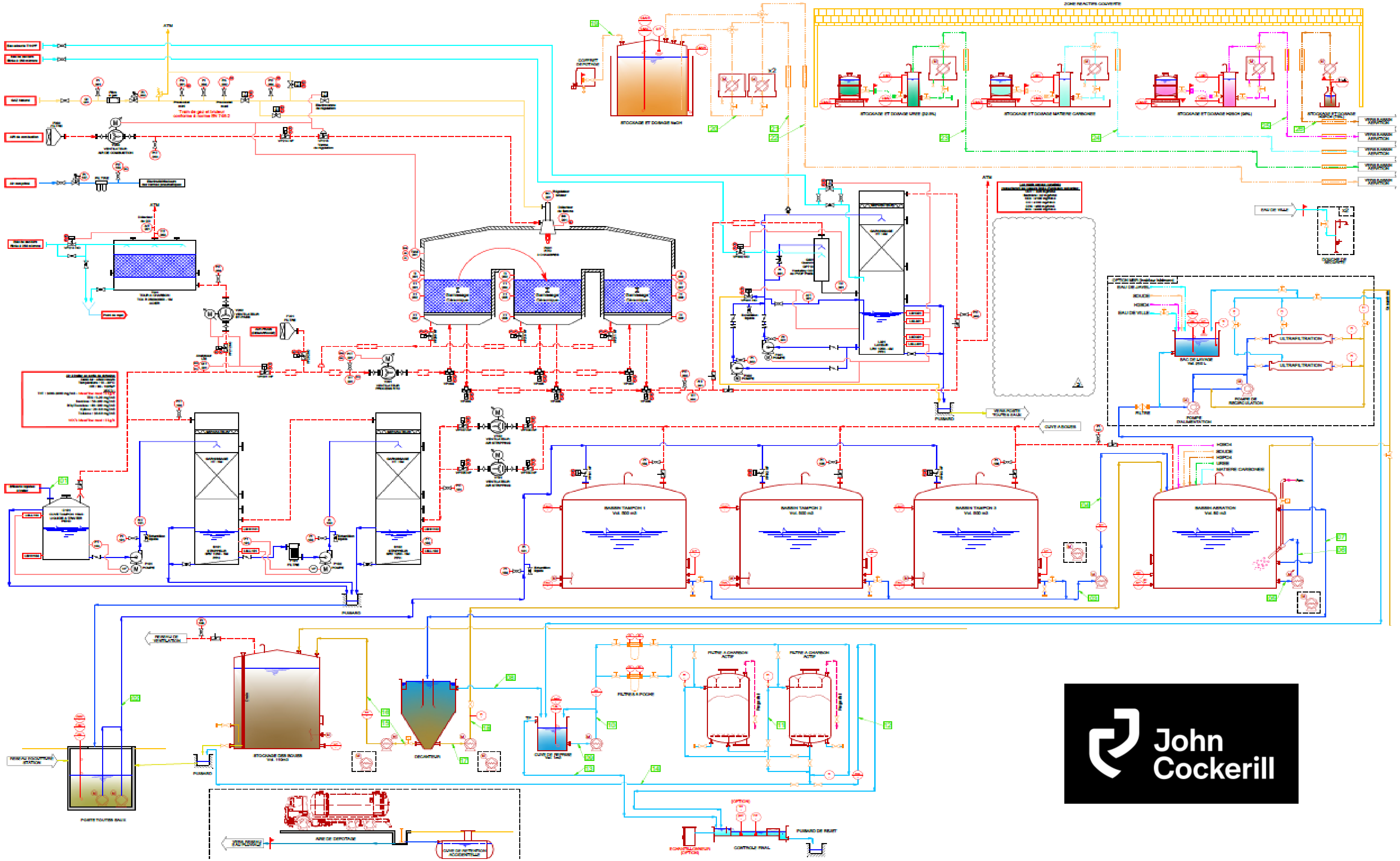
# Case 1 : Recovery and treatment of NMP

## Usine ACC/Nersac
## Gigafactory ACC/Douvrin

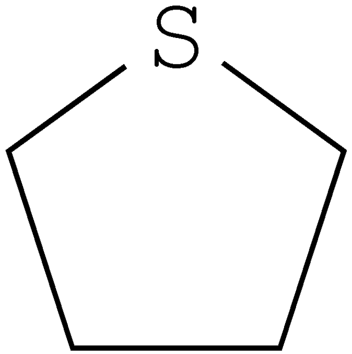


# Case 1 : Recovery and treatment of NMP


# Case 2. Elimination of hydrocarbons and odours from a waste water treatment plant in Gas industry



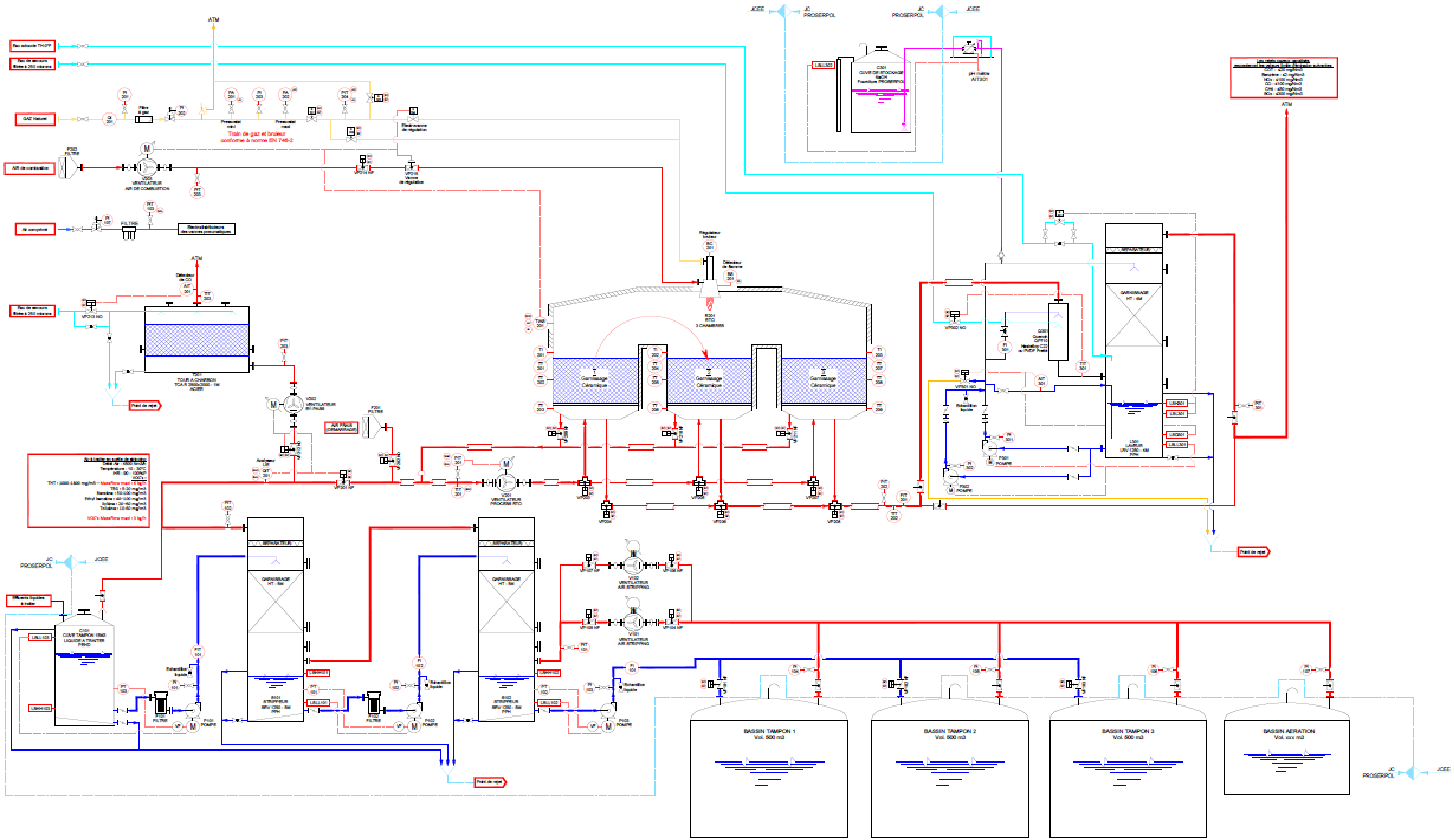
# Case 2 : Stripping tests of the waste water

Le stripping, correspond à l'entraînement de gaz ou produits volatils dissous dans l'eau par l'action d'un autre gaz, en réalisant en fait une désorption.


Tétrahydrothiophène – THT – $C_4H_8S$

# Case 2. Elimination of hydrocarbons and odours from a waste water treatment plant in Gas industry



# Case 2. Elimination of hydrocarbons and odours from a waste water treatment plant in Gas industry

# Definition of VOC

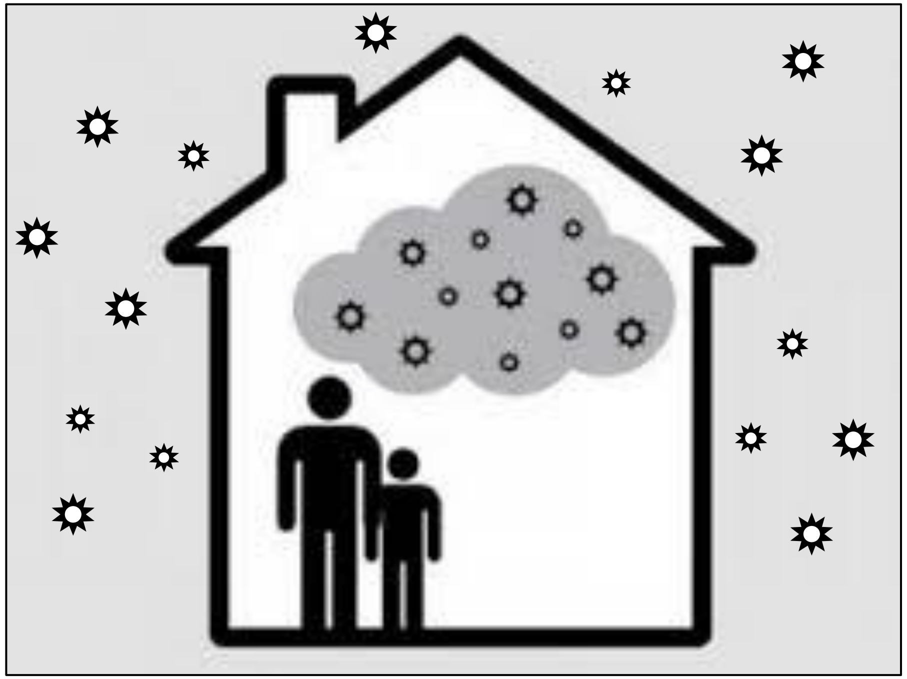
## VOC: Volatile Organic Compounds

**Compounds in gaseous state, or which evaporate readily during use under standard temperature and pressure conditions (293.15 K and 0.01 kPa)**

