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## Study of the durability of repair mortars submitted to acid attacks

Sophie Travailleur

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École Nationale des Travaux Publics de L'État

# **STUDY OF THE DURABILITY OF REPAIR MORTARS SUBMITTED TO ACID ATTACKS**

A Thesis in  
Materials engineering  
by  
**Lucy Sophie TRAVAILLEUR**

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Submitted in Partial Fulfilment  
of the Requirements  
for the Degree of  
Master in Sustainable Territorial Planning Engineering

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## ABSTRACT

This study was carried out in order to acquire a better understanding of the behaviour of repair mortars when they are submitted to acid attacks. Above all, this study focuses on the case of an repair mortar that contains polymers. The main objectives of this study were to highlight the influence of the presence of polymers in the case aggressive agents attack the material, and to determine the parameters that main be responsible for the durability of the material. In order do so, three mortars were selected: two repair mortars (one containing polymers – the Monotop 412 SFG - and another one without polymer additions – the Monotop 412 S) and a conventional mortar (CEM 52.5 R) in order to make a comparison.

A first step consisted in characterising all of the mortars. Indeed, since repair mortars were used, there was a lack of information about their composition. Making a characterisation of each mortar was essential in order to predict and understand their behaviour when submitted to acids. All of the mortars were characterised from a mechanical point of view, as well as from microstructure and durability points of view. The different tests that have been carried out were: flexural and compressive strength tests, mercury intrusion porosimetry, differential thermal analysis, electrical resistivity, chloride migration and capillary absorption. The different tests have pointed out outstanding properties for the Monotop 412 SFG (which contains polymers) in terms of durability, even if no significant improvement was notices in terms of mechanical properties. They have also highlighted no improvement in the capacity of the Monotop 412 SFG to resist freeze/thaw cycle than a conventional mortar. This part has allowed highlighting that the Monotop 412 SFG has a microstructure that makes it more difficult for aggressive agents to penetrate into the material.

A second step consisted in submersing all of the three mortars into two different acid solutions (an acetic acid solution and a lactic acid solution). After one month of submersion, some characterisation tests were carried out in order to qualify the reaction of each mortar. From a visual point of view, it has been determined that the Monotop 412 SFG is the one that presents the best resistance to acid attacks in both cases (acetic acid and lactic acid). Indeed, for both solutions, theses samples were the least degraded after one month of attack. Moreover, the conventional mortar was the most deteriorated. It also appears that lactic acid attack is more intense for mortars than acetic acid attack is, in accordance with their pKa values. It attacked the gel, changing its stoichiometry, and leading to an increase in volume of the specimens. Three different tests were carried out in order to confirm these observations: mercury intrusion porosimetry, differential thermal analysis and a titrimetric method. However, the tests have pointed out a change in microstructure for both repair mortars while the conventional mortar was maintaining its microstructural properties. According to the tests, the properties of both repair mortars were worsened as a result of acid attacks. It can also be underlined that the results were worst in the case of lactic acid attack.

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## GENERAL INTRODUCTION

Cement-based materials are ones of the most widely used in the fields of construction and civil engineering. The use of cement-based materials goes back over a period of several decades. The composition of these materials has evolved at the same time as the requirements from the industry have changed. Nowadays, cementitious materials are asked to be stronger and more flexible in order to fulfil both technological and structural demand from modern constructions. In this context, many different types of additions are now employed; among them are accelerators, filler additions or polymer-based materials.

Polymer materials have been used over centuries. They are now widely employed to produce materials and finished product for the industry. Construction industry has showed many interest in the combinations between polymers and cementitious material in the 1950's – 1960's, with the use of polymer concrete and polymer impregnated concrete. At that time, the improvement in physical properties of the final product was already demonstrate, which has reinforce the use of such materials for repair and bridge overlay. Later, in the 1970's – 1980's those materials have seen their used being increased in order to improve service life and strength of the structures. Indeed, depending on the types, polymers are known to improve particular properties, allowing thus satisfying new requirements.

Nevertheless, even if we are now able to produce high quality and high property cement-based materials, the question of its durability is still being essential to engineers and industrials which are looking for longer service life and less maintenance for the structures. Structure durability is a major factor in civil engineering as well as in industrial engineering, and this is closely linked to concrete durability (or that of any cement-based material which is used for the construction of the structure). The degradation of cementitious materials can have different sources. In particular, it can be due to the development of biological activity or to the influence of an aggressive medium. Many areas are concerned by the phenomena of deterioration of cement-based structures because of these types of attacks. Many studies have been carried out in order to understand the causes of such degradations and the mechanisms involved, in order to increase the durability of concrete in those cases. The cases of agricultural and agro-food industries as well as the case of biological activity have been especially studies over the past few years. However, to the best of our knowledge, this case has not been studied for polymer-modified concrete or mortars yet.

In the light of the above, this master's thesis is the first step of a more general work which aims to provide a better understanding of this phenomenon in order to increase the durability of polymer-modified cementitious materials. Thus, the subject of this Master's thesis has been defined collaboration with the IFTTAR (French Institute for sciences and technologies of Transportations, Planning and Networks) that I will join soon in order to deepen the investigations in the framework of a PhD-project. The main objectives of this Master's thesis are the following:

- Characterise repair mortars in comparison with a conventional mortar;

- Understand the behaviour of those mortars in the case of an acid attack and the influence of the presence of polymers in the composition of the mortars;
- Identify the key parameters that help explaining the differences in behaviour.

To do so, three mortars will be considered, among which two repair mortars (one containing polymers, and another one formulated without polymers) that will be compared to a conventional mortar. They will be submersed into different acids in order to see the consequences of acid attacks.

This report will start by a bibliographical study that constitutes the first chapter. In it, a reminder of what is essential to know about cementitious materials will be done, including their composition, structure and characterisation. A focus will also be done on some aspects of chemistry of cementitious materials. Another part will focus on the modifications of cementitious materials, in particular on the case of the use of polymers. In this part, the different types of polymers that can be employed will be detailed as well as their properties. A summary of the main results of some studies for two different types of polymers will finally be made.

In the second chapter, the experimental approach will be detailed. We will begin with the preparation of the samples. In this part, we will characterise the mortars that have been selected, and how the mortars have been prepared in each case according to the type of the sample. The dosing used and the curing conditions will also be described. Another part will focus on the acid solutions. In this part, we will justify the choice of the two types of acids and give some data on them. We will then detail how the solutions have been prepared. Finally, the attention will be paid to the different tests that will be carried out, including mechanical tests, durability capacity and microstructure characterisation tests. The different test will be presented as well as the main result they allow accessing to. The machine used for each test and the Standard that have been applied will also be specified.

In the third chapter, the results that allow characterising all of the three mortars after their hardening will be presented. In this chapter, the mechanical properties will be regarded by the realisation of compression and flexural strength tests. With regard to the microstructure characterisation, the mercury intrusion porosimetry and the differential thermal analysis will be carried out. Finally, regarding the durability capacities, three tests will be carried out: electrical resistivity, chloride migration and capillary absorption. The results will be compared for all of the three mortars and a discussion will be made.

In the final chapter, the different mortars will be submitted to acid solutions. Two different solutions have been prepared and each mortar will be submersed in both solutions for one month. The effect of these attacks will then be highlighted by means of characterisation tests. In this part three tests will be carried out: mercury intrusion porosimetry, differential thermal analysis and a titrimetric method. The results obtained will be exposed and compared. A discussion will help pointing the main conclusions out.

Finally, a synthesis of all of the main results and conclusions will be made. We will also point out the future areas of investigation.



## **CHAPTER I: STATE OF THE ART**

### **INTRODUCTION**

Concrete is one of the most used materials. It is widely employed in civil engineering and in construction for its good resistance properties (above all against water, in comparison with steel, or wood), but also because of its cost. Over the past few decades, different processes have been put into place in order to improve the properties of concrete. Among them are the modifications of concrete by the addition of polymers. This type of modification is said to improve the performances of concrete and above all the resistance of concrete to chemical attacks.

Nevertheless, nowadays the structures made of concrete are more and more submitted to different types of attacks that lead to their degradation. These attacks are becoming more and more frequent due to favourable conditions (global warming, increase in the temperature worldwide). In particular, the effect of biogenic species has to be taken into account since the conditions are becoming favourable to their development. The effects of such attacks can be seen on the facades that suffer an important deterioration, or on some facilities that suffer degradation due to a wild environment. The action of such species is traduced by an acid attack of the structure, leading to its deterioration. To our best knowledge, this phenomenon has not been studied yet in the case of materials modified by the addition of polymers. However, in order to be able to apprehend such a study, it is essential for us to have some data about the mechanisms involved, and the previous studied that have been handled on traditional concrete.

In what follows, we will focus on the composition of a traditional concrete. We will also highlight the phenomena involved on the hydration process and on the transport process of the material. Then, we will focus on the different ways to modify it by adding polymers. Finally, we will focus on the attack of original cementitious material by organic species and the reported studies about this subject.

### **1 PART I: REMINDERS AND GENERALITIES ABOUT CEMENTITIOUS MATERIALS**

There are different types of cement-base materials. The first one, the cement paste, is made by mixing cement and water. The second one, the mortar, is obtained by combining fine aggregates (maximum aggregate size of 2mm) thanks to a hydraulic binder (which is the cement paste). The last one, the concrete, is obtained by combining both fine and coarse aggregates thanks to a hydraulic binder (which is the cement paste). This can be resumed by saying that cementitious materials are made with three main components, which are aggregates, cement and water, and some additives when necessary.

## 1.1 COMPOSITION AND STRUCTURE OF CEMENTITIOUS MATERIALS

### 1.1.1 Reminders of cement chemistry notations

Many different components enter into account in the composition of cement. In order to make easier the description of chemical composition as well as chemical reactions, a specific simplified notation has been developed, as shown below (cf. Table 1). This simplified notation is the one that will be used in this Master's thesis.

NAME	FULL NOTATION	SIMPLIFIED NOTATION
Lime	CaO	C
Iron oxide	Fe <sub>2</sub> O <sub>3</sub>	F
Alumina	Al <sub>2</sub> O <sub>3</sub>	A
Silica	SiO <sub>2</sub>	S
Sulphate	SO <sub>3</sub>	Ŝ
Water	H <sub>2</sub> O	H
Magnesium oxide	MgO	M
Sodium oxide	Na <sub>2</sub> O	N
Potassium oxide	K <sub>2</sub> O	K

Table 1 – Cement chemistry notations for raw materials

### 1.1.2 Cement

According to the European Standard EN 197-1, "cement is a [...] finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water".

Cement is one of the most important components that enter into account for the realisation of mortar or concrete. It plays an essential role in the behaviour of cementitious materials. Cement is a hydraulic binder, which is mainly made up from:

- Calcareous material which is the source of CaCO<sub>3</sub> (it can also contain impurities such as iron or alumina);
- Argillaceous material which is the source of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and some Fe<sub>2</sub>O<sub>3</sub>.

These two types of materials are the major contributors to the composition of cement; even though gypsum and eventually other mineral additives can take part of the composition of the cement.

#### ▪ *Production process*

The production process of cement consists in the grinding of the different raw materials into a fine powder, the mixing of the materials, and the burning in kilns at very high

temperature. This burning process leads to the production of clinker. Clinker will be then grinded with some additives, leading to the production of cement. The calcination process has several stages:

- Drying (up to 100°C): evaporation of free water.
- Preheating (100°C-750°C): evaporation of the water in the raw feed (clay) and changes in the crystal structure, leading to the activation of silicates.
- Calcination (750°C-1000°C): decarbonation of calcium carbonate (CaCO<sub>3</sub>).
- Burning (1000°C-1450°C): partial melting of the mix, formation of belite and appearance of a liquid phase which helps the reaction between belite and free lime, leading to the formation of clinker (cf. Table 2).
- Cooling of the clinker (1450°C-1300°C): crystallisation of the main liquid phase leading to the formation of aluminate phase (C<sub>3</sub>A and C<sub>4</sub>AF) and a little quantity of belite (C<sub>2</sub>S).

NAME	FULL NOTATION	SIMPLIFIED NOTATION
Tricalcium silicate (alite)	3 CaO.SiO <sub>2</sub>	C <sub>3</sub> S
Dicalcium silicate (belite)	2 CaO.SiO <sub>2</sub>	C <sub>2</sub> S
Tricalcium aluminate (celite)	3 CaO.Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A
Tetracalcium aluminoferrite (browmillerite)	4 CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	C <sub>4</sub> AF
Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O	C $\hat{S}$ H <sub>2</sub>

Table 2 – Principal products of the cement production process

Alite is the most abundant compound in the cement. It is in form of polygonal crystals which diameters are between 20 and 50µm. Belite is present in cement and, as well as alite, it is in form of rounded crystals. Tricalcium aluminate can adopt either a cubic form, or an orthorhombic form, depending on the sodium content. Finally, tetracalcium aluminoferrite is in the form of a solid solution (composed of massive and elongated crystals embedded in the interstice between alite and belite (OUESLATI, 2011)).

▪ **Principal constituents**

Cements are made up with principal components, in which some secondary components are added. Gypsum is also often added in small quantities during the manufacturing of cement in order to regulate the cement setting. The principal components of cement are the following:

- Portland cement clinker;
- Blastfurnace slag S;
- Silica fume D;
- Natural pozzolana P and industrial pozzolana (i.e. natural calcined pozzolana) Q;
- Siliceous fly ash V and calcareous fly ash W;
- Burnt shale T;

- Limestone L (that does not exceed 0.50% by mass) and LL (that does not exceed 0.20% by mass).

The secondary components are inorganic mineral materials. They can be natural or derived from the clinker production process. The percentages of these constituents define different types of cement, which are listed and classified in the EN 197-1 Standard, as shown below (cf. Table 3).

TYPES OF CEMENT	CLINKER	OTHER PRINCIPAL COMPONENTS	SECONDARY COMPONENTS
CEM I (Portland cement)	95 - 100%	0%	0 - 5%
CEM II (Portland-composite cement)	65 - 94%	6 – 35% S/D/P/Q/V/W/T/L/LL	0 - 5%
CEM III (Blastfurnace cement)	5 - 64%	36 – 95% Slag	0 - 5%
CEM IV (Pozzolanic cement)	45 - 89%	11 – 55% D/P/Q/V/W	0 - 5%
CEM V (Composite cement)	20 - 64%	18 - 50% S/P/Q/V	0 - 5%

Table 3 – Types of cement according to the EN 197-1 Standard

As seen in the table above, clinker is essential to the realisation of any type of mortar. According to the production process, there are four main phases that enter into account in the chemical composition of clinker: alite ( $C_3S$ ) which represents 40-60% of the chemical composition, belite ( $C_2S$ ) which represents 20-30% of the chemical composition, and the aluminate phase ( $C_3A$  and  $C_4AF$ ) which represent 7-14% and 5-12% respectively. The composition of each phase can be evaluated by means of Bogue's Method. This method assumes that in the clinker, only these four phases are present, and defines the proportion of each phase (cf. Equation 1). It has to be underlined that the percentages obtained with this method are relative.

$$\%C_3S = 4.0710 CaO - 7.6024 SiO_2 - 6.7187 Al_2O_3 - 1.4297 Fe_2O_3$$

$$\%C_2S = -3.0710 CaO + 8.6024 SiO_2 + 5.0683 Al_2O_3 + 1.0785 Fe_2O_3$$

$$\%C_3A = 2.6504 Al_2O_3 - 1.6920 Fe_2O_3$$

$$\%C_4AF = 3.0432 Fe_2O_3$$

Equation 1 – Bogue's equations for potential composition

### **1.1.3 Additions**

Additions are finely ground materials (e.g. inorganic materials, pozzolanic materials or materials with a latent hydraulicity) which are added to cementitious materials in order to improve their physical and/or chemical characteristics. Additions are defined and characterised in the EN 206-1 Standard. Two main types of additions are identified:

- The substantially inert additions (type I);
- The pozzolana or latent-hydraulic additions (type II).

According to the European Standard, the performance of a concrete with an addition of mineral must be similar to the performance of a concrete without addition. To this end, the concept of equivalent binder has been introduced (cf. Equation 2). The EN 206-1 Standard defines the values of the coefficient K according to the addition which is used. It allows computing the water, taking into account the presence of additions (using the water/(cement + K x addition) ratio instead of the water/cement ratio). The values of K vary according to the country.

$$Leq = C + K.F$$

Equation 2 – Equivalent binder

Where:

Leq is the amount of binder;

C is the cement content per m<sup>3</sup>;

F is the addition content per m<sup>3</sup>;

K is a weighted coefficient (depends on the addition).

### **1.1.4 Aggregates**

Aggregates form the skeleton of the concrete. They are essential in order to obtain a good material from the point of view of dimensional stability, stiffness, abrasion resistance and economy. They are granular, inert and inorganic materials. They can be natural (i.e. made from minerals that come from alluviums or solid rocks that have only suffered mechanical transformations), artificial (i.e. made from minerals that are the result of an industrial process which includes thermal transformations among others), or recycled (i.e. after the treatment of an inorganic material previously used in the construction).

The grain size used is essential to obtain a good compactness. With regard to mortars, the maximum grain size used according to the EN 196-1 Standard is of 2mm. With regard to concrete, a mix of fine and coarse aggregates is used, and the proportions depend on the dosing chosen. Aggregates constitute 80% of a concrete, and 70% in the case of mortar, with respect to the total volume when hardened.

The interface between aggregates and the cement paste (cf. Figure 1) has a thickness of about some micrometres and is characterised by a water/cement ratio higher than the average in the paste. Consequently, in this area, the interfacial water is increased due to the surface exudation of the aggregates. So, the interfacial transition zone between the

aggregate and the cement paste matrix presents a particular interest since the adherence between the aggregate and the paste influences the resistance capacity of the material.

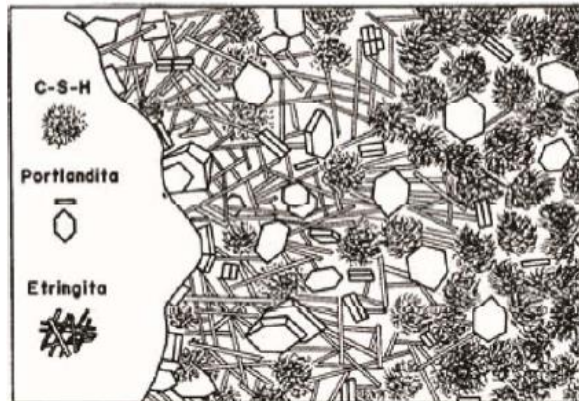


Figure 1 – Interface between an aggregate and the cement paste

Source: (MEHTA & MONTEIRO, 1986)

### 1.1.5 Water and additives

Water is a well appropriated solvent for the realisation of cementitious materials (if those are inorganic material; in the case of mortars with a polymeric matrix, the solvent will be combined with the resin). Two types of water are used for the realisation of cementitious materials: the mixing water and the curing water. The first one enters into account in the cement hydration reactions, and gives a good workability to the cement. In this case, the dosage is essential since putting too much water will leads to an excessive porosity (which has a bad influence on the mechanical resistance), and putting not enough water will leads to a partial hydration of the material. The second one is used to allow the development of new hydration processes compensating the evaporation losses.

Additives (or admixtures) can be added while mixing the cementitious material components. Their function is to modify one or several properties of the final material. They can be either organic chemical compounds, or inorganic chemical compounds. They are incorporated respecting in general proportions which do not exceed 5% of the total cement weight. The improvements achieved with additives have an influence on both fresh and hardened states of the cementitious material. The EN 934-2 Standard classifies the additives according to their main functions (cf. Table 4).

FUNCTIONS	ADDITIVES	DETAILS
Modification of workability (rheology)	Plasticisers (water reducing); superplasticisers (high-range water reducing)	Reduce water at equal consistence, or increase in consistence at equal w/c ratio
Modification of	Set accelerating admixtures	Reduce the initial setting time

hardening and setting	Hardening accelerating admixtures	Increase the development of initial resistances
	Set retarding admixtures	Increase the initial and final setting times
Modification of some particular properties	Air entraining admixtures	Entrain the formation of micro air-bubbles uniformly distributed into the mass
	Water retaining admixtures	Reduce the bleeding
	Water resisting admixtures	Reduce the capillary absorption

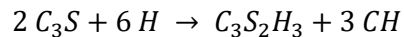
Table 4 – Classification of additives according to the EN 934-2 Standard

## 1.2 CHARACTERISATION

### 1.2.1 *Hydration of the principal constituents of cement*

#### ▪ *Case of alite*

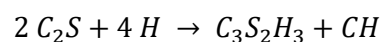
Alite is in form of solid phase which forms a crystal lattice with impurities. This compound hydrates and hardens quickly. So, it has a high mechanical resistance at short age and it is responsible for initial set and high early strength in Portland cement. Alite reacts by means of an exothermal reaction producing calcium silicate hydrate gel and calcium hydroxide (cf. Equation 3). This mechanism can be decomposed into the dissolution of  $C_3S$ , the precipitation of the silicate ions leading to the formation of calcium silicate hydrate, and finally the precipitation of the calcium ions in the form of calcium hydroxide.



Equation 3 – Hydration of alite

#### ▪ *Case of belite*

Belite is a compound which hydrates and hardens slowly. Thus, it has good long-term mechanical resistance and it contributes to strength at ages beyond seven days. Belite reacts by means of an exothermal reaction which evolves less heat than alite. As well as alite, it produces also calcium silicate hydrate gel and calcium hydroxide in fewer quantities than alite does (cf. Equation 4). It has to be underlined that several polymorphs of belite exist:  $\alpha$ - $C_2S$ ,  $\alpha_H$ - $C_2S$ ,  $\alpha_L$ - $C_2S$ ,  $\beta$ - $C_2S$  and  $\gamma$ . Nevertheless, only the  $\beta$ - $C_2S$  has significant hydraulic properties (it is the dominant form in the Portland cement, which is the most commonly used).

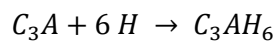


Equation 4 – Hydration of belite

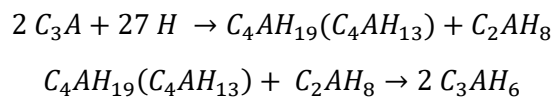
▪ **Case of the aluminates**

Aluminates compose the phase which is the most reactive towards water. This phase reacts quickly. This rate has to be controlled so that the cement can be shaped.

The tricalcium aluminate ( $C_3A$ ) contributes a little to the early strength development. It releases an important amount of heat during the first few days. Its hydration depends on the presence of gypsum. The tricalcium aluminate is normally highly reactive. In presence of water, it reacts to produce a stable hydrate: the cubic hydrargarnet (cf. Equation 5). This reaction can be decomposed in a two step-mechanism (cf. Equation 6). The first step leads to the formation of a hexagonal hydrate ( $C_2AH_8$ ) and finally to the formation of the cubic hydrargarnet ( $C_3AH_6$ ). The formation of the latest cubic structure is the one that allows the hydration process continuing (MONTEAGUDO VIERA, 2014). The hydration process leads to different products in present of sulphates (coming from the gypsum).

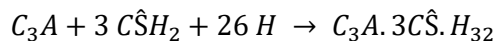


Equation 5 – Reaction of tricalcium aluminate with water

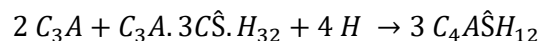


Equation 6 – Decomposition of the reaction between tricalcium aluminate and water

As we may see, the presence of gypsum leads to the formation of ettringite crystals (cf. Equation 7). This reaction takes place until the gypsum is totally consumed (the gypsum is generally totally consumed before the tricalcium aluminate). It has to be underlined that gypsum causes a decrease in the rate of the reaction. At this stage, the tricalcium aluminate starts reacting with the ettringite (cf. Equation 8), which dissolution leads to the formation of calcium monosulfoaluminate hydrate (AFm). Consequently, the tricalcium aluminate has a great impact on the vulnerability of the cement to the sulphate attacks. That is the reason why the tricalcium aluminate content is approximately of 10% for cement, and 5% for the cements exposed to sulphate solutions (MONTEAGUDO VIERA, 2014).



Equation 7 – Hydration of tricalcium aluminate in presence of gypsum

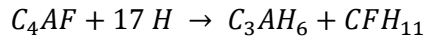


Equation 8 – Hydration of tricalcium aluminate in presence of ettringite

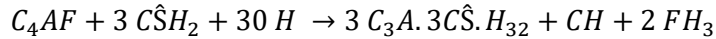
The tetracalcium aluminoferrite ( $C_4AF$ ) contributes slightly to strength but hydrates quickly. It reduces the melting temperature of the raw materials in the kiln. The hydration process of the tetracalcium aluminoferrite is essentially the same as tricalcium aluminate, replacing the aluminates by aluminoferrites in the products of the reactions (cf. Equation 9, Equation 10 and Equation 11). It has to be underlined that in the case of tetracalcium



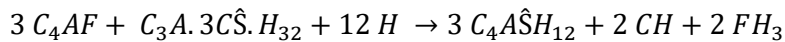
aluminoferrite hydration, the rate of reaction is slower than in the case of the tricalcium aluminate hydration process.



Equation 9 – Reaction of tetracalcium aluminoferrite with water



Equation 10 – Hydration of tetracalcium aluminoferrite in presence of gypsum



Equation 11 – Hydration of tetracalcium aluminoferrite in presence of ettringite

Finally, we may say that gypsum plays an important role on the hydration process of the aluminate phase since it allows slowing down the reaction between the aluminates and the water while producing ettringite.

These characteristics can be summed up as show in the table below (cf. Table 5). Moreover, in terms of kinetics for the hydration process, the following relation can be established:  $C_3A > C_3S > C_4AF > C_2S$ .

COMPONENTS	HYDRATION SPEED	HYDRATION HEAT	MECHANICAL RESISTANCE	CHEMICAL RESISTANCE
C <sub>3</sub> S	High	High	High and rapid	Acceptable
C <sub>2</sub> S	Low	Low	High and late	Good
C <sub>3</sub> A	Instantaneous	High	Limited	Very poor
C <sub>4</sub> AF	High	Low	Limited	Good

Table 5 – Characteristics of the main components in cement

Source: (MASSANA GUITART, 2010)

### 1.2.2 Hydrated components of the solid phase

As seen above, the principal components of solid phase are the calcium silicate hydrate gel and the calcium hydroxide (Portlandite). However, other products are found in lower proportions (cf. Table 6).

NAME	FULL NOTATION	SIMPLIFIED NOTATION
Calcium hydroxide	Ca(OH) <sub>2</sub>	CH

Calcium silicate hydrate gel	$x\text{CaO}\cdot y\text{SiO}_2\cdot z\text{H}_2\text{O}$	CSH
Ettringite	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$	$\text{C}_3\text{A}\cdot 3\text{C}\hat{\text{S}}\cdot \text{H}_{32}$ (AFt)
Calcium monosulfoaluminate hydrate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot \text{CaSO}_4\cdot 12\text{H}_2\text{O}$	$\text{C}_4\text{A}\hat{\text{S}}\text{H}_{12}$ (AFm)

Table 6 – Principal hydrated components of cement paste

- **Calcium silicate hydrate gel**

The calcium silicate hydrate gel is the main product of the hydration process and represents between 50% and 60% of the total volume of the hydrated cement paste. It is produced during the hydration of the silicates (tricalcium silicate and bicalcium silicate). It is the principal responsible for many properties of cementitious materials, including mechanical properties, hardening and durability. The CSH gel has a structure which is mainly amorphous and which can vary over time (many models have been realised to understand the morphology of the microstructure of the CSH gel but it still no being well defined). It has to be underlined that the stoichiometry of the CSH gel can vary according to its production mode (produced by the hydration of the silicates, pozzolanic reaction or synthesis). The bonds involved in CSH gels are ionic bonds; however, the bond linked Si-O is ionic and covalent at the same time. The silicon is at the centre of a tetrahedron whose apexes are four oxygens (cf. Figure 2).

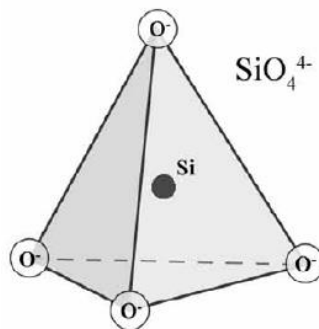


Figure 2 – Structure of the silicates in the CSH gel

Source: (MONTEAGUDO VIERA, 2014)

- **Calcium hydroxide**

The calcium hydroxide crystals develop in form of a hexagonal network, and represent between 20% and 25% of the total volume of the hydrated cement paste (in the Figure 3 below, the calcium hydroxide is represented with an X, the CSH gel with a # and the pore with a 0). An important parameter in the morphology of the calcium hydroxide is the water/cement ratio. The forces evolved in the bonds are weak. Thus, calcium hydroxide does not influence the mechanical properties of the hardened cement. However, it plays an important role in the alkalinity of the material. The calcium hydroxide may be important in the case of attacks by acid components, leading to the lixiviation of the material in contact with water.

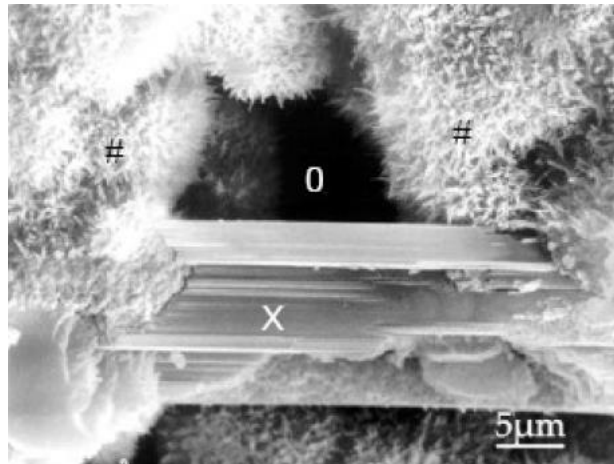


Figure 3 – Calcium hydroxide crystal between calcium silicate hydrates

Source: (REGOURD &amp; HORNAIN, 1975)

#### ▪ *Aluminate hydrates*

The ettringite is part of the AFt family (i.e. Aluminate – Ferrite – tri, where “tri” is linked to the three moles of  $\text{CaSO}_4$ ), in which it represents the most important phase. It has the structure of a hexagonal prism. In the Portland cement, the ettringite grows during the first hours of hydration, with a maximum at 24 hours. Then, the AFm phase starts to be produced while the ettringite content decreases.

The AFm phase (i.e. Aluminate – Ferrite – mono, where “mono” is linked to the mole of  $\text{CaSO}_4$ ) contains the calcium monosulfoaluminate hydrate. It presents a laminar structure and may have a hexagonal form.

The characteristics of the main components in solid phase can be summed up in the following table (cf. Table 7).

COMPONENT	PROPORTION IN CEMENT PASTE VOLUME	ORIGIN	CHARACTERISTICS
CSH	50 – 60%	Hydration of $\text{C}_3\text{S}$ and $\text{C}_2\text{S}$	Mechanical properties of resistance
CH	20 – 25%	Hydration of $\text{C}_3\text{S}$ and $\text{C}_2\text{S}$	Alkaline reserve of the cementitious material
Ettringite	15%	Hydration of $\text{C}_3\text{A}$ and gypsum	Durability in sulphated media

Table 7 – Characteristics of the main components of solid phase

### 1.2.3 Aqueous phase and porous structure

According to SEREDA's study (SEREDA, et al., 1980) three different types of water contained in the cement paste can be identified: chemically-combined water, physically-bounded water (gel water) and free water (capillary water).

The chemically-combined water is the one which reacts chemically with the cement particles. In this case, the elimination of the chemically-combined water leads to the drying of the products and the decomposition of the hydrate products.

The gel water is located in the gel pores. This type of water is associated to the laminar structure of the CSH gel. Its elimination is linked to the shrinkage of the structure.

The capillary water is located in the capillary pores: either in the large ones or in the little ones. Its elimination is not linked to any change in the dimensions of the cement paste.

Cementitious materials are porous media with a solid phase and different types of voids that can be filled with air or solutions. The parameters involved in the formation of the porous structure of cementitious materials are the following: the degree of hydration, the water/cement ration, the amount of cement, or the compaction. Different studies have been realised and have allowed identifying and classifying the pores (cf. Table 8). If we refer to the table, the pores that influence the most the cementitious materials are the mesopores and the macropores since they affect the shrinkage, the permeability and the strength of the material.

IUPAC		P. MEHTA, 1986		S. MINDESS et al, 2002	
Name	Size	Name	Size	Name	Size
Micropores	Up to 2 nm	Interparticle space between CSH sheets	1 nm to 3 nm	Micropores "inter layer"	Up to 0.5 nm
				Micropores	0.5 nm to 2.5 nm
Mesopores	2 nm to 50 nm			Small (gel) capillaries	2.5 nm to 10 nm
		Capillary pores (low w/c)	10 nm to 50 nm	Medium capillaries	10 nm to 50 nm
Macropores	> 50 nm	Capillary pores (high w/c)	3 $\mu$ m to 5 $\mu$ m	Large capillaries	50 nm to 10 $\mu$ m
		Entrained voids	50 $\mu$ m to 1 mm	Entrained air	0.1 mm to 1 mm

Table 8 – Classification of the porous network

Source: (ALIGIZAKI, 2005)

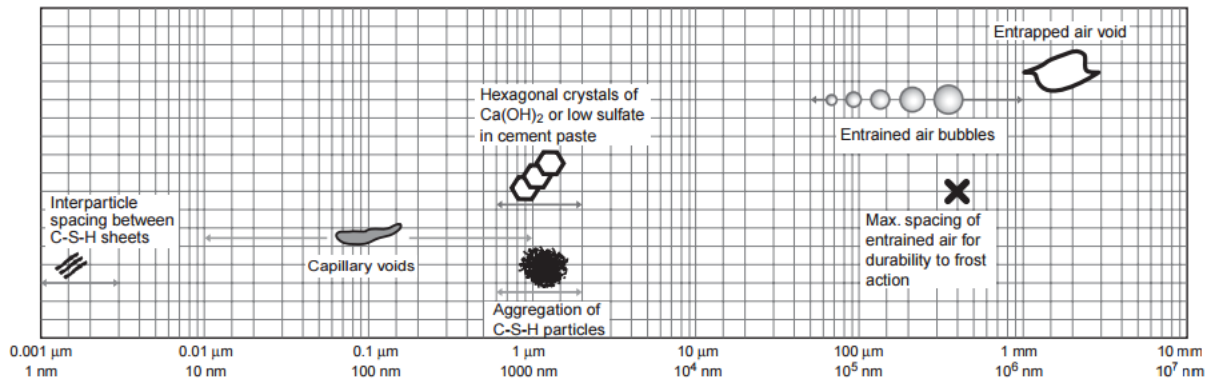


Figure 4 – Dimensional range of solids and pores in a hydrated cement paste

Source: (MEHTA & MONTEIRO, 1986)

According to the figure above (cf. Figure 4) the morphology of the porous structure plays an important role on the durability of the material. Indeed, interconnected pores and open porosity make easier the access and transport of both gases and liquids exposing the material to severe troubles.

Micropores (or gel pores) are those who stay in between the sheets of CSH gel. According to MINDESS's classification (cf. Table 8) their sizes are in the range 0.5nm–2.5nm. Their volume increases as hydration products grow. They may modify both shrinkage and creep of the cementitious material, but have no influence on the resistant capacity of the material, or on its durability.

