NATURSEA-PV
NOVEL ECO-CEMENTITIOUS MATERIALS AND COMPONENTS FOR DURABLE, COMPETITIVE, AND BIO-INSPIRED OFFSHORE FLOATING PV SUBSTRUCTURES

D2.1 – Raw materials

Project information

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V1.1	16/10/2023	First draft with contributions from TEC and EHU
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V1.4	31/10/2023	First complete version with the contribution from UBX
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V1.6	28/11/2023	Final version reviewed by TEC
V1.7	11/10/2024	Conclusions section added

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List of abbreviations

AAB	Alkali Activated Binders
AAC	Alkali Activated Cement
AA-UHPC	Eco-UHPC using a tailor made Alkali Activated Binder in place of cement.
Eco-UHPC	Ultra High Performance Concrete with reduced environmental impact
FA	Fly Ash
GGBS	Ground Granulated Blast Furnace Slag
KPI	Key Performance Indicator
LCOE	Levelized Cost Of Energy
LOI	Loss On Ignition
OPC	Ordinary Portland Cement
PV	PhotoVoltaic
MFFT	Minimum Film Formation Temperature
MMA/BA	Poly (Methyl Methacrylate)-co-(Butyl Acrylate)
SCM	Supplementary Cementitious Material
SF	Silica Fume
Tg	Glass transition Temperature
UHPC	Ultra High Performance Concrete
WP	Work Package

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1 Executive Summary

This report includes the raw materials selected for the development of WP2, the selection criteria, and the experimental results that support them. The document is divided in two main sections:

- Materials for the development of eco-UHPCs (section 3).
- Materials for the development of bio-based coatings (section 4).

2 Introduction

The strategic objective of NATURSEA-PV is to improve the overall lifetime, reliability and maintainability of marine substructures for offshore floating photovoltaic (PV), to reduce degradation and failure rates, and thus investment risk and Levelized Cost Of Electricity (LCOE). This implies, among other things, the development of new circular materials (eco-UHPC) and bio-based coatings specially designed for marine conditions and with a smaller environmental impact than existing solutions. To that end, production costs and scalability of the proposed solutions will also be part of the Key Performance Indicators (KPI) for the selection of the most suitable materials and coatings, in addition to the overall performance.

Two different approaches will be explored in parallel for the development of the **new eco-UHPCs**. The replacement of traditionally used CEM I and CEM II cements with other commercial varieties (type III, IV…) with lower carbon footprint, and the use instead of low-environmental-impact alkali activated binders (AAB) specifically developed in the project for this application. In both cases, FORMEX®, the proprietary UHPC currently used by PREFFOR, will be used as reference material. The use of recycled aggregates and fibres will also be considered.

In the case of the **bio-based coatings**, monomers derived from the biomass will be used to synthesize the waterborne coatings. Different monomers of different glass transition temperature (Tg), hydrophobicity and bio-content will be explored, in order to obtain a hydrophobic coating with a high bio-content and good mechanical properties. Additionally, zwitterionic monomers will also be used in the synthesis of the waterborne coating with the objective of obtaining coating with antifouling properties.

This report includes the raw materials selected for the development of WP2, the selection criteria and the experimental results that support it. The document is divided in two main sections:

- Materials for the development of eco-UHPCs.
- Materials for the development of bio-based coatings.

3 Materials for the development of eco-UHPC

UHPC is a variety of concrete characterized by values of compressive strength exceeding 120 MPa and very good durability in aggressive environments. In order to reach such properties, it is necessary to maximize the compacity of the material, which requires the use of very low water to cement ratios, and a careful selection of aggregates and supplementary cementitious materials. In this sense, it is particularly important to pay attention to the granulometric curves of all the components of the concrete to ensure smaller particles fit in the space between the larger ones. However, the main differences with regular concrete are that the proportion of cement of UHPCs is considerably larger, the absence of coarse aggregate, and the use silica fume as supplementary cementitious material (SCM). In addition, UHPCs are usually reinforced with steel microfibres that increase strength and toughness and reduce the probability of explosive failure under compression.

Considering the carbon footprint and cost of each of the components of UHPCs, we will follow a stepwise approach for the development of the eco-UHPC, starting with the component with the largest impact. Therefore, we will explore first the replacement of the CEM I and CEM II cements commonly used by other

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varieties with lower environmental impact: CEM III, CEM IV and, alkali activated binders. Then, we will also explore the substitution of the steel microfibres by second life steel fibres. The use of recycled aggregates will only be considered at a later stage if time and project resources allow for it.

3.1 Reference material

The reference UHPC in NATURSEA-PV is FORMEX®, the proprietary UHPC currently used by PREFFOR for the production of precast elements. Therefore, the performance, cost, and environmental impact of FORMEX® will be used along the project as reference values for comparison with those of the new eco-UHPCs. In addition, the components (aggregates, silica fume…) and mix composition of FORMEX® will be used as a starting point for the development of the eco-UHPCs.

FORMEX® is currently being produced using two grades of fine silica sand with a particle size below 4 mm, densified silica fume, a last generation superplasticizer, steel microfibres, and cement CEM I OPC. Particle size distribution of the silica fume was measured by dynamic light scattering using propan-2-ol as solvent. For the measurement a small amount of material (about 2E-3 vol.%) was dispersed in the solvent manually and using an ultrasonic bath for a minimum of 30 min. Obtained results show that as received particles are strongly agglomerated, with an average particle size over 200 μm, Figure 3.1. However, ultrasonication reduces particle size considerably giving place to a trimodal distribution with the main peak centred at 10 μm, and two more peaks at 0.6 μm and 60 μm. It is also interesting to stress that although the relative volume of agglomerated particles is large, the number of particles of that size is small. In fact, if we represent the same data in terms of relative number of particles (Figure 3.2), the particle size distribution of as received and sonicated sample become unimodal and centred at about 7 μm and 0.3 μm respectively.

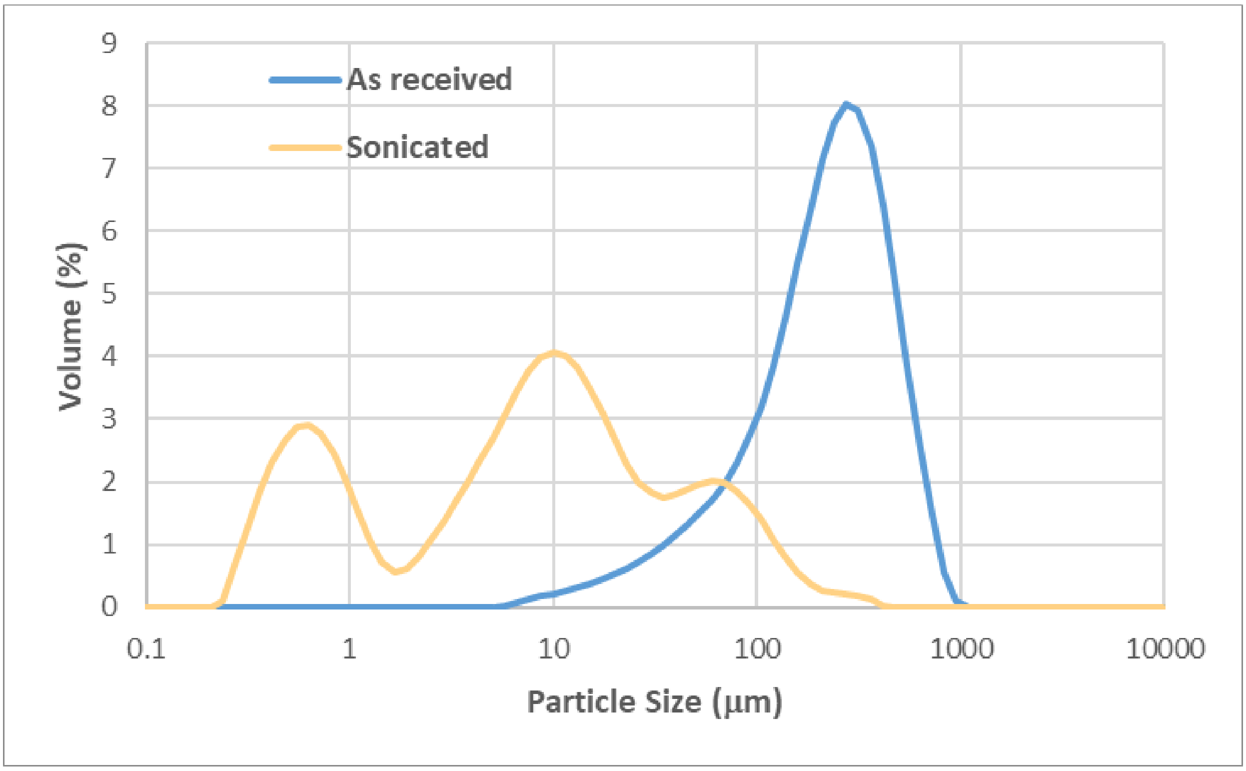

Figure 3.1 Particle size distribution of densified silica fume as received and after sonication in an ultrasonic bath for more than 30 minutes.

