



Effects of mineral and chemical admixtures on high-strength concrete in seawater

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Abstract

The effects of mineral and chemical admixtures namely fly ash, ground granulated blast furnace slag, silica fume and superplasticizers on the porosity, pore size distribution and compressive strength development of high-strength concrete in seawater curing condition exposed to tidal zone were investigated. In this study, three levels of cement replacement (0%, 30% and 70% by weight) were used. The total cementitious content used was 420 kg/m³. A water/binder ratio of 0.4 was used to produce concrete having a target compressive strength ranging between 54 and 63 MPa at the age of 28 days. At the age of 364 days, the compressive strength of the specimens produced ranged between 59 and 74 MPa. The pore size distribution of both high-strength concrete (MSS-0 and MSS-40) was significantly finer and the mean volume pore radii (MVPR) at the age of 6 months were reduced about three times compared to NPC concrete. Results of this study indicate that both concrete mixes (30% and 70%) exhibited better performance than the NPC concrete in seawater exposed to tidal zone. Hence, it is believed that both high-strength concrete produced would withstand severe seawater exposure without serious deterioration. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: High-strength concrete; Compressive strength; Pore size distribution; Porosity; Admixtures

1. Introduction

Long-term durability of structures has become vital to the economics of all nations. Concrete for the twenty-first century can be much stronger, more durable and at the same time cost and energy efficient. Failure of concrete in a period less than its design life may be caused by external factors such as the environment to which it has been exposed or by a variety of internal causes. External factors may be physical or chemical in nature, such as weathering, extreme variation of temperatures, abrasion and exposure to aggressive chemicals. Internal causes may lie in the choice of materials or inappropriate combination of materials. Of all the causes of lack of durability in concrete, the most important is excessive permeability and porosity. Permeable

concrete is vulnerable to attack by almost all classes of aggressive agents [1].

The durability of concrete in a marine environment has drawn the attention of engineers and scientists for over a century because seawater action can result in major damage to marine and offshore structures [2]. The most essential factor governing concrete durability is considered by many authors to be the penetration rate of water, gas and ions, which depends on the microstructure and porosity and above all on the permeability of cement paste [3–5]. The long-term performance of concrete can be achieved through the incorporation of supplementary cementitious material. Such concrete, due to its compactness and extremely low void structure, leads to higher strength and low permeability. This results in greater resistance to chemical and environmental attack [6,7]. Concrete incorporating pozzolanic and cementitious materials placed in aggressive environment exhibits a substantial increase in durability due to the reduced amount of larger pores [8,9]. The mechanism is that when pozzolanic materials are added, calcium hydro-

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Table 1
Detail of mix proportion

| Type of mixes | Water (kg/m ³) | Cement (kg/m ³) | Fly ash (kg/m ³) | Silica fume (kg/m ³) | GGBF slag (kg/m ³) | Fine aggregate (kg/m ³) | Coarse aggregate (kg/m ³) | SP (l/m ³) |
|---------------|----------------------------|-----------------------------|------------------------------|----------------------------------|--------------------------------|-------------------------------------|---------------------------------------|------------------------|
| NPC | 170 | 420 | 0 | 0 | 0 | 590 | 1220 | 1 |
| MFSS-0 | 170 | 294 | 105 | 21 | 0 | 590 | 1220 | 1 |
| MFSS-40 | 170 | 126 | 105 | 21 | 168 | 590 | 1220 | 1 |

xide Ca(OH)₂ is transformed into secondary calcium silicate hydrate (C-S-H) gel [10], causing the transformation of larger pores into finer pores as a result of pozzolanic reaction of the mineral admixtures.

2. Experimental

Three concrete mixtures as detailed in Table 1 were used in this study. All mixtures had the same total cementitious content and free water/binder ratio. The mixtures were proportioned to have the same amount of fine and coarse aggregates. Superplasticizer was added to give constant workability with a slump of 150–200 mm. The main variable in the mixtures was the cementitious content. The objective was to identify the composition of cement matrix that would produce not only high strength but also durable concrete.

2.1. Materials

Type 10 ordinary Portland cement, fine aggregates of washed mining sand conforming to BS 882 [11] and crushed granite coarse aggregates of nominal size 20 mm were used. Class F fly ash originally from local Power Station was used. Silica fume and GGBF slag were provided by cement manufacturer in Malaysia. The chemical compositions of the cement replacement materials are given in Table 2. The superplasticizer was sodium naphthalene formaldehyde base with the specific gravity of 1.19–1.21 kg/l, pH 8–9 and solid content of 39.0–41.0%. It conformed to Type F of ASTM C494 [12].

