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Posted Date: 7 August 2024

doi: 10.20944/preprints202408.0507.v1

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The Influence of Sodium Benzoate as Corrosion Inhibitor on Physical and Mechanical Properties of Concrete: Kinetics Study

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Abstract: This research aims to explore the use of sodium benzoate C6H5-COOH as corrosion inhibitor added to the mixing water of concrete, and test the mechanical performances of five types of concretes over several time periods, 7, 28, 56 and 90 days, in the absence and in the presence of limestone fillers. Hence the results confirm the increase in this resistance over time. Through this, tests were carried out cement paste after addition of sodium benzoate and limestone fillers, we see clearly that the start and the and setting time of cement shift out considerably which indicates that sodium benzoate aims to delay start and end setting time of cement. In addition, Abrams cone slump tests on concrete in the fresh state were carried out in order to see the influence of the addition of sodium benzoate and tests on the cement consistencies in the absence and presence of superplasticizing adjuvant "ORAFLOW THM 17200" which has the main role of improving the workability and quality of the concrete while comparing with ordinary concrete.

Keywords: admixture; concrete; sodium benzoate; corrosion inhibitor; limestone fillers; mechanical resistance; time

1. Introduction

Reinforced concrete, given the great advantages it offers in the field of construction, is placed as the first material used in this field, however, this material undergoes degradation over time which causes its aging and alters its durability.

Usual structures resist over the years the multiple physicochemical attacks to which they are subjected. However, it happens that defects in design, implementation or accidental causes are at the origin of disorders, and the notion of durability is thus inseparable from that of quality. In the case of reinforced concrete constructions, the durability of the structure essentially depends on the corrosion resistance of the reinforcements.

Corrosion of reinforced concrete was first recognized at the beginning of the 20th century and it has worsened in recent years with the widespread use of skyscrapers. There Corrosion of reinforcing steel in concrete is not only a very expensive problem, but it also endangers structural safety. To fix this problem, the use of corrosion inhibitors in concrete in recent decades has seen remarkable success in protecting reinforced concrete structures from corrosion especially for those carried out in aggressive environments.

Among these pathologies which attack the concrete material, corrosion of reinforcement remains the problem of concern to researchers and specialists in this field. In addition to the physico-chemical alterations appearing on concrete facings, the corrosion of reinforcements affects the durability of constructions, which leads civil engineers to practically find rapid solutions to remedy the harmful consequences of this phenomenon. The costs of rehabilitating structures damaged by corrosion are very high, as a result developed countries devote a special annual budget linked to corrosion [1]. Among the effective means of combating this pathology, the use of corrosion inhibitors remains a better alternative which has proven remarkable results in the medium and long term over the last two decades [2].

These corrosion inhibitors are chemical or plant-based products used preventively as additives to mixing water when making fresh concrete, or by impregnation on hardened concrete facings [3]. There are several categories of corrosion inhibitors, we distinguish, aminoalcols, carboxylates, molybdates and phosphates [4], Calcium nitrite, Sodium nitrite, Hexamine and Diethanolamine which have proven a remarkable improvement in compressive strength and to traction by flexion [5]. Marketed inhibitors were tested in order to determine their effectiveness via the corrosion of reinforcements, and thus their influence on the mechanical performance of the concrete samples which incorporate them [6].

The work we undertake is essentially experimental in nature and is part as part of a research theme whose main objective is, on the one hand, the study of the quality of concrete made from local materials, namely: cement from BeniSaf as well as aggregates from the Algerian national company of aggregates (E.N.G) while integrating inhibitor product aimed at protecting the reinforcements of the corrosion in the presence and absence of adjuvants which have the main role of improving the workability and quality of the concrete.