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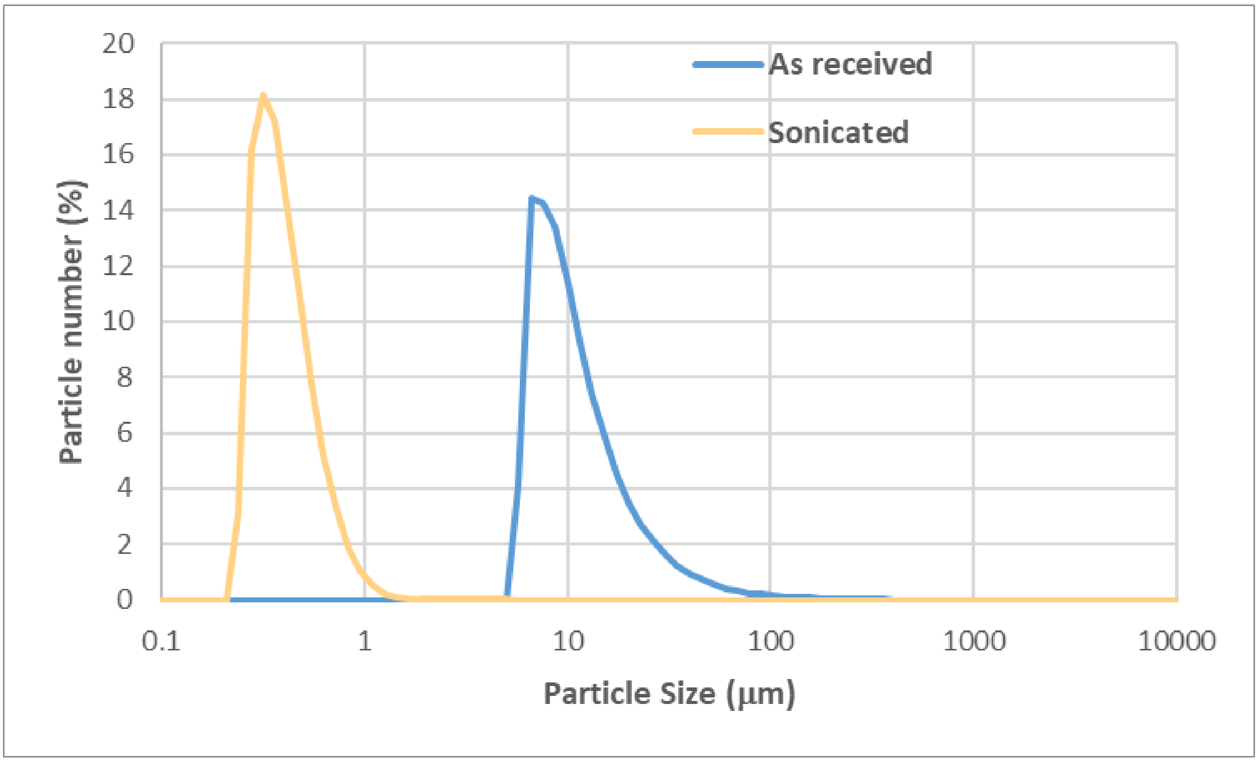

Figure 3.2 Particle size distribution of densified silica fume as received and after sonication in an ultrasonic bath for more than 30 minutes.

PREFFOR has supplied both, already premixed FORMEX® (cement + sand + silica fume) and its individual components to UBX and TEC for their use along the project. In addition, RDC has provided advice about water and superplasticizer dosage, as well as the mixing procedure.

Small batches of FORMEX® were prepared using the different mixers that will be used in the project in order to validate their suitability for mixing UHPC, and to set the reference values of strength obtained using each of them. First trials proved that planetary mortar mixers available in TEC are less efficient than the concrete mixers, making it necessary to increase the amount of water approximately by 10 wt.% to obtain a similar consistency. Figure 3.3 shows pictures and strength values of UHPC prepared with the concrete mixer. Obtained results fulfil the proposed set of minimum requirements:

- Mini slump: cone spread in the range of 18-21 cm after 30 seconds with no segregation of fibres or aggregates.
- Open time: at least 20 minutes.
- Compressive strength at 24 hours: 65 MPa for 10 cm cubic samples.
- Compressive strength at 28 days: 130 MPa for 10 cm cubic samples.

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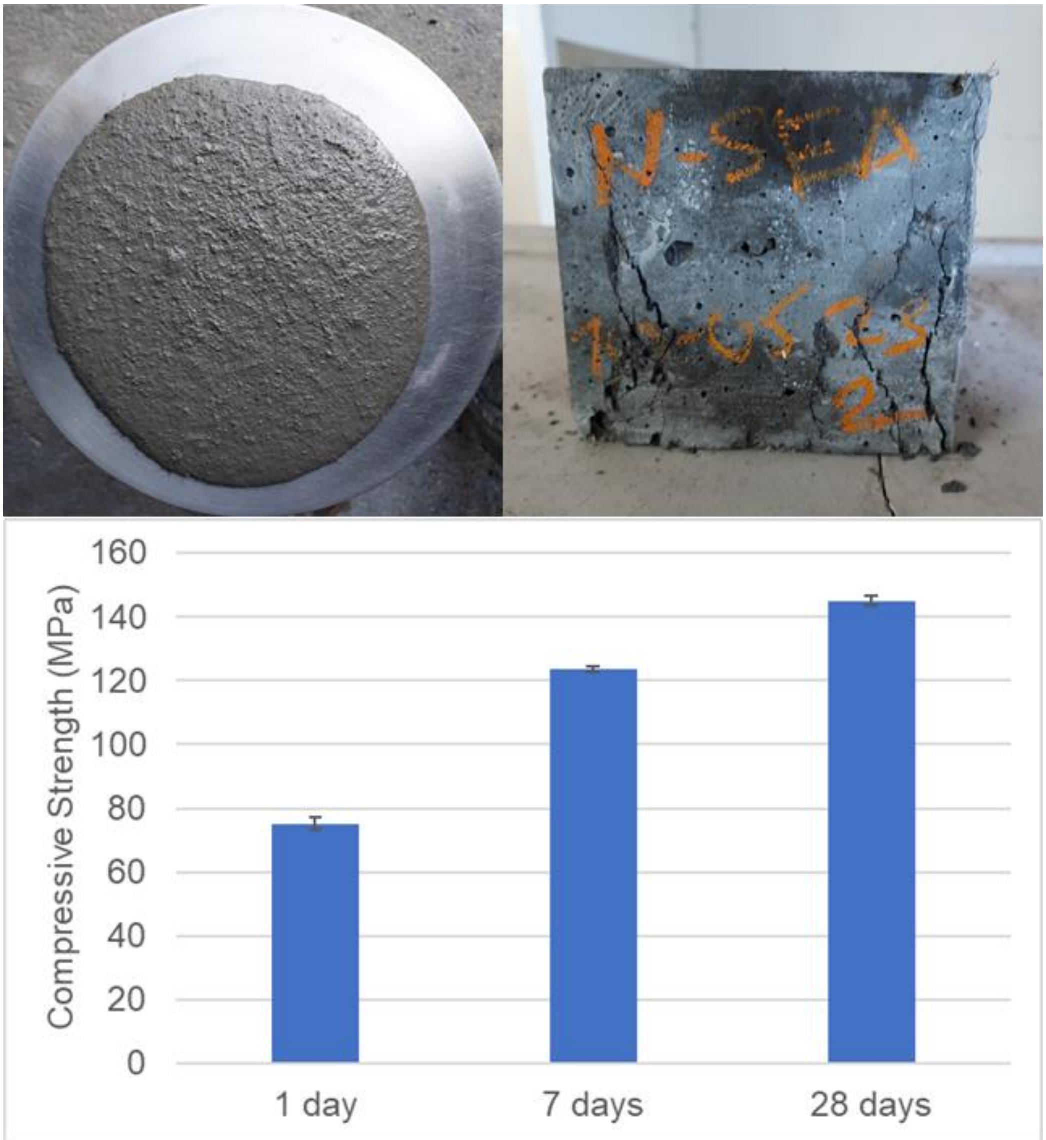

Figure 3.3: Pictures of the mini slump test after 30 seconds and a 10 cm cubic sample after the compressive strength test. The results of the compressive strength test are also shown as a function of curing time. Each value is the average of at least 3 samples and error bars show the standard deviation.

