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Early Age Stiffening of Cement Paste Using Ultrasonic Wave Reflection

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Synopsis: Ultrasonic wave reflection (UWR) has been used to monitor hydration and strength development of concrete. UWR measures the changes in reflected ultrasonic waves at the interface between a buffer material and hydrating cement paste. To monitor the subtle changes during early hydration it is necessary to use a buffer with low acoustic impedance, close to that of cement paste. In this research, UWR measurements on hydrating Type I portland cement are performed using a high impact polystyrene (HIPS) buffer. Both S-waves and P-waves are analyzed simultaneously to develop and extend the use of UWR to monitor early stiffening of cement paste. The penetration resistance test (ASTM C 403) and temperature rise of cement paste are used to correlate stiffening characteristics. The UWR responses show good correlation with results from temperature rise and penetration resistance. The onset of stiffening is the same for penetration resistance and both P- and S-wave UWR, and nearly the same for temperature rise. It is found that the HIPS buffer can provide sensitive measurement on the early age stiffening of cement paste.

Keywords: cement paste; penetration resistance; stiffening; temperature rise; ultrasonic wave reflection (UWR)

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RESEARCH SIGNIFICANCE

Ultrasonic wave reflection has been used to monitor stiffening of cement paste and concrete. Most of the past research used a single transducer (either P- or S-wave) with a buffer material that has higher acoustic impedance compared to that of the fresh cement paste. This research uses high impact polystyrene (HIPS) buffer, whose acoustic impedance is very close to that of cement paste, with two transducers (both P- and S-wave). The testing setup presented in this research can provide more sensitive measurement of the changes in hydrating cement paste at very early ages, which is important for monitoring abnormal setting activity.

1. INTRODUCTION

The ASTM C 403 Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance, the so-called Proctor test, is applied to mortar extracted from concrete. However, this technique has been extended to measure the setting of the cement paste by Struble et al. [1]. They showed that penetration resistance detects changes in penetration resistance prior to initial set and thus correlates well with the setting process. An advantage of the penetration resistance test is that any w/c can be used, even when segregation and bleeding occurs. However, the conventional penetration resistance test is likely to miss some valuable information because it measures data only at discrete time periods.

The ultrasonic wave reflection technique (UWR) measures ultrasonic wave pulses that are reflected at the interface between a buffer material and cement paste. This technique can measure the stiffening of cement paste continuously and shows promise as an alternative to penetration resistance for monitoring very early stiffening and set of cement paste.

Shear wave UWR has been used to monitor hydration and strength development. However, most of the work is concentrated on concrete [2, 3]. In addition, the buffer materials that were used, steel [4] and fused quartz [5], have relatively high acoustic impedances. Use of a buffer material with low acoustic impedance and low ultrasonic energy attenuation is expected to enhance the sensitivity to changes during the early hydration period. More recently, Subramaniam et al. [6, 7] used PMMA as the buffer material to study the setting behavior of cementitious materials, where they used S-wave reflection. S-wave UWR allows detection of the hardening process only after initial set. Since P-waves can also penetrate liquid, the use of P-waves is necessary to detect subtle changes of the cement paste during the very early hydration period, before the occurrence of initial set. Öztürk et al. [8] used P-wave reflection with a PMMA buffer. However, the acoustic impedance of PMMA is still high compared to that of fresh cement paste.

The objective of this research is to develop and extend the use of UWR to monitor stiffening of cement paste during the very early hydration period. The setting and hardening behavior was measured as a function of time. Both P- and S-wave reflections were used to monitor stiffening. To increase the sensitivity of the UWR test method, we employed high impact polystyrene (HIPS) as a buffer, because its acoustic impedance is very close to that of cement paste. The P- and S-wave responses are interpreted and compared to results from penetration resistance and temperature rise.

2. EXPERIMENTAL PROCEDURES

2.1. Mixing

The cement used for the test was ordinary Type I portland cement, whose chemical composition is presented in Table 1. The mixing water was stored in a container for at least 1 day to bring it to room temperature (approximately 23 ºC, 73 ºF). Cement pastes of w/c 0.5 were prepared by mixing 1500 g (3.3 lb) cement and 750 g (1.65 lb) water using a paddle mixer[†]. The mixing procedure was changed slightly from the procedure for mixing cement paste in ASTM C 305, Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency. The paste was first mixed for 30 seconds at the lowest speed level (140±5 rpm). The mixer was stopped for 30 seconds to 60 seconds in order to scrape down cement paste adhering to the side of the mixing bowl[‡]. As soon as scraping was finished, the paste was mixed for 90 seconds at the intermediate speed level (285±10 rpm)[§].