Mesopores (or capillary pores) are formed during the hydration process, when voids are not filled in with hydration products or anhydrous cement. They change as the components hydrate. According to MINDESS's classification, their sizes are in the range 2.5nm–50nm. Their sizes increase with the water/cement ratio, and depend on the amount of hydrated cement and the degree of hydration. They may affect the durability of the cementitious material, as well as its transport capacity (especially when an interconnected network is formed by the mesopores). In the case of mesopores, water has the possibility to freeze (which does not succeed with the micropores due to their sizes).

Finally macropores (or Hollow shell pores) are formed by the air bubbles which remain trapped. According to MINDESS's classification, their sizes are superior to 50nm. They do not affect the permeability of the material and if they are not connected, they may not influence the durability of the material. However, they might negatively affect the mechanical resistance of the material. They can be avoided by realising a good compaction of the material.

#### 1.2.4 *Transport phenomena in porous materials*

In porous materials, transport mechanisms help aggressive agents (liquid compound, gas compound or ions that are dissolved in an aqueous phase) to enter the material leading to its deterioration. The transport phenomena are realised through permeability, diffusion, capillary absorption or convection (cf. Figure 5).

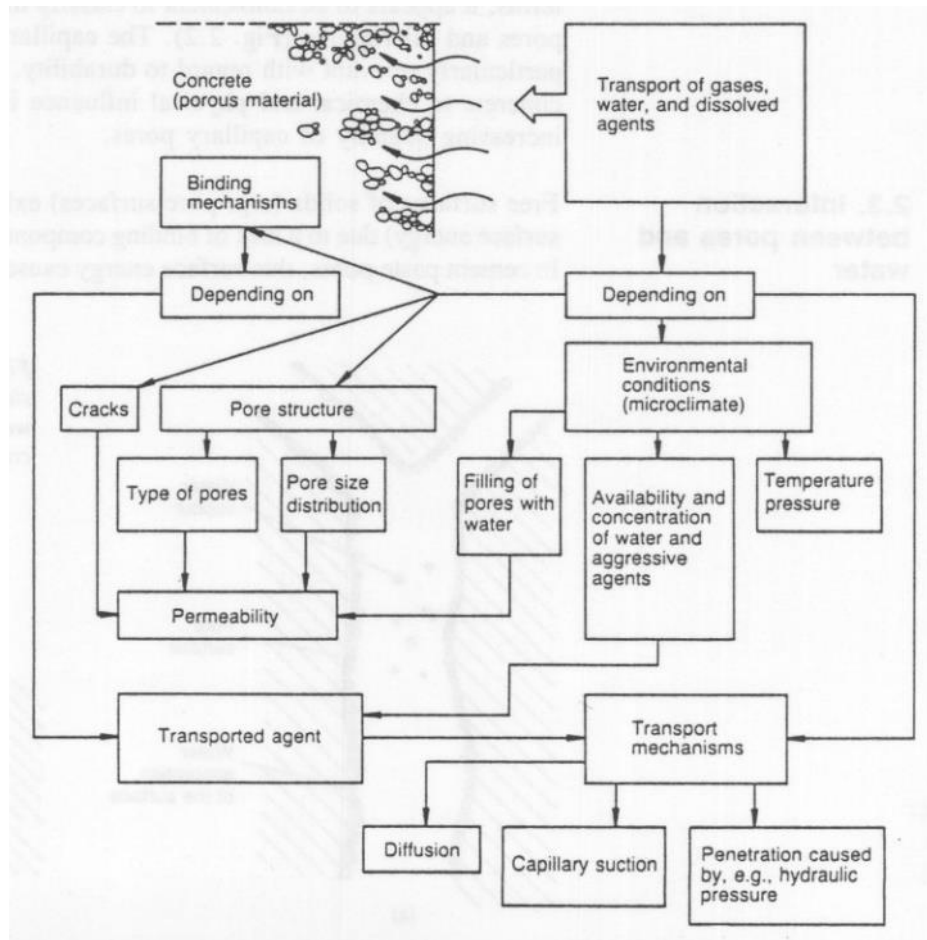


Figure 5 – Transport phenomena in concrete

Source: (Comité Euro-International du Béton, 1992)

### ▪ **Permeability**

Permeability is linked to a pressure gradient, leading to the formation of a movement in the material. Thus, permeability occurs if a flux of the aggressive agent is created in the material. Regarding this mechanism, the form and structure of the pore (types of pores, size distribution) have a great influence. It has to be underlined that the water/cement ratio, as well as the curing process plays an important role for the permeability of the material (a low w/c ratio and a good curing process lead to a low permeability of the material). The gas permeability is the parameter to study in order to quantify the permeability due to a pressure gradient. Darcy's Law (cf. Equation 12) is the basis for the determination of the permeability applies to a flux of fluid.

$$v = - \frac{k}{\mu} \cdot \frac{\partial p}{\partial L}$$

Equation 12 – Darcy's Law

Where:

v is the average speed of the flux (m/s);

$k$  is the coefficient of permeability ( $m^2$ );

$\mu$  is the dynamical viscosity of the fluid ( $N.s/m^2$ );

$\frac{\partial p}{\partial L}$  is the variation of the pressure related to length  $L$  ( $N/m^2/m$ ).

▪ **Diffusion**

Diffusion is related to a chemical potential gradient (concentration gradient) in a saturated or partially saturated material. Indeed, the presence of a concentration gradient in the specie leads to the creation of a movement. Consequently, a global transport occurs from the points of higher concentration to the points of lower concentration. Fick's Laws describe the transport by diffusion in a saturated material (cf. Equation 13). The diffusion coefficient quantifies the transport capacity. It has to be mentioned that diffusion is a slow transport mechanism in comparison with permeability or capillary absorption. Yet, it can be rapid enough to cause the deterioration of the material.

$$J = -De \cdot \frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = De \cdot \frac{\partial^2 C}{\partial x^2}$$

Equation 13 – Fick's First and Second Laws

Where:

$J$  is the particle flux of the specie considered ( $mol.m^{-2}.s^{-1}$ );

$De$  is the diffusion coefficient ( $m^2.s^{-1}$ );

$C$  is concentration of the specie considered ( $mol.m^{-3}$ ).

▪ **Capillary absorption**

In the case of capillary absorption, the liquid transport is due to surface tension of water (which acts on capillary pores). This mechanism is related to the porous structure as well as the humidity of the material. The combination of the surface tension, the atmospheric pressure and the electromolecular forces leads to the penetration and the movement of the liquid water within the porous material. The capillary rise depends on the radius of the pore and the density of the capillary liquid, as it is explained in Jurin's Law (cf. Equation 14).

$$h = \frac{2 \cdot \gamma}{r \cdot g \cdot \rho} \cdot \cos \theta$$

Equation 14 – Jurin's Law

Where:

$h$  is the height (cf. Figure 6) (m);

$\gamma$  is the surface tension of the interface ( $\text{N}\cdot\text{m}^{-1}$ );

$r$  is the radius of the tube (m);

$g$  is the acceleration due to gravity ( $\text{m}\cdot\text{s}^{-2}$ )

$\rho$  is the density of the liquid ( $\text{kg}\cdot\text{m}^{-3}$ );

$\theta$  is the contact angle (rad);

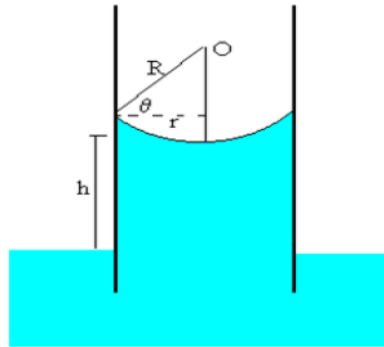


Figure 6 – Height corresponding to the capillary rise

Source: (NESTOR EDUARDO, 2015)

The weight of water absorbed per area unit can be determined by combining Darcy's Law and Laplace's Law (cf. Equation 15).

$$Ca = \frac{M}{S \cdot \sqrt{t}}$$

Equation 15 – Coefficient of capillary absorption

Where:

$Ca$  is coefficient of capillary absorption;

$M$  is the absorbed water mass (kg);

$S$  is the surface of the basis of the specimen ( $\text{m}^2$ );

$t$  is the time (s).

- **Convection**

Finally, convection is a transport mode produced when two areas of the material have different temperature. In the hot area, the fluid tends to decrease its density (by increasing its volume). To homogenise its properties, the fluid moves from the hot areas to the cold areas.



### 1.3 CHEMISTRY OF CEMENTITIOUS MATERIALS

#### 1.3.1 Cement hydration process

Cement hydration process is characterised by a succession of steps between the ions that come from the dissolved reactive products entering in contact with water, evolving dissolution, transport or chemical reactions. First of all, the dissolution occurs, leading to the formation of an aqueous phase. Then, the components are transported through the pores. The ions liberated during the dissolution will then precipitate (when saturated) leading to the formation of the hydrates.

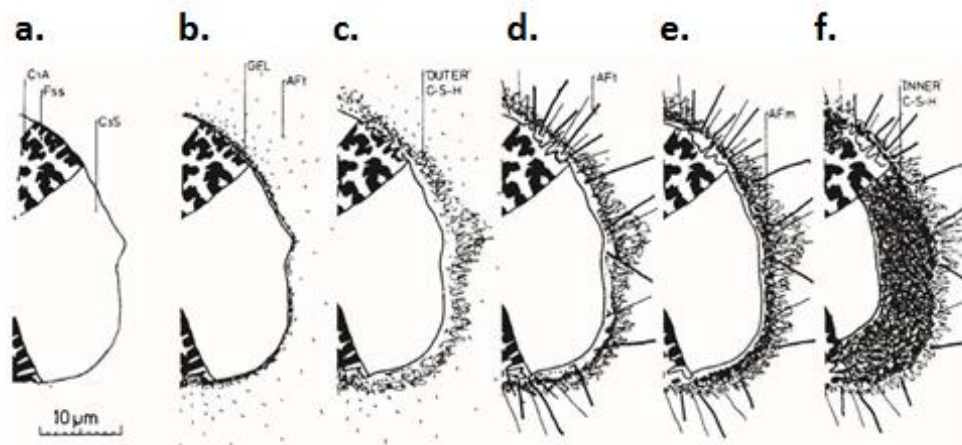


Figure 7 – Hydration process of Portland cement

Source: (SCRIVENER, 1984)

The figure above allows having a better understanding of the hydration process in cement (cf. Figure 7). The figure a. shows the different phases at the beginning. Then, in figure b. (during the ten first minutes of the hydration process), there is a reaction between the aluminates and the gypsum leading to the formation of a gel at the surface; then, ettringite (AFt phase) starts growing upon the gel. In figure c. (ten hours after the beginning of the process), the tricalcium aluminate produces the called “outer CSH”, which is CSH gel growing from the surface. At 12 hours, we have reached the cohesion point where the grains start to occupy the voids. In figure d. (18 hours), we can see that the tricalcium aluminate continues to react with the gypsum provoking more formation of ettringite (as we may see the needles of ettringite are longer) while the CSH gel starts to penetrate the grain. In figure e. (evolution after 13 days), at this stage, the tricalcium aluminate reacts with the ettringite (since the gypsum has been totally consumed) leading to the formation of the AFm phase (calcium monosulfaluminate hydrate); at the same time, the CSH gel continues to grow into the grain. Finally, in figure f. (2 weeks), we can clearly see the called “inner CSH” which is the CSH gel formed within the grain.

The cement hydration process can also be described by the two following periods: the setting and the hardening. The first one occurs once the water is put in contact with the cement during the first few hours. It consists of the increase in the cement paste consistency

until it reaches the properties of a solid. Both beginning and ending of setting define the rheological changes in the material. The hardening occurs after the setting.

The hydration of cement evolves several steps. It is possible to have an idea of the different stages by measuring the evolution of the heat of hydration over time, as represented on the figure below (cf. Figure 8) that shows a typical evolution of heat over time for classical Portland cement. Each step will be described from the kinetics point of view in the following paragraph.

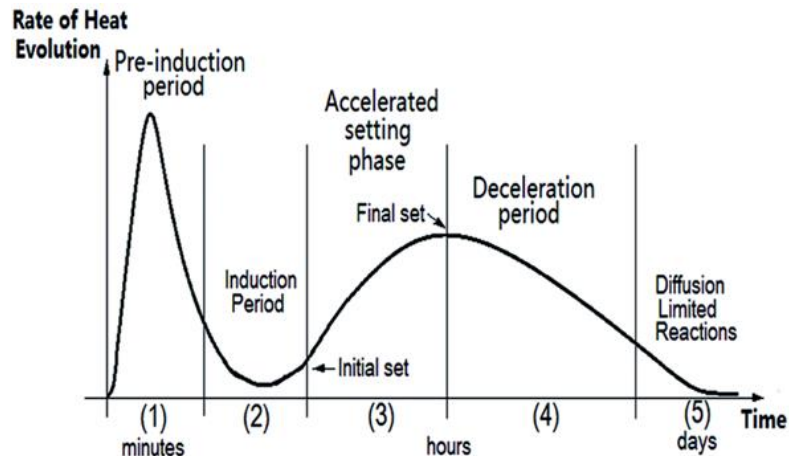


Figure 8 – Heat evolution during hydration process

Source: (ZHANG, et al., 2015)

### 1.3.2 Kinetics of cement hydration

As it appears above (cf. 1.3.1) five periods can be identified.

#### ▪ *Pre-induction period*

This step occurs in the first minutes of the reaction (15 to 20 first minutes). The pre-induction period is characterised by the rapid dissolution of ionic species and the formation of the CSH gel on the surface while the  $C_3S$  is being quickly dissolved.  $C_2S$  reacts very little during this period.  $C_3A$  and  $C_4AF$  react and lead to the formation of the AFt phase. The precipitation of calcium hydroxide is the sign that the induction period is starting. This step is characterised by very fast rate kinetics and an important loss of heat (cf. Figure 8).

#### ▪ *Induction period*

Also called “dormant period”, it occurs in the first few hours of the reaction. At this stage, the reaction continues. The amount of calcium hydroxide increases until it reaches a maximum and then starts to be reduced. This period is characterised by a slowdown in the rate of reaction (cf. Figure 8). At this stage, the cement paste has plasticity and workability characteristics. Many different hypotheses have been emitted to explain the end of the induction period:

- A possible weakening of the barrier due to ageing;
- A possible diffusion of ions occurring across the barrier by osmosis;
- A possible gradual weakening of the electrical double layer;
- A possible slowdown in the nucleation of calcium hydroxide due to the nuclei approaching their critical size.

▪ ***Acceleration stage***

This stage occurs between 3 and 12 hours after the mixing. At this stage, the  $C_2S$  begins to react significantly. The ions precipitate in the form of CSH gel and calcium hydroxide. The calcium hydroxide starts precipitating and the AFt phase continues to grow. During this period, the rate of hydration starts to increase again (cf. Figure 8). During this period, the cement starts setting. The end of this phase can be explained according to the following hypotheses:

- The nucleation and growth of the CSH gel;
- The growth of a stable layer of CSH gel;
- Break of the initial barrier;
- Nucleation of the calcium hydroxide.

▪ ***Post-acceleration period***

This stage occurs after 6 to 24 hours (for the cement made with clinker at normal temperature). AFt is converted into AFm.  $C_2S$  increases substantially its contribution, which leads to a reduction in the formation of calcium hydroxide. In general, the process starts to slowdown as it starts to be controlled by the diffusion (cf. Figure 8).

▪ ***Diffusion***

This stage is mainly controlled by the diffusion and transport processes within the porous matrix. Slow hydration reactions occur during the diffusion period. Even though its beginning and its end cannot be clearly defined, we can say that dense CSH gel structures (in comparison with those formed previously) are formed during this stage.

The process in terms of consumption and production of the different species can be summed up in the figure below (cf. Figure 9). Alite, as it is the main compound, determines to a larger degree the hydration process of cement. Indeed, alite is the principal responsible for the formation of CSH gel as explained above (cf. 1.2.1 and 1.2.2). As represented on the figure below, the CSH gel is the most important product of the hydration process; it is responsible for the resistance of the cement paste.

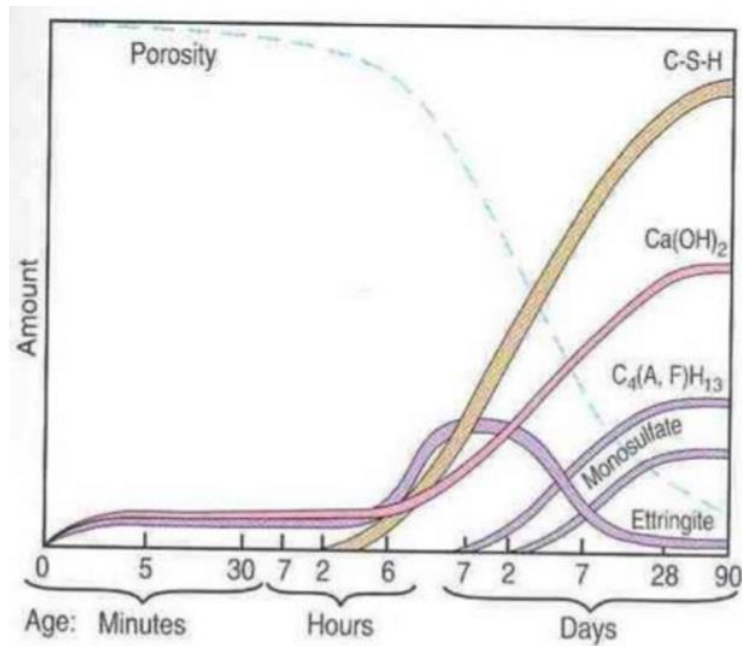


Figure 9 – Evolution of the hydration process in terms of amount of products formed

Source: (Front Desk Architects, 2011)

Many parameters can influence the kinetics of the hydration process:

- The composition of the phases of the cement;
- The quantity of gypsum in the cement and its form;
- How fine is the cement;
- Water/cement ratio;
- Curing conditions:
- Hydration temperature;
- Use of chemical admixtures.

The study of the kinetics of hydration process is carry out by the study of the degree of hydration (i.e. the fraction that has entirely reacted with water, relative to the total quantity of cement in the sample) related to the time.

## **2 PART II: MODIFICATION OF CEMENTITIOUS MATERIALS**

Nowadays, in order to achieve the structural and technological requirements linked to the construction area, chemical additive are developed and used. Among them, the polymers are more and more requested. The basic reason why polymers are employed in cementitious materials is because they are able to modify both physical and chemical characteristics of the cementitious material (MILLER, 2005). They are particularly used for repairing and protecting the concrete structures.

## 2.1 STANDARDS FOR THE REPAIR OF CONCRETE STRUCTURES

With regard to the legislation in force about the repair of concrete structures, both Spain and France use a European Standard: the EN 1504. This Standard, in force since 2009, defines the principles and methods of the repair of concrete structures. It counts 10 different parts (cf. Table 9).

<b>EN 1504-1</b> Definitions	<b>EN 1504-6</b> Anchoring reinforcing steel bars
<b>EN 1504-2</b> Surface protection systems for concrete	<b>EN 1504-7</b> Reinforcement corrosion protection
<b>EN 1504-3</b> Structural and non-structural repair	<b>EN 1504-8</b> Quality control and conformity assessment
<b>EN 1504-4</b> Structural bonding	<b>EN 1504-9</b> General principles for the use of products and systems
<b>EN 1504-5</b> Concrete injection	<b>EN 1504-10</b> Site application of products and quality control of the works

Table 9 – Parts of the EN 1504 standard

This Standard has been based on the most common causes of degradation of the concrete and the probable combination of causes in order to establish the principles detailed in the 9<sup>th</sup> part. Indeed, it can be reminded that the degradation of the concrete can be due to the degradation of the concrete itself, or to the corrosion of its reinforcement. The defects in the concrete itself can be due to a mechanical process (impacts; overload; movements such as settlement, explosion or vibration), a chemical process (alkali-aggregate reaction; aggressive agents such as sulphates, soft water or salts; biological activities) or a physical process (freeze/thaw cycle; thermal cycle; salts crystallisation; shrinkage; erosion; wear). Regarding the reinforcement corrosion, it can be due to a carbonation process, corrosive contaminants at mixing (sodium chloride; calcium chlorides) or from external environment (sodium chloride; other pollutant), or stray currents.

Knowing this, the Standard defines 11 principles: the 7 first principles concern the degradation of the concrete itself, while the others are about the corrosion of the reinforcement (cf. APPENDIX A – Principles defined in the EN 1504 Standard). In particular, the third part of the EN 1504 Standard defines mortars for concrete restoration. It is one of the most important principles since in this part the repair mortars are defined and classified. Four types of repair mortars are identified, from higher to lower performances:

- Class R4 mortar (structural repair mortar);
- Class R3 mortar (structural repair mortar);
- Class R2 mortar (non-structural repair mortar);
- Class R1 mortar (non-structural restoration mortar).

The Standard defines the minimum requirements that each mortar has to satisfy in order to be used for structural or non-structural restoration work. Those requirements are based on the performance characteristics of the mortars, according to various tests (cf. APPENDIX B – Class of restoration mortars according to the performance characteristics).

Three types of mortar are generally used to repair concrete structures: cementitious concrete, polymer cementitious concrete, or epoxy cementitious concrete. We will now focus on polymer cementitious concrete, in which the polymers help to improve some of the properties of the products.

## **2.2 COMPOSITION OF POLYMER-MODIFIED MORTARS**

A polymer-modified mortar is a cement mortar which has been mixed with a polymeric admixture. This admixture can integrate polymers in the concrete mix in various different forms:

- Polymer latex;
- Redispersible polymer powder;
- Water-soluble polymer;
- Liquid polymer.

In such materials, the polymerisation process occurs within the mortar or concrete. When polymers are introduced to a mortar or a concrete, it is essential to obtain a monolithic matrix phase made by a network structure in which the cement hydrate phase and the polymer phase interpenetrate. This phenomenon is the result of both cement hydration and polymer film formation process, where the polymer film formation is the coalescence of both polymer particles and polymerisation of resins. The co-matrix phase obtained is the one that gives the good properties observed in polymer-modified mortar and concrete. In what follows, the different types of admixtures will be described (OHAMA, 1998) and its properties will be highlighted.

### **2.2.1 *Polymer latexes***

Polymer latexes are formed with polymer particles with very small diameter (from 0.05 to 5 $\mu$ m). They are generally a copolymer system produced by emulsion polymerisation (except for the natural rubber latex which is directly taken from the rubber trees and concentrated, and the epoxy latex which is produced by emulsifying an epoxy resin in water). The polymer latexes are classified as shown below (cf. Figure 10). It has to be underlined that both elastomeric and thermoplastic latexes form continuous polymer film when they dry; they are also the polymer latexes more commercially available.

The principle of polymer modification using polymer latexes is based on the cement hydration and polymer film formation processes. Generally, the cement hydration comes first, once the cement is in contact with water. Consequently to these processes, a co-matrix is formed (cf. Figure 11). It can be noted that chemical reactions take place between the particles surfaces of reactive polymers. The increase in the bond between cement hydrates and aggregates, produced by the reactions, leads to an improvement in terms of properties of hardened latex-modified mortar and concrete.

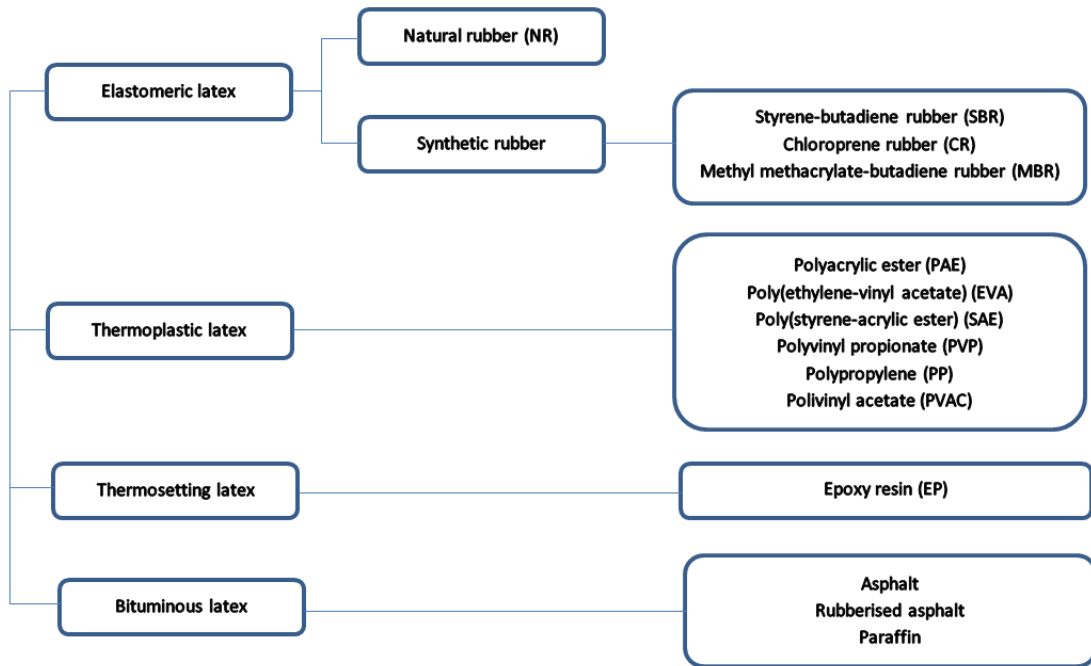


Figure 10 – Classification of polymer latexes

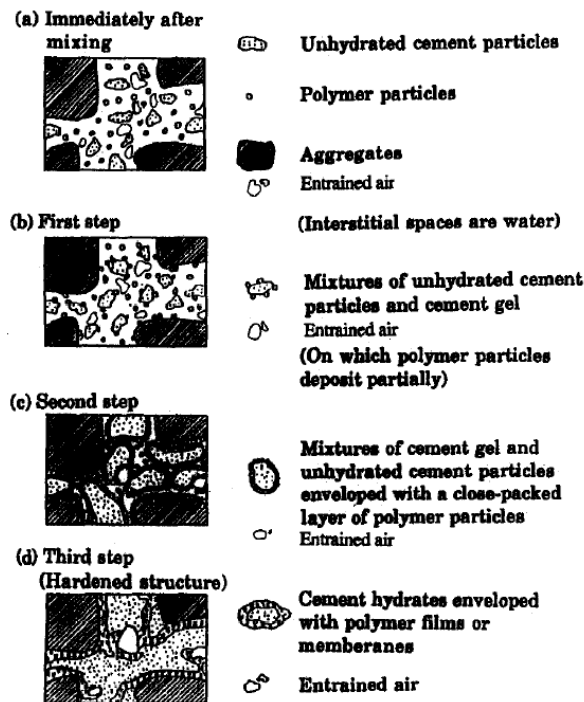


Figure 11 – Simplified model of the polymer-cement co-matrix formation

Source: (OHAMA, 1998)

### 2.2.2 Redispersible polymer powders

Redispersible polymer powders are usually free-flowing powder made from polymer latexes which particles sizes are in a range of 1 to 10µm. They are made by a two-step process which involves producing the polymer latexes (which is in this case the raw material,

and is formulating with bactericides, spray-drying aids and antifoaming agents), and spray-drying them to obtain the powder. It can be noted that, due to the anti-blocking aids, redispersible powders have an ash content of 5 to 15%. This type of polymer admixture re-emulsify once they are placed in water under agitation. Consequently, they are dry-blended with the cement and aggregates. They can be classified as shown below (cf. Figure 12). The principle of polymer modification using redispersible polymer powders is almost the same as polymer latexes. The difference is that in this case, the redispersion of the polymer powders is taken into account. Indeed, when wet mixing the preparation (polymer powders, cement and aggregates) with the water, the re-emulsified polymer powder have the same behaviour as the latexes.

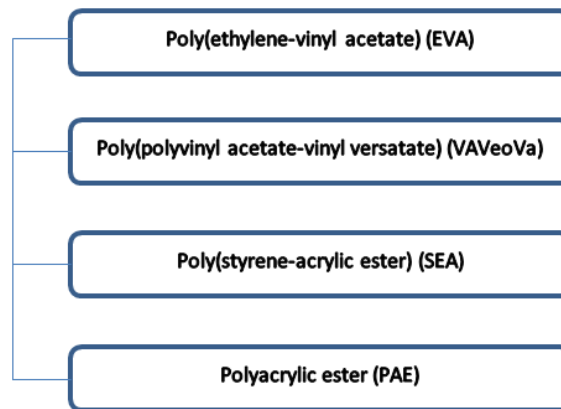


Figure 12 – Classification of redispersible polymer powders

### 2.2.3 Water-soluble polymers

Water-soluble polymers are powdered polymers which are soluble in water. They can be classified as shown below (cf. Figure 13).

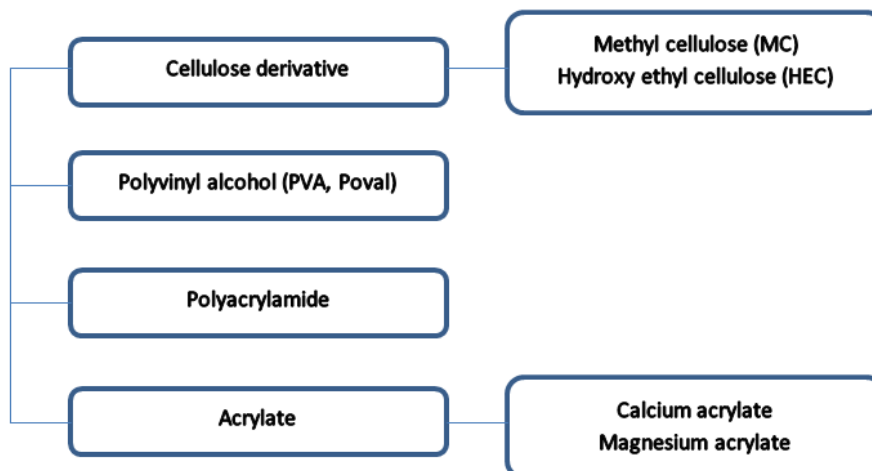


Figure 13 – Classification of water-soluble polymers (monomer)



While mixing the cement mortar or concrete, they can be added either in the form of powders or in the form of aqueous solutions. This leads to an increase in workability and in the viscosity of the water phase in the modified system.

#### 2.2.4 *Liquid polymers*

Liquid polymers can be either a viscous polymeric resin or an unsaturated polyester resin. They can be classified as shown below (cf. Figure 14). They are added while mixing the cement mortar or concrete (at the same time as the hardener or the catalyst) and the accelerator. In this case, the polymerisation is initiated by the presence of water, which leads to the formation of a polymer phase, while at the same time the cement hydration takes place. Therefore, a co-matrix phase is formed, in which cement hydrates and polymers interpenetrate, improving the properties of the material.

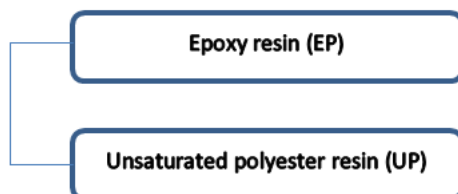


Figure 14 – Classification of liquid polymers

### 2.3 PROPERTIES AND CHARACTERISTICS

As told above, the introduction of polymers in cementitious materials such as mortars or concrete modifies physical and chemical properties of the material, and has a positive effect on its durability. From all the types of polymer developed before, polymer latexes are among the most employed in the industry. Besides, water-soluble polymers play an important role on the rheology of the cementitious material. Consequently, we will especially focus on the characteristics and properties of both polymer latexes and water-soluble polymers.

#### 2.3.1 *General characteristics and control parameters*

The formation of a co-matrix phase, mentioned above, is typical of polymer-modified mortars. The composite mechanism has been studied and may be summed up in the figure below (cf. Figure 15). It can be seen that a microstructure is formed and polymer particles are distributed in it. The interface between cement particles is filled with spherical polymer particles and the hydrated products are stacked around the polymer particles.

In a study realised with redispersible powder (styrene/acrylic), it has been highlighted that the synergy between the cement and the polymer gives the good properties observed in the polymer-modified materials (SCHULZE, 1999). Indeed, cement acts as an inorganic binder and is responsible for the compressive strength (mechanical stability). As the same time, the redispersible powder acts as an organic binder and is responsible for the internal tensile strength and for the adhesion-bond strength at the interfaces. These properties may be influenced by several parameters including:

- The type of polymer;
- The polymer/cement and water/cement ratios;
- The air content;
- The curing conditions.

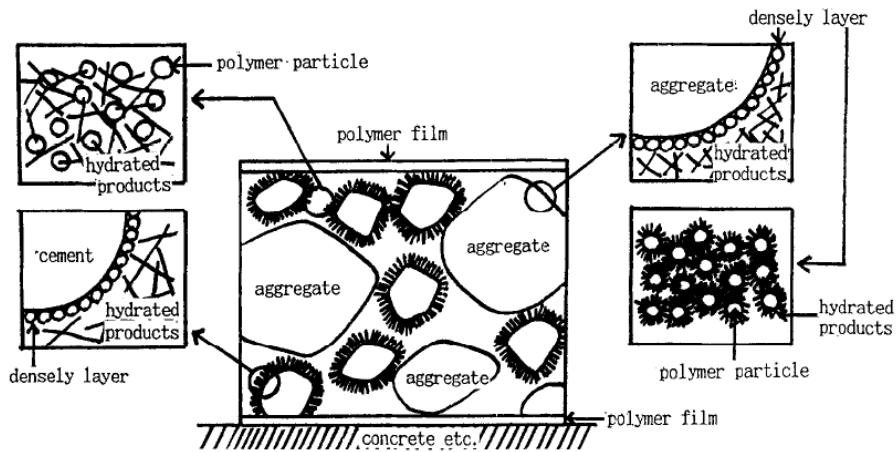


Figure 15 – Model of composite mechanism

Source: (SAKAI &amp; SUGITA, 1995)

### 2.3.2 Properties

With regard to fresh mortars, it has been showed that the workability and water retention of polymer-modified materials is improved in comparison with ordinary mortars. Besides, those materials present a very good resistance to bleeding and segregation. However, an excess of entrained air can leads to a reduction in the strength of the material (OHAMA, 1998).

With regard to hardened mortars, it has been showed that polymer-modified materials present a higher flexural strength in comparison with unmodified materials, but no improvement in compressive strength occurs. In the case of the flexural strength, it has been showed that after 28 and 90 days of a storage at normal climate, the flexural strength decreases slightly (SCHULZE, 1999). Nevertheless, after storage under water, flexural strength decreases significantly with the increasing of the water/cement ratio. In addition, the improvement of the following properties has been observed for polymer-modified materials in comparison with conventional cementitious materials: impact resistance, abrasion, or freeze/thaw durability. Those materials are dependent on the temperature as the polymer is. Hence, both thermal resistance and incombustibility of the polymer-modified material are variable according to the type of polymer used and the polymer/cement ratio. According to OHAMA, polymer-modified materials (using latexes) resist alkalis and various salts except sulphate, but have not a good resistance to organic solvents.

