



Valorization of stainless steel slag Zero Waste Concept

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SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT



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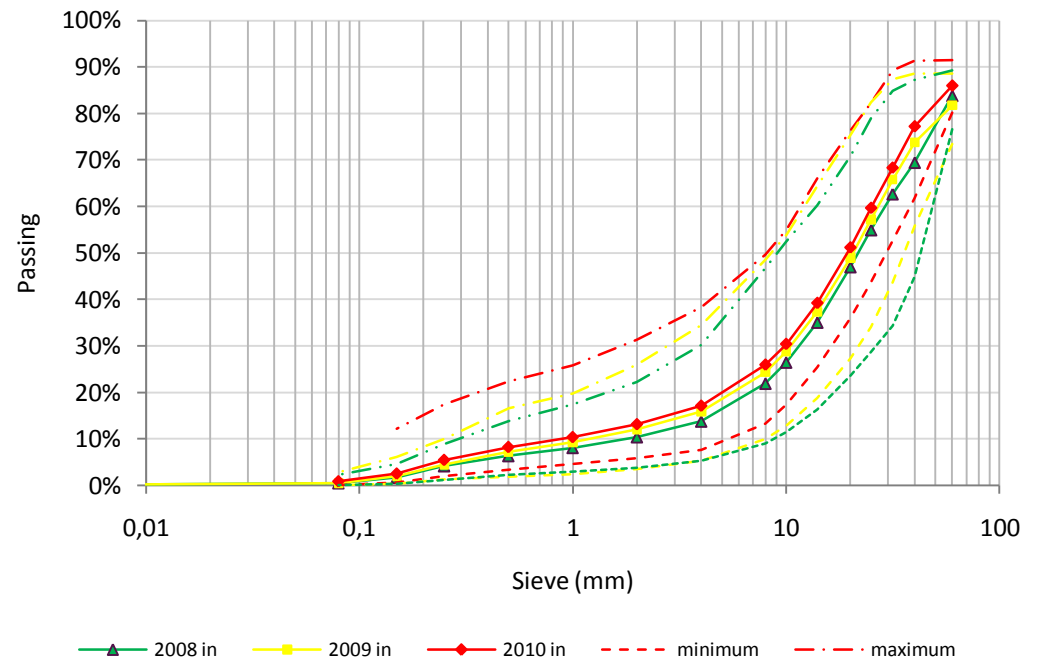
Valorisation of stainless steel slag



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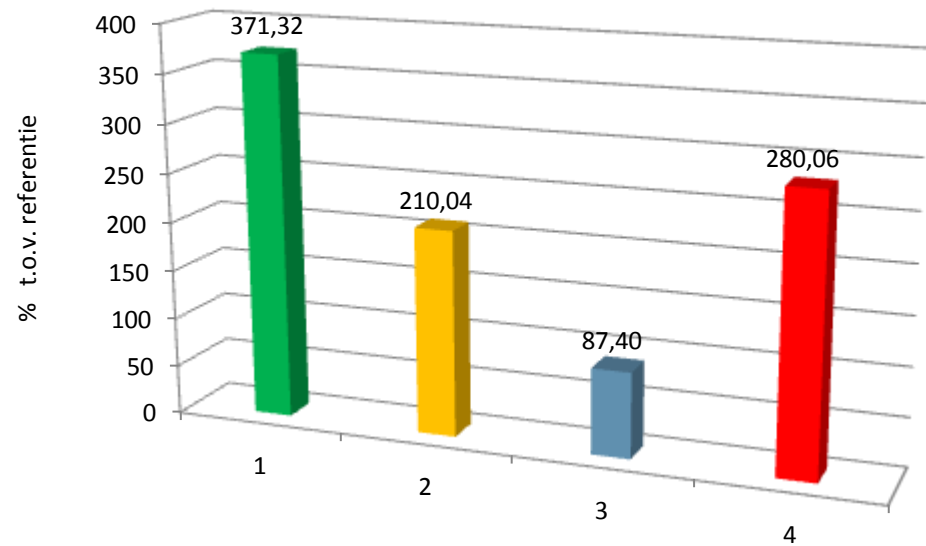
Valorisation of stainless steel slag

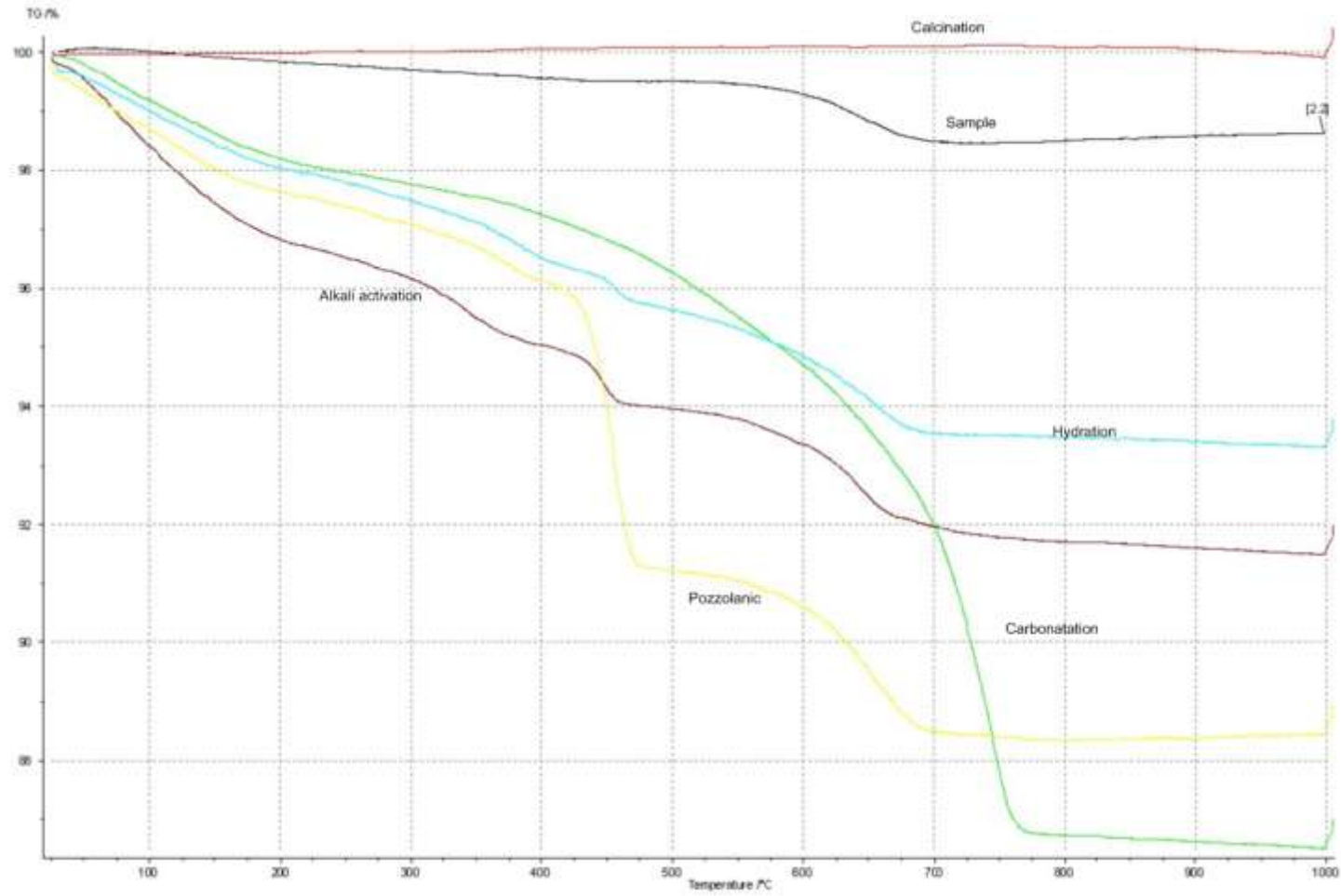


RECMIX

9

Binding capacity (% t.o.v. referentie)		Papieras Oudergem EC1	Referentie
1. Carbonatation	CaO _{eq} verbruikt	371,32	LD slak
2. Pozzolanic	H ₂ O _{C-S-H}	210,04	Tras (Mendig)
3. Hydratation	H ₂ O _{C-S-H}	87,40	CEM I
4. Alkali activation	H ₂ O _{C-S-H}	280,06	Orcem slak



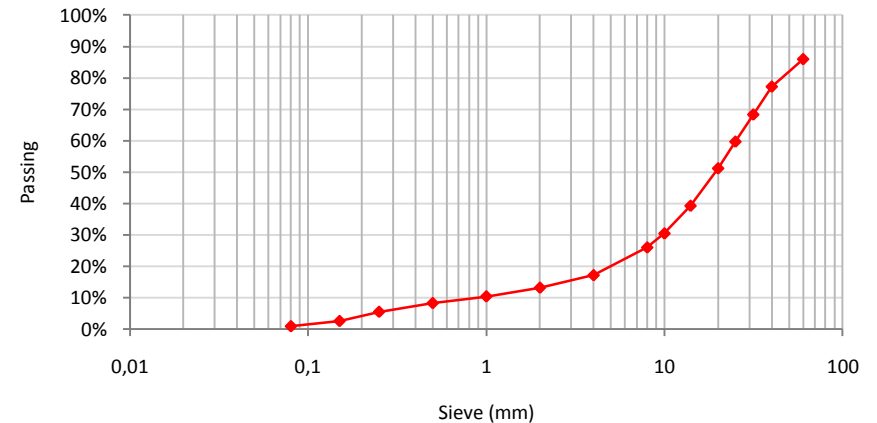
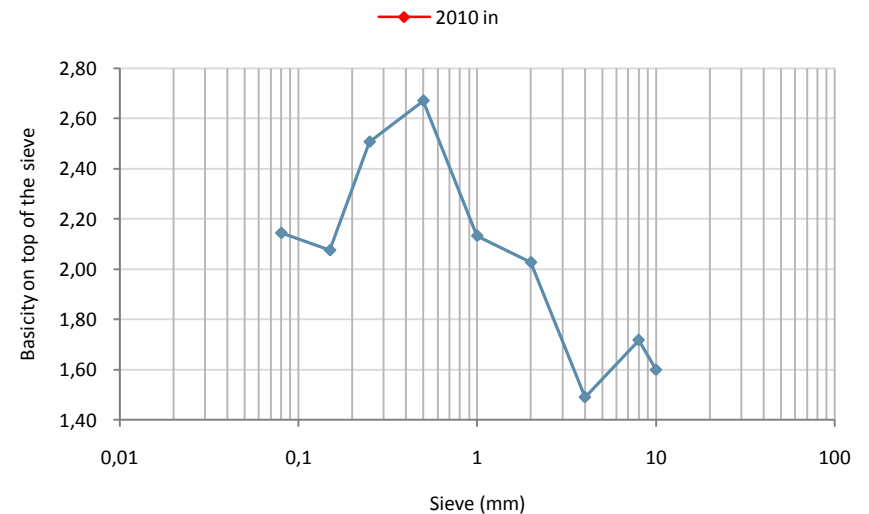


Slag: grain size – [CaO]/[SiO₂]



Sieve (mm)	(%)	CaO (%)	SiO ₂ (%)	[CaO]/[SiO ₂] (%)
10	69,60	43,49	27,20	1,60
8	74,00	42,83	24,93	1,72
4	82,90	42,83	28,74	1,49
2	86,80	42,83	21,13	2,03
1	89,60	43,42	20,36	2,13
0,5	91,80	42,99	16,10	2,67
0,25	94,50	47,44	18,93	2,51
0,15	97,50	51,87	25,00	2,07
0,08	99,10	57,50	26,82	2,14
0,001	100,00	54,82	27,01	2,03

$$\sum \frac{[CaO]}{[SiO_2]} = 1,70$$

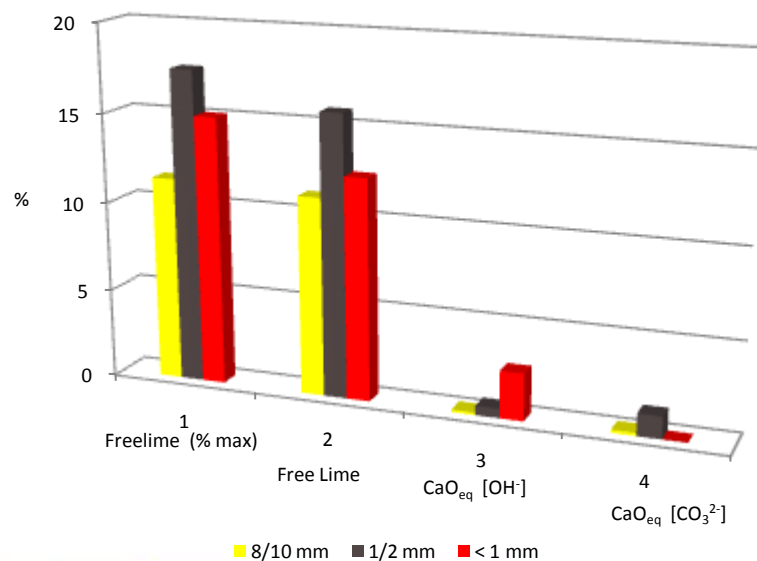
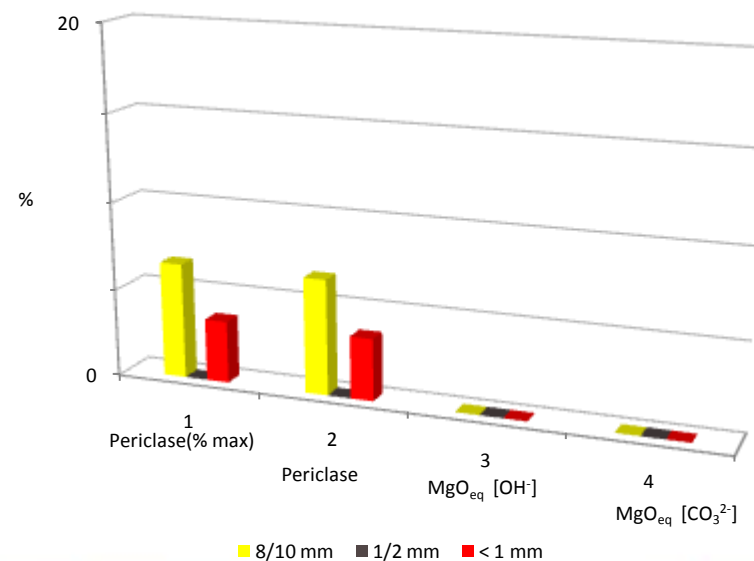