According to Nada (2008) [7], For the addition of sodium benzoate in concrete. (1% by weight of cement) there is no reduction in compressive strength at the ages of 28, 60 and 90 days, and the samples performed higher than the reference mixture (C25) by approximately 12%, 15% and 14% 28, 60 and 90 days respectively. Indeed, following the conclusions of Nada (2008) [7]. The use of sodium benzoate as corrosion inhibitor in concrete at 2% and 3% by weight of cement affects the resistance to compression at early ages (28 days) with a considerable reduction of 15% for addition of 2% and 11.5% for an addition of 3%, however, an increase in compressive strength of approximately 7% up to 17% at the age of 90 days was noted, which means that the compressive strength of this mixture increases with the age of the concrete in question. Likewise, concrete admixed with sodium benzoate revealed an increase in splitting tensile strength of approximately 10%, 16.6% and 17% for concrete specimens with respectively 1%, 2% and 3% of adjuvant by weight of cement [7].

The same author states that concrete mixtures with sodium benzoate presented a increase in the modulus of rupture of approximately 13%, 18% and 24% for proportions of 1%, 2% and 3% by weight of cement respectively.

So, in this research, we looked to integrate limestone fillers in order to increase mechanical performance of concrete.

Much research has linked the presence of limestone fillers with the evolution of resistance. The majority of them suggest that the resistance would be improved, or at least equivalent in the case of addition. Explaining in particular an improvement in mechanical properties by densification of the matrix obtained [8].

On the other hand, the incorporation of limestone fillers constitutes an important parameter which enhances the compactness of concrete by filling pore voids, corrosion inhibitors. So, our work focuses on the impact of the addition of an optimal concentration of sodium benzoate on the mechanical performance of concretes in the short term and long term while integrating new generation adjuvant and also limestone fillers.

2. Materials and Methods

2.1. Preparation of Concrete Specimens

After characterizing the construction materials used in the preparation of concrete, the Dreux Gorisse method was used for the formulation of this concrete, The specimens used in this study are: reference concrete, concrete+sodium benzoate and concrete+sodium benzoate+ adjuvant. Limestone fillers are products obtained by fine grinding of natural rocks (limestone, basalt, bentonite, etc.) having a calcium carbonate $CaCO_3$ content greater than 75%. These products, designated commercially as limestone fillers, are fine powders with particle sizes controlled and whose largest grains do not exceed 80 microns.

The Dosage of its constituent is given in Table 1.

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Table 1. Formulation of concrete [9].

Constituants : Dosage (Kg/m³)									
	Sand	Cement	Water	Gravel 4/8	Gravel 8/16	Gravel 16/25	Sodium Benzoate	fillers	Adjuvant
B0	807.22	350	177	168.29	405.91	393.32			
B1	807.22	350	177	168.29	405.91	393.32	5.101		
B2	807.22	350	177	168.29	405.91	393.32	5.101	38.88	
B3	807.22	350	177	168.29	405.91	393.32	5.101		1.75 L
B4	807.22	350	177	168.29	405.91	393.32	5.101	38.88	1.75 L

In this study five types of concrete were prepared: B0: Reference concrete; B1: Concrete+ Sodium benzoate; B2: Concrete + Sodium benzoate + Limestone fillers; B3: Concrete+ Sodium benzoate+ Adjuvant; B4: Concrete+ Sodium benzoate+ Adjuvant+ limestone fillers;.

The characteristics of limestone fillers used in this research are summarized in Table 2.

Table 2. Characteristics of limestone fillers [10].

Shape	Powder
Appearance	Homogeneous
Absolute density	2.75
Mass surface	2416cm2/g

The recommended rate of limestone fillers which offers greater resistance is obtained at a filler percentage of 10% calculated by the formula: F/C+F = 10%.[11].

After mixing the different constituents, we proceed to fill the 11x22 cylindrical specimens as well as the 10×10×40 cm3 prismatic specimens according to the NA 2600 standard intended for compression and tension tests by flexion respectively after the curing period.

These tests were carried out at 7, 28, 56 and 90 days in the absence and presence of an optimal concentration of the corrosion inhibitor, also the limestone fillers and superplasticizing adjuvant "ORAFLOW THM 17200".

