NO_x Adsorption, Fire Resistance and CO_2 Sequestration of High Performance, High Durability Concrete Containing Activated Carbon

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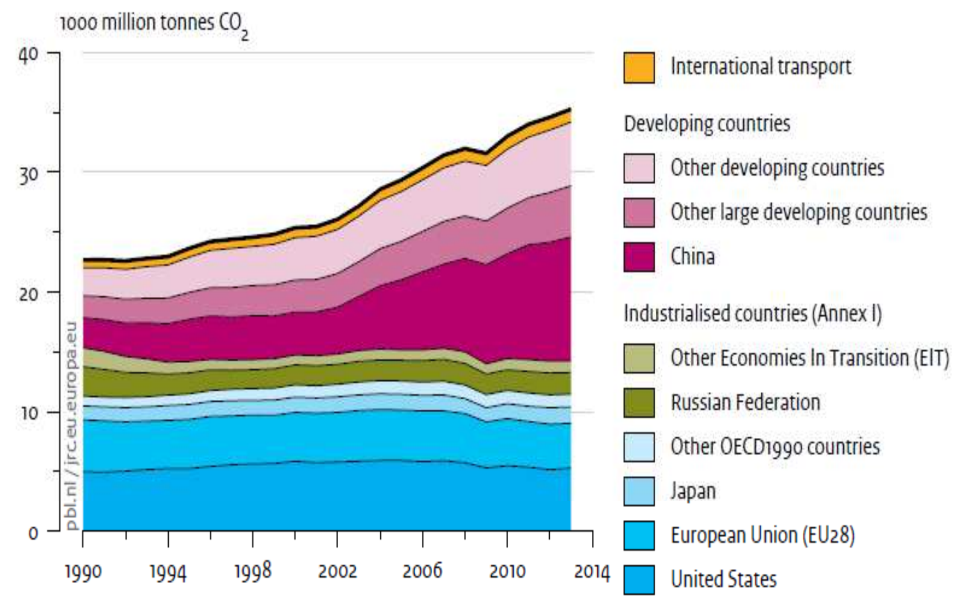
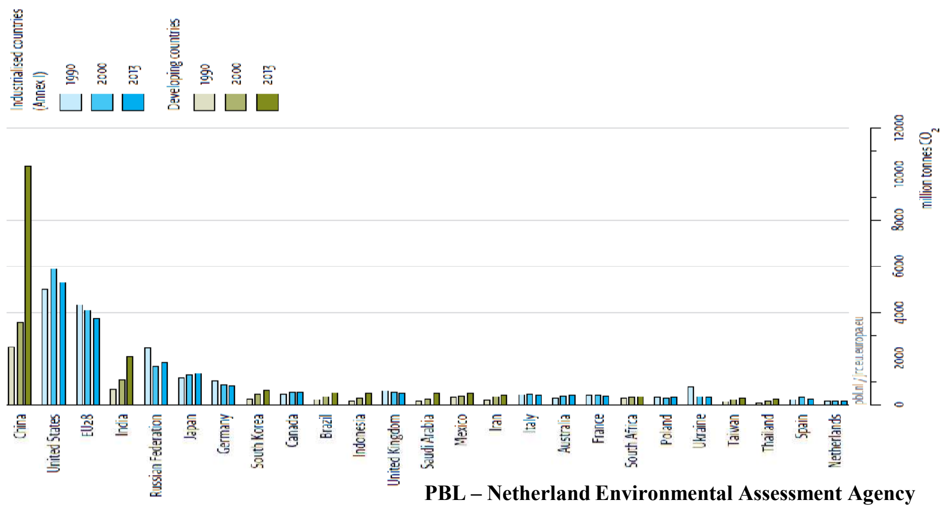
❑FOSSIL FUEL AND CEMENT PRODUCTION ACCOUNT FOR THE MAJORITY OF CO_2 EMISSIONS ON OUR PLANET

❑TODAY'S GLOBAL AVERAGE EMISSIONS RATE FROM CLINKER MANUFACTURING IS 0.9 kg OF CO_2 PER kg OF CLINKER (APPROXIMATELY 0.74 kg OF CO_2 PER kg OF CEMENT)

❑THE WORLD'S CONCRETE PRODUCTION IN 2010 WAS ROUGHLY 19 Gton WITH AN ESTIMATED ANNUAL GROWTH RATE OF ABOUT 10%

❑CONSIDERING THAT 0.130 KG OF CO_2 PER kg OF CONCRETE ARE EMITTED BY THE FINAL PRODUCT THE ANNUAL EMISSION OF CO_2 FOR CONCRETE PRODUCTION IS ESTIMATED AT 2.47 Gton





PBL – Netherland Environmental Assessment Agency

REDUCTION OF CO_2 EMISSIONS FROM THE CEMENT (AND CONCRETE) INDUSTRY ?

