SEACON

Infravation
An Infrastructure Innovation Programme

D1.1 Report on properties and sources of alternative materials

Binders

Reference cement

A limestone portland cement, widely used for structural applications in Italy (66% of the market share), which consists of 84% portland cement clinker, 10.3% ground limestone and 5.7% gypsum, was considered as reference. The strength class of this cement is 42.5 MPa and according to European standard EN 197 it is designated as: CEM-II/A-LL 42.5R.

Seacon cement

A cement, contaminated with chloride ions, was specifically produced for this project. This cement has a composition similar to the reference one, but the ground limestone was replaced by a secondary material from the cement production, containing higher amount of Cl^-. The SEACON cement can not be considered conforming to EN 197-1, due to the chloride content that exceeds the threshold of 0.1%.

Fly ash

Fly ashes was used in the concrete mixtures, in order to improve the durability by reducing the mobility of the chloride ions, and by binding part of the dissolved alkalis. Fly ash is an amorphous material, therefore XRD analysis can not give additional information.

Table 1 reports the mineralogical composition of the two cements and of the secondary material, used to produce the SEACON one, determined by quantitative XRD Rietveld analysis.

Table 1- Mineralogical composition determined by quantitative XRD Rietveld analysis

wt.%	***Reference cement***	***SEACON cement***	***Secondary material***
C_2S	11.29	14.07	-
C_3S	55.93	53.14	7.52
C_3A	4.38	3.33	3.33
C_4AF	9.61	9.52	-
Periclase	1.66	2.04	1.32
Lime	0.30	4.25	49.28
Gypsum	3.25	3.77	-
Calcite	8.64	3.02	13.15
Dolomite	1.19	0.73	2.25
Quartz	0.41	1.45	10.41
Arcanite	2.02	1.53	1.81
Langbeinite	1.14	2.04	7.28
Portlandite	0.18	1.11	2.24
Ettringite	-	-	0.85
Aphthitalite	-	-	0.56

SEACON cement contains a higher amount of lime if compared with the reference one, due to the high content of this element present in the secondary material. Also the Portlandite amount is grater in SEACON cement than in the reference one.

A chemical analysis was carried out on cements and fly ash (Table 2). The most interesting value is the chloride content, that represents the major difference between the two cements.

Table 2- Chemical tests

wt.%	***Reference cement***	***SEACON cement***	***Fly ash***
LoI	5.88	3.86	5.62
SiO_2	18.39	19.03	56.58
Al_2O_3	4.28	4.54	26.22
Fe_2O_3	3.05	3.24	5.41
CaO	61.03	61.03	1.49
MgO	2.75	2.78	0.85
SO_3	3.34	3.69	0.07
Na_2O	-	-	0.42
K_2O	0.88	1.19	1.77
TiO_2	0.19	0.20	-
P_2O_5	0.05	0.05	-
ZnO	0.01	0.01	-
SrO	0.04	0.04	-
Mn_2O_3	0.09	0.09	-
Cl	0.02	0.23	-
M.E.	-	0.02	1.57

Table 3 shows the results obtained through physical tests performed on the two cements. The main difference between them is their reactivity, in fact SEACON cement presents minor setting times.

Table 3 – Physical tests on the two cements

Physical tests		**Units**	***Reference cement***	***SEACON cement***
Setting times	Water	%	28.6	28.4
	Initial setting time	min	210	140
	Final setting time	min	310	220
Laser granulometric analysis	Residue to 8 µ	%	74.2	73.1
	Residue to 24 µ	%	38.1	38.9
	Residue to 40 µ	%	12.6	15.2
Specific gravity		g/cm^3	2.98	2.98
Blaine fineness		cm^2/g	3220	2805
Flow		%	99	83
Compressive strength (Reference mortar)	2 d	MPa	26.3	26.2
	7 d	MPa	39.4	38.7
	28 d	MPa	52.2	48.7

An hydration study was also performed, through XRD analysis, on the pastes prepared using the two cements mixed with freshwater and seawater, to determine the evolution of the mineralogical phases during time.
The cements were hydrated and the pastes were submitted to the XRD analysis from the beginning to 28-days curing.
The tables below report the amounts of the main phases (legend: -=0, *≤1%, **1÷15%, ***15÷30%, ****>30%).

