Effect of polymer latexes with cleaned serum on the phase development of hydrating cement pastes

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ABSTRACT

The effects of polymer latexes on cement hydration were investigated by the combination of isothermal calorimetry, in-situ XRD and Cryo-SEM. Two model latexes with varied amounts of anionic charges were used for measurements after cleaned by dialysis to remove the serum components. This study confirms that in-situ XRD technique can be successfully adapted to hydrating cementitious systems in the presences of polymer latexes to quantitatively follow evolution of mineral phases involved in cement hydration. Results show that both polymers retard aluminate reaction and depress silicate reaction, by delaying the dissolution of C_3A, anhydrite and gypsum and consequently the formation of ettringite, and reducing the dissolution of C_3S and the formation of C-S-H. The anionic colloidal polymers exhibit more pronounced retardation effect on aluminate reaction than on silicate reaction due to stronger electrostatic interaction between the polymer particles and the positively charged aluminate phases. The more charged latex shows stronger retardation.

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1. Introduction

Latex polymers, including styrene–butadiene copolymer (SBR), styrene–acrylate copolymer (SA) and ethylene–vinyl acetate (EVA) copolymer, in forms of either aqueous dispersion or re-dispersible powder have been for long used in cement mortar as well as in concrete to improve various properties such as workability, adhesion to substrate, mechanical strength, ductility, cracking resistance, impermeability and durability [1–6]. It has been often reported that the addition of polymer latexes significantly influences the cement hydration kinetics and the hydration products. In most cases, polymer latexes retard cement hydration to different extents [7,8]. In our previous study [9], we have raised the question "How do the polymer particles retard cement hydration?". By using well characterized SA polymer latexes, it was shown that the type and density of charges on surface of polymer particles are the main decisive factors for the retarding effect of polymer latexes on cement hydration. We proposed the retardation mechanism of polymer latexes as the following two manners: 1) *Chemical retardation*, that involves complexation of R–COO⁻ with calcium ions, by which the concentration of free calcium ions in aqueous phase of hydrating

cement paste is reduced, and thus the induction period is prolonged; 2) *physical retardation*, which is mostly related to the covering layer on hydrating cement surface due to adsorption of polymer particles. The adsorbed polymer skin on mineral surface, which has been clearly observed by means of confocal laser scanning microscope [9], may inhibit the nucleation and growth processes of hydration products and, thus decelerates the hydration rate during the acceleration period. The adsorption mechanism of polymers on the surface of cement grains was also studied by Plank et al. [10]. Baueregger et al. [11] recently focused on the impact of SBR polymers on cement hydration and concluded that Ca^{2+} complexation plays a key role in the interaction between polymers and cement hydration. Larbi and Bijen [12] also concluded from their research in 1990 that there must be an interaction between metal ions in cement pore solution and the carboxylic groups of the polymer.

On the other hand, cement hydration has been known as dissolution–precipitation processes, including mainly silicate reaction and aluminate reaction [13]. During the early hydration of cement, the silicate reaction majorly includes the dissolution of C_3S phase and the formation of C-S-H, while the aluminate reaction comprises the dissolution of C_3A, sulfate phases and the formation of ettringite. When a polymer latex is added into a cement paste, what are the impacts of polymer particles on each reactions during cement hydration, however, stay undiscovered. Silva et al. found that EVA polymer decreases the portlandite amount in a hydrating Portland cement paste, due to the

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consumption of Ca^{2+} ion by the polymer [14]. By using soft X-ray transmission microscopy, they also reported that the dissolution of C_3S was hindered by EVA polymer [15] and during early hydration stage in C_3A system, the formation of ettringite crystals was inhibited by the EVA polymer particles [16].

With respect to the methodologies and techniques for investigation of cement hydration, isothermal calorimetry has been a powerful and easy technique to provide overall information of the kinetics of cement hydration. A typical calorimetry curve for ordinary Portland cement, is usually characterized as five stages, the initial stage, the induction period, the acceleration period, the deceleration period and the long-period of slow reaction [17]. However, information about reaction of each phase is unobtainable from calorimetric methods. In recent years, Jansen and Neubauer et al. have intensively contributed to enable a better interpretation of the calorimetric data by following the time-dependent phase evolution during early hydration of cement using the technique of in-situ XRD [18–23]. It has been clearly shown that during the early cement hydration, the heat flow of a hydrating cement paste is contributed mainly by two reactions, the silicate reaction and the aluminate reaction. The silicate reaction includes the dissolution of C_3S and the formation of C-S-H and CH. Thanks to the fact that the dissolution of C_3S and the formation of C-S-H are synchronously taking place, the heat generation of the silicate reaction can be simply calculated by the measurement of alite content and using the enthalpy of silicate reaction of -561 J/g alite. The aluminate reaction contains the dissolution of C_3A and calcium sulfate phases (gypsum, basanite and anhydrite), and the formation of ettringite. It has been found that these dissolution and precipitation processes do not run synchronously. Thus, the heat flow generated by the aluminate reaction has to be subdivided into the individual dissolution and precipitation processes. They have concluded that the main hydration peak in the acceleration period is mainly contributed by the silicate reaction as well as the formation of ettringite, while the second hydration peak (or shoulder), which is usually called sulfate depletion peak, is produced by the recommended C_3A dissolution.

