

Early Age Stiffening of Cement Paste Using Ultrasonic Wave Reflection

by C. Chung, J.S. Popovics, and L.J. Struble

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 °C, 73 °F). 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/(ft²·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

$$F_1(f) = S_T d_1 r d_2 \quad (1)$$

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

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

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

[†] 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.

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

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 mm², 323 mm², 161 mm², 65 mm², 32 mm², and 16 mm² 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:

$$R_p = P/A \quad (4)$$

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

- 1) Struble, L. J., Kim, T.-Y., and Zhang, H., Setting of Cement and Concrete. *Journal of Cement, Concrete, and Aggregate*, 2001, Vol. 23, No. 2.
- 2) Öztürk, T., Rapoport, J., Popovics, J.S., and Shah, S.P., Monitoring the setting and hardening of cement-based materials with ultrasound, *Concrete Science and Engineering*, 1, Vol. 1, pp.83~91, 1999.
- 3) Rapoport, J., Popovics, J.S., Subramaniam, K.V., and Shah, S.P. Using ultrasound to monitor stiffening process of concrete with admixtures, *ACI Materials Journal*, Vol. 97, No. 6, pp. 675-683, 2000.
- 4) Voigt, T., *The Application of an Ultrasonic Shear Wave Reflection Method for Nondestructive Testing of Cement Based Materials at Early Ages*, Ph.D. Dissertation, Universität Leipzig, 2004.
- 5) Sun, Z., *Monitoring the Early Age Properties of Cementitious Materials with Ultrasonic Wave Reflection Method at Macro- and Micro-structural Levels*, Ph.D Dissertation, Northwestern University, 2005.
- 6) Subramaniam, K.V., and Lee, J.J., Ultrasonic assessment of early-age changes in the material properties of cementitious materials, *Materials and Structures*, Vol. 40, pp. 301-309, 2007.
- 7) Subramaniam, K.V., and Lee, J.J., and Christensen B.V., Monitoring the setting behavior of cementitious materials using one-sided ultrasonic measurements, *Cement and Concrete Research*, Vol 35, pp. 850-857, 2005.
- 8) Öztürk, T., Kroggel, O., Grubl, P., and Popovics, J.S., Improved ultrasonic wave reflection technique to monitor the setting of cement-based materials, *NDT&E International*, Vol 39, pp. 258-263, 2006.

- 9) Chung, C. W., Popovics, J. S, and Struble, L. J., Ultrasonic wave reflection measurements on aqueous solutions with varying concentrations, Submitted to *Ultrasonics Sonochemistry*, Oct 2008.
- 10) Taylor, H.F.W., *Cement Chemistry*, Academic Press, Thomas Telford edition, 1997.

Table 1 – The composition of type I portland cement^{†††}

	content (%)
SiO ₂	20.2
Al ₂ O ₃	4.8
Fe ₂ O ₃	3.4
CaO	63.3
MgO	2.4
SO ₃	3.1
Total alkalis	0.59
C ₃ S	67.12
C ₂ S	7.37
C ₃ A	6.97
C ₄ AF	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

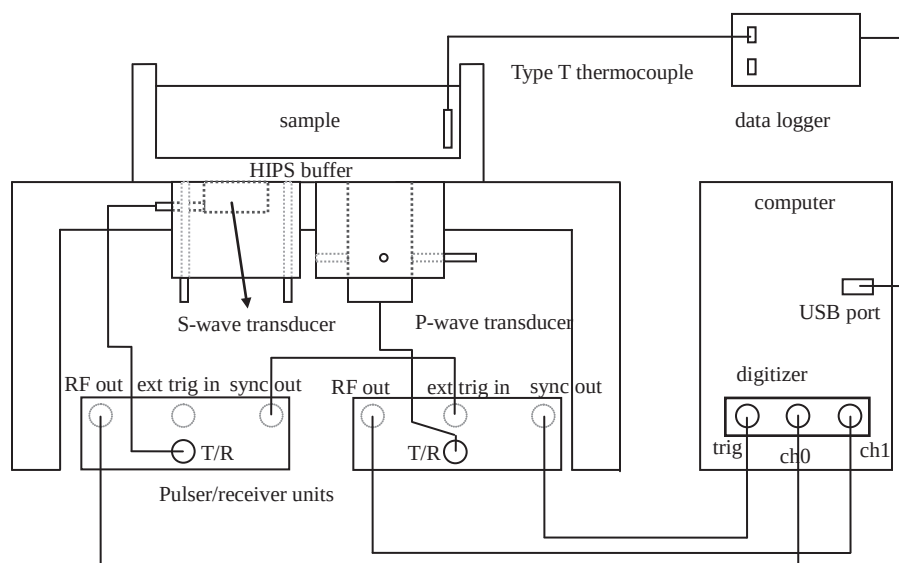


Figure 1 – Schematic drawing of UWR testing setup

^{†††} This information is provided by the manufacturer.

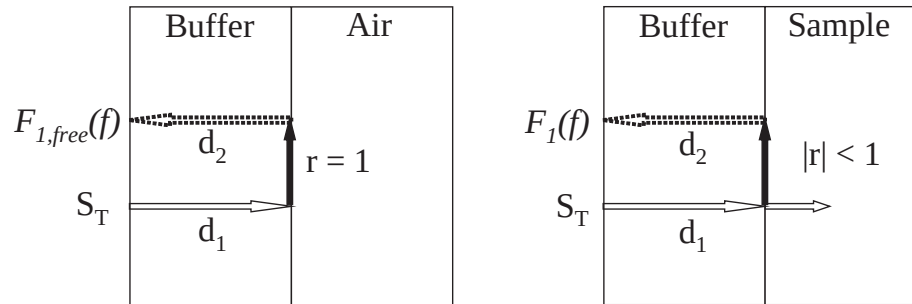


Figure 2 – Illustration of self-compensating procedure to calculate the reflection coefficient

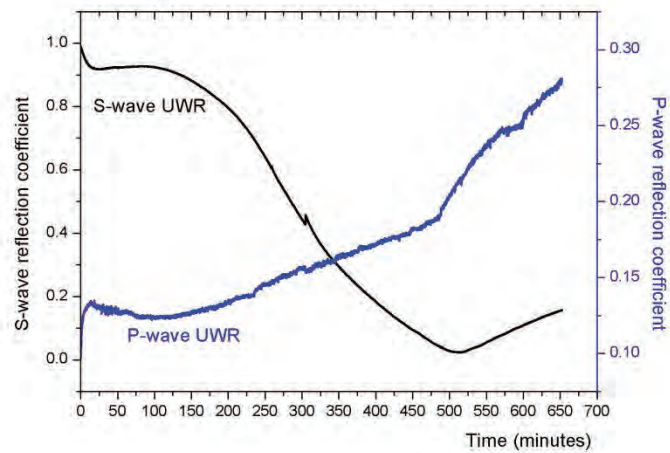
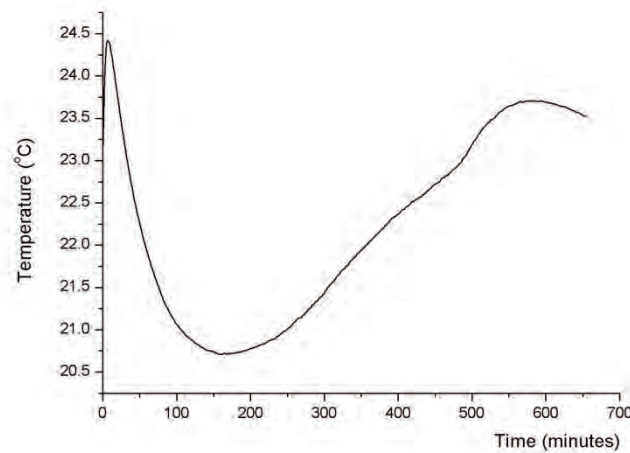


Figure 3 – P- and S-wave UWR response of w/c 0.5 cement paste

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

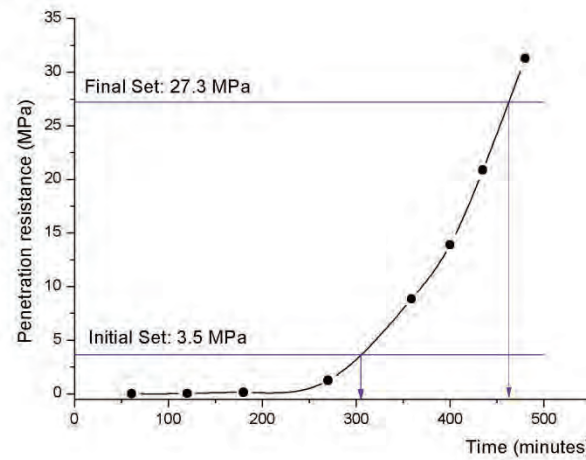


Figure 5 – Penetration resistance data of w/c 0.5 cement paste (penetration resistance ranges from 0 to 5076 psi, conversion factor 1 MPa = 145 psi)

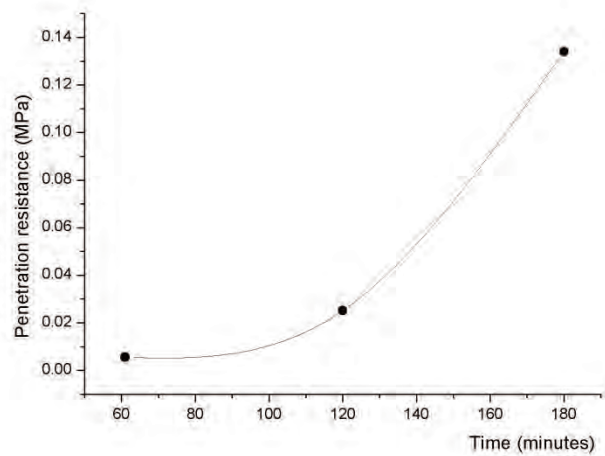


Figure 6 – Penetration resistance data of w/c 0.5 cement paste during first 3 hours (penetration resistance ranges from 0 to 20 psi, conversion factor 1 MPa = 145 psi)

Experimental Study on Restrained Drying Shrinkage Cracking of Concrete Using Acoustic Emission

by M. Ozawa, S. Uchida, T. Kamada, and H. Morimoto

Synopsis: Drying shrinkage cracking can occur in concrete due to volumetric changes caused by temperature and moisture gradients. The purpose of this study is to acquire fundamental data on the relationship between internal relative humidity and drying shrinkage cracking. The detection of drying shrinkage cracking was performed using the Acoustic Emission method. It was found that the AE measurement technique was successful at detecting drying shrinkage cracking.

Keywords: acoustic emission; drying shrinkage cracking; internal relative humidity; restrained condition

Biography

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Toshiro Kamada is a Professor in the Division of Global Architecture at Osaka University, Japan. He received his Doctor of Engineering degree in 1997 from Tokyo Institute of Technology, Japan. He is chairman of Technical Committee for Improvement of reliability of nondestructive testing of concrete, JSCE, and Technical Committee for NDIS of testing of concrete using elastic wave, JSNDI. His research interests include Maintenance of civil structures and Nondestructive testing of concrete.

Hiroaki Morimoto is a Professor at Gifu University Gifu, Japan. He received his PhD in civil engineering from Kyoto University in 1990. His research interests include cracking of concrete due to volume changes.

INTRODUCTION

Cracking of concrete caused by tensile stresses due to volume changes reduces the durability of concrete structures significantly. Volume changes can arise from drying shrinkage, temperature change, autogenous shrinkage, and so on. Drying shrinkage is a prime factor in controlling volume changes of concrete members, and is directly associated with moisture transfer in concrete.

In the JSCE¹ standard, the cracking criterion is defined as the ratio of the critical tensile stress to the axial tensile strength. Wittmann et al.² investigated crack criteria using fracture mechanics and numerical simulation. Their numerical model was validated by comparison with experimental results obtained from ring tests carried out on mortar specimens of different hygro-mechanical properties. The model identified optimum values for different material properties (e.g. moisture diffusivity, coefficient of shrinkage, elastic modulus, and fracture energy) that must be controlled to avoid cracking. Van Breugel et al.³ investigated experimentally the evolution of stresses in hardening concrete and the risk of cracking with a Temperature-stress testing Machine (TSTM). Their experimental data showed that self-induced cracking and load-induced cracking at early ages can occur at stress/strength ratios of $\eta = 0.75$ and 0.88 , respectively. The commonly-applied crack criteria were discussed. The effects of aging stress-strain relationship, micro-cracking and stress relaxation on crack formation were studied with concrete specimens cut out from an axially-restrained slab. The aspect of reliability-based cracking criteria was also discussed by Rostásy⁴. Methods of measuring internal moisture gradient have also been proposed by Izumo⁵, who investigated the relationship between drying shrinkage and internal moisture gradient of mortar specimens containing fly ash. Jensen⁶ measured chemical shrinkage and internal relative humidity (RH) on cement past of different water-binder ratios. Ueda et al.⁷ conducted drying shrinkage cracking tests according to the draft of Japan Industrial Standard (JIS) in order to propose a method for the prediction of drying shrinkage cracking. Pirsawetz et al.⁸ investigated early crack formation and the cracking progress due to autogenous shrinkage and thermal dilation using acoustic emission (AE) techniques on hardening silica fume cement paste and mortar samples made with a low water/binder ratio. Couch et al.⁹ reported that AE may be used to determine the time when the fluid-solid transition occurs in a cement paste, which is often referred to as time-zero. Nagataki et al.¹⁰ measured AE on reinforced concrete beams dried by a heater in order to induce cracks caused by drying shrinkage on the bottom surface of the beam. Maji et al.¹¹ employed three different non-destructive and non-invasive techniques (e.g. Holographic Interferometry, Speckle Photography, and Acoustic Emission) to study the fracture process in concrete. Bisschop et al.¹² evaluated three different 'destructive' microscopy methods (e.g. pre-impregnation, post-impregnation, and ESEM) for detecting drying shrinkage micro-cracks on cut cross-sections of specimens. Chariton et al.¹³ monitored early-age damage development in restrained cementitious mortar specimens using acoustic emission. Kim et al.¹⁴ reported the use of acoustic emission for monitoring early age cracking in restrained fiber reinforced mortars. Akhter et al.¹⁵ conducted an experimental study using restrained ring tests on concrete specimens of different geometries and boundary conditions, and evaluated cracking using the AE method.

RESEARCH SIGNIFICANCE

Although many studies on drying shrinkage and related cracking have been conducted, drying shrinkage cracking of concrete structures still continues to be a severe problem. The purpose of this study is to acquire fundamental data on the relationship between internal relative humidity and restrained drying shrinkage cracking, which was detected and quantified by using the acoustic emission method.

EXPERIMENTAL INVESTIGATION

In this study, all concrete specimens were sealed immediately after casting with a wet cloth and cover sheet to prevent evaporation of water. After 96 days of wet curing, the specimens were exposed to the drying environment on three faces only. The reason to start drying at an age of 96 days was to focus on drying shrinkage at a time when cement hydration was almost completed. Measurements of concrete strains, internal relative humidity, and acoustic emissions were recorded by a data logger every five minutes during the drying period.

Materials

Table 1 gives the mixture proportions of the concrete used in this study. Ordinary Portland cement with a specific surface of $3,360 \text{ cm}^2/\text{g}$ and a density of 3.15 g/cm^3 was used as the cement at a water-cement ratio (W/C) of 0.57, which is commonly used in Japan for normal concrete applications. The aggregates were river sand with a density of 2.62 g/cm^3 and a fineness modulus of 2.63, and crushed stone with a density of 2.61 g/cm^3 and a maximum size of 25 mm (1 in.), respectively, both of which were obtained from Nagara River, Japan. **Table 2** shows the obtained slump and air content. The 5% air content was required by JSCE standard for adequate freeze-thaw resistance. **Table 3** shows the compressive strength and modulus of elasticity measured on concrete cylinders at the age of 106 days (i.e. immediately after cracking of the corresponding restrained shrinkage specimen).

Specimens

Table 4 shows the two types of specimens prepared for the drying shrinkage cracking tests. **Figure 1** and **Photo 1** show the geometry of the restrained specimen (dog-bone shape), including locations of strain gauges, humidity sensors and acoustic emission sensors. The restrained specimen, made according to the Japan Industrial Standard¹⁶, measured 750 mm in length (30 in.), and had a mid-length cross-sectional area of 100 x 50 mm (4x2 in.). The restraining system consisted of four steel pipes (each 213 mm^2 (0.33 in.^2) in net cross-section) and two thick steel plates. Embedded strain gauges ($\phi 17 \times 54 \text{ mm}$ ($\phi 5/8 \times 2 \text{ in.}$)) were used to measure the longitudinal strain at the centre of the specimen cross-section. Non-heating ceramic humidity sensors were used to measure internal relative humidity in the concrete specimen (Naito¹⁷; Ozawa et al¹⁸) at depths of 15 mm ($5/8 \text{ in.}$) and 50 mm (2 in.), and were protected by a vapor-permeable membrane. Crack propagation was monitored by acoustic emission sensors applied at the surface of the concrete specimen as illustrated in **Figure 1**.

Figure 2 and **Photo 2** show the geometry of the unrestrained specimen, including the locations of strain gauges. This free specimen measured 100 x 100 x 750 mm (4x4x30-in.).

