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Sustainable concrete mix design for a target strength and service life

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Abstract. Considering the well known environmental issues of cement manufacturing (direct and indirect levels of CO_2 emissions), clinker replacement by supplementary cementing materials (SCM) can be a very promising first step in reducing considerably the associated emissions. However, such a reduction is possible up to a particular level of SCM utilization, influenced by the rate of its pozzolanic reaction. In this study a (4-step) structured methodology is proposed in order to be able to further adjust the concrete mix design of a particular SCM, in achieving additional reduction of the associated levels of CO_2 emissions and being at the same time accepted from a derived concrete strength and service life point of view. On this note, the aim of this study is twofold. To evaluate the environmental contribution of each concrete component and to provide the best possible mix design configuration, balanced between the principles of sustainability (low environmental cost) and durability (accepted concrete strength and service life). It is shown that such a balance can be achieved, by utilising SCM by-products in the concrete mix, reducing in this way the fixed environmental emissions without compromising the long-term safety and durability of the structure.

Keywords: compressive strength; concrete; environmental cost; optimization; service life; supplementary cementing materials; sustainability

1. Introduction

Today, the cement and concrete industry is the dominant type of materials industry within the construction sector. Concrete is recognized to be the most widely used construction material, second only to water in total volumes consumed annually by society. It has been estimated that its average consumption is about 1 tonne per year per every person on the planet (Flower and Ganjayan 2007). Latest estimations from CEMBUREAU (2011) show a 0.7% rise in the EU construction activity in the first quarter of 2011, with the index of cement manufacturing showing a positive trend since the beginning of 2011. It is predicted that global demand for cement is expected to rise 4.1% yearly through 2013, to 3.5 billion metric tonnes in 2013. In general, at the

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rate of cement consumption before the effects of the economical crisis and based on the early signs of improvement, the demand for concrete (hence of cement) is expected to rise to about 16 billion tonnes a year by 2050 (WBSCD 2009, Zampini 2009).

Such levels of demand however, are associated with significant environmental burden. It is well known that any type of construction material entails certain aspects of environmental cost (in the form of carbon dioxide and other gasses emissions and energy consumed) from its manufacturing stage to its end-use (fixed environmental cost). In producing concrete the main emissions to air are associated with the cement-making process, where during the stage of clinker formation, CO_2 and other greenhouse gases are emitted to the atmosphere (CEMBUREAU 2009). These types of emissions are both raw material-related and energy-related. Raw material-related emissions are produced during limestone decarbonation and account for about 50% - 60% of total CO_2 emissions (Ecosmart Concrete 2008, WBSCD 2005). Energy-related emissions are generated both directly through fuel combustion and indirectly through the use of electrical power. It is estimated that burning of 1 tonne of clinker releases up to 0.97 tonnes of CO_2 (Habert *et al.* 2010, IEA 2010). Considering that on average 900 kg of clinker are used to produce 1 tonne of cement, the CO_2 emissions per tonne of cement are estimated in the magnitude of 0.87 tonnes (Ecosmart Concrete 2008, WBSCD 2005). Just to get an indication on the overall magnitude of related emissions, it should be noted that the construction sector accounts for a considerable share of the total EU final energy consumption (more than 42%) and produces more than 35% of all the greenhouse emissions (WBSCD 2005, 2009), with cement manufacturing contributing 5% of the global man made CO_2 emissions.

Bearing all of the above in mind, increasing emphasis should be placed on investigating and enforcing ways and methodologies to make the cement and the construction industry in general a more environmental friendly sector. On that note, altering the nature of clinker, or reducing the clinker content of cement with other constituents, should influence directly the levels of the derived CO_2 emissions. Several innovative new types of cements with altered clinker properties are being (and have been) developed, including carbon-negative cement based on magnesium silicates (rather than limestone as the Ordinary Portland Cement) (Ruffolo *et al.* 2010), cement produced in a reactor by rapid calcination of dolomitic rock in superheaded steam (Sweeny and Sceats 2009) and cement based on a mixture of calcium and magnesium carbonates and hydroxides (Bren 2011), with however limited appeal on the cement manufacturing companies. Reasons for such a withheld acceptance can be found on the fact that it is estimated that their substantial benefits on the reduction of the associated emissions will by fully utilized in a time frame of 5-10 years from today (WBSCD 2005, 2009). Overall, they do not provide a feasible economical and operational solution on tackling the environmental burden of cement manufacturing, today.

What is actually promising is direct reduction (up to a certain extent) of the clinker content in cement through utilization of industrial by-products as supplementary cementing materials *SCM* (fly ash, silica fume, rice husk ash, ground granulated blast-furnace slag). It has been estimated that 18% replacement of Portland cement results in a 17% reduction of the CO_2 emissions and that, if just 30% of cement (Ecosmart Concrete 2008) used globally were replaced with SCMs, the rise in CO_2 emissions from cement production could be reversed (Fig. 1).

However, equally important on achieving a “green” mix design, by utilizing industrial by-products as cement replacement materials, is to be able to further “fine tune” this particular mix

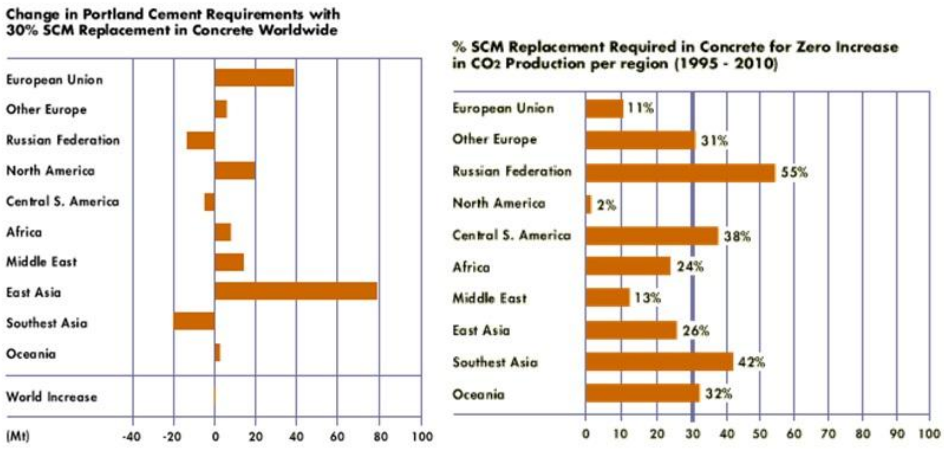

Fig. 1 Effect of SCM utilization in CO_2 emissions, after (Ecosmart concrete 2008)

design in order to safeguard certain concrete strength and service life requirements. The challenge is to be able to guarantee not only reduced environmental contribution but also, accepted mechanical properties, workmanship (workability), strength development and service life of a structure utilizing an environmentally friendly cement type.

Previous research studies (Antiohos *et al.* 2007, Demis and Papadakis 2012, Papadakis and Demis 2013) have identified the high added values of SCM incorporation in concrete strength and service life under harsh environmental factors. Considerable amount of work on developing analytical models for the evaluation of SCM in concrete using the concept of efficiency factors (or k-values, to compare the relative performance of supplementary cementing materials on concrete durability) by Papadakis (1999a,b, Papadakis *et al.* 2002) has identified the high-added value of certain types of these materials (as Type II additives in CEM I type of cement) and their pozzolanic properties on cement and mortar and their effects they entail on early concrete strength and volume stability (Antiohos *et al.* 2007, Papadakis and Tsimas 2002).