**Methane ≠ other VOC's known as NMVOC's** (Non-Methane VOCs)

**Examples**

| | |
|---|---|
| **Benzene, toluene, xylene** | **Acetone** |
| **Dichloromethane** | Etc. |



# Nature of VOC’s

**Any 'solvent' used alone or in mixture without altering its nature, as a cleaning or degreasing agent, solvent, dispersing medium, viscosity adjuster, plasticiser or preservative.**

## Solvent families

- Aliphatics (heptane, hexane, pentane, mineral spirits, etc.)
- Aromatics (benzene, toluene, xylene, etc.)
- Alcohols (ethanol, methanol, butanol, IPA: isopropyl alcohol, etc.)
- Ketones (acetone, MEK: methyl ethyl ketone, MIBK: methyl isobutyl ketone, cyclohexanone, etc.)
- Esters (ethyl, butyl, isopropyl acetates, etc.)
- Halogenated (perchlorethylene, trichlorethylene, dichloromethane, etc.)

## Other VOC member families

- plasticisers (DOP: dioctyl phthalate, etc.)
- nitrogen compounds (amines, nitriles, etc.)
- sulphur compounds (mercaptans, dimethylsulphide, etc.).

# VOC treatment techniques

## Oxidation-destruction techniques

### Thermal

- Recuperative
  Regenerative
- Catalytic

### Biological

- Biofiltration
- Bioscrubbing

## Recovery techniques

- Adsorption
  gas/solid
- Condensation
- Absorption
  gas/liquid
- Permeation
  (membranes)

# Thermal oxidation

**"Thermal Oxidation"**

All VOCs can be converted by total oxidation to inorganic compounds.

**Depending on the elementary composition of the volatile organic compound to be destroyed, the compounds formed are:**

- either only $CO_2$ and $H_2O$,
- or a mixture containing $CO_2 + H_2O$ + the oxidation products of other atoms (N → NOx, Cl → HCl, S → $SO_2$, etc.).
  - Secondary pollutants to be taken into consideration (formation of acid gases requiring the installation of wet scrubbers)

# Thermal oxidation

## Parameters used to optimise thermal oxidation

- Temperature
- Oxygen content
- Turbulence
- Residence Time
- Pollutant concentration

## 3T rule

$$C_nH_m + (n + m/4)\ O_2 \rightarrow n\ CO_2 + m/2\ H_2O + \text{Energy}$$

where n and m represent the respective proportions of carbon and hydrogen in the hydrocarbon in question.

# Thermal oxidation

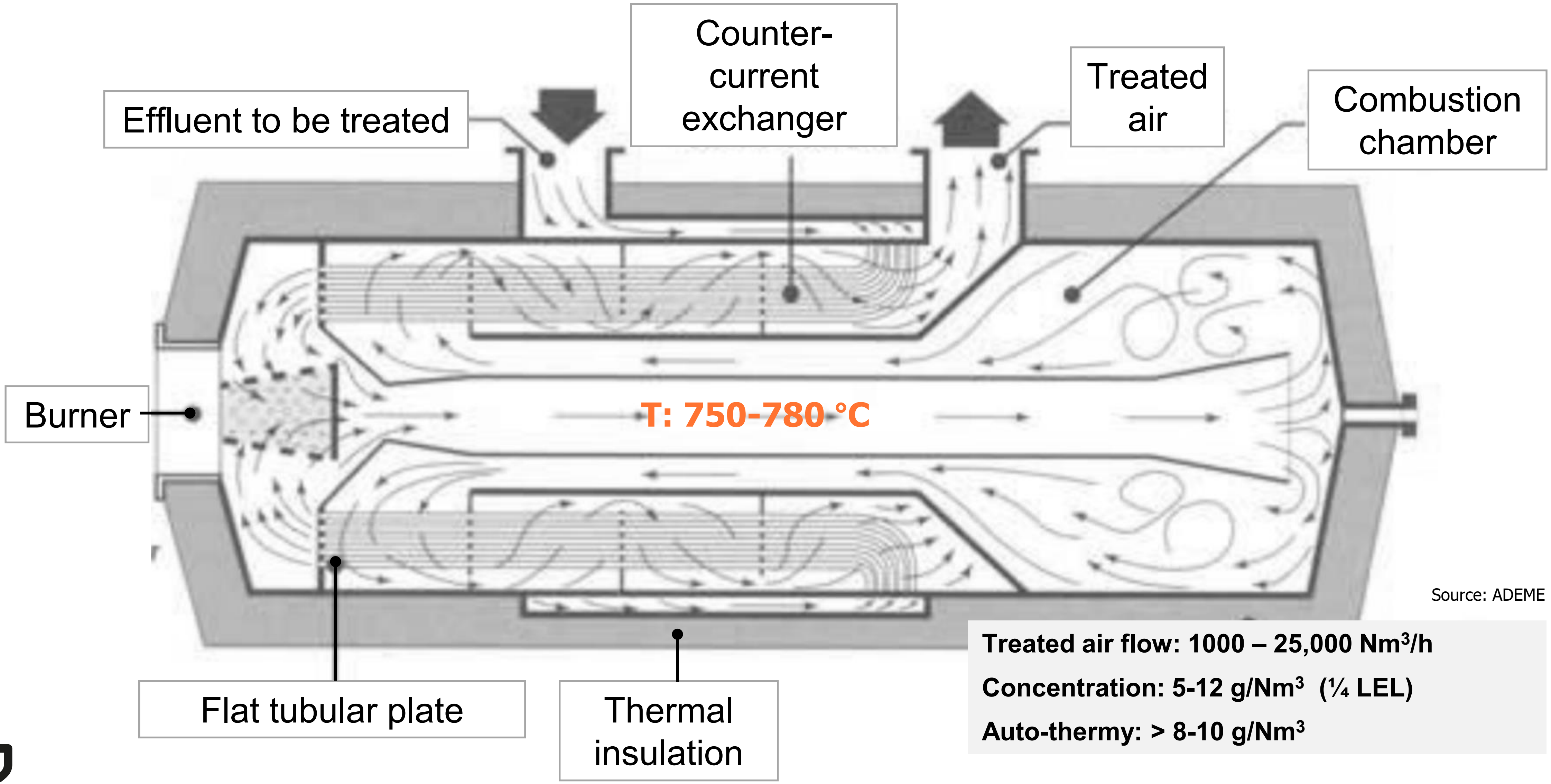
**In this ideal scheme, combustion results in the production of only $H_2O$ and $CO_2$ (non-toxic gas)**

$$VOC + O_2 \rightarrow CO_2 + H_2O + \Delta h$$

| | | | |
|---|---|---|---|
| 300 – 400°C: with catalysts | 750 – 780°C: recuperative thermal | 810 – 830°C: regenerative thermal | Heating power = (Volume flow) x (fresh air density) x Cp x (Delta T) / 3600 |

# Recuperative thermal oxidation

## Schematic diagram




Source: ADEME

**Treated air flow: 1000 – 25,000 $Nm^3/h$**

**Concentration: 5-12 $g/Nm^3$ (¼ LEL)**

**Auto-thermy: > 8-10 $g/Nm^3$**

# Recuperative thermal oxidation

## Operating principle

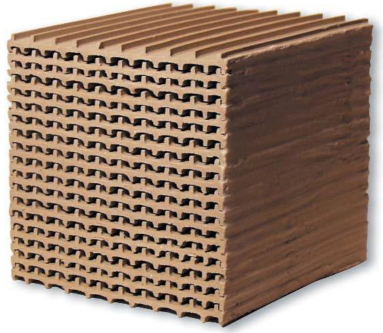
1. The effluents are sucked or pushed into the purifier using a fan
2. They pass through an exchanger which heats the gas flow to between 250 and 500 °C
3. They circulate through the combustion chamber, which guarantees:

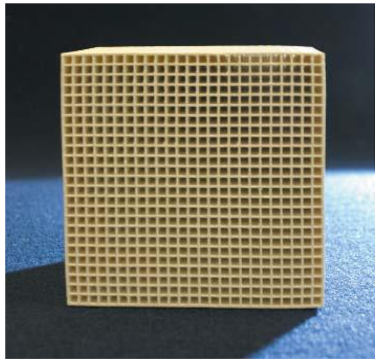
   - a sufficiently long **residence time** to completely oxidise the volatile organic compounds (1.0 to 2.0 s for non-halogenated compounds).
   - **combustion T°**: between 750 and 850 °C in general and exceeding 1000 °C in the case of halogenated hydrocarbons.
   - **turbulence**, which allows efficient mixing between VOCs and oxygen, along with homogeneous temperature distribution.