2.2. Ultrasonic wave reflection (UWR)

As soon as cement paste was mixed, it was poured into the ultrasonic wave reflection testing apparatus shown in Figure 1. Separate 2.25 MHz P- and 0.5 MHz S-wave transducers were attached at the bottom of the container. The container was made of 6.25 mm (0.25 in.) thick HIPS, and the bottom panel of the container acted as the buffer for the ultrasonic waves. HIPS was selected since it has a relatively low acoustic impedance (2.27 MRayls, 0.466×10^6 lb/(ft^2·s)) that is similar to that for fresh cement paste, thus increasing sensitivity to small changes in acoustic impedance during the early hydration process. HIPS is also chemically resistant to most chemicals and does not absorb or soften in water. The transducers were clamped using set screws to assure firm contact with the buffer. The HIPS container was supported by a frame made of PMMA. The transducer was connected to the pulser/receiver unit[**], and the pulser/receiver unit was connected to a digitizer[††], which was connected to computer for data collection and analysis.

The changes in early age properties of cement paste can be monitored through the reflection coefficient of ultrasonic waves at the interface between buffer material and cement paste. The reflected time domain pulses were windowed for a duration of 5 μs, and zero-padded to the length of 10 μs on each side. Hundred of these time domain signals were averaged and converted into the frequency domain signal using the Fast Fourier Transform (FFT) algorithm. However, the amplitudes of the reflections are influenced not only by the transmission losses at the interface between the buffer and the sample, but also by the coupling of the transducer to the buffer material. To eliminate these influences and to isolate the reflection coefficient, we first tried to use the self-compensating procedure developed by Öztürk et al. [2], which measures the ratio of the first peak to the second peak intensity, both expressed in terms of frequency. However, P-wave amplitudes were so weak that only the first peak could be measured with HIPS buffer. Therefore, we used an alternative self-compensating procedure, which incorporates only the first reflected wave pulses.

Figure 2 illustrates propagation of ultrasonic waves between transducer and cement paste within the buffer. The Fourier transform of the first reflected pulse in terms of frequency f is given by

$$F_1(f) = S_T d_1 r d_2 \tag{1}$$

where S_T is the transducer function including variables specific to the transducer and variables due to coupling, r is the normal incidence reflection coefficient at the buffer-cement paste interface, and d_1 and d_2 are the material and geometric signal losses along the propagation path through the buffer to and from the interface, respectively. Since the reflection coefficient at the buffer-air interface is nearly unity for P-waves, the Fourier transform of the first reflected pulse in the free boundary case is

$$F_{1,air}(f) = S_T d_1 d_2 \,. \tag{2}$$

Dividing the reflection from cement paste by that from air, we can obtain the reflection coefficient r

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[†] The brand name of a paddle mixer is Hobart.

[‡] According to ASTM C 305-99, the time for scraping is 15 seconds, but in this experiment 15 seconds was not sufficient to finish scraping. Therefore the scraping time was increased to 30 or 60 seconds according to the consistency of the mixture.

[§] The intermediate speed range was selected because the paste tended to splash at the fastest speed.

[**] Pulser/receiver unit used in this experiment is Olympus Panametrics PR-5077.

[††] The high speed digitizer used in this experiment is National Instrument 5102 PCI type. It has 8–bit 2–channels with 20 MS/s sampling rate.

$$\frac{F_1(f)}{F_{1,air}(f)} = \frac{S_T d_1 r d_2}{S_T d_1 d_2} = r\,. \tag{3}$$

2.3. Temperature rise

The temperature history of the cement paste was recorded during UWR measurements. The purpose was to compare the temperature rise with UWR results. The advantage of this setup is that the direct relationship can be established between UWR and temperature rise during cement hydration. The use of isothermal calorimetry was not considered in this research since isothermal calorimetry uses very small amount of specimen (1~2 g, 0.035~0.07 oz), and the condition of cement paste for UWR measurement is greatly different from isothermal condition. Thus, the only temperature rise in UWR container was monitored.

As shown in Figure 1, the calorimetry system consisted of a type T thermocouple that was attached to the inside of the UWR testing container, a data logger[‡‡] which connects a thermocouple wire into the computer through a USB port, and its operating software for data acquisition. The container was open to the air during measurements, and therefore it was considered neither isothermal nor adiabatic. In fact, the test condition was closer to isothermal calorimetry since the total temperature rise was only about 4 °C (7 °F).