What is needed is to be able to achieve an optimum, balanced approach, between sustainability and durability design of reinforced concrete structures. After all, the very definition of sustainability (CEN EN 15643 2011) as "*the ability of a system (a structure) to be maintained for the present and future generations*" incorporates to a great extend the end result of the durability design (*maintenance of a structure for the present and future*). It should be noted, that the linkage between durability and sustainability is also emphasized, on the newly imposed EN Standards on the sustainable assessment of buildings (CEN EN 15643 2011), where a combination of the assessments of *environmental and economic performance* taking into account the *technical* and *functional requirements* of a *building* is approached, and on the next generation structural codes (*fi*b 2010), where repair and maintenance of concrete structures, will be subjected to strict requirements both with regard to environmental, economical and service life constraints.

The question that needs to be answered is how their relationship is affected. How a 30% reduction in clinker content (for example) or a reduction in the overall cement or water content affect the service life of a structure? Does an accepted sustainable design (from an environmental aspect point of view) provides automatically a durable design that meets certain target values, or certain modification in the mix design have to be made (and to what extent).

The scope of this particular study is to provide answers to the previously mentioned questions, on the relation between sustainable and durable design of reinforced concrete. To achieve this, a (4-step) structured methodology is proposed on estimating the reduction of environmental cost (in principle) and the strength and service life of concrete incorporating cement replacement materials, aiming to achieve the best possible (optimum) mix design configuration. Although the previously mentioned methodology is presented in detail in Section 3 of this study, it can by summarized as follows. Upon defining a set of design parameters, in terms of concrete compressive strength and service life, a typical (referenced as control) mix design (no SCM) is selected that produces strength and service life values higher than the design parameters, but at a high environmental cost. The aim is to reduce considerable that cost, without compromising on strength or service life. To achieve this, a particular SCM is utilized at certain incremental percentages and the environmental and service life properties are calculated. On reaching a rate of pozzolanic reaction bellow 1, further fine-tuning of the concrete compositional parameters is achieved resulting in reduced environmental cost and at the same time strength and service life values higher than the predefined ones. As it is also mentioned in Section 3, on every step, the service-life, and compressive strength, evaluation was made using a software tool, based on proven predictive models (according to performance-related methods for assessing durability) developed and validated by some of the authors of this study (Demis and Papadakis 2012, Papadakis *et al.* 1991, 2007, Papadakis and Demis 2013) well published and awarded by the ACI, for the estimation of concrete service life when designing for durability under harsh environments.

On this note, fly ash and silica fume were evaluated as Type II additives on a common CEM I type of cement. The first step however is the estimation of the environmental output of concrete incorporating these types of materials, as it illustrated in the following section.

2. Estimation of concrete environmental cost

It was previously mentioned that in producing concrete the main emissions to air are associated with the cement manufacturing process. However, other concrete constituents also contribute in that sense. In general, it can be said that the CO_2 emissions from concrete production are the summation of the emissions from, the chemical conversion process in clinker production (during cement manufacturing), from the energy consumption due to fossil fuel combustion (also during cement manufacturing), from the electrical energy required for the grinding of any additive materials and from the energy required (in terms of fuel consumption) for the transportation of the raw materials and of the final product. Overall, the initial environmental cost of concrete $E_{I,conc}$ (expressed in kg CO_2 / m^3 of concrete) taking under consideration every environmentally contributing parameter from the materials supply to concrete production, delivery and casting can be expressed as

$$E_{I,conc} = E_M + E_P + E_T + E_G \quad (1)$$

where E_M is the environmental cost of materials, E_P the environmental cost for concrete production, E_T the environmental cost for concrete transportation, delivery and E_G the cost for concrete casting, placing and finishing (all expressed in kg CO_2 / m^3 of concrete).

A more precise estimation of the environmental footprint (environmental factors) of each individual concrete component, based on the literature and on data derived from the Greek branch of a multi-national cement manufacturing company, is presented in this section. The total fixed environmental footprint of concrete materials ($E_{M,}$ kg CO_2 / m^3 of concrete) can be calculated as

$$E_M = C \cdot E_c + \Sigma(SCM \cdot E_{SCM}) + A \cdot E_A + W \cdot E_W + D \cdot E_D \tag{2}$$

where C, SCM, A, W, and D: are the contents (in kg / m^3 of concrete) of cement, supplementary cementing materials, aggregate, water and admixtures, respectively, in the concrete volume, and E_C, E_{SCM}, E_A, E_W, and E_D: their corresponding environmental costs (in kg of CO_2 / kg of material).

By taking under consideration the chemical equation of complete combustion of coal (Eq. (3)), where 94 kcal/mol of energy is produced (Q), since it is an exothermic reaction, the amount of CO_2 produced from energy consumption of 1kWh is calculated as 0.404 kg (1 cal is equal to 1.162 $\cdot 10^{-6}$ kWh, hence 94 kcal equal to 0.109 kWh producing 44 g of CO_2).

$$C + O_2 \rightarrow CO_2 + Q \tag{3}$$

The related to cement production CO_2 emissions vary from 0.65-0.92 tonnes per tonne of cement produced based on a cement plant with a modern technology and equipment, according to the literature (Flower and Ganjayan 2007, Hoenig *et al.* 2007), or from 0.61 – 0.80 according to data from cement manufacturing companies (ACC 2010, CRH 2011, Heidelberg Cement 2009, Holcim 2011, Italcementi Group 2011, Lafarge 2011) (Table 1). It should be noted that the levels of CO_2 emissions derived from cement manufacturing companies (Table 1) represent the average levels of emissions produced of the total range of different cement types produced annually by each company. Hence, they do not reflect on the actual levels of emissions of a CEM I type of cement.

For the purposes of this study, based on operational and production data from the Greek branch of a multi-national cement-manufacturing company, the level of CO_2 emissions from cement manufacturing was accurately estimated. By taking into account data as, the amount of cement produced (1,700,000 t/year), the electrical energy required (500,000 kWh/day) the level of CO_2 emissions measured (3,801,000 kg/day) and the total days of operation per year (335), the total CO_2 emissions were calculated to be in the range of 1,341,005 t/year. Hence in order to produce 1 t of cement 0.79 t of CO_2 are emitted into the atmosphere. In addition to the later, the derived CO_2 emissions from transportation should be added. Considering that on average 2.74 kg of CO_2 is emitted per litre of fuel, using vehicle transport, and that fuel consumption is estimated to be 1 lt / 3 km for 5 t of raw materials, the overall emissions arise from transportation are estimated to be 0.183 kg / km / t of raw material (GHG Protocol 2001).

According to data from a cement manufacturer (ItalCementi 2011), in order to extract, process and grind aggregates the overall CO_2 emissions are estimated to be 5.96 kg / t of aggregates (considering that 2.53 kWh are required for the production of 1 tonne of aggregates and that 9 lt of fuel are required for the transportation of a 5 tonnes shipment, resulting in 4.94 kg of CO_2 / t of aggregates).

