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L'influence de la pouzzolane naturelle dans la durabilité des bétons locaux – Revue de la littérature-

Soutenu, le 28/6 /2020, devant le jury composé de :

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الجمهورية الجزائرية الديمقراطية الشعبية

PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA

وزارة التعليم العالي والبحث العلمي

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Dr. Moulay El-Taher University of saida

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Wassim Kalloub

THE INFLUENCE OF NATURAL POZZOLAN ON THE DURABILITY OF LOCAL CONCRETE

Defended on 28/6/2020 , before the jury composed by:

Dr. Belouadi L.	MCA	President
Dr. Touil M.	MCB	Supervisor
Dr. Derfouf M.	MCA	Examiner

Thanks and appreciations:

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Finally, we would like to express our deep gratitude to our parents who have always supported us and to all who participated in the production of this dissertation. As well as all of the teachers who contributed to our training.

Greetings:

I dedicate this humble work as proof of respect and gratitude:

To my dearest mom, ask God to protect her for me, I can't thank her enough For what she does for me

To my dear father, I would like to share this success with him, ask God to protect and keep him. Thanks to his encouragement to give and his great sacrifices, It impossible to express my respect, my deep feelings and my feelings towards him. I ask God to bless him, hoping to be always proud of me.

To my dear uncle, Dr. Haroun, ask God to protect him for the support he provided me.

- To my dear brothers, ask god protect them and keep them for me

- To my sisters and all my little and big family.

- To all my teachers, their generosity and support oblige me to show them my deep respect and loyal consideration.

- To all my friends and colleagues, they will find here the testimony of an infinite fidelity and friendship.

Ahmed Sabra

Greetings

I dedicate this humble work as proof of respect and gratitude:

To my dearest mom,

To my dear father,

I would like to share this success with him, ask God to protect and keep him.

- To my dear brother ask god protect him

- To my sisters and all my little and big family.

- To all my teachers,

- To all my friends.

Wassim Kalloub

Abstract

This work is talking about the natural pozzolan as basic components in building materials. It aims to shed light on the benefit from these materials in terms of improving the properties of concrete, it is useful in economic savings, and it is environmentally friendly. In this work, it was clarified, the definition of cement, its components, properties and reactions, and the materials that are added to the cement to become processed cement. And we clarified the results of treating concrete with additions especially natural pozzolan based on studies conducted in several countries, where each study was aimed at clarifying the change of concrete properties in several aspects such as: fresh properties, mechanical resistance, durability and others.

الملخص

هذا العمل يتحدث عن البوزولان الطبيعية كمكون أساسى في مواد البناء. فإنه يهدف إلى تسليط الضوء على الإستفاده من هذه المواد من حيث تحسين خصائص الخرسانة ، إنها مفيدة في التوفير الاقتصادي ، وهي صديقة للبيئة .

في هذا العمل تم توضيح ، تعريف الاسمنت ومكوناته وخصائصه و تفاعلاته ، والمواد التي تضاف للإسمنت ليصبح إسمنت معالج . ووضحنا نتائج معالجة الخرسانة بالإضافات و خاصة بالبوزولان الطبيعي استنادا على دراسات أجريت في عدة دول ، حيث كل دراسة كان تهدف إلى توضيح تغيير خصائص الخرسانة في عدة جوانب مثل : الخرسانة الطازجة المقاومة الميكانيكية المتانة وغيرها .

Résumé

Ce travail parle de la pouzzolane naturelle en tant que composants de base des matériaux de construction. Il vise à faire la lumière sur les avantages de ces matériaux en termes d'amélioration des propriétés du béton, il est utile dans les économies économiques, et il est respectueux de l'environnement. Dans ce travail, il a été clarifié, la définition du ciment, ses composants, ses propriétés et réactions, et les matériaux qui sont ajoutés au ciment pour devenir du ciment traité. Et nous avons clarifié les résultats du traitement du béton avec des ajouts en particulier la pouzzolane naturelle sur la base d'études menées dans plusieurs pays, où chaque étude visait à clarifier le changement des propriétés du béton sous plusieurs aspects tels que: propriétés fraîches, résistance mécanique, durabilité et autres.

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INTRODUCTION

INTRODUCTION

Constantly developed since the end of the 19th century, reinforced concrete is today the most widespread building material in the world. The buildings of the Greeks and Romans were made with materials whose primary components were: a mixture of sand, stones, crushed clay bricks and calcined lime. Thus, man has come to design the concrete of today which is made from an intimate mixture of cement, aggregates (fine and ultrafine), additives and water.

These constituents are dosed, according to their own properties, whose important reaction is based on the microstructure of the cement paste by the formation of calcium silicates (CSH), calcium hydroxide or portlandien (CH) and calcium sulfoaluminates (AFt and AFm) in order to obtain a solid product called concrete and whose physical and mechanical characteristics can be much higher than those of the most resistant rocks. Today, more than 6 billion cubic meters of concrete are poured worldwide each year. This material makes it possible to build works of all kinds. Thus, the issue of sustainable development in terms of design, formulation and implementation of concrete has become in a few years a major challenge for the scientific world and the construction industry. The emergence at national and international level of the environmental challenges of sustainable development has notably highlighted the significant quantities of CO_2 emissions generated by the manufacture of Portland cement. These greenhouse gas emissions are linked, on the one hand, to energy consumption during the cooking and grinding of clinker and, on the other hand, to the decarbonation of limestone.

The cement industry would thus today be responsible for around 7% of CO_2 emissions linked to human activities. This relatively large contribution and the strong global growth in cement production have led several research teams to look into alternative binders with a lower CO_2 footprint.The principle of manufacturing such binders consists in particular in reducing the share of clinker by replacing it with mineral additions.

These latter, natural products (pozzolana, filler, etc.) or industrial co-products (blast furnace slag and fly ash), are added to the clinker during the grinding phase or directly in the concrete mixer as a substitution for part of the cement .

The industrial development of these modern concretes, with reduced environmental impact, requires a significant research effort in order to better understand their long-term behavior, and particularly in the presence of aggressive environmental agents.

In Algeria importance is given to mechanical strength while neglecting the durability of concrete which is an essential criterion for the structures.

As part of our work, we are mainly interested in the valuation of cement additions such as natural pozzolan, which is currently one of the most recent developments in the production of cement, because its use brings an improvement on the mechanical properties of materials. cementitious

(mortar and concrete). In general, its use reduces the consumption of clinker, contributing in a simple and economical way to solve environmental problems such as CO_2 reduction, control of the environmental impact and the recovery of pozzolan. which is in large quantity in Algeria. This on the one hand and on the other hand to improve certain performances of our concretes in terms of durability.

This dissertation is structured in four chapters:.

The first chapter is devoted to bibliographic research on cement, we will opt for research on cement in general: in the anhydrous state (chemical component, manufacturing, etc.), in the hydrated state by developing the microstructure of cementitious paste, in particular concrete, we approach the formation of hydrates, the description of the porous network and these characteristics, and the influence of additions on the microstructure of concrete. We also define its environmental impact and the solutions to remedy it.

The second chapter is dedicated to a bibliographic research on cementitious additions and their importance for improving the performance of cementitious materials.

The third chapter relates specifically to the analysis of the influence of natural Pozzolan and its various effects on the performance of concrete, while citing the various physico-mechanical and durability works accomplished in this field.

Finally, a general conclusion takes up the main analyzes identified during this study and reports on the practical interests that flow from them.

Chapter 1. State of the art –Cementitious material

Chapter 1. State of the art - Cementitious material

I.1:Description of cement

Cements usually are also called hydraulic binders because they have the property of hydrating in the presence of water and because this hydration transforms the binding paste, which has a more or less fluid starting consistency, into a solid practically insoluble in water. In common parlance, the term cement can be a source of confusion when used to denote both: - cement powder (for example as sold in bags); - cement paste when it is mixed with water; - the product obtained after hardening. In all that follows, we will distinguish these different states by calling:

- Anhydrous cement, the cement powder before it is mixed with water; hydrated cement, the compounds, insoluble in water, obtained by chemical combination of water with the grain of anhydrous cement;
- Fresh cement paste, the mixture of water and anhydrous cement before hydration has resulted in making a solid called hardened cement paste; the expression "hardening cement paste" will be used to designate the cement paste in its transformation from a more or less fluid state to a solid state (https://www.britannica.com)

I.2:Anhydrous cement

I.2.1:Raw materials

Usual cements are made from a mixture of approximately 80% limestone ($CaCO_3$) and 20% clay ($SiO_2 – Al_2O_3$). Depending on the origin of the raw materials, this mixture can be corrected by iron oxide or other materials providing the required alumina and silica supplement, the raw materials used to make cement are composed mainly of lime (CaO) of silica (SiO_2), alumina (AL_2O_3) and iron oxide (Fe_2O_3), lime is generally provided by carbonate rocks which represent 80% of the raw food (Table I.1). Alumina, silica and iron oxide are provided by formants approximately 20% of the raw food. (Belkacem, 2019).

Table I.1:Raw materials composition. (Belkacem,2019)

Raw material	*Formula Chemical*	*Abbreviation*	*Proportion*	*Source of raw material*
Lime	CaO	*C*	*77 at 80%*	*Clay, limestones,*
Silica	SiO_2	*S*	*10 at 15%*	*Clay, limestones, basalt, silicate Calcium, sand*
Alumina	Al_2O_3	*A*	*5 at10%*	*Clay, aluminum ore*
Iron oxide	Fe_2O_3	*F*	*2 at 3%*	*Clay, iron ore*

I.2.2:Cement manufacturing process:

Cement manufacturing is a complex process that requires know-how, mastery of tools and production techniques, rigorous and continuous quality controls. This process includes the following manufacturing steps:

The cement manufacturing process consists of grinding a mixture of raw materials (limestone + clay) and then bake them in a large rotary oven at a temperature of around 1450 °C

From the quarry to the cement storage silos, the material goes through five main stages:

1- Extraction of raw materials.

2- Storage and crushing of raw materials.

3- Cooking to obtain the clinker.

4- Crushing of the clinker and additives to obtain the cement.

5- Packaging and shipping.

i) Raw material extraction and preparation:

Raw materials are extracted from the rock walls of an open pit by blasting, shovelling or bulldozing. The rock is recovery by dumpers to a crushing plant. To produce quality cements raw materials must be very carefully sampled, dosed and mixed so as to obtain a perfectly regular composition over time .

ii) Drying and grinding:

The raw materials are then dried and crushed very finely. We get the flour. This one will later be introduced into the oven in powder form or previously transformed into granules.

The mixture of limestone, sand clay and iron ore is dosed to feed the two raw mills, the product resulting from grinding is called raw flour, it is stored in two homogenization silos of 8000 tonnes each. (Adam , 2000)

iii) Flour cooking and clinker storage:

Whatever the technique developed for the preparation of the vintage, the cooking facilities are similar and it exists as following:

1-The preheating zone

2- The cooking zone

3- Decarbonation

4- The clinkerization zone

5- The cooling zone

Before introduction into the oven, the flour is heated to about 800 °C in a preheater cyclones.

The physico-chemical phenomena during cooking are as follows:

1- At 100 °C: evaporation of mechanical water or free water.

2- Between 450 and 550 °C: Evaporation of water of constitution (chemical) or crystalline.

3- From 650 °C: Formation of calcium aluminates and ferrites.

$$\boldsymbol{3CaO+Al_2O_3 \rightarrow 3CaO.Al_2O_3\ (C3A: Celite)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\boldsymbol{I-1})$$

$$\boldsymbol{2CaO + CaO.Fe_2O_3 + CaO.Al_2O_3 \rightarrow 4CaO\ Al_2O_3\ Fe_2O_3\ (C4AF: F\acute{e}lite)} \ldots\ldots\ldots\ldots\ldots (\boldsymbol{I-2})$$

4- From 700 °C: Decomposition of limestone

$$\boldsymbol{CaCO_3 \rightarrow CaO + CO_2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\boldsymbol{I-3})$$

5-Around 800 °C: Formation of bicalcium silicate(2CaO, SiO_2)

$$\boldsymbol{CaO + SiO_2 \rightarrow 2CaO.SiO_2\ (C2S: belite)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\boldsymbol{I-4})$$

From 1250 ° C: the tricalcium silicate called "Alite" begins to appear from lime and Belite.

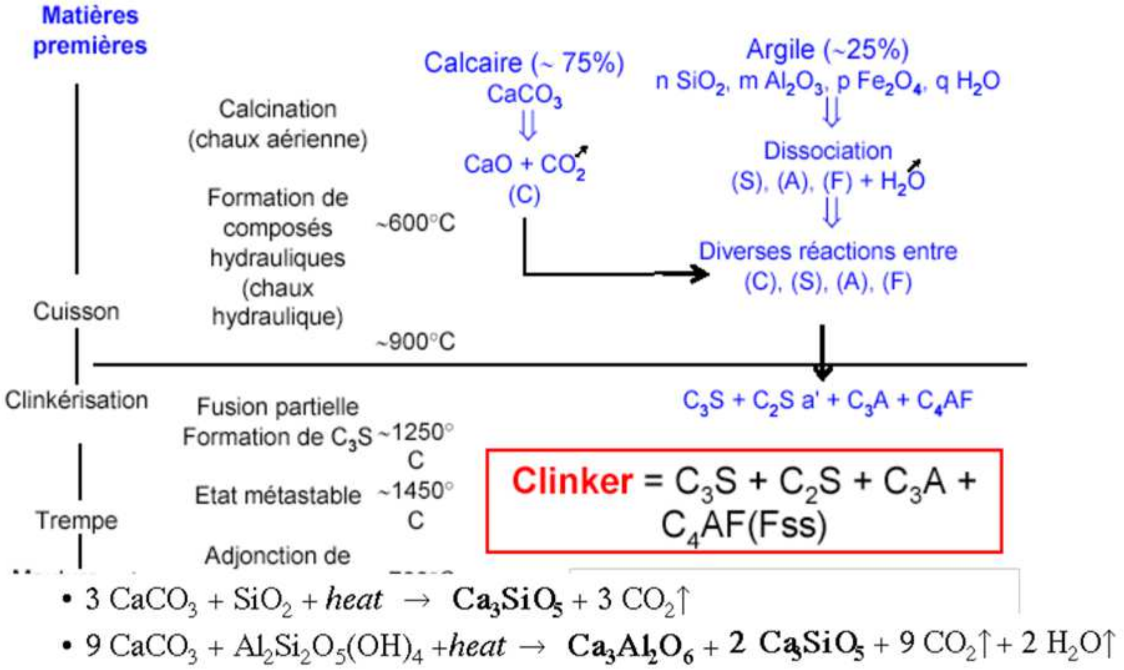
$$2CaO + 2CaO\ SiO_2 \rightarrow 3CaO\ SiO_2\ (C3S: Alite)\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (I - \text{Err�ur ! Sign�t non défini.})$$

Between 1260 and 1450 °C: appearance of the first liquid.

T = 1450 °C: Clinkering

(Belkacem ,2019).

