Deliverable T2.2.1 – Sediment as a pozzolanic material : formulation and lab tests of eco-solutions report

Mars 2022

Armines-Center of Douai

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1. Formulation of concretes based on ternary binders

Introduction

This chapter is the subject of a combination of the two previous parts. Indeed, the objective of this part is to formulate concretes incorporating 20% of the O dredging sediments as a substitute for sand, whose granular skeleton optimization was carried out in the PP part. These concretes will be made from ternary binders from industrial by-products whose composition is defined in part pp, and their durability will be investigated.

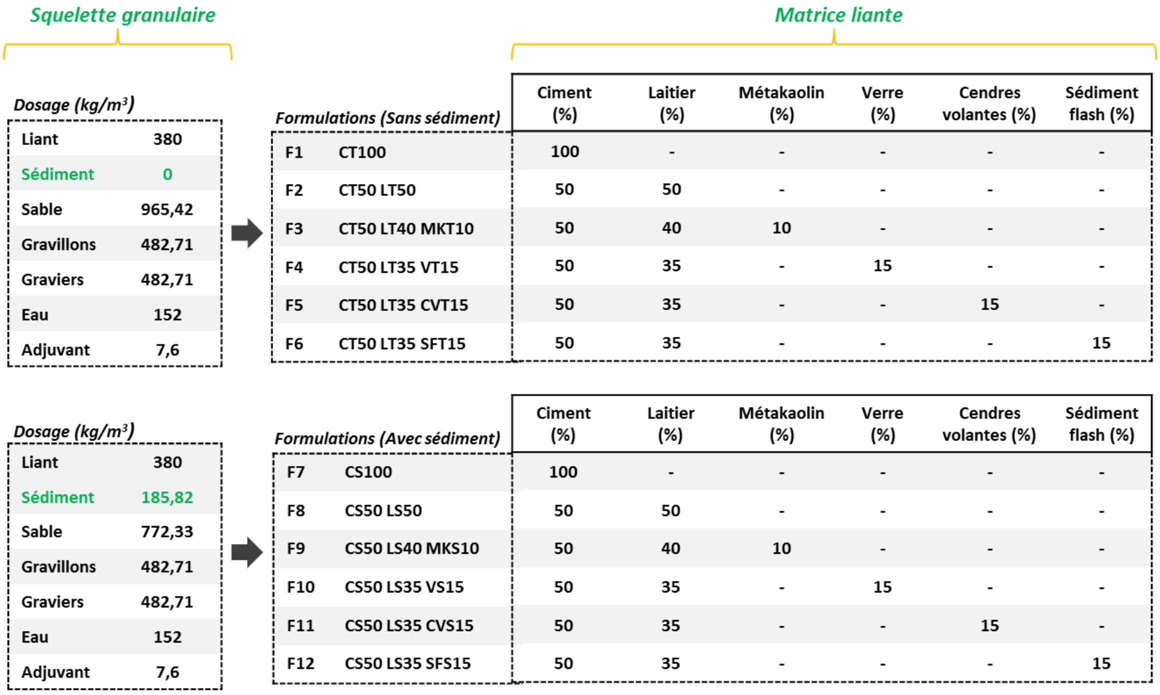
After the formulation of the concretes, they will be characterized in the fresh state through the following tests: the measurement of apparent density, the collapse at the Abrams cone and the occluded air content. They will also be characterized in the hardened state through mechanical performance tests: simple compressive strength, indirect tensile strength, evaluation of the elastic modulus (Young's modulus) and measurement of apparent density. The hardened characterization tests will be carried out at several deadlines: 14, 28, 90 and 120 days. The results will be interpreted and confronted with the constraints set out in the specifications of the CEMTF guide relating to the realization of artificial riprap intended for the rehabilitation of the banks.

The evaluation of the durability of the different formulations will also be discussed in this section. Some tests will be carried out on concrete formulations such as water-accessible porosity and long-term mechanical strengths. Further durability tests will be carried out on concrete equivalent mortars (CEM) for questions of practicability and material available in the laboratory. The durability tests carried out are the resistance to freeze/thaw, the resistance to internal sulfatic attacks (ISR) and external attacks (ESR) as well as the alkali-aggregate reaction (AAR).

Summary of formulations studied

In order to study the effect of the use of ternary binders in concrete incorporating sediments, two groups of formulations will be studied: the first group will consist of 6 control formulations, with 100% sand and 0% sediment O. The second group will also consist of 6 formulations, and will incorporate 20% O sediment as a substitute for sand.

For the binding matrix, each group (1 and 2) will be composed of a control formulation, composed of 100% CEM I 52.5 N cement, a formulation based on a binary binder: 50% cement + 50% slag, and 4 other formulations based on ternary binders (one formulation per type of addition). All formulations are summarized in Figure 1.



Squelette granulaire

Matrice liante

Dosage (kg/m³)

Liant	380
Sédiment	0
Sable	965,42
Gravillons	482,71
Graviers	482,71
Eau	152
Adjuvant	7,6

Formulations (Sans sédiment)		Ciment (%)	Laitier (%)	Métakaolin (%)	Verre (%)	Cendres volantes (%)	Sédiment flash (%)
F1	CT100	100	-	-	-	-	-
F2	CT50 LT50	50	50	-	-	-	-
F3	CT50 LT40 MKT10	50	40	10	-	-	-
F4	CT50 LT35 VT15	50	35	-	15	-	-
F5	CT50 LT35 CVT15	50	35	-	-	15	-
F6	CT50 LT35 SFT15	50	35	-	-	-	15

Dosage (kg/m³)

Liant	380
Sédiment	185,82
Sable	772,33
Gravillons	482,71
Graviers	482,71
Eau	152
Adjuvant	7,6

Formulations (Avec sédiment)		Ciment (%)	Laitier (%)	Métakaolin (%)	Verre (%)	Cendres volantes (%)	Sédiment flash (%)
F7	CS100	100	-	-	-	-	-
F8	CS50 LS50	50	50	-	-	-	-
F9	CS50 LS40 MKS10	50	40	10	-	-	-
F10	CS50 LS35 VS15	50	35	-	15	-	-
F11	CS50 LS35 CVS15	50	35	-	-	15	-
F12	CS50 LS35 SFS15	50	35	-	-	-	15

Figure 1. Composition of concrete formulations based on ternary binders.

Characterization of concrete formulations based on ternary binder

Fresh characterization

Abrams cone subsidence test (NF EN 12350-2:2019)

The results of the Abrams cone subsidence tests are presented inTable 1 below. The results show that the addition of sediments leads to a loss of workability, this finding being valid for all formulations. This decrease in workability is attributed to the high water demand of sediments.

We also find that SF and MK formulations have lower subsidence than the rest of the formulations. Indeed, the water demand of these two additions is significant, which leads to a decrease in the amount of water available and therefore a reduction in subsidence.

However, in the light of the specifications which require a minimum subsidence of 50 mm, all formulations satisfy this condition.

Table 1. Subsidence of concrete at the Abrams cone.

Formulation	Sagging (cm)	Formulation	Sagging (cm)
CT100	Spread	CS100	80
CT50 LT50	Spread	CS50 LS50	95
CT50 LT40 MK10	65	C50 LS40 MK10	55
CT50 LT35 V15	90	CS50 LS35 V15	75
CT50 LT35 CV15	Spread	CS50 LS35 CV15	97
CT50 LT35 SF15	65	CS50 LS35 SF15	52

Occluded air content (NF EN12350-7:2019)

The results of the occluded air content are presented inTable 2.

From these results, it is noted that the introduction of sediment O as a sand substitute is accompanied by a slight increase in the content of occluded air. This result is expected in view of the amount of water added to compensate for the water demand of the sediments. It is also noted that for both groups of formulations and overall, the use of ternary binders did not result in a large difference in occluded air content.

Table 2. Occluded air content of concrete formulations.

Formulation	Occluded air content (%)	Formulation	Occluded air content (%)
CT100	4,20	CS100	5,55
CT50 LT50	3,25	CS50 LS50	5,35
CT50 LT40 MK10	4,10	C50 LS40 MK10	6,25
CT50 LT35 V15	4,65	CS50 LS35 V15	6,45
CT50 LT35 CV15	3,85	CS50 LS35 CV15	6,00
CT50 LT35 SF15	4,05	CS50 LS35 SF15	5,10

Apparent density in the fresh state (NF EN 12350-6:2019)

The results for measuring the apparent densities of the different formulations are presented inTable 3 below.

The results show a decrease in the apparent density of all sediment-based formulations compared to control formulations. This is explained by the fact that the actual density of substituted sand is higher than that of sediment, in particular because of the organic matter contained in the latter. It should also be noted that for both groups of formulations, the use of ternary binders is accompanied by a decrease in density: indeed, the absolute densities of additions are overall 20% lower than that of cement.

Table 3. Density (M.V.) apparent to the fresh state of concrete formulations.

Formulation	Apparent M. V. (kg/m^3)	Formulation	Apparent M. V. (kg/m^3)
CT100	2542,50	CS100	2395,87
CT50 LT50	2443,12	CS50 LS50	2333,75
CT50 LT40 MK10	2426,38	C50 LS40 MK10	2330,87
CT50 LT35 V15	2406,25	CS50 LS35 V15	2328,12
CT50 LT35 CV15	2412,87	CS50 LS35 CV15	2334,13
CT50 LT35 SF15	2429,62	CS50 LS35 SF15	2337,12

Hardened characterization

The formulation of concretes for characterization in the hardened state was carried out according to the NF EN 206 standard. Cylindrical specimens 11 cm in diameter and 22 cm in height were made (Figure 2). For each of the 12 formulations, 22 specimens were formulated to be characterized in the hardened state at 14, 28, 90 and 120 days. The specimens were demoulded after 24 hours and stored in water at 20 °C until the end of the test.

The tests that have been carried out in this part are the compressive strength, the indirect tensile strength, the determination of young's modulus and the porosity accessible to water.

Figure 2. Cylindrical concrete specimens 11 cm × 16 cm.

Direct compressive strength

The results of the compressive strengths are summarized in Figure 3.

The results of the compression tests show that the substitution of 20% sand by sediment induces a loss of strength for all formulations. Several elements can explain this decrease in compressive strength: on the one hand, sediments contain organic matter and chemical elements such as heavy metals that can alter the hydration of cement and additions; and on the other hand, the decrease in density and the increase in porosity are also elements that can justify this decrease in resistance.

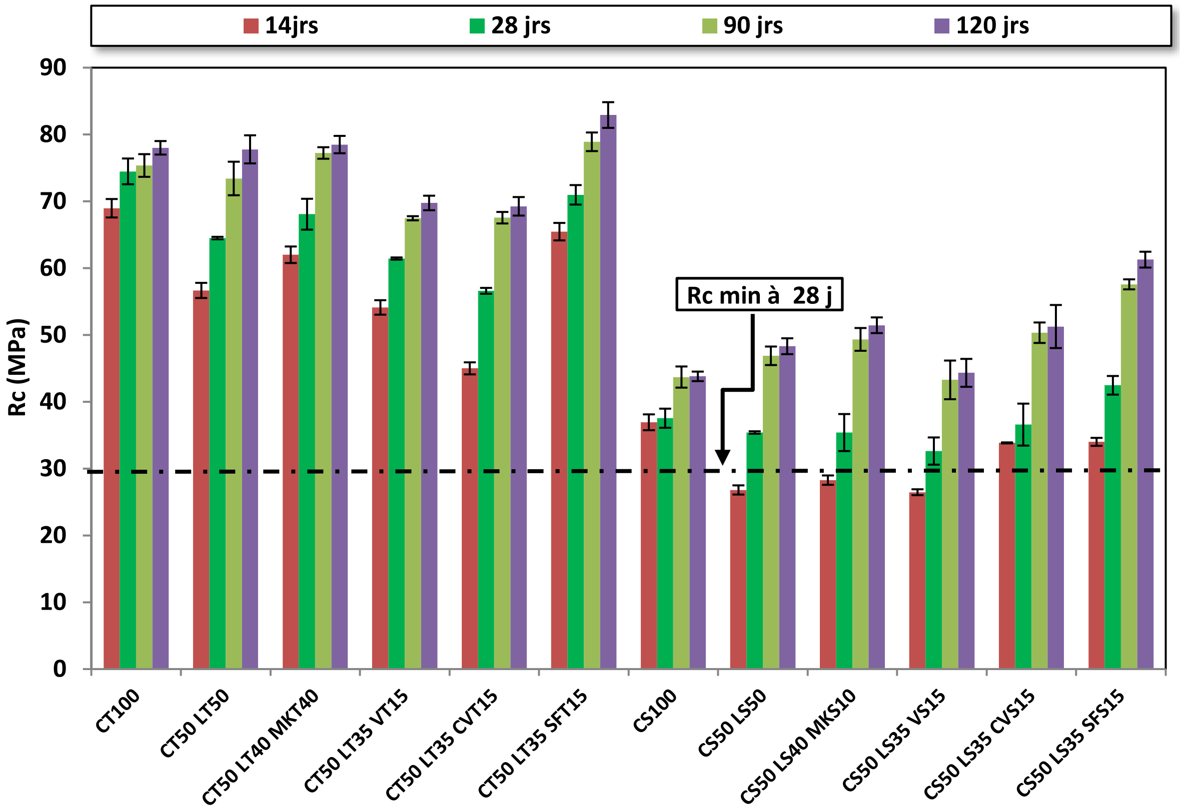


Figure 3. Simple compressive strength of concretes.

There is also an increase in resistance as a function of time for the different formulations, due to the hydration of the cement and additions. This increase is more pronounced for formulations containing slag: indeed, the binary formulation C50 L50 and ternary formulations have an average increase of 18% in strength between 28 and 120 days while this increase is 5% for control concretes. This increase is due to the pozzolanic reaction of additions, a consumption of portlandite having been demonstrated in chapter PP by the ATG trial.

Similarly, the use of ternary binder reduces the loss of strength caused by the presence of dredged sediments. This is because once the concrete has hardened, the sediment has less impact on hydration. Indeed, the setting of the cement will mobilize the sediments and reduce the diffusion of chemical elements inhibitors of the hydration reaction (for example zinc). It is then that the reactions of the additions, which arrive later, will occur.

Sediment-based ternary formulations have the best mechanical characteristics, which testifies to the high reactivity of sediments treated with flash calcination. This activity is related to the physical and chemical aspect of these sediments: indeed, the particle size of the sediments is very fine and the treatment by flash calcination makes it possible to obtain spherical particles, the compactness of the mixture is therefore improved as well as the mechanical characteristics. On the other hand, chemical activation can be suspected, the presence of elements such as sodium sulphates Na_2SO_4 in sediments can play a role of slag activator in particular. The activation of certain clay phases of sediments (kaolinite in particular) by flash treatment also contributes to accentuating the pozzolanic reaction and therefore to the improvement of mechanical performance.

Finally, since the specifications of the CEMTF guide recommend a minimum strength of 30 MPa for concrete intended for the manufacture of artificial riprap in concrete blocks, all the formulations studied meet this requirement.

Crack resistance

The results of the splitting resistance of the formulations are presented inFigure 4 below.

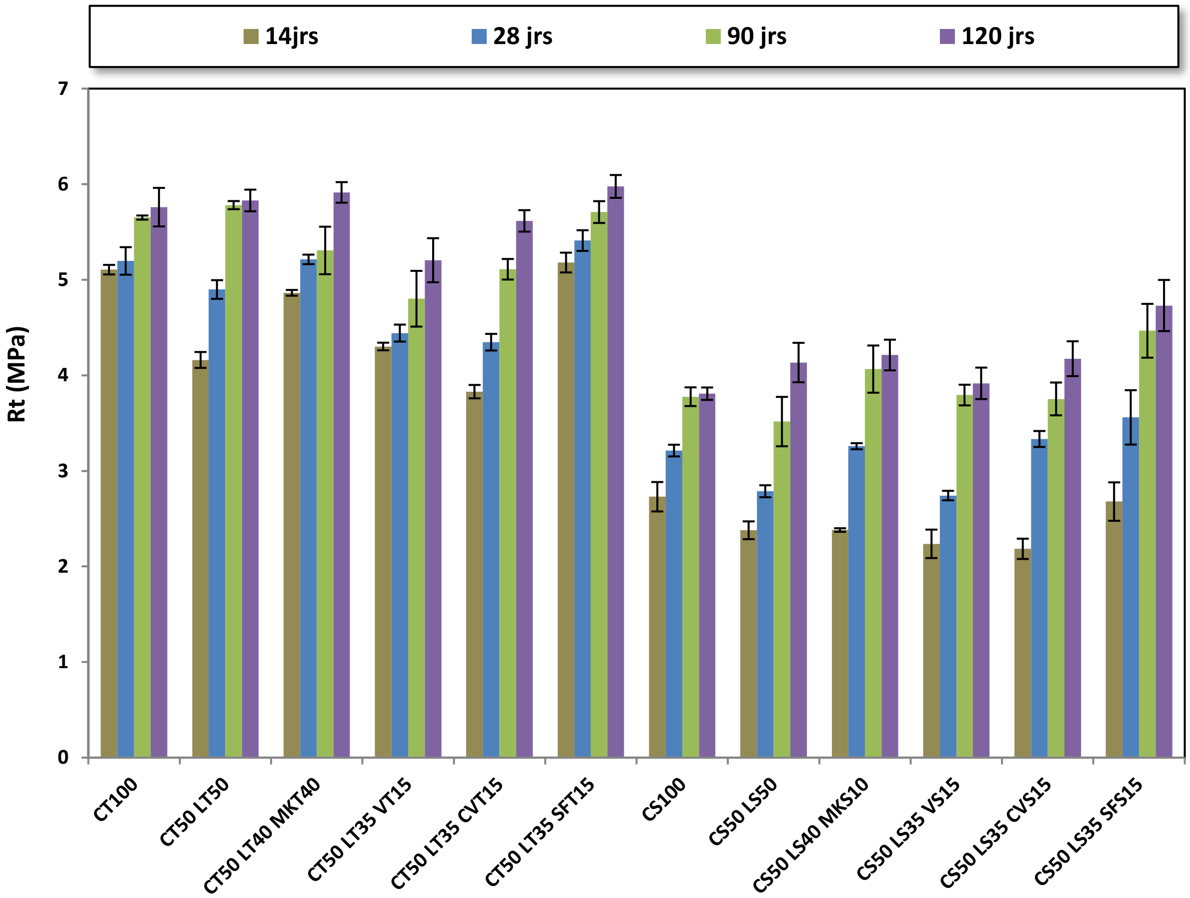


Figure 4. Tensile strength of concrete formulations.

