SOME EFFECTS OF LIMESTONE FILLER AS A PARTIAL SUBSTITUTE FOR CEMENT IN MORTAR COMPOSITION

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Abstract

Limestone filler is a raw material that is already used in several applications like paints, bricks, bituminous mixes, … Moreover, and particularly in Belgium, classical additions like fly ashes and blast furnace slags become rare. There is a need for new additions that could have a positive effect on the properties of the fresh and hardened cementitous composites.

Substitution of limestone filler in Portland cement and blast furnace slag cement has been realized between 15 and 27 % in mass.

In addition to the characterization of the powder itself – specific mass, specific surface and laser granulometry – the problem of the water demand has been analysed: it seems that it remains constant with the substitution rate. Electric conductivity has also been performed in order to study the evolution of the "dormant" period.

Tests on hardened mortars concerned the mechanical properties, the evolution of the porosity and the durability. The i factor indicates a higher value and the porosity seems to be better in the case of blast furnace slags cements, partially due to a very low diameter of the slags particles.

Oxygen permeability doesn't seem to be influenced by the filler while capillary absorption increases with substitution rate. Finally, carbonation rate, sulphate resistance and chloride penetration show quite interesting behaviours, leading to the conclusion that this material needs more investigations in order to define optimum application conditions in cementitous matrixes.

Keywords: limestone, filler, substitution, mortar

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1. Introduction

In Belgium, classical additions for concrete like fly ashes and blast furnace slags, are becoming rare. Limestone filler is quite abundant and already used in several applications. The idea of this research is to use limestone filler in substitution of the cement in mortars compositions. Limestone filler is actually cheaper and less polluting than cement. So, we studied the effects of such a substitution. Two cements (Portland cement and blast furnace slag cement) and four rates of substitution (0, 17, 23 and 27 % by mass) were tested, i.e. eight mixtures.

The first part of this paper talks about the materials used and justifies the proportions in the mixtures. The second part discusses the tests results. The cement paste was first analysed with regards to its water demand and the electric conductivity gave us information about the hydration process. Afterwards, tests were carried out on fresh and hardened mortar in order to determine properties like porosity, mechanical performances (strengths and shrinkages), permeability to oxygen, capillary absorption and durability (carbonation rate, sulphate resistance and chloride penetration). The activity index of the limestone filler based on compressive strengths was determined but, as it refers only to a mechanical property, an interaction ratio was also calculated in order to assess the effect of the limestone filler on each measured property.

2. Materials and mixtures

2.1. Materials

A normalized sand (CEN EN 196-1) and water tap were used. The Portland cement was of CEM I 42.5 R HES type and the blast furnace slag cement was re-composed with 65 % (by mass) of Portland cement and of 35 % of blast furnace slag (bfs). The filler came from a limestone quarry. Table 1 shows the mineralogical composition, the specific mass and the specific surface of the three powders that composed the binders. Figure 1 presents their particle size distribution.

Table 1: Mineralogical composition (% by mass), specific mass (kg/m³) and surface (m²/kg)

	Portland cement	**Blast furnace slag**	**Limestone filler**
CaO	62.8	38.46	98.1 ($CaCO_3$)
SiO_2	19.3	35.08	0.533
Al_2O_3	5.1	13.47	0.166
Fe_2O_3	3.1	0.51	0.082
MgO	0.8	8.5	0.35
SO_3	3.1	0.1	0.085
Specific mass	3 090	2 890	2 700
Specific surface	385	440	305

2.2. Mortar compositions

All the compositions have the same sand and water contents. Water demand and consistency tests showed indeed that these two properties remained constant whether limestone filler was incorporated or not. It was then decided to use a water-to-binder ratio of 0.45 (by mass) for all the mixtures. Four substitution rates were tested with the two cements (0, 17, 23 and 27 % by mass). Table 2 presents the eight compositions tested.