This process is summarized in fig. below :



- $3\ CaCO_3 + SiO_2 + heat \rightarrow \mathbf{Ca_3SiO_5} + 3\ CO_2\uparrow$
- $9\ CaCO_3 + Al_2Si_2O_5(OH)_4 + heat \rightarrow \mathbf{Ca_3Al_2O_6} + \mathbf{2\ Ca_3SiO_5} + 9\ CO_2\uparrow + 2\ H_2O\uparrow$

Figure I.1:Process of cement manufacturing and chemical reaction.

I.2.3: Chemical composition

In an anhydrous state Portland cement is essentially composed of clinker, its chemical composition consists of two large families of oxides, the first of the calcination of the clay and giving an acid character to the cement such as SiO_2, Fe_2O_3 , Al_2O_3, etc. The second results from limestone in the form of CaO, having a basic chemical character. In simplified form, the main chemical constituents resulting, as well as their cementitious notation, are illustrated in Table I-2.

The cements commonly used in civil engineering contain the majority of Portland clinker, at the origin of the binding properties of cement or of the composite binder. This clinker consists of a mass proportion at least equal to 2/3 (standard NF EN 197-1) of calcium silicates (C_3S and C_2S), the remaining part containing C_3A and C_4AF. Portland cement is ground to typically produce a specific surface of approximately 350 m^2/kg (Baron and Sauterey,1995) .

Table I.2:Main anhydrous phases of a Portland cement and their properties in a cement paste. (Touil ,2017)

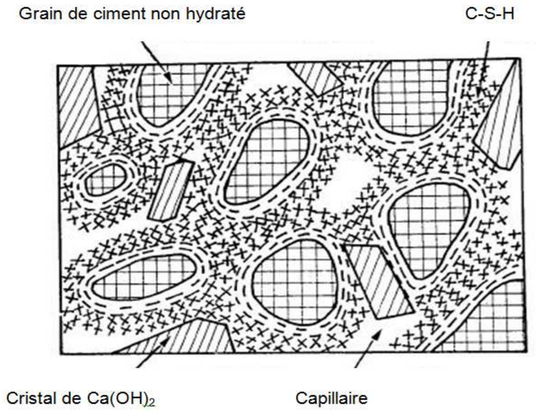
Compound	Chemical composition	Cement rating	% by mass of cement	Reactivity	Contribution resistance
tricalcium silicate a lite	3CaO.SiO2	C3S	40-80	high	High or young age
bicalcium silicate belite	2CaO.SiO2	C2S	0-30	lent	Raised in the long term
tricaleium aluminate	3CAO.Al2O3	C3A	3_15	high	Raised at a very young age
tetracalc aluminoferrite	4CAO.Al2O3.Fe O3	C4AF	4_15	Lent	Very weak

I.3:Microstructural evolution of cement from the early age to maturity

I.3.1:Hydration of cement and its microstructure

Hydrated cement paste is the result of the chemical reaction between water and cement (the hydration reaction). In fact, several mechanisms are at the origin of the hydration reaction: adsorption, hydrolysis, dissolution, salvation, crystallization.

This chemical reaction process is very complex where the main cement compounds C_3S, C_2S, C_3A, C_4AF in the presence of gypsum (as setting regulator) react to form new insoluble compounds leading to the formation of hardened cement paste, medium porous compound of hydrated solid phases and an interstitial porous solution. The hydration of the various phases of the cement takes place simultaneously at different kinetics. These reactions are exothermic. At the end of hydration, the main components formed are shown in Figure I-2 and will be briefly detailed later. (Touil ,2017)



FigureI.2:Schematic representation of the hydrated cement paste (Touil ,2017)

The main Portland cement compounds, alite (C_3S) and belite (C_2S), react with water to form hydrated calcium silicates (C-S-H) and calcium hydroxide (CH). The C_3S reaction is given as follows (Equation l-6):

$$C_3S + (3-x+y)\,H \rightarrow CxSHy + (3-x)CH \qquad (I-6)$$

where x is the C / S ratio, y is the H/S ratio. According to the literature, the C/S ratio varies from 0.8 to 2 (Neville, 2002) (Zhang, 2007). This variation is mainly due to the hydration conditions (excess of water, temperature, etc.) and to the various ions formed such as the alkalis, the aluminas and the sulfates incorporated in the C-S-H (Ballonis and al, 2009).

Hydrated calcium silicates (C-S-H)

Hydrate Calcium Silicates (CSH) very important hydrate constituting 50 to 70% of the paste present in the form of an amorphous gel with the property of being welded to the surrounding materials by bridges of calcium or hydrogen ions and thus achieving a real sticks in the matrix. This cohesion of C-S-H is due, in part, to the Van der Walls forces between the colloidal particles of C-S-H. it is a gel which largely influences most of the properties of the dough, in particular mechanical and durability.

The gel of C-S-H is porous, the gel pores, are in fact the spaces which contain water adsorbed on the surfaces between the sheets. They are very small in size (20 Å to 30 Å) (Figure I-3). The specific surface of C-S-H is very high and can be evaluated from 100 to 700 m^2 / g. (Neville, 2000).

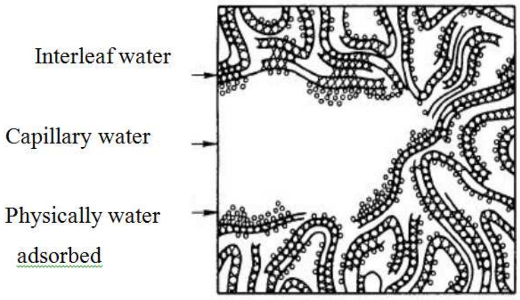


Figure I.3:Schematic representation of C-S-H and the state of the water associated with it (Metha,1986).

- The water in the gel pores is not "free" because it is strongly retained on the sheets by surface forces. Since the gel pores are extremely fine, they contribute very little to the permeability of the paste and the concrete.

At equilibrium, the pH of the solution containing C-S-H is very alkaline and is close to 12.5. At lower pHs, there may be leaching of Ca^{2+} ions. The C-S-H then undergo transformations which can increase their porosity and decrease the mechanical properties (Brahim,2017).

Calcium hydroxide or portlandite (CH)

Calcium hydroxide (Ca $(OH)_2$) or portlandite derived from silicates (see eq. I-6), and reacting with alkaline sulfates has a crystal structure constituting 25 to 27% of the cement matrix, giving it 90% of its alkalinity.

However, this phase is the most soluble phase among all hydrates. Its solubility in water is around 1.4 g/L. Its dissolution balance is responsible for maintaining the high pH in the interstitial solution. the high pH is due to the presence of OH- ions from alkaline bases and lime, the solubility of which depends precisely on the concentration of OH- ions. During the structuring of the paste, the interstitial solution is gradually enriched with alkaline bases NaOH and especially KOH, while the lime concentration decreases and becomes negligible in the long term: this explains why the pH remains above 13 while a saturated lime solution has only a pH of 12.5 (Taylor, 1997). In the presence of alkalis (Na +, K +), these elements fix the pH of the interstitial solution between 13.5 and 14. The portlandite then fixes only the total concentration of calcium (21 mmol/kg) in solution. Equilibrium of portlandite indicate that the concentration decreases significantly with increasing pH (Neville, 2000).

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^- \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (I-7)$$

Thanks to the presence of lime which will be partly in equilibrium of precipitation precipitation in the porous network filled with excess mixing water that it will be possible to drown the steel reinforcements in the interstitial solution of the concrete which will passivate steels and inhibit their corrosion. Portlandite Ca $(OH)_2$ is a mineral stable in basic medium and plays an essential role for the durability of concrete but contributes little to the development of its mechanical resistance. Finally, note that the amounts of CSH and Ca $(OH)_2$ depend on many factors, essentially the W/C ratio and the degree of maturation (Hansen, 1986).

Calcium sulfoaluminates (AFt and AFm)

The alumina phases mainly occur in C_3A and C_4AF. C_3A plays an important role in the rapid hydration of cement pastes. C_4AF reacts much more slowly. The alumina present in hydration products is in two forms calcium sulfo-aluminates (or Ettringite) and also monosulfates (AFt and AFm); they represent 5 to 15% of a hydrated paste. The consumption of sulfates during the formation of AFt and AFm implies that the alkalis are present in the form of caustic soda or potassium soluble in the interstitial solution.

Ettringite is a stable mineral in the system, however monosulfoaluminate even under normal conditions is not a stable form and participates little in the development of resistance. Furthermore, the coexistence of these two minerals controls the content of aluminate and sulfate in solution at low contents (Balonis and al, 2009).

Paste-aggregates interface (Transitionnal Zone Interface: ITZ)

In a concrete, the bond that is established during hydration between the cement paste and the materials it coats, results in a particular paste area called "transition halo" or paste-aggregate interface(). Its thickness increases with the size of the aggregate but is always less than 50 micrometers. In this area, the cement paste has a weaker cohesion, due to a local excess of water, characterized by a high W/C ratio, because at the time of mixing, a liquid film is adsorbed on the surface of the aggregate, which makes its porosity higher than that of the dough. Both from the mechanical point of view and from the point of view of durability or permeability, these zones constitute the “weak links” of the material (Buil,1993). The pores, coarser than this area compared to the rest of the dough, become a preferred path for mass transport.

I.3.2: Structure and porosity of concrete

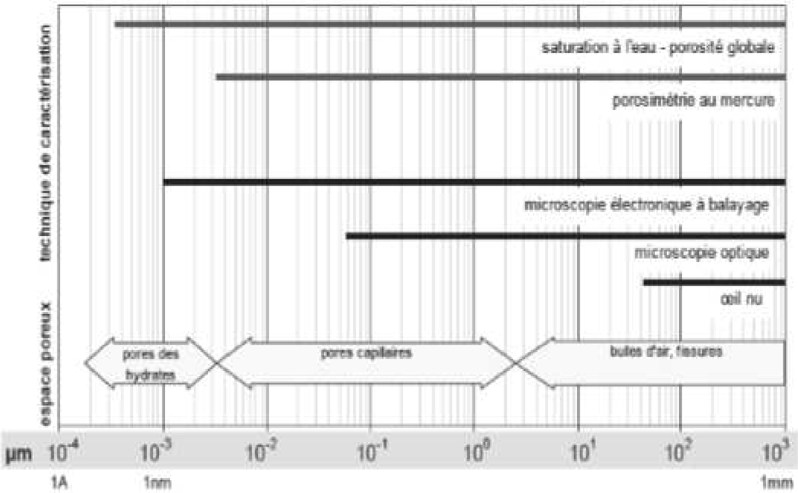
During the cement hydration process, the different hydrates form and develop in the spaces between the initial anhydrous cement grains. This mode of filling the original voids creates a very complex porous network (Baroghel,1994). The porous network of a cementitious material covers a wide range of scales (from the picometer to the centimeter).

Pores are commonly listed in two categories:

- “Capillary” pores, vestiges of the intergranular spaces of fresh dough. They are directly linked to the W/C ratio and are detectable by mercury prosimetry, they have a pore size between 0.1 and 10 µm. This porosity occupies up to 30% of the volume of a cement paste for the case of an W/C ratio = 0.65 (Verbeck,2005).
- However, it is preferable that the capillary pore network is made up of the smallest possible pores because the degree of interconnection is lower (Quenard,1999).
- Consequently, the permeability through the material is then considerably reduced because there are fewer preferential paths for the passage of liquids, gases or potentially aggressive ions.

- The pores relating to hydrates, inter and intra-crystallites (or inter-sheet spaces) and in particular C-S-H (Baroghel,1994).
- They are inherent in the formation of hydrates and independent of the W/C ratio, and are significantly smaller than the previous 0.1 to 10 nm (porosimeter test). On this scale, the surface effects such as capillary pressure or absorption in the pores are preponderant in front of transport phenomena such as diffusive transport. Powers evaluated the porosity included in the C - S - H gel at 28% (Powers,1960).

To these two families of pore size, the voids due to air bubbles, and the cracks (diameter greater than 1 µm) must be added. Figure I.4 illustrates the different types of voids in concrete and the fields of use of the main methods for characterizing porous media (Baroghel and al ,1994).



FigureI.4:Porosity at different scales in concrete and main techniques for investigating porous media (BAR,94).

The porous structure of hydrated cement paste and hardened concrete can be characterized with different parameters such as porosity, pore size distribution, connectivity or pore tortuosity. These parameters influence both the mechanical properties and the durability of the concrete through the transfer properties (Brahim,2017)

I.4:Cement additions

Cement additions are increasingly used to replace Portland cement. In fact, during the production of the latter, large quantities of CO_2 are released (1 kg of CO_2 emitted per kg of clinker produced) (Gartner, 2010).

In fact, the additions from mineral additions and industrial co-products make it possible to considerably reduce the ecological impact and to enhance the latter on the one hand. On the other hand, the additions can bring beneficial modifications to the properties of the material in terms of resistance and durability in a healthy or aggressive environment. These cement additions which, like Portland cement, have binding properties. They are called pozzolans and react with calcium hydroxide (Ca $(OH)_2$) released by calcium silicates to form new C-S-H. This reaction is called pozzolanic reaction and is schematized as follows:

$$\boldsymbol{Pozzolan + Ca\ (OH)2 \rightarrow C - S - H} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \boldsymbol{(I-8)}$$

Several researchers have concluded that the pozzolanic reaction brings certain modifications in the chemical environment of concrete and causes a very significant change in the physical structure of hardened cement paste.

At the substitution levels normally used, the major changes relate to the reduction in the Ca/Si ratio (approximately 1.2 or less) in the C-S-H phase and the consumption of portlandite (Kocaba, 2007).

in general, the chemistry of cement additions is characterized (with the notable exception of fine limestone) by a calcium content lower than that of a Portland cement (Fig. I.5).

However, the strong presence of silica in these types of cement additions influences the quantity and type of hydrates formed. On the other hand, additions rich in alumina increase the absorption of alumina in C-S-H and the amounts of aluminate containing the hydrates. This microstructuring is significantly different from that formed in the paste of a Portland cement and therefore the volume, the porosity and finally the durability of these materials (Lothenbach and al, 2011).

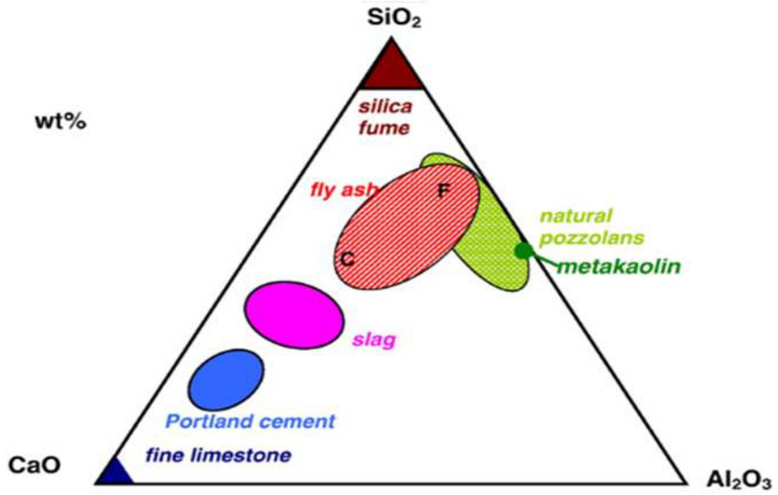


Figure I.5 : diagram of the main phases of cement and these additions

It is also noted that increasing the volume of CSH can lead to a reduction in the volume of hair pores while the volume of gel pores can increase. In addition to the refining of the pore size, the decrease in the volume initially occupied by the CH consumed and filled by the CSH can lead to an improvement in the mechanical properties (Hooton, 1986) (Mehta and al 2006) (Stefanovic and al , 2007).

and improved resistance to sulphate attack and penetration of chlorides in hardened pasta (Hooton, 1986) (Mehta, 1981).

