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Using ultrasonic wave reflection to monitor false set of cement paste

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The standard mechanical penetration approach for monitoring cement paste stiffening (Vicat needle method, ASTM C191) does not distinguish responses associated with false set of cement paste caused by secondary gypsum formation. The objective of this research is to determine whether ultrasonic wave reflection, using a testing set up with high measurement sensitivity, could be used to monitor false set of cement paste. Penetration resistance, P-wave, and S-wave reflection coefficients were measured on cement pastes with water-to-cement ratio 0.5. The S-wave reflection coefficient showed a sharp and abrupt linear drop associated with secondary gypsum formation, thereby indicating that S-wave ultrasonic wave reflection can be used to monitor false set of cement pastes. False set could not be distinguished in penetration resistance or P-wave UWR test data.

1. Introduction

After cement is mixed with water, the resulting paste gradually stiffens, i.e., gains rigidity, typically over a few hours [1]. The stiffening of portland cement paste is due to microstructural development, typically caused by the hydration of alite (an impure form of tricalcium silicate, Ca_3SiO_5) [1] to produce calcium silicate hydrate (C-S-H), which acts to bridge cement grains [2] and leads to a percolated and interconnected particle network at relatively low degrees of hydration [3,4].

Stiffening gradually progresses until set occurs. Although set times are extremely important in practice, since stiffening is a gradual process, definitions of initial and final set times are subjective, and the values of set times depend on the measurement method used [5]. Generally, initial and final set times are defined to be equal to the times paste or concrete reaches various values of penetration resistance in standard tests [6–8]. In practice, it is commonly accepted that initial set is the time when the cement paste starts to lose its fluidity, and final set is the time when it starts to exhibit some measurable strength. Set occurs after a significant amount of microstructural development has progressed and when a percolation of total solids is achieved [9].

Set times are typically measured using mechanical penetration-based measurements, such as ASTM C191 [6], C266 [7], and C403 [8]. Set times of cement paste depend strongly on the water-to-cement ratio (w/c), typically increasing with increasing w/c [10–12], probably because solid percolation occurs faster at a higher solid volume fraction. Before normal setting occurs, cement pastes occasionally exhibit abnormal premature stiffening. Two kinds of premature stiffening are generally recognized: flash set and false set [13,14]. Flash set is a rapid stiffening behavior accompanied by high heat generation. The resulting microstructure cannot be broken apart by further mixing, as the material has developed some mechanical strength, although subsequent strength development is poor [1]. Flash set is caused by formation of calcium hydroaluminate (hydroxyl-AFm) due to the absence of sufficient sulfate to regulate C_3A hydration [15,16]. False set is a rapid stiffening behavior that is typically not accompanied by high heat generation, and the resulting rigidity can be overcome by further mixing, and the subsequent strength development is not greatly affected [1]. False set is often seen in cements with high levels of calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$), which reacts to form secondary gypsum ($CaSO_4 \cdot 2H_2O$) [17,18]. As the dissolution rate of hemihydrate is much higher (approximately three times) than the dissolution rate of gypsum [10], the pore solution becomes quickly supersaturated in sulfate ions and secondary gypsum precipitates quite rapidly. Stiffening is associated with interlocking needle-like gypsum crystals and reduction in water content [1].

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ASTM C451 [13] and C359 [14] are standard tests to diagnose premature stiffening (false or flash set) in cement pastes and mortars. Similar to ASTM C191, these are mechanical penetration tests that utilize the Vicat needle. The depth of needle penetration is measured shortly after mixing (5 min for paste and 11 min for mortar), and flash and false set are identified using the ratio between the first and second penetration depths [13,14]. Penetration measurements are discrete and they are seen to damage the microstructure in the vicinity of the penetration [19]. Additionally, these standard procedures require normal consistency, which is an uncommonly stiff mixture. Determining the w/c for normal consistency is somewhat tedious and difficult; but more importantly, normal consistency mixtures have very low w/c, and, as stated earlier, set behavior depends strongly on w/c [10–12]. Therefore, the standard procedures are not satisfactory because they do not measure the stiffening response at ordinary w/c levels. An alternative penetration test is ASTM C403 [8], which utilizes Proctor needles. It has been previously shown that the Proctor test is more appropriate than tests based on the Vicat needle for measuring stiffening of cement paste, in part because it does not require low w/c [5,19].

Ultrasonic wave reflection (UWR) is an alternate method for monitoring stiffening of cement paste. In contrast to penetration measurements, UWR measurements using shear waves (S-waves) are continuous (the automated measurements were taken every 5 s), sensitive to particle flocculation [20], and do not significantly damage the developing paste microstructure [21]. Several studies [22–28] have used S-wave UWR to monitor setting of cement-based materials, but these have typically utilized a high impedance buffer that leads to reduced early age sensitivity. A few researchers have determined the setting time of cement pastes and concretes using high-sensitive, low-impedance buffers such as polymethyl methacrylate (PMMA) [29,30] and high impact polystyrene (HIPS) [10,21,31,32]. P-wave UWR response depends on solution concentration and density [33] and therefore can be also used to characterize early stiffening and setting behavior of cement pastes [21,34]. Detailed reviews on UWR test devices, methods, and applications are provided elsewhere for the interested reader [35,36]. It must be pointed out that, apart from UWR, ultrasonic transmission methods have also been used to measure early age cement properties [37,38] and transmission and reflection methods can be used in conjunction [26].

