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Grits as a Partial Cement Replacement for Concrete

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ABSTRACT

The paper pulp industry produces several waste materials, most of which are dumped to landfill causing economic and environmental problems. Grits is one such material and research is being carried out on mortar, to ascertain applicability of Grits in concrete as a partial cement replacement material.

As grits contain mainly calcium carbonate and amorphous material is absent, this waste material will only act as filler. Therefore fineness is of the upmost importance and two sets of tests were carried out with grits ground to different fineness. Strength and durability-related results of mortar with 10% cement replacement by grits generally indicated relatively small differences to control, improving with fineness.

Therefore if sulphates are controlled and chlorides reduced through prior treatment this waste material, if ground to sufficient fineness may be used as filler for concrete. Applying grits even in small dosages will avoid dumping and therefore contribute to sustainability in construction.

INTRODUCTION

Cementitious materials, mainly in the form of concrete, are the most successful materials in the world. Every year more than $1 m^3$ is produced per person worldwide. The huge volumes of cement and concrete produced mean that cement production accounts for some 5-8% of man-made CO_2 emissions. Therefore there is increasing pressure to innovate to improve sustainability [Scrivener and Kirkpatrick, 2008]. Concrete must keep evolving to satisfy the increasing demands of all its users. Reuse of post-consumer wastes and industrial by-products in concrete is necessary to produce "greener" concrete. Recycling by-products is an environmental-friendly method for large quantities of materials that may otherwise pollute land, water, and air [Mehta, 1994].

The Kraft process (Figure 1) corresponds to a technology for conversion of wood into wood pulp consisting of almost pure cellulose fibers for paper production. Grits are produced during the clarifying process of black liquor which is recovered into white liquor needed for the digesting process of wood chips. They are in particular, produced during the causticizing process which is part of the pulp mill chemical recovery circuit. Grits are the insoluble materials removed from slakers after the reaction between green liquor and lime produced in this phase (slaker grits).

Grits have been used for soil stabilization [Pereira et al.a, 2006], as raw material for clinker [Castro et al., 2009] and as sand replacement in mortar [Gemelli et al., 2001] but not, to the authors knowledge, as cement replacement.

