Monitoring Apparent pH Value in Geopolymer Concrete Using Glass Electrode

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Abstract –

Geopolymer concrete (GPC) is estimated to reduce 80% carbon footprint in construction projects compared with ordinary Portland cement (OPC). Previous studies on GPC have been focusing on assessment of paste or mortar while the long-term durability of GPC has not been extensively investigated yet. This research aims to monitor carbonation process of GPC by measuring in-situ apparent pH value under accelerated carbonation test in laboratory environment. Glass pH electrode is typically applied for liquid medium and considered to be unsuitable for OPC due to high alkaline condition. We have endeavoured to test the glass electrode in GPC assuming the alkalinity in GPC would be much lower than OPC. Two pH probe sensors were embedded into GPC specimens with different depth and seal condition. After 18 hours heat cures and 7 days curing in ambient environment, one of GPC specimens was then relocated to a carbonation chamber with 1% carbon dioxide concentration. The glass electrodes were found to survive the GPC environment with real-time apparent pH value registered since the GPC specimens were poured. It is also observed that the apparent pH values were affected significantly by the level of humidity inside the concrete. Saturation experiments were then conducted to provide valid pH readings. As a result, we successfully monitored pH decreasing from 11.1 to 10.76 after three months carbonation experiment. The results are also validated by comparing against the data acquired by traditional concrete grinding test. The research features the first trial of its kind and has contributed to comprehensive understanding about corrosion mechanism of the new GPC material.

Keywords –

pH glass electrode, Geopolymer concrete, Carbonation, Long-term monitoring

1. Introduction

The contribution to carbon emissions from the ordinary Portland cement concrete (OPC) is second only to fossil fuels [1]. With growing environmental demands in terms of low carbon, geopolymer concrete (GPC) has emerged as environmentally construction material with great potential to substitute OPC [2]. The GPC utilises industrial waste as binder to cast concrete, e.g. fly-ash, slag and mud, etc. It potentially contributes to a maximum reduction of 80% carbon dioxide (CO_2) emission in construction projects compared with OPC. With similar mechanical properties to OPC, GPC also exhibits some superior characteristics such as stable state exposed to the high temperature and acid. Despite many advantages compared to the conventional concrete, there are also several challenges faced by this new material [4] [11]. There are still many fundamental issues to be addressed for GPC, e.g. lack of a complete standard or handbook commonly used globally; the corrosion mechanism of reinforcing steel in GPC is not well understood, which could be very different with traditional concrete [9]; and limited previous studies assessed long-term durability of GPC in terms of carbonation process.

Concrete carbonation is one of the primary reasons for steel corrosion in reinforced concrete structures [13]. Steel reinforcement in OPC is naturally protected by the high alkalinity pore solution (pH value being 12.5-13.5) in which induces an oxide passive film is formed on the reinforcement surface to protect it against corrosion. Carbonation process when occurs will cause a rapid decay and shorten the service life of concrete structure [1]. This can be evoked under the exposure to normal situation while carbon dioxide from atmosphere diffused into concrete and reacted with the hydrated cement in concrete [16]. The process is usually described as a simple chemical function, as given in Equation 1.

$$\mathrm{Ca(OH)_2} + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

Carbonation itself doesn't cause the damage to concrete, which only lowers the alkalinity concentration of the pore solution and the passive film protection tends to be disappeared along with the decreased pH value in concrete. Therefore the pH value in concrete is well regarded as a key parameter indicating the level of corrosion [12]. As reported by Schieβl, if pH value in concrete drops bellows 9, the passive film protection will lose in the greater surface area of reinforcement. Accordingly, long-term monitoring of pH value in the range from pH 9 to 13 with a resolution of about 0.5 pH units is relevant for early detection of a potential corrosion condition [10].

Carbonation is often assumed to be related to the diffusion gas though the porous concrete. The diffusion rate normally depends on the material properties, moisture and concertation of the carbon dioxide. As the properties of the concrete vary, the carbonation rate will also be different [13]. An easy model was developed for calculating the time-dependent depth according to Fick's first law of diffusion:

$$X=A\sqrt{t} \qquad (2)$$

Where the X is the depth of the carbon dioxide front, A is the rate of carbonation, t is the time.