In line with the findings made on compressive strengths, a loss of indirect tractive strength is recorded for the different formulations when incorporating the dredged sediments. The causes of this drop in strength are the same as those mentioned for simple compressive strength. It is also noted that at a young age (14 days), resistance to splitting is quite low for formulations containing the slags. These catch up with the resistances of the cement-based formulation alone after 28 days and then exceed it in the long term (120 days). Similar trends are found in the literature. It is also noted that formulations based on ternary binders have splitting resistances comparable to that of the control, and even better for the formulation based on flash sediment.

Elastic modulus of compression plasticity (NF EN 12390-13)

The compression elastic cutting modulus was evaluated according to standard NF EN 12390-13 on cylindrical specimens (11 × 22 cm) at several deadlines (14, 28, 90 and 120 days). The principle of this test is to subject the specimens to axial loading/unloading cycles in compression and then to record the deformation of these using three displacement sensors (Figure 5). The elastic secant modulus represents the slope of the stress/strain curve obtained for each specimen and is given by theEquation 11:

$$\sigma = E \times \varepsilon \qquad \textit{Equation 1}$$

With σ : the stress applied to the specimen,
E : Young's module,
ε : longitudinal deformation.

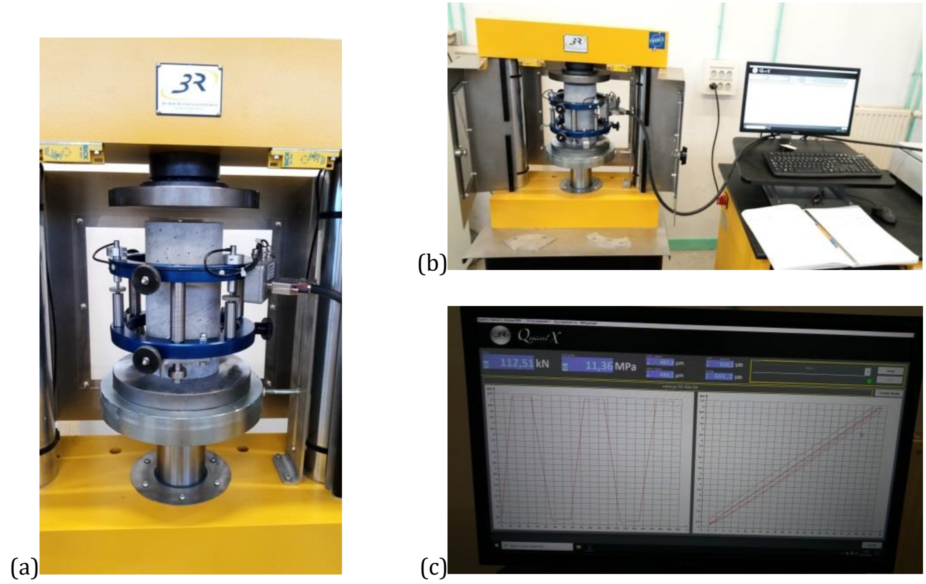


Figure 5. Measurement of the elastic modulus secant of concretes: (a) deformation measurement sensors; (b) device used; (c) loading/unloading cycles and stress/strain curve.

The stress level of the applied cycles is determined from the measurement of the compressive strength on so-called "accompanying" specimens tested at the same deadline. f_c

The loading/unloading cycles carried out on the specimens were applied according to the diagram shown in Figure 6

with σ_a : the upper limit of stress: $\sigma_a = f_c/3$,
σ_b: the lower limit of stress: $10\ \%\ f_c \le \sigma_b \le 15\ \%\ f_c$,
σ_p: the pre-load constraint: $.0{,}5\ MPa \le \sigma_p \le \sigma_b$

The stress increase is (0.6 ± 0.2) MPa/s, the stabilized elastic modulus is determined during the third cycle.

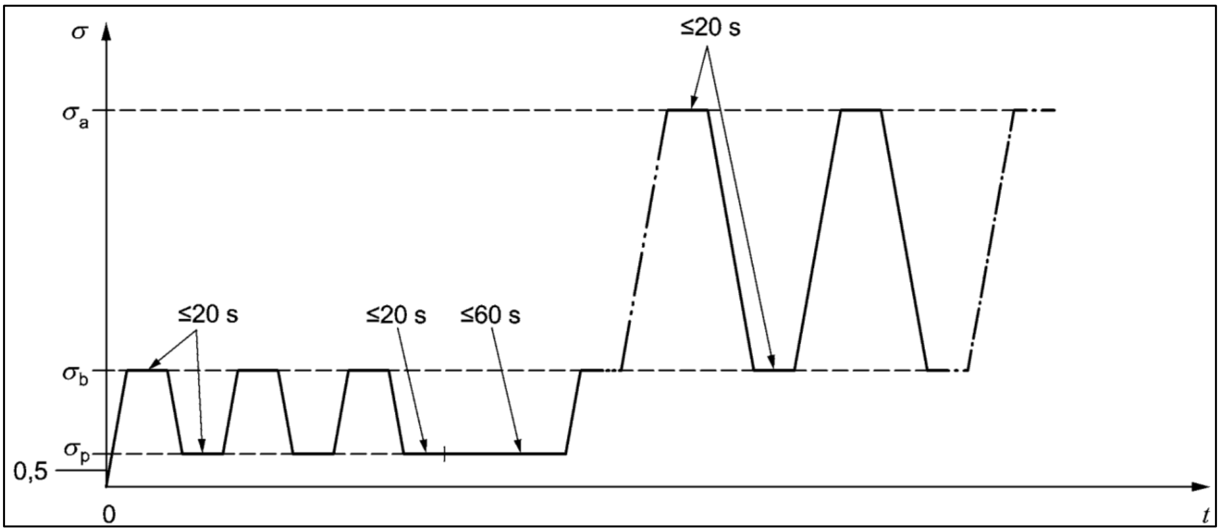


Figure 6. Cycle for the determination of the cutting modulus of elasticity of concrete (NF EN 12390-13).

The force cycles applied to the specimens at 28 days and an example of the stress-strain torque are presented in Figure 7 and Figure 8 respectively below.

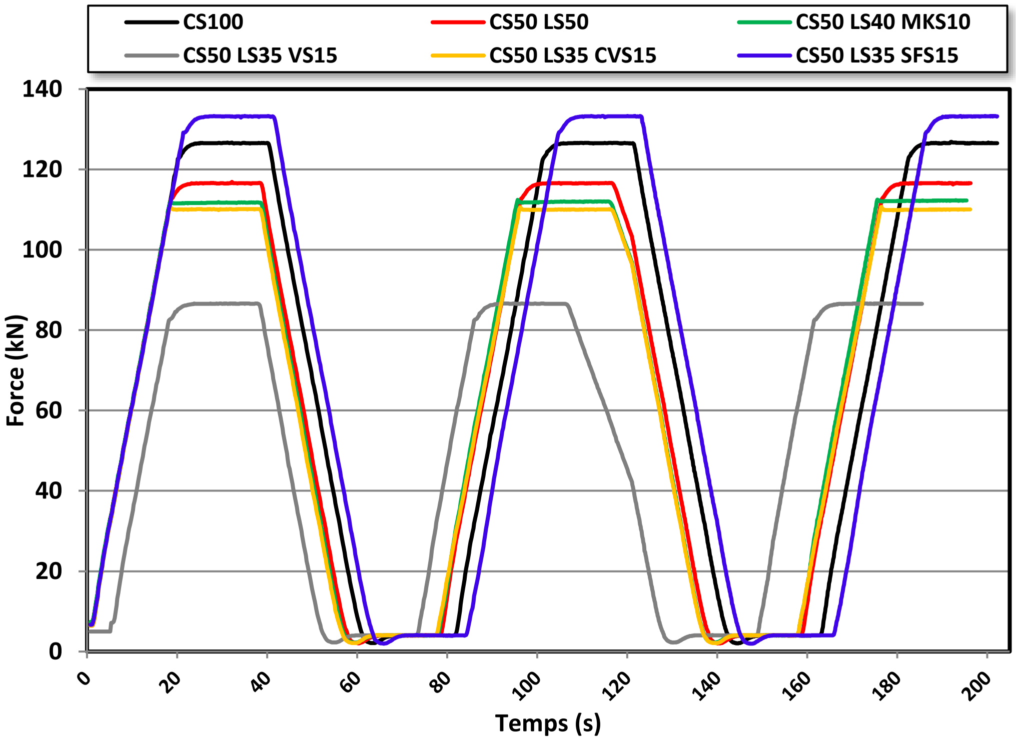


Figure 7. Loading/unloading cycle profile applied to the different specimens at 28 days.

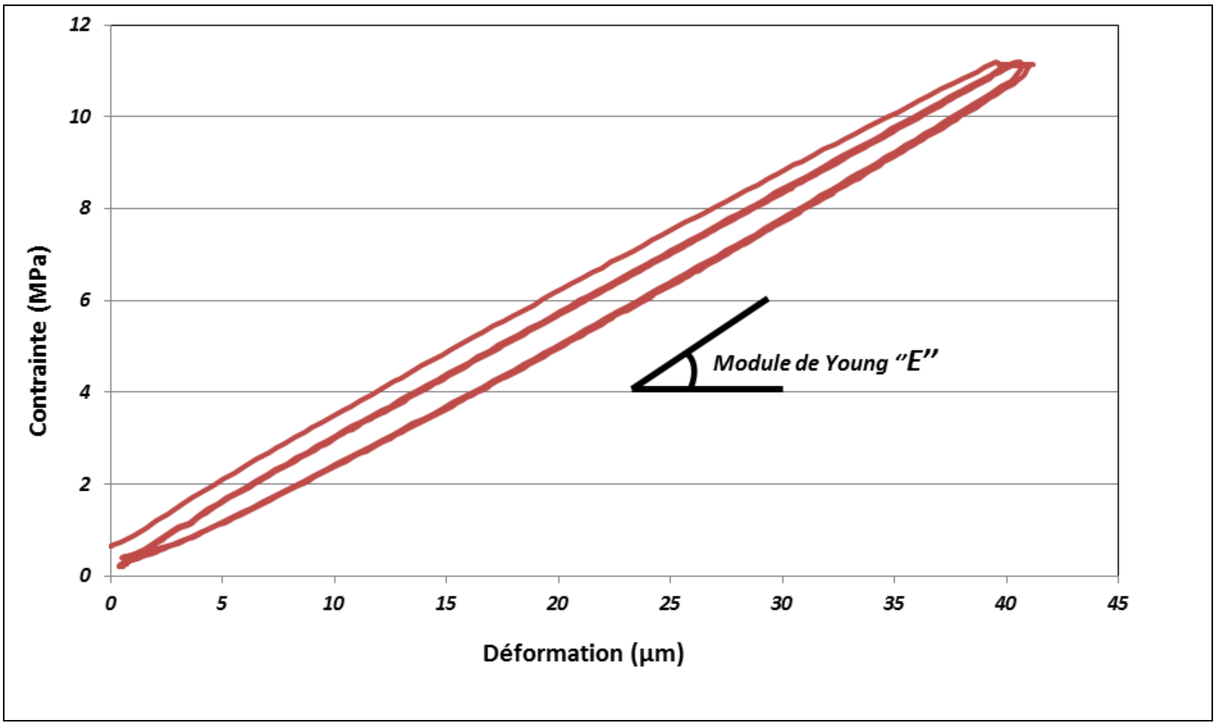


Figure 8. Loading/unloading cycles for measuring Young's modulus

The values of Young's modulus obtained for the different formulations are shown in Figure 9 below.

Young's modulus of the formulations studied are quite close to that of the control formulation (100% sand) at 14 days: it varies between 35 GPa and 40 GPa, or even 45 GPa for the flash sediment formulation. For formulations incorporating sediment (group 2), Young's modulus is around 25 GPa, an average decrease of 30% at this time. Young's modulus of ternary formulations in the 2nd group is weak at 14 days compared to control formulations. This is due to the latent hydration of additions, while cement hydrates faster. On the other hand, in the long term, it would appear that sediments have less impact on Young's modulus for ternary formulations than for 100% cement formulation.

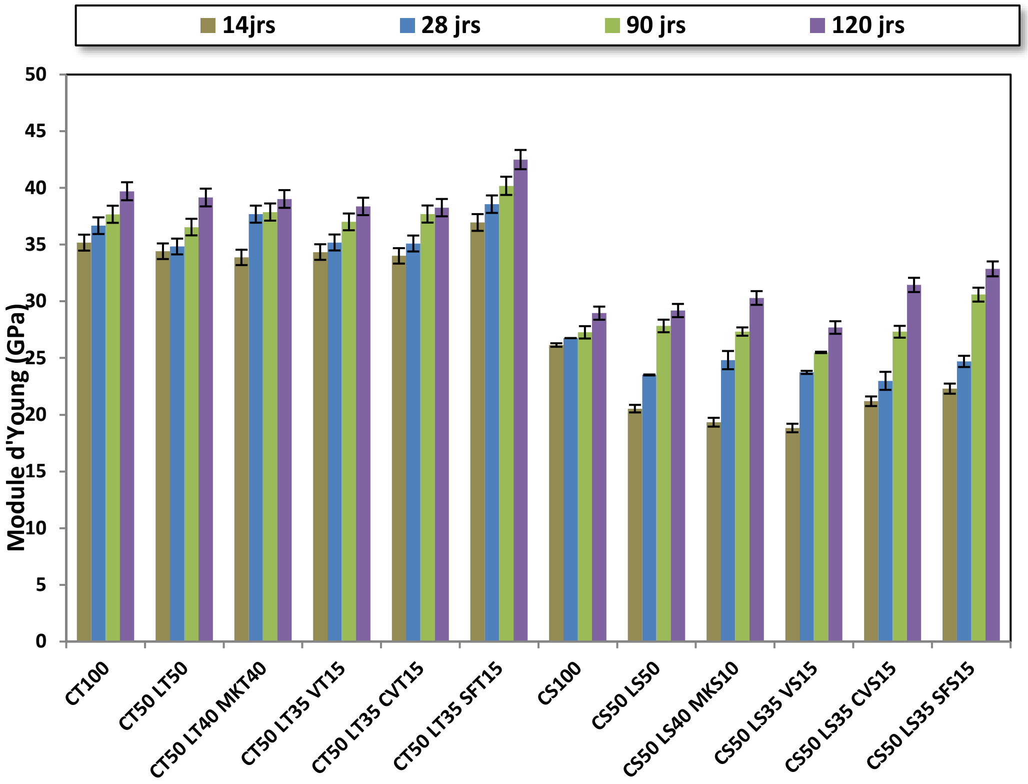


Figure 9. Young's module of the different concrete formulations at 14, 28, 90 and 120 days.

Porosity accessible to water (NF P18-459)

The measurement of porosity is a revealing indicator of the durability of a concrete, many being the mechanisms of damage to concrete structures related to the porosity and tightness of the latter [1]. Indeed, when a concrete is subjected to external attacks, for example, aggressive agents penetrate the concrete and diffuse through the porous network. They react with concrete components and interstitial solutions that lodge in the pores – reactions often favored by the presence of water or moisture – and lead to major degradation that can affect the proper functioning of the structure [2].

By definition, the porosity of a material represents the volume of the pores of that material in relation to its apparent volume. It is expressed as a percentage (%). The porosity can be either open (interconnected or not), closed, or total (the sum of the previous two) (Figure 10). According to OLIVIER *et al.* [3], the durability of concrete is particularly associated with open porosity, and more specifically with interconnected open porosity. Indeed, it is this type of porosity that allows the penetration of aggressive agents.

