NEWSLETTER September 2013

SEVENTH FRAMEWORK PROGRAMME

The Consortium		
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EDITORIAL

Welcome to the Month 19 edition of the **ECO-CEMENT Newslette**r. We hope this will provide an overview of the development of the project, and encourage you to become engaged with the project by following its progress, or even better by making contact with project partners and keeping in touch with those closest to your areas of interest.

As well as being distributed by email and hard copy, the newsletter is also available as a download from the project website at www.eco-cement.euunder the "newsletter" top-menu item.

We also welcome feedback from anyone interested in our project. Please select the relevant contact person from the list above. If your comment is about the newsletter itself, then please feel free to send your comments to lsanchez@essentium.com and tiano@icvbc.cnr.it

Laura Sánchez
Project Manager, Grupo Essentium

ECOCEMENT CONCEPT

Increased public awareness of the threats posed by global warming has led to greater concern over the impact of anthropogenic carbon emissions on the global climate. The current level of carbon dioxide (CO2) in the atmosphere is approaching 380 ppm 1(particles per million). Without drastic market, technological, and societal changes CO2concentrations are projected to increase to over 800 ppm by the end of the century. Since the pre industrial revolution, both changes in land-use patterns and the intensity of our development activities have had a notable impact on atmospheric CO2 concentrations. The largest source of anthropogenic carbon emissions is from fossil fuel combustion, and energy consumption is rising due to our growing economy's demand for fuel. Non-energy related industrial activities also produce a significant quantity of process-related CO2 emissions through the transformation of raw materials. Of these, cement manufacturing and iron and steel production are the most carbon intensive.Industrial waste is now global concern, causing environmental and economic harm. Industries are rapidly trying to find a solution, searching for optimal ways to manage waste and to change the most common practices as landfill or incineration. Industrial waste is very heavy burden for the environment, where a significant proportion of this industrial waste is attributable to construction and demolition waste.

*I*n order to mitigate the threats mentioned above (greenhouse gas emissions and waste management) ***ECO-CEMENT Project*** will allow recovering valuable resources from industry, capturing carbon dioxide and transforming both products into ecological cement that can be use in construction or novel environmental applications.

The idea is based on the nature's way of creating natural formations through bacterial contribution to carbonate precipitation: extensive sedimentary rock masses as limestone or marble and calcareous sandstone in marine, freshwater and terrestrial environments. Natural carbonation occurs by the reaction between atmospheric CO_2 and alkaline materials, which is called "weathering".The difference of ECO-CEMENT respect to nature principles is that the microbial carbonate precipitation reaction takes a relatively short period of time instead of millions of years.

OBJECTIVE

The main objective of ECO-CEMENT is to develop novel bio-mimetic technology for enzyme-based microbial carbonate precipitation through the revalorization of industrial waste as raw materials, in order to produce eco-efficient environmental cement. The Bio-mimetic Technology will convert industrial waste, mainly cement waste and others by-products, into high strength, ecological cement using microbial carbonate precipitation via urea hydrolysis.

The Ecocement group during the Florence general meeting

SCHEDULED EVENTS IN THE PROJECT

Date	Description	Partners
October 2013		
9th – 11th	Review Meeting - SOST – Brussels (Belgium)	All
March2014		
-	4th General Assembly - G. Essentium. Madrid (Spain)	All
July 2014		
-	Workshop – NEU Pafos (Cyprus)	All

PROJECT DIFFUSION

Conference events in which will be started to diffuse, in specialized scientific areas, the Ecocement concept and the first laboratory results

N°	PARTNERS	Title	Location	Date
1	**CNR - ICVBC**	**SAIE 2013** **International Building Exhibition** http://www.saie.bolognafiere.it/it/	**Bologna (Italy)**	**October 16-19 2013**
2	**To be defined**	**9th International Masonry Conference** http://www.9imc.civil.uminho.pt/	**Guimarães, Portugal**	**July 7-9, 2014**

PROJECT DEVELOPMENTS: ***WP3 - Requirements analysis of microbial process for a suitable and cost-effective Eco-Cement production***
[Work Package 3]

The ECO-CEMENT project is focused in one of the most promising alternatives to produce a Portland cement substitute: the "Microbial induced calcium carbonate precipitation (MICP)" by the use of ureolytic bacteria. These bacteria are widely available in the soil and natural environment, can be easily controlled and have the ability to produce cementation at a comparatively much faster rate.