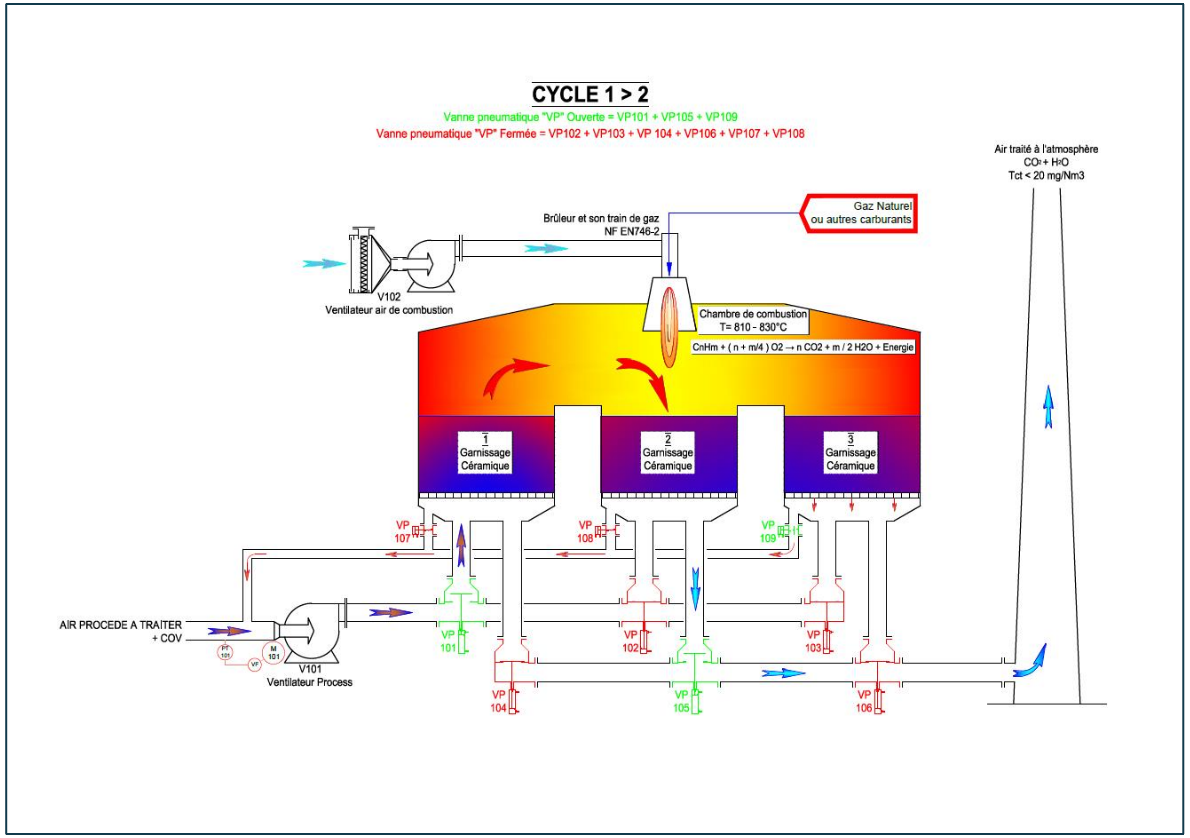
A secondary heat exchanger can be fitted to increase calorie recovery, for example by heating a thermal fluid or producing steam.

# Regenerative thermal oxidation

## Schematic diagram








**High thermal efficiency:**
up to 95% heat recovery

**Bed height**: 900-1200 mm

**Rate of flow**: 0.75-0.90 m/s

**Contact time** in the chamber:
0.8-1.3 s

# Regenerative thermal oxidation

## Operating principle

The scrubber generally consists of **3 ceramic beds** used to preheat the solvents, along with a combustion chamber with a burner. The number of beds is determined by the volume to be treated and the desired efficiency.

The effluents pass through the first ceramic bed and are heated to a temperature close to the combustion temperature **(810/830 °C)**. Air then passes through the combustion chamber where a burner provides supplemental energy if necessary. The purified air passes through the second ceramic bed where it is cooled. The third bed is purged by the already treated hot air. This purge air is reinjected into the first bed to avoid pollutant discharge to the atmosphere when the beds are swapped. When bed number 1 is cooled, the flow of effluents is reversed.

This reversal can be programmed over time, for example every two minutes or according to bed temperature. The effluents to treat are then introduced through bed number 2 and exit through bed number 3. Bed number 1 is in purge phase.

**Process limitations ➔**

Large facility

Not suited to short operating times

# Regenerative thermal oxidation

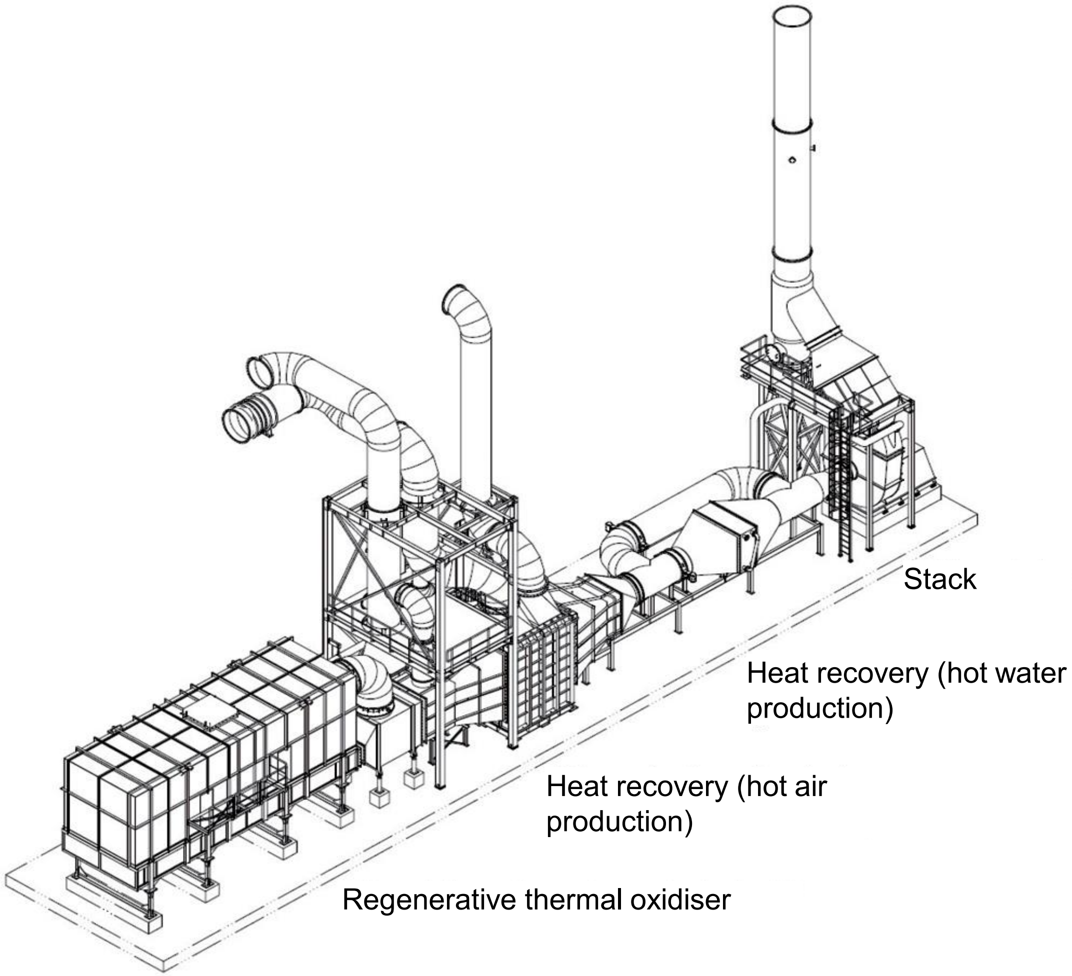
## RTO on galvanising line

**Flow rate: 55,000 $Nm^3/h$ at 200 °C + energy recovery**

**Solvents: toluene, xylene, solvesso 100/150**

# Regenerative thermal oxidation

## RTO on galvanising line

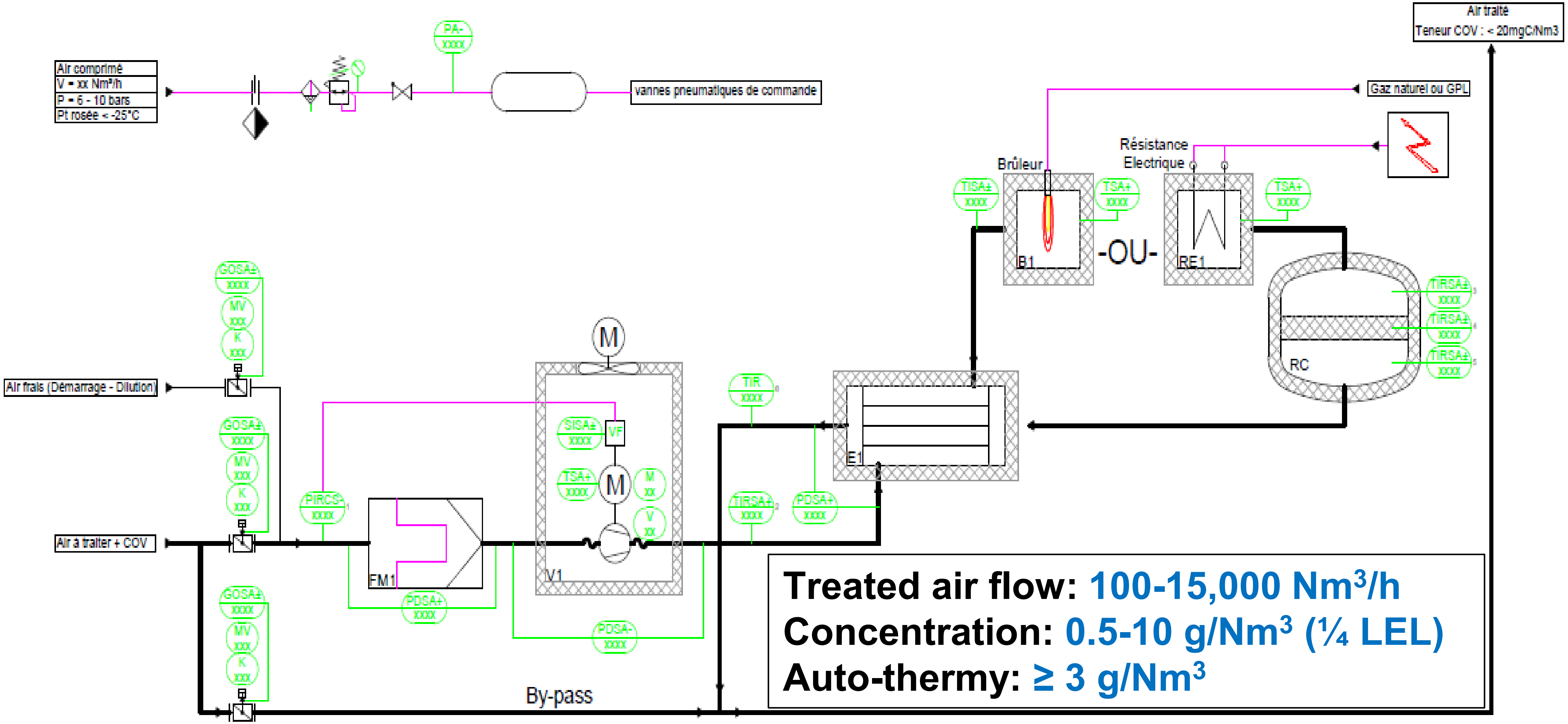



# Regenerative thermal oxidation

| HIGH EFFICIENCY (98-99.8%)<br>HIGH THERMAL RECOVERY (≥ 95%) | REDUCED PRODUCTION OF SECONDARY<br>POLLUTANTS (CO, $NO_X$) | SIMPLE AND EASY MAINTENANCE | AUTOMATIC OPERATION | POSSIBLE ENERGY RECOVERY | DESIGN ADAPTED TO HIGH AND<br>LOW VOC CONCENTRATIONS |
|---|---|---|---|---|---|

