ABSTRACT

The use of integral high performance concrete of the cementitious additions as the fly ash, the silica fume or the cementitious hydraulic slag increased considerably during two last decades. The works in HPC last longer and involve maintenance costs less low than those out of ordinary concrete. Moreover, the HPC uses less cement, which decreases the CO₂ emissions. A vaster use of the integral high performance concrete of the cementitious additions could thus involve benefit as well environmental as financial and build more durable works.

In the current state, research on the concretes with high performances in Algeria is especially centered on their formulations in order to produce concretes of better resistances and durable.

However, an optimal composition depends on several parameters, in particular on the choice of the ingredients. The effect of the cementitious additions and their smoothness remains little undertaken. This is why we propose in this work, to formulate of high performances concretes with and without cementitious addition. And, to treat the influence of the slag of the iron and steel plant of El-hadjar (Algeria), finely crushed and substituted for part of cement, on the physicomechanical characteristics of the elaborate concretes. The mode of conservation is the gypsum water (corrosive condition).

KEYWORDS

HPC, Slag, Durability, Sulphate.
1 INTRODUCTION

The concrete of high resistances to fact the object of many research, since strong a long time, from the very start of the century, the concretes of resistance higher than 50 MPa were obtained on building site, result very meritorious if one compares the quality of materials available at the time to that of cements and aggregates of today. However, for a few years, a renewed interest has appeared, in the whole world, for the concrete with high performances, obtained thanks to the use of thinners and silica smoke. The reason of this new reversal must be sought, makes some not only in the possibility of reducing the structures by an increase in the pressures in services, but rather in the improvement of the durability of material in service in chemically aggressive mediums [Mekki 2002].

The action of sulphated underground water offers the simplest case of an aggression giving rise to expansive new compounds starting from the components of cement. The calcium sulphatic combines with aluminates of cement to form a salt (the ettringite) or salt of Candlot C₃A.3CaSO₄.32H₂O, whose crystallization accompanied by expansion causes the cracking of the concrete. It facilitates the penetration of the aggressive agents to the reinforcements which are, in their turn attacked.

It is possible to modify the microstructure of the concrete by incorporating mineral products. These cementitious additions modify the microstructure of the concrete in term of physical and chemical characteristics. The pozzolanic mechanism of reaction of the cementitious additions can be briefly described like the reaction of silica with the lime released by the hydration of cement, in the presence of water. It results from it from the C-S-H with poor Ca/Si report/ratio. Although this reaction is prompt and early, it is limited by the quantity of water in the HPC.

The slag of blast furnace is a by-product of the manufacture of the cast iron in blast furnaces starting from flux and coke, iron ore (the oxides FeO, Fe₂O₃, Fe₃O₄ in variable proportions) possibly. One collects it liquid towards 1550°C above the cast iron. The vitrified slag, granulated is a product hydraulic, i.e. likely to give by basic activation, of the stable products of hydration. It is obtained by brutal cooling by water under pressure; it is a sand of granulometry 0/5 mm.

In the slag cements, the clinker is the principal activator of the slag; however the first produced hydrates will be those of the clinker; C-S-H and Ca(OH)₂ which uniformly cover the grains with the slag and the clinker ; thereafter the lime excess activates the hydration of the slag with a texture C-S-H similar to that of cements; it then results from it from calcium silicate hydrates and hydrated aluminates tetracalcic [Baron and Olivier [1997]; Jiang and Grandet [1989]].

What allows the solubilization of a new quantity of products until a concentration involving a new precipitation of hydrated compounds. It is this repetition of the cycle dissolution - concentration - precipitation (several years), which constitutes the catch and the hardening of the slag vitrified [Alexandre and Sebileau [1988].

Resulting precipitations are normally intended to seal the large pores; however, precipitations of the slag cements are fixed and impermeable whereas those of Portland cements are not it. Consequently the ordinary concrete is more porous than the concrete with the slag [ACI [1974]; Venuat [1971]].

[Sarkar et al. 1970] had shown that with a ground slag with a smoothness of 800 m²/kg, one obtains a significant reduction of the heat of hydration of cement, a high-strength concrete and with more compact structure. [Péra et al.1988] showed that more the granulometry of the slag is high, better are its performances.
2 EXPERIMENTAL

2.1 Materials

2.1.1 The Cement
The Portland cement used is a CPA CEM I 52,5 of the factory Saint Pierre Lacour, whose chemical composition is deferred on table 1.

