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Effects of seawater-neutralised bauxite refinery residue on properties of concrete

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ABSTRACT

Various industrial by-products, such as fly ash, ground granulated blast-furnace slag and silica fume, have been used in concrete to improve its properties. This also enables any environmental issues associated with their disposal. Another material that is available in large quantities and requiring alternative methods of disposal is the Bauxite Refinery Reside (BRR) from the Bayer process used to extract alumina from bauxite. As this is highly caustic and causes many health hazards, Virotec International Ltd. developed a patented technology to convert this into a material that can be used commercially, known as Bauxsol™, for various environmental remediation applications. This use is limited to small quantities of seawater-neutralised BRR and hence an investigation was carried out to establish its potential utilisation as a sand replacement material in concrete. In addition to fresh properties of concrete containing seawater-neutralised BRR up to 20% by mass of Portland cement, mechanical and durability properties were determined. These properties indicated that seawater-neutralised BRR can be used to replace natural sand up to 10% by mass of cement to improve the durability properties of concrete without detrimentally affecting their physical properties. Combining these beneficial effects with environmental remediation applications, it can be concluded that there are specific applications where concretes containing seawater-neutralised BRR could be used.

1. Introduction

Concrete is used in very large quantities throughout the world, but only 10–20% of the concrete is the binder. The other 80–90% is aggregate. Therefore, the use of alternative aggregates can play a key role in aiding the construction industry to reduce the long-term ecological and environmental impact. Consequently, there have been concerted efforts to increase the use of waste materials in concrete. To address the environmental costs associated with quarrying, the UK Government introduced the Aggregates Levy in April 2002 [1] to reduce the demand for primary aggregate. This was done by minimising the wastage of construction materials and maximising the use of alternatives to primary aggregates. However, these alternative aggregates must be strong and durable for the intended applications. Throughout the past two decades numerous types of alternative aggregates have been investigated [2–5], some of which specifically consider replacing fine aggregate in concrete [6,7]. The latter was an attempt to utilise some of the industrial waste materials in concrete as fine aggregate. Bauxite Refinery Reside (BRR) is such an industrial waste material.

The production of 1 tonne of alumina from bauxite by the Bayer process typically creates 1–1.5 tonnes of bauxite refinery residue (BRR). Globally it is estimated that the alumina refining industry generates some 70 million tonnes of BRR per annum [8,9]. The BRR has a $\text{pH} > 13.5$ and is highly caustic in nature [10]. Consequently, it is essential to neutralise BRR to minimise the potential environmental impacts and there are various methods for neutralising it. McConchie et al. [11], developed a new method (Basecon™ technology) for neutralising the BRR, which is based on seawater neutralisation. The neutralisation of BRR by Basecon™ converts soluble alkalinity into low soluble minerals (essentially Ca and Mg hydroxides, carbonates and hydroxy-carbonates). The removal of hydroxides to low soluble forms reduces the pH to less than 9, where the hydroxyl ions are primarily controlled by reaction with Mg in the seawater to form brucite and hydrotalcite. The Basecon™-neutralised BRR is currently being marketed by Virotec International Plc under the trade name Bauxsol™.

Currently, seawater-neutralised BRR is mostly used in environmental treatment and remediation projects, such as the neutralisation of acid and metal trapping, arsenate removal from water and phosphate and phenol removal from aqueous solution [12–15]. However, only relatively small quantities of seawater-neutralised BRR are used in environmental remediation compared with the quantities produced, and for the alumina industry to become more

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sustainable, much larger quantities need to be consumed in some other manner. Seawater-neutralised BRR does not have any pozzolanic property [16] and, hence, cannot be used as a supplementary cementitious material. Therefore, its use in concrete as a sand replacement material was investigated in this study. As seawater-neutralised BRR is produced from the waste of alumina industry, it is expected to be cheaper than the natural sand.

While using alternative materials for aggregates, the properties of fresh concrete are vital primarily because they affect the choices of equipment for handling and compaction in addition of affecting the properties of hardened concrete. Compressive strength is obviously an important mechanical property of concrete. This is due to the fact that in most structural applications concrete is employed primarily to resist the compressive forces. However, the tensile strength of concrete does also have a fundamental role in the fracture mechanism. Drying shrinkage can play a significant role in applications of concrete in large slabs on grade and containment structures. As concrete is a porous material, the transport properties of concrete are also important. Therefore, a detailed study to investigate the effects of replacing natural sand by seawater-neutralised BRR on fresh properties (workability and water demand), strength development (compressive and flexural), drying shrinkage, transport and durability properties of concrete was carried out, results of which are reported and discussed in this paper.