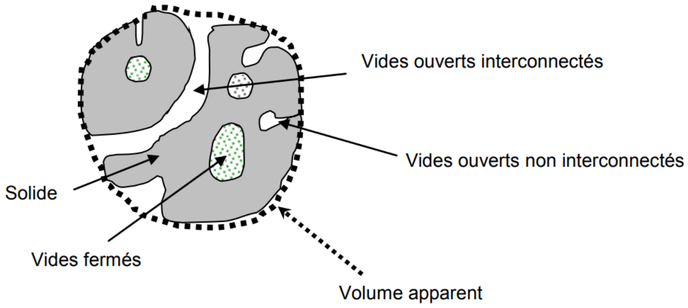


Figure 10. Descriptive diagram of porosity in concrete [3]*.*

There are several methods for determining the porosity of concrete. For open porosity, the most used method is that of porosity accessible to water, described in the NF P18-459 standard. The principle of this method is to vacuum saturate concrete samples for 48 hours under a pressure of 25 mbar, then to carry out the various weighings (Figure 11):

- Hydrostatic weighing: it corresponds to the mass of the sample completely immersed in water;
- The mass in the air: it represents the mass of the specimen in the humid state;
- Dry mass: this is the mass of the test tube body after drying in an oven ventilated at 105 °C.

The porosity accessible to the water noted Φ can then be deduced from these weighings according to theEquation 22:

$$\Phi(\%) = \frac{\mathrm{M_{air}} - \mathrm{M_{sèche}}}{\mathrm{M_{air}} - \mathrm{M_{eau}}} \qquad \textit{Equation 2}$$

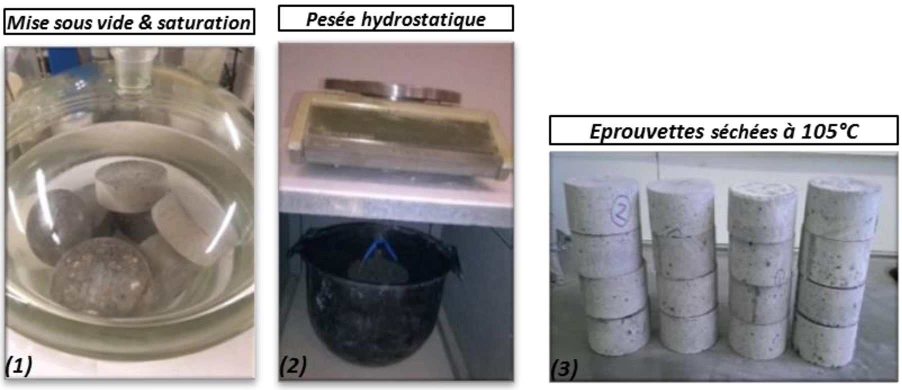


Figure 11. Measurement of porosity accessible to water on concretes.

The tests were carried out at 28, 90 and 120 days and the results obtained for the different formulations are presented in the Table 44:

Table 4. Water-accessible porosity of concrete formulations.

Formulation	Porosity accessible to water (%)		
	28 days	90 days	120 days
CT100	8,41	8,32	8,11
CT50 LT50	8,98	7,49	7,16
CT50 LT40 MK10	8,73	7,66	6,74
CT50 LT35 V15	9,61	8,22	8,17
CT50 LT35 CV15	10,42	8,60	7,89
CT50 LT35 SF15	8,63	7,13	6,27
CS100	14,96	14,54	13,92
CS50 LS50	14,21	13,03	12,66
C50 LS40 MK10	12,62	12,12	11,27
CS50 LS35 V15	13,15	12,35	11,33
CS50 LS35 CV15	12,34	12,21	11,42
CS50 LS35 SF15	12,62	12,20	11,21

The overall porosity of the 28-day formulations ranges from 8.41% for the CT100 formulation to 10.42% for the CT50 LT35 CV15 formulation. This overall porosity decreases at the 90-day and 120-day deadlines, especially for formulations based on ternary binders. Indeed, for these formulations, the porosity decreases by about 20% from 28 to 120 days while it decreases by only 4% for the CT100 formulation. Thanks to the pozzolanic reactivity of additions, the consumption of portlandite for the formation of C-S-H helps to fill the pores initially present, reduces their size and thus improves the durability of concretes.

Figure 12 shows the increase in overall porosity in concrete with the incorporation of dredged sediments. Indeed, it goes from 7% on average for all formulations, to more than 11%. The organic matter content, the water content, the heterogeneity of the sediments as well as their impact on the hydration of the cement are all parameters that contribute to the increase in total porosity. On the other hand, the impact of sediments seems to be mitigated by the use of ternary binders: indeed, the latter have porosities accessible to water lower than those of CS 100 and CS50 LS50 concretes.

Flash sediment formulations have the lowest porosities; this suggests that we will have a good resistance to aggressive agents and therefore a good durability.

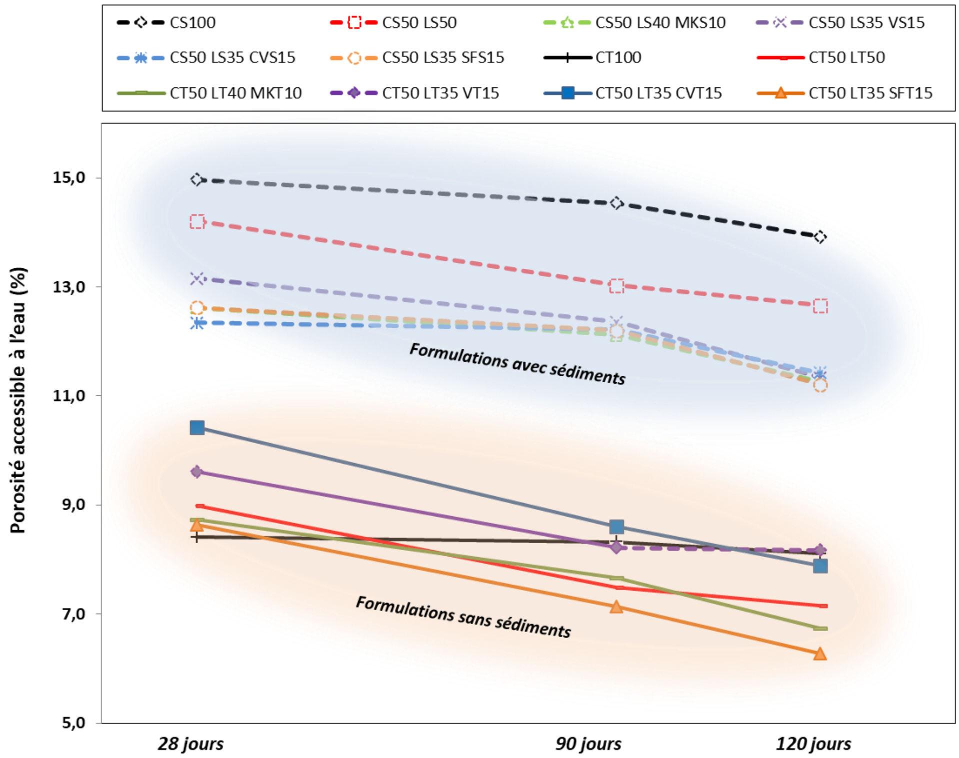


Figure 12. Porosity accessible to concrete water at different deadlines: 28 days, 90 days and 120 days.

Towards an assessment of the sustainability of the formulations studied

Method of the Concrete Equivalent Mortar (CEM)

The equivalent concrete mortar method is a method that was initially used by the CTG (Italcementi Group, Les Technodes, Guerville, France) and then developed as part of the Calibé National Project [4] before being published by SCHWARTZENTRUBER *et al.* [5] in 1999. One of the objectives of this project was to develop a simple, reliable and less expensive method for determining the properties of concrete in the fresh state. This method therefore aimed to limit the number of wastes made during the implementation of concrete formulations, in particular the optimization of dosages in superplasticizer. This method consists in designing mortars whose composition is deduced from the composition of the reference concrete and whose rheological properties are correlated [5].

The principle of the CEM method states that it is possible to obtain a mortar whose rheological properties are correlated with those of concrete by replacing aggregates whose dimensions are greater than 5 mm by sand of the same nature as that used in concrete and whose quantity would reproduce the same granular surface as that of the aggregates removed [6] (Figure Figure 13).

For this deduction to be valid, the following must be respected:

- The nature of cement and its dosage are the same in concrete and its CEM;
- Keep the same E_{eff}/C ratio, and therefore take into account the absorption of aggregates;
- The dosage and nature of the mineral additions must be the same;
- Use an admixture of the same nature as that used for the formulation of concrete and keep the same dosage and the same mode of introduction.

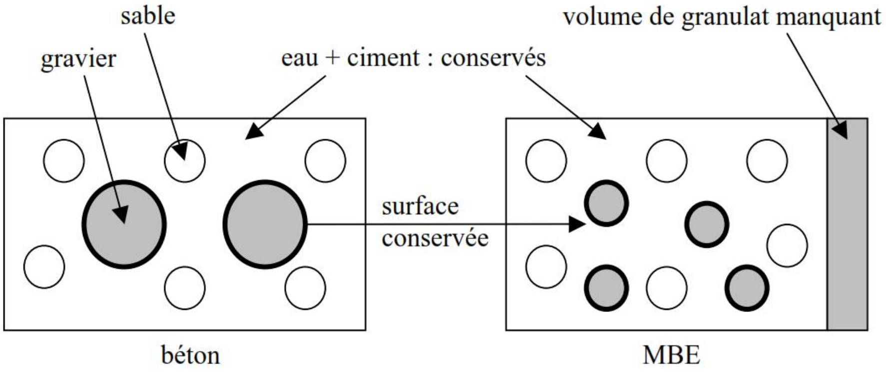


Figure 13. From concrete to equivalent mortar [7].

According to [8], it appears from the results of the CALIBÉL National Project that the CEM method is applicable to concretes whose subsidence is between 5 and 25 cm, and can be considered optimal for concretes whose subsidence is between 10 and 22 cm. However, although correlations have been established between the rheological properties of concrete and its equivalent mortar, the latter remain universal and must be determined experimentally for each composition.

In this part, the CEM method was used to formulate mortars equivalent to concrete with the aim of evaluating their durability through certain specific tests (freeze/thaw, internal and external sulfatic attack, alkali-aggregate reaction, etc.), the objective being to assess the impact of the presence of sediments in the cementitious matrix on its sustainability indicators, and particularly to analyze this effect in the case of matrices based on ternary binders. The use of TEMEs will therefore make it possible to evaluate these parameters reliably and easily.

- Formulation of mortars by the CEM method

The composition of the mortars that will be formulated will be deduced from the composition of the concretes previously formulated in part pp. As mentioned above, the equivalent mortar of a concrete cannot be obtained by simply sieving a fresh concrete with a sieve of 5 mm since part of the water and cement paste adheres to the aggregates. The CEM method makes it possible to recompose an equivalent mortar that will have the same total granular surface. For this, it will be necessary to calculate the total granular area of each fraction (sand 0-4 mm, gravel 4-8 mm and gravel 8-14 mm) and also take into account the water demand of the different granular constituents. For the binding part of the formulation, the quantity of each addition will be deducted from the total volume occupied by the cement.

As a reminder, the composition of formulations based on 100% cement (CT100 and CS100) shown in Table Table 5 below.

Table 5. Composition of the CT100 and CS100 formations.

Constituents (kg/^{m3})	Concrete Witness	Formulation based on 20% Sed. O
Sediment	0	185,82
Sand (kg)	963,015	772,33
Gravel	481,508	482,71
Gravel	481,508	482,71
Cement	380	380
Water	152	152 + saturation water
Adjuvant	7,60	7,60

Determination of the specific surfaces of each component

In order to determine the specific area of each granular slice, it is necessary to calculate the area of each granular slice of the different components.

During the characterization phase, it was found that the absorption of gravel and gravel is different from that of sand (results shown in Table Table 6). In order to take account of this difference in absorption, the density of saturated aggregates with a dry surface was calculated. The results are presented in Table Table 6. The amount of aggregates removed must then be compensated by an addition of sand so as to preserve the same specific surface. The latter will be corrected via the saturated density at dry surface to take into account the difference in absorption.

The results of the soaked density are presented in the Table 66.

Table 6. Dry surface density of aggregates.

	S (0/4 mm)	G1 (4/8 mm)	G2 (8/14 mm)
Absolute density (T/m3)	2,65	2,65	2,65
Absorption coefficient (%)	1,02	0,55	0,55
Saturated density dry surface(T/m3)	2,68	2,66	2,66

The corrected specific area is calculated by the Equation 33:

$$\text{Surface spécifique}_{\text{corrigée}} = \frac{\sum \text{surfaces}_{/\text{tranches}} * \text{M.V.}_{\text{absolue}}}{\text{M.V.}_{\text{saturée surface sèche}}} \qquad \textit{Equation 3}$$

Table 7. Measurement of the total specific area: sand 0/4.

Tamis (mm)	Passants cumulés (%)	Dmoyen (mm)	Refus par tranche (%)	Surface par tranche (mm^2)
0,08	*0,63*	*0,04*	*0,63*	*3,57E+05*
0,16	*5,9*	*0,12*	*5,27*	*9,94E+05*
0,315	*20,43*	*0,24*	*14,53*	*1,39E+06*
0,63	*43,73*	*0,47*	*23,3*	*1,12E+06*
1,25	*61,56*	*0,94*	*17,83*	*4,29E+05*
2,5	*87,54*	*1,88*	*25,98*	*3,14E+05*
3,15	*93,99*	*2,83*	*6,45*	*5,17E+04*
4	*99,5*	*3,58*	*5,51*	*3,49E+04*
5	*100*	*4,50*	*0,5*	*2,52E+03*
			Total :	4,685E+06
Surface spécifique corrigée (m^2/kg) :		**4,638**		

Table 8. Measurement of the total specific area: grit 4/8 mm.

Tamis (mm)	Passants cumulés (%)	Dmoyen (mm)	Refus par tranche (%)	Surface par tranche (mm^2)
3,15	*2*	*2,825*	*2*	*1,60E+04*
4	*5,7*	*3,58*	*3,7*	*2,34E+04*
5	*40,735*	*4,50*	*35,035*	*1,76E+05*
6,3	*83,955*	*5,65*	*43,22*	*1,73E+05*
8	*100*	*7,15*	*16,045*	*5,08E+04*
			Total :	*4,40E+05*
Surface spécifique corrigée (m^2/kg) :		**0,437**		

Table 9. Measurement of the total specific area: gravel 8/14.

Tamis (mm)	Passants cumulés (%)	Dmoyen (mm)	Refus par tranche (%)	Surface par tranche (mm^2)
5	*1,15*	*4,5*	*1,15*	*5,79E+03*
6,3	*3,915*	*5,65*	*2,765*	*1,11E+04*
8	*15,185*	*7,15*	*11,27*	*3,57E+04*
10	*43,8*	*9,00*	*28,615*	*7,20E+04*
12,5	*72,465*	*11,25*	*28,665*	*5,77E+04*
14	*100*	*14,25*	*27,535*	*4,37E+04*
			Total :	*2,26E+05*
Surface spécifique corrigée (m2/kg) :		**0,225**		

Once the total specific areas in (m^2/kg) have been obtained for each component (Table 7, Table Table 8, Table Table 9), the specific area for 1 m3 of concrete must be calculated. This can be obtained by a simple multiplication by knowing the dosage in (kg/m3) of each constituent. The specific area missing (to be compensated) will be equal to the total area of the aggregates that have been removed, this is calculated in Equation 4 and is equal to 318.8 m^2/m^3 of concrete.

$$\text{Specific area to be compensated} = \text{Specific surface of aggregates} = (481.508 \times 0.437 + 481.508 \times 0.225) = 318.8\ \text{m}^2/\text{m}^3\ \text{concrete} \tag{Equation 4}$$

Therefore, the amount of sand to be added in order to maintain a granular surface equal to that of the formulated concrete, is equal to: (318.8/ 4.638) = 68.74 kg.

The volume that will be occupied by the sand will automatically be less than that occupied by the aggregates. As a result, the calculation of dosages will be reduced to the equivalent cubic meter of mortar. The composition of the CT100 and CS100 concretes and their respective equivalent mortars is presented in the Table 1010.

Table 10. Composition of concrete and its equivalent mortar.

Constituents (kg/^{m3})	Concrete		CEM	
	0% sediment	20% sediment	0% sediment	20% sediment
Sediment	–	193,01	–	290,72
Sand (kg)	963,015	770,41	1450,505	1160,40
Sand added	–	–	103,54	103,54
Gravel	481,508	481,508	–	–
Gravel	481,508	481,508	–	–
Cement	380	380	572,36	572,36
Water	152	152	228,94	228,94
Adjuvant	7,60	7,60	11,45	11,45

For verification, the water/cement ratio, the rate of sand substitution by sediment and the total cement/specific area ratio were recalculated (Table 11 and Table 12).

Table 11. Verification of sediment-free formulations.

	Concrete	Equivalent mortar
W/C report	= 152/380 = **0,4**	= 228,94/572,36 = **0,4**
Ratio of cement to total granular specific area	= 380/(963,015×4,638+481,508 ×0,437 +481,508×0,225)= **0,07942**	= 572,36/((1450,505+103,54) ×4,638)) = **0,07942**

Table 12. Verification of formulations based on 20% sediment O.