When fly ash is used as a SCM, since it is a by-product of coal burning in electrical power stations, the emissions associated with power generation are not considered of being part of the environmental burden of fly ash. A small amount of energy required for the grinding of the raw material into very fine powder and for its transportation, are the only sources of greenhouse gasses. According to the literature (IPPC 2010, US Environmental Protection Agency 2008) the

Table 1 Cement production data and CO_2 emissions from the industry
(ACC 2010, CRH 2011, Heidelberg Cement 2009, Holcim 2011, Italcementi Group 2011, Lafarge 2011)

Reference	Cement produced (million t/year)	Electrical energy consumed (kWh/t cement)	CO_2 emissions	
			(t/year)	(t/t cement)
CRH 2011	15.6	180	10.3×10^6	0.735
Heidelberg 2009	3.90	131	3.70×10^6	0.739
Holcim 2011	144.3	100	$102. \times 10^6$	0.608
Italcementi 2011	71.8	122	34.4×10^6	0.708
Lafarge 2011	145	-	98.0×10^6	0.611
ACC 2010	-	118	43.1×10^6	0.798

previously mentioned energy requirement is estimated to be in the order of 20 kWh per tonne of fly ash produced, hence 8.06 kg of CO_2 per tonne of fly ash (emissions from transportation, similar to cement transportation, should also be added). In the case of silica fume, since it is available from limited regions on European level, the related emissions arise from its transportation. For reasons of simplicity, since the aim of the current study is to produce an estimation of the environment impact of concrete the previously mentioned source of emissions are assumed to be twice of those of fly ash transportation.

As far as water is concerned, the only source of emissions arises from the electrical energy required to pump the water, which in this study is considered to be negligible. Since no admixtures were used on the mix design of the different concrete configurations used in this study, the environmental impact of admixtures is ignored.

In this way, based on the proportions of the concrete constituent materials used and on the environmental factors, as derived above, the overall environmental cost of concrete was calculated. These calculations were incorporated on every step of the structures methodology presented in the following section.

3. Structured methodology for concrete mix design optimization

A schematic illustration of the (4-step) methodology proposed in this study, for the evaluation of the effectiveness of industrial by-products as cement replacement materials in achieving a robust mix design (in terms of concrete properties and service life) with minimum environmental cost is presented in Fig. 2.

The concept can be briefly described as follows:

•For given design parameters, as concrete compressive strength and service life (e.g., 40 MPa and 50 years), an initial set of concrete compositional parameters (CCP; cement, water, aggregate) is selected (achieving the target values) but with an initial high environmental cost (Step 1). This particular mix design is referenced as the control mix (with 95% clinker, no SCM) and its corresponding properties as the control values (strength, service life, environmental cost).

•A particular SCM is utilized as cement replacement material (Step 3) at a certain percentage (e.g. 10%, 20%, 30% for fly ash and 5%, 10%, 15% for silica fume, since it is a more intense pozzolanic material than fly ash). The environmental cost and the corresponding concrete properties are calculated, per incremental step of SCM addition. In order to provide a level of comparison in terms of concrete properties of the utilization of SCM (with the control mix, from

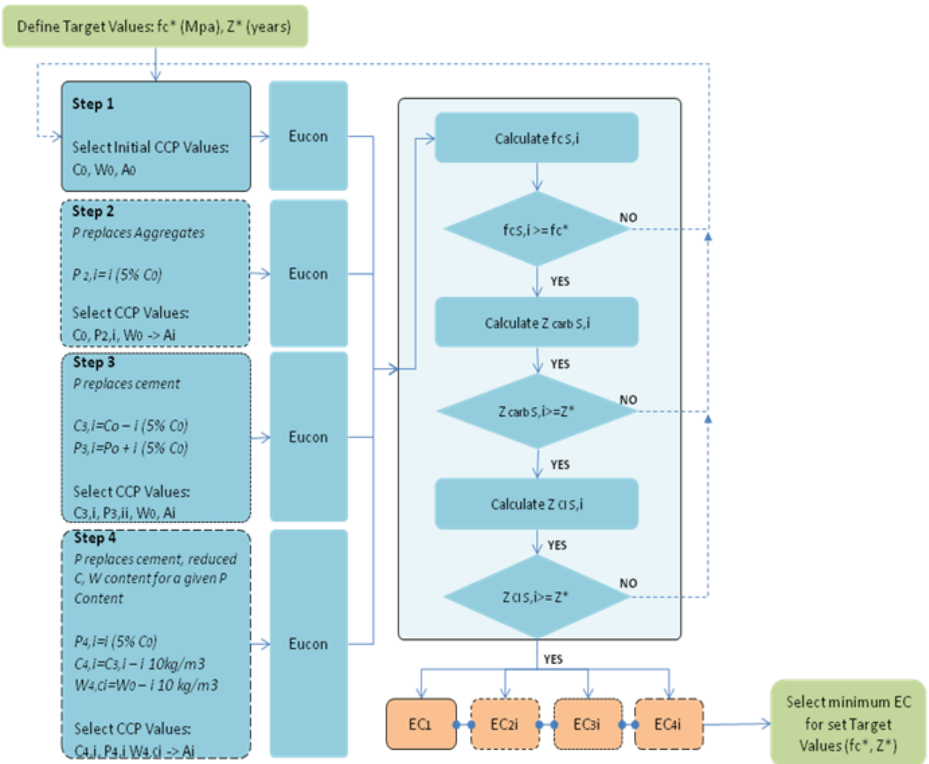

Fig. 2 Logical diagram of structured methodology for obtaining CCP values for minimum environmental cost (EC) with optimum strength and durability properties (C, P, W: cement, SCM and water contents, in kg/m3; Zcarb, ZCl-: service life in carbonation and chloride exposure, in years)

step 1), these materials are also inserted in the mix as aggregate replacement materials (Step 2). Eventhough they do not replace cement, hence we do not achieve a reduction in environmental cost, at the same time we do not particularly increase it, since the aggregate associated levels of CO_2 emissions are very small (5.96 kg / t of aggregates).

•Based on the best performed mix design configuration from Step 3 (in terms of environmental cost and target values) further reduction in the CCP properties is achieved (Step 4), through incremental reductions of cement (10 kg per step) and water (10 kg per step, for each decrease in cement content). In essence we are altering the water-to-cement (*w*/*c*) ratio of the best performed mix at Step 3, keeping at the same time the percentage of SCM constant.

In terms of service life as indicators of performance, the critical time for initiation of corrosion due to the action of carbon dioxide from the atmosphere (and the corresponding depth of carbonation), as well as the critical time for initiation of chloride induced corrosion (and the adequate concrete cover needed in order to sustain a chloride free concrete cover for a period of 50 years), were selected.

On every step, the service-life, and compressive strength, evaluation was made using a software tool, based on proven predictive models (according to performance-related methods for assessing durability) developed and validated by some of the authors of this study (Demis and Papadakis 2012, Papadakis *et al.* 1991, 2007, Papadakis and Demis 2013) well published and awarded by the

ACI, for the estimation of concrete service life when designing for durability under harsh environments. Concrete service life is reliably predicted using fundamental mathematical models that simulate the basic deterioration mechanisms of reinforced concrete (carbonation, chloride penetration). Principles of chemical and material engineering have been applied to model the physicochemical processes leading to concrete carbonation, as well as the processes of chloride diffusion in the aqueous phase of pores, their absorption and binding in the solid phase of concrete and their desorption.

4. Utilization of structured methodology for concrete mix design optimization

4.1 Step 1: selection of initial CCP values

A compressive strength of 40 MPa and a service life of 50 years were selected as the defined target values. A typical CEM I mix (w/c: 0.5, cement content: 300 kg/m^3, crushed aggregates of 31.5 mm maximum size, no additives, no admixtures), water cured for 28 days, was selected as the control mix. Its overall environmental contribution was calculated to be 311.47 (kg CO_2/m^3 of concrete). The control mix produced a concrete compressive strength of 44.6 MPa and gave a service life of 119.9 years under carbonation exposure (for a concrete cover: 30 mm) and 53.1 years under chloride exposure (for a concrete cover: 30 mm). These values (environmental cost, strength and service life) are regarded as the reference (control) values on every mix design optimisation procedure followed in the current study.