2. Experimental programme

2.1. Materials

The cement used was class 42.5 N Portland cement (PC) supplied by Blue Circle, complying with BS EN 197-1:2000 [17] as a CEM I material. The coarse aggregate was crushed basalt with 20 mm and 10 mm size fractions mixed in the ratio 2:1 by mass and the fine aggregate used was medium graded natural sand complying with BS EN 12620: 2002 [18], except where seawater-neutralised BRR was used as a partial substitute. Both types of natural aggregates were obtained from local sources in Northern Ireland and seawater-neutralised BRR was supplied by Virotec International from their plant at Portoscuso, Sardinia, Italy.

The specific gravities of PC, seawater-neutralised BRR and natural sand are presented in Table 1. These data show that seawater-neutralised BRR has a specific gravity similar to the natural sand. The chemical composition of PC and seawater-neutralised BRR is summarised in Table 2 and this shows that seawater-neutralised BRR contains six major constituents, namely Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O and CaO. Particle size distributions presented in Fig. 1, show that seawater-neutralised BRR has a size distribution much finer than that of the natural sand. Moreover, it can be observed that 95% of its particles are <10 μm and substantially finer than that of the PC. X-ray diffraction (XRD) patterns of seawater-neutralised BRR (Fig. 2) shows that its mineralogy is dominated by hematite, with some silicates and aluminium oxy-hydroxide, with minor TiO_2 (rutile and anatase).

The scanning electron micrographs of seawater-neutralised BRR and natural sand particles are shown in Figs. 3a and 3b respectively. These figures show that seawater-neutralised BRR is an agglomeration of very small particles and appears to be much more porous in nature than the natural sand, and has a clay or iron oxy-hydroxide coating.

Table 1
Physical properties of materials used.

Materials	Specific gravity
PC	3.18
Seawater-neutralised BRR	2.75
Natural sand	2.72

Table 2
Chemical composition of PC and seawater-neutralised BRR.

(%)	PC	Seawater-neutralised BRR
SiO_2	21.41	24.06
Al_2O_3	5.11	20.01
CaO	61.50	2.64
Fe_2O_3	2.61	29.60
MgO	1.78	0.95
SO_3	3.03	0.90
Na_2O	0.33	7.45
K_2O	0.61	0.68
TiO_2	0.37	5.81
P_2O_5	0.16	0.14
Loss of ignition	2.64	7.76

2.2. Mix proportions

The investigation on physical properties of fresh and hardened concrete was carried out using specimens in three series, viz. Series A, Series B and Series C. For all these three series, natural sand was replaced with seawater-neutralised BRR at 0%, 5%, 10%, 15% and 20% by mass of cement. Cement content is a major factor affecting the fresh and hardened properties of concrete [19] and in order to eliminate the effect of this factor, the cement content was kept constant for all the three series. For Series A, the W/C was held constant, but for Series B the slump was held constant by adjusting the water content, and for Series C, both the W/C and the slump were held constant by adjusting the dosage of a superplasticiser. BS EN 206-1 [20] indicates that the maximum permissible W/C is between 0.45 and 0.55 in mixes designed for exposure in aggressive environments. Therefore, the W/C used for Series A was 0.55. Details of the mix proportions for all the three series are summarised in Tables 3–5 respectively.

Details of the mix proportions used for preparing the mortar bar for testing alkali–silica reactivity is provided in Table 6. As the mortar bars in alkali–silica reactivity test were prepared using potentially reactive aggregates, these aggregates were graded in accordance with the requirements prescribed in ASTM C 1260-94 [21] (Table 7). The mix proportions for concrete for other durability testing were the same as that of Series A.