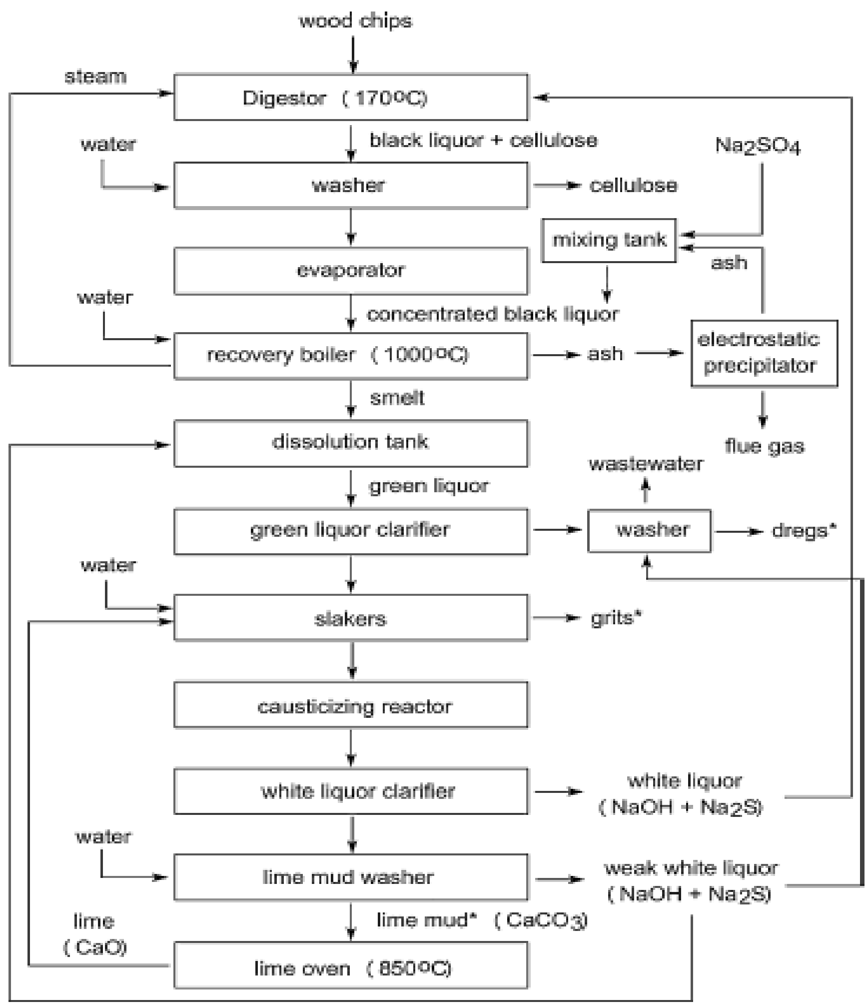


Fig. 1. Flowsheet of the Kraft process under study

EXPERIMENTAL PROGRAMME

A first phase of the program, previously published [Garcia and Sousa-Coutinho, 2009] concerned examining the material per se. Several tests were carried out such as chemical and mineralogical analysis, SEM – Scanning Electron Microscopy and laser particle size distribution. Mechanical properties were also determined in mortar produced with 10% replacement of ground grits. The second phase presented in this paper deals with durability – related properties of mortar with grits, namely absorption by capillarity, resistance to accelerated carbonation, resistivity and chloride ion penetration. Alkali silica and sulphate testing is also being carried out.

Grits and Ground Grits

Grits waste material was obtained from Portucel-Soporcel pulp paper industry plant at Cacia where they are deposited in controlled landfills (Figure 2). Grits consist of gray lime sludge with a Water Content of 15% to 25%.

Fig. 2. Paper pulp industry plant and Grits

Grits material was dried in an oven at 105 ± 5 º C. In a first study the waste material was ground in Los Angeles equipment, and then sieved and only particles under 250 micrometers were considered and named GRTa. The second study comprised grits material ground in a ceramic ball mill for 24 hours and named GRTb.

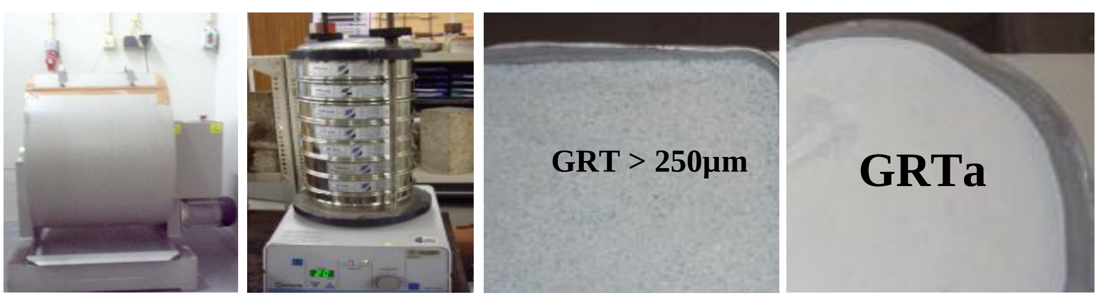


Fig. 3. Los Angeles ground Grits (GRTa)

Fig. 4. Ball mill ground Grits (GRTb)

Chemical analysis, XRD and SEM

X-Ray Diffraction revealed that this material does not contain amorphous matter and mineralogical analysis of Grits is shown in Figure 5 and Table 1. Chemical Analysis presented by Cacia plant is shown in Table 2 and according to NP EN 196-2, it is shown in Table 3. SEM - Scanning Electron Microscopy including EDS spectrums from different areas (Figure 6) disclose that GRTb particles are fairly homogeneous chemically. SEM for cement used is also presented (Figure 7). GRTb particles of intermediate size are scarce which is in accordance with the grading curve obtained by laser diffraction technique (Figure 9). Figures 8 and 10 show the particle size distribution of GRTa and CEM I 42,5 R used, respectively, where it can be seen by comparing values in Table 4, that although GRTb is finer than GRTa, this material should have been ground even further to fineness greater than cement for enhanced filling effect.