All sample preparations were processed in a similar manner, according to European Standard EN 196-1 [1]. Water was first introduced in the mechanical blender. The dry mix solids (cement + filler) were then added to the water solution and mixed for 30 seconds at low speed; sand was added and mixed for 30 seconds. Then the mixing proceeds in a sequence of three steps: 30 seconds mix at high speed, 90 seconds in rest, 60 seconds mix at high speed. The mortar was cast into moulds, cured with plastic sheet and after 24 hours, the hardened mortar was demoulded.

Table 2: Mortar compositions

Cement used	% filler	Name	Portland Cement (kg/m³)	Bfs (kg/m³)	Filler (kg/m³)	Sand (kg/m³)	Water (kg/m³)	Air (%)
Portland P	0	P0	504	0	0	1513	227	3.86
	17	P17	429	0	77	1518	228	3.23
	23	P23	390	0	114	1512	227	3.40
	27	P27	368	0	138	1520	228	2.79
Bfs cement L	0	L0	329	177	0	1519	228	3.13
	17	L17	277	149	77	1510	227	3.38
	23	L23	253	137	114	1512	227	3.08
	27	L27	238	128	138	1514	227	2.91

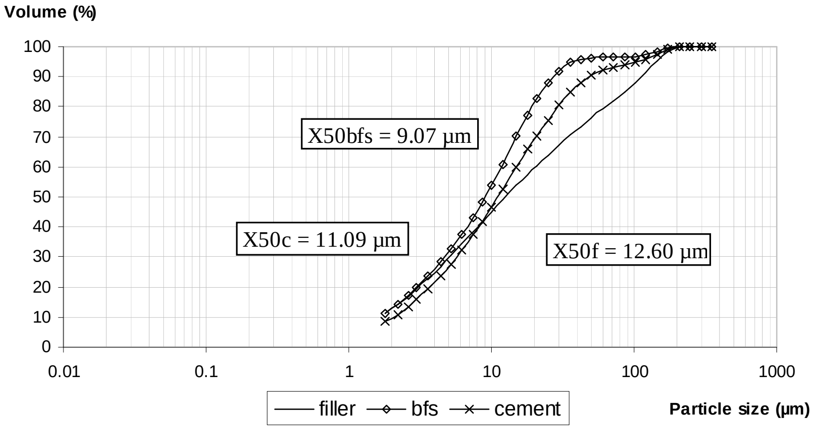


Figure 1: Particle size distributions of the three powders

3. Results and discussion

3.1. Tests on cement paste and fresh mortars

The tests on cement paste concern first the water demand and the electric conductivity. The water demand (Figure 2) is characterized by the factor β (expressed by mass): it varies from 0.31 to 0.35 for all the mixtures tested. It is not a significant variation so we can conclude that the water demand remains constant with the substitution of cement by limestone filler.

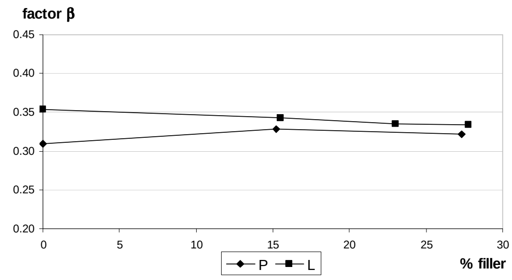


Figure 2: Water demand (factor β expressed by mass) for P and L samples

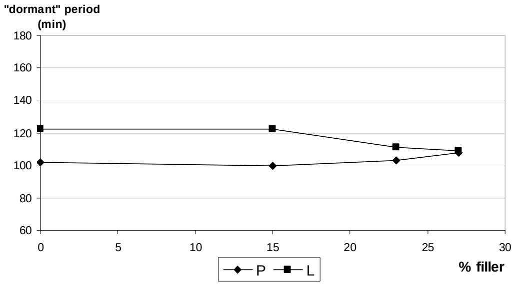


Figure 3: The "dormant" period for P and L samples

Because it is dependant on the ions dissolved in the solution, the measure of the evolution of the electric conductivity over time can give information about the hydration process. The "dormant" period is representative of the setting time: at the end of this period, the setting really begins. As shown on figure 3, the "dormant" period, i.e. the setting time, is shorter for the L-mixtures when the binder contains filler. It can be the sign of the formation of carboaluminates that accelerate the setting [2]. We can also see that the duration of the "dormant" period is longer for the L-mixtures than for the P-mixtures. This is due to the latent characteristic of the blast furnace slag.