Material characterization	8/10 mm	1/2 mm	< 1 mm
SiO ₂ (%)	24,93	20,36	27,01
Fe ₂ O ₃ (%)	1,26	6,09	0,25
CaO (%)	42,82	43,42	54,82
MgO (%)	2,40	6,01	5,03
Al ₂ O ₃ (%)	3,49	4,69	0,00
Reactivity			
$\frac{([CaO] + [MgO] + [Al_2O_3])}{[SiO_2]}$ Din spec. > 1	1,95	2,66	2,22
$\frac{([CaO] + [MgO])}{[SiO_2]}$ EU spec. > 1	1,81	2,43	2,22
$\frac{([CaO] + 0,5 [MgO] + [Al_2O_3])}{[SiO_2]}$ Keil > 2,5	1,91	2,51	2,12
$20 + [CaO] + 0,5 [MgO] + [Al_2O_3] - 2[SiO_2]$ J.Cleret D'Langavant > 20	17,65	30,40	23,32

Slag: reactivity



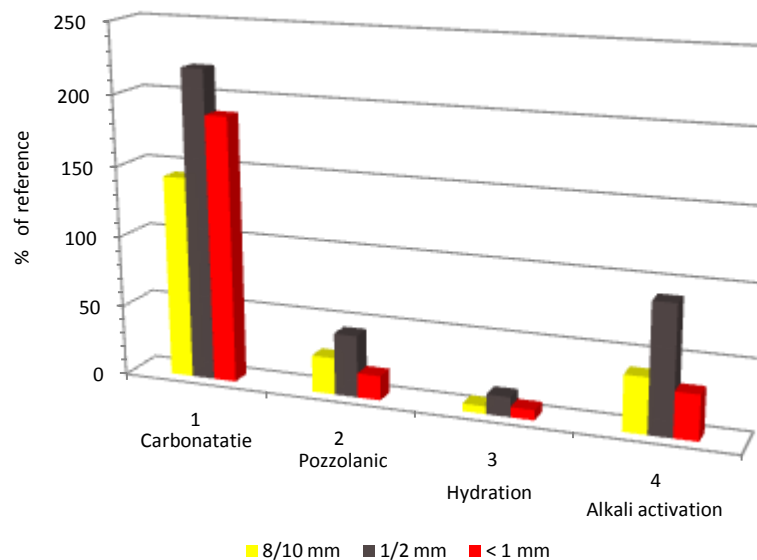
Material characterization	8/10 mm	1/2 mm	< 1 mm
Amorph (%)	11,31	12,56	13,98
Free Lime (% max.)	11,43	17,55	15,04
Free Lime (%)	11,11	15,77	12,39
CaO _{eq} (OH ⁻)	0,14	0,53	2,65
CaO _{eq} (CO ₃ ²⁻)	0,18	1,25	0,00
Free MgO (% max.)	6,58	0,00	3,54
Free MgO (%)	6,58	0,00	3,54
MgO _{eq} (OH ⁻)	0,00	0,00	0,00
MgO _{eq} (CO ₃ ²⁻)	0,00	0,00	0,00



Slag: binder capacity

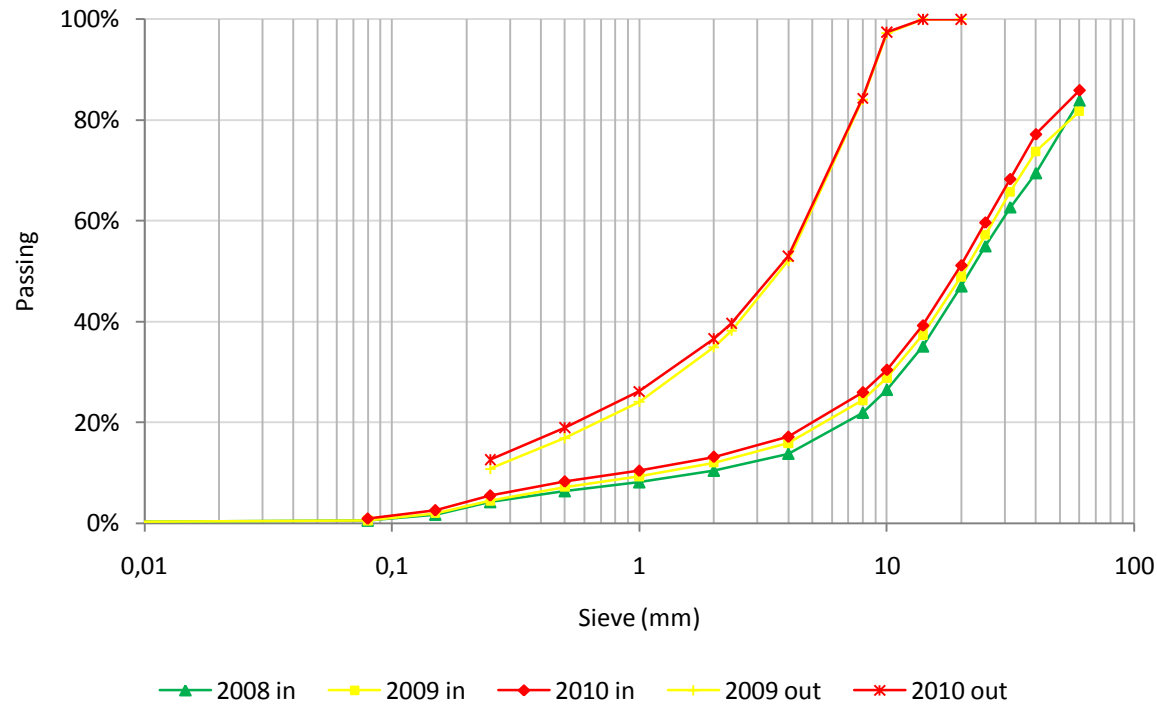


Binder capacity	% of reference 8/10 mm	% of reference 1/2 mm	% of reference < 1 mm	Reference
1. Carbonatation (CaO_{eq} used)	142,92	219,38	187,96	LD slag (1 mm)
2. Pozzolanic ($\text{H}_2\text{O}_{\text{C-S-H}}$ strength devel.)	26,05	43,70	17,23	Tras (Mendig)
3. Hydration ($\text{H}_2\text{O}_{\text{C-S-H}}$ strength devel.)	5,42	13,99	7,17	Cem I
4. Alkali activation ($\text{H}_2\text{O}_{\text{C-S-H}}$ strength devel.)	39,20	90,34	31,82	GBS (NI)

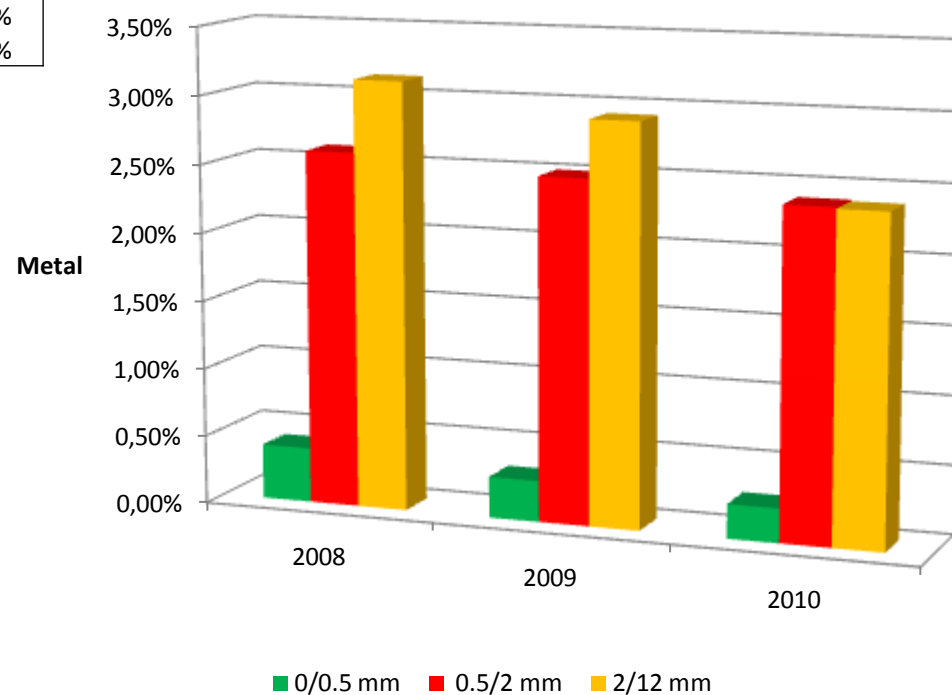




Valorisation of stainless steel slag: Stinox



	Metal	2008	2009	2010
Stinox aggregate (2008: 2/12 mm) (2009-2010: 2/10 mm)	Free	0,03%	0,02%	0,01%
	Bounded	3,10%	2,90%	2,37%
	Total	3,13%	2,92%	2,38%
Sand				
0,5/2 mm	Total	2,60%	2,50%	2,39%
0/0,5 mm	Total	0,40%	0,30%	0,25%



Stinox: chemical composition, physical characteristics

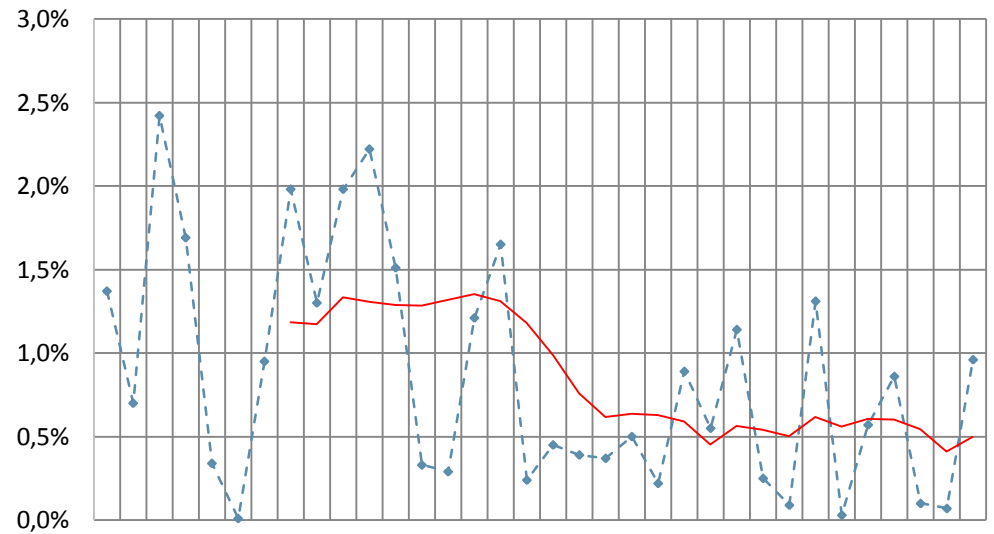


	Minimum (%)	Maximum (%)
CaO	42,0	50,0
SiO ₂	25,0	32,0
MgO	9,0	13,0
Al ₂ O ₃	1,6	5,0
Cr ₂ O ₃	1,1	6,0
Fe ₂ O ₃	0,6	6,0
MnO	0,6	1,9
TiO ₂	0,5	1,6
Na ₂ O	0,0	0,6
Free CaO	0,05	2,40
Periclase	0,32	1,54

	Minimum	Maximum
Organic substances (%)	0	0,4
Loss on ignition (%; 1000 °C)	0	6,5
Bulk density (kg/dm ³)	3,1	3,3
Water absorption (%)	1	3,5
Shape Index (%)	0,52	0,55
Swelling (%)	0	1
MDE (%)	7	11
LA (%)	15	20
PSV (%)	53	78



Swelling: 30/10/2010 - 15/03/2011



- Shaking test (DIN 38414-S4)
  - Particle size < 10mm
  - Demineralised water (pH = 7)
  - L/S = 10
  - 5rpm
  - 24h