3.2 Materials for the development of eco-UHPCs using commercial cements.

As already mentioned, we will follow a stepwise approach for the development of the eco-UHPC which starts with the replacement of the CEM I and CEM II cements commonly used, by other varieties with lower environmental impact: CEM III, CEM IV and, alkali activated cements. Therefore, the first step in this approach was the identification of potential eco-cement suppliers.

Nowadays, most cement producers include in their portfolio low CO_2 cements. Besides, there are some relatively new companies focused mainly on the production of eco-cements and derived products. The list of contacted companies is included in Table 3.1. As a result, we have received four different cements that will be used for the development of the eco-UHPC. Three of the cements are Ordinary Portland Cements (OPC): CEM III/A 42,5 N/SRC, CEM III/B 42,5 N-LH/SR, and CEM IV/A(P) 42,5 SR. On the contrary, the fourth one is one of the few alkali-activated cements (AAC) commercially available.

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Table 3.1 List of cement producers identified and contacted in the project.

SUPPLIER	ECO-CEMENT FAMILY	WEBPAGE
CEMENTOS CRUZ	CKLEEN	https://cementoscruz.com/ckleen/
CEMEX	VERTUA	https://www.cemex.es/cemento/ecologico-vertua
HOLCIM	ECOPLANET	https://www.holcim.es/ecoplanet-cemento-sostenible
ECOCEM	ECOCEM	https://ecocem.fr/en/
HOFFMAN	HOFFMANN	https://www.ciments-hoffmann.com/hoffmann-green-solutions/
DB GROUP	CEMFREE	https://www.cemfree.com/
CEMENTIR GROUP	FUTURECEM	https://www.cementirholding.com/en/our-business/products-and-solutions/grey-cement

3.2.1 Characterization of the eco-cements

The three selected OPCs are sulphate resistant, which makes them suitable for marine applications. In the case of the AAC cement there is no such classification, but the producer suggested this particular cement due to its good performance in terms of strength and durability.

The mineralogical composition of the cements was determined by x-ray diffraction using Rietveld refinement method (only for the OPCs) and corundom as standard material. Obtained results (Table 3.2) confirm that the three OPCs can be classified as sulphate resistant according to UNE-EN 197-1 due to their low content of C3A and C3A+C4AF. There is also a very good correlation between the proportion of amorphous material and the proportion of supplementary cementitious materials (SCM) of the OPCs: 36-65 wt.% for CEM III/A; 66-80 wt.% for CEM III/B; 11-35 wt.% for CEM IV/A. The AAC is almost completely amorphous, Figure 3.5.

Table 3.2 Mineralogical composition of the cement obtained by x-ray diffraction and Rietveld refinement method.

PHASE	CEM III/A (wt%)	CEM III/B (wt%)	CEM IV/A (wt%)	AAC (wt%)
Amorphous	47.5±0.9	62.2±0.9	23.2±0.8	100**
Beta-C2S	3.1±0.6	5.0±0.6	8.2±0.9	
C3S	37.3±0.7	23.2±0.5	46.6±0.8	
C3A	2.0±0.3	2.6±0.3	4.6±0.4	
C4AF	6.9±0.4	3.8±0.3	7.4±0.5	
Quartz	0.2*	0.3	0.5*	
Calcite	1.4±0.2	1.9±0.3	3.2±0.4	
Mg calcite			1.5±0.8	
Akermanite	1.5±0.3	0.9*	0.4*	
Diopside			4.5±0.6	

*The error for values below 1% is of the same order of magnitude than the value itself.

**Rietveld method was not applied in this case, but the diffractogram (Figure 3.4) showed that there were no crystalline phases.

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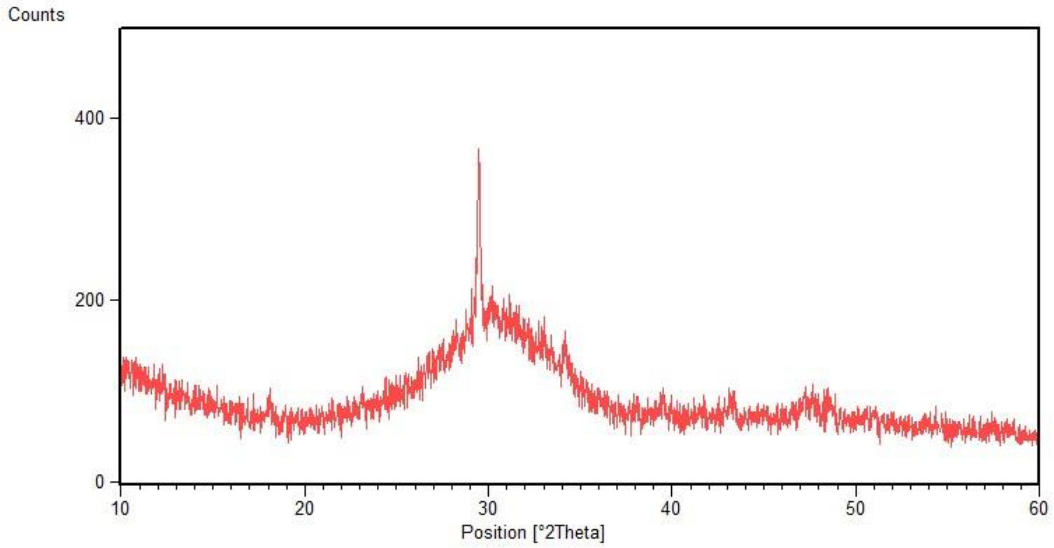

Figure 3.4 X-ray diffractogram of the alkali activated cement.

The elemental composition of each of the cements was determined by x-ray fluorescence, Table 3.3. The addition of the SCM reduces the Ca/(Si+Al) molar ratio of the cements, which in turn might reduce the corrosion protection of the steel reinforcements, particularly in the case of CEM III/B. Obtained values are 1.8, 1.4 and 2.24 for CEM III/A, CEM III/B and CEM IV/A respectively.

The composition of the AAC is compatible with the use of slag as main component. In addition, this cement showed high values of Na_2O and LOI (loss on ignition), which can be attributed to the alkali activator.

Table 3.3 Elemental composition of the eco-cements obtained by x-ray fluorescence.

COMPOUND	CEM III/A (wt.%)	CEM III/B (wt.%)	CEM IV/A (wt.%)	AAC (wt.%)
CaO	56.05	50.52	58.13	40.59
SiO_2	22.57	25.30	21.63	30.66
Al_2O_3	8.89	11.37	5.19	9.24
MgO	3.93	4.72	2.66	5.38
SO_3	2.88	3.43	2.87	1.43
Fe_2O_3	2.61	1.78	4.74	0.438
K_2O	0.708	0.435	0.961	0.417
TiO_2	0.414	0.477	0.8	0.729
MnO	0.385	0.563	0.0948	0.203
P_2O_5	0.0822	0.0601	0.344	---
ZnO	0.0328	0.0214	---	---
CuO	0.0248	0.0444	0.0299	0.021
Cl	0.0244	0.0288	0.0363	0.0176
Cr_2O_3	0.0146	---	0.0106	---
Na_2O	---	0.255	0.743	5.47
L.O.I.*	1.36	0.98	1.74	5.39

*Loss on ignition

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Particle size distribution of the cements was measured by dynamic light scattering using propan-2-ol as solvent. For the measurement a small amount of material (about 2E-3 vol.%) was dispersed in the solvent using an ultrasonic bath for a minimum of 30 min. Obtained results show that all cements have a bimodal distribution (Figure 3.5) with the main peak centred at around 20 µm, and a second one slightly below 1 µm. AAC contains also some large, agglomerated particles that can even be seen by the naked eye. Although most of these particles dispersed upon sonication, some of them persisted.