2.2. Inhibitor Tested

Sodium benzoate (C_6H_5-COOH), is a preservative frequently used in the food industry, cosmetics, pharmaceuticals and even as an inhibitor of corrosion. It is a mono-carboxylate type agent which binds with a single anion (RCOO-). [12]

Sodium benzoate is the known organic inhibitor, due to its remarkable effectiveness against corrosion of steels. It is not toxic and does not present any dangers during its use. especially at low concentrations.

The product is stable and reactive with acids, slightly reactive with water and metals.

The concentrations added to the mass of fresh concrete have already been confirmed in previous studies, they gave maximum efficiencies against the corrosion of treated steels, they are summarized in Table 3.

Table 3. Concentration of the inhibitos [13].

Inhibitor	Concentration (mol/l)	Molar mass (g/mol)
C6H5-COOH	0.2	144.11

The dosage of the superplasticizer is: 0.5% (of the weight of cement)

2.3. Tests Carried Out on Fresh Concrete

1) Cement consistency and setting tests:

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2) Cement consistency test: In order to determine the quantity of water necessary to have a standardized consistency of the cement, this test was carried out using Vicat probe according to NA 230 standard.

3) Cement setting test: Using the Vicat needle, the start and end times of setting were recorded at a temperature of 20°C for the following samples:

- Reference cement paste
- Cement paste + Sodium Benzoate C6H5-COOH
- Cement paste + Sodium Benzoate+ limestone fillers

4) Slump test

The Abrams cone slump test was carried out according to the Algerian standard NA431 for each formulation on a fresh reference concrete and also on concretes containing the optimal concentrations of C6H5-COOH in the absence and in the presence of fillers and superplasticizer for the five types of concrete tested in this study in the fresh state.

2.4. Tests Carried Out on Hardened Concrete

2.4.1. Non-Destructive Testing: Dynamic Auscultation

This method makes it possible to measure the propagation time of an ultrasonic pulse passing through the concrete and also the propagation speed which will give indications on the concrete strength and identify the quality of the concrete.

The wave propagation speed is calculated by the following formula:

$$S = \frac{d}{t}$$

Where: d: height of the test specimen (cm)
t: propagation time (s)

While the resistance is calculated by the following equation:

$$R = 0{,}342 . e^{1{,}004 . S}$$

5) Storage of test specimens:

As part of this study, we used a single method of concrete conservation. The test pieces were completely immersed in water at an ambient temperature of 20°C ±2°C (Figure 1), in accordance with standard NA 426. In the meantime to prepare them for compressive and flexural strength tests at 7 days, 28 days, 56 days and 90 days.

Figure 1. Method of storing samples.

2.4.2. Destructive Measurements

a- Compression strength tests

These compressive strength measurement tests are carried out on 11x22 cm cylindrical specimens by a mechanical press in accordance with requirements of standard NF EN 206-1 following the different time limits. These tests are realized for the five types of concrete: B0, B1, B2, B3 and B4.

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Compressive strength is calculated by the following formula:

$$R_c = \frac{P}{S} \text{ (KN/cm}^2\text{)}$$

Hence: P represents the applied load (KN)

S: crushed surface of the sample (cm2)

B: Bending tensile tests

The tensile strength by three-point bending is obtained using the following formula:

$$RT = \frac{3\,F\,L}{2\,b\,h^2} \text{ (KN/cm}^2\text{)}$$

F: The applied load (KN)

b: The side of the prismatic test piece (cm).

h: height of the prismatic test piece (cm).

3. Results and Interpretations

Part one: cement tests

3.1. Consistency Tests and Cement Setting

The results obtained relating to the cement consistency and setting tests in the absence and presence of optimal concentrations of sodium benzoate are summarized in Table 4.

Table 4. Physico-mechanical properties of cement.