Monitoring equipment

(i) AE Measurement system¹⁹

Figure 3 shows an outline of the acoustic emission measurement system, which was used to record and analyze the waveform parameters, and a close-up view of the measured area, which had a length of 200 mm (8-in.). AE sensors were longitudinally placed 125 mm (5-in.) away from the center of the cracking test area. AE signals, detected by 150-kHz resonant sensors, were amplified to 50 dB by a pre-amplifier, with the threshold value set to 50 dB.

(ii) Non-heating ceramic humidity sensor^{17,18}

Photo 3 shows the sensing element of the non-heating ceramic humidity sensor used in the present study, which consists of a humidity sensing element (ceramic), a resistor (measuring element), and a circuit board for temperature correction. The sensor unit is operated at 5V DC. The range of relative humidity and sensitivity are 20-90% and $\pm 3\%$, respectively. In this study, it was assumed that the change in RH was an indication of the change in moisture in concrete.

RESULTS AND DISCUSSION

Time-related changes in temperature and relative humidity of concrete

Figure 4 shows the ambient air temperature and internal concrete temperature recorded during the drying period, which started after 96 days of wet curing. This figure shows that the internal concrete temperature matched the ambient air temperature, which ranged from 8 to 16°C (46 to 60 °F).

In Figure 5 shows the ambient air relative humidity and the internal concrete relative humidity recorded during the drying period. In this figure, the ambient RH varied from 37% to 75% during the drying period, with an overall average of 55%. Since the RH sensors could not measure above 90% RH, the data in Figure 5 can only confirm that the internal concrete RH at depths equal to or greater than 15 mm was above 90% for the period of time monitored.

Concrete strain and stress

Figure 6 shows the time-related changes in the strains of restrained and free specimens. This figure reveals that the strain in the restrained specimen was -133×10^{-6} after drying for 9.7 days (time of specimen failure), and the corresponding strain in the free specimen was -205×10^{-6} . This means that the sum of elastic and creep strains at failure was 72×10^{-6} .

The drying shrinkage stress development in the restrained specimen was determined using the following calculation procedure:

$$\Delta \varepsilon_e = \Delta \varepsilon_r - \Delta \varepsilon_{cr} - \Delta \varepsilon_f \quad (1)$$

$$\Delta \sigma_c = A_g / A_{cr} \times \Delta \varepsilon_e \times E_c / (1 + \phi_c) \quad (2)$$

where

$\Delta \varepsilon_r$ = strain measured restrained concrete specimen;

$\Delta \varepsilon_f$ = strain measured in free concrete specimen;

$\Delta \varepsilon_{cr}$ = creep strain;

$\Delta \varepsilon_e$ = elastic strain;

$\Delta \sigma_c$ = concrete stress at the cracking test area (MPa) (1MPa=145 psi);

A_g = cross section of specimen at gauge location (mm^2) (1mm=0.039 in.);

A_{cr} = cross section of specimen at cracking test area (mm^2);

ϕ_c = tensile creep coefficient;

E_c = modulus of elasticity of concrete (MPa).

The modulus of elasticity of concrete at the ages of 96-106 days was assumed to be constant and equal to the measured value of 27.7 MPa (Table 3). The creep coefficient was estimated as a function of drying time (Fig. 7) from previous data obtained on an identical concrete tested under similar drying and loading conditions (Ozawa et al.¹⁸). The stress in the cracking area was considered to be twice as that found at the strain gauge location ($A_g/A_{cr} = 2$).

Figure 8 shows the calculated mean concrete stress of the specimen cross section using equations (1) and (2) in an iterative procedure. This figure reveals that tensile stress developed gradually as drying occurred. After 9.7 days of drying, the specimen failed at a maximum tensile stress of 1.4 MPa (200 psi.). This uniform restrained shrinkage stress combined to additional internal restraint tensile stress due to a strong moisture gradient near the surface (<15 mm (5/8 in.)) was the reason for cracking at this low tensile stress level.

Acoustic emission measurement results and crack propagation

Figure 9 shows the time-related changes in mean concrete stress and the cumulative AE hit counts. This figure shows that the concrete stress and the accumulated AE hit counts both increased with drying time. The time of crack emergence occurred when the accumulated AE hit counts increased drastically at a drying time of 9.7 days.

Previous studies (Chariton et al.¹³; Kim et al.¹⁴; Akhter et al.¹⁵) have shown that the acoustic energy release

rate can be used to describe the development and propagation of crack in restraint concrete specimens. Figure 10 shows the time-related changes in the amplitude of AE hits. The drying period was divided into three time periods: Period A1 is from 0 to 2 days, Period A2 is from 2 to 9 days, and Period A3 is from 9 to 13 days. During Period A1, AE hits were generated by micro-cracking caused by rapid drying shrinkage at the surface of the specimen. The maximum amplitude of AE hits was 90 dB. During Period A2, a relatively-small number of AE hit counts were generated, at which time the drying on the surface seemed to approach a stationary state, and slowly progressed deeper in the specimen. During Period A3, a large number of AE hits were generated due to further development of micro-cracks as result of continued drying, and the specimen failed when the intrinsic tensile stress reached the specimen tensile strength. In particular, AE hits were concentrated at drying period of 9.7 days, which coincided with the observed specimen failure, confirming that the AE method can be applied for the monitoring of the drying shrinkage cracking process.

Figure 11 shows the relationship between the amplitude of AE hits and source locations within the cracking test area. During Period A1, AE hits were generated over the entire cracking test area. During Period A2, the AE hit count was small. During Period A3, AE hits concentrated near the center of the cracking test area. More specifically, the maximum amplitude of AE hits was 85 dB in the center of the cracking test area. Previous studies (Couch⁹, Chain¹³) have also reported similar observations regarding the location of acoustics events as a function of drying time.

Figures 12 and 13 show the top and side views of surface crack generation in the test area, respectively. It could be confirmed that AE hit locations concentrated at the observed crack positions. Using the AE method, it was thus possible to evaluate the time at which drying shrinkage cracks occurred both at the surface and deep within the concrete specimen.

CONCLUSIONS

In conclusion, this study used the acoustic emission method for detecting cracking due to drying shrinkage. After 9.7 days of drying, the specimen failed at a measured average stress of 1.4 MPa (200 psi). This average restrained shrinkage stress combined to additional internal restraint tensile stress due to a strong moisture gradient near the surface (<15 mm (5/8 in.)) was the reason for cracking at this low tensile stress level.

AE hit locations were found to concentrate at the observed crack positions at the top and on the sides of the specimen, confirming that the AE method can be used to evaluate the time at which drying shrinkage cracks occur both at the surface and deep within the concrete specimen.

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REFERENCES

1. JSCE, Standard specification for design and construction of concrete structures, *Japan Society of Civil Engineer*, SP 1-2 Japan (in Japanese).
2. F.H. Wittmann, G. Marinola, H. Sadouki, Material properties influencing early cracking of concrete, *Control of cracking in Early age concrete*, Mihashi&Wittmann (eds.), Swets&Zeitlinger, Lisse, 2002, p. 3-18.
3. K. Van Breugel, P. Lura, Predicting cracks in hardening concrete using stress-based cracking criterion, *Control of cracking in Early age concrete*, Mihashi&Wittmann (eds.), Swets&Zeitlinger, Lisse, 2002, p.317-324.
4. F.S. Rostásy, M. Krauß, Effects of stress-strain relationship and relaxation on restraint, stress crack formation in young concrete members, *Control of cracking in Early age concrete*, Mihashi&Wittmann (eds.), Swets&Zeitlinger, Lisse, 2002, p. 305-316.
5. K. Izumo, T. Nawa, Shrinkage strain of mortar using fly ash under two different temperature, *JSCE Journal*, No. 739, V. 60, 2003, p. 221-236, (in Japanese).
6. O.M. Jensen, Autogenous Phenomena in Cement Based Material, Aalborg University, Doctoral Thesis, 2005.
7. K. Ueda, Y. Sato, C. Kiyohara, S. Nagamatu, H. Hasegawa, Drying shrinkage cracking of concrete kept under dry air conditions from early ages, *Control of cracking in Early age concrete*, Mihashi&Wittmann (eds.), Swets&Zeitlinger, Lisse, 2002, p. 317-324.
8. S. Pirskawetz, F. Weise, and P. Fontana, Detection of early-age cracking using acoustic emission, *International RILEM Conference on Volume Change of Hardening Concrete, Testing and Mitigation*, Technical University of Denmark, Lyngby, Denmark, August 2006, p. 385-392.
9. J. Couch, P. Lura, O.M. Jensen, J. Weiss, Use of acoustic emission to detect cavitation and solidification (time

- zero) in cement pastes, *International RILEM Conference on Volume Change of Hardening Concrete, Testing and Mitigation*, Technical University of Denmark, Lyngby, Denmark, August 2006, p. 393-400.
10. S. Nagataki, N. Otsuki, T. Kamada, G. Yazakai, M. Kawashima, Evaluation of Drying Shrinkage Cracks in Concrete by Destructive Testing Methods, *Proceeding of Regional Symposium on Infrastructure Development in Civil Engineering*, Thailand, December 1995, p. 94-108.
 11. A.K. Maji, S.P. Shah, Application of Acoustic Emission and Laser Holography to Study Micro-Fracture in Concrete, *ACI Special Publication*, SP112-05, 1988, p. 83-109.
 12. J. Bisschop, J.G. M. Van Mier, How to study drying shrinkage micro-cracking in cement-based materials using optical and scanning electron microscopy?, *Cement and Concrete Research*, 32, p. 279-287, 2002.
 13. T. Chariton, W.J. Weiss, Using Acoustic Emission to Monitor Damage Development in Mortars Restrained from Volumetric Changes, *ACI Special Publication*, SP206-13, 2002, p. 205-217.
 14. B. Kim, W.J. Weiss, Using Acoustic Emission to Quantify Damage in Restrained Fiber-reinforced Cement Mortars, *Cement and Concrete Research*, 33, 2003, p. 207-214.
 15. B.H. Akhter, J. Weiss, The role of specimen geometry and boundary conditions on stress development and cracking in the restrained ring test, 36, 2006, p. 189-199.
 16. T. Shiire, Y. Aoyagi and K. Kawase, Testing Method on Cracking of Concrete Due to Restrained Drying Shrinkage, *Concrete Journal of JCI*, Vol. 23, No. 3, 1985, p. 40-54 (in Japanese).
 17. Y. Nanto, *Sensor and Basic technology*, Kougaku-Tosyo, June 2000, p. 72-96 (in Japanese).
 18. M. Ozawa, M. Kasuya, H. Morimoto, Relationship between creep and chemical potential of concrete, *Proceeding of International Conference on CONCREEP8, Creep, Shrinkage and Durability of Concrete and Concrete Structures*, Editor of T. Tanabe, CRC Press, Alkema Book, Vol. 1, 2008, p. 73-79.
 19. Y. Niwa, M. Ohtsu, *Characteristics and Theory of Acoustic Emission*, Morikita Publishing Co. Ltd, 1988 (in Japanese).

Table 1 – Concrete mixture proportion
(1 kg/m³ = 1.6858 lb/yd³)

Water-Cement Ratio	Unit Weight (kg/m ³)				
	Fine		Coarse		Admixture
	Water	Cement	Aggregate	Aggregate	
0.57	180	316	851	926	0.825

Material	Properties	Density (g/cm ³)
Water	Tap water	1.00
Cement	Ordinary Portland cement	3.13
Fine aggregate	River sand	2.61
Coarse aggregate* (max. 25 mm (1 in.))	River stone	2.62
Admixture	Air-Entraining & Water-Reducing agents:	1.27

Table 2 – Properties of fresh concrete
(1mm=0.039 in.)

Slump (mm)	Air content (%)
90	5.0

Table 3 – Strength and elastic modulus at 106 days
(1MPa=145psi)

Compressive strength (MPa)	Splitting Tensile strength (MPa)	Elastic Modulus (GPa)
37.9	3.3	27.7

Table 4 –Detail of specimens
(1mm=0.039-in.)

Category of specimen	Specimen size (mm)	Shape	Number
Restrained specimen	150x100x750 (min. cross section of test area: 100x50)	Dog bone	1
Free specimen	100x100x750	prism	1

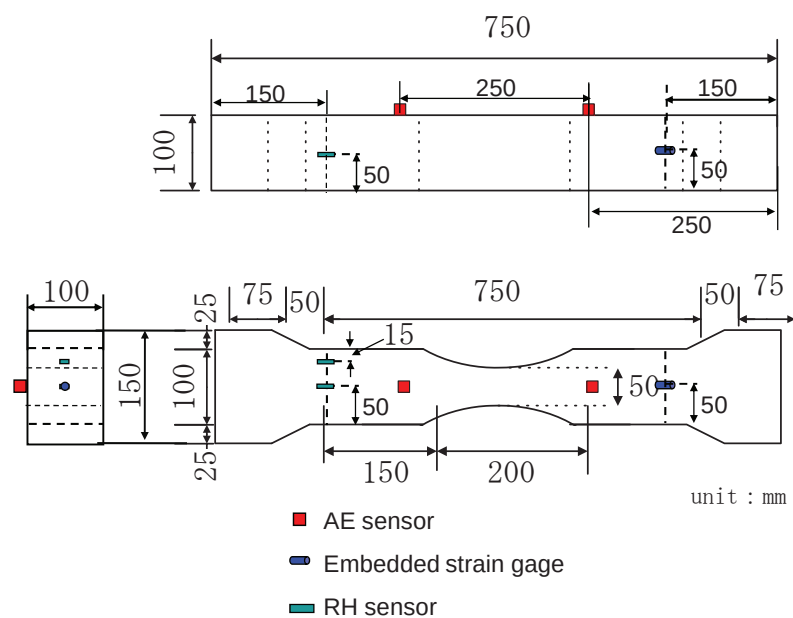


Fig. 1 – Detail of restrained specimen
(1mm=0.039 in.)

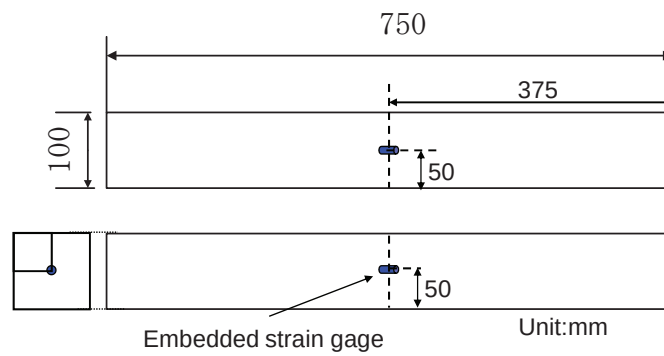


Fig. 2 – Detail of free specimen
(1mm=0.039 in.)



Photo 1 –Outline of restrained specimen

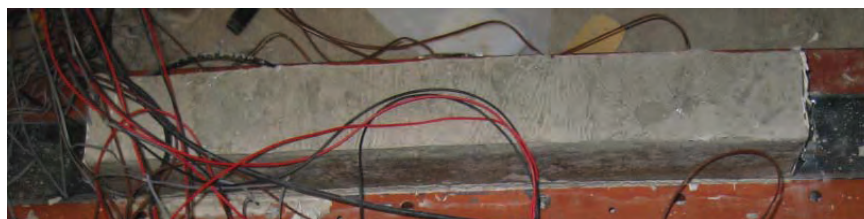


Photo 2 –Outline of free specimen

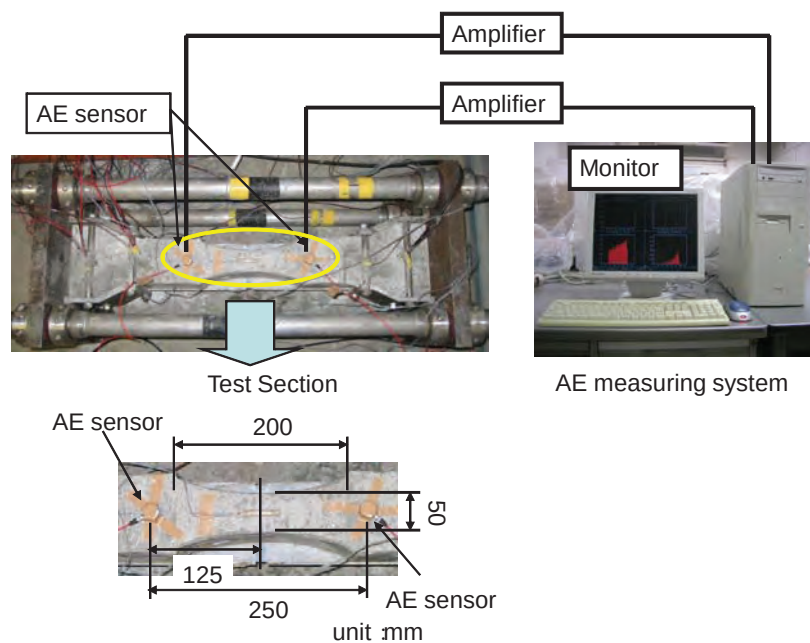


Fig. 3 – AE measurement system
(1mm=0.039 in.)



