A TUMBLER AND PORE WATER EXPRESSION DEVICE TO PREPARE HOMOGENEOUS SAMPLES FOR THE EXTRACTION OF FREE CHLORIDE IN CEMENT PASTE

D.J. DELPORT, S.S. POTGIETER-VERMAAK AND J.H. POTGIETER

ABSTRACT

Corrosion of rebar in concrete is commonly associated with the free chloride in the pore water in the cement matrix. Knowing the quantity of chloride in concrete is important because chloride can promote corrosion of steel reinforcement when moisture and oxygen are present. The problem of physical extraction and the measurement of the free chloride content in pore water solutions extracted from cement pastes has received attention in literature but has not been explained in full detail. However, the variability of results obtained from the different methods used by various investigators only serves to confuse the issue. This investigation describes the use of a tumbler designed to prepare homogeneous samples and the use of a pore water expression device designed to extract free chloride in cement paste and concrete samples.

Keywords: Tumbler, Homogeneous samples, Cement, Chloride

1. INTRODUCTION

The cement industry plays a major role in the world industry. Analytical techniques are central to its success (Potgieter-Vermaak, 2002). One major problem in this field is the lack of preparation of good homogeneous cement paste samples for research purposes. A well-prepared sample yields accurate results. When conflicting results are obtained, in most cases, greater focus is placed on the analytical technique rather than on the method of sample preparation of the sample. This is evident in the variety of alternative procedures that have been developed for measuring chloride in cement-related materials described in the literature (Sakai et., 2006, Buckley et al., 2007, Delport, 2010, Castellote et al., 2001, Climent et al., 2004, Yun et al., 2004 and Potgieter et al., 2007). The variability of the results obtained by using the different methods suggested by the various investigators only serves to confuse the matter. One possible cause for this lack of reliable repeated results could be due to the insufficient detailed attention paid to the preparation of samples and specifically with regard to the homogeneous setting of the cement paste samples. Homogeneous setting of the cement paste specimens constitutes an important part of the sample preparation method. Sedimentation of the cement samples must be avoided during hydration or setting. Sedimentation, in this case, refers to the cement particles settling, out of suspension, under gravity. The water in the mixture, which contains the bulk of the free chloride, would collect at the top of the cast, while the cement solids would settle at the bottom.

This could result in a chloride concentration gradient throughout the cement paste and means that the hardened cement that was in contact with the water would contain a higher concentration of total free chloride than the cement near the bottom of the cast. In other words, the distribution of free chloride throughout the hardened cement specimen would be uneven, and thus not representative of the actual concentration in the sample.

In the literature, certain researchers have mentioned that the freshly mixed cement specimens were rotated slowly about a horizontal axis for a day in order to avoid sedimentation (Byfors, 1986 and Tritthart, 1989a). This device, the so-called tumbler, used for such a purpose is not commercially available and must therefore be custom built. No reference that described the design and rotational velocity, or any that proved that the use of such a device did in fact promote a homogeneous setting of the cement paste, could be found.

Thus, the first aim of this investigation was to design and build a tumbler to ensure the homogeneous setting of cement samples by making use of a slow rotating action about a horizontal axis, moreover, to minimise the negative sedimentation effect of rotating horizontally about a horizontal axis. The chloride analyses performed on the specimens by means of the pore water extraction device, would establish the homogeneity of chloride distribution throughout a sample.

2. SAMPLE PREPARATION

The cement samples were made by mixing ordinary Portland cement (OPC) with a specific amount of distilled water (measured by mass of cement or binder) in order to achieve a water to cement/binder ratio of 0.6:1. An important consideration before deciding on a suitable water to cement ratio, was the working range (maximum 25 MPa) of the available press (Furnell Testing Press, provided by Dick King Laboratories) and the typical ranges taken by compilers of the standard method of the Rilem Technical Committee (Rilem, 2002). A known concentration of chloride was added to the de-ionised water as sodium chloride (NaCl) prior to mixing.

