Research Article

### Durability against freeze-thaw cycle of natural pozzolan concrete

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#### Abstract

In this research, an attempt was made to produce several types of mixing rate materials by the implementation of the procedure adopted. The evolution of the damage factor due to freezing, under loading of 20 to 60% of the flexural breaking load at 28 days, was determined during the freeze-thaw cycles. A study of the microstructure of materials gives explanations of the phenomena involved. A durability factor, was calculated from the damage factor after 40 freeze-thaw cycles and, in an original way, revealed the relative importance of characteristics of the materials affecting their frost resistance. Freeze-thaw stability tests were conducted for 400 cycles or until specimens deteriorated.

Keywords: Natural pozzolan; freeze-thaw; compressive strength; light concrete; scaling

#### 1. Introduction

The durability of concretes depends on several factors (T. Peter et al, 2013; A. Tehmina et al, 2013; M.N. Kamran, 2015), including the chemical aggressions, the mechanical and thermal stresses. With regards to the effect of successive freeze - thaw cycles, complex phenomena are involved and can be summarized as follows: an important thermal gradient appears, the water present in the three forms is redistributed in the matrix, and the microstructure and the interfaces between aggregates are modified. Owing to the intrinsic evolution of the material, it can be assumed that its thermal characteristics will accordingly evolve. Many studies have been carried out to elucidate the frost behavior of concrete. Work reporting the state of the knowledge on this object is published elswhere (R. Martin, 2016; Z. Kamyab H et al, 2011). In particular, the mechanisms related to the formation of crystals (B. Himangshu et al, 2016), or the freezing of cementitious materials in the presence of salts have been described (A. Usherov-Marshak et al, 2000). From the theoretical point of view, an approach based on the thermodynamics of irreversible processes (J.L. Garden et al, 2008) seems to be suitable to better understand the occurring phenomena. Models directed to this approach have been already developed (D. Jou et al, 1999).

The objective of the present research is to quantify the influence of ice on the transfer mechanisms and the microstructural characteristics of lightweight pozzolan concrete. Indeed, it is of much interest to experimentally highlight the effects of the freeze-thaw cycles on porosity and on mechanical resistance.

In our experimental study, a wide range of materials with various properties was used to demonstrate the influence of a particular parameter per series of tests, while keeping in mind that the variation of such parameter often makes changes in properties with regards to the characteristics of the hydrated binder.

#### 2. Materials used

To analyze the influence of four parameters on the composition of the concrete, the materials used concerns:

1) The cement whose weight and chemical composition together with specific surface will be determined. A study on the mixing rate of the cement will be also performed;

2) The pozzolans in emphasizing on the influence of their physicochemical characteristics;

3) The sands whose chemical characteristics might have an influence to the sustainability.

#### 2.1 Water

ASTM C1602 (ASTM C1602, 2009) includes provisions for drinking water and is used for mixing and curing concrete specimens as7.

The two cements used have different chemical compositions but they have similar surface areas. Their physical and chemical characteristics are summarized in Table 1.

#### 2.2 Cement (C)

#### Table 1 Physical and chemical properties of Cement

		c1	c2	
Specific gravity (g/cm3)		3.11	3.20	ASTM C 188-03
Specific surface (cm2/g)		3750	4430	ASTM C 204-05
Setting time initial (min)		30	157	ASTM C 191-04
Compressive strength (MPa)				
	1 d	10.5	10.4	
	3 d	21.6	21.3	
	7 d	28.0	33.5	
	28 d	42.0	43.6	
Chemical composition, % by mass				
	SiO <sub>2</sub>	19.77	22.20	
	Al <sub>2</sub> O <sub>3</sub>	5.12	3.70	
	$Fe_2O_3$	3.31	4.60	
	CaO	64.26	64.80	
	MgO	0.73	0.80	
	K <sub>2</sub> O	0.60	0.30	
	SO <sub>3</sub>	3.21	2.10	
	Na <sub>2</sub> O	0.23	0.30	
	TiO <sub>2</sub>	0.33	0.20	
	MnO	0.11	0.10	
	$Cr_2O_3$	0.01		
	$P_2O_5$	0.33	0.20	
	LOI	1.99	0.70	
Potential composition in %				
	C <sub>3</sub> S	67.70	57.64	
	C <sub>2</sub> S	5.70	20.25	
	C <sub>3</sub> A	7.97	2.03	
	C <sub>4</sub> AF	9.93	13.80	