2.3. Manufacturing, curing and conditioning of specimens

2.3.1. Specimens for compressive and flexural strength test

Test specimens for compressive and flexural strength were cast by filling appropriate moulds, reported in the following sections, in approximately two equal layers and compacting each layer using a vibrating table. The compaction was considered to be complete when air bubbles stopped appearing on the surface. After the second layer was compacted, the specimens were finished lightly with a metal float, covered with a plastic sheet and kept in the casting room at 20 (±1) °C for 24 h. Specimens were then demoulded and transferred to a water bath maintained at 20 (±1) °C for curing them in water. After 2-days of water curing the specimens were wrapped in polythene sheet and kept in an environmental chamber at 20 (±1) °C and 40 (±1)% RH, where they remained until required for testing. One-day old specimens were tested immediately after demoulding, whereas specimens at the three days were tested immediately after removing from the water bath. This curing regime was employed as it encourages the hydration reactions whilst preventing calcium hydroxide leaching. In addition, the adoption of a 2-days water curing was expected to

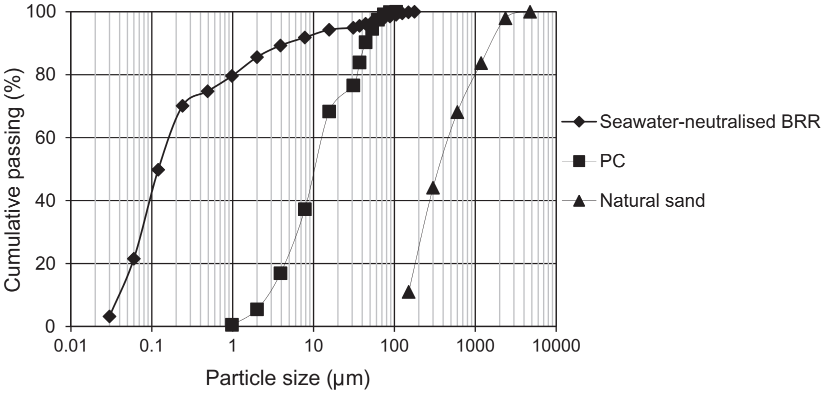

Fig. 1. Particle size distributions of PC, natural sand and seawater-neutralised BRR.

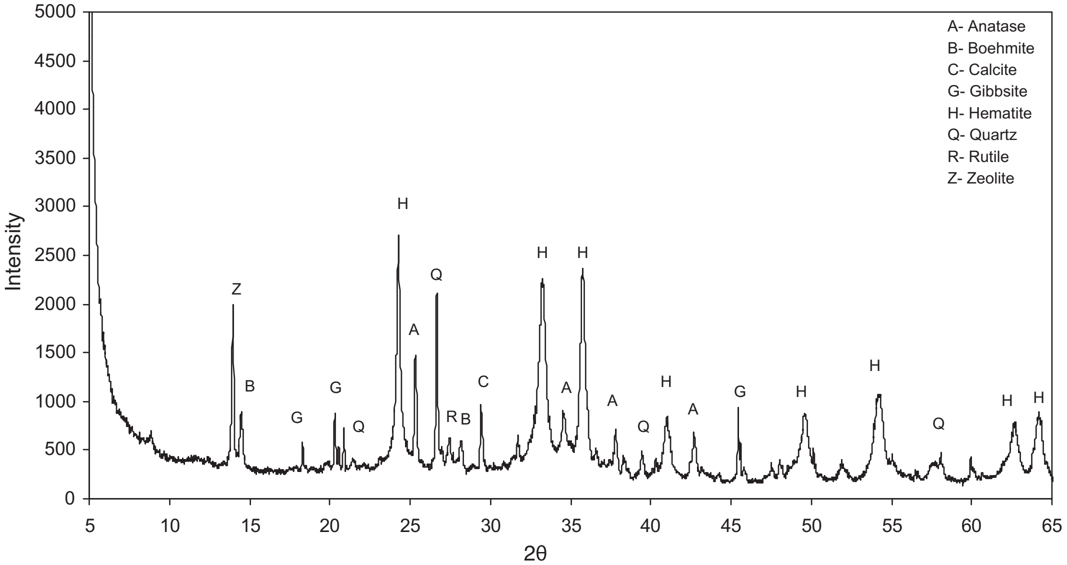

Fig. 2. XRD pattern of seawater-neutralised BRR.