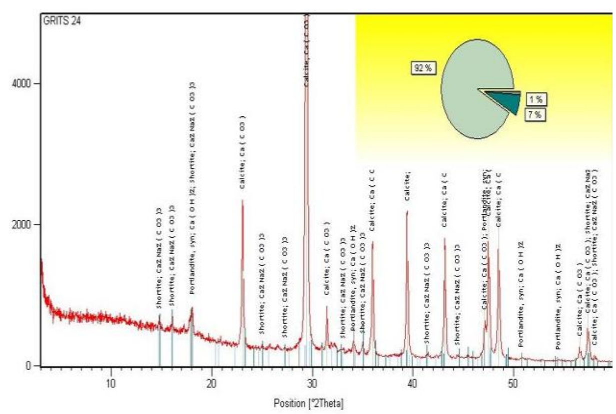


Table 1. Semi quantitative Mineralogical analysis of GRT

Minerals	Formula	%
Calcite	$CaCO_3$	92
Portlandite	$Ca(OH)_2$	1
Sodic calcic carbonate	$Ca_2Na_2(CO_3)_3$	7

Fig. 5. X-Ray diffraction of GRT

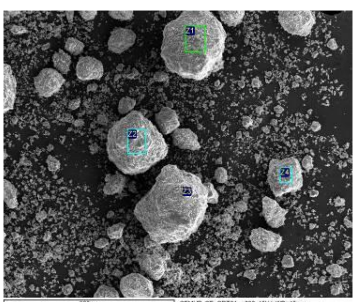
Table 2. Characterization of grits Factory Cacia

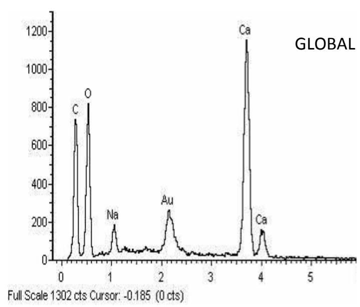
	Parameter	Average
	Apparent density (g/cm^3)	1,3
% gross weight	Humidity	12,1
	Solids (105$\pm$3º C)	87,9
% Solids	Fixed solids (550$\pm$25º C)	94,6
	Volatile solids (550$\pm$25º C)	5,4
	Total phosphorus (P)	0,69
	Sulphates (SO_4^{2-})	0,17
	Soluble sulphides	0,07
	Calcium (Ca)	39,81
	Magnesium (Mg)	0,26
	Sodium (Na)	0,59
	Potassium (K)	0,03
	Iron (Fe)	0,36
	Aluminium (Al)	0,37
	Manganese (Mn)	0,012

Table 3. Chemical analysis (NP EN 196-2) of GRT

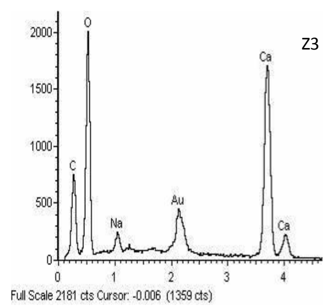
Components	(%)
LOI	42 ± 2
Insoluble Residue	1,2 ± 0,2
SiO_2	0,40 ± 0,07
Al_2O_3	< 1 [l.q.]
Fe_2O_3	0,11 ± 0,01
MgO	0,54 ± 0,06
CaO	56 ± 3
Na_2O	3,0 ± 0,3
K_2O	0,11 ± 0,01
MnO	0,008 ± 0,004
SO_3	0,31 ± 0,02
Cl	0,15 ± 0,02

EDS spectrum of GRTb particles (Figure 6) show predominance of calcium (Ca) and oxygen (O) and some sodium (Na) therefore in agreement with chemical analyses.