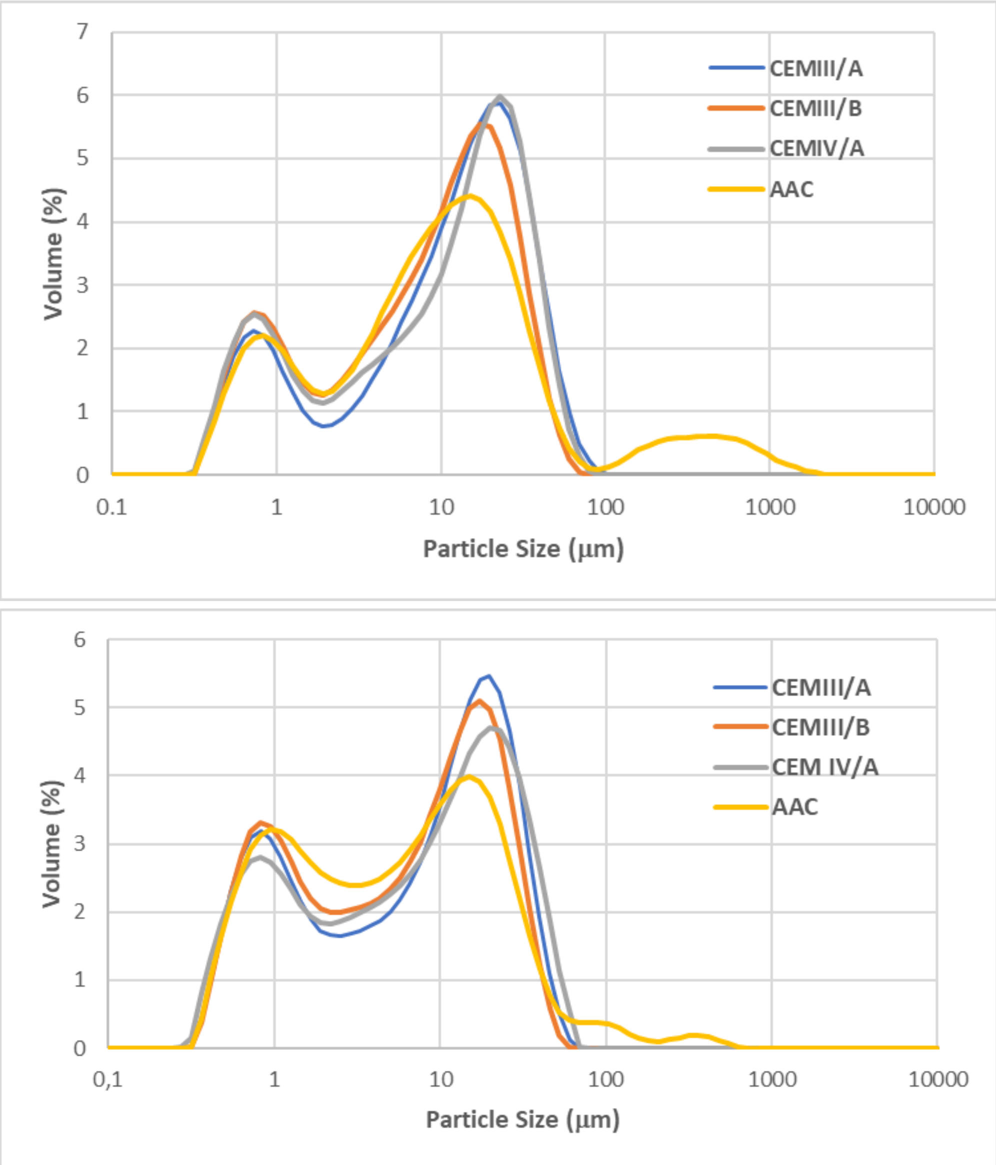

Figure 3.5 Particle size distribution of the cements measured by dynamic laser scattering before (top) and after (bottom) sonication.

3.2.2 Selection of the superplasticizer

One of the key points in the design of UHPCs is the selection and dosage of the water reducing admixtures, generally, last generation superplasticizers. In this sense, there are three main aspects to take into account:

- First of all, the superplasticizer must be compatible with the used cement. In order to do so, we have reached an agreement with an admixture producer, who will provide us superplasticizers especially formulated for the eco-cements.

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- Secondly, the superplasticizer must reduce water demand without reducing early strength development. In the case of this project, the objective is to obtain a compressive strength over 65 MPa after 24 h from mixing.
- Finally, the effect of the superplasticizer must be maintained for a certain time in order to provide enough time for filling the moulds. This is the so-called open time, and, in this project, it has been set at a minimum of 20 minutes.

In order to test the effect of the superplasticizer on the rheology and hydration of the cements, we studied cement pastes, with and without superplasticizer. The proportion of superplasticizer was adjusted so that the cone spread obtained with the mini slump test equalled the value (110±10 mm) obtained for a cement paste with w/c=0.4 and no superplasticizer. This allowed us to get a first idea of the compatibility between the eco-cements and the superplasticizers. So far, only two superplasticizers have been tested, the one currently used by PREFFOR and another one specifically formulated for NATURSEA-PV. However, further collaboration with the admixture producer is expected in the coming months.

The heat flow curves presented in Figure 3.6 show that the admixture has an important accelerating effect on AAC, resulting on the complete disappearance of the dormant period. This is made evident by the displacement of the calorimetric peak to the left and the increase of heat flow both at the peak and at the initial minimum placed at approximately 1.2 h. This result indicates that the superplasticizer is not suitable for this cement because the paste lost its fluidity completely after a few minutes, making it difficult even to carry out the slump test. In fact, almost no fluidity gain was observed independently of the proportion of superplasticizer used (up to 1 wt.% by weight of cement).

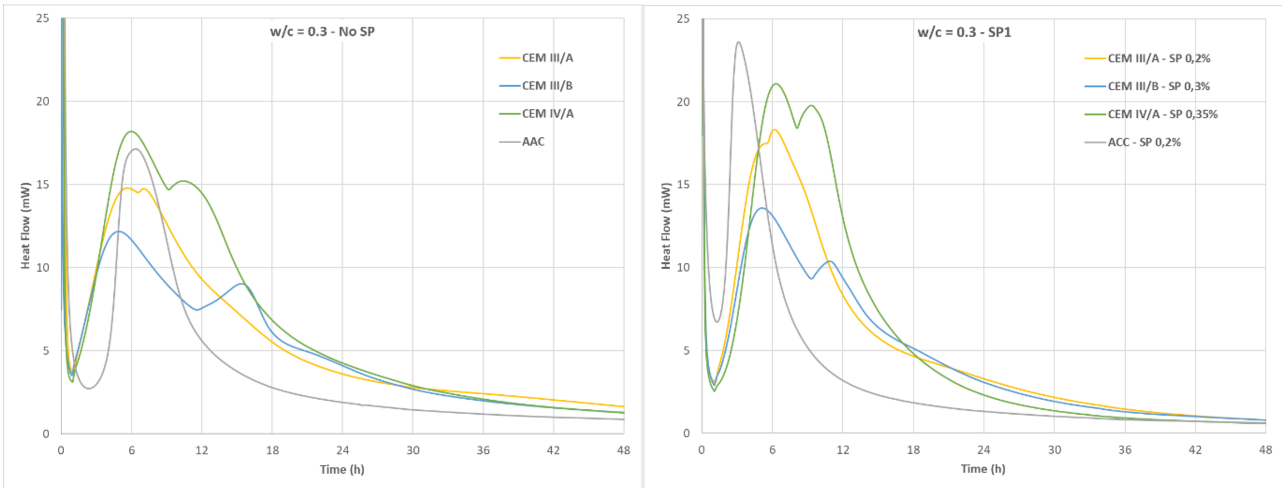

Figure 3.6 Calorimetric curves of cement pastes with w/c=0.3 in absence (left) and presence (right) of superplasticizer. The proportion of superplasticizer by weight of cement used in each case is indicated in the name of the samples.

