Eco-Efficient Ternary Mixtures Incorporating Fly Ash and Metakaolin

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ABSTRACT: With the growing awareness of environmental problems, particularly with regard to energy efficiency and greenhouse gas emissions, the construction and the cement industry has had a prominent place, the latter being responsible for about 7% of CO_2 emissions into the atmosphere. Knowing that cement production contributes about one tone of CO_2 for every tone produced, it remains paradoxical that concrete, the product most consumed by humans, exceeded only by water, cannot find a credible, more efficient and greener replacement material for portland cement. Considering the available technological solutions, involving the energy efficiency of cement intensive production or the demand for alternative fuels for cement manufacture, a simpler solution might be the rationalization of resources by cement replacement by alternative materials. There is already a kind of concrete (high volume fly ash concrete) with very limited applications until nowadays but with intrinsically environmental advantages. However, the reduced early strength of this type of concrete is a limiting factor for its widespread usage. In this context, a study was developed in mortars with binary and ternary mixtures where significant volumes of cement were replaced by fly ash, and also, simultaneously, for another addition: metakaolin. In this paper, one present the main advantages and drawbacks of the simultaneous use of these two mineral additions which synergy may cause very interesting performance characteristics even with high volumes of cement replacement. These ternary mixtures show very promising performances, allowing large volumes of cement replacement, maintaining or improving both mechanical and durability performances. These binders could be a viable solution for obtaining an eco-efficient enhanced performance concrete for widespread usage in construction as an alternative for conventional concrete.

1 INTRODUCTION

Nowadays, the world ecosystem is constantly faced with ever-larger ecological problems associated with the emissions of CO_2. It is well known that for every tonne of portland cement produced, approximately one tonne of CO_2 is released into atmosphere, which means that the portland cement industry contributes for about 7% of the total CO_2 emissions. Also, other adverse environmental impact of portland cement production refers to the high energy consumption. After aluminium and steel, the manufacturing of portland cement is the most energy intensive process (Malhotra & Mehta (2002)).

However, the emission of CO_2 and the energy consumption are only two of the many problems we are facing nowadays. The inadequate durability of reinforced portland cement concrete structures and the increase on the volume of construction in the last few decades has resulted in a rampage of our natural resources. The availability of resources is finite and therefore we must alert the industry to take into account the sustainability of construction.

The concrete industry, due to its large size, is the ideal home for economic and safe incorporation of millions of tonnes of industrial by products such as fly ash (FA) from coal combustion thermoelectric power plants. Therefore large scale cement replacement in concrete by FA will be highly advantageous from the standpoint of cost, economy, energy efficiency, durability, and overall ecological and environmental benefits (Malhotra & Mehta (2002)).

The worldwide production of coal combustion products is estimated to be about 1300 million tonnes per year of which at least 70% (900 million tonnes) is FA which is suitable to use as a pozzolan in concrete or other cement based products (Mehta (1999)). Unfortunately, only about 20% of the worldwide available FA is being used by the cement and concrete industry. To achieve a sustainable development of the concrete industry, the rate of the use of pozzolanic and cementitious by-products will have to be accelerated (Malhotra & Mehta (2002)). Reusing greater amounts of FA in concrete mixtures and replacing higher quantities of cement will certainly help to reduce a major problem of environmental impact. Incorporating high volumes of FA in concrete is one of the possible ways for making green concrete.

High volume fly ash concrete (HVFAC) (percentage of replacement of cement weight by fly ash greater than 50%) mechanical and durability characterization was already been evaluated (Camões (2006), Sirivivatnanon & Ho (2003), Malhotra & Mehta (2002)) and bibliography document some practical applications (Sirivivatnanon & Ho (2003), Bilodeau & Seabrook (2001), Langley (2001)) that permits to classify this kind of concrete in the field of conventional concrete. Design requirements related to mechanical characteristics will be perfectly fulfilled and with this type of concrete it will be possible to build more durable structures while contributing significantly to the construction sustainability (Camões (2006)).

According to Malhotra (2002), the following characteristics are typical for HVFAC: a minimum of 50 to 60% fly ash by mass of cementitious materials; low water content, generally less than 130 kg/m^3 of concrete; cement content not more than 200 kg/m^3 of concrete, but generally about 150 kg/m^3; low water/cementitious ratio, generally less than 0.35.