#### Table 2 Physicochemical characteristics of sands

Elements	s1	s2
Mineralogical composition	Limestone	Silica and limestone mixture
Origin of sands	Rolled with rounded grains	Rolled with rounded grains
Particle size distribution	Rolled 0/4 mm	Rolled 0/4 mm
Los Angeles Trial	33	25
Micro-Deval wear test	20	8
% Water absorption rate	4.1	4.5

#### 2.3 Sand (S)

The influence of the sand on the resistance of mortars to freeze-thaw cycles will be investigated. To carry out this study, two sands were chosen. Their physicochemical characteristics are set out in Table 2. The differences of properties of these two sands are expected to bring new elements concerning the importance of the factors listed above.

#### 2.4 Pouzzolane (p)

A specific method called "powder method" was implemented to investigate slag samples reduced to powders. It uses monochromatic X-rays. The equipment employed is a SIEMENS diffractometer using a monochromatic CuKa radiation at a wavelength  $k = 1.7903 \text{ A}^\circ$ , a voltage of 40 kV and a current of 30 mA. Fig 1 and 2 show the exploitation of the diagrams relating to the two samples.

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Fig.1 p1 X-ray diffraction analysis



Fig.2	p2 X-ray	diffraction	anal	ysis
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Elements	p1	p2
SiO <sub>2</sub>	48,70	44,63
Al <sub>2</sub> O <sub>3</sub>	20,12	13,04
Fe <sub>2</sub> O <sub>3</sub>	01,13	12,48
CaO	10,58	12,08
MgO	09,81	09,56
K20	01,10	01,33
SO3	00,00	00,02
TiO2	02,81	02,29
MnO	00,22	00,21
Na <sub>2</sub> O	02,78	02,40
$Cr_2O_3$	00,10	00,11
$P_2O_5$	00,64	00,71
LOI	02,00	01,15
τοται	99 99	100.01

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Some differences were observed between the products. These include a notable preponderance of augite peaks for pozzolans in sample p1. Moreover, the diffractogram obtained from the product of the sample p2 showed more or less diffuse bands instead of fine lines. The vertices, however, correspond to the diffraction lines of the same crystallized phases. Comparative chemical analysis of these 2 materials is given in Table 3.

Several materials consisting of pozzolans will be compared as for their relative efficiencies by taking into account the characteristics of each pozzolan, such as the chemical nature of the reactive material, the pozzolanic activity, the physical characteristics and the effect of cement-pozzolan couple.

Photographs of the Pozzolan samples and sand are shown in Fig. 3.



(a) Pozzolan p2

Fig.3 Pozzolan and sand samples

**3 Experimental approach** 

The experimental approach is presented as follows:

- At first, we will focus on studying the influence of the nature of the cement. The mortars will be made from the two selected cements, the pozzolan and the sand, respectively. These choices are guided by practical reason because this pozzolan is readily available and characteristically controlled, and by the fact that the role of quartz aggregates in the resistance to freezethaw cycles has never been hypothesized yet. Quartz is an inert material with no chemical interaction with the cement matrix.

- The results obtained during assays focusing on the influence of the characteristics of these two binders on frost resistance, will help making the choice of the cement for the study of other parameters. This choice will be dictated by the fact that the selected cement must not be durable after the internal frost resistance test, so that the cement supply is zero, and the effect of other factors is amplified.

- The role of pozzolan in the frost resistance will be undertaken on the cement chosen.

- The study of the additions of sand will be realized on the fixed basic formulation composed of a cement and a pozzolan.