About 5 % of the global carbon emissions originate from the manufacturing of cement. These emissions are expected to increase strongly throughout the next decades [1]. Also the total amount of industrial waste is a global concern, causing environmental and economic harm. Therefore, industries are searching for optimal solutions regarding their waste management.
To mitigate these threats, the EU project Eco-Cement addresses the recovery of valuable waste resources from industry, capturing CO_2 and transforming both into ecological cement that can be used in construction or novel environmental applications. The Eco-Cement concept is based on natural calcite formation created by bacteria. One aspect of Eco-Cement is to investigate the enzyme based microbial carbonate precipitation through the valorisation of industrial waste, in order to produce eco-efficient environmental cement.
A reduction in the medium costs without loss of urease activity is possible by the substitution of laboratory grade yeast extract with different industrial by-products: *Corn Steep Liquor (CSL); Torula Yeast; Brewery waste yeast (BWY); Sludge Biomass from WWTP, Lactose Mother Liquor (LML); Whey or butter milk (Mazada- Permeado).*
The project research suggests that LML and Mazada can serve as the better ***nutrient source for the growth of the bacteria*** and also for calcite precipitationas the final level of urease activity produced is sufficient for cementation. These materials are a good source of nutrients that can support growth and urease activity of *Sporosarcina Pasteurii*. The availability of this waste is guaranteed by a regular supply and abundance of dairy industries across Europe. ***Using LML or Mazada instead of standard media does not only reduce the cost but also serves as eco-friendly technology to prevent environmental pollution***.
As ***alternative Urea*** we successfully tested a commercial ***fertilizer*** with an average cost of 0.3 €/kg. It is clear that this is not a commercial by-product but it is cheap. Further possible sources coming from the chicken drop matter are under test, even if these could require pre-treatments due to the presence of pathogens, viruses, etc. that increase the overall process cost.
Cement Kiln Dust **(CKD)**, is the ***source of solid alkaline industrial waste in cement plants*** As cement industry waste processing is of crucial significance within the project, different types of cement kiln dust were investigated.
As first step the vitality of *Sporosarcina pasteurii, Bacillus subtilis, and Bacillus megaterium* was tested in the presence of CKD. The results revealed, that only *S. pasteurii* resisted the cement waste CKD.
The bacterial strain *Sporosarcina pasteurii* has demonstrated a high level of urease enzyme activity and to be tolerant to high concentrations of calcium and ammonium ions.
The carbonate precipitation efficiency of this bacterium, via urea hydrolysis, was evaluated by the use of gravimetric analytics and characterized by X-Ray diffraction. The analysis confirmed the presence of mainly calcite crystals. The results also showed that calcite precipitation immediately occurred when calcium chloride was added to the bacterial suspension.

For the experiment the biomass was growth in the classic organic nutrient medium (30 g/L CASO Broth, Sigma Aldrich) enriched with urea (20 g/L, Sigma Aldrich) inoculated with *S. pasteurii* (1.3×10^9 CFU/ml) and let to grow overnight at 30°C under continuously and horizontally shaking (150 rpm).
The bacteria growth was checked using the following methods: optical density at 600nm (OD_{600}) and ATP, while the bacterial urease activity was checked by Nessler assay method (total ammonium content) (Figs. 1 - 2).
The bacterial calcite precipitation was checked using the calcein (10 mg/L, Sigma Aldrich), a fluorescent dye able to bind to the calcite of new formation (Figs. 3, 4).

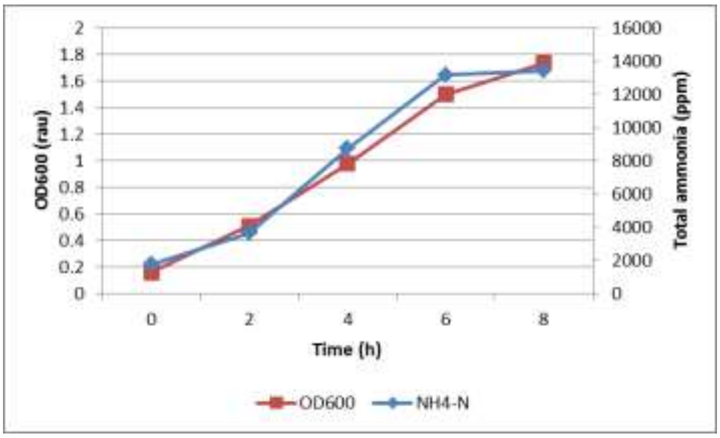

Figure 1: Graph of optical density andtotal ammoniumversus time: representation of the values of ammonium generated by *S.pasteurii* cultures at 330 mM concentration of urea. The initial OD_{600} was 0.0773

