Construction and Building Materials 25 (2011) 1572–1579

Contents lists available at ScienceDirect

Construction and Building Materials

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

Early hydration of calcium sulfoaluminate cement through electrical resistivity measurement and microstructure investigations

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ARTICLE INFO

Article history:
Received 7 March 2010
Received in revised form 12 August 2010
Accepted 17 September 2010

Keywords:
Electrical resistivity
Calcium sulfoaluminate cement
Hydration
Ettringite (AFt)
Monosulfate (AFm)
Transformation

ABSTRACT

The electrical resistivities of the calcium sulfoaluminate (CSA) cement pastes at different water to cement (W/C) ratios, over a period of 1440 min (or 24 h) were measured by a non-contacting electrical resistivity apparatus. The electrical resistivity–time curve decreased slightly after mixing, and then increased sharply around the setting time, followed by two peaks, and finally developed at a very low rate up to 1440 min. The porosity plays a dominant role in the electrical resistivity development of the CSA cement paste in the earlier period of hydration (before the initial setting time), while the ion concentration plays a major role at the later period (after the second peak). The electrical resistivity–time curve demonstrates the process of ettringite formation and transformation to monosulfate in the CSA hydration system, and this is confirmed by the SEM and XRD observations. The high temperature and the insufficiency of gypsum in the CSA cement system during hydration result in the decomposition of ettringite at the first peak, while at the second peak the decomposition of ettringite is due to the lack of gypsum. The relationship between W/C and electrical resistivity at 1 h follows a negative trend but a positive trend is observed at 24 h. The relationship between the compressive strength and the electrical resistivity at 24 h for the different W/C ratios follows a negative relationship.

1. Introduction

Calcium sulfoaluminate (CSA) cement is produced by burning mixtures of limestone, bauxite and gypsum at 1300–1350 °C [1,2]. CSA cement has many advantages, such as a low burning temperature, low CO_2 emissions, high early strength, high frost resistance, and high corrosion resistance. It can be used to stabilize industrial wastes and immobilize heavy metals [3–9]. China produced more than 1.2 million tons of CSA cement in 2009.

The main minerals of CSA cement are yeelimite or tetracalcium trialuminate sulfate ($C_4A_3\bar{S}$), belite (C_2S) and gypsum ($C\bar{S}H_2$), and the minor phases are calcium aluminate, tricalcium aluminate, ferrite, mayenite or gehlenite [2,10,11]. The main crystal products are ettringite (AFt) and monosulfate (AFm), and the main gel products of the hydration of CSA cement are the C–S–H phase, Al_2O_3 (aq) and Fe_2O_3 (aq).

When CSA cement hydrates, ettringite is formed rapidly according to the following two reactions [2]:

In the absence of calcium hydroxide,

$$3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + 2(CaSO_4 \cdot 2H_2O) + 34H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 4Al(OH)_3 \quad (1)$$

In the presence of calcium hydroxide,

$$3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + 8(CaSO_4 \cdot 2H_2O) + 6Ca(OH)_2 + 74H_2O \rightarrow 3(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O) \quad (2)$$

The C–S–H gel comes from the hydration of belite as follows:

$$2CaO \cdot SiO_2 + 2H_2O \rightarrow C{-}S{-}H + Ca(OH)_2 \quad (3)$$

It is worth noting that reaction (2) will occur if the gypsum content in the CSA hydration system is adequate. If the gypsum is absent, reactions (4) and (5) will occur as follows:

$$3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + 18H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O + 4Al(OH)_3 \quad (4)$$

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O + 2(CaSO_4 \cdot 2H_2O) + 16H_2O \quad (5)$$

The hydration behavior of CSA cement is complicated and the most important reactions are the formation and the transformation of ettringite. The hydration of CSA cement has been reported in the literature [3,10–17] and the methods used in CSA cement research were mentioned, such as near-infrared (NIR) spectroscopy [10], nuclear magnetic resonance (NMR) [14], energy dispersive X-ray (EDS) analysis [15] and electrical resistivity measurement [16]. Glasser [17] divided the hydration process of the CSA cement into

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doi:10.1016/j.conbuildmat.2010.09.042

four stages according to the heat evolution curves. Research outcomes on the relationships between compressive strength, water to cement ratio and electrical resistivity have not been reported.

Extensive investigations have shown that the electrical resistivity measurements can provide more detail, with a high accuracy, on the overall behavior of the hydration of cement-based materials. It is a powerful non-destructive testing technique that is capable of providing information on hydration reactions, microstructural characteristics and the transport properties of cement-based materials [18–21].

In the present study, the hydration process of CSA cement is investigated using electrical resistivity monitoring and microstructure observations in order to obtain more details of the hydration mechanism. The first aim of this work is to study the hydration mechanism of CSA cement using electrical resistivity measurement, microstructure observations and compressive strength testing. The second aim is to obtain relationship between compressive strength and electrical resistivity as well as relationship between the water to cement ratio and the electrical resistivity at various hydration ages.