1. INTRODUCING INNOVATIVE STRUCTURAL DESIGN, IMPROVING DURABILITY OF STRUCTURES IN ORDER TO EXTEND THEIR SERVICE LIFE
2. USING PRECAST ELEMENTS THAT CAN BE ASSEMBLED/DISASSEMBLED EASILY
3. SPECIFYING SUPPLEMENTARY CEMENTITIOUS MATERIALS (PULVERIZED FUEL ASH - PFA, GROUND GRANULATED BLAST-FURNACE SLAG – GGBS, POZZOLANAS, CALCINED CLAYS, ETC.)
4. ADAPTING STRUCTURAL/DURABILITY AND QUALITY CONTROL REQUIREMENTS ACCORDINGLY
5. USING RECYCLED MATERIALS
6. REDUCING CEMENT DOSAGE
7. UTILIZING THE HEAT CAPACITY OF CONCRETE TO SAVE ENERGY FOR HEATING/COOLING OF BUILDINGS
8. MAKING CONCRETE A CARBON SINK BY INCORPORATING CARBON-BASED (VEGETAL / ANIMAL ORIGIN) COMPOUNDS IN ITS MATRIX THAT WOULD OTHERWISE DECOMPOSE IN AEROBIC ENVIRONMENT TO PRODUCE CO_2

WHAT IS BIO-CHAR?

- ORGANIC MATTER THERMALLY CRACKED BETWEEN 400°C AND 600°C IN ABSENCE OF OXYGEN BY MEANS OF A PYROLYSIS PROCESS → BIO-CHAR

- FEEDSTOCK MATERIAL: WOOD, COCONUT SHELLS, CROPS, ANIMAL WASTE, ETC.

- THE CONTENT OF PURE CARBON (C) IN THE CHAR MAY VARY, GENERALLY IN EXCESS OF 70% OF TOTAL CHAR WITH THE REMAINING % MADE OUT OF ASH CONTAINING SILICON, CALCIUM, IRON AND NEGLIGIBLE AMOUNTS OF ALKALIS (NA + K)

- THE GLOBAL YEARLY QUANTITY OF DEAD WOOD ON OUR PLANET IS ESTIMATED ROUGHLY AT 67 Gton OF BIOMASS, WHICH IS ABOUT 11% OF ALL BIOMASS

- A VAST AMOUNT OF THIS DEAD BIOMASS IS CURRENTLY BURNED IN OPEN AIR, PARTICULARLY IN THIRD WORLD OR DEVELOPING COUNTRIES, LEADING TO LARGE SCALE (REGIONAL) PHENOMENA OF POLLUTING HAZE

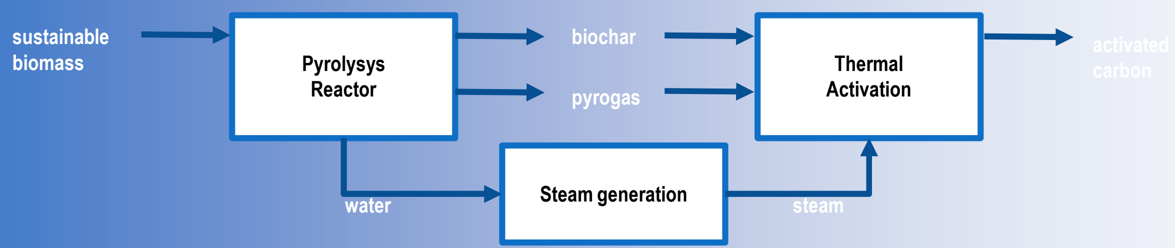
- IT CAN BE ESTIMATED THAT FROM 1.0 ton OF DEAD WOOD MATTER, APPROXIMATELY 0.3 ton OF BIO-CHAR CAN BE PRODUCED