According to Malhotra & Ramezanianpour (1994) HVFAC exhibits adequate strength development characteristics both at early and later ages. However, there are other authors like Gillies (2001) reporting that some HVFAC developed lower strengths at 3 and 7 days of age but achieved higher ultimate strengths when properly cured. Furthermore, experience shows that faster construction is not always less expensive. Poor-quality concrete, with its honeycombs and many cracks, frequently requires costly repairs and results in litigation. Poorly built structures have a tendency to deteriorate faster, especially when exposed to aggressive environments. Thus, owners must pay a higher life-cycle cost.

Compressive strength values will differ depending on the materials and proportions used but one can say that typically HVFAC have 28 days strength of approximately 35 MPa and 91 days strengths of about 45 MPa (Burden (2006)). The compressive strength tests made by Camões (2006) indicate that concrete with about 35 MPa strength at 28 days can be produced using 160 kg/m^3 of cement and 400 kg/m^3 of binder content (C400) which is sufficient for the majority of the structural concrete constructions' applications. Furthermore the author said that this kind of concrete can also be used when higher strength is needed. CANMET also reports that HVFAC can be used for high strength applications (Burden (2006), Bilodeau & Seabrook (2001)).

These concretes seem to be highly durable ones once they show reduced gas and water permeability, capillary absorption, high resistance against chloride penetration, low heat of hydration and reduced drying shrinkage (Burden (2006), Camões (2006) and Malhotra & Mehta (2002)). Mehta (2004) reported that the addition of high volumes of FA in concrete reduces the water demand, improves the workability, minimizes cracking due to thermal and drying shrinkage, and enhances durability to reinforcement corrosion, sulphate attack, and alkali-silica expansion. In this type of concrete it is expected that the very low permeability of HVFAC offsets any marginal reduction in the concrete's pH due to its large quantities of mineral admixtures (Malhotra (2002), Malhotra & Mehta (2002)). However it is well known and accepted between researchers that carbonation depth increases as FA content increases (Burden (2006), Jiang, et al (2000)) because the rate at which concrete carbonates is a function of, among others, the mass of CH available for reaction (Burden (2006), Joshi & Lohtia (1997)). In fact, as the permeability of the concrete is reduced by the addition of FA, it may be expected to become harder for CO_2 to penetrate the concrete. However, FA reduces permeability by reacting with CH. This reaction reduces the amount of material available for reaction with CO_2. Thus less CO_2 has to penetrate to neutralize the concrete.

HVFAC have some drawbacks that prevent presently their widespread usage. The main potential problems associated with implementation of these concretes are: i) slower strength development along time and reduced early age strengths; ii) greater sensitivity to curing process; iii) high plastic shrinkage of this type of concrete having a very low water/binder ratio; iv) reduced carbonation resistance.

Considering the presented disadvantages the low early strength may be considered critical because can extend the period before demoulding and consequently retard the construction, which can lead to an increase of the overall costs.

In order to overcome these disadvantages, in this work one propose incorporating in concrete, adding together with a very high quantity of FA, other mineral addition that prevent or minimize these adverse factors and thus enable wider application of an eco-efficient concrete.

In contrast to portland cement, metakaolin (MtK) presents very interesting environmental properties and the good-will of their addition in concrete was already been studied and proven (Justice (2005), Badogiannisa et al (2004), Fernandes (2004), Kosmatka et al (2003)).

MtK is a highly reactive pozzolan classified as ultra-fine with an average diameter around 1-2 microns. The presence of MtK has a huge effect on the hydration of cement. When portland cement alone hydrates, typically 20-30% of the resulting paste mass is CH. However, when MtK is added, it reacts rapidly with these newly forming CH compounds to produce supplementary calcium silicate hydrate. The pozzolanic reaction of MtK is considered to be very effective and similar than silica fume. Thus, the partial replacement of cement by MtK will increase the performance of concrete either in early or at long term ages. The optimum cement replacement content is less than 20%. Some authors indicate 5% (Justice (2005)) and for Portuguese MtK Fernandes (2004) report the value 15%.

The addition of MtK results in a substantial performance improvement of the concrete, both at young and long term ages. Thus, it is expected that the cumulative addition of MtK in HVFAC can contribute for solving problems associated with reduced early age strength. However there are few references about activated HVFAC (Xiaosheng et al (2007)).