	Concrete	Equivalent mortar
Substitution rate	= 193,01/(193,01+770,41)×100 = **20 %**	= 290,72/(290,72+1160,40) ×100 = **20 %**
W/C report	= 152/380 = **0.4** (+ saturation water)	= 228.94/572.36 = **0.4** (+ saturation water)
Ratio of cement to total granular specific area	=380/(770,41×4,638+481,508 ×0,437 +481,508×0,225) = **0,09764**	= 572,36/((1160,40+103,54) ×4,638)) = **0,09764**

Freeze/thaw resistance

Among the pathologies that can limit the life of a concrete structure, the exposure of structures to freeze/thaw cycles is one of the means of degradation that can have strong consequences on their durability. Depending on the severity of the gel, several exposure classes can be defined, the French standard XP P 18 305 to define three classes of gels:

- Low: exposure of up to two days per year to a temperature below -5°C;
- Severe: exposure above a temperature below 10°C for a period exceeding 10 days/year;
- Moderate: exposure between low and severe.

When concrete is exposed to freeze/thaw cycles, two degradation modes can be observed depending on its strength and degree of exposure [9]:

- Internal frost: the latter results in a swelling of the concrete, or even the appearance of microcracking in the case of extreme degradation. Microcracks occur in the cementitious pulp and contribute to the weakening of the mechanical performance of the structure, in particular by reducing the adhesion between the cementitious paste and the aggregates;
- Concrete chipping: this is a less explored mode of degradation compared to internal frost but which causes very harmful effects for the structures. This degradation occurs on the surface and results in a loss of material. This is often aggravated by the presence of an aggressive agent such as salt (NaCl) especially during de-icing.

Although these two degradation modes are relatively well identified, the mechanisms of deterioration of concrete subjected to the action of frost are still not clearly defined and distinguished. Indeed, it is accepted that the transition of water from liquid to ice is accompanied by a volume increase of about 9% [10],but this phenomenon is not the only reason for degradation of concrete subjected to cold. Many studies claim that it is rather the movement of internal water that is the main cause of this degradation. In a porous medium, the transition temperature of the water from the liquid phase to the solid phase is inversely proportional to the size of the pores in which the water is confined. This is explained by the fact that the layer of water that is in contact with the wall does not freeze, due to the interactions that occur there [11]. Thus, water contained in large pores freezes faster than water enclosed in small pores. This delayed formation of frost will result in the creation of a thermal gradient that will promote the migration of water from hot to cold areas on the other hand; and on the other hand to the increase in the ion content of the unfrozen interstitial solution, which creates an influx of water to the small pores to balance the concentrations according to the law of osmosis.

In addition to these phenomena of thermo-differential expansions and water transport, there is the effect of swelling forces caused by the formation of the gel and which tend to push water out of the pore. The concrete therefore undergoes pressures of water forces so great that they exceed the tensile force of the cement paste and cause cracks and consequent damage. The main element for the prevention of frost/thaw degradation is therefore not the volume of air bubbles but rather the spacing factor $\bar{L}$, commonly known as "L bar", defined as the average half-distance between two walls of air bubbles – in other words, the distance that water would have to travel to reach the air bubble that will serve as an expansion vessel (Figure Figure 14). The value of $\bar{L}$ can be evaluated according to ASTM C 457-98. However, a quick indication of the quality of concrete can be achieved by calculating the air driven from concrete to the fresh state. Generally, the amount of occluded air required to obtain a satisfactory $\bar{L}$ is 4 to 8% for concretes with a d_{max} of 0/20 mm, and it is 5 to 9% for concretes whose d_{max} varies from 0 to 15 mm [12]. There is a consensus among researchers that a volume of air equal to 9% of the volume of the mortar is needed to prevent the effects of freezing. Indeed, the amount of the dough increases with the decrease in the maximum diameter of the aggregates, and therefore the amount of occluded air required is inversely proportional to the maximum diameter of the aggregates used in the formulation of concrete.

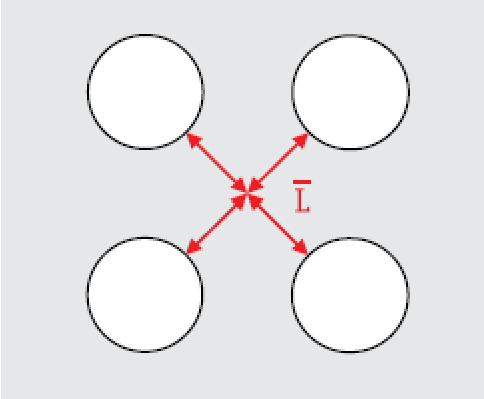


Figure 14. Spacing factor $\bar{L}$ [10].

Taking into account the risks of freezing/thawing attack is therefore essential when formulating concrete to ensure the proper functioning of structures throughout their lifetime. Recommendations to best prevent this degradation were defined in the technical guide entitled *Recommendations for the durability of hardened concrete subjected to frost* and developed by a working group led by the Central Laboratory of Bridges and Roads LCPC in 2003.

Among these recommendations, the use of CEM I or CEM II/A and B cement with a minimum dosage of 385 kg/m^3 is recommended to prevent disorders related to the action of frost. The use of mineral additions as an addition to cement or as a partial substitution is possible, among them are limestone additions, slags, silica fumes, etc. However, it should be noted that ashes are not recommended. It is also advisable not to exceed 30% of the total mass of cement. Specifications for aggregates, including sand, are also provided in this technical guide.

The W/C ratio is also one of the factors that have the most influence on freeze/thaw resistance. Indeed, the reduction of the latter will have the consequence on the one hand of reducing the quantity of water available in the cementitious pulp likely to be transformed into ice, and on the other hand, the reduction of porosity and the improvement of mechanical resistance. These are all factors related to the decrease in the W/C ratio that improve the frost resistance of concretes designed with low W/C ratios. For traditional concretes, an W/C ratio of less than 0.45 is recommended for concrete subjected to frost and glaze, and an W/C of less than 0.5 for concrete exposed to frost only [13]. The recommendations are summarized inTable 13 [12]."

Table 13. Recommendations for concrete subjected to frost.

Characteristics	Specification for concrete subjected to frost
Cement	CEM I, CEM II/A and B; 52.5N and R, 42.5 N and R
Dosage in cement, concrete with D_{max} = 20 mm	385 kg/m^3
E/C report	0,5
Additions	Slag (30%), silica smoke (10%), limestone additions (15%) etc.
Absorption coefficient gravel	1,2 % maximum
Spacing factor $\bar{L}$	≤ 250 µm
Compressive strength	≥ 30 MPa

In this study, freeze/thaw resistance was evaluated according to the P 18-425 standard for moderate freeze attacks within the meaning of the classification established in XP P 18 305. The standard is applicable regardless of the degree of water saturation of the concrete.

In addition, only resistance to internal frost was studied, the presence of de-icing salts or flaking resistance were not investigated. This evaluation was carried out on prismatic specimens (4×4×16cm), three specimens were made for each formulation to ensure the reproducibility of the results. The specimens were fitted with swelling measuring pads on the ends to monitor dimensional variations (Figure Figure 15). 12 mortar formulations equivalent to the 12 concrete formulations were formulated (6 with sediment and 6 without sediment). After making the test pieces, they were demoulded after 24 hours and then stored in water for 54 days at 20°C. At the end of this period of treatment in the water, the test pieces were taken out and left to dry in the open air for 1 hour in an air-conditioned room at 20° C. The assessment of the action of the freeze/thaw cycles is evaluated through measurements of mass, dimensional variation, as well as the longitudinal resonance frequency of the different specimens. Initial measurements of each of these three parameters were made before introducing the samples into the climate chamber for the application of freeze/thaw cycles.

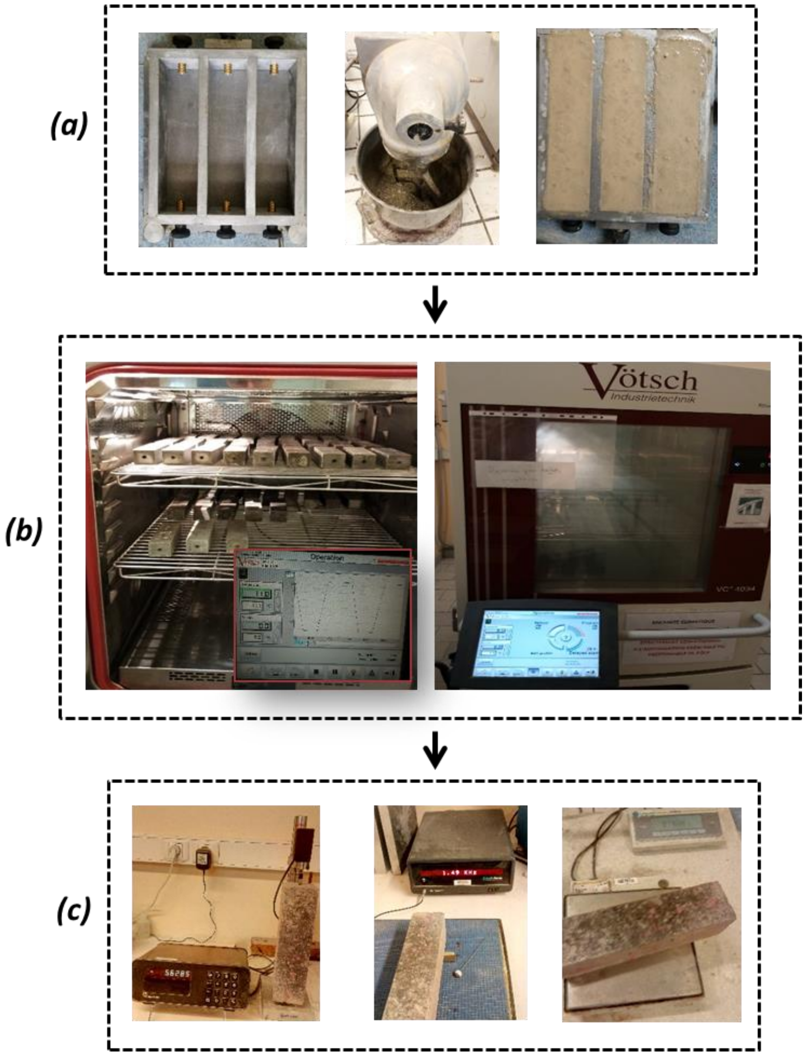


Figure 15. (a) preparation of test pieces; (b) application of 300 thaw freeze cycles; (c) elongation measurement, frequency measurement and mass monitoring.

The exposure level targeted in this study was moderate freezing, the cycles that were applied to the test pieces are freeze in air and thaw cycles in air. The temperature profile applied complies with nf p 18-425 (Figure Figure 16). The samples were subjected to 300 cycles over 6 hours. The climatic chamber was set to lower the temperature from +9°C to -18°C at the heart of the specimen in 1 h (27°C/h) and then stabilize at this temperature for 1 h 30. This phase corresponds to the freezing phase. The temperature then increased with the same speed before stabilizing at +9°C for 2 h 30. This time allowed sufficient time to take out the specimens and carry out the various measurements.

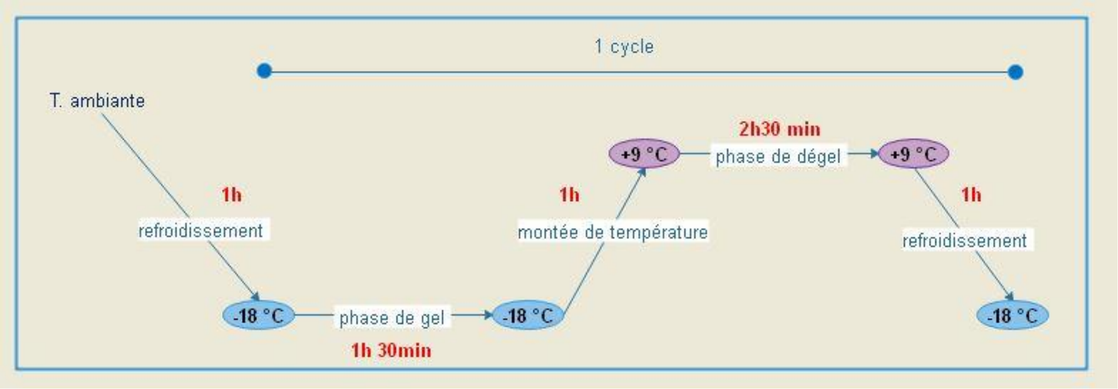


Figure 16. Temperature profile of freeze/thaw cycles.

The criteria for evaluating frost resistance are elongation and resonance frequency. The elongation is expressed according to the Equation 55.

$$\varepsilon_L = \frac{\Delta_L}{L_0} = \frac{L_t - L_0}{L_0}\ x\ 10^{+6} \qquad \textit{Equation 5}$$

With: relative elongation in μm/m;ε_L

L_t : the length of the test piece at maturity t in m;

L_0 : the initial length of the test piece before the start of the test in m.

The square ratio of resonance frequencies is calculated by the Equation 66.

$$\text{Square ratio of resonance frequencies} = \frac{{F_t}^2}{{F_0}^2}\ x\ 100 \qquad \textit{Equation 6}$$

with, the resonance frequencies measured at time $F_t F_0$ t and .t_0

The criteria to be met are specified in the following Table 14 , the elongation measurements are carried out after 300 freeze/thaw cycles, the factor 0.8 is introduced in order to take into account the heterogeneity of the manufacture.

Table 14. Criteria for premature termination of the trial.

	Control value
Relative elongation	≤ 500 μm/m
Square ratio of resonance frequencies	≥ 60

The results of measuring the elongation obtained after 300 freeze/thaw cycles are shown in Figure Figure 17.

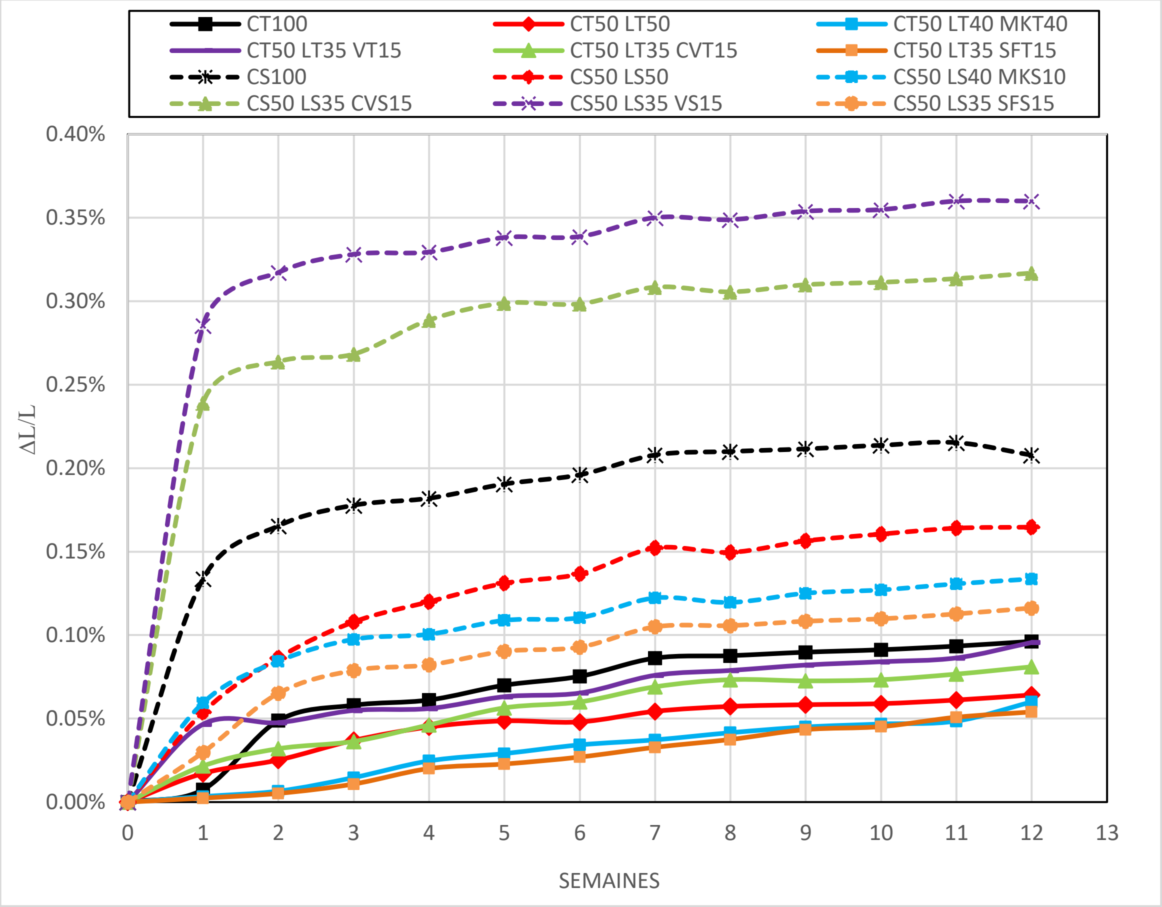


Figure 17. Relative elongations of test pieces subjected to freeze/thaw cycles.