In the case of the other cements, there was also some increase in the intensity of the peaks of the heat flow curves (Figure 3.6), but the dormant period was not substantially reduced.

Comparison between the calorimetric curves of both superplasticizers (Figure 3.7) showed very small differences between them making it impossible to reach any conclusion.

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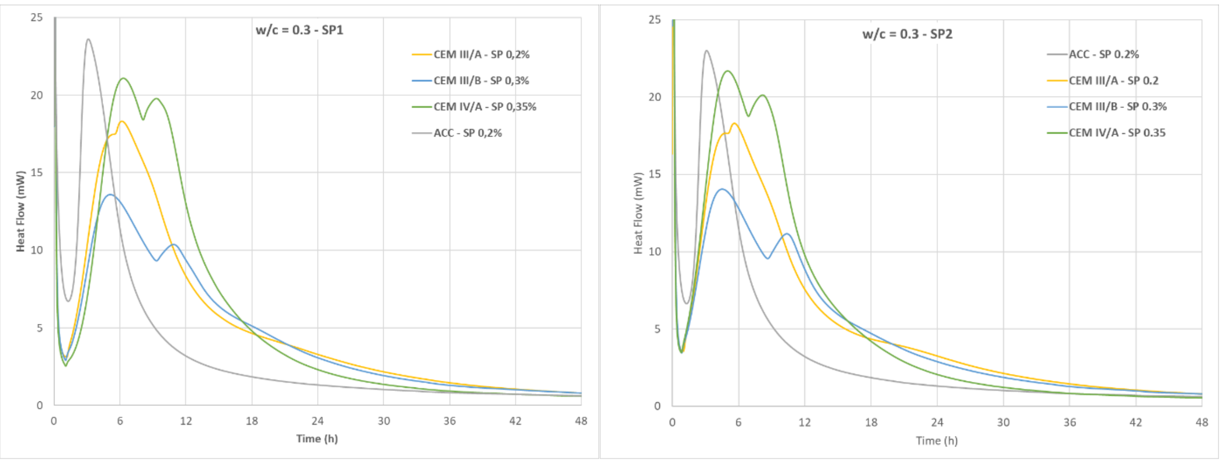

Figure 3.7 Comparison of the calorimetric curves of cement pastes with w/c=0.3 prepared using the same proportion of the two superplasticizers tested so far. The proportion of superplasticizer by weight of cement used in each case is indicated in the name of the samples.

The values of compressive strength after 24 h (Figure 3.8) are in good agreement with the calorimetric measurements, with the CEM IV/A having the largest strength at such age. No significant effect is observed as a consequence of the use of the superplasticizers, although it could be due to the small dosages used. At later ages, the difference in strength between all the cements is substantially reduced. The reduction in strength after 28 days of curing of ACC and CEM IV with superplasticizer was attributed to experimental error, as made evident by the large error bars. In the particular case of ACC, this was due to two main reasons: the low workability of the pastes, and the adherence of the hardened cement to the moulds. Both effects resulted in test specimens with relatively large defects in the form of large pores or broken edges.

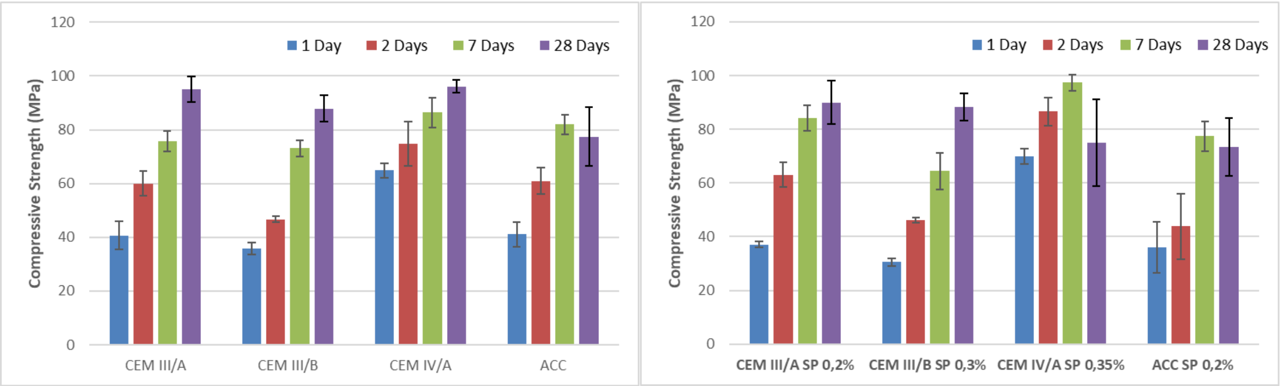

Figure 3.8 Compressive strength of cement pastes with w/c=0.3 in absence (left) and presence (right) of superplasticizer SP1. The proportion of superplasticizer by weight of cement used in each case is indicated in the name of the samples.

3.3 Materials for the development of eco-UHPC using alkali activated cements.

For the development of the eco-UHPC using alkali activated binders (AA-UHPC), we will start using the same sand, superplasticizer and silica fume mentioned in previous sections. The proportions of binder (cement + silica fume), fine sand, and coarse sand will also be maintained. On the contrary, commercial cements will be replaced by a tailor-made alkali activated binder (AAB).

3.3.1 AAB components

Raw materials selected for the preparation of the AAB were:

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- **Ground Granulated Blast Furnace Slag (GGBS):** GGBS is a glassy by-product of blast furnace iron-making. It mainly contains calcium silico-aluminate with high reactivity characteristics, see Table 3.4. Its pozzolanic reaction can be activated by several methods, but the main hydration product is an amorphous calcium silicate gel that may also contain alkali ions. Used GGBS complies with NF EN 15167-1, and its Blaine fineness is 4500 cm^2/g. Particle size distribution of the GGBS is presented in Figure 3.9.
- **Fly Ash (FA):** The fly ash supplied by SURCHISTE is a quality assured fly ash conforming to EN 450-1 2005: Fineness Category N, with a loss of ignition less than 7% (LOI Category B). It's elemental composition and particle size distribution are presented in Table 3.4 and Figure 3.9 respectively.
- **Alkaline Activator (AA):** The employed AA was a sodium silicate (Na_2SiO_3) solution commercialized under the name of Betol 47 T. Betol 47 T is an inorganic binder derived from a specially modified sodium silicate, entirely devoid of any volatile organic additives, see Table 3.4. Its dry content constitutes roughly 44.5%. At a temperature of 20°C, its density is approximately 1.55 g/cm3, while its pH level rests around 12.5. Notably, its viscosity at 20°C is estimated to be about 450 millipascal-seconds (mPas).

Table 3.4 Composition of the materials used for the preparation of the AABs.