The large amount of portlandite in cement pastes is reported to cause concrete instability when exposed to aggressive media and at high temperatures. Studies of the penetration of chlorides and the development of the microstructure by additions have shown a reduction in the size of the critical pores (Diamond, 1999) (Zhang,1998).

However, the filling effect of the cement additions can also be contributing to the young age where no reaction of the (inert) additions occurs. This very significant factor in the hydration changes has been studied by showing that the hydration kinetics are dominated by the filling effect or the particles of additions first fill the voids between the grains of cement resulting from the immobilization of water then acting as nucleation sites by promoting the increase in CSH which can reduce the pores of cement paste (Gutteridge and al,1990) (Gutteridge and al, 1976).

Furthermore, it has been indicated for pastes with a high percentage of replacement of the cement which generates a high porosity for the hydrated paste at an early age with often a reduction in the rate of heat of hydration (Mehta, 1986)(Taylor, 1997).

Finally, among pozzolanic materials, widely accepted as valid ingredients for sustainable concrete, have been the subject of a classification extended to inorganic, natural (pozzolan, metakaolin, ..) or artificial (fumée de silica, fly ash, blast furnace slag, etc.) (Lea,2004).

I.5 : Environmental Effects of Cement Manufacturing:

The cement industry alone is responsible for about a quarter of all industry CO_2 emissions, and it also generates the most CO_2 emissions per dollar of revenue (fig. I.6). About two-thirds of those total emissions result from calcination, the chemical reaction that occurs when raw materials such as limestone are exposed to high temperatures. (Touil ,2017)

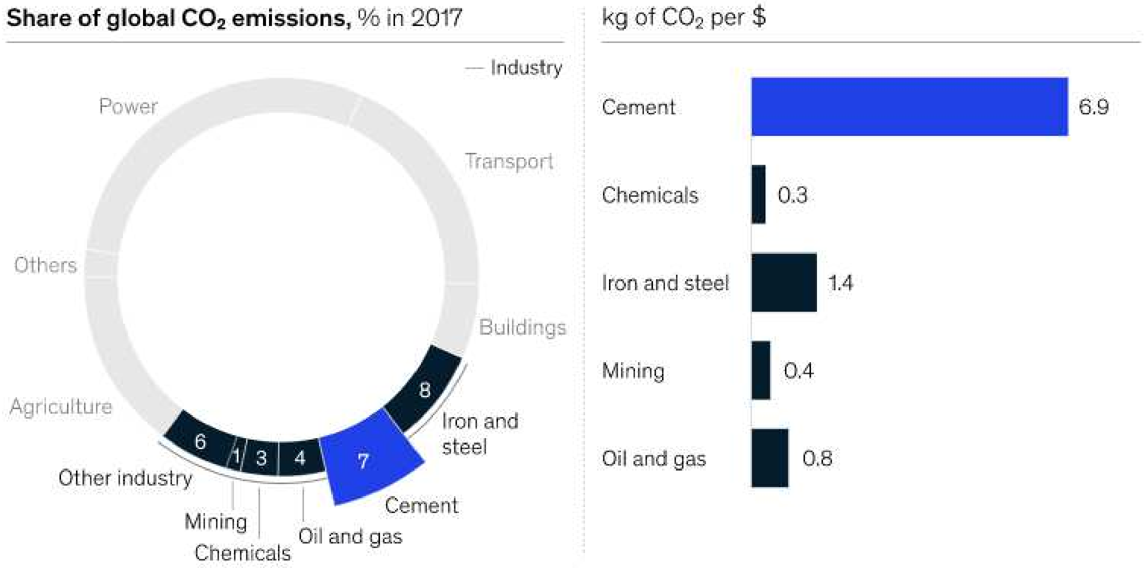


Figure I.5 : cement production is major source of global CO2 emissions. (Touil ,2017)

Measured data of the European cement kiln emissions show that cement industry contributes substantially to environmental pollution.

In addition to material pollutants, noise emission is also associated with almost all the processes involved in cement manufacturing. these environmental impacts contribute to abiotic depletion, global warming, acidification, and marine ecotoxicity (C. Chen and al, 2010).

Cement is produced by utilizing an extensive amount of raw materials treated and reacted at extreme conditions such as high temperatures. the high-temperature processes are called pyroprocessing processes where raw materials are heated at high temperatures for solid-state reactions to take place, which utilize fuel sources such as coal, fuel oil, natural gas, tires, hazardous wastes, petroleum coke, and basically anything combustible (Branquinho and al, 2008).

Some cement manufacturing plants utilize the organic waste generated in other industries such as rubber processing industries. As such, cement industry contributes to a significant extent of anthropogenic carbon dioxide emissions, which is in the range of 5–7% of total anthropogenic carbon dioxide emissions (Lei and al, 2011).

In the clinker burning process, in order to produce 1 tonne of clinkers, 1.52 tonnes of raw materials are used on average. 0e balance of 0.52 tonne of raw materials is converted mainly to carbon dioxide by the processes such as

$$\boldsymbol{CaCO_3 \rightarrow CaO + CO_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\boldsymbol{I-9})$$

This is a serious global environmental problem since increase in carbon dioxide in the atmosphere has direct consequences on global warming. In addition to CO2, other key polluting substances emitted to air by the cement industry include dust, other carbon oxides such as carbon monoxide (CO), nitrogen oxides (NOxs), sulphur oxides (SOxs), polychlorinated dibenzo-p-dioxins, dibenzofurans, total organic carbon, metals, hydrogen chloride, and hydrogen fluoride, which are serious health-hazardous substances and some are hilariously odorous. (Schuhmacher and al,2004).

However, the type and amount of air pollution caused by the cement industry depend on various parameters, such as inputs (the raw materials and fuels used) and the type of process used in the industry. As for water pollution, the contribution from cement industry may be insignificant through the storage and handling of fuels that may contribute to soil and groundwater contaminations. (Al-Khashman and al, 2006).

I.6 Conclusion

In order to reduce the amount of raw materials, particularly in the manufacturing of specialized cement types as described above, supplementary cementitious materials such as coal fly ash, slag, and natural pozzolans such as rice husk ash and volcanic ashes are used. This will not only reduce the waste materials generated for landfilling but also the cost of cement production. However, cement is an essential material for human survival nowadays. As such, there is no alternative, but the production of cement is mandatory. At the same time, controlling pollution created

by cement industry is also very important. In the next section, we discuss ways to reduce quantities of cement by means additions cement.

Chapter 2. Additions effects and interaction with cement

Chapter 2. Additions effects and interaction with cement

II.1: Introduction

The improvement of certain properties of cementitious materials calls for materials of a mineralogical nature called "mineral additions". As a mass replacement of cement, the mineral additions are incorporated directly into the cement mixtures; paste, mortar and concrete.

This substitution can be advantageous, not only from the economic point of view, but also from the rheological point of view and sometimes from the mechanical and durability point of view.

A mineral addition is defined by European standard EN 206-1 as being:

"A finely divided mineral material used in concrete to improve certain properties or to give it specific properties. "

Among the mineral additions used in cement matrices, there may be mentioned:

- Fly ash.
- Blast furnace slag.
- Limestone fillers.
- Silica fumes.

The European standard EN 206-1 considers two types of additions:

Type I additions: Almost inert additions, they have no chemical action on cementitious matrices.

The general suitability for use as Type I additions is established for:

- Fillers conforming to the pre-standard prEN 12620: 2000;
- Pigments in accordance with standard EN 12878.

Type II additions: These are the additions of latent pozzolanic or hydraulic character, they present, even partially, hydraulic or pozzolanic properties in the presence of cement and water.

The general suitability for use as type II additions is established for:

- Fly ash conforming to standard EN 450;
- Silica fumes in accordance with the pre-standard prEN 13263: 1998.

The general fitness for use for concretes used in France is established for the following standardized additions:

- Fly ash for concrete conforming to standard NF EN 450-1;
- Silica fumes conforming to standard NF P 18-502;
- Ground vitrified slag from class B blast furnaces in accordance with standard NF P 18-506
- Limestone additions in accordance with standard NF P 18-508;
- Category A siliceous additions, in accordance with standard NF P 18-509.

 Limestone additions in accordance with standard NF P 18-508

Limestone additions are dry finely divided products, obtained by grinding and / or selection, coming from deposits of limestone rocks which can be dolomitic, massive or loose. Two of these characteristics are particularly significant to complete this definition:

 A minimum content of total carbonates (limestone + dolomite), as well as a minimum content of calcium carbonate.

 A minimum value of the activity index.

The limestone additions conforming to standard NF P18-508 are of type I according to standard EN 206-1 and are substitutable for cement in the sense and under the conditions of this standard.

 Siliceous additions in accordance with standard NF P 18-509

The siliceous additions are finely divided products, made up of more than 96% (lower specified value) and more than 93.5% (lower absolute limit value), by silica expressed as SiO2 measured on dry product and obtained by grinding and / or selection of quartz or synthetic cristobalites.

The siliceous additions conforming to standard NF P18-509 are of type I according to standard EN 206-1 and are substitutable for cement within the meaning and under the conditions of this standard.

 Silica fumes conforming to standard NF P 18-502

Silica fume is a finely divided amorphous powder resulting from the production of silicon alloys or containing silicon. It is driven from the combustion zone of the ovens by the gases, towards the collection system.

The standard distinguishes two classes A and B; Class A silica fumes being the richest in silica and are finer. Silica fume of class A or B, conforming to the standard is an addition of type II within the meaning of standard EN 206-1 and is substitutable for cement within the meaning and conditions of this standard.

However, given the great finesse of these additions and their very high reactivity with the portlandite released by the hydration of the cement, their proportion is limited to 10% and their use is reserved for concretes containing a superplasticizer.

 Fly ash for concrete conforming to standard NF EN 450-1

Fly ash is a fine powder mainly consisting of glassy particles of spherical shape, resulting from the combustion of pulverized coal in the presence or not of co-fuels, having pozzolanic properties and composed essentially of SiO2 and Al2O3; the proportion of reactive SiO2 constituting at least 25% of the mass. Fly ash conforming to standard NF EN 450-1 are type II additions within the meaning of standard EN 206-1, and are substitutable for cement within the meaning and according to the conditions of this standard.

 Blast furnace ground vitrified slag conforming to standard NF P 18-506

Ground vitrified slag comes from the grinding of granulated or pelletized vitrified slag, a co-product of the production of cast iron and obtained by quenching molten blast furnace slag.

The following are excluded from the standard: unhardened crystallized and therefore unvitrified pig slags used as ballast or as aggregates and also steelworks slags and all slags of non-ferrous metals which may contain elements harmful to concrete such as salts metallic.

The standard distinguishes two classes of slag A and B; the latter is the most reactive, its fineness being higher. Slags conforming to standard NF P 18-506 are type II additions within the meaning of standard EN 206-1, but only class B slags are substitutable for cement within the meaning and according to the conditions of this standard.

II.2 : Effects of mineral additions on cement matrices:

By their fineness and by their more or less significant reactivity in the presence of cement, the mineral additions generate significant modifications on the properties of cement materials in the fresh and hardened state. The mechanisms behind these modifications are particularly complex, however, several recent studies in this area (Baron and al, 1997) (Lawrence P and al,2005) (Boudchicha and al,2007).

agree to distinguish three main effects of additions in a cementitious material:

- A granular effect resulting from the modifications brought by the addition on the granular structure of the material in the presence of water and possibly of adjuvant and which acts on the rheological properties and the compactness of cementitious materials in the fresh state.

- A physico-chemical and microstructural effect generated by the multiple interactions between the addition particles and the cement hydration process and which acts on the evolution of the hydration of the cement during setting and hardening.
- A purely chemical effect specific to certain additions in a cement medium (essentially present in the case of type II additions according to standard EN 206-1), which acts during the hydration of the cement and which interacts strongly with the effect physico-chemical and microstructural.

A superposition can be the result of the intervention of different effects simultaneously, influencing the properties in the fresh and hardened state of the cementitious material. This makes it difficult to assess the contribution of mineral additions to the performance of cementitious materials.

Gran The granular or filler effect:

The "granular" effect, also called the "filler" effect, is by definition the incorporation of mineral addition into a cementitious material to modify the granular skeleton of the mixture. These modifications can result from the stacking capacity of the fine or ultrafine particles of the addition with the other solid grains of the mixture and / or from the intensity of friction between the different particles of the mixture. Taking into account factors such as morphology, textural surface, granular distribution and zeta potential of the addition particles used; which influence the rheology of cementitious materials, the granular effect can be favorable or unfavorable (Boudchicha and al,2007) (Felekoglu B and al, 2006)

According to Gallias, the granular effect concerns the stacking of the solid particles of the addition with the other solid particles of the granular skeleton of the concrete (cement, sand). (Gallias,2011)

According to Baron and Ollivier, It is explained, at times, wrongly of a limestone addition activity is by what is called "filler effect"; intuitively, we imagine that the fine grains of the powder slip between the larger grains (those of sand), that they thus increase the compactness and, consequently, the resistance ". An important characteristic of fresh concrete is its porosity, if we vary the dosage of fine elements of concrete (all grains less than 63 micrometers, whether they belong to cement, addition or aggregates), we observe the existence of an optimal dosage for which the porosity of fresh concrete is minimal. For a concrete whose maximum dimension of the largest aggregate is 20 mm, this optimal dosage of fine elements is of the order of 350 kg / m3. Consider a concrete with a cement dosage of 250 kg / m3 and lacking fine elements; if added to it in the form of, for example, an addition, the amount of water required to achieve a given consistency decreases, and so does the porosity of fresh concrete(Baron et al,1997).

If, in addition, the cement dosage is kept constant, it follows an increase in resistance resulting directly from the decrease in the W / C ratio. The granular effect is said to be favorable when the particles of the addition modify the intergranular frictions little and manage to fill the porosities of the granular skeleton (cement and aggregates) by releasing the water contained in these pores, this effect leads either to improvement of the consistency of the fresh mixture at a constant quantity of water, ie reduction of the quantity of water for a given consistency by improving the compactness of the mixture and the mechanical performance of the hardened material.

A granular effect is said to be positive when the particles of the addition fill the space left empty by the other particles (Gallias,2011).

Some researchers have shown that the spherical shape of the fly ash particles is one of the parameters that improves the rheology of cementitious materials, for a given fluidity, increasing the fluidity of the mixture with a reduced amount of water. The spherical shape also reduces the surface area ratio by the volume of the particles, which generates a reduced demand for water in the mixture (Felekoglu B and al, 2006).

Zhang and Han have shown that the flow stress increases with the amount of ultrafine addition incorporated, but the viscosity of the dough varies with the nature and the amount of addition. When the rate of substitution of cement by additions of silica smoke, fly ash or limestone is less than 15%, the viscosity of the dough is reduced remarkably.