- Column test (NEN 7343)
  - Particle size $< 4\text{mm}$
  - Acidified demineralised water ($\text{pH} = 4$)
  - $\text{L/S} = 10$
  - $\sim 3\text{weeks}$



Stinox: leaching behaviour



DIN

Libelle	Stinox 2/14	Stinox 2/14
Parameters (mg/L)		
As	< 0,005	< 0,005
Al	13,8	10,2
Sb	< 0,009	< 0,009
B		
Ba		
Cd	< 0,0012	< 0,0012
Co	< 0,001	< 0,001
Cr	0,199	0,019
Cr6+	0,143	0,011
K	< 1,2	1,21
Cu	< 0,0025	< 0,0025
Hg	< 0,0001	< 0,0001
Mo	0,113	0,169
Na		
Pb	< 0,006	< 0,006
Ni	< 0,005	< 0,005
Se	< 0,005	< 0,005
Sn		
Ti	< 0,003	< 0,003
V	0,007	0,009
Zn	< 0,006	< 0,006
F ⁻	8,49	8,71
Cl ⁻	1,7	4,9
Br ⁻	< 0,05	< 0,05
SO ₄ ²⁻	1,14	0,37
CN ⁻	< 0,0024	< 0,0024

NEN

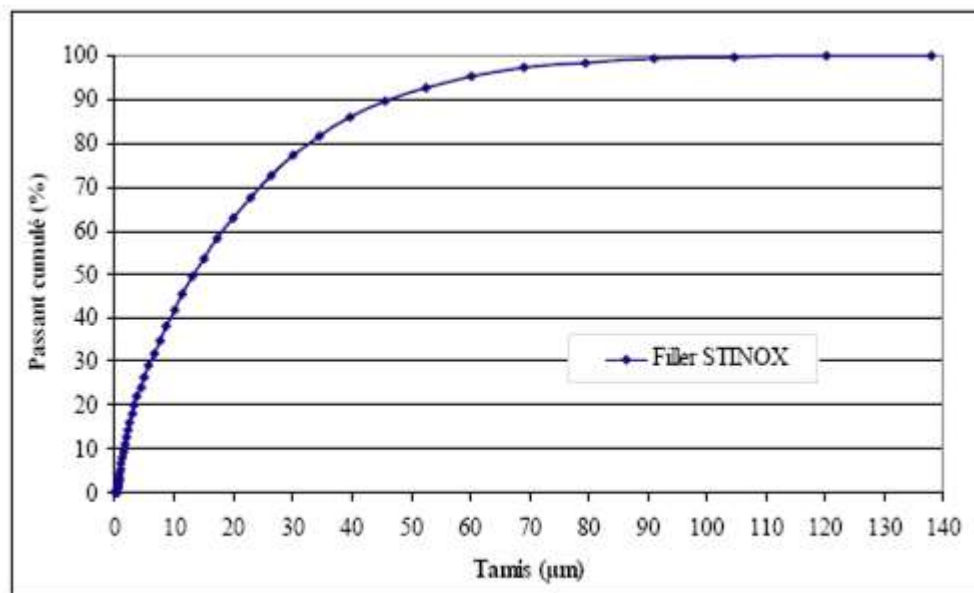
Libelle	Concrete	Asphalt
Parameters (mg/L)		
As	< 0,01	< 0,01
Al	0,087	1,3
Sb	< 0,001	0,0066
B	< 0,5	1,2
Ba	1,25	0,064
Cd	< 0,001	< 0,001
Co	0,00015	< 0,00003
Cr	0,02	0,022
Cr6+	< 0,025	< 0,025
K	40,5	5,4
Cu	< 0,01	< 0,01
Hg	< 0,0005	< 0,0005
Mo	0,0398	0,0299
Na	20,1	7,3
Pb	< 0,005	< 0,005
Ni	< 0,002	< 0,002
Se	< 0,005	< 0,005
Sn	< 0,0005	< 0,0005
Ti	< 0,01	< 0,01
V	< 0,001	0,0099
Zn	< 0,02	< 0,02
F ⁻	0,93	1,89
Cl ⁻	5	16
Br ⁻	< 0,5	< 0,5
SO ₄ ²⁻	< 3	19
CN ⁻	< 0,005	< 0,005

Libelle	Stinox 0,5/2	Stinox 2/14
Parameters (mg/kg)		
As	0,005	0,0051
Al	0,77	2,26
Sb	< 0,005	< 0,005
B	80,1	130
Ba	6,47	6,5
Cd	0,0023	0,002
Co	< 0,001	< 0,001
Cr	0,88	0,7
Cr6+	0,29	0,58
K	22,5	19,8
Cu	< 0,1	< 0,1
Hg	< 0,001	0,0012
Mo	2,02	1,69
Na	267	299
Pb	< 0,002	< 0,002
Ni	0,02	0,02
Se	0,029	0,035
Sn	< 0,006	< 0,006
Ti	< 0,11	< 0,11
V	< 0,01	< 0,01
Zn	< 0,1	< 0,1
F ⁻	30,9	62,5
Cl ⁻	228	181
Br ⁻	< 10	< 10
SO ₄ ²⁻	< 50	< 50
CN ⁻	0,051	0,04

Libelle	Concrete	Asfalt
Parameters (mg/kg)		
As	0,0052	0,0082
Al	0,49	3,33
Sb	< 0,006	0,033
B	< 10	22,8
Ba	15,1	0,11
Cd	< 0,002	< 0,002
Co	0,0023	< 0,001
Cr	0,31	0,44
Cr6+	0,23	0,46
K	437	65,7
Cu	< 0,1	< 0,1
Hg	< 0,001	< 0,001
Mo	0,46	0,36
Na	300	123
Pb	< 0,002	< 0,002
Ni	0,02	0,02
Se	0,016	0,015
Sn	< 0,006	< 0,006
Ti	< 0,11	< 0,11
V	< 0,01	0,17
Zn	< 0,1	< 0,1
F ⁻	7,62	18,1
Cl ⁻	120	155
Br ⁻	< 10	164
SO ₄ ²⁻	< 50	76,1
CN ⁻	0,048	0,042



Fillinox: grain size distribution



Courbe granulométrique du filler STINOX (analyse au granulomètre laser)



