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Optimization of the SO_3 content of an Algerian Portland cement: Study on the effect of various amounts of gypsum on cement properties

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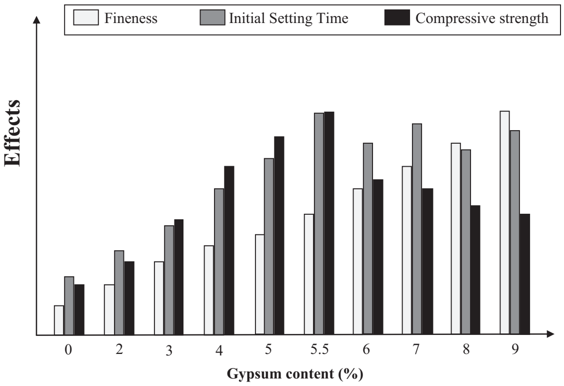
HIGHLIGHTS

- Gypsum is a cement setting regulator, it is also a cement hydration accelerator.
- The use of gypsum at the optimum content, improves several cement properties.
- Its use below or above the optimum, affects adversely the cement properties.
- The optimum gypsum content is not fixed at 5%, it varies from a cement to another.
- The optimum gypsum content depends mainly on: SO_3 %, C_3A %, Alkali % and cement SSB.

GRAPHICAL ABSTRACT



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ABSTRACT

Portland cement CEM I is obtained from (95–97%) of clinker and (3–5%) of gypsum, according to EN 197-1 (2011) standard. Sulfur trioxide SO_3 is the main component of gypsum (Calcium Sulfate Dihydrate $CaSO_4 \cdot 2H_2O$), it may also originate from clinker, the previous standard has limited its content in cement at 4%. It is known that the gypsum acts as a cement setting regulator, however, an appropriate gypsum quantity (optimum) may improve other properties such as: mechanical response, dimensional variations and hydration process. This optimum gypsum content is related to several parameters, namely: SO_3 %, cement SSB (specific surface Blaine), C_3A % and alkali %. The aim of this work is to find, through an experimental protocol, the optimum gypsum content of an Algerian Portland cement CEM I. 10 variants containing various % of gypsum were formulated, where properties of anhydrous cements, cement pastes and normalized cement mortars were studied. Results show that when gypsum is added below or above the optimum, water demand for normal consistency, setting times, compressive strength, heat of hydration, swelling, drying shrinkage and hydration degree were adversely affected. It has been experimentally demonstrated that this optimum gypsum content is 5.5% by weight.

Cement chemistry abbreviations: S, Silica, SiO_2; A, Alumina, Al_2O_3; F, Ferric Oxide, Fe_2O_3; C, Calcium Oxide, CaO; $\bar{S}$, Sulfur Trioxide, SO_3; H, Water, H_2O; C_3S, Tricalcium Silicate, $3CaO \cdot SiO_2$; C_2S, Dicalcium Silicate, $2CaO \cdot SiO_2$; C_3A, Tricalcium Aluminate, $3CaO \cdot Al_2O_3$; C_4AF, Tetracalcium Aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$; $C\bar{S}H_2$, Gypsum (calcium sulfate dihydrate) $Ca_2SO_42H_2O$; C-S-H, Calcium Silicate Hydrate, $CaO\text{-}SiO_2\text{-}H_2O$; CH, Calcium Hydroxide, $Ca(OH)_2$; $C_6A\bar{S}_3H_{32}$, Ettringite, $3CaO \cdot Al_2O_3.3CaSO_432H_2O$; $C_4A\bar{S}H_{12}$, Monosulfoaluminate, $3CaO \cdot Al_2O_3 \cdot CaSO_412H_2O$.

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1. Introduction

The Portland cement CEM I is a powdery substance made from clinker and gypsum. Clinker is formed after firing a raw mill of limestone and clay at around 1450 °C, where chemical reactions take place to form essentially, calcium silicates (C_3S, C_2S) and aluminates (C_3A, C_4AF). Cement hydration is the chemical process that allows these minerals to react with water, giving rise to new cementitious compounds called hydration products, where the major phases are: calcium silicate hydrates (C-S-H) and calcium hydroxide (CH). On complete hydration, 50–70% by weight of ordinary Portland cement is converted to C-S-H and up to 28%, to CH [1]. Contrary to CH crystals that do not participate much in the matrix resistance, C-S-H is the main compound of cement bonding properties. This mineral with a low crystallinity degree, even amorphous, is formed from reactions of C_3S and C_2S with water according to reactions 1 and 2.

$$2C_3S + 11H \rightarrow C-S-H + 3CH \tag{1}$$

$$2C_2S + 9H \rightarrow C-S-H + 2CH \tag{2}$$

The tricalcium aluminate (C_3A) has a very high reactivity with water, which is the main cause of flash setting. Without gypsum in the binder, it can dissolve rapidly in water leading to an intermediate phases of hexagonal calcium aluminate hydrates (C_2AH_8, C_4AH_{19} and C_4AH_{13}) which turns into a more stable phase, Hydrogarnets C_3AH_6, according to reactions 3 and 4.

$$2C_3A + 27H \rightarrow C_2AH_8 + C_4AH_{19} \rightarrow 2C_3AH_6 + 15CH \tag{3}$$

$$2C_3A + 21H \rightarrow C_2AH_8 + C_4AH_{13} \rightarrow 2C_3AH_6 + 9CH \tag{4}$$