The workability of mortars was evaluated according to flow rate test [3]: the results show that the consistency remains constant for all the mixtures, which is in accordance with water demand evaluation.

3.2. Hardened mortar tests

First of all, the "open" porosity was determined by a water absorption test [4] (Figure 4). Water absorption is growing between 0 and 15 % of substitution of cement by limestone filler. Between 15 and 27 %, it doesn't seem to evolve. Compositions containing blast furnace slags show a lower "open" porosity; which is probably due to the lower diameter of the blast furnace slag particles.

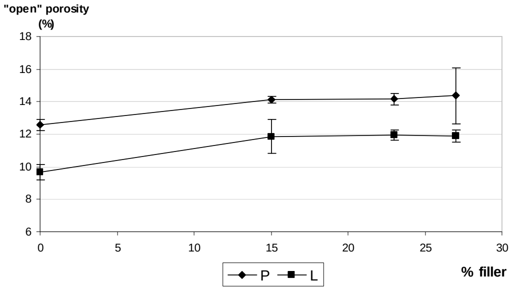


Figure 4: "open" porosity for P and L samples, measured by water absorption

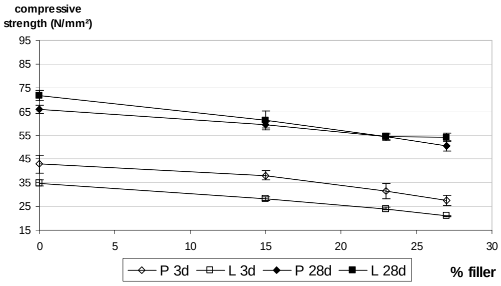


Figure 5: Compressive strength at 3 and 28 days for P and L samples

3.2.1. Mechanical properties

The first mechanical properties are the compressive and flexural strengths [1]. The results of the flexural strength tests were not reliable so we didn't take them into account. According to the literature, limestone filler should improve the transition zone between aggregates and cement paste and reduce its thickness [2]. Flexural strength is a function of the tensile strength, which depends on the thickness of the transition zone. Theoretically, flexural strength should be improved by the limestone filler and more investigations are needed about this subject, i.e. scanning electron microscope investigations.

The compressive strength decreases when cement is replaced by limestone filler (Figure 5). This is due to the decrease of the cement content and the rising of the water-to-cement ratio as substitution increases. Figure 5 shows also the well-known difference between the two cements tested: blast furnace slag cement presents a lower strength at early age (- 19 %) but a higher strength at 28 days (+ 9 %) than the Portland cement.

The i factor (or activity index) can be calculated as the ratio of the compressive strength of a mortar where 25 % (by mass) of cement are replaced by limestone filler (with a water-to-binder ratio of 0.5) and the compressive strength of a normalized mortar [5]. The i factor of the filler is 0.70 when Portland cement is used and 0.76 when the blast furnace slag cement is used. For a water-to-cement ratio of 0.5, the loss of strength at 28 days is greater for the Portland cement than for the bfs cement when 25 % of the cement are replaced by limestone filler. The i factor only takes into account a *mechanical property* and is calculated for a constant water-to-binder ratio. Inspired by the literature [6], we calculated an interaction ratio which relates properties to the cement content (Equation 1).

$$\mathrm{II} = \frac{S_{\%} / C_{\%}}{S_0 / C_0} \qquad (1)$$

where II is the interaction ratio,
S is the measured property,
C is the cement content,
the index % refers to a composition which contains x % of limestone filler,
the index 0 refers to a composition without filler.

The interaction ratio shows the effect of the limestone filler, considering the cement content. For the compressive strength, it shows that the filler has a positive effect on the P-mixtures for all the substitution rates tested and on the L-mixtures, from 24 to 27 % (Figure 6).