#### Table 4 Concretes composition

Name		А			В			(	С			l	D	
Specimens n°	1	2	3	1	2	3	1	2	3	4	1	2	3	4
Dosage (Kg/m3)	250	300	350	350	350	450	400	425	350	450	450	450	450	450
Sand river	69	231	162	105	292	332	252	191	359	72	237	291	139	71
Cement	81	92	124	115	116	115	132	132	109	147	123	114	136	137
fines	00	00	00	00	00	00	13	34	45	50	98	110	136	156
Water	120	120	160	160	155	160	172	173	175	173	187	136	221	216
Pea gravel	537	493	537	537	357	300	384	469	259	537	332	231	401	465
Density (Kg/m3)	1286	1396	1400	1330	1690	1748	1544	1522	1793	1463	1789	1780	1747	1732

When working on ordinary concretes, the main objective is to make and obtain concretes with the minimum porosity to resist to the penetration of water. In fact, these concretes have the best mechanical resistances. Concerning the lightweight aggregate concretes, the objective is to obtain mixture rules compatible with the composition of ordinary concretes and having a low density, and good physical and mechanical characteristics. Given the scale at which the tests were conducted, the use of the experimental design method was disregarded as it requires the attribution of bound values to the influencing factors. The experimental volumetric method was conducted

according to ASTM C33-03 (ASTM C33-03, 2003). The choice of compositions is based on previous works, as reported by Durán -Herrera et al (2011) for an experimental basis. The various concrete compositions are listed in Table 4.

Different compounds were studied by conducting slump tests, as per ASTM C 143 (ASTM C 143, 2014). Several studies on the frost behavior of concretes have been undertaken. Works on this subject have been published (Z. Kamyab H et al, 2011; S. Hamoush et al, 2011).

In the present study, a cycle that can be assimilated to that recommended by Bodet (R. Bodet, 2014) was performed. It is inspired by North American experimental work (ASTM Standard C666/C666M-03, ASTM Standard 2008). Each concrete formula, 3 prisms  $100 \cdot 100 \cdot 400$  mm are made. This approach was adapted to our control and acquisition devices. The freezing and thawing were carried out under saturation state by water. This test is the one used to qualify the concrete formulations during the study and control tests in cases of severe frost with a high degree

of saturation according to the NF EN 206-1 standard (Norme NF EN 206-1, 2004).

The thermal cycles are as follows:

- The gel stage at -15 ° C is kept for 2 hours

- The thaw stage at + 6 ° C is carried out for 1 h

- The cycle time of 8 hours allows to perform 3 cycles per day

When the surface is damaged and the concrete breaks up into slats, the degradation is called « flaking» (S. Jacobsen *et al*, 1997). The chipping of the concrete is due to the formation of ice lenses which produces stresses at the periphery of the material. Frost damage, and more particularly scaling (S. Jacobsen *et al*, 1997), occurs mainly in humid regions (surface of the material saturated with water) where winter conditions are severe (severe freezing).

The flaking assay consists in subjecting the test pieces covered by the NaCl solution, to 56 consecutive

cycles of freeze-thaw for 24 hours (between +20 and -20 ° C). At each measurement deadline (every 7 cycles, as well as after 56 cycles), the specimens are brushed, and the loose particles are collected and washed. These particles are then dried in an oven at  $T = 105 \pm 5$  ° C overnight and are weighted to determine their dry mass. After that, the NaCl solution is renewed and the test piece is returned to the enclosure. The cumulative mass (g/m<sup>2</sup>) of particles came off the surface of the specimen (called accumulated mass of flaking) is thus calculated as a function of the number of cycles.

#### **4** Results and Discussion

The results obtained from the compositions  $c^2 + p^2 + s^1$  after conducting several trials, are presented below. The freeze-thaw cycles are illustrated in the following figure:



Fig.4 Evolution of compressive strength at 28 days of concretes without fines during the freeze-thaw cycle



Fig.5 Evolution of the 28-day mechanical strength of the C series concretes during the freeze-thaw cycle.

