Les “Mardis” de la Chimie Durable

Sur le thème des matériaux

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Levers for reducing the environmental impact of cements and cementitious materials

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CEMENT – Definition and applications

CEMENTS

OPC - Ordinary Porland Cement
CAC – Calcium Aluminate Cement
CSAC – Calcium SulfoAluminate Cement

OPC-Ordinary Portland Cement
. Clinker: $(CaO)_x(SiO_2)_y(Al_2O_3)_z(Fe_2O_3)_U$
C3S (Alite) – C2S (Belite) – C3A – C4AF
. Additives
. CMs: Secondary Cementitious Materials

+

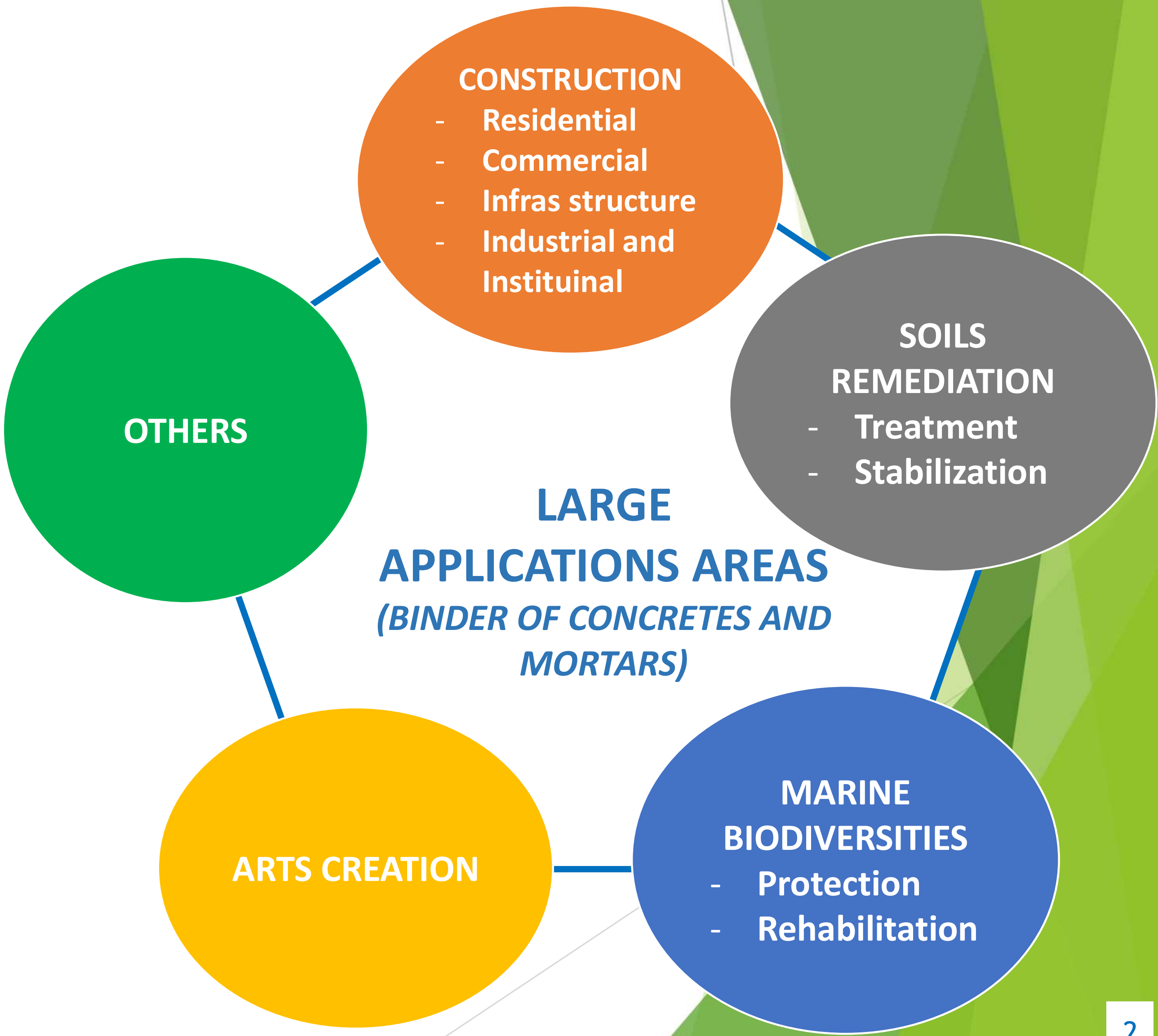
WATER

↓

HYDRATED CEMENT
Hydrated OPC: « C-S-H »

Special mineral glue with exceptional properties:

- Insolubility in water
- Very high adhesive properties
- Very high mechanical performance (CS: 150 Mpa)
- Very long durability (50 to 100 years)



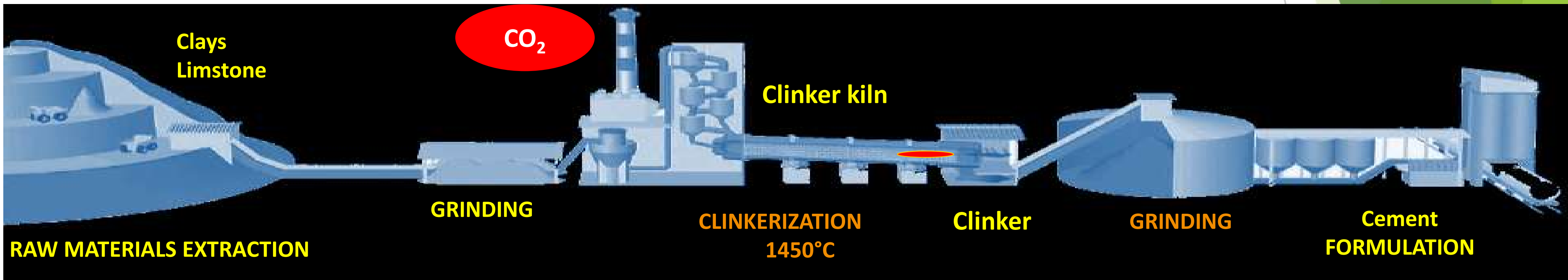
Ordinary Portland Cement (OPC) production
Clinker substitution with CMs

CMs (Secondary Cementitious Materials)
. Gypsum
. Coal fly ash, Vegetable ashes
. Granulated blast furnace slag
. Silica fume, Pozzonana

RAW MATERIALS (7 Gt/Y)
- **Clay (20%): 1,43 Gt/Y**
- **Limestone (80%): 5,72 Gt/y**