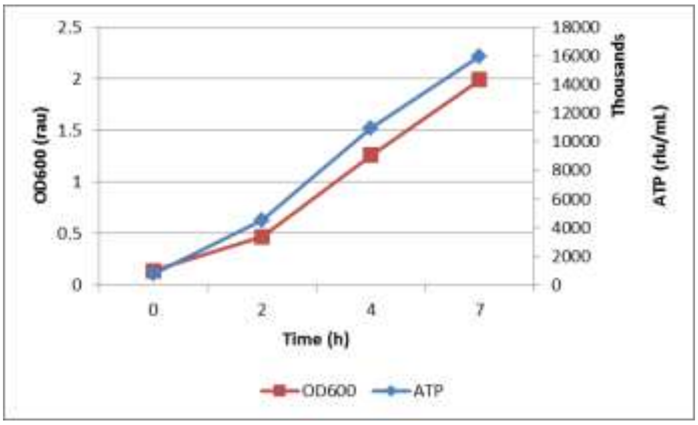

Figure 2: Graph of optical density and ATPversus time: bacterial biomass development in time under optimal conditions (CASO + Urea, 30°C). The initial OD_{600} was 0.1372.

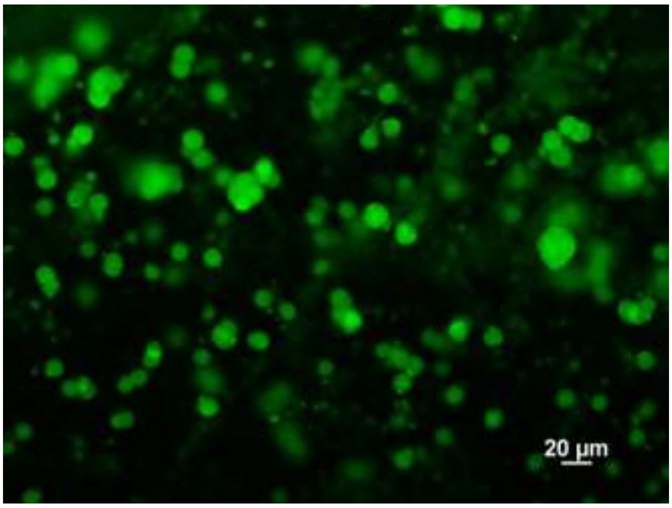

Figure 3: Fluorescence Image of S*. pasteurii* and calcein in the presence of free calcium as calcium chloride

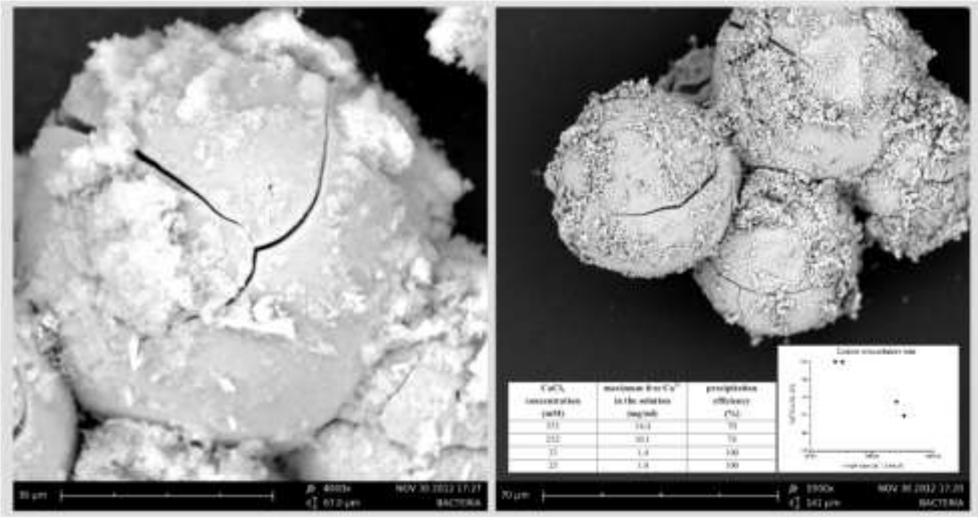

Figure 4 – SEM images of new bioenzymatic calcite

The CKD is the dust which passes out of the top of the preheater with the exhaust gases. In principle, the CKD characteristics suggest its suitability to be reused a calcium source in our project.CKD is produced in all cement kilns; however, the quantity produced is dependent on plant-specific operating conditions. In general, the amount of CKD produced for every 100 tons of clinker can be estimated to be about 9 tons.

