RINOPOLYCRETE - TOWARDS A CEMENT-FREE AND FULLY RECYCLED CONCRETE

PROJECTO FCT

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Recycled inorganic polymer concrete - Towards a cement-free and fully recycled concrete
(RInoPolyCrete)

Task 2 - Report 4

Alkali activation electric arc furnace slag mortars: Methodology, optimization of mix design, and schedule

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ACRONYMS

EAFS	Electric arc furnace slag
AAEAFS	Alkali activated electric arc furnace slag
FA	Fly ash
AAM	Alkali activated material
NaOH	Sodium hydroxide
SiO_2	Silicon oxide
Na_2O	Sodium oxide
Na_2SiO_3	Sodium silicate
WRA	Water reducing admixture

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1 Introduction

The experimental work described in this report concerns the use of alkali activated electric arc furnace slag (EAFS) in mortars, the optimization of the alkaline activator to achieve maximum mechanical performance and interaction between EAFS and fly ash (FA). It describes the several stages, starting with EAFS preparation used in the campaign, as well as the other materials typically used in the production of alkali activated materials (i.e. aggregates, FA, and alkaline activators). It presents the mix design of all planned mortars, including also those based on alkali activated FA. The testing methodology of fresh and hardened mortars is also presented, including fresh bulk density; slump; dry bulk density; shrinkage; flexural strength; compressive strength; water absorption by capillary action and by immersion; carbonation.

2 Material

2.1 Electric arc furnace slag collection and sampling

EAFS is a by-product of steel manufacturing collected from the Siderurgia Nacional de Portugal, provided by HARSCO. It presents an extensive particle size distribution and requires preparation and grinding in order to be used as binder. The oxide chemical composition, obtained from X-ray fluorescence (XRF), of the raw material is presented in Table 1. This material presents an apparent density of 3770 kg/m^3.

Table 1: Chemical composition of EAFS (%)

Fe$_2$O$_3$	CaO	SiO$_2$	Al$_2$O$_3$	MgO	MnO$_2$	Cr$_2$O$_3$	TiO$_2$	P$_2$O$_5$	SO$_3$	Na$_2$O	BaO	K$_2$O	V$_2$O$_5$	CuO	ZnO
28.48	28.18	17.66	10.13	5.66	5.44	2.38	0.65	0.42	0.33	0.19	0.17	0.03	0.11	0.02	0.02

The procedure to prepare EAFS is the following:

1. Dry the material at 100 °C for 24h to eliminate any moisture stored in the material.

2. Once the material is fully dried, the grinding process starts. It is divided into three stages:

   A. Crushing machine - this stage starts by sieving EAFS and classifying those particles larger than 4 mm to be crushed in the crushing machine located at the Mining and Geotechnical Laboratory at IST, Universidade de Lisboa.

B. Cylinder mill - Once all particles' size is below 4 mm, they are placed in the cylinder mill for further processing.

C. Ball mill - 20 kg of EAFS are placed with 56 kg of abrasive load (i.e. steel balls with sizes between 0.5 and 2 inches) for 2 hours. This results in a powder form of EAFS.

Figure 1: Preparation and grinding process of EAFS

2.2 Fly ash

FA, supplied by EDP - Gestão da Produção de Energia, S.A. at the Sines Production Centre factory. This precursor does not require preparation stages for its use. The chemical composition of FA is shown in Table 2.

Table 2: Chemical composition of FA

Fe_2O_3	CaO	SiO_2	Al_2O_3	MgO	SrO	Cr_2O_3	TiO_2	P_2O_5	SO_3	Na_2O	BaO	K_2O	V_2O_5	Zr	ZnO
6.90	2.27	56.27	25.47	1.83	0.10	0.48	1.14	0.44	0.80	1.29	0.18	2.74	0.05	0.03	0.02

2.3 Fine aggregate

Two types of fine siliceous aggregates will be used for mortar making. The first type is coarse sand 0/4, and the second type is fine sand 0/1. The bulk density, water absorption, humidity, and size must be considered prior the use of these fine aggregates.

2.4 Alkaline activator

In this experiment, the alkaline activator is prepared in terms of a liquid solution. Reactive

grade sodium hydroxide pellets (NaOH), with 98% purity and a density of 2.13 g/ml, which is in solid state, then dissolved in a solvent: tap water complying with the Directive 98/83/CE [1]. A commercial solution of sodium metasilicate is also used in this study, which has a sodium oxide (Na_2O) content of $8 \pm 0.6\%$ and silicon oxide (SiO_2) of $26.4 \pm 1.5\%$; water content $65.6 \pm 2\%$ and relative density of 1.355 g/ml.