The curves inFigure 17 show that all formulations recorded swelling due to the action of the gel. However, these results also show that the substitution of sand by dredged sediment is disadvantageous in terms of freeze/thaw resistance. Indeed, formulations containing sediment record swelling greater than control formulations (without sediment). This can be explained by the fact that these formulations contain more water that can freeze. This amount of water, which corresponds to the water demand of the sediments (estimated at more than 35%), will therefore be transferred from the warmer areas to the colder areas as a result of freeze/thaw cycles and will create significant stresses, which will consequently lead to cracks in the concrete. In addition, it has been found that the introduction of sediment increases the total porosity of concrete, which promotes the transfer of the interstitial solution. An improvement in freeze/thaw resistance has been observed when using ternary binders: in fact, the latter show less swelling than the binary binder and the cement-based control only. This improvement is even more marked for the formulations C50 L35 S15 and C50 L35 MK 15: this type of binder records the least swelling. The combination of these additions makes it possible to improve the hardened characteristics of the concretes, in particular the tensile strengths, and therefore the cracks are limited. On the other hand, as noted in Chapter XX, the use of ternary binders contributes to the refinement of the porosity of the binding paste. Thus, the water contained in the pores freezes less in these formulations than for the control formulations. Improved pore distribution for ternary binder formulations contributes significantly to improved durability. Indeed, a better distribution of pores reduces the distance $\bar{L}$ that the water must travel to reach the nearest expansion vessel.

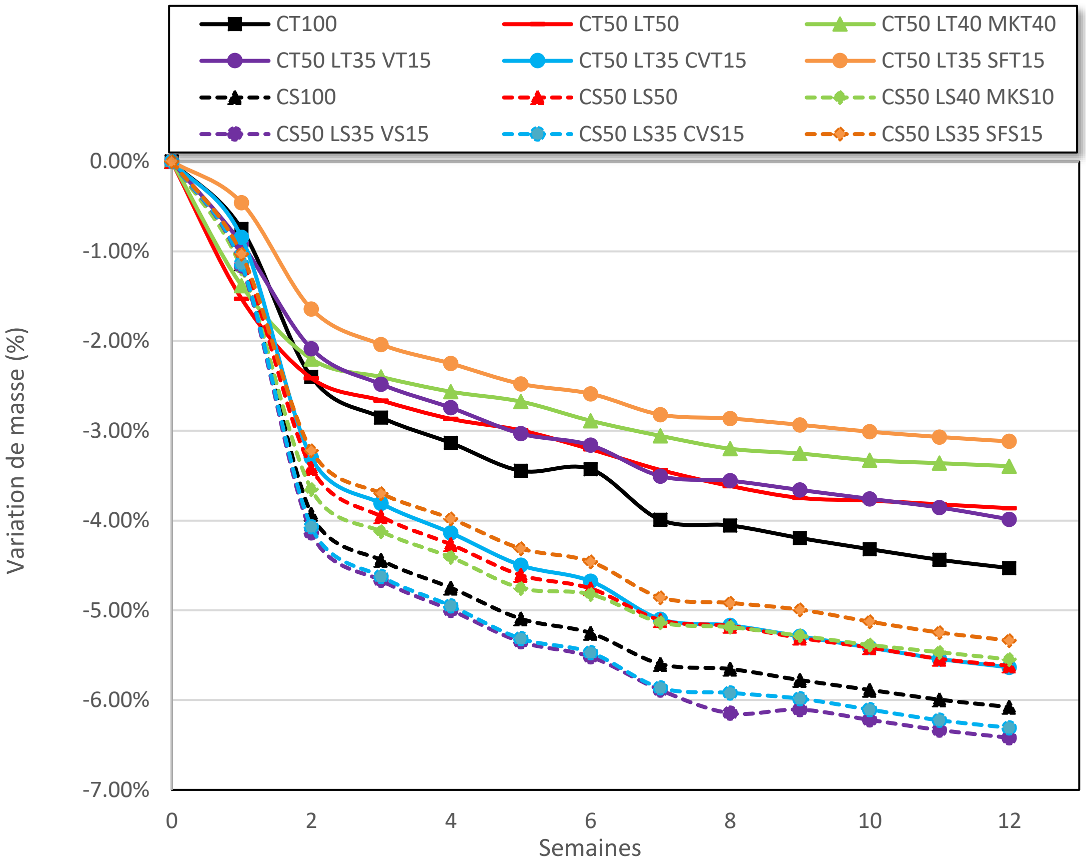


Figure 18. Mass change after 300 freeze/thaw cycles.

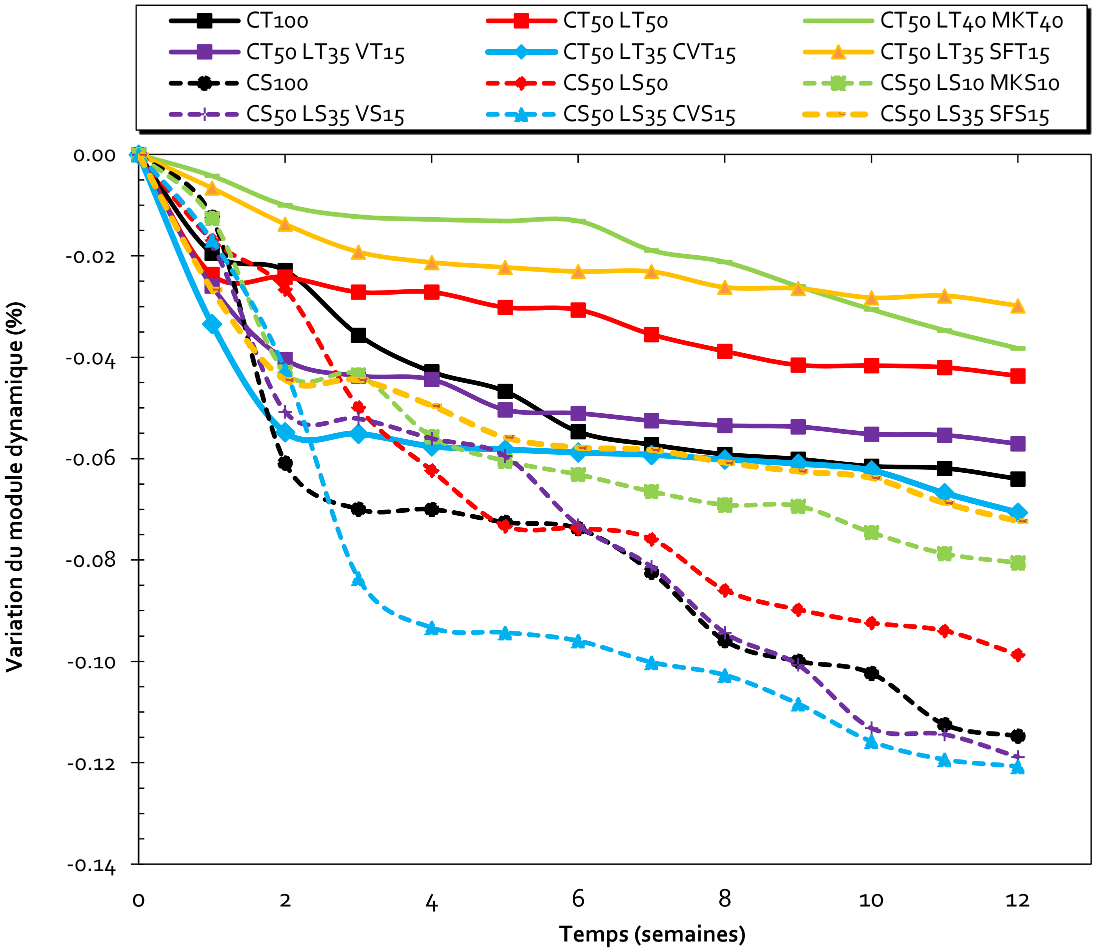


Figure 19. Variation in the dynamic modulus of test pieces subjected to freeze/thaw.

Changes in mass and dynamic modulus are shown in Figure Figure 18 and Figure Figure 19.

In accordance with the results obtained on the length variation, a loss of mass, accompanied by a decrease in the dynamic modulus was observed for the different formulations. Sediment-based formulations are the most impacted by the action of freeze/thaw cycles; this results in a greater loss of mass and a decrease in the dynamic modulus than in formulations made from sediment alone.

However, with regard to the limit of elongation for the premature termination of the test set at 500 µm/m (0,5 %), all formulations meet this requirement and are even below the value of 0,4 %. This value corresponds to the control limit value which takes into account the heterogeneity of manufacturing in the laboratory and on site; it is obtained by considering a factor of 0.8. This good resistance to freeze/thaw cycles is attributed in particular to the use of an equivalent binder dosage of 385 kg/ m^3 (in accordance with the requirements of the 2003 LCPC Technical Guide), and also to the use of a low W/C ratio (< 0.45).

Internal sulphatic reaction ISR:

Concrete structures can be subjected to several types of degradation during their service life. Among these degradations, some are of external origin, caused by climatic conditions such as freeze/thaw, or by chemical exposure such as chloride attacks on reinforcements, etc. Other pathologies can form from the inside of concrete, so they are endogenous in nature. Among them, we can mention alkali-aggregate reactions, and internal sulphatic attacks (ISR), the latter being also called DEF for "*delayed ettringite formation*", translated into French as "formation différée d’ettringite".

ISR develops in hardened concrete when it undergoes significant heating during its formulation. This exposure period can vary from a few hours to a few days. In general, the minimum temperature for which the risk of developing an ISR should be considered is approximately 65°C [14]. This value should not be taken as a threshold limit, but should be reconsidered depending on the chemical composition of the cement and the environment to which the concrete is exposed.

These temperature conditions can be encountered when setting up mass concrete parts where the heat of cement hydration becomes very important, and also in concrete prefabrication plants where they are heated in order to accelerate the setting and hardening and thus unpack faster. During the rise in temperature at a young age, the latter hinders the "normal" setting of the cement by modifying the hydration reactions between gypsum and C_3A (tricalcium aluminates) and preventing the formation of primary ettringite, because at this temperature it becomes unstable[15]. Once the temperature drops back to room temperature, ettringitis precipitates especially in the presence of humidity. However, the concrete will have already hardened and this delayed formation of ettringite then leads to swelling and internal cracking in the concrete. Before explaining the development process of ISR, it is important to recall the different categories of ettringitis [16]:

- Primary ettringitis: this is one of the hydration products of cement. It is the result of the reaction of calcium sulphates introduced in the form of gypsum and tricalcium aluminates C3A. This reaction, which aims to regulate the setting of cement, gives rise to primary ettringite. This ettringitis does not constitute any disorder because it develops when the concrete is still fresh. It even gives a certain cohesion to fresh concrete and improves its mechanical strength.
- Secondary ettringitis: it develops in hardened concrete when it is the result of the phenomena of dissolution/recrystallization of primary and delayed ettringitis. It grows in the porous network of concrete and no risk of expansion is present. However, when it develops as a result of the external or internal contribution of sulphate, the formation of secondary ettringitis could be accompanied by swelling or even cracking of the concrete.
- Delayed ettringite: as explained above, it is the result of heating the concrete from an early

age, which interferes with the formation of primary ettringite that subsequently develops in hardened concrete in the presence of moisture. The development of this type of ettringitis as well as the mode of degradation of concretes subjected to this type of pathology is detailed in the rest of this study.

There are several parameters that affect ISR; the primacy of these is not established but the influence of each parameter on the development of the ISR is proven. Below is a brief explanation of the role of some of these parameters [15][16][17][18][19]:

- Alkalis: Alkalis, mainly K^+ and Na^+ come mainly from cement and mineral additions. They have a considerable impact on the development of ISR: their presence in large quantities modifies the pH of the environment and leads to a decrease in the stability domain of ettringitis. This effect is all the more important the higher the temperature. The amount of sulfate ions adsorbed during hydration of C3S is accelerated by the high concentration of alkalis, which increases the risk of delayed formation of ettringite. In addition, studies have shown that the presence of alkalis, including potassium hydroxide (KOH), has a retarding effect on the reaction of C3A with sulfates from gypsum which contributes to the formation of primary ettringite. This effect can be explained by the formation of an impermeable layer preventing the reaction of C3A with SO_4^{2-} ions. Some of these ions will then be found either in a free form in the interstitial solution or combine with other elements. At high temperatures, SO_4^{2-} ions are adsorbed by C-S-H, this adsorption being favored by the presence of alkalis. Once the temperature is lowered, the sulfate ions are released and then react with the aluminate ions from the decomposition of hydrated sulfoaluminates (initially formed by normal reaction between sulfates and aluminates) and thus form expansive ettringite [15].
- Sulphates: the sulphates found in the cementitious paste come mainly from the gypsum added for the regulation of the setting. Sulphates combine with aluminates to form ettringite. As indicated above, it is the presence of sulphates in free form in the interstitial or adsorbed solution on the C-S-H that is at the origin of the precipitation of ettringite. In general, in order to prevent degradation by ISR, cements with a maximum sulphate content of 3% are recommended.
- Aluminates: C3A and C4AF are the origin of aluminates in cement. Aluminates play an important role because they contribute to the formation of ettringite and therefore ISR. In order to limit the development of ISR, a molar ratio of $SO_3/AL_2O_3 < 0.67$ is recommended, this value not representing a limit threshold but beyond 1 a particular vigilance must be observed.
- The nature of the aggregates: the effect of the nature of the aggregates lies mainly in the ITZ transition zone of cement and aggregates. Indeed, depending on the nature of the aggregates, the expansion of this area may be different, and the response developed to swelling related to an ISR is therefore not the same. For example, siliceous aggregates lead to more significant swelling

than for calcareous aggregates; this can be explained by the fact that the presence of alkalis allows the partial dissolution of aggregates, which promotes the fixation of hydration products. On the other hand, the amount of water that can be mobilized at the contact surface of the aggregates is greater than in the rest of the dough: this area is therefore more porous and will be the favorable place for the transfer of SO_4^{2-} ions - which contribute to the development of ettringite.

- The W/C ratio: the influence of the W/C ratio can be envisaged from two different angles: the first is to say that the reduction of the W/C ratio would reduce the porosity of the cementitious matrix and therefore the ion transfer on the one hand and the improvement of compressive strengths on the other hand. On the other hand, the reduction of porosity limits the free space in which ettringite can develop, and the formation of a small amount of ettringite could cause very high pressures inside the cement paste. There is therefore no scientific consensus on this issue, contradictory findings have been made in the literature.
- Water and adjuvants: wasting water and adjuvants are also important parameters that can be involved in the development of an ISR. Indeed, if the sulphate content of the wastewater is limited to 2,000 mg/L to prevent the effect of an internal sulfatic attack, adjuvants for their part, and in particular superplasticizers, can be a source of significant concentration of sulfates especially because of their high solubility in water.
- Temperature effect: Temperature increase is essential for the development of ISR and its impact is widely studied in the literature[20][16][18][21]–[24]. The maximum cure temperature, the duration of the heating, as well as the cross-influences of the temperature and other aforementioned parameters are all elements that have a significant impact on the development of the ISR.

Concrete intended for hydraulic structures must be formulated in such a way as to be sulphate resistant. The use of dredged sediments in concrete formulation can have an influence on the development of ISR, elements [1]such as water demand, the presence of organic matter, sulphates and the effect on mechanical strength and porosity are all parameters that can induce ISR.

As part of this study, the ISR was studied to assess the possible disorders that could result from the introduction of dredged sediments into concrete. Indeed, on the one hand, during the characterization phase, the percolation tests carried out on the raw sediments showed that sediment O has a sulphate concentration of more than 110 mg/kg of dry matter, which makes it an additional source of sulphates. On the other hand, it was found that the introduction of sediments is accompanied by a decrease in mechanical strength and a change in the porosity and amount of water available in concretes. This part will therefore make it possible to evaluate the

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[1] In the case of sulphate intakes external, the risk of Sulphatic attack will be studied in the ISR section.

influence of these different parameters on the development of ISR. The use of mineral additions in partial substruction of cement, will probably have an impact on the ISR.

The choice of treatment conditions was made with reference to existing work in the literature. Indeed, there is no normative texte in France relating to the evaluation of the ISR. On the other hand, technical guides allowing the implementation of a method of evaluation of this reaction are available. The evaluation carried out in this study was therefore essentially based on the recommendations of the report "LPC test method N°66: reactivity of a concrete vis-à-vis an internal sulfatic reaction" [17].

The tests shall be carried out on prismatic specimens 4×4×16 cm fitted with studs for the measurement of swelling. Equivalent mortars are formulated according to STANDARD NF EN 196-1. For each formulation, three specimens are tested and an average of the three values is considered.

The profile of the curing temperature applied to the samples subjected to the RSI is shown in Figure 20. These thermal cycles can be broken down into 4 phases:

1. The pre-setting period: after the implementation of the mortar formulations, they are stored for 1 hour at a temperature of 20° C.
2. Temperature rise phase: during this phase, the samples undergo a temperature increase with an average speed of 20°C/h at the heart of the specimen.
3. Isothermal period: during this phase, the temperature is kept constant at 85° C for 12 h; the duration of this cycle and the maximum temperature are chosen in such a way as to guarantee the deceleration of the ISR.
4. Cooling phase: this step reduces the heating of the specimens until it reaches room temperature.

Before the test pieces are introduced into the climatic chamber, they must be protected in order to avoid desiccation of the mortars. In this study, the mussels were wrapped in aluminum foil (Figure 21). Similarly, in order to ensure a relative humidity RH > 90% throughout the duration of the thermal treatment, a tank filled with a sufficiently large amount of water was introduced into the enclosure.