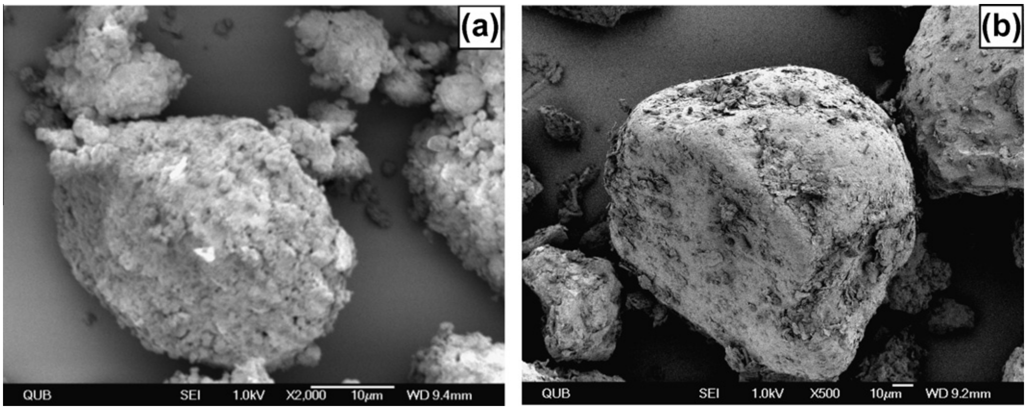

Fig. 3. SEM of (a) seawater-neutralised BRR particles at 2000× magnification, and (b) natural sand particles at 500× magnification.

simulate a curing regime that is normally used for most concrete structures.

2.3.2. Specimens for drying shrinkage test

Three 40 × 40 × 200 mm prisms with an indentation at the centre of the two longitudinal ends were cast for each mix to determine the drying shrinkage of concrete. Specimens were demoulded after 24 h and two 6.5 mm diameter stainless steel balls cemented into the indentations. Prisms were then covered with damp hessian cloth and covered with plastic sheeting. After a further 24 h, the covers were removed and the stainless steel balls were wiped clean. Prisms were then immersed in water at 20 (±1) °C for 5 days. At the

Table 3
Mix proportions for Series A.

Mix ID	PC (kg/m^3)	Water (kg/m^3)	Seawater-neutralised BRR (kg/m^3)	Natural sand (kg/m^3)	Coarse aggregate (kg/m^3)	
					10 mm	20 mm
BX0	400	220	0	700	360	720
BX5	400	220	20	680	360	720
BX10	400	220	40	660	360	720
BX15	400	220	60	640	360	720
BX20	400	220	80	620	360	720

Table 4
Mix proportions for Series B.

Mix ID	PC (kg/m^3)	Water (kg/m^3)	Seawater-neutralised BRR (kg/m^3)	Natural sand (kg/m^3)	Coarse aggregate (kg/m^3)	
					10 mm	20 mm
BX0	400	220	0	700	360	720
BX5	400	226	20	678	359	718
BX10	400	228	40	657	358	716
BX15	400	235	60	634	357	714
BX20	400	240	80	612	356	712

Table 5
Mix proportions for Series C.

Mix ID	PC (kg/m^3)	Water (kg/m^3)	Seawater-neutralised BRR (kg/m^3)	Natural sand (kg/m^3)	Coarse aggregate (kg/m^3)		SP[a] (%)
					10 mm	20 mm	
BX0	400	220	0	700	360	720	0
BX5	400	220	20	680	360	720	0.15
BX10	400	220	40	660	360	720	0.28
BX15	400	220	60	640	360	720	0.32
BX20	400	220	80	620	360	720	0.47

[a] SP – superplasticiser by mass of PC (polycarboxylate based).

Table 6
Mix proportions for mortar bar.

Mix ID	PC (g)	Natural sand (g)	Seawater-neutralised BRR (g)	Water (g)
BX0	1000	2750	0	620
BX5	1000	2700	50	620
BX10	1000	2650	100	620
BX15	1000	2600	150	620
BX20	1000	2550	200	620

Table 7
Requirements for aggregates grading as per ASTM C 1260-94 [15].

Sieve size		
Passing	Retained on	Mass (%)
4.75 mm	2.36 mm	10
2.36 mm	1.18 mm	25
1.18 mm	600 μm	25
600 μm	300 μm	25
300 μm	150 μm	15

end of this, (i.e., when specimens were 7 days old) they were removed from the water bath and the initial length was measured. The prisms were then stored in a constant temperature room at 20 (±1) °C and 40 (±1)% RH until required for measuring the length change.

2.3.3. Specimens for testing transport properties

Three 250 × 250 × 110 mm concrete blocks were made for each of the mix of Series A for this test. The blocks were cast using the method that was used for casting the specimens for the flexural and compressive strength tests and were stored in an environmental chamber at 20 (±1) °C and 40 (±1)% RH for 100 days. Prior to testing, the blocks were dried in a drying cabinet at an environment of 40 (±1) °C and 20 (±1)% RH for 2 weeks, then cooled at a constant temperature of 20 (±1) °C and 40 (±1)% RH for 1 day.