2.5 Water reducing admixture

The water reducing admixture (WRA) to be used in the campaign is SikaPlast-717, consists of a synthetic organic water-based naphthalene dispersant, having density of 1.21 ± 0.03 kg/dm^3 and a pH of 10 ± 1.

3 Methodology

3.1 Aggregate particle size distribution

The aggregate particle size distribution will be analysed according to EN 933-1 [2]. The equipment used for this test are the following.

- Test sieves;

- Tightly fitting pan and lid, for the sieves;

- Ventilated oven, thermostatically controlled to maintain a temperature of (110 ± 5) ºC, or other suitable equipment for drying the aggregates, provided it does not cause any particle size breakdown;

- Washing equipment;

- Balances or scales, accurate to ± 0.1 % of test portion mass;

- Trays, brushes;

- Sieving machine.

The procedure is the following:

- Place the test portion in a container and add sufficient water to cover the test portion;

- Agitate the sample with sufficient vigour to result in complete separation and suspension of the fines;

- Wet both sides of a 0.063 mm sieve reserved for use in this test only and fit a guard sieve (e.g. 1 mm or 2 mm) on top. Mount the sieves in such a way that the suspension passing the test sieve can be run to waste or, when required, collected in a suitable vessel. Pour the contents of the container on to the top sieve. Continue washing until the water passing the 0,063 mm test sieve is clear;

- Dry the residue retained on the 0,063 mm sieve at (110 ± 5) ºC to constant mass. Allow to cool, weigh and record as M_2;

- Pour the washed and dried material (or directly the dry sample) into the sieving column. The column comprises a number of sieves fitted together and arranged, from top to bottom, in order of decreasing aperture sizes with the pan and lid;

- Shake the column, manually or mechanically. Then remove the sieves one by one, commencing with the largest aperture size opening. Shake each sieve manually ensuring no material is lost by using a pan and lid for example:

- Transfer all the material that passes each sieve onto the next sieve in the column before continuing the operation with that sieve. Sieve overloading shall be avoided;

- To avoid overloading of sieves, the fraction of normal weight aggregates retained at the end of the sieving operation on each sieve (expressed in grams) should not exceed:

$$\frac{A \times \sqrt{d}}{200}$$

Where,

A is the area of sieve, in square millimetres;

d is the aperture size of the sieve, in millimetres.

- The sieving process shall be considered as finished when additional sieving does not lead to a change of mass of the retained material on any sieve by more than 1,0 % by mass;

- Weigh the retained material for the sieve with the largest aperture size and record its mass as R_1;

- Carry out the same operation for the sieve immediately below and record the mass retained as R_2;

- Continue with the same operation for all the sieves in the column, in order to obtain the masses of the various lots of retained materials and record these masses as R_3, R_4, R_i, R_n;

- Weigh the screened material, if any, remaining in the pan and record its mass as P;

- Record the various masses on a test data sheet;

- Calculate the mass retained on each sieve as a percentage of the original dry mass M_1:

- Calculate the cumulative percentage of the original dry mass passing each sieve down to the 0.063 mm sieve exclusive;

- Calculate the percentage of fines f passing the 0.063 mm sieve in accordance with the following equation:

$$f = \frac{(M_1 - M_2) + P}{M_1} \times 100$$

Where,

M1 is the dried mass of the test portion, in kilograms;

M2 is the dried mass of the residue retained on the 0.063 mm sieve, in kilograms;

P is the mass of the screened material remaining in the pan, in kilograms.

For dry sieving:

$$f = \frac{100\,P}{M_1}$$

3.2 Mix design

The experimental campaign will be divided into two stages. In the first one, an optimization of

the alkaline activator will be carried out based on the mortar's mechanical performance. The variables are presented in Table 3. To achieve an optimum activator for EAFS, the Na_2O/precursor mass ratio will vary between 0.04 and 0.12. The SiO_2/Na_2O will vary between 0 and 2.0. A fixed curing temperature and time of 70 °C and 24 hours, respectively, will be applied to all mortars.