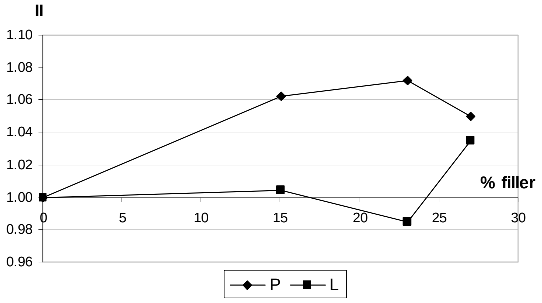


Figure 6: Interaction ratio for the compressive strength for P and L samples

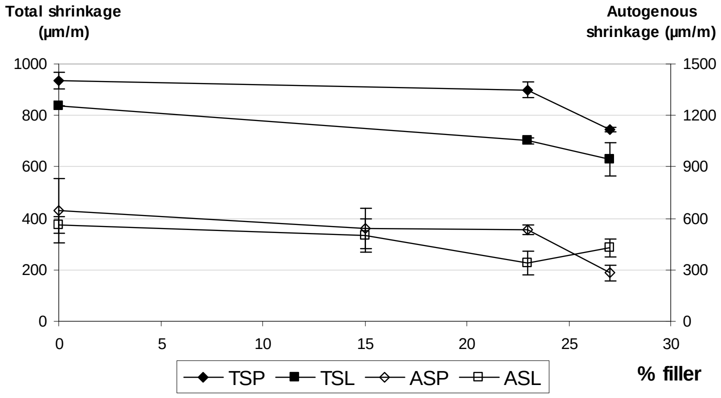


Figure 7: Total and autogenous shrinkages after 28 days for P and L samples

Another important property is the shrinkage of the mortar. The total shrinkage was measured on specimens stored at 20 °C and 65 % HR [7]. It decreases as the substitution increases (Figure 7). This is due to the decrease of the cement content and raise of the water-to-cement ratio as the substitution rate increases (considering that the cement content decreases when cement is substituted by limestone filler). If the quantity of cement is smaller, the autogenous shrinkage has to be lower. Portland cement presents more shrinkage than the bfs cement (Figure 7). The L-mixtures lose more water during the test and they have less chemical shrinkage.

The autogenous shrinkage was measured on specimens that had been coated by aluminium foil and epoxy paint (Figure 7). The autogenous shrinkage generally decreases as the substitution rises. This is also due to the lower cement content and the higher water-to-cement ratio, which keeps a high internal humidity high and induces a lower chemical shrinkage.

The interaction ratio calculated according to equation 1 shows a negative effect of the filler on the total shrinkage but a positive effect on the autogenous shrinkage for P-mixtures from 24 to 27 % and for L-mixtures between 16 and 26 % of substitution (Figures 8).

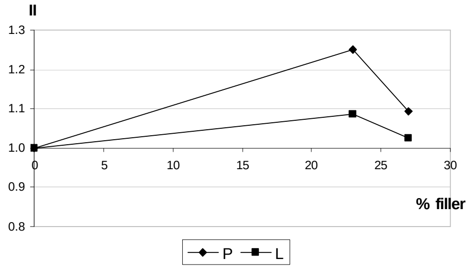


Figure 8a: Interaction ratio for the total shrinkage for P and L samples

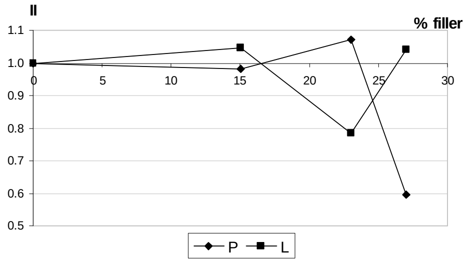


Figure 8b: Interaction ratio for the autogenous shrinkage for P and L samples

3.2.2. Porosity properties

In order to determine permeability to oxygen, a cylindrical specimen is drilled and put into the permeability test device (Figure 9). A pressure is imposed at the bottom of the sample and permeability to oxygen is determined from the oxygen flow measured at the top side [8]. This test shows that the oxygen permeability remains constant for all the compositions. The limestone filler doesn't seem to have any influence. This property depends on the interconnected pores and is not related to the "open" porosity described before: this "open" porosity was indeed determined by a water absorption test and the molecules of oxygen have smaller dimensions than those of water.

