



Retardation mechanism of anionic asphalt emulsion on the hydration of Portland cement

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HIGHLIGHTS

- Retardation effect of anionic asphalt emulsion on cement hydration was confirmed by setting time, hydration heat and electrical resistivity.
- The results of MIP and SEM validated that cement-asphalt paste is more porous in comparison to pure cement paste.
- ESEM was employed to observe the adsorption of asphalt membrane onto the surface of cement grains.
- Hydrogen bonds formed between different water molecules in anionic asphalt emulsion reduced the reactivity of water molecules with cement.

ARTICLE INFO

Article history:

Received 9 May 2017

Received in revised form 14 December 2017

Accepted 22 December 2017

Keywords:

Anionic asphalt emulsion

Cement hydration

Retardation

Water reactivity

ABSTRACT

Cement-asphalt (CA) mortar, a grouting material consisting of Portland cement (PC), asphalt emulsion, sand, water and other related admixtures, has been widely used as a cushion layer material in the construction of High-Speed Railways (HSR) during the past decade in China due to its excellent damping property. The fresh and hardened properties of CA mortar are closely related to the PC hydration in the presence of asphalt emulsion. However, the retardation effect introduced by the anionic asphalt emulsion on the hydration process of PC has not been fully understood. In this paper, the effect of an anionic asphalt emulsion on the early hydration process of CA paste was first investigated by setting time test, isothermal conduction calorimeter and electrical resistivity. The MIP and SEM were then employed to characterize the microstructure evolution of the CA paste. Based on the data and observation obtained from the experimental study, three possible retardation mechanisms introduced by the anionic asphalt emulsion on the PC hydration were then assessed in this paper, including (i) selective adsorption by anionic emulsifier via electrostatic attraction, (ii) coating formed by the demulsification of anionic asphalt emulsion, and (iii) reduced reactivity of water molecules in anionic asphalt emulsion.

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1. Introduction

Cement-based materials have been widely used in civil engineering because of their superb compressive strength and locally available supply of raw materials. However, the brittleness incurred from the high modulus of elasticity of cement-based materials have hindered their applications in certain areas where some level of ductility, in particular, damping property, is required [1–5]. Asphalt is a flexible material with excellent deformation

capacity. However, its low compressive strength forms a barrier for some applications [6,7].

As a kind of inorganic-organic composite, cement-asphalt (hereafter CA) mortar, which consists of Portland cement, asphalt emulsion, water and other related admixtures, is able to combine the high compressive strength of cement and the superb flexibility of asphalt [8–11]. As a result, in recent decades, CA mortar has been extensively used as a grouting material in the cushion layer of the slab track system of High-Speed Railways (HSR) in China, primarily due to its excellent damping property [12–15].

In the formulation of CA mortar, asphalt emulsion, instead of asphalt, has to be adopted to modify the properties of PC paste, as this can ensure a good compatibility to be achieved between

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the cement particles and the asphalt molecules. In general, two kinds of asphalt emulsion, including cationic and anionic asphalt emulsions, can be employed to formulate the CA mortars, and the properties of CA mortar can be strongly affected by the type of asphalt emulsion used. This is because the hydration of silicate phases, such as C_3S and C_2S , could be hindered in the presence of cationic asphalt emulsion due to the adsorption of cationic asphalt emulsion onto the negatively charged surface of the silicate phases via electrostatic attraction, leading to a reduction in the strength of CA paste. On the contrary, the anionic asphalt emulsion is primarily adsorbed onto the positively charged surface of aluminate phases, such as C_3A and some small parts of silicate phases [16]. Therefore, the anionic asphalt emulsion could only exert some slight hindrances to the hydration of C_3S and C_2S . As it is the hydration of C_3S and C_2S that mainly contributes to the strength development of PC paste, it could be deduced that anionic asphalt emulsion is more suitable than cationic asphalt emulsion for formulating CA mortars when a higher strength is required (such as the Type II CA Mortar as specified in the current Chinese Standard) [17–19]. However, the effect of anionic asphalt emulsion on the hydration of PC has not been fully understood. Although some researchers have reported that the anionic asphalt emulsion can retard the hydration of PC [20–22], the retardation mechanism has not been fully explored. Nonetheless, a good understanding of the retardation mechanism introduced by the anionic asphalt emulsion to the hydration of PC is considered essential to the wider industrial application of the CA mortars because it could affect the rheological property and the microstructural evolution of the CA mortar. Therefore, in this paper, an anionic asphalt emulsion was used to formulate a type II CA mortar where a relatively higher strength is required under the current Chinese Standard for High-Speed Railway [19,23,24]. The effect of this anionic asphalt emulsion on the early hydration process of the PC paste was firstly investigated by setting time test, isothermal conduction calorimetry and electrical resistivity. Additionally, the MIP and SEM were also employed to characterize the microstructure evolution of the CA paste. Based on the data and the observation obtained from aforementioned tests, three possible retardation mechanisms introduced by the anionic asphalt emulsion on the PC hydration were then assessed and discussed.