2.4. Penetration resistance

As soon as the cement paste was mixed, it was placed in a plastic container for penetration testing. Specimens were maintained in a horizontal alignment, with no inclination. Penetrations were measured using a mechanical universal testing machine[§§] equipped with the proper needles and a 1 kN (200 lbf) load cell. Measurements were made in triplicate and averaged.

The penetration test uses six needles (645 mm^2, 323 mm^2, 161 mm^2, 65 mm^2, 32 mm^2, and 16 mm^2 in cross section and less than 90 mm in length, which corresponds to 1 $in.^2$, 0.5 $in.^2$, 0.25 $in.^2$, 0.1 $in.^2$, 0.05 $in.^2$, and 0.025 $in.^2$, respectively). The largest needle is used for the first measurement and needles are changed as needed until the smallest needle has been used. Each needle penetrates to a depth of 25 mm (1 in.) for 10 seconds. The penetration resistance is given by:

$$R_P = P/A \tag{4}$$

where R_P is the penetration resistance, P is the load applied to penetrate 25 mm (1 in.) depth, A is the load bearing area at the time of measurement. Changing the Proctor needles requires a subjective decision from the tester, so an experienced technician may give less damage to the cement mixture and thereby derive better results.

3. RESULTS

3.1. Ultrasonic wave reflection

Figure 3 presents typical P- and S-wave UWR curves of w/c 0.5 cement paste. In the S-wave response, an initial decrease in the S-wave reflection coefficient is observed during the first 20 minutes. It is likely that either cement flocculation or segregation has caused this rapid drop, but further experiments are necessary to determine the cause of this response. After this initial decrease, the S-wave reflection coefficient shows a plateau for 100 minutes. Then, starting at about 120 minutes, the S-wave reflection coefficient decreases substantially. This is likely associated with the beginning of building mechanical interconnections between particles. The inversion of the curve, the point where the shear wave acoustic impedance of cement paste exceeds that of the HIPS buffer, occurs around 500 minutes.

The signal of P-wave UWR has a lower signal to noise ratio, compared to S-wave UWR; this is due to the low P-wave amplitude during the entire test because the P-wave acoustic impedance of HIPS is so close to that of cement paste. The P-wave UWR shows an initial increase in its reflection coefficient during the first 20 minutes, corresponding very well in time to the initial decrease observed in the S-wave reflection coefficient. After this, a slow decrease is observed for about 60 minutes. This decrease could be due either to the inversion of the curve or to an increase in the concentration of pore solution in cement paste. We have found that increasing the concentration of solution gives rise to linear decrease in the P-wave reflection coefficient when measured using HIPS buffer [9]. The pore solution of early age cement paste is known to increase its concentration over the first few hours, possibly up to about 300~400 mM in total ionic strength [10]. Based on our earlier work [9], this drop in P-wave UWR is found to

[‡‡] The data logger used in this experiment is Pico Technology TC-08, a USB type data logger.
[§§] The testing device used for penetration test is Instron 4500 testing apparatus.

be reasonable. Therefore, this slow decrease is more likely to be attributed to the increase in solution concentration.

After this period, the P-wave UWR shows almost no change for about 40 minutes. Then, at about 120 minutes, the P-wave reflection coefficient starts to increase. The time of this increase corresponds very well with the time of the decrease in S-wave reflection coefficient. After this point, the P-wave reflection coefficient generally increases as a function of time. As with the decrease in the S-wave reflection coefficient, this increase in the P-wave coefficient is thought to reflect the gradual building of mechanical interconnections between particles. In addition, the P-wave reflection coefficient increases more rapidly at around 500 minutes. However, the P-wave reflection coefficient shows a disruption at around 580 minutes. These changes are also observed in the temperature rise, presented in the following section. However, these changes in slope are not observed in the S-wave UWR. Unlike the S-wave curve, no clear inversion was observed, perhaps indicating that the P-wave acoustic impedance of HIPS was less than that of the cement paste throughout this time period.