# Catalytic oxidation

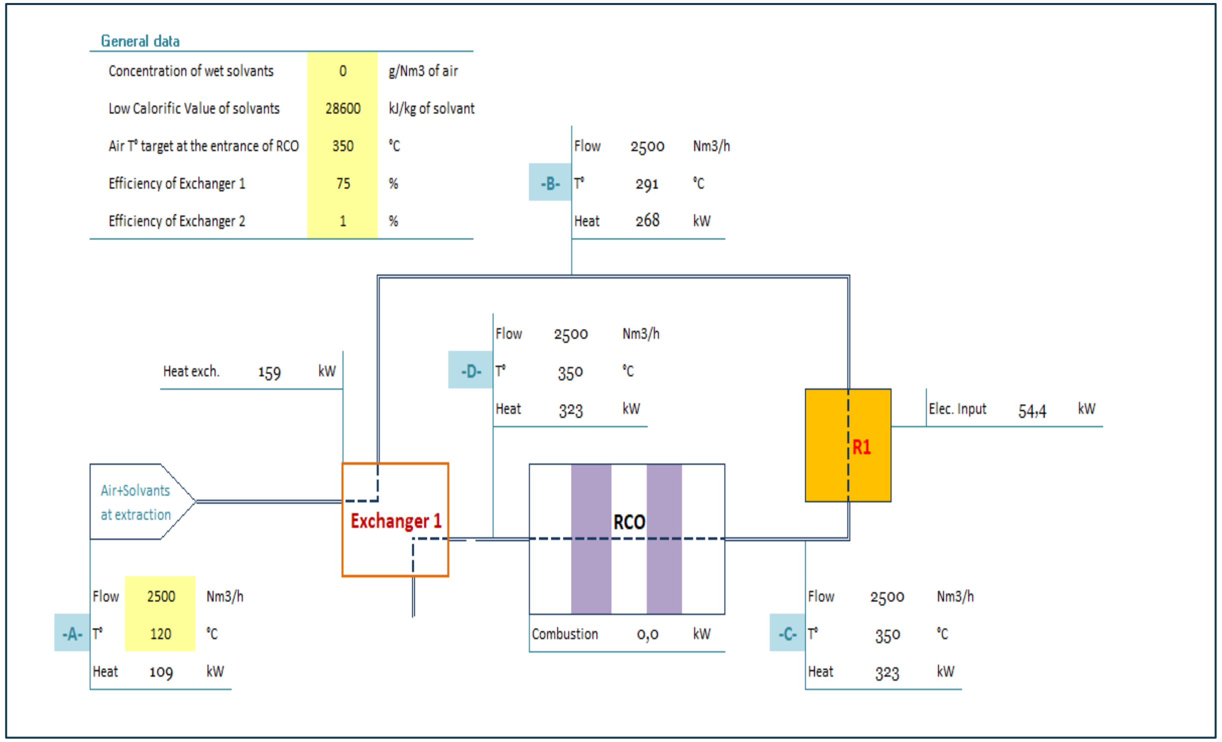
## Schematic diagram

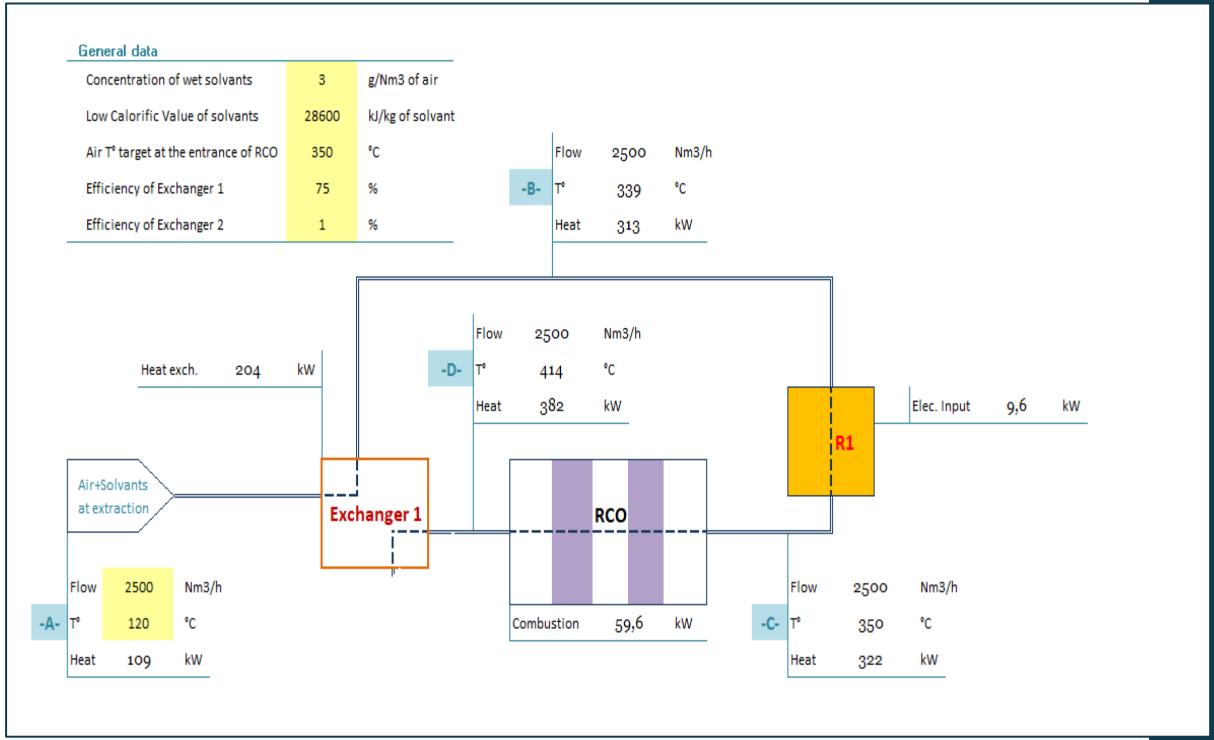



**Treated air flow: 100-15,000 Nm$^3$/h**
**Concentration: 0.5-10 g/Nm$^3$ (¼ LEL)**
**Auto-thermy: ≥ 3 g/Nm$^3$**

# Catalytic oxidation

## Heat balance



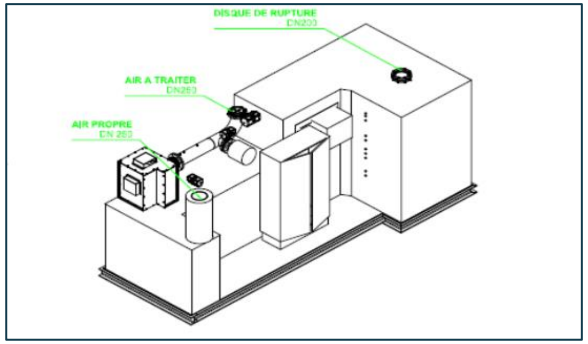



# Catalytic oxidation

## Characteristics

- **Metallic oxide catalysts**
  copper, nickel, cobalt, chromium, iron, molybdenum, tungsten
  **T: 270-330 °C**
- **Noble metal catalysts**
  platinum, palladium, rhodium
  **T: 350-420 °C**
- **Hourly space velocity:**
  air flow/catalyst volume ratio
  **10,000 to 25,000 $h^{-1}$**

The catalyst is not consumed during the reactions.
Under certain operating conditions however, its activity may be reduced and cause a drop in system performance (chemical poisoning, clogging, loss of material by attrition, thermal effect, etc.).