Table 4- Mineralogical composition of the paste prepared using Reference cement and fresh water

Reference cement + water								
Time of hydration	*0h*	*2h*	*4h*	*8h*	*24h*	*48h*	*7d*	*28d*
Residual anhydrous clinker	* * *	* * * *	* * * *	* * * *	* * *	* * *	* * *	* * *
Ettringite	*	*	*	* *	* *	* *	* *	* *
Portlandite	-	-	*	* *	* * *	* * *	* * *	* * *
Calcite	* *	* *	* *	* *	* *	* *	* *	* *
Amorphous	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *
Gypsum	*	*	*	-	-	-	-	-
Minor phases	*			*	*	*	*	*

The XRD analysis performed on the reference cement mixed with freshwater shows:

- the presence of Gypsum until 4 hours
- the formation of Portlandite after 4 hours of hydration
- the formation of Ettringite since the beginning of hydration and its increase after 8 hours

Table 5- Mineralogical composition of the paste prepared using Reference cement and seawater

Reference cement + Seawater								
Time of hydration	*0h*	*2h*	*4h*	*8h*	*24h*	*48h*	*7d*	*28d*
Residual anhydrous clinker	* * * *	* * * *	* * * *	* * *	* * *	* *	* *	* *
Ettringite	* *	* *	* *	* *	* *	* *	* *	* *
Portlandite	-	*	*	*	* *	* *	* *	* *
Hemicarbonate	-	-	-	-	-	* *	* *	* *
Calcite	* *	* *	* *	* *	* *	* *	* *	* *
Friedel’s salt	-	-	-	-	-	* *	* *	* *
Amorphous	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *
Gypsum	* *	* *	* *	* *	*	-	-	-
Minor phases	* *	* *	* *	* *	* *	* *	* *	* *

The XRD analysis performed on the reference cement mixed with seawater shows:

- the presence of Gypsum until 24 hours
- the formation of Portlandite after 2 hours
- the formation of Ettringite since the beginning of hydration
- the formation of Hemicarbonate and after 48 hours
- the formation of the Friedel’s salt after 48 hours

Table 6- Mineralogical composition of the paste prepared using Seacon cement and fresh water

Seacon cement + water								
Time of hydration	*0h*	*2h*	*4h*	*8h*	*24h*	*48h*	*7d*	*28d*
Residual anhydrous clinker	* * * *	* * * *	* * *	* * *	* * *	* *	* *	* *
Ettringite	* *	* *	* *	* *	* *	* *	* *	* *
Portlandite	* *	* *	* *	* *	* * *	* * *	* * *	* * *
CaO	*	*	*	*	-	-	-	-
Calcite	*	*	*	*	* *	* *	* *	* *
Amorphous	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *	* * * *
Gypsum	* *	* *	* *	* *	*	-	-	-
Minor phases	*	*	*	*	-	-	-	-

The XRD analysis performed on the Seacon cement mixed with freshwater shows:

- the presence of Gypsum until 24 hours
- the presence of free lime (CaO) until 8 hours
- the formation of Portlandite since the beginning of hydration and its increase after 24 hours
- the formation of Ettringite since the beginning of hydration

Table 7- Mineralogical composition of the paste prepared using Seacon cement and seawater

Seacon cement + Seawater

Seacon cement + Seawater								
Time of hydration	*0h*	*2h*	*4h*	*8h*	*24h*	*48h*	*7d*	*28d*
Residual anhydrous clinker	****	****	****	***	***	***	***	***
Ettringite	**	**	**	**	**	**	**	**
Portlandite	**	**	**	**	**	**	**	**
Hemicarbonate	-	-	-	-	-	**	**	**
CaO	*	*	*	*	-	-	-	-
Calcite	*	*	*	*	**	**	**	*
Amorphous	****	****	****	****	****	****	****	****
Gypsum	**	**	**	*	*	-	-	-
Minor phases	**	**	**	**	**	**	**	**

The XRD analysis performed on the Seacon cement mixed with seawater shows:
- the presence of <u>Gypsum</u> until 24 hours
- the presence of free lime (<u>CaO</u>) until 8 hours
- the formation of <u>Portlandite</u> and <u>Ettringite</u> since the beginning of hydration
- the formation of <u>Hemicarbonate</u> and after 48 hours

The use of seawater, for the presence of chloride ions and carbonates, causes the formation of AF_m phase, the Friedel's salt and the Hemicarbonate. This is probably due to the lack of sulphates needed to produce Ettringite (AFt phase: $\boldsymbol{C_6A\bar{S}_3H_{32}}$).