## 2.4 PREVIOUS STUDIES ABOUT POLYMER-MODIFIED MATERIALS

As seen previously, different types of polymers can be used in order to modify the properties of a cementitious material. In this context, as much formulations as polymer types

can be employed. In what follows, two mortar formulations will be presented, according to two thesis works. On one hand, the attention will be drawn to the case of redispersible polymer powders (GONZALEZ LUCAS, 2014); on the other hand, the attention will focus on the case of water-soluble polymers (BRUMAUD, 2011). These studies will give us more information about the properties of the modified material using two types of polymers and an example of dosing for the use of redispersible polymer powders.

#### **2.4.1 Case of redispersible polymer powders**

In this first case, redispersible polymer powders have been used. The main objective was to find out a justification in the use of polymer-modified mortars as repair mortars. In this case, the interest lies in the formulation (that is to be used in the industry for the preparation of repair mortars) and in the properties obtained.

The study consisted in the testing of different mortars modified with polymer addition (between 0 and 25%) taking as reference a conventional mortar without polymer or any addition. The criteria to determine the best formulation were the following:

- The mortar has to be classified as R4 for mechanical performances and durability according to the Standard in force;
- The mortar has to remain competitive (i.e. the polymer addition has to be not too high).

After having tested various mortars, with different compositions, the one which best satisfy the Standard requirements has been determined. It is a monocomponent mortar, class R4 (according to the EN 1504 Standard), reinforced with fibres derived from acrylamide (between 0.1 and 0.3% in mass), containing 3.2% of redispersible polymer. This mortar has been selected because it satisfies the EN 1504 requirements for a repair mortar (class R4) with a polymer addition that leads to an economical optimum in comparison with the other tested mortars.

This study leads to the conclusion that, to be able to obtain a repair mortar according to the Standard and satisfying an economical optimum, the optimal polymer content in this case is from 2.0 to 3.5% in total mass. Moreover, the water/cement ratio has to be in the order of 0.40 - 0.42 (more broadly, the water/cement ratio has to be inferior to 0.5). Finally, in order to improve the resistance of the mortar and to reduce costs, a particular stone skeleton has been used.

With regard to the properties of the repair mortar, it has been shown that the polymer-modified mortar has better properties in terms of adherence. Moreover, it presents a lower porosity and a smaller pore size susceptible to be attacked, which leads to a better behaviour against abrasion and capillary absorption. Its lower permeability allows a better behaviour against sea water, sulphate attacks and carbonation.

This study confirms the conclusion about the better behaviour and properties of a polymer-modified material. Besides, it gives us an idea of the composition of a mortar modified by the addition of a redispersible polymer powder used in the industry that provides the best properties.

#### **2.4.2 Case of water-soluble polymers**

In this second case, water-soluble polymers, specifically cellulose ether, have been used. The main objective was to study the rheology of solutions which contain cellulose ether, and to determine the influence of cellulose ether on various parameters among which the viscosity of the interstitial fluids, or its flow threshold.

In her study, BRUMAUD C. shows the existence of a concentration threshold and two different behaviours for the interstitial solution. Below the threshold, the solution behaves as a Newtonian fluid and the parameter that influences this behaviour is the molar mass of the polymer. Above the critical concentration, the interstitial solution behaves as a shear thinning fluid and inter molecular interactions are developed. In this case, an increase in the pH or the presence of species coming from the dissolution of the cementitious material has an influence on the rheology. According to her study, the parameters responsible for the viscosity of the interstitial fluid are the dosing of the polymer, its molar mass and its type. Her study has also confirmed the delaying effect of cellulose ether by highlighting the limitation of the germination and growth of the CSH due to the adsorption of the polymer. Besides, according to her study, another effect of the adsorption of the polymer is the disappearance of the Van der Waals interactions and the development of bridging interactions.

Finally, she has shown that an improvement on water retention for monolayer mortars can be achieved by increasing the dosing of the molar mass of the polymer, or by increasing the degree of substitution of the polymer. Moreover, an improvement in the adhesion capacity can be achieved with a high molar mass and a low degree of substitution. But a particular attention has to be paid to the molar mass since a high molar mass leads a decrease in the sag resistance of the mortar.

This study allows us understanding the effect of water-soluble polymers on modified mortars. It highlights the delaying effect of such polymers and shows the impact on rheology (presence of a concentration threshold that delimits a Newtonian behaviour for the interstitial fluid on one hand, and a shear thinning behaviour on the other hand).

### **3 PART III: ACID ATTACK OF CEMENTITIOUS MATERIALS**

Cementitious materials are widely employed in the industry where they are really exposed to various potential attacks (including salts attacks, acid attacks, etc.) which can be due to an aggressive environment or freeze/thaw cycles among others. It has to be reminded that concretes are generally alkaline by nature, with pH = 13 approximately. But, in case they are attacked by acid solutions, the decrease in the pH disturbs the equilibrium in the cement matrix and can causes severe damages to the material.

### 3.1 DURABILITY OF CEMENTITIOUS MATERIALS

#### 3.1.1 Generalities about the durability of cementitious materials

Concrete structures are well-known to be submitted to many different actions. But when thinking about its durability, the loads and mechanical actions are not the only ones that have to be taken into account. Indeed, the environment plays an important role on the capacity of the structure to support the external actions and to last the whole service life it has been designed for. Many definitions of the concept of durability have been given by different organisms. In general, durability is seen as the capacity of a structure to resist the external actions it is exposed to and which can damage it during its service life. In this respect, durability is closely linked to the performance of the concrete structure (cf. Figure 16). As we can see on the figure below, different mechanisms can lead to a decrease in the performances of the cementitious material either by a deterioration of the proper material, either by a deterioration of its reinforcement. Those mechanisms can be: physical actions, chemical and biological actions of corrosion (in the case of reinforced material).

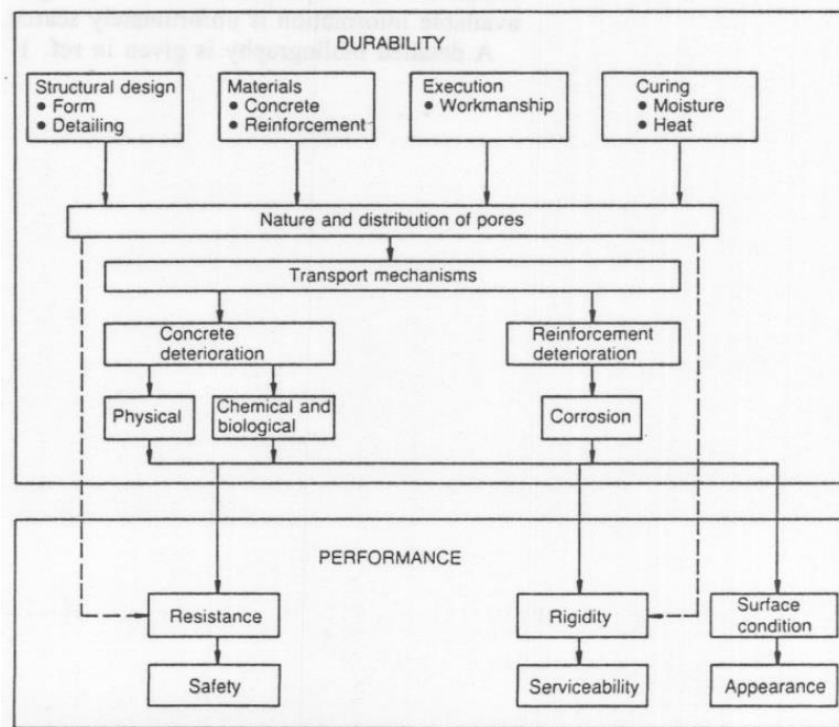


Figure 16 – Relationship between concrete durability and performance

Source: (Comité Euro-International du Béton, 1992)

#### 3.1.2 Chemical attack of cementitious materials

In what follows, we will focus on the deterioration of cementitious materials by chemical attacks. Chemical attack is here considered as the penetration of aggressive agents into the cementitious material which leads to the deterioration of the material as the agents react with the proper components of the considered material. Chemical attacks of a cementitious material (and more broadly of concrete) may cause different damages depending on the configuration. REGOURD and HORNAIN have determined a classification of the damages

observed on concrete according to the configuration of the chemical attack; this classification is presented below (cf. Figure 17). The classification makes it clear that the transport mechanisms play an important role in the deterioration of concrete; thus the porous structure is essential in the understanding of penetration of aggressive agents into the material.

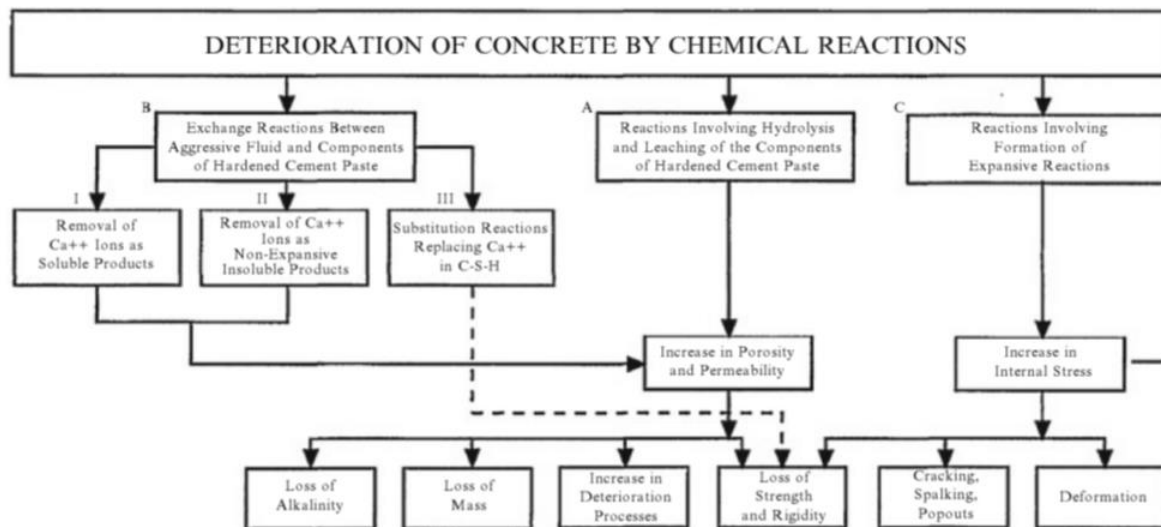


Figure 17 – Deterioration of concrete by chemical reactions

Source: (REGOURD, 1981)

It has to be reminded that cementitious materials consist of a basic medium in which the hydrated cement paste compounds are unstable (owing to the equilibrium between the dissolution of the hydrated compounds and the porous solution). In presence of organic or inorganic acids, an acid/base reaction occurs between the acid in presence and the hydrated and/or anhydrous components of the cement paste. This reaction may modify the equilibrium and lead to the decomposition of the components.

REARDON has determined the expected decomposition of the cement paste according to the pH variations in the porous solution, as shown in the table below (cf. Table 10). As we may see, for a pH below 12 to 12.5, the modifications begin in the cement paste and for pH below 9 a total decomposition of the CSH (which gives durability and resistance to the cement paste) occurs. The intensity of the chemical attack depends on the pH of the solution, on the solubility of the formed salts, on the type of acid and its concentration in the solution, on the nature of the binder and on the dissociation constant of the acid (MASSANA GUITART, 2010; PEREIRA GARCIA, 2008; BERTRON, 2004).

pH	EXPECTED CHANGES IN THE CEMENT PASTE
12 – 12.5	- Dissolution of both calcium hydroxide and hydrated calcium aluminate, and eventual dissolution of the calcium monosulfoaluminate hydrate - Precipitation of ettringite
10.6 – 11.6	- Precipitation of gypsum

10.6	- Decomposition of ettringite and formation of $\text{Al}(\text{OH})_3$ and gypsum
8.8	- Decomposition of the CSH to form silica gel

Table 10 – Expected changes in the cement paste according to pH variation

Source: (REARDON, 1990)

Chemical attacks can have different forms including:

- Leaching, which is caused by the dissolution and leaching of the  $\text{Ca}^{2+}$  contained in the cement paste;
- Acid attack by means of ionic exchange which is due to the concentration of protons that decompose the calcareous compounds of the cement paste;
- Acid attack by means of bacteria which secrete acids;
- Sulphate attack.

Thus, many different types of attack can occur and cause damages to the cementitious material. In what follows, we will exclusively focus on attacks by organic acids.

### 3.1.3 Case of organic acids

Cementitious materials are exposed to organic acids in many different environments. For instance, organic acids are very present in agricultural and agro-food industries and in sewage waters. Yet, concrete structures can also be degraded by organic acids coming from the secretions of bacteria or the excretion of microorganisms. In this case, the degradation does not only occur in sanitation facilities or in facilities dedicated to production, storage and treatment of effluents in agricultural and agro-food industries, but also on buildings (in their façades as well as inside the proper structure).

Many studies have been realised in order to explain the mechanisms of degradation of organic acids in agricultural and agro-food facilities. The acids mostly identified are the following (cf. Table 11).

NAME OF THE ACID	CHEMICAL FORMULA	pKa (25°C)
Lactic acid	$\text{C}_3\text{H}_6\text{O}_3$ $\text{CH}_3\text{-CH-OH-COOH}$	3.86
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$ $\text{CH}_3\text{-COOH}$	4.76
Valeric acid	$\text{C}_5\text{H}_{10}\text{O}_2$ $\text{CH}_3\text{-(CH}_2\text{)}_3\text{-COOH}$	4.80
Butyric acid	$\text{C}_4\text{H}_8\text{O}_2$ $\text{CH}_3\text{-(CH}_2\text{)}_2\text{-COOH}$	4.81
Iso-butyric acid	$\text{C}_4\text{H}_8\text{O}_2$ $(\text{CH}_3)_2\text{-CH-COOH}$	4.85

Propionic acid	$C_3H_6O_2$ $CH_3-CH_2-COOH$	4.87
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Table 11 – Some organic acids: formula and pKa

These acids are weak acids within the classification of acids; however they lead to a very strong attack. In particular, the lactic acid has the lowest pKa of all these considered above; consequently, it is more aggressive than the others. Besides, we can see that acetic acid, valeric acid, butyric and iso-butyric acids and propionic acid have comparable pKa. According to BERTRON et al, the acetic acid can be considered as representative of them all. They react with the hydrates (i.e. calcium hydroxide, CSH gel, hydrated aluminates) and/or anhydrous compounds of the cement paste and form soluble salts. The dissolution of  $Ca^{2+}$  causes the leaching of the material. In particular, the solubility of the calcium salts formed during this process (and which is the most important element in ordinary cement pastes) impacts the structure of the proper cementitious matrix. However, all the salt can possibly be formed, so they have to be all taken into account (cf. Table 12). We can see that the salts that are formed are soluble into water. Thus, they are unlikely to crystallise in the pores if the material is submerged into a solution of organic acids.

SPECIES	FORMULA	SOLUBILITY IN COLD WATER (g/100mL)	SOLUBILITY IN HOT WATER (g/100mL)
Lactic acid	$Ca[C_3H_5O_3]_2 \cdot 5H_2O$	3.1 (0°C)	7.9 (30°C)
	$Al[C_3H_5O_3]_3$	Very soluble	-
	$Mg[C_3H_5O_3]_2 \cdot 3H_2O$	3.3	16.7 (100°C)
	$Fe[C_3H_5O_3]_3$	Soluble	Very soluble
	$Na[C_3H_5O_3]$	Soluble	Very soluble
	$K[C_3H_5O_3] \cdot xH_2O$	Soluble	-
Acetic acid	$Ca[C_2H_3O_2]_2$	37.9 (0°C)	29.7 (100°C)
	$Al[C_2H_3O_2]_3$	Soluble to slightly soluble	Decomposed
	$Mg[C_2H_3O_2]_2$ or $Mg[C_2H_3O_2]_2 \cdot 4H_2O$	Very soluble or 120 (15°C)	Very soluble or $\infty$
	$FeOH[C_2H_3O_2]_2$	Insoluble	-
	$Na[C_2H_3O_2]$ or $Na[C_2H_3O_2] \cdot 3H_2O$	119 or 76.2 (0°C)	170.15 (100°C) or 138.8 (50°C)
	$K[C_2H_3O_2]$	253, 20°C	492 (62°C)
Valeric acid	$Ca[C_5H_9O_2]_2$	8.28	7.39
	$Na[C_5H_9O_2]$	Soluble	-



Butyric acid	$\text{Ca}[\text{C}_4\text{H}_7\text{O}_2]_2 \cdot \text{H}_2\text{O}$	5	Slightly soluble
Isobutyric acid	$\text{Ca}[\text{C}_4\text{H}_7\text{O}_2]_2 \cdot 5\text{H}_2\text{O}$	20	Slightly soluble
Propionic acid	$\text{Ca}[\text{C}_3\text{H}_5\text{O}_2]_2 \cdot \text{H}_2\text{O}$	49	55.8
	$\text{K}[\text{C}_3\text{H}_5\text{O}_2] \cdot \text{H}_2\text{O}$	207 (16°C)	359

Table 12 – Solubility of salts

Source: (BERTRON, 2004)

Another process which has to be taken into account is the complexation of cations. This is important in the attack process since the formation of cations is predominant in comparison with the formation of the salts. The complexes formed have a great influence on the equilibria since they can shift the equilibria in favour of an acceleration of the reactions between the cementitious matrix and the acids. That is the reason why the formation constants have to be taken into account while thinking about the attack of cementitious materials by organic acids (cf. Table 13).

LIGAND	Log(Ki)
Lactate anion	1.42
Acetate anion	0.6

Table 13 – Formation constant for the  $\text{Ca}^{2+}$  cation (20°C)

Source: (BERTRON, 2004)

In this respect, the consequences of the reactions in the situation of a cementitious material which is submerged into a solution of organic acids may be the increase in both porosity and permeability of the material. Thus, a loss in mass and a reduction of the mechanical properties are, among others, the phenomena that may be observed on the cementitious material.

### 3.2 MECHANISMS OF ORGANIC ACID ATTACKS

Many studies have been realised in order to determine the mechanisms in action when an attack of a cementitious material by organic acids takes place. According to the studies that we are aware of, it has been highlighted that the mechanisms of such attacks (in the case in which the material is submerged) are similar to those of attacks by pure water or strong acids (BERTRON, 2004).

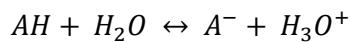
#### 3.2.1 Reminders about acid/base reactions

As the cementitious matrix is a basic medium, in presence of an acid an acid/base reaction occurs between this acid and the hydrates and/or anhydrous of the cement paste. An acid/base reaction can be summed up by the following reaction (cf. Equation 16). The products formed by means of an acid/base reaction are salts and water.



Equation 16 – Reminders of an acid/base reaction

Two types of acids may be distinguished: strong acids and weak acids. When put in solution, strong acids are completely dissociated. But in the case of weak acids, a partial dissociation of the acid occurs as it is summed up in the following equation. (cf. Equation 17). In this case, the dissociation constant plays an important role since it gives an idea of the force of the acid once it is in solution. It is common to use a logarithmic scale to characterise a weak acid (cf. Equation 18). In our study, this plays an important role in the behaviour of salts.



Equation 17 – Partial dissociation of weak acids

$$K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{A}^-]}{[\text{AH}]}$$

$$pK_a = -\log K_a$$

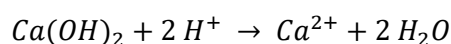
Equation 18 – Dissociation constant of a weak acid

### 3.2.2 *Mechanisms of an attack by organic acids*

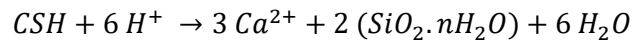
Firstly, it is important to remind that the cement hydration produces calcium silicate hydrate and calcium hydroxide as main products (cf. Equation 3, Equation 4). When a cementitious material is submersed into an aggressive solution, two types of phenomena occur:

- The spread of chemical species ( $\text{Ca}^{2+}$  in this case) in the pores due to the appearance of a gradient of concentration between the aggressive solution and the interstitial water;
- The beginning of dissolution and precipitation reactions.

If the aggressive solution is made of organic acid, the acid/base reactions leads to the formation of protons  $\text{H}^+$  (cf. Equation 17). In its presence, the dissolution of the hydrated phases will be accelerated. The CH is the first to be attacked since it constitutes the most unstable phase (cf. Equation 19). Then, the ettringite is attacked. When there are enough protons (CH is then totally consumed), the CSH gel is attacked and decomposed into a silica gel (cf. Equation 20). The decomposition of the CSH gel causes severe damages to the cementitious material in a structural point of view since the silica gel produced presented a lack of resistance.



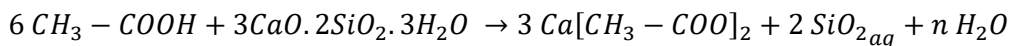
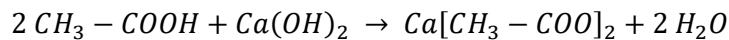
Equation 19 – Acceleration of the lixiviation of CH by  $\text{H}^+$  ion



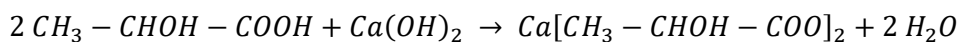
Equation 20 – Attack of the CSH by the H<sup>+</sup> ion

If we consider the particular cases of acetic and lactic acids, when they are put in presence of the cementitious material, they will form calcium acetate salt and calcium lactate salt as explained below.

The reaction of acetic acid with the hydrated phase of a cementitious material leads to the formation of a soluble calcium salt: the calcium acetate (cf. Equation 21). It first reacts with the calcium hydroxide, then with the CSH gel. In the latter case, it leads to the formation of three times more salt than in the reaction with calcium hydroxide. Lactic acid, when reacts with calcium hydroxide, leads also to the formation of a soluble calcium salt: the calcium lactate salt (cf. Equation 22). It has to be underlined that lactic acid also reacts with the CSH gel. These calcium salts, if they are insoluble, will slow down the attack since they will precipitate in the voids, limiting the amount of calcium that enters into solution. On the contrary case, if these calcium salts are soluble, they will be easily removed from the attack front, weakening the structure of the cement paste. This is what happens with the organic acids considered, in particular with acetic acid and lactic acid. Indeed, when calcium lactate or calcium acetate salts are formed and leach the cementitious material, they lead to an increase in the porosity of the material and a drop in the pH level in those pores. As a result, the cement hydrates gradually become unstable and a disintegration of the material occurs.



Equation 21 – Formation of calcium acetate salts



Equation 22 – Formation of calcium lactate salts

### 3.2.3 Consequences for the cementitious material

Owing to the attack of the material by organic acids, it has been showed that areas with constant chemical and mineralogical composition appear within the degraded parts. The degraded areas have suffered decalcification whose intensity depends on the pH (cf. Table 14) and whose porosity has significantly increased. The fact that these substances are easily erodes leads to the disintegration of the concrete. Therefore, the attack of cementitious materials by acids depends more on the solubility of the calcium salts of the organic acids than on the pH of the solution. The disintegration of the concrete depends also on:

- The porosity of the cement paste: the higher the porosity will be the more aggressive will be the attack.
- The fluid transport through the concrete.

pH RANGE	PHENOMENA	REMARKS
pH < 7 - 8	Almost total decalcification due to the dissolution of CH and the decalcification of the CSH gel	
pH = 4 - 5	Almost total decalcification of the peripheral areas	Same characteristics as the materials submitted to strong acids

Table 14 – Intensity of the decalcification according to the pH

Source: (BERTRON, 2004)

As a result, an acid attack can be basically diagnosed by the absence of calcium dioxide in the cement paste, or by the appearance of a surface dissolution of the cement paste, which exposes the aggregates. Moreover, it appears that the outside area of the attacked material is made of an amorphous zone which is composed almost entirely of silica, aluminium and iron oxide (BERTRON, 2004).

It has been showed (DE BELIE, et al., 1997) that there are three main factors in acid resistance of concrete:

- The chemical composition of cement paste;
- The alkalinity;
- The permeability (that determines the extent to which acids can penetrate into concrete).

Moreover, previous studies have highlighted the good influence of mineral additions such as fly ash, silica fumes or blast-furnace slag.

### 3.3 PREVIOUS STUDIES ABOUT ORGANIC ATTACKS

The attack of traditional concrete by acids is a topic that has been studied a lot in the last few years; in particular, the case of organic acids coming from the agriculture. It allows highlighting the consequences of the exposition of concrete to some organic acids. We can focus on the conclusions coming from BERTRON et al, OUESLATI regarding the effect on livestock manure and silage seepage (BERTRON, 2004; OUESLATI, 2011; DE WINDT, et al., 2015). Besides, we can lay interest on MASSANA's works regarding pig slurry (MASSANA GUITART, 2010).

#### 3.3.1 *Studies on the effect of livestock manure and silage seepage*

In her study, BERTRON A. has focused on acids coming from livestock manure (i.e. acetic, propionic and butyric acids principally) and silage seepage (i.e. acetic and lactic acids), in a determined pH range (between 6 and 8 for manures, and always lower than 4 for silage seepage) in order to reproduce the phenomena for that case. She has shown that the relative aggression of those acids depends basically on their dissociation constant and that the complexation reactions tend to increase the speed of the reactions between acids and the cementitious matrix (complex formation is overriding compared with salt formation).

Moreover, according to her results, the lactic acid has the most aggressive behaviour (in accordance with its pKa value), while the other acids are equivalent in terms of aggression. Consequently, a solution constituted by acetic acid at pH = 4 is representative of what really happens in the case of manure. She has also shown that when submerge the cementitious material into organic acid solutions, the attack produced is similar to an attack by means of strong acids and the following observations can be done:

- The degraded area suffers an almost complete decalcification and is constituted exclusively by silicon, iron and aluminium;
- The hydrated and anhydrous phases are dissolved in the degraded area (alite and belite are entirely dissolved whereas  $C_4AF$  is preserved in the inner part of this area, and dissolved in the external part of the degraded area);
- The degraded area is amorphous and has a high porosity and a poor mechanical resistance. However, since the area is not entirely dissolved, it forms a semipermeable membrane and helps to slowdown the kinetics of the following degradation.

According to her results, in order to improve the durability of the cementitious material in such conditions, the quantities of calcium and magnesium have to be limited (since they are highly leachable in such conditions) while the silicon, aluminium and iron contents have to be increased. In cases in which salts are formed (e.g. partial submersion) they do not lead to a specific cracking of the material. In the case of an acid attack of the material, the consequences that can be drawn are: an increase in both permeability and porosity of the material; a mass loss; a loss of alkalinity, resistance and rigidity; an increase in the degradation process. In real conditions, she has shown that even though in the case of manure the bacteria respiration is overriding compared with the acid effects, in the case of silage seepages, the mechanisms are similar to those highlighted before.

In his study, OUESLATI O. determines the formulas of cementitious materials that have the best performances when submitted to organic acid attacks and evaluates the importance of additions in the stability of a cementitious matrix in an acid medium. To do so, he focuses on the submersion of his samples into acetic acid solutions that simulate the action of livestock manures.

In his study, he has demonstrated the importance of the chemical composition of the cementitious matrix in order to minimise the solubility of the material in an acid medium. Indeed, the most adapted composition is the one that is rich in silicon, aluminium and iron and poor in calcium and magnesium (that are highly leachable). This result is in total accordance with those highlighted in BERTRON's study. According to his study, the degree of hydration is an essential parameter in the case of the organic acid attack of cementitious materials since it plays an important role in the stability of the cement paste in an acid medium. He has shown that the chemical and mineralogical stability of both anhydrous and hydrated phases is improved with a longer curing period (from 3 months to 1-2 years). A long curing period has also a good influence on the decrease produced in the mechanical properties due to the acid attack.

In his study, he has also focused on the effect of an acid attack on the corrosion of the material. He has shown that both permeability and porosity are essential parameters in terms of corrosion of the material: a high porosity facilitates the entrance of aggressive agents

leading to the depassivation of the reinforcing (as a consequence, rust propagates). So finally, it seems that porosity and chemical composition are the main control parameter in terms of durability of the proper material, and resistance to corrosion in acid media.

### **3.3.2 *Studies on the effect of pig slurry***

Different studies have been realised to understand the behaviour of cementitious materials exposed to pig slurry. In such media, short-chain fatty acids such as formic, acetic, propionic, butyric and isovaleric acids are in presence.

In his study, MASSANA J. has determined the behaviour of cementitious materials subjected to pig slurry (that contains among others acetic acid, butyric acid, propionic acid and bacteria). To do so, he has submersed the materials in pools containing pig slurry, at two different depths and with different conditions of dissolved oxygen availability. His goal in this study was to determine the compositions that resist the best to such media.

In his study he has drawn three conclusions that may present an interest for our study. Firstly, he has shown that the concentration of dissolved oxygen does not play a role in the degradation process. Besides, according to his results, a protective layer is formed and is characterised by a decrease in porosity and an increase in the quantity of calcite. Finally, he has observed a mitigation of the deterioration due to leaching and precipitation reactions. Indeed, this phenomenon is due to the superposition of hydration process of the cementitious material and the puzzolanic reaction (in there are fly ashes). This has an important influence on the aggressiveness of the attack.

## **CONCLUSION OF THE CHAPTER**

In this chapter, three main points were tackled. Firstly, the composition and the characteristics of cementitious materials were reminded. A focus was made on the transport mechanisms that may have an influence in the case of an attack by aggressive agents. Then, the modification of cementitious materials, especially in the case of addition of polymers was developed. In this part, the different types of polymers that can be used and the properties of the resulting material were pointed out. In general, the addition of polymers into a cementitious matrix leads to an improvement on the properties of the material, giving it more resistance. Finally, a special interest was given to the degradation of cementitious material by organic acid attacks. After having reminded the processes involved when an organic aggressive agent attacks the material, the mechanisms of the degradation and the consequences linked were highlighted. In this part, the main species that can be encountered in those cases were listed (acetic acid, lactic acid, propionic acid, butyric acid among others). Considering all these species, lactic acid can be distinguish since it has a lower pKa in comparison with the others and is more aggressive. The different studies realised on this topic have allowed showing that the submersion of the material in a solution made of acetic acid at pH 4 is a good way to recreate the conditions of an attack by the other acids in the case of agricultural or agro-food media. The studies have also pointed out the importance porosity and permeability.

To the best of our knowledge, any studies have been realised to study the degradation of a polymer-modified cementitious material submitted to acid solutions. According to all the information collected in the three parts of this chapter, a lower impact of aggressive agents can be expected on polymer-modified materials in comparison with traditional cementitious material. Indeed, according to the different studies realised, the addition of polymer leads to a decrease in the porosity. In order to confirm our hypotheses and to have a better understanding of the mechanisms evolved, we will realise an experimental campaign in what follows. In the next chapters, we will test two repair mortars and compare them to a conventional mortar. After being characterised, they will all be submitted to two different acid solutions.





## CHAPTER II: EXPERIMENTAL APPROACH

### INTRODUCTION

In this study, we are looking for a better understanding of the degradation of polymer-modified mortars when they are submitted to aggressive media. In the previous chapter, we have seen that in many situations, the cementitious materials are exposed to acid attacks. These attacks cause severe damages to the material. In the experimental campaign, we consider three different mortars (a conventional mortar and two repair mortars among which one contains polymers). The three of them are submitted to two different aggressive media and their reaction are studied and compared.

In this chapter, in a first part we present the materials used, and how the samples were prepared. Then, we give more details about the aggressive media that have been selected, characterising the species used and the conditions of exposition of the mortars to the aggressive agents. Finally, we detail the experimental approach that have been adopted and present all the tests that will be carried out during the campaign. All the tests have been selected in order to give relevant information about the mechanical resistance of the mortars, their microstructure and their durability capacities.

### 1 PART I: PREPARATION OF THE SAMPLES

#### 1.1 TYPES OF MORTARS

Three different mortars have been selected for this Master's thesis. The idea was to be able to compare the results using a conventional mortar without any additions and two different repair mortars commercialised by SIKA S.A.: one without polymers and the second one modified with polymers. They are described in the table below (cf. Table 15).

TYPES OF MORTAR	CHARACTERISTICS	ORIGIN
CEM I 52.5 R	Conventional mortar with a water/cement ratio of 0.5	
SIKA Monotop 412 S	Low shrinkage repair mortar with one component reinforced with fibres (R4 class)	SIKA
SIKA Monotop 412 SFG	Low shrinkage repair mortar with one component, containing corrosion inhibitor, polymers and reinforced with fibres (R4 class)	SIKA

Table 15 – Characteristics and origin of the mortars

Since for the repair mortar the preparation already includes both cement and aggregates, the three mortars cannot be described with the water/cement relation. However, it is possible to compare their water/solid ratio (cf. Table 16). As we may see, this ratio remains in the same range for the three mortars that have been selected.

MORTARS	WATER/SOLID RATIO
CEM I 52.5 R	0.125
SIKA Monotop 412 S	0.144
SIKA Monotop 412 SFG	0.140

Table 16 – Water/solid ratios according to the mortar types

Since the two repair mortars (cf. Figure 18) which have been used are commercialised mortars, we do not have access to the detailed composition (types of polymers and additions used, dosing of the different components, etc.). That is the reason why a first step, consisting in characterising the mortars is necessary. It will help us acquiring precious data about the behaviour of the repair mortars, and predicting their expected behaviour once exposed to aggressive media. In what follows, we will refer to these mortars as “Monotop 412 S” and “Monotop 412 SFG” respectively.



SIKA Monotop 412 S

SIKA Monotop 412 SFG

Figure 18 – Repair mortars

## 1.2 DOSING AND PREPARATION OF THE SAMPLES

For the realisation of the different tests, two types of samples have been made: prismatic samples and cylindrical samples. The dimensions and conception procedure of the samples are detailed in what follows.

### 1.2.1 Prismatic samples

#### ▪ Description of the samples

The prismatic samples are used for the mechanical testing (compression and tensile tests) and the electrical resistivity test. Then, from them, the samples for the mercury intrusion porosimetry and the differential thermal analysis are extracted. They have the following dimensions (cf. Figure 19).

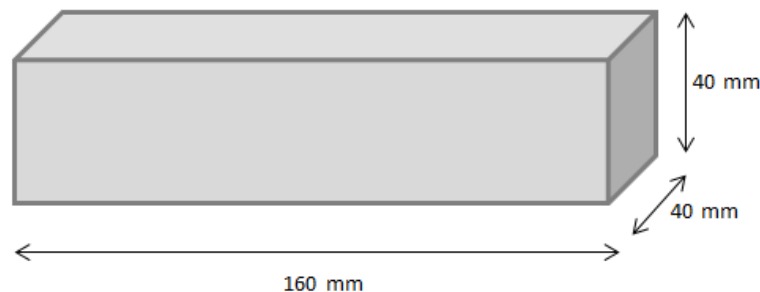


Figure 19 – Dimensions of the prismatic samples

#### ▪ Dosing

For the realisation of the prismatic samples, the dosing which has been used is described in the table below (cf. Table 17).

MORTARS	CEMENT	SAND	WATER
CEM I 52.5 R	450 g	1350 g	225 g
Monotop 412 S	1748 g		252 g
Monotop 412 SFG	1754 g		246 g

Table 17 – Dosing for the preparation of prismatic samples

#### ▪ Realisation of the samples

The dosing used was enough to realise three samples. For the need of the study, six samples for each mortar were necessary. Consequently, the process was repeated three times for each mortar. The prismatic samples have been realised according to the EN 196-1 Standard, whose process is described in what follows.

