Optimized bio-mitigation of CO₂ in cement industry
Laboratory of Process Engineering for Environment and Food (UMR-CNRS 6144)
(Laboratoire de Génie des Procédés-Environnement-Agroalimentaire)

- Around 190 persons, with 40 persons working on bioprocesses applied to microalgae, from biology to the refining of microalgal biomass

- A public R&D facility dedicated to the development of microalgal industry

University of Nantes (GEPEA, AlgoSolis) in Europe…

**ALGO**

**SOLIS**

MICROALGAE R&D FACILITY

- RAW BIOMASS CHARACTERIZED
  - Algo-Refinery (liquefaction, methanisation, ...)
- REFINED BIOMASS (PROTEINS, LIPIDS, SUGARS, PIGMENTS, HYDROCARBON, ...)
- Extraction techniques
- Water treatment / medium recycling

**Flowchart**

- Selection and optimization of strains
- Controlled large scale production
- Harvesting techniques
- Extraction techniques

**Building Information**

- Total surface: 3000m²
- Biomass production area: 1500m²
- (350m² in thermostated greenhouse)
- Downstream processing R&D unit: 240m²

**Total funding budget (infrastr. & equip.): 3.8M€**

- Greenhouses for microalgae cultivation
- Biomass conditioning and storage area
- Photobioreactors area
- Low-cost cultivation systems
- Solar outdoor cultivation area
Carbon sources for microalgae growth

Natural feeding

\[ \text{CO}_2 \text{ from air} \quad \rightarrow \quad \text{Current atmospheric concentration 0.0395\%} \]

Artificial feeding (CO\(_2\) enrichment)

- Carbonates
- Bicarbonates
- Purified \(\text{CO}_2\)
- \(\text{CO}_2\) effluent from plants

\[ \quad \rightarrow \quad \text{Purified \(\text{CO}_2\) or chemicals can be expensive for large scale system} \]

\[ \quad \rightarrow \quad \text{The use of flue gas (5 to 20\% of \(\text{CO}_2\) + \(\text{SO}_2\), \(\text{NOx}\), ash) can induce possible toxic effects and the need of dedicated feeding strategies (gas pretreatment…)} \]

But huge quantities available, and it enables the « Waste to value » concept to be introduced!
Main issues of growing microalgae on flue gas

Implementation and optimization of microalgae cultivation on flue gas implies to:

1. Understand and control the mechanisms of CO₂ dissolution and its assimilation by microorganisms

2. Investigate the effects of other compounds contained in the flue gas on both medium (pH) and biological response (additional nutrient, toxicity)

So as to develop optimized cultivation systems with appropriate CO₂ feeding strategies
Investigation of CO$_2$ dissolution and of its assimilation by microalgae

Results issued from B. Le Gouic PhD Thesis
Carbon assimilation by microalgae: main aspects

An important remark:
- Only dissolved carbon is assimilated (aqueous micro-organisms)
- Dissolved inorganic carbon (DIC) is the main parameter (and not %CO₂ in the gas phase)

CO₂ in the gas phase (CO₂(g))

- CO₂ solubility / gas-liquid mass transfer
- Chemical equilibrium of carbon species

Dissolved inorganic carbon (DIC)

- Photosynthesis, CCM
- Biomass assimilation

Biomass
**CO₂ gas-liquid mass transfer**

**Gas-liquid mass transfer**

Two-film concept (Lewis et Whitman)

- CO₂ poorly soluble in water
- Diffusion of CO₂ in liquid is 4 orders of magnitude slower than in the air
- Function of the cultivation system/injection device
- Mass transfer coefficient
- Driving force
- Influenced by %CO₂ and DIC

**Carbon dissociation in liquid phase**

- CO₂, HCO₃⁻, CO₃²⁻
- Carbon species evolution as a function of pH value
- The pH value is a key parameter of available DIC

**DIC (mM)**

Total DIC evolution as a function of pH value
Investigation of CO₂ dissolution and DIC assimilation by microalgae in lab-scale PBR

On line monitoring of biomass growth and gas-liquid mass transfer for various CO₂ feeding strategies in well-controlled environment (pH, light, culture medium)
Development of predictive models of CO\(_2\) mass transfer and effect of DIC on microalgae growth in photobioreactors

- Mass balance: \( \frac{dC_{CO_2}}{dt} = N_{CO_2} - (r_{CO_2}) - D_c (C_{CO_2} - C_{CO_2}^*). \)
- Modeling of gas-liquid mass transfer: \( a_n N_{CO_2} = k_i a(y_x) \left( \frac{y_{CO_2} P}{H} - \frac{C_T}{K} \right) \)
- Modeling of carbon dissociation in liquid phase: \( K = 1 + \frac{K_1}{[H^+]^2} + K_2 [H^+] \)
- Modeling growth limitation by light and carbon source: \( r_x = f(q_0, D_c, C_T) \)
- \( r_{CO_2} = Y_{CO_2/X} \cdot r_x \)
Examples of results: Influence of carbon limitation on Chlorella vulgaris growth