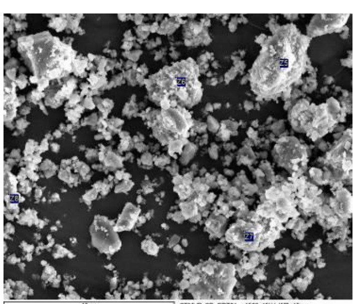

GRTb 200 times enlarged

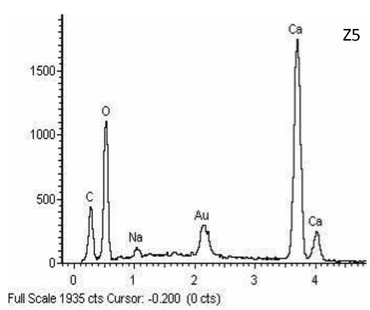


Spectrum for GLOBAL

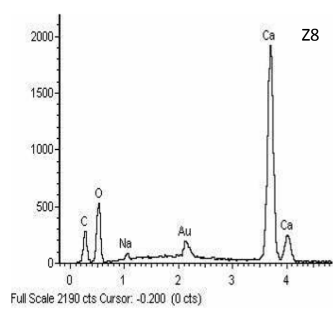


Spectrum for Z3


GRTb 1500 times enlarged

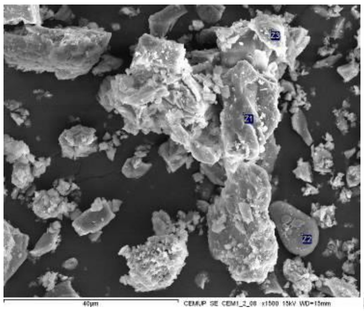


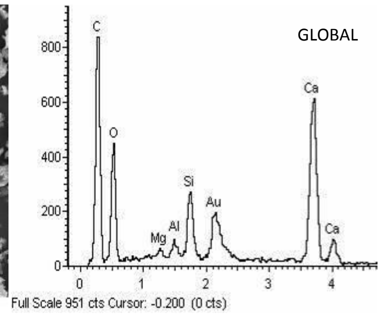
Spectrum for Z5

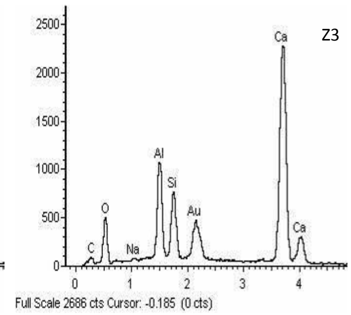


Spectrum for Z8

Fig. 6. SEM photos and EDS spectrums for GRTb







CEM I 42,5 R 1500 times enlarged | Spectrum for GLOBAL | Spectrum for Z3

Fig. 7. SEM photos and EDS spectrums for CEM I

Table 4. Laser particle size distribution curves (dXX-diameter for which XX% of the particles are smaller, by volume)

	GRTa	GRTb	CEM I 42,5 R
	Diameter (µm)		
d10	9,165	3,081	2,186
d50	28,235	18,005	16,557
d90	171,31	95,924	41,354

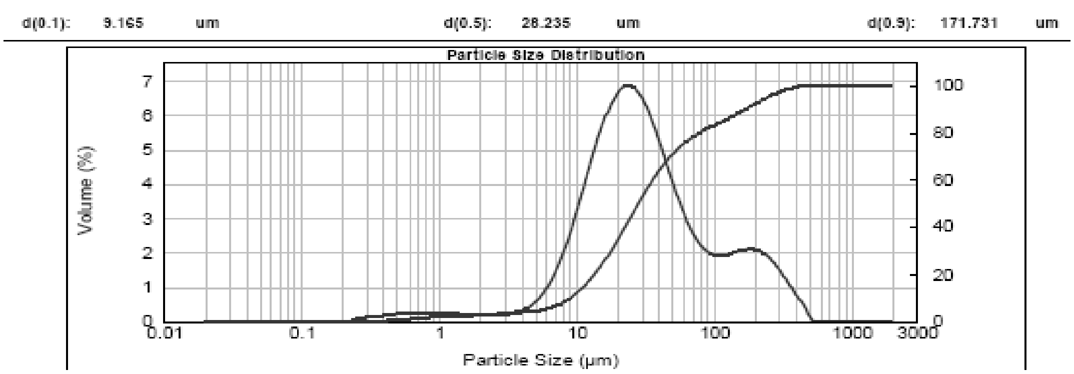


Fig. 8. Laser grading curve for Grits (GRTa)

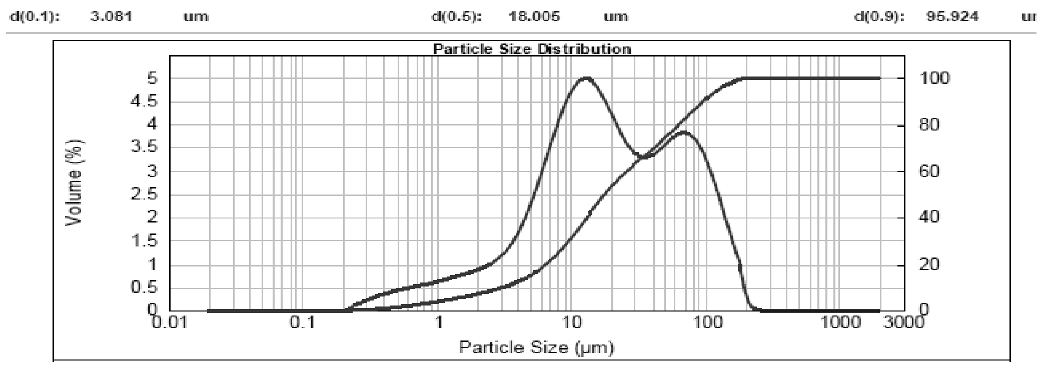


Fig. 9. Laser grading curve for Grits (GRTb)

