

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/275353761>

SELF-COMPACTING CONCRETE CONTAINING LIMESTONE AND A WASTE OIL-REFINERY CATALYST

Conference Paper · January 2014

CITATION

1

READS

106

3 authors:



Ines Laginha

University of Lisbon

2 PUBLICATIONS 2 CITATIONS

[SEE PROFILE](#)



Pedro Raposeiro da Silva

Instituto Politécnico de Lisboa

45 PUBLICATIONS 208 CITATIONS

[SEE PROFILE](#)



Carla Costa

Instituto Politécnico de Lisboa

31 PUBLICATIONS 257 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Recognition of physical-mechanical properties as a basis for evaluating wood in old buildings [View project](#)



EcoZement [View project](#)

SELF-COMPACTING CONCRETE CONTAINING LIMESTONE AND A WASTE OIL-REFINERY CATALYST

Inês Laginha, Pedro Silva, Carla Costa^(*)

Área Departamental de Engenharia Civil, Instituto Superior de Engenharia de Lisboa, Portugal
{ineslaginha, silvapm, carlacosta}@dec.isel.pt

ABSTRACT

This paper describes research on viability of producing self-compacting concretes (SCCs) with ternary blends of powder materials comprising cement, limestone powder (L) and a waste catalyst generated at the fluid cracking catalytic unit (FCC) by the oil-refinery industry. For this purpose, an experimental program was conducted to iteratively design mixture proportions of SCCs using 30% (v/v) limestone powder and 0-30% (v/v) of waste FCC catalyst as partial cement replacements in the powder materials blends. Tests of fresh-state SCCs were conducted for slump flow, V-funnel, and L-box. Compressive strength tests of hardened SCCs were conducted at 3, 7, 14 and 28 days of curing time. Results showed that SCCs containing high volumes - up to 60% (v/v) - of both additions, limestone and waste FCC catalyst, in powder materials blends achieve adequate self-compactability in compliance with European standard EN 206-9. Moreover, waste FCC catalyst incorporation in concretes composition leads to compressive strength gains.

Besides standard requirements being fulfilled and the improvement in the concrete performance, the ample availability of the waste FCC catalyst (around 500 kton) in oil refineries worldwide make this waste a potential steady supply for the concrete industry. As such, large-scale manufacturing of innovative SCCs with recycle waste FCC catalyst is feasible in the future, making a significant contribution to lower the carbon footprint of the construction materials.

Key-words: Self-compacting concrete, limestone, waste oil-cracking catalyst, ternary concrete mixtures.

INTRODUCTION

The development of self-compacting concrete (SCC) is considered a technological breakthrough in the concrete material's domain that occurred in the last decades. Among several benefits that SCC can provide, a very significant one is its ability to address environmental, technological and economic issues in an integrated way. Namely, SCC typically incorporates significant amount of additions in its powder materials with various potential positive effects on concrete performance. Such use of the additions, namely if they are industrial wastes, also concurs to the reduction of the environmental impact of the cement industry, mitigates solid waste disposal of in landfills and turns a polluting waste into a product with added-value for building materials industry.

In this regard, one of the goals of this ongoing project is the viability assessment of using a waste catalyst - originated by the fluid catalytic cracking (FCC) unit during the oil refinery process - as a pozzolanic addition to produce SCC. This waste is produced on a fairly large scale of around 500 kton in oil refineries worldwide, of which 20% is originated in European refineries [1]. Thus, the potential use of this waste as a steady supply for industrial production of cement-based materials - namely in SCC's manufacturing - can make major contributions towards a more sustainable construction. However, besides the outstanding pozzolanic properties already identified in the waste FCC catalyst [2-4], the majority of this waste catalyst is still disposed in landfills which is the least environmentally preferred option.

Our previous results using waste FCC catalyst as addition in SCCs production [3] revealed that it is possible to produce SCCs incorporating up to 25% (v/v) in their powder materials, as well as that this waste incorporation typically leads to better compressive strength performance. Higher levels of cement replacement were experimented without success due to the occurrence of segregation and bleeding in the SCCs fresh-states. This limit in this waste content incorporation in the SCCs composition was mainly attributed to the high water absorption ability presented by the FCC catalyst [4].