Mixture	Consistency test %	Start setting time (mn)	End setting time (mn)
Reference cement	24	168	278
Cement+ Fillers	24	167	275
Cement +Sodium Benzoate	23	198	303
Cement +Sodium Benzoate+Fillers	24	186	297

According to the results in Table 4, we see that the addition of Sodium Benzoate to cement tends to considerably shift the start and end of setting times when comparing with a sample without inhibitors, which could be beneficial when transporting fresh concrete. Although limestone fillers slightly reduce the start and end setting time. We can see clearly that the addition of limestone fillers means to regulate the start setting time and also the end setting time of cement, the benefic role of these additions is to keep the homogenous texture of cement. Therefore, it remains greater while compared with reference cement sample.

Referring to [10], the effect of adding of 5 to 28% of limestone powder to cement on the properties of fresh concrete tends to reduce the setting time when the filler rate increased and also decrease the amount of water and probably do not have an air-entraining effect. Limestone fillers have a good affinity with the cement matrix. Furthermore, they give the fresh concrete water conservation which limits segregation and bleeding. Several authors have noted that, for a constant dosage of cement (or a W/C ratio constant), the addition of limestone filler contributes to reducing the viscosity of a cement paste (despite the increase in the volume concentration of solids), before causing an increase viscosity when its dosage exceeds a certain critical value, which depends on the W/C ratio [10].

Part two: Fresh concrete

3.2. Slump Test

The results of the slump test on the different types of concrete made are given in Table 5.

Table 5. Results of the slump test.

Type of concrete	Slump or spreading (cm)

B0	Reference concrete	2
B1	Concrete +Sodium Benzoate	2
B2	Concrete +Sodium Benzoate+Limestone Fillers	5
B3	Concrete +Sodium Benzoate+ adjuvant	19
B4	Concrete+ Sodium benzoate+ Adjuvant+ limestone fillers	18

According to the results in Table 5, we see that the slump of the reference concrete is 2cm, which suggests that it is a firm concrete, and this even by incorporating the corrosion inhibitor, we can conclude that the sodium benzoate tested in our study does not influence the properties of our concrete in the fresh state.

Although the addition of the adjuvant marks a remarkable jump in slump which goes from 2cm to 19cm, this spreading confirms that our concrete becomes fluid in the presence of adjuvant. This result is logical since it is a new generation superplasticizer.

Also, we remark that the addition of limestone fillers changed the state of the fresh concrete, it went from a firm concrete (concrete + sodium benzoate) to a plastic concrete. According to [10] The effect of limestone results in greater compactness of the granular skeleton and will therefore have effects on the properties of concrete both in the fresh and hardened states.

However, the addition of superplasticizer adjuvant means to change the state of fresh concrete, it passes from a firm state in the presence of sodium benzoate to a plastic state after addition of limestone fillers to a fluid state, when incorporate the superplasticizer adjuvant; it will be benefic when pouring concrete with dense reinforcements.

3.3. Non-Destructive Testing: Dynamic Auscultation

The results of the dynamic auscultation tests are summarized in Table 6.

Table 6. Results of dynamic monitoring tests for made concretes .

Time (days)		Reference concrete	Concrete +Sodium Benzoate	Concrete +Sodium Benzoate+ fillers	Concrete +Sodium Benzoate+ adjuvant	Concrete +Sodium Benzoate+ Fillers+ adjuvant
7	Speed (Km/s)	4.27	4.26	4.28	4.30	4.32
	Resistance (Mpa)	25.00	24.7	25.65	25.12	25.83
28	Speed (Km/s)	4.50	4.41	4.55	4.52	4.54
	Resistance (Mpa)	31.43	28.83	32.17	31.07	32.24
56	Speed (Km/s)	4.87	4.49	4.74	4.67	4.69
	Resistance (Mpa)	45.44	31.03	35.08	36.23	33.11
90	Speed (Km/s)	4.87	4.71	4.76	4.65	4.72
	Resistance (Mpa)	45.44	41,10	42.69	41.89	42.78