In this context an experimental study has been developed aiming the performance characterization of ternary HVFA mixtures. The tests were performed on mortar samples due to the obvious advantages that this solution presents in comparison to concrete (lesser material waste, greater ease at producing the compositions and maneuvering the molds and samples, lesser occupied space by the samples, etc.) and that usually can be summarized in a decrease of man-hours necessary to this experimental study. However this work aims to contribute for the knowledge of eco-efficient concretes and not mortars. In fact, this option was made taking into account that the mortar specimen's results may be extrapolated to estimate the performance of the corresponding concretes (Camões et al (2005), Camões (2002) and Daczko (1999)).

2 EXPERIMENTAL PROGRAM

The tested mixes are presented in Table 1. The cement (C) used was a CEM II/B-L 32.5N produced by CIMPOR which was replaced by MtK MIBAL-C, FA from Pego thermal power station or by both (FA + MtK) simultaneously. The binder content is considered the sum of cement and mineral additions used (B = C + FA + MtK), W represents the water added and SP the superplasticizer. A commercial available 3th generation copolymer SP was used.

Table 1. Studied mortar mixtures.

Mix	Name	Materials						
		B [kg/m^3]	C [%]	MtK [%]	FA [%]	M [kg]	W/B [-]	SP [%B]
I	PATTERN	484	100	0	0	1457.9	0.55	0
II	10%MtK	484	90	10	0	1449.1	0.55	1.5
III	20%FA	484	80	0	20	1422.8	0.55	0
IV	40%FA	484	60	0	40	1387.6	0.55	0
V	60%FA	484	40	0	60	1352.5	0.55	0
VI	10%MtK+20%FA	484	70	10	20	1414.0	0.55	0
VII	10%MtK+40%FA	484	50	10	40	1378.8	0.55	0.4
VIII	10%MtK+60%FA	484	30	10	60	1343.6	0.55	1.5

In order to evaluate the mortar's behavior in fresh state one submit it to flow table test according to EN 1015-3 (2004). At the hardened state the mechanical behavior was evaluated through flexural and compressive strength tests (EN 196-1 (2005)). For flexural tests, series of 3 specimens with 40x40x160 mm^3 for each age of testing (3, 7, 14, 21, 28 and 90 days) were used. Consequently, compressive strength was obtained from 6 40x40x(±80) mm^3 specimens.

The durability performance was evaluated through chloride migration (LNEC E463 (2005)) and water absorption by capillarity tests (EN 1015-18 (2002)). Chloride migration tests were done in 3 specimens of 50 mm height and 100 mm of diameter at 28 and 90 days of age. Water absorption by capillarity was carried out using 3 cubic samples with 50 mm of edge at 7, 14, 21, 28 and 90 days of age. The reading period was carried out between regular intervals decreasing with time until a 90 days period was reached. To determine the capillary absorption coefficient only the first 4 hours were considered.

3 MINERAL ADDITIONS

3.1 *Metakaolin*

MtK is a pozzonalic addition and derives from the thermal activation of kaolin clay at about 750/800ºC. The methakaolin used was extracted from Barqueiros, Portugal, located in the Barcelos Council and named Mibal-C. This deposit in Barcelos is of sedimentary nature with brute reserves estimated in millions of tons (Pinto (2004)). In Table 2 one can see its main properties.

Table 2. Properties of the used metakaolin, MIBAL – C (Pinto (2004)).

Characteristic		MIBAL - C
Particle Dimension [%]	< 30 μm	99 ± 3
	< 10 μm	93 ± 5
	< 5 μm	82 ± 5
	< 2 μm	68 ± 6
Chemical Composition [%]	SiO_2	47.0
	Al_2O_3	37.1
	Fe_2O_3	1.3
	K_2O	2
	Na_2O	0.2
	MgO	0.15
	TiO_2	0.3
	CaO	0.1

Characteristic		MIBAL - C
Unburnt	Loss on ignition [%]	12.75
Humidity [%]	Initial	32 ± 3
	Granules	18 ± 2
	After drying	< 2
After drying parameters	Burnout	0.09
	Flexural resistance (110ºC) [MPa]	2.45 ± 0.49
	After burnout flexural resistance [MPa]	13 ± 3
	Water absorption [%]	10 ± 2
Others	Density [g/cm^3]	2.4 – 2.7
	Suspension's pH	6 – 9

Table 3. Properties of the used fly ash, PEGOP (Camões (2006)).