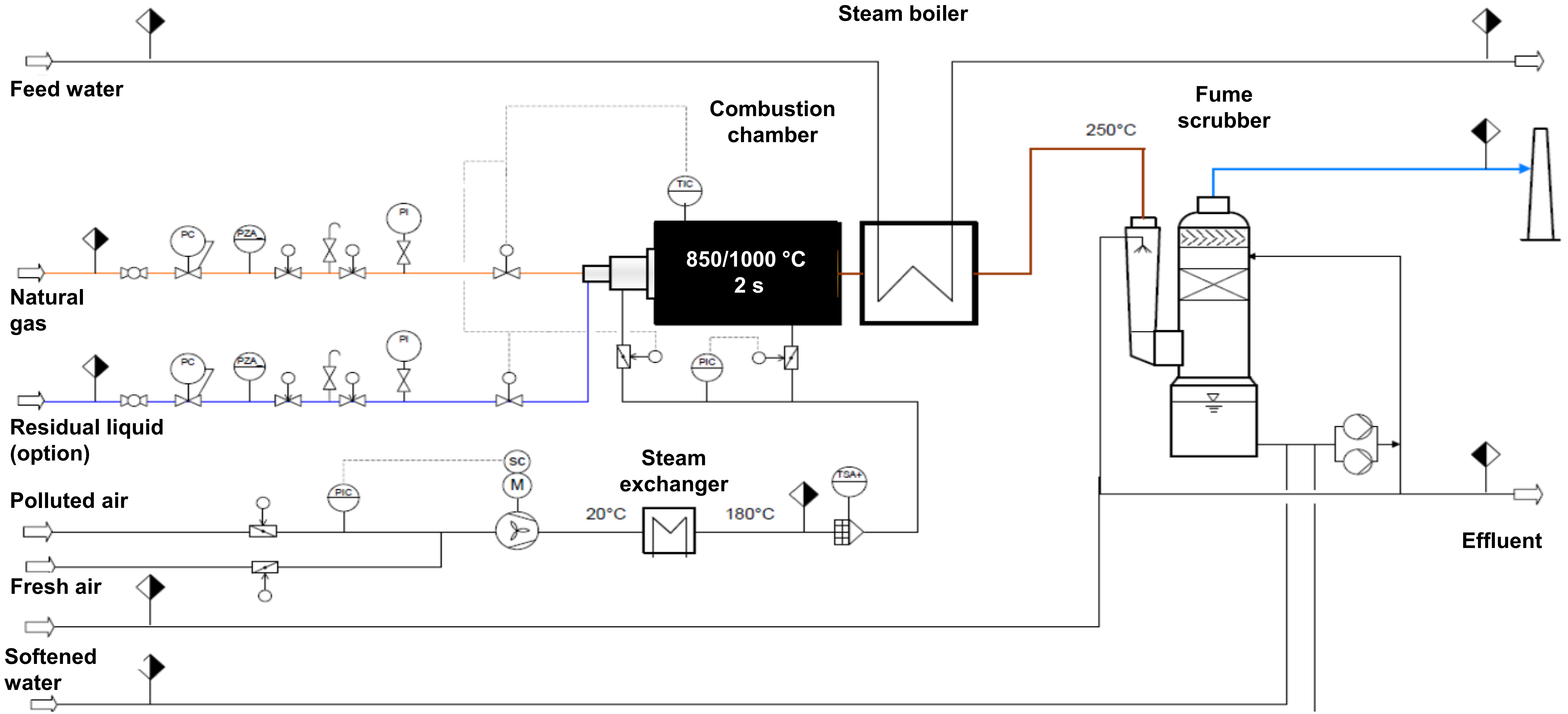



# Catalytic oxidation
## Facilities




# Thermal oxidation of halogenated compounds

## Schematic diagram



# Treatment on activated charcoal

## Single use

Suitable for treating a large number of organic solvents

Loading rate or **adsorption capacity** depends on many pollutant-related parameters

In general, ACGs are single use

**For flow rates of 100 – 10,000 m³/h**

- With max. concentrations of 200-400 mg/m³
- Daily mass flow (24h cycle)

If quantity of VOC released > 2/4 kg/h ⇨ solution not viable due to cost of new ACGs + SIW treatment

# Treatment on activated charcoal

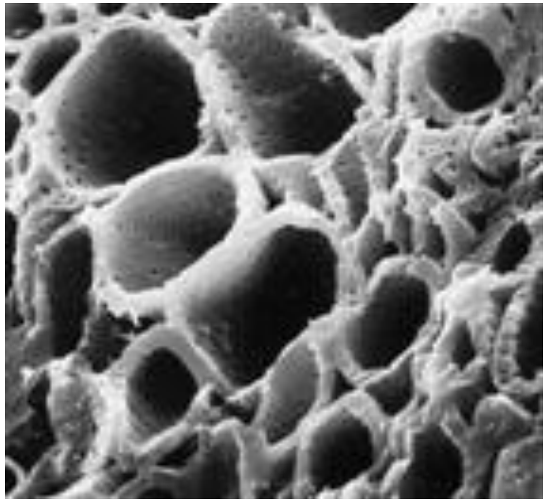
## Single use

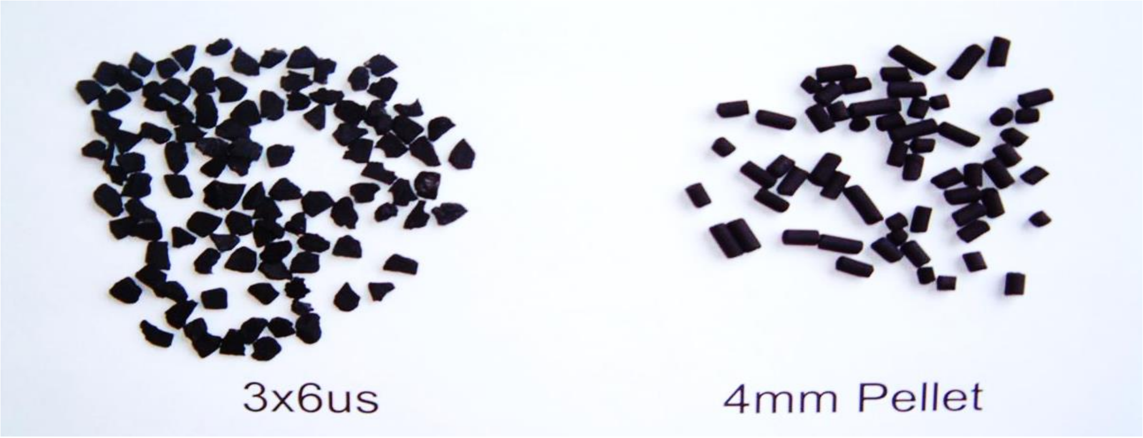
# Adsorption onto regenerative activated charcoal

## Characteristics

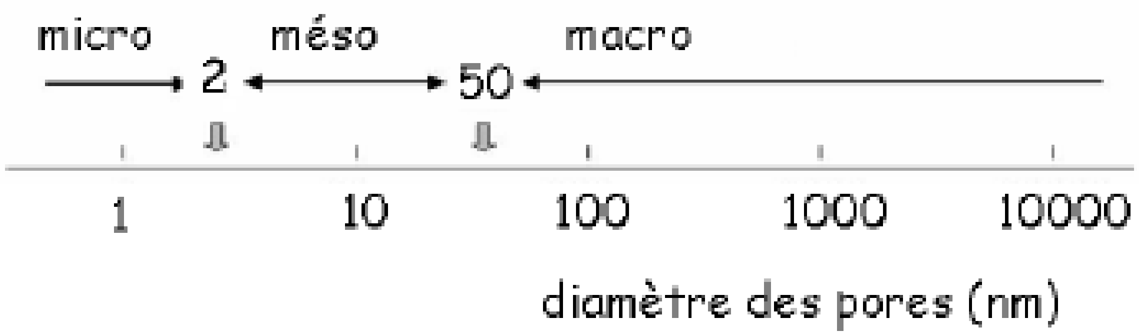
For ACGs in adsorption-desorption mode: use a Ø4 or 5 mm extrudate
S BET: 1100-1250 m²/g

For small molecules, use ACGs (micro-porous – coconut granules)






**2 types of granules: crushed and extruded**



# Adsorption onto regenerative activated charcoal

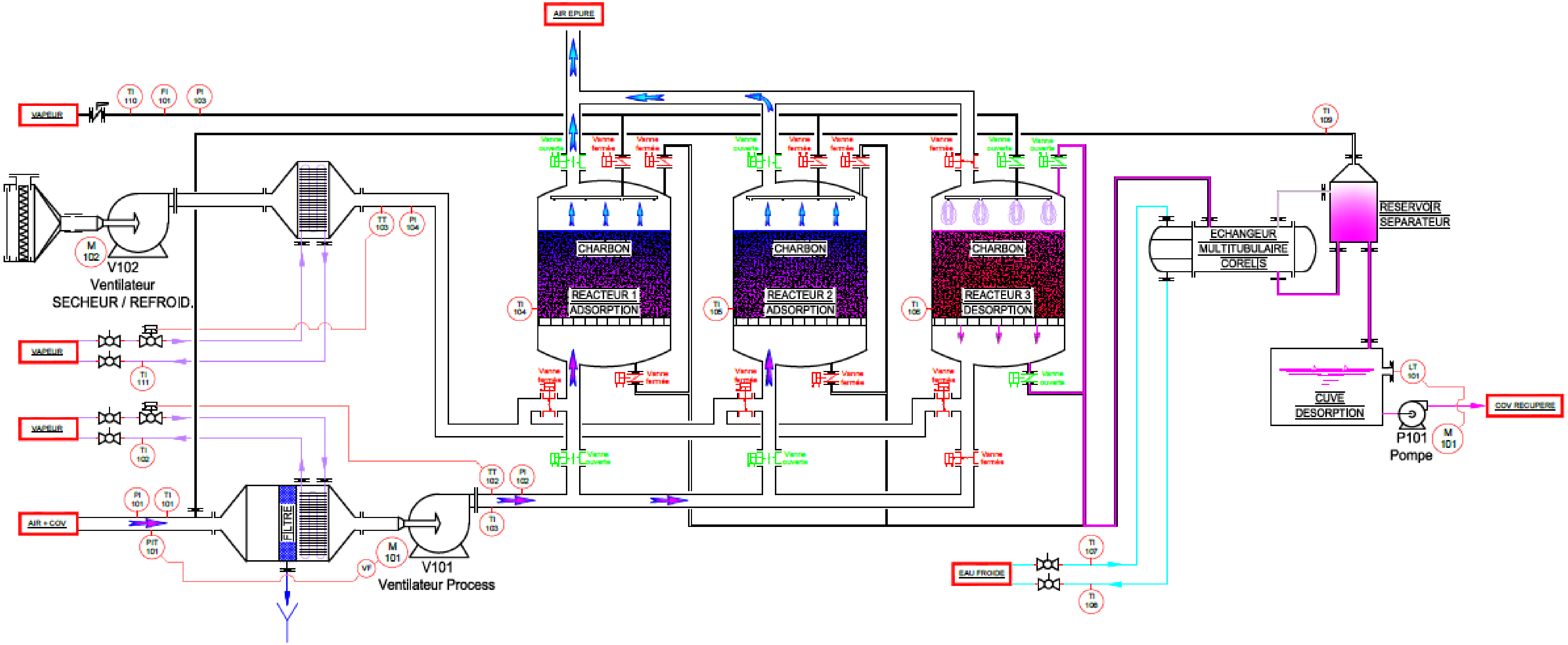
## Basic information

- Adsorption generally occurs between 20 and no more than 40°C.
- After steam is passed through for desorption, the activated charcoal load is ventilated to dry and cool it before a new adsorption cycle.
- Steam desorption is very widespread. It is primarily used for non-soluble VOCs for which solvent-water separation is easy. Desorption with hot inert gas (nitrogen) avoids the disadvantages of water (soluble VOCs and risks of corrosion).
- Avoid " drowning " by operating at too high relative humidity because the capillarity of the water then opposes adsorption.
- At least 2 activated charcoal beds in alternating operation
- One bed is in **adsorption phase** by filtration of gaseous effluents, while the other is in **regeneration phase** (desorption).
- When using regenerative charcoal, **the loading rate is lower, < 10% or even 5-7%**
- Regeneration phase in 3 successive stages:
  - Saturated bed stripping with low-pressure steam (between 125 and 150 °C) or hot inert gas (between 170 and 300 °C)
  - Liquid phase condensation of the vapour mixture (water and VOCs)
  - Water – solvent separation
    - by simple settling for water-insoluble solvents
    - otherwise by stripping/distillation.