A 9-10 fold increase in productivity is observed simultaneously to dissolved inorganic carbon appearance in the medium

**Air injection:** Unstable culture
- $C_{X_{\text{max}}}$ = 0.33g/L
- $P_x$ = 8.6 g.m$^{-3}$.j$^{-1}$
- % pigments = 2.05%
- No DIC in the liquid phase

**Injection of 2.25% (mol) of CO$_2$:***
- $C_{X_{\text{max}}}$ = 3.5g/L
- $P_x$ = 77 g.m$^{-3}$.j$^{-1}$
- % pigments = 5.14%
- From 0.1 to 0.2 mM in the liquid phase
Examples of results: analysis of carbon fluxes in the process and growth C-limitation modeling

Carbon flux in the photobioreactor

- Total amount of carbon per produced biomass (kg): 4.38 kg CO$_2$/kg
- Abatement of the gas phase: 46%

Modeling of photosynthetic growth limitation by the carbon source

$$r_X = r_{X,\text{photolim}} \frac{\text{DIC}}{K + \text{DIC}}$$

$$K = 0.033 \text{mM}$$

$r_X$: Biomass growth rate (light + Csource)
$r_{X,\text{photolim}}$: Biomass growth rate (light only – can be obtained from photosynthetic growth model, see Pruvost and Cornet, 2012)
Examples of results: Development of engineering tools to optimize CO₂ fixation in PBR

Simulation of a direct flue-gas injection in a PBR

Increasing the gas phase CO₂ content increases DIC

This increases growth up to a given limit where growth reveals to be only light-limited

Then, carbon accumulates in the liquid phase

Maximum biofixation is achieved for optimal growth conditions (no C limitation)

A too high CO₂ content in the flue-gas decreases the yield of gas epuration

An optimal running region exists, combining maximal gas epuration with maximum biofixation (here, around 4000ppm in CO₂)
Examples of results: Development of flue-gas feeding strategies

Objective: Investigate the interest of a multi-stage production units

Case study: Cement plant with $y_{(CO_2)}$ of 16% and $Q = 250L.min^{-1}$

A series of 6 enclosed RWs of 100m$^2$ each allows combining high CO2 abatement (>90%) while keeping biomass productivity close to its maximal limit value (80%)
Integration of microalgal culture in actual CO$_2$ emitting industry – Investigation of the effects of flue gas composition on biology

Results issued from AlgoSource Technologies projects
In-site investigation of flue-gas effect on microalgal growth

*In-site implantation of a mini-lab with direct connection to an emitting cyclone tower (coll. with Ciment Calcia)*

- Cyclone tower of the Gargenville’s cement plant
- Sampling line connected to chimney stack
- Experimental platform
- Photobioreactor (small scale studies)

13% of CO₂ + various compounds
Development of a feeding strategy: Investigation of toxic effects of metal compounds transferred to the liquid phase

Arthrospira platensis

An interesting species, because of its intrinsic value and its growth in alkaline medium (better C dissolution)

Comparison of the Arthrospira platensis culture aspect before (left) and after (right) the addition of precarbonated solution

Evolution of the volumetric productivity of Arthrospira platensis with progressive increase in cement plant precarbonated medium

Progressive addition of precarbonated medium obtained from flue gas (saturated solution containing metals)

Loss of productivity

% of precarbonated medium in the feeding medium

Productivity (g/L/d)

Time (d)
Development of the experimental set-up

Integrated set-up composed of 2 PBR (1 with pure CO₂, 1 with flue-gas) operated in parallel to test various feeding/pretreatment strategies of the flue-gas
Example of results: Microalgae culture on flue gas

Long-term culture of *A. platensis* with appropriate flue-gas feeding strategy (results obtained in the cement plant)
Conclusion and perspectives

AlgoSource Technologies in collaboration with University of Nantes (GEPEA, AlgoSolis R&D platform) has developed an integrated approach for the rational and optimized integration of microalgae culture in flue-gas emitting industry

- With appropriate considerations, flue gas can be used to produce microalgae: a stable production was achieved in a cement plant with productivities similar to the case with pure CO₂ (corresponding here to a maximal biofixation as fixed by available light)

The current effort is focused on issues related to the actual implementation of microalgal culture on flue-gas

- Development of adapted business models (i.e. waste to value approach)
- Impact of metal fixation on harvested biomass and extracted products quality
- Development of feeding strategies able to maintain maximal growth in time-varying flue-gas emissions (need to council the various dynamics of the process (flue-gas emission → gas-liquid mass transfer → solar microalgae growth)
Examples of ongoing projects

AlgoSource Technologies is currently applying this methodology and knowledge for the actual development of its waste-to-value approach (conversion of flue-gas in valuable microalgae compounds)

- Cimentalg project (ADEME) – 1.6M€
- Ciments Calcia
  Italcementi Group
- Integration of a 300m² biofacade in a waste processing plant (Nantes, France - www.alcea.fr) for simultaneous microalgal production and flue gas partial treatment

- Symbio2 project (FUI) – 5M€
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Thank you for your attention

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