Table 3: Operationalization of the variables

Factor	Unit of measurement	Variation				
Na_2O/precursor	%	4	6	8	10	12
SiO_2/Na_2O ratio	Dimensionless	0	0.5	1.0	1.5	2.0
Curing temperature	°C	70				
Curing time	Hours	24				

In the second stage, the interaction between the EAFS and FA will be determined by varying their proportions (100/0; 75/25; 50/50; 25/75; 0/100). The concentration of the alkali activator for each mix will be interpolated from the optimum solutions determined in the first stage.

The amount of each constituent is calculated based on some volumetric and mass ratios, using the densities of each of the raw materials. The binder/aggregate volumetric ratio (V_B/V_A) is of 0.33. The mass ratio of SiO_2/Na_2O will be of 0, 0.5, 1.0, 1.5, or 2.0. The mass ratio of water/binder (M_W/M_B) will be fixed and equal to 0.4. The mass WRA/precursor ratio will be of 1% and Na_2O/binder will be of 4%, 6%, 8%, 10%, and 12%.

3.3 Production procedure

Mortar production will be based on EN 196-1 [3], as shown in Table 4==Error! Reference source not found.==, with slight adaptations. Once the mix is ready to be moulded, the steps below will be followed:

- First, place the mould in its position and tie it well to the compaction apparatus (Figure 2);

- Once the mould is fixed, use the trowel to pour mortar filling half of the mould;

- Adjust the electric compaction apparatus to have 60 strokes for the first half layer;

- Then pour the second layer to fill the mould;

- Once again adjust the compaction apparatus to have 60 strokes to fully compact it;

- Remove the excess mortar that will show up on the top layer (Figure 3);

- Remove the mould carefully to an undisturbed place and cover it with a plastic bag to avoid water loss.

Table 4: Mortar production procedure

Equipment	Procedure
Electrical mixer and mixing bowl	1 - Weigh the materials according to the design mix.
Trowel	2 - Prepare the NaOH solution 24 hours before mixing day.
Mass scale with an accuracy of 0.01 g	3 - Moisturize the bowl, pour the NaOH solution with the EAFS into the bowl, and mix for 1 minute.
Mortar moulds (40 x 40 x 160 mm³)	4 - Add the fine aggregates into the mixing bowl gradually, allow mixing for 2 more minutes.
Compaction apparatus	5 - If required, use a plastic paddle to return unmixed materials stuck to the wall of the bowl and mix for 1 more minute.
Volumetric container	

Figure 2: Molding mortar - Shaking table

Figure 3: Excess layers of mortar removed from the top surface

3.4 Curing conditions

Once the mortars are moulded and wrapped with plastic film, they are transported to thermal curing for 24 hours in the oven at a temperature of 70 °C. At the end of this stage, the mortars are demoulded and placed in their designated curing conditions depending on the desired test method, as shown in Table 5.

Table 5: Curing conditions, test methods and number of specimens of the experimental campaign

Test	Standard	Number of specimens	Curing conditions
Accelerated carbonation	EN 13295 [4]	4	14 days in wet chamber then another 14 days in dry chamber; place in carbonation chamber until testing age.
Shrinkage	EN 1015-13 [5]	2	Specimens placed in dry chamber after demoulding until the end of the test.
Flexural strength	EN 1015-11 [6]	9	Specimens placed in wet chamber until testing age.
Compressive strength			

3.5 Fresh state performance

3.5.1 Bulk density

The density of the fresh mortar is performed by compacting mortar into a volumetric container. The ratio of mass/volume is determined as shown in Table 6 (EN 1015-6 [7]).

Table 6: Bulk density - Equipment, procedure, and calculation

Equipment	Procedure	Equations
Container with a known volume (V)	1 - Weigh the empty container (M_1)	Fresh mortar density $\rho = \dfrac{M_2 - M_1}{V}$
	2 - Fill the container with mortar at 1/3 height; Drop the container to the floor at an approximate height (7 to 10 cm) for 10 time, to reduce air voids and compact the mortar	
Trowel	3 - Repeat step 2 by filling the container up to 2/3 height	
	4 - Fill the container with mortar to its full; Remove the excess material on to surface with the trowel and compact the surface	
Mass scale with an accuracy of 0.01 g	5 - Weigh the full container (M_2).	

3.5.2 Workability

The mortars' workability will be evaluated via their slump according to EN 1015-3 [8]. The equipment and procedure are shown in in Figure 4 and Table 7.