2. Experiments

2.1. Materials

The CSA cement used in this study was commercial Chinese rapid hardening calcium sulfoaluminate cement. The chemical compositions of the CSA cement are shown in Table 1 and the X-ray diffraction (XRD) analysis of the cement is shown in Fig. 1. CSA pastes with *W*/*C* ratios of 0.4, 0.45 and 0.5 were prepared with a machine mixer for electrical resistivity and compressive strength testing, scanning electron microscopy (SEM) and XRD tests.

2.2. Electrical resistivity

The electrical resistivity of the paste was measured by a non-contacting electrical resistivity apparatus that was invented by Li and Li [22] and manufactured by Hong Kong Brilliant Concept Technologies, and the principle of the measurement was given in Ref. [18]. The tests were conducted at a temperature of 20.0 ± 2.0 °C. Each paste was mixed for 4 min in a planetary-type mixer at 45 rpm and was then cast in a ring-shaped plastic mould (1.67 L) that was closed during the tests to prevent water evaporation. The data were automatically recorded by a computer up to 1440 min and the sampling interval was 1 min. The data were calibrated by the height of the paste after demoulding.

2.3. Compressive strength

The paste samples were prepared with the same mix proportions as those used in the bulk resistivity tests. Cubic specimens of size 40 × 40 × 40 mm were cast, demoulded, and then cured at 20.0 ± 2.0 °C and 95 ± 5% relative humidity, for compressive strength tests at 24 h. Six specimens were prepared for each cement paste. The compressive tests were conducted in a compression testing machine at a loading rate of 2.4 kN/s.

Table 1
Chemical composition of CSA cement (wt.%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	TiO_2	Others	LOI
6.64	22.26	2.46	44.27	17.90	0.75	1.34	0.63	3.49

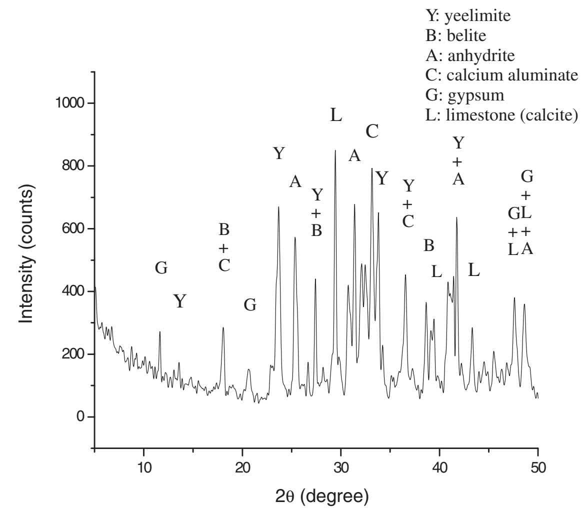

Fig. 1. X-ray diffraction analysis of CSA cement.

2.4. SEM and XRD

The paste samples with *W*/*C* = 0.4 were selected for the investigation by SEM (JEOL, JSM-5610LV) and XRD (Japan Rigaku Corporation, D/Max-RB). All the samples were immersed in acetone to stop hydration at the designated ages and then were dried in vacuum at room temperature.

2.5. Temperature

The inner temperature of CSA cement paste was measured with a mercury thermometer embedded in the central part of the sample.

3. Results and discussions

3.1. The electrical resistivity curve

3.1.1. At a certain W/C ratio

The electrical resistivity and the temperature development up to 1440 min for the paste having *W*/*C* = 0.4 were measured simultaneously and are shown in Fig. 2. From the trend of the resistiv-

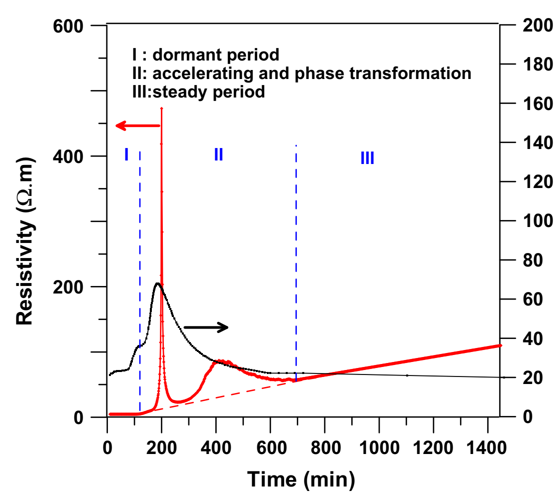

Fig. 2. The temperature and electrical resistivity development of CSA cement paste (*W*/*C* = 0.4).