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Adsorption kinetics of retarding admixtures on cement with time controlled addition

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ABSTRACT

Retarders are widely used in construction materials to control the setting and hardening. The present study focuses on changes in the rheological behavior, the admixture adsorption and the pore solution composition with a controlled addition of sodium gluconate and ethylenediamine tetra(methylene phosphonic acid) (EDTMP) in cement.

The adsorption of the sodium gluconate was influenced by time of addition of dosage. Delayed addition induced a depot effect which was reduced by the ongoing hydration whereas the adsorption of EDTMP was not affected by time of dosage. Nearly the complete admixture concentration was directly adsorbed on clinker phases or first hydration products.

For sodium gluconate, an interaction with ferrite containing clinker phases and a calcium complexing mechanism were suggested. In contrast, EDTMP seemed to have no significant influence on the calcium concentration. With regard to the sodium concentration a fast adsorption of sodium gluconate was determined. Furthermore, a competitive adsorption between dissolved sulfate and retarder molecules or a complex formation mechanism is supposed.

1. Introduction

The setting and hardening behavior of a wide variety of inorganic binders used as construction materials (e. g. cement or plaster) is controlled by the addition of different retarding and accelerating admixtures. Usually, both admixtures are combined with each other to yield a precise adjustment of the setting and hardening behavior for practical applications like cementitious tile adhesives, self-leveling screeds etc. However, till today an exact separation of the setting and hardening process is not controllable because of which, the applied retarders will influence both, the setting and hardening process.

Retarding admixtures can be classified due to their basic materials in inorganic and organic admixtures. Inorganic retarders are based on borates, phosphates, fluorine silicates and chemical compounds based on zinc. Phosphate based admixtures retard the hydration kinetics of the aluminate as well as silicate reaction in cementitious binders due to the formation of hardly soluble complexes with dissolved ions in the pore solution. Due to the subsequent precipitation of these complexes on available surfaces of clinker and first hydration products, further ion dissolution and ongoing cement hydration is hampered [1–5].

Basic materials for organic retarders are sucrose, glucose and sugar

containing admixtures like lignosulfonates as well as hydroxyl carbon acids [1–3]. Sucrose retards the hydration by stabilizing hexagonal aluminate hydrates and their conversion to stable phases. With regard to its dosage, different concentration levels between 0.03 and 1.0 wt% of cement are reported [6–9]. Beside the admixture concentration the retarding effect of sucrose is influenced by the addition time. With direct addition, the hydration of C₃A and formation of AFt is accelerated whereas a delayed addition retards the hydration reactions [9–11]. Compared to sucrose, the C₃A hydration is less influenced by glucose. However, the higher stability of the glucose derivate in the high alkaline pore solution retards the hydration in a sufficient way [8]. In general, different mechanisms of sugar based retarding admixtures are reported in the literature, e.g. [12–15].:

- Adsorption on portlandite and prehydrated surfaces and development of a surface coating, which prevents hydrolysis and nucleation and/or
- precipitation of hardly soluble calcium complexes from pore solution, subsequent inhibition of the hydrolysis by these precipitations and prevention of nucleation.

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Juilland and Gallucci [16] investigated the nucleation and growth of C-S-H in presence of sucrose. They assumed that the onset of the acceleration period is mainly driven by the composition of the pore solution as well as the precipitation of portlandite. Dodson and Farkas [17] studied the retardation effect of a delayed addition of different retarding admixtures on cement. With delayed addition, a decrease in the consistency and lower sulfate concentration in the pore solution was observed. Similar results are reported by Rickert [18,19] and Goetz [20]. They proposed a mechanism similar to the competitive adsorption between superplasticizer molecules and dissolved sulfate ions in the pore solution. The slightly retarding effect by the direct addition of the admixtures is induced by an unspecific adsorption on first-formed C-A-H, AFm and AFt phases. By the delayed addition of the retarder, firstly the hydration of C₃A and subsequent surface growth was completed. Retarder molecules in pore solution adsorb preferentially on first-formed hydration products.

The influence of the aluminate and sulfate content of the cement on the retarding mechanisms of different hexitols was recently published by Nalet and Nonat [21]. Furthermore, they have investigated the complexing power and adsorption of different retarders like sugar derivatives, amino-carboxylates and phosphonates on C-S-H phases. In this research, all retarders showed a complexation of calcium and hydroxide ions. Furthermore, amino-phosphonates, D-gluconate and D-glucitol also complex silicate ions [22].