4.2 Steps 2 and 3: replacing aggregates or cement by SCM

On every mix design a constant volume unit (1 m^3) of concrete was chosen as a common basis. When an SCM was added to this unit, then an equal volume of another component, either cement (Step 3) or aggregate (Step 2), was removed in order to keep the same total volume and the common comparison basis. Several mix design configurations were considered (Table 2), where each time addition of a Type II additive took place, at certain proportions, as cement and as aggregate replacement. In the case of fly ash 10, 20 and 30% replacement levels of the control cement mass were chosen, while in the case of silica fume, since it is a more intense pozzolanic material than fly ash (hence the degree of pozzolanic reactions drops bellow one for lesser quantities than fly ash) 5, 10 and 15% replacement levels were used. The water content (kg/m^3) was kept constant for all specimens.

Overall, in terms of concrete and durability properties, it was seen (Tables 2 and 3) that when SCM were used for cement or aggregate replacement, the derived strength and service life values were higher than the target values initially set (40 MPa and 50 years). When SCM were used as aggregate replacement, incorporation of calcareous fly ash (CFA) in CEM I type of cement, produced a better performance than siliceous fly ash (SFA) (Fig. 3). Addition of 30% of CFA produced similar service life (more than 200 years for carbonation exposure) values to SFA but increased the compressive strength considerably higher (Table 3) than SFA, compared to control (44.4% strength increase for CFA, compared to 13% increase for SFA). Additionally and more important the derived strength values were 61% and 26% higher than the target strength value initially set (40 MPa) in the case of CFA and SFA correspondingly. Silica fume (SF) although it produced concrete and durability values higher than the target set values, compared to FA it did not

Table 2 Mix design, service life indicators and environmental cost (Steps 1-3)

SCM type	SCM (%)	C (kg/m^3)	W (kg/m^3)	w/c	A (kg/m^3)	P (kg/m^3)	f_c (MPa)	Z_{carb} (years)	Z_{Cl-} (years)	E_C (kg CO_2 /m^3 con.)	ΔE_C (%)
Control	*0*	*300*	*150*	*0.5*	*1925*	*-*	*44.6*	*119.9*	*53.1*	*311.47*	*-*
SFA						Replacing aggregates					
s-fa 1a	10	300	150	0.50	1890	30	47.4	175	187.5	311.52	0.02
s-fa 2a	20	300	150	0.50	1856	60	50.3	>200	>200	311.58	0.03
s-fa 3a	30	300	150	0.50	1821	90	50.4	>200	>200	311.63	0.05
						Replacing cement					
s-fa 1c	-10	270	150	0.56	1915	30	41.8	98.4	81.3	281.67	-9.57
s-fa 2c	-20	240	150	0.63	1905	60	38.0	74.3	106.3	251.87	-19.14
s-fa 3c	-30	210	150	0.71	1895	90	31.7	47.6	45.8	222.07	-28.70
CFA						Replacing aggregates					
c-fa 1a	10	300	150	0.50	1896	30	51.4	180.2	118.8	311.56	0.03
c-fa 2a	20	300	150	0.50	1866	60	58.0	> 200	>200	311.64	0.05
c-fa 3a	30	300	150	0.50	1837	90	64.4	> 200	>200	311.72	0.08
						Replacing cement					
c-fa 1c	-10	270	150	0.56	1920	30	45.8	102.3	70.8	281.70	-9.56
c-fa 2c	-20	240	150	0.63	1916	60	46.9	86.2	93.8	251.94	-19.11
c-fa 3c	-30	210	150	0.71	1911	90	48.0	72.2	187.5	222.16	-28.67
SF						Replacing aggregates					
sf 1a	5	300	150	0.50	1908	15	50.8	135.3	137.5	311.39	-0.03
sf 2a	10	300	150	0.50	1890	30	56.9	146.5	>200	311.30	-0.06
sf 3a	15	300	150	0.50	1873	45	62.0	164.8	>200	311.21	-0.08
						Replacing cement					
sf 1c	-5	285	150	0.53	1920	15	48.0	102.9	81.3	296.46	-4.82
sf 2c	-10	270	150	0.56	1915	30	51.4	85.2	143.8	281.45	-9.64
sf 3c	-15	255	150	0.59	1910	45	51.2	70.9	156.3	266.43	-14.46

SCM: Replacement level (%) with supplementary cementing material
C: cement content (kg/m^3) *W:* Water content (kg/m^3)
A: aggregate content (kg/m^3) w/c: Water/cement ratio
P: SCM content (kg/m^3) of fly ash *FA* (siliceous "*SFA*" or calcareous "*CFA*") and of silica fume *SF*
f_c: Concrete compressive strength (MPa)
Z_{carb}, Z_{Cl-} Service life for carbonation and chloride exposure, respectively (years)
E_C, ΔE_C: Environmental cost (kg CO_2 / m^3 of concrete) and change (%) compared to control

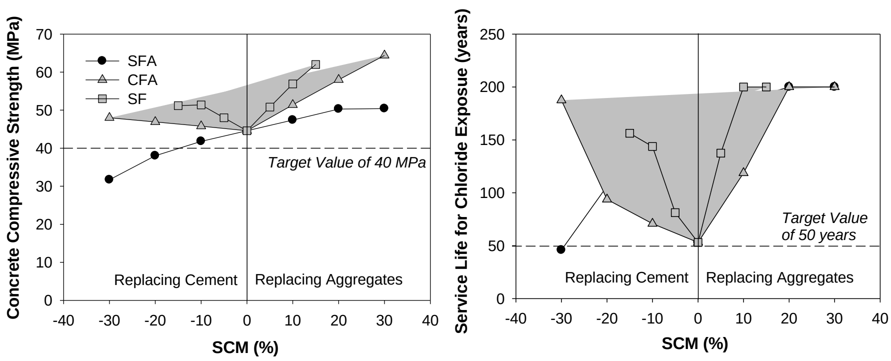

Fig. 3 Comparison of SF and FA performance in terms of target values for strength and service life

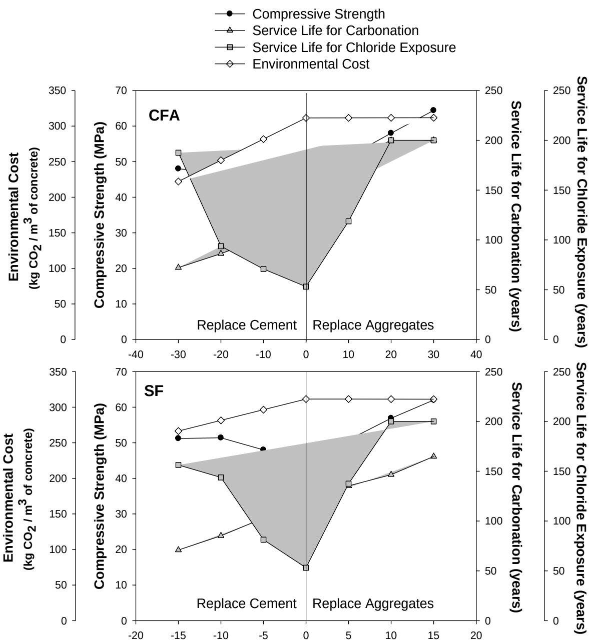

Fig. 4 Overall performance of CFA and SF mixes in terms of environmental cost, concrete strength and service life properties