Therefore, aiming to increase the additions content on the SCC composition, this paper describes research on fresh-state characteristics, as well as on compressive strength of SCCs produced with ternary powder materials blends of cement, limestone powder and waste FCC catalyst. The main idea lying beneath this challenge is that the synergy between both additions (limestone and waste catalyst) may allow the compensation of their mutual shortcomings. Namely, when limestone is used as addition in concretes production their compressive strengths tend to decrease due to the dilution effect associated to the reduction in the cement content [6-8], but on the other hand, typically, the workability in their fresh-states, increases [7, 8]. Whereas, the waste FCC catalyst - which is an aluminosilicate with a huge specific surface area - tend to enhance concrete strengths [3, 4] but on the other hand, decreases their workability [4, 9].

A concrete mixture can only be classified as SCC if its fresh-state characteristics as specified in European standard EN 206-9 (presented in Table 1) are fulfilled. Taking into consideration these requirements, the preliminary results obtained in the present study showed that it is possible to produce SCCs with high level - up to 60% - of simultaneous incorporation of both additions, limestone and waste FCC catalyst.

Table 1 - Acceptance criteria of SCCs fresh-state characteristics as specified in the European standard EN 206-9.

	Class	Value
<i>Flowability evaluation test:</i>		
Slump flow (SF) (mm)	SF1	550-650 mm
	SF2	660-750 mm
	SF3	760-850 mm
<i>Viscosity evaluation tests:</i>		
Slump flow/ t_{500} (sec)	VS1	< 2.0 s
	VS2	\geq 2.0 s
V- funnel (sec)	VF1	< 9 s
	VF2	9-25 s
<i>Passing ability evaluation test:</i>		
L-box	PL1	\geq 0.80 with 2 bars
	PL2	\geq 0.80 with 3 bars

EXPERIMENTAL PROGRAM

Materials

The powder materials used in this study were: commercial Portland cement type CEM I 42,5R (C), according to European standard EN 197-1 of industrial origin from the CIMPOR Company (Portugal); waste fluid cracking catalytic (FCC) catalyst, produced by Portuguese refinery company PETROGAL S.A. at Sines; and, powdered limestone (L) quarried in Rio Maior (north of Lisbon, Portugal).

Table 2 lists the bulk chemical compositions and physical properties of the powder materials. Chemical composition was obtained by X-ray fluorescence spectrometry (using a PANalytical model Axios equipment). Loss on ignition (LOI) was evaluated following European standard EN

196-2. Specific density was determined by helium pycnometry using an AccuPyc 1330 instrument from Micromeritics. Specific surface area was determined by nitrogen adsorption-desorption isotherm at 77 K using a Micromeritics ASAP 2000 apparatus. Particle size distribution was obtained by laser diffraction using a *CILAS PSA 1064* equipment. Cumulative particle size distributions of cement, limestone and waste FCC catalyst are represented in Figure 1.

Table 2 - Chemical composition (% w/w) and physical properties of the powder materials.

	Cement (C)	Limestone Powder (L)	waste FCC catalyst
Chemical Composition (% w/w)			
SiO ₂	19.41	0.20	39.59
Al ₂ O ₃	5.45	0.20	52.81
Fe ₂ O ₃	3.23	0.06	0.55
CaO	62.57	55.10	0.09
MgO	1.91	0.32	0.19
SO ₃	2.89	0.00	0.23
K ₂ O	1.10	0.01	0.04
Na ₂ O	0.00	0.02	0.68
TiO ₂	0.27	0.02	0.82
P ₂ O ₅	0.10	0.01	0.06
MnO	0.05	0.00	0.00
SrO	0.07	0.00	0.00
Cl ⁻	0.02	0.00	0.01
LOI ⁽¹⁾	2.68	43.52	1.48
TOTAL	99.75	99.46	95.07
Physical Properties			
Specific density (g/cm ³)	3.18	2.60	2.71
Specific surface area (m ² /g)	1.05	0.71	150.00
Mean particle size (μm)	26.57	71,15	86.05
d ₅₀ ⁽²⁾	21.48	70.47	79.86
d ₉₀ ⁽³⁾	2.33	198.91	46.95

¹ Loss on ignition, evaluated following European standard EN 196-2.

² 50% (v/v) of particles have diameters smaller than the presented value.

³ 90% (v/v) of particles have diameters smaller than the presented value.