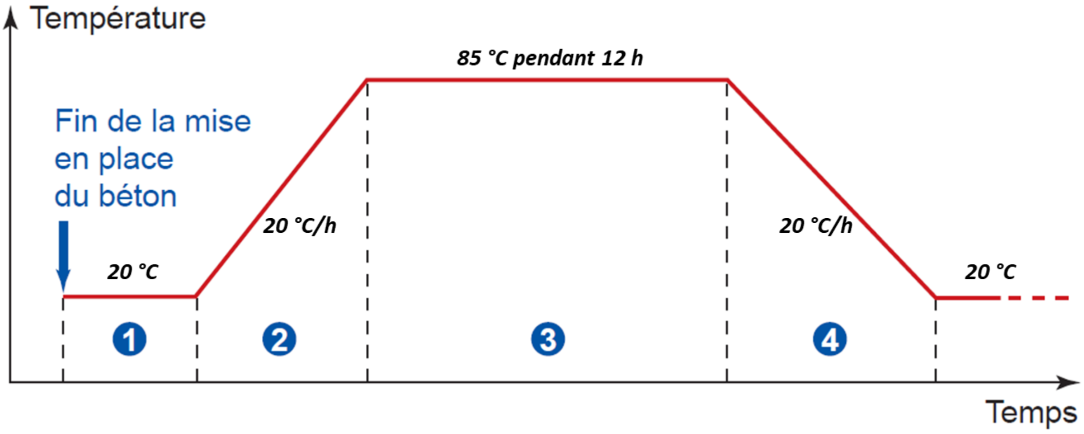

Figure 20. Cure temperature profile of samples for ISR (adapted from [17]*).*

Once the heat treatment is complete, the specimens are demoulded and the initial measurements are made. The monitoring will be carried out through longitudinal strain measurements, mass monitoring and the evolution of the dynamic modulus through the measurement of longitudinal resonance frequency.

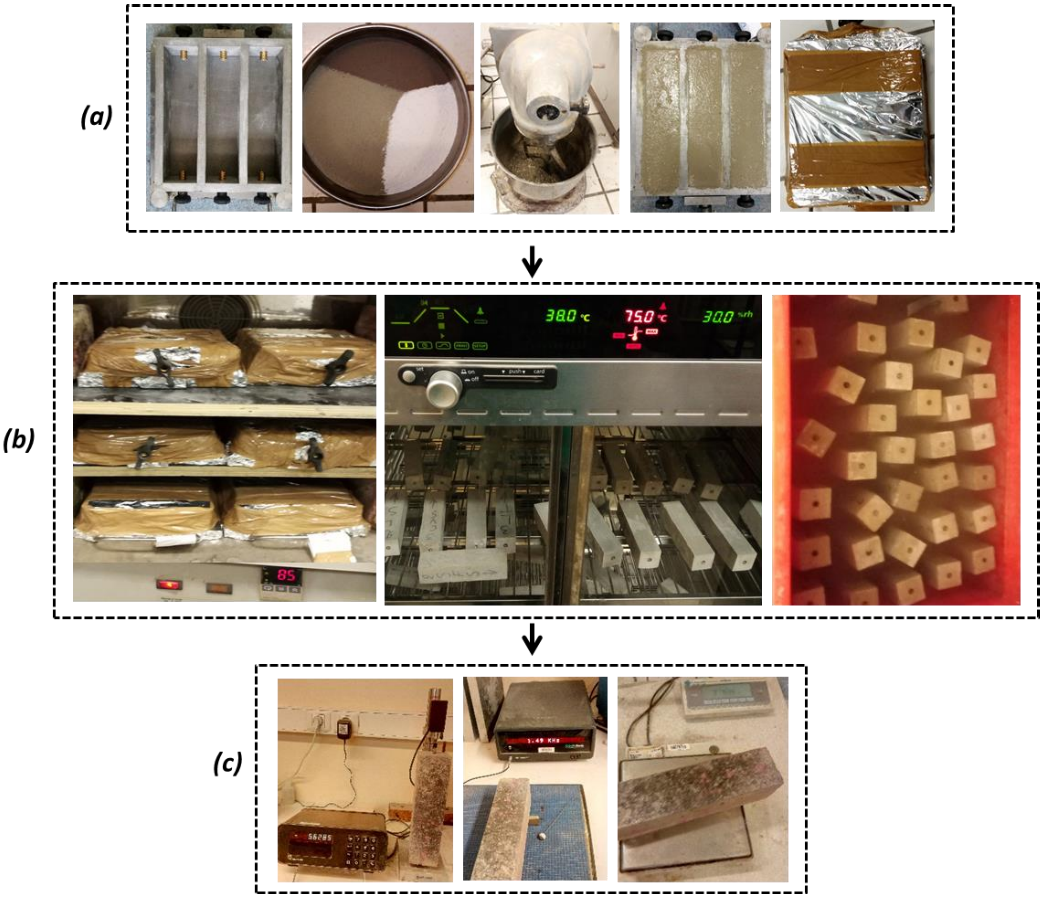

Figure 21. Illustration of the steps involved in setting up the ISR trial. (a) preparation of test pieces; (b) heat treatment and drying/wetting cycle; (c) monitoring of longitudinal deformation, mass variation and resonance frequency.

In accordance with the LPC method N°66, 2007, two drying/humidification cycles were applied. Each cycle lasts 14 days and consists of two phases (Figure 22):

1. Drying for 7 days in a climatic chamber set at 38 ± 2 °C and a relative humidity RH < 30%.
2. Total immersion in water for a week.

The water tank in which the specimens are kept must be well insulated so as to have a minimum loss of water: in fact, the specimens must be kept in the same water so as not to alter the chemical balance of the samples. The objective of these cycles is to accelerate the precipitation kinetics of ettringitis.

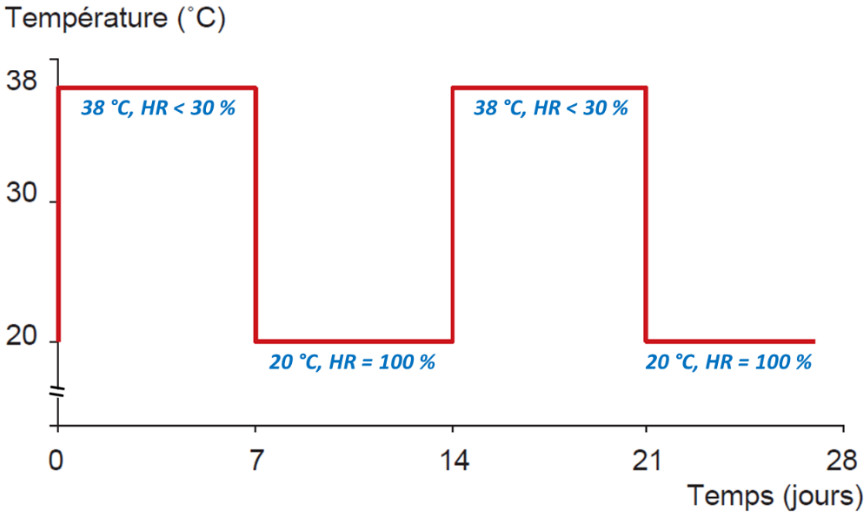

Figure 22. Drying/humidification cycles applied for RSI.

For concrete to be considered resistant to ISR, two criteria must be met at 3 and 12 months (Table 15).

Table 15. Criteria for resistance to sulphatic attacks.

Parameter	Criterion
Mean longitudinal deformation after 12 months	< 0,04 %
Average monthly change after 3 months and	< 0,004 %
Individual longitudinal deformation after 12 months	0,04 – 0,07 %
Average monthly change after 12 months	< 0,004 %

Signs of degradation of structures affected by an ISR take a long time to appear, sometimes it can take years to see them. In this study, and for reasons of time constraints, only the results obtained up to 4 months were presented. The dimensional variations of the specimens tested are shown in Figure 23.

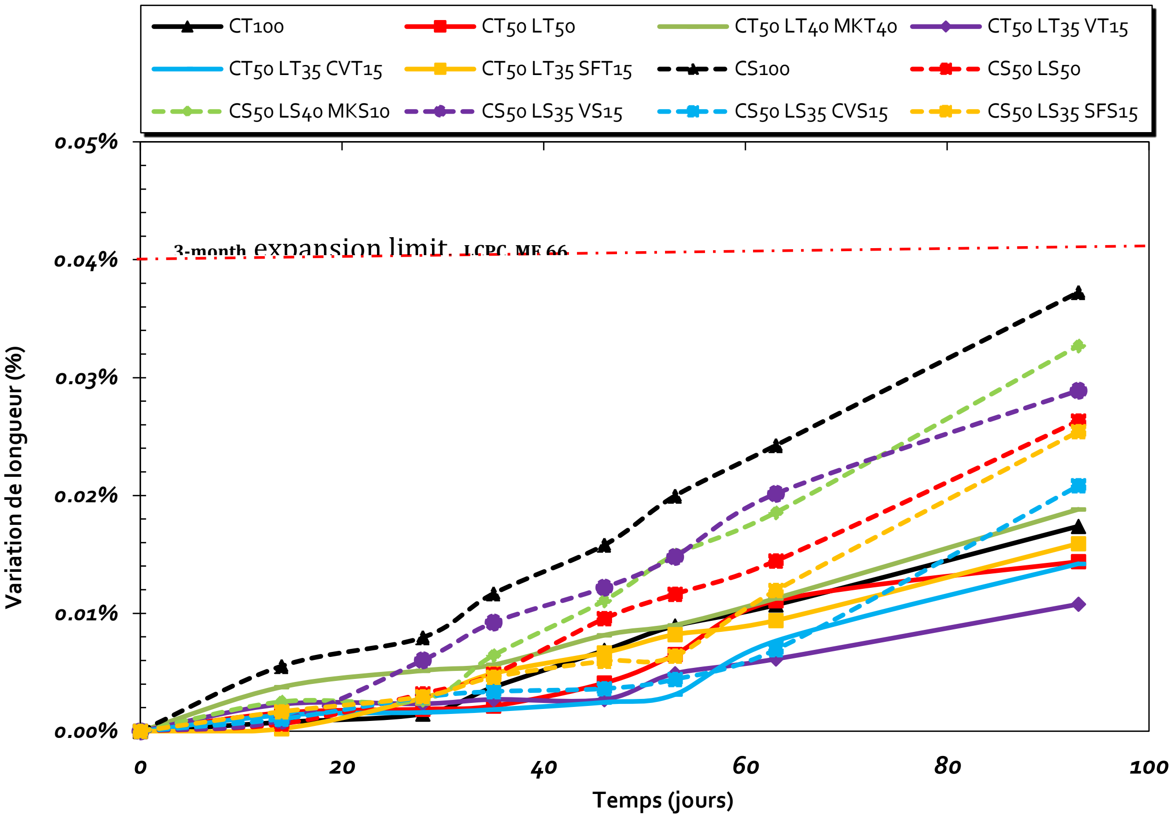

Figure 23. Follow-up of the expansion of specimens subjected to internal sulfatic attack.

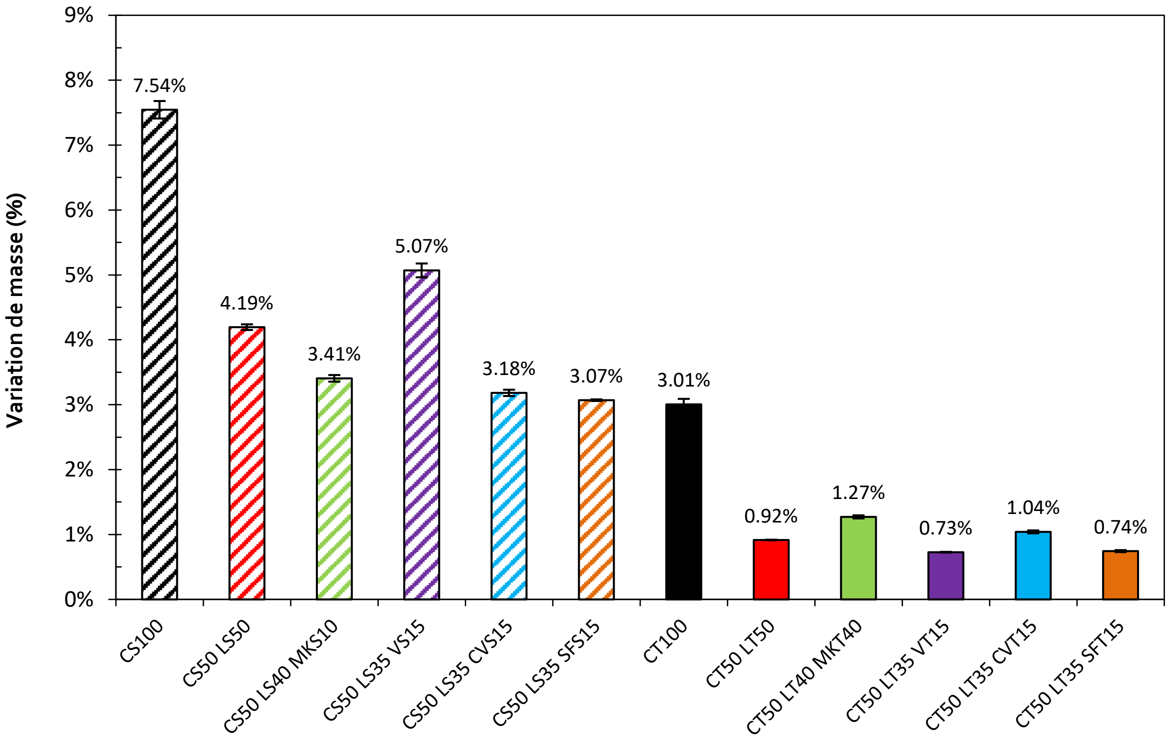

Figure 24. Mass variation of specimens subjected to an ISR after 4 months of follow-up.

These initial results show that after 4 months, formulations containing dredging sediments appear to be less resistant than control formulations, as a length variation of between 20 µm/m and 38 µm/m is observed with sediments, while control formulations do not exceed 18 µm/m.

Several factors can explain this expansion: on the one hand, sediments are a source of extra sulphate in the composition of concrete. As mentioned earlier, delayed ettringite is formed by combining sulfates with aluminates. On the other hand, the nature of the sediments and their demand for water are also the source of this more important deformation: around the sediment grains, the water content and porosity are more important than in the rest of the cement paste. This promotes ionic exchanges as well as the formation of expansive ettringitis. Also, because of the low resistance of this contact zone between the dough and the sediment, the dilation that occurs there is more important. Formulations based on 100% cement are also the ones that swell the most.

The use of ternary binders with a low C_3A content contributes to the improvement of ISR. It is also noted that the use of ternary binder, especially based on sediment treated by flash calcination, contributes strongly to the improvement of ISR. Indeed, due to their pozzolanic power, sediments treated by flash calcination significantly improve the mechanical performance of concrete and its durability. The reduction of the total porosity, as well as the refinement of the pore size are also the elements that can justify the improvement of the durability of concretes based on ternary binders. Figure Figure 24 shows a relatively large mass loss in formulations containing dredged sediments compared to control formulations (100% sand). It is also noted that formulations based on ternary binders record lower mass losses than control mortar (100% cement).

Finally, in the LCPC ME66 test method [17], the 3-month expansion limit was set at 0.04% for the prevention of disorders due to ISR. All formulations meet this requirement even beyond 3 months. Follow-up should be continued for up to 12 months to ensure that ISR is not likely to occur; nevertheless, the indicative criterion measured at 4 months is satisfactory.

External sulphatic reaction ESR

The problem related to the attacks of external sulfates is old and has been widely discussed in the literature. However, often the reactions involved in this type of degradation are presented as complex and dependent on several factors that are difficult to dissociate. In France, since 1958, sulphate-resistant cements have been included in the NF P15-313 standard; this was modified in 2006 by the implementation of the standard NF P15-317 "Cement for work at sea" on cement for maritime works. Despite these standards, research on degradation processes and their effect remains topical, especially those focusing on the properties of ion transfers, and the combined effects of parameters that trigger ESR.

The debradation of structures by ESR – just as in the case of ISR – is caused by the formation of expansive ettringite which exerts stresses on the concrete, involving cracking and swelling of it. Moreover, although the degradation mechanisms are similar, the origin of the sulphates necessary for the formation of ettringite is not the same: in the case of ESR, sulphates come from the external environment, in particular soils, groundwater, river water, maritime waters, etc. The degradation process can be summarized in two mechanisms: the first is physical, related to the transfer of aggressive agents and their penetration into the cementitious matrix; the second is chemical, consisting of the combination of sulphate ions with cement products.

Among the sulphates to which the structures may be exposed, sodium sulphates (Na_2SO_4) are most often encountered in nature. These are absorbed by the contact surface of the concrete and penetrate through the porosity and cracks found in the paste and the ITZ surface (Figure 25). The chemical degradation process occurs by combining sodium sulphates SO_4^{2-} with portlandite $Ca(OH)_2$ to form gypsum ($CaSO_4{\cdot}2H_2O$) (Equation 7). The latter combines with C_3A ($3CaO{\cdot}Al_2O_3{\cdot}12H_2O$) and form of ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) (equation 8).

$$Na_2SO_4{\cdot}10H_2O + Ca(OH)_2 \longrightarrow CaSO_4{\cdot}2H_2O + 2NaOH + H_2O \qquad \textit{Equation 7}$$

$$3(CaSO_4{\cdot}2H_2O) + 3CaO{\cdot}Al_2O_3{\cdot}12H_2O + 14\,H_2O \longrightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O + Ca(OH)_2 \qquad \textit{Equation 8}$$

If the expansion of ettringitis is clearly highlighted, that of gypsum is still controversial. In any case, the chemical reactions induced by the introduction of sulphates into concretes trigger reactions that transform the hydration products into products harmful to the structures. According to ZHANG *et al.* [25], the impact is not limited to this transformation but also occurs a decalcification of hydrated calcium silicates (S-C-H).