2.2. Specimen preparation and curing

Cube moulds (100-mm) were used to cast specimens. Castings of cubes were conducted in two layers. Each layer was compacted by internal vibration. Immediately after vibration of the top layer, the excess concrete was removed and the top surface was leveled and smoothed using a trowel. After 24 h, the specimens were removed from the moulds and marked for later identification. After demoulding, the specimens were cured in a water curing tank at room temperature for 7 days and then transferred to the seawater curing condition. The location of the seawater condition chosen was at the Selat Tebrau, Johor Bahru, Malaysia. This curing regime was employed to investigate the effect of aggressive chemical exposure on concrete

together with the effect of the tidal zone. The specimens were subjected on an average to 18 h of wetting and 6 h of drying per day. The average water temperature was approximately 25 °C.

2.3. Testing program

The three mixtures of concrete containing various levels of cement replacement of 0%, 30% and 70% by weight were tested for compressive strength development. The tests were conducted at ages 28, 63, 91, 182, 273 and 364 days. These tests were performed in accordance with Ref. [13].

Tests for the porosity and pore size distribution were conducted at ages 63, 91 and 182 days. The porosity and pore size distribution of concrete mortar remnants were determined using Mercury Intrusion Porosimetry (MIP). Specimens to be tested were collected from the cubes and selected mortar remnants free from aggregate. The MIP can be used to determine the distribution of pores over a range of about 7–0.0018 μm (70,000–18 Å) radius. The apparatus

Table 2
Chemical constituents of OPC, FA, GGBF slag and silica fume

| Chemical constituents | OPC (% by weight) | Fly ash (% by weight) | GGBF slag (% by weight) | Silica fume (% by weight) |
|---|-------------------|-----------------------|-------------------------|---------------------------|
| Silicon dioxide (SiO ₂) | 20.1 | 48.7 | 28.2 | 92.3 |
| Aluminum oxide (Al ₂ O ₃) | 4.9 | 27.8 | 10.0 | 2.7 |
| Ferric oxide (Fe ₂ O ₃) | 2.5 | 9.2 | 1.8 | 1.4 |
| Calcium oxide (CaO) | 65.0 | 3.0 | 50.4 | 0.5 |
| Magnesium oxide (MgO) | 3.1 | 1.9 | 4.6 | 0.3 |
| Sulfur oxide (SO ₃) | 2.3 | 0.9 | 2.2 | 0.1 |
| Sodium oxide (Na ₂ O) | 0.2 | 1.3 | 0.1 | 0.1 |
| Potassium oxide (K ₂ O) | 0.4 | 2.4 | 0.6 | 0.1 |
| Titanium oxide (TiO ₂) | 0.2 | 1.1 | – | – |
| Phosphorus oxide (P ₂ O ₅) | 0.9 | 0.3 | – | – |
| Loss on ignition (LOI) | 2.4 | 3.9 | 0.2 | 1.8 |

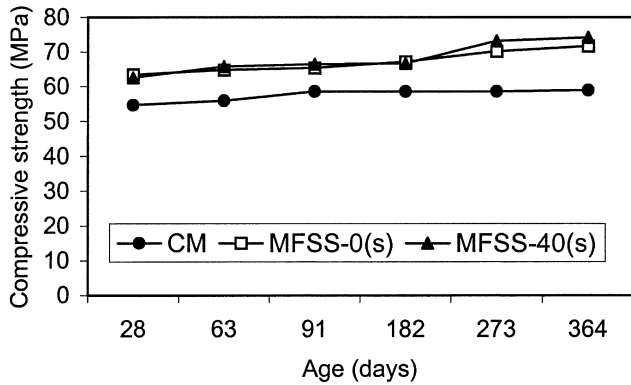


Fig. 1. Compressive strength against age.

has a 412-MPa (60,000 psi) pressure capacity. The porosimeter generally forces mercury to penetrate into the specimen tested by applying pressure in a continuous ram. The volume changes of the mercury in the high-pressure cavity were measured using computerized data acquisition system. The pore radius into which mercury intrudes in a given sample as a function of pressure is given by the Washburn [14] equation:

$$r = |2\gamma(\cos \vartheta)|/P$$

where r = radius of the intruded pores (\AA), γ = surface tension of mercury (480 erg/cm^2), ϑ = angle of contact between mercury and the pore walls (140°) and P = pressure at which a given increment of mercury intrudes the pore system (MPa).