The chloride concentration was calculated as a mass percentage of the cement content or combined cementitious binder. The cement paste sample was mixed with a Hobart mixer and poured into quality plastic tube bags, which had been sealed at one end. The plastic tubing containing the cement paste was then placed in polyvinylchloride (PVC) pipes. The plastic tubing was subsequently sealed at the other end by wire ties or a knot. Each sample, conveniently called a “bullet”, consisted of a PVC pipe, 50 mm in diameter and 180 mm in length (Figure 1). The PVC pipe was cut perpendicular to its length in order to make it easier to remove the hardened cement paste samples.

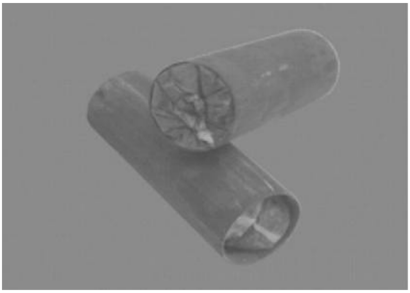

Figure 1. Cement in plastic bags inside PVC pipes, (bullet)

3. TUMBLER DESIGN

The frame of the tumbler was made with 50 mm by 50 mm square tubing. A 110 V dc motor, equipped with a gearbox to reduce the rotational speed of the output shaft, was used to supply rotational motion. Since the main power supply is 220 V, a transformer was used to step it down to 110 V. A schematic drawing of the tumbler is presented in Figure 2, and the real image in Figure 3. In the control box, a voltage variable transformer was used to control the rotational speed of the 110 V dc motor.

The revolution of the tumbler drum with the step down gearbox was measured with a tachometer to be 106 rpm. A 68 mm pulley was connected to the gearbox output shaft. A fan belt connected the motor pulley to the pulley attached to the specimen drum shaft, the diameter of which was 200 mm. This increase in pulley size between the motor output shaft and the drum shaft had the effect of reducing the speed of the cement sample drum by a factor of 0.34, relative to the speed of the motor shaft. The homogeneous setting of the specimen drum, measured with a tachometer, indicate an optimum rotational speed of 36 rpm.

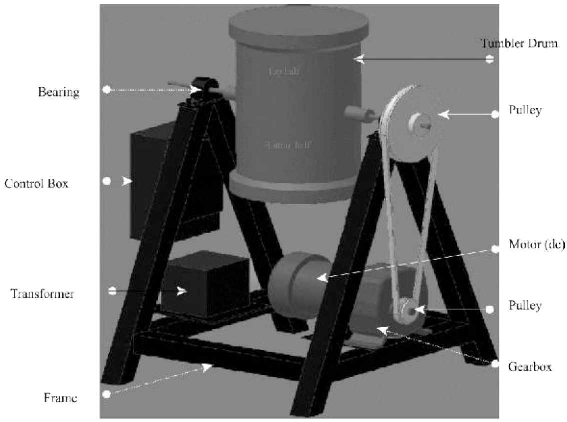

Figure 2. Schematic representation of the tumbler assembly

The tumbler controls featured a power switch, a digital timer and a switch to toggle between the timer control and direct operation. The tumbler could be set to operate for up to 24 h, in increments of 30 min by adjusting the timer. The control box also featured a voltage variable transformer, which was added with the intention to control the rotational speed if necessary.

The drum container was made from an aluminium alloy pipe, with an inside diameter of 250 mm and a length of 450 mm, with wooden lids on both sides. The lids were closed by means of a threaded steel rod that passed through the centre of the drum and the lids and tightened with nuts. A shaft was attached to the drum container perpendicular to its centre line. This design caused the drum to rotate vertically about a horizontal axis.