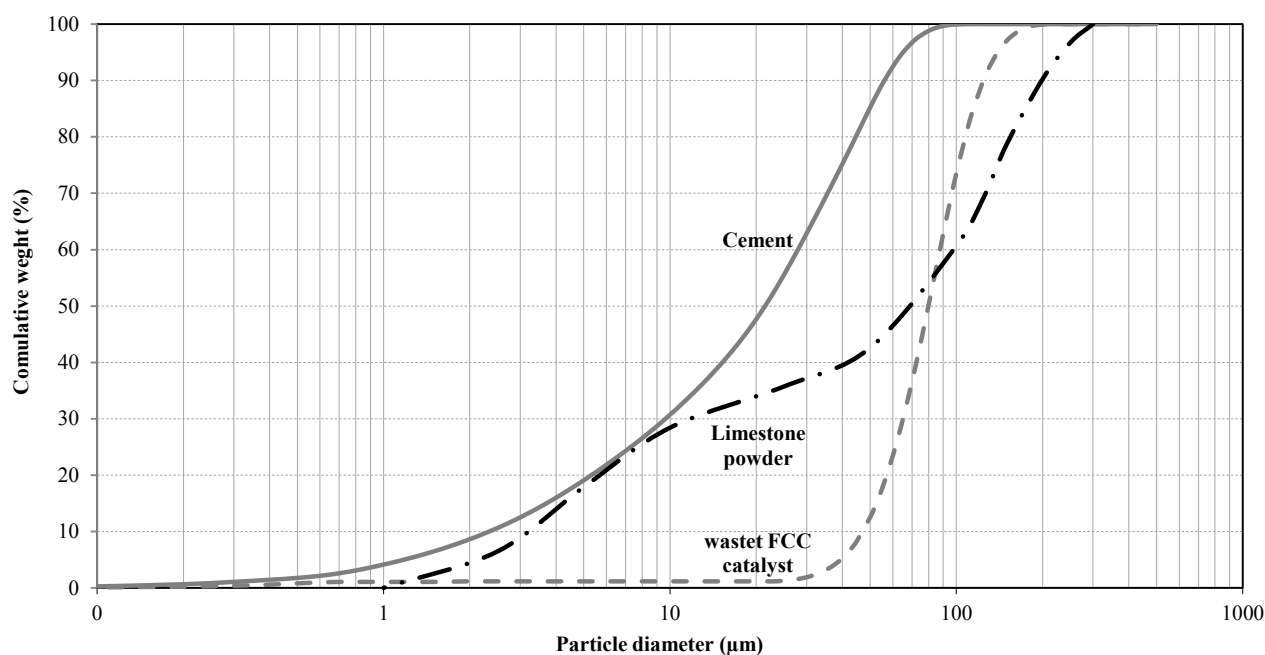


Figure 1 - Cumulative particle size distributions of cement (C), limestone powder (L) and waste FCC catalyst.

Four different aggregates (according to European standard EN 12620) were used: two natural siliceous sands (one finer and one coarser, Sand_{0/2} and Sand_{0/4}, respectively) and two crushed limestone aggregates (La1 and La2). The mixture proportion of the two sands - used as fine aggregate - as well as the mixture proportion of the two crushed limestones - used as coarse aggregate - were determined experimentally in order to obtain maximum bulk densities. Figure 2 presents cumulative particle size distributions of fine and coarse aggregates.