Concretes B1, B2 and A3 reach almost the same level of significant influ compressive strength after 40 cycles. The result of concrete A2 analysis shows that the freeze-thaw cycle has a modification of

significant influence on the compressive strength (cs) of concrete A2, but without producing any significant modification on the other concretes. It can be

concluded that concrete A2 and B3 have a very low permeability, which hinders the movement of water, that is to say, no macroporosity and a powerful air bubble system allied to the tortuosity of the network of pores. The reduction in the mechanical strength of concrete A1 is fast, but the ruin of the test specimens is obtained just after the 40 freeze-thaw cycles.

The compressive strength of A3 to B1 concretes drop to around 20% even in the absence of fines. This is due to a lower dosage of the cement so that the percentage of sand does not fill the voids of large granulates. With a succession of freeze-thaw cycles, the A1 concretes have an almost perfect elastic nature, which means the decrease of resistance is low compared to the resistance before the 40 cycles of freezing. The decrease in tensile strength (ts) is always greater than that in compression, showing the preponderant damage of the interface matrix cement\_aggregate.

From the 10th cycle, the reduction of the mechanical strength is observed on all the concretes. C4 concrete is durable at 40 freeze-thaw cycles. After the first 30 cycles of freeze-thaw, it was observed a slight decrease in resistance followed by a stabilization of the behavior. The resistance of C1 concrete changes only after the 35th cycle. The very low content of freezing water may be given as fitting explanation to these observations. These results show that these two concretes are still resistant to freeze-thaw cycles.



Fig.6 Evolution of mechanical strength at 28 days of D-series concretes during freeze-thaw cycle

**Table 5** Influence of the maximum size of coarse aggregate on the mechanical strength of concretes (in MPa)without fines after 40 freeze-thaw cycles

Dmax (mm)	A1		A2		A3		B1		B2		B3	
	CS	ts	CS	ts	CS	ts	CS	ts	CS	ts	CS	ts
05	3.30	0.67	7.32	1.60	9.31	1.30	9.22	1.36	9.43	1.00	8.20	1.20
10	3.31	0.67	7.43	1.62	10.81	1.45	9.27	1.36	11.12	1.88	9.99	1.45
15	3.32	0.67	7.52	1.64	12.52	1.95	9.51	1.38	12.02	2.23	10.78	1.99
20	3.45	0.68	7.80	1.65	12.99	2.01	9.72	1.40	13.24	2.58	11.25	2.35
25	3.56	0.69	7.92	1.66	14.56	2.51	9.85	1.52	14.27	3.45	12.89	2.69

The analyses of the results of the D4 and D3 concretes indicate that the resistance to freeze-thaw cycles drops significantly when the percentage of pozzolanic fines is equal to or greater than that of the cement. The fines bring about several sites of weakness where fissures are preferentially and more easily initiated. Therefore, the microcracks result from drying and not from the gel. The decrease of strength of C1, B2 and B3 concretes, which have high proportions of sand, may be inferred from their high quantity of fast freezing water. Moreover, their moderate mechanical strength supports neither the volume increases nor the stress induced during freeze thaw cycles. In order to obtain results on "the influence of the maximum size of the aggregate on concrete compression", the first 50 freeze-thaw cycles were considered. The reassurance

of the non-deterioration of all the specimens occurs in these cycles. Specifically, our test is conducted just after the 40 freeze-thaw cycles.

The strengths of concrete A1 increases as long as the rate remains low. These are due to the lack of vacuum filling of the cement used. The strengths of concrete A3 are satisfactory because the values of the resistance increase more and are higher compared to those of A1 to B3.

Generally, the evolution of mechanical strengths as a function of the size of the aggregate shows the insufficiency of the values of air occluded on the concrete. The knowledge of the microstructure is helpful to describe the durability to the internal gel, although the more chemical role of the material is not taken into account.