3.2. Temperature change

The temperature during UWR measurement is presented in Figure 4. The measured temperature in this experiment increases due to exothermic hydration reactions and then decreases due to heat loss to the environment. However, it is not clear how much these two effects counteract each other. First of all, the initial temperature of the cement paste when it was poured into the UWR testing container was about 24.5 °C (76 °F). The temperature decreased from this value until 150 minutes. During this period, the cement paste was in the induction period, so it approached the room temperature (approximately 20 °C, 68 °F). At 150 minutes, the temperature started to rise again, indicating the onset of hydration. It is often considered that the onset of hydration marks initial set, although it probably rather coincides with the onset of stiffening. However, the simultaneous cooling probably delayed somewhat the temperature rise due to hydration. In addition, an increase in slope is observed at about 500 minutes, which matches the increase observed using P-wave UWR shown in Figure 3. This response is not observed with S-wave UWR.

3.3. Penetration resistance

The penetration resistance is presented in Figure 5. The cement paste shows rapid stiffening starting at 270 minutes, reaches initial set at about 300 minutes and final set at about 480 minutes. However, it should be noted that the values of initial and final set using penetration resistance are defined in ASTM C 403 for mortar extracted from concrete, not for paste. The time for initial set does not correspond to any specific changes in either UWR or temperature rise.

The penetration data in Figure 5 are replotted in Figure 6 on an expanded scale. Although the penetration measurements were taken only every hour, it can be seen that the penetration resistance starts to increase at about 120 minutes. This time marks the onset of stiffening and correlates well with the findings of UWR and temperature rise.

4. DISCUSSION

Some amount of bleeding was observed during penetration resistance testing. This phenomenon may affect stiffening behavior. The cement paste tested using UWR never showed any bleeding, although these specimens were not even exposed to any kind of agitation after mixing. In addition, the values of penetration resistance given in ASTM C 403 for initial and final set are arbitrary values and are only defined for penetration resistance. Therefore, it is not possible to define initial and final set for UWR and calorimetry using values in penetration resistance test.

The time for onset of stiffening[***] measured by the various methods shows excellent correlation. The results are summarized in Table 2. The initial set measured by ASTM C 191 Test Method for Time of Setting of Hydraulic Cement by Vicat Needle is 119 minutes[†††], a value that is quite similar to the results in Table 2, although this method allows only a very low w/c paste. The Vicat method only allows us to measure the time of setting, not the onset of stiffening, so results can be a reference but cannot be correlated with results from the other techniques. It should be also noted that the time for onset of stiffening measured by 4 different methods can have some uncertainties. The estimation of onset of stiffening is based on the rough judgment based on the graph, not based on the detailed microstructural analysis.

As noted in the Introduction, many researchers have used S-wave UWR to monitor stiffening of cement paste

[***] It should be noted that the time for onset of stiffening is not based on the specific studies on the hydration of cement paste, but based on the rough judgment using graphs from experimental results. Therefore, the uncertainty in estimating the time for onset of stiffening may exist.

[†††] The initial and final set values were provided by the cement manufacturer on the mill sheet.

and concrete [2, 3, 4, 5, 6, 7]. None of them reported the initial decrease in S-wave reflection coefficient as reported here. Thus it appears that the testing setup described here is providing a more sensitive measure of stiffening in fresh cement paste.

Only one study, Öztürk et al. [8], used P-wave UWR to monitor stiffening of cement paste. They found that the P-wave reflection coefficient with PMMA buffer started to decrease from their initial value and showed a clear inversion at about 200 minutes. Their results did not show the three important findings that we have observed: 1) an initial increase during 0~20 minutes which is attributed to cement paste segregation or flocculation, 2) a slow decrease during 20~80 minutes which is attributed to changes in chemical composition in pore solution, and 3) a plateau during 80~120 minutes before the onset of stiffening. In addition, the more rapid increase at about 500 and disruption at 580 minutes which corresponds to temperature changes have not been reported by Öztürk et al. [9]. Although a direct comparison between our results and those of Öztürk et al. is difficult because they used a w/c, close to 0.3, and their P-wave UWR response with PMMA is distinctly different than our results with HIPS.

Ultrasonic wave reflection coefficients using polymeric buffer materials such as HIPS may be susceptible to the temperature changes. The temperature rise during the UWR measurement may change acoustic impedance of the HIPS and thus affect the wave reflection response. In this research, the temperature rise during the measurement (4 °C, 7 °F) was considered to be negligible, but compensation for temperature may need to be performed when temperature rises significantly.