# Adsorption onto regenerative activated charcoal

## Schematic diagram

PHASE 1
ADSORPTION REACTEUR 1 & 2
DESORPTION REACTEUR 3

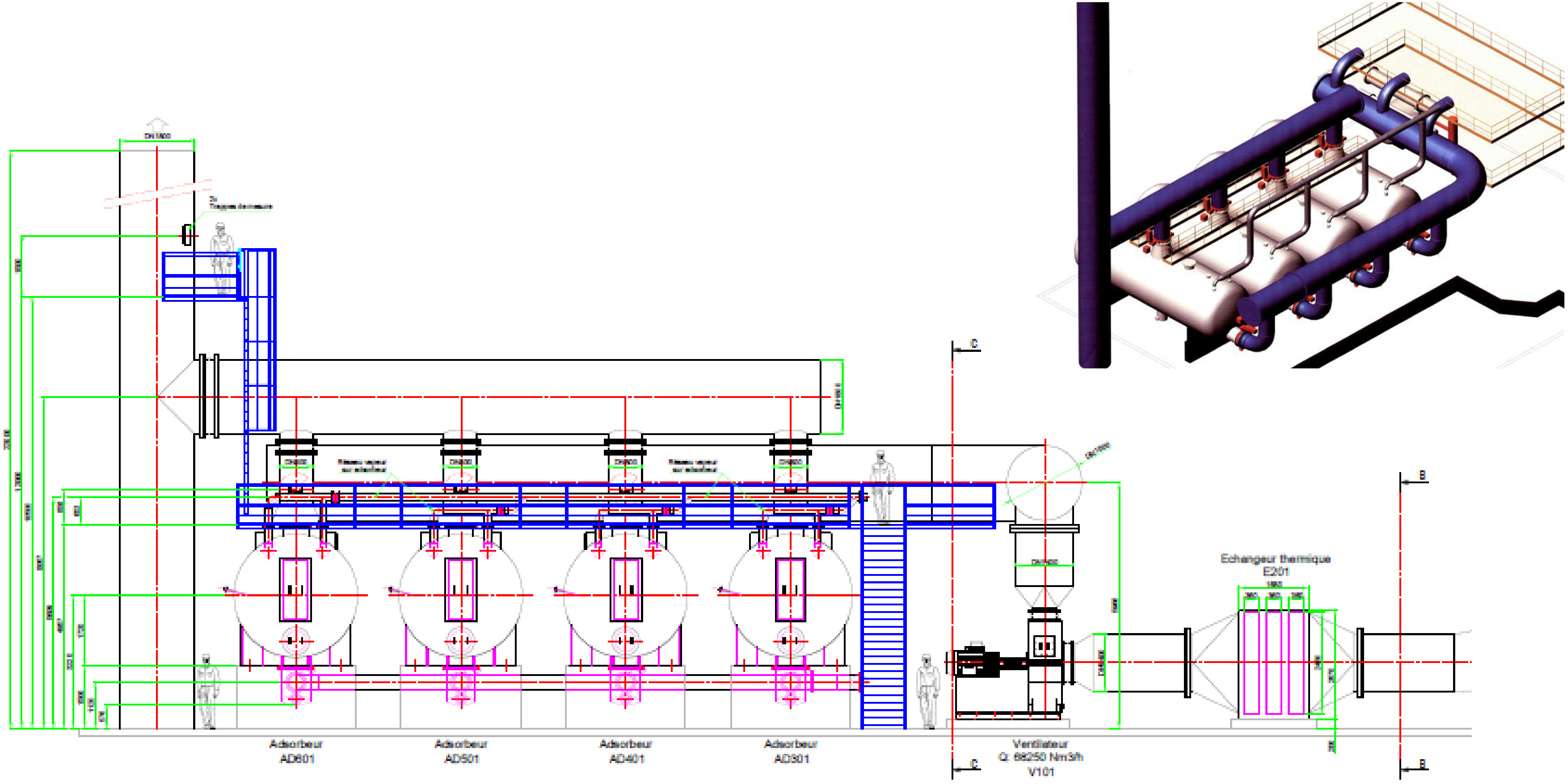


# Adsorption onto regenerative activated charcoal

## Solvent recovery in gravure press and packaging

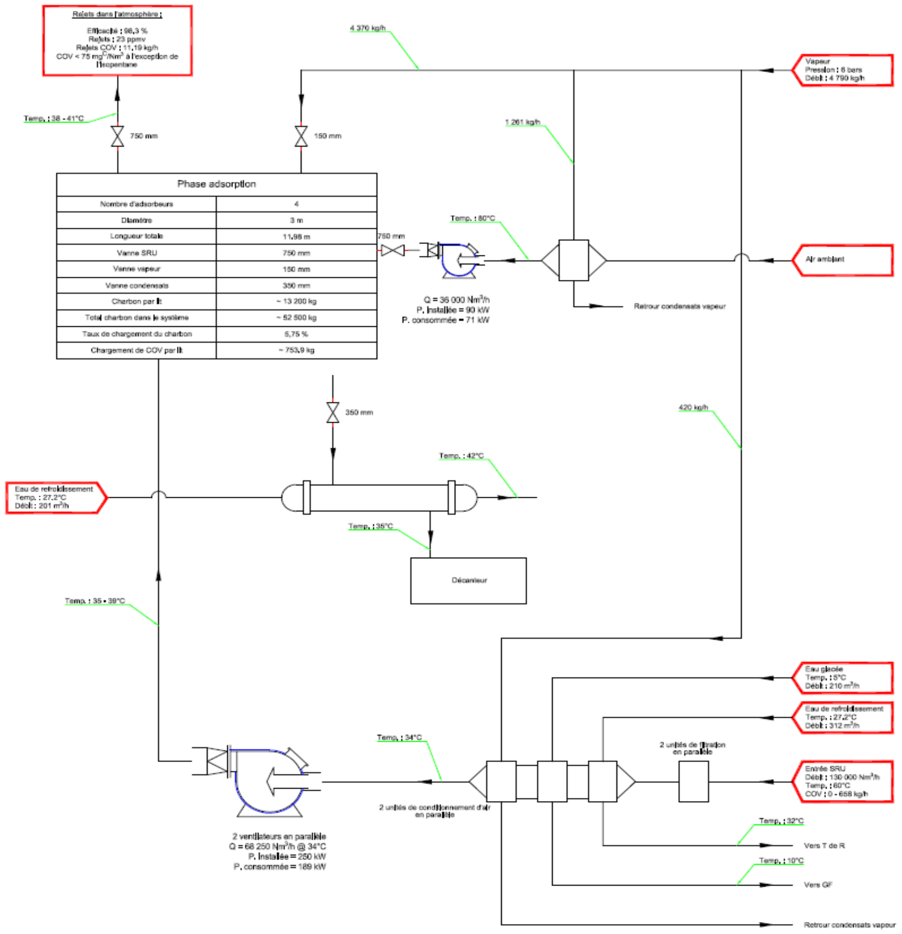
# Adsorption onto regenerative activated charcoal