Photo 3 –Ceramic RH sensor (with temperature-correction circuit)

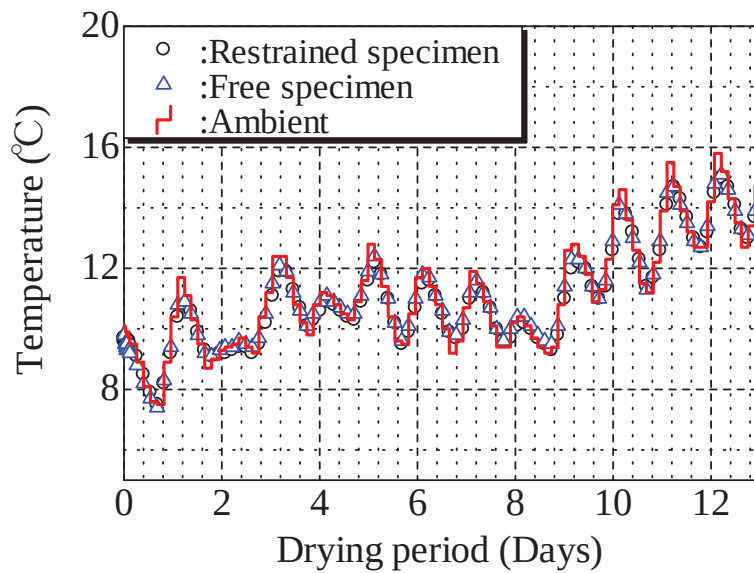
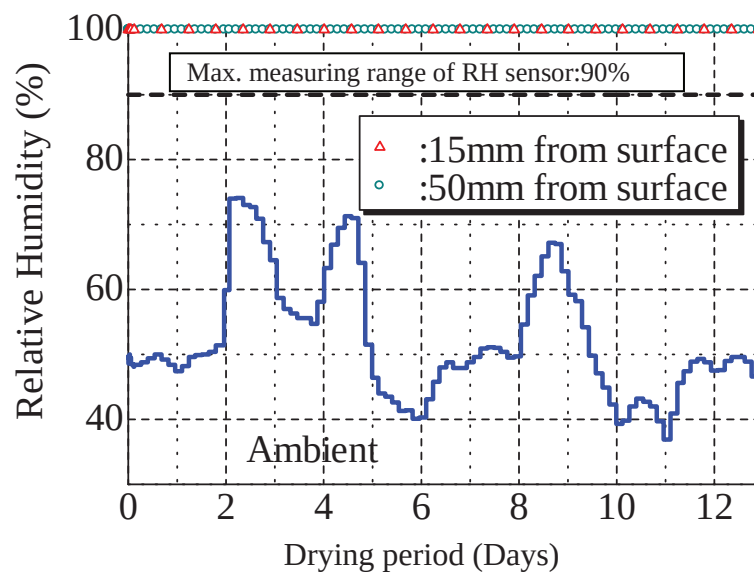


Fig. 4 – Relationship between temperature and drying period

Fig. 5 – Relationship between relative humidity and drying period
($^{\circ}\text{F}=9/5^{\circ}\text{C}+32$; 1mm=0.039 in.)

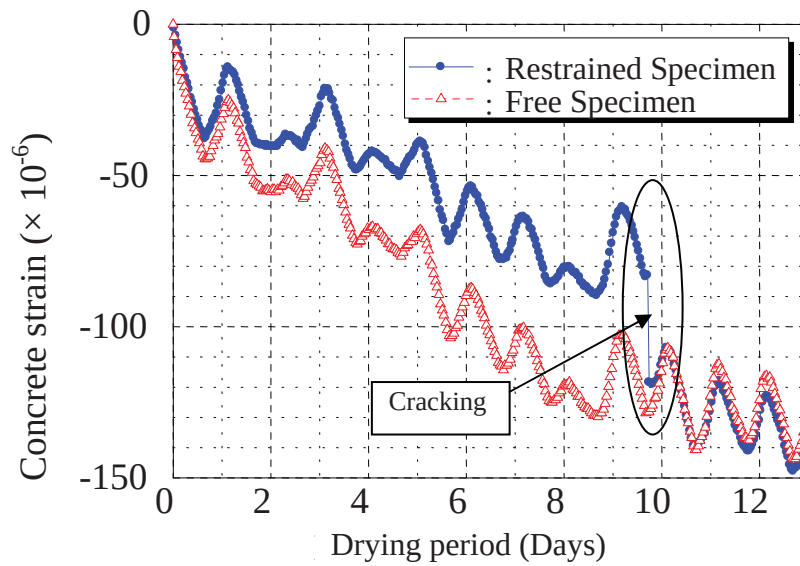


Fig. 6 – Relationship between concrete strains and drying period

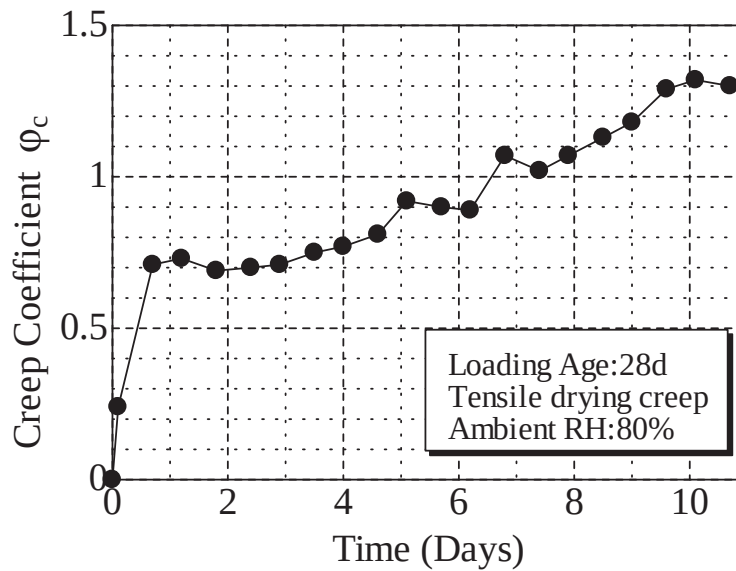


Fig. 7 – Relationship between tensile creep coefficient and drying/loading time

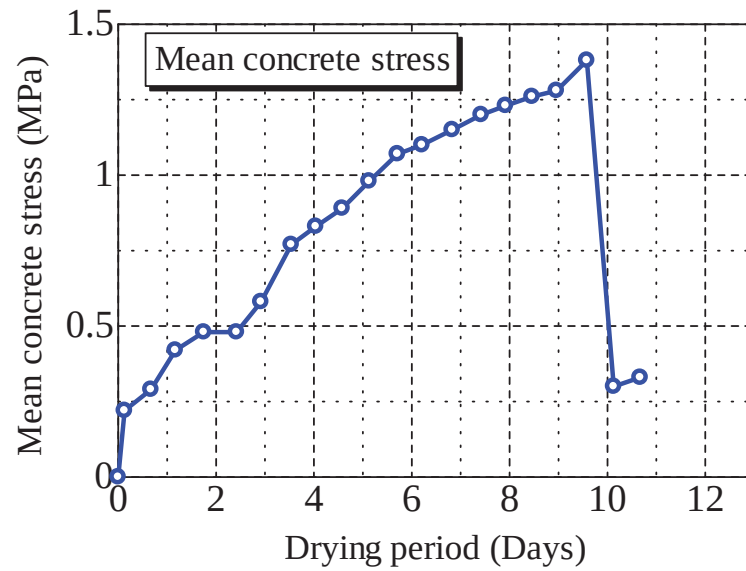


Fig. 8 – Relationship between mean concrete stress and drying period
(1MPa=145psi)

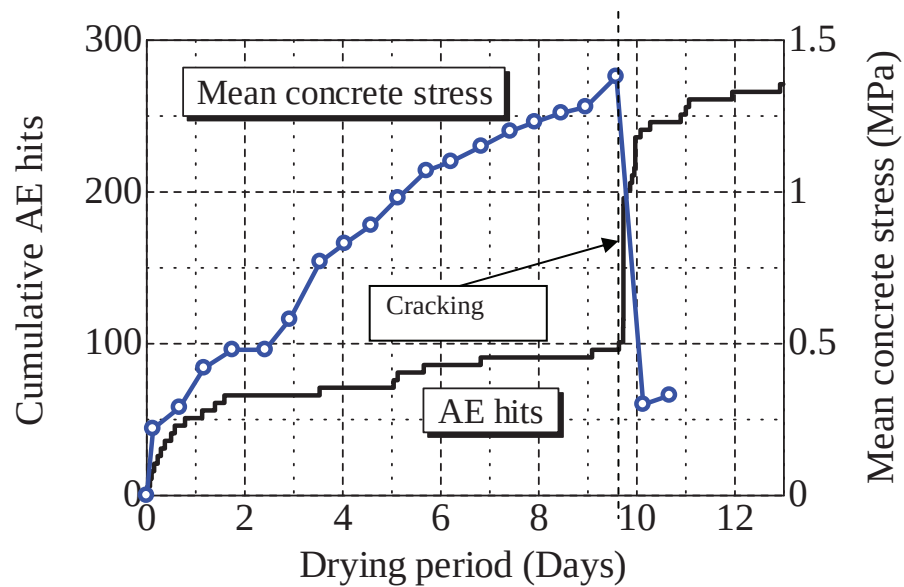


Fig. 9 – Relationship between cumulative AE hit counts and mean concrete stress over drying period

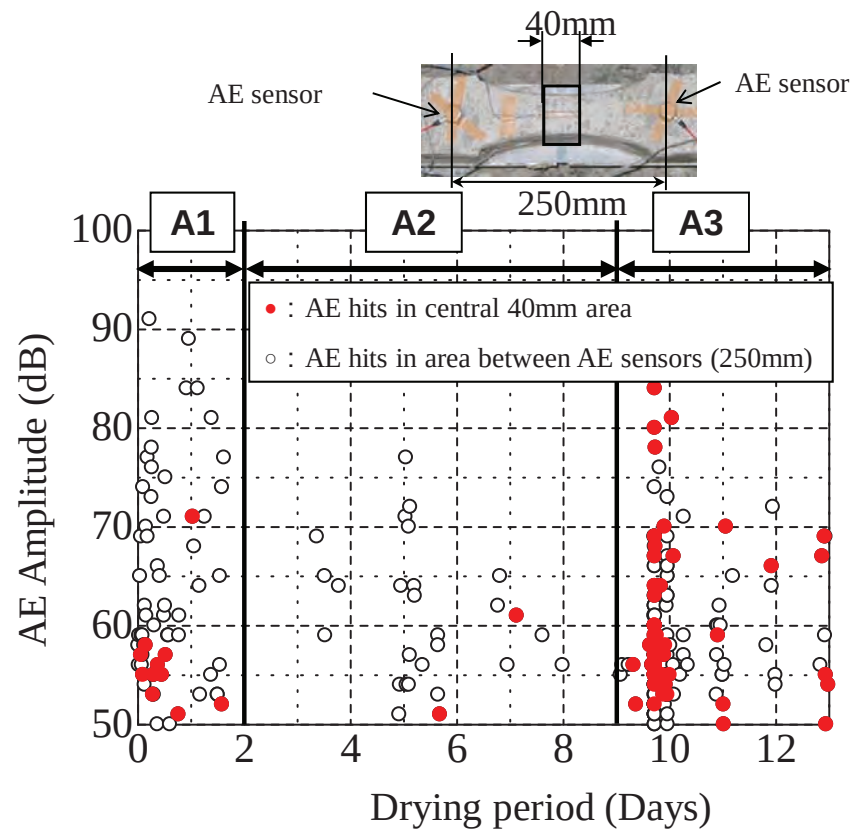


Fig. 10– Relationship between AE amplitude and drying period
(1mm=0.039 in.)

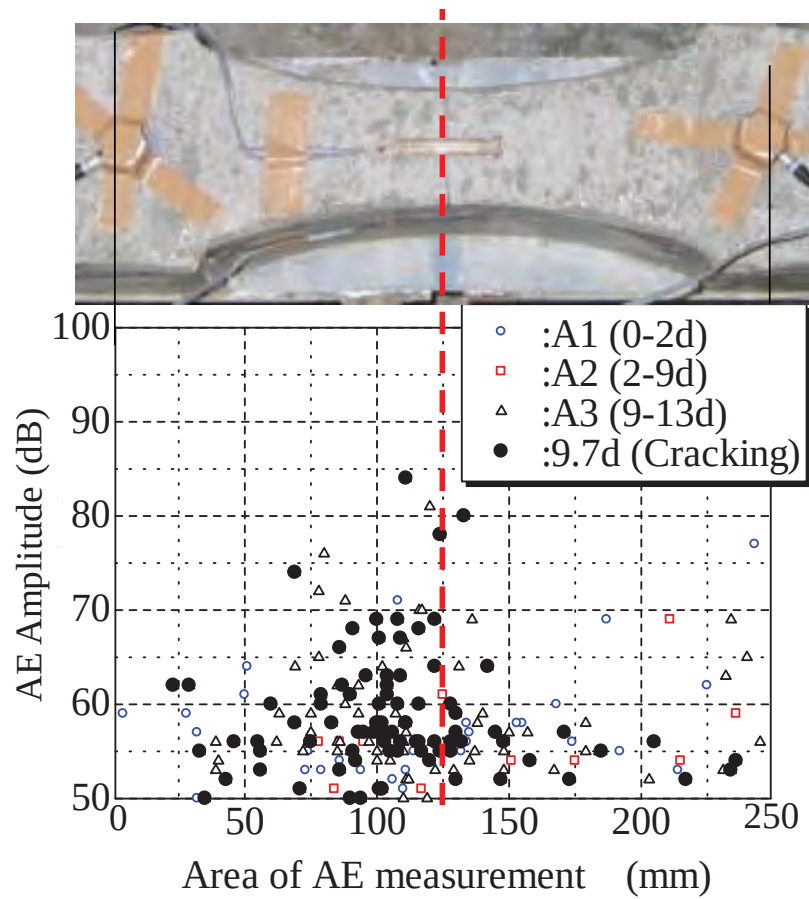


Fig. 11 – Relationship between AE amplitude and area of measurement
(1mm=0.039 in.)

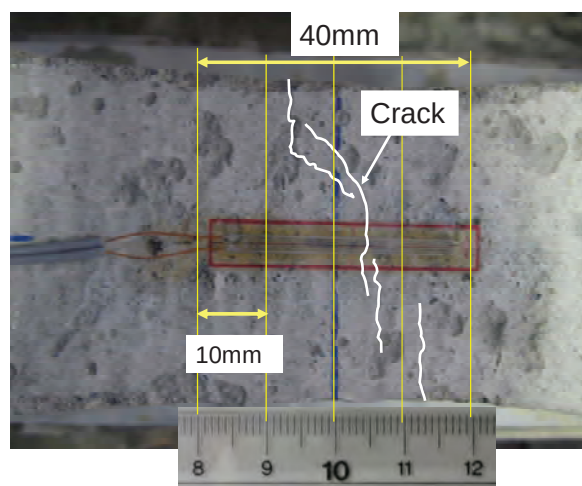


Fig. 12 – Observation of cracking (top view). (1mm=0.039 in.)

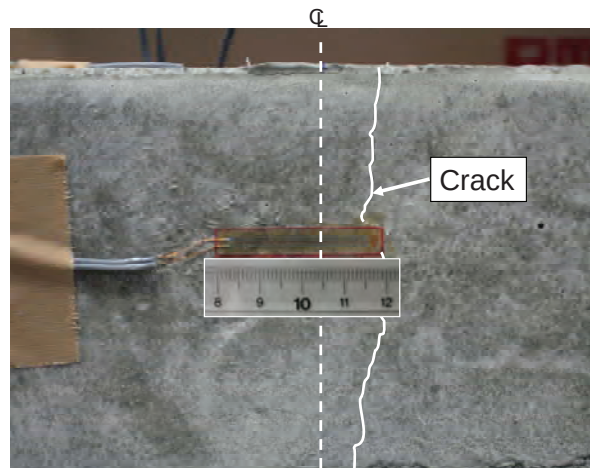


Fig. 13 – Observation of cracking (side view)

Continuous Ultrasonic Assessment of Elastic Modulus of Cementitious Materials through Setting and Early Strength Gain

by K.V. Subramaniam and J. Lee

Synopsis: An ultrasonic method for continuously assessing changes in the shear modulus of hydrating cementitious materials after casting, through setting and early strength gain, is presented. In the test method, reflected shear waves from the interface between the material of the form and the cementitious material are monitored. The test procedure for obtaining the ultrasonic test data and the inversion subroutines for assessing the shear modulus of the cementitious material at different stages of hydration are described. Results from a test program showing the response of ultrasonic signals of 1 MHz frequency reflected from the interface between the form and mortar are presented. A form made of polymethyl-methacrylate (PMMA), was used in the study. The observed experimental trends are explained considering reflection at the interface between two visco-elastic materials. It is shown that shear modulus can be determined immediately after casting and the increase in shear modulus can be sensitively monitored through setting and early strength gain. The shear modulus assessed at 1 MHz exhibits a five orders of magnitude increase in the first 24 hours after casting. The rate of increase in the shear modulus is the most rapid before initial set. The rate of modulus decreases steadily through final set and early strength gain. It is shown that there is a complete phase reversal in the reflected waves with time. The reversal corresponds in time with the final setting time determined using ASTM C 403 and it occurs when the shear modulus of the mortar is almost equal to the shear modulus of PMMA.

