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Role of the filler on Portland cement hydration at early ages

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ABSTRACT

The effects of mineral additions, quartz (*Q*) and limestone (*C*) *fillers*, on Portland cement (PC) hydration are ultimately reflected in the mechanical behavior and durability of the resulting concrete. The physical and chemical interactions involved may expedite or retard the hydration rate. The present paper describes the hydration mechanism in Portland cements containing crystalline mineral additions (*fillers*, non-pozzolanic), based on the reaction rates and amount of products formed. The mineralogical composition of the Portland cements used determines their differential behavior when exposed to sulfate or attacked by chloride, separately. Ground quartz, *Q*, and limestone, *C*, were the mineral additions chosen. The results show that *direct* and *non-direct* stimulation of the hydration reactions increase with the replacement ratio and, obviously, as a result of the concomitant physic *dilution* effect. Mixing water would be responsible for *direct* stimulation. *non-direct* stimulation, in turn, would occur very early in PC hydration, for the positive and negative electrostatic charge acquired by the particles of *filler* during grinding and/or initial mixing, and subsequently the zeta potential is generated as PC hydration progresses.

On the other hand, it has also been demonstrated that both of the *fillers* interact chemically as specified below. Hence, *Q filler* is influenced by the portlandite of any PC, OPC and/or SRPC (due to its randomly inner texture totally compact, but above all, to its *acid* chemical character) to originate CSH-gels, although in a very slowly way, and for this reason, its chemical interaction is *specific* for the portlandite and *generic* for any PC of C_3A significant content. Whereas, *C filler* interacts chemically mainly with the C_3A to originate different carboaluminate types, and for this reason, its chemical interaction is *specific* for the C_3A only.

Consequently, overall system behavior varies depending on the crystalline mineral addition, the type of PC and the replacement ratio.

1. Introduction

Although perfections continue to be introduced in the existing qualitative and quantitative models for Portland cement paste hydration mechanisms [1–3], the main outlines are in place [4]. Moreover, there are models describing the hydration mechanisms for tricalcium silicate and tricalcium aluminate in the presence of pozzolanic additions [5,6]. Pozzolanic additions are natural or artificial materials with capacity to interact chemically with hydration products from Portland cement (pozzolanic activity), as a consequence the capillary pore network becomes segmented and a particle size reduction of the calcium hydroxide is produced [7]. The use of such mineral additions contribute to less consumption of natural resources entailed and a lower amount of energy needed to manufacture blended cements.

The development of cement manufacture with pozzolanic additions (i.e., amorphous and/or vitreous) has led to the gradual inclusion of crystalline mineral additions known as *fillers*, some of which interact physically and/or chemically with Portland cement or its reaction products, while others do not [8].

In light of the lack of consensus among researchers about the physical and/or chemical interaction of siliceous and/or calcareous *fillers* on Portland cement hydration at early ages in this case, this additional research has been carried out with the aim of clearing up their respective behavior.

Initially, such siliceous and/or calcareous *fillers* were used in response to the need to control bleeding in concretes with low cement content. Their effect on early age hydration of the Portland cement to which they were added was subsequently analyzed and studied [9] but not completed. The main conclusion drawn from these studies is that they stimulate hydration in the initial

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stages when their particles are moistened by the mixing water. This hydration mechanism has been termed as *direct* stimulation [9] to differentiate it from the *non-direct* one whose explanation and justification is an aim of this new study. Finally, the use of *fillers* has become so widespread that they have been standardized as well as their blended cements too [10].

On the other hand and with regard to the *filler*, the particle surfaces are positively or negatively charged during grinding with Portland clinker and gypsum and/or when mixing process with water and aggregates, consequently and respectively attracting OH^- and Ca^{2+} ions [11] very at the start of the hydration. This first layer of anions or cations in turn attracts a second cluster of Ca^{2+} or OH^- ions, respectively. As the ionic layer thickens, the electrostatic force of the particles declines [12]. Besides this, the following much more important consideration has to be also taken into account when the hydration moves forward: *all inorganic particles assume a charge when dispersed in water*.

