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Tunisian gypsums: Characteristics and use in cement

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ABSTRACT

Gypsum materials of hundred meters thickness and interbedded with marine claystones and limestones from different paleogeographic sectors in the Tunisian territory are studied to assess their suitability for cement production. For this reason, thirty representative samples are analysed by chemical, physical and geotechnical tests. The obtained results for the studied gypsum materials are compared to Tunisian and European norms and with the local cements, currently marketed and which obey international norms. Indeed, for all samples hydraulic modulus HM, silica modulus SM and alumina modulus AM vary from (2.37–2.44), (2.48–2.68) and (1.45–2.5), respectively; whereas the required values for these modulus are (1.5–2.5), (2–3) and (1.5–2.5). The same behavior is observed for mineralogical analyses of C_3S, C_2S, C_3A and C_4AF and compressive strength at different ages.

Briefly, Tunisia contains important reserves of gypsum scattered and spread over the Tunisian territory and can be used for cement production.

1. Introduction

Tunisia is a sedimentary country which is rich with useful substances and can be used in the field of building materials. The gypsum for example, can be used in the manufacture of the hydraulic binders. ASTM C 150 limits the SO_3 content for Types I and II cements to 3.0%, for Type III cement 3.5% and for Types IV and V cements to 2.3%. Alexander et al. (1979) stated that “according to surveys published by CEMBUREAU and Cement and Lime Manufacture, the limit in various national standards ranges from 2.5 to 5.0% SO_3, depending on cement fineness or composition or both”. Gypsum renders workability to mortar more concrete by keeping the cement in plastic state at an early age of hydration (Bhanumathidas and Kalidas, 2004). This is achieved by changing the course of hydration of calcium aluminate that manifests as retardation in cement hydration. This is how gypsum is identified as a set regulator or retarder, as known popularly. Nevertheless, gypsum also contributes for strength acceleration in the early stages of hydration. This dual role of gypsum is discussed in this study. Gypsum is the set retarder for ordinary portland cement (OPC). Without gypsum, ground clinker exhibits flash setting in a few minutes, due to the rapid hydration of calcium aluminates to form calcium aluminate hydrate (CAH). On the one hand, the present paper sheds light on the mineralogical and geochemical characteristics of gypsum sediments in three different sectors (Sidi Bouzid, Gabes, Tataouine) in Tunisia. In this context, the authors give an extensive trial to have a reasonable coverage of sampling in order to have a collective idea about gypsums in the three formations from the south to the north; Mestaoua in Tataouine, Bouhedma in Gabes and Jebs in Sidi Bouzid. On the other hand, we study the cements properties with this gypsum addition. The obtained mixtures can be evaluated by comparing them to the norms and to the local cement and it is formed by 91% of clinker, 5% of limestone and 4% of gypsum. The chemical and mineralogical compositions of the cement and raw materials of local cement are reported in Table 1. The recorded values for gypsum show that the chemical ratios meet the norm NF − P15−302, except the alkalis ($K_2O + Na_2O$) and silica (SiO_2) contents which exceed its requested values. The limestone rock contains 92.3% of $CaCO_3$ and 3.76% of

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Table 1
The mineralogical and chemical analyses of cement and raw materials from local cement (regarded as a witness or benchmark). C_3S: Tricalcium-silicate; C_2S: Dicalcium-silicate; C_3A: Tricalcium-aluminate; C_4AF: Tetracalciumalumino-frite.

Elements oxide	Chemical analyses (±2%)			
	Clinker	Limestone	Gypsum	Cement
CaO	65.71	51.97	29.93	64.63
SiO_2	20.98	3.76	8.49	19.62
Al_2O_3	4.64	0.77	0.98	4.82
Fe_2O_3	3.64	0.51	0.48	3.08
SO_3	1.73	0.37	38.23	3.31
MgO	1.14	0.30	0.56	1.13
Na_2O	0.11	0.06	0.15	0.12
K_2O	0.58	0.11	0.20	0.65
TiO_2	0.01	–	–	–
Cl^-	0.018	0.040	0.026	0.047
$CaCO_3$	–	92.3	–	–
LOI at 500 °C	0.04	–	19.91	0.06
LOI at 950 °C	0.19	41.97	16.89	2.34
Mineralogical analyses (±5%)				
C_3S	C_2S	C_3A	C_4AF	
59.9	15.9	7.79	9.64	

Table 2
The geotechnical parameters of Tunisian cement (regarded as a witness or benchmark). HM: Hydraulic modulus; SM: Silica modulus; AM: Alumina modulus.