- **Hemicarbonate →** $\boldsymbol{C_4A\bar{C}_{0.5}(OH)^{-}_{0.5}nH}$
- **Friedel's salt →** $\boldsymbol{C_4ACl_2H_{10}}$

It is unclear why the Friedel's salt is only formed by Reference cement combined with seawater, therefore other investigations will be necessary.

Portions of paste were also taken at different curing time (0, 2, 4, 8, 24, 48 hours, 7 and 28 days), dehydrated at 40°C for 24 hours, grinded and submitted to the TGA analysis to quantify the evolution of the Portlandite amount more precisely, Fig.1.

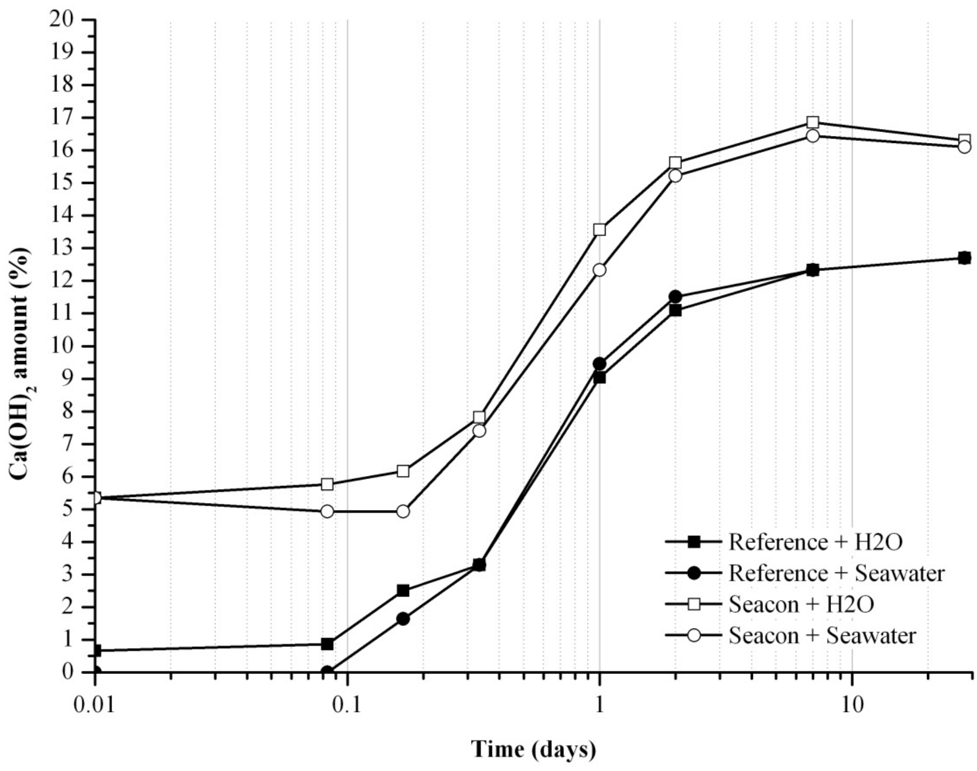

Figure 1- TGA analysis

The Portlandite amount present in the samples, from TGA analysis, is an index of the reaction progress, in fact Portlandite is the main hydrated phase of the CSH reaction. Figure 1 shows the higher reactivity of the Seacon cement compared with the reference one. However the use of freshwater or seawater does not involve substantial differences.

Aggregates

Natural aggregate

As natural aggregates, two siliceous sands (0-2 and 0-4 mm) and one gravel (4-12.5 mm), from Torrazza concrete plant (TO), were employed.