Table 1. Chemical composition of cement CEM I 52,5

<table>
<thead>
<tr>
<th>Elements</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>MgO</th>
<th>SO3</th>
<th>K2O</th>
<th>Na2O</th>
<th>IR</th>
<th>PF</th>
<th>CaO1</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>64,50</td>
<td>21,01</td>
<td>4,90</td>
<td>2,80</td>
<td>0,90</td>
<td>3,00</td>
<td>0,90</td>
<td>0,20</td>
<td>0,20</td>
<td>1,10</td>
<td>0,45</td>
</tr>
</tbody>
</table>

The mineralogical composition of this cement calculated by Bogue’s method is as follows:
- C3S ............... 65,94 %
- C2S ............... 10,47 %
- C3A ............... 8,24 %
- C4AF ............... 8,52 %

2.1.2 The Slag
The slag used is a by-product of the manufacture of the cast iron, factory of El-hadjar' Annaba'. It is a sand of granulometry 0/3 mm, granulated slag cooled with the jet of water, vitrified i.e. amorphous. Table 2 gives its chemical composition. It is tiny room powders some until obtaining a large surface specific compared to cement.

The slag of El-hadjar has the advantage of being rather acid (the CaO/SiO2 report/ratio varies within the limits of 0,95 - 1,04); it is relatively stable. The result of the micro-analysis (figure 1) comes to confirm this assumption.

Table 2. Chemical composition of slag.

<table>
<thead>
<tr>
<th>Elements</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>MgO</th>
<th>SO3</th>
<th>K2O</th>
<th>Na2O</th>
<th>IR</th>
<th>PF</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>39,77</td>
<td>41,69</td>
<td>7,05</td>
<td>1,41</td>
<td>5,49</td>
<td>0,15</td>
<td>0,44</td>
<td>0,10</td>
<td>0,12</td>
<td>0,11</td>
</tr>
</tbody>
</table>

Other physical properties: Specific surface = 8 500 cm²/g.

Figure 1. Micro-analysis (x2000) of slag.
In addition to its pozzolanic capacity, the slag with such a granularity (specific surface doubles cement), will ensure the thickening of the matrix: these particles can fit between the cement grains [Behim et al. 2002].

### 2.1.3 Aggregates

Obtaining the characteristics necessary for the concrete passes imperatively by the settling of optimal compositions of the various aggregates.

These aggregates for a great part are rolled: quaternary deposit of Unpleasant (Ille and Vilaine, France), primarily siliceous in the form of quartz and, for a weak part, crushed: corneal and metabarzite.

For this work, after preliminary tests relating to as well the rheology of the mixtures of concrete as its crushing as a hardened material, the choice was concerned the aggregates of class 3/8 and 8/15.

As for sand used, it is a coarse river sand, whose fineness modulus is worth 2.47.

### 2.1.4 The Additive

The additive used is a plasticizing water reducer for concretes with high performances in conformity with standard NF EN 934-2 provided by company SIKA.

The SIKAMENT FF 86 allows the concrete clothes industry very weak report/ratio W/C having mechanical resistances very high in all term and in particular to the youths.

### 2.2 Formulation

The final composition of High Performances Concrete (HPC) without addition and that of High Performances Concrete with addition of slag (HPCS), after optimization [Chaïd et al. 2004] are reported on table 3.

#### Table 3. Compositions of concretes with and without slag.

<table>
<thead>
<tr>
<th>Components</th>
<th>Cement</th>
<th>Sand</th>
<th>Gravel 3/8</th>
<th>Gravel 8/15</th>
<th>Water</th>
<th>Additive</th>
<th>Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HPC)</td>
<td>500 kg/m³</td>
<td>573 kg/m³</td>
<td>130 kg/m³</td>
<td>915 kg/m³</td>
<td>150 l/m³</td>
<td>8 l/m³</td>
<td>-</td>
</tr>
<tr>
<td>(HPCS)</td>
<td>425 kg/m³</td>
<td>573 kg/m³</td>
<td>130 kg/m³</td>
<td>915 kg/m³</td>
<td>150 l/m³</td>
<td>8 l/m³</td>
<td>75 kg/m³</td>
</tr>
</tbody>
</table>

The procedure of malaxation to make the concrete specimens is the following:

1 - The aggregates and the binder (cement + slag) are mixed dry during for one minute.

2 - The mixing water is added with a third of the volume of superplastifiant and malaxation continues for 2,5 mn.

3 - The remaining superplastifiant is added with a final malaxation of one minute.

The concrete specimens are preserved in their mould in wet place (20°C, 95% HR) during 24 hours. They then undergo immersed in gypsum water at 20° C until the fixed terms.

The physical, mechanical and microstructural characteristics of the concretes with and without addition of slag are compared.

T 11, Durability of the HPC Cured in Sulphate Environment, Rabah Chaïd et. al.
3 FINDINGS AND ANALYSIS

3.1 Densities and mechanical resistance

Figure 2 shows the evolution of the density of the various concretes preserved in gypsum water. One note a thickening of the concrete with slag addition. Indeed, the high grinding of the slag, combined with its interaction with Portlandite to form no soluble calcium hydrosilicates, favors the increase of the compactness of the hardened concrete. This explains the increase of its density compared to the control concrete.