This research aims to assess performance and accuracy of the pH electrode in measuring apparent pH value GPC. The traditional electrode was embedded in GPC to measure the pH value throughout the entire life since concrete casting. It features the very first trial of a long-term pH monitoring system for GPC. It contributes to a comprehensive understanding about corrosion mechanism of the new GPC material and is potentially applicable for field measurement if the results of laboratory experiment prove to be successful and reliable.

2. Review on pH measurement

It is essential to measure the pH value to estimate the likelihood and start time of corrosion as the pH value is the only parameter that can directly indicate the corrosion state. Currently, most commonly used methods to measure the pH value in concrete are destructive, such as percussive drilling, X-ray and thermo-gravimetric analysis [18]. These methods require removals of concrete dust or sample from different depth of the testing structure and bring back to analysis in a laboratory. The construction industry uses a simple test, which involves spraying the phenolphthalein indicator solution onto the freshly cored concrete sample and measuring the carbonated depth of the concrete [3]. However, none of those methods is able to provide continuous measurement; the use of destructive methods to obtain pH information of the material is no longer accepted for long-term monitoring [5].

In-situ monitoring systems allow continuous monitoring over an extended time periods by embedding the sensing probe within permanent bodies. [20]. Due to the harsh condition of concrete in terms of the high pressure and high alkalinity condition, continuously measuring the pH value within concrete is always a very difficult task. The sensor has to be durable enough and requires many unique characteristics, such as high chemical and pressure resistance and a suitable measureable pH range. Since Werner reported the fibre optical pH sensor has the potential to measure the high pH value from 9~13 in 1990s, a few studies has been continued in developing the fibre optical pH sensor in concrete. This sensor is designed by use of an appropriate pH indicator attached to porous substrates allowing the ions exchange with the concrete structure. This matrix has the ability to respond the pH change as the colour difference and, consequently, the optical sensor will measure the light intensity. Although a few fibre optical pH sensors have been embedded in concrete to measure the pH value for several months, the development has not exceeded the status of prototyping and there is no commercial product available so far [6][21]. More importantly, it suffers from certain drawbacks, such as inconsistent response in different pH range [17]. As dye will easily leach leading to a signal drifting, a complex operation procedure in designing process is required. Meanwhile the fibre optical pH sensor has not been able measure pH value above 12 effectively [3] [15].

Usually, the pH value in solution is determined using an electrode which includes working electrode, reference electrode and temperature sensor. The pH electrode contacts with the solution by a special pH sensitive glass membrane which develops a voltage proportional to the pH value. Previous results in concrete showed that this type of sensor is not suitable for the OPC. The main problem is the sensor designed for the solutions might be not respond to the dry condition and easily leads to false readings. The high alkalinity concentration in concrete could break the sensor body in hours [15][21]. The conclusion is made based on the test results in conventional concrete while GPC tends to have a much lower alkalinity condition due to the different compositions. However, the pH electrode has never been tested in GPC even though the sensors have been commercially available for decades.

With technical advances in the pH electrode sensor, manufacturers use special glass membranes to measure high alkaline values which makes almost zero alkalinity error with pH value below 12. More importantly, periodically re-wetting the sensor by water can possibly eliminate the shift of readings [19].

An Emerson pH glass probe (Model: General

Purpose 3900) was evaluated in geopolymer concrete in this study. A rugged surface encloses the temperature, reference and working electrode into one sensor body, which provides a stable condition for electrode with high chemical and pressure resistance. The measurable pH range from 0-14 is suitable for entire carbonation process from the fresh concrete to cure and carbonation condition. The measurement unit is quite sensitive with a 0.01 unit of resolution, and therefore it is possible to monitor the pH change within the concrete throughout the service life.