The process of physical degradation is manifested by the crystallization of sodium sulphates in the pores of concretes that occurs according to *Equation 9*. This crystallization causes an increase in stress on the walls of concrete pores and causes internal cracks where these stresses exceed the maximum tensile strength of concrete.

$$Na_2SO_4 + 10H_2O \longrightarrow Na_2SO_4{\cdot}10H_2O \qquad \textit{Equation 9}$$

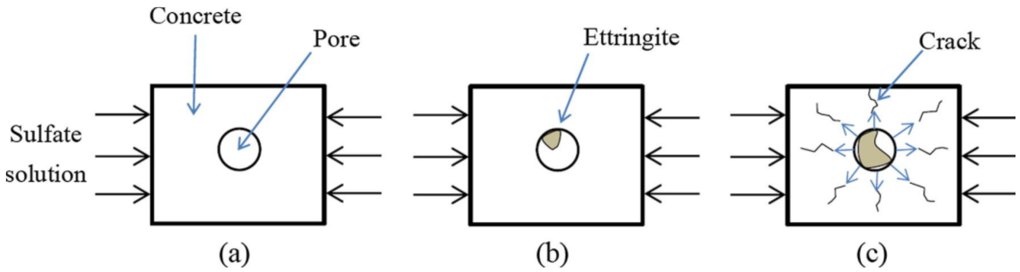

Figure 25. Degradation process by CSR: (a) penetration of sodium sulphates into the pores of concrete; (b) expansive ettringitis formation; (c) cracking of concrete [26].

The development of a ESR is conditioned in particular by the[2] sulphate concentration of the environment in contact with the concrete, the permeability of the concrete, the chemical composition of the cement and the pH of the interstitial solution of the concrete [27].

In the literature, different protocols have been applied to assess the resistance of concretes to external sulphatic attack: some authors apply a total immersion of the specimens in a sulphate solution, while others opt for drying/wetting cycles. Indeed, the drying of the specimens accelerates the transfer movements and consequently the degradation occurs rapidly. The following Table 16 summarizes some of the protocols applied in the literature.

Table 16. Summary of some protocols applied for the evaluation of the ESR of concretes.

Reference	Protocol applied
GAO *et al.* [28]	*72-hour cycle* • Drying at 60°C for 45 hours followed by 3 hours at room temperature • Immersion in a 5% solution by mass of Na_2SO_4 for 21 h then 3 h in ambient air
ZHANG *et al.* [25]	*7-day cycle* • Immersion in the 5% Na_2SO_4 solution for 24 hours • Drying for 6 days at a temperature of 20°C and a relative humidity of 40% < RH < 70%
ZHANG *et al.* [26]	*7-day cycle* • Immersion in the 5% Na_2SO_4 solution for 3 days • Drying at T = 23°C and RH = 50% for 4 days
ZHANG *et al.* [26]	• Total immersion in the 5% Na_2SO_4 solution

In the case of this study, some of the artificial concrete riprap will be in contact with river water, with the ground and potentially with groundwater upwelling. These elements constitute a very favourable environment for the development of ESR. The verification of the resistance of concrete against external sulphatic attack (ESA) is therefore of great importance to ensure the good durability of the structure. When the concretes are put into service, 3 cases of exposure of the structure can be distinguished. The first corresponds to the total and permanent exposure of concrete to the sulphate source – this is the case of concrete blocks that will be completely immersed. The second case corresponds to a permanent but partial exposure; and the third case, aux concrete blocks which will be exposed periodically with high frequencies. The latter case seems to be the most damaging, so it would be substantial to apply a wetting/drying cycle here.

Based on these data, the protocol used in this study was inspired by the work of ZHANG *et al.* [26]. The chosen protocol is composed of cycles of one week, a total immersion of the specimens in a

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[2] So, its ability to let in sulfate ions (SO_4^{2-}).

solution dosed at 5% by mass of sodium sulphate Na_2SO_4 for 3 days, then the application of a drying for 4 days at 20° C and at a RH of 50%. As mentioned above, this wetting/drying alternation will promote ion transport and accelerate the ESA development process. The water used is distilled water, and the solution is renewed every 30 days.

The tests are carried out on mortars whose composition has been deduced from the CEM method. Measuring pads were placed on the ends of the specimens in order to be able to measure any dimensional variations of the specimens. In addition to these measurements, the esa's monitoring of the degradation of the specimens was carried out by periodic taking of the masses of the specimens as well as the measurement of longitudinal frequencies. After formulation of the specimens, they were introduced into the water for 54 days before the test was carried out. For material availability and time constraints, only formulations containing dredged sediments were tested. The curves representing the expansion of specimens subjected to external sulfatic attack as a function of time are shown in Figure 26.

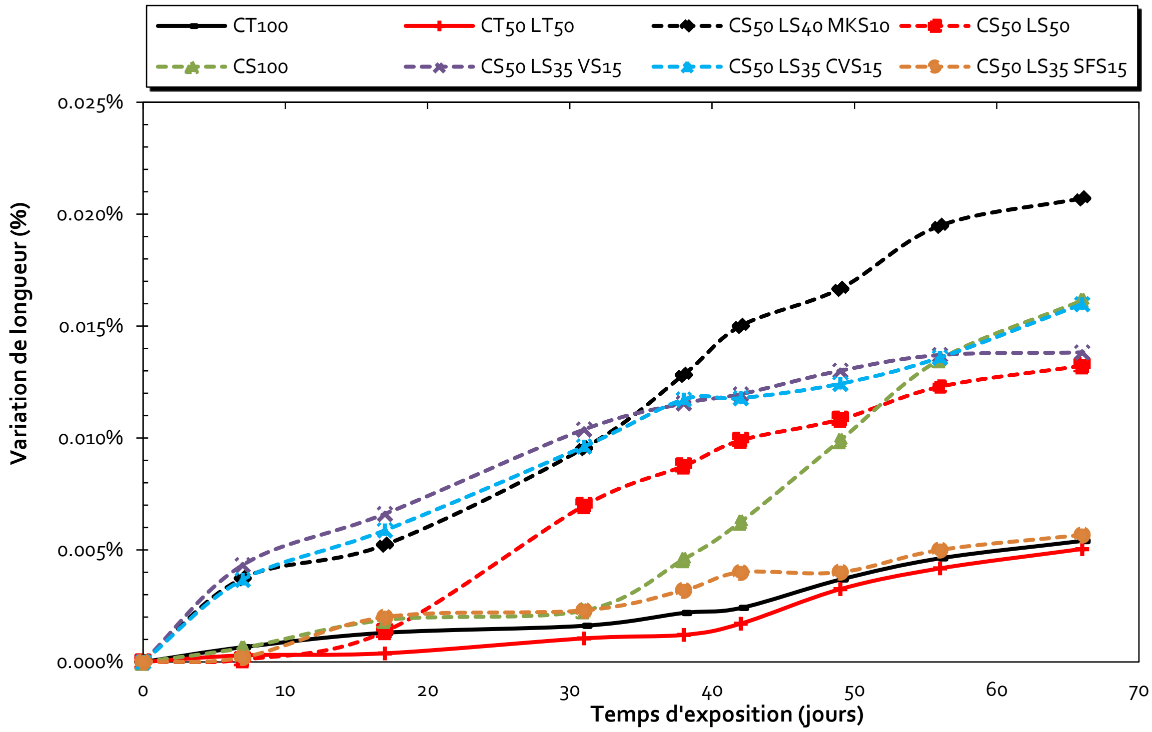

Figure 26. Expansion of specimens subjected to external sulfatic attack.

This expansion is the result of the formation of delayed ettringite in the cementitious paste and at the contact interface between the binding matrix and the grains of sand and sediment. As mentioned earlier, this area is a very favorable space for the development of expansive ettringitis. The ternary binder formulation CS100 LS35 SF15 has the least deformations while the formulation based on 100% cement CS100 is the one that deforms the most. Since the tests began after 54 days of maturation in water, this difference in dimensional variation highlights the improvement in mechanical and durability characteristics brought about by the use of ternary binders. Indeed, thanks to the pozzolanic activity of additions, which react with portlandite to form C-S-H, the effect of these additions is twofold. On the one hand, the amount of portlandite available to react with sulfates is reduced, so there will be fewer expansive products. On the other hand, the production of C-S-H makes it possible to fill the porosity possibly present in the cementitious paste, which will contribute on the one hand to limit the ion transfer via the interstitial solution, and on the other hand to strengthen the mechanical characteristics of the concrete and therefore its resistance to the stresses generated by the development of expansive products, especially during the crystallization of sodium sulfates.

It is also noted that the introduction of sediments leads to greater expansion. This is due on the one hand to the porosite which is more important for these formulations – and donc the sulfate ions will penetrate the structure of the concrete more easily. On the other hand, the weakening of mechanical strength due to the presence of sediments, will lead to greater cracking and therefore to more consequent deformations.

Figure 27 shows that the longitudinal deformation is accompanied by a mass gain for all the specimens. These results were expected because the more concrete is attacked and cracks begin to form, the easier it will be for the sulphate-laden solution to penetrate the concrete body. This mass gain, although important, can be attributed to the solution that lodges in the concrete. A decrease in the dynamic modulus was also observed on the different formulations as a function of the time of exposure (Figure 28). This decrease is 1% for formulations that do not contain sediment and about 4% for other formulations. This testifies to the development of cracks inside the specimens tested as a function of time.

Although signs of degradation have been observed on the different test tubes, all the forms can be considered resistant to sulfatic attacks and the risk of degradation of this pathology is very low.

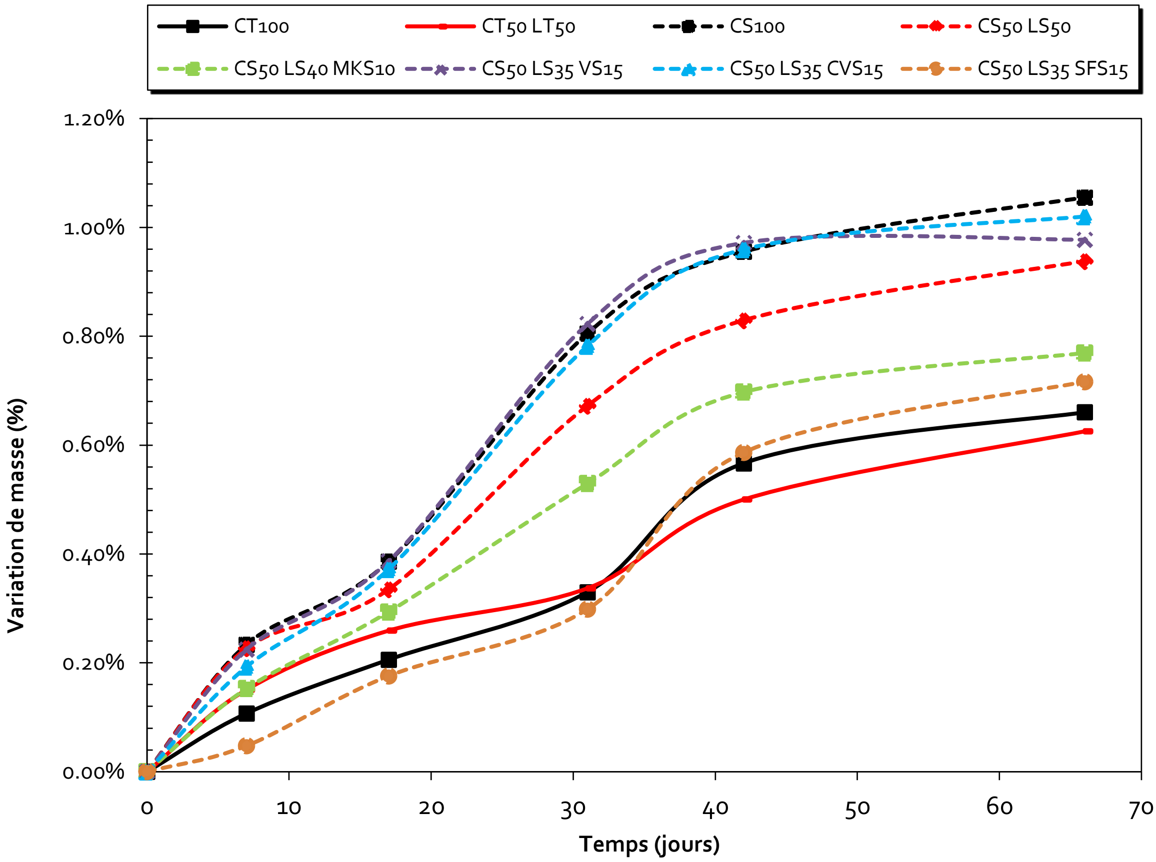

Figure 27. Variation in length of specimens subjected to external sulfatic attack.

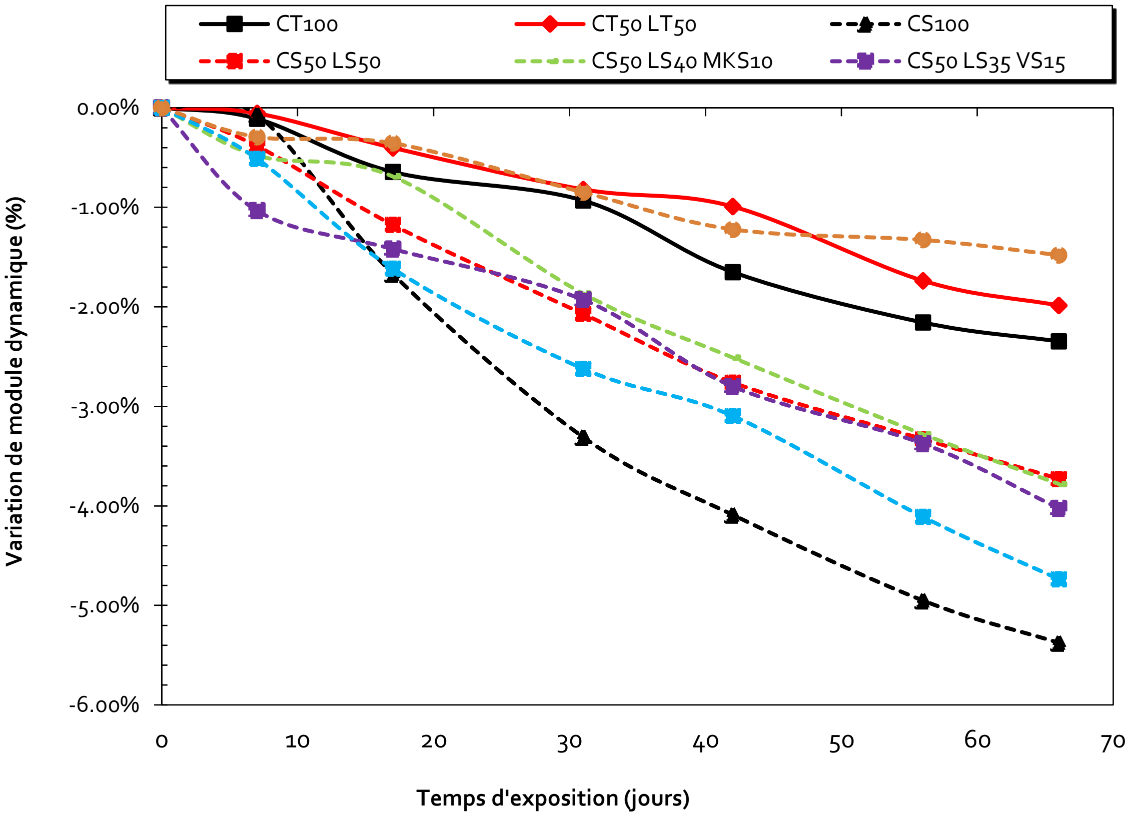

Figure 28. Dynamic modulus variation of specimens subject to ESR.

Alkali-reaction (NF P 18-454)

The alkali-reaction is one of the degradations that could affect the durability of concrete structures. Commonly known as the "alkali-aggregate reaction" (AAR), it occurs between alkalis (sodium Na^+ ions and/ or potassium K^+ ions) with the so-called "reactive" silica that comes from aggregates.

In France, the first findings of dam degradation by the AAR were observed in 1970. As early as 1994, recommendations were published by the LCPC to limit the risk of this pathology [29]. These principles have been incorporated into standard NF EN 206-1 on concrete[26].