2.3.4. Specimens for testing alkali–silica reactivity

This test was also carried out for Series A only. Six 25 × 25 × 285 mm mortar bars with an indentation at the centre of the two longitudinal ends were manufactured using potentially reactive aggregates. After 24 h, the mortar bars were removed from the moulds and two 6.5 mm diameter stainless steel balls were cemented into indentations at the ends of the bars. The bars were then covered with damp hessian cloth and then with a plastic sheet to cure. After 24 h, the covers were removed from the bars and the balls were wiped clean. The bars were then immersed in water in a metallic storage container and kept in an oven at 80 (±1) °C for a period of 24 h. The bars were then removed from the oven and their length measured using a length comparator; this initial measure is the 'zero' reading. The bars were then placed in 1 N NaOH at 80 (±1) °C and the change in length was measured using a length comparator at 3, 5, 7, 9, 11 and 14 days post immersion in the hydroxide solution.

2.3.5. Specimens for testing carbonation

Four 50 mm diameter cores were cut from each of the three 100 days old 250 × 250 × 110 mm blocks (Series A) manufactured for determining transport properties of concrete. That is, altogether twelve cores were cut for each mix. The cores were coated with an epoxy emulsion on both the curved surface and the trowel-finished face, leaving only the surface formed by the mould uncoated for carbon dioxide penetration during the test. Three coats of the epoxy were applied by allowing 24 h curing between the coats. The cores were then dried in a drying cabinet at a constant temperature of 40 (±1) °C and 20 (±1)% RH for two weeks. However, before placing cores in the carbonation chamber, they were cooled at a constant temperature of 20 (±1) °C and 40 (±1)% RH for 1 day.

2.3.6. Specimens for testing sulphate attack

Nine 100 mm concrete cubes were manufactured for each of the mixes of Series A (Table 3). The cubes were cast using the same method that was used for casting the specimens for the compressive strength. After curing, the cubes were kept in two different solutions, viz. 10% Na_2SO_4 and 10% $MgSO_4$, for a period of 180 days.

2.3.7. Specimens for testing chloride ingress

Three 100 mm diameter cores were cut from each of the three 100 days old 250 × 250 × 110 mm blocks (Series A) manufactured for determining transport properties of concrete. The cores were cut to have a thickness of 50 (±2) mm before being kept in an oven at 40 (±1) °C for 14 days. One day prior to testing, the specimens were cooled for 24 h at 20 (±1) °C. After cooling the specimens were placed in a vacuum container for vacuum treatment, where the absolute pressure in the vacuum container was reduced to a pressure in the range of 10–50 mbar within a few minutes. This vacuum was maintained for 3 h and then with the vacuum pump still running, the container was filled with a saturated $Ca(OH)_2$ solution (by dissolving an excess of $Ca(OH)_2$ in de-ionised water at 20 (±1) °C). The vacuum was then maintained for a further hour before allowing air to re-enter the container. The specimens were then kept in the solution for 18 (±2) h before putting them in the migration test cell.

2.3.8. Specimens for testing salt-scaling

One 100 mm diameter core was taken from each of the three 250 × 250 × 110 mm blocks (Series A) manufactured for determining transport properties of concrete; resulting in three cores to be tested for each mix. Between 2 and 7 days before saturating, the cores were coated with an epoxy emulsion (supplied by Larsen, Belfast under the trade name Sikaguard 38) on the curved surface, leaving both ends of the core uncovered. The use of the epoxy ensures that there is no lateral scaling of test specimens. Two coats of the epoxy were applied by allowing 24 h between the coats.

2.4. Test methods

2.4.1. Workability and air content of concrete

The workability of concrete in the fresh state was measured using the slump test and the flow table test in accordance with BS EN 12350-2:2000 [22]. The air content of concrete in its fresh state was measured using the pressure gauge method.

2.4.2. Compressive and flexural strength of concrete

The compressive and flexural strength tests were conducted as per BS EN 12390-3:2002 [23] and BS EN 12390-5:2002 [24] respectively. One day prior to the test (except in the case of both the 1 day and the 3 days strength tests), the specimens were removed from the polythene sheet and immersed in a water tank for 24 h. Immediately before testing, the specimens were removed from the water bath and the surface-water was removed using a dry cloth. This was done to ensure that the specimens were tested at a saturated-surface dry (SSD) condition.

2.4.3. Drying shrinkage of concrete

The drying shrinkage of concrete was determined as per BS EN 1367-4:1998 [25] by measuring the length change of the 40 × 40 × 200 mm prisms using a length comparator at the age of 14, 28, 56, 91 and 180 days.