3. Experimental Program

3.1. Design of Instrumentation

This pH sensor system consists of two pH probes, one data analyser and two data loggers, as shown in Figure 1. The probe is composed of a working electrode, reference electrode and temperature sensor included in one body. The data logger automatically records the pH readings in different environments from the two sensors. The overall potential of the measuring electrode equals the potential of the internal reference electrode plus the potential at the glass membrane surface. The working electrode is able to proportionally indicate the pH value while the potential of reference electrode is dependent. The overall voltage of the cell depends on the measured sample. Working and reference electrode will exhibit an iso-potential and this usually designed to be 0 mv at pH 7.0. Prior to the use of system, it is necessary to calibrate the sensor first before embedding it into concrete. As the cell voltage is a linear function of pH value, two buffer solutions were used with pH 4 and 10. The calibration slopes for sensor 1 and 2 were 57.8 and 57.6 respectively.

Figure 1. Experiment setup of the pH Sensor System (Emerson Ptd.)

3.2. GPC Material and Batching

The specimens are 50Mpa in design grade and produced by homogeneous paste from the mixture with fly ash and activator (Table 1). The fly-ash classification follows the ASTM standard C618. For concrete mixing, the priority procedure is to prepare the alkaline activator 24 hours before the casting day. The activator used was the mixture of 12M sodium hydroxide and sodium silicate solution while the aggregate used is 10 mm basalt and Sydney sand. The material mixing followed restrict sequence from coarse to fine, then the activator and free water.

Table 1 Concrete Mixing

Materials	Density (Kg/^{3}m)	Percentage
Coarse aggregate (10mm basalt**)**	1221.2	50.105
Fine aggregate	620.8	25.471
Fly ash	271.6	11.143
Kaolite	77.6	3.184
Slag	38.8	1.592
NaOH	55.3	2.269
Na2SiO3	138.7	5.691
Water	13.3	0.546
Total	N/A	100

3.3. Experiment Setup

After calibrating the pH sensors, the next step is the sensor embedment. Two concrete cylinders were built with same 100 mm diameter and 200 mm height. A magnet-stand was used to attach to the concrete steel mould and fix the sensor location, as shown in Figure 2. The sensors were embedded into different depths of 100 mm and 20 mm from the bottom surface respectively. Upon the sensor location is confirmed, the concrete was directly poured from the top and vibrated. To reach the expected strength shortly, both geopolymer concrete cylinders were heat cured at 75°C in a heat chamber for 18 hours.

Once the heat curing process finished, different treatments were applied into the individual concrete sample. Table 2 is shown the difference dispose methods between the 1st and 2nd specimen. The first specimen cylinder stayed at a plastic mould to isolate any contact with environment which intends to keep the inner moisture from evaporating quickly. The 2nd specimen was de-moulded and wrapped with the seal tap except bottom surface which was in contact with the environment. Both concrete cylinders were placed on the 25°C and 63% relative humidity for 7 days curing. But only the 2nd specimen was transferred to the carbonation chamber for investigating the carbon dioxide front at 20 mm depth. Environment in the chamber was set to 23°C temperature, 65% relative humidity with 1% carbon dioxide concentration. Meanwhile, another sample stayed in the controlled ambient condition with 23°C as a reference. The different measurement depth and seal condition in this experiment were designed to investigate the moisture and carbonation influence on the pH readings. It is obvious that the 1st specimen will provide a much more wet measurement environment for the pH sensor, while the moisture of 2nd specimen will decrease quickly due to the evaporation from bottom.

Figure 2. set-up of pH sensor embedment

Table 2 Experiment Plan

Items	Sealed condition	Embedment Depth	Carbonated
1st specimen	Sealed	100mm	No
2nd specimen	Leave bottom surface	20mm	YES

It should be noticed that the conventional pH glass sensors are designed to measure the pH in water or liquid solutions. When a non-water solvent is present in appreciable quantities, the pH reading will be shifted from the expected value by effects of the non-water solvent on the pH. Therefore, the concrete samples need to be wetted to reduce the errors of reading.

The compression strengths of 7 days and 28 days are 48.5 Mpa and 52.94 Mpa respectively. The specific test procedure followed the AS1012.9-1999 standard.

4. Results and Discussions

4.1. pH value in Curing process

Figure 3 shows the pH values of the two specimens during curing process. After concrete was poured, pH readings were 12.4 and 12.2 for the 1st and 2nd specimens respectively. Both specimens recorded a sharp decrease during the heating process as the temperature increased from 25°C to 75°C. Temperature compensation was already add into the data analyser to eliminate the error induced by the sensor. However, chemical equilibrium of the components affected the pH value in addition to the temperature effect.