Overall, the data examined indicated that there exists no average*Cement kiln dust***.**This highlights the importance of fully characterizing a particular CKD before recommending for its reuse as part of the ECO-CEMENT project. Different samples from different kilns were collected to produce statistically significant results. Preliminary results have evidenced, that not all the samples analysed were suitable, as the calcium found was mainly calcite without CaO and Ca $(OH)_2$(see Table 1).

Waste samples before biocalcification	Table 1: Mineralogical composition by XRD				
	Calcite ($CaCO_3$)	Lime (CaO)	Calcium silicate	Quartz (SiO_2)	Others
CKD1 (Holcim sample B)	-	XX	XX	-	KCl, K_2SO_4, $NaK_3(SO_4)_2$, $CaSO_4$
CKD2 (Holcim sample C)	XXX	-	-	XX	KCl
CKD3 (Bypur)	-	XX	X	X	KCl, K_2SO_4
CKD4 (EGR dust)	XXX	X	-	XX	KCl,
CKD5 (Vassilikos)	XXX	-	-	XX	-

X= traces XX= moderate XXX=abundant

Powder of different types of CKD before and after biocalcification process were analysed with a PAN analytical diffractometer X'Pert PRO with radiation CuK_{a1}= 1,545Å, operating at 40 KV, 30 mA, investigated range 2Θ, 3-70°, equipped with X' Celerator multirevelatory and High Score data acquisition and interpretation software (Tab. 1, Fig. 5).

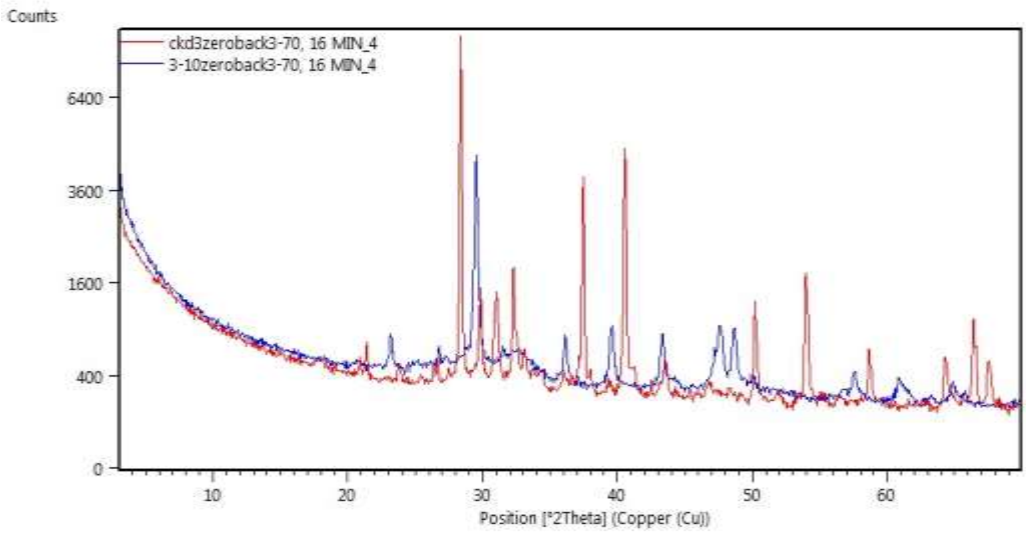

Figure 5: Example of XRD spectra of the CKD3 before and after the bacterial treatment. The graph shows the conversion of the calcium oxide (available calcium ions) into calcium carbonate due to the biocalcification process.

Preliminary biocementation experiments with varying mixtures of bacterial cultures, CKD, calcium sources and hydraulic binders were carried out (Fig. 6) t.

Fig. 6: Preliminary biocementation products

Mechanical tests on the preliminary biocementation “bricks” indicated promisingfeatures for the ecocement products (Fig 7).

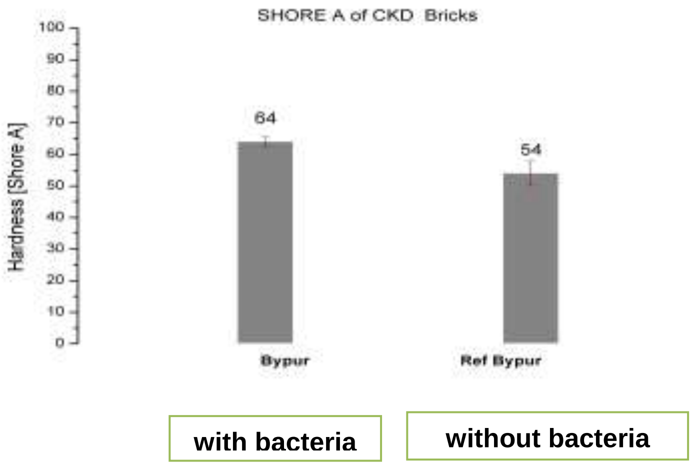

Fig. 7: Results of Shore A measurements of biocementation bricks made with CKD, medium, $CaCl_2$and with/without *S. pasteurii*.