In the case of crystalline silica (*Q filler*, in this work), this is due to surface silanol, Si–OH, groups losing a proton. The aqueous phase becomes slightly acidic (since it receives protons) whilst the silica surface becomes negative (due to the formation of $Si–O^-$). The charged particle surface then attracts a layer of counter-ions (ions of the opposite charge) from the aqueous phase. In the case of silica, positive ions (Ca^{2+} mainly, in this work) will crowd the surface. Due to ionic radii considerations, the strongly adsorbed counter-ions will not fully offset the surface charge. A second layer of more loosely held counter-ions then forms. At a certain distance from the particle surface, the surface charge will be fully balanced by counter-ions. Beyond this point, a bulk suspension with a balance of negative and positive electrolyte exists. The size of the double layer will depend firstly on the amount of charge on the particle surface. A large charge, whether positive or negative, will result in a large double layer that stops particles getting close to each other because of the electrostatic repulsion between those particles carrying the same electrical charge. This situation is typical of stable (deflocculated) suspensions having a low viscosity. Conversely, a low surface charge requires fewer counter-ions and smaller double layers. Accordingly, particles then tend to flocculate which leads to high viscosity suspension. The zeta potential (mV) can be related to the energy needed to shear the particle and its inner layer of counter-ions away from the outer layer/bulk medium. This phenomenon has been illustrated in Fig. 1. In short, as it was mentioned earlier that particle charge influences the double layer size and so the zeta potential.

Furthermore, the surface charge of calcium carbonates is scarcely changed by the change in pH under the conditions that the activity of CO_3^{2-} or Ca^{2+} is kept constant. Consequently, the hydrogen ion is not the surface charge controlling ion. It has also been reported by Sawada [13] that the surface charge of the calcium carbonate shifts to positive side with the decrease in pH. These experiments were conducted under the conditions that the equilibrium concentrations of lattice ions are not kept constant. Thus, the change in the potential is the result of the decrease in the carbonate ion concentration, $[CO_3^{2-}]$, caused by its protonation, i.e., the increase in the $[Ca^{2+}]$ concentration.

In addition, the surface properties of crystals are significantly altered by the conditions of the way of preparation and history of the crystals. Particularly, the crystal surface created by crush is very rough and active (both *fillers*, the *Q* and the *C* specially, in this work). The rate of crystal growth on rough surface is much higher than that on the smooth surface and that surface is more favorable for adsorption. Consequently, attention is called for the comparison of the thermodynamic and kinetic data between the crystals from different origins and treatment even if they have the same polymorph.

Finally and with regard to the calcite, $CaCO_3$, (ground limestone or *C filler* in this work) it presents three polymorphous [14]: the thermodynamically most stable, calcite (solubility product: $K_{sp} = 10^{-8.48}$ at 25 °C), less stable, aragonite ($K_{sp} = 10^{-8.34}$), and the most unstable polymorph, vaterite ($K_{sp} = 10^{-7.91}$). Sawada [13] has demonstrated by different concentrations of phosphate, that the chemical species adsorbed on the vaterite surface are negatively charged one, $[Ca^{2+} \cdot PO_4^{3-}]$, whereas, the chemical species adsorbed on the calcite surface are electrically neutral one: low phosphate concentration $[(Ca^{2+})_3(\cdot PO_4^{3-})_2]$, and high phosphate concentration $[(Ca^{2+})(\cdot PO_4^{2-})]$, (note that the portlandite is also non-charged species, i.e. electrically neutral one). In other words, calcite requires the adsorption of electrically neutralized species. Conversely, the vaterite surface is positive and thus the adsorption of negatively charged species is reasonably explained.

For all these reasons, this new research has been conducted, therefore, to determine the optimal replacement ratio for *fillers* depending on Portland cement, mortar or concrete requirements. In addition, the present paper describes a possible mechanism for their interaction with Portland cement based on previous studies that support its validity [15].

2. Objective

The present paper aims:

– to determine type of interaction between *fillers* (siliceous and/or calcareous) and Portland cement, during its hydration at early ages, and in the former case, whether it is of physical – by *direct*

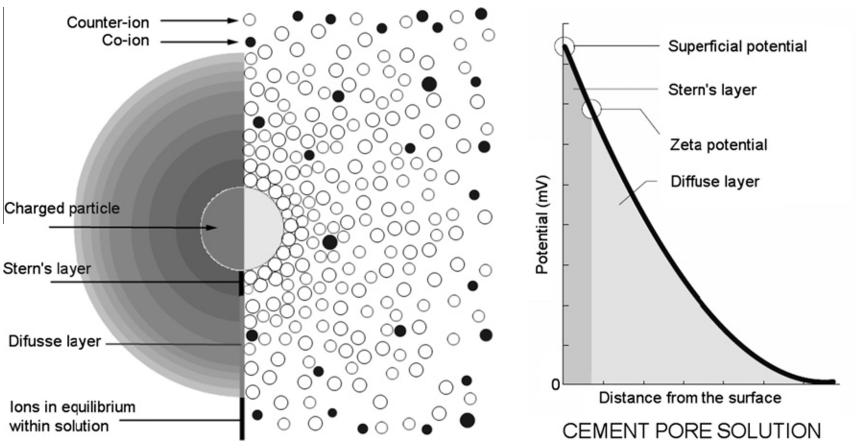

Fig. 1. Electrostatic phenomenon in a solution for a charged particle. Graphical description of the Zeta potential.