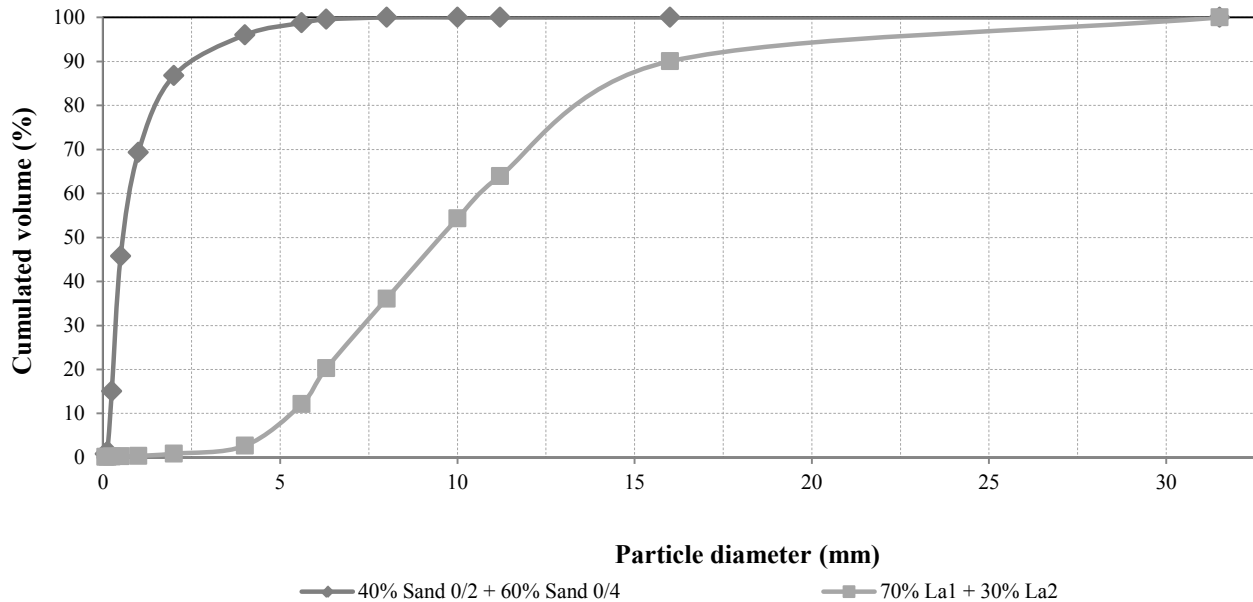


Figure 2 - Cumulative particle size distributions of fine and coarse aggregates.

The superplasticizer (Sp) used is a third-generation high-range water reducing admixture complying with European standard EN 934-2. This Sp consists of modified polycarboxylates and is supplied in liquid form with density of 1.07. Tap water was used, in accordance with European standard EN 1008.

Proportioning the SCCs mixtures

A two-stage experimental program was conducted for the mixture proportioning of the SCCs using waste FCC catalyst and limestone as partial cement surrogates in the powder materials blends. Actually, four different blends of powder materials were considered: one made with 30% (v/v) of cement replaced with limestone; and three other mixtures with cement partially replaced simultaneously with 30% (v/v) L and with 10, 20 and 30% (v/v) of waste FCC catalyst. Details about the mixture proportioning procedure can be found elsewhere [10]. In brief, the first stage consisted in mortars preparation as well as in mini slump-flow and mini v-funnel testing in order to iteratively evaluate the parameters: V_w/V_p (volumetric ratio between water and powder materials) and $Sp/p\%$ (weight ratio, in percentage, between the superplasticizer and powder materials), to achieve adequate flow requirements for each considered powder materials blend (slump flow diameter of 257 ± 6 mm and V-funnel flow time of 8.23 ± 0.54 sec). For calculation purposes, in mortars preparation V_p/V_s ratio (volumetric ratio between powder materials and fine aggregate) of 0.75 and V_v (volume of voids) of $0.03 \text{ m}^3/\text{m}^3$ were kept constant.

The second stage of the experimental program consisted in SCCs preparation with same additions incorporation level in the powder materials blends. Besides the experimental parameters considered in the previous stage, the following conditions were also assumed: V_m/V_g (volumetric ratio

between mortar and coarse aggregates) of 2.427; V_g (absolute volume of coarse aggregate) of $0.268 \text{ m}^3/\text{m}^3$; and V_m (absolute volume of mortar) of $0.702 \text{ m}^3/\text{m}^3$. The SCCs mixing procedure adopted is described elsewhere [10].

Table 3 presents the parameters determined in the mortars stage of the experimental program as well as the mixture proportions used to produce the SCCs. The SCCs mixtures are identified by a code that indicates the amount of each addition present in the powder materials blend as follows: 30L represents the mixture in with 30% of cement replaced with L (used as reference mixture to evaluate the effect of waste catalyst on SCCs properties); and 30L_10FCC; 30L_20FCC and 30L_30FCC represents respectively the mixtures with cement replaced, simultaneously, with 30% of L and with 10, 20 and 30% of waste FCC catalyst.

Table 3 - Parameters - V_w/V_p and $Sp/p\%$ - determined in mortars stage of experimental program and mixture proportions of SCCs.