In the case of the conventional mortar, the sand is already in the right proportion (in a little bag of 1350 g of sand). The mixing is realised in a kneading machine with a vertical axis. For the elaboration of these samples, the different steps in the process were the following:

- Introduction of the water in the machine;
- Introduction of the cement and timer start for a 30 s slow mixing;
- Introduction of the sand and 30 s of slow mix;
- Quick mixing of the components for 30 s;
- Rest for 90 s;
- Quick mix for 30s.

In the case of the repair mortars, the cement and the sand are already mixed. The instructions were to mix the preparation with the correct volume of water for 3 minutes. So, the process has been modified accordingly. The steps were the following:

- Introduction of the water in the machine;
- Introduction of the preparation and timer start for a 60 s slow mixing;
- Quick mixing for 30 s;
- Slow mixing for 60 s;
- Quick mixing for 30 s.

Once the mortar is ready, it is placed into the moulds (which have been previously oiled in order to make easy the demoulding). The process consists in:

- Fill in half of the mould;
- Compact by tamping (60 times);
- Fill in the entire mould;
- Compact by tamping (another 60 times).

Cylindrical samples used for mercury intrusion porosimetry and differential thermal analysis are extracted from the previous prismatic samples as shown on the figure below (cf. Figure 20Figure 21). The cylindrical samples used for porosimetry and differential thermal analysis have the following dimensions:  $\varnothing$  10mm for a 40mm length.



Figure 20 – Cylindrical samples for porosimetry and DTA

### 1.2.2 Cylindrical samples

#### ▪ Description of the samples

The cylindrical samples are used for the chloride migration test, the capillary absorption test and for the resistance to acid attacks. They have the following dimensions (cf. Figure 21). To make it easier, cylindrical samples of 200mm in length have been realised and then cut to obtain the required length of 50mm (cf. Figure 22). This process allows saving time by realising several samples at the same time.

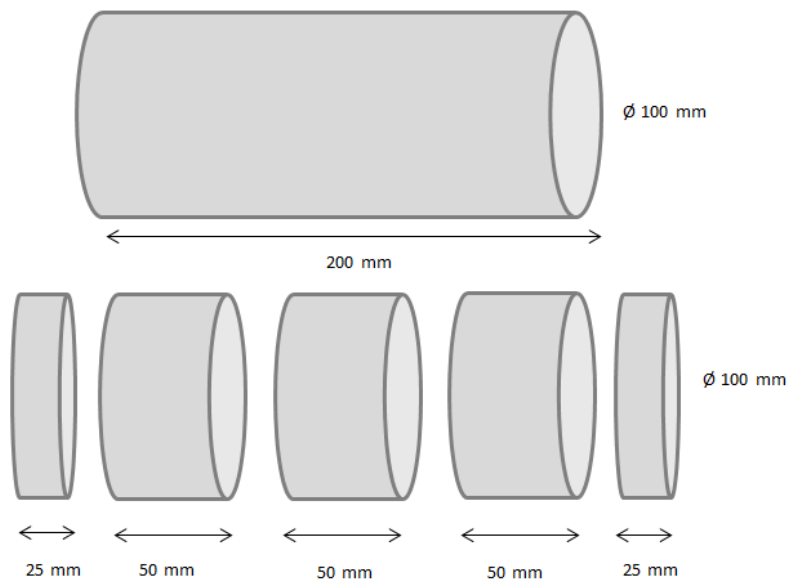


Figure 21 – Dimensions of the cylindrical samples

#### ▪ Dosing

For the realisation of the cylindrical samples, the dosing which has been used is described in the table below (cf. Table 18).

MORTARS	CEMENT	SAND	WATER
CEM I 52.5	675 g	2025 g	338 g
Monotop 412 S	2622 g		378 g
Monotop 412 SFG	2631 g		369 g

Table 18 – Dosing for the preparation of cylindrical samples

▪ **Realisation of the samples**

The same process was used to realise the different mortars for both cylindrical samples and prismatic samples. The only difference is that in the case of cylindrical samples, the compaction of the mortars have been realised by vibration. The process was the following:

- Fill in half of the mould;
- Compact by vibrating for 25 seconds;
- Fill in the entire mould;
- Compact by vibrating another 25 seconds.

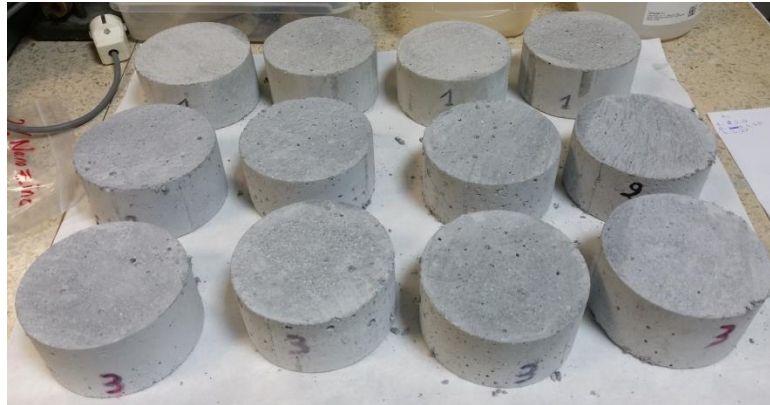


Figure 22 – Cylindrical samples

**1.2.3 Curing of the samples**

Curing of the samples is carried out according to the UNE 83966 Standard. Both prismatic and cylindrical samples have been entirely filled in with the mixing and put in a curing chamber. They have been removed from the moulds after 24 hours and maintained in the curing chamber under water until their use for the tests. The conditions in the curing chamber are the following: a temperature maintained at  $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and a relative humidity of 84%. All the samples have been let in the curing chamber until the reach of the 28 days of curing. Then they have been treated according to the standard in force for each type of test.

**2 PART II: ACID MEDIUM**

In this investigation work, the main objective is to characterise the attack of different cementitious materials by acid agents. To do so, two acid media have been selected, in order to recreate the conditions of such attacks. These media are presented in what follows.

**2.1 CHOICE OF ACIDS**

**2.1.1 Justification of the selected acids**

According to the remarks made in the Chapter II about the acid attacks of ordinary cementitious materials, we have decided to test our mortars in a solution made of acetic acid

and a solution made of lactic acid. These acids have been selected because they are present in agro-food and agricultural industries. Both acetic and lactic acids are weak organic acids. However, their pKa are relatively high with regard to inorganic acids. That is the reason why they are very aggressive for mortars. Besides, their salts are soluble, which will contribute to the aggressiveness of the attack. The choice of acetic acid is justified by the fact that its pKa is comparable to some other organic acids presents in agricultural and agro-food environments (such as propionic acid or butyric acid among others), and it is representative of the effect of the combination of different acids in presence in such environment. With regard to the lactic acid, it has been selected because it is more aggressive than the others due to its lower pKa; so, we can expect a more severe attack in this case, with a different mode of attack.

### 2.1.2 Characteristics of the selected acids

In the following table (cf. Table 19) the two acids that will be used for the aggressive solutions are presented. As explained in the previous chapter, these species are weak acids, whose salts are soluble in water (cf. Table 12).

SPECIES	FORMULA	pKa
Acetic acid	$C_2H_4O_2$	4.76
Lactic acid	$C_3H_6O_3$	3.86

Table 19 – Formulas and pKa of acetic and lactic acids

The titration curves of both acids are presented below (cf. Figure 23). They have been realised for an acid concentration of 0.28mol/L. We can see that both present a buffer zone. In the case of acetic acid, this area is located in the range  $3.76 < \text{pH} < 5.76$ , while for the lactic acid, it is in the range  $2.5 < \text{pH} < 5$ .

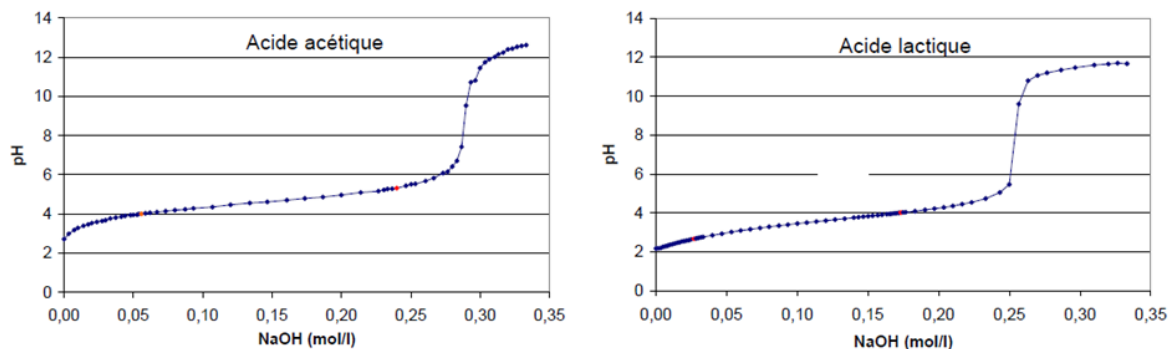
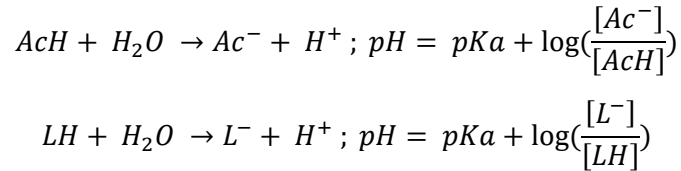


Figure 23 – Titration curves for acetic and lactic acids

Source: (BERTRON, 2004)

It is important to work with a pH range that is included in the buffer zone. There are many ways to achieve this. However, when enough acid is put in contact with the cementitious

material, a buffer acetic/acetate and lactic/lactate is established respectively in the cases of acetic acid and lactic acid. It tends to equilibrium with a pH located in the buffer zone, according to the reactions that take place (cf. Equation 23). For this reason, there is no need to add soda in order to maintain the pH in this buffer zone.



Equation 23 – Evolution of the pH of the acid solution toward the buffer zone

## 2.2 PREPARATION OF THE ACID SOLUTIONS

The objective is to recreate the aggressive environment the materials are submitted to in real cases. To do so, the materials will be submersed in the different media. To have an accelerated reaction, both acids will be at a concentration of 2mol/L. At this concentration, as soon as the acid solution is put in contact with the mortar, the acids will immediately react with the calcium hydroxide, leading to the formation of soluble salts (acetate and lactate). In such media, if the quantity of acetic acid and lactic acid is sufficient, the equilibrium between the ions leads to a pH approaching 4.7 in the first case, and 3 in the case of lactic acid. Those pH are reasonable according to the titration curves (we take the advantages of the buffer area). The samples will be submersed in both solutions for at least 3 weeks in order to be able to observe the degradation of the cementitious materials.

## 3 PART III: CHARACTERISATION TESTING

### 3.1 MECHANICAL PROPERTY CHARACTERISATION TESTING

Mechanical properties of a material can be characterised by its resistance in compression and its tensile strength. Both tests are realised according to the EN 196-1 Standard.

#### 3.1.1 *Flexural strength test*

In order to determine the flexural strength of the hardened mortars, we have used the EN 12390-6 Standard and tested the mortars at 7 days and 28 days of curing. The test used for this study was a three point tensile strength test developed by IBERTEST. This machine has two guide rollers spaced 100mm apart. A charge roller is at the same distance of both guide rollers and has the same diameter (cf. Figure 24). As shown on the figure below, the samples used for this test were prismatic samples. They have been broken into 2 pieces during this test, and each piece has served for the compression test (presented after).



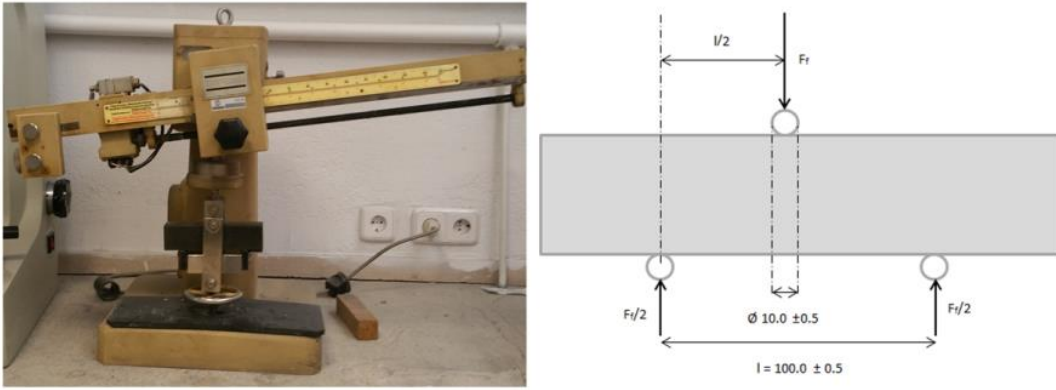


Figure 24 – Loading device

In order to determine the flexural strength, the following computing has to be done (cf. Equation 24). The value of the tensile strength is the average of all the values obtained, in case several samples have been tested for the same material (all manufactured under the same conditions).

$$R_f = \frac{1.5 \times F_f \times l}{b^3}$$

Equation 24 – Determination of flexural strength

Where:

$R_f$  is the flexural strength (MPa);

$F_f$  is the load applied in half of the prism (N);

$l$  is the distance between supports (mm);

$b$  is the length of the square section of the prism (mm).

### 3.1.2 Compression test

Once the prisms have been broken during the tensile strength test, they are submitted to the compression test, realised with an IBERTEST press, whose maximum capacity reaches 1500kN. The compression test system is composed by two faces that impose a charge upon the portions of prisms (cf. Figure 25). The charge is applied as described on the figure below. This test allows determining the value of the maximum failure tension. However, this tension can be computed from the maximum breaking load (also given by the test) as shown below.

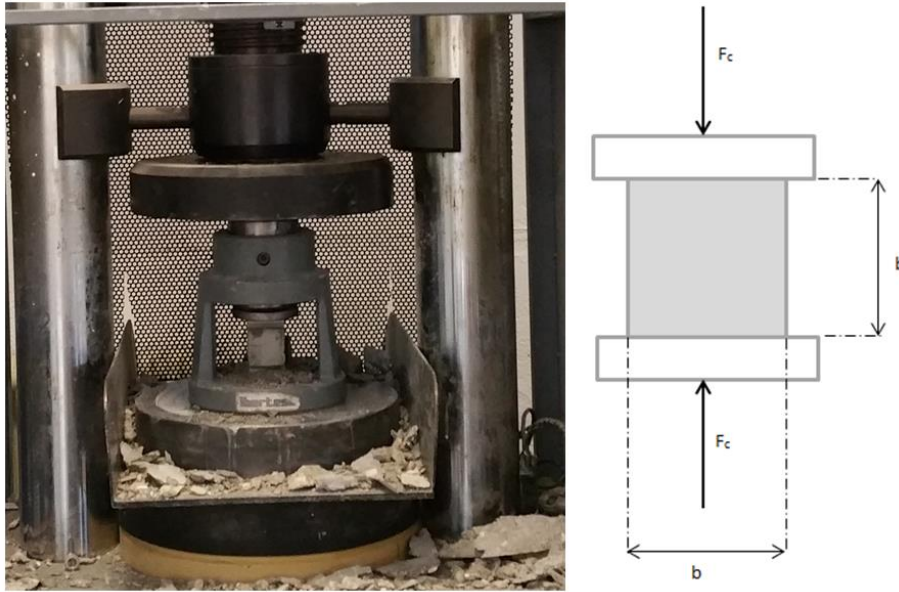


Figure 25 – Compression test device

The charge is applied at a constant speed of  $2.4\text{kN/s} \pm 0.2\text{kN/s}$  and increases uniformly along the test and until the material fails. The compression strength can be computed using the following formula (cf. Equation 25). As well as for the tensile strength, the compression strength of the material is the average of all the values obtained.

$$R_c = \frac{F_c}{b^2}$$

Equation 25 – Determination of the compression strength

Where:

$R_c$  is the compression strength (MPa);

$F_c$  is the maximum breaking load (N);

$b$  is the length of the square section of the prism (mm).

### 3.2 MICROSTRUCTURE CHARACTERISATION TESTING

The characterisation of the microstructure of the sample is essential in our case since it will help to determine the capacity of the aggressive agent to enter the material, as well as the physical properties of the proper material (according to the temperature) and many other relevant information about the sample. Three different tests are described below: the mercury intrusion porosimetry method, the differential thermal analysis and the titrimetric method.

### 3.2.1 Mercury intrusion porosimetry method (MIP)

The mercury intrusion porosimetry method is a test which is carried out to characterise the microstructure of a material. It is based on the determination of its porous structure (and thus the ability of the material to allow aggressive agents penetrating through the network of pores and capillaries) by means of mercury intrusion. This technique uses the mercury which is a heavy metal that does not wet most of solid substances. This method allows having information about a large range of pore sizes (from 2.5-5nm to 100 $\mu$ m) and about the distribution of the pores.

To allow the mercury entering the material, it is necessary to apply pressure to counteract the effect of the mercury surface tension (cf. Figure 26). As we may see, this method assumes that the drops have cylindrical geometry and it only considers the pores that the mercury has access to (i.e. the opened pores).

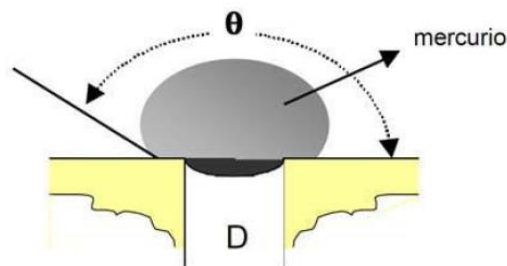


Figure 26 – A drop of mercury entering a pore

Source: (MASSANA GUITART, 2010)

The pressure that needs to be applied can be expressed as shown below (cf. Equation 26).

$$p = \frac{-4 \cdot \gamma \cdot \cos \theta}{D}$$

Equation 26 – Washburn's equation

Where:

$p$  is the required pressure to allow the penetration of mercury into the a pore (N/nm<sup>2</sup>);

$\gamma$  is the surface tension of the mercury (485 N/nm);

$\theta$  is the contact angle between the mercury and the pore surface (130°);

$D$  is the diameter of the pore (nm).

This method also allows obtaining values of the total porosity (cf. Equation 27), the critical pore diameter (i.e. the most continuously repeated pore diameter; cf. Equation 28), the threshold diameter (i.e. the most important pore size in which the first increase in mercury intrusion can be noticed) and the distribution of pores according to their diameters. Another

relevant parameter is the tortuosity. It is the ratio between the actual length that a fluid particle has to run to join two points in the porous medium and the direct line between those two points.

$$P_t = 100 \cdot \frac{V_p}{V_s}$$

Equation 27 – Total porosity

Where:

$P_t$  is the total porosity (%);

$V_p$  is the pore volume ( $\text{mm}^3$ );

$V_s$  is the sample volume ( $\text{mm}^3$ ).

$$\varnothing = \frac{4 \cdot V}{A}$$

Equation 28 – Average pore diameter

Where:

$\varnothing$  is the average pore diameter (mm);

$V$  is the pore volume ( $\text{mm}^3$ );

$A$  is the sample surface ( $\text{mm}^2$ ).



Figure 27 – Mercury Intrusion Porosimetry device

This test is realised according to the ASTM D4404-84 Standard, using a Porosimeter Micromeritics, Autopore IV 9500 model (cf. Figure 27). This porosimeter has a maximum pressure that reaches 33000 psi (i.e. approximately 227.5 MPa) and allows having

information about pores whose size is in the range 5nm – 180µm. To do so, cylinders of 10mm in diameter are extracted from the prismatic samples (cf. 1.2.1). Before starting the test, the samples are entirely dried (in an oven).

### 3.2.2 Thermogravimetric analysis

Thermogravimetric analysis is a method used in order to determine quantitatively the hydrated products of a cementitious material. It is based on two processes: differential thermal analysis (DTA) and thermogravimetry (TG). Thermogravimetry consists on the measurement of the sample mass, while differential thermal analysis is based on the detection of thermal variations when either physical or a chemical changes occur in the material. This thermal change is measured thanks to the difference of temperature that exists between the sample and an inert reference material (alumina  $\text{Al}_2\text{O}_3$  is generally used); it can be expressed as a function of time or temperature.

The differential thermal analysis allows quantifying the hydrated compounds of the hydrated cement paste and characterising some of the properties of the studied material. This is possible to realise since the dehydration and decarbonation processes of the different products are identifiable by the temperature ranges (cf. Table 20). The data obtained allow identifying and describing the different compounds and determining the degree of hydration.

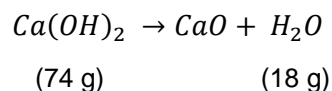
COMPOUNDS	TEMPERATURE RANGES
Calcium silicate hydrate gel ( $\text{C}_x\text{H}_y\text{S}_z$ )	120°C – 180°C
AFt family (including ettringite)	130°C – 150°C
Gypsum	145°C – 165°C
Calcium monosulfoaluminate hydrate (AFm)	170°C – 190°C
Hydrated calcium aluminates ( $\text{C}_x\text{A}_y\text{H}_z$ )	250°C – 300°C
Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )	400°C – 500°C
Carbonates ( $\text{CaCO}_3$ )	550°C – 700°C

Table 20 – Identification of hydrated products according to the temperature

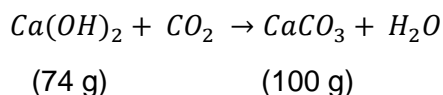
Source: (RIVERA LOZANO, 2004)

According to the temperature, one type of water or another evaporates leading to the dehydration of one of the components of the cementitious matrix. Losses of carbon dioxide also occur and correspond to the calcite.

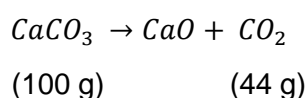
To determine the quantity of calcium hydroxide, it is usual to compute the weight loss in the range of 400°C – 500°C. The reaction which takes place is the following (cf. Equation 29). The weight loss per mole of water is 18 g and is due to the dehydroxilation of 1 mole of calcium hydroxide (74 g). Nevertheless, the carbonation of a part of the calcium hydroxide can occur and has to be considered. In this case, the following reaction takes place (cf. Equation 30). This is the reason why the quantity of calcium hydroxide has to be adjusted according to the quantity of carbonates.



Equation 29 – Dehydroxilation of the calcium hydroxide



Equation 30 – Carbonation of the calcium hydroxide



Equation 31 – Decomposition of the carbonates

The decarbonation reaction (cf. Equation 31) usually occurs between 550°C and 800°C. As we may see, each mole of carbon dioxide is produced by the decomposition of one mole of calcium carbonate (which comes from the carbonation of calcium hydroxide).

The quantity of calcium hydroxide is finally computed according to the following equation (cf. Equation 32).

$$\text{Ca(OH)}_2 = \frac{74 \cdot x}{18} + \frac{74 \cdot y}{44}$$

Equation 32 – Computation of the quantity of calcium hydroxide

Where:

x is the mass in gram lost due to the dehydroxilation of the calcium hydroxide;

y is the mass in gram lost due to the decarbonation reaction.

This test is realised using the Simultaneous Thermal Analyser SETARAM, LABSYS EVO model (cf. Figure 28), with a scale which precision is 0.1µg. The temperature range considered for this study is from 40°C to 1100°C and the heating rate is 10°C/min. In order to realise this test, the samples need to be in powder form, with a size that is below 0.5mm. To do so, cylinders extracted from the prismatic samples are grinded after being totally dried.

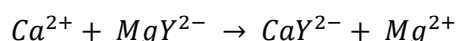


Figure 28 – Thermogravimetric and differential thermal analysis device

### 3.2.3 *Titrimetric method*

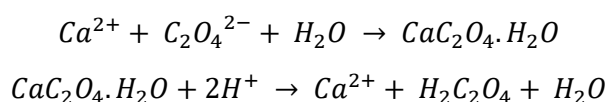
The titrimetric method is part of quantitative chemical analysis used to determine the quantity of a compound. This quantity is found by measuring the volume of a dissolution (whose concentration is known) necessary to make this constituent react. This method can be achieved by the formation of a complex, or by the formation of a precipitate, among other methods. It is really often used to determine the quantity of calcium present in a solution.

The valuation of calcium by the formation of a complex is generally carried out using the EDTA (i.e. ethylenediaminetetraacetic acid,  $C_{10}H_{16}N_2O_8$ ). EDTA is a hexavalent ligand, noted  $Y^{4-}$  in its ionic form. The EDTA combines with the metallic ions to form a metallic complex (e.g.  $Ca^{2+} + H_2Y^{2-} \rightarrow 2H^+ + CaY^{2-}$ ). This method involves the use of a coloured indicator. The most widely used is the Eriochrome black indicator (EBT), but other indicators are also used (such as murexide). In order to determine the quantity of calcium using EDTA, a little quantity of magnesium ions (that is known) is added at the EDTA before evaluating the calcium. The  $Ca^{2+}$  reacts with the EDTA as well as with the  $MgY^{2-}$  (cf. Equation 33). The  $Mg^{2+}$  forms the red complex Mg-BET which reacts with the first excess of EDTA.



Equation 33 – Valuation of calcium by formation of a complex

The valuation of calcium by precipitation can be carried out by means of the formation of oxalate monohydrate ( $CaC_2O_4 \cdot H_2O$ , cf. Equation 34). The precipitated is separated, and this compound is then dissolved in  $H_2SO_4$ . The  $H_2SO_4$  solution is evaluated with a solution of  $KMnO_4$ . The stoichiometry makes it easy to compute the quantity of calcium since each  $Ca^{2+}$  corresponds to a molecule of  $H_2C_2O_4$ .



Equation 34 – Valuation of calcium by precipitation

### 3.3 DURABILITY CHARACTERISATION TESTING

The characterisation of the durability of the material have been realised through three different tests: the electrical resistivity (realised according to the UNE 83988-1 Standard), the chloride migration (realised according to the NT BUILD 492 Standard) and the capillary absorption (realised according to the UNE 83982 Standard). A description of each test is made in what follows.

#### 3.3.1 *Electrical resistivity*

The electrical resistivity is an indirect measure of the connectivity and the size of the pores. Resistivity is a volumetric property of the material that indicates its resistance to electrical loads; it depends on the geometrical characteristics of the sample.

With the measure of the electrical resistance, it is possible to determine the electrical resistivity (cf. Equation 35).

$$\rho_e = \frac{S}{L} \cdot R_e$$

Equation 35 – Electrical resistivity

Where:

$\rho_e$  is the electrical resistivity ( $\Omega \cdot m$ );

$R_e$  is the electrical resistance ( $\Omega$ );

$S$  is the area of the sample through which the electrical load passes ( $m^2$ );

$L$  is the height of the sample (m).

The ASTM C1202 Standard allows qualifying the chloride penetrability of the sample thanks to the electrical resistivity measure. A table is given by the manufacturer to link the electrical load with the chloride penetrability (cf. Table 21).

<b>ELECTRICAL LOAD (ASTM C1202)</b>	<b>ELECTRICAL RESISTIVITY (UNE 83988-1)</b>	<b>CHLORIDE PENETRABILITY</b>
> 4000 C	< 5 $\Omega \cdot cm$	High
2000 to 4000 C	5 to 10 $\Omega \cdot cm$	Moderate
1000 to 2000 C	10 to 20 $\Omega \cdot cm$	Low
100 to 1000 C	20 to 200 $\Omega \cdot cm$	Very low
< 100	> 200 $\Omega \cdot cm$	Negligible

Table 21 – Qualification of the chloride penetrability according to the electrical load

Source: (NESTOR EDUARDO, 2015)



It has to be underlined that the electrical resistivity indicates the quality of the concrete through its porosity characterisation; it is also an indicator of the degree of saturation of the material (useful for the control of the degree of cure).

To realise this study, the prismatic samples are used. The resistance is measured on both faces of the samples. This test is realised according to the UNE 83988-1 Standard.

### 3.3.2 Chloride migration

The chloride migration process is based on the fact that when an external electric potential is axially applied through the sample, the chlorides located outside have to move into the sample. The penetration depth can be observed by the formation of insoluble silver chlorides (once the test is finished, the sample is cut and silver nitrate is added into the rupture area). The migration coefficient is given by the measure of the penetration depth (cf. Equation 36).

$$D_{nssm} = \frac{0.0239 \cdot (273.15 + T) \cdot L}{(U - 2) \cdot t} \cdot (x_d - 0.0238 \cdot \sqrt{\frac{(273.15 + T) \cdot L \cdot x_d}{U - 2}})$$

Equation 36 – Migration coefficient

Where:

$D_{nssm}$  is the migration coefficient for non-steady state ( $\times 10^{-12}$  m<sup>2</sup>/s);

T is the average temperature (average of initial and final temperature) of the anode solution (°C);

L is the thickness of the sample (mm);

U is the absolute value of the applied voltage (V);

t is test duration (hours);

$x_d$  is the average of the values of penetration depth (mm).

This test is realised according to the NT BUILD 492 Standard. The cylindrical samples of 50mm in length are used. The samples are put in contact with dissolution of calcium hydroxide, according to the Standard. The samples are then submersed in a sodium chloride solution. The testing device (cf. Figure 29) is connected to a voltmeter.



Figure 29 – Chloride migration device

### 3.3.3 Capillary absorption

The capillary absorption test allows measuring the capacity of the material to absorb water by capillary action (that depends on the network of interconnected pores within the material). The coefficient of capillary absorption can be expressed by the means of this method (cf. Equation 37).

$$K = \frac{\delta_a \cdot \varepsilon_e}{10 \times \sqrt{m}}$$

$$\varepsilon_e = \frac{Q_n - Q_0}{A \cdot h \cdot \delta_a} ; m = \frac{t_n}{h^2}$$

Equation 37 – Capillary absorption coefficient

Where:

K is the coefficient of capillary absorption ( $\text{kg}/\text{m}^2 \cdot \text{min}^{1/2}$ );

$\delta_a$  is the density of water ( $1 \text{ g}/\text{cm}^3$ );

$\varepsilon_e$  is the effective porosity of the concrete ( $\text{cm}^3/\text{cm}^3$ );

m is the resistance to water penetration by capillary absorption ( $\text{min}/\text{cm}^2$ );

$Q_n$  is the weight of the sample when reaching the saturation for  $t = t_n$  (g);

$Q_0$  is the weight of the sample before starting the test for  $t = t_0$  (g);

A is the sample area exposed to water ( $\text{cm}^2$ );

h is the sample thickness (cm);

In order to realise this test, cylindrical samples of 50mm in length are used. The test is carried out according to the UNE 83982 Standard. The samples are put in contact with water (5mm height). The mass is then measured after 5 min, 10 min, 15 min, 30 min, 1h, 2h, 3h, 4h, 6h and then every 24h until 18 days (at least).

### 3.4 TESTING PROGRAMME

The experimental campaign that will be followed in this study is presented on the figure below (cf. Figure 30). This campaign has two different phases: firstly it will consist in characterising all the mortars after hardening and then the resistance of each mortar to acid attacks will be tested. For each mortar, a sample will be kept in normal conditions and tested while two samples will be submitted to two different acid media presented in the following Part II, and then they will be tested.

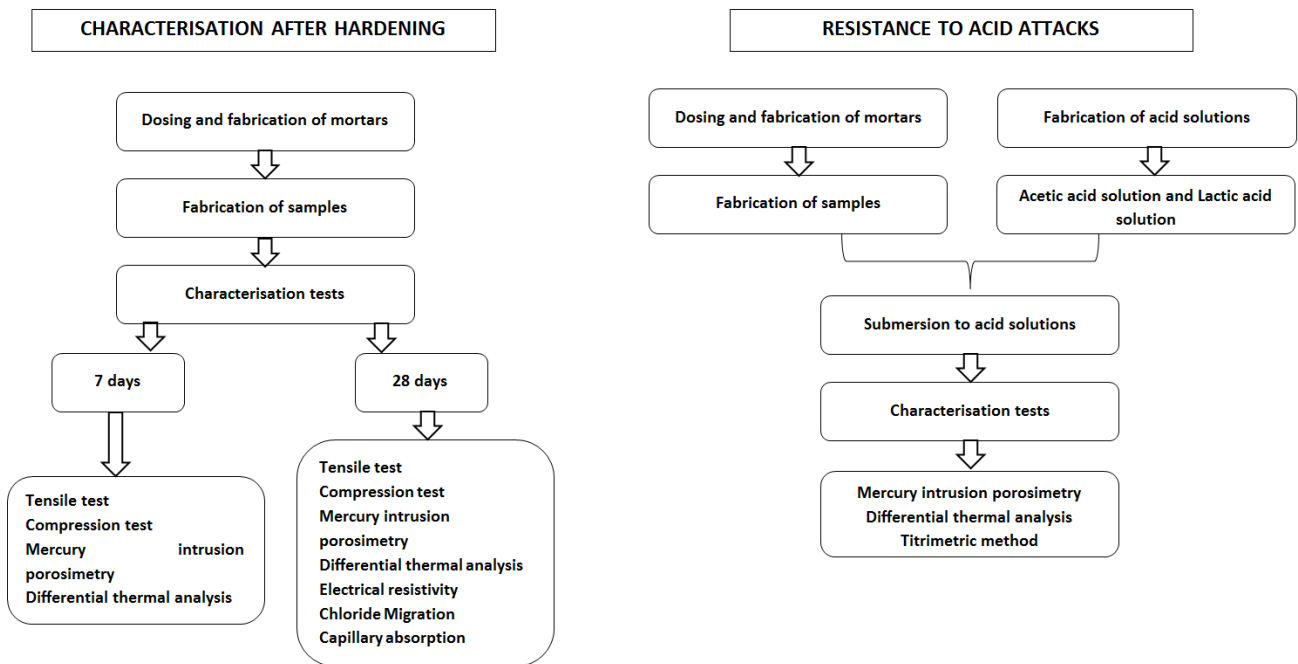


Figure 30 – Experimental campaign



## **CHAPTER III: CHARACTERISATION AFTER HARDENING**

### **INTRODUCTION**

This chapter is the first step of the experimental campaign. In it, all the results of the tests that have been carried out in order to characterise the three mortars after hardening are presented. This characterisation is important since we do not have a lot of information about the two repair mortars. It will allow us understanding what are the capacity of both repair mortars in comparison with a conventional one, and what kind of behaviour can be expected once they are submitted to aggressive agents. According to the information given in Chapter II, we may expect better properties for the repair mortar since it contains polymers. We may expect higher mechanical properties, but also a less porous structure. To confirm these assumptions, different tests have been realised. Firstly, mechanical testing has been done and leads to the determination of tensile and compression strengths. Then, a special interest has been laid to the characterisation of the microstructure of the mortars and their durability capacities. To do so, the campaign has included mercury intrusion porosimetry, thermogravimetric analysis and electrical resistance on one hand; chloride migration and capillary absorption on the other hand.

### **1 PART I: MECHANICAL PROPERTY CHARACTERISATION**

In the following part, the results of the mechanical testing are reported. Two different tests have been realised: a compression test and a tensile test. Both have been realised at 7 and 28 days of curing for each mortars.

#### **1.1 Flexural strength test**

The flexural strength has been measured for the three mortars at 7 and 28 days of curing (cf. Figure 32). It has to be underlined that the failure of the two repair mortars has been very different in comparison with the conventional mortar failure. Indeed, while the conventional mortar has failed suddenly, in the case of the repair mortars, both parts of the samples remained together (cf. Figure 31). This phenomenon can be explained by the presence of fibres in the two repair mortars that have allowed maintaining both parts together, leading to a smoother failure.