WATER (1.43 km^3/Y)

ENERGY (22.5 GJ/Y)
- **Fuels (Coke)**
- **Electricity power**



GHG EMISSION (3.57 Gt CO_2 –eq/Y)

PORTLAND CEMENT (4.6 Gt/Y)
- CEM I : 95% of Portland clinker
- CEM II/A or B : 65% of Portland clinker
- CEM III/A, B or C : 36 to 80% of furnace slag
- CEM IV : Pozzonana Cement
- CEM V : Composite Cement
- CEM VI : Composite Cement_NF EN 197-5 (50% less clinker, Le Teil)

➔ **Clinker substitution with secondary materials (CMs) can reduce annual global CO_2 emissions by up to 1.3 gigatons**
(Sabbie A. Miller et al. 2022)

Ordinary Portland Cement (OPC) production

Altenative fuels

- **Target: 30 to 70% of alternative fuels**

Coffee Husk

Palm Kernel Shell

Rice Husk

Obsolete Seeds

Municipal wastes

Water Treatment Plant Sludge

End-of-life products

- **Precaution and recommendations**

- *Networks organization for wastes collecting and pre-treating*
- *Control of mineral composition (Heavy metal and Phosphorous content)*
- *Appropriate treatment of combustion gas*

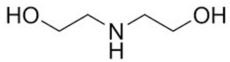
Ordinary Portland Cement (OPC) production

Grinding Aid Agents

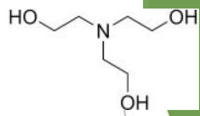
- **Synthesis Grinding Aid Agents (Small & polar molecules)**

DG

DEA



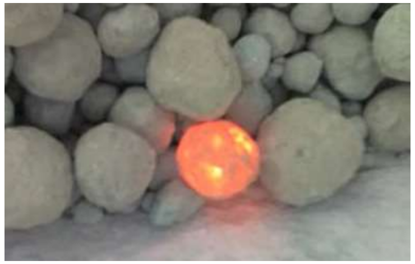
TEA



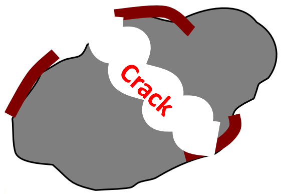
Amine acetate

250 to 400g of GAA/T of cement or > 1,5 Mt/Y

Limestones
CMs
Clinker (C3S-C2S-C4A-C4AF**)**



Cements, CMs
Blaine: 2800 – 5000 cm²/g
Particles size: 10 – 80 µm



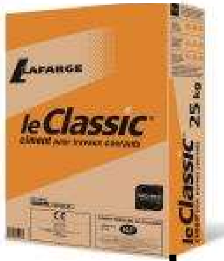
- Surface adsorption & improving breakage
- Reducing electrostatic energy
- Cleaning balls mill

- Improving the separation of fine particles
- Reduce energy consumption
- Increase production capacity
- Improve28-day compressive strength by +3.7 MPa

- **Biobased Grinding Aid Agents**
- Crude Glycerol & Derivatives of Glycerol from biodiesel & oleochemical industries
- Aminoacids, hydroxyacids and by-products from food industries
- ...

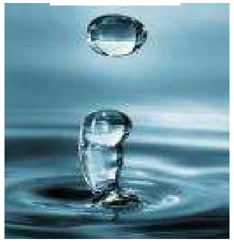
Concretes & mortars

Cement

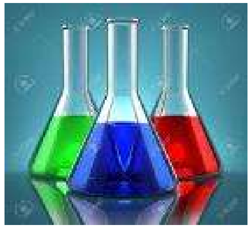


Aggregates, sands

Water



Admixtures



Metal fiber

Synthetic fiber

Natural fiber (CHRYSO®Fiber UF500)