3. Results and discussion

When pozzolanic and cementitious materials are added, $\text{Ca}(\text{OH})_2$ is transformed into additional C-S-H gel. This forms a basis for improvement of both strength and

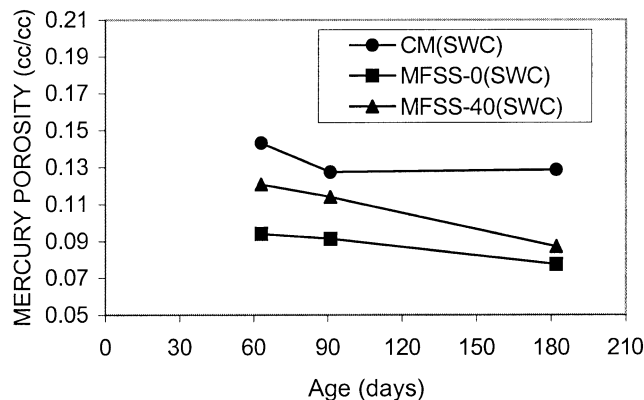


Fig. 2. Total intruded volume against age.

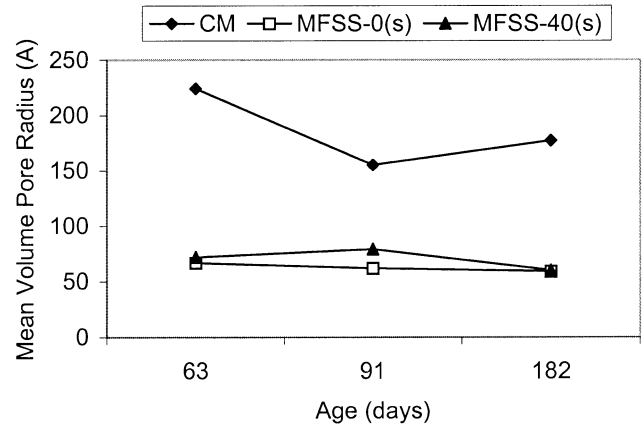


Fig. 3. Mean volume pore radius against age.

durability of concrete. The compressive test results for all mixes are presented in Fig. 1. The test results show that all mixes were able to develop the required strength of 50 MPa at 28 days. In fact, mixes MFSS-0 and MFSS-40 achieved strength values of about 60 MPa and above. From Fig. 1, it is revealed that at 28 days and beyond up to 364 days, both blended mixes MFSS-0 and MFSS-40 achieved higher compressive strength than the OPC control mix (CM) mixture.

The results of porosity for OPC CM, MFSS-0 and MFSS-40 under the effects of curing period ranging between 63 and 182 days are shown in Fig. 2. From Fig. 2, it is evident that the total pore volume decreases with increasing age. The result of OPC CM shows that the decrease in total porosity is about 8% between ages 63 and 182 days. Similarly, the results of mixes MFSS-0 and MFSS-40 show the decrease in total porosity of about 15% and 27%, respectively, which is about 1.8 and 3.2 times larger in reduction in total porosity as compared to the CM. This seems to suggest that mixes MFSS-0 and MFSS-40 contribute in producing additional hydration products to fill-up voids due to pozzolanic reaction. Thus, total porosity of these mixes is significantly reduced.

Mean volume pore radius (MVPR) refers to the minimum radius of pore intruded when half of the total intrusion has taken place. From Fig. 3, it is clear that at age 63 days, the control concrete mix shows higher value of MVPR, which is about 224 \AA . After that, MVPR value dropped, and at the age of 182 days, it reaches 177 \AA . For mixes MFSS-0 and MFSS-40, MVPR values are found to be significantly smaller as compared to the CM concrete. At the age of 63 days, both mixes MFSS-0 and MFSS-40 achieved MVPR values of about 67 and 77 \AA , respectively, which are about 3.3 and 3.1 times smaller than the CM concrete. At the age of 182 days, both mixes MFSS-0 and MFSS-40 achieved the MVPR values of about 59 and 60 \AA , respectively, which are about three times smaller than the CM concrete.