Figure 31 – Failure of a repair mortar during the tensile test

For both ages, the repair mortar without polymer addition (Monotop 412 S) presents the lowest tensile strength and the repair mortar with polymer addition (Monotop 412 SFG) has the highest one. In general, the Monotop 412 SFG has similar values than the reference mortar.

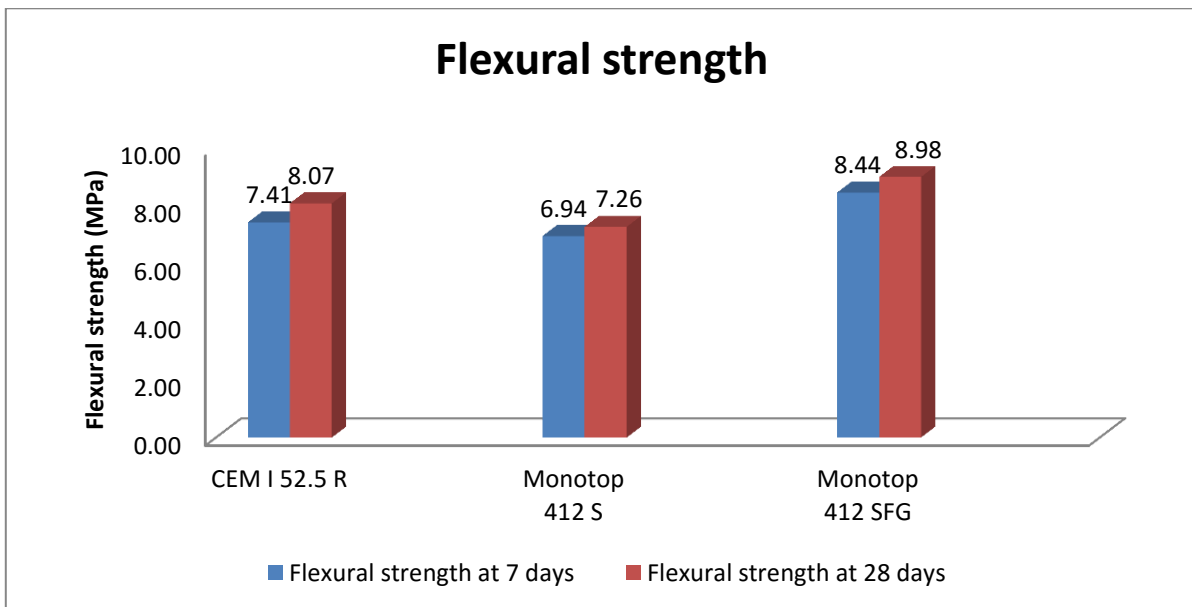


Figure 32 – Flexural strengths

We can note the percentage of variation of the different values that have been obtained at 7 days with those at 28 days:

- The value of the conventional mortar (CEM I 52.5 R) has increased a 8.5%;
- The value of the repair mortar without polymer addition (Monotop 412 S) has increased a 4.6%;
- The value of the repair mortar with polymer addition (Monotop 412 SFG) has increased a 6.4%.

We can also compute the percentage of variation of the flexural strength in comparison with the reference mortar (cf. Table 22 where the values at 7 days of curing appear in blue while the values at 28 days of curing appear in red). This table confirms the tendency observed in the graphs: the repair mortar that contains polymer has the highest values in

comparison with the two other mortars. Besides, the conventional mortar has a higher resistance to tension than the Monotop 412 S which does not contain polymers.

Flexural strength 7 days Flexural strength 28 days	Monotop 412 S	Monotop 412 SFG
CEM I 52.5 R	- 6.34 % - 10.04%	+ 13.90% + 11.28%
Monotop 412 S	-	+ 21.61% + 23.69%

Table 22 – Comparison of flexural strengths

### 1.2 Compression test

As well as for the tensile strength, the compression test has been realised at the ages of 7 and 28 days for the three types of mortars. The results are presented in the following graph (cf. Figure 33).

We can see that at 7 days of curing, the conventional mortar is the one who has the lowest compression strength, and the repair mortar with polymer addition has the highest one. At 28 days, the repair mortar with polymer additions still has the highest compression strength while the repair mortar without polymer addition presents the lowest compression strength. As well as for the flexural strength, the values obtained for the Monotop 412 SFG are similar to those obtained for the conventional mortar after 28 days of curing.

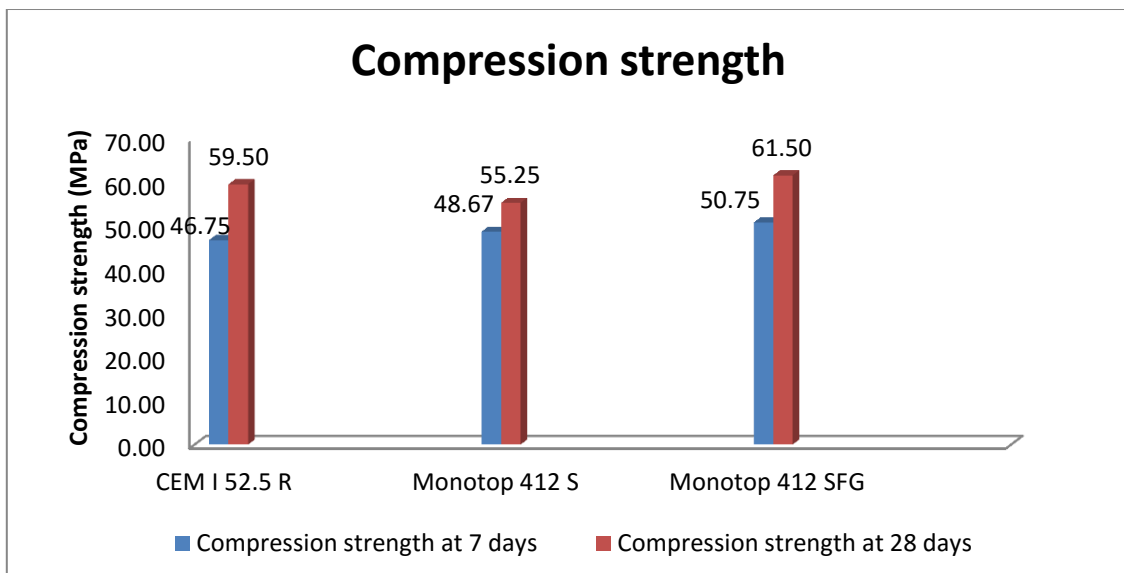


Figure 33 – Compression strengths

If we compare the values at 7 days with those obtained at 28 days, we may note that:

- The value of the conventional mortar (CEM I 52.5 R) has increased a 27.3%;

- The value of the repair mortar without polymer addition (Monotop 412 S) has increased a 13.5%;
- The value of the repair mortar with polymer addition (Monotop 412 SFG) has increased a 21.2%.

As well as for the tensile strength, we can also compare the percentages of variation of the compression strength for each mortar in comparison with the conventional one which constitutes our reference (cf. Table 23 where the values at 7 days of curing appear in blue while the values at 28 days of curing appear in red). This table confirms the observations made above. As we may see, the Monotop 412 SFG, which contains polymers has the highest resistance in compression at both ages (7 days and 28 days). Moreover, after 28 days of curing, the conventional mortar reached a higher resistance in compression than the Monotop 412 S.

<b>Compression strength 7 days</b>	<b>Monotop 412 S</b>	<b>Monotop 412 SFG</b>
<b>Compression strength 28 days</b>		
<b>CEM I 52.5 R</b>	+ 4.11%	+ 8.56%
	- 7.14%	+ 3.36%
<b>Monotop 412 S</b>	-	+ 4.27%
		+ 11.31%

Table 23 – Comparison of compression strengths

## **2 PART II: CHARACTERISATION OF THE MICROSTRUCTURE AND THE DURABILITY**

In the following part the results of the tests carried out to characterise the microstructure and durability capacity of each mortar are given. We have realised several tests: mercury intrusion porosimetry, thermogravimetric analyse and electrical resistivity test at 7 and 28 days of curing for each mortar. At 28 days of curing, chloride migration and capillary absorption tests have also been realised.

### **2.1 Mercury intrusion porosimetry**

In what follows, we can see the curves representing the logarithm of the differential intrusion and the cumulative intrusion volume over pore diameter. These curves have been plotted for 7 (cf. Figure 34) and 28 days (cf. Figure 35) of curing for all of the three mortars considered.

As we may see, the Monotop 412 SFG which contains polymers is the mortar that presents the major variation between the results obtained after 7 days of curing and those obtained after 28 days of curing. We can also note that the CEM I 52.5 R presents an only pore size located between 0.01 and 0.1µm. However, the two repair mortars present two pore sizes: the first one is located in the range 0.01-0.1µm, while the second one is in the



range 0.1-1 $\mu$ m. All the pores correspond to macropores (large capillaries) and mesopores (small and medium capillaries) as we may see on Table 8. Finally, according to the curves, we can say that the conventional mortar has a homogeneous distribution of pore size while the two repair mortars present a bimodal distribution of pore size. Besides in the care repair mortars, the pores are smaller even if there is a part of large pores.

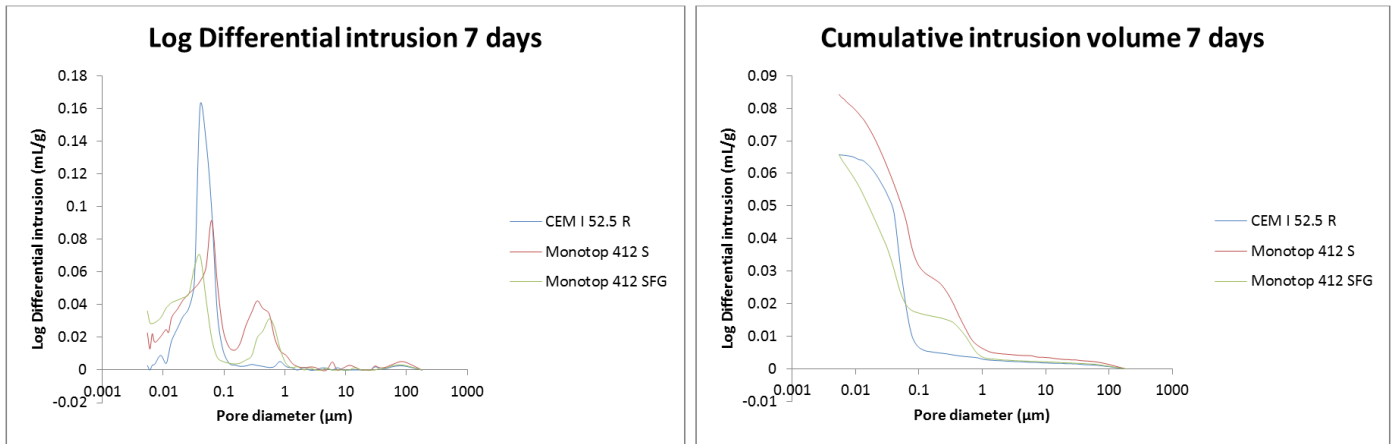


Figure 34 – Differential intrusion and cumulative intrusion volume at 7 days

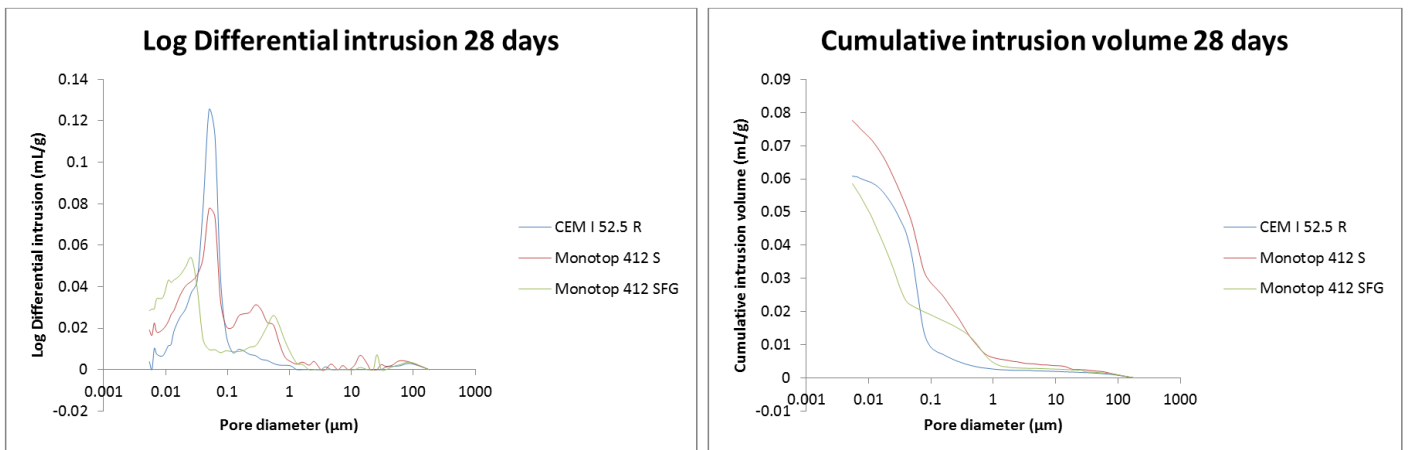


Figure 35 – Differential intrusion and cumulative intrusion volume at 28 days

The following figure (cf. Figure 36) shows the evolution of the total porosity of each mortar at 7 and 28 days of curing. Firstly, we can note that there is little variation between the results obtained after 7 days of curing and those obtained after 28 days of curing, regardless the type of mortar; which means that the microstructure does not evolve much between 7 and 28 days of curing. We can also note that, as predicted, the total porosity decreases with the curing age for all of the three mortars. Besides, the highest values of porosity are obtained for the Monotop 412 S. The values of porosity of the Monotop 412 SFG are the lowest at 7 days and at 28 days, even if they are in the same order of magnitude than the values obtained for the reference mortar, which is in accordance with the previous studies (cf. Chapter I).

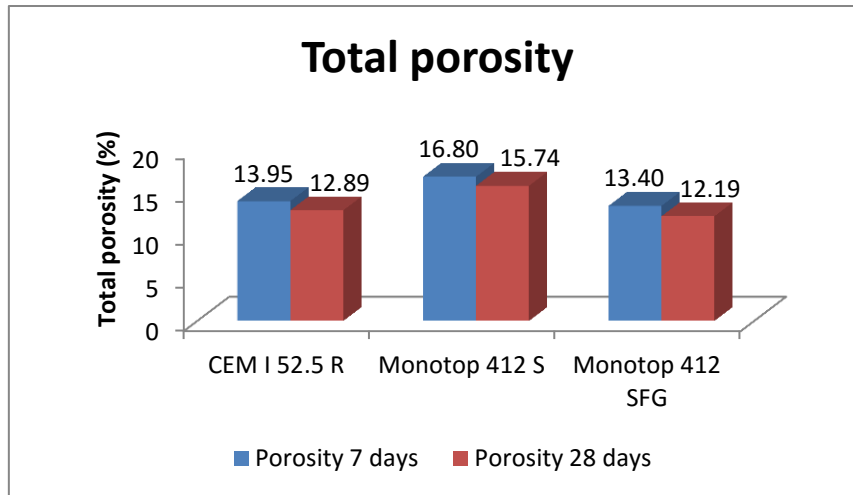


Figure 36 – Total porosity

Another relevant data is the distribution of pores. This data allows characterising the porous matrix. Four types of pores can be distinguished according to S. MINDESS et al. classification (cf. Table 8):

- Macropores:  $10\ \mu\text{m} < \emptyset$ .
- Large capillaries:  $50\ \text{nm} < \emptyset < 10\ \mu\text{m}$ .
- Medium capillaries:  $10\ \text{nm} < \emptyset < 50\ \text{nm}$ .
- Small capillaries:  $5\ \text{nm} < \emptyset < 10\ \text{nm}$ .

This graph has been realised at 7 and 28 days of curing (cf. Figure 37). It shows a similar evolution of porosity for both CEM I 52.5 R and Monotop 412 SFG; which means that the mechanical properties are similar for both mortars. We can note that large and medium capillaries are the most important part of the pore distribution for the three mortars. At 28 days, the Monotop 412 SFG is the one that presents the highest proportion of capillaries. If we compare the evolution with respect to the curing age, we can note that in general, the proportion of capillaries tends to decrease at 28 days of curing in comparison with the values obtained at 7 days of curing. Between 7 and 28 days of curing, medium capillaries tend to decrease while large capillaries increase, except for the Monotop 412 SFG which decreases slightly its percentage of both medium and large capillaries. The mortar that changes the most its microstructure between 7 and 28 days of curing is the CEM I 52.5 R (with a decrease in medium capillaries and an increase in large capillaries).

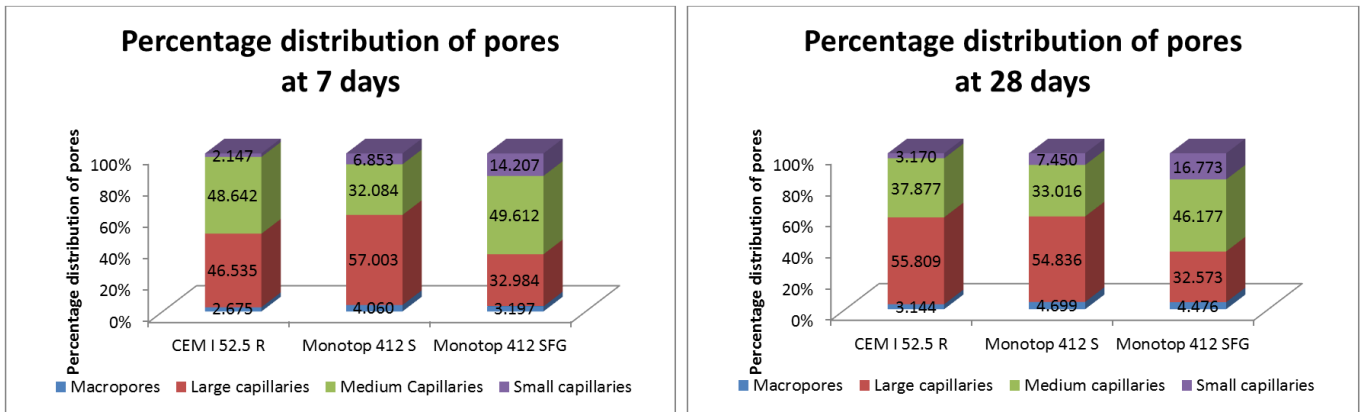


Figure 37 – Percentage distribution of pores

The last graph shows the evolution of the tortuosity over the curing age (cf. Figure 38). What is important to notice is that the tortuosity increases with the curing age. This data is relevant as it shows that the penetration of aggressive agents will be more difficult at 28 days of curing than at 7 days of curing. Moreover, if we compare the three mortars, we can see that the conventional mortar is the one that shows the highest value of tortuosity at 28 days of curing, and the Monotop 412 SFG has the lowest one. The slight variation of tortuosity after 7 and 28 days of curing in the case of the Monotop 412 SFG indicates that the mortar no longer hydrates (after 7 days, it has already its definitive microstructure).

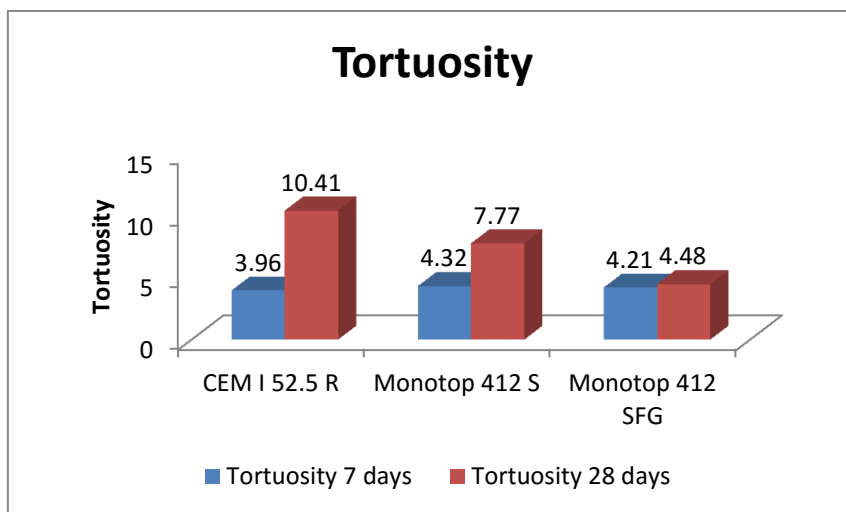


Figure 38 - Tortuosity

## 2.2 Differential thermal analysis

The differential thermal analysis is based on the variation of temperature. The analysis allows distinguishing four main zones:

- Zone 1 (40-140°C approximately): this area corresponds to the loss of free water and interlaminar water.
- Zone 2 (140-400°C approximately): this area corresponds to the water loss due to the CSH gel.

- Zone 3 (400-500°C approximately): this area corresponds to the water loss due to the calcium hydroxide.
- Zone 4 (500-1100°C approximately): this area corresponds to the decarbonation, but almost 40% is due to a part of calcium hydroxide that took more time to decompose. The interesting part in this zone is the one that corresponds to calcium hydroxide.

The analysis has been realised at 7 days and at 28 days. The results are presented in the sets of curves below (cf. Figure 39 and Figure 40). In the curves we can note that the Monotop 412 SFG, which contains fibres, presents a peak that does not appear on the curves of the others two mortars. It appears at both ages (7 and 28 days of curing), at approximately 730°C (737.6°C at 7 days of curing and 735.1°C at 28 days of curing). We can suppose that it corresponds to the burning of the polymer. This assumption has to be confirmed since we do not know the composition of the mortar; in particular we do not know which type of polymer enters into the composition of the Monotop 412 SFG. However, we think that the main compositional difference between the CEM I 52.5 R and the Monotop 412 SFG is due to the presence of polymer, which leads to a difference in the DTA. Besides, we can note a difference in the shape of the curves for the two repair mortars in the area corresponding to carbonates, and CSH gel. The same differences are observed after 7 days of curing as well as after 28 days of curing.

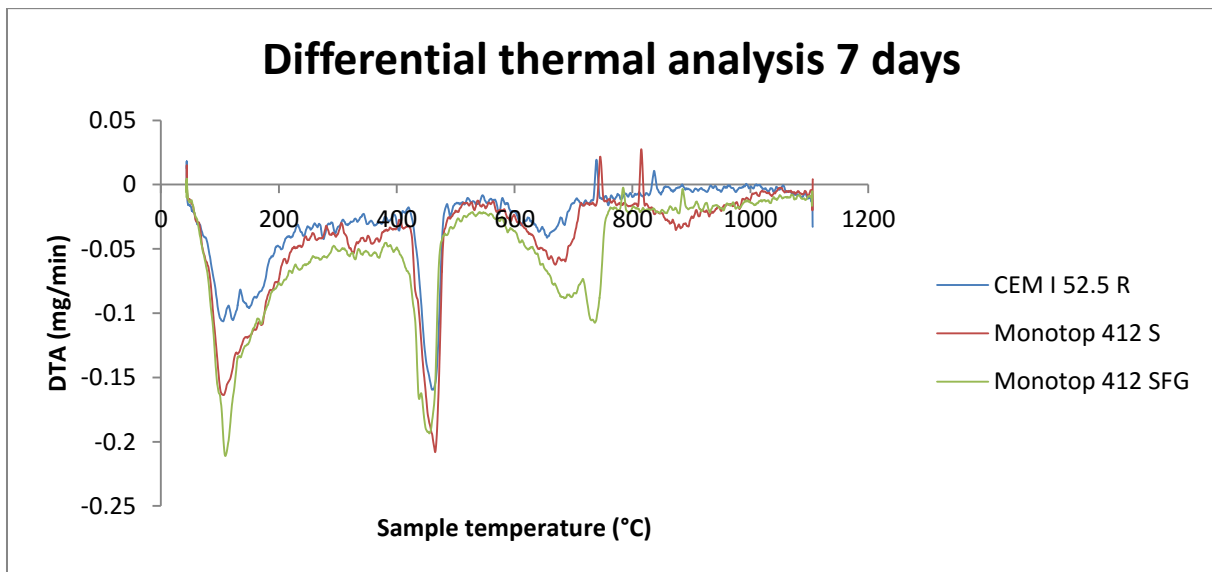


Figure 39 – Differential thermal analysis at 7 days

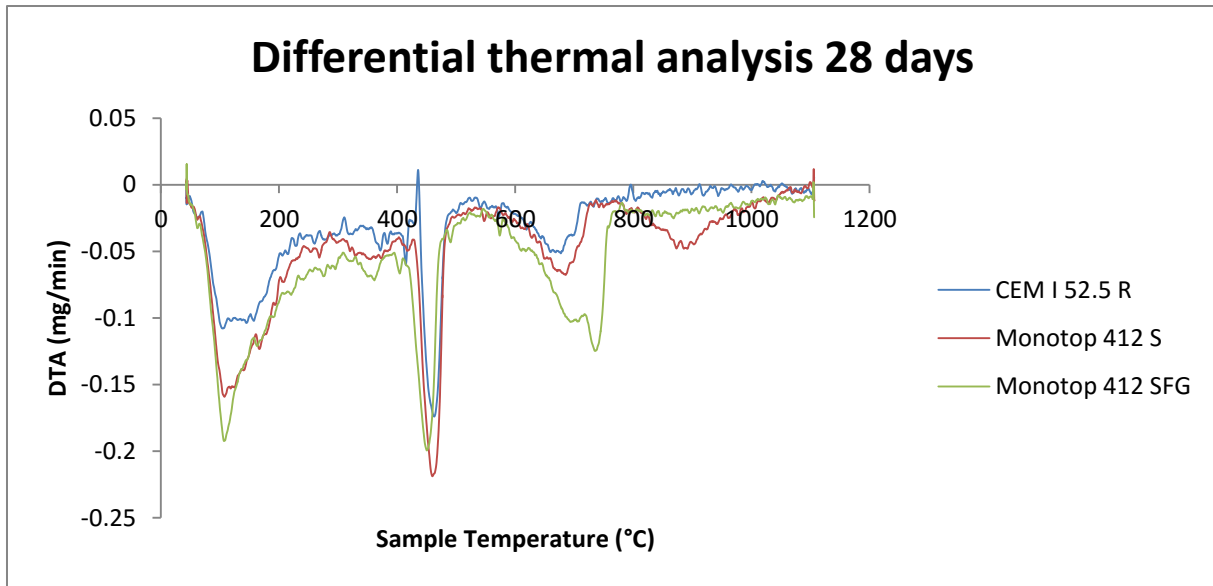


Figure 40 – Differential thermal analysis at 28 days

According to the curves, it is possible to determine the water loss expressed with respect to the initial weight (cf. Figure 41). We can note that the conventional mortar presents the lowest values in each phase while the repair mortar with polymers has the highest ones. If we compare these results with those obtained after 28 days of curing, we can see that the tendency remains the same and the losses remain in the same order of magnitude. However, the evolution of the behaviour with respect to the temperature is little as we may see only slight differences on the two graphs. This remark applies to all mortars regardless of its nature.

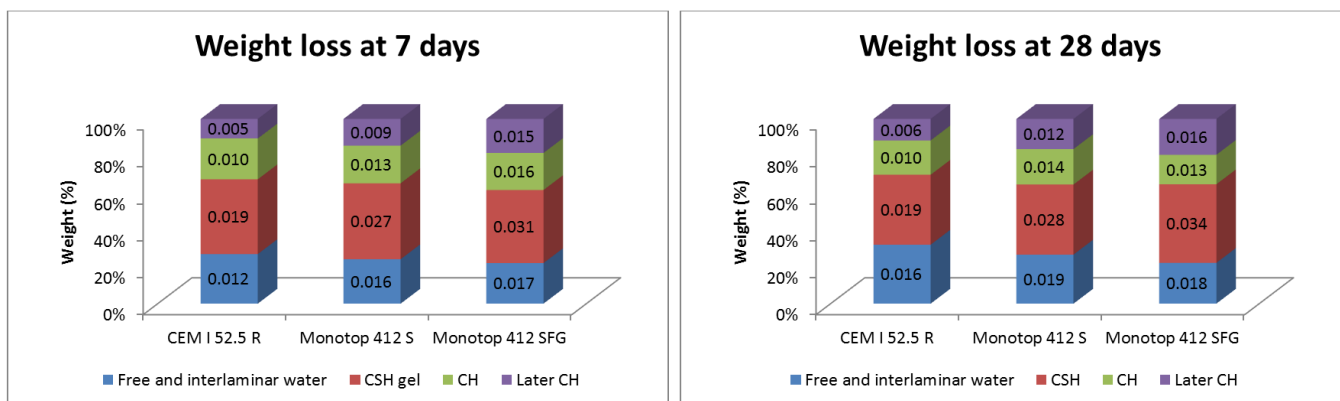


Figure 41 – Weight loss after 7 and 28 days of curing

It is possible to compare the variation of water between all the mortars at 7 days and at 28 days (cf. Table 24 where the values in blue correspond to the case of 7 days of curing and the values in red correspond to the case of 28 days of curing). These values are computed in the table below for both water loss due to the CSH gel and water loss due to the calcium hydroxide. In the case of water loss due to calcium hydroxide, the values are given for the section 3 and the section 4 (notation: section 3 / section 4).

<b>Water loss 7 days</b> <b>Water loss 28 days</b>	<b>Monotop 412 S</b>	<b>Monotop 412 SFG</b>
Water due to CSH gel		
<b>CEM I 52.5 R</b>	+ 42.11% + 47.37%	+ 63.16% + 78.95%
<b>Monotop 412 S</b>	-	+ 14.81% + 21.43%
Water due to calcium hydroxide		
<b>CEM I 52.5 R</b>	+ 30.00% / + 80.00% + 40.00% / + 100.00%	+ 60.00% / + 200.00% + 30.00% / + 166.67%
<b>Monotop 412 S</b>	-	+ 23.08% / + 66.67% - 7.14% / + 33.33%

Table 24 – Comparison of water losses

As we have seen (cf. Table 24 and Figure 41) the two repair mortars lose more water than the conventional one. With regard to the free and interlaminar water loss and the water loss due to CSH gel, they can be due to a major quantity of both waters in the repair mortars than in the conventional one. They can also be due to the fact that there are more difficult to remove from the conventional mortar than from the repair ones. Regarding the water loss due to calcium hydroxide, it is also higher in the case of both repair mortars; which can be linked to a major quantity of CH in those mortars in comparison with the conventional mortar.

### 2.3 Electrical resistivity

The resistivity of the three mortars has been measured at 7 and 28 days of curing. According to the graph (cf. Figure 42), we can say that the tendency remains the same after 7 days and after 28 days of curing. Indeed, the repair mortar with polymer additions has the highest values of resistivity, while the conventional mortar has the lowest one. As we know, a high value of resistivity is linked to a small porosity and a high mechanical resistance. According to this data, we can conclude that the Monotop 412 SFG has smaller pores than the two other mortars. This assumption is in accordance with the results obtained with the MIP (cf. Figure 37). Besides, all the values are higher than 200Ω.cm. So we may say that the chloride penetration can be neglected (cf. Table 21).

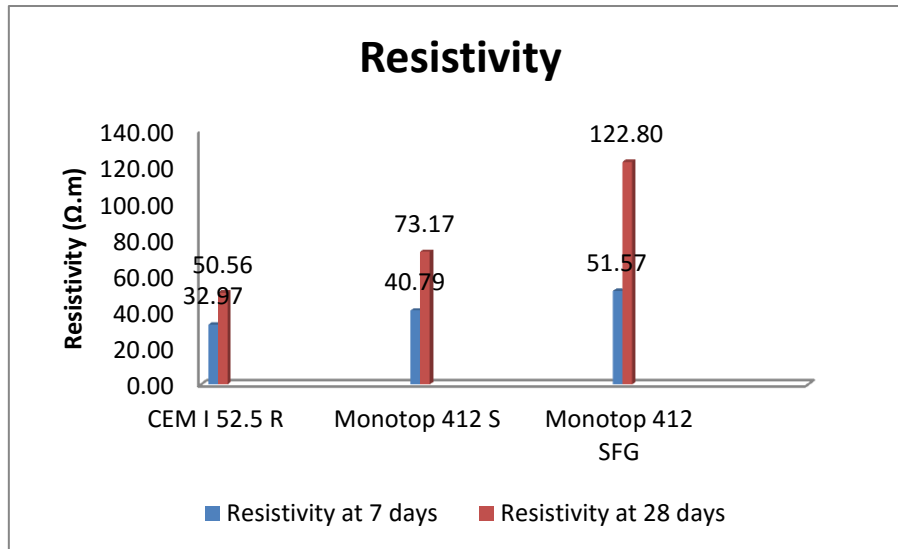


Figure 42 – Resistivity

As we have done for compression and tensile strengths, we can highlight the increase between 7 days and 28 days of curing:

- The value of the conventional mortar has increased a 53.4%;
- The value of the repair mortar without polymer addition has increased a 79.4%;
- The value of the repair mortar with polymer addition has increased a 138.1%.

The comparison between the variations in resistivity with respect to the conventional mortar can also be done (cf. Table 25 where the values at 7 days appear in blue while the values at 28 days appear in red).

<b>Resistivity 7 days</b> <b>Resistivity 28 days</b>	<b>Monotop 412 S</b>	<b>Monotop 412 SFG</b>
<b>CEM I 52.5 R</b>	+ 23.72% + 44.72%	+ 56.41% + 142.88%
<b>Monotop 412 S</b>	-	+ 26.43% + 67.83%

Table 25 – Comparison of resistivities

## 2.4 Chloride migration

The chloride migration test has been realised on the samples after 28 days of curing. It has allowed observing that the conventional mortar is the one that presents the highest penetration depths (cf. Figure 43 where the sample n°1, n°2 and n°3 correspond respectively to the conventional mortar, the Monotop 412 S mortar and the Monotop 412 SFG mortar) and consequently, the highest migration coefficient. From a visual point of view, the repair mortar that contains polymers seems to be the most efficient regarding this test (cf. Figure 44).



Figure 43 – Penetration depths

This test has allowed computing the value of migration coefficient for each mortar. The graph below confirms the observations made. According to the migration coefficient, we can say that a cementitious material is a good one when its migration coefficient is lower than  $10 \times 10^{-12} \text{ m}^2/\text{s}$ , which supposes that the service life of this material is high. So, we may say that all the tested mortar have a good behaviour regarding the chloride resistance (even the conventional mortar whose value reaches  $10.01 \times 10^{-12} \text{ m}^2/\text{s}$ ). However, the repair mortar with polymer additions (Monotops 412 SFG) presents the best properties regarding the chloride migration test. These results are in total accordance with those obtained with the electrical resistivity.