Keywords: hydration; mortar; setting time; shear modulus; ultrasonic shear wave; visco-elastic

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INTRODUCTION

After casting, cementitious materials exhibit a continuous change in the mechanical properties produced by the hydration reaction. There is also a change in state, from a fluid to a solid, which occurs in the first few hours and is associated with setting. There is a gradual development in the rigidity through setting and early strength gain. Currently, changes in the material properties of the cementitious material after mixing are followed using different techniques, each with its own limitations and applicability. Before setting, the elastic and viscous moduli of the material are obtained from rheological measurements¹. These measurements however cannot be directly performed on concrete and the onset of setting defines a practical limit for their application. The increase in penetration resistance with time is currently used to quantify changes in stiffness through setting. The procedure for determining the penetration resistance from mortar has been standardized in ASTM C 403². The penetration resistance method also cannot be directly applied to concrete and does not provide for direct evaluation of useful mechanical properties. After final setting, the elastic material properties of concrete are usually obtained using mechanical tests²⁻⁴ or vibration-based measurements performed on standard specimens^{5,6}.

Techniques which provide for (a) continuous monitoring of early age elastic material properties of cementitious materials through setting and early stiffening, (b) are non-invasive, and (c) have the potential for directly monitoring concrete, are currently unavailable or are under development. A test device for monitoring the through thickness ultrasonic compression wave velocity in concrete after casting was recently developed by Reinhardt et al.⁷. The development of elastic material properties of concrete was assessed from the observed change in compression wave velocity with time. This technique however does not provide sufficient sensitivity before setting, while the concrete is in a fluid state. A one-sided ultrasonic technique, similar to the one presented in this paper, has been used by other researchers⁸⁻¹¹ to study the early hydration in cementitious materials. The amplitude of the ultrasonic wave reflection at the interface between cement paste and an elastic substrate material was shown to be sensitive to the kinetics of hydration reaction. Microwave-based techniques have also been proposed for monitoring the strength gain of concrete^{12,13}. The dielectric properties obtained from a microwave measurement however do not provide for direct determination of the mechanical properties of the cementitious material.

A one-sided ultrasonic test procedure, which consists of continuously monitoring the waves reflected at the interface of polymethyl methacrylate (PMMA) and the cementitious material, is presented in this paper. Since the material properties of the cementitious material change with time, monitoring the reflected waves off of the PMMA-cementitious material interface provides a convenient way to assess these changes. The reflected waves at the PMMA-mortar interface are used to monitor changes in the state of the cementitious material as reflected in its acoustic properties. Analytical framework for (a) interpreting the observed trends and (b) for determining the increase in the shear modulus of the hydrating cementitious material, using the information provided by the reflected stress waves is presented. Finally, the test procedure and the analytical framework are used to study the development of the shear modulus of mortar as a function of time/age. It is shown that the changes in the shear modulus can be monitored sensitively after casting using the ultrasonic technique. The technique presented in this paper provides continuous information about any cementitious material after casting, through setting, and early strength gain.

BACKGROUND

The experimental test setup for wave reflection measurements is shown in [Figure 1\(a\)](#). The measurements in the test procedure introduced in this paper are based on determining the changes in the amplitude, $r(f)$, and phase, $\Delta\Phi$, of an incident wave after reflection at the PMMA-mortar interface ([Figure 1\(b\)](#)). Reflection of a wave at any bi-material interface introduces a change in the amplitude and the phase of the incident wave. The exact change in the amplitude and phase introduced by the reflection depends upon the frequency dependent material properties of the

two media in contact. Considering an incident wave $A(f)$, at the mortar-PMMA interface, the reflected wave is given as ¹⁴

$$\text{reflected wave} = \left[r(f)e^{i\Delta\Phi} \right] A(f) = \frac{Z_{\text{mortar}} - Z_{\text{PMMA}}}{Z_{\text{mortar}} + Z_{\text{PMMA}}} A(f) \quad (1)$$

where $r(f)$ is the change in amplitude of an incident wave at frequency f , Z_{mortar} and Z_{PMMA} are the acoustic impedances of mortar and PMMA, respectively and $\Delta\Phi$ is the phase change introduced after one reflection at the PMMA-mortar interface. $r(f)$ is also known as amplitude reflection factor ¹⁰. The acoustic impedance of a material is given as

$$Z = \sqrt{\rho G} \quad (2)$$

where ρ and G are the density and the shear modulus of the material, respectively. In materials which exhibit frequency dependent elastic material properties, the acoustic impedance is a complex number and both $r(f)$ and $\Delta\Phi$ vary with frequency.

EXPERIMENTAL SETUP AND TEST PROCEDURES

The composition of the mortar used in the experimental work had the following proportion by weight of the constituents: cement: water: fine aggregate = 1.0 : 0.4 : 2.0. Type I cement was used and the fine aggregate comprised of river sand. In the test setup, the mold was 12.5 mm (0.5 in) in thickness. The mold was cylindrical in shape, with height and inner diameter equal to 50 mm (2.0 in) and 75 mm (3.0 in), respectively. The average ambient temperature was equal to 25 °C (77°F) and the maximum temperature change produced by the hydration was equal to 2 deg C (3.6 deg F). The temperature of the mortar was recorded by placing a thermocouple approximately in the center of the specimen.

After mixing, the cementitious material was placed in a mold made of PMMA. Ultrasonic signals were introduced in the PMMA using a broad-band ultrasonic transducer with a central frequency equal to 1MHz. The ultrasonic transducer was attached to the bottom of the mold using a rapid setting epoxy. A pulser-receiver provided the excitation signal to the ultrasonic transducer. The ultrasonic signal received back at the transducer after reflection at the PMMA-mortar interface was digitized by the oscilloscope. An averaging procedure, which allowed for eliminating the random noise in the signal was adopted while collecting the time-domain signal ¹⁰. The test procedure comprised of averaging 100 signals in the time-domain. The time-averaged signal was then transferred to the computer over a GPIB interface. The time domain signal was windowed and transformed into frequency domain using the FFT algorithm. The phase angle at a given frequency component was obtained by unwrapping the phase obtained from the FFT. The amplitude and the phase angle obtained from the FFT at different frequencies were recorded and stored.

The reflected wave signals were collected at the PMMA-water interface prior to placing the cementitious material. The mold was filled with water for this measurement. The mold was then emptied of the water and the surface of the PMMA was dried using absorbent paper before placing the mortar. The reflected signals were collected and stored every ten minutes up to 20 hours after casting. The required parameters, $r(f)$ and $\Delta\Phi$, were obtained from the frequency-domain data using the self-calibrating procedure, which allows for removing the influence of geometric and material signal losses along the signal path ¹⁵. In the frequency domain, the stress wave signals received after a single reflection at the PMMA-water and PMMA-mortar interface can be represented as a simple product of terms

$$F^{\text{PMMA-water}} = s(f)d_1(f)d_2(f) \text{ and } F^{\text{PMMA-mortar}} = s(f)d_1(f)d_2(f)r(f) \quad (3)$$

where F is the magnitude of FFT of the captured time domain signal, $d_1(f)$ is the geometric and material signal losses in the couplant, $d_2(f)$ is the material signal losses along the signal path in the PMMA, $S(f)$ the input source function, and $r(f)$ is the amplitude reflection factor at the PMMA-mortar material interface. Therefore the amplitude reflection factor, $r(f)$, can be determined by normalizing the reflected magnitude off the PMMA-mortar interface with the reflected amplitude off the PMMA-water interface as shown below

$$r(f) = F^{\text{PMMA-mortar}} / F^{\text{PMMA-water}} \quad (4)$$

The amplitude reflection factor, $r(f)$, determined using Equation 4 defines the ratio of the amplitudes of incident and reflected waves at frequency f that is reflected from an interface between two materials. Since the amplitude reflection factor for shear wave reflection at the PMMA-water interface should have a magnitude equal to 1.0, Equation (4) allows for evaluating $r(f)$ from PMMA-mortar interface.

The phase change at any given frequency introduced by the reflection at the PMMA-mortar interface can be extracted by subtracting the phase angle of the stress wave recorded after one reflection at the PMMA-water interface from that at the PMMA-mortar interface¹⁶. Change of phase, $\Delta\Phi$, introduced by the reflection of stress wave at the PMMA-mortar interface can be calculated as shown below

$$\Delta\Phi = \pi - (\phi^{\text{PMMA-mortar}} - \phi^{\text{PMMA-water}}) \quad (5)$$

where $\phi^{\text{PMMA-mortar}}$ and $\phi^{\text{PMMA-water}}$ are the phase angles obtained from the FFT of the time domain signals collected after one reflection at the PMMA-mortar interface and the PMMA-water interface at the corresponding temperature, respectively.

The choice of PMMA as the material for the mold was based on having the ability to sensitively determine early age changes in the shear stiffness of the cementitious materials. After mixing, the cementitious materials are in a fluid state and have very small shear stiffness. Further, early changes in stiffness are also of a small magnitude. Since the shear stiffness is directly related to the acoustic impedance, sensitive detection of small changes in the acoustic impedance, which has a small magnitude requires that the acoustic impedance of the base material should be as low as possible. Another requirement for the material of the mold is that it should be chemically inert to the cementitious material. PMMA was found to be suitable for this purpose because of its low acoustic shear impedance and chemical inertness to cement and products of hydration.

PMMA is known to exhibit sensitivity to temperature changes¹⁰. Since hydration is an exothermic reaction, the changes in phase and amplitude produced by a change in temperature were experimentally determined by filling the PMMA mold with water, which was heated to identical temperatures as those recorded from the mortar samples. At 1 MHz, while a 10 deg C (18 deg F) change in temperature produced a 2% change in $r(f)$ the change in $\Delta\Phi$ was more significant. The temperature of the bottom and top faces of the PMMA were recorded using thermocouples. The temperature difference between the top and bottom surfaces after placing the mortar inside the mold was found to be insignificant during the test. The phase change produced by varying temperature in PMMA as a result of hydration are compensated by using the phase angle recorded after reflection at the PMMA-water interface at the same temperature as that of the mortar sample. The change in phase produced by temperature effects was subtracted from the total phase change recorded after one reflection at the PMMA-mortar interface.

EXPERIMENTAL RESULTS

The reflection factor ($r(f)$) and the phase change in the stress wave (Φ) introduced by reflection at PMMA-mortar interface, captured after one reflection at the PMMA-mortar interface at the resonant frequency of the transducer (1MHz) are plotted in Figure 2(a). The amplitude reflection factor determined at 1 MHz is referred to as $r(1)$ in the text. The distinctive features in the $r(1)$ response have been labeled O, A and B. After mixing, there is a steady decrease in the magnitude of $r(1)$ up to the occurrence of feature A, where $r(1)$ appears to level off for a short time. Following A, the magnitude of $r(1)$ continues to decrease up to Point B. Point B corresponds with the minimum recorded value of $r(1)$. After B, $r(1)$ starts to increase and the observed trend indicates a continued increase after 20 hours. The occurrence of features A and B in $r(1)$ response measured at the PMMA-mortar interface has previously been shown to correspond in time respectively with the initial and final setting times determined using the pin penetration method⁹.

The phase change, $\Delta\Phi$, due to reflection at the PMMA-mortar interface is shown in Figure 2(b). The $\Delta\Phi$ obtained from Equation 5 is plotted in the figure. $\Delta\Phi$ is close to 180 degrees for approximately 4 hours, following which $\Delta\Phi$ exhibits a slight increase. The observed increase in phase corresponds approximately with the occurrence of feature A in the $r(1)$ response. Following this slight increase, there is a steady decrease in the value of $\Delta\Phi$ up to 20 hours where it appears to be approaching an asymptotic value close to 0 degrees. In the first few hours up to the occurrence of feature A in $r(1)$ response, there is a significant decrease in $r(1)$ while $\Delta\Phi$ is relatively constant. Thus it can be concluded that early changes in the microstructure which result in a loss of workability are reflected in the amplitude of the incident wave. There is a rapid drop in $r(1)$ between Points A and B, which corresponds with a fast decrease in $\Delta\Phi$. This suggests a rapid change in both the amplitude and the phase of the incident wave through the setting. After Point B, both $r(1)$ and $\Delta\Phi$ change at a steady and slower rate.

The ultrasonic measurements were obtained from mortar mixtures containing admixtures to investigate sensitivity of the technique to the varying rates of hydration. Figure 4 shows comparisons of the $r(1)$ and $\Delta\Phi$

measured from the control and mortar samples containing accelerator and retarder. The compositions by weight of other constituents were identical for the three mortar mixtures. It can be seen that the basic trends in the response of the three mixtures are similar. Changes in the rate of hydration introduced by admixtures are reflected in both $r(1)$ and $\Delta\Phi$. The accelerator/retarder added to the mortar mixture produces a shift to the left/right indicating a more rapid/slower change in the material properties.

INTERPRETATION OF TEST RESULTS

Reflection of a stress wave at the PMMA-mortar interface produces a change in both the amplitude and the phase when compared with the incident wave (shown schematically in [Figure 1\(b\)](#)). The exact change in the amplitude and phase introduced by the reflection depends upon the frequency dependent material properties of the two media in contact. Since the material properties of PMMA are invariant with time, changes in the amplitude reflection factor are produced by changes in the acoustic impedance of the mortar with time.

A simple analysis is now attempted, which considers a simplistic representation of the mortar and PMMA as visco-elastic materials. This idealization of the both mortar and PMMA as visco-elastic materials has been shown to be reasonable and it also allows for explaining the observed two-stage trend in $r(1)$, i.e. an initial decrease followed by an increase^{10,14}. The shear modulus of a visco-elastic material is represented by a complex number, i.e. the shear modulus (G) has real and imaginary parts, which are equal to the storage (G') and loss moduli (G''), respectively ($G = G' + iG''$). The change in the amplitude ($r(f)$) and phase ($\Delta\Phi$) of an incident wave produced by reflection of shear waves at the interface of two visco-elastic materials, is obtained as¹³.

$$R = r(f)e^{i\Delta\Phi} = \frac{\sqrt{\rho_{\text{mortar}}}\sqrt{G_{\text{mortar}}}e^{i\frac{\phi_{\text{mortar}}}{2}} - \sqrt{\rho_{\text{PMMA}}}\sqrt{G_{\text{PMMA}}}e^{i\frac{\phi_{\text{PMMA}}}{2}}}{\sqrt{\rho_{\text{mortar}}}\sqrt{G_{\text{mortar}}}e^{i\frac{\phi_{\text{mortar}}}{2}} + \sqrt{\rho_{\text{PMMA}}}\sqrt{G_{\text{PMMA}}}e^{i\frac{\phi_{\text{PMMA}}}{2}}} \quad (6)$$

where, R is the reflection coefficient, $r(f)$ is the amplitude reflection factor, $\Delta\Phi$ is the change in phase introduced by the reflection, ρ_{mortar} and ρ_{PMMA} are the densities of mortar and PMMA, respectively. G_{mortar} and G_{PMMA} are the shear moduli of mortar and PMMA, respectively given as, $G_{\text{mortar}} = \sqrt{(G'_{\text{mortar}})^2 + (G''_{\text{mortar}})^2}$, $G_{\text{PMMA}} = \sqrt{(G'_{\text{PMMA}})^2 + (G''_{\text{PMMA}})^2}$. ϕ is the phase angle for the material, $\phi_{\text{mortar}} = \tan^{-1}(G''_{\text{mortar}}/G'_{\text{mortar}})$, $\phi_{\text{PMMA}} = \tan^{-1}(G''_{\text{PMMA}}/G'_{\text{PMMA}})$, G' and G'' are the storage and loss moduli of the material at 1 MHz.

The shear modulus of mortar can now be obtained from the expression given in Equation 6 and is given as

$$\left| \frac{G_{\text{mortar}}}{G_{\text{PMMA}}} \right| = \left(\frac{\rho_{\text{PMMA}}}{\rho_{\text{mortar}}} \right)^2 \left| \frac{1 + r(1)e^{i\Delta\Phi}}{1 - r(1)e^{i\Delta\Phi}} \right|^2 \quad (7)$$

In Equation 7, $r(1)$ and $\Delta\Phi$ are experimentally measured changes in amplitude and phase angle after reflection at the PMMA-mortar interface, respectively.

Prior to performing an inversion to determine the material properties of mortar using the experimental data, it is essential to perform a sensitivity analysis of the parameters involved. The variations in $G_{\text{mortar}}/G_{\text{PMMA}}$ as a function of $r(1)$ for different values of $\Delta\Phi$ computed using Equation 7 are shown in [Figure 3](#). The specific gravities of PMMA and mortar were assumed to be equal to 1.1 and 2.4, respectively. Since G_{PMMA} is invariant with time, this plot shows the variation in G_{mortar} as a function of $r(1)$ for different $\Delta\Phi$. It can be seen that $r(1)$ is sufficiently sensitive to changes in G_{mortar} . It can be seen that small changes in $r(1)$ correspond with a large change in G_{mortar} for values of $\Delta\Phi$ different than $\pi/2$. This analysis indicates that it is practically feasible to obtain the values of G_{mortar} from the measured change in $r(1)$.