The objective of the present research is to highlight the adsorption behavior of different retarding admixtures as well as the pore solution composition by a time controlled addition to different cement types. The benefit of a time controlled addition of different chemical admixtures in cementitious materials has been published by the authors previously [23–27]. Beside the retardation, retarders are well known to induce a slightly liquefying effect with improved rheological properties [28]. The retarder adsorption was determined by the analysis of the organic carbon content in pore solution and investigations of the rheological behavior of cement pastes. Furthermore, the ion composition of the pore solution was investigated by chemical analysis via optical emission spectroscopy.

2. Materials and methods

2.1. Materials

The effect of two commercially available retarders for concrete applications based on sodium gluconate (Na-Glu) and ethylenediamine tetra(methylene phosphonic acid) (EDTMP) were studied by time and dosage controlled addition. The material properties of the retarders are given in Table 1. The retarders were added to three different cements according to DIN EN 197-1 [29], an ordinary Portland cement with high sulfate resistance (OPC, CEM I 42.5 R SR3), a Portland slag cement with early strength development (CEM II/A-S 52.5 R) and a blast furnace slag cement (CEM III/A 42.5 N). All cement types were based on the same cement clinker from one rotary kiln. The objective behind the cement selection was to determine the effect of the slag content in the cement while avoiding any influences of the clinker composition. The chemical analyses as well as the technical data of the cements are given in Table 2. An exemplary coding of the different investigated mixtures

Table 1
Material properties of the retarders (manufacturer's data).

Retarder	Na-Glu	EDTMP (Na ₅ salt)
Basic material	D-Gluconic acid	Ethylenediamine tetra(methylene phosphonic acid)
Active agent [wt%]	≥ 99.0	31.0
True density [g/cm ³]	1.79	1.34

Table 2

Chemical and mineralogical clinker phase composition of the cements used [wt%] (manufacturer's data).

	CEM I 42.5 R-SR3	CEM II/A-S 52.5 R	CEM III/A 42.5 N
CaO	62.90	57.60	52.30
SiO ₂	20.10	21.40	25.40
Al ₂ O ₃	3.45	5.64	6.74
Fe ₂ O ₃	4.61	2.82	2.24
MgO	3.51	4.34	4.96
K ₂ O	0.55	0.84	0.87
Na ₂ O	0.20	0.28	0.28
SO ₃	2.88	3.38	3.09
C ₃ S	57.54	49.00	35.70
C ₂ S	17.64	9.90	6.30
C ₃ A _{cubic}	1.76	1.90	1.30
C ₃ A _{ortho}	0.65	5.60	3.90
C ₄ AF	14.38	7.80	5.00
LOI	2.62	1.85	1.72
Slag content	–	17.10	39.00
Specific gravity [g/cm ³]	3.18	3.10	3.03
Blaine value [cm ² /g]	4370	5380	5220
Specific BET surface [m ² /g]	1.21	1.72	1.77

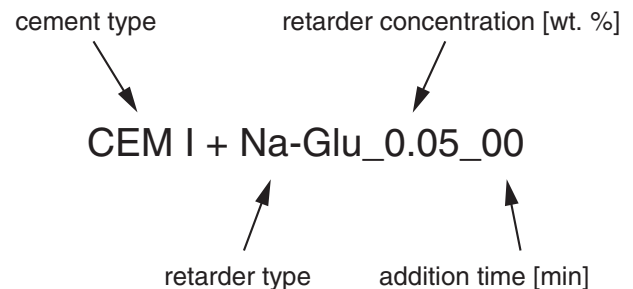


Fig. 1. Sample code applied in the study.

is given in Fig. 1.

2.2. Surface growth behavior

The specific surface development of the plain cement during the early cement hydration was characterized by nitrogen adsorption analysis based on the work of Brunauer et al. [30] (BET analysis; Carlo Erba Instruments, Sorptomatic 1900). For the sample preparation, 10 g of cement was blended with 5 ml deionized water in a vortex mixer for 60 s. For further experimentations, 100 ml isopropanol was added to the samples to stop the cement hydration and was mixed for another 60 s. Subsequently, the samples were stored for seven days and then decanted and vacuum dried for another seven days before analysis.

2.3. Rheological analysis

To investigate changes in the rheological behavior, cement pastes with a water to cement ratio (w/c) between 0.35 and 0.60 were mixed with a mortar mixer according to DIN EN 196-1 [31]. The retarders were dosed with a concentration of 0.05 and 0.15 wt% of cement directly, respectively 5 or 15 min after addition of the water. The mixing procedure was 90 s of mixing, 60 s scraping the paste off the walls of the bowl, addition of the retarders after 5 or 15 min if necessary and followed by 90 s of mixing.

The rheological measurements were carried out with a rotational viscometer (Viskomat NT, Schleibinger Germany) with a cement paste probe. The samples were sheared with a step profile at 100, 80, 60, 40 rpm each step for 3 min. Afterwards, the rheological characteristics yield stress and viscosity (relative device-dependent values) were

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