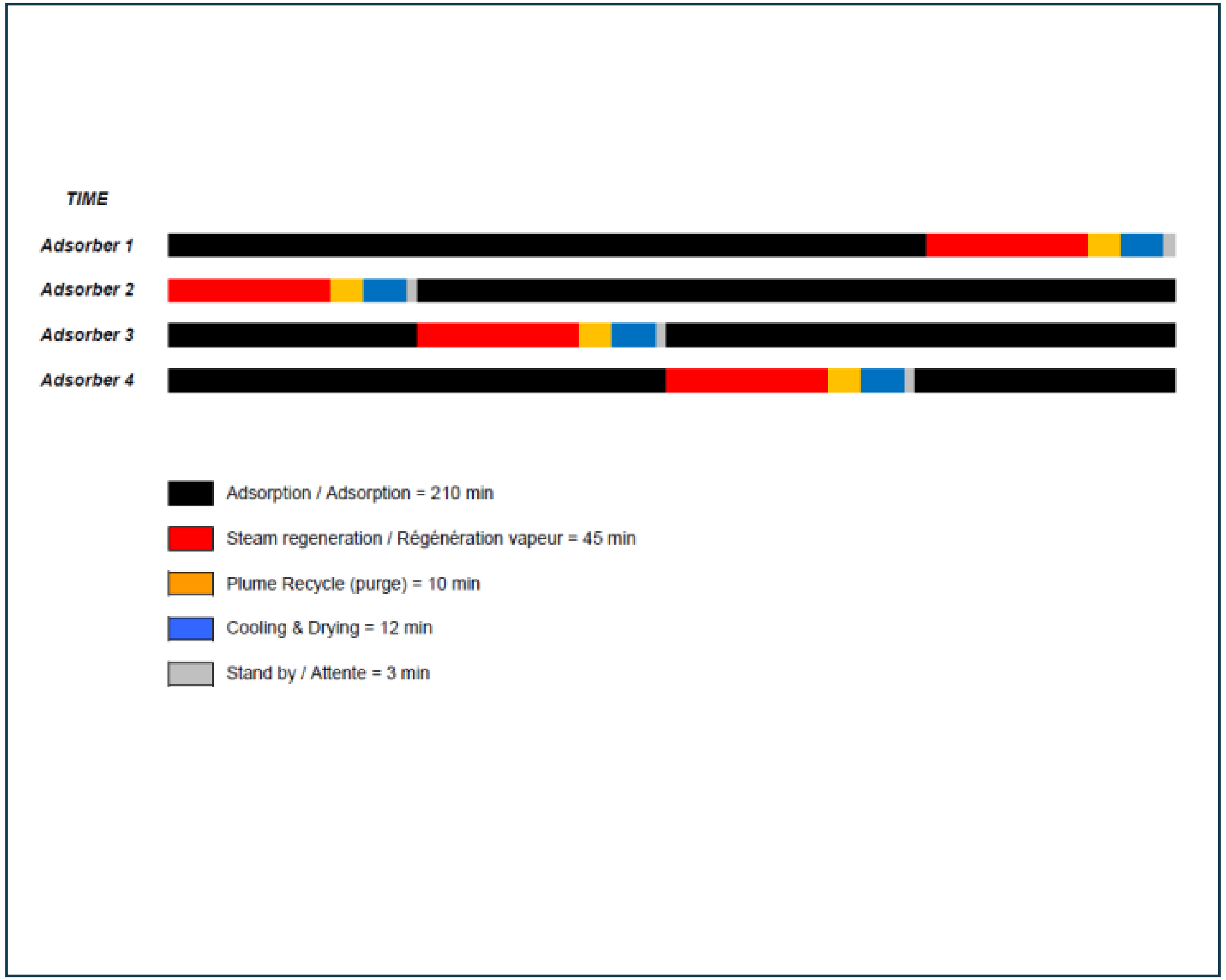
## Standard layout



# Adsorption onto regenerative activated charcoal

## Material balance / Cycle management



# Adsorption onto regenerative activated charcoal

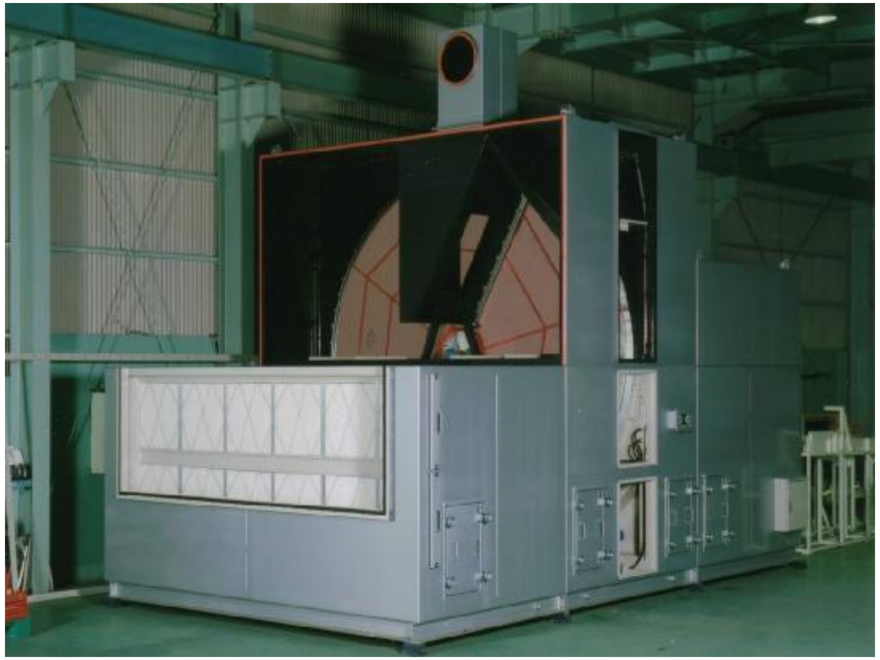
## Solvent recovery on skid unit

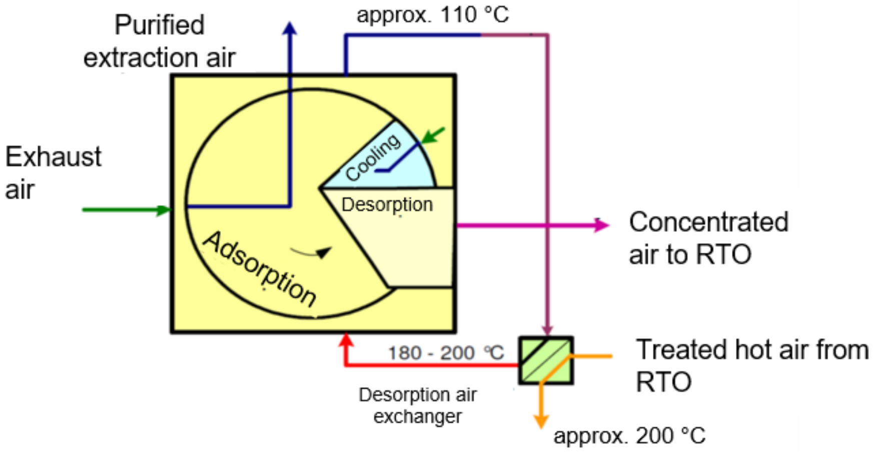
Flow rate:  680 $Nm^3/h$ nitrogen
Mass flow: 70 kg/h heptane

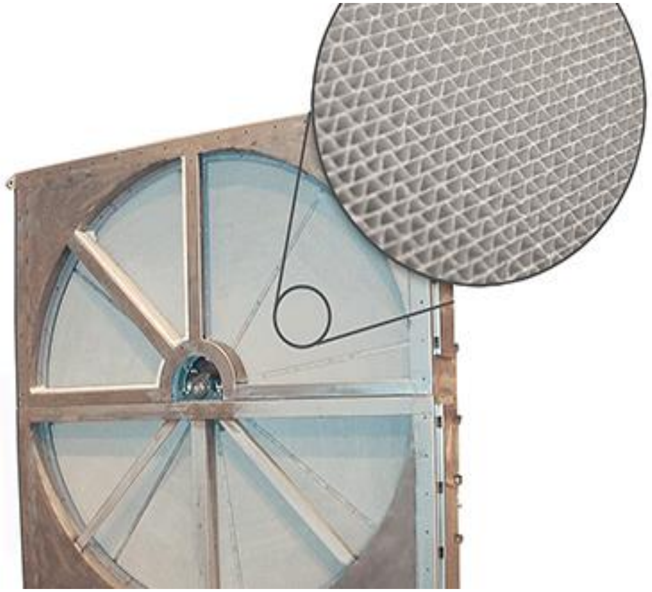
Flow rate: 1200 $Nm^3/h$ process air
Mass flow: 5-20 kg/h
1.2 DCE + / 0.2-0.8 kg/h $SO_2$

Flow rate: 400 $Nm^3/h$ nitrogen
Mass flow: 10-30 kg/h trichlorethylene

# Adsorption on roto-concentrator (zeolites)





The rotor-concentrator / thermal oxidiser is the most cost-effective technology for treating large volumes with low VOC concentrations. The real savings come from reduced operating costs.

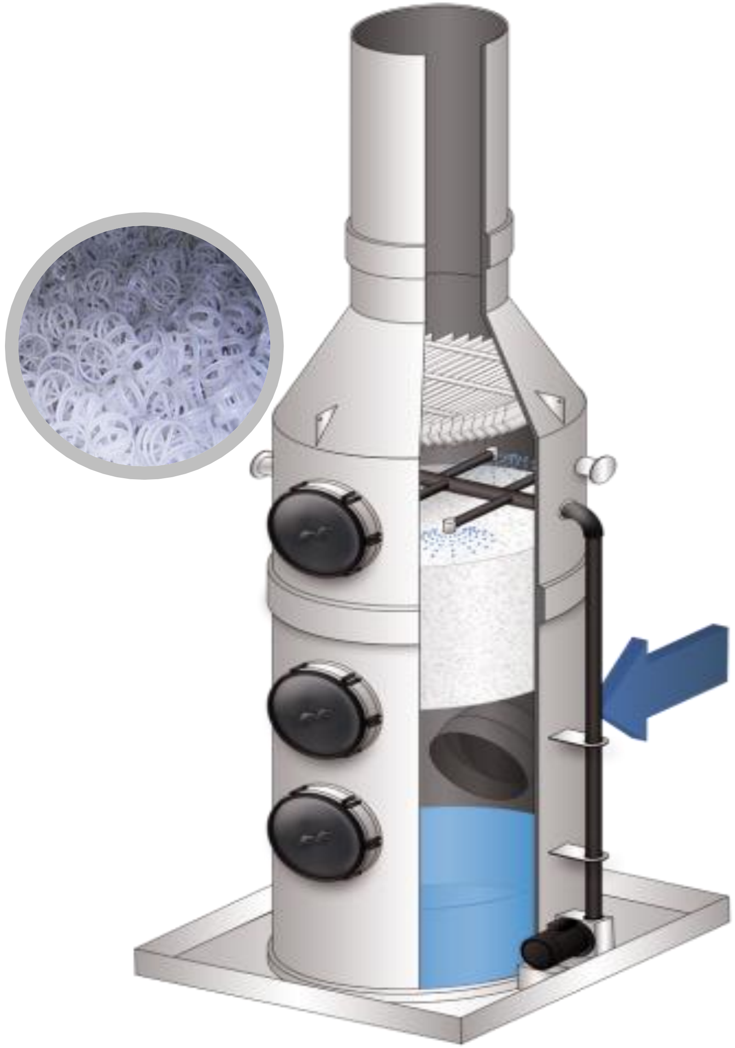
**The primary industrial applications are as follows:**
Painting booths (aeronautic – automotive – industry)
Semi-conductor industry HVAC
Dryer-based packaging industry HVAC

# Absorption

## General

Absorption corresponds to the washing of a gas with a liquid, often aqueous solution ➔ transfer of pollutants from the gas phase to the liquid phase. It relies on the physical equilibrium that exists when a gas phase containing a given substance is contacted with a liquid phase in which this substance is soluble.

The choice of washing liquid will determine the amount of material transferable from G phase to L phase.



