A SUSTAINABLE CONCRETE WITH NATURAL POZZOLAN

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Deterioration of the concrete

Physical
- Structural loading
- Thermal shock
- Swelling
- Shrinkage
- Abrasion
- Leaching ...

Chemical
- Carbonation
- Alkali - aggregate
- Ions chlorine Attack
- Sulfatic Attack ...

Expansion, Cracking, Alteration
Solutions: Supplementary cement materials: SF, FAsh ..... 
Algeria: exist: laitier (washes of siderurgique industry) and natural pozzolan,
Effect of natural pozzolan on concrete resistance to sulfate attacks.

Pozzolan is from the region of BENI SAF in the west of Algeria.

The conference is organized in two parts
1- Attacks mechanisms + effects on durability in general.
2- Experimental program and results
- Sulfate attack is a chemical aggression.
- Water presence
- Permeability concrete
- Sulfate ions $\text{SO}_4$ is associated to different cations depending of environment (soil, sea water... etc)
• **SOILS**  gypsum (sulphate de calcium).
  gypsum not very soluble in water  ------ slow attack

• **SEA WATER SEA, UNDERGROUND WATER**
  Sulfates de magnesium (MgSO4)
  ------- the most aggressive because very soluble in water , also (K2SO4 - Na2SO4).

• **AGRICULTURAL SOILS**
  ammonium sulfates (NH4)2SO4
  also K2SO4, MgSO4)

• **CANALISATIONS:**  H₂S (gas) react with aerial bacteria and product sulphates ion SO₄
sulphates attacks

Internal

Gypseous or sulfurous Granulats
Addition of gypsum to clinker
Hydration reaction energy in massive concrete

External

soils
Under ground water and sea water
Industrial pollution
Bacteriological transformation

Destructive expansion
sulfates Attack

Characteristics of the concrete

Environement

Process of assessment of the aggression

Transfer of the ions sulphate controlled by the permeability and diffusity of the material.

Chemical reactions between the components of the cement and the $\text{SO}_4^{2-}$ ions

Expansion phenomenon
Apparition of new crystalline phases
Schematic presentation of the attack to the sulphates

- **Water**
- **Pores, capillary**
  - High E/C, mauvaise cure
  - **Microcracking**
    - (structural loading, heat and cold, drying and watering cycles)

**AES : External Attack Sulphate**
Chemical interactions

I) Secondary gypsum formation

Ionic substitution between the portlandite and the sulphates

Case of the sulphate of Na$_2$SO$_4$ sodium

$$\text{Ca(OH)}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} + 2\text{NaOH}$$

(Secondary gypsum, expansion)

II) Secondary ettringite formation

Starting from the residual anhydrous C3A

$$\text{C}_3\text{A} + 3\text{CaSO}_4\cdot2\text{H}_2\text{O} + 26\text{H}_2\text{O} \rightarrow \text{C}_3\text{A.3CaSO}_4\cdot32\text{H}_2\text{O}$$

(Ettringite, expansion)

from hydrated aluminates (Monosulfoaluminates)

$$\text{C}_3\text{A}.\text{Ca(OH)}_2\cdot\text{xH}_2\text{O} + 2\text{Ca(OH)}_2 + 3\text{SO}_4 + 11\text{H}_2\text{O} \rightarrow \text{C}_3\text{A.3CaSO}_4\cdot32\text{H}_2\text{O}$$

(Ettringite, expansion)
Case of the magnesium sulphate MgSO$_4$

1. Formation of expansive product

$$\text{Ca (OH)$_2$ + MgSO}_4 \rightarrow \text{CaSO}_4 + \text{Mg(OH)$_2$} \text{ (Brucite, weak solubility)}$$

$$\text{C}_3\text{A} + 3\text{CaSO}_4.2\text{H}_2\text{O} + 26\text{H}_2\text{O} \rightarrow \text{Ca}_3\text{A.3CaSO}_4.32\text{H}_2\text{O} \text{ (Ettringite, expansion)}$$

Substitution of the Ca$^{2+}$ ions by the Mg$^{2+}$ ions in the C-S-H

$$\text{C-S-H} + \text{MgSO}_4 \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + (\text{C , M})\text{-S-H} \text{ (weakly cohesive)}$$

Consequences are an expansion et cracking due to secondary ettringite and a resistance loss due to the consumption of CSH. The silicate of hydrated magnesium (Mg-S-H) formed doesn't have any binding properties, and therefore the hydrated becomes soft and disjointed.
Primary ettringite = formed in beginning cement hydration. Not nocive but indispensable to regulate cement prise.

Secondary ettringite = Expansive,
- molar volume is to 3 à 8 higher than primary ettringite molar volume.
- crystallize in hard concrete
Experimental programm
The study was conducted on three types of concrete: an ordinary concrete BO, a high performance concretes BHP (with superplastizer) and a concrete with pozzolan BHPZ. Following parameters were studied:

Expansion, shrinkage, chloride penetration and strength, of concrete specimens immersed in the solution containing 5% NH4SO4 ammonium sulphate.
MATERIALS

Cement: CEMII/A 42.5

Surface spécifique ...3400-3650 cm²/g

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>minéralogy Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>60.88</td>
<td>24.3</td>
</tr>
</tbody>
</table>

Tab1: Chemical and minéralogy composition of the cement

Sand: Rolled siliceous sand of 3,5 mm maximum aggregate size.

Density = 2, 60

Aggregates: class 3/8 and 8/16 of silico-chaky origin (carrer)

Density = 2, 50
I.4) Natural pozzolan of volcanic origin.