Mix description	30L	30L_10FCC	30L_20FCC	30L_30FCC
<i>Parameters determined in mortars stage of the experimental program:</i>				
V_w/V_p	0.85	0.87	0.95	1.10
$Sp/p\%$	1.37	1.00	0.90	1.54
<i>Mixture proportions (kg/m^3) of SCCs:</i>				
Powder materials:				
Cement	475	406	330	251
Limestone powder	141	144	154	170
Waste FCC catalyst	0	58	113	161
Water	181	185	197	217
Fine aggregate ($0.6\text{Sand}_{0.2}+0.4\text{Sand}_{0.4}$)	744	742	724	690
Coarse aggregate ($0.6\text{La}_1+0.4\text{La}_2$)	746	746	746	746
Superplasticizer - Sp	9	9	5	9
Water/Powder materials ratio (w/w)	0.29	0.30	0.33	0.37

Fresh-state SCCs tests

The following tests were performed on fresh SCCs: slump flow, V-funnel and L-box. The procedures used are described, in European standard 12350, respectively, in parts 8, 9 and 10.

Compressive strength test

The test procedure used in the determination of the compressive strength is described in European standard EN12390-3. This test was performed at 3, 7, 14 and 28 curing days. For that purpose, 150 mm cubic moulds were used, which were kept in a wet chamber ($20 \pm 2 \text{ }^\circ\text{C}$ and $\text{RH} \geq 95\%$) after demoulding, at 24 hours. The specimens were tested immediately after being taken from the curing chamber. The test was performed in three moulds for each mixture composition and test age with a 3000 kN hydraulic press and a loading rate of $0.6 \pm 0.2 \text{ MPa/s}$.

RESULTS AND DISCUSSION

Fresh-state properties of SCCs:

Results of fresh-state properties of SCCs namely, flowability (slump flow diameters), viscosity (V-funnel flow and t_{500} times) and passing ability (L-box height ratios) are presented in Figure 4, Figure 5 and Figure 6, respectively. Same figures also show the corresponding SCCs classification for each fresh-state property, according to European standard EN 206-9.

As can be seen in Figure 4, slump flow diameter values of SCCs were measured in the range 530-788 mm. As such, SCCs meet the consistency requirements set out in European standard EN 206-9, although for the SCC mixture 30L_10FCC the tolerance of $\pm 50 \text{ mm}$ admitted for slump flow diameter values in the standard EN 206-9 had to be considered.

As presented in Figure 5, the values of the t_{500} flow times were measured in the range 2.84 - 7.54 s and V-funnel times in the range 4.76 - 11.85 s. Therefore, all mixtures satisfy the requirement sets out in European standard EN 206-9.

As can be seen in Figure 6, the L-box passing ability ratios of SCC mixtures were observed in the range 0.54-0.84. The SCC mixture 30L_10FCC was found to be out of European standard EN 206-9 which recommends this value must be higher than 0.8 (Table 1), in order to mitigate the risk of blockage during the concrete application. Thus, the mixture 30L_10FCC cannot be considered as a SCC, according to EN 206-9. However, as previously stated, this paper presents preliminary results of the ongoing investigation fostering the production of SCCs using both limestone powder and waste FCC catalyst as additions. Therefore, it is our understanding that this SCC mixture proportion can still be improved, in order to achieve better passing ability, to allow for PL1 value to reach 0.8.