2.4.4. Transport properties of concrete

The transport properties of concrete were evaluated in terms of air permeability and sorptivity of concrete, which were determined using the Autoclam permeability system [26].

2.4.5. Alkali–silica reactivity

The alkali–silica reactivity of concrete was determined using ASTM C 1260-94 [21]. The difference between the 'zero' reading and the reading at each test age was calculated to the nearest 0.001% of the initial length and was recorded as the expansion of the bars for that period.

2.4.6. Accelerated carbonation

The cores prepared for the carbonation test were placed in a carbonation chamber at an elevated CO_2 content of 5 (±1)% (by volume) and controlled temperature and humidity of 20 (±1) °C and 55 (±1)% RH respectively. After a period of 6 and 9 weeks of exposure, three cores per mix were removed and split longitudinally. A 1% phenolphthalein indicator solution was then sprayed on the freshly broken concrete surfaces and after a period of 24 h, the non-carbonated portion was detected by the formation of a pink colour. The depth of carbonation (i.e., the depth up to the pink colour region) was measured using Vernier callipers to an accuracy of 0.5 mm at three locations across the split core surfaces, resulting in a total of nine measurements, which were then averaged and reported as the carbonation depth.

2.4.7. Sulphate attack

The sulphate attack on concretes was determined by immersing 100 mm cubes in sulphate solutions (10% Na_2SO_4 and 10% $MgSO_4$) for a period of 56 and 180 days and determining the compressive strength at the end of each period of exposure. An average of three cube results was determined for each testing condition and reported.

2.4.8. Chloride ingress resistance

Among the various test methods available to assess the chloride ingress resistance of concrete, the non-steady state migration test is considered to have a sound theoretical basis and reliability [27]. Therefore, the non-steady state migration test in accordance with NT BUILD 492-1999 [28] was used to determine the chloride ingress resistance of seawater-neutralised BRR concretes.

2.4.9. Salt-scaling

The capillary suction of de-icing solution and freeze thaw (CDF) test [29] was used to evaluate the resistance of concrete to salt-scaling. The amount of scaling per unit surface area due to a number of well-defined freeze and thaw cycles in the presence of sodium chloride was used to estimate the salt-scaling resistance of concrete.

3. Results and discussion

3.1. Fresh properties of concrete

The slump and flow properties of fresh concrete are shown in Figs. 4a and 4b (Series A) respectively. The data in these figures show that, at a fixed W/C of 0.55, slump and flow decreased with increasing seawater-neutralised BRR content suggesting increased water demand with increased seawater-neutralised BRR content. The water demand at a fixed slump of 90 (±5) mm (Series B) is shown in Fig. 4c. From this figure, it can be seen that there is a uniform increase in the water demand with the increase in the seawater-neutralised BRR content. These data sets (Figs. 4a, 4b and 4c) show that when seawater-neutralised BRR was used as a sand replacement material, the water demand increased. This increased water demand is thought to reflect the increased particle surface area provided by the fine-grained seawater-neutralised BRR compared to that of natural sand (Fig. 1), which, therefore, requires more water for inter-particle lubrication. When other waste materials, for example, fly ash (FA) and ground granulated blast-furnace slag (GGBS) are used as supplementary cementitious materials (SCMs) in concrete, the workability increases [30,31], whereas the use of silica fume (SF) and metakaolin (MK) reduces the workability [32]. However, when FA is used as a sand replacement material, the workability decreases [33,34]. The function of sand in concrete is to assist in providing workability and uniformity in the mix. It also assists the cement paste in holding the coarse aggregate particles in suspension. The action promotes plasticity in the mix and prevents segregation of the cement paste and coarse aggregate. However, the reduction in slump obtained using seawater-neutralised BRR is most likely due to its increased surface area. Furthermore, unlike water added to natural sand during concrete production, water in seawater-neutralised BRR containing mix may not be as readily available to lubricate the mix, because it may be either held within the fine-particle aggregates or it may be chemically bound with the seawater-neutralised BRR, which is somewhat hygroscopic in nature [13].