Compressive strength (MPa)		
At 2-day age	At 7-day age	At 28-day age
12.3	24.1	38.0
Specific modules		
HM	SM	AM
2.24	2.53	1.27

SiO_2. The chemical compositions of cement show acceptable contents and which is tolerated by the norm NT47–01, 2005 the average ratio of CaO, SiO_2, Al_2O_3 and Fe_2O_3 are 64.63, 19.62, 4.82 and 3.08%, respectively. Mineralogical analysis shows that the C_3S, C_2S, C_3A and C_4AF are 59.9, 15.9, 7.79 and 9.64%, respectively. These values meet the norms NT 47–01, 2005.

The geotechnical parameters of cement are mentioned in Table 2. The norm NT 47–01, 2005 of the compressive strength at 7 – day age and 28 – day age requires at least 16 and 32.5 MPa, respectively. The measured values follow the norm NT 47–01, 2005.

Based on the values of chemical oxides, we can calculate the different specific modulus; hydraulic modulus $HM = CaO/(SiO_2+Al_2O_3+Fe_2O_3)$, silica modulus $SM = SiO_2/(Al_2O_3+Fe_2O_3)$ and alumina modulus $AM = Al_2O_3/Fe_2O_3$ The modulus reported in Table 2 and show that they are suitable to statistical limits.

This research aims at assessing the impact of different Tunisian gypsums on cement properties.

2. Materials and methods

The Samples used in this work are taken from three sites of the south and the center of Tunisia in the form of intact carrots pack in PVC tubes to avoid any contamination coming from the external environment. These analyses were carried out by using the samples without modification, to keep the originality of materials with a view to their use as raw materials. They were initially dried at 105 °C until a constant weight was achieved, and they were powdered for 30 min. X–ray diffraction (XRD) patterns were recorded on a Philips X'Pert diffractometer at the Center of Researches and Technology of Energy (CRTE) using CuKα radiation (1.5418 Å) on powder samples. The accelerating voltage and filament current were maintained at 40 kV and 40 mA, respectively. For the semi-quantitative analysis of the samples, the relative abundance of minerals was estimated from the intensity of the main reflections. The experimental was error ±5%.

The major element compositions (SiO_2. Al_2O_3. Fe_2O_3. K_2O. Na_2O. MgO. CaO. MnO and TiO_2) were determined by atomic absorption spectroscopy. The standard deviation for chemical analyses was ±2%.

Loss on ignition (LOI) was measured from total weight after ignition at different temperatures for 2 h.

At the outgoing of the drier, the green samples were weighed (m_1) and fired at different temperatures, the weight is m_2. The

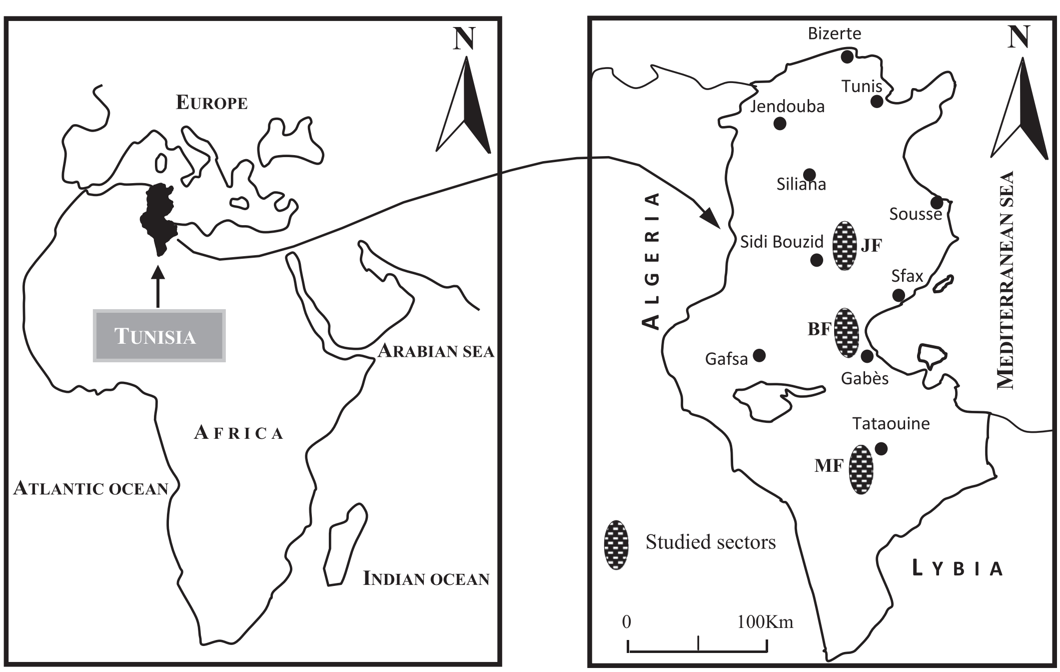

Fig. 1. The geographic situation of the studied sectors; (JF): Jebs Formation, (BF): Bouhedma Formation and (MF): Mestaoua Formation.