Table 3 Comparison of strength and servie life values to initial set target values (Steps 1-3)

SCM type	SCM	f_c	Δf_c	f_c > set value	Z_{carb}	ΔZ_{carb}	Z_{carb} > set value	Z_{Cl-}	ΔZ_{Cl-}	Z_{Cl-} > set value
	(%)	(MPa	(%)	(%)	(years	(%)	(%)	(years	(%)	(%)
Contro	*0*	*44.6*	-	-	*119.9*	-	-	*53.1*	-	-
SFA	Replacing aggregates									
s-fa 1a	10	47.4	6.3	18.5	175	46.0	>150	187.5	252.	>150
s-fa 2a	20	50.3	12.8	25.8	>200	66.8	>150	>200	276.	>150
s-fa 3a	30	50.4	13.0	26.0	>200	66.8	>150	>200	276.	>150
	Replacing cement									
s-fa 1c	-10	41.8	-6.3	4.5	98.4	-17.9	96.8	81.3	52.9	62.5
s-fa 2c	-20	*38.0*	-14.8	-5.0	74.3	-38.0	48.6	106.3	100.	112.5
s-fa 3c	-30	*31.7*	-28.9	-20.8	*47.6*	-60.3	-4.8	*45.8*	-13.7	-8.3
CFA	Replacing aggregates									
c-fa 1a	10	51.4	15.2	28.5	180.2	50.3	>150	118.8	123.	137.5
c-fa 2a	20	58.0	30.0	45.0	>200	66.8	>150	>200	276.	>150
c-fa 3a	30	64.4	44.4	61.0	>200	66.8	>150	>200	276.	>150
	Replacing cement									
c-fa 1c	-10	45.8	2.7	14.5	102.3	-14.7	104.6	70.8	33.3	41.7
c-fa 2c	-20	46.9	5.2	17.3	86.2	-28.1	72.4	93.8	76.5	87.5
c-fa 3c	-30	48	7.6	20.0	72.2	-39.8	44.4	187.5	252.	275.0

Table 3 Continued

SF		Replacing aggregates								
sf 1a	5	50.8	13.9	27.0	135.	12.8	>150	137.5	158.	>150
sf 2a	10	56.9	27.6	42.3	146.	22.2	>150	>200	276.	>150
sf 3a	15	62	39.0	55.0	164.	37.4	>150	>200	276.	>150
		Replacing cement								
sf 1c	-5	48	7.6	20.0	102.	-14.2	105.8	81.3	52.9	62.5
sf 2c	-10	51.4	15.2	28.5	85.2	-28.9	70.4	143.8	170.	>150
sf 3c	-15	51.2	30.0	28.0	70.9	-40.9	41.8	156.3	194.1	>150
Δf_c: ΔZ_{carb} ΔZ_{Cl-}:	Change in concrete compressive strength and service life values compared to control (%)									
> set value	Percentage of concrete compressive strength and service life above target values set (40 MPa, 50 years)									

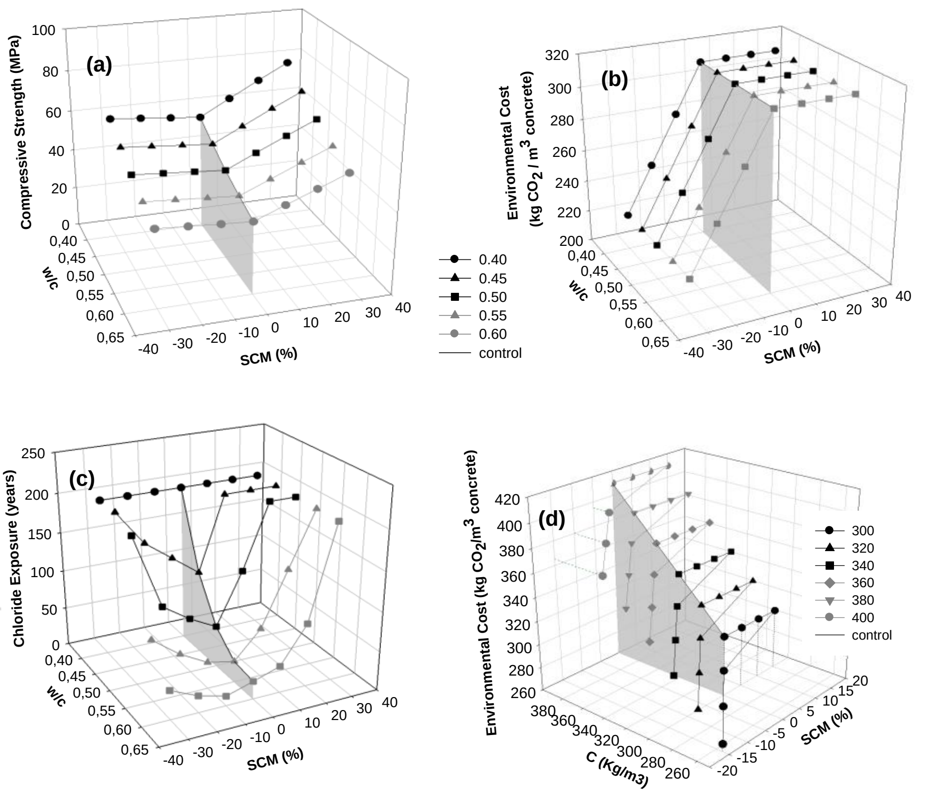

Fig. 5 Overall performance of SCM in terms of environmental cost (b), concrete strength (a) and service life properties (c) for a range of w/c ratios and for different initial cement content (d)

proved to be as effective in inhibiting carbonation exposure. The service life was increased, but to a lesser extend. To draw a level of comparison between performances, 10% addition of SF increased the service life for carbonation by 22.2% (compared to the control value of 119,9 years of the control mix), compared to the 46% and 50.3% increase observed when 10 % of siliceous and calcareous fly ash was added.

In the case where SCM were used as cement replacement materials, the service life to carbonation exposure was decreased for every type of SCM used. In other words, the corresponding carbonation depth values calculated by the models utilised in this study were increased, with increasing content of SCM. As far as chloride exposure is concerned (Fig. 3(b)), specimens incorporating SCM whether aggregate or cement was substituted, produced increased service life values compared to control. Silica fume proved to inhibit chloride diffusion more efficiently than FA. A staggering 170% increase on the service life (compared to control) was noticed for 10% SF utilization, in contrast to 33.3% and 52.9% increases in the cases of CFA and SFA (correspondingly). Is should also be noted, that at higher levels of SFA (30 %) the service life values to both carbonation and chloride exposure dropped below the target service life value initially set (of 50 years). The reasons for such a performance are explained in the following section.

In terms of environmental performance, utilization of 30% FA, as cement replacement material, reduced the concrete environmental footprint by 28.7% (to 222.07kg CO_2 / m^3 of concrete), compared to a 14.5% reduction achieved when 15% of SF was utilized. Of course, when SCM were used as aggregate replacements the environmental output of concrete did not change. A comparative assessment of every strength, durability and environmental cost indicator, calculated in this study, for CFA and SF is given in Fig. 4. In this way, the reduction of environmental cost observed can be weighted against the strength and service life values.