Carachteristic		PEGOP	Carachteristic	PEGOP
Chemical composition	LOI [%]	7.30	*Cl^-* [%]	0.00
	SiO_2 [%]	60.87	*free CaO* [%]	0.00
	Al_2O_3 [%]	20.40	*Na_2O* [%]	0.55
	Fe_2O_3 [%]	7.82	*K_2O* [%]	1.92
	total CaO [%]	2.72	*P_2O_5* [%]	1,14
	MgO [%]	1.40	*TiO_2* [%]	1.29
	SO_3 [%]	0.22	*Total SiO_2+Al_2O_3+Fe_2O_3* [%]	89.09
Physical properties	Density [kg/cm^3]	2360	*Fineness > 45 μm* [%]	27.30
	Blaine's specific surface [m^2/kg]	387.9	*Humidity* [%]	0.16
			Water demand	0.297

3.2 *Fly ash*

The FA used was produced by Pego Power Station located in Portugal, with an average loss on ignition (LOI) which varied between about 6% and 9%. These high LOI values belong to the upper class (category C) established by EN 450:2005 or may exceed the proposed limit. However, studies have shown that, at least for this FA, the high LOI is not impeditive of its use on concretes (Camões (2006), Camões et al (2003) and Camões et al (2002)). Table 3 shows the main properties of the FA used.

4 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 *Workability*

The flow tests used to assess the workability of the mixes provided the results shown in Fig. 1.

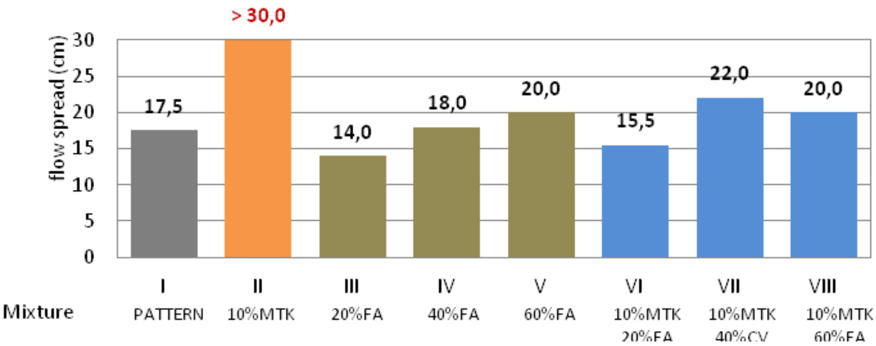


Figure 1. Flow table test results.

These test results has provided some atypical values as SP was used only in some mixes (II, VII and VIII). The usage of this admixture was due to difficulties in the mixing process when MtK was used once, as it is known, its presence makes the mixtures less workable (Pinto (2004)). On the contrary, incorporating larger quantities of FA originates higher workability. In practice one can say that the synergic effect of these two additions complement each other as FA provide a mitigating effect of this disadvantage of using MtK.

4.2 *Mechanical strength*

In Fig. 2 one can see the evolution of compressive and flexural strength along time. These values were obtained from 3 to 90 days of age. The flexural test results present greater sensitivity than compressive strength tests maybe because of the effect of sample's imperfection that affects more the flexural than the compressive strength.

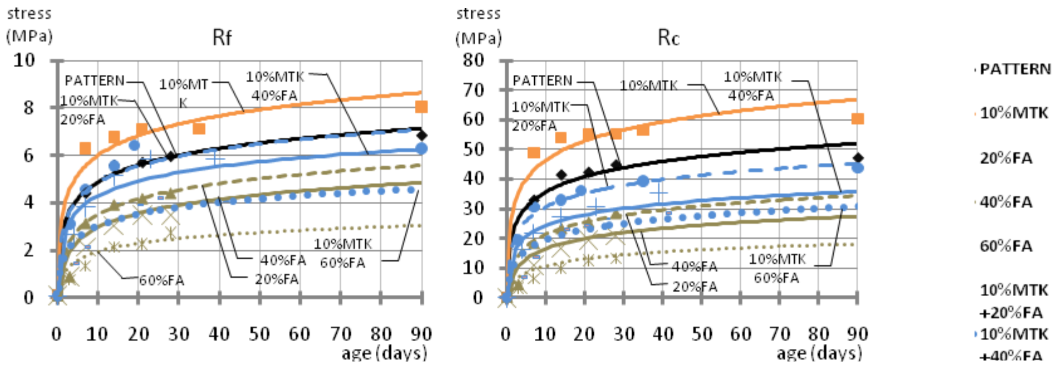


Figure 2. Mechanical strength test results.