## **Table 6** Influence of the maximum size of coarse aggregates on the mechanical strength (in MPa) of C-seriesconcretes after 40 freeze-thaw cycles

Dmax (mm)	С1		С2		СЗ		<i>C4</i>	
	CS	ts	CS	ts	CS	ts	CS	ts
05	13.05	1.01	13.02	1.39	13.52	1.02	15.76	1.70
10	13.45	1.12	13.10	1.39	13.68	1.05	15.79	1.71
15	13.87	1.33	13.12	1.39	13.91	1.05	16.00	1.84
20	14.01	1.56	13.14	1.40	14.12	1.23	16.06	1.90
25	13.98	1.43	13.14	1.40	14.16	1.23	15.79	1.87

# **Table 7** Influence of the maximum size of coarse aggregate on the mechanical strength (in MPa) of D-seriesconcretes after 40 freeze-thaw cycles

Dmax (mm)	D1		D2		D3		D4	
	CS	ts	CS	ts	CS	ts	CS	ts
05	13.05	1.25	14.42	1.05	16.50	1.35	18.45	1.71
10	13.45	1.30	14.56	1.12	16.53	1.35	18.52	1.71
15	13.72	1.32	14.63	1.13	16.59	1.35	18.65	1.72
20	13.82	1.33	14.78	1.15	16.63	1.36	18.82	1.72
25	13.99	1.34	14.86	1.17	16.65	1.36	18.93	1.73

#### Table 8 Scaling cumulated mass

Name		А			В				С			Γ	)	
Specimens n°	1	2	3	1	2	3	1	2	3	4	1	2	3	4
Scaling cumulated mass after 56 cycles M (g/m <sup>2</sup> )	5069	4416	3157	3109	2403	3007	981	839	4198	302	1038	4037	699	622

Table 9 classifications of concretes relating to freeze-thaw cycles

N°	Compressive strength before freeze thaw cycles	Compressive strength after 300 freeze thaw cycles	Scaling cumulated mass after 56 cycles
1	D4	C4	C4
2	D3	C1	D4
3	C4	A2	D3
4	D1	B1	C2
5	D2	C2	C1
6	C3	D2	D1
7	C2	D4	B2
8	C1	A3	B3
9	B3	D1	B1
10	B2	B2	A3
11	B1	D3	D2
12	A3	С3	C3
13	A2	B3	A2
14	A1	A1	A1

All the results show that the strength of the C series rises slightly depending on the size of coarse aggregate except C3 concrete which increases with an average percentage about 15%. This concrete can be used to make an optimal concrete.

A fluctuation occurs on the strength of concrete C4 and C1, whereas that of C2 is constant. In fact, these materials have a very small pore volume in the field of capillaries where the pore network is very thin, and they are thus initially unsaturated at heart. This last point results from the fact that it is very difficult to saturate the specimens of these concretes after a drying phase. The compactness of the material and the low permeability to water limit indeed the penetration of external water to a very superficial layer.

In this series, more significant gains in mechanical strength were observed and allow considering a good resistance to double thermo-mechanical stress. Even after the freeze-thaw cycles, a number of results on resistances greater than 10% to 20% compared to

those before freeze-thaw cycles were obtained. The size of the coarse aggregate can be inspired by the reformulation of the optimal concrete.

The cumulative mass of peeling at the end of the 56 cycles is reported in Table 8.

The classification of the 14 concretes studied, based on the average compressive strength at 28 days, the relative elongation after 300 cycles of freeze-thaw gel (without salts) and the cumulative peeling mass after 56 cycles of freezing thaw (with salts) is given in Table 09.

#### Conclusion

The results of our experimental assays suggest that, when the pozzolan concrete is subjected to freeze-thaw cycles, it undergoes deterioration *via* two different processes. The first one induced by the internal gel in the concrete is characterized by a loss of rigidity which increases significantly and finally leads to more or less long term rupture of the sample. The mechanism involved does not begin from the application of stress for all concretes. However, once initiated, the damage expands quickly for all of them. The second one is accompanied with a decrease in resistance from the first freeze-thaw cycles, but it advances very slowly later.

The important parameters which govern the composition of the formulation of the durable gel pozzolan concretes are the nature of the cement, the dimensions of the aggregates and the use of low mixing rate. The best results were obtained with low specific surface cement C3A poor and rich in C2S. However, change in the average size of the large pozzolan aggregate from 5 cm to 10 cm increases the scoria concrete strength up to 8% after 40 freeze-thaw cycles. It is also worth mentioning that limestone and silico-calcareous sands offer better frost resistance than for inert siliceous sand.

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