Material	SiO_2 (wt.%)	Fe_2O_3 (wt.%)	Al_2O_3 (wt.%)	K_2O (wt.%)	Na_2O (wt.%)	MgO (wt.%)	SO_3 (wt.%)	CaO (wt.%)
GGBS	37.6	0.33	10.26	0.26	0.22	6.93	0.03	43.9
SF	90-95	<1	<1	<4	<4	<3	<1	<1
Betol	27.7	-	-	-	16.72	-	-	-
FA	50.82	6.07	26.29	4.32	0.61	1.66	-	1.67

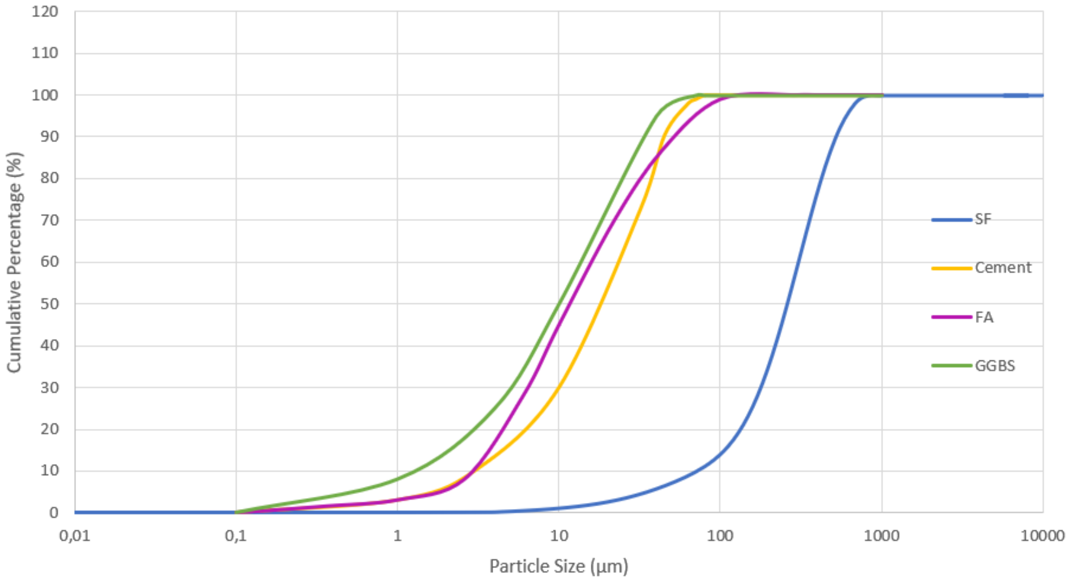

Figure 3.9 Particle size distribution of the reference cement and the main components of the AAB: Fly Ash (FA), Ground Granulated Blast Furnace Slag (GGBS), and Silica Fume (SF).

3.3.2 Mix design of the AA-UHPC

The composition of the AABs used for the preparation of the AA-UHPCs are included in Table 3.5. The objective behind this was to achieve the desired rheological and mechanical properties using the minimum

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amount of binder. Mixes labeled W20, W40, and W100 all contained the same amount of binder (1150 kg/m3) and an equivalent quantity of alkali activator (AA) and aggregates, but with differing water content (20, 40, and 100 kg/m3). For the other mixes G6F25 to G2F6, we replaced the cement with a combination of ground granulated blast furnace slag and fly ash in different proportions. The proportion of binder in the concrete was also varied from 1000 kg/m^3 to 800 km/m^3, maintaining constant the amount of SF.

Table 3.5 Composition of the materials used for the preparation of AA-UHPCs. AA indicates the total weight of Betol 47 T, i.e. it includes the dry and evaporable fractions. "b" stands for the sum of GGBS, FA, and SF. "w" includes added water and the evaporable fractions of AA (55.5 wt.%) and SP (65 wt.%).

AA-UHPC	GGBS (kg/m^3)	FA (kg/m^3)	SF (kg/m^3)	SP (l/m^3)	Water (kg/m^3)	AA (kg/m^3)	AA/b (kg/kg)	w/b (kg/kg)
W20	632	368	150	28	20	328.2	0.29	0.19
W40	632	368	150	28	40	328.2	0.29	0.21
W100	632	368	150	28	100	328.2	0.29	0.26
G6F25	600	250	150	0	40	300	0.3	0.21
G85F0	850	0	150	0	60	300	0.3	0.23
G8F0	800	0	150	0	100	300	0.32	0.28
G6F2	600	200	150	0	100	300	0.32	0.28
G4F4	400	400	150	0	100	300	0.32	0.28
G2F6	200	600	150	0	100	300	0.32	0.28

Figure 3.10 shows the results of the slump tests of G6F25 to G2F6 mixes. It can be observed that as the amount of fly ash is increased in the mix the flowability of the mixes also increases. This might be due to the typical spherical shape of this type of particles that induce a lubricating effect. On the contrary, in the case of W20, W40 and W100 mixes, the slump test could not be carried out because mixes lost their fluidity almost instantaneously after mixing. In fact, setting strength development took place so fast that it was also impossible to prepare strength test specimens.

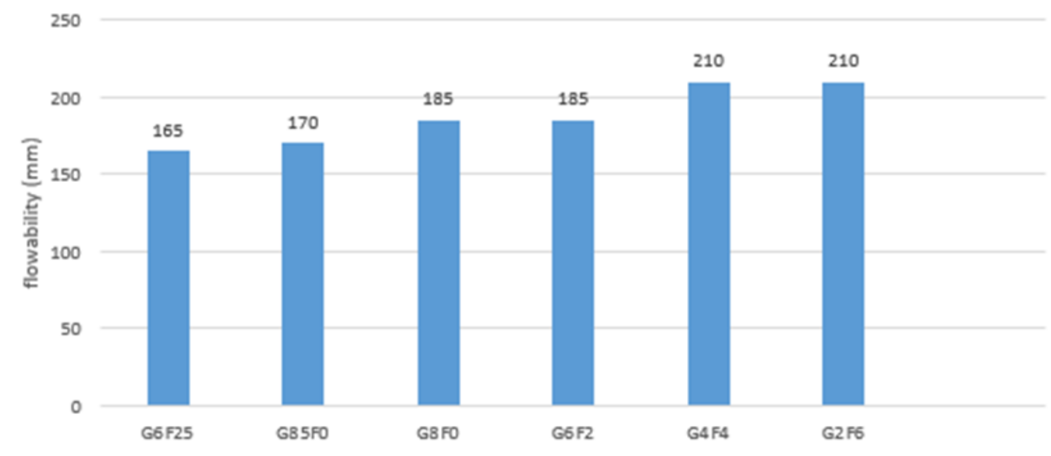

Figure 3.10 Cone spread measurement of G6F25, G85F0, G8F0, G6F2, G4F4, G2F6 mixes.

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Figure 3.11 shows the compressive strength at 28 days curing of the specimens of G6F25, G85F0, G8F0, G6F2, G4F4 and G2F6 mixes. It can be observed that as the substitution of GGBS by fly ash increases (from G6F25 to G2F6) the compression strength is reduced. This is especially clear in the mixes G6F2, G4F4 and G2F6, where the compressive strength reduces from 120 MPa to 70 MPa as the fly ash substitution is increased and the water content is the same in all the mixes. Such reduction could potentially be attributed to several factors.

GGBS and fly ash each possess unique chemical and physical properties that influence their contributions to the strength of alkali activated concrete. GGBS, being a by-product of iron production, typically contains latent hydraulic properties that contribute to long-term strength development. On the other hand, fly ash, derived from coal combustion, can have varying levels of pozzolanic reactivity and may exhibit differing effects on early-age and long-term strength.

This observation underscores the intricate nature of AA UHPC mix design and the need to carefully evaluate the behavior of different supplementary materials when making substitutions. It's a also reminder that the performance of concrete mixes is influenced by a combination of factors, including material properties, proportions, curing conditions, and the specific context of their application.

It has been observed that the compressive strength of alkali activated UHPC is influenced by the Si/Al. This ratio refers to the proportion of reactive silicate to aluminate components in the binder material. According to the values presented in Table 3.6 the relationship is clear: as the Si/Al ratio increases, the compressive strength of the alkaline activated UHPC also increases.

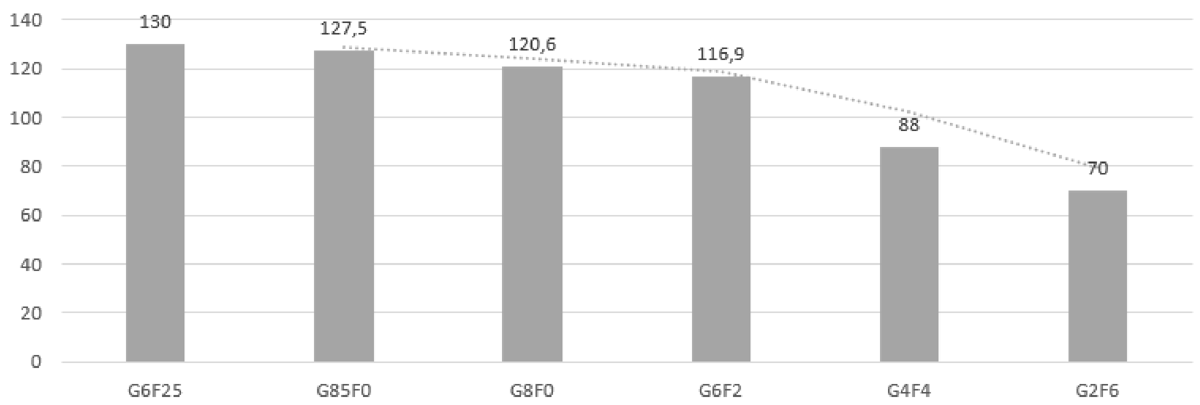

Figure 3.11 Compression strength of G6F25, G85F0, G8F0, G6F2, G4F4, G2F6 mixes at 28 days.