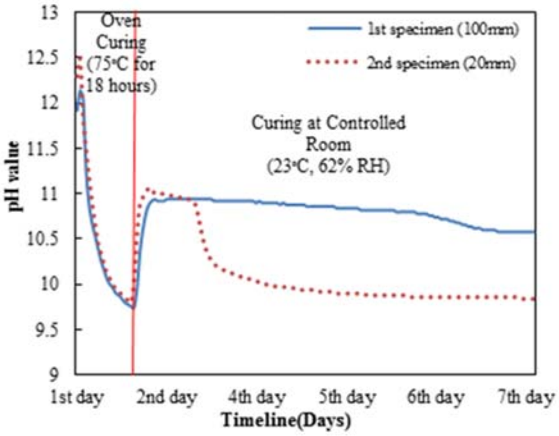

Figure 3. pH value during the heat and normal curing process

Both pH readings gradually recovered as the specimens cooled down to ambient temperature. The initial pH value of harden concrete was 11.1. In the next few days of curing process, a significant decrease was observed for the 2nd specimen in which the bottom can directly contact with the environment while the 1st specimen only experienced a slight drop at the same time due to different sealed condition. pH readings experienced a major change are not considered to be correct for the fresh concrete. The shift of pH readings is more likely caused by the moisture loss in terms of the evaporation and geopolymersation reaction within the concrete. Due to gradual loss of the water content within concrete, the resistance of the sensor increased substantially which induced a small current output and reflected a lower pH value. The specimens were then saturated to investigate and calibrate the moisture effect.

4.2. pH Value during Carbonation Process

After the pH reading of the 2nd specimen stayed constant in the dry condition, it was transferred to the accelerated carbonation chamber with 1% carbon dioxide and 65% relative humidity. The specimen was placed in the chamber for 6 weeks. To ensure the decreasing result is more reliable, another pH measurement method with percussive drilling was also introduced. The drilling test of concrete sample conducted every two weeks since the carbonation and all the samples were prepared from the same concrete batch. Figure 4 shows the pH value comparison between the sensor measurement and percussive drilling at the exact 20 mm depth of the concrete cylinder. The initial pH value tested by drilling test was 11.45 and the decreasing curve was presented mostly like a linear function and, eventually come to 11.04 after six weeks carbonated. By comparison, a very similar pattern was found in the raw data of sensor measurement result although the pH readings were not correct due to the loss of moisture. It decreased from 9.84 to 9.42, the decreasing values in two methods were almost the same being 0.41 and 0.42 pH unit respectively. The humidity within the concrete already kept constant and only had limited effect to the pH readings. Therefore the change of pH reading is mostly because of the carbonation.

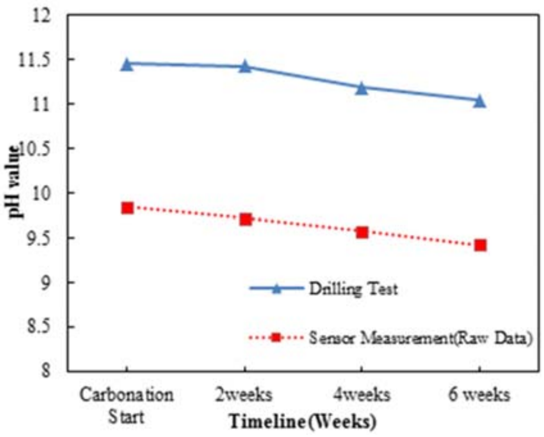

Figure 4. Comparison of 6 weeks carbonation value from raw pH sensor readings and drilling test

