Cement and Concrete Research 90 (2016) 137–143

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Retarding effectiveness of hexitols on the hydration of the silicate phases of cement: Interaction with the aluminate and sulfate phases

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ARTICLE INFO

Article history:
Received 9 March 2016
Received in revised form 1 September 2016
Accepted 8 September 2016
Available online xxxx

Keywords:
Adsorption
Aluminate
Cement
Complexation
Retardation
Stereochemistry

ABSTRACT

This study focuses on the relationship between the retardation generated by hexitols (D-glucitol, D-galactitol and D-mannitol) on the hydration of the silicate phases of a white cement and on their interactions with the aluminate and sulfate phases. The impact of the aluminate and sulfate content of cement on their retarding effect was identified. The consumption of the stereoisomers as well as their effects on the ionic composition cement in suspension were studied and compared. The results showed that the aluminate and sulfate content of cement reduces the retarding effect of hexitols on the hydration of its silicate phases. Moreover, they adsorb differently on hydrating cement and complex with ions in solution. The impacts of the adsorption of these alditols on ettringite and of their complexation with aluminate ions in solution on their retarding effect on the hydration of the silicate phases of cement are discussed.

1. Introduction

Ordinary Portland Cement (OPC) is composed of silicate, aluminate and sulfate phases which interact between each other during its hydration. Alite (impure tricalcium silicate, C_3S) and belite (C_2S) are the silicate phases mainly composing OPC and are responsible for its setting. The latter can be retarded by using chemical admixtures such as lignosulfonates, carbohydrates and sugar derivatives. Although used since decades, these organic additives are often considered from a performance point of view by focusing on their retarding effectiveness on the setting time of OPC [1–9]. Nevertheless, with the diversity of existing cements and with the increasing levels of Supplementary Cementitious Materials of cement in modern concrete, the knowledge on the interactions between chemical admixtures and mineral surfaces and their influence on the hydration mechanisms of cement seems to be a subject of priority [10,11].

The retarding effect generated by several polysaccharides (dextrin, starch) and saccharides derivatives (D-gluconate, D-glucitol) on the hydration of OPC were reported to be sensitive to its composition and particularly to its aluminate content [1,4,8]. Several setting retarders were also shown to be adsorbed on aluminate hydrates [1,12,13]. Moreover, the presence of D-gluconate was also revealed to enhance the concentration of aluminate ions during the hydration of OPC in suspension [1]. Hence, some setting retarders change the ionic composition of the solution and interact with aluminate hydrates when hydrating OPC. However, the impacts of the different interactions of the organic molecules with the aluminate phases of OPC on the hydration of its silicate phases are not well identified and understood.

This present study intends to contribute to fill this gap of knowledge by focusing on the interactions of hexitols during the hydration of a white cement and on their effects on the hydration rate of its silicate phases. Table 1 details the structure of the organic molecules studied that are D-glucitol, D-galactitol and D-mannitol which differ from one another in the stereochemistry of their hydroxyl groups. The retarding effects of these organic molecules on the hydration of pure C_3S and of the silicate phases present in cement were first identified by isothermal calorimetry and compared. Secondly, the influence of the aluminate content of cement on the retardation caused by hexitols on the hydration of its silicate phases was assessed. Thirdly, the consumption of these sugar alcohols during the hydration of cement was revealed by Total Organic Carbon measurement. Then, the impacts of these organic compounds on the ionic concentration of cement and C_3S suspensions measured using the Inductively Coupled Plasma – Atomic Emission Spectroscopy are compared. Finally, the relation between the different interactions of hexitols relative to the aluminate phase of cement and their retarding effect on the hydration of its silicate phases are discussed.

2. Experimental procedures

2.1. Materials

The preparation of all pastes, suspensions and solutions was made with water which was both distilled and deionised. The molecules

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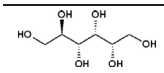
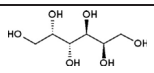
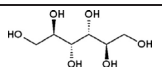
http://dx.doi.org/10.1016/j.cemconres.2016.09.018
0008-8846/

Table 1
Chemical structures of the molecules studied.

D-glucitol	D-galactitol	D-mannitol
		

studied were D-glucitol (≥98%), D-galactitol (≥99%) and D-mannitol (≥98%) from Sigma Aldrich in powder form.

A white cement and a C_3A–gypsum-hemihydrate mixture both from Lafarge as well as C_3S from Mineral Research Processing were used. Table 2 indicates the physical and chemical characteristics of these minerals. In all the following the study, the C_3A–gypsum-hemihydrate mixture will be called aluminate-sulfate mixture. White cement with different C_3A contents was made by adding different amounts of the aluminate-sulfate mixture to the initial white cement in order to increase its C_3A content from 2.7 to 15%.

Calcium oxide used to make saturated lime solutions was obtained after decarbonation of calcium carbonate (98.5–100%, VWR AnalaR NORMAPUR) at 1000 °C for 24 h. Saturated lime suspensions were first made by equilibrating an excess of freshly decarbonated lime to water kept at 25 °C in a thermoregulated bath during minimum 24 h. Finally, the saturated lime solutions were obtained by filtering the saturated lime suspensions (0.1 μm cellulose ethers, Merck Millipore).