(Zhang and al,2000).

Other contradictory results have shown that the granular effect becomes unfavorable when the particles of the addition considerably modify the intergranular friction in cement mixtures or fail to fill the porosities of the granular skeleton. A negative granular effect when the particles of the addition separate the other particles (Gallias,2011).

Bessa has shown by studying the contribution of mineral additions to the physical, mechanical and durability properties of mortars, that the granular effect of mineral additions on the formulations of non-adjuvanted mortars depends first of all on the fineness and the quantity of l " addition introduced (figure II.1)(Anissa Bessa and al,2004).

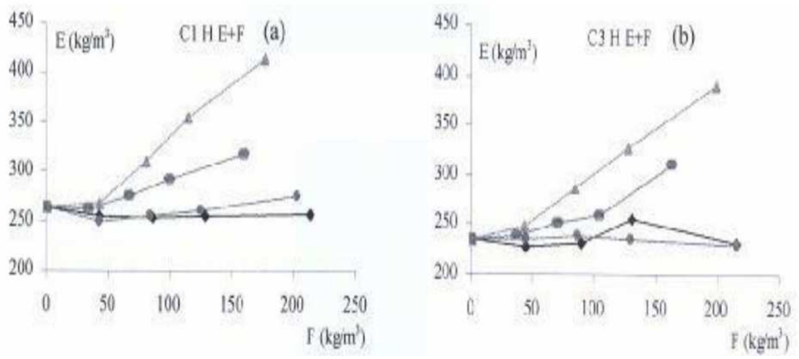


Figure II.1 : Water requirement of CEM II mortars - non-adjuvant additions according to the dosage of mineral additions, according to Bessa(Anissa Bessa-Badreddine,2004)

Gallias has shown by studying the effect of fine mineral additions on the water requirement of cement pastes, that the introduction of high proportions in cement pastes of standardized consistency creates a higher need for water (Fig. II.2).

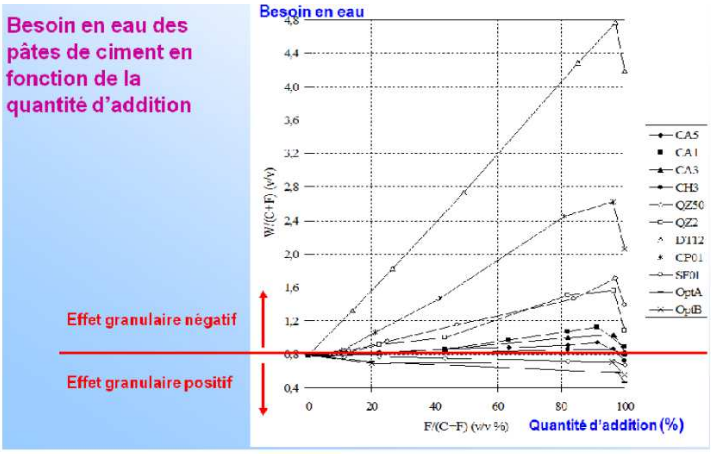


Figure II.2 : Water requirement of cement pastes according to the amount of addition according to (Gallias,2011)

Despite a multitude of available experimental results relating to the granular effect of additions in cement mixes, we don't currently have an approach sufficiently constructed and thorough, capable of predicting whether or not a given addition can produce a favorable granular effect in a formulation. A fortiori we do not know on which criterion we must support the choice of additions, in particular limestone additions and siliceous capable of improving the mechanical properties by optimizing the granular mixture.

It therefore follows that when the particles of mineral additions modify little the friction between the grains and fill the porosities of the granular structure (cement and aggregates) by releasing water contained in these pores, the granular effect becomes favorable and leads to the improvement of the fluidity fresh mixture for a constant amount of water, or reducing the amount of water for a given consistency and improving the compactness of the mixture and the mechanical strengths. But, when the particles of the mineral additions strongly modify the friction between the grains in cement mixtures or do not fill the porosities of the granular structure, the granular effect becomes unfavorable. (Gallias,2011)

- A physico-chemical and microstructural effect

The physicochemical and microstructural effect concerns the modifications between the particles of mineral additions and the hydration process of the cement and on the structure of hydrated products, this effect is also called "physical surface effect".(Lawrence P and al, 2005).

By Baron and Ollivier , adding limestone has no chemical reaction, the acceleration
of hydration is due to a physical effect explained by the germination of hydrated calcium silicate CS-H that occurs more easily in the presence of fine limestones this easier germination leads to a faster precipitation of CSH and therefore, also, more precipitation of portlandite Ca (OH) 2. The reactions between cement and water are faster in the presence of powder limestone and therefore, at all times, there are more hydrates formed. However, the excess hydrates, compared to the control without addition, decreases as the hydration is more advanced and becomes zero when hydration is complete. A distinction must therefore be made between the progress of the hydration reactions of the cement (chemical phenomenon) and the development of resistance (physical phenomenon) which depends on the quantity of hydrates formed by the hydration but also on the way these hydrates are assembled, their arrangement in space and their connections (Baron and al,1997).

As a hypothesis, two consequences result from germination due to contact with the surface of the additions: the first is the acceleration of hydration, the second is the modification of the assembly of hydrates favorable to resistance. For the siliceous additions, the quartz particles can constitute preferential nucleation sites in particular for the crystallization of portlandite crystals .
(Benzet and al,1999).

Lawrence et al have shown by studying the effect of inert mineral additions on the hydration of mortars, that the short-term hydration degree of mortars containing chemically inert additions was always greater than that of reference mortars without additions, and thus confirmed the improvement of the hydration of the cement with inert mineral additions(Lawrence and al, 2005).

Several hypotheses have been put forward to explain the action of additions on the cement hydration process. Some authors have shown that the presence of mineral additions in a cement mixture leads to an increase in the effective W / C ratio and leads to the acceleration of the hydration process or even that it allows better dispersion of the grains of cement leading to a more efficient structuring of the cement matrix (Lawrence,2000). Other authors consider that the presence of mineral additions multiplies the possibilities of germination of hydrated cement products and thus facilitates the formation of a solid structure guaranteeing the first mechanical resistance (Memon A and al,2002) (Manjit S,1999).

Caré has shown that the presence of mineral additions accelerates the hydration reactions of the cement and promotes the properties of the hardened material at young ages, especially since the particles are fine, however this favorable effect seems to fade with the weather.

In general, the physicochemical and microstructural effect of mineral additions acts essentially on the development of mechanical resistance at young ages as well as on the physical and microstructural properties of hardened cementitious materials. Chimique The chemical effect:

While the physico-chemical and microstructural effect generally concerns all mineral additions regardless of their mineralogical nature, the chemical effect is intimate linked to their mineralogical composition and concerns the capacity of additions characterized by pozzolanic and / or hydraulic properties, to react with water and anhydrous constituents or hydrated cement to form new mineral phases which can contribute to the evolution of mechanical resistance in the same way as hydrated cement products. This beneficial effect is a function of many parameters and can appear at different ages depending on the chemical or mineralogical composition of the addition, its specific surface and the type of cement.

The current European standardization defines the chemically active additions as being of type II by taking into account either their latent hydraulic reactivity (this is the case of blast furnace slag), or their pozzolanic activity (this is the case of smoke from silica and fly ash, among the additions with specific standardization). This chemical activity primarily results in a gain in mechanical strength (Caré et and, 2002).

According to Gallias the chemical effect concerns the chemical reactivity of certain active mineral additions in contact with cement (pozzolanic reaction and / or hydraulic reaction). Certain components of the additions (reactive silica, reactive alumina) react with the hydrated products of the cement and form new products which contribute to the cohesion of the concrete and its resistance to attack (Figure II.3)(Gallias,2011)

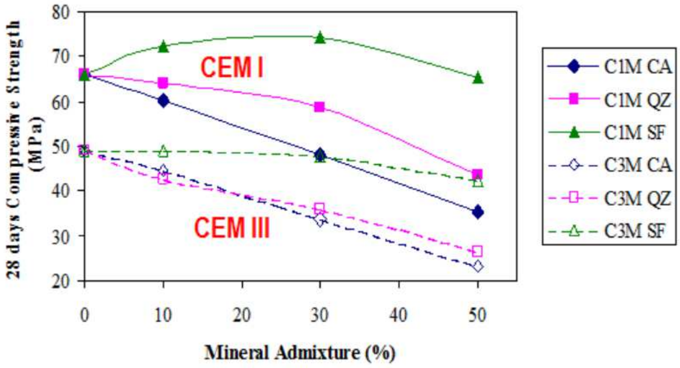


Figure II.3 : Influence of the type of cement and the amount of addition on the compressive strength of concrete, (Gallias,2011)

According to Baron and Ollivier the limestone additions also exhibit reactivity in the presence of hydrated cement products and form hydrated calcium carboaluminates.(Baron and al,1997).

In the long term, the researchers confirmed, by comparing the evolution of the mechanical strengths of the mortars made with two fly ash and a lime addition, that the chemical activity of the lime additions is however significantly lower than that of the siliceous additions of pozzolanic nature. .

The pozzolanic reaction mainly concerns silica fumes, siliceous fly ash (Class F), natural pozzolans or calcined shales. The amorphous silica present in these various additions reacts, in the presence of water, with the "portlandite" which is produced by the hydration of the cement to form the hydrated calcium silicates C-H-S according to the chemical reaction:

$$S + x.CH + y.H \rightarrow CxSHx + y \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II - 1)$$

It should be noted that the finest particles of quartz (considered a priori as inert in a cement medium) whose diameter is less than 5 µm can also exhibit similar pozzolanic activity (Benzet and al,1999).

The hydraulic activity relates more particularly to blast furnace slag and fly ash (class C) which, due to the basic nature of the cement environment, can produce HSCs whose C / S ratio differs from that of HSCs resulting from the reaction pozzolanic. For limestone additions, calcite (CaCO3) reacts with the aluminates of the cement (C3A, C4AH13) in the presence of water to form a hydrated calcium monocarbonate of the type (C3A. Ca OH3. 11H2O), crystallizing into fine hexagonal platelets (Baron and al,1997).

Boudchicha et al , by studying the effect of the activity of mineral additions on the compressive strengths of mortars, showed that the activity coefficients of these additions were very variable and depended on their mineralogical nature, on the rate of substitution of cement. and the age of mortar. Limestone additions have the highest activity coefficient at 07 days and silica smoke at 28 days at 10% of the cement substitution rate.

As a result, the chemical effect, when favorable, is complementary to the physicochemical and microstructural effect. Its action on the properties of the hardened material is measured by the modification of the volume and the nature of the hydrated products formed. However, their strong synergy prevents any clear distinction between these two effects. For this reason, these two effects can be combined in a single broader concept which is that of the contribution of mineral additions to the binding activity of cement (Baron and al,1997).

II.3:Effect of mineral additions on the properties of mortars and concretes

In this part we will analyze the effects of the different mineral additions on fresh and hardened mortars and concretes in general and limestone additions in particular.

II.3.1:Silica smoke

Are by-products from the manufacture of silicon or ferrosilicon. They are in the form of silica microspheres having average diameters of 0.1 µm. the specific surface varies from 20 to 25 m2 / g. Silica fumes are characterized by a vitreous structure (very reactive product) with a high silica content (from 75 to 95%).

Silica fumes act in concrete in three ways: physical, physico-chemical and pozzolanic action. Indeed, the physical action consists in driving out the water which is between the particles of cement, which plasticizes the concrete having an E / L ratio of 0.15 to 0.20. The physicochemical action is manifested by clogging of the pores of 0.1 mm in diameter from the age of 7 days, which makes the silica smoke concrete completely impermeable.

Action on fresh mortars and concretes:

De Larard et al have shown that the favorable effect of silica smoke on the granular stack of cementitious materials was represented by a variation in the workability of a mortar as a function of the amount of silica smoke incorporated, (FIG. II. 4) (De Larard and al,1986).

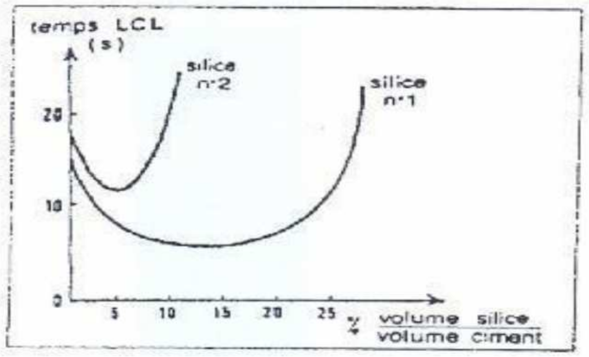


Figure II.4 : Effect of silica smoke on the workability of a mortar according to De Larard and al,1986)

Some researchers have shown that for cement dosages of 200, 300 and 400 kg / m3, it is possible to add up to 2, 4 and 6% of silica smoke respectively without increasing the concrete stiffness threshold with an improvement in the plastic viscosity. This is attributed to the improved dosage superior reverse the phenomenon by increasing friction between the fines. Concrete becomes very rich, very sticky and very cohesive.

Action on hardened mortars and concretes:

The pozzolanic action of silica smoke allows, by reacting very quickly with the lime released during hydration, to produce a very dense CSH which allows gains in compressive strength from the age of 7 days (Chahinez,2009) (Manai,1995).

Kwan has shown that the compressive strength of mortars at 28 days, whatever the water / binder ratio, increases with the content of silica smoke up to the limit of 15% of substitution of cement by addition (Figure II. 5).(Kwan, 2000).

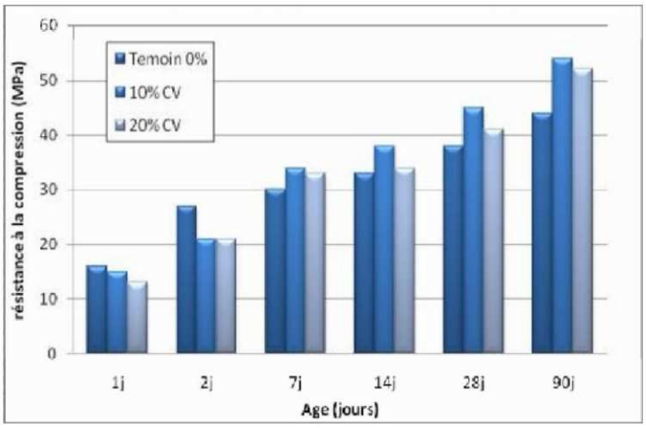


Figure II.5 : Variation in compressive strengths at 28 days of mortars as a function of the silica smoke content for different water / binder ratios, according to Kwan (Kwan, 2000)

Demirboga showed by studying the influence of mineral additions on the compressive strength of mortars, that the incorporation of 10% silica smoke, resulted in an improvement in compressive strength at 7.28 and 120 days.

According to the research work that we have seen previously, we note that the introduction of the addition of fumed silica has no positive effect on the mechanical strengths at young ages of mortars and concretes, on the other hand, a very significant improvement. medium and long term mechanical resistance has been shown. (Demirboga, 2003).