- IF ONLY 1% OF BIO-CHAR (BY MASS OF CONCRETE) WERE INCORPORATED IN CONCRETE, IT CAN BE CALCULATED THAT ROUGHLY 0.5 Gton OF CO_2 WOULD BE SEQUESTRATED YEARLY BY THE CONCRETE SINK CORRESPONDING TO ABOUT 20% OF THE TOTAL CO_2 YEARLY EMISSIONS GENERATED BY THE CEMENT INDUSTRY

THE INCORPORATION OF BIO-CHAR IN CEMENTITIOUS MATERIALS IS A RELATIVELY NOVEL CONCEPT AND RECENT STUDIES FOCUSED MAINLY ON:

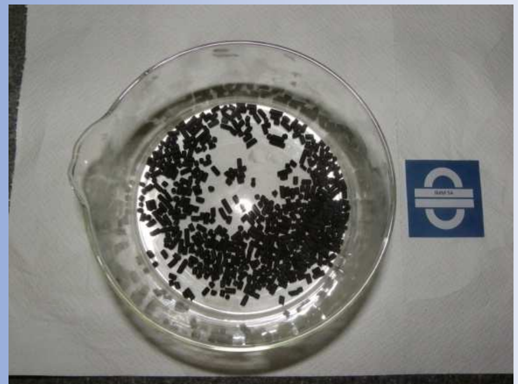
- ❑ASSESSING THE OPTIMUM DOSAGE OF BIO-CHAR IN CONCRETE SO AS NOT TO NEGATIVELY AFFECT ITS MECHANICAL PROPERTIES WHEN CONCRETE IS USED AS A CARBON SINK
- ❑THE EFFECTS OF BIO-CHAR INCORPORATION IN PLASTERS FOR THE CONTROL OF HUMIDITY
- ❑ OTHER RECENT STUDIES AIMED TO DETERMINE THE NO_X ADSORBING PROPERTIES OF CONCRETE MANUFACTURED WITH ACTIVATED CARBON

ACTIVATED CARBON IS THERMALLY-TREATED-IN-PRESENCE-OF-WATER-VAPOR CHAR DERIVING FROM WOOD BIOMASS TO PRODUCE A HIGH SPECIFIC SURFACE (B.E.T > 800 m^2/g) AND HIGHLY POROUS STRUCTURE WITH NOTICEABLE FLUID ADSORBING AND ABSORBING PROPERTIES



PILOT PLANT (A*TTT*EROM Technology®)

PELLETS



MICROSTRUCTURE

THE END PRODUCT (ACTIVATED CARBON) IS WIDELY USED IN AGRICULTURE, IN POLLUTANTS REMOVAL TECHNOLOGIES, IN FILTERING PROCESSES, AIR PURIFICATION SYSTEMS AND IN THE FOOD AND PHARMACEUTICAL INDUSTRY AMONGST OTHERS

THE OBJECTIVE OF THIS RESEARCH:

- DEFINING POSSIBLE BENEFICIAL PROPERTIES OF ACTIVATED CARBON FOR CONCRETE IN TERMS OF ITS ADSORBING/ABSORBING PROPERTIES
- KEEPING IN MIND THE LONG TERM (STABLE) STORAGE POTENTIAL OF CONCRETE STRUCTURES FOR THE CARBON CONTAINED IN THE CHAR

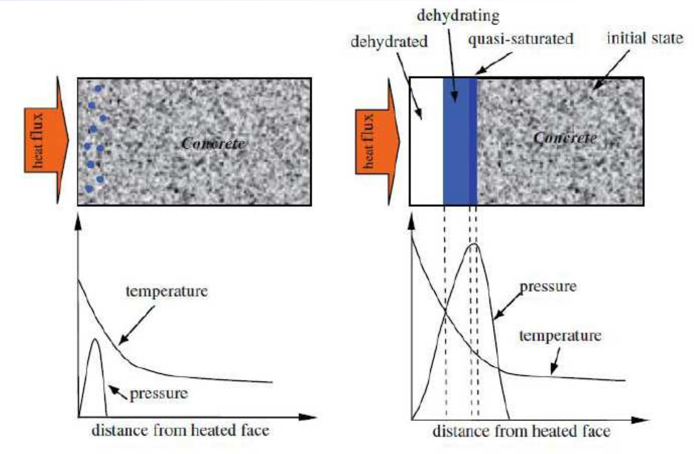
OF PARTICULAR INTEREST:

- ADSORPTION PROPERTIES OF THE ACTIVATED CARBON AND ITS NOTICEABLE NO_x ADSORBING PROPERTIES AS ALREADY DETERMINED BY OTHER RESEARCHERS (Horgnies, M., Serre, F., Dubois-Brugger, I. and Gartner,)

- NO_2 HIGHLY REACTIVE AND HAZARDOUS GAS OF THE NO_X GROUP
- TENDS TO CONCENTRATE IN ROAD TUNNELS
- IN BRIGHT SUNLIGHT AND AT TEMPERATURES ABOVE 21°C PHOTOLYSIS OF NO_2 PRODUCES OZONE (O_3)
- NO, ANOTHER VERY UNSTABLE GAS OF THE NO_X GROUP, CAN IN TURN REACT WITH OXYGEN (O_2 AND O_3) TO FORM NO_2
- DURING RUSH HOUR IN METROPOLITAN TUNNELS, THE CONCENTRATION OF NO_2 CAN BE SEVERAL ORDERS OF MAGNITUDE GREATER THAN THE CONCENTRATION LIMIT SET BY THE EPA IN 2010, THAT OF 100 PPB (1PPB = 0.1 PPM)

OF PARTICULAR INTEREST:

❑WATER VAPOR ADSORPTION BY CHAR PARTICLES COULD DISSIPATE SOME OF THE INTERNAL VAPOR PRESSURE DEVELOPED DURING EXPOSURE OF CONCRETE TO FIRE WHICH CAUSES DISRUPTIVE SPALLING



- WATER IN THE CONCRETE COVER REACHES THE BOILING POINT DURING FIRE
- WATER VAPOUR MIGRATES INWARDS
- GAS MIGRATION STOPS WHEN WATER WITHIN THE CONCRETE IS STILL IN LIQUID FORM (MOISTURE CLOG)
- INTERNAL PRESSURE BUILDS UP WITHIN FIRST cm FROM SURFACE
- WHEN PRESSURE EXCEEDS TENSILE STRENGTH OF CONCRETE SPALLING OCCURS
- REBARS ARE EXPOSED AND MAY YIELD LEADING TO STRUCUTRAL INSTABILITY

- POLYPROPILENE (PP) FIBERS HAVE BEEN LONG USED TO PREVENT SPALLING
- MELT/SUBLIMATION AT ~160°C – 170°C LEAVES CONNECTED CAPILLARITY
- VAPOUR CAN ESCAPE
- PRESSURE IS RELIEVED

THE GENERAL IDEA:

IF CONCRETE CONTAINING ACTIVATED CARBON WERE EXPOSED TO A NO_X POLLUTED ENVIRONMENT OF A ROAD TUNNEL, IT COULD NOT ONLY IMPROVE THE FIRE RESISTANCE OF THE CONCRETE LINING, BUT IT WOULD PROVIDE THE REDUCTION OF HAZARDOUS GASES SUCH AS NO_2 PRODUCED BY VEHICLES

- WE COMPARED PROPERTIES OF A C50/60 XF4, XC4, XD3, XA3 (ACCORDING TO EN 206-1 STANDARD) FIRE RESISTING CONCRETE MIX (WITH PP FIBERS) USED FOR THE CONSTRUCTION OF THE VIADUCTS OF THE HIGH SPEED RAILWAY SYSTEM IN SWITZERLAND (ALPTRANSIT PROJECT)

- A REFERENCE MIX WAS CAST WITH AND WITHOUT ACTIVATED CARBON

- WHEN ACTIVATED CARBON WAS USED, PP FIBERS WERE OMITTED FROM THE MIX

THE FOLLOWING PROPERTIES WERE COMPARED WITH VARYING DOSAGES OF ACTIVATED CARBON:

- COMPRESSIVE (CUBE) STRENGTH AND TENSILE STRENGTH
- ELASTIC MODULUS
- FREEZE-THAW RESISTANCE
- CHLORIDE DIFFUSION
- CAPILLARY PERMEABILITY
- SULPHATES RESISTANCE
- ACCELERATED CARBONATION
- FIRE RESISTANCE (SPALLING DEPTH AND TEMPERATURE PROFILES)
- NO_X ADSORPTION TESTS

THE MIX DESIGN
(patent 9646 CH 01)

Component	Dosage	% By mass of concrete
	Reference mix	Comparative mix
CEM II / A-D 52.5R	350 kg/m³	16.5%
Pulverized Fuel Ash	40 kg/m³	--
HRSP*	--	1.27%
Activated Carbon (AC)	--	0.48% /1.06% /1.43%
Superplasticizer	4.9 kg/m³	0.33%
Air Entrainer	0.14 kg/m³	0.01%
PP fibers	2.0 kg/m³	--
Silceous-Calcareous CA - Ø $_{max}$ 32 mm	270 kg/m³	3.45%
Silceous-Calcareous CA - Ø max 16 mm	684 kg/m³	32.9%
Silceous-Calcareous CA - Ø max 8 mm	576 kg/m³	18.5%
Silceous-Calcareous FA - Ø max 4 mm	268 kg/m³	13.6%
Entrained air	4%	8% ÷12%
Free water – W/C	165 kg/m³ – 0.41	5.9% - 0.33

HIGHLY REACTIVE SILICEOUS POZZOLANIC COMPOUND

TEST RESULTS

Concrete requirements C50/60 XF4, XD3, XC4					
	Comparative mix			Reference mix	
Parameter	0.48% AC	1.06% AC	1.43% AC		Limits
Elastic Modulus (SIA 262/1 - G) [MPa]	41800	41300	41900	40400	--
Flexural Strength (SN EN 12390-5) [MPa]	5.0	5.4	5.4	4.9	--
Shrinkage (364-day) (SIA262/1-F) [με]	419	452	458	423	--
Freeze - Thaw Resistance (SIA262/1-C) [g/m²]	200	70	80	40	$\leq$ 200
Resistance to Chlorides Penetration (SIA 262/1 - B) [m²/s]	$2.3 \cdot 10^{-12}$	$2.2 \cdot 10^{-12}$	$1.7 \cdot 10^{-12}$	$3 \cdot 10^{-12}$	$\leq 10 \cdot 10^{-12}$
Absorption by Capillarity (SIA 262/1-A) [g/(m²·h)]	6.8	4.5	4.2	5.7	$\leq$ 10
Resistance to sulphates (SIA 262/1-D) [‰]	0.36	0.31	0.46	0.32	$\leq$ 1.2
7-day Compressive Strength (SN EN 12390-3) – [MPa]	52.3	51.3	53.0	50.0	--
28-day Compressive Strength (SN EN 12390-3) – [MPa]	71.8	65.8	61.8	65.3	$\geq$ 64
Coefficient of carbonation (SIA 262/1-I) - [mm/√year]	--	1.38	--	--	$\leq$ 4.5

FIRE TESTS

SEVERAL FACTORS AFFECT THE EXPLOSIVE SPALLING OF CONCRETE:

- HEATING RATE AND PROFILE
- SECTION SIZE AND SHAPE
- MOISTURE CONTENT
- PERMEABILITY
- AGE
- STRENGTH
- COMPRESSIVE STRESS BEFORE AND DURING HEATING
- RESTRAINT TO THERMAL EXPANSION
- AGGREGATE TYPE AND SIZE
- CRACKING
- REINFORCEMENT