Concrete Ready Mix Plant & Transport

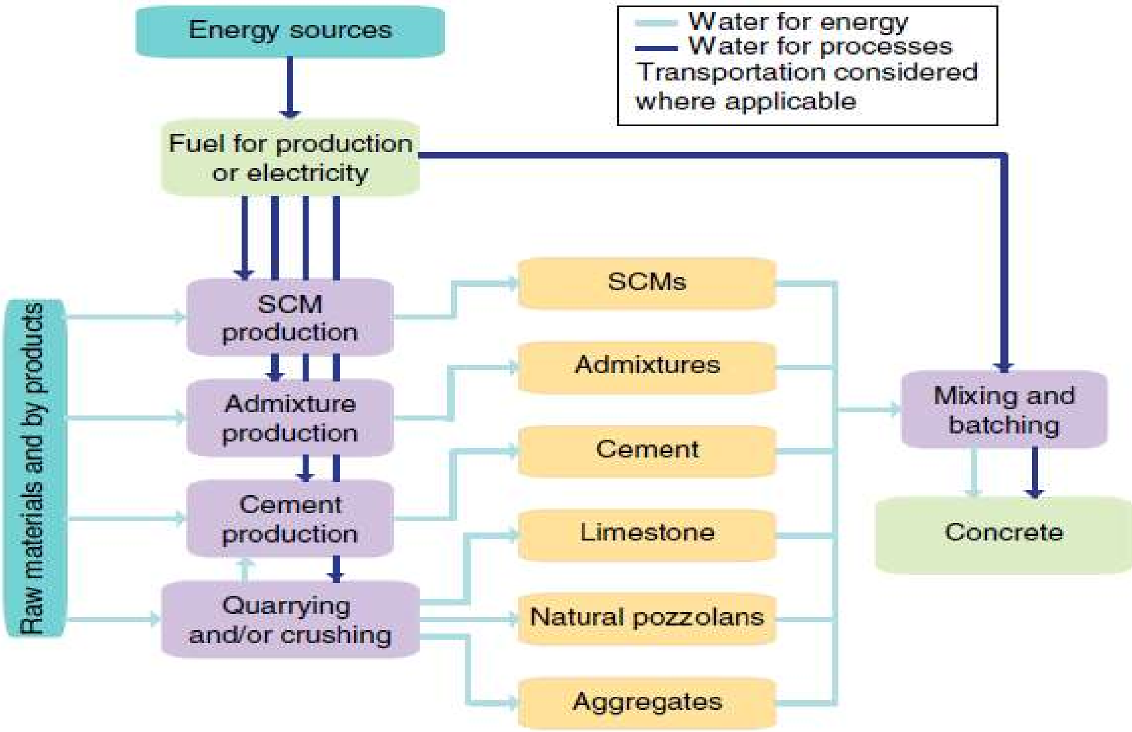
ENERGY

FORMULATION

WASTES
Return concretes
Washwater

Concretes, Mortars, Coatings

Concretes & Mortars_Economical and environmental impact



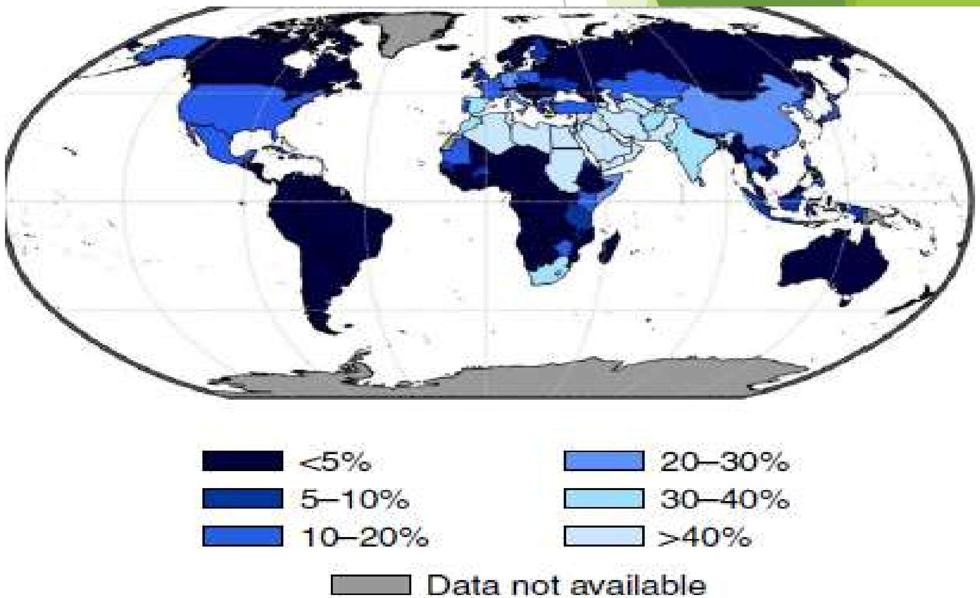
Concrete flow diagram

Sabbie A. Miller 2018 (California Univ.)

Keys words:

Concretes production:	**6 Gm³/Y or 6 km³/Y**
Aggregates:	**> 25 Gt/Y**
Water withdrawal:	**65.7 km³** of water
Water consumption:	**16.6 km³** of water
Embodied energy:	**14.7 GJ**
GHG:	**2.73 Gt** CO_2 -eq.

➔ **Treatment & recycling of wastewater is imperative!**



Global water stress by country

Reduction of fresh water withdrawal for aggregates making

Aggregates production: 25 Gt/Y (World); 400 Mt/Y (French)

CRUSHING - SCREENING

WASHING

150 to 200 kg of dry sludge/t of aggregates

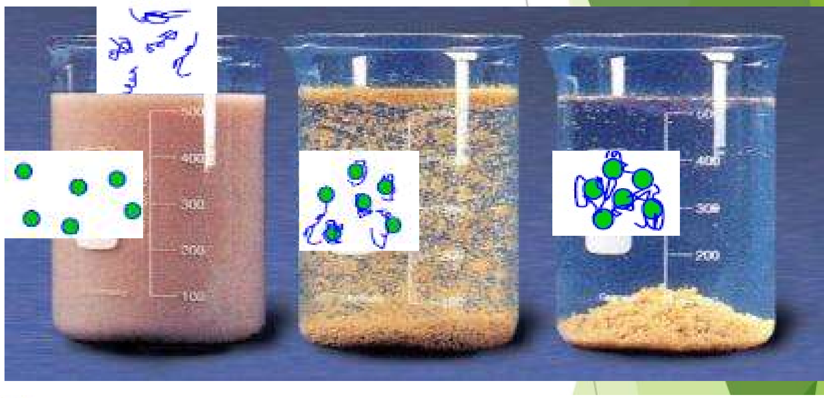
Fillers | Sand | Coarse aggregate | Gravel

AGGREGATES WASHING:

- Use from 1 to 2m^3 of water/T of aggregate
- Used water contains a lot of small particles

➔ Needing to use the floculent agent to treat used water

FLOCULATING OF SLUGDE



Floculent agent (polymers): Polymelamineformol, PolyAcrylamide…

- **Weaknesses of the current floculent agents:**
- Environmental impact < = 1000 mg/L of treated water
- Price of synthesis molecules

Good prospects for the biodegradable and biobased molecules (Chitosan, Starches, cellulose derivative)

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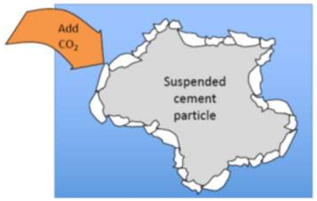
Reduction of fresh water withdrawal for concrete making

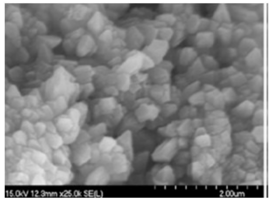
- **Recycling of Return concrete (1 – 1,5%) & Concrete washwater (more than 100L/m³) beneficiation using CO_2**

CARBON CURE™

• Washing of trucks produces up to **800 L** of wash water per load.
• About **270 kg** of solids are typically washed from a truck.
• Investigated CO_2 mineralization in washwater solids to allow increased use as mix water

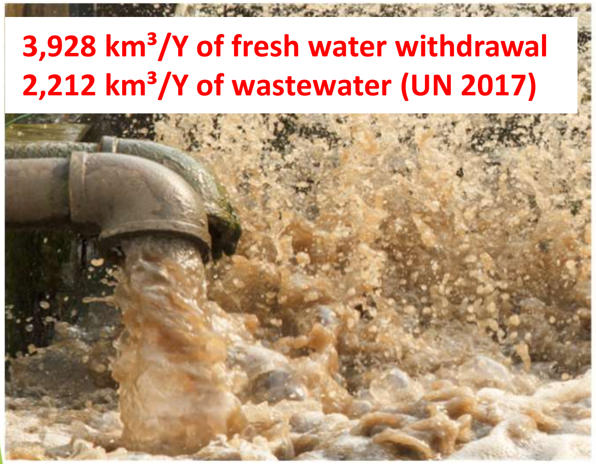


$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$



➔ ***CO_2 capture potential: 0.5 to 0.7 Gt CO_2/Y***

- **Reuse treated wastewater for concrete making**



TREATMENT
. Aerobical
. Anaerobical
. Oxydation (O_3)
. Ultrafiltration

Treated water

➔ **Treated water is very good quality for concrete making, even as drinking water. But we need the permission of states**