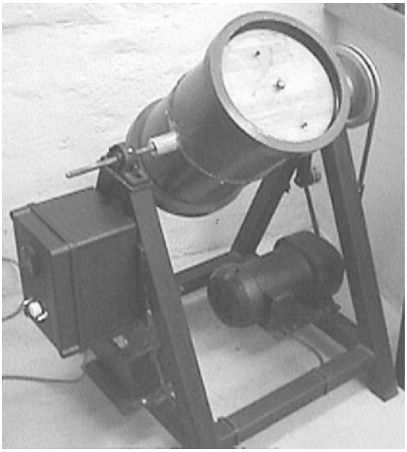

Figure 3. Photographic image of the tumbler design

An aluminium plate was placed in the centre of the drum container, thereby dividing it into two sections at the axis of rotation. The PVC sample cylinders were placed in the aluminium drum container lengthways. The container could hold 24 cement paste samples, 12 in each half (see Figure 4).

Figure 4. Tumbler loaded with samples

4. PORE WATER EXPRESSION DESIGN

The device was designed, in principle, similar to that of a piston and sleeve usually found in the engine of a car. It consisted of four components, namely the plunger, body, Teflon seal and base plate (Figure 5). The whole device, except the Teflon seal, was made of mild steel. The dimensions of the plunger were 54 mm in diameter and 135 mm in length. The body was machined to achieve 120 mm in diameter and 150 mm in length. A centre diameter of 55 mm was cut out to make space for the plunger. A recess of 15 mm, with a centre diameter of 65 mm, was cut out of the top of the body through which to pull the plunger out, by hand, if necessary. The base plate was machined to a size of 125 mm in diameter and 21 mm in length. The top of the base plate was recessed so as to accurately fit the body onto it and to prevent it from sliding. On the side, at the top of the base plate, a 3 mm hole was drilled at an angle of 45º for the expressed water to be collected. A Teflon seal was placed between the sample and the plunger in order to prevent the water from being pressed out of the top of the device.

4.1 Pressing procedure

The sample was placed in the pore water expression device and slowly pressed at ±100 $kPa.s^{-1}$. The first drop of water appeared at 20 ±5 MPa for a water to cement ratio of 0.6:1. The samples were pressed using a slow increase in pressure of 500 $Pa.s^{-1}$. It proved to be beneficial not to press continuously but to wait for a few minutes at various intervals during the pressing in order to allow for the flow of the water to permeate between the solid particles and the outer surface.