Table 7: Workability - Equipment and procedure

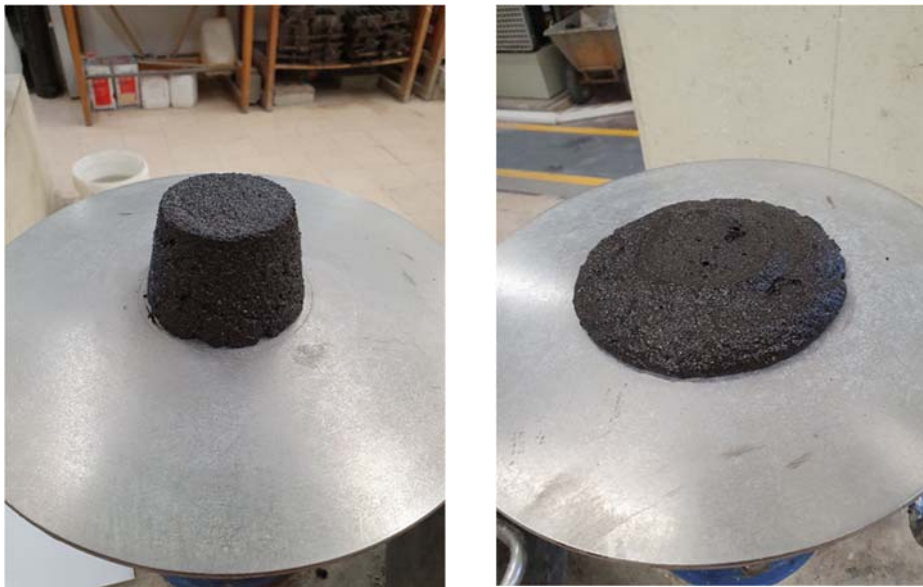| Equipment	Procedure
Mortar flow table	1 - Centre the slump cone on the workability table
Tamper	2 - Fill the cone with the first layer and drop the tamper 10 drops for compaction
Trowel	3 - Repeat step 2
Scoop	4 - Fill the cone to its full and compact the top surface with the trowel
Calliper	5 - Remove the slump cone mould; blow the table for 15 jolts (**Error! Reference source not found.**)
Mortar slump cone	6 - Use the calliper to measure to opposite diameters and take the average result

Figure 4: Slump test

3.6 Hardened state performance

3.6.1 Dry bulk density

The dry bulk density of mortars will be measured in accordance with EN 1015-10 [9]. The equipment and procedure are shown in Table 98.

Table 8: Dry bulk density - Equipment, procedure, and equations

Equipment	Procedure	Equations	
Mass scale	1 - Dry the specimens in the oven at temperature of 100 °C; until there is no change in mass by > 0.2%	Dry bulk density	$\rho = \dfrac{M_{s\,dry}}{V_s}$
Oven	2 - Measure the mass of the prism specimens		
Calculator	3 - Take the average mass of those specimens of the same family		

3.6.2 Shrinkage

The shrinkage of hardened state mortars is measured according to EN 1015-13 [5]. The apparatus and procedure of this test is shown in Table 9.

Table 9: Shrinkage test - Equipment and procedure

Equipment	Procedure
Shrinkage measuring equipment	1 - Demould the specimens and place it in the dry chamber
	2 - Use the shrinkage measuring equipment daily for 7 days
	3 - Use the shrinkage measuring equipment every 3 days for 21 days
Scale with 0.01 g precision	4 - Use the shrinkage measuring equipment every 7 days until the end of testing period

3.6.3 Flexural strength

The flexural strength test is performed on a hardened state mortar prism simply supported at both ends and load is applied at mid-point as presented in

Figure 5. Table 10 shows the equipment used for flexural strength, procedure, and equations according to EN 1015-11 [6].

Table 10: Flexural strength - Equipment, procedure, and equations

Equipment	Procedure	Equations	
Flexural and compression strength equipment.	1 - Align the specimen correctly to apply the flexural load at the mid-point	Flexural strength	$fi = 1.5 \dfrac{F_i \; x \; L}{b_i \; x \; d_i^2}$
	2 - Apply the flexural load until the peak and failure of the specimen at maximum of 30 N/s		

Figure 5: Flexural strength

3.6.4 Compressive strength

In this test, the same two halves of the specimen from the previous test will be used and aligned with a 40×40 mm^2 compressor. The hydraulic jack will start to compress the specimen until failure (Figure 6). This test is done according to EN 1015-11 [6] and as shown in Table 11.