Functionnal admixtures for concrete making

No concrete without organic admixtures (EN 934-2)

Concrete production: 6 Gm³/Y (World); 215 Mm³/Y (Europe)
Global Admixtures market: 13.5 Billions USD/Y

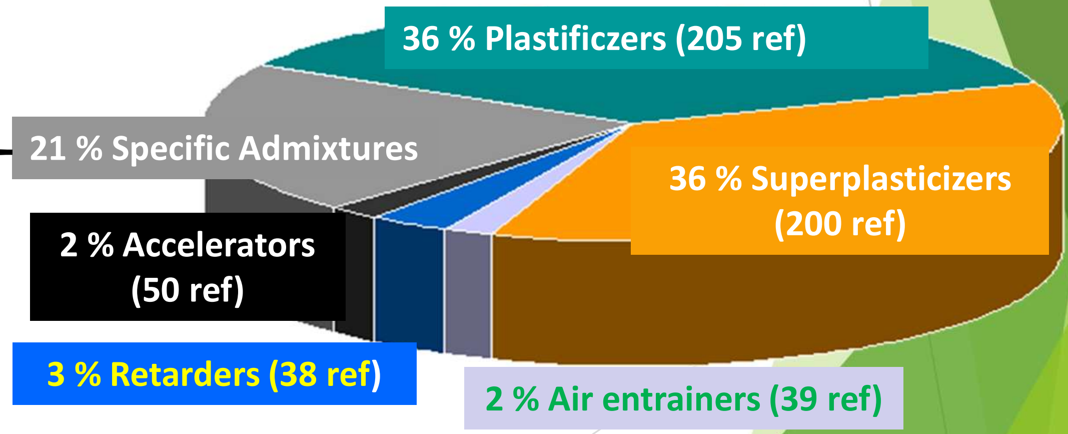
Why to admix a material ?

- **To adapt to local raw materials (**polluted sand, Specific cement…)
- **To adapt /optimize production processes (**Acceleration, retardation, workability…)
- **To provide specific properties** (freeze/thaw resistance, shrinkage/cracking, insulating…)

European production of Admixtures : 850 000 t/Y

Specific Admixtures

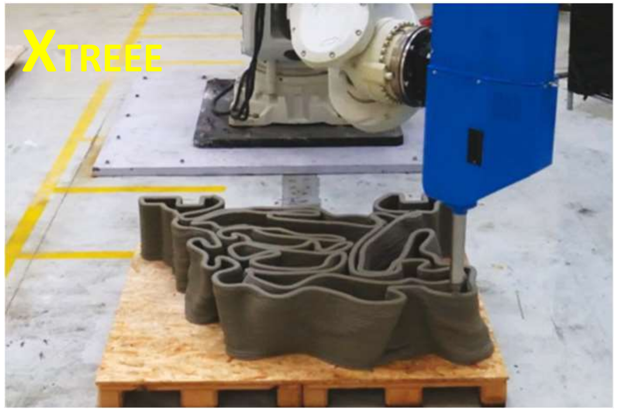
- Water retaining agents
- Viscosity modifiers
- Anti-Shrinkage agents
- Foaming agents
- Demolding Agent
- Curing agent…

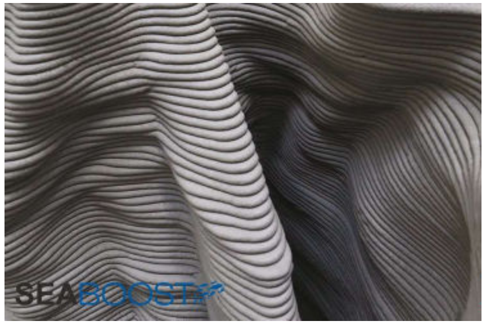


Right materials for right application thank to functionnal admixtrures

Airium®, an insulating cement foam

Bio-inspired concrete thank to **3D PRINTING TECHNOLOGIES** to the rescue of marine biodiversity _ **Calanques Marseille**





➔ **Specific admixtures & additives are essential for theses applications**

Functional admixtures for concretes & mortars

(Super)plastisizers

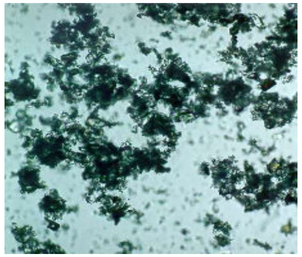
Without dispersing agents, cement particles agglomerate (flocculation)

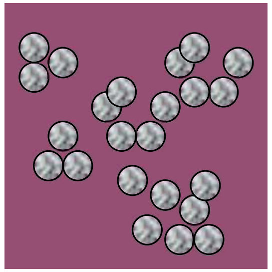
➔ Lose of fluidity of concrete

A dispersing agent breaks down these flocs by repulsive forces between cement particles

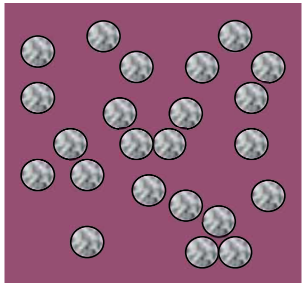
➔ Increasing fluidity

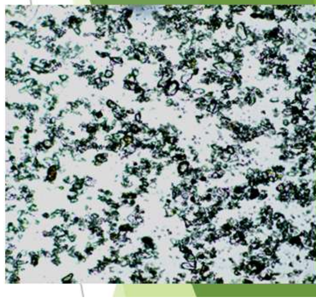
Flocculated state



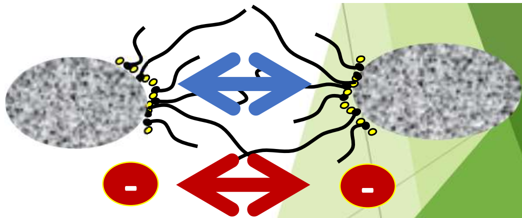


Dispersed state





Steric or electrostatic dispersing of cement particles



A good dispersing agent allows:

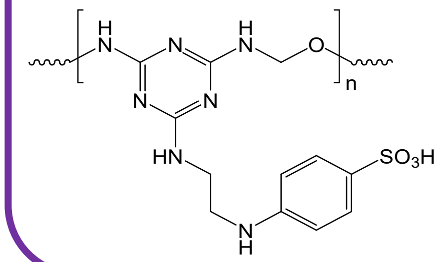
- *to obtain a self-compacting and self-leveling concrete*
- *easy to use, aesthetic and ergonomic, delivering high quality results.*