5. CONCLUSIONS

From the results presented in this research, the following conclusions have been drawn:

1) Both P- and S-wave UWR showed the same type of change during first 20 minutes. In addition, the onset of early stiffening was observed at 120 minutes for both P- and S-wave UWR.
2) The P-wave UWR showed different response from the S-wave UWR. With the P-wave, a slow decrease was monitored between 20 ~ 80 minutes followed by a gradual increase. A more rapid increase was observed at 500 minutes and a disruption at 580 minutes. It was found that P-wave UWR can monitor such changes which S-wave UWR cannot, thus making P-wave UWR worthwhile as a complementary measurement.
3) The P-wave UWR, S-wave UWR, temperature rise, and penetration resistance all showed similar times for the onset of early stiffening.
4) The initial set time obtained from temperature rise was somewhat later than the onset of stiffening observed with UWR and penetration resistance.
5) Using HIPS as the buffer provides increased sensitivity of UWR to monitor early stiffening of cement paste.

6. References

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Table 1 – The composition of type I portland cement[‡‡‡]

	content (%)
SiO_2	20.2
Al_2O_3	4.8
Fe_2O_3	3.4
CaO	63.3
MgO	2.4
SO_3	3.1
Total alkalis	0.59
C_3S	67.12
C_2S	7.37
C_3A	6.97
C_4AF	7.00
Fineness (Blaine, m^2/kg)	379
Initial set (minutes)	119
Final set (minutes)	263

Table 2 – The comparison of the onset of stiffening measured by various techniques

	Time for onset of stiffening (minutes)
S-wave UWR	120
P-wave UWR	120
Temperature rise	150
Penetration resistance	120

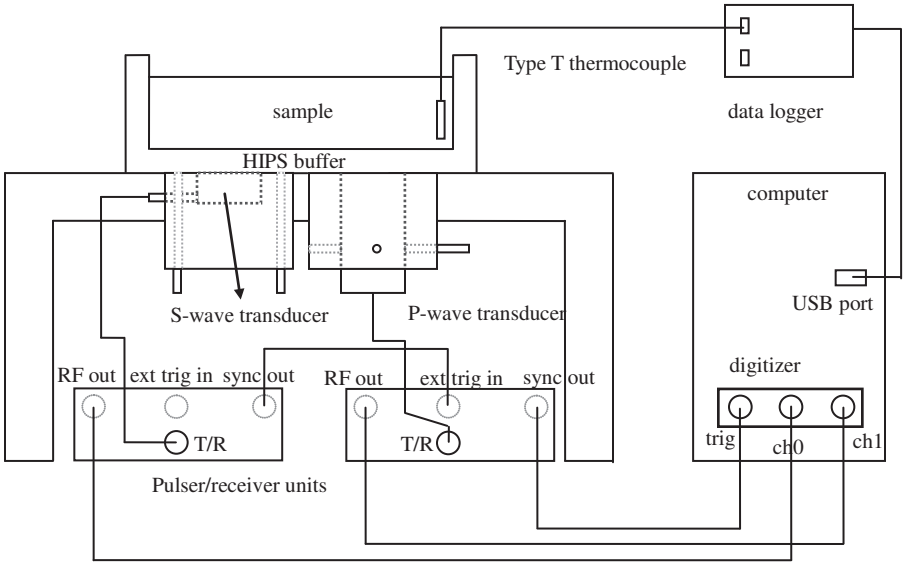

Figure 1 – Schematic drawing of UWR testing setup

‡‡‡ This information is provided by the manufacturer.

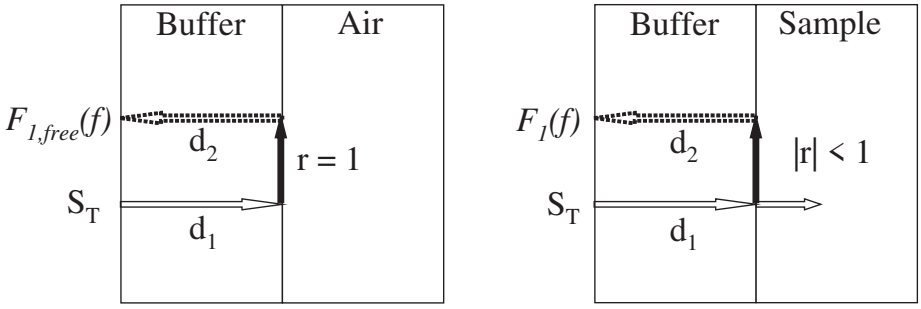

Figure 2 – Illustration of self-compensating procedure to calculate the reflection coefficient