Table 11: Compressive strength - Equipment, procedure, and equations

Equipment	Procedure	Equations	
Flexural and compression strength equipment.	1 - Align the specimen correctly to apply the compressive load	Compressive strength	$c_i = \dfrac{C_i}{A_i}$
	2 - Apply the compressive load until the peak and failure of the specimen at maximum of 30 N/s		

Figure 6: Compressive strength

3.6.5 Water absorption by capillarity

The water absorption coefficient due to capillary action is determined according to EN 1015-18 [10]. The increase in mass will be determined and capillarity is characterized by water absorption coefficient A_w as shown in Table 12.

Table 12: Water absorption by capillarity - Equipment, procedure, and equations

Equipment	Procedure	Equations
Mass scale	1- Dry the specimen to constant mass in the oven	
Minimum of 20 cm depth basin	2- Cut the mortar specimen in half	
Trowel	3- Expose the cut cross-sectional surface (40x40 mm) in basin filled with water at depth of 5 mm to 10 mm	
Absorbing filter paper	4- Cover the basin to avoid evaporation of water throughout the test	Water absorption coefficient [kg/m²h^0.5] $A_w = \dfrac{M_i - M_t}{A_i \times \sqrt{t}}$
Water	5- Set a timer for 10 minutes and remove all specimens	
Timer	6- Use the filter paper to wipe the excess water on the surface and record the mass of the specimens	
Oven (60 ± 5 °C)	7- Repeat the process for (30, 60, 90, 180, 300, 480 and 1400 minutes)	

3.6.6 Water absorption by immersion

Water absorption by immersion test is performed and measured in percentage of the voids in the mortar presented in Table 13 according to LNEC E-394 [11]. Figure 7 shows the four different stages of the test when applying water to immerse the mortar samples.

3.6.7 Carbonation

For the accelerated carbonation test, the mortar is placed in the carbonation chamber containing $5 \pm 0.1\%$ of CO_2 at room temperature (23 ± 3 °C) with a relative humidity of $60 \pm 5\%$. This process allows identifying the resistance against carbonation. The depth of carbonation is measured by applying a phenolphthalein indicator of broken pieces of the specimen according to LNEC E-391 [12] also shown in Table 14. Natural carbonation is also tested in the dry chamber or in a room where the specimens are exposed to CO_2, this process is slower than the accelerated carbonation.
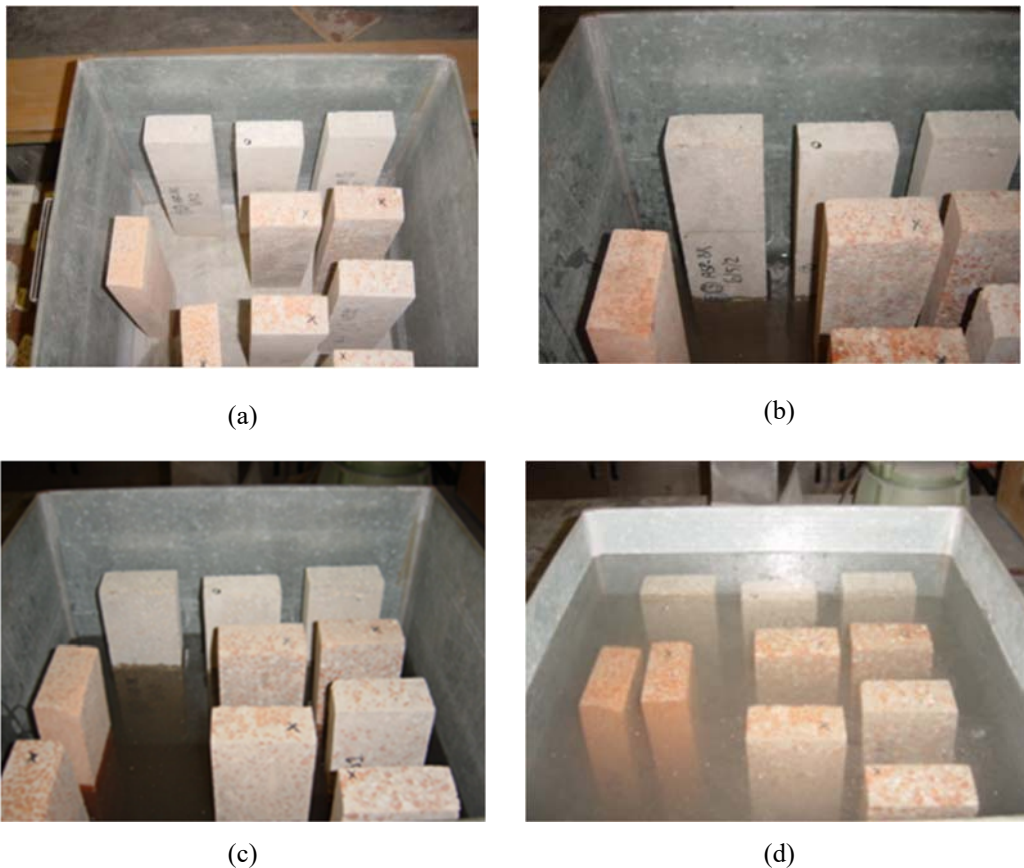