According to the results in Table 6, we note that the addition of sodium benzoate reduces the compressive strength of concrete at young age by 21%, this result remains to be confirmed by destructive measurements. Whereas for other ready-made concretes, the addition of the inhibitor or adjuvant does not significantly influence the mechanical resistance at 7 days. Furthermore, at 28 days we see that the addition of the inhibitor reduced this resistance by 2.6% when comparing to the reference concrete, although the addition of the adjuvant comes to remedy this problem and it exceeds even that of a reference concrete of 2.35%. At 56 days, these resistances are practically lower than those of a reference concrete, of the order of 18.2% with the addition of sodium benzoate, the contribution of the adjuvant remains beneficial and tends to enhance these resistances. In the longer term 90 days, the compressive strengths of concrete with inhibitors decrease by 9.55%, the adjuvant has no negative effects on the evolution of the strengths according to these results which remain to be confirmed at using destructive testing.

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By analyzing the results illustrated in Figure 2, we note that the resistances recorded using non-destructive methods: ultrasound reach their maximum values at 90d, these resistances are slightly lower compared to the reference concrete not exceeding 10%, the adjuvant used improves workability and does not affect these resistances according to these non-destructive tests. Through these results, we note that the limestone fillers added to the concrete increase its resistance at 28 days, but the presence of corrosion inhibitors at an optimal concentration slightly reduces these resistances, we note that sodium benzoate decreases the resistance when comparing with a Reference concrete even in the presence of limestone fillers. We can see that limestone fillers tends to increase compressive strengths compared to the other formulations. Some authors, such as Campitelli and Florindo [8] who studied the beneficial effect of fillers on mechanical properties. The addition of filler introduced at the time of grinding would lower the strength performance of cements, even for the optimum SO_3 present in the cement, whatever the percentage of addition or the fineness thereof. Concurrent grinding with fillers does not promote good particle distribution in size. In particular the greater part of clinker in the large particles would not favor the development of resistance in young adulthood [14].

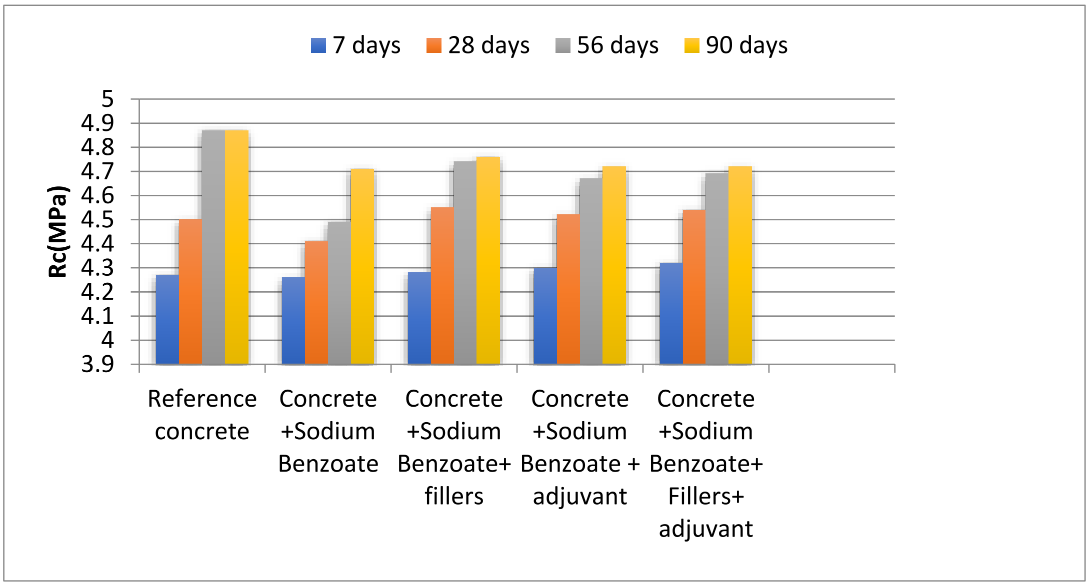

Figure 2. Evolution of ultrasonic compressive strengths.