![Figure 2. Evolution of the densities of the concretes according to the cured time.](image)

Figure 3 shows the increase in resistance, with respect to the period of conservation in gypsum water. It is definitely higher for the concrete with the addition of slag (HPCS). After 365 days of conservation, the constraint reached is about 100 MPa, whereas for the concrete without addition (HPC) it is only 69 MPa.

The thorough grinding of the slag supported the increase in the compactness of the HPCS, which explains the increase in its density compared to the HPC. On the physicomechanical level, the slag reacts by its fineness and its pozzolanic activity, thus generating a more coherent skeleton and consequently a more resistant and more durable concrete in gypsum water.

![Figure 3. Evolution of the compressive strengths according to the cured time.](image)
3.2 Internal Structure

The reactions known as pozzolanic are faster because of the very low dimension of the reactive particles. On the one hand the newly formed products are more easily dispersed or better set out in materials; on the other hand their composition is more favorable to the incorporation of alkaline in their crystalline structure.

The microstructure of cement with addition of slag is characterized by a dense matrix with a growth of the C-H-S on the surface of the particles of the slag. Compared with cement, products of hydrations of the cement mixture - slag also have a weak Ca/Si ratio but rich in magnesia and alumina [Sarkar and XU [1996].

The observation under the scanning electron microscope (Figure 4) enabled us to examine the microstructure of the hydrates formed within the concretes after 365 days of hardening. A microstructure relatively improved in the concretes with addition of slag was noticed with interfaces relatively more densified and rich in C-S-H, characteristic of the high quality concretes.

![Figure 4. SEM Observation of the internal structural of concrete specimens after 365 days of curing.](image)

However, one can notice some plates of the lime and the presence of needles of ettringite in the cavities of the HPC. For the HPCS, the matrix having become very dense, it does not support the blooming of certain products, which thus find a free field only in the bubbles of air and the interfaces stamps aggregates.

The analysis by x-ray diffraction (Figure 5) illustrates the various crystalline phases. Which are identical for the concretes with and without slag. However, the hydration of the anhydrous compounds of the slag concrete is considerably slowed down, contrary to that of the concrete without addition. This is the consequence of the thickening of the matrix. By supporting the formation of a more compact skeleton (structure) and consequently of much higher chemical resistances.
In addition, the incorporation of the finely crushed slag also generates a granular effect related to the induced modifications on compactness of the granular skeleton. This effect acts during the hardening of the concretes and influences the extent of the modifications made on the porosity of the cementitious matrix. This explains the high propagation velocities of wave measured on the slag concrete specimens compared to the concrete without addition (Figure 6), on various terms with an increasing rise and this in spite of the character prejudicial of the medium of conservation (gypsum water).

**Figure 5.** Radiogram of different concretes cured in gypsum water.

**Figure 6.** Evolution of propagation of sound velocities through the concretes according to the cured time.
3.3 Concrete Skin

On the surface of the specimens preserved in gypsum water one observe an important deposit of gypsum needles (Figure 7), covering almost all the surface of the concrete of control unlike that of the slag concrete where the presence of the calcite crystals on the surface of the concrete is relatively more noticed compared to the concrete of control.

In addition, one note that the slag which presents the strongest contribution to the mechanical resistance also contributes in reducing the degradation of the external surface of the concrete specimens preserved in gypsum water and consecutively contributes to increase their chemical resistance.

![Figure 7. SEM observation of the surface of concrete specimens cured in gypsum water.](image)

In other words, the addition of slag contributes to the reinforcement of the connections in the cementitious matrix and also contributes to its chemical resistance by the formation of an impermeable layer made up of calcite crystallites.

A considerable deposit of the gypsum needles observed on figure 7 for the concrete of control puts in danger the permeability of the skin of concrete without addition of slag, this yield weaker chemical resistance.

CONCLUSION

The study undertaken in this communication deals with the study of degradation of the concretes with and without addition of slag by the sulphates ions.

The thorough grinding of the slag has favoured the increase in the compactness of the concretes. This explains the increase in their resistance compared to the resistance of the concrete without addition.

The observation by the scanning electron microscope enabled us to examine the microstructure of the hydrates formed within the concretes after of 365 days of hardening. A microstructure relatively improved in the concretes with addition of slag has been noticed with interfaces relatively more densified and rich in C-S-H.

The incorporation of the finely crushed slag also generates a granular effect related to the modifications induced on compactness of the granular skeleton. On the physicochemical aspect, the slag entails the formation of a concrete skin relatively more impermeable and, consequently a more durable concrete.

In conclusion, it is important to emphasis on the fact that the influence of the fineness of the slag becomes more and more significant, when one seeks to manufacture more powerful concretes.
REFERENCES