Observing Fig. 2 one can see an already known effect of cement replacement by FA: the delay on the strength development and for these HVFA mixes the drastically reduction at early strength. This effect is due to the reduced availability of calcium hydroxide (derived from cement hydration) to react with FA and because it is a very slow chemical reaction.

Contrasting to FA, MtK magnifies both flexural and compressive strength even in early ages, and for all FA content tested. Unlike FA, MtK reacts very quickly with calcium hydroxide being the responsible for the high early age strength obtained. At a later phase, as FA slowly reacts with calcium hydroxide, FA controls the long term strength development. In Fig. 3 this fact is well demonstrated as it can be observed that with 10% of MtK addition in the ternary mixtures the compressive strength of the binary mixtures (with just cement and FA) has been substantially ameliorated. It is also known that the greater compactness is associated with a higher strength, which may indicate that the mixtures showing better performance will be more compact, and from this perspective, MtK being a much more thinner and reactive material may have a predominant effect.

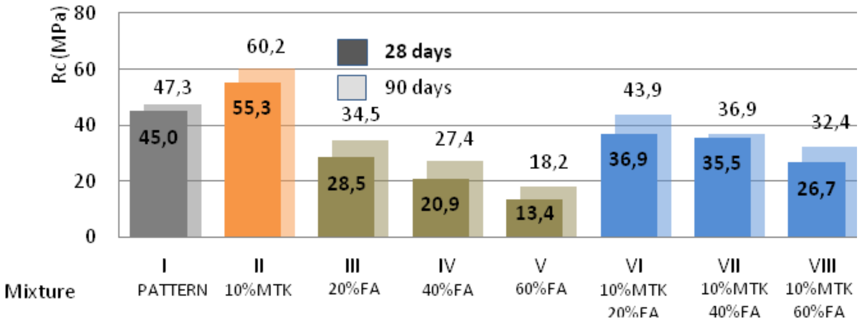


Figure 3. Compressive strength (R_c) at 28 e 90 days of age.

4.3 *Durability indicators*

In Fig. 4 one can see the coefficient of chloride diffusion obtained from rapid migration tests.

Analyzing the results achieved it's possible to observe that all mixtures made with mineral additions presented better performance than the standard one. This effect was already expected hence FA fix chloride ions. According to Camões (2002) a first part is chemically bonded and is incorporated in the cement hydration products. Another part is physically fixed and is absorbed by micro-pores surface. Just a third part called "free chlorides" is free to move and is responsible for steel reinforcement corrosion. Also the increase in the aluminates provided by the presence of FA in the binder is expected to be responsible for better performance (Camões (2002)) once they reacts chemically with chloride ions and reduce the free chloride content.

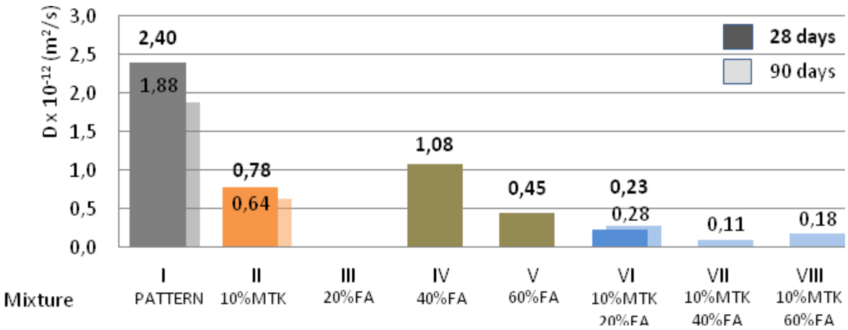


Figure 4. Coefficient of chloride diffusion (D) at 28 e 90 days of age.

The obtained results showed the high potential of the addition of 10% of MtK and all the ternary mixes showed enhanced performance than the FA binary ones due to the presence of MtK.