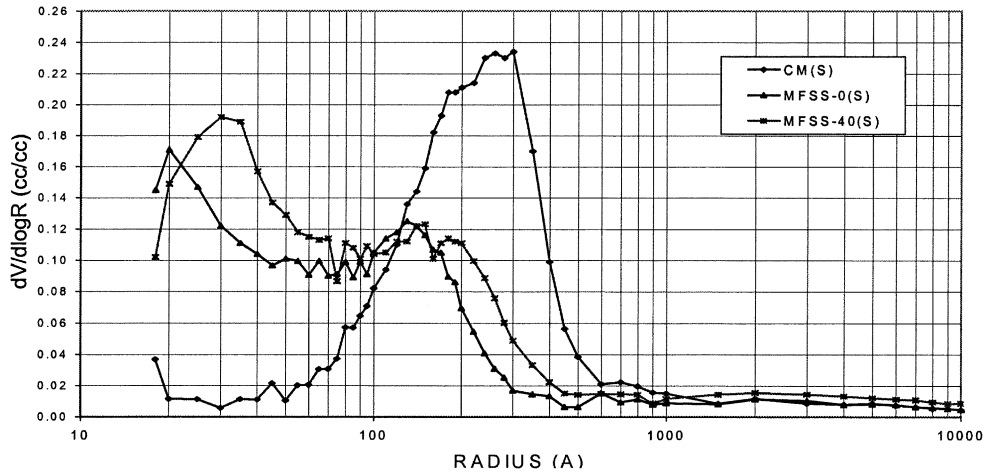


Fig. 4. $dV/d\log R$ against radius at 63 days.

The first derivative distribution results are shown in Figs. 4 and 5. From these figures, it is clear that age has a significant effect on the size and shape of peaks. With increasing age, the height of the peaks and the area beneath are reduced. The trend is almost similar at ages between 63 and 182 days. From the figures, it is evident that for blended mixtures the peaks significantly shifted towards the finer pore size radii region with respect to increasing age. At the same time, it is also observed that the peaks at the small pore radii are shifted to finer pore sizes with increasing age. Hence, from above observations, it is evident that by the addition of pozzolanic and cementitious materials, namely, fly ash, silica fume and GGBF slag, pore refinement or transformation of larger pores into finer pores occurs. These findings are in agreement with the results from previous researchers [9,10,15].

4. Conclusions

From the above discussion, the following conclusions can be drawn:

- For all mixes (CM, MFSS-0 and MFSS-40), the compressive strength development progresses, and at the age of 28 days, CM achieved 54 MPa while MFSS-0 and MFSS-40 achieved about 63 MPa. At the age of 364 days, mixes CM, MFSS-0 and MFSS-40 achieved 59, 72 and 74 MPa, respectively.
- Concrete containing 30% and 70% cement replacement by weight achieved lower values of total intruded volume at all ages up to 6 months compared to OPC concrete.
- Both blended mixes showed more significant pore refinement compared to the OPC concrete.
- The pore size distribution in the blended mixes was significantly refined. The MVPR at the age of 6 months

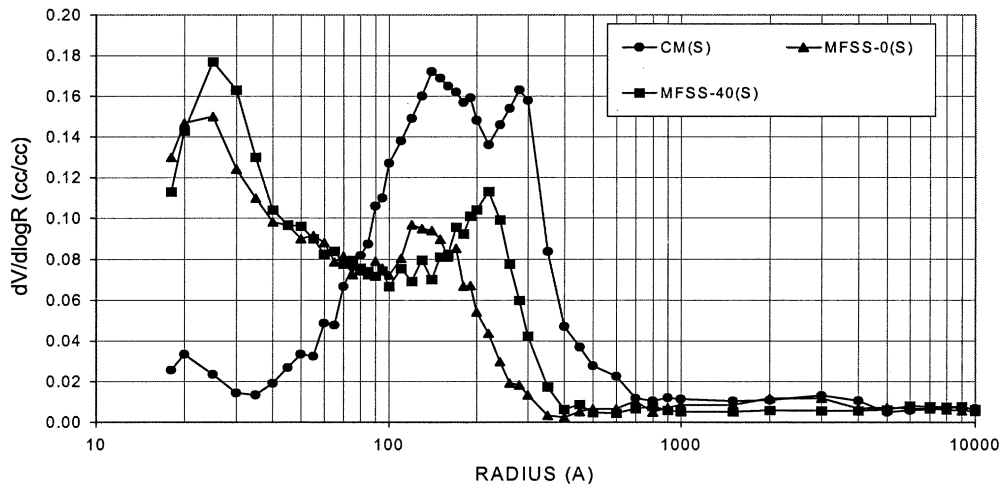


Fig. 5. $dV/d\log R$ against radius at 182 days.

were reduced to about three times less compared to OPC concrete.

- Both blended mixes showed significant effect of age upon the size and shape of peaks of first derivative distribution curve. With increasing age, the height of peaks and area beneath are reduced and shifted towards the finer pores as compared to OPC concrete.

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