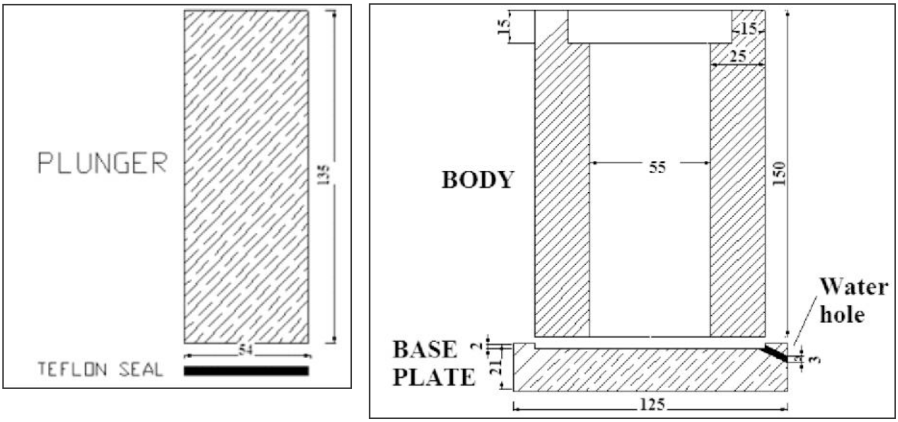

Figure 5. Schematic sketch of pore water expression device

5. RESULTS AND DISCUSSION

In an initial design the rotation axis was horizontal about a horizontal axis (see Figure 6) and operated at a rotational speed of 77 rpm. Visual inspection of the specimens rotated in the first tumbler showed signs of heterogeneous setting (see Figure 7). This was evident by the presence of what appeared to be flow lines in the sections cut from the specimens. The presence of these flow lines could be explained by the high rotational speeds employed by the design (77 rpm), which would cause significant centrifugal forces in the cement paste. These forces would cause segregation of the cement paste and mixing water. The electric motor was replaced with another motor with a lower rpm, resulting in a tumbling speed of 21 rpm. With the lower speed of the rotation, no significant improvement was observed in the segregation occurring in the samples. In addition most of the sample end sections were more brittle than the rest of the body, thus confirming particle segregation. Since it was clear that setting was not homogeneous, chloride concentrations of different sections of these specimens were not determined, as this would be done only for homogenous samples. The longitude and perpendicular cuts of the samples were made with a diamond grinder blade.

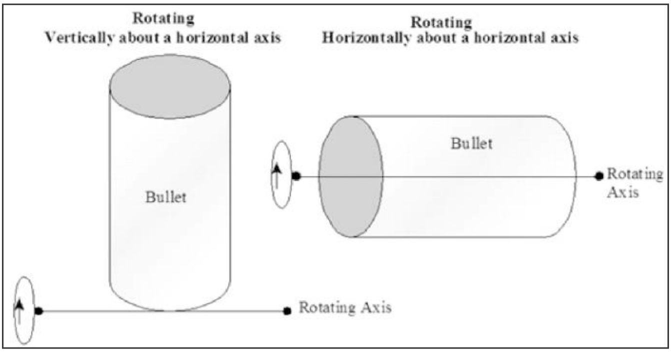

Figure 6. Schematic representation of the two different sample rotational axis orientations used

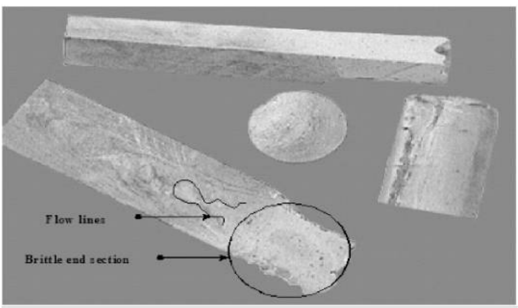

Figure 7. Photographic image of different sections of a cement paste sample that was rotated in the initial tumbler design.

The final tumbler design took into consideration the shortcomings of the first design. In this design, made drum rotates vertically about a horizontal axis (Figure 6). After the first batch of specimens were rotated for the predetermined time of 12h, visual inspection of the samples of this design displayed clear signs of homogeneous setting. This was evident in the uniform colour and texture of the longitude and perpendicular cuts of the inspected specimens (Figure 8). In order to verify that these specimens did in fact set homogeneously, it was decided that the free chloride concentration of the different sections of these specimens would be determined after seven days of curing.

After seven days of curing, three specimens were taken from the mixing batches. Each sample of the mix consisted of 1% chloride in the form of NaCl and water to cement ratio of 0.6:1. A Metrohm Chloride (6.0502.120) Iron Selective Electrode (ISE) with a Ag/AgCl reference electrode (6.0726.107) was used for the potentiometric measurements of the express pore water. Each specimen was dry cut with a diamond grinder blade. The different sections (bottom, middle and top) were pressed at 20 Mpa. The pore water for each of the sections was placed in separate sample bottles for analysis.

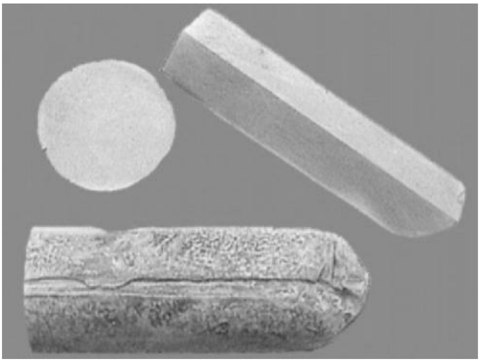

Figure 8. Photographic image of different sections of the hardened cement paste sample that was rotated with the tumbler base on the second design

The potentiometric analyses were performed by pipetted 1.0 ml of the sample into 50 ml of de-ionised water. The results obtained, clearly indicated that good repetition (< 3% RSD) was achieved between the different sections of each sample as well as between the three different samples from different batches (Table 1). The mV readings were not converted to absolute chloride concentrations, but merely used to indicate the degree of reproducibility and repeatability between the different sections and samples (top, middle and bottom).