Changes in ρ_{mortar} with time are insignificant and therefore $\rho_{\text{PMMA}}/\rho_{\text{mortar}}$ can be treated as a constant in Equation 7. The density of each mortar mixture was determined using samples of hardened mortar. The change in the shear modulus of mortars assessed at 1MHz as a function of time is shown in [Figure 4](#). The high-frequency values of G_{PMMA} and ϕ_{PMMA} , assessed at 1MHz are currently not available. However, since G_{PMMA} is relatively invariant with time, the shear modulus of mortar, G_{mortar} , has been normalized with respect to G_{PMMA} in [Figure 4](#). The measured change in $r(1)$ is also plotted on the graph for comparison. It can be seen that the changes in the shear modulus can be monitored very sensitively from a very early age. There is five orders of magnitude increase in the

total increase in shear modulus in the first 24 hours. It should be noted that the G_{mortar} obtained by from the inversion of the ultrasonic signals is the high frequency shear modulus assessed at 1 MHz. The noise in the G_{mortar} in the first few hours can be explained considering the results of the sensitivity analysis. When the ratio of the acoustic impedance of the two materials in contact is low, a large change in the modulus of the softer material produces a small change in the measured $r(f)$. Conversely, small changes corresponding to the noise in the $r(f)$ measurements are reflected as large variations in the shear modulus. The large variations notwithstanding, the general trend indicates an almost continuous increase in G_{mortar} after casting.

It has previously been shown that the occurrence of Features A and B in the $r(1)$ response correspond approximately in time with the initial and final setting times determined using the pin penetration method given in ASTM C 403⁹. Since the initial setting time approximately corresponds with the emergence of a solid phase, the changes in G_{mortar} up to the occurrence of feature A in the $r(1)$ response correspond to changes in the stiffness in the fluid stage. The early changes in the material properties result in a gradual loss in the workability and eventually to set. It is interesting to note that there is a significant, almost 30% drop in $r(1)$ up to the occurrence of feature A. The total increase in $G_{\text{mortar}}/G_{\text{PMMA}}$ in the same time is more than two orders of magnitude. There appears to be a rapid, almost exponential increase in G_{mortar} after mixing up to Point A.

The increase in G_{mortar} after Point A in the $r(1)$ response provides an indication of the stiffness change through setting. The increase in G_{mortar} appears to be continuous through the occurrence of Feature B in the $r(1)$ response. Shear modulus of mortar equals that of PMMA after the occurrence of Feature B. After Point B, while there is approximately 30% increase in $r(1)$ up to 20 hours, there is an almost six-fold increase in G_{mortar} . The rate of increase in G_{PMMA} slows down after initial set through final set and early strength gain.

It has previously been shown that the lowest point the $r(1)$ response occurs when the acoustic impedance of the cementitious material is equal to that of PMMA^{9,10}. At Point B in the $r(1)$ response, the G_{mortar} is therefore a fixed percentage of G_{PMMA} , which is given by the inverse ratio of the densities of the two materials. The Point B in the $r(1)$ response besides providing a convenient point for determining the final set also gives a point of reference for assessing the shear modulus of the mortar. This is illustrated in Figure 5, where the ratio $G_{\text{mortar}}/G_{\text{PMMA}}$ is plotted along with $r(1)$ for mortar mixtures containing accelerator and retarder. Since the difference in densities for the two mixtures is insignificant, the $G_{\text{mortar}}/G_{\text{PMMA}}$ for both mixtures is approximately equal at point B of their $r(1)$ responses.

Changes in G_{mortar} reflect the changes in the rate of hydration produced by the admixtures present in the mortar; the mortar mixture containing accelerator/retarder exhibits a more rapid/slower increase in shear modulus when compared with the control. The observed trend in G_{mortar} suggests a two-stage process. The most rapid increase in the modulus occurs in the first few hours prior to initial set. There is a period of time when the measured shear modulus levels off for a brief period of time before continuing to increase. The rate of increase in shear modulus steadily decreases after initial setting. The changes in the shear modulus up to initial setting correspond with the evolution of microstructure until a solid skeleton emerges from within the fluid medium. Solid reaction products which emerge due to hydration are responsible for this transformation. Once sufficient connectivity is achieved between the solid reaction products, also known as percolation threshold in the literature, setting is initiated¹⁶. Further increase in the shear modulus of the material corresponds with changes in the stiffness and porosity of the solid skeleton comprised of the hydration products. The experimental trends in measured modulus suggest that the feature A is associated with the emergence of a solid skeleton within the material. Initially, before the emergence of a solid structure, the hydration reaction occurs in a fluid medium. The decrease in the rate of shear modulus with time after initial setting suggests a change to a diffusion controlled reaction where the reaction rate depends upon the diffusion of water through a solid porous network.

CONCLUSIONS

An ultrasonic technique for continuous monitoring of a cementitious material from an early age is described in this paper. Following a reflection at the PMMA-mortar interface, there is a continuous change in both the phase and the magnitude of the incident wave. The observed changes in the reflected waveforms with time can be interpreted to provide information about the change in the shear modulus, with time after casting. Based on the results presented in this paper, the following conclusions can be drawn:

1. The measured change in the shear modulus determined from the ultrasonic measurements allows for sensitive detection in the change in the reaction kinetics introduced by admixtures.

2. Initially after mixing the material properties of the mortar are reflected in the changes in the measured amplitude reflection factor. In this early period there is a continuous increase in the shear modulus of the material. The early changes in the material properties result in an increase in the stiffness of the fluid, which leads to a gradual loss in the workability and eventually to set.
3. The shear modulus of mortar increases at a very rapid, almost exponential rate before initial set. The rate of increase in the shear modulus is the most rapid before initial set. The rate of modulus decreases steadily through final set and early strength gain.

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REFERENCES

1. L.J. Struble, H. Zhang, W.G. Lei, 'Oscillatory Shear Behavior of Portland Cement Paste during Early Hydration', *Conc. Sci. Eng.* 2 (2000) 141-149.
2. ASTM C 403, Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance, (ASTM, Philadelphia, 2000) 214-218.
3. ASTM C 39, Test Method for Compressive Strength of Cylindrical Concrete Specimens, ASTM, (Philadelphia, ASTM 2000) 18-21.
4. ASTM C 469-94, Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression, (ASTM, Philadelphia, 2000) 242-245.
5. K.V. Subramaniam, J.S. Popovics, S.P. Shah, Determining Elastic Properties of Concrete Using Vibrational Resonance Frequencies of Standard Test Cylinders, *Cem. Conc. Aggreg.*, 22(2) (2000) 81-89.
6. X. Jin, Z. Li., Dynamic Property Determination for Early Age Concrete, *ACI Mater. J.* 98(5) (2001) 365-371.
7. H.W. Reinhardt, C.G. Grosse, A.T. Herb, Ultrasonic Monitoring of Setting and Hardening of Cement Mortar – A New Device, *Mat. Struct.* 33 (2000) 580-583.
8. T. Özutürk, J. Rapoport, J.S. Popovics, S.P. Shah, Monitoring the Setting and Hardening of Cement-Based Materials with Ultrasound, *Conc. Sci. Eng.* 11 (1999) 83-91.
9. K.V. Subramaniam, J. Lee, B. Christensen, Monitoring the setting behavior of Cementitious Materials using One-Sided Ultrasonic Measurements, *Cem. Conc. Res.*, 35 (2005) 850-857.
10. K.V. Subramaniam, J. Lee, Ultrasonic Assessment of Early-Age changes in the Material Properties of Cementitious Materials, *Materials and Structures, RILEM*, 40(3) (2007) 309.
11. M.I. Valič, J.S. Stepišnik, A Study of Hydration of Cement Pastes by Reflection of Ultrasonic Shear Waves. Part I: Apparatus, Experimental Method and Application Examples, *Kov. Zlit. Tech.*, 32 (6) (1996) 551-600.
12. van Beek A., Dielectric Properties of Young Concrete, PhD Thesis, Delft University, 2000.
13. R. Zoughi, S.D. Gray, P.S. Nowak, Microwave Nondestructive Estimation of Cement Paste Compressive Strength, *ACI Mater. J.* 92 (1995) 64 -70.
14. P. Kielczynski, W. Pajewski, Reflection of an Obliquely Incident SH Plane Wave at a Plane Interface between an Elastic Solid and Viscoelastic Liquid, *J. Acoust. Soc. Am.* 81(3) (1987) 599-605.
15. J.D. Achenbach, I.N. Komsky, Y.C. Lee, Y.C. Angel, Self-Calibrating Ultrasonic Technique for Crack Depth Measurement, *J. Nondestr. Eval.* 11 (2) (1992) 103-108.
16. G. Ye, K. van Bruegel, A.L.A. Fraaij, Three-dimensional Microstructure Analysis of Numerically Simulated Cementitious Materials, *Cem. Conc. Res.*, 33(2) (2003) 215-222.

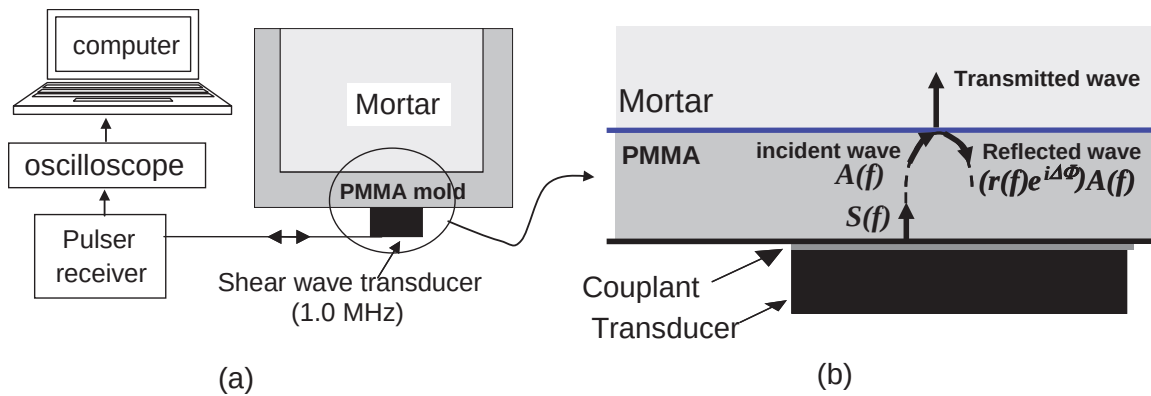


Figure 1 -- (a) Schematic figure of the experimental test setup for wave reflection measurements, (b) Wave reflection at the PMMA-mortar interface showing the change in the amplitude and phase introduced by the reflection.

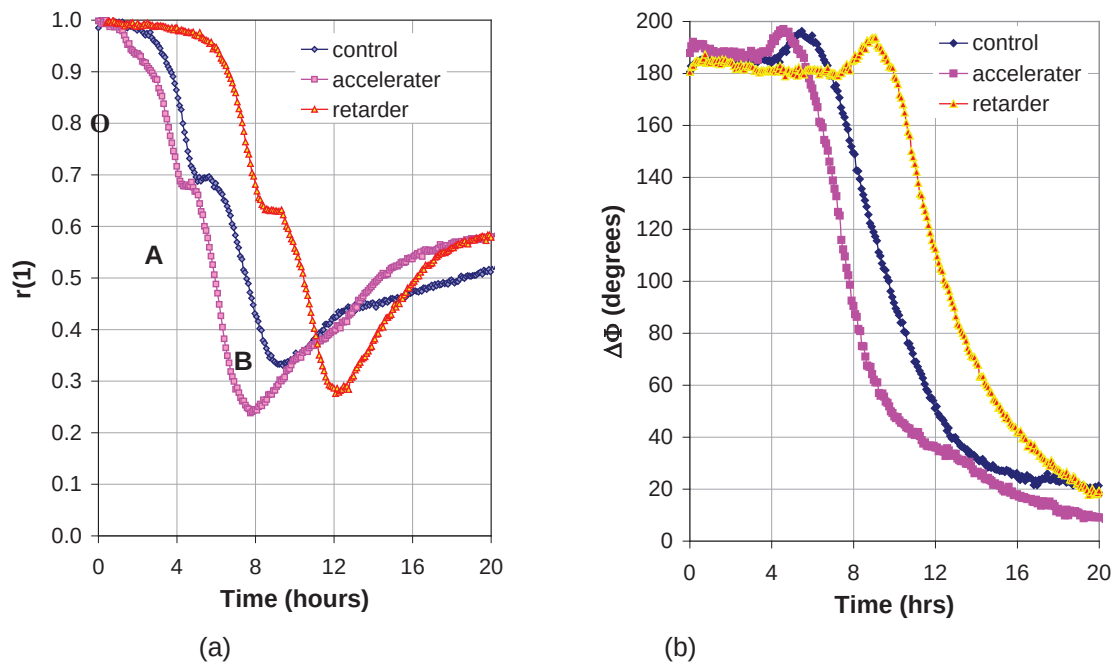


Figure 2 -- Ultrasonic wave response after one reflection at the PMMA-mortar for different mortar compositions, (a) $r(1)$ as a function of time, (b) $\Delta\Phi$ as a function of time.

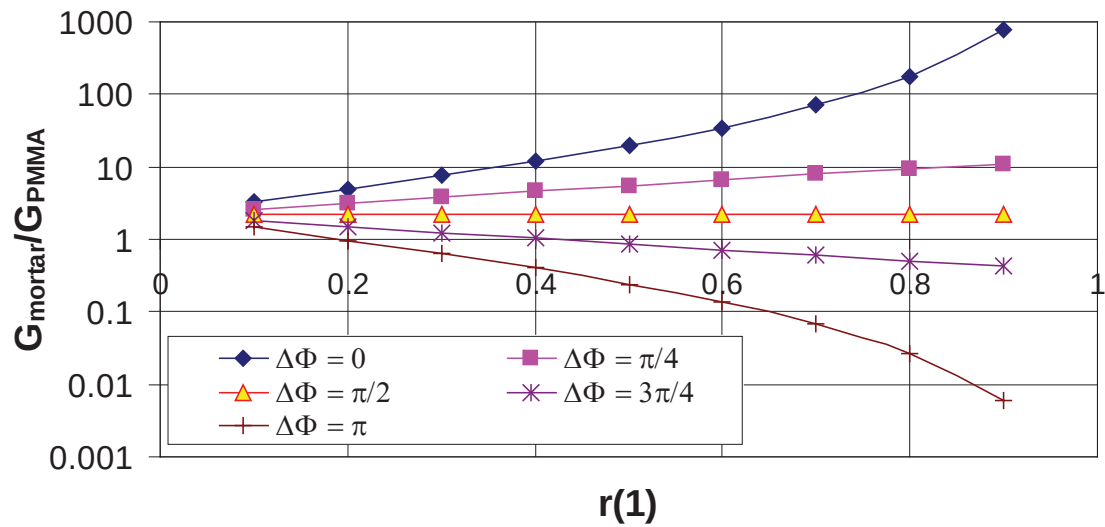


Figure 3 -- Variation of G_{mortar} as a function of $r(1)$ for different $\Delta\Phi$.

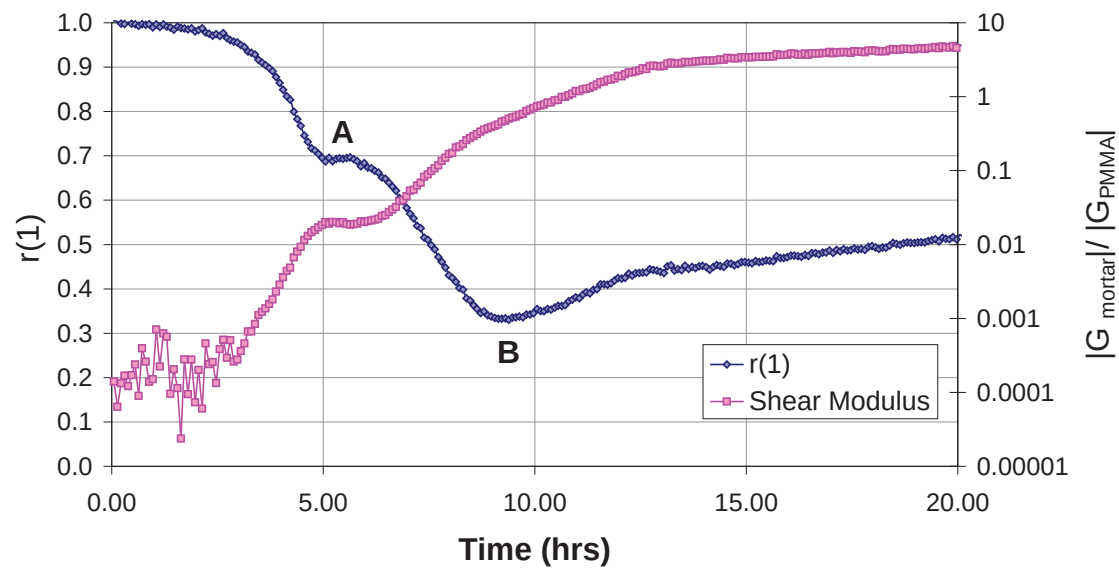


Figure 4 -- Change in the shear modulus of mortar assessed at 1MHz as a function of time.