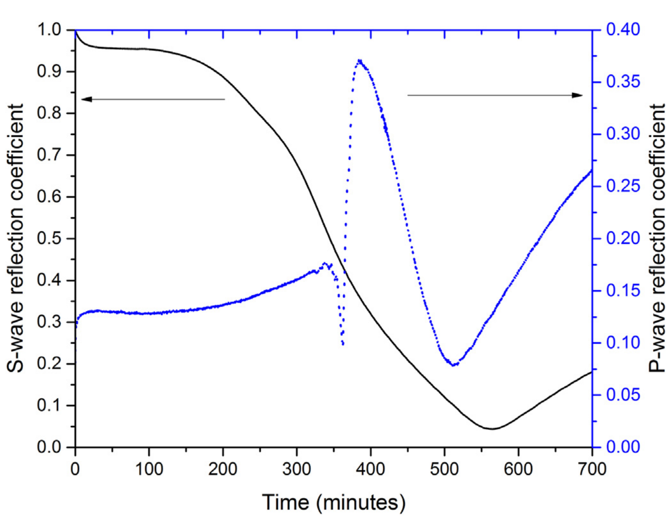

Fig. 1. Typical P-wave and S-wave UWR responses of ordinary type I cement paste with w/c 0.5.

Typical S-wave and P-wave UWR responses of an ordinary cement paste using HIPS buffer from studies conducted in our laboratory are presented in Fig. 1. A detailed interpretation of these responses is provided elsewhere [10,21] and only a short summary is presented here. The S-wave response can be generally categorized into four stages: (a) an initial slight drop in reflection coefficient starting from a high value of reflection coefficient r (~1), associated with the flocculation of cement particles (from approximately 0 to 20 min after mixing), (b) a flat or slightly decreasing portion indicating a low rate of stiffening, which broadly corresponds to the induction period of cement hydration (from approximately 20 to 200 min after mixing), (c) a steeply descending portion that reflects rapid stiffening (from approximately 200 to 550 min after mixing), and (d) the “inversion” in the curve, which occurs when the tested material (paste) becomes acoustically harder than the buffer, resulting in a change in the sense of the reflection coefficient and direction of the curve (approximately 550 min after mixing). Initial set occurs at around the beginning part of stage c (when the tested material exhibits acoustic impedance of 0.09 MRayls, approximately 200 min after mixing), and final set occurs around midway in stage c, at the inflection point of the curve, after which the rate of stiffening decreases as a function of time (approximately 350 min after mixing) [10].

The P-wave UWR shows a different response from S-wave UWR, but can also be categorized into four different stages: (a) an initial increase in reflection coefficient starting from a relatively low value (~0.3) associated with settlement of cement particles, followed by a flat or slightly increasing portion of the curve due to slow microstructural development and densification (from approximately 0 to 300 min after mixing), (b) a wide peak consisting of a rapid increase and decrease in the reflection coefficient owing to partial debonding of contact between paste and buffer caused by under-pressure of water at the time of final set (from approximately 300 to 400 min after mixing), (c) a fairly rapid decrease in the reflection coefficient associated with a gradual reestablishment of the bond between paste and buffer (from approximately 400 to 500 min after mixing) (d) a gradual increase in the reflection coefficient over time, associated with full recovery from partial debonding and progressive hydration over time [21]. The partial debonding response is associated with two inversions in the curve, which occur when the tested paste becomes acoustically harder than the buffer, resulting in a change in the sense of the reflection coefficient and direction of the curve [21].

The S-wave response is directly related to hydration and mechanical stiffening, and both initial and final set can be found from S-wave curves [10,23,26,39]. The P-wave response is related to material density and not always directly correlated to hydration and stiffening since P-waves can penetrate through the matrix of un-percolated particles. However, time of final set can be easily distinguished from the P-wave curves using the starting point of the partial debonding, and these times match the times from S-wave curves [21,34]. Initial and final setting times from S-wave UWR [10] and final set time from P-wave UWR [21] are well correlated with corresponding times from the Proctor penetration resistance test.

To date, both S- and P-wave UWR techniques have been used only to characterize ordinary setting and stiffening. The objective of this research is to explore the applicability of UWR to detect premature stiffening of cement paste at very early ages associated with secondary gypsum formation, the so-called false set. The stiffening of the cement paste was measured at w/c 0.5 using both P- and S-wave UWR, and the Proctor penetration resistance test [8] was performed for comparison.