Table 2.1: Potentiometric (mV) results of the different sections of the specimens used to determine homogeneous hardening in cement mixtures

Specimen number	Top Section (mV)	Middle Section (mV)	Bottom Section (mV)
1	153	154	153
	158	153	158
	154	156	155
Average	155±3	154±2	155±2
2	150	152	155
	155	154	152
	156	155	156
Average	154±2	153±2	154±2
3	155	155	154
	154	156	155
	155	153	156
Average	155±2	155±2	155±2

6. CONCLUSIONS

By changing the rotational axis of the drum to a vertical position to rotate about a horizontal axis of the tumbler, it was possible to obtain homogeneous cement paste samples. This visual inspection was verified by potentiometric analysis. Thus, the design met its objective to prepare homogeneous samples.

It was also possible to separate the pore water of the hardened cement from the solid particles by squeezing out the water under high pressure. This method has been used previously in order to investigate the composition of pore water (Tritthart, 1989a). The advantage of this method is that comprehensive information can be obtained not only regarding the chloride content, but also the type and concentration of other species dissolved in the pore water.

7. REFERENCES

BUCKLEY, L.J., CARTER, M.A., WILSON, M.A., SCANTLEBURY, J.D. 2007. Methods of obtaining pore solution from cement pastes and mortars for chloride analysis. Cem and Concr Res.37: 1544-1550.

BYFORS, K. 1986. Chloride binding in cement paste. Nordic Concr. Res. 5: 27-38

CASTELLOTE, M., ALONSO, C., ANDRADE, P., CASTRO, P. & ECHEVERRIA, M. 2001. Alkaline leaching method for the determination of the chloride content in the aqueous phase of hardened cementitious materials. Cem. and Concr. Res. 31: 233 - 238.

CLIMENT, M.A., de VERA, G., VIQUEIRA, E.,& LOPEZ-ATALAYA, M.M. 2004. Generalization of the possibility of eliminating the filtration step in the determination of acid-soluble chloride content in cement and concrete by potentiometric titration. Cem. and Concr. Res. 34: 2291-2295.

DELPORT, D.J. 2010. The effect of mineral admixtures on free chloride in cement. D-Tech, dissertation, TUT, Pretoria, S.A.

POTGIETER, S.S & MARJANOVIC, L. 2007. —A further method for chloride analysis of cement and cementitious materials ICP-OES. Cem. and Concr. Res. 37: 1172 - 1175.

POTGIETER-VERMAAK, S.S. 2002. The determination of major, minor and trace elements in cement and cement-related materials. D-Tech, dissertation, TUT, Pretoria, S.A.

RILEM TC 178-TM, 2002. Testing and modelling chloride penetration in concrete. Analysis of total chloride content in concrete. Mat. and Struct. 35: 583 - 585.

SAIKAI, N., KATO, S. & KOJIMA, T. 2006. Thermogravimetric investigation on the chloride binding behaviour of MK-lime paste. Thermochimica Acta. 444: 16-25.

TRITTHART, J. 1989a. Chloride binding in cement. I. Investigations to determine the composition of pore water in hardened cement. Cem. and Concr. Res. 19: 586-594.

YUN, H., PATTON, M.E., GARRET, H.J. Jr., FEDDER, K.G., FREDERICK, K.M., HSU, J., LOWE, I.J., OPPENHEIM, I.J. & SIDES, P.J. 2004. Detection of free chloride in concrete by NMR. Cem. and Concr. Res. 34: 379 - 390.