Superplasticisers are well-known additives that can assist in overcoming the increased water demand, allowing increased workability with reduced water content. Fig. 4d shows the superplasticiser requirements to obtain a slump of 90 (±5) mm with a fixed W/C (0.55). It can be seen that the dosage of superplasticiser increased with the increase in the seawater-neutralised BRR content, because increased seawater-neutralised BRR content increases the

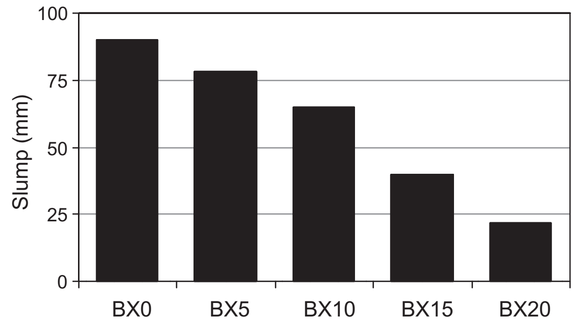

Fig. 4a. Slump of concrete at fixed W/C (0.55) (Series A).

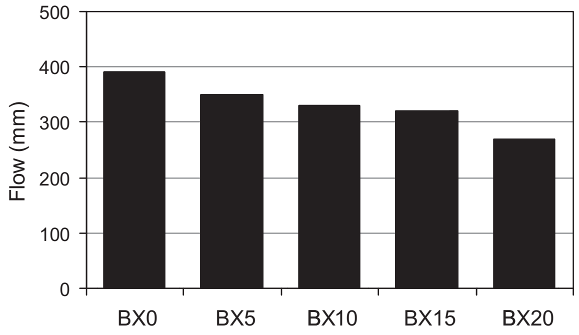

Fig. 4b. Flow of concrete at fixed W/C (0.55) (Series A).

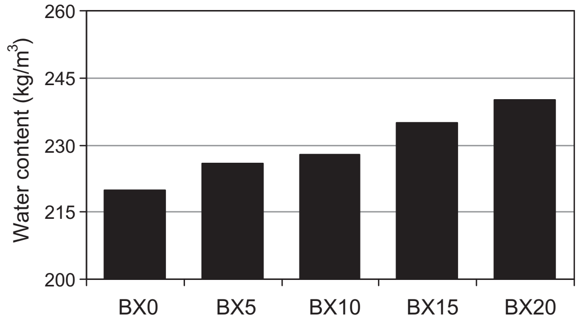

Fig. 4c. Water demand of concrete at a fixed slump of 90 (±5) mm (Series B).

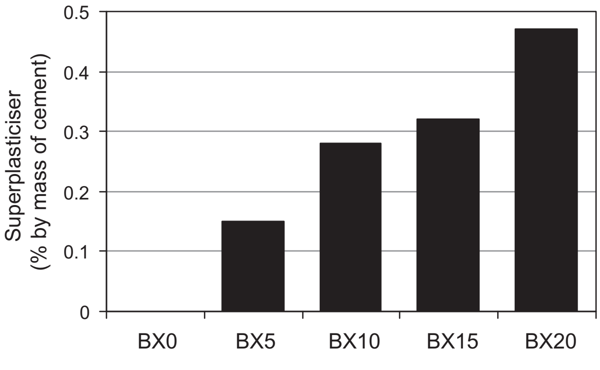

Fig. 4d. Dosage of superplasticiser at fixed W/C (0.55) and slump (90(±5)) mm (Series C).

water demand. Although for mix BX20 the quantity of superplasticiser required was 0.47% by mass of cement, the addition rate is well within a typical range that is added to concretes. Therefore, it can be said that although a reduction in workability occurs with the use of seawater-neutralised BRR, this can be readily overcome through the use of a suitable superplasticiser.

3.2. Physical properties of concrete

3.2.1. Compressive strength development of concrete

The compressive strength data of concretes at the age of 3, 7, 28, 91 and 180 days for Series A, B and C are presented in Figs. 5a, 5b and 5c respectively. These figures show that although there is no substantial improvement in concrete strength with the use of seawater-neutralised BRR as a sand replacement material, there is no detrimental effect on the strength either. However, the reduced workability in Figs. 4a and 4b and the increased water demand in Fig. 4c indicate that seawater-neutralised BRR based concretes need to be added with a suitable superplasticiser in order to achieve the required workability.

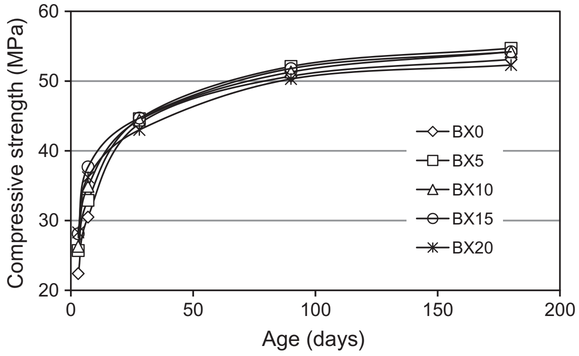

Fig. 5a. Compressive strength of concrete for Series A.