Table 3.6 Si/Al and compression strength (f'c) values. Si/Al was calculated taking into account the SiO_2 and Al_2O_3 content in GGBS, FA, SF, and AA.

	G6F25	G85F0	G8F0	G6F2	G4F4	G2F6
Si/Al (kg/kg)	4.18	5.72	5.85	4.44	3.65	3.14
f'c (MPa)	127.5	130.0	120.6	116.9	88.0	70.0

Summing up, these results show that addition of fly ash improves the flowability of the mix but can reduce the compressive strength, therefore, it is necessary to find the optimum proportion. Besides, obtained values of strength and flowability are close to the objective values, 130 MPa and 180-210 mm respectively.

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3.4 Recycled steel fibres for the development of eco-UHPC.

A first batch of 200 kg of recycled steel fibres with an average length of 13 mm was directly purchased from its manufacturer. As it can be observed in Figure 3.12, fibre length is not homogeneous, and they are twisted. Fibres are also accompanied by some rubber particles and a few metallic particles and small wires.

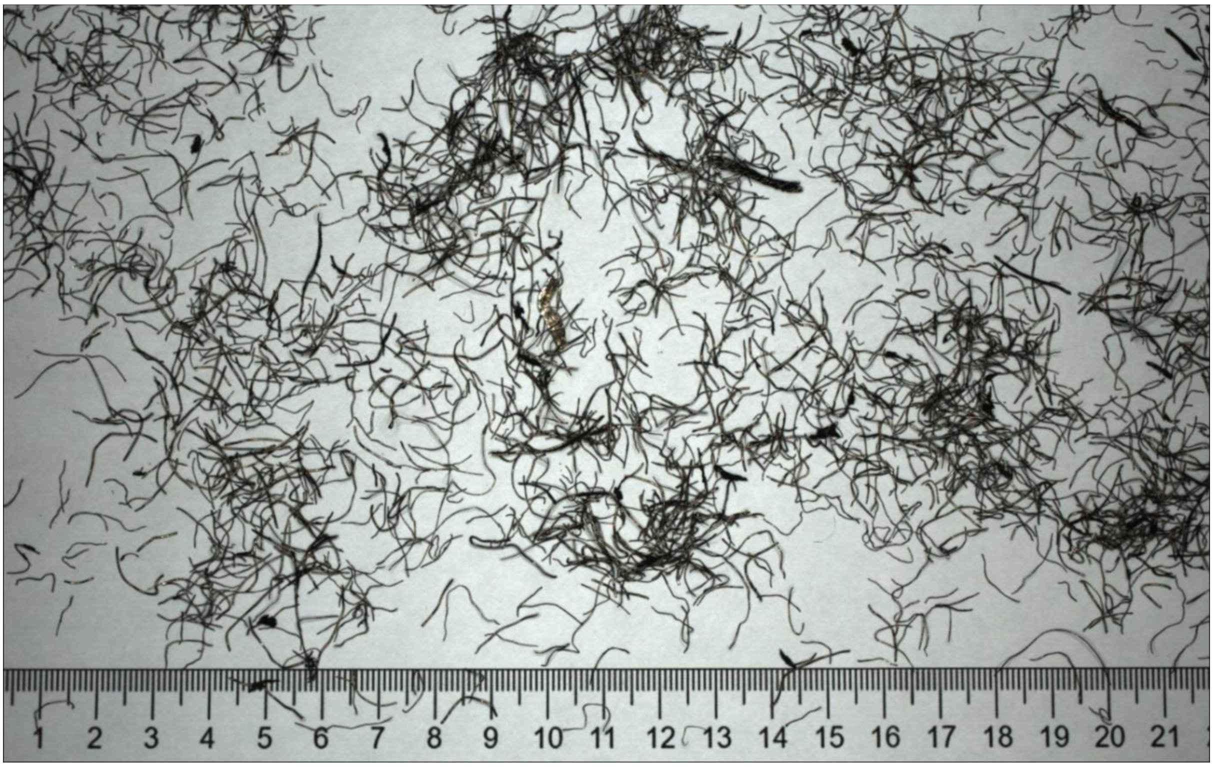

Figure 3.12 Photo of the recycled fibres.

In order to test the performance of the recycled fibres, we prepared UHPC cubic samples using exactly the same materials and procedures as for the reference UHPC but changing the type of fibres used. However, water to cement ratio had to be increased 10 wt.% compared to the reference UHPC to obtain similar workability before adding the fibres. We do not have an explanation yet for the increase in water demand because all materials and methods used were the same. Mixing took place outdoors, but conditions were mild in all cases.

During mixing, recycled fibres did not show any problem of entanglement. The overall appearance of the prepared samples was similar to that of the reference material and compressive strength values were also very close at all ages, see Figure 3.13. The slightly lower values of strength after 7 days and 28 days might be due to the increase in w/c. Nevertheless, obtained value is still larger than the 130 MPa set as objective.

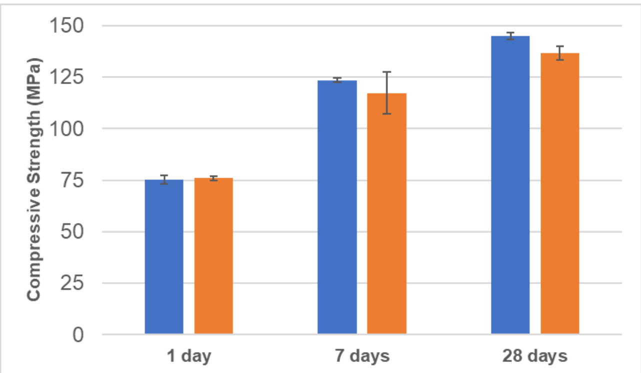

Figure 3.13 Compressive strength of the reference UHPC (blue bars) and a similar concrete prepared with recycled fibres (orange bars).

4 Materials for the development of bio-based coatings

As sustainability and environmental concerns become more prominent, the development and utilization of bio-based monomers is growing considerably. Thus, the list of monomers from bio-sources can be extensive. However, not all of them are suitable to polymerize via emulsion polymerization, and only few of them can be obtained commercially at a competitive price. Because of that, different bio-based monomers were explored and a list of potential monomers for the development of the coating is presented.

4.1 Reference material

As reference material, a latex (a dispersion of polymer particles in water) of poly(methyl methacrylate)-co-(butyl acrylate) (P(MMA-co-BA)) has been selected. This latex is widely used for coating applications due to its excellent weather resistance, adhesion, and durability. The reference latex was synthesised by seeded semi-batch emulsion polymerization of methyl methacrylate (MMA) and butyl acrylate (BA) two commercial monomers derived from petroleum. A polymeric film was prepared using the P(MMA-co-BA) latex and its thermal and water resistance properties were assessed. Table 4.1 presents the glass transition temperature (Tg), the minimum film formation temperature (MFFT), the water uptake and the contact angle of the film (before and after being immersed in water for 5 days). Additionally, the P(MMA-co-BA) films presents a young modulus of around 2 MPa and a tensile strength of around 10 MPa depending on the surfactant and initiator employed in the synthesis.

Table 4.1 Properties of the reference material.

	Tg (ºC)	MFFT (ºC)	Water-uptake after 7 days (%)	Contact Angle before water (º)	Contact angle after water immersion (º)
P(MMA-co-BA)	18	10	20 ± 1	52 ± 3	76 ± 6

4.2 Selection of bio-based monomers

In order to obtain a waterborne bio-based coating with good mechanical and film forming properties, a bio-based latex will need to be synthesized combining soft and hard bio-based monomers. The objective will be to obtain a hydrophobic bio-based latex, with a high bio-content and good film forming and mechanical properties. Table 4.2 presents the molecular structure, the bio-content, the commercial availability, the Tg of the homopolymers, and the hydrophobicity of the selected bio-based monomers.