The Rietveld refinement of in-situ XRD data enables to quantitatively track the evolution of various phases involved in cement hydration, including clinker phases and hydration products such as ettringite and C-S-H. The combination of the calorimetric technique and the in-situ XRD allows a much deeper insight into the cement hydration in the presence of polymer particles. In this paper, we choose two model well-characterized latexes with varied surface charge of polymer particles to investigate their impacts on the evolution of each mineral phase during early cement hydration in detail, using the combination of heat flow calorimetry, in-situ XRD and Cryo-SEM. The studies of early cement hydration in the presence of polymer by using the combination of such methods are rare in literature. Hence it is the intention of the authors to close this gap with this publication.

2. Experimental

2.1. Materials

Portland cement, CEM I 52.5 R-Milke® premium complying DIN EN 197–1 was provided by Heidelberg Cement AG. The Blaine value of the cement is 590 m^2/kg. The chemical and mineralogical compositions of the cement are indicated in Table 1. Phase composition of the cement was determined by means of X-ray diffraction and Rietveld-refinement. Chemical composition was measured using XRF analysis.

Two styrene–acrylate co-polymer model latexes which were synthesized via emulsion polymerization and cleaned by dialysis technique to remove the free surfactant, salts and oligomers remaining in aqueous phase to avoid their influences on cement hydration, were used in this study. The detailed synthesis and characterization methods have been described in our previous publication [9]. The main properties of these two polymer latexes are listed in Table 2 and schematically

Table 1
Chemical and mineralogical compositions of cement.

Oxide	wt.%	Phase	wt.%
SiO_2	22.7	C_3S	62.5
Al_2O_3	3.7	C_2S	14.3
Fe_2O_3	1.4	C_3A	8.3
CaO	67.2	C_4AF	2.1
MgO	0.7	Anhydrite	3.6
K_2O	0.7	Bassanite	1.1
Na_2O	0.2	Gypsum	1.3
SO_3	3.1		
LOI	1.3		

described in Fig. 1 [9]. As indicated in Fig. 1, the major difference between the two latexes is the surface charges of polymer particles. Both polymer particles are negatively charged attributed to the anionic emulsifier and the persulfate initiator used in synthesis. Both latexes exhibit "hairy colloidal particle" due to the co-polymerization of the water soluble monomers during synthesis of the latexes. The surface of polymer particles in L2 is enriched in carboxylate groups, which are mainly contributed by the functional monomer methacrylic acid (MAA), while the co-monomer methyl poly(ethylene glycol) methacrylate (MPEGMA) in L1 leads to the particle surface less negatively charged due to introduction of the macro-monomer. Our previous study has clearly shown that the two latexes exhibit different adsorbing behaviors on surface of cement grains and thus different impacts on cement hydration. Namely, L2 presents high adsorbing tendency on cement surface and L1 has less adsorbing capability [9]. Deionized (DI) water was used in all experiments of this study.

2.2. Paste experiments

2.2.1. Hydration kinetics of cement pastes by iso-thermal calorimetry

TAM-air micro-calorimeter (TA Instruments®, USA) was employed to monitor the heat evolution in cement pastes to investigate the influences of polymer latexes on cement hydration. Before test, the calorimeter was regulated at constant temperature of 23 $\pm$ 0.02 °C and then equilibrated for 24 h. Cement paste was prepared by thoroughly mixing 5.0 g cement with DI water and polymer latex in an ampoule. Water–cement ratio (W/C) of the cement paste was fixed at 0.41 and polymer dosage in cement paste was fixed at 12% by weight of cement (bwoc). It should be mentioned that the polymer dosage in this paper was counted by mass of polymer solid in the latex, excluding the mass of the aqueous phase of the latex. Thereafter, the freshly mixed cement pastes were promptly placed into the channels of the calorimeter. The heat evolution within 72 h was recorded. It should be mentioned that external stirring of the cement pastes with placing inside the calorimeter after some minutes will lead to non-meaningful heat signal during the very initial period. Therefore, the calorimetric data within 20 min are not reliable and were not considered for evaluation of data and discussion of the results.

2.2.2. Quantitative in-situ XRD measurement

The quantitative phase evolution over hydration time was determined by means of X-ray diffraction. To this end the cement paste for investigation was mixed and prepared in a special sample holder and measured at constant temperature of 23 $\pm$ 0.02 °C over the first 50 h of hydration with 10 min scan step.

Since the water and the polymer added into the cement paste are non-crystalline phases a method for quantification of absolute amounts for each crystalline phase based on Rietveld refinement was chosen [20,21,24]. This method allows an individual quantification of each phase without any normalization of all crystalline phases to 100 wt.%. The method is described in detail elsewhere [20,21,24].

When working on cement pastes with polymers, one has always to keep in mind that the mass attenuation coefficient of the sample