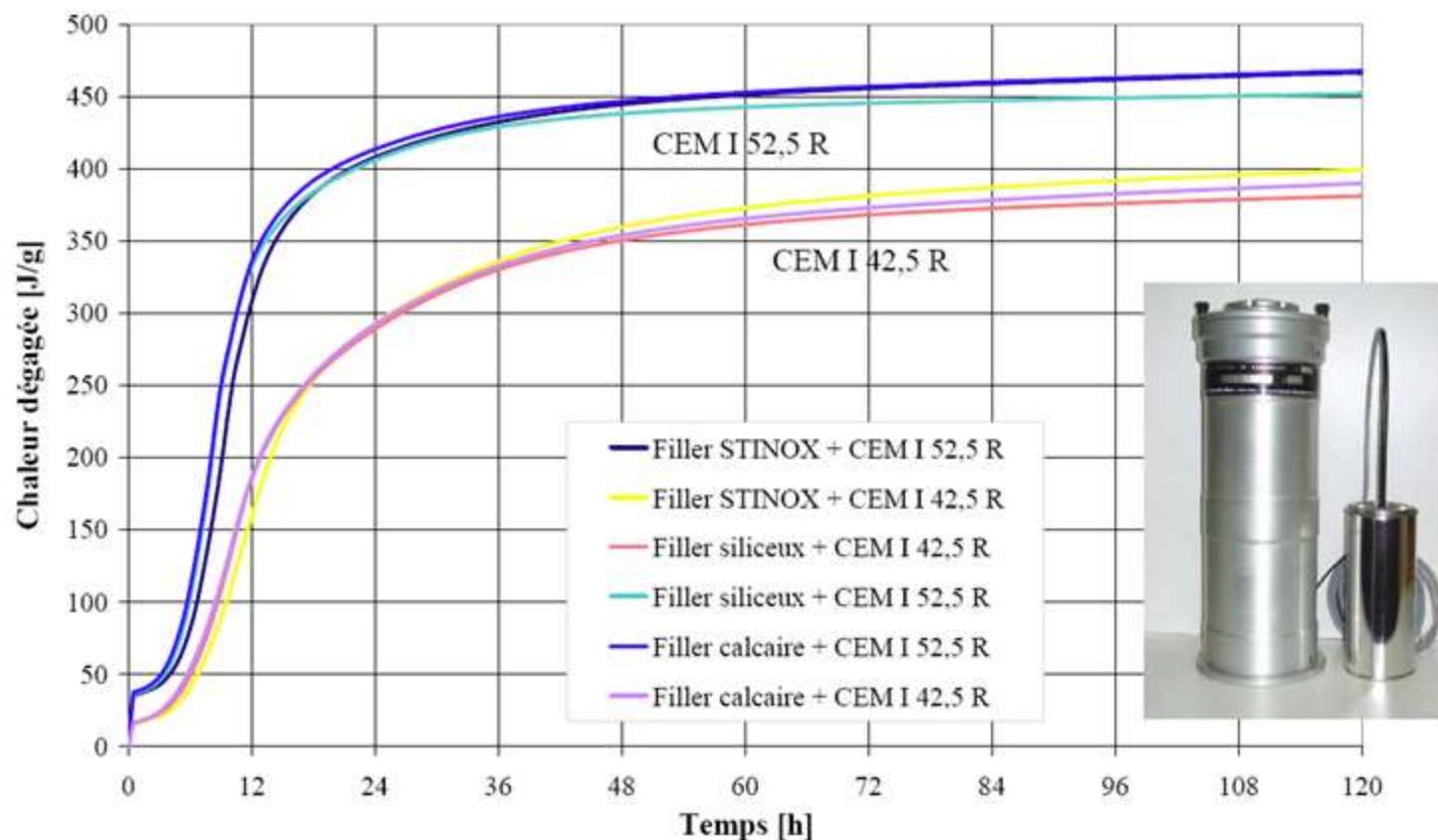
Fillinox: workability of fresh concrete

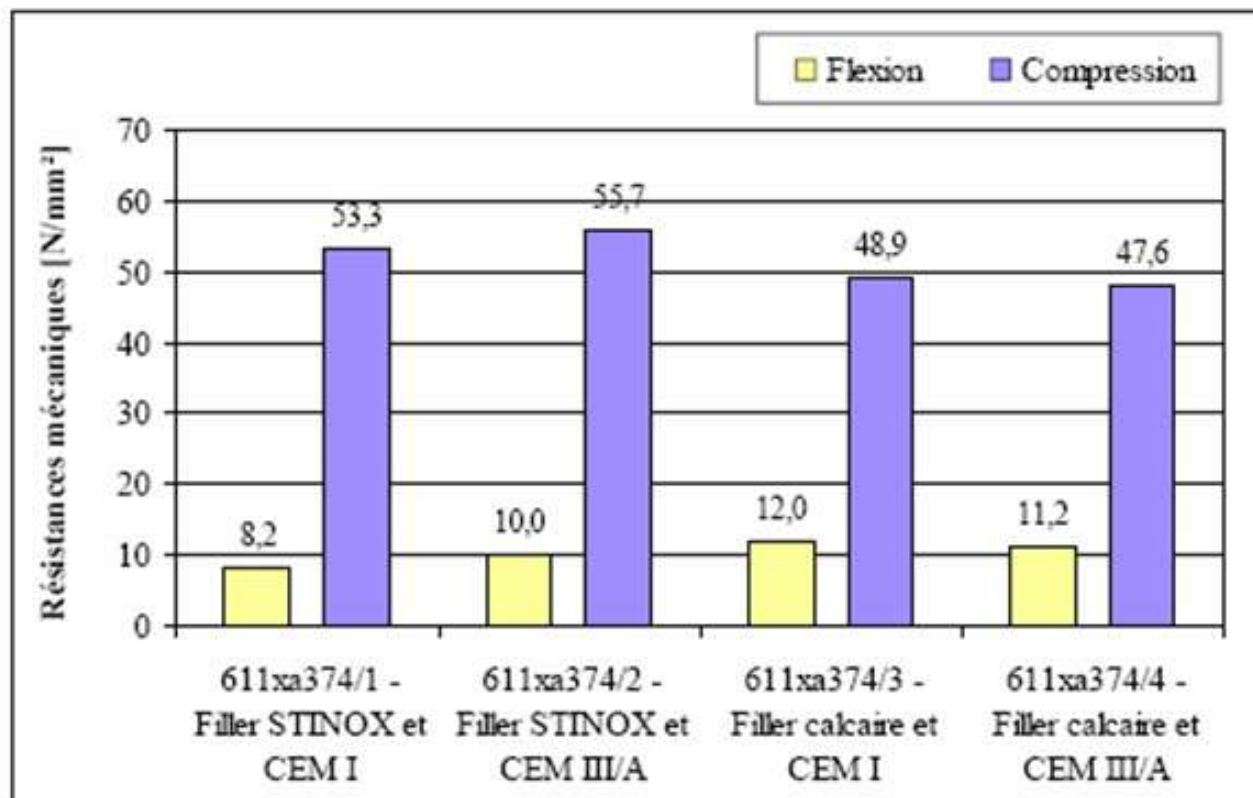


Limestone filler + CEM

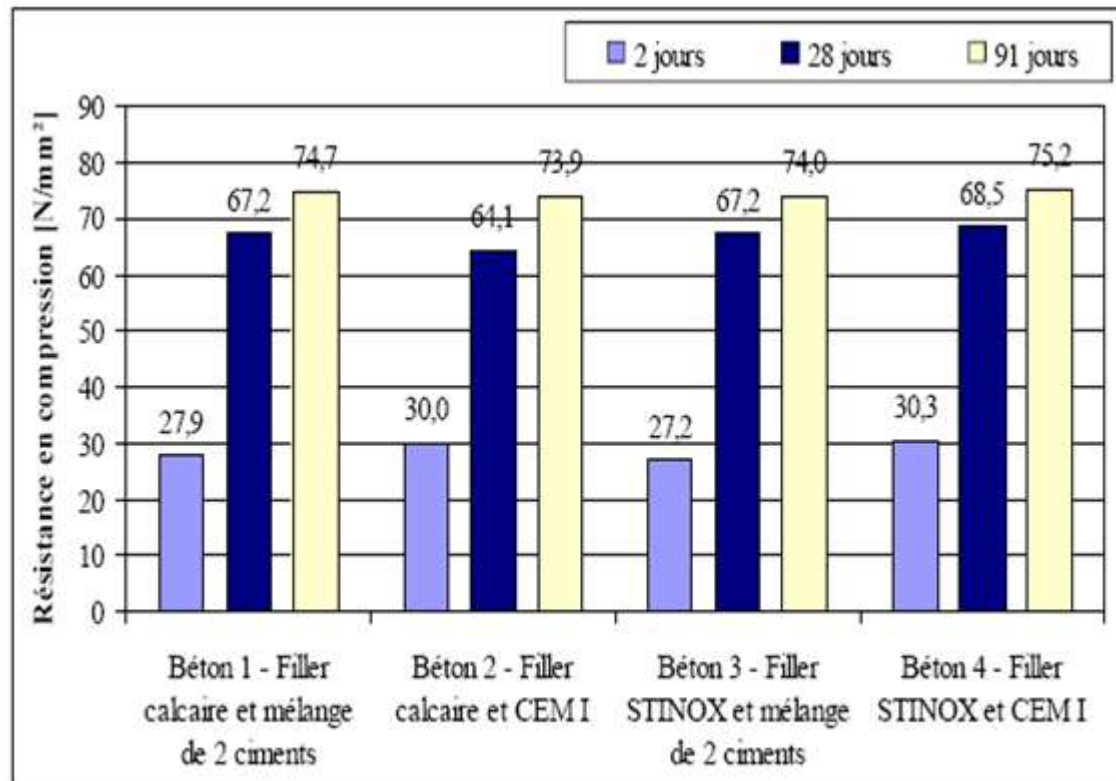


Stinox filler + CEM



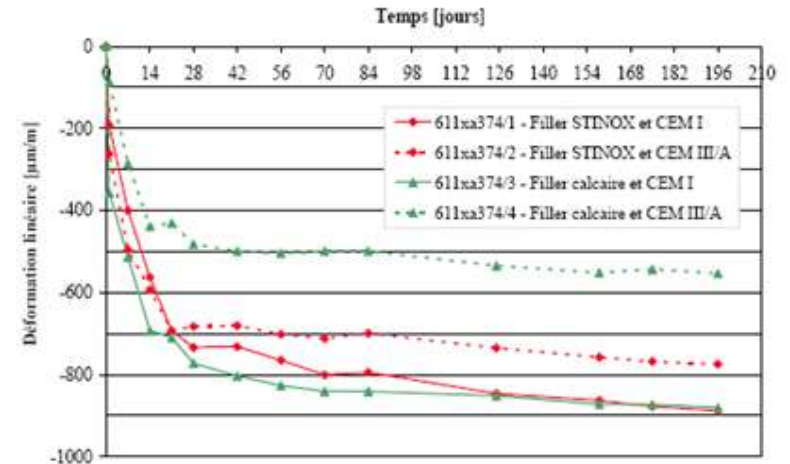


- Résistances mécaniques à 28 jours des mortiers (moyennes de 3 prismes)

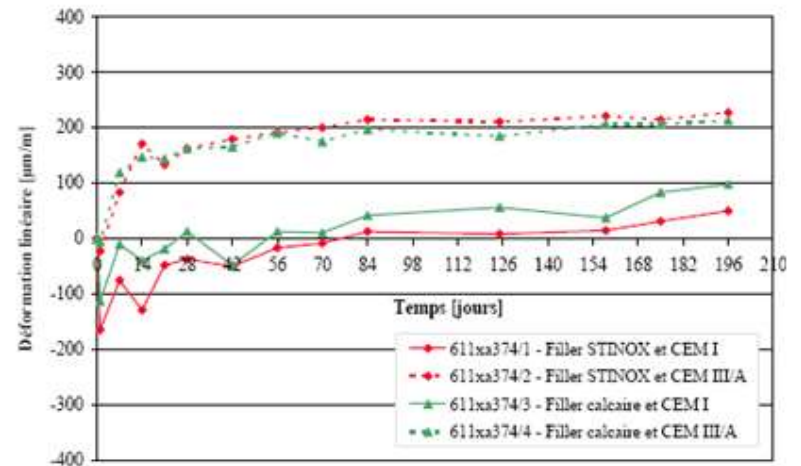


Résistances en compression des bétons (conditions normalisées)

Fillinox: swelling and shrinking of concrete

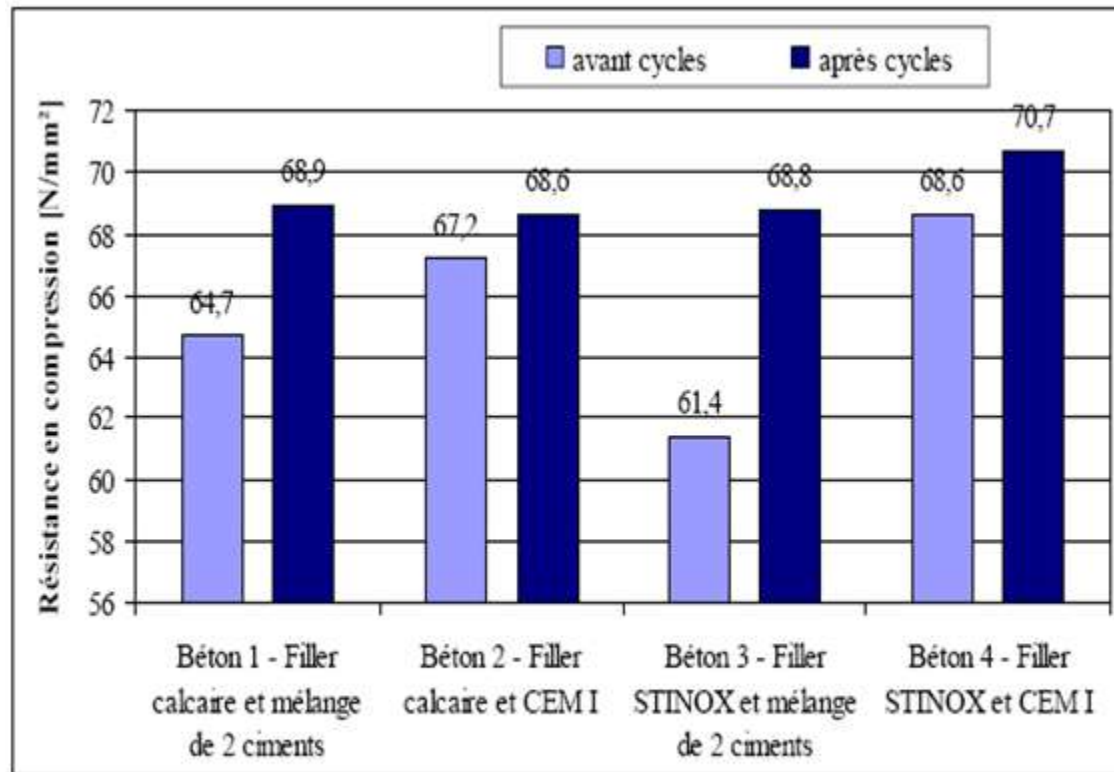


Essai de retrait des mortiers (moyennes de 3 prismes)



Essai de gonflement des mortiers (moyennes de 3 prismes)

Fillinox: resistance of concrete to freezing and thawing



Résistances en compression des bétons (avant et après cycles de gel/dégel)

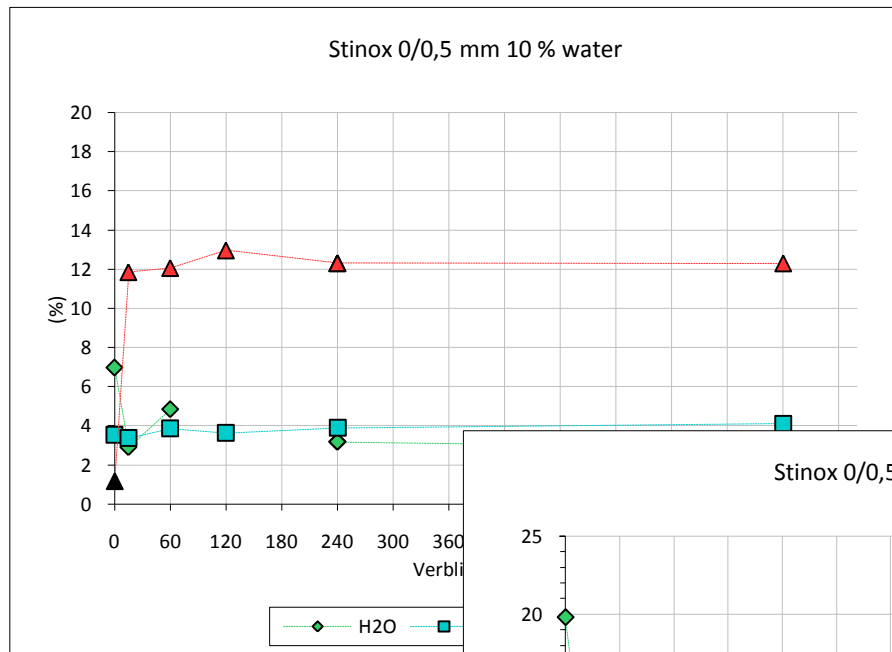
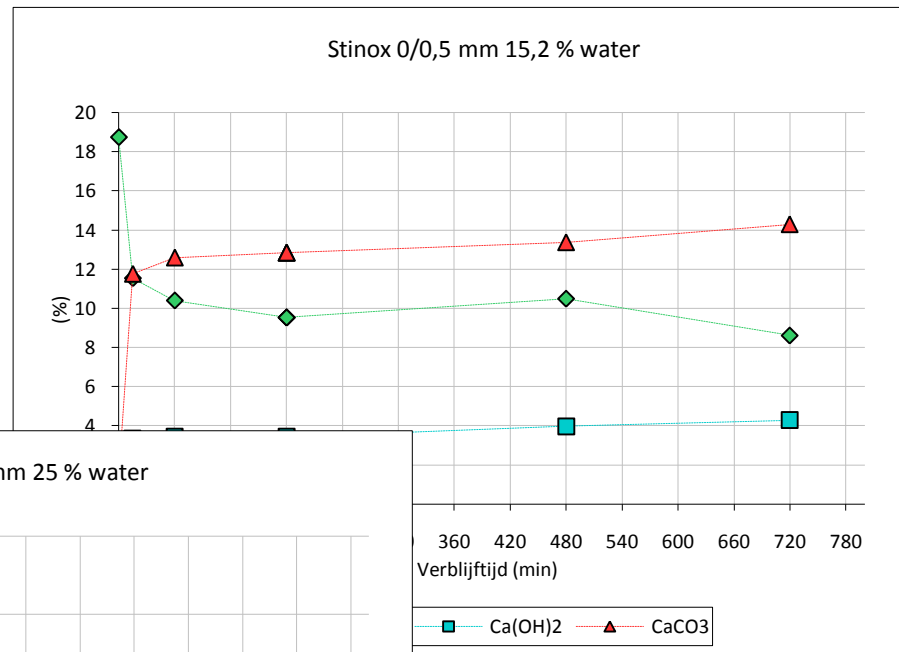
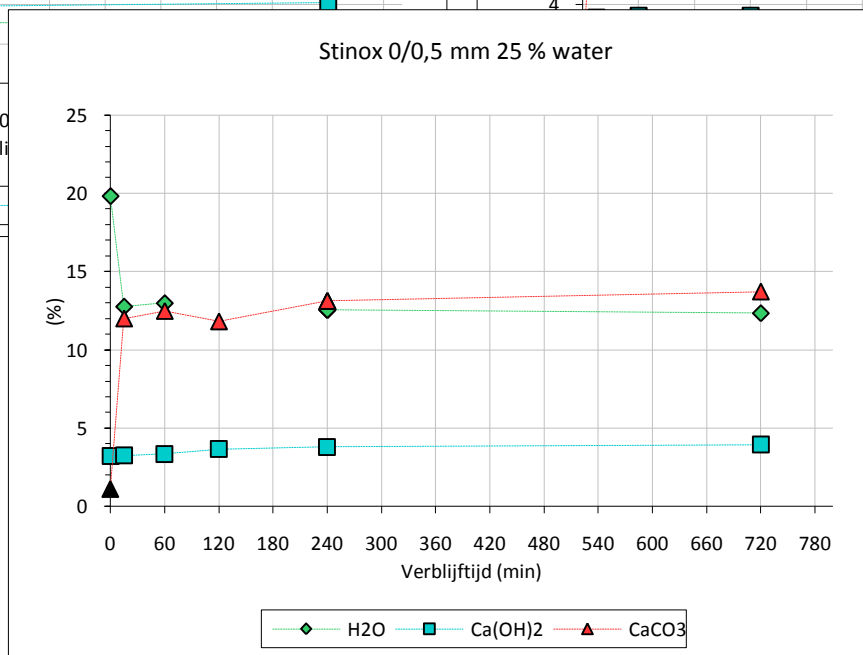
Fillinox: leaching behaviour of concrete