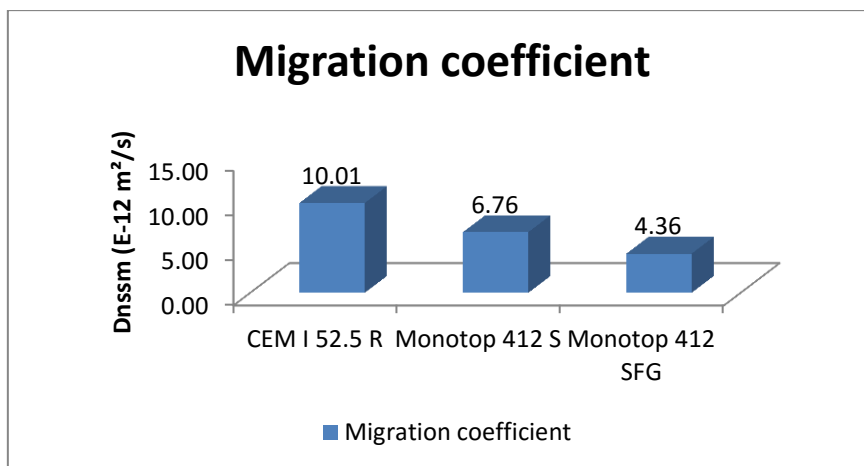


Figure 44 – Migration coefficient

According to the graph above, it is relevant to determine the percentage of variation of the migration coefficient of each mortar with respect to the others (cf. Table 26). So we may note that the Monotop 412 SFG, that contains polymers, has a coefficient which is more than twice as low as the conventional mortar. This data is important as it indicates how good its behaviour is regarding chloride migration.



	Monotop 412 S	Monotop 412 SFG
CEM I 52.5 R	- 32.47%	- 56.44%
Monotop 412 S	-	- 35.50%

Table 26 – Comparison of chloride migration coefficients

## 2.5 Capillary absorption

The capillary absorption coefficient is closely linked to the resistance to freeze/thaw. This test has been carried out in order to have an idea of the resistance of the mortars to freeze/thaw cycles, according to the reduced time we had for this study. The capillary absorption test has been realised after 28 days of curing (cf. Figure 45). According to the graph, the conventional mortar is the one that presents the highest capillary absorption coefficient, while the Monotop 412 S mortar has the lowest one. In any case, both repair mortars have lower capillary absorption coefficient than the conventional mortar. However, the results obtained show that there are not so much differences between the mortars regarding the capillary absorption coefficient. According to the microstructure of repair mortars, the values could have been much higher due to the smaller pores, but the presence of a part of large pores allows maintaining the resistance in the order of values than a conventional mortar.

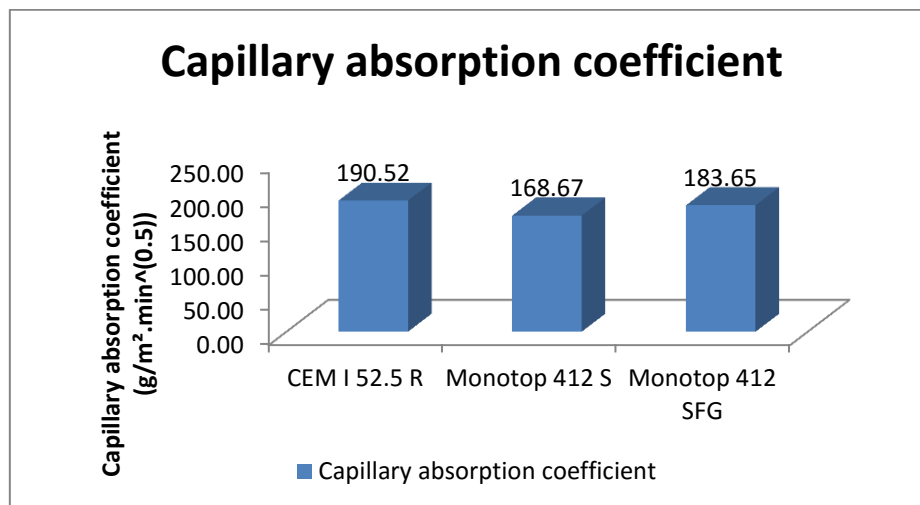


Figure 45 – Capillary absorption coefficient

We can also compute the percentage of variation of the capillary absorption coefficient (cf. Table 27). As we may see, the values obtained are not really different from one mortar to another. This also confirms the observation made while highlighting the good performance of the Monotop 412 S regarding capillary absorption.

	<b>Monotop 412 S</b>	<b>Monotop 412 SFG</b>
<b>CEM I 52.5 R</b>	- 11.47%	- 3.61%
<b>Monotop 412 S</b>	-	+ 8.88%

Table 27 – Percentage of variation of the capillary absorption coefficient

### **3 PART IV: DISCUSSION**

Regarding the mechanical properties, we can compare the values obtained with the test by those given on the product sheet (cf. APPENDIX C – Extract from the product sheet of the Monotop 412 S and APPENDIX D – Extract from the product sheet of the Monotop 412 SFG). If we do so, we may say that in general we obtained higher values than predicted by the manufacturer for both repair mortars. This tendency can be observed after 7 days of curing, as well as after 28 days of curing in all of the cases except for the Monotop 412 S in flexural strength test (whose values are lower than predicted). In general, we can say that repair mortars have good mechanical properties. However, regarding mechanical properties, the Monotop 412 SFG has a resistance that is comparable with the reference mortar. No significant improvement has been noticed due to the presence of polymers.

Regarding the microstructure, two different tests have been carried out: mercury intrusion porosimetry and differential thermal analysis. Regarding the mercury intrusion porosimetry, the highest value of total porosity is obtained for the Monotop 412 S (without polymer). In general, this value tends to decrease with the curing age, which seems to be normal. Besides, we obtained lowest values for the Monotop 412 SFG, as we were expecting because of the presence of polymers, which start having an influence after 28 days of curing. The value obtained for the Monotop 412 SFG is comparable to the one obtained for reference mortar. However, the distribution of pores is different for the two repair mortar as it is a bimodal distribution, with smaller pores than the CEM I 52.5 R, but with a part of large pores. The conventional one has the highest percentage of large capillaries while the Monotop 412 SFG has the highest percentage of medium capillaries. Moreover, we can say that, in general, the Monotop 412 SFG has smaller pores than the others. Finally, the tortuosity has a tendency to increase with the curing age, which is normal and shows that the penetration of aggressive agent is more difficult after 28 days of curing than it is after 7 days of curing. However, the Monotop 412 SFG presents the lowest values of tortuosity. Besides, between 7 days and 28 days, its tortuosity only increases a 6.41%. This means that this mortar has its definitive microstructure after 7 days of curing.

Regarding the differential thermal analysis, the curves obtained have in general the same shape for all of the mortars. The main differences are observed in the zone corresponding to carbonates and the one corresponding to CSH gel. Another difference appears for the Monotop 412 SFG that contains polymers. Indeed, a peak is located at approximately 730°C (this peak does not appear for the other two mortars). We can assume that it is due to the burning of the polymer. Besides, the water losses are mostly due to CSH gel and CH. For all of the three mortars, these losses have a tendency to increase with the curing age.

Finally, regarding durability capacities, three tests have been carried out: electrical resistivity, chloride migration and capillary absorption. Regarding the electrical resistivity, both repair mortars obtained higher values of electrical resistivity in comparison with the conventional mortar. The results also show that the highest value of electrical resistivity is obtained with the Monotop 412 SFG (more than twice higher than the reference mortar), which means that it has smaller pores than the two other mortars. This result is in accordance with those obtained with the PIM method. The results also highlight the increase of the resistivity with the curing age for all the testes mortars.

Regarding the chloride migration test, we were expected to obtain the lowest migration coefficient for the Monotop 412 SFG that contains polymers. The results are in accordance with our assumptions. It confirms that the mortar containing polymers will allow with more difficulties the entrance of aggressive agents and allows having the same conclusions with had with the electrical resistivity. It allows thinking that this mortar will have a better behaviour than the others in the case of an aggressive attack since it presents very good properties in terms of durability.

Regarding the capillary absorption test, the results show that the behaviour is more or less the same for all of the mortars. Due to the smaller pores of the two repair mortars, the values obtained could have been much higher; but the presence of a part of large pores in both mortars allows obtaining finally values that are comparable than the one obtained for the reference. Consequently, we may say that apparently no significant improvement can be expected from the Monotop 412 SFG in comparison with a conventional mortar in terms of resistance to freeze/thaw.

### **CONCLUSION OF THE CHAPTER**

In conclusion, we may say that the tests carried out in this chapter show that the repair mortar that contains polymer has a tendency to present better properties than the others, above all in terms of durability. The mechanical properties of the Monotop 412 SFG are similar to those obtained with a conventional mortar. However, it presents a microstructure that makes it more difficult for aggressive agent to enter the material than it is for the other mortars. Nevertheless, no significant improvement has been highlighted regarding the resistance to freeze/thaw; the values are in the same order of magnitude than the one obtained for a conventional mortar. For these reasons, we can expect a better behaviour of the Monotop 412 SFG in presence of aggressive agents. Besides, since all of the repair mortars have better properties than the conventional mortar in terms of durability, we can expect to see the most important degradations occurring for the conventional mortar. These assumptions have to be confirmed. In the next chapter, the three mortars will be submitted to aggressive media. By carrying out some tests, we will try to determine in what extent we are right.



## **CHAPTER IV: RESISTANCE TO ACID ATTACKS**

### **INTRODUCTION**

The previous chapter has allowed us highlighting the properties and characteristics of each studied mortars. Thanks to this chapter, we have an idea of the behaviour that each mortar can adopt (according above all to their microstructure and durability capacities) and we can predict their reaction once submitted to acid attacks. The objective of this chapter is to study the real behaviour of these mortars when they are submersed into an aggressive medium. To do so, two different solutions are considered: a lactic acid solution and an acetic acid solution. A sample of each mortar is submersed into the lactic acid solution on one hand and the acetic acid solution on the other hand. According to the results obtained in the previous chapter, we may expect a better resistance to acid attack from the repair mortar that contains polymers (i.e. the Monotop 412 SFG). The worst behaviour can be expected for the conventional mortar since its structure allows an easier penetration of agents. After one month of submersion, each sample will be tested in order to be characterised from both microstructural and durability points of view. In this respect, three different tests are realised: mercury intrusion porosimetry, thermogravimetric analysis and titrimetric method.

### **1 PART I: DEGRADATION PROCESS**

The degradation process can be observed and described with eyes. It can be noticed that the behaviours of the mortars submersed into acid solutions depend on the type of acid as well as on the type of mortar. These observations that have been made are detailed below.

#### **1.1 Lactic solution**

According to the characteristics of lactic acid, it is normally the most aggressive solution in comparison with the acetic one, as we have seen previously. In the case of the lactic solution, the degradation of the three mortars is visible as it leads to a severe deterioration of the mortars once they are submersed into the solution.

It has to be reminded that this attack took place with a very low pH (cf. Figure 46), according to the buffer zone on lactic acid. During the entire submersion, the pH has varied around 2 to 2.5 (knowing that the buffer zone is located between pH=2.85 and pH=4.85). According to these curves, we have not reached the buffer zone, which means that the concentration of lactic acid was much higher than the concentration of the lactate ion (around 1/30).

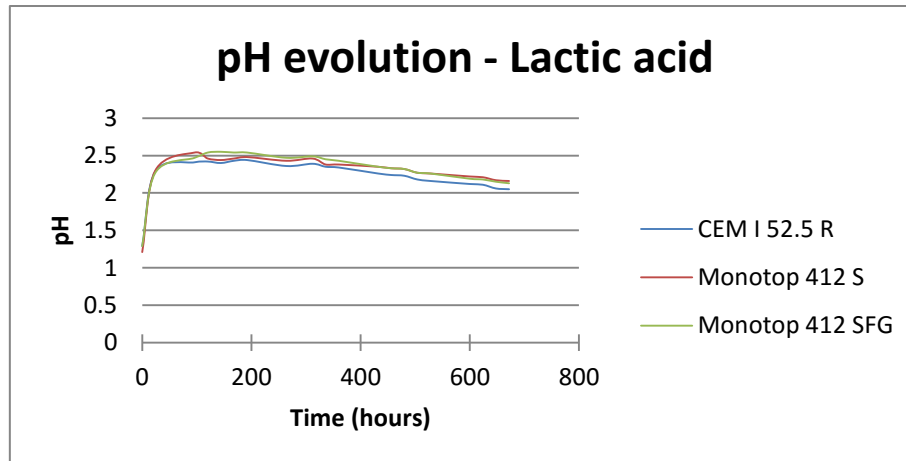


Figure 46 – Evolution of the pH for lactic acid solution

After 10 days of submersion, we can note that while the conventional mortar and the repair one that does not contain polymers begin to decompose and disintegrate, the repair mortar that contains polymers just presents cracks (cf. Figure 47). At this stage, the better resistance of the mortar that is modified with polymer addition seems to be obvious.

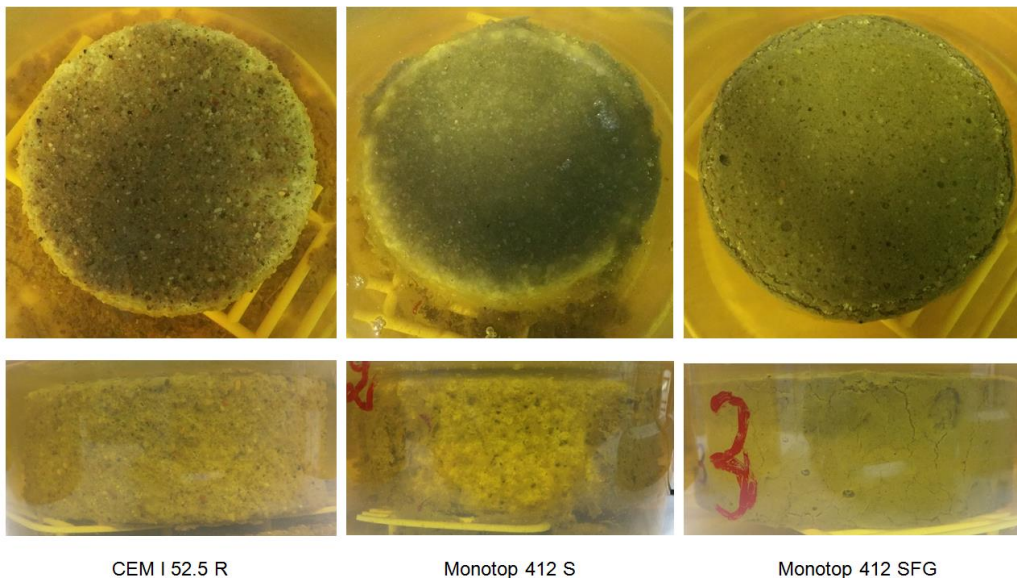


Figure 47 – Mortars after 10 days of submission into lactic acid

We can also note that the lactic solutions became yellow when put in contact with the mortars. This can be due to the complexation of one or several ions present in the composition of the three mortars (since the change in colour can be noted in all of the cases). According to the composition of the CEM I 52.5 R (which is known), we can suppose that this coloration is due to ferrous lactate. It can also be underlined that the coloration is more important for the repair mortars (the most coloured solution corresponding to the Monotop 412 SFG that contains polymers).

After one month of submersion, a visual observation allows saying that all of the three mortars have suffered structural damages. The conventional mortar appears to be the least resistant against lactic acid attack as it present the most extended damages. We can see that a great part of the mortar (in the circumference) has been disintegrated. This phenomenon is also observed on the Monotop 412 S. On the contrary, the mortar containing polymers is the one that seems to have resisted the best (cf. Figure 48). Submitted to the same medium than the others, the effects of the attack take more time to be visible. After one month of submersion, the circumference has stated degrading but the specimen remains keeping its structure. Besides, the diameter of all samples has changed (cf. Table 28). In the case of the CEM I 52.5 R and the Monotop 412 SFG, the diameter has increased in the same proportions in both upper and lower faces. However, the Monotop 412 S presents a different diameter on its upper face than on its lower face. It has to be noticed that the Monotop 412 SFG presents the highest increase in diameter. This can be due to the combination of some compounds with water, leading to the formation of insoluble compounds (different from the salts that are soluble).

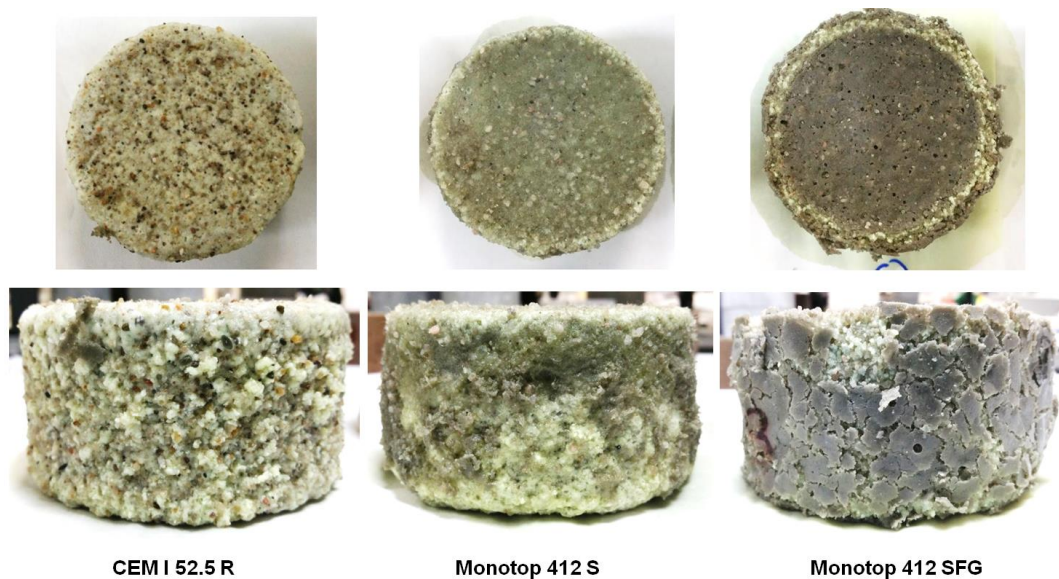


Figure 48 – Mortars after 1 month of submersion into lactic acid

MORTAR	DIAMETER	VARIATION
CEM I 52.5 R	105 mm	+ 5%
Monotop 512 S	95 mm (upper face) 105 mm (lower face)	- 5% (upper face) + 5% (lower face)
Monotop 412 SFG	110 mm	+ 10%

Table 28 – Diameters of the samples after 1 month of submersion into lactic acid

## 1.2 Acetic acid

In the case of acetic acid, the attack occurs at a more elevated pH as shown on the curves below (cf. Figure 49). In this case, the pH varies around 4 to 4.5, knowing that the buffer zone is comprised between  $\text{pH}=3.75$  and  $\text{pH}=5.75$ . Regarding these curves, it has to be mentioned that the solution in which the Monotop 412 S is submitted has an acetic acid concentration of  $1.43\text{mol/L}$  since it has been more diluted. The only effect is that the buffer zone has been reached earlier than for the two other solutions. That is the reason why the pH curve for the Monotop 412 S has not the same tendency than the two other curves, and has higher values. Nevertheless, it does not influence the degradation process.

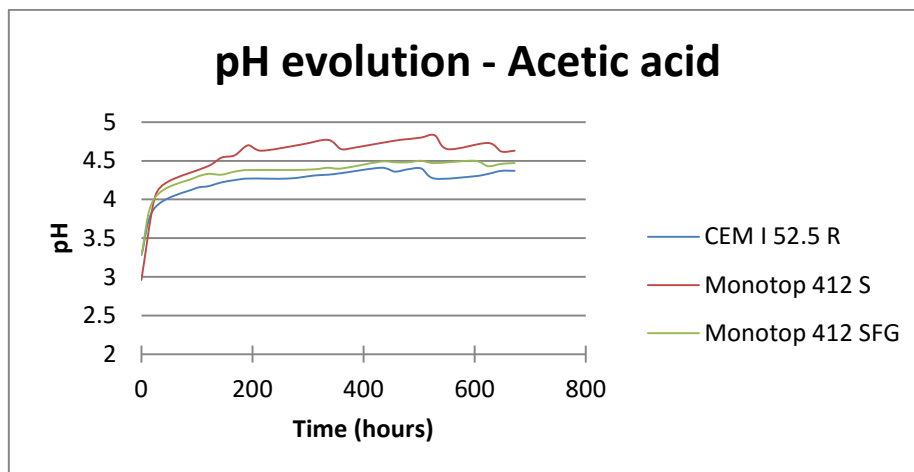


Figure 49 – Evolution of the pH for acetic acid solution

In the case of acetic acid attack, after two weeks of submersion, the three mortars are still being intact as a visual level. The samples do not seem to suffer dissolution in their peripheral area during all the experiment, as it occurs in the case of lactic acid attack. However, it can be noticed that the coloration of the acetic solutions changes when the mortars are submersed into them (cf. Figure 50). Indeed, in all cases, the solutions become red. As well as for the lactic acid, we can suppose that this is due to a complex reaction that evolves the ferric acetate. This supposition can be done by looking at the composition of the conventional mortar which is known. We can generalise to all of the three mortars since in all cases this red coloration appears. It has also to be mentioned that the coloration is stronger for the repair mortars (in comparison with the conventional mortar) and the coloration is the strongest for the Monotop 412 SFG which contains polymers.



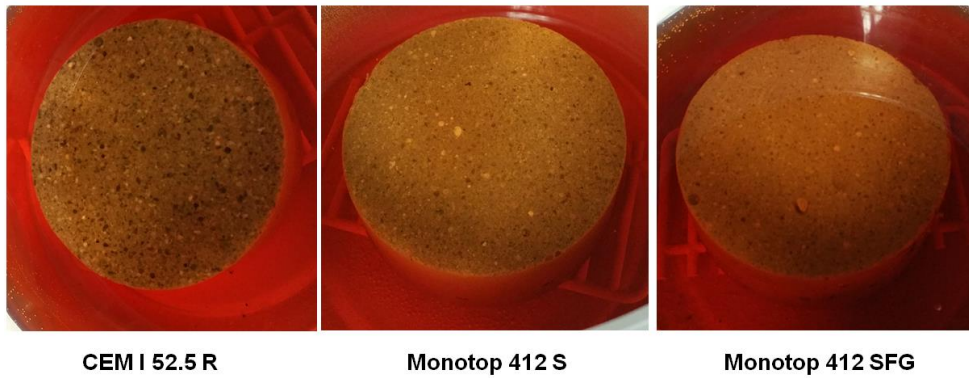


Figure 50 – Mortars after 10 days of submersion into acetic acid

After one month of submersion, the mortars are still intact and there is no sign of degradation from a visual observation (cf. Figure 51). However, after the specimens have been put out of the solution and the samples extracted to realise the tests, some cracks appear and the degradation becomes visible (cf. Figure 52). The samples are still maintaining their dimensions (100mm diameter) and forms, but the effect of the attack can be clearly viewed. Moreover, it appears that the thickness of the degraded zone is less important in this case than it is in the case of lactic acid attack. This confirms, from a visual point of view, the fact that the attack with acetic acid is less aggressive than it is with lactic acid. Once again, the CEM I 52.5 R seems to be the most deteriorated from a visual point of view.

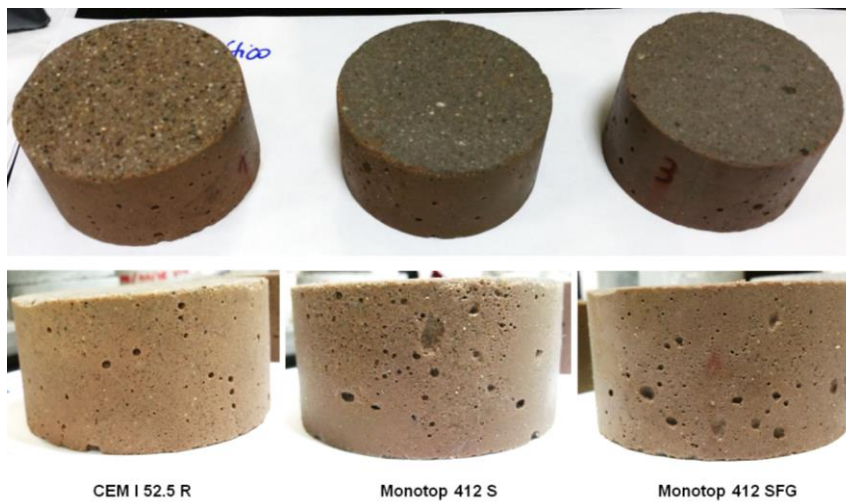


Figure 51 – Mortars after 1 month of submersion into acetic acid

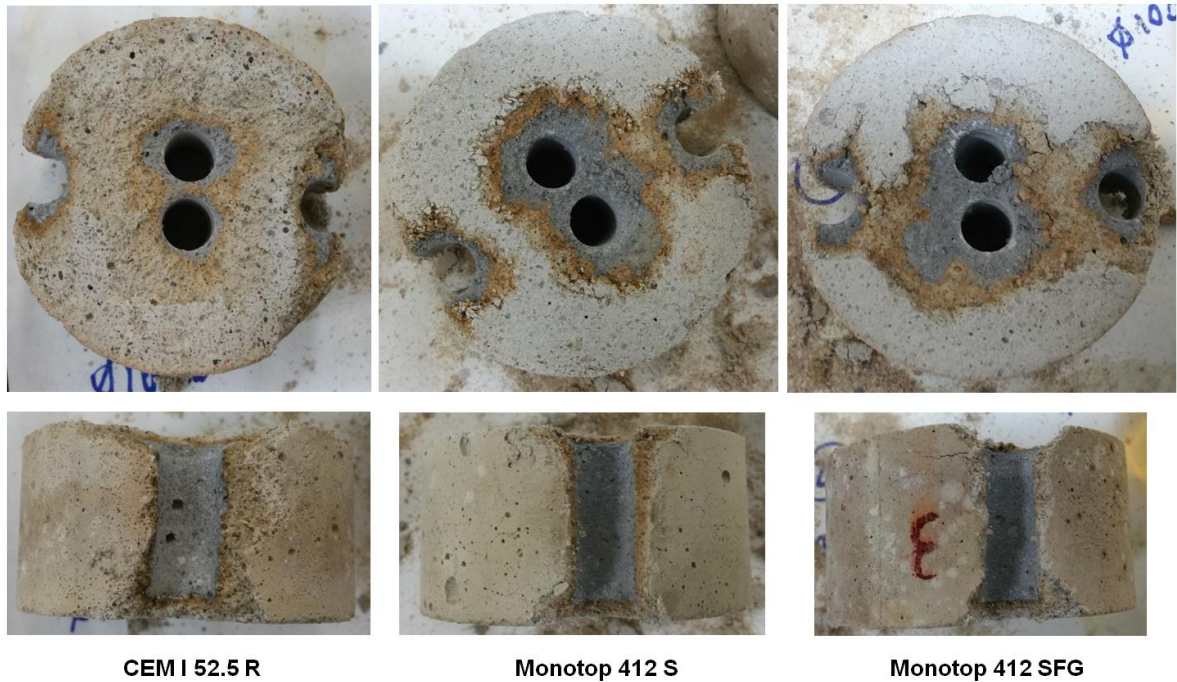


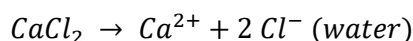
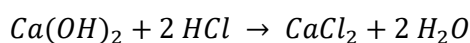
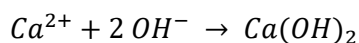
Figure 52 – Mortars submitted to acetic acid after drying

## **2 PART II: CHARACTERISATION TESTING**

In order to characterise the state of each mortar after their submersion into acid solution, three tests seem to be relevant: the titrimetric method, the mercury intrusion porosimetry and the thermogravimetric analysis. All these tests have been carried out and their results are presented in what follows.

### **2.1 Titrimetric method**

As we know, when put in the solutions, the compounds of the material will react, decomposing the calcium hydroxide first. Consequently, calcium should be present in the solution. That is the reason why the realisation of a titration can be useful in this study. The objective in this part is to determine the quantity of calcium present in each solution after one month of submersion. Indeed, as we have observed, the mortars have been degraded (above all in the case of the lactic acid). That is the reason why we may assume that there was an exchange between the solution and the mortars, leading to the presence of calcium in the solution. Because of the coloration of both acetic and lactic solutions, we were not able to apply directly the EDTA method (using murexide as coloured indicator). Consequently, in order to evaluate the quantity of calcium in solution, we have first mixed the dissolution (that contains the calcium ions) with soda. Then, the CH formed has been dissolved in hydrogen chloride. Since the  $\text{CaCl}_2$  formed is soluble in water, we have been able to separate the calcium ions from the hydrogen ones (cf. Equation 38).



Equation 38 – Steps to the realisation of titrimetric method

Doing this, we have finally been able to evaluate the quantity of the calcium by means of EDTA method. To realise this study, the solutions have been mixed with soda (cf. Table 29). In all cases, this step leads to the formation of a suspension. Once the solution is filtered, the suspension is put to dry.

SOLUTION	QUANTITY OF SOLUTION	QUANTITY OF SODA	pH	OBSERVATIONS
Lactic acid				
CEM I 52.5 R	50 mL	100 mL (2mol/L)	12.71	Formation of a white suspension (precipitate) and heat up
Monotop 412 S			12.76	
Monotop 412 SFG			12.60	
Acetic acid				
CEM I 52.5 R	50 mL	90 mL (2mol/L)	12.67	Formation of a white viscous suspension (precipitate)
Monotop 412 S			13.15	
Monotop 412 SFG			12.56	

Table 29 – Proportions of soda added to the solutions

### 2.1.1 Lactic acid

In the case of lactic acid, after the precipitate has dried, it becomes a yellowish solid in all cases. A first indication on the capacity to resist acid attack can be given by the weight of the compound formed by the addition of soda. We can assume as a first approximation that this solid is made of CH, although it does not seem to be. In order to be comparable, these weights have to be considered according to the quantity of CH initially present in the samples. These quantities have been highlighted by the DTA realised after 28 days of curing (cf. Figure 41). This figure shows a higher content of CH in the repair mortars in comparison with the conventional mortar. With these data, we are able to compute the theoretical weight of CH formed (cf. Table 30). As we can see, both repair mortars have formed less precipitate than predicted theoretically. This result shows a better resistance for both mortars. It has also to be underlined that the Monotop 412 SFG presents the better resistance according to this result. Then, the calcium titration has been realised. The results show that in all cases, the calcium concentration reaches 0.0073mol/L (cf. Table 31). The concentration obtained is the same concentration for all of the mortar. So we can say that the observations made with the weights are valid and the Monotop 412 SFG resists the best to lactic acid attack. However, this value is much lower than expected (we were expected approximately 0.0134mol/L).

MORTARS	WEIGHT MEASURED	THEORETICAL WEIGHT	COMPARISON
CEM I 52.5 R	0.914g		
Monotop 412 S	1.074g	1.485g	- 27.65%
Monotop 412 SFG	1.173g	1.656g	- 29.21%

Table 30 – Quantity of CH formed in the lactic acid solution

SOLID	WEIGHT	QUANTITY OF HCl	CALCIUM CONCENTRATION
1 (CEM I 52.5 R)	0.104g	100mL (0.05mol/L)	0.0073mol/L
2 (Monotop 412 S)	0.109g		
3 (Monotop 412 SFG)	0.107g		

Table 31 – Calcium concentration in lactic acid solutions

So we may wonder where the calcium ions that do not appear here in the solution are. In order to find an explanation, we have realised the titration of the most external parts of the specimens: the one that have been detached, and the one that have still adhered to the specimen (cf. Figure 48). We have realised the evaluation of calcium content in these solid phases according to the UNE-EN 14629 Standard. The solids have been grinding and put at  $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for 24h. Then, they have been put at room temperature until their cooling. 2g of each part have been dissolved according to the Standard (100mL of distilled water and 10mL of  $\text{HNO}_3$  at 0.5mol/L have been added). The mix has been put to ebullition and filtered as the Standard requires. We have finally realised the calcium titration. In the case of the part that was totally detached from the specimen, the quantity of calcium was too low to be detected. However, 0.0109mol/L have been measured in the other part (that was adherent to the specimen). This result explains why the calcium was not in solution. As this external part was in solidarity with the specimen, we can assume that it was belonged to the CSH gel (whose stoichiometry has changed).

### 2.1.2 Acetic acid

In the case of acetic acid, after drying, the precipitate becomes a white solid (that looks like CH) in all cases. As well as for lactic acid, we can compute the quantity of CH formed by the addition of soda. These values have to be compared with the theoretical ones, computed in accordance with the initial CH content of each mortar. As we can see on the table below (cf. Table 32), the two repair mortars resist well to acetic acid attack. Besides, the Monotop 412 SFG is the one that resists the best in this case. These observations have to be confirmed with the realisation of the proper titration.

The results of the calcium titration show that the calcium concentration reaches 0.0109mol/L for the CEM I 52.5 R and the Monotop 412 S, and 0.0097mol/L for the Monotop

412 SFG. Once again, the calcium concentration is lower than expected, but the values obtained are reasonable. This can be due to the presence of other ions (Mg, Fe, Al). Besides, the Monotop 412 SFG has the lowest concentration, which is in accordance with our assumptions.

MORTARS	WEIGHT MEASURED	THEORETICAL WEIGHT	COMPARISON
CEM I 52.5 R	4.30 g		
Monotop 412 S	3.45 g	6.99g	- 50.64%
Monotop 412 SFG	4.91 g	7.79g	- 63.00%

Table 32 – Quantity of CH formed in the acetic acid solution

SOLID	WEIGHT	QUANTITY OF HCl	CALCIUM CONCENTRATION
1 (CEM I 52.5 R)	0.106g	100mL (0.05mol/L)	0.0109mol/L
2 (Monotop 412 S)	0.107g		
3 (Monotop 412 SFG)	0.103g		0.0097mol/L

Table 33 – Calcium concentration in acetic acid solutions

### 2.1.3 Comparison

If we compare the results obtained for the lactic acid solutions and those obtained for the acetic acid solutions, many differences can be highlighted. The aspect of the solid that is formed is different: it is a white solid in the case of acetic acid solutions, while it is a yellowish solid in the case of lactic acid solutions. Moreover, the weights of solid obtained are higher in the case of acetic acid solids. The calcium concentrations obtained in the latter case are also higher than they are in the case of lactic acid solutions (with a factor of 1.5). A better understanding of what happened can be obtained by realising a DTA of the solids formed. Since the solids seem to be the same regardless the type of mortar, we can assume that the results obtained for the solid coming from CEM I 52.5 R (whose composition is known) are generalizable to all of the mortars submersed in the same solution (cf. Figure 53).

According to the curves, we can clearly see the differences with the sample that has not been exposed to aggressive agents. Regarding the case of acetic acid attack, we can see that a huge part belongs to CH, and carbonation (later CH). We can assume that the calcium found in the acetic acid solutions comes from calcium hydroxides. However, regarding the lactic acid attack, there is no calcium hydroxide and almost all of the calcium belongs to carbonation (only the inaccessible calcium from CH appears). Besides, the CSH gel presents a different structure, which means that it has been attacked during the submersion and its stoichiometry has changed. This confirms the hypothesis that has been made regarding lactic acid solutions: the CSH gel has been attacked, its stoichiometry has changed and it is the one that retains the calcium on the peripheral area of the specimens.