There are three types of alkali-reaction: the alkali-silicate reaction, the alkali-carbonate reaction, and the alkali-silica reaction (ASR). Sar is the most common reaction. The steps of degradation of concrete by an alkali-silica reaction are presented inFigure 29. First, the OH^- ions found in the interstitial solution of the concrete act on the unstable silica of the aggregates by destroying the bonds (≡ Si−O−i≡; ≡ Si−OH), which will cause the silica to dissolve. This is accompanied by a release of negative charges (O^-) and will lead to the consumption of positively charged alkalis (Na^+ and K^+) to balance the charge in the vicinity of the reactive aggregates. This combination will form a silico-alkaline (Si–O–Na) and silico-calco-alkaline (C-K-S-H) gel, which will give rise to localized pressures that can cause cracks and swelling in the concrete: this is phase 2 of the degradation process by AAR. Finally, other elements that enter phase 3 of the degradation process and that have a central role in the formation of the expansive gel, are the calcium ions Ca^+. Indeed, the latter play a role of regulators of the amount of dissolved silica because they replace aux alkaline during the formation of the gel and thus release them to react again, which helps to make the reaction last. Studies have shown that the presence of more Portlandite $Ca(OH)_2$ helps to increase notamment swelling by maintaining a high pH [30]. Nevertheless, the mechanism of swelling related to AAR is still unanimous in the scientific community, several theories having been put forward in order to try to solve the problem: gonflement by crystallization pressure, hypothesis of electrical repulsive forces and osmotic swelling, swelling of porous bodies, etc. Among these hypotheses that of swelling by imbibition of water states that the gel formed from the reaction between reactive silica and alkalis, has the characteristic of adsorbing water and forming a swelling fluid [29].

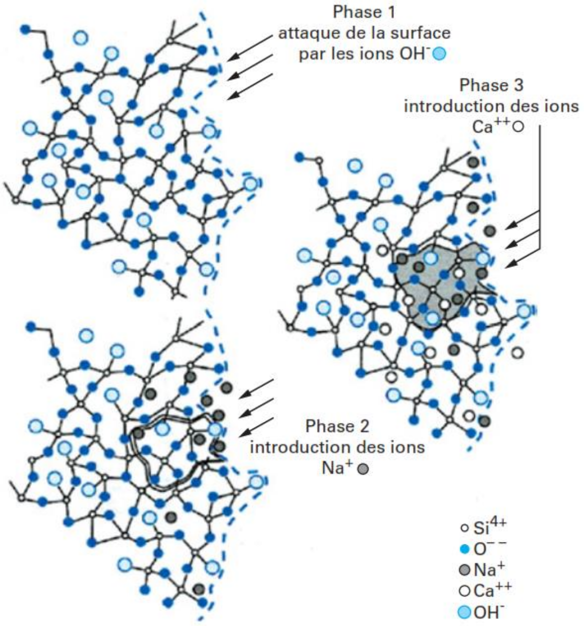

Figure 29. Stages of formation of the gel resulting from the alkali-reaction.

The main conditions that favor the formation of an AAR are:

- A sufficiently humid environment (> 80%);
- A high concentration of soluble alkalis: the higher the alkaline content, the greater the swelling;
- The presence of reactive silica provided in particular by reactive aggregates.

These three elements are considered essential for the de-launch of the AAR. Nevertheless, it is important to emphasize the role of certain parameters in the development of AAR [29][30][31][32][32]:

Aggregates: The type of aggregates is naturally important for the development of a AAR, with aggregates being the source of active silica that reacts with alkalis. The NF P18-594 standard of July 2015 defines the test method for the evaluation of the reactivity of aggregates and fascicle P18-542 specifies 3 classes of aggregates according to their reactivity: non-reactive (NR); potentially reactive (PR) and potentially reactive pessimum effect (PRP), the pessimum effect being presented as the interval for which it is found that for the same amount of alkalis, there is an amount of reactive silica that would cause maximum swelling.

Impact of porosity: the impact of porosity in the development of AAR is difficult to measure since it can be located at several levels in concrete (in aggregates, in cementitious pulp, the transition phase, pre-existing cracks, etc.). Nevertheless, its importance, especially at the level of the properties of transfer of the swelling gel through the connected pores, is proven.

Influence of particle size: the influence of the particle size of siliceous aggregates on swelling is one of the parameters highlighted in the literature. It would seem that the larger the particle size, the less swelling. The hypothesis put forward to explain this phenomenon is based on the fact that crushing makes it possible to make the initially closed pores accessible, and therefore allow a greater migration of alkalins to reactive silica.

Influence of water: if sometimes the water initially available in the pores of the aggregates is sufficient for the development of AAR, the amplitude of the swelling is all the more important as there is more free water during the formation of the gel. This influence is explained in particular by the fact that water acts as a transport vector for alkaline bases. At the level of the real scale, for the same structure, it was found that the swelling was greater for the submerged part than for cell which was not.

Temperature effect: according to LARIVE [29],, temperature plays a role in the development of AAR in the kinetics of reactions. However, the strength of silica is sensitive to the rise in temperature: the more it increases plus the solubility also increases; it is therefore difficult to say that the effect of temperature is limited to the change in the kinetics of reactions.

Influence of additions: Mineral additions are known for improving the durability properties of concretes when these additions are optimized. In the case of AAR, the addition of mineral addition occurs at several levels and depends on the physical and chemical characteristics of each addition. Indeed, these have an impact on the porosity of concretes: the addition of fine particles makes it possible to improve, by filtering effect and by production of C-S-H, the porosity and thus reduce the ion exchanges in the interstitial solution. Similarly, the pouzzoulanic reaction reduces the amount of portlandite in concrete and consequently reduces the amount of calcium ions. The latter also reduces the amount of alkalis available in the solution as well as the pH of the solution. The effect of additions also depends on the chemical composition of the additions: an addition richer in amorphous silica or with fewer alkalis would necessarily have a greater impact.

In this study, the alkali-aggregate reaction test was performed to assess the effect of sediment presence on swelling mechanisms. Indeed, as mentioned above, the amount of water available, porosity, particle size and chemical composition are all parameters influencing the formation and development of AAR and on which the presence of sediment will have a direct impact. The effect of using a ternary binder will also be investigated.

The test is carried out according to the standard NF P 18-454 of December 2004 on the reactivity of a concrete formula vis-à-vis the alkali-reaction. Its principle is based on the recommendations for the prevention of disorders due to alkali-reaction [33]. It makes it possible to evaluate the reactive potential of a concrete or mortar by monitoring the longitudinal deformation on three prismatic specimens of dimensions 4×4×16 cm or 7×7×28 cm, over-calibrated and subjected to special pressure and temperature conditions in order to accelerate and the degradation process.

For each formulation, 4×4×16 CEM mortar specimens were formulated according to NE EN 196-1. During the preparation of the test pieces, an amount corresponding to 4%[3] Na_2SO_4 equivalent soda was added to the spoil water in order to obtain the required alkaline content. The test pieces were then stored under water at 20°C for 60 days.

48 hours before the test, the specimens were removed from the water for the determination of the initial measurements: measurement of dimensional variation, mass variation and dynamic modulus through the measurement of the resonance frequency. The samples were then placed in an autoclave set at 120°C and 0.15 MPa for 5 h (Figure 30). New measurements were then carried out to identify possible disorders related to AAR.

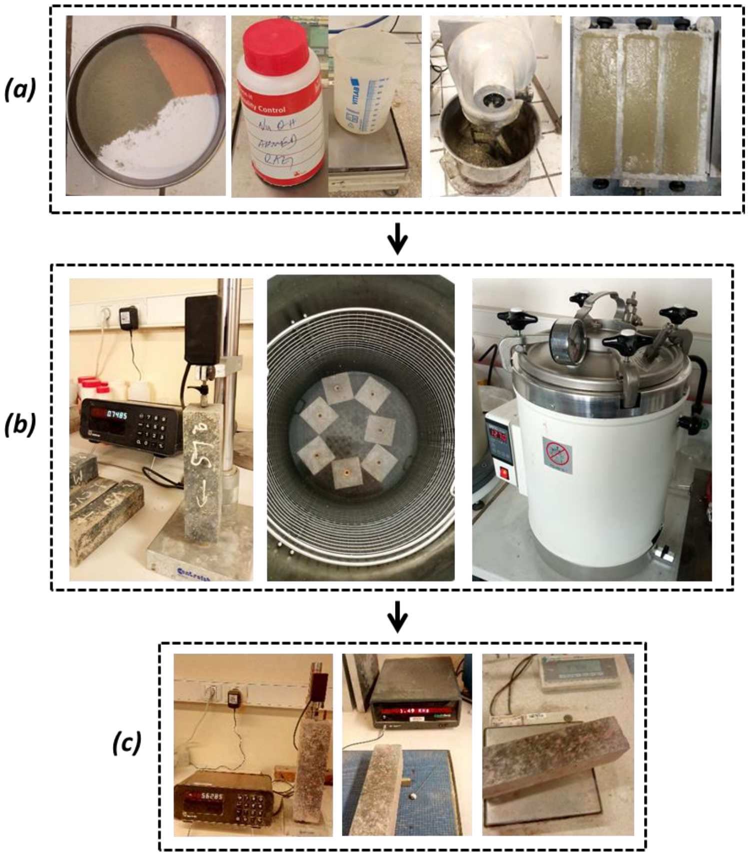

Figure 30. (a) manufacture of test pieces; (b) initial measurement and autoclaving; (c) measurement of dimensional variations, mass and resonance frequency.

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[3] Compared to the mass of the binder.

The results of these tests are presented in Figure 31.

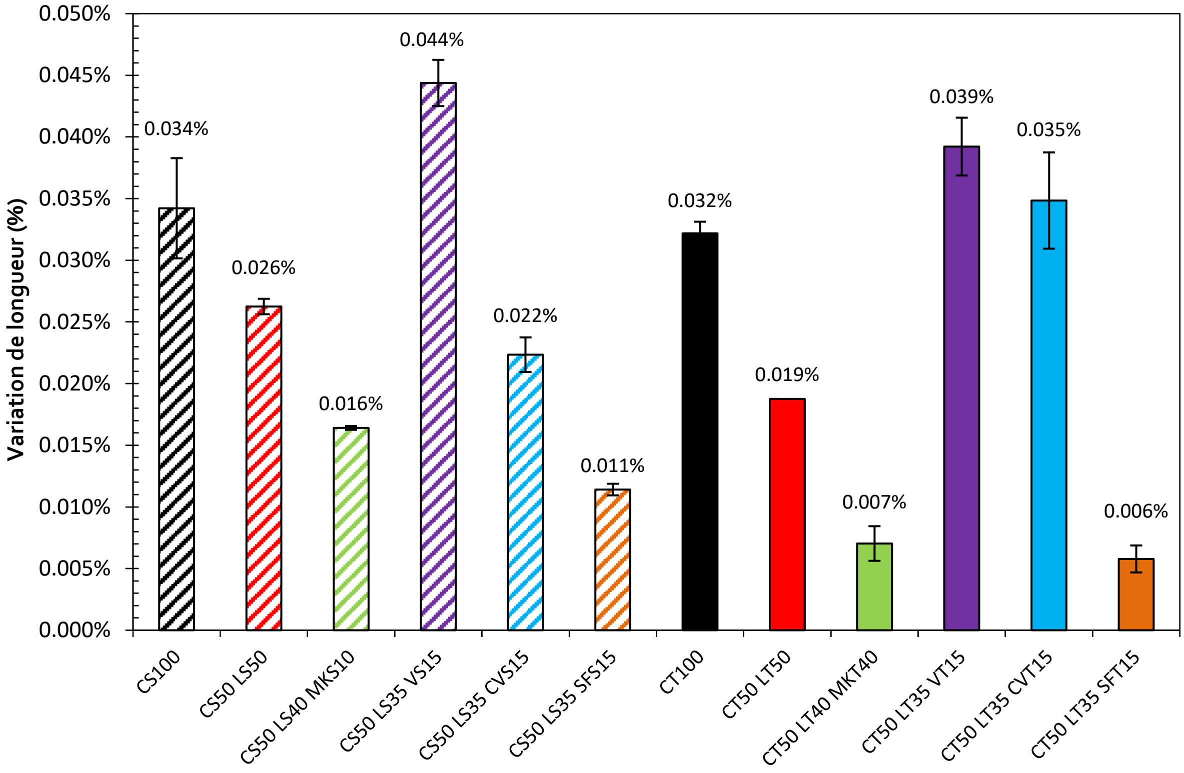

Figure 31. Longitudinal deformation of specimens after autoclaving.

Based on these results, sediment-containing mortar formulations show slightly higher swelling than control formulations. Several hypotheses can be made about this difference. On the one hand, sediments are composed of more than 50% quartz (SiO_2), which is a source of silica. This silica combines with alkaline ions to form a fluid that swells in the presence of moisture. In this way, the sediment increases the risk of AAR development. On the other hand, the presence of sediments causes a number of disorders such as increased porosity, lower mechanical resistance, alteration of the ITZ transition zone, etc. The attenuation of the characteristics of the mortars is at the origin of this amplified swelling.

It is also noted that, apart from the formulation based on glass waste, formulations based on ternary binders contribute strongly to the reduction of relative swelling, in particular the formulation based on calcined sediment by flash technique. The latter thus has swellings of 0.011% and 0.006% for CS50 LS35 SFS15 and CT50 LT35 SFT15 respectively against 0.034% and 0.032% for formulations based on 100% cement (CS100 and CT100) (Figure 31)." This clear improvement is attributed to several elements: on the one hand, the improvement of mechanical characteristics and porosity in the matrix; and on the other hand, the consumption of portlandite constituting a source of Calcium Ca^+ ions that combine with alkalis and promote swelling.

It is also noted that glass-based formulations have swellings greater than the controls. Indeed, during the characterization phase, it was found that the glasses are rich in sodium oxide (Na_2O) which is an important source of Na+ ions. However, as noted above, the greater the amount of alkaline ions available in the interstitial solution, the greater the risk of developing AAR degradation. The same observation can be established for the formulation CT50 LT35 CVT15 since flying ashes contain a significant amount of potassium oxide (K_2O).

Finally, with regard to the threshold value of the elongation to 0.15% defined in the standard NF P 18-454, all formulations meet this requirement and are non-reactive. The addition of sediment does not in itself constitute a risk of development of degradation by AAR.

Conclusion

In this part, concrete formulations based on ternary binders and control formulations were made. The study involved two groups of formulations, the first consisting of 100% sand, and in the second, 20% sand was substituted by sediment. A characterization of the concrete in fresh and hardened state as well as an evaluation of certain sustainability indicators were carried out. The main conclusions that can be drawn are:

- Fresh characterization showed that the incorporation of dredged sediments into concrete has an adverse impact on fresh characteristics, resulting in loss of workability, increased occluded air content and decreased absolute density. The use of ternary binders would seem to mitigate this impact. It is also noted that all formulations meet the requirements set out in the specifications.
- The hardened caraterization of the concrete formulations highlighted the impact of sediments on the mechanical performance of the concrete. Indeed, losses of compressive and flexural strength as well as a decrease in the dynamic modulus were observed for all formulations. It has also been found that the use of ternary binders contributes significantly to the improvement of the mechanical characteristics of concrete in the long term. In particular, the formulation CT50 LT35 SF15 records a 6% gain in compressive strength compared to the formulation containing 100% cement (CT100) at 120 days. This strength difference is even greater in "Group 2" formulations incorporating sediments, where the 120-day compression strength gain is about 40%. For artificial concrete riprap, a minimum resistance of 28 days of 30 MPa is recommended; all formulations have compressive strengths that exceed this value.
- The durability of the different formulations was achieved through the evaluation of the porosity accessible to water, the freeze/thaw test, the resistance to internal and external sulfatic attacks and the alkali-aggregate reaction test. The results of accessible porosity to water show that the use of sediment as a substitute for sand contributes significantly to the increase in overall

porosity in concrete. The use of ternary binders reduces this porosity in the long term, which will improve the durability of these formulations. Indeed, the results obtained on the freeze/thaw test showed that the formulations based on ternary binders all have lower swellings than those of the control formulations (CT100 and CS100). This improvement in resistance to freeze/thaw cycles is attributed in particular to the reduction in pore size and the improvement of mechanical characteristics. Elsewhere, all formulations are considered to be frost/thaw resistant because they have an elongation below the normative threshold of 500 µm/m.

The results of internal sulfatic attack tests have shown that formulations based on ternary binders allow a considerable improvement in ISR. Indeed, the reduction of the amount of C3A, the improvement of the porosity, and the latent characteristics of the additions are all parameters that allow this improvement. However, it is noted that all formulations record swellings of less than 0.04% at 3 months of follow-up, which presages a good resistance to internal sulfatic attacks.

Similarly, the external sulfatic attack was evaluated, highlighting the positive impact of the use of ternary binders. Indeed, because of the pozzolanic reactivity of additions, they are doubly beneficial: on the one hand, portlandite likely to react with sulfates is less available because it is consumed by the pozzolanic reaction; on the other hand, this reaction makes it possible to densify the structure and therefore to reduce porosity and consequently ion exchanges, without forgetting the improvement of mechanical performance. All these elements make ternary binder formulations have a better resistance to external sulphatic attacks compared to control formulations. Furthermore, although the use of dredged sediments tends to decrease resistance to ESR, all formulations are considered resistant to external sulfatic attacks.

The alkali-aggregate reaction was evaluated for the different formulations. The results show that ternary binder formulations, including C50 L35 SF 15, have the lowest swelling. This improvement is attributed to the consumption of Portlandite $Ca(OH)_2$, a source of ions that combine with alkalis and promote swelling. Improved porosity and mechanical strength are also factors justifying this strength. Although the use of glasses as a source addition of Na^+ ions as well as the presence of sediment tend to increase swelling, no formulation exceeds the 0.15% relative elongation threshold defined in the standard. The use of sediment as a substitute for sand does not pose a risk to the development of AAR.

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