2.2. Methods

2.2.1. Study of the effect of hexitols on the hydration rate of C_3S and white cement with different C_3A contents

The heat flow released during the hydration of the different mineral powders in presence of hexitols was monitored by isothermal calorimetry (TAM AIR) at 23 °C. 1 g of powder was mixed with 0.4 mL of aqueous solutions with and without sugar alcohols (Liquid to Solid ratio, L/S = 0.4). All these pastes were stirred for 2 min at 3200 rpm in different plastic ampoules. Then, the latter were immediately capped and inserted in the calorimeter.

The impacts of hexitols on the calorimetric curves monitored during the hydration of C_3S and cement were different than the ones observed during the hydration of cement with different C_3A contents. Hence, they were analyzed differently as described below.

2.2.1.1. Definition of the retardation generated by hexitols on the hydration of C_3S and cement. Fig. 1 shows the typical calorimetric curves obtained for C_3S and cement pastes with and without D-glucitol. It represents the evolution of the heat flow resulting from the reactions of dissolution of the anhydrous phases and of the precipitation of hydrates over time. Hence for pure C_3S, the calorimetric curve reveals the heat flow released by the hydration of the silicate phase whereas for cement, it reveals the heat flow released by the overall hydration of the silicate, aluminate and sulfate phases. Nevertheless, the peak observed during the hydration of C_3S and cement on the calorimetric curves indicates the acceleration of the hydration of the silicate phases which are the main phases of these two mineral compounds. The shape of the calorimetric curves measured during the hydration of C_3S and cement pastes stays the same in presence of the different hexitols in the range of concentration studied (0–54 mmol/L in cement and 0–11.3 mmol/L in C_3S pastes) compared to their respective reference without additive as can be seen for D-glucitol, Fig. 1. However, the molecules lengthen the induction period during the hydration of C_3S and cement pastes compared to the one of their respective reference. Given that hexitols do not change the shape of the calorimetric curve obtained during the hydration of C_3S and of cement, the retardation was defined as being the difference in time between the maximum heat flow of the samples with alditol and the reference without additive as indicated in Fig. 1. Finally, the retardation induced by different concentrations of hexitols on the hydration of C_3S and on the one of the silicate phases present in cement was measured by using this method.

2.2.1.2. Definition of the time ending the induction period when hydrating cement with different C_3A contents with and without alditols. Fig. 2 represents the calorimetric curves obtained during the hydration of cement pastes with 5% of C_3A with and without D-glucitol (20.3 mmol/L). The variation of the percentage of C_3A in cement pastes with hexitols was sometimes changing the shape of the calorimetric curves. In this case, instead of considering the time at the maximum heat flow, the time ending the induction periods was taken into account. This time has been arbitrarily taken being equal to the one found at the intersection between the slope of the calorimetric curve at the inflexion point during the acceleration period (highest acceleration) and the x-axis as shown in Fig. 2, the recorded calorimetric curves are given in suplementary material. Using this method, the concentration of the different hexitols was kept constant (20.3 mmol/L) but the percentage of C_3A of the initial cement was increased from 2.7% to 15%.

2.2.2. Adsorption measurements of hexitols during the hydration of cement in suspension

The adsorption of the different organic molecules was measured during the hydration of cement in suspension with L/S = 5 (150 mL of saturated lime solution and 30 g of cement). These suspensions were stirred in thermoregulated cells at 25 °C and under a continuous nitrogen gas atmosphere to prevent the formation of calcium carbonate. Samples of the cement suspensions were collected over time and were centrifuged at 9000 rpm for 5 min in Nalgene tubes. Finally, the supernatants were filtered with a syringe filter (0.2 μm PTFE, VWR). A small known quantity of orthophosphoric acid (85%, Analar Normapur, VWR) was added to the filtrates before their analysis. The adsorption of the organic molecules was determined by using the depletion method. The non adsorbed portion of molecules remaining in the acidified filtrates was measured by analyzing the Total Organic Carbon (TOC) of these solutions (Shimadzu TOC analyser V_{CPN}).

The adsorption of polyols on cement in suspension was measured over time and was stable during the induction period. Hence, the value at this plateau of adsorption was used to determine the adsorption of a molecule on cement for a given initial concentration.

Table 2
Physical and chemical parameters of the different mineral phases.

	Cement	C_3S	C_3A–gypsum-hemihydrate
Specific surface area (m^2/g)	0.4[a]	0.5[b]	0.3[b,c]
Mono. alite (%)	66.1	–	–
Tric. alite (%)	0.0	100.0	–
Belite (%)	24.2	–	–
Ferrite (%)	0.4	–	–
Cub. aluminate (%)	2.0	–	80.5
Ortho. aluminate (%)	0.7	–	–
Lime (%)	0.3	–	–
Gypsum (%)	0.2	–	9
Hemihydrate (%)	0.7	–	15.0
Anhydrite (%)	1.0	–	–
Calcite (%)	2.4	–	–
Portlandite (%)	1.8	–	–
Quartz (%)	0.1	–	–

– = not measured items.
[a] Blaine method.
[b] Calculated from particle size distribution assuming that the density of particles is homogeneous with the size, that the particles are spherical and considering these different densities (C_3S: 3210 kg/m^2 and C_3A: 3030 kg/m^2). The PSD has been measured by Laser Diffraction (Malvern mastersizer 2000) in ethanol (≥99.5%, Sigma Aldrich). The particle size distributions are given in supplementary material of this paper.
[c] The proportion of $C_3A/CaSO_4$ has been chosen to correspond to a properly sulphated cement. The hemihydrate/gypsum proportion has been measured from Rietveld analysis of the XRD pattern. It was initially fixed at 50/50.