II.3.2 Fly Ash

Fly ash is a fine powder that is a by product of burning pulverized coal in electric generation power plants. Fly ash is a pozzolan, a substance containing aluminous and siliceous material that forms cement in the presence of water. When mixed with lime and water, fly ash forms a compound similar to Portland cement. This makes fly ash suitable as a prime material in blended cement, mosaic tiles, and hollow blocks, among other building materials. When used in concrete mixes, fly ash improves the strength and segregation of the concrete and makes it easier to pump.

Fly ash is in the form of glassy, solid or hollow spherical particles. The particle size ranges from 1 to 200 µm and, in general, 50% of the particles have a diameter of less than 30 µm. their Blaine specific surface varies between 250 and 400 m2 / kg (an area similar to that of cements).

The ASTM C-618-80 standard groups fly ash into two main classes according to their chemical composition:

- Class F rich in oxide ($SiO_2 + Al_2O_3 + Fe_2O_3 > 70\%$) with a low lime content ($CaO < 10\%$). It is qualified as silicoaluminous with a low pozzolanic potential.
- Class C rich in lime ($CaO > 10\%$), with an oxide content greater than 50%.

It is qualified as silica-limestone with a high pozzolanic potential.

II.3.2.1 Application for Fly Ash

Fly ash can be used as prime material in many cement-based products, such as poured concrete, concrete block, and brick. One of the most common uses of fly ash is in Portland cement concrete pavement or PCC pavement. Road construction projects using PCC can use a great deal of concrete, and substituting fly ash provides significant economic benefits. Fly ash has also been used as embankment and mine fill, and it has increasingly gained acceptance by the Federal Highway Administration.

The rate of substitution—of fly ash for Portland cement—typically specified is 1 to 1 1/2 pounds of fly ash for 1 pound of cement. Accordingly, the amount of fine aggregate in the concrete mix must be reduced to accommodate the additional volume of the fly ash.

II.3.2.2 The Different Types

There are two common types of fly ash: Class F and Class C. Class F fly ash contain particles covered in a kind of melted glass. This greatly reduces the risk of expansion due to sulfate attack, which may occur in fertilized soils or near coastal areas. Class F is generally low-calcium and has a carbon content less than 5 percent but sometimes as high as 10 percent.

Class C fly ash is also resistant to expansion from chemical attack. It has a higher percentage of calcium oxide than Class F and is more commonly used for structural concrete. Class C fly ash is typically composed of high-calcium fly ashes with a carbon content of less than 2 percent.

Currently, more than 50 percent of the concrete placed in the U.S. contains fly ash. Dosage rates vary depending on the type of fly ash and its reactivity level Typically, Class F fly ash is used at dosages of 15 to 25 percent by mass of cementitious material, while Class C fly ash is used at dosages of 15 to 40 percent.

Benefits Fly ash can be a cost-effective substitute for Portland cement in many markets. Fly ash is also recognized as an environmentally friendly material because it is a by product and has low embodied energy, the measure of how much energy is consumed in producing and shipping a building material. By contrast, Portland cement has a very high embodied energy because its production requires a great deal of heat. Fly ash requires less water than Portland cement and is easier to use in cold weather. Other benefits include:

* Produces various set times
* Cold weather resistance
* High strength gains, depending on use
* Can be used as an admixture
* Considered a non-shrink material
* Produces dense concrete with a smooth surface and sharp detail
* Great workability
* Reduces crack problems, permeability, and bleeding
* Reduces heat of hydration
* Allows for a lower water-cement ratio for similar slumps when compared to no-fly-ash mixes
* Reduces CO_2 emissions

Disadvantages Smaller builders and housing contractors may not be familiar with fly ash products, which can have different properties depending on where and how it was obtained. Additionally, fly ash applications may face resistance from traditional builders due to its tendency to effloresce along with concerns about freeze/thaw performance. Other concerns about using fly ash in concrete include:

* Slower strength gain
* Seasonal limitation
* Increased need for air-entraining admixtures
* Increase of salt scaling produced by higher proportions of fly ash

(https://www.thebalancesmb.com)

Action on fresh mortars and concretes :

It is reported that certain fly ash can have a delaying effect of the order of one or more hours on the setting of cement, probably due to the release of sulfates (SO4) present on the surface of the fly ash particles, those these have an unfavorable chemical effect. Thus, only the start of setting is offset, the time interval between setting and hardening remaining unchanged. This delay can be advantageous in the case of concreting in hot weather; otherwise it may be necessary to use a setting accelerator (Neville,2000) .

A slight improvement in the fluidity of mortars by the addition of fly ash was observed by Chahinez A This improvement relates to the rate of substitution of cement by fly ash (CV); flow time decreases with increasing substitution rate as illustrated in Figure II.6. (Chahinez,2009)

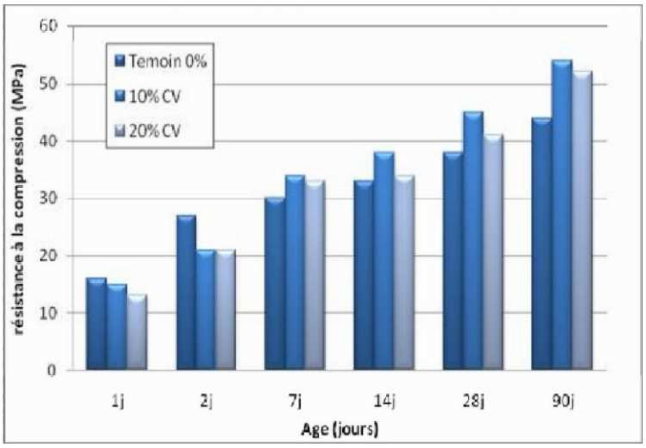


Figure II.6 :Variation in flow as a function of the rate (Chahinez,2009)

As reported by several authors: fly ash prevents cement particles from forming in blocks.

Lange & al concluded that for a given fluidity, the introduction of a specific amount of fly ash reduced the amount of water and increased the fluidity of the mixture. This behavior has been explained by the spherical shape of the particles which facilitate granular stacking and reduce inter-particle friction (Lange and al, 1997).

The spherical shape also reduces the ratio of the surface by the volume of the particles, which generates a reduced demand for water (Felekoglu and al,2000)

Action on hardened mortars and concretes :

Chahinez A showed that the mortar based on 20% fly ash developed lower resistance compared to that with 10% fly ash; and lower compressive strengths at a young age and higher at 90 days compared to the reference mortar (Chahinez,2009).

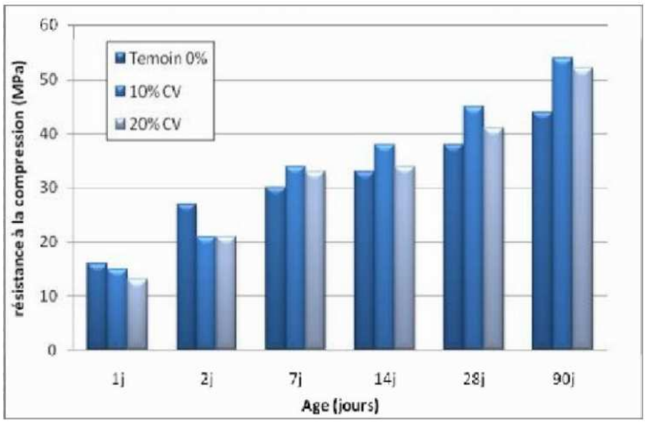


Figure II.7 : Variation in compressive strength as a function of age for the two substitution rates of Chahinez A fly ash (Chahinez,2009)

Demirboga showed by studying the influence of mineral additions on the compressive strength of mortars, that fly ash caused a decrease in compressive strength at all ages and for all quantities. (Demirboga,2003).

II.3.3 Blast furnace slag

Slag is a by-product of the production of pig iron in blast furnaces of steel factories. These are lime silico-aluminates treated in different ways at the outlet of the blast furnace:

- By sudden cooling in water or in the air: this prevents crystallization and allows its use in cements and concretes like pozzolan,
- By slow air cooling: this gives a crystallized material without any binding power which is used as aggregates for road works and in concrete.

Action on fresh mortars and concretes

Boudchicha A et al have shown, we study the variation in demand for SP1 superplasticizer for mortars made from two cements C1 and C2 partially substituted by additions of granulated blast furnace slag (BFS) of fineness of 2900 cm² / g have a greater demand for superplasticizer than limestone and pozzolan additions and which increases with the rate of cement substitution.

(Boudchicha and al ,2013).

Action on hardened mortars and concretes Demirboga showed by studying the influence of mineral additions on the compressive strength of mortars, that granulated blast furnace slag produced a reduction in compressive strength at 28 days and an improvement at 120 days (Demirboga and al,2003). Toufik Boubekeur and al have shown that the substitution of cement by slag gave low compressive strengths at young age (2 to 7 days) (Boubekeur and al,2010). This is due to the low hydraulic activity of the granulated slag from El Hadjar However, the resistance of cements to slag is similar to that of CEM I at 90 days, particularly for cements with 20% and 30% slag (Boubekeur and al, 2010) (Sadok and al, 2008).

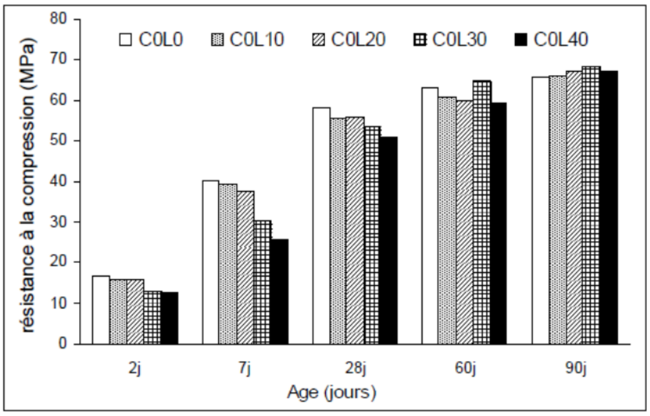


Figure II.8 : Effect of the percentage of slag on the compressive strength (Boubekeur and al, 2010)

However, it has been shown that hydration of a mixture of Portland cement and slag, containing more silica than Portland cement alone, produces more C-S-H and ettringite. The microstructure resulting from the hydrated cement paste is dense. However, the initial hydration of the slag is very slow because it is linked to the production of portlandite during the hydration of Portland cement.

The porosity and the porous distribution of concrete based on slag are different from that of Portland cement concrete. At a young age, the porosities are comparable. In the long term, the slag reacts with portlandite to form hydrates. The latter fill the interfoliar voids and make the pores discontinuous (FEL ,1986).

II.3.4 Limestone fillers

The products designated in the trade as fillers are fine powders with controlled particle size, the largest grains of which do not exceed 80 microns obtained by grinding or spraying certain rocks (limestone, basalt, bentonite, fly ash, etc.). Fillers differ from each other by:

- their origin, their chemical and mineralogical compositions, their structural defects, the impurities which they contain.
- their fineness, the shape of the grains, their surface condition. their hardness, their porosity.

Limestones can have different geological origins, metamorphic (these are marbles) or sedimentary. They can also exist in several polymorphic forms (calcite, aragonite, vaterite).

Their chemical composition is that of calcium carbonate ($CaCO3$) but they can also contain magnesium (in the form $Ca Mg (CO3) 2$), if it reacts with dolomitic limestones.

The use of limestone fillers in the cement and concrete industry is fairly recent. Limestone additions in cementitious matrices have already been the subject of several studies, mainly in France and the United States of America (Manai,1995)(Boudchicha , 2011)

Action on fresh mortars and concretes Limestone additions, in the presence of hydrated cement products, form hydrated calcium carboaluminates, Baron and Ollivier (Baron and al,1997).

Chahinez A has shown, by studying the workability of mortars of limestone fillers, a significant improvement in the fluidity of the mortars obtained by the mass substitution of cement with two percent of the limestone addition 10% and 20%. However, this improvement is independent of the cement substitution rate (Figure II.9) (Chahinez,2009).

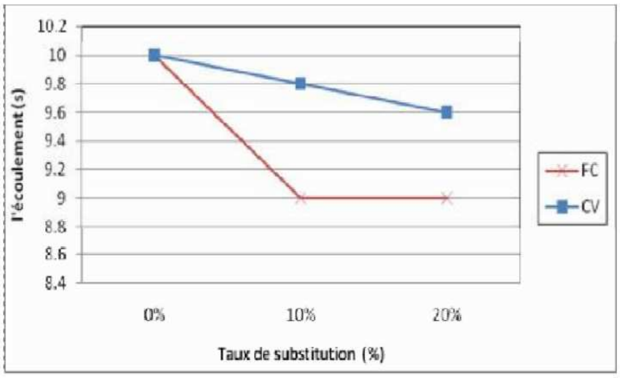


Figure II.9 : Variation of the flow as a function of the rate (Chahinez,2009).

This improvement in consistency has also been shown by Boudchicha and al , for substitution rates below 20% and a fineness of limestone additions below 5500 cm² / g.

Chahinez A has shown, by studying the mechanical resistance of limestone fillers mortars, that at 7 and 14 days; mortars with limestones give slightly higher resistances to mortar without addition (control mortar) and that this advantage is not sustainable because for deadlines mortars containing the limestone addition have the same resistance for a given substitution rate. The figure shows that the mortar based on 20% of the addition has developed the most low resistance compared to 10% (Figure II.10) .

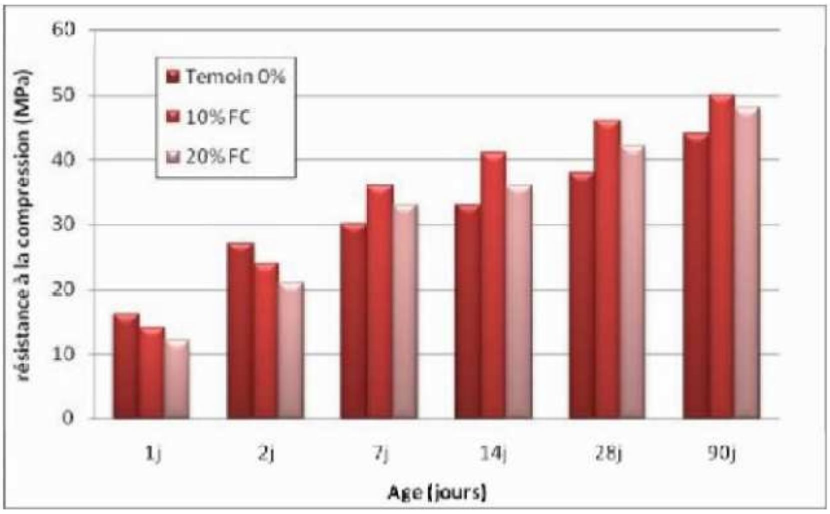


Figure II.10 : Variation in compressive strength as a function of age (Boubekeur and al, 2010)

Toufik Boubekeur et al have shown that the compressive strength is similar to that of 15.96% control mortar for a 10% replacement of limestone at 2 days, then it decreases 37% for a 20% limestone substitution. At 28 days of age, compressive strength decreases by 11% and 20% with the increase in the percentage of limestone from 10% to 20% respectively (Boubekeur and al, 2010).