Recycled concrete aggregate (RCA)

In order to simulate a highly chloride contaminated recycled concrete aggregate, old specimens stored from previous researches, were utilized. About 200 kg of chloride-contaminated concrete, made with Portland cement, *w/c* ratio of 0.5, crushed limestone aggregate and chloride contamination ranging from 1% to 5% by mass of cement, were crushed and sieved to obtain a fraction passing between 4 mm and 12.5 mm.

Natural contaminated aggregates were not used, it would not be helpful for the investigation due to their low chloride content.

Eluate analysis was performed on RCA to evaluate the possible release of the aggregate in water. After a 15 minutes-stay of the material under agitation in water, the values, found by means of ionic chromatographer, are:
- 0.39 g/l of chloride
- 0.03 g/l of sulphate

Table 8 – Physical tests on natural aggregates and RCA

	Unit	***Sand 0-2 mm***	***Sand 0-4 mm***	***Gravel***	***RCA***
Water absorption	%	1.0	1.0	1.0	5.3
Density	kg/m^3	2690	2680	2740	2574
Moisture	%	4.3	4.6	2.5	2.0

Water

Fresh water

Tap water was used.

Seawater

Natural seawater, collected from the Mediterranean sea near Gogoleto (GE, Italy), was used.
The ionic chromatography was performed on seawater to determine the chloride and sulphate content.
Figure 2 shows the chromatographic track of seawater. The sulphate content is equal to 3.20 g/l, and the chloride one 22.96 g/l

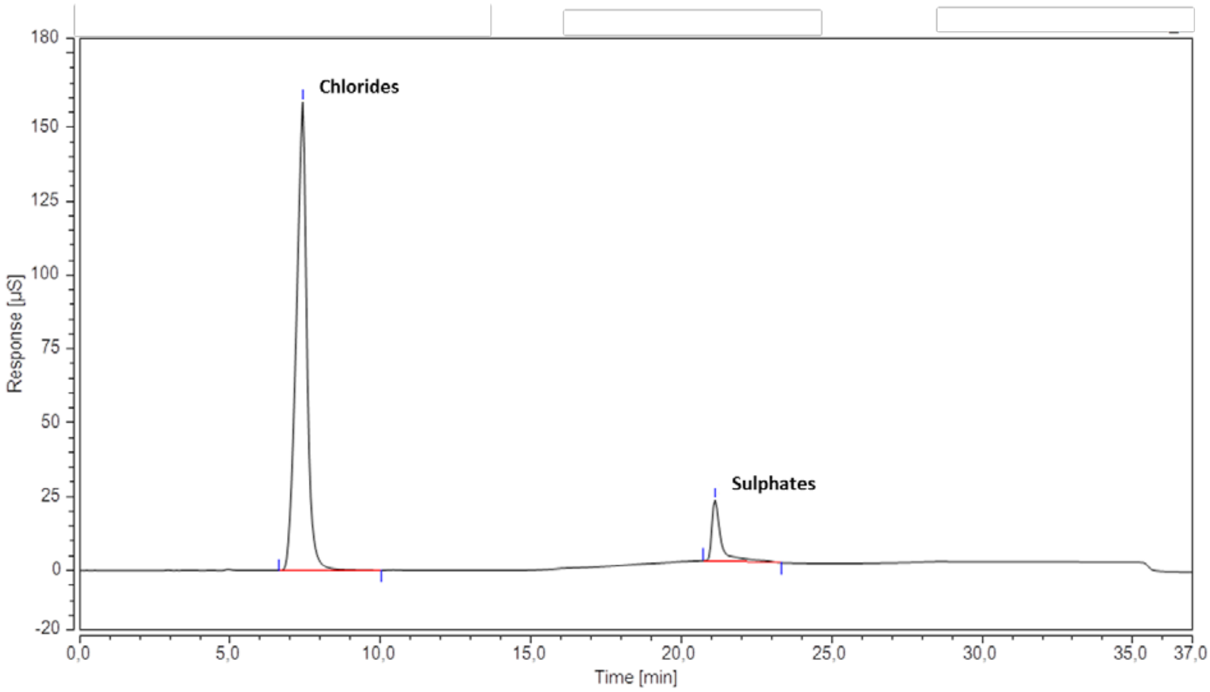

Figure 2- Chromatographic track of seawater