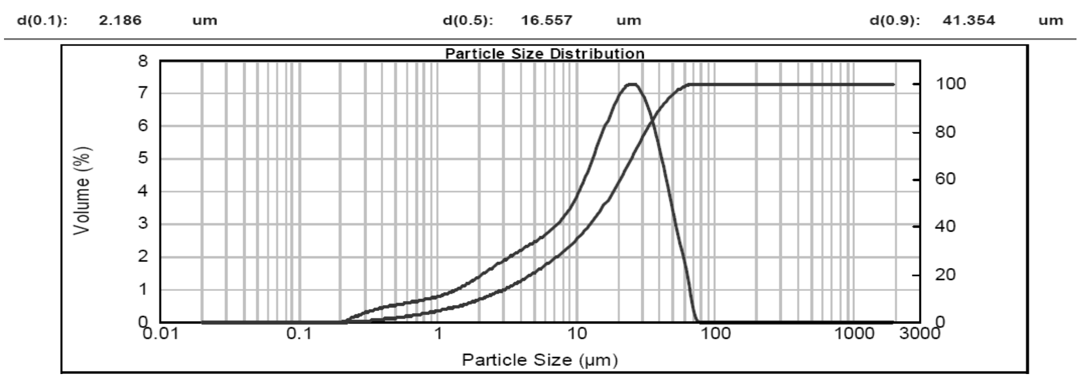


Fig. 10. Laser grading curve for cement used

MORTAR PRODUCTION

Tests were carried out in two steps with two types of equivalent mortars being produced at each step, a control mortar (CTL) with 100% of Portland cement and a mortar with 10% cement replacement with ground grits, GRTa in the first step and GRTb in the second step. The ratio “binder: sand: water” for the all types of mortar was 1:3:0.5 by weight. Standardized CEN sand provided in 1350 gr. sealed bags was used. Workability was measured following the procedure described in ASTM C 109/90. Similar workability (CTL±10mm) was obtained for all types of mortar (Table 5).

Several prismatic, cubic and cylindrical test specimens were produced for the various tests to be carried out with each type of mortar. Standard procedure described in EN 196-1 was generally used. Specimens were demoulded the next day and then cured in accordance with the standard procedure, in water at 20 ºC.

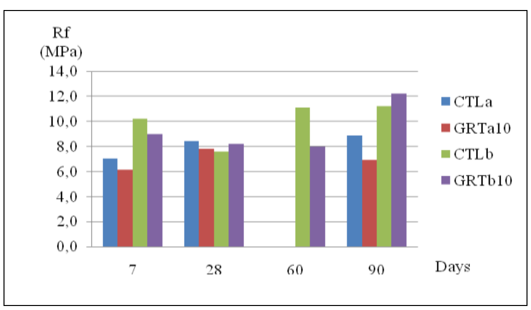
Fig. 11. Flow test

Table 5. Mixture proportions of mortars

Mortar type	CTLa	CTLb	GRTa10	GRTb10
CEM I 42,5R, g	450	450	405	405
GRT, g			45	45
Standard Sand, g	1350	1350	1350	1350
Water, g	225	225	225	225
Flow, mm	215,9±3,7	223,4±3,1	219,1±5,1	213,9±7,5

Density, Strength and Activity Index

Density at 7 and 28 days strength was determined at 7, 28, 60 and 90 days, following the standard procedure described in NP EN 196-1. Results are shown in Table 6 and Figure 12 and 13. Activity Index (AI) of a certain percentage of cement replacement by an addition corresponds to comparing strength of mortar produced with that percentage replacement with the strength of equivalent mortar with no cement replacement, at the same age, produced in exactly the same conditions. AI was determined at 90 days. Results are shown in Table 6.