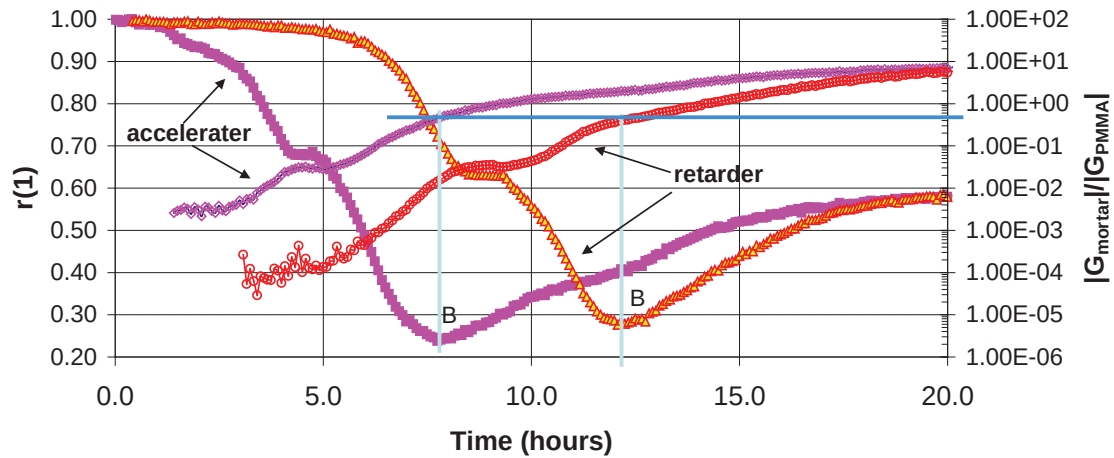


Figure 5 -- Change in the shear modulus assessed at 1MHz of mortar mixtures containing accelerator and retarder as a function of time.

Early Age Properties Development of Concrete with Different Slag Contents

by A. Darquennes, S. Staquet, A. Kamen, M.-P. Delplancke-Ogletree, and B. Espion

Synopsis: Slag cement concrete is characterized by many advantages, which leads to its intensive use in the construction industry in Belgium. However, it may exhibit a high sensitivity to cracking at early age in case of restrained shrinkage. The understanding of this behavior involves an in-depth analysis of the early age deformations. Firstly, an experimental investigation of the mechanical properties (compression strength, elastic modulus) and the microstructure evolution (hydration kinetic and hydrates development) was performed on three concretes containing different slag proportions (0%, 42% and 71% of the mass of binder), but with identical total binder content, in order to understand the effect of slag on these parameters. Secondly, the autogenous deformations were measured from casting time on concrete cylinders under isothermal conditions. The apparent activation energy and the time of initial set were also evaluated in order to analyse these deformations. The apparent activation energy is used to convert the actual age into equivalent age to express the concrete properties independently of the temperature variations. The time of initial set from which the strains are expressed is determined by ultrasonic detection and by the Kelly-Bryant method.

Keywords: autogenous deformation; blended cements; hydration; mechanical performance; microstructure; setting time

44 Darquennes et al.

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INTRODUCTION

Slag cement concrete is widely used in Belgium. It has several advantages in comparison with Portland cement concrete such as a lower hydration heat and a lower permeability^{1,2}. Furthermore, the production of this cement is more respectful of the environment than the production of Portland cement because less carbon dioxide is emitted into the atmosphere. This cement is used for a wide variety of constructions such as bridges, roads, buildings, tanks, etc. However, some structures built with slag cement concrete have exhibited early age cracking due to restrained shrinkage resulting from autogenous, thermal and drying components³. This phenomenon may jeopardize the durability and the functionality of the structure. In order to limit the risk of cracking, it is necessary to study in depth the early-age behavior of slag cement concrete, which is not well known.

CEMENTS CHARACTERIZATION

Three cements were used: a Portland cement CEM I 52.5 N, and two blended cements, namely CEM III/A 42.5 LA and CEM III/B 42.5 HSR LA. They differ by their slag content but the clinker of all three cements has the same origin. The blended cements (CEM III/A and CEM III/B) contained 42% and 71% of slag respectively. Moreover, their specific area and their density are similar (Table 1). The concretes associated with these three cements are indicated in this paper: P-95, SA-42 and SB-71 respectively. In the tested concretes, the water-binder ratio (w/b) and the binder (*i.e.* clinker + slag) content are kept constant and equal to 0.45 and 375 kg/m³ (23.41 lb/ft³) respectively. Aggregates with six different fractions were used. The concrete mixture proportions are given in Table 2.

Slag and clinker

The chemical slag composition includes compounds of calcium, silicon, aluminium, magnesium and iron. These elements are also detected in the clinker composition in different proportions. Indeed, the slag is characterized by a lower calcium content and a larger silicon content than the clinker composition. The percentage of these elements influences strongly the slag behavior. The reactivity of slag¹ was characterized by means of the chemical modulus and the hydraulic factor (Table 3) by using the percentage of the main elements of slag determined by XRF (Table 4). These ratios define the acid or basic character of the slag. They are also an acceptance criterion for the use of a slag in cement production⁴ and they have to be higher than 1 and 1.4 respectively. The studied slag is basic and it matches the acceptance criterion. Slag quality is also considered as acceptable if the ratio of slag solubility in basic solution (R) is higher than 0.18. This condition is also verified for the studied slag (Table 3). Slag hydraulicity⁵ is calculated on basis of oxides percentages using different expressions (Table 3): Keil ratio, Langavant ratio, I_h ratio and Tetmayer modulus. According to these relations, the studied slag is characterized by a good hydraulicity, except for Langavant ratio which gives an ordinary hydraulicity.

XRD analysis of the slag (Fig.1) revealed crystalline phases such as merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, akermanite $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$, gehlenite $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$ and rankinite $\text{Ca}_3\text{Si}_2\text{O}_7$. Moreover, the diffuse bands in the diffraction diagram between 23°C and 38° are characteristic of a partially crystallized slag. However, the vitreous appearance of the slag confirms its reactivity. Generally, it is considered that the hydraulicity of slag decreases with the increase in the content of its crystalline phases. But some crystalline phases like merwinite crystals allow improving the slag

hydraulicity by increasing the Al_2O_3 content⁵. Therefore, a total vitrification of slag would not be a criterion for an optimal reactivity.

The clinker is composed of four main elements (Ca, Si, Al and Fe) (Table 4) and several minor elements (Mg, Ti, Mn, K, Na and P) which govern the physico-chemical and mechanical properties of the cement. The proportions of the main mineral phases of clinker C_2S , C_3S , C_3A and C_4AF were calculated by means of the Bogue formulas, which yielded : 2%, 70%, 8% and 11% respectively.

MECHANICAL PROPERTIES

The ability of concretes to counteract stresses induced by restrained shrinkage depends, among other parameters, on the concrete stiffness. Compressive strengths and static elastic moduli were measured on three cylindrical samples [diameter $\varnothing = 100$ mm (3.94 in.), and height $h = 200$ mm (7.87 in.) for strength and $h = 350$ mm (13.78 in.) for modulus] kept at 20°C (68°F) and 90% relative humidity (RH) at 1, 2, 3, 4, 5, 6, 7, 14 and 28 days. The dynamic elastic modulus is determined on three prismatic samples [400x100x100 mm³ (15.75x3.9x3.9 in.³)] stored under the same conditions by measuring the mechanical resonant frequencies. The dynamic elastic modulus is determined using the resonant frequency in either the flexural or longitudinal mode of vibration as described in ASTM E1876-99⁶. At 1 day, the value of the compressive strength decreases with the slag content: 26 MPa (3771 psi) for P-95, 14 MPa (2030 psi) for SA-42 and 3.4 MPa (493 psi) for SB-71 (Fig.2). From 1 to 3 days, the compressive strength increase is 23 MPa (3336 psi) for SB-71 and 15 MPa (2176 psi) for SA-42 and P-95. At 7 days, the compressive strength of SB-71 [45 MPa (6527 psi)] is only slightly lower than the strength of SA-42 and P-95 [47 MPa and 49 MPa (6817 psi and 7107 psi) respectively]. At 14 days, the compression strength is similar for the three concretes. The low compressive strength evolution of SB-71 is linked to its low C_3S content⁷ and to the evolution of the hydration reaction of this kind of cement^{8,9}. This reaction consists of two subreactions: clinker reaction and slag reaction. Indeed, the hydration of slag cement concretes depends upon the breakdown and the dissolution of the glassy slag structure by hydroxyl ions released during the hydration of clinker and also the alkali content in cement⁵. Moreover, its hydration consumes calcium hydroxide and uses it for additional C-S-H. Thus, the hydration products resulting from the clinker reaction (portlandite) is needed for the slag reaction. So, this reaction is delayed for cements containing high slag content. Thus, during the first week, the compressive strength evolution of SB-71 is slower than the development of the strength of the Portland cement concrete.

The evolution of the static elastic modulus is quite similar for P-95 and SA-42 (Fig.3). Their static modulus increases between 1 and 7 days from 31 GPa ($4.5 \cdot 10^6$ psi) to 41 GPa ($5.9 \cdot 10^6$ psi) but beyond this age, it increases slowly. However, SB-71 shows a different behavior: a very low value at 1 day [18 GPa ($2.6 \cdot 10^6$ psi)] and a large rise during the first week [23 GPa ($3.3 \cdot 10^6$ psi)]. Beyond 7 days, it evolves slowly like P-95 and SA-42. Thus, the static elastic modulus evolution is similar to the compressive strength evolution. The dynamic modulus values are close to the static modulus values for SA-42 and SB-71, but they are larger than the static elastic modulus for P-95 [maximal difference of 5 GPa ($7.3 \cdot 10^5$ psi)].

HYDRATION PROGRESS

It has just been noticed that the mechanical properties evolution of the slag and Portland cement concretes depends strongly on the evolution of their hydration reactions. Thus, they are studied by means of several experimental techniques: adiabatic calorimetry, TGA-DTA and SEM-EDX.

Adiabatic calorimetry

Description of the device: The heat of hydration was measured on concrete specimens by means of an adiabatic calorimeter developed at the Université Libre de Bruxelles. This adiabatic calorimeter (Fig.4) consists of a copper cylindrical tank with water circulation (3). An insulating air layer (2) separates the sample (1) from the tank (3)¹⁰. The temperature regulation is controlled by thermocouples embedded in the sample (1). A thermostatic bath controls the temperature of the circulating fluid to ensure a homogeneous temperature in the device. Moreover, the thermal exchange between the calorimeter and the environment is limited by the insulation surrounding the device.

Results: The adiabatic temperature evolutions in the core of massive concrete samples show that P-95 is characterized by a faster release of heat than the two other concretes. The maximal temperature increases with the

clinker content: 55.6°C (132°F) for SB-71, 63.4°C (146°F) for SA-42 and 65.8°C (150°F) for P-95. The cumulative heat and the heat flow evolutions are determined from the temperature curves (Fig.5). The progress of the hydration reactions is defined as a fraction of the heat emission. By using the cumulative heat of hydration in a finite elements program such as FEMMASSE¹¹, the temperature evolution and the degree of advancement of hydration (defined as Q/Q_{∞}) can be predicted in any form of concrete specimen or element. The heat flow evolution (Fig.5) shows a first high peak associated to the heat of dissolution. Then, the hydration reaction goes through a dormant period characterized by a minimal heat flow. This period is long for SB-71 (6.67 h) while shorter but similar for SA-42 (4.5 h) and P-95 (5.25 h). After this time, initial setting begins and a second peak related to the cement hydration appears at 14.58 h for P-95, 20.25 h for SA-42 and 27.9 h for SB-71. However, the heat flow evolution of SB-71 shows a change in slope at about 13.5 h corresponding to the beginning of an acceleration period of the slag hydration². The maximal heat flows are lower for SA-42 and SB-71 than for P-95, being 8.98 J/gh, 6.49 J/gh and 13.95 J/gh respectively. The surface below the heat flow curve is equal to the total emitted heat and this surface decreases strongly for SB-71, with this mixture producing less heat during hydration than SA-42 and P-95.

TGA-DTA

Mortar samples coming from the concretes were analysed by differential thermal analysis (DTA) and thermogravimetry (TGA). The hydration was stopped at four ages (2, 3, 7 and 28 days) using two solvents (ethanol and ether). The samples were crushed. The tests were performed under helium atmosphere over the temperature range 20°C-1000°C (68°F-1832°F) with a heating rate of 10°C/min (50°F/min). Three major periods¹² of sample decomposition are distinguished during this temperature increase:

- from 20°C (68°F) to 400°C (752°F): water loss from the capillary pores and hydrates decompositions in the cement paste;
- from 400°C (752°F) to 600°C (1112°F): dehydroxylation of the portlandite;
- from 600°C (1112°F) to 880°C (1616°F) : decarbonation of the calcite;

The first phase characterizes the evaporation of the free water and the beginning of chemically bound water departure. The temperature threshold between the two kinds of water is set to 145°C (293°F).

After 2 days of curing, the total mass loss increases with the clinker content (Fig.6). The DTA curves show an endothermic reaction related to the water loss between 30°C (86°F) and 200°C (392°F). This peak is lower for SA-42 and SB-71 than for P-95. From 130°C (266°F) to 170°C (338°F), two endothermic reactions (A and B) are observed for SA-42 and P-95. This is related to the dehydration of gypsum¹³ and C-S-H. A second endothermic peak located between 450°C (842°F) and 550°C (1022°F) is observed and is linked to the decomposition of portlandite into free lime. The amplitude of this peak decreases with the slag content in the cement. At 570°C (1058°F), the curves present an additional peak. According to Mounajed et al¹³, this peak is attributed to a transformation in the quartz structure from α quartz to β quartz. The last peak between 700°C (1292°F) and 900°C (1652°F) characterizes the decomposition of the calcium carbonate and its amplitude increases with the clinker content. From 2 days to 28 days, the curves are characterized by the same peaks and the mass loss between 145°C (293°F) and 1000°C (1832°F) increases with the hydration advancement. The mass content of portlandite $\text{Ca}(\text{OH})_2$, chemically bound water w_{el} and calcite CaCO_3 were determined on basis of the mass loss at different temperature intervals¹² (Table 5). The results (Table 5) show a higher content of portlandite in P-95 at 2 days than in SA-42 and SB-71. In SA-42, the portlandite content increases rapidly between 2 and 3 days. Then, its rise slows down. However, the portlandite content is continually increasing for SB-71, while the portlandite content in P-95 measured on several samples is constant after 2 days. At 28 days, SA-42 and SB-71 have the same portlandite content. The low portlandite content of SB-71 at 2 and 3 days is probably related to its consumption by the pozzolanic reaction. P-95 is characterized by a larger content of chemically bound water and calcite than SA-42 and SB-71 at 2 days. This large calcite content of P-95 is related to its use for the clinker grinding. Thus the calcite content decreases with increasing slag content. But these values are also influenced by the fine aggregate. After 2 days, the content of chemically bound water of SA-42 and SB-71 increases during the hydration advancement. Moreover, the degree of advancement of the hydration reaction (defined as $w_{el}/w_{el}(\infty)$) and the degree of advancement of the slag hydration can be predicted by using the chemically bound water and portlandite contents respectively measured by TGA-DTA at different ages¹⁴. Pane and al¹⁴ also suggest that w_{el} is proportional to the heat of hydration. Further experimental tests are needed to connect these data (adiabatic calorimetry, TGA-DTA) together in this study and to determine the degree of the hydration reaction which is related to compressive strength development¹⁵. Indeed, it seems appropriate to link the evolution of materials properties and the development of their microstructure with the hydration degree because age is not an intrinsic parameter to monitor the physical and chemical processes.

SEM-EDX

Fracture surfaces of concrete were analysed by scanning electron microscopy (SEM) using a JEOL 6100 microscope to compare the morphology of the hydration products at 2, 3, 7 and 28 days. The aim of this analysis is to study the influence of slag on the nature and the evolution of the hydration products. Three main hydration products are essentially implied in the hydration reaction: C-S-H, portlandite and ettringite. At 2 days, the hydration reaction of P-95 and SA-42 is already well advanced in comparison with SB-71. P-95 and SA-42 present the three main hydration products (Fig.7). SB-71 presents mainly ettringite needles at 2 days and the C-S-H hydrate presence increases at 3 days (Fig.8). At 7 days, an evident dissolution of slag in SB-71 is observed (Fig.9) and corresponds to the increase in portlandite measured by TGA-DTA. The EDX analysis of this slag shows that its Ca/Si ratio is twice as low as compared to the Ca/Si ratio of the hydration products. This difference tends to confirm that the slag dissolution results from a migration of its components. At 28 days, the hydration products of these mixtures form a dense and packed matrix. This analysis of the microstructural evolution corroborates the slowdown of the advancement of the hydration reactions of the slag cement concretes observed by adiabatic calorimetry and ATG. This behavior is well related to the initialization of the pozzolanic reaction which retards the hydration of silicate phase¹⁶. Moreover, the slag cement hydration seems to give the same reaction products as the Portland cement.