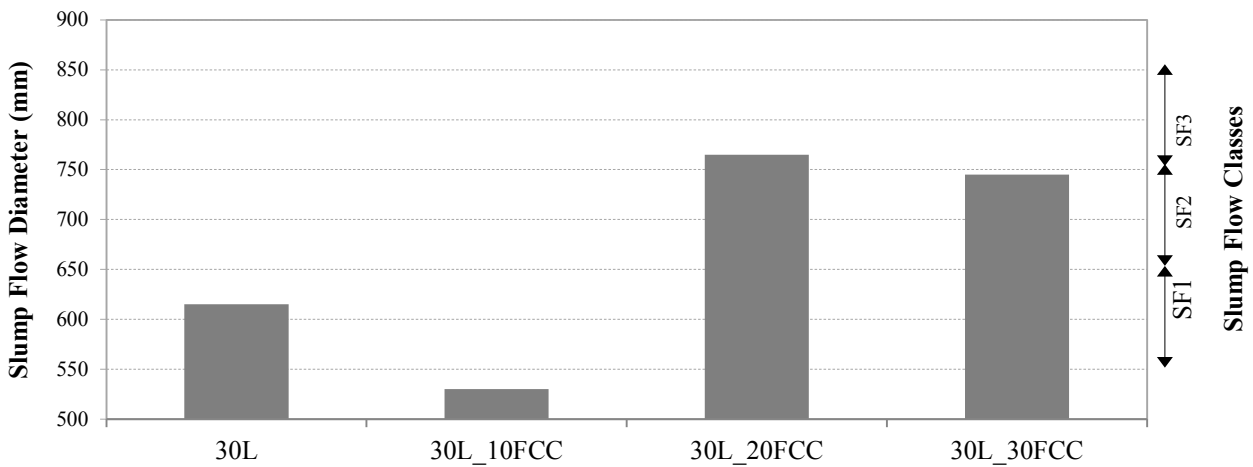


Figure 4 - Slump flow diameter of concrete mixtures and correspondent slump-flow classification (according to European standard EN 206-9).

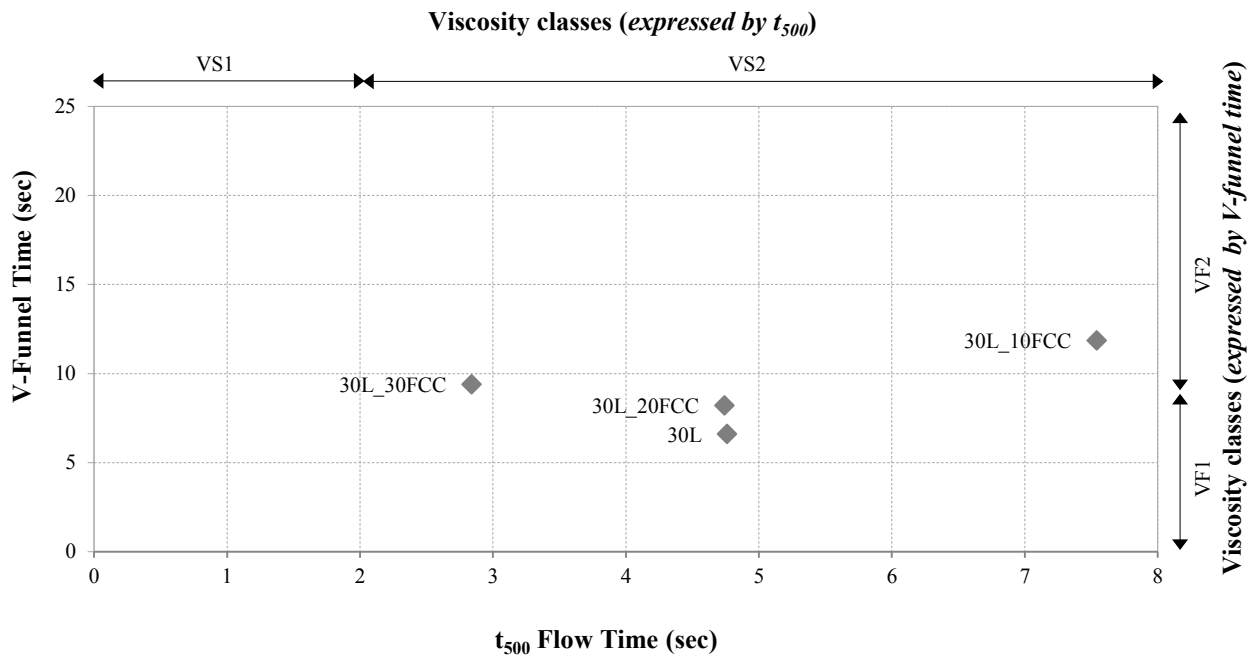


Figure 5 - t_{500} flow and V-funnel flow times of concrete mixtures and correspondent viscosity classification (according to European standard EN 206-9).