Main families of plasticizers (dispersing agents) for ready-mix concrete

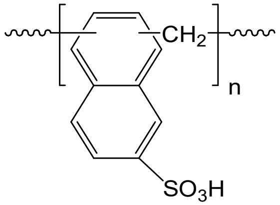
Anionic water-soluble molecules or polymers

Superplasticizers 1st Generation

Melamine-based polycondensates
MSF, PMS

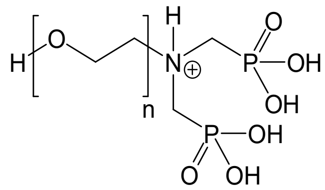


(**N**aphtalene **S**ulfonated **F**ormaldehyde) based polycondensates **NSF, PNS**

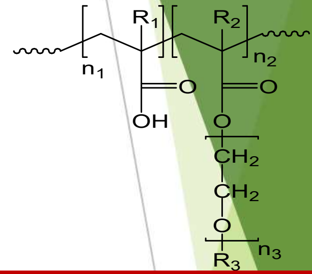


Superplasticizers 2nd Generation

Diphosphonate polyox

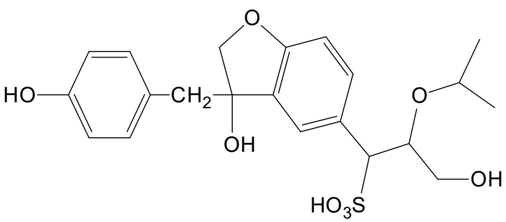


Poly(**C**arboxylate de **P**olyéthylène glycol) **PCP** or **PCE**



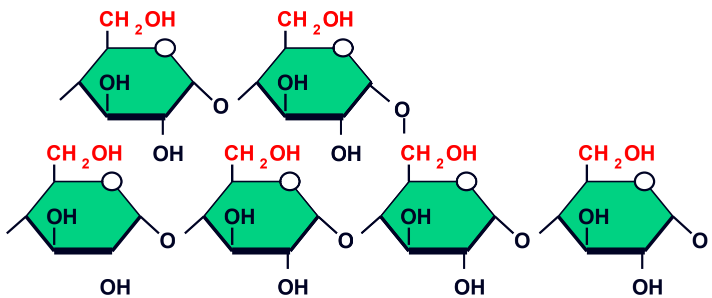
Bio-based plasticizers

LignoSulfonates, LS

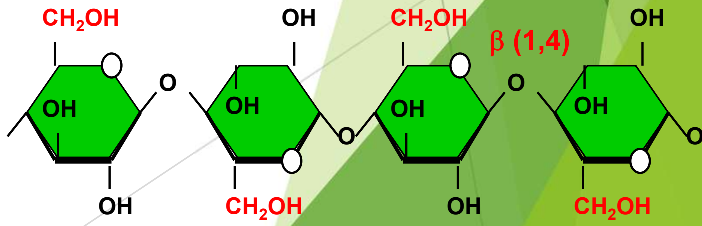


Sulphonated or carboxylated olysaccharides (Cellulose, starches, gums)

Starches derivatives (*Branched structure*)



Cellulose derivatives *(Linear structure)*



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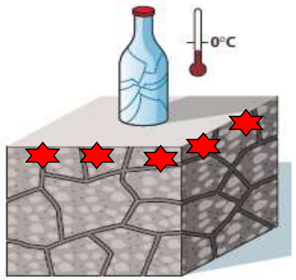
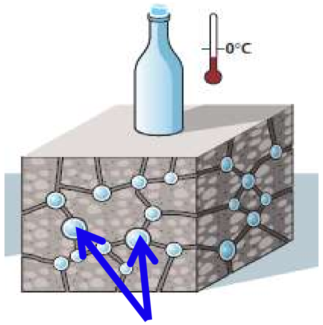
Concrete Resistance to freeze-thaw attack thank to Air Entraining Agent (AEA)

USA: Reparation costs due to freeze-thaw cycles and chloride ingress are estimated to **16 to 24 billions dollars** + 400 Millions dollars per year.



The frozen water volume increases by 9% and cause the cracks of concrete (Powers 1945)



➔ Creation a well network micro-bubbles of air increases the frost resistance of certain concretes by decreasing the internal tensions in capillaries

Air bubbles network

- **Air Entraining Agent has to create and stabilize the air bubbles network**
- **3 families distinguished by their 'polar' head:**

AEA = Surfactant 

- Sulfonates and sulfates based (Synthetic compounds)
- Non ionic based (PEO)
- **Bio-Based molecules (Fatty carbocylic acids…)**

Cement-based insulating materials

Contexte: Global insulation market: 82 Bn € in 2017
External wall insulation (new & retrofit): 5.7 Bn m^2/year

Airium® a technology developed and patented by LafargeHolcim R&D center nearly of Lyon France

Airium ® is an cement-based insulating foam, so light as a chocolate foam and very fluid.

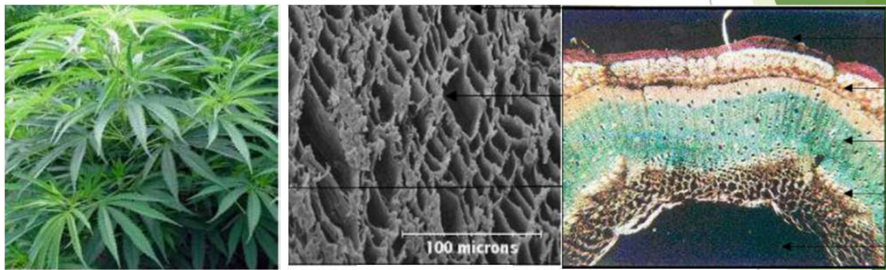
Thermal conductivity = 0,04 to 0,12 W/m.K

Insulating Bloc

Insulating Screed

Biobased Insulating Block

Hemp wood

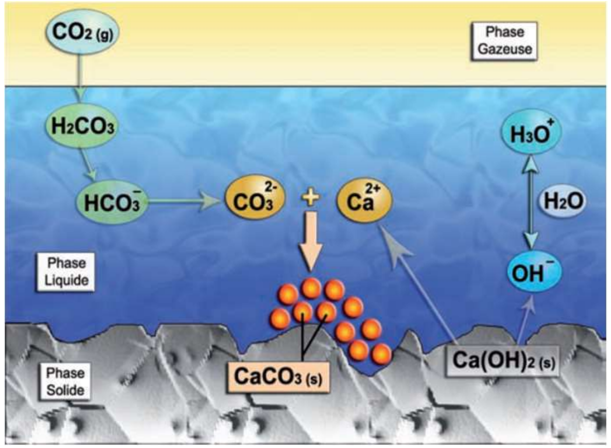


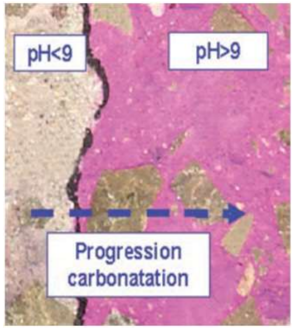
Cement

FORMULATION
With as well as possible control of the interaction « Binder/Biomasse »