3.4. Destructive Testing

a- Compression tests

The results of the compressive tests on concrete specimens for different types of concrete made are given in Table 7.

Table 7. Compressive strengths by destructive measurements.

Type of concret	Compressive strengths (MPa)			
	7 days	28 days	56 days	90 days
Reference concrete	16.96	23.48	37.05	37.88
Concrete +Sodium Benzoate	19.22	23.58	27.54	30.09
Concrete +Sodium Benzoate + limestone fillers	19.78	24.98	29.49	31.30
Concrete +Sodium Benzoate+Adjuvant	19.43	24.78	28.46	29.12
Concrete +Sodium Benzoate + limestone fillers +adjuvant	24.81	26.7	30.49	30.30

Through results illustrated in Table 7, we can see that at early age 7 days, of concrete, compressive strength for reference concrete is the lower compared with the other samples, however

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its better improved for concrete with sodium benzoate+ limestone fillers + adjuvant. It shifts from 31.64% compared to reference concrete. For the same type of concrete, in the long term 56 and 90 days, the compressive strengths decrease when compared with the reference concrete.

In order to better compare the evolution of the compressive strengths for the different concretes made over the time periods studied, we have drawn the histogram illustrated in Figure 3.

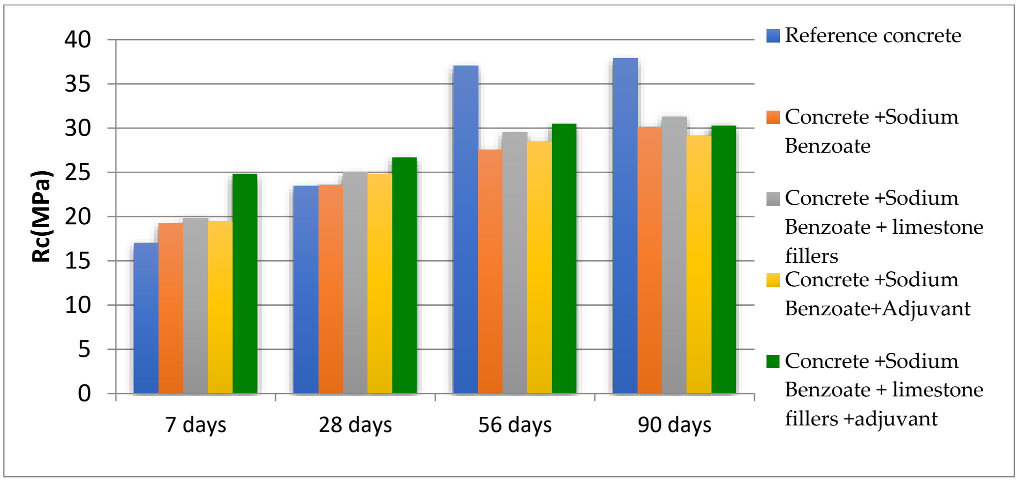

Figure 3. Evolution of compressive strengths by destructive measurements.

The results in Figure 3 represent the compressive strengths by destructive measurements for the different concrete compositions at well-specified time periods. We note that for a young concrete "7 Days", the resistance of a concrete with sodium benzoate is higher than the other ready-made concretes as well as that of the reference concrete by 35.29%. For the latter, its resistance is lower than that of other concretes, we can therefore conclude that sodium benzoate has a positive influence on the mechanical properties of concrete at 7 days.

While at 28 days, we see that the compressive strength of a concrete with sodium benzoate is similar to the resistance for reference concrete, the highest value was recorded for concrete with sodium benzoate, limestone fillers and adjuvants, when comparing with reference concrete, also, the addition of the adjuvant did not considerably improved the mechanical resistance of concrete incorporating corrosion inhibitor.