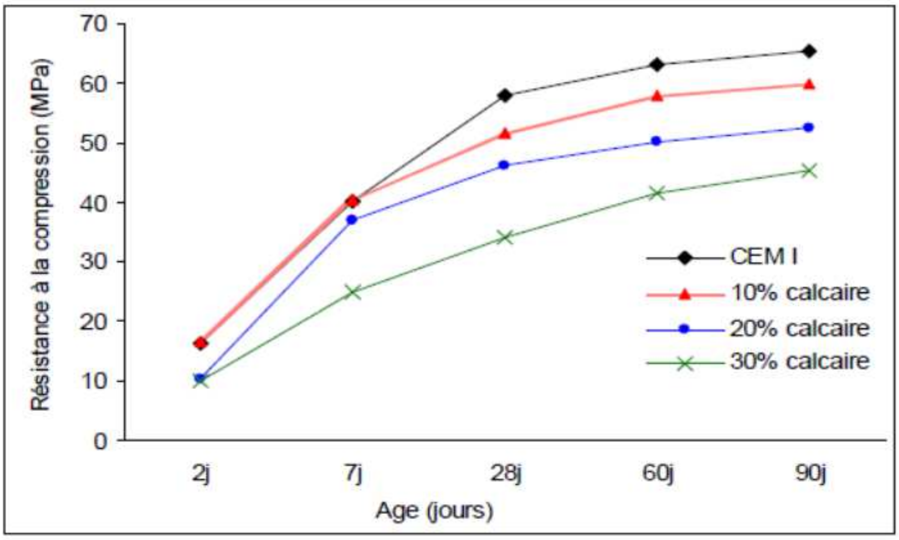


Figure II.10 : Evolution of the compressive strength as a function of the age of the mortars containing the limestone (Boubekeur and al, 2010).

Boudchicha et al have shown that the incorporation of limestone additions in mortars makes it possible to improve the strengths at 07 days up to 18% to 10% of the rate of substitution of cement by the addition, but this improvement is not maintained at 28 days and the strengths of the mortars with lime additions are lower than those of the reference mortar (Boudchicha and al,2007).

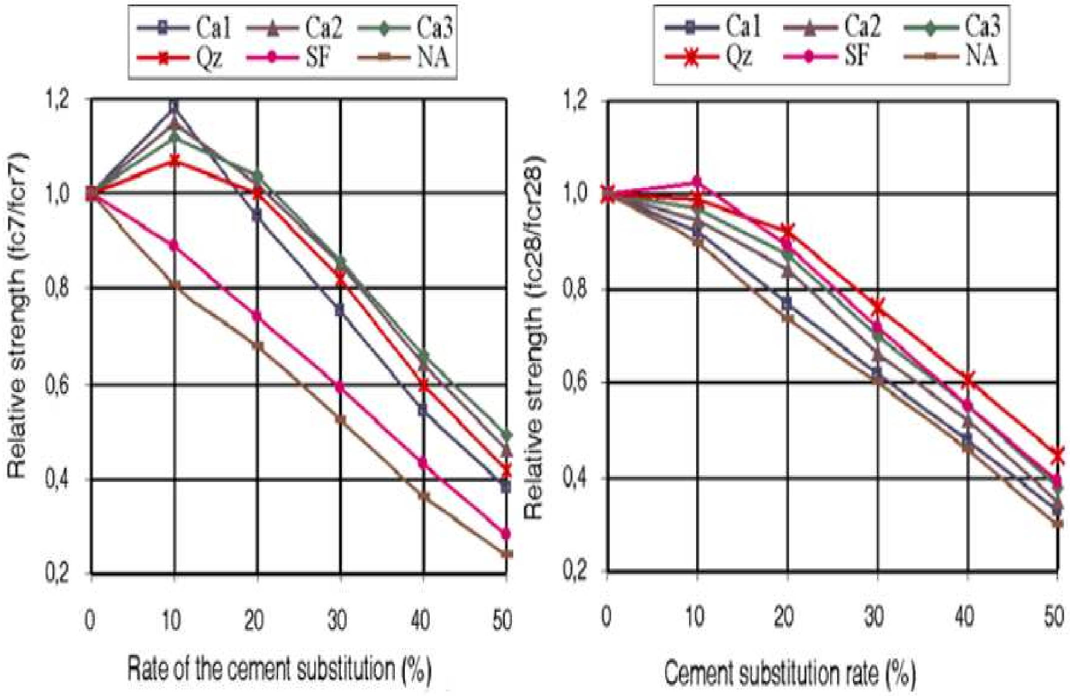


Figure II.11 : Effect of substitution of cement by additions on compressive strengths at 07 and 28 days according to Boudchicha et al (Boudchicha and al, 2007).

The researchers therefore confirmed that the mechanical strengths of mortars made with limestone additions are low compared to those of mortar without addition in the longer term.

II.3.5 Pozzolan

Pozzolans are materials, natural or artificial, capable of reacting in the presence of water with lime hydroxide to give rise to new, stable compounds, not very soluble in water and having binding properties (M Venuat, 1989).

Action on fresh mortars and concretes

Aichouba et al have shown by studying the effect of natural pozzolan from Béni-saf on the properties of a lime-based cement, that the substitution of cement by pozzolan from 10% to 30% generates an increase in normal consistency , a decrease in setting time.(Aichoube and al, 2005)

Action on hardened mortars and concretes Houhou and Mazghiche have shown by studying the influence of the pozzolanic addition on the mechanical behavior of the cement paste, that most of the evolution of the mechanical resistance and consequently of the pozzolanic effect which is associated with it produced from the age of 7 days(Houhou and al,2002).

Aichouba et al have shown by studying the effect of natural pozzolan from Béni-saf on the properties of a lime-based cement, that the substitution of cement by pozzolan from 10% to 30% generates a reduction in mechanical resistance to young ages and long-term conservation of these resistances (Aichoube and al, 2005).

II.4 Conclusion

The bibliographic study on the effects engendered by the various additions on mortars and concretes, makes it possible to note that the additions can bring significant modifications to the fresh and hardened state of cementitious materials. These modifications can result from a granular, physicochemical or chemical effect which depends on the nature of the addition, its fineness, or its morphology.

In this study, we propose to study the contribution that can generate an addition such as natural pozzolan and its different effects on the physico-mechanical properties and durability on the performance of a concrete, using the natural pozzolan of Béni-Saf. This will be discussed in the next chapter.

Chapter III. Analysis of natural pozzolan and its effects on concrete

Chapter III. Analysis of natural pozzolan and its effects on concrete

III.1 INTRODUCTION

In this chapter, a general description is devoted to natural pozzolan with a highlight of the interest of its use as a cement addition, in particular the aspects of pozzolan, while bringing clarifications on these characteristics and its activity.

Second, an analysis of the effects of natural pozzolan on the performance of concrete is described.

III.2 DESCRIPTION OF POZZOLAN

III.2.1 History of pozzolan

Origin of the term “pozzolan”—was fine-grained pumice they first sourced,from Pozzuoli, in Italy. When mixed with lime (still the key componentof Portland cement today) and aggregate, the pumice based concrete hardened into the most enduring man-made construction material ever.Pumice pozzolan not only mitigates such chemical forces, but improves the strength and abrasion resistance ofconcrete, creating a durable construction material after the manner of theRomans.

Modern engineers “rediscovered” the benefits of pozzolanic concrete early in the 20th century. When the coal-fired power generation industrywas looking for a market to use the fly ash they were scrubbing from theirstacks, they discovered that fly ash had a similar chemistry to pumice pozzolan. Adding fly ash to concrete became an inexpensive means of significantly improving the performance and life span of modern concrete.

While fly ash works as a replacement pozzolan, the original pozzolan,natural pumice, remains the superior choice. Minerals pozzolans arethe same as the natural, sustainable pumice pozzolan used by the Romansuse —carefully refined—resulting in a pozzolan that greatly enhancesconcrete chemistry and that performs consistentlyafter. Minerals pozzolans should be part of the toolbox of any engineer interested (www.crminerals.com).

Nowadays, the use of additions can be by the artificial pozzolan material essentially composed of silica, alumina and iron oxide having treatment to ensure its pozzolanic properties. In the other hand, natural pozzolan is widely used in some countries which has quarries such as: Saudi, turkey,Algeria, etc...

In Algeria, natural pozzolan is available at the Béni-Saf site in the Ain-Temouchent Wilaya.

III.2.2 Natural pozzolan

Pozzolans are loose or weakly cohesive pyroclastic rocks originating from volcanic eruptions of the explosive or sedimentary origin type. It consists of the basic elements of the cement components ,SiO2, A12O3 and Fe2O3 and those components are important for reducing the degree of clinker in manufacturing cement and increase the strength of concrete. The particles of this type of rock are in a glassy state or at least in a special state of instability or reactivity which makes them sensitive to attack by calcium hydroxide

Today, pozzolanic materials are enjoying a renaissance as supplementary cementing materials in Portland cementspastes and may replace part of the clinker in order to enhance the performance of the hydrated cement. When Portland cement clinker is produced there is a significant amount of CO_2 emitted from the calcination of the limestone.(D. Bajare and al, 2013). Inorder to reduce the emission of CO_2, reduction of the cement amount in concrete production and usage of pozzolansis an advantage (E. R. Dunstan Jr , 2011)

III.2.2.1 A description of some pozzolan materials

There is a description of the different substances that are classified as natural pozzolan,including:

III.2.2.1.1 Calcined clay

Calcined clay is a naturally occurring raw material comprised essentially of alumino-silicate minerals. Examples of clay are kaolinite, dickite, halloysite, and illite . Calcined clays have been used as manufactured pozzolans in concrete for many years, In the midwestern United States, calcined kaolinite clays have been documented in the literature as containing a mixture of approximately 85 to 90 percent metakaolin, 5 to 10 percent quartz, and residual thermally treated mixed clays of illite and montmorillonite or smectite. Higher purity calcined clays (greater than

95 percent metakaolin), specifically kaolinite, are discussed in 4.4 on metakaolin . (Barger and al. 1997**)**

Figure III.1 : Calcined clay (bpzoological.com)

III.2.2.1.2: Calcined shale

The raw material is shale or slate, which consists largely of alumino silicate clay minerals. In addition, there may be varying amounts of calcite (limestone), quartz, feldspar, and mica.

Reported cases of calcined shale being used as a pozzolan date back to as early as 1932. Calcined shale has been commercially available in the Mid-Atlantic and midwestern United States since the mid-1990s (Neal and al ,2002**)**.

Figure III.2 : Calcined shale (www.cementequipment.org)

III.2.2.1.3 Diatomaceous earth

Diatomaceous earth is composed of the siliceous skeletal remains of microscopic aquatic plants called diatoms. All diatomite has pozzolanic reactivity to varying degrees. Diatomite is a highly reactive pozzolan due to its high content of amorphous silica and its high specific surface area. It has a specific surface area approximately 10 times higher than that of portland cement, Lacustrine, or freshwater deposits of diatomite, appear to have higher pozzolanic reactivity. Diatomite can be calcined and finely ground to achieve optimum pozzolanic reactivity and performance characteristics . (Christensen and al. 2001).

Figure III.3 : Diatomaceous earth (Diatoms,2011).

III.2.2.1.4 Metakaolin ($Al_2O_3 \cdot 2SiO_2$)

It is a natural pozzolan produced by heat treating kaolinite clays. Kaolinite has a chemical composition of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. When it is heat treated, in the temperature range of approximately 1100 to 1650°F (600 to 900°C) .

Figure III.4 : Metakaolin (www.researchgate.net)

Although the use of metakaolin as a pozzolanic mineral admixture has been known for many years, its use has grown rapidly since the mid-1980s. In the United States, metakaolin and HRM are primarily manufactured from deposits of kaolin found in Georgia . (Murat and al ,1985).

III.2.2.1.5 Opaline shales

Opaline shales are described as cherts, shales, and clays containing substantial quantities of opaline silica and sometimes nearly pure opal .Opal is found in the Ardennes and Meuse Valleys in France and is still used in that region. The material is usually calcined at temperatures of approximately 1620°F (900°C) before it is used as a pozzolan or as a component of portland-pozzolan cement(Davis,1950).

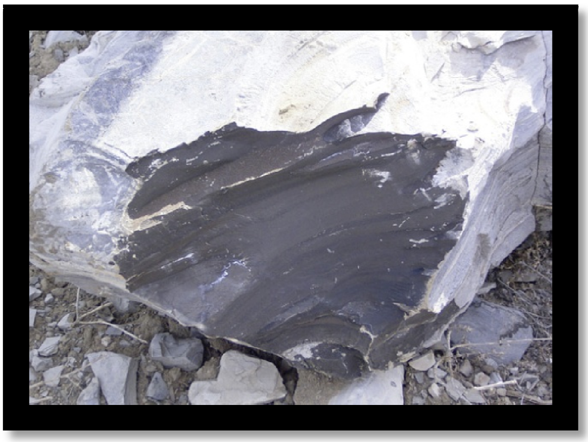


Figure III.5 : Opaline shales (https://www.geol.umd.edu)

III.2.3 Chemical interaction cement/pozzolan

Pozzolans are materials that consist predominantly of silica and alumina (D. J. Cook,1986) and are able to combine with portlandite in the presence of water to produce new reaction products exhibiting a binding character (Martinez-Ramirez and al ,2006).water to form C-S-H (calcium silicate hydrate) and portlandite – $Ca(OH)_2$. A small portion of portlandite enters intoreactions with alumina and sulphates to form compounds such as ettringite. Therefore not all of the portlanditeproduced is available or free to react with pozzolans (N.Toropovs and al,2014) (S. Popovic et al ,1998) has been noted in the research by Massazza, that approximately 22% of free portlandite is available in the system(F. Massazza) . Moreover, it has been found that adding calciumto pozzolan, which has a low calcium /silica ratio, enhances the hydration reaction for the formation of calcium silicatehydrate (C-S-H) gels and improves the mechanical strength of high-performance concrete (C. Isaia and al, 2003). Materials that exhibit pozzolanic activity can decrease the hydration heat by means of cement substitution, whichincreases the heat generated during hydration due to the pozzolanic reaction (M. Frias, 2000).

Pozzolans are known to increase the durability (Rojas and al ,2002) lower the hydration heat, increase the resistance tosulphate attack and reduce the energy cost per cement unit (.C. Shi ,1998) In the scientific research work by other scientists (Allahverdi and al,2011) it has been proved that by addition of metakaolin with pozzolanic character to the the four principal minerals comprising **PC** (C_3S, C_2S, C_3A and C_4AF), in the reaction with PC hydratation products calcium silicates appear in the structure,the binding time is accelerated in the early stage of hydration. Giergiczny has detected that by replacing half of PCamount in the composition with metakaolin – the shrinkage and amount of cracks diminishes for the concrete samples (Z.Giergiczny,2004). Consequently, the present study focuses on modification of cement pastes with binary and ternary cement pastesystems in order to determine effects on properties of cement and concrete.

III.3PROPERTIES OF NATURAL POZZOLAN

III.3.1 Pozzolanic activity

Pozzolanic activity is defined as the ability of natural or by-product materials to produce components having binding property as a result of their reaction with calcium hydroxide (CH) in presence of moisture (F. Massazza,1998).

The pozzolanic activity is characterized by two distinct aspects:

- The total amount of calcium hydroxide that a pozzolan is able to fix.
- The speed of fixation of calcium hydroxide by the pozzolan . (Massaza F,1976).