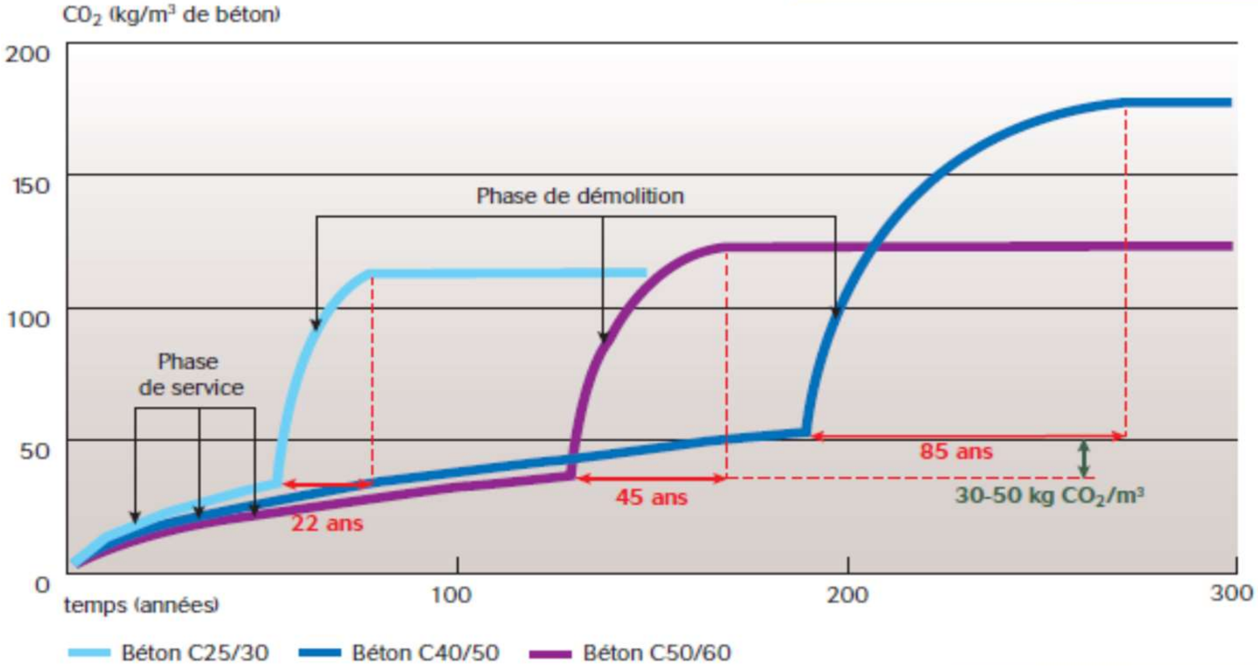
Thermal conductivity: 0,05 to 0,1 W/m.K
Conpressive Strength : 0,1 to 3 MPa

Recarbonatation of demolition concretes





Mécanisme de carbonatation au niveau de la solution interstitielle du béton (IFSTTAR).



Quantité de CO_2 fixée au cours des phases de service et de démolition-exposition pour les trois classes du béton (la taille des granulats est de 10 mm) (N. ROUSSEL).

Stock de bétons de démolition avant traitement.

Remarques:

- **C**apacité de capture du CO_2 par le béton recyclé : de 120 à 180 kg du CO_2/m^3
- La recarbonatation du béton est lente en phase de service et s'accélère en phase de démolition
- L'objectif du projet FASTCARB est d'accélérer la recarbonatation par un procédé intégré sur site en utilisant le CO_2 émis par des cimenteries.

Levers for Ordinary Portland Cement (OPC) production

CO_2 capture, carbonatation & valorization

PROJET FASTCARB ET RECARBONATATION)DES GRANULATS DE BETON RECYCLES (GBR)