- Density = 2.65

- Specific surface = 9500 cm²/g

L'indice d'activité de la pouzzolane utilisée a été déterminé selon
la norme EN 450

- \( i = \frac{R_c(MZ25)}{R_c(MZ0)} = 0.82 \)

la pouzzolane étudiée est donc réactive

<table>
<thead>
<tr>
<th>Eléments</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>P.A.F</th>
<th>R.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>44.95</td>
<td>16.91</td>
<td>9.47</td>
<td>14.59</td>
<td>3.76</td>
<td>0.20</td>
<td>1.35</td>
<td>1.34</td>
<td>4.30</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Tab2: Chemical composition of the pozzolan
R.X.D results revealed the predominance of feldspars and pyroxene and a small amount of hematite and clay.

Important quantity of portlandite developed during the cement hydration in concrete

Pozzolanic reaction continuous by consumption of the portlandite liberated during the cement hydration in concrete
1.5) Reducing superplasticizer of water

Superplasticiser: a local production, a high reducing water superplasticizer of the 3rd generation derived from polycarboxylates. The manufacturer’s use recommendations is 0.5 to 2% of the cement weight.
## 11) Composition of the concretes

<table>
<thead>
<tr>
<th>Sand</th>
<th>Gravel 3/8</th>
<th>Gravel 8/16</th>
<th>Cement (C)</th>
<th>Water (W)</th>
<th>W/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>763,5</td>
<td>137</td>
<td>837</td>
<td>425</td>
<td>212,5</td>
<td>0,5</td>
</tr>
</tbody>
</table>

**Tab5: Composition of the ordinary concrete in Kg /m³ (OC)**

<table>
<thead>
<tr>
<th>Sand</th>
<th>Gravel 3/8</th>
<th>Gravel 8/16</th>
<th>Cement C</th>
<th>Water W</th>
<th>W/ C</th>
<th>MF30</th>
</tr>
</thead>
<tbody>
<tr>
<td>763,5</td>
<td>137</td>
<td>837</td>
<td>425</td>
<td>107,66</td>
<td>0.3</td>
<td>26,48 l 28,33 Kg</td>
</tr>
</tbody>
</table>

**Tab6: Composition of the HPC in Kg /m³ (HPC)**
Tab 7: Composition of the HPC with addition of pozzolan in Kg /m³ (HPCZ)

<table>
<thead>
<tr>
<th>Sand</th>
<th>Gravel 3/8</th>
<th>Gravel 8/16</th>
<th>PZ 5%</th>
<th>C</th>
<th>W</th>
<th>W/C</th>
<th>MF30</th>
</tr>
</thead>
<tbody>
<tr>
<td>763,5</td>
<td>137</td>
<td>837</td>
<td>21,25</td>
<td>403,75</td>
<td>107,66</td>
<td>0,3</td>
<td>26,48 (l)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28,33 (Kg)</td>
</tr>
</tbody>
</table>

II.1) Specimen preparation, curing and testing

After mixing the concrete, the specimens were kept in the moulds and covered for 24 hours in the air laboratory. After demoulding, the specimens were subjected to 28 days of curing in water at 23 ± 2°C before being subjected to sulphate solutions. The concrete specimens were immersed in 5% NH₄SO₄ ammonium sulphate which was renewed every 30 days.
II.2) Evolution of the mechanical resistances

II.2.1) Compressive strength

**Fig 13:** Evolution of the compressive strength of different types of concrete in water

**Fig 14:** Evolution of the compressive strength of different types of concrete in sulphated solution
II.2.3) Permeability to the chloride ions
Charge passed in the concrete specimen kept in sulphate environment
One can note that the compressive and tensile strength of the concretes with additions of pozzolan are all superior to the ordinary concretes and high performance concretes without addition. The permeability to the chloride ions of the concretes with addition of pozzolan is lower to the ordinary concretes and high performance concretes without addition.

**II.2.4) Expansion**

![Graph showing expansion of different kinds of concrete in the sulphated solution](image)

**Fig 19: Expansion of different kinds of concrete in the sulphated solution**
The results show that the concretes undergo an expansion, nevertheless the one of the ordinary concrete is accentuated more than the one of the concretes with or without addition of pozzolan. The ordinary concrete with a W/C report = 0.5, present a matrix very porous that facilitates the penetration of the solution charged of ions sulphate in its interior. These, in presence of aluminate anhydrous tricalcique of hydrates or of aluminized them hydrated react to form the secondary, chatty ettringite the expansion.
II.2.5) Skrinkage

*Fig 20: Autogenous skrinkage of different types of concrete*

*Fig 21: Drying skrinkage of different types of concrete*
The skrinkage high performance concretes that they are with or without addition and having an W/C report = 0.3 are weaker than the one of the ordinary concrete prepared with an W/C report = 0.5.

The natural pozzolan used for the confection the high performances concrete with addition (HPCZ) acts by its very advanced fineness, its latent property and by its heat of hydration. The effect combined of these three parameters generates a sensitive increase of the skrinkage to the first ages. To means term, the supplementary CSH descended of the reaction pouzzolanique generate a reduction of the distortion due to the skrinkage. Indeed, the dense structure of the concretes due to the reduction of the measurements and percentage of the pores prevents the migration of the water.
Conclusion

The addition of natural pozzolan in combination with an appropriate dosage of superplasticizer gave a high strength concrete (70 MPa). The experimental analysis of some aspect of sustainability showed that the concrete also has good performance with regard chlorides permeability and resistance to sulphates.