(a)

(b)

(c)

(d)

Figure 7: Water absorption by immersion - (a): lines marked with no immersion; (b): 1/3 immersed; (c): 2/3 immersed; (d): fully immersed

Table 13: Water absorption by immersion -Equipment, procedure, and equations

Equipment	Procedure	Equations
Mass scale	1- Mark the specimen at 1/3 and 2/3 height	
Minimum of 20 cm depth basin.	2- Place the specimens in the empty basin; Pour water to the height of 1/3 of the specimens for 1 hour	
Water vessel	3- Pour water until 2/3 of the specimens for another hour	Water absorption by immersion
Absorbing filter paper	4- pour water until all specimens are immersed; water level shall not exceed 25mm of the specimen's height	$M_1 \rightarrow$ Air saturated mortar
Water	5- Keep the specimens in the basin for 24 hours, so that the change in mass is less than 0.1%	$A = \dfrac{m_1 - m_3}{m_1 - m_2} \; x \; 100$
Timer	6- Dry the surfaces of the specimens with the filter paper and weigh the mass as M_2	
Oven (105 ± 5 °C)	7- Dry the specimens in the drying oven until the mass is constant and record the mass as M_3	

Table 14: Carbonation - Equipment and procedure

Equipment	Procedure
Thermal chamber	1- Place the samples in the thermal chamber for 24 hours
Wet chamber	2- Transport the specimens in the wet chamber until the 14th day from mixing
Dry chamber	3- Transport the specimens in the drying chamber until testing age for natural carbonation; and move out those for accelerated carbonation after 14 days
Carbonation chamber	4- Transport those specimens moved out from the dry chamber to the carbonation chamber until testing age
Phenolphthalein solution	5- The depth of the carbonation is measured on the split face of the prisms, using the phenolphthalein indicator. The depth of the carbonation (mm) is the average depth of the 4 sides

4   Quantity and scheduling

The optimization process (all stages of the campaign) for both precursors EAFS and FA are quantified with a 20% factor of safety of the materials and scheduled to be done in 6 months in total and is presented in Table 15 and Table 16. A total of 48 mixes are expected to be produced (24 containing EAFS and 24 with FA). Each mix is expected to have a total of 5 L of mortar (5 moulds - 1 L/mould). 9 specimens will be casted for mechanical performance, 4 specimens for carbonation, and 2 for shrinkage.

Table 15: Total quantity of materials required for the experimental campaign

Materials	100 % EAFS (kg)	100% FA (kg)	Total (kg)
FA (kg)	0.00	52.50	52.50
EAFS (kg)	78.51	0.00	78.51
SP (kg)	0.39	0.26	0.66
Water (kg)	18.31	12.21	30.52
NaOH (kg)	5.34	3.57	8.92
Na_2SiO_3 solution (kg)	19.96	13.40	33.36
Fine sand 0/1 (kg)	49.42	56.63	106.06
Coarse sand 0/4 (kg)	114.45	131.14	245.59

Table 16: Experimental campaign schedule

Activities	Months
	1 2 3 4 5 6 7 8 9
Preparation and grinding EAFS	
Fine aggregate characterization	
Mortar manufacturing and thermal curing	
Fresh state tests (Density & workability)	
Bulk density	
Flexural strength	
Compressive strength	
Shrinkage	
Carbonation	

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