Gypsum is an indispensable component in the cement manufacture, it's used mainly for regulating the setting time of cement. However, some of the mechanical properties of cement, namely strength, shrinkage and expansion in water may be affected by its level in the matrix [2]. Also, and in order to reduce the grinding energy required to produce cement, the gypsum is often added to the clinker upon its cooling and during the final grinding process in cement plants. Gypsum is a transparent or translucent sulfate mineral composed of calcium sulfate, found and mined, primarily from sedimentary deposits. Usual form of gypsum in nature is Dihydrate ($CaSO_4{\cdot}2H_2O$), more rarely Anhydrite ($CASO_4$), but Hemihydrate ($CaSO_4.1/2H_2O$) is extremely unusual due to its unstable character.

To obtain cement, the sulfate source can be determinative. It is known that anhydrite dissolves very slowly in water, which affects the formation of ettringite and consequently, the resistance evolution, particularly at a very early age [3,4]. According to Agabgbou et al., [5], mechanical properties of cement pastes and mortars were more affected when hemihydrate is used, especially, in terms of dimensional variations where a greater drying shrinkage was found. In the field of cement industry, term of gypsum refers generally to calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$). The gypsum content in cement is expressed in terms of its trioxide sulfate (SO_3) level. Portland cement contains usually around 5% of gypsum, but its level from SO_3 must be less than 4%, according to the European standard EN 197-1.

In the presence of water, gypsum reacts quickly with C_3A (Reaction (5)) to generate an Aft phase known as Ettringite ($C_6AS_3H_{32}$). The retardation mechanism of gypsum is forming these very fine grained crystals of ettringite, which develop a protective film on the cement particle surface to reject the movement of water [6] and delay the setting time of cement.

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \tag{5}$$

After exhaustion of gypsum, the residual C_3A reacts with the formed ettringite giving rise to an AFm phase (calcium monosulfoaluminate) according to reaction 6:

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H_2O \rightarrow 3C_4A\bar{S}H_{12} \tag{6}$$

Similarly, the tetracalcium aluminoferrite (C_4AF) reacts without (Reaction (7)) and with gypsum (Reactions (8) and (9)), but more slowly than C_3A and releasing a lower hydration heat.

$$C_4AF + 10H \rightarrow C_3AH_6 + CH + FH_3 \tag{7}$$

$$C_4AF + 3C\bar{S}H_2 + 30H \rightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \tag{8}$$

$$2C_4AF + C_6A\bar{S}_3H_{32} + 12H \rightarrow 3C_4A\bar{S}H_{12} + 2CH + 2FH_3 \tag{9}$$

The effect of gypsum on the hydration of C_3S is widely studied by Menetrier et al., [7]. It has been demonstrated that the dissolution rate of C_3S increased in the presence of gypsum. Kurdowski [8], reported that the gypsum accelerates the C_3S hydration mainly in the pre-induction period, its effect on cement hydration takes two aspects. It improves the amount and constitution of C-S-H gel, on the other hand, the C-S-H cohesiveness, being the function of C/S ratio, is reduced.

In some recent studies, it appears that the authors have chosen arbitrarily the percentage of gypsum in the formulation of their cements. Although these percentages vary between 3 and 5, the SO_3 content in gypsum varies from one research to another (Table 1). In cementitious system, a low gypsum content should not ensure sufficiently the retardation effect, while high gypsum level will affect considerably the cement strength and its dimensional stability. Moreover, the gypsum over dosage may have long term negative consequences that adversely affect the durability of cement concrete causing its serious damage.

Leklou et al. [14] reported that the Delayed Ettringite Formation (DEF) is a type of Internal Sulfate Attack (ISA) observed in cementitious materials and caused by heat-induced decomposition and/or prevention of normal ettringite formed during the initial hydration of cement at elevated temperature (above about 70 °C) and its re-crystallization in the hardened matrix. This physico-chemical phenomenon induces an expansion of the cement paste and leads to cracks in concrete. These cracks result in a decrease of the mechanical performances and durability parameters of the material.

High content of gypsum in cement may be considered as one of the main causes of DEF. That's why and according to Paris et al. [15], limiting sulfate additions in cement is common to avoid DEF. The same authors noted that when excess soluble sulfates do not react completely, and when temperature reaches 70 °C, the DEF phenomenon occurs. In the set concrete, the unbound sulfates present in the microstructure react to form more voluminous chemical products, causing internal stresses in the concrete to build until cracks in the hardened concrete are formed, thus, compromising the structure. Furthermore, the high gypsum content favors the internal corrosion of concrete, particularly intensive for cements with high is C_3A content and low fineness [8]. Therefore to limit this risk of expansion, especially in areas like Algeria where climatic conditions (high temperature, sun exposure and humidity) favor ettringite re-crystallization and DEF, it would be advantageous to avoid the use of cements with high sulfate contents.

In reality, there is an optimum % of gypsum, which ensure for the matrix, a maximum strength and minimum shrinkage without excessive expansion in water [2,6]. According to Soroka and Abayneh [2], the gypsum content involves two opposing effects. Gypsum was shown to accelerate the cement hydration, particularly