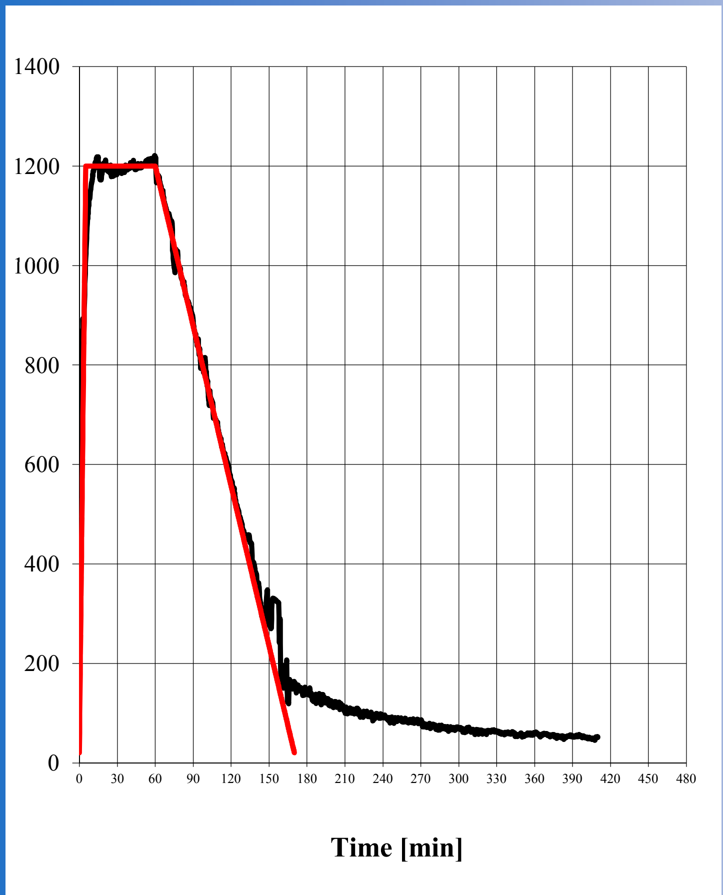
TWO SEPARATE FIRE TESTS WERE CONDUCTED BY EFECTIC NETHERLANDS UNDER DIFFERENT CONDITIONS

- RABT FIRE CURVE FOR RAILWAYS
- NO RESTRAINT TO THERMAL EXPANSION
- SMALL VOLUME (0.6 X 0.6 X 0.4 m^3)
- NO REINFORCEMENT

- RABT FIRE CURVE FOR RAILWAYS
- RESTRAINT TO THERMAL EXPANSION
- LARGER VOLUME 1.2 X 1.2 X 0.3 m^3)
- REINFORCEMENT (ø 16 mm, S = 150 mm, C = 60 mm)

- RABT ZTB (RAILWAYS) FIRE CURVE
- NO RESTRAINT TO THERMAL EXPANSION
- SMALL VOLUME (0.6 X 0.6 X 0.4 m^3)
- NO REINFORCEMENT

- C50/60
- Air: 7%



Exposed face before fire

Exposed face after fire

PARAMETER	VALUE/RESULT
Age (days)	35
Moisture content (%)	3.9
T @ 60 mm depth @ 45 minutes (°C)	128
Maximum spalling depth (mm)	22

- RABT ZTB (RAILWAYS) CURVE
- RESTRAINT TO THERMAL EXPANSION
- LARGER VOLUME (1.2 X 1.2 X 0.3 m^3)
- REINFORCEMENT (ø 16 mm, S = 150 mm, C = 60 mm)

- C30/37
- Air: 11%

The frame

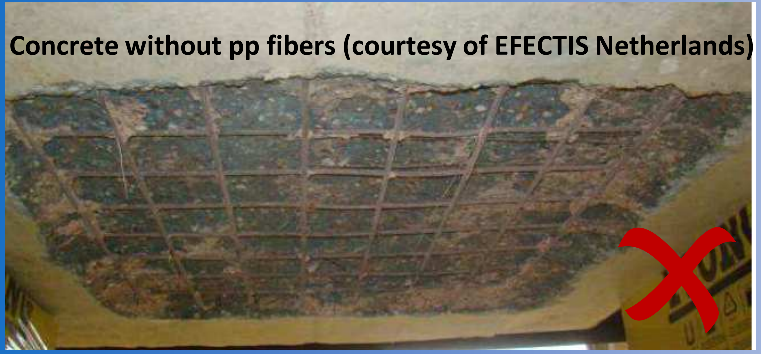
Exposed face

- RABT ZTB (RAILWAYS) CURVE
- RESTRAINT TO THERMAL EXPANSION
- LARGER VOLUME (1.2 X 1.2 X 0.3 m^3)
- REINFORCEMENT (ø 16 mm, S = 150 mm, C = 60 mm)