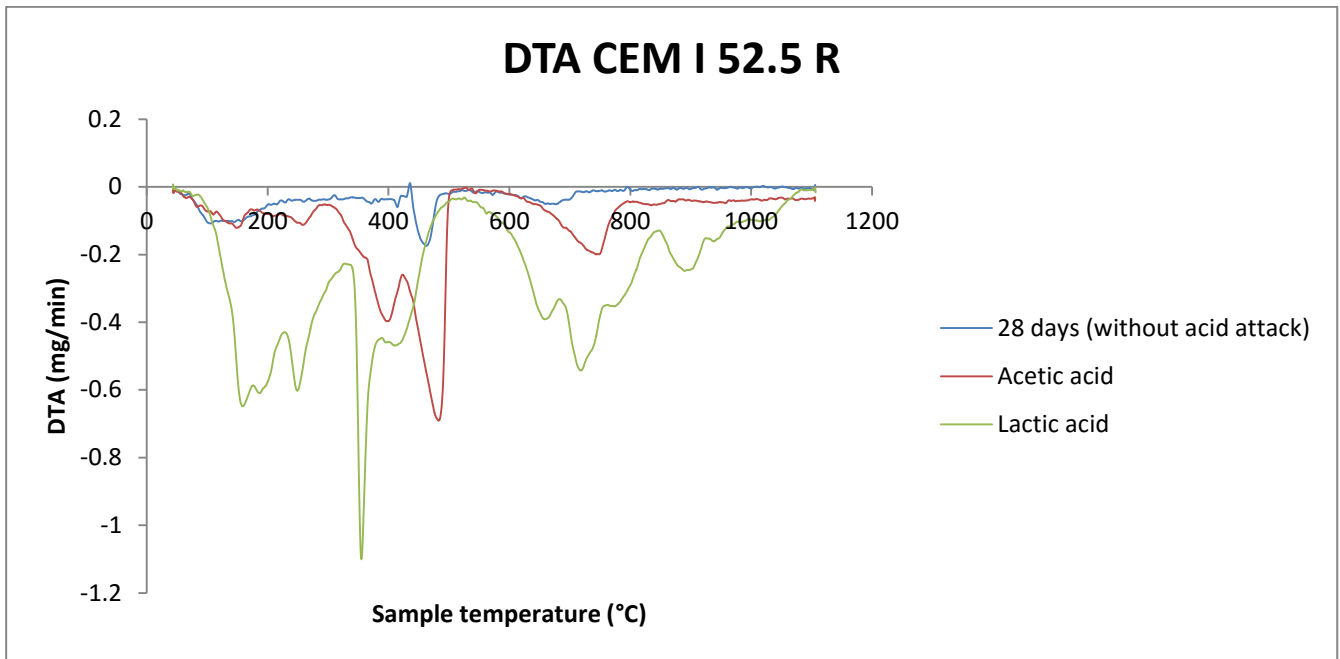


Figure 53 – DTA of the solid formed in the case of CEM I 52.5 R

## 2.2 Mercury intrusion porosimetry

### 2.2.1 *Lactic acid*

The mercury intrusion porosimetry has been realised on samples extracted from the centre as well as from the periphery of each specimen (cf. Figure 54 and Figure 55). According to the curves, we can note a change in the microstructure of the specimens due to lactic acid attack. Indeed, each mortar has a bimodal distribution (from 0.01 to 0.1 $\mu\text{m}$  and from 0.1 to 1 $\mu\text{m}$ ). In the case of the conventional mortar, there is an increase in the pores around 0.5 $\mu\text{m}$  and 1 $\mu\text{m}$ . The same phenomenon occurs in the case of the Monotop 412 S, in addition with an increase in the pores around 10 $\mu\text{m}$  and 50 $\mu\text{m}$ . In the case of the Monotop 412 SFG, there is an increase only in the pores around 10 $\mu\text{m}$  and 50 $\mu\text{m}$ . The most significant changes can be observed at the centre of the specimens, which means that according to microstructure, the centre of the specimens have suffered the most the attack by lactic acid.

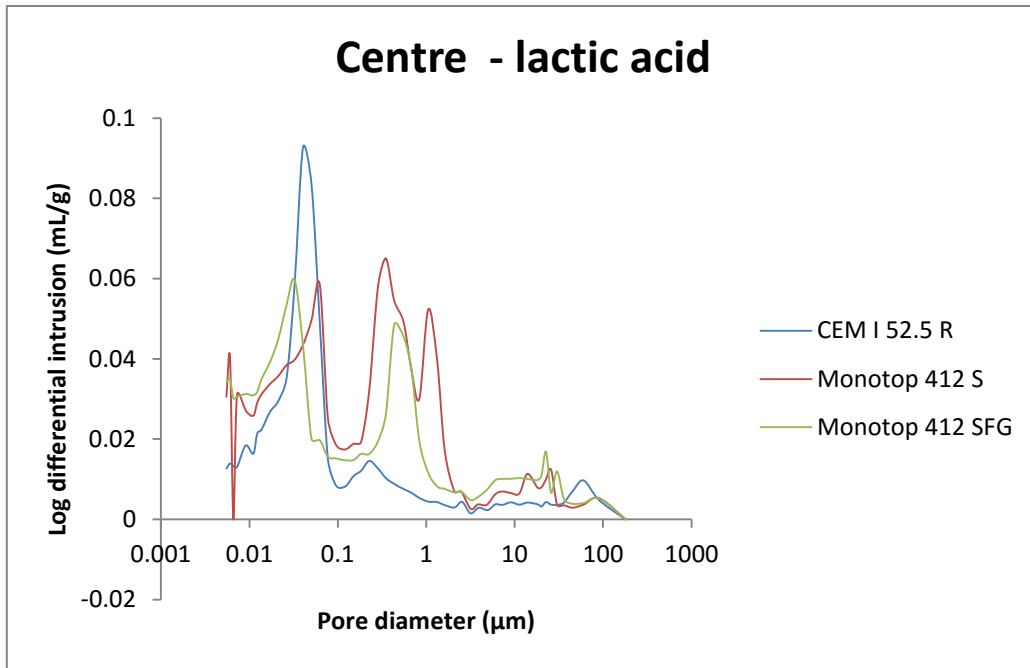


Figure 54 – PIM at the centre of the sample (lactic acid)

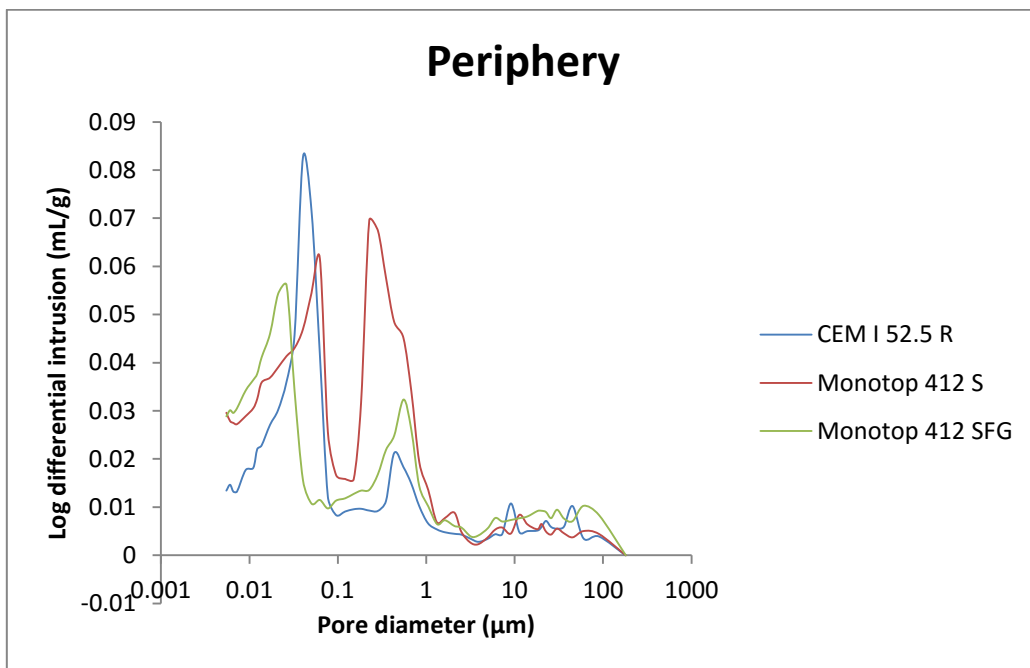


Figure 55 – PIM on periphery (lactic acid)

The results of total porosity show that the conventional mortar has the lowest porosity at the centre as well as in the periphery of the specimen, while the Monotop 412 S reaches the highest values in both cases. In general, the porosity is higher in the centre of the specimen than it is in the peripheral area (even if the difference is not relevant in the case of the CEM I 52.5 R). In general, the porosities obtained after lactic acid attacks are higher than in the case the specimen are not attacked (cf. Figure 36). These results confirm the effects of the attack on the microstructure of the specimens. According to these results, the CEM I 52.5 R

is the one that has kept more or less the same properties in terms of microstructure. However, the repair mortars have suffered important changes, leading to worst properties.

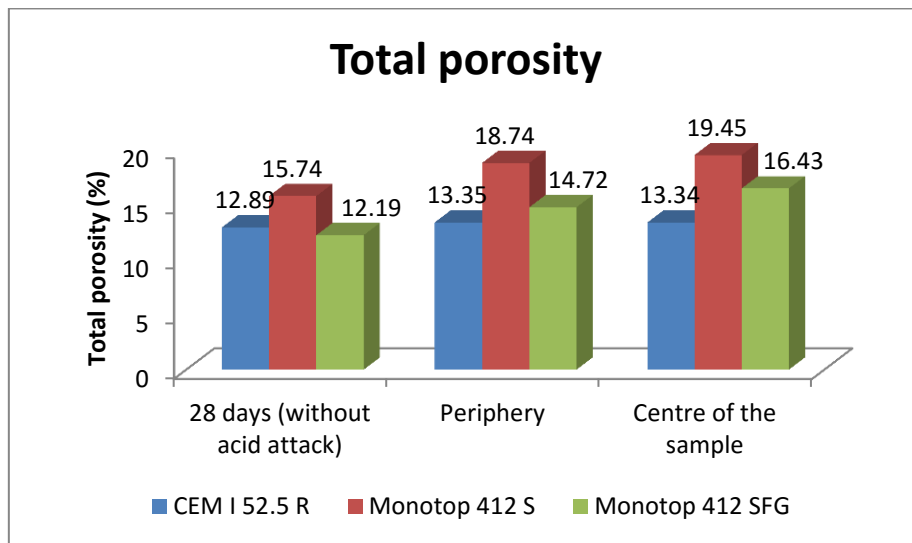


Figure 56 – Total porosity at the centre and in the periphery (lactic acid)

If we compute the tortuosity we can note that for all of the mortars, the tortuosity is higher in the centre of the sample than it is in the periphery. This explains why the peripheral area has been disintegrated while the centre of the specimen has kept its integrity. The mortars that decrease the most their tortuosity after lactic acid attack are the CEM I 52.5 R and the Monotop 412 S (being value of the reference mortar that decreases the most). Besides, while in the periphery the lowest values are obtained with the CEM I 52.5 R and the highest one with the Monotop 412 SFG, in the centre of the specimens, this trend is reversed. Besides, the values obtained are higher in comparison with the results obtained after 28 days of curing (cf. Figure 38), except for the Monotop 412 SFG whose tortuosity has remained in the same order of magnitude.

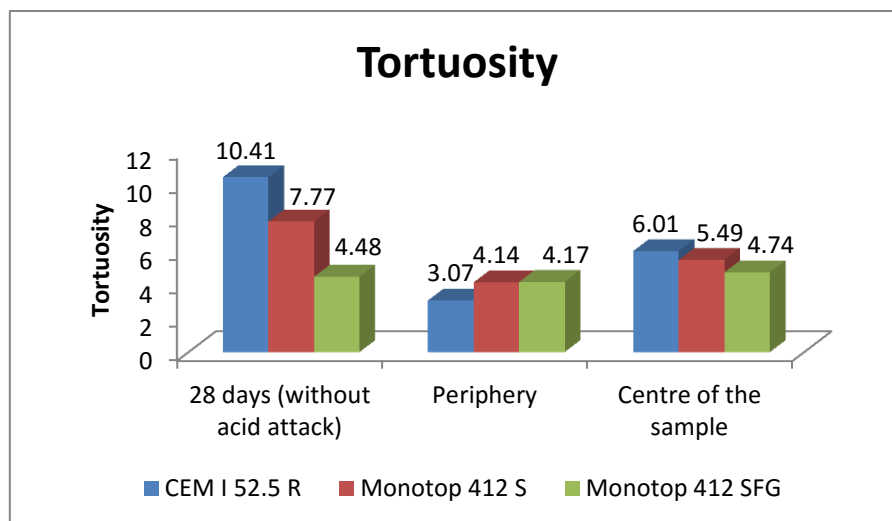


Figure 57 – Tortuosity at the centre and in the periphery (lactic acid)



According to pore distribution, some differences can be observed in comparison with the case the mortars have not been attacked (cf. Figure 37). In the case of the Monotop 412 S, only the percentage of medium capillaries has decreased. In the case of the Monotop 412 SFG, the percentages of macropores and large capillaries have increased, while the other values have decreased. CEM I 52.5 R has increased its percentage of macropores. However, in general, the Monotop 412 SFG still has smaller pores than the other mortars.

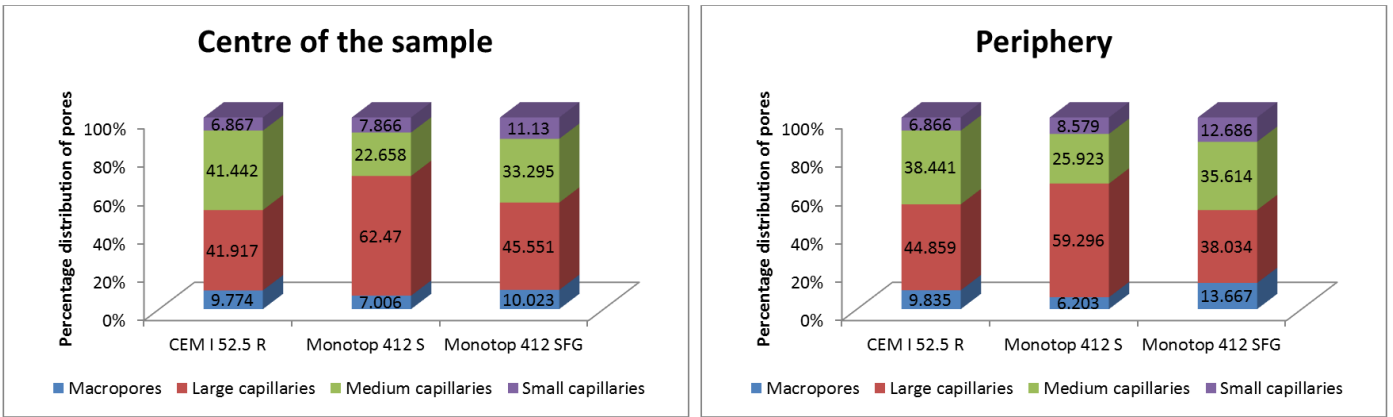


Figure 58 – Pore distribution at the centre and in the periphery (lactic acid)

### 2.2.2 Acetic acid

In the case of acetic acid attack, the curves have also been plotted for samples extracted from the centre of the specimens as well as from the peripheral area (cf. Figure 59 and Figure 60). The CEM I 52.5 R still has a homogeneous distribution of pores (0.01-0.1 $\mu$ m), while the repair mortars present basically a bimodal distribution (0.01-0.1 $\mu$ m and 0.1-1 $\mu$ m). We can note more differences in microstructure in the centre of the specimens.

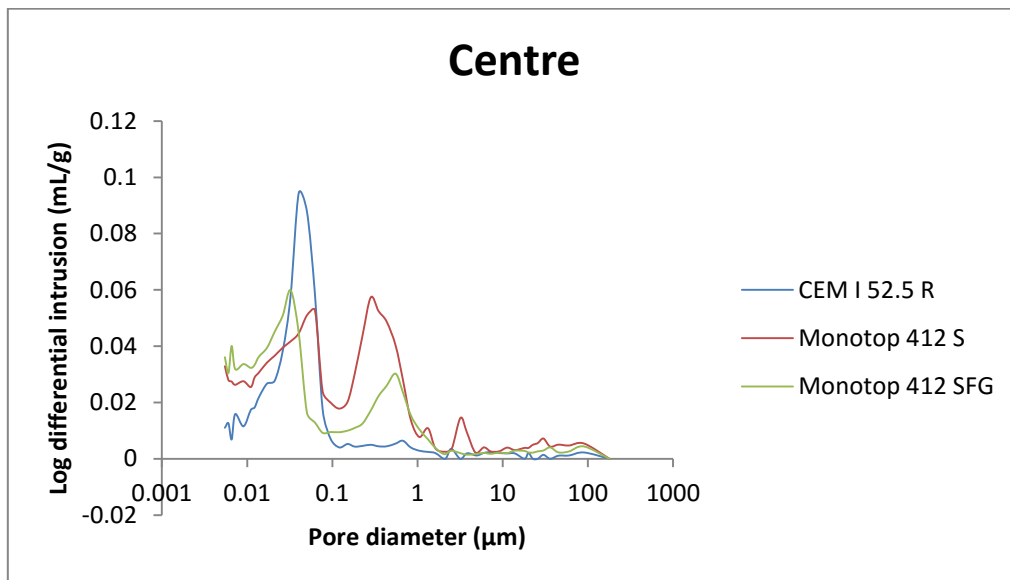


Figure 59 – PIM at the centre of the sample (acetic acid)

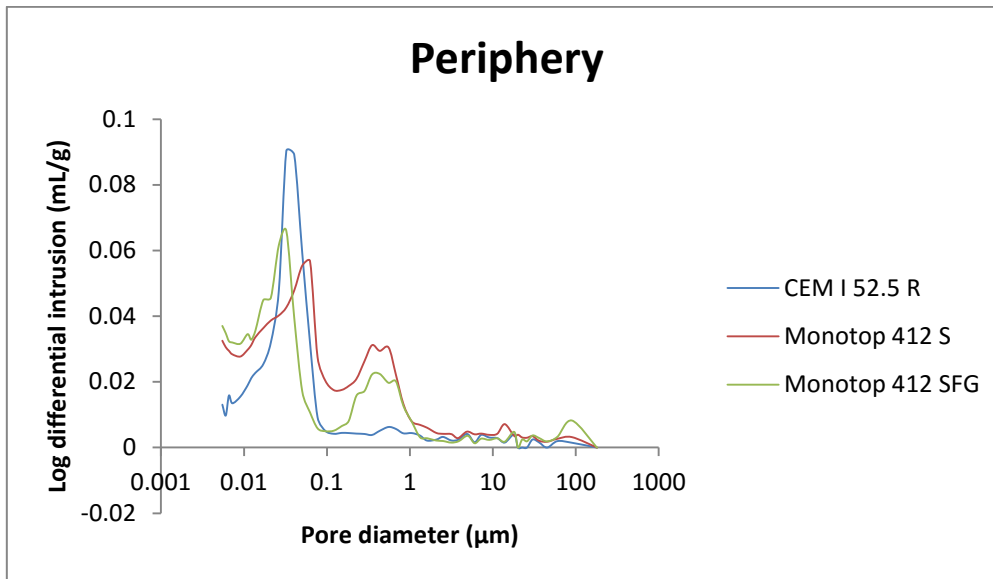


Figure 60 – PIM on periphery (acetic acid)

The total porosity has also been computed for samples extracted in the centre and the periphery of the specimens (cf. Figure 61). If we focus on the total porosity, we can see that the values remain in the same range than in the case of 28 days of curing without acid attack. The differences are very slight, even if they are more pronounced in the case of the Monotop 412 S. According to this result, the mortar the most degraded is the Monotop 412 S, while the CEM I 52.5 R resists well the attack. This result shows that the attack has been more important for the Monotop 412 SFG than for the CEM I 52.5 R, even though the Monotop 412 SFG has other properties that are better than the reference mortar (mechanical resistance, resistivity, chloride migration). In addition, if we compare these values with those obtained in the case of lactic acid attack, we can see that the increase is more reduced in this case. It confirms the fact that the attack by lactic acid has been more aggressive than the attack by acetic acid (that changes less the microstructure than lactic acid attack does).

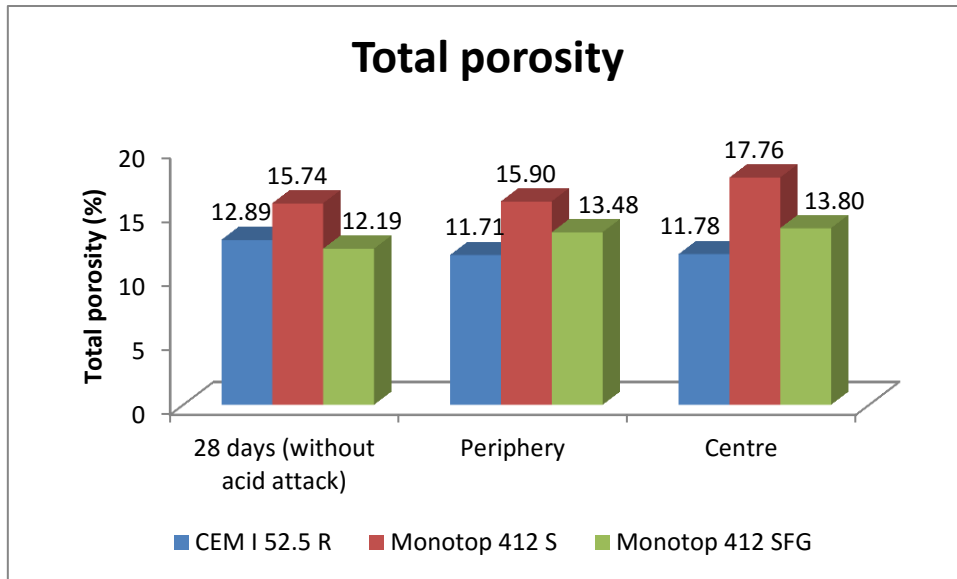


Figure 61 – Total porosity at the centre and in the periphery (acetic acid)

According to the tortuosity (cf. Figure 62) the values have slightly decreased in comparison with those obtained after 28 days of curing without acid attack. The difference is more relevant in the case of the CEM I 52.5 R than it is for the repair mortars. This indicates that the samples have been attacked (with a more aggressive attack for the reference mortar). Besides, for both repair mortars, the values are higher in the peripheral area than they are in the centre of the specimens.

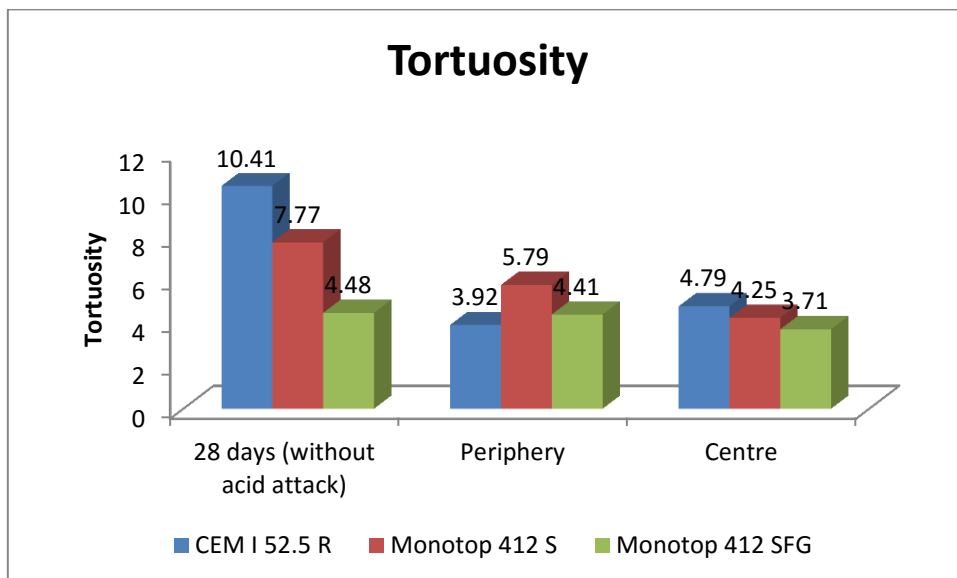


Figure 62 – Tortuosity at the centre and in the periphery (acetic acid)

According to the pore distribution (cf. Figure 63), in comparison with the one obtained after 28 days of curing without aggressive attack, the distribution remains in the same range of values for both repair mortars. However, the conventional mortar presents a remarkable

decrease in its percentage of large capillaries, and an increase in its percentages of small and medium capillaries.

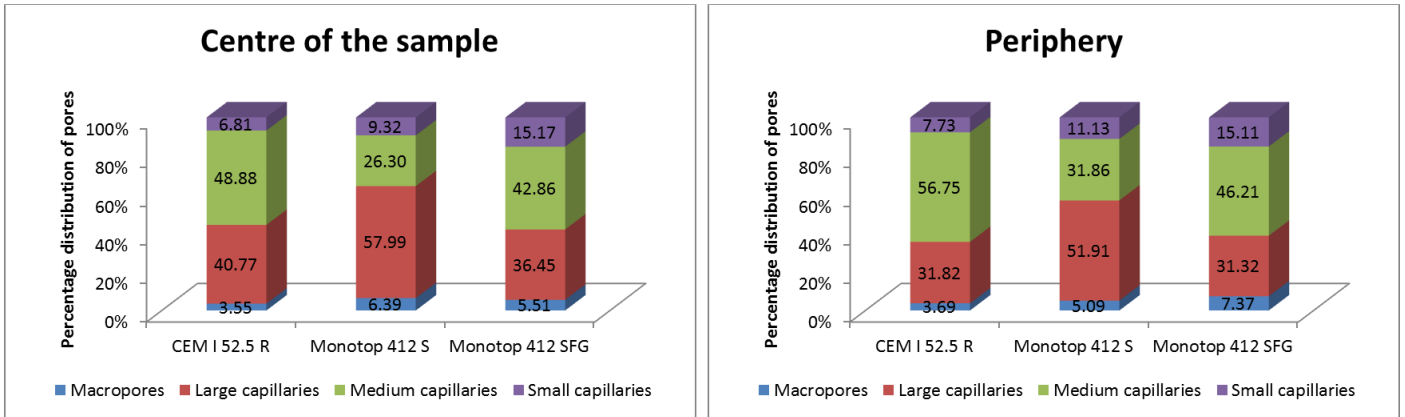


Figure 63 – Pore distribution at the centre and in the periphery (acetic acid)

## 2.3 Thermogravimetric analysis

### 2.3.1 Lactic acid

The differential thermal analysis has been realised for samples located in the centre of the specimens as well as on the peripheral area of each specimen (cf. Figure 64 and Figure 65). In the curves, we can see, in the case of the Monotop 412 SFG, a peak at approximately 750°C. As we have assumed previously, we can say that it corresponds to the burning of the polymer.

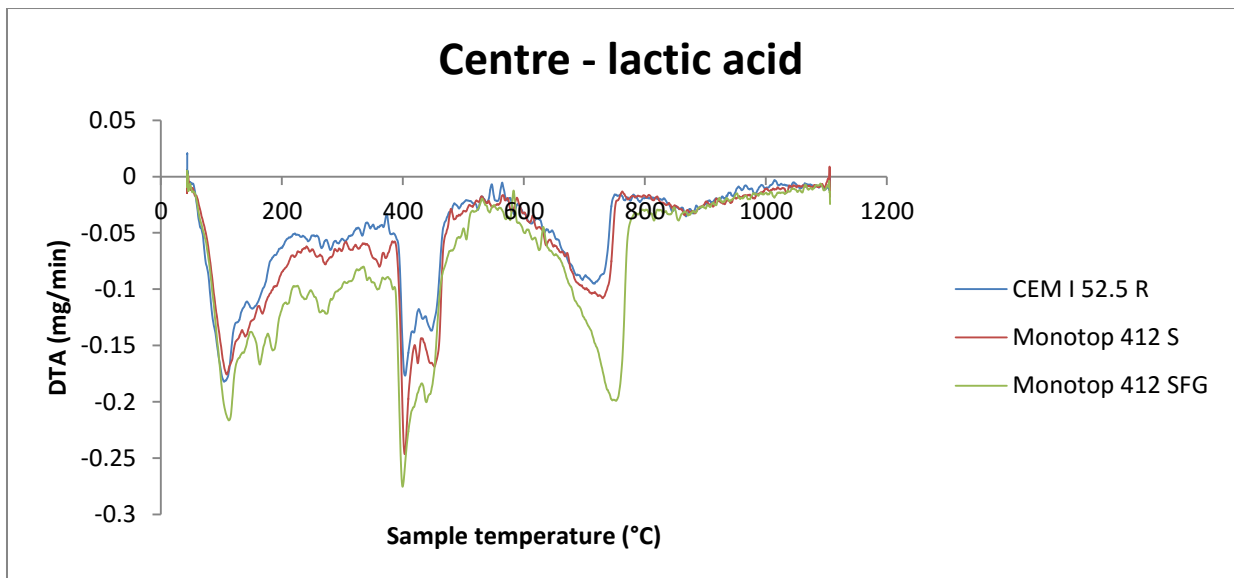


Figure 64 – DTA at the centre of the sample (lactic acid)

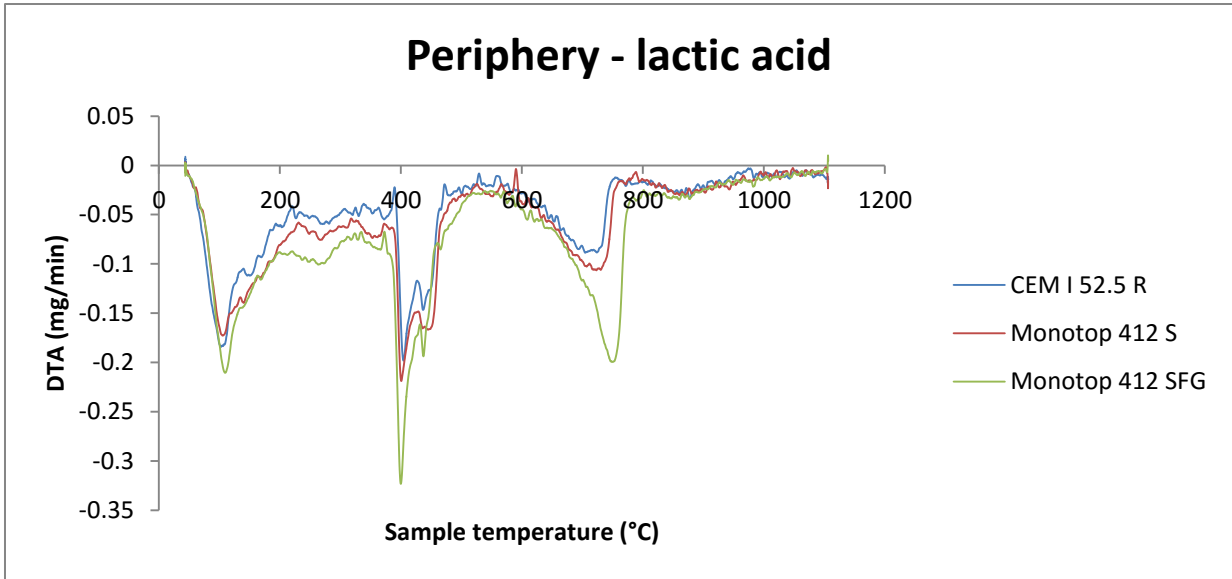


Figure 65 – DTA on periphery (lactic acid)

According to these curves, it is possible to compute the weight losses corresponding to each section described on the previous chapter (cf. Figure 66). However, to compare the results obtained in terms of loss of water, we have to relate the data with those obtained in the case the mortars were not attacked. The results are showed in the table below where the data from the centre of the sample appear in blue while those from the peripheral area appear in red (cf. Table 34). As we can see, all of the samples lose more weight than they do when they are not attacked. In the centre of the sample, the Monotop 412 SFG loses more from CSH gel and CH than the others, being the Monotop 412 S that loses the least. However, in the periphery of the sample, the Monotop 412 SFG loses the least from CSH but the most from CH.

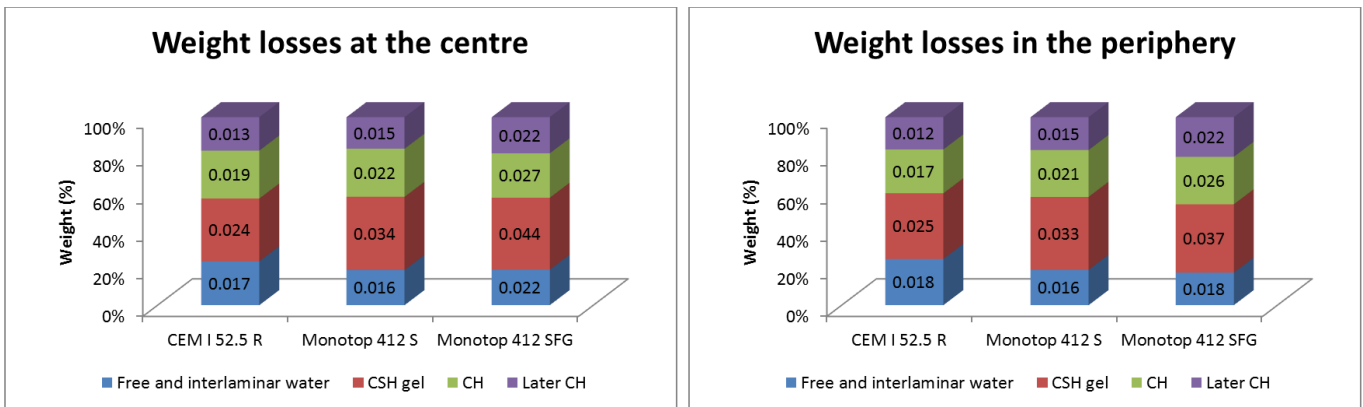


Figure 66 – Weight losses at the centre and in the periphery (lactic acid)

<b>Weight loss centre</b> <b>Weight loss periphery</b>	<b>CSH gel</b>	<b>CH</b>	<b>Later CH</b>
CEM I 52.5 R	+ 26.32% + 31.58%	+ 90% + 70%	+ 116.67% + 100%
Monotop 412 S	+ 21.43% + 17.86%	+ 57.14% + 50%	+ 25% + 25%
Monotop 412 SFG	+ 29.41% + 8.82%	+ 107.69% + 100%	+ 37.5% + 37.5%

Table 34 – Comparison of weight losses (lactic acid)

### 2.3.2 Acetic acid

As well as in the case of lactic acid, the curves have been plotted for samples extracted from the centre of the specimens and from the periphery of the same (cf. Figure 67 and Figure 68). We can detect a peak at approximately 730°C in the case of the Monotop 412 SFG. As we have explained before, it can be linked to the possible burning of the polymer.