III.3.1.1 Reaction with lime

The different materials described in the preceding paragraphs all have the property of reacting with calcium hydroxide, in the presence of water, to form compounds having binding properties. From the point of view of this property the influence of silica and alumina cannot be dissociated. There are siliceous materials, with very little alumina, which fix large quantities of lime very quickly, but which give only weak mechanical resistance. The presence of reactive alumina considerably increases the mechanical resistance, especially in the short term.

Two main theories have been put forward to explain the properties of pozzolans:

- The basic exchange: pozzolanas would have the property of exchanging their alkalis for calcium. This property is the same as that possessed by ion exchange resins used to demineralize water (permutation).

- The direct combination: the progressive combination of lime with pozzolana.

However the second could be confirmed in several ways unlike the first which is not really valid because studies have shown that the ions play only a secondary role. However, the study of the reaction product has proved difficult and the compounds identified to date are very numerous. The reaction of certain artificial pozzolans can for example be represented by the following equation:

$$2\,(Al2O3\,.\,2\,SiO2) + 7\,Ca\,(OH)\,2 \rightarrow 3\,CaO\,.\,2\,SiO2.\,aq\;+ 2\,(2\,CaO\,.\,Al2O3\,.\,SiO2\,.\,aq)$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III-1)$$

III.3.1.2 Evaluation of the Pozzolanic activity

Various tests have been proposed and used to evaluate pozzolanic activity. Currently, two types of tests are generally used. They are based on two factors:

a- The mechanical strength of mortar and concrete made with lime or portland-pozzolan cement mixtures.

b- The reaction of calcium hydroxide in hardened pozzolanic cement.

Test methods based on mechanical strength are given by ASTM standards. Independently of the standard methods for determining the effectiveness of a pozzolan, one can simply compare the mechanical resistance of two sets of mortar test pieces, one made by replacing part of the cement (for example 30%) with the pozzolan and the other by an inert powder. The tests are carried out at 14, 28 and 90 days for example. If the mortars containing the pozzolan have higher mechanical strengths, the pozzolan is therefore active. An accelerated test method based on the lime reaction to assess whether a binder satisfies the designation of pozzolanic cement, was proposed by Fratini in 1950. This currently universally accepted test consists in comparing the quality of calcium hydroxide present in the aqueous solution in contact with the hydrated binder, with the amount of calcium hydroxide which can saturate a medium of the same alkalinity. Also Pozzolanic cements always give undersaturated lime solutions.

III.3.2 Chemical composition

The composition is slightly different from experiment to experiment ; to get more details on this part we take the works made in many regions in algeria.

III.3.2.1 Chemical compostion from studies of (N.Kaid)

A large deposit (160 km long) of pyroclastic rocks of volcanic origin is found in the north-west of Algeria, between the border with Morocco and the Oran' Sahel . A few studies have shown that these rocks have pozzolanic properties, so they are currently used in cement plants to produce composite cements containing between 15% and 20% NP. Usually, only the mechanical characteristics are checked. Knowledge of the performance of this NP in terms of durability still remains limited , in this table shows the chemical composition of NP of Beni-saf (N. Kaid and all)

Table III.1 : Chemical composition of natural pozzolan (N. Kaid and all)

	CEM 1 52.5 R	Natural pozzolan (NP)	
		Beni-Saf	Typical range NP (115-171)
Chemical composition (%)			
SiO_2	19.9	46.8	43-72
Al_2O_3	5.6	18.8	9-20
Fe_2O_3	2.5	10.5	1-12
CaO	64	9.2	1-15
Mgo	1.8	3.8	0.5-7
SO_3	3.1	0.2	0-1.4
Na_2O	0.1	0.8	0.5-11
K_2O	0.7	0.5	0.2-8
Loss on ignition	1.7	6.5	0.2-19

III.3.2.2 Chemical compostion from studies of (Yassine) .

The natural pozzolan was obtained from a source in north-western Algeria and was composed of zeolite and plagioclase, which are mineralogical materials containing large quantities of SiO2 and Al2O3. A number of cements were prepared in which portland cement (OPC) was replaced by NP in the
range of 0–25% (Yassine and al ,2012) .

Table III.2 : Chemical and physical properties of cement and NP (Yassine and …,2012)

Chemical composition (X-ray fluorescence)	OPC	NP
SiO_2(%)	21.35	47.21
Al_2O_3(%)	63.89	18.85
Fe2O3(%)	4.59	9.99
CaO(%)	5.52	10.84
MgO(%)	1.37	438
SO3(%)	0.41	0.5
K2O(%)	2.72	0.2
Na2O(%)	0.13	0.81
LOL(%)	2.47	3.91

III.3.3 Physical properties :

The water requirement and setting time were determined by Vicat Probe and Vicat needle apparatus. The effect of replacement of 10–40% of cement with natural pozzolana is an increase in the water demand necessary for maintaining consistency. This might be due to the relatively high fineness and flocculent structure of the natural pozzolana. The increase in natural pozzolana content slightly reduces the initial setting time. This is contrary to expectation and is difficult to explain. However, a negligible effect is also reported by other researchers for low cement replacement levels (up to 20%) using a higher activity natural pozzolana. The soundness of the samples show a gradual increase with the increase in replacement level, but the values measured are less than the maximum of 10 mm tolerated by the European standard specifications . (Ghrici and al , 2006) .

Table III.3 : Physical properties of the mixed used . (Ghrici and al , 2006)

	Natural pozzolan (%)				
	0	10	20	30	40
Water demand for standard consistency (%)	27.6	28	28.5	30.6	31.5
Initial setting time (min)	152	146	143	137	109
Final setting time (min)	257	225	200	192	185
Soundness (mm)	0.5	0.55	0.6	0.7	0.9

III.4 EFFECT OF NATURAL POZZOLAN ON CONCRETE

III.4.1 Influence of natural pozzolan on properties of fresh concrete

III 4.1.1 Influence of natural pozzolan on properties of fresh concrete From studies of (Laoufi) .

The pozolan used in this study was taken from Bani Saf.

The results of these physical characterization tests of standardized cement pastes with and without GNP are presented in Table III.4 It is clear from this table that cement pastes with different pozzolan levels require more water to obtain of a consistency similar to that of the dough without PNB (P0), moreover, the greater the percentage of PNB and the greater the demand for water. This increase in the normal consistency of pozzolanic pastes is probably due to the gradual increase in the specific surface area of the binder, which naturally leads to a strong call for water molecules to wet the whole dough. (Laoufi L and al, 2016).

Table III.4 : Influence of PNB on normal consistency and setting time (Laoufi L, 2016)

Designation of pastes	Natural pozzolan (%)	Consistency (mm)	Start of setting (h: min)	End of setting (h: min)
P0	0	24.00	2.23	3.45
P10	10	25.00	2.35	3.57
P20	20	25.50	2.50	4.10
P30	30	26.00	3.25	4.15

III 4.1.2 From studies of (Ghrici)

In order to analyse the effect of duration of initial curing on the compressive and flexural strengths, specimens were cured for 1, 3, 7, or 14 days before being left in the outdoor hot environment until the age of testing of either 28 or 90 days. The effect of duration of curing is summarised in Table 5 and Fig. 4. It seems that the period of initial moist curing has a significant effect on the mechanical properties as natural pozzolana does not react as rapidly as the cement. Longer curing periods allow sufficient moisture for continued hydration resulting in higher strength. A curing period of 7 days improved the compressive strength at 90 days of age up to 82% of that of continuous humid curing of mortars containing 30% of natural pozzolana as compared to only 53% with one day curing. This shows the importance of proper curing for strength development especially in concretes containing pozzolans as cement extenders. However, the increase of compressive strength when the period of initial moist curing increase from 7 to 14 days, is negligible and one can conclude that a minimal period of initial moist curing of 7 days could be sufficient. Prolonged moist curing may be required not only to achieve full development of strength but also for durability-related properties as inadequate curing has been found to hinder the refinement of pore structure and retduction of the permeability of concrete and produce a large increase in the absorptivity of concrete. A similar trend to that observed for compressive strength seems to be followed by the flexural strength results. However, the results show that the flexural strength is less sensitive than the compressive strength to inadequate curing . (Ghrici and al , 2006)

Table III . 5 Effect of initial curing on the flexural strength (MPa) at 28 days and 90 days of age (Ghrici and al , 2006) .

	Water cured		Exposure in hot environment							
			1 day curing		3 day curing		7 day curing		14 day curing	
	28 day	90 day	28 day	90day	28 day	90 day	28 day	90 day	28 day	90 day
0%	8.13	8.87	4.28	5.04	5.82	7.47	5.98	7.86	6.32	8.36
10%	8.52	8.82	4.38	5.22	5.46	7.56	6.02	7.96	6.35	8.74
20%	7.65	9.3	3.78	4.78	5.72	7.99	5.82	8.31	6.19	9.1
30%	7.07	7.9	3.11	4.66	4.45	6.19	4.92	7.17	4.56	8.13
40%	7.07	7.65	2.39	2.76	3.01	3.54	3.82	6.17	4.12	7.25

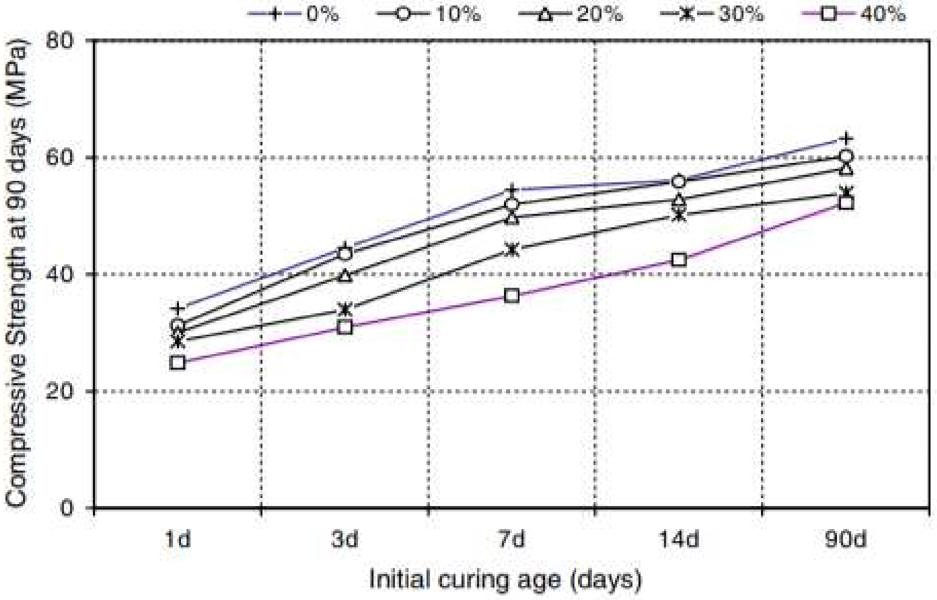


Figure III.6 : Effect of the initial curing age on the compressive strength at 90 days .
(Ghrici and al , 2006)

III.4.2 Influence of natural pozzolan on properties of hard concrete

III.4.2.1 Compressive strength

The development of the compressive strength with age for cement blended with different levels of cement substitution is shown in Figure 8. In all cases, the strengths of the mortars increased with age. Natural pozzolan induced compressive strength reductions in mortar at all levels of replacement at 2, 7, 28, 90 and 360 days, except for 20% NP replacement of OPC, which increased the compressive strength a little at 360 days. However, reductions were 9, 11 and 17% due to 15, 20 and 25%, respectively, of NP replacement of OPC at 90 days. Reductions due to NP replacement at early ages increased with increases in NP level and decreased with curing time. Many researchers have reported that adding pozzolanic material, such as silica fume and natural pozzolan, slows down the appearance of the strength in the early curing period This could be explained by the slowness at room temperature of the pozzolanic reactions of the glassy particles in the natural pozzolan with the Ca(OH)2 released during cement hydration. However, its pozzolanic reactivity could be improved or modified by employing the appropriate activation and (or) treatment (Caijun, 2001). The optimization of the use of natural pozzolanic material is still under investigation and results are expected to be published later. In addition, due to the continuation of this reaction and the formation of a secondary C-S-H that enhances the paste–aggregate interface and decreases the capillary porosity of the mortar, a greater degree of hydration is achieved, resulting in strengths at 360 days of age which are comparable to those of ordinary portland cement specimens. Substituting high percentages of pozzolan for cement (more than 20%) leads to considerable compressive strength reduction. This is in agreement with previous research

which reported that the use of NP beyond 20% replacement resulted in a slight decrease in the compressive strength. This shows that pozzolan has a negative effect on the compressive strength when used at high doses. In other words, some of the substituted pozzolan cannot take part in the pozzolanic reaction with cement hydration products and remains inactivated in the mixture, thus reducing its resistance. So, from the point of view of compressive strength and regarding Figure

9, it can be concluded that the 20% substitution rate is an optimal one and any additional substitution will cause considerable reduction in compressive strength.(Yassine and al,2012).

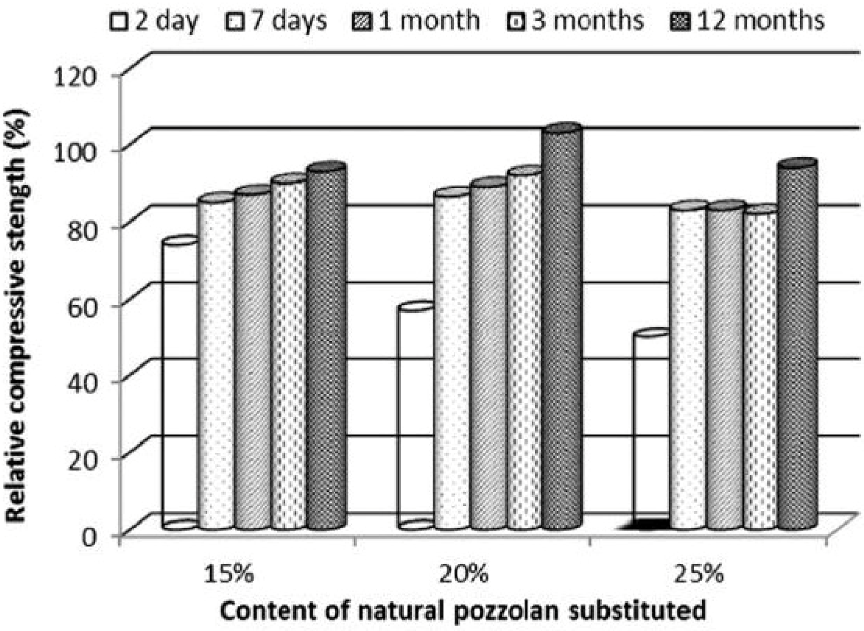


Figure III.7 : Relative strength for various binders. .(Yassine and al,2012).