It can be seen that even though in terms of environmental cost CFA outperformed SF (28.7% reduction compared to a 14.5% reduction for SF), in terms of concrete properties SF performed better than FA in general. A 10% utilization of SF increased the concrete compressive strength by 15.2% (compared to the control value of 44.6 MPa), in contrast to a mere 2.7% increase achieved when CFA was used. In terms of service life, for chloride exposure each SCM gave comparable significant increases to control. For carbonation exposure however, the service life was reduced compared to the control value (119.9 years) but remained higher than the target set value (of 50 years) by 41.8% and 44.4% when SF and CFA were used respectively.

Such a behavior, in terms of reduction in environmental cost and trends in service life and strength was also noticed for,

•different w/c ratios (Fig. 5(a)), other than the control value of 0.5, but for the same initial cement content (300 kg/m^3 concrete, as in the control mix),

•different initial cement content from (300 up to 400 kg/m^3) for w/c ratio of 0.5 (Fig. 5(b)).

The rate and the overall reduction in environmental cost was very similar on every different mix design with either different w/c ratio (but for the same cement content) or with different initial cement content (but for the same w/c ratio), since the cement replacement level follows the same incremental increase. Overall the 28.7% reduction in environmental cost (in the case of FA) is achievable with a 30% utilization of SCM as Type II additive (with accepted strength and service life properties).

Considering the fact that at higher SCM replacement levels, the degree of the pozzolanic reaction drops quickly below one, the question is, how can we further reduce the environmental cost without compromises on strength and durability properties? Such a solution is attempted on "Step 4" of the methodology previously described (Fig. 2) and utilized in this study, for the optimum mix design configuration in terms of environmental cost at one end and concrete and durability properties at the other.

4.3 Step 4: further reduction of w and/or c contents

As it was previously described, on the best performed mix design configuration from Step 3 further reduction in the CCP properties can be achieved, through incremental reductions of cement (by 10 kg/m^3) and water (per 10 kg/m^3), for each decrease in cement content. Overall, we are altering the w/c ratio of the best performed mix at Step 3, keeping at the same time the percentage of SCM constant.

Table 4 Strength and Durability indicators compared to initially set target values for strength and service life, of a 20% CFA mix (Step 4)

	C kg/m^3	W kg/m^3	A kg/m^3	f_c MPa	f_c> set value%	Z_{carb} years	Z_{carb} > set value %	Z_{cl-} years	Z_{cl-} > set value %	E_c kg CO_2/ m^{3}con	ΔE_c%
Control mix	*300*	*150*	*1925*	*44.6*	-	*119.9*	-	*53.1*	-	*311.47*	-
20% SCM mix	**240**	**150**	**1916**	**46.9**	**17.3**	**86.2**	**72.4**	**93.8**	**87.5**	**251.94**	**19.11**
	240	**140**	1942	50.6	26.5	118.1	136.2	187.5	>150	252.09	19.06
C stable	240	130	1967	54.8	37.0	175.4	> 150	262.5	> 150	252.24	19.02
W-10-40 kg/m^3	240	120	1994	59.7	49.5	203	> 150	200	> 150	252.40	18.97
	240	110	2020	65.1	62.8	203	> 150	200	> 150	252.56	18.92
	230	**140**	1949	48.6	21.5	95.6	91.2	118.8	137.5	242.13	22.26
C- 10 kg/m^3	230	130	1976	52.8	32.0	136.5	> 150	237.5	> 150	242.29	22.21
W-10-40 kg/m^3	230	120	2001	57.4	43.5	203	> 150	200	> 150	242.44	22.16
	230	110	2028	62.8	57.0	203	> 150	200	> 150	242.60	22.11
	200	**140**	1974	42.7	6.75	53.3	6.6	70.8	41.7	212.28	31.85
C – 40 kg/m^3	200	130	2000	46.4	16.0	71.3	42.6	118.8	137.5	212.44	31.80
W-10-40 kg/m^3	200	120	2026	50.7	26.8	102.4	104.8	200	> 150	212.59	31.75
	200	110	2052	55.6	39.0	163.3	> 150	200	> 150	212.75	31.70
C – 70 kg/m^3	**170**	**120**	2051	43.8	9.50	51.1	2.2	106.3	112.5	182.74	**41.33**
W-10-40 kg/m^3	170	110	2077	48.3	20.8	73.3	46.6	200	> 150	182.90	**41.28**

Table 5 Strength and Durability indicators compared to initially set target values for strength and service life, of a 30% CFA mix (Step 4)

	C kg/m^3	W kg/m^3	A kg/m^3	f_c MPa	f_c > set value %	Z_{carb} years	Z_{carb} > set value %	Z_{cl-} years	Z_{cl-} > set value %	E_c kg CO_2 / m^{3}con	ΔE_c %
Control mix	*300*	*150*	*1925*	*44.6*	-	*119.9*	-	*53.1*	-	*311.47*	-
30% SCM mix	**210**	**150**	**1911**	**48**	**20**	**72.2**	**44.4**	**187,5**	**> 150**	**222.16**	**28.67**
	210	**140**	1937	51.8	29.5	97.6	95.2	200	> 150	222.32	28.62
C stable	210	130	1963	56.1	40.25	141.7	> 150	200	> 150	222.47	28.57
W-10-40 kg/m^3	210	120	1989	61	52.5	200	> 150	200	> 150	222.63	28.52
	210	110	2015	66.5	66.25	200	> 150	200	> 150	222.78	28.47
	200	**140**	1945	49.9	24.75	78.6	57.2	200	> 150	212.37	31.82
C stable	200	130	1971	54	35	110.9	121.8	200	> 150	212.52	31.77
W-10-40 kg/m^3	200	120	1997	58.8	47	171.1	> 150	200	> 150	212.68	31.72
	200	110	2023	64.2	60.5	200	> 150	200	> 150	212.83	31.70
C stable	**160**	**120**	2030	46.1	15.25	57	14	200	> 150	172.87	**44.50**
W-10-40 kg/m^3	160	110	2056	50.6	26.5	78.6	57.2	200	> 150	173.03	**44.45**

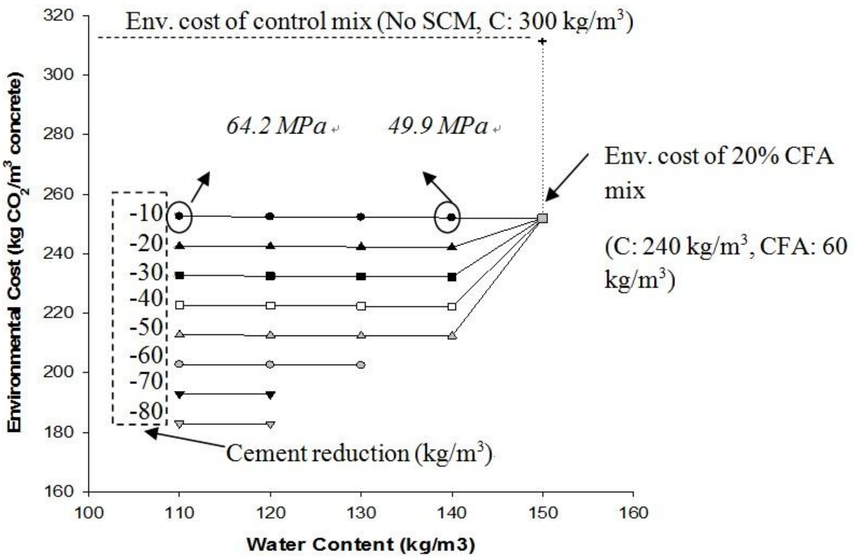

Fig. 6 Effect of step/step reduction of cement and water contents on the environmental cost of a 20% CFA mix