The capillary absorption [9] is characterized by the sorption coefficient (the slope of the line representing water absorption by surface unit as a function of the square root of the immersion time). The sorption coefficient increases with the substitution rate (Figure 10). This result can be related to the "open" porosity.

The interaction ratio shows a negative effect of the limestone filler for the P-mixtures and a positive effect for the L-mixtures between 0 and 25 % of substitution for the permeability to oxygen. The interaction ratio for the capillary absorption shows a negative effect of the limestone filler on the porosity characteristics tested for all the compositions (Figures 11).

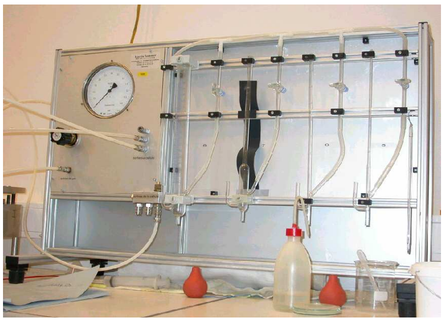


Figure 9: Permeability test device

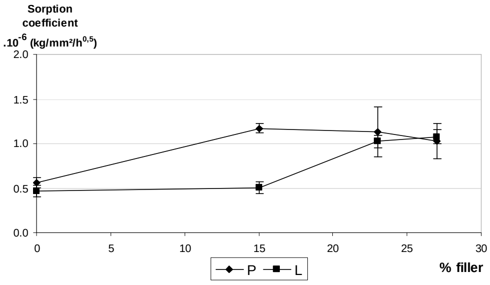


Figure 10: Sorption coefficient for P and L samples

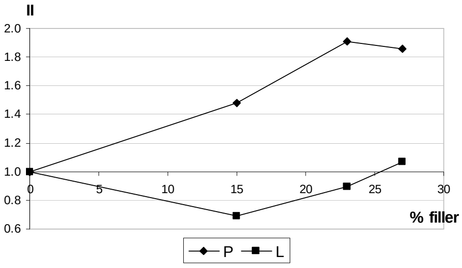


Figure 11a: Interaction ratio for the intrinsic permeability for P and L samples

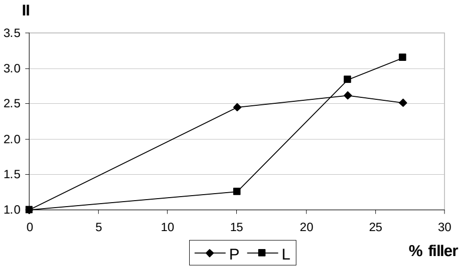


Figure 11b: Interaction ratio for the sorption coefficient for P and L samples

3.2.3. Durability

The durability of the mixtures was analysed with regards to the carbonation rate, the chloride penetration and the sulphate resistance. These properties are dependant on the open porosity that permits or not the intrusion of aggressive agents. The transport mechanism is the diffusion: the aggressive agent is moving according to a difference of concentration.

The carbonation is a reaction between lime and carbon dioxide and it induces a decrease of the pH of the interstitial solution of concrete. The carbonation rate is determined with phenolphthalein test [10]. Figure 12 shows the carbonation depth of the compositions tested after 3 months of exposure to CO_2 (1 % concentration and 60 % R.H.). The carbonation depth increases as the filler content rises. We can relate this result to the "open" porosity: when it increases, the molecules of CO_2 can penetrate easier into the mortar.

The effectiveness of limestone fillers was evaluated by means of two other durability tests [11]: chloride diffusion (1) and sulphate attack (2):

- (1) Rates of diffusion of Cl^- and Na^+ ions into cement mortars are monitored using two compartment diffusion cells (Figure 13). Mortar blocks 10 mm thick are sawed from 8 cm diameter specimens and stored in Ca(OH)2 saturated solution. Prior to the test, each specimen is polished with 600-grade emery paper, rinsed with de-ionized water and surface dried with a tissue before being fitted into the diffusion cell. After fitting with epoxy resin and sealing with silicon paste, the cells are filled at one side with $Ca(OH)_2$ solution and at the other side with 3 M NaCl in saturated $Ca(OH)_2$ solution. At periodic intervals, chloride concentration is determined by titration from a 10 cm³ sample of the solution.