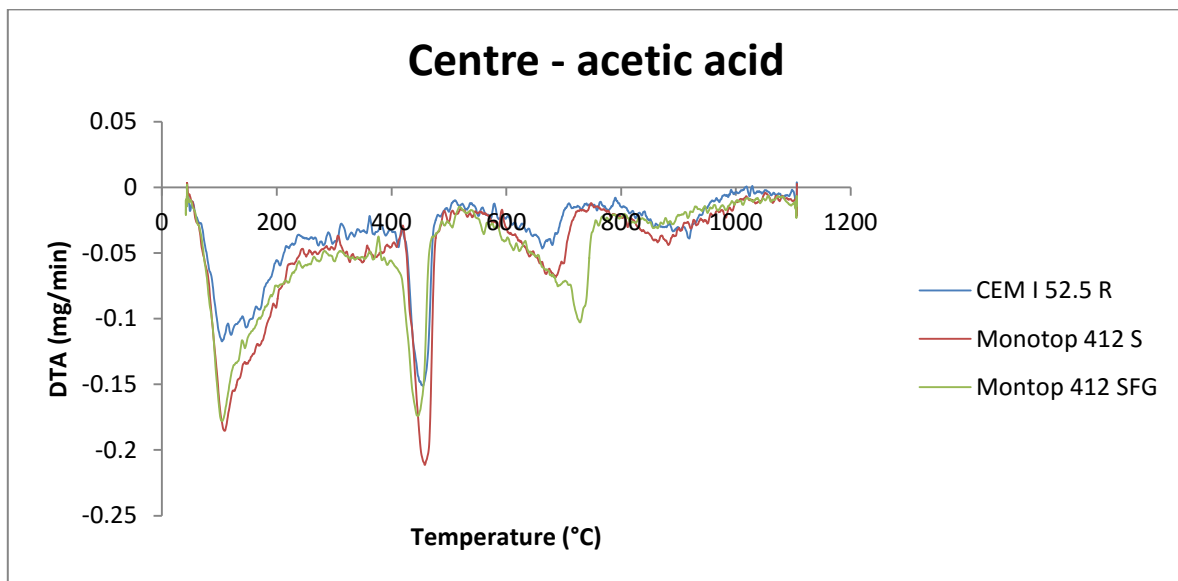


Figure 67 – DTA at the centre of the sample (acetic acid)

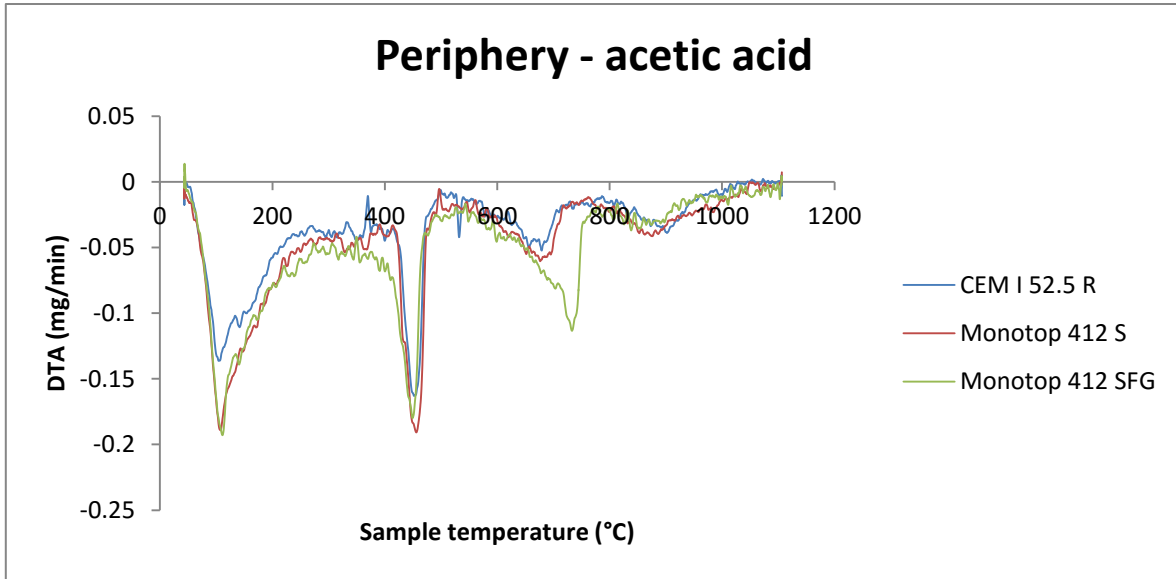


Figure 68 – DTA on periphery (acetic acid)

The weight losses have been computed (cf. Figure 69). We can note that they tend to be similar on the periphery and on the centre of the samples. These results have to be considered in comparison with those obtained in the case the samples were not attacked by aggressive agents. These results are showed in the table below (cf. Table 35). As we can see, in the centre of the specimens both CEM I 52.5 R and Monotop 412 S lose more from CSH gel than they used to, while the Monotop 412 SFG loses less. Regarding CH, both CEM I 52.5 R and Monotop 412 SFG lose more (being the Monotop 412 SFG that loses the most) while the Monotop 412 S loses the same as it used to. In the peripheral area, the CEM I 52.5 R loses more from CSH gel whereas the two repair mortars lose less. Finally, regarding the CH, the Monotop 412 S loses the same while the CEM I 52.5 R loses more and the Monotop 412 SFG loses less.

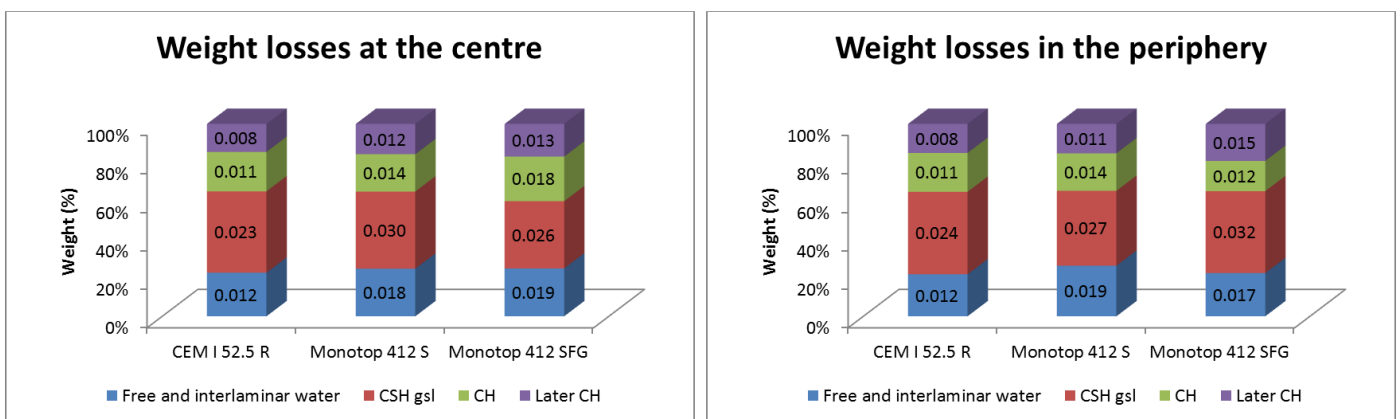


Figure 69 – Weight losses at the centre and in the periphery (acetic acid)

<b>Weight loss centre</b> <b>Weight loss periphery</b>	<b>CSH gel</b>	<b>CH</b>	<b>Later CH</b>
CEM I 52.5 R	+ 21.05% + 26.32%	+ 10% + 10%	+ 33.33% + 33.33%
Monotop 412 S	+ 7.14% - 3.57%	+ 0% + 0%	+ 0% - 8.33%
Monotop 412 SFG	- 23.53% - 5.88%	+ 38.46% - 7.69%	- 18.75% - 6.25%

Table 35 – Comparison of weight losses (acetic acid)

If we compare these results with those obtained in the case of lactic acid attack (cf. Table 34), we can see that the combined water losses (due to CSH gel, CH and later CH) are much higher in the case of lactic acid attack than they are for acetic acid attack. This higher weight loss can be linked to the fact that a more aggressive attack leads to the weakening of the bonds of combined water in each phase. This result is in accordance with the visual observations that have been made.

### **3 PART III: DISCUSSION**

The visual observations have highlighted a more aggressive attack in the case of lactic acid than it is in the case of acetic acid from a structural point of view. Indeed, in the case of lactic acid all of the specimens have suffered a structural deterioration. In the case of acetic acid, the negative effects of the aggressive agent have not been visible until the specimens have been removed from the solutions. In the case of lactic acid attack, the deterioration of the samples has appeared from the early days. All of the specimens that have been put in contact with lactic acid have suffered a change in their structure (they have increased in volume), which can be due to the combination with water, leading to the formation of insoluble compounds. Since the CSH gel is known to be the most stable part of a cementitious material, we can assume that it has been attacked in the case of lactic acid. In both cases (lactic and acetic acids) it seems that the conventional mortar has suffered the most the acid attack, while the Monotop 412 SFG has resisted the best. Indeed, it has to be mentioned that both lactic and acetic acid solutions have changed colour when the specimens were submersed: the lactic acid solution has become yellow and the acetic acid solution has become red. Since this phenomenon has occurred in all cases, regardless of the type of mortar, it is due to a compound that is common to each mortar and that has probably reacted with the acids. On the basis of the composition of the conventional mortar, we can assume that this change is respectively due to ferrous lactate and ferric acetate.

Regarding the titrimetric method, an approximate evaluation has consisted in determining the weight of solid formed after the addition of soda in the solutions. In the case of acetic acid solutions, a white suspension has been formed after the addition of soda. Once this



suspension has dried, it has become a white solid. After having comparing the weights and realising the titration, it seems that once again the Monotop 412 SFG has resisted the best. In the case of lactic acid solutions, a white and viscous suspension has been formed in all of the cases. After drying, this suspension has become a yellowish solid. Besides, in this case, the suspension has formed little quantity of solid. After having realised the calcium titration, the quantities obtained were really lower than expected. The realisation of the calcium titration in the external part of the sample has confirmed that the calcium was not in the solution, but had remained in the sample.

The DTA of the solids has allowed pointing out the fact that in the case of lactic acid solutions, the CSH gel has been attacked and has changed stoichiometry. Ions such as aluminium, magnesium or iron are in presence. Besides, in this case, calcium hydroxide does not appear to be. Nevertheless, in the case of acetic acid attack, the shape of the curves presented fewer differences. All of the calcium was coming from calcium hydroxide and a little part from carbonation. In this latter case, the CSH gel does not seem to have suffered a change in stoichiometry. This result can be linked to the structural degradations observed in the case of samples submersed into lactic acid, and not on those submersed into acetic acid. Besides, since other ions seem to be in presence, they can have reacted with the CSH gel, leading to the formation of other compounds (insoluble). This could explain the increase in volume of the samples submersed into lactic acid. According to the titration of the most peripheral area of the specimen submersed into lactic acid solution, since most of the calcium ions was in the peripheral area, it probably belongs to the CSH gel whose stoichiometric was modified by the lactic acid attack. These results explain why the quantities of calcium that have been detected in lactic acid solutions were so low.

Regarding the DTA and MIP, many differences were observed as well as some similarities with the results obtained after 28 days of curing. The DTA shows the same shape of curves in all cases. We also notice a peak in the case of the Monotop 412 SFG, at 730-750°C. As we have assumed before, it can be linked to a possible burning of the polymer. In the case lactic acid, all of the curves present a bimodal distribution of pore (0.01-0.1µm and 0.1-1µm). Furthermore, in the case of the repair mortars, the total porosity has increased after the attack and the values are higher in the centre of the specimens than it is on the periphery. In the case of the reference mortar, the porosity has remained more or less in the same order of magnitude. This result shows that in the case of an exposition to organic acids, the reference mortar manages to keep its microstructure almost intact, while the repair mortars suffer a change in microstructure (leading to worst properties). The tortuosity has also increased after the attack, except for the Monotop 412 SFG whose values remains in the same order of magnitude. These values are also higher in the centre of the specimens. Regarding the acetic acid attack, the curves of both repair mortars present a bimodal distribution of pores (0.01-0.1µm and 0.1-1µm) while the conventional mortar has a homogeneous distribution of pores (0.01-0.1µm). In addition, the values of total porosity remain in the same range for all of the mortars; the differences noticed are very slight. The tortuosity has decreased; but this is a slight change in the case of the Monotop 412 SFG.

### **CONCLUSION OF THE CHAPTER**

As a conclusion we can say that the attack of mortars realised with lactic acid is very different than the one realised with acetic acid. Indeed, lactic acid attack leads to a structural deterioration of the specimens. The dimensions of the specimens change and their peripheral area is being disintegrated. The solution changes colour as the supposed ferrous lactate react. The CSH gel is being attacked and its stoichiometry change as well; the new CSH gel retains the calcium, so that it is not present in the solution. Yet, in the case of acetic acid attack, the specimens remain intact until they have dried. This is only at this moment that the effects of the aggression appear. The specimens keep their dimensions and structural integrity. The solution becomes red as the supposed ferric acetate react, which means that the attack has only reached the step of dissolution of calcium hydroxide and aluminates (the CSH gel has not suffered changes). Due to the attack, the microstructure of both repair mortars has changed, leading to a worsening of their properties.

## GENERAL CONCLUSION

This Master's Thesis dealt with the durability of repair mortars submitted to acid attacks. The bibliographical study has highlighted the necessity to investigate on the behaviour of polymer-modified mortars when submitted to aggressive environment. In particular, the case of the effect of organic acid was not treated for polymer-modified materials. The state of the art has also highlighted the good properties of polymer-modified materials in terms of mechanical resistance and durability. In order to answer this necessity in investigation, this Master's Thesis has focuses on a polymer-modifies repair mortar (the Monotop 412 SFG), in comparison with another repair mortar (the Monotop 412 S, that does not contain polymers) and a conventional mortar (the CEM I 52.5 R). The experimental campaign has been divided into two distinct parts: the characterisation of the mortars and the resistance of those mortars to acid attacks.

Since the composition of both repair mortars was just estimated, a first step has consisted in characterising them in comparison with the conventional mortar. Different tests were carried out in order to characterise the mortars according to their mechanical properties, their microstructure and their durability capacities. On one hand, the mechanical tests highlighted that the mechanical properties of the Monotop 412 SFG did not present significant improvement in comparison with the reference mortar. These properties were comparable in both cases. On the other hand, this mortar presented lower porosity than the others, with smallest pores. Both Monotop 412 S and Monotop 412 SFG presented a bimodal distribution of pores (0.01-0.1 $\mu$ m and 0.1-1 $\mu$ m), with smaller pores that the reference mortar and a part of large pores. From a durability point of view, the Monotop 412 SFG presented better capacities than the others, with a much higher resistivity and a lower chloride migration coefficient. However, according to the results obtained for the capillary absorption test, no improvement was notices due to the presence of polymers. The presence of large pores in both repair mortars allows reaching capillary absorption coefficients that are similar to the one obtained with a conventional mortar. In general, the results obtained thanks to the characterisation tests allow thinking that the polymers have a positive influence on the properties of the mortar (above all in terms of durability), making it more difficult for aggressive agent to penetrate the material.

A second part has consisted in submersing the mortars into acid solutions: an acetic acid solution and a lactic acid solution. The mortars were submersed for one month. The results have shown that both repair mortars suffered changes in microstructure due to the acids. The results were worst in the case of lactic acid attack. Indeed, in the case of the acetic acid attack, the consequences of the acid have been visible after the drying of the specimens. All of the specimens have maintaining their dimension and structural integrity. The reaction of the ferric acetate has been observed as the solution has become red. In the case of lactic acid attack, the attack has been different as all of the specimens have suffered structural degradation. In the first weeks of submersion, the deterioration of the specimens has been observed. In this case, the CSH gel has been attacked and its stoichiometry has changed,

which can explain the structural degradation of the specimens. The specimens have increased their volume after the attack, probably due to the combination with water leading to the formation of insoluble compounds. Furthermore, in this case, the CSH gel that has changed its stoichiometry retains the calcium ions. Hence, these ions are not present in the solution as they are in the case of acetic acid attack. Finally, as well as for the acetic acid attack, the reaction of ferrous lactate has been observed as the solutions have become yellow. In general, the reference mortar has kept its properties in both cases (lactic and acid attack), while the two repair mortars have suffered a worsening of the microstructural properties.

This study has allowed confirming many of the assumptions made about the positive impact of the presence of polymer in the durability of the cementitious material. Nevertheless, some points need to be explored in future investigations. We may say that some of the future areas of investigation can be the following:

- Testing different polymer-modified mortar in order to determine the role of each compound and to confirm the burning of the polymer detected on the DTA results. These mortars can be made of different polymer types or their polymer contains can be different.
- Testing the resistance of mortars to acid attacks for different curing ages (90 days, 1 year, 3 year for instance) in order to determine the effect of curing age on the capacity of the mortars to resist aggressive attacks.
- Testing polymer-modified mortars that do not contains fibres in order to determine the contribution of the polymers and the contribution of the fibres.
- Realising a model of both attack modes in order to predict the durability of the repair mortars.

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## APPENDIX A – Principles defined in the EN 1504 Standard

Principle	Definition of the principle	Methods based on the principle
<b>Degradation of the concrete itself</b>		
Principle n°1 (PI)	<p>Protection against the ingress</p> <p>Reducing or preventing the ingress of aggressive agents (water, chemical agents, biological agents, vapours, gases, etc.)</p>	<p>1.1 Impregnation</p> <p>1.2 Surface coating with and without crack bridging capability</p> <p>1.3 Local bandaged cracks</p> <p>1.4 Crack filling compound</p> <p>1.5 Transferring cracks into joints</p> <p>1.6 Erecting external panels</p> <p>1.7 Use of membranes</p>
Principle n°2 (MC)	<p>Moisture control</p> <p>Adjusting and maintaining the moisture content in the concrete within a specified range of values</p>	<p>2.1 Hydrophobic impregnation</p> <p>2.2 Surface coating</p> <p>2.3 Sheltering or overcladding</p> <p>2.4 Electrochemical treatment</p>
Principle n°3 (CR)	<p>Concrete restoration</p> <p>Restoring the original concrete of an element of the structure to the originally specified shape and function;</p> <p>Restoring the concrete structure by replacing part of it</p>	<p>3.1 Applying mortar by hand</p> <p>3.2 Recasting with concrete</p> <p>3.3 Spaying concrete or mortar</p> <p>3.4 Replacing elements</p>
Principle n°4 (SS)	<p>Structural strengthening</p> <p>Increasing or restoring the structural load bearing of an element of the concrete structure</p>	<p>4.1 Adding or replacing embedded or external steel bars</p> <p>4.2 Installing bonded rebars in preformed or drilled holes in the concrete</p> <p>4.3 Plate bonding</p> <p>4.4 Adding mortar or concrete</p> <p>4.5 Injecting cracks, voids or interstices</p> <p>4.6 Filling cracks, voids or interstices</p> <p>4.7 Prestressing – post tensioning</p>
Principe n°5 (PR)	<p>Resistance to physical attack</p> <p>Increasing in the resistance to physical or mechanical attack</p>	<p>5.1 Overlays or coatings</p> <p>5.2 Impregnation</p>

Principle n°6 (RC)	Resistance to chemical products Increasing in the resistance of the concrete surface to the deteriorations by chemical attack	6.1 Overlays or coatings 6.1 Impregnation
<b>Corrosion of the reinforcement</b>		
Principle n°7 (RP)	Restoring or preserving of the passivity Creating chemical conditions in which the surface of the reinforcement is maintained in or is returned to a passive condition	7.1 Increasing cover to reinforcement with additional cementitious mortar or concrete 7.2 Replacing contaminated or carbonated concrete 7.3 Electrochemical realkalisation of carbonated concrete 7.4 Realkalisation of carbonated concrete by diffusion 7.5 Electrochemical chloride extraction
Principle n°8 (IR)	Increase in the resistivity Increasing the electrical resistivity of the concrete	Limiting moisture content by surface treatments, coatings or sheltering
Principle n°9 (CC)	Cathodic control Creating conditions in which potentially cathodic areas of reinforcement are unable to drive an anodic reaction	Limiting oxygen content (at the cathode) by saturation or surface coating
Principle n°10 (CP)	Cathodic protection	Applying electrical potential
Principle n°11 (CA)	Control of the anodic areas Creating conditions in which potentially anodic areas of reinforcement are unable to take part in the corrosion reaction	11.1 Painting reinforcement with a coatings containing active pigments 11.2 Painting reinforcement with barrier coatings 11.3 Applying inhibitors to the concrete

## APPENDIX B – Class of restoration mortars according to the performance characteristics

Test n°	Performance characteristics	Test method	Requirements			
			Non-structural		Structural	
			Class R1	Class R2	Class R3	Class R4
1	Compressive strength	EN 12190	≥ 10 MPa	≥ 15 MPa	≥ 25 MPa	≥ 45 MPa
2	Chloride ion content	EN 1015-17	≤ 0,05%	≤ 0,05%	≤ 0,05%	≤ 0,05%
3	Adherence bond	EN 1542	≥ 0,8 MPa	≥ 0,8 MPa	≥ 1,5 MPa	≥ 2,0 MPa
4	Contrasted expansion/shrinkage	EN 12617-4	No requirement	Bond strength after test ≥ 0,8 MPa	Bond strength after test ≥ 1,5 MPa	Bond strength after test ≥ 2,0 MPa
5	Durability – resistance to carbonation	EN 13295	No requirement		$d_k \leq$ control concrete	
6	Modulus of elasticity	EN 13412	No requirement		≥ 15 GPa	≥ 20 GPa
7	Thermal compatibility freezing/thawing	EN 13687-1	Visual inspection after 50 cycles	Bond strength after 50 cycles ≥ 0,8 MPa	Bond strength after 50 cycles ≥ 1,5 MPa	Bond strength after 50 cycles ≥ 2,0 MPa
8	Thermal compatibility storms	EN 13687-2	Visual inspection after 30 cycles	Bond strength after 30 cycles ≥ 0,8 MPa	Bond strength after 30 cycles ≥ 1,5 MPa	Bond strength after 30 cycles ≥ 2,0 MPa
9	Thermal compatibility dry cycles	EN 13687-4	Visual inspection after 30 cycles	Bond strength after 30 cycles ≥ 0,8 MPa	Bond strength after 30 cycles ≥ 1,5 MPa	Bond strength after 30 cycles ≥ 2,0 MPa
10	Slip resistance	EN 13036-4	Class I: > 40 units with damp test; Class II: > 40 units with dry test; Class III: > 55 units with damp test			


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Appendix B – Class of restoration mortars according to the performance characteristics

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11	Thermal expansion coefficient	EN 1770	Not required if tests 7, 8 or 9 are carried out, otherwise declared value	
12	Capillary absorption (permeability to water)	EN 13057	No requirement	$\leq 0,5 \text{ kg.m}^{-2}.\text{h}^{-0,5}$

## APPENDIX C – Extract from the product sheet of the Monotop 412 S

Construcción	<b>Hoja de Datos del Producto</b> Edición 21/07/2014 Identificación n.º 2.2.3 Versión n.º 2 Sika MonoTop®-412 S		2.2.3
	<b>Sika MonoTop®-412 S</b> Mortero de reparación estructural. Clase R4		
	<b>Descripción de Producto</b>	Sika MonoTop®-412 S es un mortero de reparación estructural de un componente, reforzado con fibras, de baja retracción que cumple con los requisitos de la clase R4 de la UNE-EN 1504-3.	
	<b>Usos</b>	<ul style="list-style-type: none"> <li>■ Adecuado para trabajos de reparación de hormigón (Principio 3, método 3.1 y 3.3 de la UNE-EN 1504-9). Reparación de desconchones y daños del hormigón en edificios, puentes, infraestructuras y superestructuras.</li> <li>■ Adecuado para trabajos de refuerzo estructural del hormigón (Principio 4, método 4.4 de la UNE-EN 1504-9). Incremento de la capacidad portante de las estructuras de hormigón mediante la adición de mortero.</li> <li>■ Adecuado para la conservación o restauración del pasivado (Principio 7, método 7.1 y 7.2 de la UNE-EN 1504-9). Incremento del recubrimiento con mortero adicional y sustitución del hormigón contaminado o carbonatado.</li> </ul>	
	<b>Características/Ventajas</b>	<ul style="list-style-type: none"> <li>■ Excelente trabajabilidad.</li> <li>■ Adecuado para aplicación a mano y por proyección.</li> <li>■ Se puede aplicar en espesores de capa de hasta 50 mm.</li> <li>■ Clase R4 según UNE-EN 1504-3.</li> <li>■ Para reparaciones estructurales.</li> <li>■ Resistente a sulfatos.</li> <li>■ Retracción muy baja.</li> <li>■ No requiere puente de unión, incluso cuando se aplique manualmente.</li> <li>■ Baja permeabilidad a cloruros.</li> <li>■ Clasificación al fuego A1.</li> </ul>	
	<b>Ensayos</b>		
	<b>Ensayos tipos iniciales</b>	Producto para la reparación de estructuras de hormigón según UNE-EN 1504-3: 2005, con declaración de prestaciones 01 03 02 04 001 0 000069 1053, con certificado de producción según el cuerpo notificador n° 0099-CPR-B15-0009, provisto del marcado CE.	
	<b>Datos del Producto</b>		
	<b>Forma</b>		
	<b>Apariencia/Color</b>	Polvo gris.	
<b>Envase</b>	Sacos de 25 kg.		
<b>Almacenamiento</b>			
<b>Condiciones de almacenamiento/Conservación</b>	12 meses desde su fecha de fabricación, en sus envases de origen bien cerrados y no deteriorados. En lugar seco y fresco, protegido de las heladas.		
<b>Datos Técnicos</b>			
<b>Base química</b>	Cemento sulforresistente, áridos seleccionados y aditivos.		
			

<b>Densidad</b>	Densidad del mortero fresco: – 2,05 kg/l.		
<b>Granulometría</b>	$D_{max}$ : 2.0 mm		
<b>Espesor de capa</b>	6 mm min / 50 mm max.		
<b>Retracción</b>	– 500 $\mu\text{m}/\text{m}$ a 20°C 65% H.R. a 28 días		(EN 12617-4)
<b>Coefficiente de dilatación térmica</b>	10,5 $\times 10^{-6}$ m/m°C		(EN 1770)
<b>Propiedades Mecánicas/Físicas</b>	a 20°C bajo condiciones del laboratorio		
<b>Resistencia a compresión</b>	(UNE-EN 12190)		
	1 día	– 16 N/mm <sup>2</sup> (MPa)	
	7 días	– 38 N/mm <sup>2</sup> (MPa)	
	28 días	– 54 N/mm <sup>2</sup> (MPa)	
<b>Resistencia a flexión</b>	(UNE-EN 12190)		
	1 día	– 4 N/mm <sup>2</sup> (MPa)	
	7 días	– 7 N/mm <sup>2</sup> (MPa)	
	28 días	– 9 N/mm <sup>2</sup> (MPa)	
<b>Requisitos</b>	Requisitos de acuerdo a la UNE-EN 1504-3 Clase R4 (Ensayado con una relación agua/polvo = 14,5%)		
	Método de Ensayo	Resultados	Requisitos (R4)
<b>Resistencia a compresión</b>	EN 12190	54,2 N/mm <sup>2</sup> (MPa)	$\geq 45$ N/mm <sup>2</sup> (MPa)
<b>Contenido de ión cloro</b>	EN 1015	< 0,03%	$\leq 0,05\%$
<b>Adherencia</b>	EN 1542	2,5 N/mm <sup>2</sup> (MPa)	$\geq 2,0$ N/mm <sup>2</sup> (MPa)
<b>Retracción restringida</b>	EN 12617-4	2,4 N/mm <sup>2</sup> (MPa)	$\geq 2,0$ N/mm <sup>2</sup> (MPa)
<b>Expansión restringida</b>	EN 12617-4	2,3 N/mm <sup>2</sup> (MPa)	$\geq 2,0$ N/mm <sup>2</sup> (MPa)
<b>Resistencia a carbonatación</b>	EN 13295	Pasa	$d_k \leq$ hormigón de control tipo MC(0,45) $d_k=4,9$ mm
<b>Módulo de elasticidad</b>	EN 13412	36,7 kN/mm <sup>2</sup> (GPa)	$\geq 20$ kN/mm <sup>2</sup> (GPa)
<b>Compatibilidad térmica Parte 2: lluvia tormentosa</b>	EN 13687-2	2,3 N/mm <sup>2</sup> (MPa)	$\geq 2,0$ N/mm <sup>2</sup> (MPa)
<b>Compatibilidad térmica Parte 4: ciclos térmicos en seco</b>	EN 13687-4	2,3 N/mm <sup>2</sup> (MPa)	$\geq 2,0$ N/mm <sup>2</sup> (MPa)
<b>Absorción capilar</b>	EN 13057	– 0,07 kg · m <sup>-2</sup> · h <sup>-0,5</sup>	$\leq 0,5$ kg · m <sup>-2</sup> · h <sup>-0,5</sup>
<b>Reaccion al fuego</b>	EN 13501-1	Euro clase A1	

## APPENDIX D – Extract from the product sheet of the Monotop 412 SFG

Construcción	<b>Hoja de Datos del Producto</b>		
	Edición 21/07/2014		
	Identificación n.º 2.2.2		
	Versión n.º 1		
	Sika MonoTop®-412 SFG		
	<b>Sika MonoTop®-412 SFG</b>		
	Mortero de reparación estructural con inhibidores de corrosión. Clase R4		
	2.2.2	<b>Descripción de Producto</b>	Sika MonoTop®-412 SFG es un mortero de reparación estructural de 1 componente con inhibidores de corrosión, polímero modificado, de baja retracción, reforzado con fibras que cumple con los requisitos de la clase R4 de la UNE-EN 1504-3.
	<b>Usos</b>	<ul style="list-style-type: none"> <li>■ Adecuado para trabajos de reparación de hormigón (Principio 3, método 3.1 y 3.3 de la UNE-EN 1504-9). Reparación de desconchones y daños del hormigón en edificios, puentes, infraestructuras y superestructuras.</li> <li>■ Adecuado para trabajos de refuerzo estructural del hormigón (Principio 4, método 4.4 de la UNE-EN 1504-9). Incremento de la capacidad portante de las estructuras de hormigón mediante la adición de mortero.</li> <li>■ Adecuado para la conservación o restauración del pasivado (Principio 7, método 7.1 y 7.2 de la UNE-EN 1504-9). Incremento del recubrimiento con mortero adicional y sustitución del hormigón contaminado o carbonatado.</li> </ul>	
	<b>Características/Ventajas</b>	<ul style="list-style-type: none"> <li>■ Mortero modificado con polímeros para aumentar la durabilidad.</li> <li>■ Excelente trabajabilidad y acabado superficial.</li> <li>■ Adecuado para aplicación a mano y por proyección.</li> <li>■ Se puede aplicar en espesores de capa de hasta 50 mm.</li> <li>■ Clase R4 de la UNE-EN 1504-3.</li> <li>■ Para reparaciones estructurales.</li> <li>■ Resistente a sulfatos.</li> <li>■ Muy baja retracción, reforzado con fibras, y por tanto con reducida tendencia a fisuración.</li> <li>■ No requiere puente de unión, incluso cuando se aplica manualmente.</li> <li>■ Contiene inhibidores de corrosión.</li> <li>■ Baja permeabilidad.</li> <li>■ Clasificación al fuego A1.</li> </ul>	
<b>Ensayos</b>			
<b>Certificados/Normativa</b>	Producto para la reparación de estructuras de hormigón según UNE-EN 1504-3:2005 con declaración de prestaciones 01 03 02 04 001 0 000070 1053, con certificado de producción según el cuerpo notificador nº 0099-CPR-B15-0009, provisto del marcado CE.		
<b>Datos del Producto</b>			
<b>Forma</b>			
<b>Apariencia/Color</b>	Polvo gris.		
<b>Envase</b>	Sacos de 25 kg.		
<b>Almacenamiento</b>			
<b>Condiciones de almacenamiento/Conservación</b>	12 meses desde su fecha de fabricación, en sus envases de origen bien cerrados y no deteriorados. En lugar seco y fresco, protegido de las heladas.		
			

<b>Datos Técnicos</b>			
<b>Base química</b>	Cemento sulforesistente modificado con polímeros, inhibidores de corrosión, áridos seleccionados y aditivos.		
<b>Densidad</b>	Densidad del mortero fresco: – 2,05 kg/l.		
<b>Granulometría</b>	D <sub>max</sub> : 2,0 mm.		
<b>Espesor de capa</b>	6 mm mín. / 50 mm máx.		
<b>Retracción</b>	– 500 m/m a 20°C 65% H.R. a 28 días		(EN 12617-4)
<b>Coefficiente de dilatación térmica</b>	10,5 × 10 <sup>-6</sup> m/m°C		(EN 1770)
<b>Propiedades Mecánicas/Físicas</b>	A 20°C bajo condiciones de laboratorio.		
<b>Resistencia a compresión</b>	(UNE-EN 12190)		
	1 día	– 13 N/mm <sup>2</sup> (MPa)	
	7 días	– 35,2 N/mm <sup>2</sup> (MPa)	
	28 días	– 55,3 N/mm <sup>2</sup> (MPa)	
<b>Resistencia flexión (UNE-EN 12190)</b>	(UNE-EN 12190)		
	1 día	– 2,7 N/mm <sup>2</sup> (MPa)	
	7 días	– 5,5 N/mm <sup>2</sup> (MPa)	
	28 días	– 7,2 N/mm <sup>2</sup> (MPa)	
<b>Requisitos</b>	Requisitos de acuerdo a la UNE-EN 1504-3 Clase R4 (Ensayado con una relación agua/polvo = 14%).		
<b>Resistencia a compresión</b>	Método de Ensayo	Resultados	Requisitos (R4)
	EN 12190	55,3 N/mm <sup>2</sup> (MPa)	≥ 45 N/mm <sup>2</sup> (MPa)
<b>Contenido de ión cloro</b>	EN 1015	< 0,03%	≤ 0,05%
<b>Adherencia</b>	EN 1542	2,6 N/mm <sup>2</sup> (MPa)	≥ 2,0 N/mm <sup>2</sup> (MPa)
<b>Retracción restringida</b>	EN 12617-4	2,5 N/mm <sup>2</sup> (MPa)	≥ 2,0 N/mm <sup>2</sup> (MPa)
<b>Expansión restringida</b>	EN 12617-4	2,4 N/mm <sup>2</sup> (MPa)	≥ 2,0 N/mm <sup>2</sup> (MPa)
<b>Resistencia a carbonatación</b>	EN 13295	Pasa	d <sub>s</sub> ≤ hormigón de control tipo MC(0,45) d <sub>s</sub> = 4,9 mm
<b>Módulo de elasticidad</b>	EN 13412	– 32,3 kN/mm <sup>2</sup> (GPa)	≥ 20 kN/mm <sup>2</sup> (GPa)
<b>Compatibilidad térmica Parte 2: lluvia tormentosa</b>	EN 13687-2	2,4 N/mm <sup>2</sup> (MPa)	≥ 2,0 N/mm <sup>2</sup> (MPa)
<b>Compatibilidad térmica Parte 4: ciclos térmicos en seco</b>	EN 13687-4	2,4 N/mm <sup>2</sup> (MPa)	≥ 2,0 N/mm <sup>2</sup> (MPa)
<b>Absorción capilar</b>	EN 13057	– 0,04 kg · m <sup>-2</sup> · h <sup>-0,5</sup>	≤ 0,5 kg · m <sup>-2</sup> · h <sup>-0,5</sup>
<b>Reaccion al fuego</b>	EN 13501-1	Euro clase A1	
<b>Información del Sistema</b>			
<b>Estructura del sistema</b>	Sika MonoTop®-412 SFG es parte de la gama de morteros de Sika® que cumplen con la Norma Europea EN 1504, compuesta por: Puente de adherencia / protección contra la corrosión:		
	– Sika MonoTop®-910 S	Uso normal	
	– SikaTop® Armatec®-110 EpoCem®	Requisitos demandados	