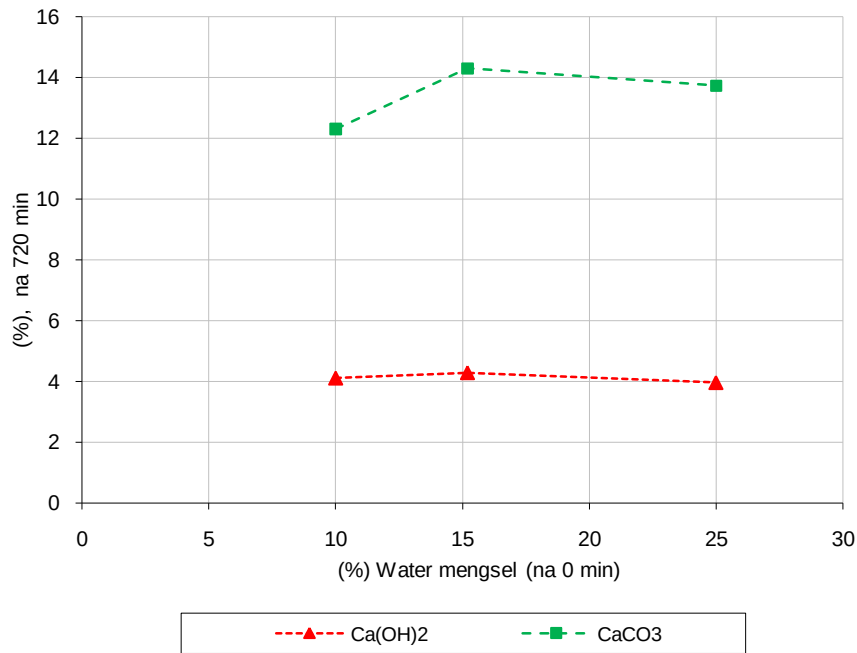
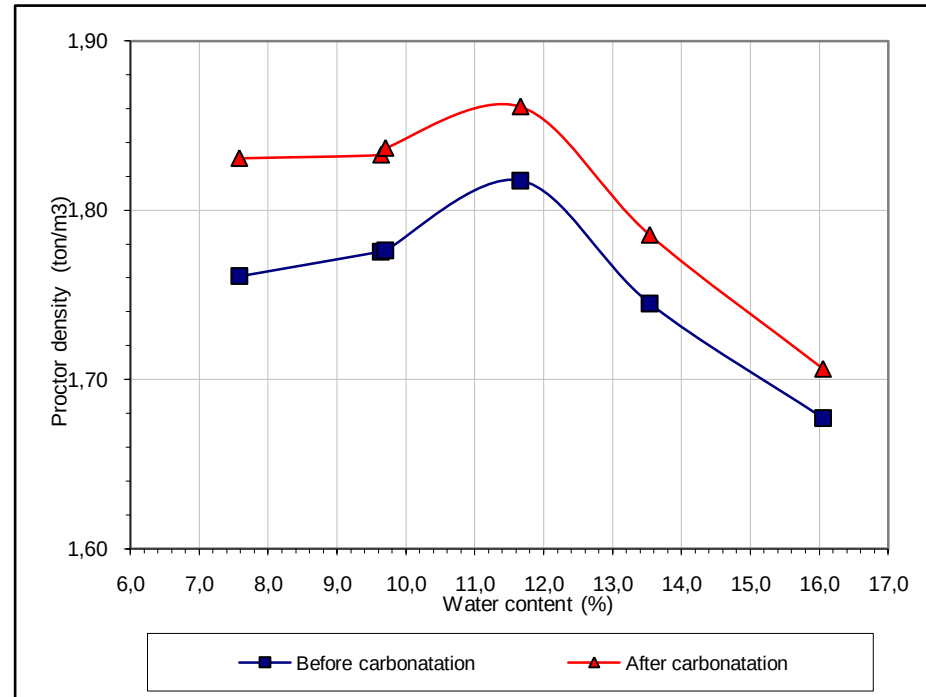
Libelle	Filler Stinox	Filler Stinox	Filler Carmeuse	Filler Carmeuse
Parameters (mg/l)				
Al	0,227	1,14	0,235	1,36
As	<0.005	<0.005	<0.005	<0.005
Sb	<0.009	<0.009	<0.009	<0.009
B				
Ba	0,81	0,746	0,838	0,83
Cd	<0.0012	<0.0012	<0.0012	<0.0012
Co	<0.001	<0.001	<0.001	<0.001
Cr	0,02	0,018	0,036	0,017
Cr6				
K	94,2	42,7	97,5	46,1
Cu	0,005	0,0031	0,0065	0,0036
Hg	<0.000100	<0.000100	<0.000100	<0.000100
Mo	0,022	0,047	< 0,008	< 0,008
Na	25,8	34,2	22,3	34,8
Pb	0,023	<0.006	<0.006	<0.006
Ni	<0.005	<0.005	<0.005	<0.005
Se	0,006	0,006	0,006	0,006
Sn	<0,009	<0,009	<0,009	<0,009
Ti	<0,003	<0,003	<0,003	<0,003
V	<0.0015	<0.0015	<0.0015	<0.0015
Zn	0,021	0,007	0,009	0,008
NH ₄ ⁺	< 0,06	0,12	< 0,06	0,06
Br ⁻	<0,05	<0,05	<0,05	0,05
Cl ⁻	1,9	3,1	1,7	3,1
CN ⁻	<0,0024	<0,0024	<0,0024	<0,0024
F ⁻	0,622	0,325	0,497	0,142
NO ₂ ⁻	0,033	0,034	0,018	0,023
SO ₄ ⁼	5,7	5,2	< 4,6	< 4,6



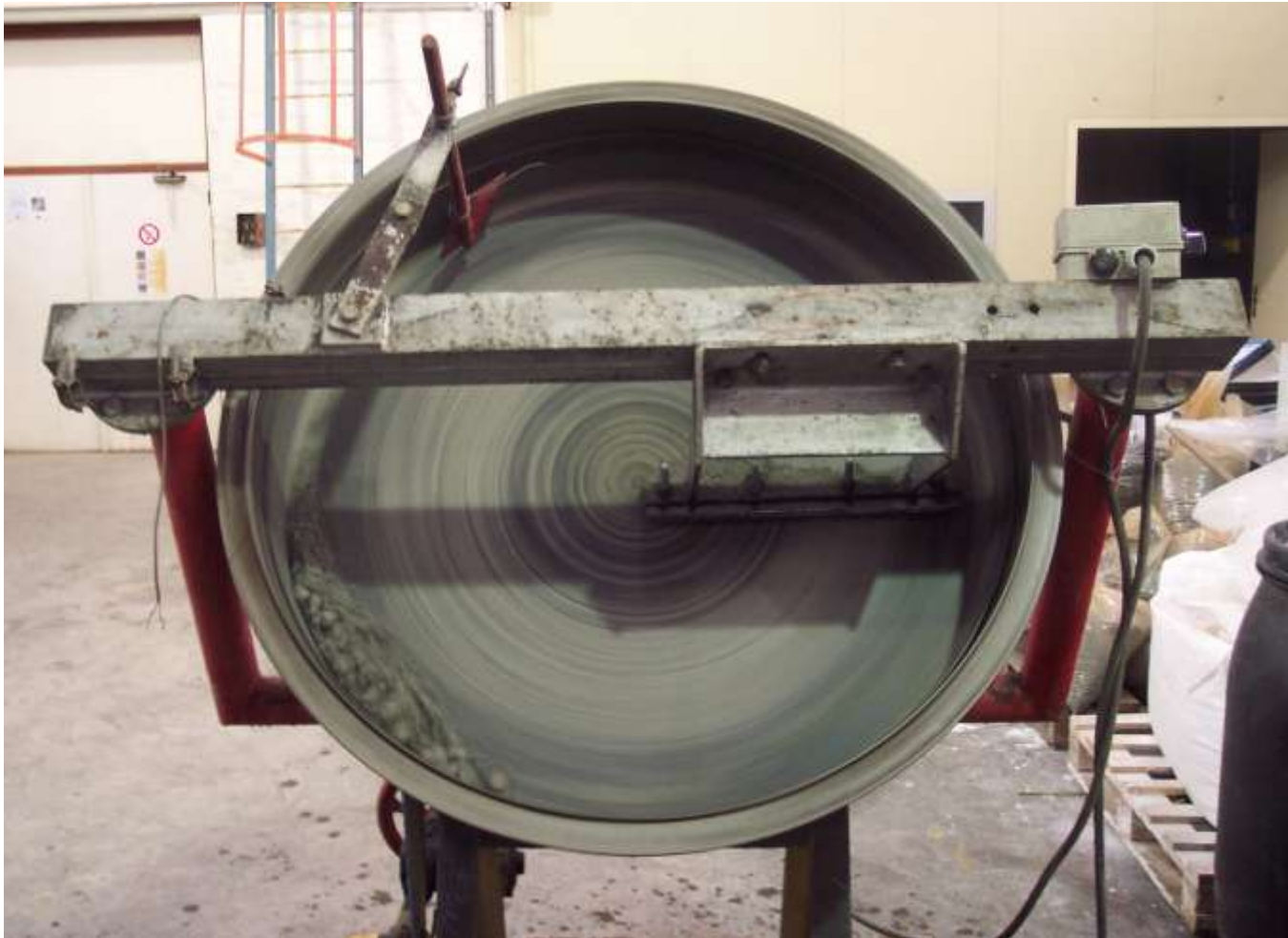
Carbonatation (2005): proctor compaction

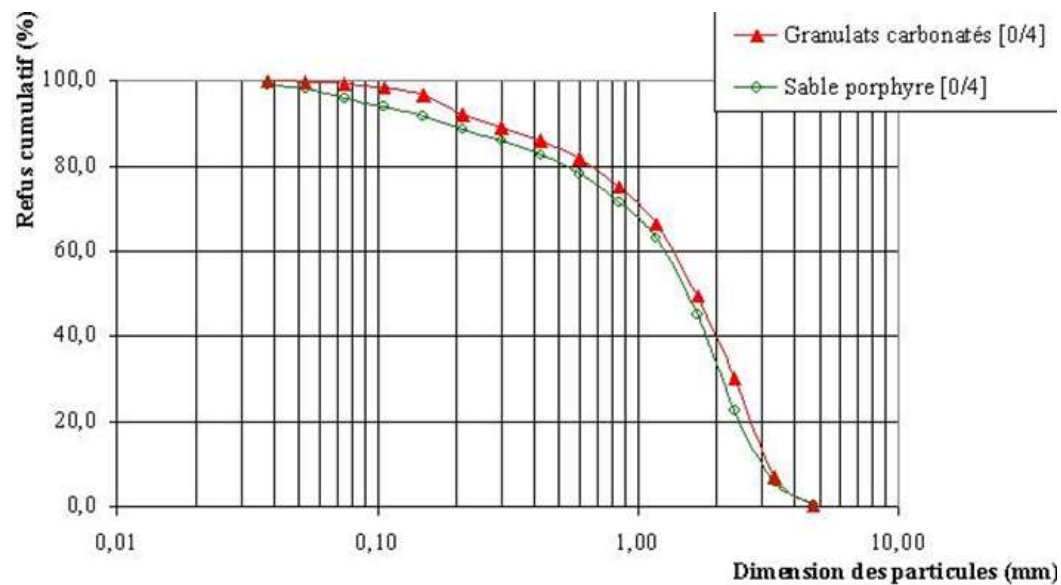


Carbonatation (2005): proctor compaction



Granulation





	Compression strength (N/mm ²)	Flexural strength (N/mm ²)
100 % Porfier	45	9
100% granulated slag	35	6