- C30/37
- Air: 11%

Exposed face at the end of the fire test

After 24 hr. from the end of the fire test



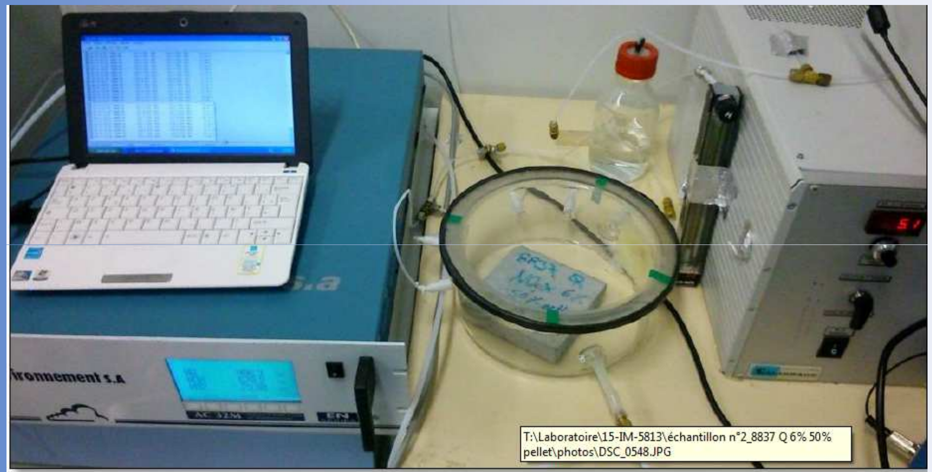
Concrete without pp fibers (courtesy of EFECTIS Netherlands)

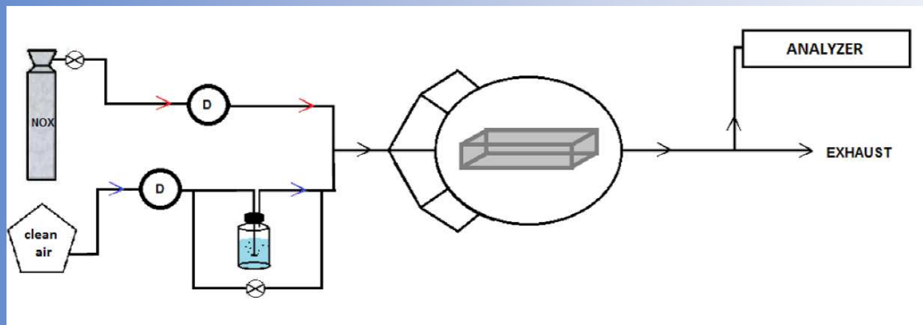
PARAMETER	VALUE/RESULT
Age (days)	44
Moisture content (%)	<3%
T @ 60 mm depth @ 45 minutes (°C)	200
Maximum spalling depth (mm)	20

NO_X ADSORPTION TEST

PERFORMED BY TERA ENVIRONMENT LABS IN FRANCE FOLLOWING THE PROCEDURE OUTLINED IN:

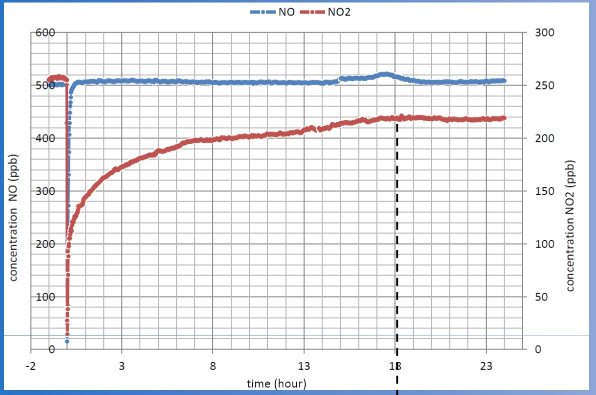
Horgnies, M., Serre, F., Dubois-Brugger, I. and Gartner, E. ***NOx de-pollution using activated carbon concrete – From laboratory experiments to tests with prototype garages*****. Proceedings of the 4th International Conference on Environmental Pollution and Remediation (2014) 65.**