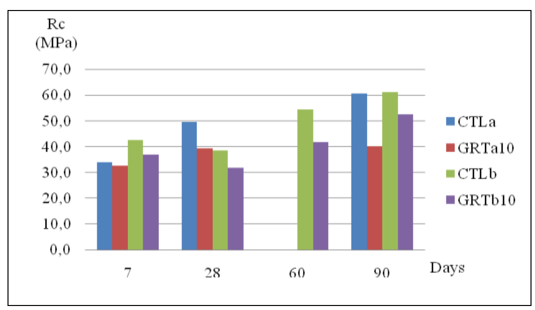


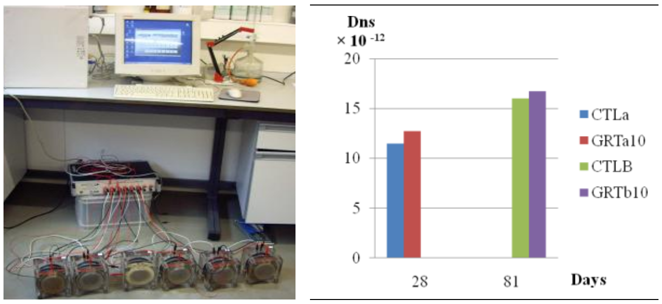
Fig. 12. Strength in flexure

Fig. 13. Strength in compression

Chloride ion penetration

Chloride ion penetration was assessed by the Luping method, which is a non-steady state migration method based on a theoretical relation between diffusion and migration. This enables the calculation of the apparent chloride diffusion coefficient (D_{ns}) from an accelerated test. This method is based on measuring the depth of colour change of a silver nitrate solution sprayed on the specimens previously submitted to a migration test. Results of this test are presented in Figure 14 and Table 6.

Resistivity
Resistivity in saturated specimens was evaluated on specimens at the beginning of the chloride ion penetration test and results are shown in Figure 15 and Table 6.



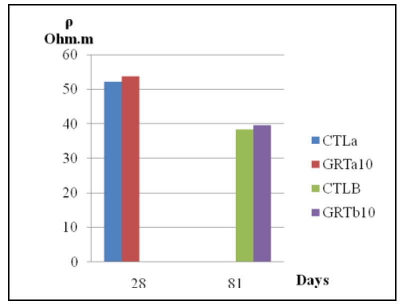


Fig. 14. Cell and D_{ns} results for Luping method **Fig. 15. Resistivity**

Absorption by Capillarity
Water absorption by capillarity was carried on 150 mm cube specimens on a 3mm water layer. Specimens were weighed at time intervals up to 4h 30min and linear regression was applied to the plots leading to sorptivity results (Figs. 16, 17 and Table 6) with correlation coefficients (R) over 0.998.

Carbonation Accelerated carbonation tests were carried out following the procedure described in LNEC E391. As only one test specimen for each mortar type was analysed, results shown in Table 6 must be considered cautiously.