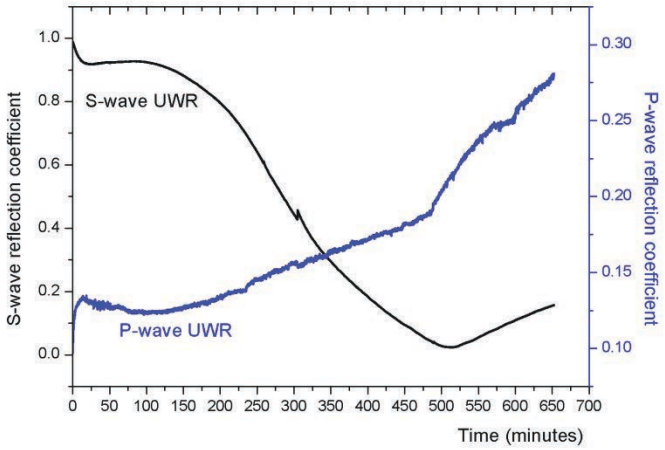

Figure 3 – P- and S-wave UWR response of w/c 0.5 cement paste

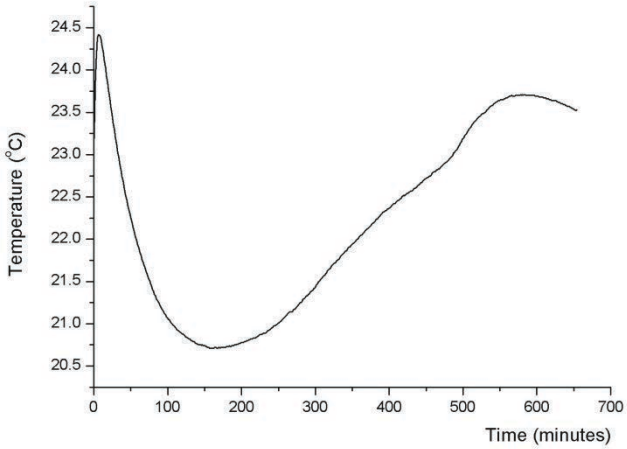

Figure 4 – Temperature change of w/c 0.5 cement paste obtained during UWR measurement (temperature ranges from 69 ~ 76 °F, conversion factor 1 °C = 1.8 °F ($1.8 \times T_c + 32$))

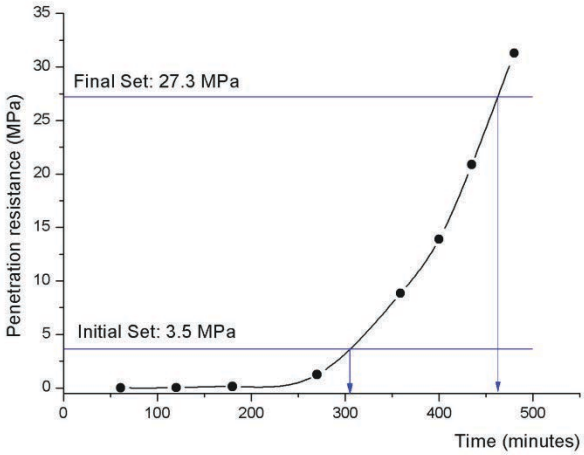

Figure 5 – Penetration resistance data of w/c 0.5 cement paste (penetration resistance ranges from 0 to 5076 psi, conversion factor 1 MPa = 145 psi)

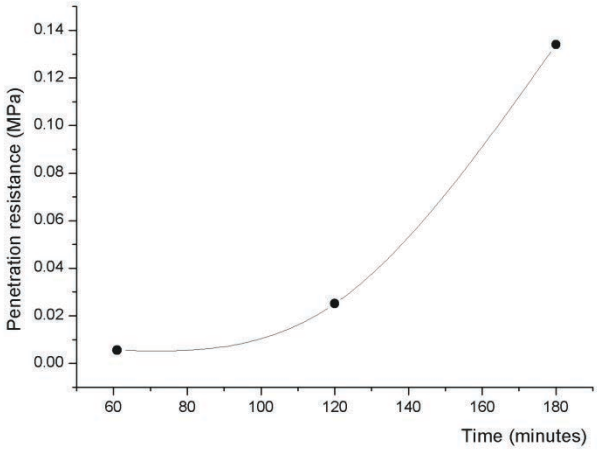

Figure 6 – Penetration resistance data of w/c 0.5 cement paste during first 3 hours (penetration resistance ranges from 0 to 20 psi, conversion factor 1 MPa = 145 psi)