4.3. Saturation Test for pH Calibration

To verify the shift of pH readings due to moisture loss, a series of saturation tests was carried out on both specimens. The specimen was submerged into the tap water for 8 hours and then enclosed with the sealed tap. After that, the specimens were placed at controlled environment and let the humidity diffusion into the inner concrete gradually. Both specimens wre saturated into tap water twice; only hydrated for few hours of each time as a concern of the alkalinity leakage. Figure 5 shows the pH readings of specimens saturated after the carbonation test finished. Since the saturation begins, the pH readings of the both specimens increased apparently in the next few weeks. However, the increasing rate was gradually slowdown in the 2nd week and, therefore a second saturation was conducted to wet concrete more properly. The pH readings of the first specimen stabilised at 11.08 in the fourth week, which was exactly the initial pH value when concrete was harden. Meanwhile, the pH reading of second specimen was 10.74 remaining a 0.34 difference to 1st specimen. Considering the same initial values obtained from both specimens at the beginning of the test, the carbonation effect after 6 weeks was considered to be the main reason causing the gap of pH readings between the two specimens.

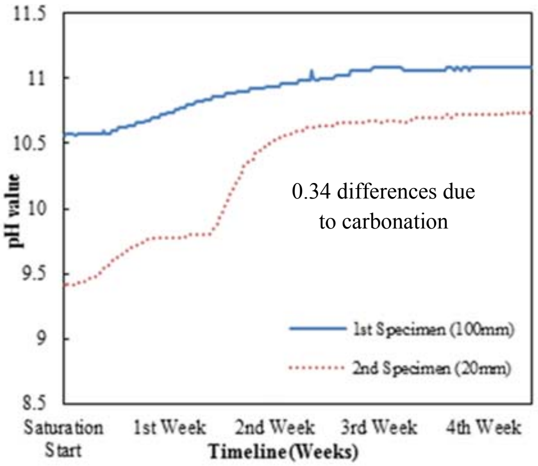

Figure 5. pH value of 2nd specimen during the saturation Test

It was also found from the saturation tests that the pH value shifting caused by the humidity loss could be reversible if the sensor probe was wetted properly. In this experiment, the pH value of 11.1 is regarded as the correct initial value. Meanwhile, the sensor measurement under the carbonation environment was considered as accurate.

Figure 6 shows the real pH value during 6 weeks carbonation. The pH readings of the sensor measurement decrease from 11.1 to 10.68 as an average weekly rate of 0.07 unit/week during the same duration.

The eventual value also contained small error compared to the value after 2nd specimen being well saturated (10.74). The difference of 0.3 pH unit was found between the two methods. This was considered to be in the acceptable range as the drop pH value due to carbonation is usually measured as a resolution of 0.5 pH unit.

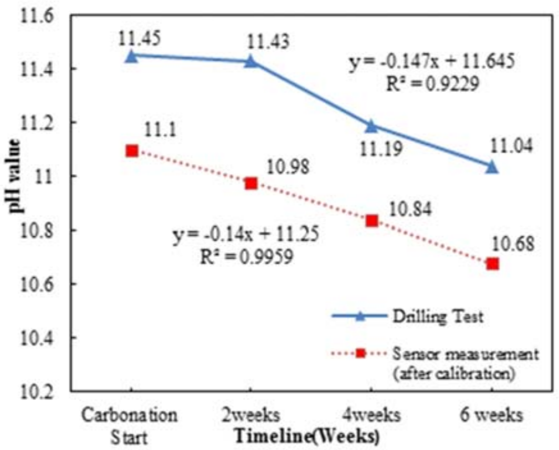

Figure 6. pH value comparison between sensor measurement and drilling test after calibration

5. Conclusion

This paper investigated continuous pH measurement by electrochemical method in geopolymer concrete for the very first time. The pH electrodes have survived the geopolymer concrete environment for 9 months since concrete casting. The pH value measured after 6 weeks carbonation test was validated by comparing to the result from drilling test. A decrease of 0.4 pH unit was recorded in both testing methods at cover depth of 20 mm. The pH readings in GPC were found to be affected by three factors: moisture, temperature and carbon dioxide diffusion rate. The dry condition induced a substantial resistance to the sensor circuit and resulted a lower pH reading. The pH readings were calibrated in this study by conducting saturation tests. Future research will investigate the relationship between the moisture loss and pH reading. A humidity monitoring sensor will be embedded in concrete to model pH drift due to humidity changes.

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