2. Raw materials, sample preparation and test methods

2.1. Raw materials

Portland cement (PC), type P.I 42.5, complying with the Chinese standard GB8076-2008, produced by Qufu China United Cement Co., LTD was used in this study. Its chemical composition is presented in Table 1.

Anionic asphalt emulsion (with a solid content of 60%) was supplied by Jiangsu Bote New Materials Co., Ltd. Its main production process can be summarized as follows: the asphalt was first heated to about 140 °C, and it was then turned into asphalt droplets following a mechanical dispersion. The anionic asphalt emulsion was finally produced through the interactions between the asphalt droplets, anionic emulsifier and water in a colloid mill. Fig. 1 illustrates schematically the processes involved in the manufacture of the anionic asphalt emulsion used in the current study.

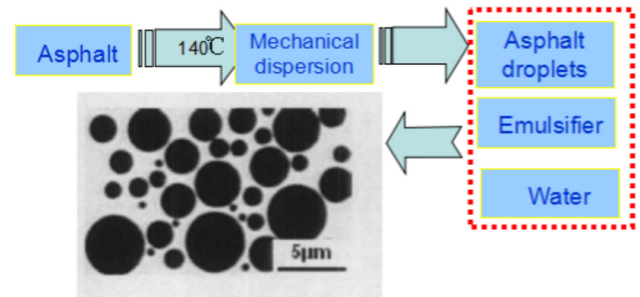


Fig. 1. Schematic diagram of the production process of anionic asphalt emulsion.

It should be noted that the anionic emulsifier is an essential component in the production of anionic asphalt emulsion. In this study, a lignin carboxylate emulsifier was employed [25], mainly due to the following two reasons: 1) the lignin carboxylate emulsifier could generate the negatively charged groups such as $-COO^-$ via ionization, which can enhance the dispersion stability of the anionic asphalt emulsion; 2) the negatively charged groups could be adsorbed onto the surface of the cement particles or the hydration products via the electrostatic attraction and this can improve the interaction between the cement particles and the asphalt emulsion. In addition, since the lignin carboxylate emulsifier is stable at high temperature, the anionic asphalt emulsion formulated with this type of emulsifier is, thus, suitable for producing cement asphalt pastes for a wider range of working temperatures.

2.2. Sample preparation

The CA pastes with different asphalt to cement (A/C) ratios, namely, 0, 0.16, 0.24 and 0.32 (the mixes are hereafter denoted as CA-0.16, CA-0.24 and CA-0.32, accordingly) were used to investigate the heat released during the early stage reaction of the CA pastes with an isothermal conduction calorimeter. Additionally, the electrical resistivity tests were carried out with CA pastes at a W/C of 0.41 and the A/C of 0 and 0.24 in order to understand the effect of anionic asphalt emulsion on the evolution of the microstructure of CA pastes. It should be noted that the amount of the water in the anionic asphalt emulsion was also considered in the calculation of W/C, and the mix ratios were selected from the real engineering applications in China.

2.3. Test methods

2.3.1. Setting time measurement

Setting time was measured according to the standard of ISO 9597:2008–Cement-Test methods – Determination of setting time and soundness, NEQ. Both the initial and final setting times of CA pastes with different anionic asphalt emulsion were measured, and the test temperature was kept at 20 °C.

2.3.2. Hydration heat measurement

The fresh CA pastes were put into a plastic bottle within 10 min after mixing, and the heat released was then measured by a self-regulated isothermal conduction calorimeter. The temperature was equilibrated at 20 °C between the specimen and the instru-

Table 1
Composition of Portland cement (wt.%).

Chemical composition								
SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SO ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂
20.47	3.48	4.41	3.33	2.49	61.43	0.14	0.55	0.30

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