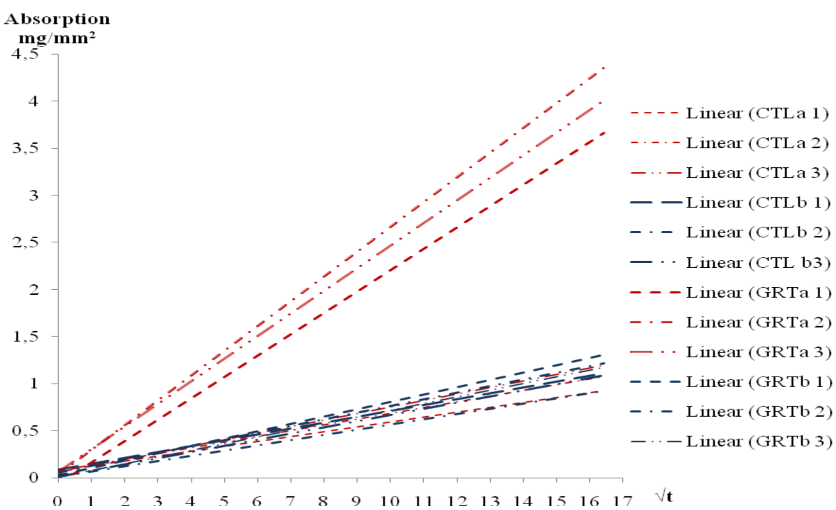


Fig. 16. Capillary absorption for the first 4-1/2 hours

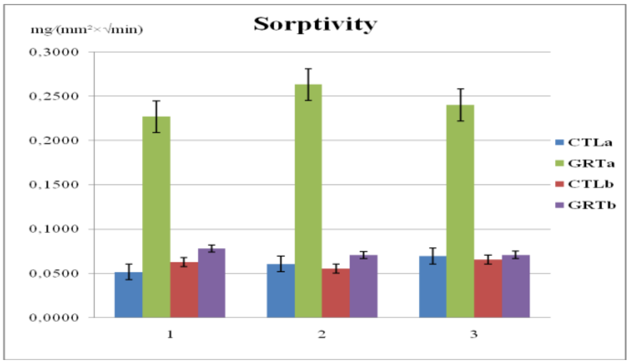


Fig. 17. Sorptivity

Table 6. Mechanical and durability results obtained for the two sets a and b each with two mortar types (CTL and GRT) as well as perfomance (+ or -) of each property for GRT mortar versus the value of property obtained for CTL mortar.

Mortar type		CTLa	GRTa10	CTLb	GRTb10	Perfom. (+/-) of GRTa10 versus CTLa	Perfom. (+/-) of GRTb10 versus CTLb
Density, strength and activity index (AI)							
Density, 7d	kg/m3	2268 ± 21	2279 ± 6	2343 ± 29	2382 ± 17		
Flexural strength, 7d	MPa	7,1 ± 0,4	6,2 ± 0,6	7,6 ± 0,7	8,2 ± 1,3	-13%	+8%
Compressive strength, 7d	MPa	34,0 ± 1,8	32,6 ± 0,6	38,6 ± 3,6	31,8 ± 2,6	-4%	-18%
Density, 28d	kg/m3	2274 ± 23	2312 ± 14	2293 ± 6	2302 ± 28		
Flexural strength, 28d	MPa	8,4 ± 0,4	7,8 ± 0,5	10,2 ± 0,7	9,0 ± 0,8	-7%	-11%
Compressive strength, 28d	MPa	49,4 ± 2,8	39,2 ± 0,9	42,6 ± 1,8	37,0 ± 1,1	-21%	-13%
Flexural strength, 60d	MPa			11,1 ± 0,6	8,0 ± 0,5		-27%
Compressive strength, 60d	MPa			54,5 ± 2,6	41,8 ± 0,7		-23%
Flexural strength, 90d	MPa	8,9 ± 0,2	6,9 ± 0,3	11,2 ± 1,5	12,2 ± 0,3	-22%	+9%
Compressive strength, 90d	MPa	60,5 ± 2,2	40,2 ± 1,2	61,2 ± 1,9	52,6 ± 2,6	-34%	-14%
AI	%		66%		86%		
Durability related properties							

Dns, $\times 10^{-12}$, 28d	m^2/s	11,5 ±0,7	12,7 ± 0,3			-10%	
Dns, $\times 10^{-12}$, 81d	m^2/s			16,0 ± 0,7	16,7 ± 0,5		-4%
Resistivity, 28d	Ohm.m	52,2 ± 0,9	53,7 ± 0,5			+3%	
Resistivity, 81d	Ohm.m			38,3 ± 1,2	39,6 ± 0,5		+3%
Sorptivity, 36d	$mg/(mm^2 \times min^{0,5})$	0,061±0,009	0,243±0,017	0,061±0,005	0,072±0,004	-298%	-18%
Carbonation, 47d	mm	4,0 ± 1,4	4,5 ± 0,4	4,0 ± 1,4	4,2 ± 0,8	-11%	-5%

X_{GRT} – test for GRT mortar, X_{CTL} – test for CTL mortar

$$\text{perfomance} = \frac{X_{GRT} - X_{CTL}}{X_{CTL}}$$

CONCLUSIONS

Grits material consists mainly of calcium carbonate with no amorphous material and therefore non pozzolanic. Although strength for GRT mortar was always under CTL it did increase with fineness thus presuming similar performance to CTL with further grinding. Except for sorptivity, durability related properties show similar performance for both GRT mortars compared to CTL, with enhanced performance for finer material. Therefore as a first conclusion if sulphates are controlled and chlorides reduced (to under 0.1%) through prior treatment this waste material, if ground to sufficient fineness may be used as filler for concrete. Applying grits even in small dosages will avoid dumping to landfill and therefore contributing to sustainability in construction.

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