Granulation



Laddle slag



AOD slag



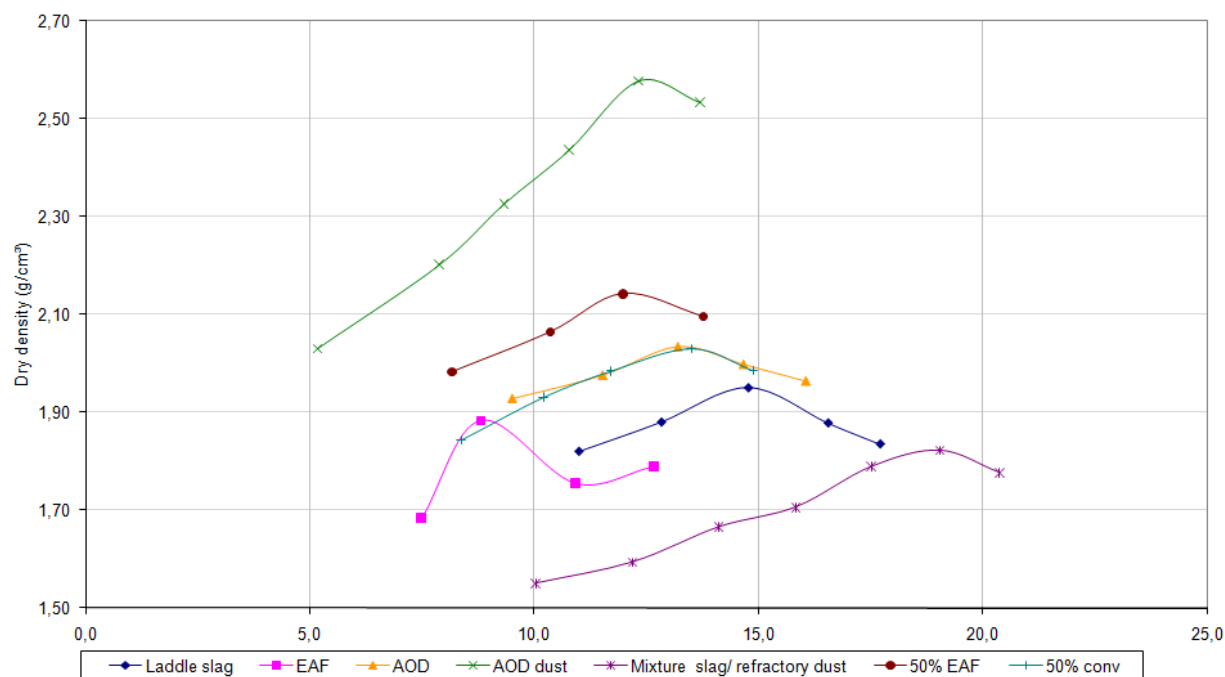
Filter dust

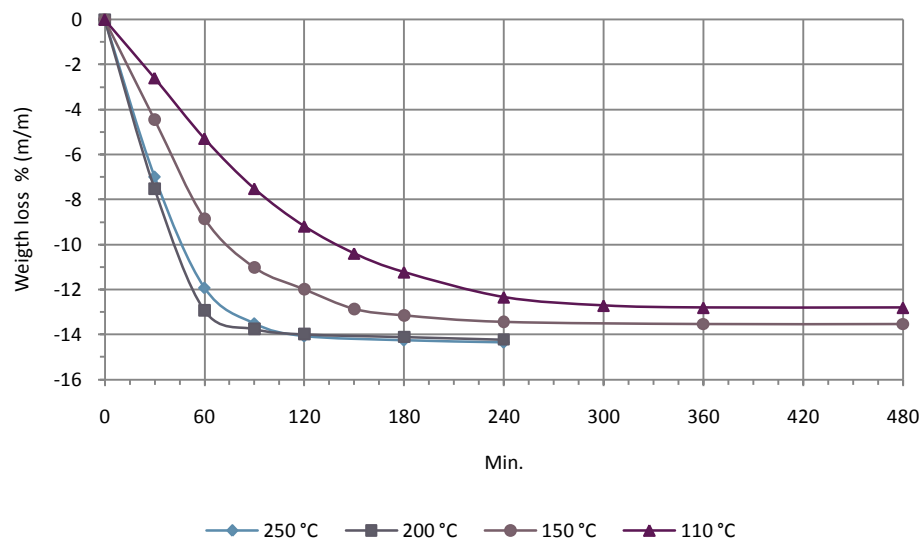
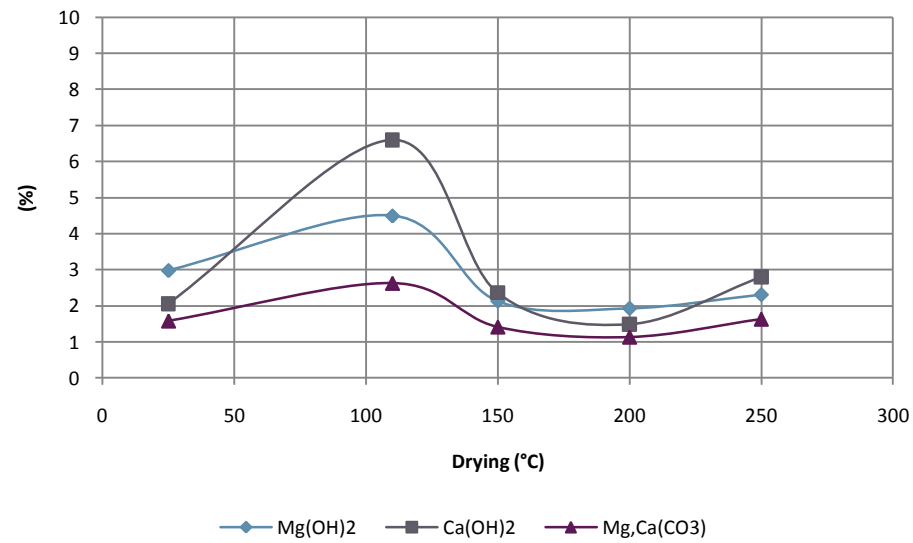


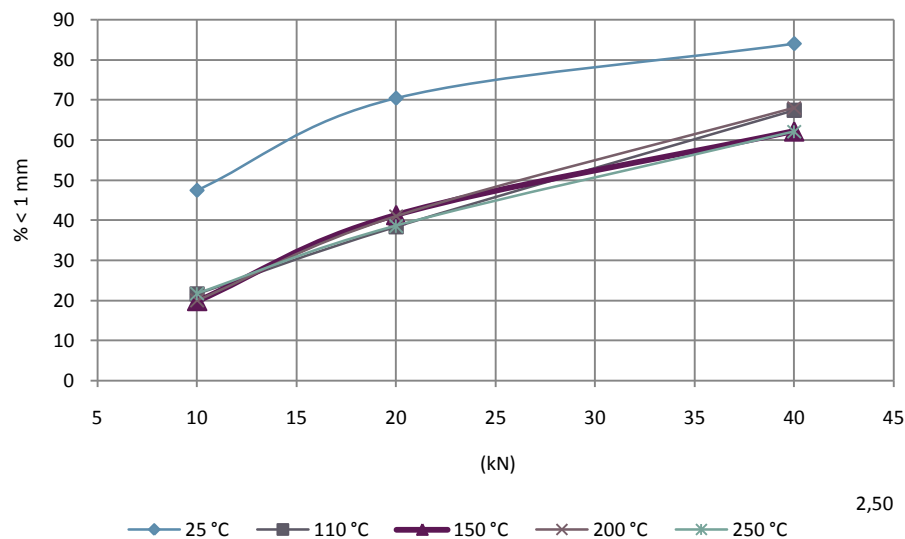
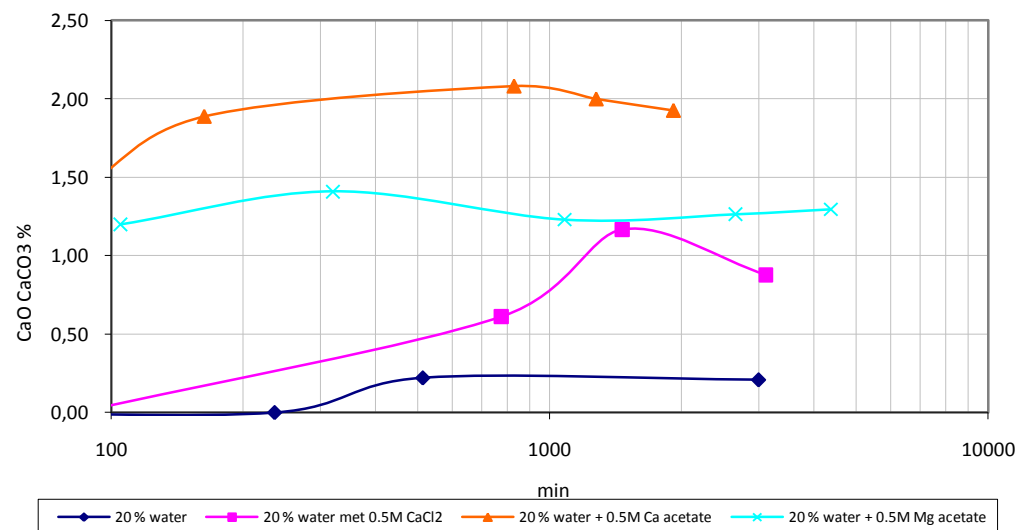
Mixture slag/refractory