III.4.3 Influence of natural pozzolan on durability of concrete

III.4.3.1 Water permeabilty

A steady flow method has been applied to test the permeability of concrete on several samples, and the time and amount of water that has passed through each sample has been monitored until a steady flow rate has been obtained. The water permeability tester is shown in FigureIII.9**.**

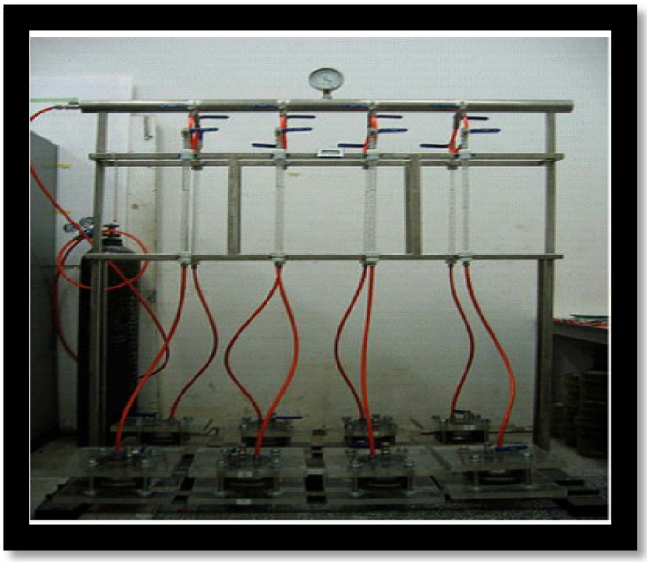


Figure III. 8 : Water permeability apparatus (Nuntachai Chusilp and al, 2009).

The water permeability and the water permeability ratio of concrete mixes are also given in TableIII.6. The water permeability ratio was defined as the water permeability of concrete containing ground bagasse ash with respect to that of the control concrete at the same age. The water permeability of the control concrete was 1.32 1012 and 1.26 1012 m/s at 28 and 90 days, respectively. These results agree with previous studies . It is also found that the water permeability values of all concretes decreased with their curing age. For example, the water permeability values of the 35BA10 concrete were 1.22 1012 and 0.73 1012 m/s, with water permeability ratios of 0.92 and 0.58, at 28 and 90 days, respectively. These results suggest that the low water permeability of concrete was affected by the pozzolanic reaction of the ground bagasse ash. Note that the compressive strengths of 35CT and 35BA10 at the age of 90 days were not very different, at 41.8 and 44.4 MPa, respectively.The Samples are in Table III.7 as showen **.** (Nuntachai, 2009)

Table III.6 : Water permeability of concrete (Nuntachai and al 2009)

Sample	Permeability* 10^-12. k (m/s) k/kcr	
	28 dayş	90 dayş
35CT	1.32-1.00	1.26-1.00
35BAIO	1.22-0.92	0.73-0.58
35BA20	1.08-0.82	0.48-0.38
35BA30	0.66-0.50	0.39-0.31

III.4.3.2 Chloride permeability

The specimens used for this test were cylindrical with diameter 100 mm and height 50 mm. The test was performed at the ages of 28 and 90 days and the tests results are shown in Fig. 4. The total passed charge was high for both specimens at the age of 28 days. The chloride ion permeability of the pozzolancontaining specimens had decreased significantly by the age of 90 days due to the natural pozzolan activities at later ages. (Najimi and al, 2008).

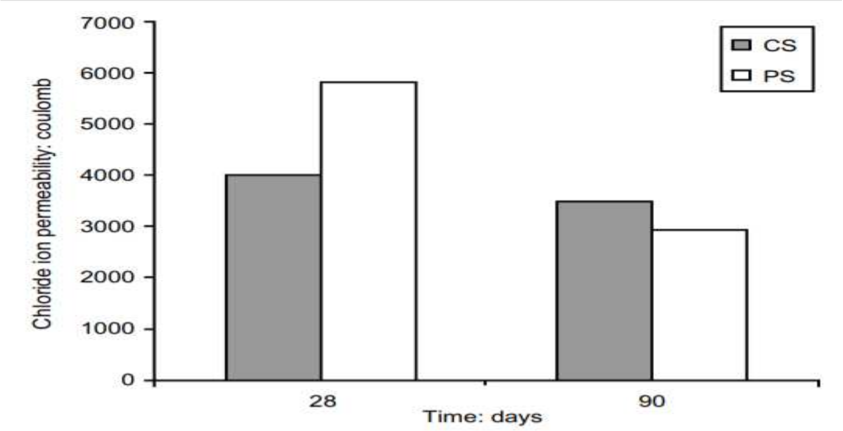


Figure III.10 : Chloride permeability (Najimi and al,2008).

III.4.3.3Porosity

A study on the porosity, led by a Touil's team, on several samples of concrete (with pozzolan and without pozzolan) as follows in Table III.7 **:**

Table III.7 : Composition des bétons (TOUIL and al, 2015).

Ingredients (Kg / m3)	BO2	BPZ5	BPZ10	BPZ15
Aggregates 04-25 mm	1109	1109	1109	1109
Sand 00-04mm	660	660	660	660
CEM Cement II 42.5	350	332.5	315	297.5
Pozzolan	-	17.5	35	52.5
E/L	0.55	0.55	0.55	0.55
Water	192.5	192.5	192.5	192.5

the characterization of the range of concretes, the substitution of part of the cement in mass proportion (5 to 15%) with pozzolan highlighted a significant reduction in the porosity of the concrete and in particular its porous distribution with a more microstructure compact while largely conditioning the transport mechanisms in concrete. In terms of durability, this is systematically confirmed by recording a reduction in the diffusion coefficients going from 5.13 to 3.57 10-12 (m2 / s) when we go from a reference concrete BO2 to a concrete with pozzolanic addition BPZ15. In Table III.10 , Results relating to the sustainability indicators of the concretes studied .

Table III.8 : Results relating to the sustainability indicators of the concretes studied(Najimi and al, 2008).

sample	Resistance Fc28 (MPa)	Porosity accessible to water (%)	Coef. diffusion From (m2 / s. E-12)	Durability class [AFGC, 04]
BO2	34.10	15.08	5.13	**Very weak**
BPZ5	31.20	13.79	3.96	**Average**
BPZ10	32.50	13.77	3.75	**Average**
BPZ15	37.00	13.06	3.57	**Average**

III.4.3.4 X-ray diffraction analysis

The rice husk ash was ground to a powder and analysed by X-ray diffraction. The diffraction diagram, Fig III.11, shows that quartz is the only crystalline phase. It is noted that the halo centred at approximately 20_ 2_ , corresponds to black calcinated amorphous organic matter or amorphous silica. As with the granulometric analysis the two ashes showed the same results.(Jauberthie, 2000)

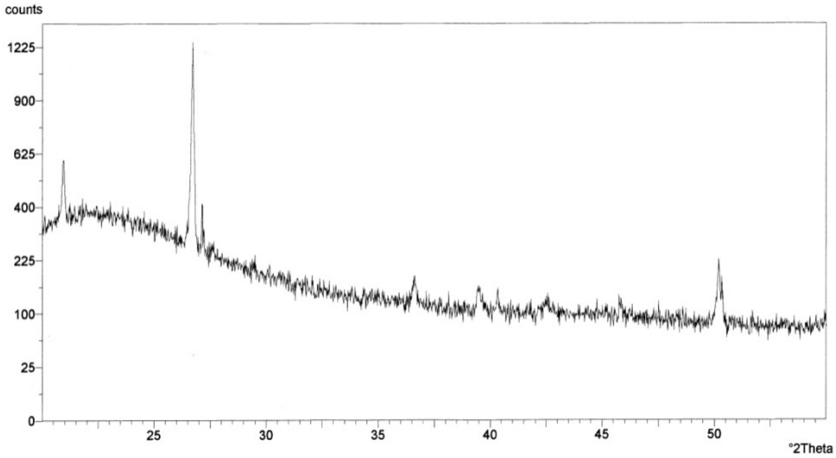
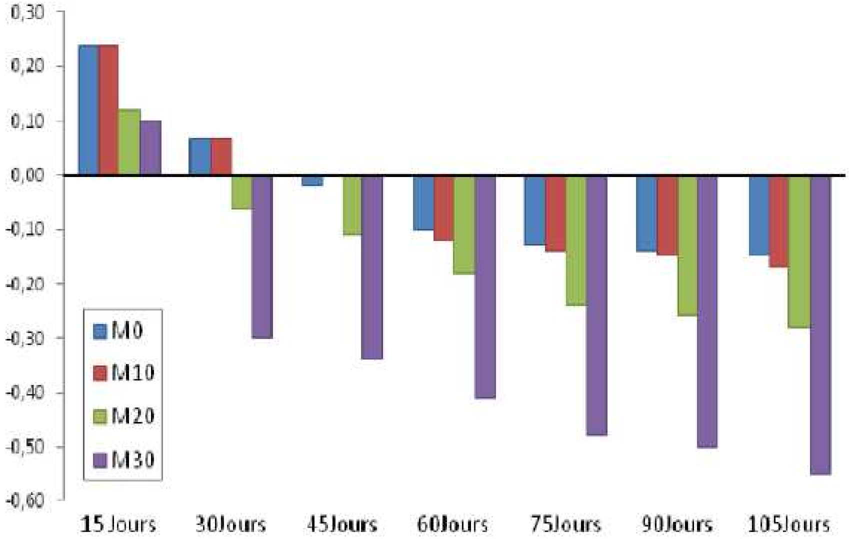


Figure III.9: X-Ray diffraction analysis of the rice husk ash K _Cu filter .(Jauberthie and al, 2000).

III4.3.5 Action of Sodium Sulfate

Figure III.10 shows the variation of the mass of the M0, M10, M20 and M30 mortar specimens made with and without the addition of PNB with different percentages 0, 10, 20 and 30% respectively, depending on the period of immersion in the 5% Na_2SO_4 solution.



Axis of x :conversion

Axis of y:variation in mass (%)

Figure III.10: Mass variation of the different mortars depending on the period of immersion in a 5% Na_2SO_4 solution (Laoufi and al)

In Figure III.10, we can see, in general, that all the mortars have shown permanent mass gains from the 4th week of storage which are represented by values with a negative sign. Prior to this date, low mass loss readings were identified for all four types of mortars, and are represented by positive signs. At 15 days, a period when the pozzolanic reaction is inactive, reductions in mass losses are recorded for the pozzolanic mortars M20 and M30 which are 0.12 and 0.10% respectively, compared to the M0 mortar without pozzolan, the latter records a loss of mass. by 0.24%. , confirm that the gradual degradation and dissolution of the cement matrix at an early age is attributed to the decomposition of calcium hydroxide and consequently to the formation of an amount of gypsum which is dissolved . (Laoufi and al)

III.5 Conclusion :

The Natural Pozzolan material is a great addition to the building, as it improves the concrete properties through durability, heat exposure, and others .

GENERAL CONCLUSION

Cement is a finely milled mineral powder, usually grey in colour. The most important raw materials for the production of cement are limestone, clay, and marl. Mixed with water, cement serves as an adhesive to bind sand, gravel, and hard rock in concrete. Cement hardens both in the air and under water, and remains in its hardened state once reached .

Cement is usually available in the form of a homogeneous bulk dry good. It's characteristics are standardised in order to ensure the required stability, reliability, and processability in the application .

Cements are classified according to their early and final strength as well as their composition. In addition to cements that consist of 100% clinker, there are so-called composite cements, in which a portion of the clinker is replaced by alternative raw materials, such as fly ash, ground slag, or limestone. As the production of clinker is energy-intensive and releases large amounts of CO2, the use of alternative raw materials can conserve natural resources and reduce CO2 emissions .

Concrete can add beauty and durability to many residential and commercial projects. It works great on driveways, patios, parking lots, walkways, roads, and so much more, and it creates a timeless look. While concrete offers many benefits, it's not always perfect. Improper processes and maintenance, as well as certain weather conditions, can cause a few common concrete problems that can affect the aesthetics or durability. Thankfully, though, most of these common concrete problems also have solutions .

Among these solutions are materials that are added with cement, which change the properties of concrete and add new features to it, and these materials are added according to the characteristic to be improved in concrete . Cement additives are materials added to cement for the optimization of the cement properties and the cement grinding process. Cement additives are classified into different product groups such as grinding aids, strength enhancers and performance enhancers .Cement additives are a popular choice because of

Positively affect the production process and the quality of cement.

* Improve defined cement properties, e.g. powder flowability, strength development, mortar workability and durability.

* Adjust the cement quality to meet the demands set by relevant standards and cement customers

* Contribute to the profitability of cement plants .

* Ensure less environmental impact by reducing utilization of energy and resources combined with minimized carbon footprint .

Among these addition :

- Fly Ash : Fly ash can be used as prime material in many cement-based products, such as poured concrete, concrete block, and brick. One of the most common uses of fly ash is in Portland cement concrete pavement or PCC pavement. Road construction projects using PCC can use a great deal of concrete, and substituting fly ash provides significant economic benefits. Fly ash has also been used as embankment and mine fill, and it has increasingly gained acceptance by the Federal Highway Administration.
- Silica smoke:Are by-products from the manufacture of silicon or ferrosilicon. They are in the form of silica microspheres having average diameters of 0.1 µm. the specific surface varies from 20 to 25 m2 / g. Silica fumes are characterized by a vitreous structure (very reactive product) with a high silica content (from 75 to 95%).
- Blast furnace slag : Pelletized blast furnace slag has been used as lightweight aggregate and for cement manufacture. Foamed slag has been used as a lightweight aggregate for Portland cement concrete. Granulated blast furnace slag has been used as a raw material for cement production and as an aggregate and insulating material.
- Limestone filler : Limestone filler is increasingly used, among other things as replacement for clinker in cement and as addition to self-compacting concrete.

Pozzolans can be used to control setting, increase durability, reduce cost and reduce pollution without significantly reducing the final compressive strength or other performance characteristic. The use of natural pozzolans results in a reduction of CO2 emissions associated with Portland cement production. A 50% Portland cement replacement by a natural pozzolan would mean a reduction of such greenhouse gas emissions in cement production by one half, which could have enormous positive consequences for the environment. Secondly, depending on the grindability (if necessary) and closeness to the construction site, natural pozzolans can significantly reduce the cost of concrete production, dam construction or production of mass housing units. As found with ancient concrete, natural pozzolans used in normal proportions typically improve concrete performance and durability. Whereas the benefits of most pozzolans used far outweigh their disadvantages . After researching the Pozzolan studies, we concluded that:

- The local natural pozzolan obtained from different sources have a similar chemical and physical properties .
- The natural pozzolan conforms with the requirements of ASTM C618 and can be designated as Class N. Strength activity index for both 7 d and 28 d comply with the specification of ASTM C 618 .
- Incorporation of natural pozzolanic material in concrete has insignificant effects on the properties of fresh concrete, namely initial slump, setting times, and slump loss .
- Natural pozzolan fineness and source did not affect the compressive strength. The compressive strength development of natural pozzolanic concrete was low as compared to Portland cement concrete up to the investigated age .
- The chloride permeability of natural pozzolanic concrete demonstrated better performance at above 90 d as compared to plain concrete. There was good correlation between porosity and the chloride permeability .

- XRD analysis shows that there is a change of the crystalline phase into amorphous phase due the natural pozzolanic reaction .

- The characterization of the range of concretes, the substitution of part of the cement in mass proportion (5 to 15%) with pozzolan has highlighted a significant reduction in the porosity of the concrete and in particular its porous distribution with a more compact microstructure while largely conditioning the transport mechanisms in concrete. In terms of durability .

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