In order to have good film forming and mechanical properties, the Tg of the bio-based latex will need to be between 12 and 18 °C and the MFFT will need to be below 18 °C. The hydrophobicity of the polymeric films will be assessed by water-uptake and contact angle measurements. The water-uptake and contact angle values of the petroleum-based P(MMA-co-BA) latex will be used as reference (Table 4.1). Therefore, bio-based latexes with a maximum water uptake of 20 % (after 7 days) and a contact angle value above 76 ± 6 º (after water immersion) will need to be synthesized.

Additionally, the mechanical properties of the bio-based films will be assessed based on the young modulus and tensile strength. Again, the values of the petroleum-based P(MMA-co-BA) latex will be used as reference (section 4.1).

The bio-based latexes presenting the best water resistance and mechanical properties will be selected to improve their formulations and incorporate functional monomers with antifouling and anticorrosive properties (section 4.3).

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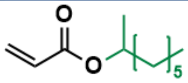
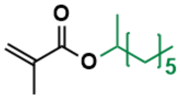
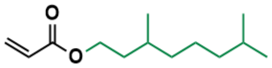
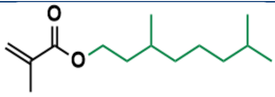
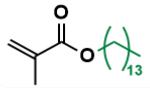
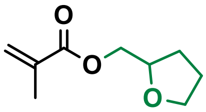
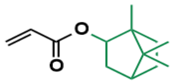
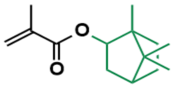
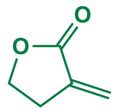
Table 4.2 Selection of bio-based monomers and their properties.

	Monomer	Molecular structure	Bio-based content (%)*	Commercial	Tg (°C)	Hydrophobicity
SOFT	2-Octyl acrylate (2OA)		73	✓	-44	Hydrophobic
	2-Octyl methacrylate (2OMA)		64	✓	5	Hydrophobic
	Tetrahydrogeraniol acrylate (ThgA)		77	✗	-46	Hydrophobic
	Tetrahydrogeraniol methacrylate (ThgMe)		71	✗	-79	Hydrophobic
	Tetradecyl methacrylate (TdMe)		78	✓	-80>	Highly hydrophobic
HARD	Tetrahydrofurfuryl methacrylate (ThfM)		56	✓	49	Low hydrophobicity
	Isobornyl acrylate (IBOA)		77	✓	94	Highly hydrophobic
	Isobornyl methacrylate (IBOMA)		71	✓	150	Highly hydrophobic
	α-methylene-γ-butyrolactone (MBL)		100	✓	195	Low hydrophobicity

*Bio-based content based on the number of carbons.

Additionally, a high-throughput screening (HTS) of extensive databases containing both soft and hard monomers will be conducted. To carry out this process, an atomic-level metadynamics approach will be employed, focusing on monitoring the interaction between monomers and the concrete's surface. This approach enables the estimation of the free energy associated with monomer adsorption on the surface, allowing for the identification of monomers with particularly high affinities for concrete. This computationally-assisted approach can guide the design of bio-based coatings that not only adhere effectively to concrete, but also deliver optimal mechanical performance and exceptional durability.

4.3 Functional monomers for antifouling and anti-corrosive properties

Biofouling occurs when living organisms attach to a surface. The adherence of the microorganisms can be avoided using a coating containing zwitterionic components. Table 4.3 presents the zwitterionic monomers that will be used in this work. These monomers were selected due their well-known antifouling performance.

Once a bio-based latex with high bio-content and good water resistance and mechanical properties is obtained, zwitterionic monomers will be introduced in the latex formulation. The incorporation is pre-formed by adding a small amount of these monomers to the bio-based monomers. The effect of adding different amount of zwitterionic monomer (1-4 % in weight based on the bio-based monomers amount) in the latex stability and antifouling properties will be evaluated.

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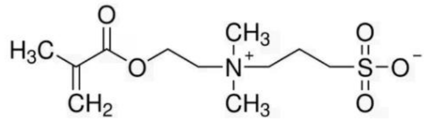
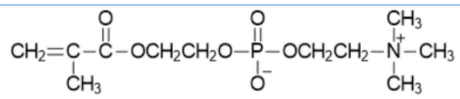
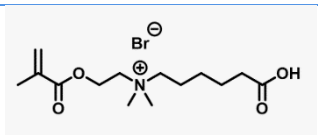
First, antifouling properties will be assessed at laboratory scale by measuring the protein adhesion into the coating surface. Then, the performance of the best performing coatings will be validated in real marine conditions at Tecnalia´s HarshLab.

Table 4.3 Zwitterionic monomers.

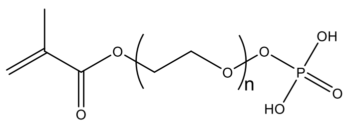
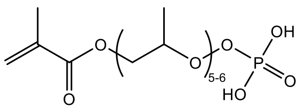
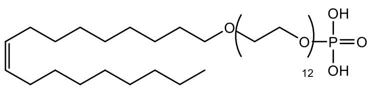
Monomer	Structure
2-Methacryloyloxy ethy ldimethyl-(3-sulfopropyl) ammonium hydroxide	
2-(Methacryloyloxy)ethyl 2-(Trimethylammonio)ethyl Phosphate (M2005)	
1-pentanaminium, 5-carboxy-N,N-dimethyl-N-[2-[(2-methyl-1-oxo-2- propen-1-yl)oxy]ethyl] bromide	

In order to inhibit the corrosion of the metallic parts, different functional monomers are required. It is known that monomers containing a phosphate functionality are able to interact with steel, leading to effective anticorrosive properties. Furthermore, the phosphate group enhances latex properties such as freeze/thaw resistance, mechanical stability, and gloss. For that reason, the monomers presented in Table 4.4 were chosen.

Anti-corrosive monomers will be introduced in the bio-based latex in the same way as zwitterionic monomers. After selecting the bio-based latex with the best water resistance and mechanical properties, a small amount (around 2 % in weight respect to the bio-based monomer) of the anti-corrosive monomer will be added to the formulation.

Anticorrosion properties of the coatings will be measured by electrochemical impedance spectroscopy (EIS) and using the anticorrosion salt spray chamber.

Table 4.4 Anti-corrosive monomers.

Monomer	Structure
Sipomer PAM 100	
Sipomer PAM 200	
Maxemul 6106-	

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5 Conclusions

Raw materials required for the developments of the new eco-UHPCs and biobased coatings were acquired and characterized. In the case of UHPC, FORMEX® was reproduced and its components and the resulting UHPC were characterized, which will serve as the reference material in the project. The obtained commercial eco-cements and the raw materials to produce the AA UHPCs were also characterized using techniques such as X-ray diffraction, X-ray fluorescence, particle size distribution etc. The analysis showed that the three of the acquired OPCs have low C3A content and hence are sulphate resistant cements which is an important property to have for marine environment. The hydration of the eco-cement pastes and the influence of superplasticizers were studied using isothermal calorimetry and the evolution of compressive strength. It was seen that one of the admixtures was suitable for the commercial AAC. More admixtures will be tested in the future to find the optimal ones to be used with each cement. Initial mix designs for AA UHPCs were made to characterize the materials. The results show that based on the mix design the workability of the mixes and the mechanical properties vary quite a lot. These formulations will serve as the starting point of further developments in this direction.

The obtained recycled fibres were found to contain rubber particles and a complete replacement in the reference mix showed a slight reduction of mechanical properties. Besides a slight increase in the amount of water required to maintain the flow, no agglomeration was observed in the mix. Further research will show the suitable amount of these recycled fibres to be used in the eco-UHPC.

For the biobased coatings, petroleum P(MMA-co-BA) latex was prepared and characterized and set as the reference. Several bio-based monomers were selected based on several characteristics, which will be further refined later using the help of computational studies. Some functional monomers which provide the antifouling and anti-corrosive properties were also identified. In conclusion, this deliverable describes in detail the different raw materials acquired for the development of eco-UHPCs and bio-based coatings and serves the base for the materials-based developments in the project.

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