APPARENT ACTIVATION ENERGY DETERMINATION

The apparent activation energy E_a was determined by means of mechanical tests for SA-42 and SB-71 in order to express the experimental results in function of the equivalent age. By applying the superposition method¹⁷, E_a was determined with the evolution of the average compressive strengths (3 samples) under three curing temperatures: 10, 20 and 30°C (50, 68 and 86°F) (Fig.10 and 11). The method implies the superposition of two curves giving the evolution of the strength for two different temperature histories in function of the equivalent age in the compressive strength intervals [0; 32 MPa (4641 psi)] for SA-42 and [0; 28 MPa (4061 psi)] for SB-71. The E_a value is obtained by minimizing the differences between the different couples of equivalent ages on this compressive strength interval (Eq.[1]).

$$\min_{E_a} \left(\sum_{f_{c_i} \in [f_{c_{inf}}, f_{c_{sup}}]} |t_{eq1i} - t_{eq2i}|^2 \right) \quad [1]$$

$$\text{With } t_{eq1i} - t_{eq2i} = \int_0^{t_{1i}} \exp \left(-\frac{E_a}{R} \left(\frac{1}{T_1(\tau)} - \frac{1}{T_{ref}} \right) \right) d\tau - \int_0^{t_{2i}} \exp \left(-\frac{E_a}{R} \left(\frac{1}{T_2(\tau)} - \frac{1}{T_{ref}} \right) \right) d\tau$$

with

t_{1i} , t_{2i} : actual ages leading to the same compressive strength value f_{c_i}

t_{eq1i} , t_{eq2i} : corresponding equivalent ages

T_{ref} : 293°K

Table 6 shows the E_a values computed for the different temperature couples. In the following experimental results and for the temperature interval of 10°C-30°C (50°F-86°F), E_a values of 42.7 kJ/mol and 46.6 kJ/mol are used for SA-42 and SB-71 respectively. For the Portland cement concrete, a value of E_a equal to 35.6 kJ/mol derived by Wirquin et al¹⁷ for the same cement, but for a different concrete and in the temperature range [10°C-40°C (50°F-104°F)] will be used.

DETERMINATION OF THE SETTING TIME

Ultrasonic and mechanical monitoring of setting

The study of the autogenous deformation needs the determination of a reference time-zero t_0 from which the strains are expressed. An under- or overestimation of the autogenous deformation may be avoided if this time is determined precisely¹⁸. In this research, the time-zero t_0 is the time at the beginning of setting evaluated by means of two techniques: an ultrasonic monitoring (Fig.12) and a device for pulling steel bars embedded in concrete called the Kelly-Bryant method²⁰ (Fig.13). The initial and final settings are determined by ultrasonic transmission measurements with equipment that was developed recently at the University of Stuttgart¹⁹. The mould is formed by two polymethacrylate walls (PMMA) kept at a distance of 5.9 cm (2.3 in.) by four screws. A foam material is used

to make a U-shaped mould. Its high damping properties are able to remove waves passing through the mould and moving around the concrete sample [concrete volume: 450 cm^3 (6.10^{-4} yd^3)]. The test is carried out in an air-conditioned room at 20°C (68°F) and the sample is protected against desiccation by a plastic foil. During the test, the ultrasonic velocity, energy and frequency spectrum evolutions in function of the concrete age are given by the software. The Kelly-Bryant method²⁰ which allows the determination of the initial concrete setting is based on the measurement of the force that is necessary to pull out a stainless steel bar from a concrete prism. Concrete is poured in a rectangular prismatic mould $10 \times 10 \times 60 \text{ cm}^3$ ($4 \times 4 \times 24 \text{ in.}^3$) placed horizontally. Stainless steel bars maintained vertically by guides are disposed in the mould. These guides are removed after the concrete casting and the vibration phase. The bars are pulled by one by one from concrete at regular time intervals with a mechanical system. The tensile force needed for pulling the bars from concrete is measured with a dynamometer. The initial setting corresponds to the first significant change of slope on the curve giving the evolution of the force in function of time.

Initial setting time determination

Several particular events in the concrete hydration reaction can be identified by analysing the velocity curve of the ultrasonic pulse passing through the concrete sample. The initial setting corresponds to the first inflection point of the velocity curve²¹. Physically, this change is related to the appearance of an interconnected path of hydrated cement particles. Thanks to this percolation, the ultrasonic transmission velocity with hardening concrete is higher than in the fresh concrete. But the ultrasonic velocity starts to increase earlier than the appearance of the initial setting and this period is also characterized by a constant value of the pulling strength (Fig.14, 15, 16). Robeyst and al²¹ suggest that this increase in velocity without increase in pulling resistance could be attributed to two reasons. Firstly, the compression ultrasonic waves pass through gases, liquids and solid. Thus, the initial velocity increase could correspond with the formation of hydration products which have no or little influence on the stiffening process and the pulling strength. These hydration products fill the pore spaces but they are not characterized by connected particles. Secondly, an internal setting process caused by gravity could create a kind of mechanical coupling in the concrete without a real bond between the particles. So, the ultrasonic velocity increases while the pulling strength stays constant. According to these two techniques, the initial setting is assumed to be the first inflection point of the velocity curves corresponding to the increase in the pulling strength. For Portland cement concrete, the final setting is usually associated to the time when the velocity reaches a value equal to 1500 m/s (0.93 miles/s)²⁰. However, De Belie and al¹⁹ observed that this threshold is not applicable for slag cement concretes. Instead, they noticed a good correspondence (with an accuracy of about 100 min) between the final setting and the second inflection point of the curve giving the velocity in function of time. Thus, the setting of SA-42, SB-71 and P-95 conserved at 20°C (68°F) (Fig.14, 15, 16) begins at 5 h, 7.5 h and 5.5 h and ends at 8.8 h, 10.5 h and 9 h respectively. The analysis of the mechanical results shows that the increase in the pulling strength is close to the first inflection point of the velocity curve: 5.5 h for SA-42, 6.9 h for SB-71 and 5.9 h for P-95. This initial setting delay of SB-71 in comparison with SA-42 and P-95 is well correlated to its long dormant period measured by calorimetric means. Moreover, all these events are located in the phase of temperature increase in the sample.

AUTOGENOUS DEFORMATION

Testing equipment

A testing equipment developed at the Université Libre de Bruxelles for measuring shrinkage from casting was used to record the autogenous deformations. Concrete is poured in a cylindrical Teflon mould wherein a plastic foil insures the water tightness and minimizes the friction between the sample and the mould walls (Fig.17). Moreover, the thermal expansion coefficient of Teflon ($80.10^{-6}/^\circ\text{C}$) is much larger than the thermal expansion coefficient of concrete ($10.10^{-6}/^\circ\text{C}$). Therefore, the mould does not counteract the concrete volume variations related to the temperature increase or decrease. The specimen is immersed vertically inside a temperature-controlled bath. The linear contractions/dilations of the sample are measured by means of two displacement transducers (Solartron LE12) placed outside the bath. They are in contact with steel plates anchored at the ends of the sample. These transducers are characterized by a measuring range of 12 mm (0.47 in.) and an accuracy of $\sim 0.4 \mu\text{m}$ ($1.57 \cdot 10^{-5} \text{ in.}$). They are mounted on a rigid frame with vertical posts in invar, a material characterized by a low dilation coefficient ($1.6.10^{-6}/^\circ\text{C}$) to reduce the effects of the ambient temperature variations on the measurements. These displacement measurements in isothermal conditions are supplemented by temperature measurements (water of the bath, ambient air, concrete) to investigate the influence of the temperature on the measured parameters (Eq.[2]). The device used in this project has been validated on a Portland cement concrete by comparison with shrinkage measurements

obtained with an equipment (BTJADE prototype, LCPC Paris) constituted by a corrugated PVC mould developed at LCPC Paris by Boulay²².

$$\varepsilon_{corrected}(t-t_0) = \varepsilon_{raw}(t-t_0) - \frac{\alpha_{invar} L_{0invar} (T_{air}(t-t_0) - T_{air}(t_0))}{L_{0concrete}} - \frac{\alpha_{steel} L_{0steel} (T_{air}(t-t_0) - T_{air}(t_0))}{L_{0concrete}} - \alpha_{concrete} (T_{concrete}(t-t_0) - T_{concrete}(t_0)) \quad [2]$$

with

t_0 : initial setting time (days)

L_{0invar} , L_{0steel} , $L_{0concrete}$: invar bar, steel link and concrete sample length (m)

α : thermal expansion coefficient (1/°C)

T : temperature (°C)

ε : deformation (m/m)

Evolution of the autogenous deformation

Figures 18, 19 and 20 show the evolution of the autogenous deformation and the dynamic elastic modulus E_{dyn} for the three concretes. For all these concretes, E_{dyn} remains low [< 10 GPa ($1.5 \cdot 10^6$ psi)] up to the initial setting (Fig.21). This E_{dyn} threshold value [10 GPa ($1.5 \cdot 10^6$ psi)] is already rather high and has to be confirmed by complementary tests. Indeed, this value depends on several parameters such as the Poisson coefficient and the velocity²³ (Eq.[3]). This equation is only valid after the initial setting. Further analysis of the risk of cracking is not directly based on the absolute value of the dynamic modulus, but on its variation in association with an autogenous shrinkage strain increase. At very early age, the evolution of the dynamic elastic modulus does not correspond to an actual stiffness evolution. However, Eq.[3] seems to give acceptable results from 1 day when they are compared to the E_{dyn} values obtained by means of the Grindosonic device. Thus, between the initial and final setting, the elastic modulus increases rapidly and reaches a value equal to about 26 GPa ($3.8 \cdot 10^6$ psi) for SA-42, 24 GPa ($3.5 \cdot 10^6$ psi) for SB-71 and 35 GPa ($5 \cdot 10^6$ psi) for P-95. During this time, the autogenous deformation remains low. It is characterized by a small expansion for P-95 ($40 \cdot 10^{-6}$ m/m) and a shrinkage equal to $-10 \cdot 10^{-6}$ m/m and $-20 \cdot 10^{-6}$ m/m for the slag cement concretes SA-42 and SB-71 respectively. Over the period considered, the autogenous strains initialized from the initial setting reach a value of $-50 \cdot 10^{-6}$ m/m for SA-42, $-119 \cdot 10^{-6}$ m/m for SB-71 and $-75 \cdot 10^{-6}$ m/m for P-95 at 28 days (Fig.18, 19, 20). Moreover while the autogenous deformation rises, the elastic modulus reaches a value of about 45 GPa ($6.5 \cdot 10^6$ psi) for all concretes at 28 days. However, the rate of autogenous shrinkage development is higher for SA-42 and SB-71 than the rate of autogenous shrinkage development for P-95. SA-42 and P-95 show a similar autogenous deformation evolution from the age of 12 days. So, the concrete which is the more prone to crack under restrained conditions is SB-71. It is due to its fast increase in elastic modulus and its rate of autogenous shrinkage from initial setting. Concrete SB-71 is also characterized by a higher autogenous shrinkage value at 28 days. But the risk of cracking depends on other factors such as the tensile strength, the creep evolution and the degree of restraint of concrete elements so that complementary tests are needed to assess the cracking risk at early age of these slag cement concretes.

$$E_d = V^2 \frac{\rho(1+\nu)(1-2\nu)}{(1-\nu)} \quad [3]$$

V : ultrasonic velocity (m/s)

ν : constant Poisson coefficient (taken equal to 0.2 in this case)

ρ : volumetric mass (kg/m³)

The autogenous deformation of the three concretes is also characterized by an expansion related to the increase in temperature inside the concrete sample. For SB-71, this phase corresponds to the second temperature rise linked to the acceleration of the pozzolanic reaction by portlandite. This behavior has been confirmed by an adiabatic calorimetry test. Moreover, SB-71 is characterized by a second expansion located at 3.5 days. This expansion may be related to an ettringitic expansion or an increase in internal hydrates C-S-H²⁴. Indeed, a concrete sample SEM observation at 2 days (Fig.8) shows a dense presence of ettringite in the cement matrix.

POROSITY

The major mechanism at the origin of the autodesiccation is the variation of the capillary depression. According to the Laplace and Kelvin laws (Eq.[4]), the intensity of the capillary depression is inversely proportional to the pore radius. A first approach to understand the behaviour of the autogenous deformation was the study of the porosity by means of a mercury porosimeter (Autopore IV Micrometrics 9510) to quantify capillary porosity and pores distribution.

$$\Delta P = P_g - P_l = \frac{2 \sigma \cos \theta}{r} = - \frac{RT \rho_l}{M} \ln(RH) \quad [4]$$

With

P_g : pressure of gas phase

P_l : pressure of liquid water

σ : superficial tension at the liquid-gas interface (0.0729N/m)

θ : wetting angle (0°)

r : pore radius

RH : internal relative humidity

ρ_l : water density

M : water molar mass [18.10^{-3} kg/mol (0.04 lb/mol)]

T : temperature [20°C (68°F)]

R : 8.314 J/mol. $^\circ\text{K}$

The size of the pores from 360 μm (0.014 in.) to 0.003 μm ($1.18 \cdot 10^{-7}$ in.) and their distribution were quantified by increasing the pressure from 345 kPa (50 psi) to 413.685 MPa (60,000 psi). The total porosity measured by this equipment only represents the pores content accessible to mercury. The concrete porosity includes the porosity of the cement paste, the aggregates and the paste-aggregate interface. To limit the influence of the aggregate porosity, the experimental tests were conducted on mortar samples extruded from concrete samples kept at 20°C and 100% R.H. at 2, 3, 7 and 28 days. The pores between 0.01 μm ($3.94 \cdot 10^{-7}$ in.) and 5 μm ($2 \cdot 10^{-4}$ in.) define the capillary porosity corresponding to the pore space between the binder grains²⁵. Initially, this porosity is larger for SB-71 and SA-42 than for P-95, but it decreases rapidly for the slag cement concretes (Table 7). At 7 days, all the concretes present the same percentage of capillary porosity. This evolution is similar to the evolution of their compressive strength. However, the evolution of the degree of hydration may be also described in function of the capillary porosity evolution²⁶ which confirms the relation between the mechanical properties and the hydration degree.

The total porosity is also subdivided in three classes as a function of their influence on the material durability: microporosity [from 0.0032 μm ($1.26 \cdot 10^{-7}$ in.) to 0.125 μm ($4.92 \cdot 10^{-6}$ in.)], mesoporosity [from 0.125 μm ($4.92 \cdot 10^{-6}$ in.) to 0.8 μm ($3.15 \cdot 10^{-5}$ in.)] and macroporosity [from 0.8 μm ($3.15 \cdot 10^{-5}$ in.) to 5 μm ($2 \cdot 10^{-4}$ in.)] (Fig.22). During the first week, the microporosity content of SA-42 and P-95 decreases, whereas it remains quite constant for SB-71. But this concrete is characterized by a large decrease in mesoporosity content during this period. Thus, during the first week, the decrease in capillary porosity is related to the decrease in microporosity and mesoporosity for SA-42, P-95 and SB-71 respectively. Beyond this period, the micro- and mesoporosity continue to decrease with the hydration advancement. According to these results, it seems interesting to realize a detailed analysis of the microporosity variations of these different concretes. The microporosity was subdivided into four intervals (Fig.23): 125-100 nm ($4.92 \cdot 10^{-6}$ – $3.94 \cdot 10^{-6}$ in.), 100-50 nm ($3.94 \cdot 10^{-6}$ – $1.97 \cdot 10^{-6}$ in.), 50-6 nm ($1.97 \cdot 10^{-6}$ – $2.36 \cdot 10^{-7}$ in.) and 6-3 nm ($1.97 \cdot 10^{-6}$ – $1.18 \cdot 10^{-7}$ in.). For P-95, the hydration advancement between 2 and 7 days is characterized by an increase in the largest pores content [size interval: 100-50 nm ($3.94 \cdot 10^{-6}$ – $1.97 \cdot 10^{-6}$ in.)] and a decrease in the smallest pores content [size interval: 50-3 nm ($1.97 \cdot 10^{-6}$ – $1.18 \cdot 10^{-7}$ in.)]. However, the microporosity evolution of SA-42 and SB-71 with time presents an increase in the smallest pores content [size interval: 6-3 nm ($1.97 \cdot 10^{-6}$ – $1.18 \cdot 10^{-7}$ in.)] and a decrease in the largest pores content [size interval: 100-50 nm ($3.94 \cdot 10^{-6}$ – $1.97 \cdot 10^{-6}$ in.)]. It results that the porosity of the slag cement concretes becomes finer than those of the Portland cement concrete and that their largest pores content continues to decrease with the hydration advancement. This phenomenon could be explained by the capacity of slag hydration products to fill the pores²⁷ because the hydration products (C-S-H) are forming a more abundant gel that can fill the porosity developed at very early age^{4,28}. Indeed, in the ternary diagram²⁹, the Portland cement is essentially in the C_3S region, whereas the slag is found essentially in the C_2S region of the diagram. Since the C_2S reaction products more C-S-H than the C_3S reaction, the resulting porosity of the slag cement mortars and concretes is extremely fine. These experimental observations are in agreement with the

literature. Some authors suggest that the Portland cement concretes includes a larger content of pores characterized over 30 nm ($3.94 \cdot 10^{-7}$ in.) than the slag cement concretes³⁰. The increase in slag content also generates a decrease in this kind of pores^{27,31}. Globally, thanks to this pore size reduction, the resistance against chloride and sulphate diffusion is better for slag cement concrete than for Portland cement concrete.