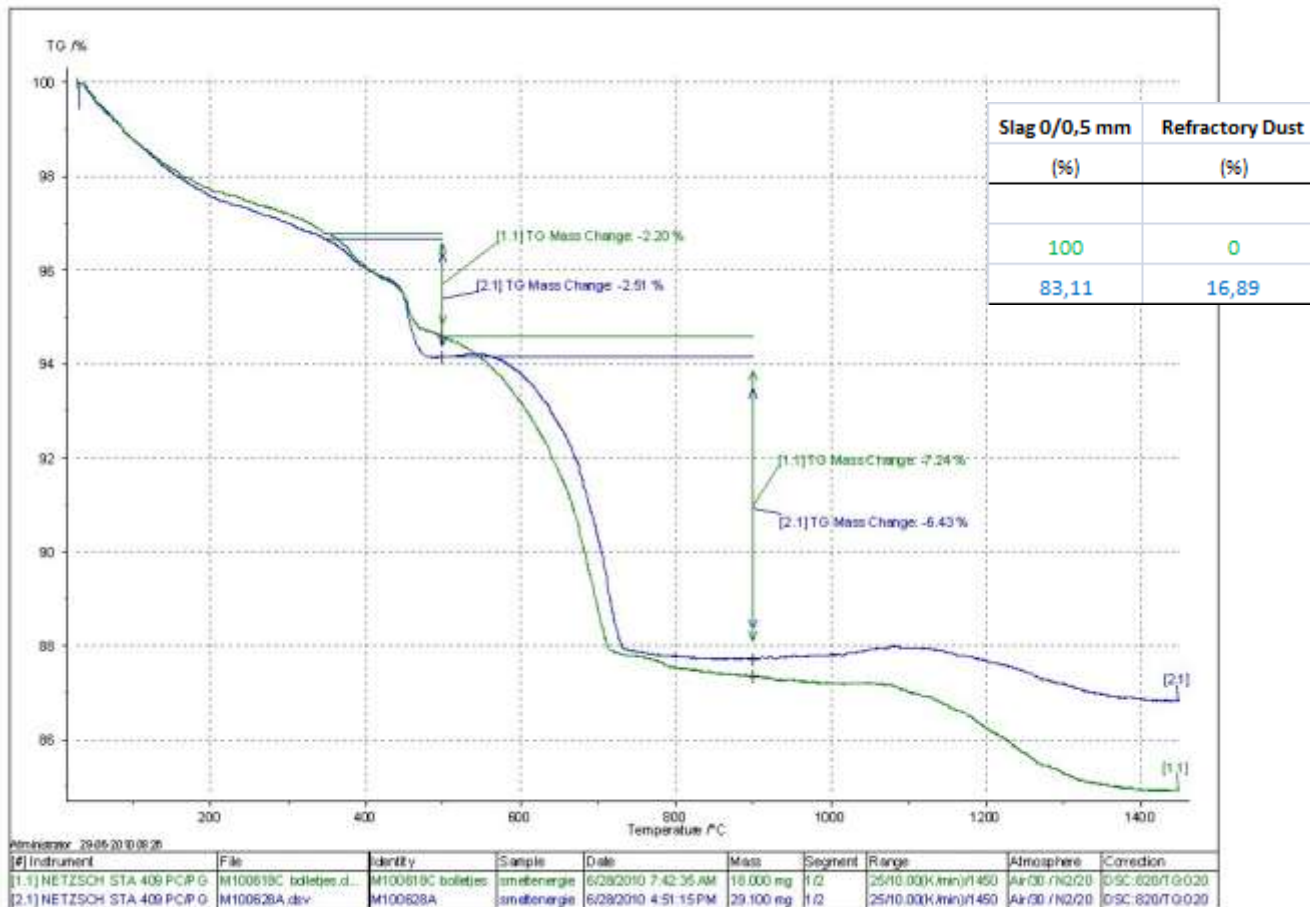


FeCr

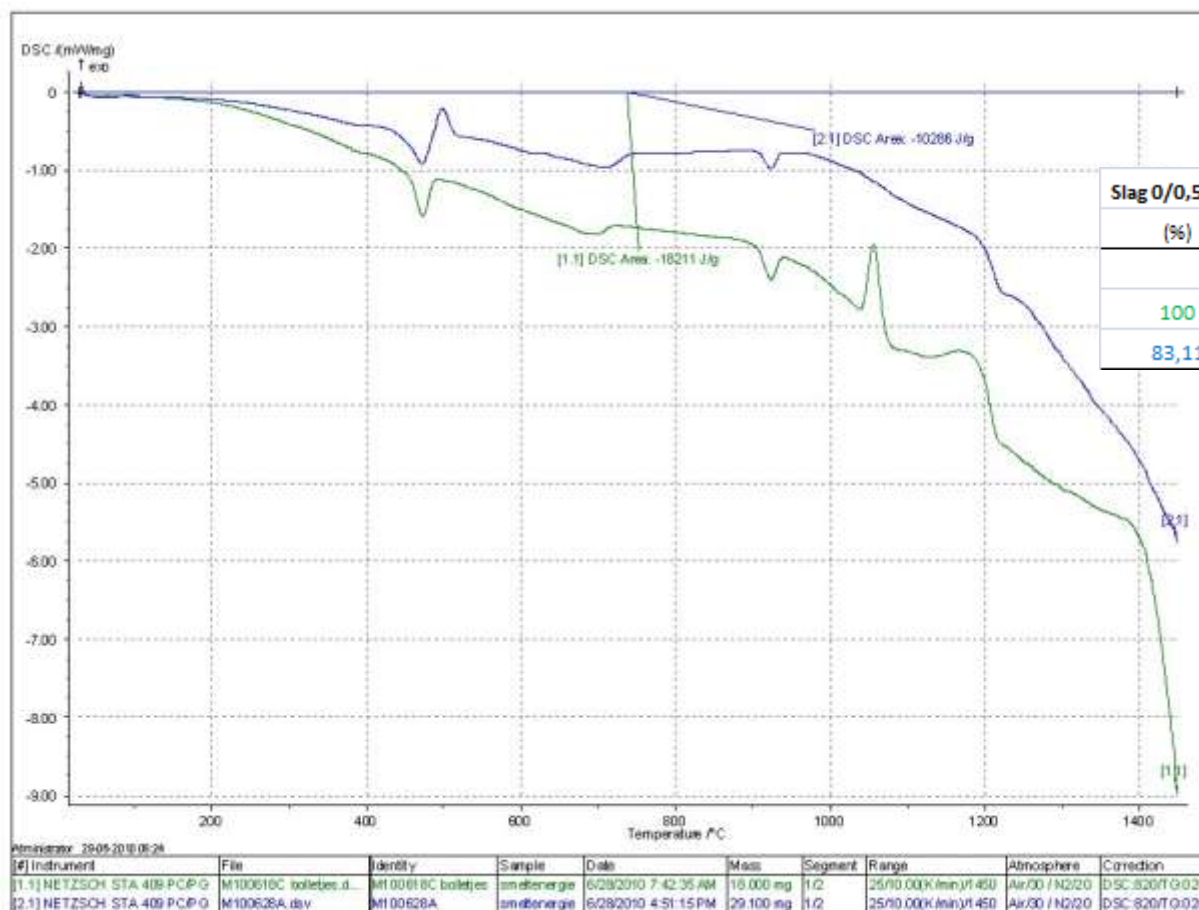








Granulation



Slag 0/0,5 mm	Refractory Dust	25 °C > 1450 °C	25 °C > 1450 °C
(%)	(%)	(kJ/kg)	(kWh/ton)
100	0	-18.211	-5,06
83,11	16,89	-10.286	-2,86

Granulation



Granulation



Granulation





Temperature: up to 250°C

Pressure: up to 150 bar

Volume: 3,25 l

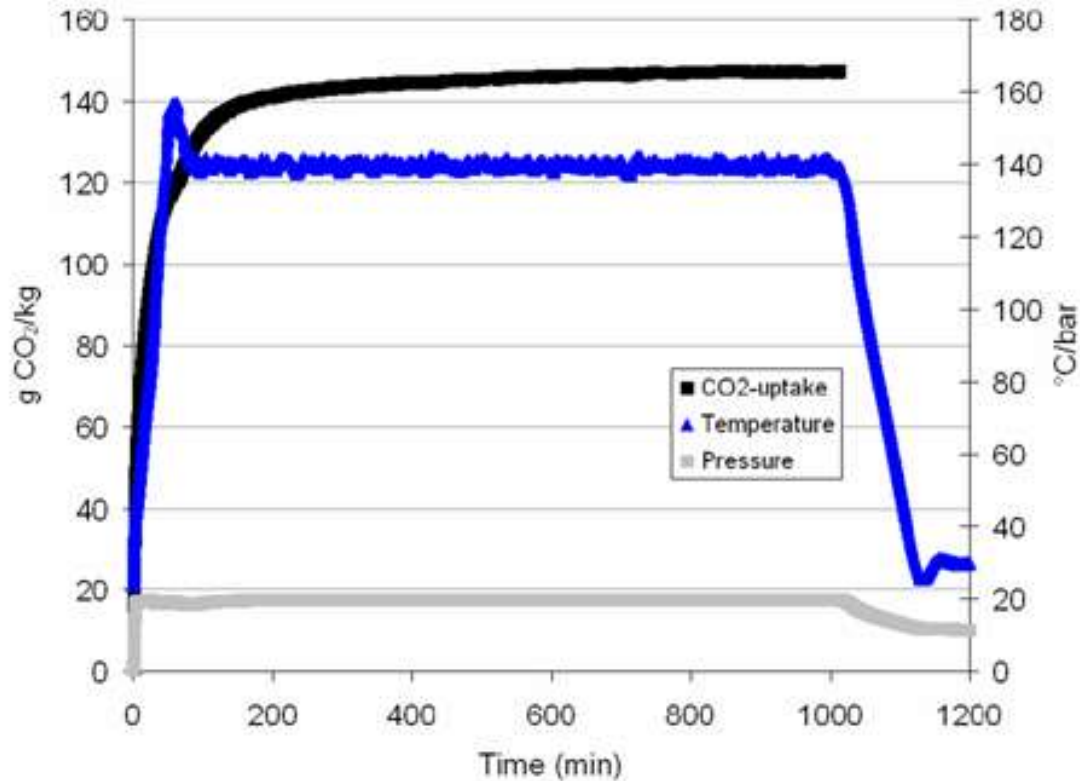


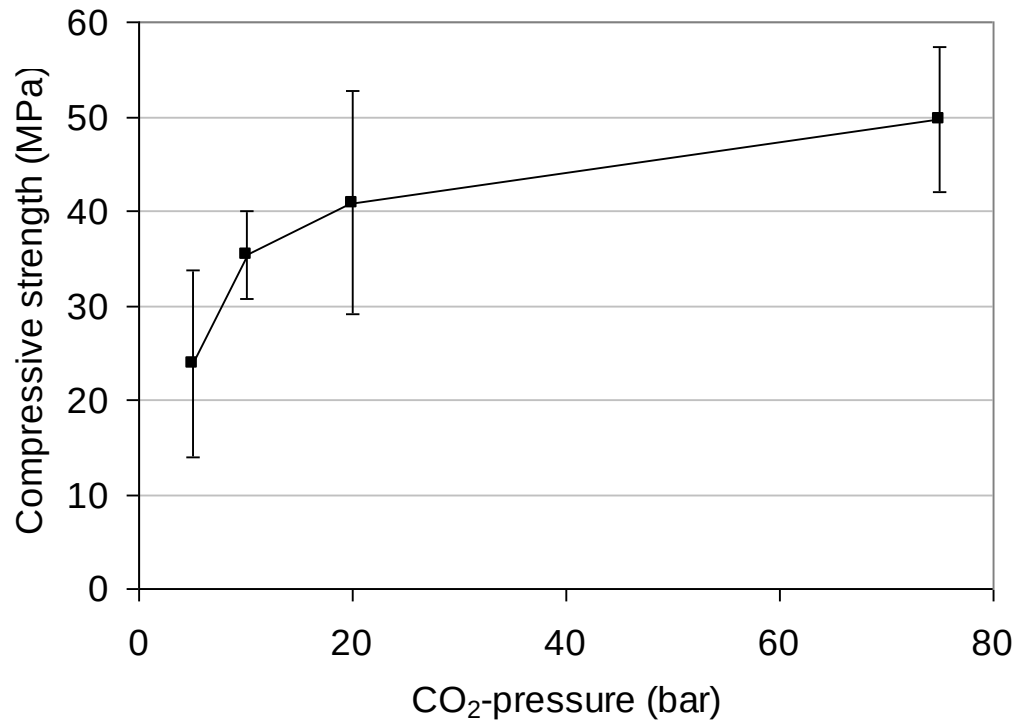
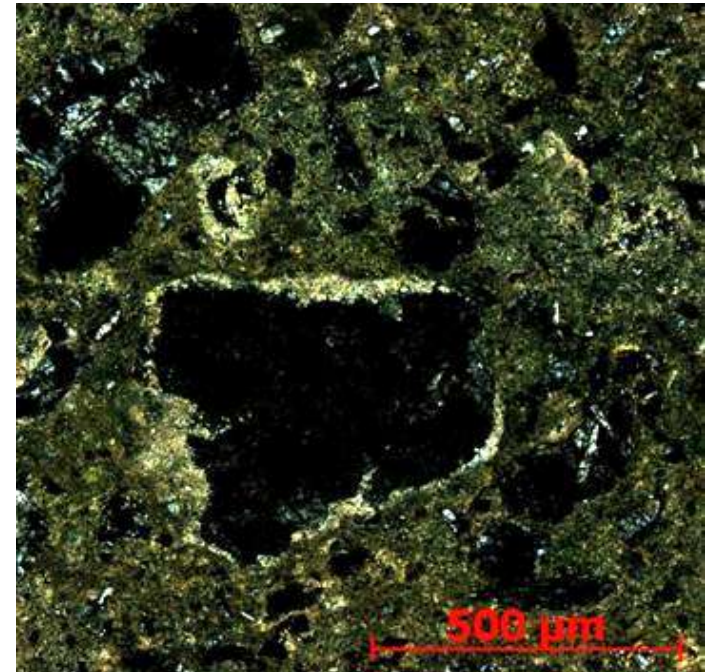
Temperature: up to 250°C