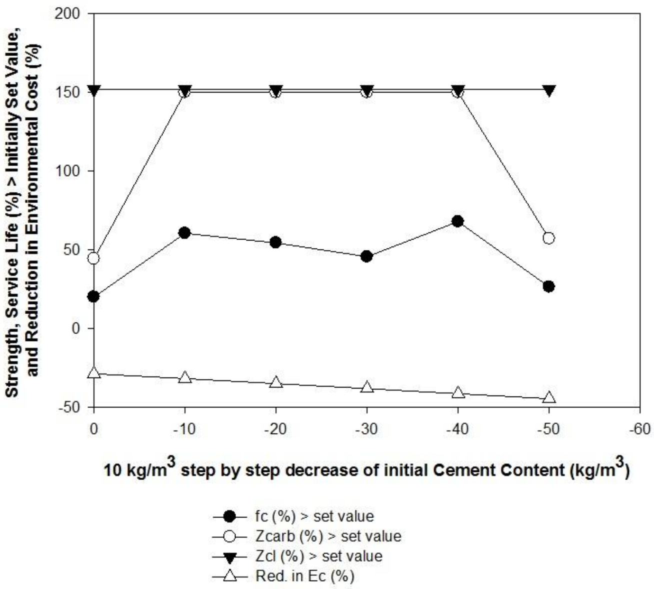

Fig. 7 Effect of step by step reduction of cement and water contents on the environmental cost and strength and service life values of a 30% CFA mix

Such a mix design configuration, in the case of FA utilization is given in Tables 4 and 5. Compared to the initial control mix (0.5 w/c ratio, 300 kg/m^3 cement content, no SCM), two CFA mix designs were further investigated (with 20% cement replacement by CFA and with 30%, illustrated in Tables 4 and 5 respectively). On each SCM mix initially the cement content was reduced by 10 kg/m^3, followed by a step by step decrease of the water content by 10 kg/m^3. These reductions, were stopped when either strength or service life values dropped below the target values initially set (40 MPa and 50 years).

It should be noted that such reductions in cement and water content (although have been approached in the literature, Newlands *et al.* 2012), might fail to meet certain minimum composition criteria (minimum cement content, maximum w/c ratio) for certain exposure classes, as defined in the relevant standard. However, better and more realistic reductions can be achieved if a mix design other than the control was selected as the base line of comparisons (e.g., with more increased cement content). After all, the main aim of this study is to demonstrate the effectiveness of altering the concrete compositional parameters (cement, water, SCM, etc.) in principle, in achieving a reduced environmental cost with accepted at the same time concrete and service life properties.

A first overall observation is that the environmental cost can be further reduced (up to 44.5%) in providing a mix design with guaranteed concrete compressive strength above 40 MPa and a service life of more than 50 years.

A closer look of the environmental and concrete strength and service life values achieved (Table 4), per step by step reductions of cement and water contents, reveals that the further reduction in cement content is associated with the desirable decrease of the environmental cost of concrete. The associated water reductions (from 10 to 40 kg/m^3) for each step by step reduction in cement content are associated with the further enhancement of strength and service life properties. Just to emphasize the validity of this particular point (illustrated in Fig. 6) it should be noted that for a 10 kg/m^3 reduction in cement content of the 30% CFA mix (from 210 kg/m^3 to 200 kg/m^3), the corresponding water content was reduced from 10 - 40 kg/m^3. Overall, for such a further cement reduction, a 31.7% decrease (on average) in environmental cost was noted (31.82% and 31.7% for 10 kg/^{3} and 40 kg/m^3 reductions in water content, correspondingly). However, in terms of water content reduction, the mix design with its water content reduced by 40 kg/m^3 provided higher compressive strength and service life values (especially for carbonation exposure) than any other smaller reduction in water (10 - 30 kg/m^3).

It can be seen, how a further (to a 30% replacement by CFA) reduction in cement content alters the environmental cost of concrete. Furthermore, Fig. 7, shows how such a reduction affects strength and service life compared to the initially set target values (of 40 MPa and 50 years). For example, a further cement content reduction by 30 kg/m^3, on a 30% CFA mix, reduces the environmental cost of concrete by 38%. More important it provides a concrete compressive strength of 58.3 MPa and a service life in carbonation and chloride exposure of more than 200 years, values higher than 45.8% and more than 150% compared to the target 40 MPa strength and 50 years service life. Hence, considerable reductions in environmental cost of concrete can be achieved, without compromising on strength and service life (in essence on structural safety).

5. Discussion

The aim of this study was to investigate the relationship of sustainable and durable design, in terms of concrete mix proportioning, in providing a valid mix design with accepted strength and service life properties, but with the minimum environmental cost. To achieve this, a (4-step) structured methodology (Fig. 2) was developed. Upon defining a set of target strength and service life values, an initial mix design is selected with 95% clinker (Step 1). Its strength and service life (in terms of carbonation and chloride exposure) values are estimated, using proven predictive models developed and validated by some of the authors of this study. In addition, its environmental output (in terms of kg CO_2/m^3 of concrete) is calculated, according to the concept described in Section 2 of this study, using data from the literature and from cement production companies. At the next step, the effectiveness of SCMs (fly ash and silica fume) as cement (clinker) and aggregate replacement materials (Steps 2 and 3) is investigated, in reducing the environmental cost and in providing accepted strength and service life properties. The best performed mix design with a certain percentage of SCM is further optimized (Step 4) in reducing further its environmental output.

When SCM were utilized as aggregate replacement materials (Step 2) their environmental output was not improved (which is expected since they do not replace clinker). However, the strength and service life in carbonation exposure were considerably increased, compared to control. When SCM replaced cement (Step 3), smaller service life values to control (hence larger carbonation depths), were produced, still higher than the target values set (50 years and 40 MPa) and their environmental output was considerably reduced (Table 2).

Although it has been noted (Atis 2003) that there is no general agreement as to whether fly ash utilization tends to lessen the rate of carbonation, similar behavior (in terms of service life values for cement replacement) as the one observed in this study, has been observed also by other researchers. (Khunthongkeaw *et al.* 2006) stated that the carbonation depth increased along with the increase in the fly ash content (became critical for 30% fly ash). On a similar note, Lo (*et al.* 2010) observed that at high PFA replacement levels (more than 40%) carbonation depth was considerably increased. The explanation for such a behavior, lays in the way these materials were incorporated into the mix. In the first case (SCM replacing aggregates), the total amount of carbonatable constituents remains almost the same, resulting in decreased porosity and lower carbonation rates (Papadakis 2000). While in the second case (SCM replacing cement), by reducing the cement and clinker content, the amount of carbonatable materials is also reduced (due to the decrease in total CaO), resulting in higher carbonation rates (Khunthingkeaw *et al*. 2006, Lo *et al*. 2009). In general SCM materials (as cement replacements) proved to be less resistant to carbonation, mainly due to their low binding capacity of CO_2, caused by their smaller concentrations of $Ca(OH)_2$, compared to control (due to the consumption by pozzolanic reaction, and lower cement content).

Under chloride exposure they all behaved much better than control. It has been noticed that specimens incorporating an SCM, whether it substitutes aggregate or cement, exhibit significantly lower total chloride content for all depths from the surface (Chalee *et al.* 2010, Hosam *et al.* 2010).