The pores distribution (Fig.24, 25, 26) is characterized by five populations of pores located at 91 μm ($3.58 \cdot 10^{-3}$ in.) for population 1, 0.3 μm ($1.18 \cdot 10^{-5}$ in.) for population 2, 0.06 μm ($2.36 \cdot 10^{-6}$ in.) for population 3, 0.03 μm ($1.18 \cdot 10^{-6}$ in.) for population 4 and 0.008 μm ($3.15 \cdot 10^{-7}$ in.) for population 5. All the concretes present a pores population at 91 μm . This kind of pores population is probably representative of material defects. The pores populations 2 and 3 characterize SA-42 and P-95 and the population 5 characterizes SA-42 and SB-71. The population 4 is only located in SB-71. Population 5 increases for the slag cement concretes and population 4 also decreases with the hydration advancement. Thus, the finer porosity of SB-71 is also confirmed by the evolution of its pores populations. The populations 2 and 3 of P-95 decrease and increase with the hydration advancement respectively. SA-42 and P-95 are qualified by the same populations but they evolve differently with time.

One possible explanation for the highest autogenous shrinkage of SB-71 could be its finer and larger porosity than the porosity of SA-42 and P-95 leading to a largest capillary depression (Eq.4). But these observations have to be confirmed by capillary depression measurements.

CONCLUSIONS

The concrete with the largest slag content (SB-71 with 27% of clinker) is characterized by a slower compressive strength evolution than the concretes SA-42 and P-95 with 58% and 100% of clinker respectively. This behavior is linked to the evolution of the hydration reaction of this kind of concrete which comprises two subreactions: clinker and slag reactions. SB-71 also shows the fastest increase in static and dynamic elastic modulus during the first week. Thus, a concrete with a large slag content presents a larger risk of cracking at early age than a Portland cement concrete. The rate of increase in the autogenous shrinkage also increases with the slag content, but the difference of behavior between SA-42 and P-95 vanishes after 12 days. This confirms the potential risk of cracking under restrained conditions due to the fast increase in elastic modulus and autogenous shrinkage for SB-71. This kind of concrete is also characterized by a finer porosity. This porosity refinement is at the origin of an increase in capillary depressions, a possible major mechanism in the autodessication shrinkage. Moreover, these experimental results underline the necessity to measure the autogenous deformation directly after casting, which was performed here with a new equipment developed at the Université Libre de Bruxelles. The correlation between the autogenous deformations and the dynamic elastic modulus highlights the consequences of the choice of the time-zero for strain measurements. Indeed, if this time is chosen equal to the final setting time, the autogenous deformation will be underestimated while the concrete has already shown a non negligible stiffness and development of strain since the initial setting. The next step of this research will be the study of restrained shrinkage on these different concretes under isothermal conditions by means of a TSTM (Temperature Stress Testing Machine) equipment.

REFERENCES

1. Bijen, J., 1998, "Blast furnace slag cement for durable marine structures", CIP Royal Library Den Haag, Stichting Betonprisma, 's-Hertogenbosch, The Netherlands, 62 pp.
2. Roy, D.M., and Idorn, G.M., 1983, "Hydration, Structure, and Properties of Blast Furnace Slag Cements, Mortars, and Concrete", *ACI Journal*, Nov-Dec, pp.444-457.
3. Darquennes, A., Staquet, S., and Espion, B., 2006, "Cracking Sensitivity of Slag Cement Concrete", 2nd *International Symposium on Advances in Concrete through Science and Engineering*, 11-13 September, Québec City, Canada, pp.311.
4. Glasser, F.P., 1991, "Chemical, Mineralogical and microstructural Changes occurring in hydrated slag-cement blends", *Materials science of concrete II*, pp.41-81.
5. Pal, S.C, Mukherjec, A., and Pathak, S.R., 2003, "investigation of hydraulic activity of ground granulated blast furnace slag in concrete", *Cement and Concrete Research*, 33, pp.1481-1486.

6. ASTM E1876-99, "Standard test method for dynamic Young's modulus, shear modulus, and Poisson's ratio by impulse excitation of vibration".
7. Kourounis, S., Tsivilis, S., Tsakiridis, P.E., Papadimitriou, G.D., and Tsibouki, Z., 2007, "Properties and hydration of blended cements with steelmaking slag", *Cement and Concrete Research*, 37, pp. 815-822.
8. Chern, J.-C. and Chan, Y.-W., 1989, "Deformations of concrete made with blast-furnace slag cement and ordinary Portland cement", *ACI Materials Journal*, 86, 4, July-August, pp.372-382.
9. Lim, S.N. and Wee, T.H., 2000, "Autogenous shrinkage of ground-granuled blast-furnace slag concrete", *ACI Materials Journal*, 97, 5, 2000, pp.587-593.
10. De Schutter, G., 1999, "Hydration and temperature development of concrete made with blast-furnace slag cement", *Cement and Concrete Research*, 29, pp.143-149.
11. van Beek, A., and Schlangen, E., 2000, "Simulating the effect of shrinkage on concrete structures", *Rilem Proceedings PRO 17 Shrinkage of Concrete*, Shrinkage 2000, pp.477-492.
12. Mounanga P., Khelidj A., Loukili A. and Baroghel-Bouny V., 2004, "Predicting $\text{Ca}(\text{OH})_2$ content and chemical shrinkage of hydrating cement pastes using analytical approach", *Cement and Concrete Research*, 34, pp.255-265.
13. Mounajed, G. and Obeid, W., 2001, "Modélisation du comportement thermo-hygromécanique des bétons à hautes températures", BHP2000 report, CSTM, 55 pp (in French).
14. Pane I. and Hansen W., 2005, "Investigation of blended cement hydration by isothermal calorimetry and thermal analysis", *Cement and Concrete Research*, 35, pp.1155-1164.
15. Hansen, W., Peng, Y., Borgnakke, C., Nouri, Y., and Biernacki, J.J., 2006, "Pozzolanic reactivity of ground granulated blast furnace slag in blended cement", *2nd International Symposium on Advances in Concrete through Science and Engineering*, 11-13 September, Québec City, Canada, pp.325.
16. Singh, N.B., Bhattachayee, K.N., and Shukla, A.K., 1995, "Hydration of Portland blended cements", *Cement and Concrete Research*, 25, pp.1023-1030.
17. Wirquin, E., Broda, M., and Duthoit, B., 2002, "Determination of the apparent activation energy of one concrete by calorimetric and mechanical means – Influence of a superplasticizer", *Cement and Concrete Research*, 32, pp.1207-1213.
18. Bjøntegaard, Ø., 1999, "Thermal dilation and autogenous deformation as driving forces to self-induced stresses in high performance concrete", Doctoral Thesis, Trondheim University, 256 pp.
19. De Belie, N., Grosse, C. and Robeyst, N., "Evolution of different ultrasound transmission parameters to monitor microstructure development in fresh concrete or mortar", *2nd International RILEM Symposium on Advances in Concrete through Science and Engineering*, September 2006, Québec City, Canada, pp.313.
20. Kelly, T.M. and Bryant, D.E., 1957, "Measuring the rate of hardening of concrete by bond pullout pins", *Proceedings of the American Society for Testing and Materials*, V.57, p.112.
21. Robeyst, N., Gruyaert, E. and De Belie, N., 2007, "Ultrasonic monitoring of setting and hardening behaviour of concrete and mortar with blast-furnace slag cement", *12^{ième} Congrès International de la chimie du ciment*, July, Montréal, Canada, pp.8-13.
22. Staquet, S., Boulay, C., and D'Aloia, L., 2006, "Autogenous shrinkage of a self-compacting VHP in isothermal and realistic temperature conditions", *2nd International RILEM Symposium on Advances in Concrete through Science and Engineering*, September, Québec City, Canada, pp.361.

23. ASTM C597-97, “Standard test method for pulse velocity through Concrete”.
24. Baroghel-Bouny, V., Mounanga, P., Khelidj, A., Loukili, A. and Rafaï, N., 2006, “Autogeneous deformations of cement pastes – Part II. W/C effects, micro-macro correlations and threshold values”, *Cement and Concrete Research*, 36, pp.123-136.
25. Mehta, P.K., 1986, “Concrete: structure, properties and materials”, Prentice-Hall, INC., New Jersey, USA, 450 pp.
26. CEB/FIP Model Code 1990, 1999, “Structural Concrete: Textbook on behaviour, Design and performance”, Vol.1, 224 pp.
27. Li, Y.X., Chen, Y.M., Wei, J.X., He, X.Y., Zhang, H.T. and Zhang, W.S., 2006, “A study on the relationship between porosity of the cement paste with mineral additives and compressive strength of mortar based on this paste”, *Cement and Concrete Research*, 36, pp.1740-1743.
28. Uchikawa, H., Hanehara, S. and Hirao, H., 1996, “Influence of microstructure on the physical properties of concrete prepared by substituting mineral powder for part of fine aggregate”, *Cement and concrete research*, 26, pp.101-111.
29. Lea, F. M., 1998, “Lea’s chemistry of cement and concrete”, 4th edition by Peter C. Hewlett, London: Arnold, 1058 pp.
30. Roy, D.M., 1989, “Hydration, Microstructure and chloride diffusion of slag-cement pastes and mortars”, *Trondheim Conference*, SP114-61, pp.1265-1281.
31. Cincotto, M.A., Melo, A. A. and Repette, W.L., 2003, “Effect of different activators type and dosages and relation to autogenous shrinkage of activated blast furnace slag cement”, *Proceedings of the 11th International Congress on the Chemistry of Cement*, 11-16 May, Durban, South Africa, pp.1878-1887.

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Table 1 — Cements characteristics

Cements	CEM I 52.5	CEM III A 42.5	CEM III B 42.5
Clinker content (%)	95	58	27
Slag content (%)	/	42	71
Limestone filler content (%)	/	/	2
Specific area (m ² /kg – ft ² /lb)	445 (2131)	447 (2140)	477 (2284)
Density (kg/m ³ - lb/ft ³)	3.09 (0.19)	3.01 (0.19)	2.93 (0.18)

Table 2 — Concretes mixtures proportions

Composition (kg/m ³ - lb/ft ³)	P-95 (CEM I 52.5)	SA-42 (CEM III/A 42.5)	SB -71 (CEM III/B 42.5)
Cement	375 (23.41)		
Water	164.6 (10.27)	166.95 (10.42)	164.9 (10.29)
Total water	169 (10.55)		
Admixture	5.63 (1.5%)	2.63 (0.7%)	5.25 (1.4%)
Sand 0/0.5	492 (30.71)		
Sand 0.5/1	126 (7.87)		
Sand 1/3	104 (6.49)		
Limestone 2/6	311 (19.41)		
Limestone 6/10	438 (27.34)		
Limestone 10/14	415 (25.91)		

Table 3 — Hydraulicity factors

Factors	Equations	Value of the studied slag
Chemical modulus	$\frac{(CaO + MgO)}{SiO_2}$	1.43
Hydraulic factor	$\frac{(CaO + MgO + Al_2O_3)}{SiO_2}$	1.76
Solubility factor R	$\frac{CaO \cdot Al_2O_3}{(SiO_2 + Al_2O_3)^2}$	0.217
Keil ratio F _{III}	$\frac{CaO + CaS + 0.5 MgO + Al_2O_3}{SiO_2 + MnO}$	1.62
Langavant ratio C	$20 + CaO + Al_2O_3 + 0.5 MgO - 2 SiO_2$	7.19
I _h ratio	$\frac{CaO + 1.4 MgO + 0.56 Al_2O_3}{SiO_2}$	1.72
Tetmayer modulus	$\frac{\frac{CaO}{56} + \frac{MgO}{40} + \frac{Al_2O_3}{102}}{\frac{SiO_2}{60}}$	1.84

Table 4 — Chemical composition of slag and clinker

Oxides (%)	Slag	Clinker
CaO	39.75	66.09
SiO ₂	34.35	19.03
Al ₂ O ₃	11.50	5.39
MgO	9.28	0.78
SO ₃	3.08	1.81
TiO ₂	0.55	0.37
K ₂ O	0.38	0.97
Fe ₂ O ₃	0.31	3.72

Table 5 — Portlandite, Chemical bound water and calcite contents estimated by TGA-DTA

$$\text{Portlandite (\%): } m_{\text{Ca(OH)}_2}(t) = \frac{|\Delta m_{400^\circ\text{C} \rightarrow 600^\circ\text{C}}(t)|}{m_c} \cdot \frac{M_{\text{Ca(OH)}_2}}{M_{\text{H}_2\text{O}}}$$

with $\Delta m_{400^\circ\text{C} \rightarrow 600^\circ\text{C}}(t)$: sample mass loss between 400°C (752°F) and 600°C (1112°F) (kg-lb)

$$m_c = \frac{m_{\text{sample}}}{(1 + W/C) \cdot (1 + \text{PaF})}$$

m_{sample} : initial sample mass (kg)

PaF : loss on ignition

w: water content (kg/m³)

c: cement content (kg/m³)

$M_{\text{Ca(OH)}_2}$: portlandite molar mass (kg/mol)

$M_{\text{H}_2\text{O}}$: water molar mass (kg/mol)

	2 Days	3 Days	7 Days	28 Days
SA-42	14	17	17	17
SB-71	9	9	14	17
P-95	31	35	32	31

$$\text{Chemically bound water (\%): } w_{\text{el}}(t) = \frac{|\Delta m_{145^\circ\text{C} \rightarrow 1000^\circ\text{C}}(t)| - |\Delta m_{600^\circ\text{C} \rightarrow 880^\circ\text{C}}(t)| - m_c \text{ PaF}}{m_c}$$

with $\Delta m_{145^\circ\text{C} \rightarrow 1000^\circ\text{C}}(t)$: sample mass loss between 145°C (293°F) and 1000°C (1832°F) (kg)

$\Delta m_{600^\circ\text{C} \rightarrow 880^\circ\text{C}}(t)$: sample mass loss between 600°C (1112°F) and 800°C (1472°F) (kg)

	2 Days	3 Days	7 Days	28 Days
SA-42	10	13	14	15
SB-71	6	8	14	17
P-95	18	19	20	20

$$\text{Calcite (\%): } m_{\text{CaCO}_3}(t) = \frac{|\Delta m_{600^\circ\text{C} \rightarrow 880^\circ\text{C}}(t)|}{m_c} \cdot \frac{M_{\text{CaCO}_3}}{M_{\text{CO}_2}}$$

with M_{CaCO_3} : calcite molar mass (kg/mol)

M_{CO_2} : carbon dioxide molar mass (kg/mol)

	2 Days	3 Days	7 Days	28 Days
SA-42	20	22	22	29
SB-71	20	21	24	27
P-95	36	34	42	66

Table 6 — Apparent activation energy value for three temperature intervals

Temperature interval (°C)	Ea (kJ/mol)	
	SA-42	SB-71
10-20	33.0	50.2
20-30	53.5	43.0
10-30	42.7	46.6

Table 7 — Evolution of the capillary porosity

	2 days	3 days	7 days	28 days
SA-42 (%)	17	15	13	12
SB-71 (%)	19	17	13	13
P-95 (%)	15	15	13	10

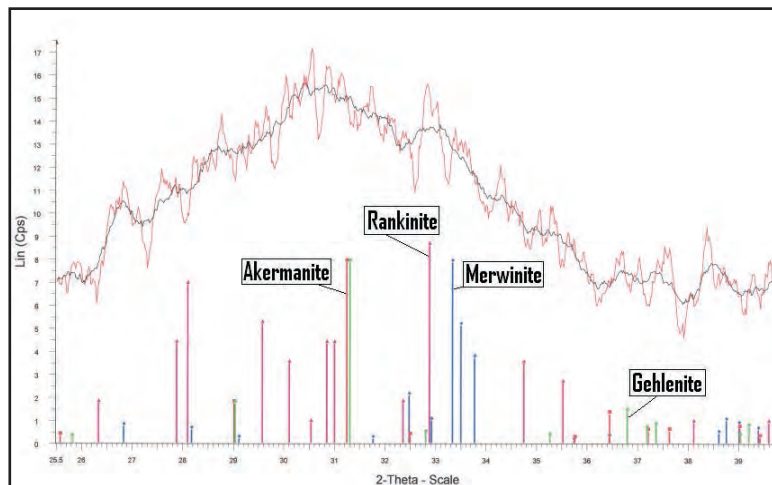


Figure 1 — XRD analysis of slag

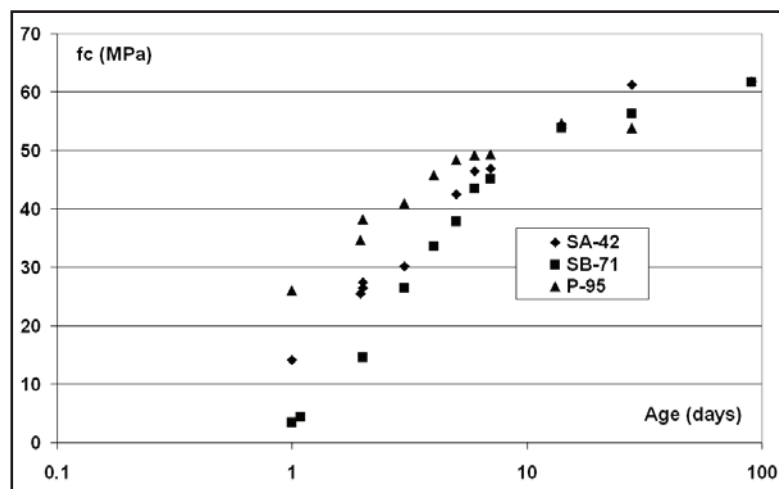


Figure 2 — Average compressive strength evolution of samples kept at 20°C and 90% R.H.