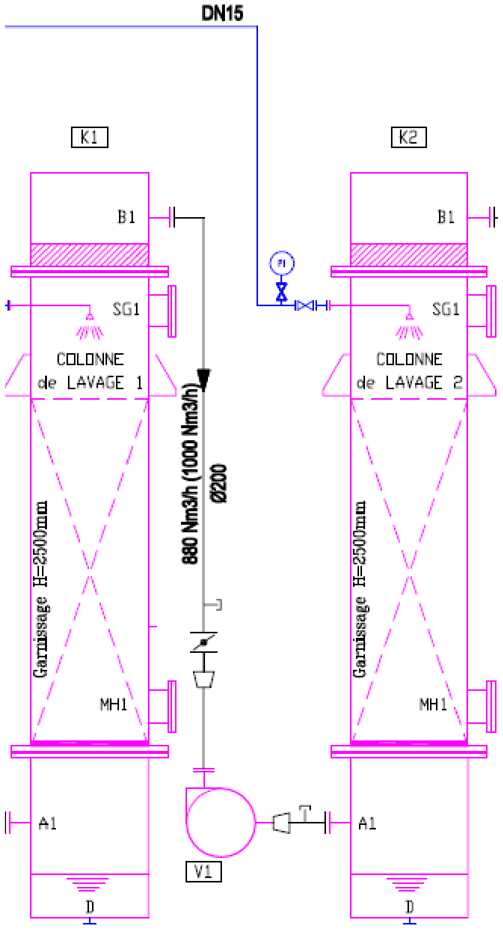
**Main aqueous washing liquids**

Water
+ acids ($H_2SO_4$, HCL)
+ bases (NaOH, KOH)
+ oxidising reagents (hydrogen peroxide, hypochlorous acid)
+ reducing reagents (sodium bisulphite)
+ organic solvents for VOCs

**Important parameters**

Temperature
Contact area
Contact time
Chemical reaction

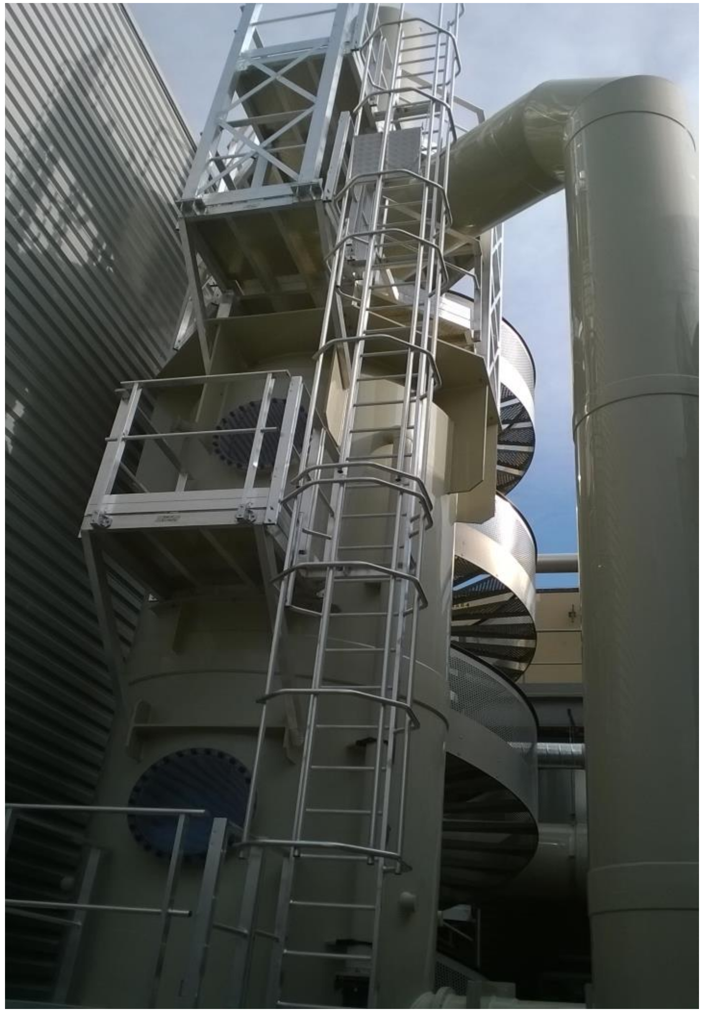
# Absorption
## DMF elimination

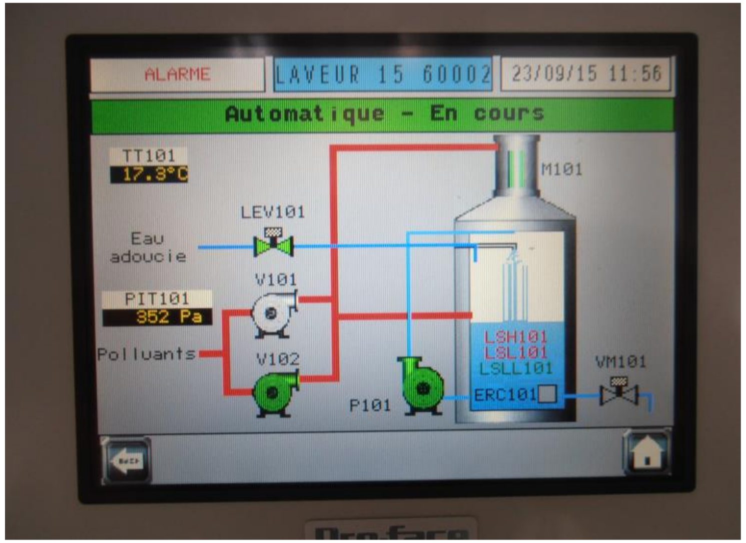



Elimination of DMF from polymer fibre extrusion lines
2 x 1200 Nm$^3$/h – DMF: 1000 – 2200 mg/Nm$^3$ input
≤ 2 mg/Nm$^3$ to atm

# Absorption

## NMP elimination

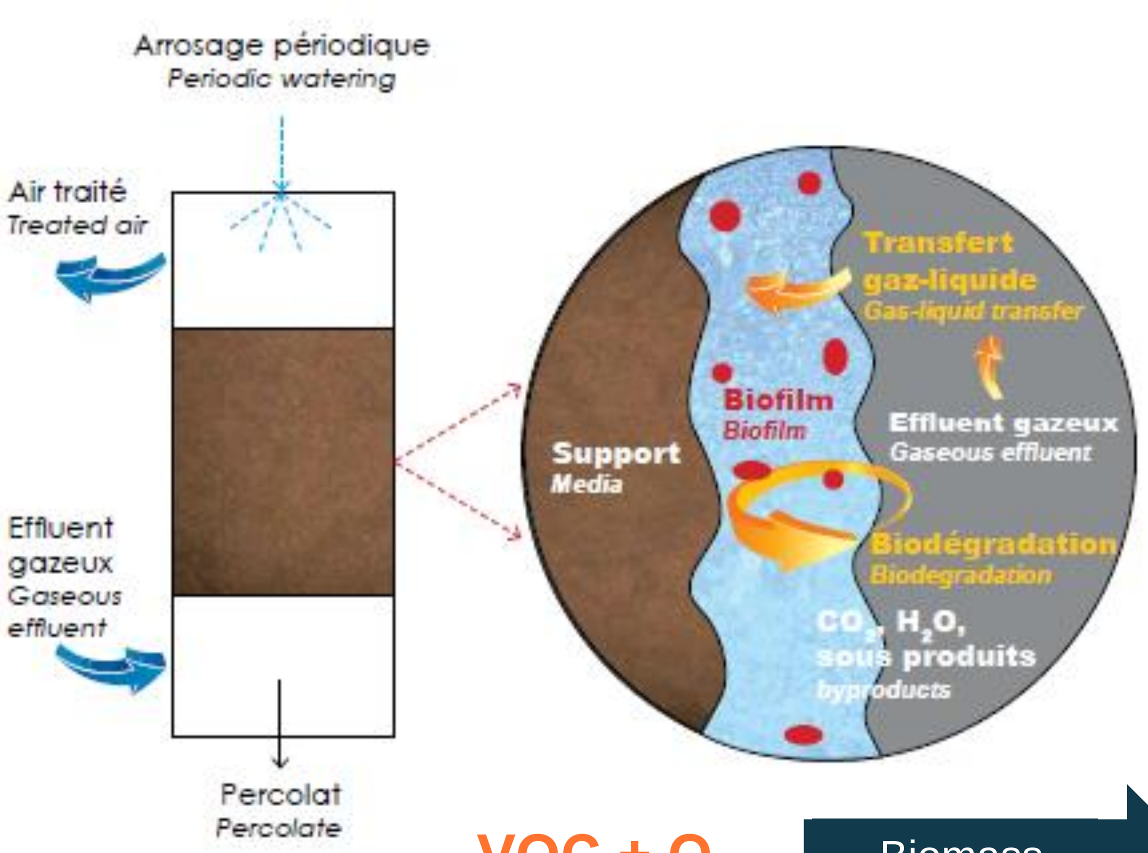





Flow rate: 20,000 $Nm^3/h$
NMP: 200 g/h input
$\leq$ 2 $mg/Nm^3$ to atm

# Biological treatment of VOCs

## Principle




Oxidation reaction of pollutants in the presence of oxygen thanks to the action of micro-organisms leading to biomass growth, along primarily with the formation of steam and $CO_2$

$$VOC + O_2 \xrightarrow{\text{Biomass}} CO_2 + H_2O + \text{heat + mineral matter}$$

# Biological treatment
## Characteristics

In the biofiltration process, the gas to be treated is first humidified to saturation, and then sent through a bed of primarily mineral matter

for VOCs. During this process, pollutants are broken down by micro-organisms that grow in the organic substrate. The humidified air prevents the biofilter from drying out and the organic matter serves as a carrier medium and as a source of nutrients for the micro-organisms.

| | | |
|---|---|---|
| Types of biodegradable VOCs: acetates, ketones, alcohols, volatile fatty acids, etc. | VOC content (200-600 mg/Nm3) | Passage speed and contact time: specific to each pollutant |

# Biological treatment
## Basic parameters

- Temperature range between 15 and **35°C**
- Relative humidity > 95%
- Relative stability of pollutant concentrations
- Complexity of the gaseous effluent to be treated:
  - Interaction between compounds
  - Relative affinity between biomass and pollutants
  - $H_2S$ > R-SH > $NH_3$ > VOC
  - Phenomena of competition, inhibition, cooperation, etc. between different specific bacteria
- Absence of dust imperative

# Biological treatment

## Facilities

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