At 56 Days, we can clearly see that the mechanical resistance of all the concretes produced is slightly lower than that of the reference concrete. Furthermore, at 90 days, the compressive strengths tend to decrease in the presence of sodium benzoate and adjuvant, they remain lower when comparing with a reference concrete. By analyzing the effect of adding limestone fillers and their influence on mechanical resistance at 28 Days, we see that they improve slightly the compressive strength resistances for concretes with sodium benzoate weather for concrete with adjuvants compared to reference concrete. According to the results obtained, the addition of limestone fillers did not really improve the compressive strengths of the concretes studied in the presence of corrosion inhibitors and adjuvants, moreover, their positive effect on flexural strengths was detected for all time periods studied.

Concerning the influence of the adjuvant used on the mechanical performance of concrete, we

We notes that at young ages, compressive strengths are slightly improved, while that at 90 days, these resistances tend to decrease. While the bending resistances in presence of adjuvants and inhibitors are slightly improved.

b- Bending tensile tests

The results obtained relating to bending strengths are presented in Table 7, they present the effect of the addition of sodium benzoate as corrosion inhibitor, adjuvant and limestone fillers on the compressive strengths for the different concrete compositions.

The results of the tensile bending tests carried out on prismatic specimens are summarized in Table 8.

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Table 8. Bending tensile strengths.

Types of concrete		Bending tensile strengths (MPa)			
		7 days	28 days	56 days	90 days
B0	Reference concrete	7.86	7.74	11.04	10.86
B1	Concrete +Sodium Benzoate	7.38	9.12	9.12	9.78
B2	Concrete +Sodium Benzoate + limestone fillers	8.31	10.02	9.36	10.2
B3	Concrete +Sodium Benzoate + adjuvant	8.33	10.05	9.34	10.6
B4	Concrete +Sodium Benzoate + limestone fillers adjuvant	8.36	11.46	11.31	11.25

In order to better compare the evolution of the Bending tensile strengths for the different concretes made over the time periods studied, we have drawn the histogram illustrated in Figure 4.

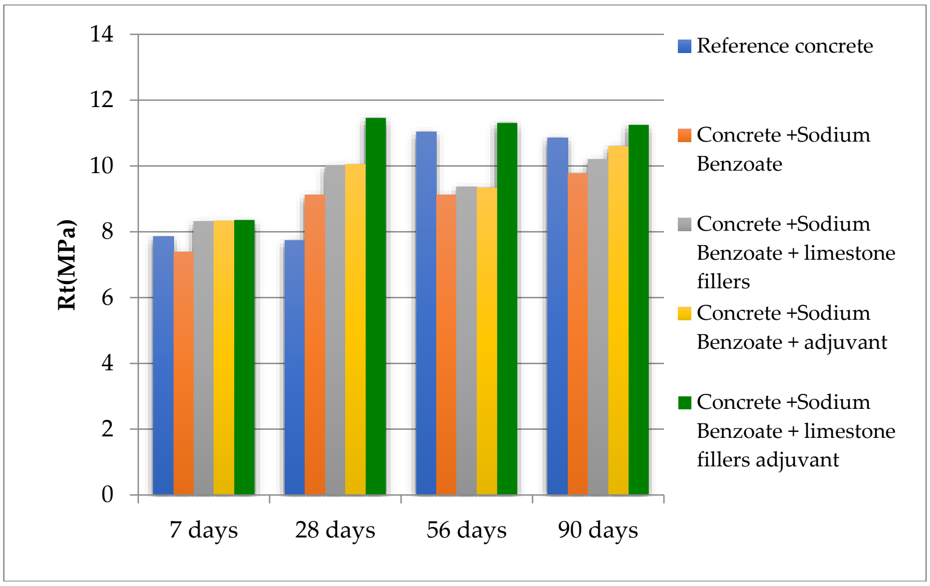

Figure 4. Evolution of tensile strengths by bending.