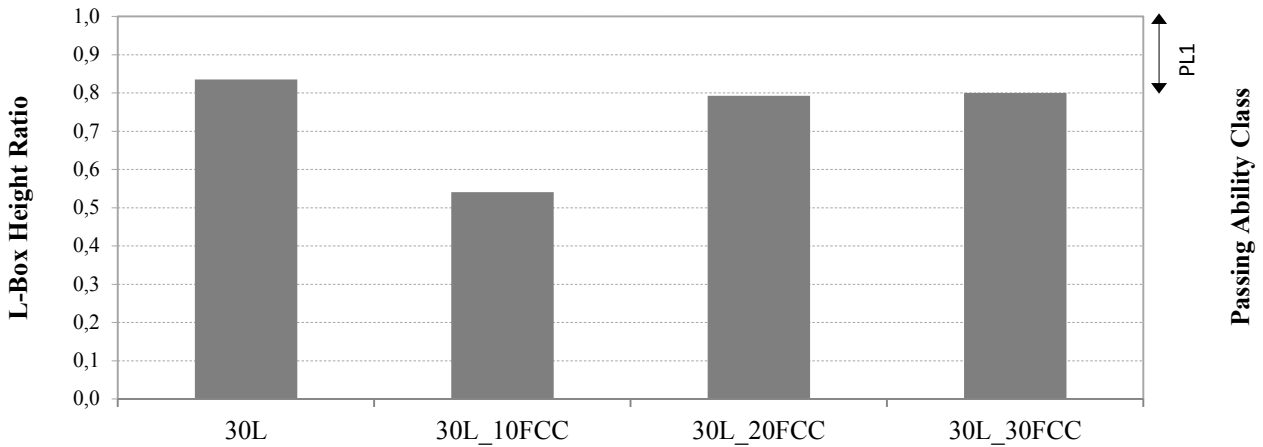


Figure 6 - L-box height ratios of concrete mixtures correspondent passing ability classification (according to European standard EN 206-9).

Compressive strength results

Figure 7 shows the compressive strength results of SCCs for different curing ages. The SCC mixture 30L_10FCC (containing both 10% of waste FCC catalyst and 30% of limestone, in powder materials composition), exhibits a strength enhancement higher than that of the SCC mixture which uses only 30 % limestone (30L), since an early age namely from the third day of curing time. During the first 14 days of curing time, the compression strengths of 30L_20 FCC and 30L_30FCC mixtures are lower than the strength of the SCC mixture 30L and decreases with the waste incorporation level. However, besides the delay in the strength development, on the 28th day of curing time, the strength of the SCC mixtures incorporating either 20 or 30% of waste FCC catalyst also reach the strengths of the L30 the SCC mixture (without waste incorporation).

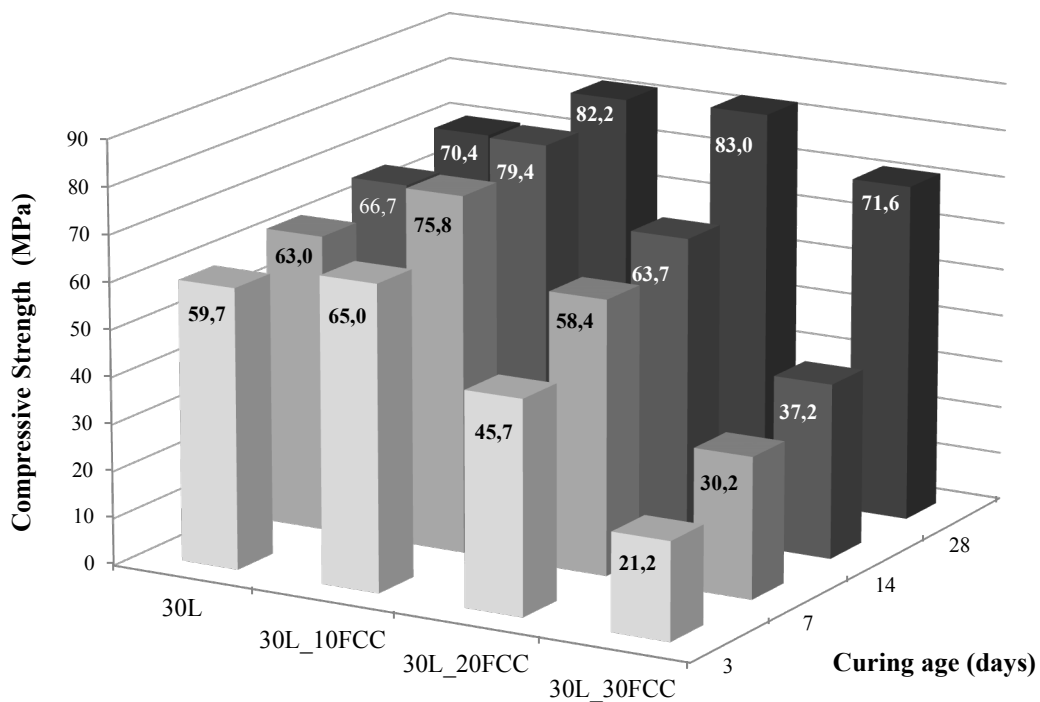


Figure 7 - Compressive strength of SCCs mixtures for 3, 7, 14 and 28 days of curing age.