Specific **(KPIs) Bioenzymatic** Key Performance Indicators together with **Energy** KPIs and**Environmental** KPIs have been addressed for determine the LCA of the project and to ensure that the Eco-Cement process is at its most effective (Table 2).

Process KPIs			
11	g CaCO3 / l	g/l	n/a*
12	g CaCO3 / kg Final Product	g/kg	n/a*
13	Biomass / Time Production	kg/hour	n/a*
14	Urea/(Time*Biomass)	kg/(hour*kg)	n/a*
15	Ca2+/Biomass	kg/kg	n/a*
16	Additives/Cement	kg/kg	n/a*
17	Cost Saving for the Recommended Medium	€/€	n/a*
Performance KPIs			
18	Compressive Strength	MPa	20-35 MPa
19	Tensile Strength	MPa	2-5 MPa
20	Flexural Strength	MPa	3.9-5.1 MPa
21	Time to Cure to OPC Strength	Days	28 Days
22	Depth of Cementation	mm	n/a*
Economic KPIs			
23	Cost	€/Tonne	€200 / t
24	Tonnes Cement / Year	Tonne/Year	890,000 t / a
25	Investment Cost Per Tonne/Annum	€/Tonne/Year	€170 / t / a
* No corresponding value for OPC			

Table 2–List of some Key Performance Indicators (from DI 2.23)

The preliminary tests made mixing the bioenzymatic component (bacteria + urea) with cement waste (CKD) have shown the effective feasibility of such kind of process: the precipitation of new biocalcite. The further experiments are undergoing in order to set up the final product: a new eco cement material. In order to improve the strength features of such material an amount of GGBS (Ground Granulated Blast-furnace Slag) or RHA (Rice Husk Ash) will be enclose in the mixture together with some inert such as sand or sepiolite.

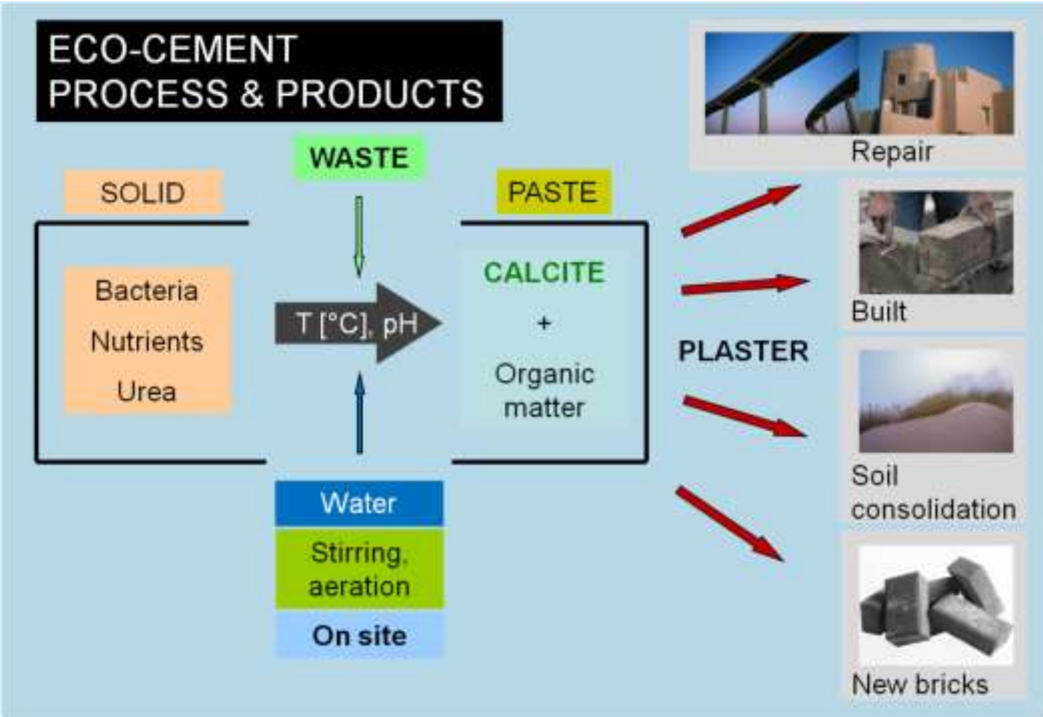

Fig 8: Schematic overview of the Eco-Cement project.