  The chloride penetration is determined by two characteristics: the evolution of the chloride content in the first cell, where there was no chloride ions at the beginning of the test, and the occurrence time (breakthrough time), which is calculated from the intercept of the concentration versus time date and corresponds to the time that is necessary to detect the first chloride ion in the first cell. When limestone filler is added, the chloride content in the first cell after 70 days increases and the occurrence time decreases (Figure 14). This may be related to the "open" porosity as for the carbonation rate. The L-mixtures don't seem to permit the chloride ions to cross the mortar slice, at least after 100 days of test.

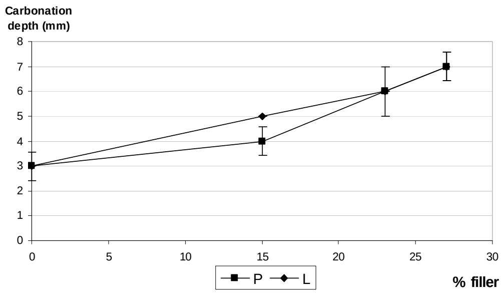


Figure 12: Carbonation depth after 3 months for P and L samples

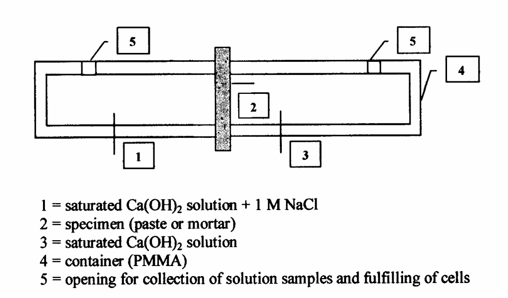


Figure 13: Experimental setup of diffusion cell

- (2) Determination of the resistance of mortars to attack by sulphate is performed according to standard P 18-837 [12]. The method involves the determination of the changes in length of prismatic specimens when stored in a standard sulphate solution. At the age of 28 days, the specimens are measured for length and placed in the sulphate solution having a concentration of 50 g/litre $SO_4^{=}$ and prepared by adding reagent grade magnesium sulphate ($SO_4Mg.7H_2O$) to water. Corresponding control specimens are placed in de-ionized water. Changes in length of the specimens are measured after storage periods of 1, 2 and 3 months at 20 ± 2°C.

  Concrete can react with sulphate by forming secondary ettringite which makes the concrete explode. The deformation is measured each month. The L-mixtures (Figure 15) sulphate resistance doesn't seem to be influenced by the limestone filler. The blast furnace slag cements are already well known to be sulphate resistant. For the Portland cement, it seems that the P-mixtures sulphate resistances are influenced by the filler, especially at a substitution rate of 15 %. More investigations are necessary to understand what is happening inside the mortars.

The interaction ratios show a negative effect of the limestone filler for these three properties (Figures 16).