According to the results illustrated in Figure 4, we note that for a young concrete "7 Days", the flexural resistance of a concrete with sodium benzoate and adjuvant is slightly higher than that of other concretes made as well as 'to that of the reference concrete of 5.41%.

While at 28 days, we see that the flexural resistance of a concrete with sodium benzoate+ limestone fillers +adjuvant is higher when compared with a reference concrete whose resistance remains the lowest when compared with the other compositions of concrete. The addition of the adjuvant improves these flexural strengths for concretes with corrosion inhibitor. However, limestone fillers remain to increase slightly this resistance

At 56 Days, according to the results illustrated in Figure 3, there is an improvement in the tensile strength for the reference concrete, but, we don't see any modification in the resistance for samples with sodium benzoate, however, limestone and adjuvant acts to regulate this parameter and increase slightly the resistance by bending of 17.39% recorded for a concrete with sodium benzoate compared to the reference concrete, on the other hand the addition of the adjuvant tends to increase this resistance by 5.97%, when comparing with a reference concrete.

Although at 90 Days, we notice that the tensile strength of the ready-made concretes is slightly lower than that of the reference concrete, in the presence of adjuvant, the resistance values improve by 6.85% compared to concretes without adjuvant.

Grinding the clinker and limestone fillers reduces the proportion of clinker in the mixture and therefore reduces the strength achieved. Finer grinding could be carried out to obtain strengths

 doi:10.20944/preprints202408.0507.v1

equivalent to a mixture without addition. But for additions between (5 and 10%), the resistances are not significantly reduced. And more intense grinding is not particularly indicated.

4. Conclusions

We studied the influence of the addition of Sodium benzoate, limestone fillers and superplasticizing adjuvant on the properties of concrete in the fresh and hardened state, as well as the addition of a superplasticizing adjuvant (THM oraflaw 17200) and limestone fillers on the evolution of mechanical resistance in the short and long term. All conclusions are summarized in the following points:

- The addition of Sodium Benzoate to cement don't modify the consistency of cement,
- The addition of Sodium Benzoate to cement tends to considerably delay the start and the end of setting times when comparing with a sample without inhibitors, which could be beneficial when transporting fresh concrete. Although limestone fillers slightly reduce the start and end setting time.
- The results obtained reveal that sodium benzoate inhibitor do not significantly influence the properties of the concrete in the fresh state according to the slump tests carried out;
- According to the results of the tests on fresh concrete, we see that sodium benzoate do not considerably influence the slump of the concrete, although the addition of adjuvant make it fluid.
- Although the addition of the adjuvant marks a remarkable jump in subsidence from 2cm at 19cm, this spreading confirms that our concrete becomes fluid in the presence of adjuvant. This result is logical since it is a new generation superplasticizer.
- We note that the resistances recorded using non-destructive methods: ultrasound reach their maximum values at 90d, these resistances are slightly lower compared to the reference concrete not exceeding 10%, the adjuvant used improves workability and does not affect these resistances according to these non-destructive tests. Through these results, we note that the limestone fillers added to the concrete increase its resistance at 28 days, but the presence of corrosion inhibitors at an optimal concentration slightly reduces these resistances
- Concerning the influence of sodium benzoate on the mechanical resistance of concrete by destructive tests at different ages; we note that sodium benzoate improve this resistance at a young age and tend to reduce it at 90 days.
- The effect of adding limestone fillers and their influence on the mechanical resistance at 28 days was also studied, it can be seen that they improve the resistance for all concrete compositions by comparing with the reference concrete,
- Concerning the influence of the adjuvant used on the mechanical performance of concrete, we note that at young ages, the compressive strengths are slightly improved, while at 90 days, these strengths tend to decrease. While the tensile strengths by flexion in the presence of adjuvant and sodium benzoate is slightly improved.

Acknowledgments: The authors gratefully acknowledge the EOLE laboratory, the University of Tlemcen, and the Directorate General for Scientific Research and Technological Development (DG-RSDT-Algeria) for supporting this work.

Disclosure statement: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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