With respect to results of coefficient of capillary absorption at 28 days (Fig. 5) one can verify that it reaches higher values for standard mixture. The inclusion of FA increases the mixture's performance but higher FA contents leads to worst behavior. When 60% of cement replaced by FA was reached its coefficient of capillary absorption was similar to the standard mix. The FA addition should work almost as filler once the pozzolanic reactions were apparently very slow. Being MtK a much thinner and reactive material than FA its addition causes good performance due to filler effect and high pozzolanic activity. Its presence in the mixture decreases the size of the bigger pores and provides more compact and therefore less permeable mixtures. Thus ternary mixtures present much lower coefficients of capillary absorption than binary ones. This synergetic effect of MtK combined with FA results in much more efficient mixtures. Nevertheless, mix VIII must be referred once its capillary absorption was significantly enhanced when compared to the other HVFA mixture tested (mix V), which was similar than the standard one.

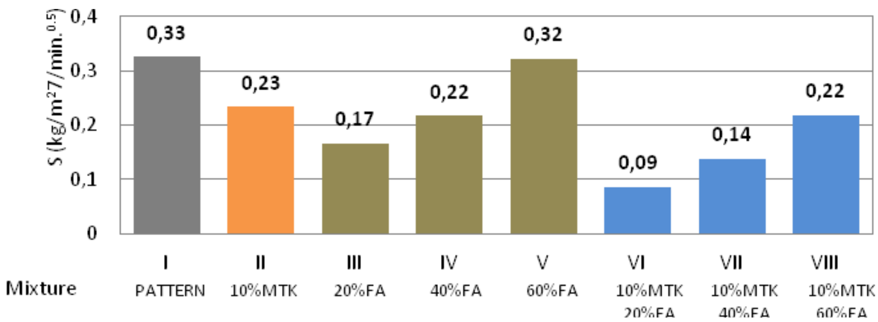


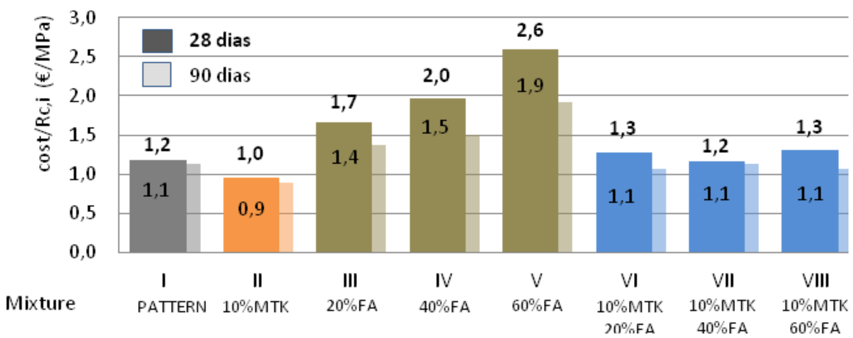
Figure 5. Coefficient of capillary absorption (S) at 28 days of age.

4.4 *Cost analysis*

For the mortar's cost only the raw material prices have been considered discarding the indirect costs. Anyways it is known that cement prices is nowadays competitive and that future additions will also have to be. For this study one have considered a value nearly 4 times lower than cement's for the price of FA and for the MtK price a value identical to the cement's. The price of sand (M) was adopted based on commercial values.

The cost/benefit ratio based on compressive strength is shown in Fig. 6. It is known that the cost of mixtures with FA is lower than the standard ones (Reis (2009) and Camões (2002)) but it is expected that HVFAC present a weak cost/benefit ratio based on compressive strength at least at early ages. This aspect is noted in Fig. 6 but interestingly one can verify that MtK corrects all the binary mixtures leading to a cost/(compressive strength) ratio similar than the standard mix.

It should be pointed out that the cost/benefit ratio here presented is the most onerous for the tested mixtures. However if one consider the results obtained in the durability indicators, the situation reverses itself and the ratios cost/benefit are undoubtedly advantageous for high volumes of cement replacements.



Material	(€/kg)
C	0.08
MtK	0.08
FA	0.02
M	0.01
W	0

Figure 6. Cost/benefit analysis based on compressive strength at 28 and 90 days of age.

5 CONCLUSIONS

Based on the obtained results one can conclude that it's possible to produce an eco-efficient HVFAC incorporating a reduced percentage of MtK capable of contributing for a decrease in the environmental impacts associated to concrete consumption. This kind of concrete presents durability or mechanical performances as good as or even better than conventional concretes even at early ages. MtK acts as a FA mechanical performance regulator. This effect is more pronounced at early ages preventing the great disadvantage of using HVFAC. This way incorporating additional MtK in HVFAC even when the pozzolanic additions have slow reactivity, seems to be a valid way for the widespread usage of this kind of eco-efficient concrete.

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