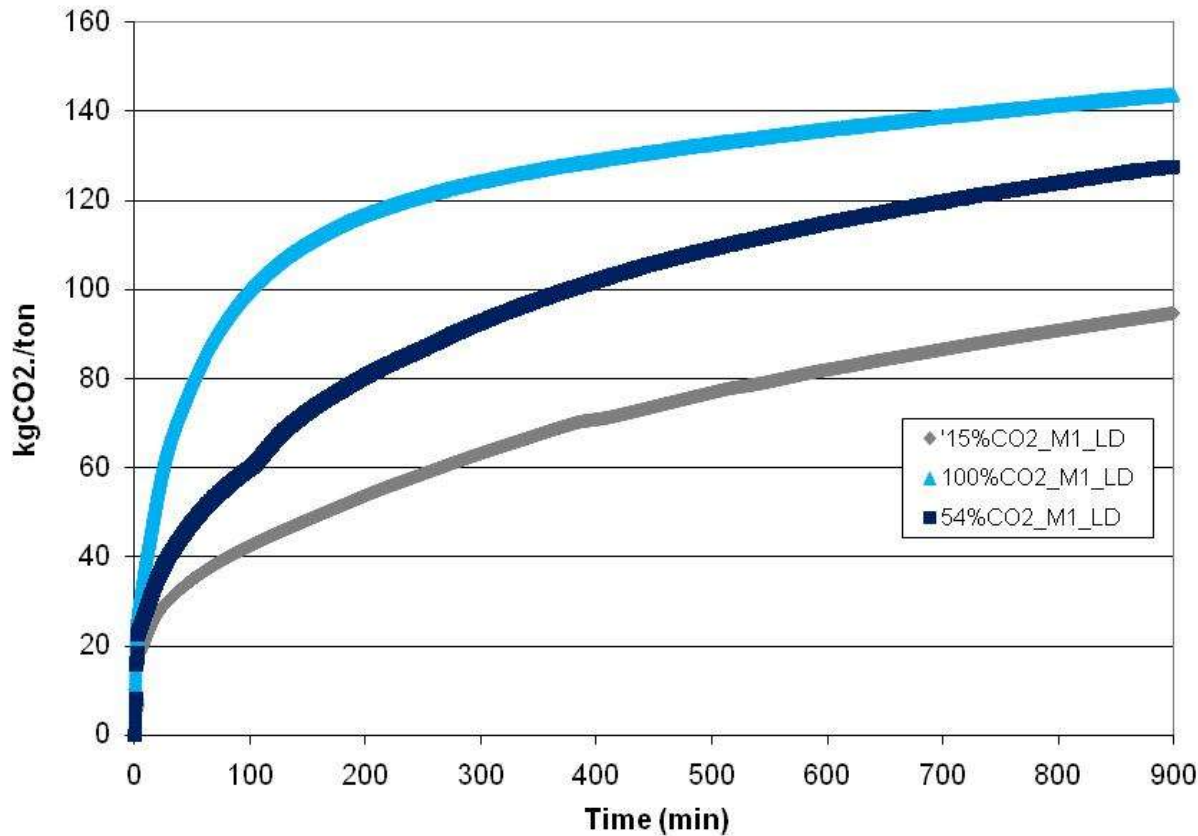
Pressure: up to 50 bar

Volume: 114 l

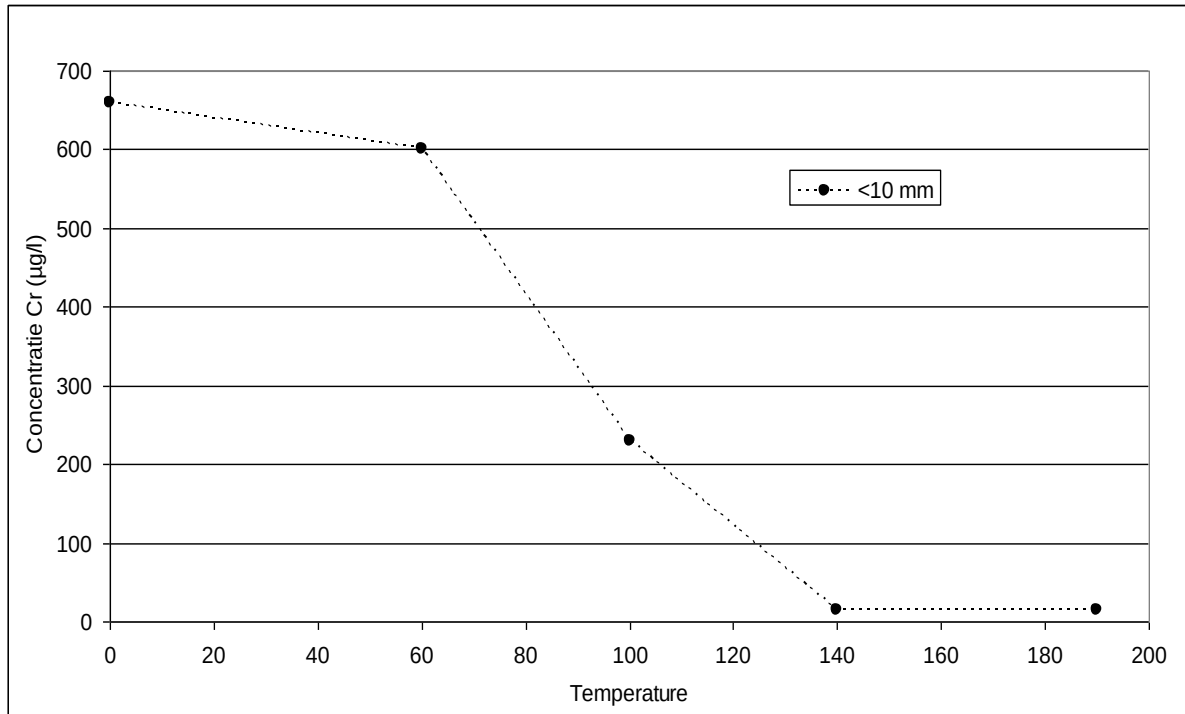
Carbstone: process parameters





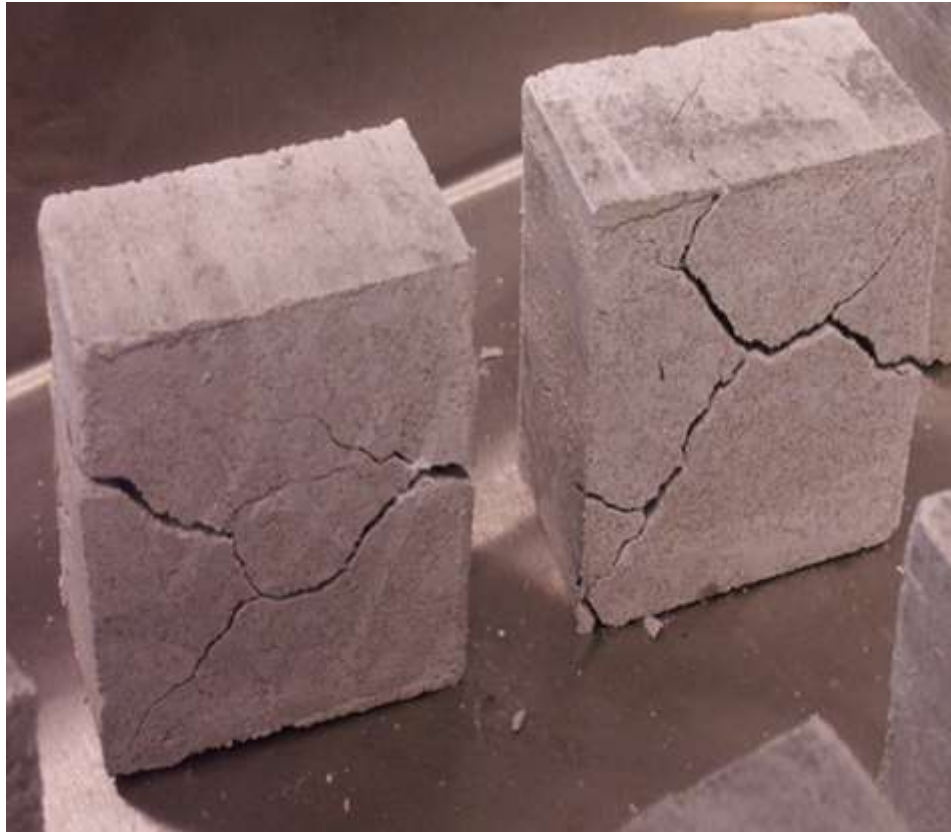


% CO2	(MPa)
15	16 (0,2)
54	36 (0,1)
100	39 (3)

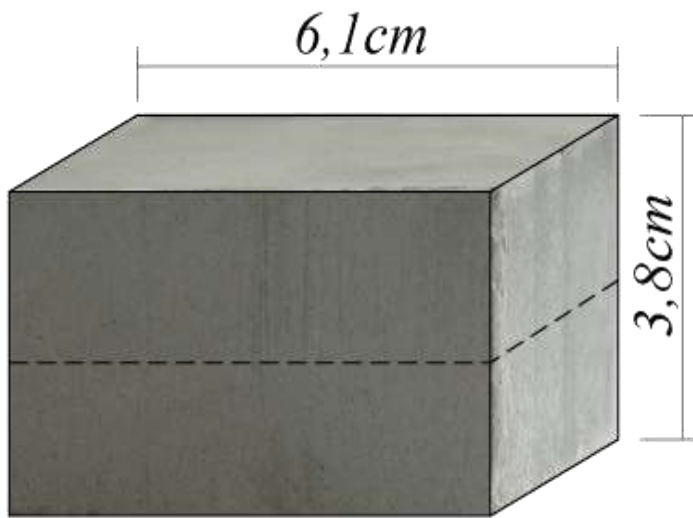
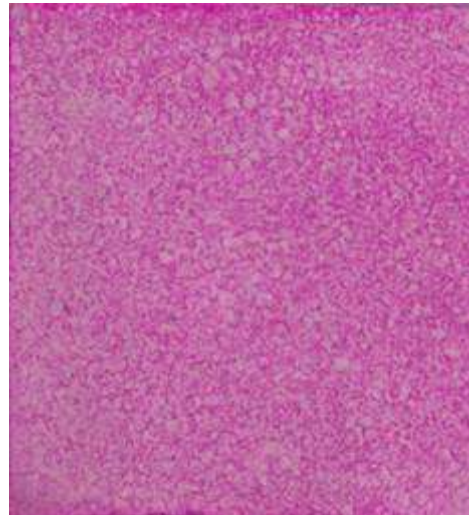


L/S 10, 24 h, batch leaching test

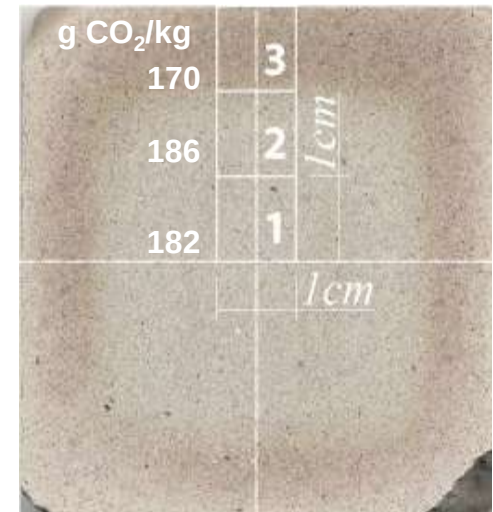
Carbstone: temperature



Carbstone: homogeneous carbonation

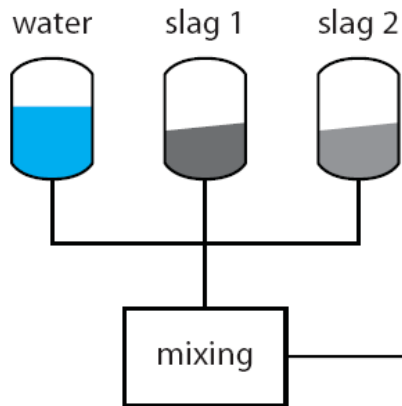


phenolphthaleine

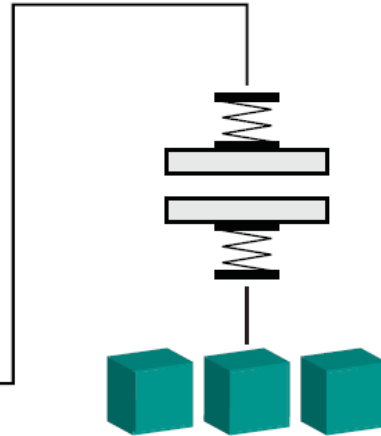


Carbstone: production process

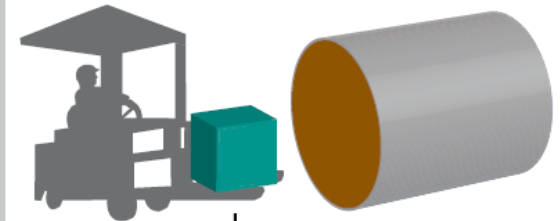
PRETREATMENT



SHAPING



CURING



Carbstone: production process



Carbstone: production process



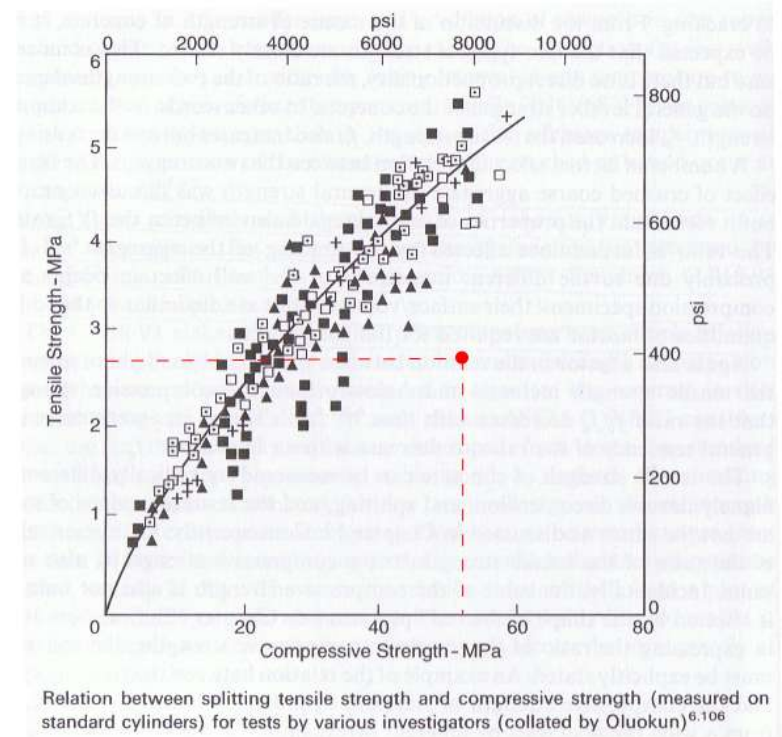
Carbstone: production process



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Compressive strength	55 Mpa
Young's modulus	17138 N/mm ²
Tensile splitting strength	2,70 MPa
Shrinkage and swell	< 300 µm/m
Frost and thaw	< 0,350 kg/m ²
Density	2010 – 2370 kg/m ³
Water absorption	10 %
Porosity	22-26%
CO ₂ -content	177-188 g CO ₂ /kg
Permeability	6,2 – 8,2 10 ⁻¹¹ cm ²



- Reference product made from stainless steel slag
  - Complies with the VLAREA-regulation for reuse as a building material (Flemish region of Belgium)
  - Complies with the Dutch regulations for building products (Building materials decree/Besluit Bodemkwaliteit)
  - Complies with the Walloon legislation for reuse (DIN-S4)

- CO₂-binding during production:
-0,30 ton CO₂/m³ carbstone blocks
- CO₂ produced during production:
+0,08 ton CO₂/m³ (energy demand 200 kWh/m³)
- CO₂ saved by not using cement:
-0,24 ton CO₂/m³ concrete block
- Total CO₂ balans:
-0.46 ton CO₂/m³ concrete block



Aperam (B)
Belgian Road Research Centre, Sterrebeek (B)
Belgian Building Research Institute, Limelette (B)
Centre Terre & Pierre, Tournai (B)
KUL, Leuven (B)
Vito, Mol (B)
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