UN CERCLE VERTUEUX ENTRE RECYCLAGE, ECONOMIE CIRCULAIRE ET PRODUCTION BAS CARBONE

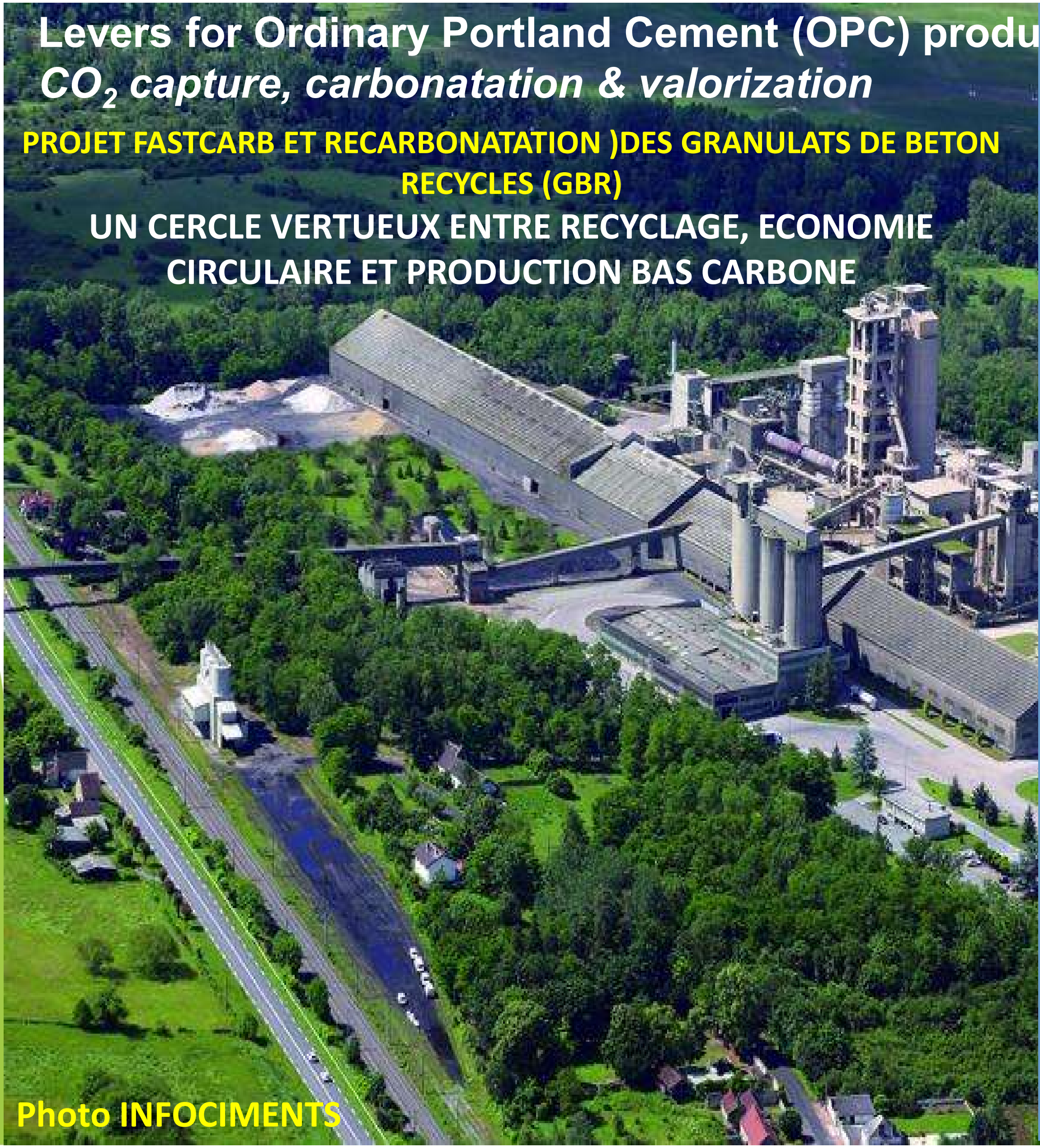
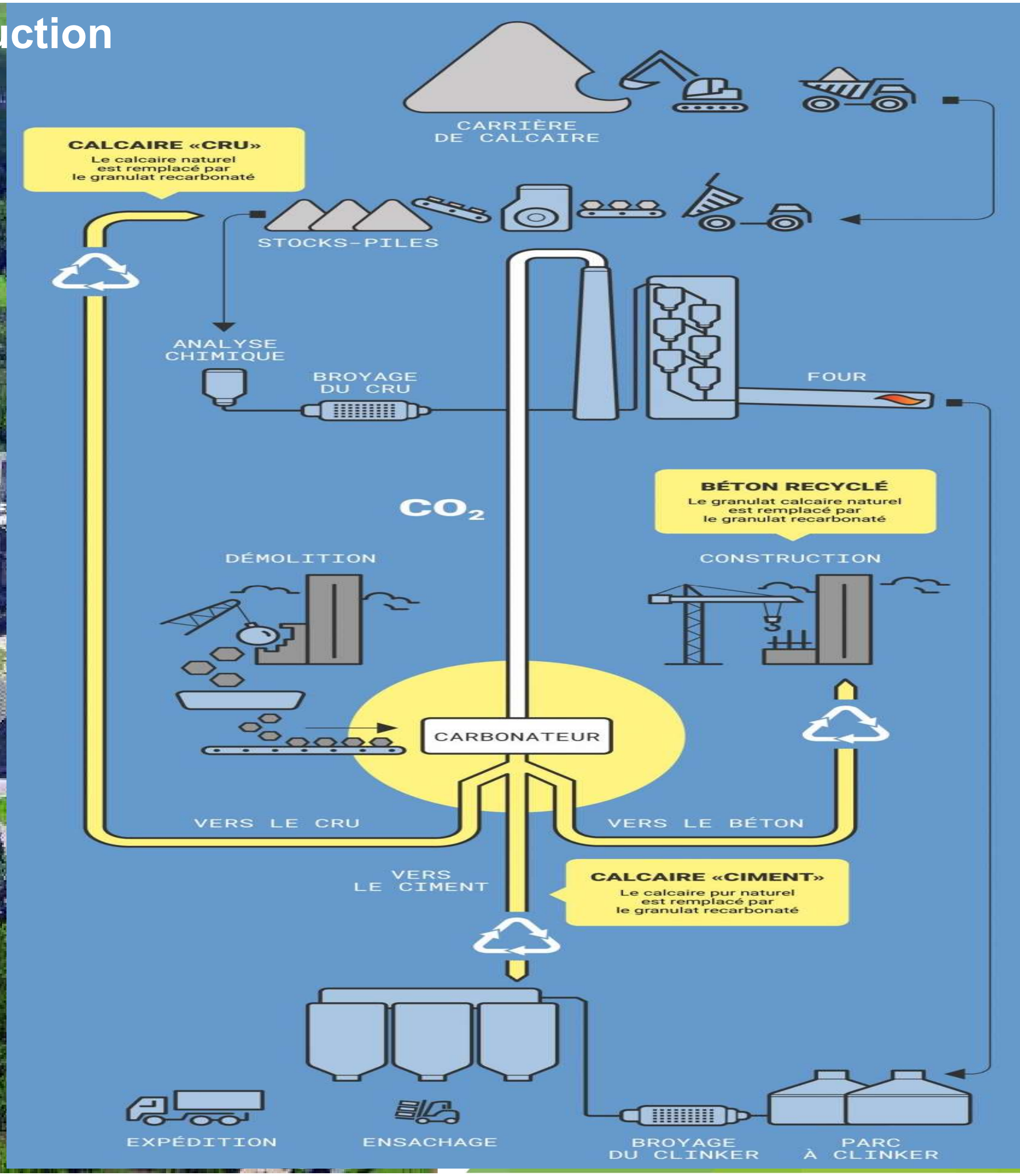
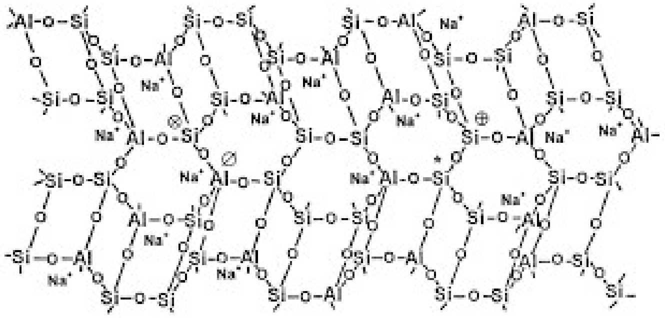


Photo INFOCIMENTS



Geopolymers as alternative binders for concrete making

GEOPOLYMER ALKALIN ACTIVATION (LOW TEMPERATURE)



Raw materials (CMs) for Geopolymers:

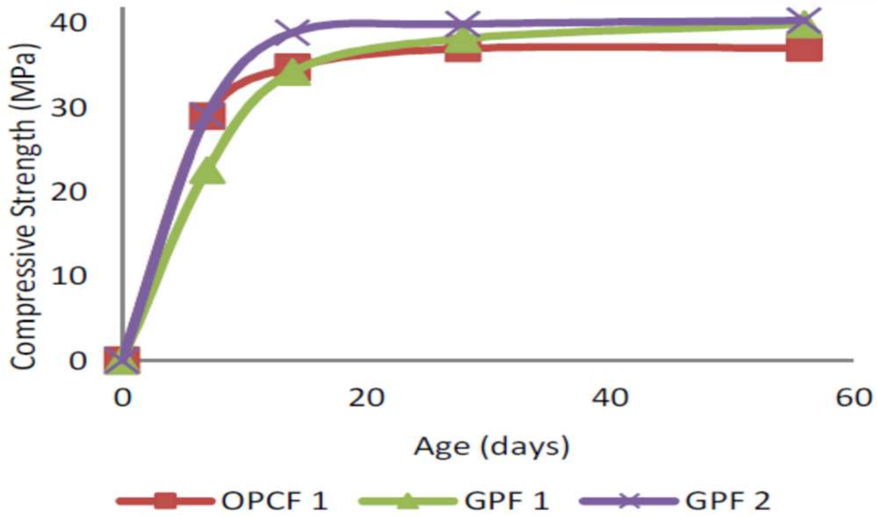
- Fly ash, Vegetable ashes
- Metakaolin
- Blast Furnace Slag
- Red Mud
- Bauxite

Chemical composition of fly ash of power plant

Chemical composition	Percentage (%)
CO_2	0.10
SiO_2	55.80
Al_2O_3	24.20
Fe_2O_3	9.10
K_2O	4.41
CaO	2.46
MgO	1.37
TiO_2	1.34
P_2O_5	0.27
BaO	0.25
Na_2O	0.21
MnO	0.18

Composition of concrete (kg/m³)

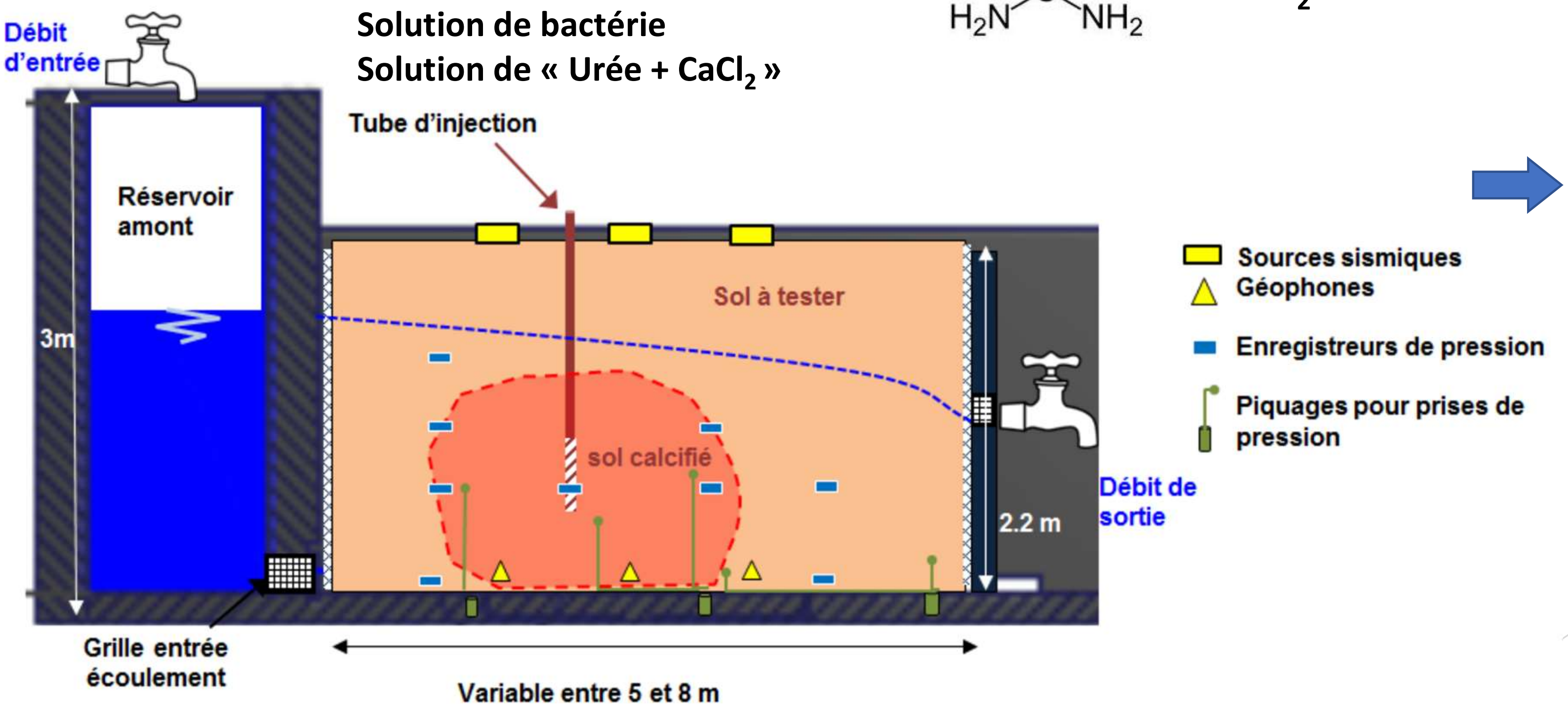
	OPCF1	GPF1	GPF2
OPC	433		
Coarse aggregate	1063	1123	1123
Fine aggregate	708.8	749	749
Fly ash		**372**	**372**
Sodium silicate		**111**	**111**
Sodium hydroxide		**45 (12M)**	**45 (16M)**



Ambient curing of concrete specimens (Lee Yee Loon 2014)

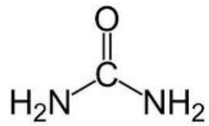
BOREAL, Bio-reinforcement of embankments by biocalcification (2019)_INDURA

STROMATOLITHES CALCIFIES, AUSTRALIE
(@BENCOOPER/LAUNCHPHOTOGRAPHY.COM)



Biocalcification

Bacterie (Sporosarcina pasteurii)



+ $CaCl_2$ + sable ➔ Bio-$CaCO_3$ /Sable

Résistance en compression:
35 MPa max

We don't lack levers to reduce the environmental impact of cements and cementitious materials !

But we need the support of governments, the commitment of industrial actors and public acceptance !

Many thanks for your attention and your participation!