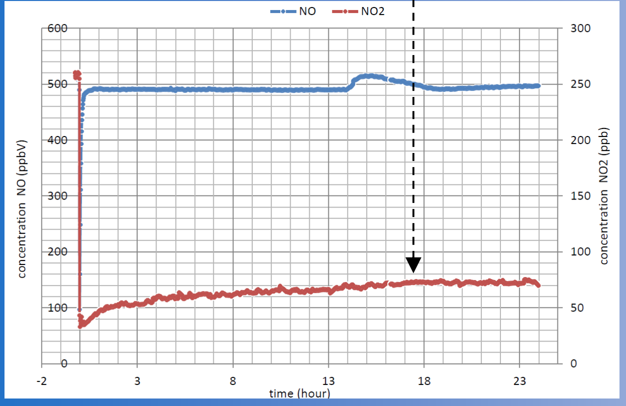
NOx ADSORPTION TEST

Without activated carbon



	Average upstream concentration	Average downstream concentration
NO_2 (ppb)*	256	219
NO (ppb)	500	509

With activated carbon



	Average upstream concentration	Average downstream concentration
NO_2 (ppb)*	258	73
NO (ppb)	510	496

*1ppb NO_2 =1.88 µg/m³

CONCLUSIONS

- ACTIVATED CARBON AS PRODUCED FROM THERMAL CRACKING OF BIOMASS HAS A HIGH SPECIFIC SURFACE AND POROUS STRUCTURE WITH NOTICEABLE FLUID (GAS AND LIQUID) ADSORBING/ABSORBING PROPERTIES

- ADDITION OF ACTIVATED CARBON TO HIGH PERFORMANCE CONCRETE IN OPTIMAL DOSAGES HAS NO EFFECT ON ITS PERFORMANCE, BOTH IN THE FRESH AND HARDENED STATE

- THE FIRE RESISTANCE OF A PATENTED HIGH PERFORMANCE CONCRETE MIX USING CALCAREOUS/SILICEOUS AGGREGATES, FREE WATER/CEMENT RATIO OF 0.33, 8÷11% ENTRAINED AIR, WITH AN HIGHLY REACTIVE SILICEOUS POZZOLANIC COMPOUND AND 1.06% ACTIVATED CARBON BY MASS OF CONCRETE, HAD VERY LIMITED SPALLING IN A FIRE TEST CONDUCTED WITH THE RABT - ZTV (RAILWAYS) FIRE CURVE

- NO STEEL REINFORCEMENT WAS EXPOSED DURING THE FIRE TEST WITH RESULTS COMPARABLE TO THOSE ONES OBTAINED WHEN CONVENTIONAL PP FIBERS ARE ADDED TO THE CONCRETE MIX

- THE NO_X ADSORBING PROPERTIES OF CONCRETE CONTAINING 1.06% ACTIVATED CARBON BY MASS OF CONCRETE HAVE BEEN INVESTIGATED, SHOWING THE EFFECT OF SUCH A CONGLOMERATE IN DRAMATICALLY DECREASING THE CONCENTRATION OF NO_2 IN THE TEST CHAMBER

- BECAUSE CONCRETE IS THE MOST WIDELY USED MATERIAL ON THE PLANET AND BECAUSE ACTIVATED CARBON IS INERT IN RESPECT OF ATMOSPHERIC OXYGEN, INCORPORATION OF 1% OF THIS MATERIAL IN CONCRETE COULD PERCEIVABLY LOWER THE CARBON FOOTPRINT OF CONCRETE, LEADING TO A MARKET OF TRADABLE CARBON CREDITS ON THE ORDER OF TENS OF BILLION OF DOLLARS IN THE NEXT DECADES

- OUR ONGOING RESEARCH IN THIS FIELD IS PRESENTLY TARGETING THE FIRE RESISTANCE (SPALLING DEPTH AND TEMPERATURE AT THE REINFORCEMENT) OF REINFORCED CONCRETE WITH ACTIVATED CARBON UNDER RESTRAINED CONDITIONS AND LONG TERM AND LARGER SCALE NO_X ADSORPTION TESTS TO CALCULATE A STEADY STATE COEFFICIENT OF ADSORPTION OF AIR POLLUTANTS FOR THE DESIGN OF A POLLUTION-ADSORBING CONCRETE LINING FOR ROAD TUNNELS

Thank you !