Silica fume proved to be most efficient in inhibiting chloride ingress, than fly ash (since a 10% replacement by SF resulted in a 170% increase of service life compared to control, than the 33.3% and 52.9% for SFA). Silica fume, composed by very small spherical particles, due to its ultra fineness and activity led to the formation of intense pozzolanic reaction products (with increased chloride ion binding capacity than fly ash) within the capillary pore spaces and as a consequence, a finer and more segmented pore system is produced (Hosam *et al.* 2010, Nochaiya *et al.* 2010).

When fly ash was used, a study pozzolanic reaction level was observed for calcareous fly ash (rate of pozzolanic reaction equal to 1) resulting in higher service life to chloride exposure (at high, 30% concentration level). CFA due to its high calcium oxide content, apart of being pozzolonic active, reacts faster than siliceous reach cement replacement materials, since it contains higher amounts of aluminate-cementing compounds (C_3A, C_4AF), leading to a more increased chloride ion binding capacity. On the contrary, when siliceous fly ash was used smaller than the control values (in both strength and service life) were obtained. Such a behaviour, can be explained by the very nature of a rich in silica material. In general, when pozzolanic materials with high active silica content are added to cement, the silica (SiO_2) present in these materials reacts with free lime released during the hydration of cement and forms additional calcium silicate hydrate (CSH) as new hydration products which improve the mechanical properties of concrete formulation (Ganesan and Thangavel 2007). However when all the available free lime is depleted, the pozzolanic reactions stops and the remaining levels of silica remain inactive. Such an observation is further reinforced by the rate of the pozzolanic reaction of SFA, which at high replacement levels (30%) drops bellow 0.5. That is the reason why at these quantities of SFA, the strength and the service life in carbonation was reduced compared to control.

In terms of environmental cost fly ash (in general) produced bigger reductions (28.7%) of the associated CO_2 emissions, compared to silica fume (14.5%). These reductions and the overall trends observed in strength and service life were also observed on other mix designs investigated, with the same content level of SCM (up to 30%) and initial cement content (300 kg/m^3), but with different *w/c* ratios (Fig. 5). Even at mix designs with different initial cement contents than control (from 300-400 kg/m^3), with the same replacement level of SCM (up to 30%) and of 0.5 w/c ratio, the percentage reductions in environmental cost was constant.

Taking under consideration that any further SCM addition would result in a bellow 1 (or even 0.5) degree of pozzolanic reaction, in order to further reduce the environmental cost incremental cement and water reductions took place (Step 4). Each reduction of cement content (by 10kg/m^3) is associated with a reduction in environmental cost, while at the other hand, the water reduction (again by 10 kg/m^3, for each cement reduction) enhances the concrete and service life properties (as illustrated in Fig. 6).

It was shown that the environmental cost of a 30% CFA mix (reduced already by 28.7% compared to the control mix) can be further reduced up to 45%, with step by step cement (by 10 kg/m^3) and additional water reductions. Such a mix design, except the considerable reduced level of associated CO_2 emissions, produces strength and service life (for chloride exposure) values of more than 26.5% and 150% above the initial target values of 40 MPa and 50 years, respectively.

Taking under consideration the effects of each incremental cement and water reduction on the associated environmental cost, strength (Fig. 8) and service life (Fig. 9) properties, in essence an area of accepted performance (in terms of strength and service life) can be defined. On each Figure, for each reduction in cement content, apart of the decrease in environmental cost, the gain in strength and service per water content reduction is also illustrated, expressed as a percentage above the initial set target values for strength (40 MPa) and service life (50 years).

For a reduction of the initial cement content of the 30% CFA mix by 30 kg/m^3, we can achieve a 38.2% reduction in environmental cost. At the same time, the associated strength would be 12.3% higher than 40 MPa for a 10 kg/m^3 water reduction and 45.8%, for a 40kg/m^3 water reduction (the corresponding service life values would be 3.4% and more than 150% for the same water reductions).

Hence the designer can adjust the mix design configuration of a particular concrete mix design incorporating SCM, in achieving further reduction in environmental cost (in addition to those achieved through clinker replacement), and at the same time can select, for this particular cement reduction the levels of required strength and service life.

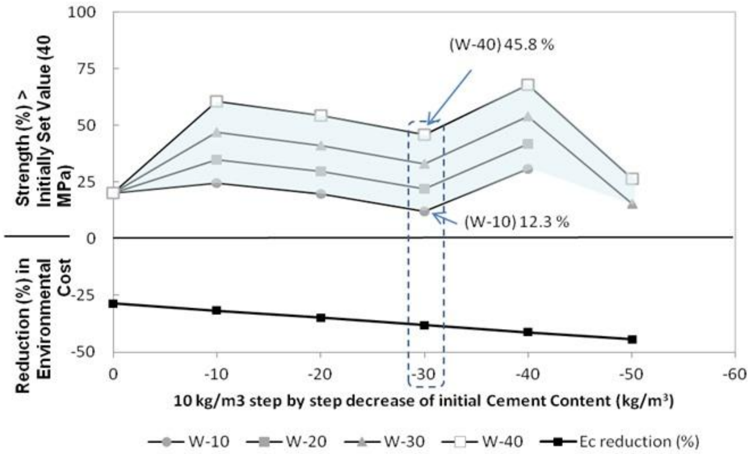

Fig. 8 Effect of reduction of water and cement contents on strength and environmental cost

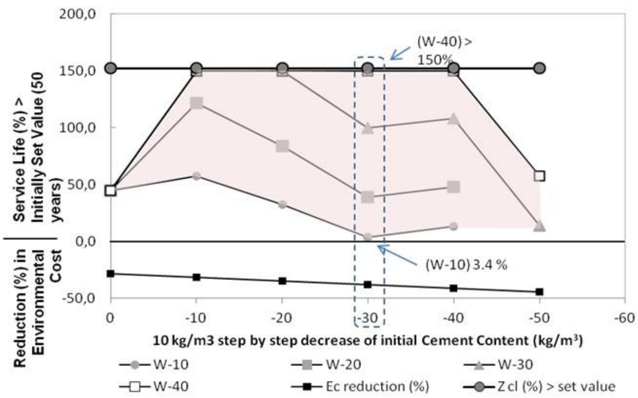

Fig. 9 Effect of reduction of water and cement contents on service life and environmental cost

6. Conclusions

Considering the increased demand for cement and concrete, in addition to the considerable levels of CO_2 emissions associated with the cement manufacturing process, a more sustainable design of concrete mixes should be enforced. Under this scope, utilization of industrial by-products as cement (clinker) replacement materials is a promising solution. In the current study, trying to investigate the relationship of sustainable and durable design, a (4-step) structured methodology was presented aiming to provide a concrete mix design with accepted strength and service life properties, but with the minimum environmental cost. The main findings, as discussed in this study can be summarized as:

•The effects of the SCM materials on the behaviour of the concrete mix differ when used as aggregate or cement replacements (in terms of service life to carbonation).

•Calcareous fly ash proved to be the most promising SCM material (for up to 30%), in providing a balanced environmentally friendly and durable solution. A further decrease in the environmental burden (up to 45%) was achieved, when the rate of the pozzolanic reaction dropped below 1.

•By taking under consideration the calculated environmental cost of a concrete mix and the derived strength and service life values, an area of accepted performance upon initially selected target values (40 MPa, 50 years) was created.

In this way, a mix design incorporating a particular type of SCM can be further adjusted in achieving an optimum sustainable and durable performance, according to the principles set in the newly imposed relevant EN 15643 Standards. It is hoped that the results of this study will pave the way for a more rigorous approach to be adopted by the research community on the level of sustainability afforded by using such types of materials.

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