The compressive strengths gain, beyond the value expected for SCC strengths considering the dilution effect (i.e, the cement content reduction due to its partial replacement with additions), are mainly attributed to the remarkable pozzolanic activity of the waste FCC catalyst [2-5]. This behavior is mostly associated to the extremely high specific surface, 150 000 m²/kg, of the catalyst particles (Table 2).

CONCLUSIONS

The following main conclusions can be drawn from the experimental results presented in this paper:

- concretes with ternary blends of powder materials comprising simultaneously, as additions, 30% of L as well as 20 and 30 % of waste FCC catalyst, comply with the requirements set out in the European standard EN 206-9 to be classified as SCCs
- from the third day of curing time, the concrete with 30% of L and 10% of waste FCC catalyst incorporations in its powder materials – 30L10FCC – exhibits a strength-enhanced higher than that of the concrete with only 30% of L as addition
- the incorporation of 10 and 20% of waste FCC catalyst, in the powder materials blend, delay the strength development during the first 28 days of curing time, but from this curing age the strength is similar with that of the SCC using only 30% of L as addition.

SCCs address environmental, technological and economic issues in an integrated way. Actually, along with their promising properties, the concretes assessed in this study are made from a waste generated, in a significant amount worldwide by the oil refining industry.

Fostering to contribute towards a large scale industrial application of these SCCs, it is currently under study a comprehensive characterization of both fresh and hardened properties to support knowledge enhancement on predictable performance and durability and, thus, to reach market acceptance.

ACKNOWLEDGMENTS

The authors, I. Laginha and C. Costa, acknowledge the support of Fundação para a Ciência e Tecnologia (FCT) and PETROGAL S.A Company through the project funding PTDC/ECM/113115/2009.

REFERENCES

1. European Cracking Catalysts Producers Association (ECCPA). "FCC Equilibrium Catalyst (including FCC catalyst fines) finds safe reuse/rework outlets in Europe". European Chemical Industry Council. p. 1-3, 2006.
2. Laginha, I., Costa C. "Environmental footprint reduction of ternary blended cements recycling industrial wastes".1st International Conference: Water, Waste and Energy Management: Salamanca, Spain. p. 1-4, 2012.
3. Payá, J.M. J., Borrachero, M.V., Garcés, P., Mellado, A., Velázquez, S., Soriano, L., Zornoza, E. "Outstanding Aspects On The Use Of Spent Fcc Catalyst In Binders", 1st Spanish National Conference on Advances in Materials Recycling and Eco – Energy, Madrid, 2009.
4. Costa, C., Marques, P,"Low-Carbon Cement With Waste Oil-Cracking Catalyst Incorporation", Cement Industry Technical Conference, 2012 IEEE-IAS/PCA 53rd Cement (doi: 10.1109/CITCON.2012.6215691): Austin, USA, p. 1-9, 2012.

5. António, J.L., Silva P., Costa, C. "Fresh Properties and Compressive Strength of self-compacting concrete containing waste fluid catalytic cracking catalyst". Concrete Innovation Conference: Paris, France. p. 1-8, 2013.
6. Laginha, I. "Reuse of Spent Catalyst exhausted from Oil-Cracking Refineries in Cement-based Materials". Msc in Civil Engineering"(in portuguese), Instituto Superior de Engenharia de Lisboa: Lisbon, Portugal. p. 1-264, 2011.
7. Uysal, M., Yilmaz. K. "Effect of mineral admixtures on properties of self-compacting concrete". Cement and Concrete Composites, 33(7): p. 771-776, 2011.
8. Hooton, R. D., Nokken, M., Thomas, M. D. A. "Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA " Cement Association of Canada Ed. (Ref. SN3053) 2007
9. Allahver A, Vakilinia, S., Gharabeglu, P. "Effects of RFCC Spent Catalyst on Some Physicomechanical Properties of Portland Cement Paste" Ceramics – Silikáty, 55 (2): p. 161-168, 2011.
10. Nepomuceno, M., Oliveira, L., Lopes, S.M.R. "Methodology for mix design of the mortar phase of self-compacting concrete using different mineral additions in binary blends of powders". Construction and Building Materials, 26(1): p. 317-326, 2012.