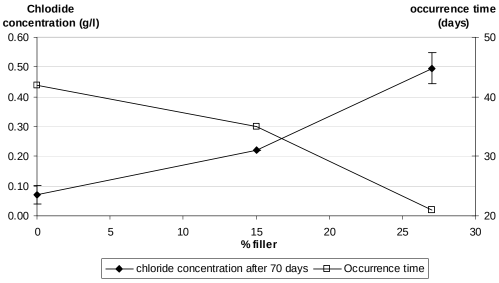


Figure 14: Chloride concentration and occurrence time for P samples

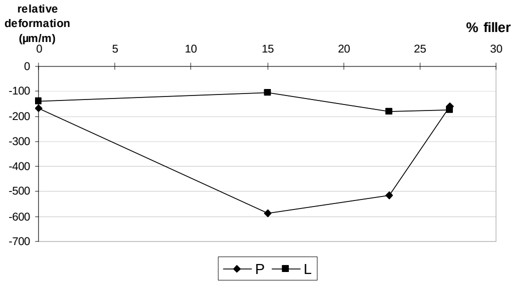
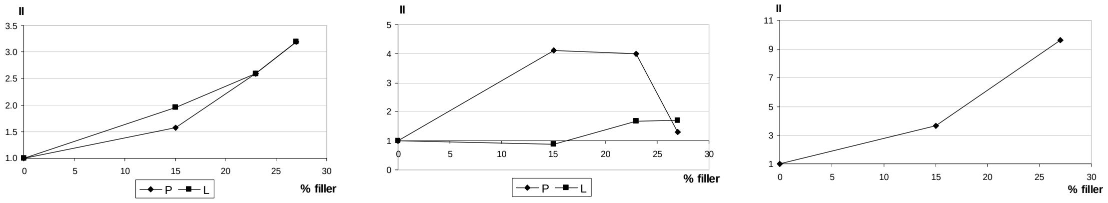


Figure 15: Relative sulphate deformation for P and L samples



a b c

Figures 16: Interaction ratios for the durability characteristics: carbonation depth (a), sulphate deformation (b) for P and L samples and chloride penetration (c) for P samples.

4. Conclusions

Some effects of limestone filler as a partial substitute for cement in mortar composition were analysed. We can draw the following conclusions from the results:

- the water demand, the consistency and the oxygen permeability remain constant with the substitution rate.
- the "dormant" period (i.e. the setting time) of the L-mixtures decreases as the substitution rate increases. This may be due to the formation of carboaluminates.
- the open porosity to water increases between 0 and 15 % of substitution and remains constant between 15 and 27 %.
- the compressive strength and the shrinkages decrease with the substitution, because of the cement content decrease.
- the capillary absorption increases with the substitution.
- the durability is not improved by the limestone filler: carbonation rate, chloride penetration and deformation due to sulphate increase as the substitution rises. More investigations are necessary to precise these conclusions.

More investigations are needed, particularly in terms of microscopic evaluation. It seems however that limestone filler can have an impact – positive or negative – on the behaviour of mortars and cannot be considered as "inert" material.

5. References

1. NBN - EN 196-1, Methods of testing cement. Part 1: Determination of strength, European Committee for Standardization, Brussels, 1995.
2. Escadeillas, G., "Fillers and limestone additions as additions for hydraulic concrete" (in French), LMDC, 1996.
3. NBN B14-207, Essais des mortiers. Consistance - étalement à la table à secousses, Belgian Institute for Standardization, Brussels, 1969.
4. NBN B15-215, Tests on concrete: water absorption by immersion, Belgian Institute for Standardization, Brussels, 1969.
5. NF P 18-508, Additions pour béton hydraulique - Additions calcaires – specifications et critères de conformité, French Institute for Standardization, Paris, 1995.
6. Tsivilis, S. and al., "A study on the parameters affecting the properties of Portland limestone cements", Cement and Concrete Composites, 21, 1999, pp. 107-116.
7. NBN B14-217, Essais des mortiers - Retrait et gonflement, Belgian Institute for Standardization, Brussels, 1970.
8. Lansival, V., "Etude de la perméabilité des bétons à l'air et à l'oxygène", Travail de Fin d'Etudes, Université de Liège, 2000, pp. 46-58.
9. prEN 13 057, Products and systems for the protection and repair of concrete structures – test methods – determination of capillary absorption, Belgian Institute for Standardization, Brussels, 1997.
10. prEN 13 295, Products and systems for the protection and repair of concrete structures – test methods – determination of resistance to carbonation, Belgian Institute for Standardization, Brussels, 2000.
11. Courard L., Darimont A., Schouterden M., Ferauche F., Willem X. and Degeimbre R., "Durability of Mortars modified with metakaolin", Cement and Concrete Research, 33(9), September 2003, pp. 1473-1479.
12. NF P 18-837, Produits spéciaux destinés aux constructions en béton hydraulique – Produits de calage et/ou scellement à base de liants hydrauliques – Essai de tenue à l'eau de mer et/ou à l'eau à haute teneur en sulfates, French Institute for Standardization, Paris, 1993.