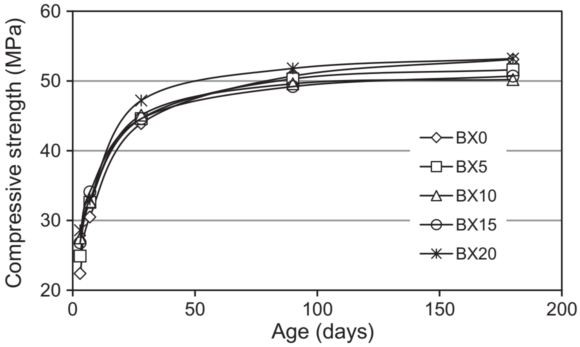

Fig. 5b. Compressive strength of concrete for Series B.

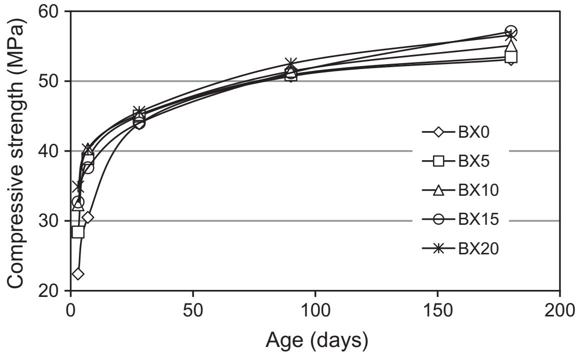

Fig. 5c. Compressive strength of concrete for Series C.

Literature on the use of various by-product materials, such as FA, GGBS, SF and MK as SCMs show a marked improvement in the long-term compressive strength of concrete [35–37]. Furthermore, when FA is used as a sand replacement material improved compressive strengths have been reported [38,39]. The marked increase in the compressive strength is mainly due to the pozzolanic reaction, whereas a non-pozzolanic material, like seawater-neutralised BRR particles lie in the concrete mix as an inert material contributing little to strength, except their possible "micro-filler effect". Nevertheless, it can be said that the use of seawater-neutralised BRR does not detrimentally affect the compressive strength of concrete.

3.2.2. Flexural strength development of concrete

The flexural strength data of concrete at the age of 3, 7 and 28 days for Series A, B and C are presented in Figs. 6a, 6b and 6c. From these data, it can be seen that for all the three series there was an improvement in flexural strength of concrete containing different quantities of seawater-neutralised BRR in the early ages of 3 and 7 days. However, the improvement decreased towards 28 days, but for all the three series there was an improvement of about 10% between the control and the highest seawater-neutralised BRR content of 20% for Series A and B, but for Series C this improvement was about 20% over the control. The effect of mineral admixtures on flexural strength of concrete is similar to that on the compressive strength [40]. Furthermore, the compressive strength data in Figs. 5a, 5b and 5c demonstrated that the strength did not vary much beyond 28 days for seawater-neutralised BRR concretes. Therefore, if flexural strength tests were performed beyond 28 days, improvements due to its use would have been marginal. Nevertheless, the replacement of sand with seawater-neutralised BRR has not caused any detrimental effect on the flexural strength of concrete, but in fact improved it modestly at early ages. This is considered to be the result of its micro-filling effect due to smaller particle sizes (Fig. 1).

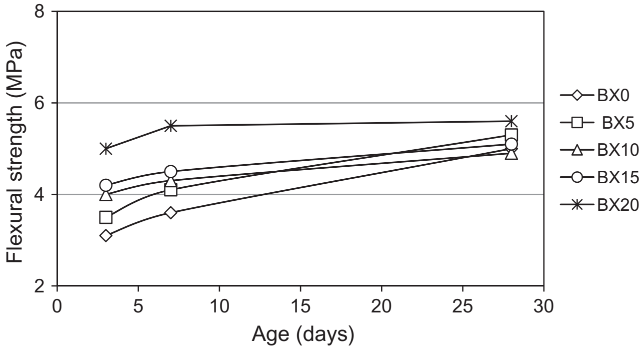

Fig. 6a. Flexural strength of concrete for Series A.

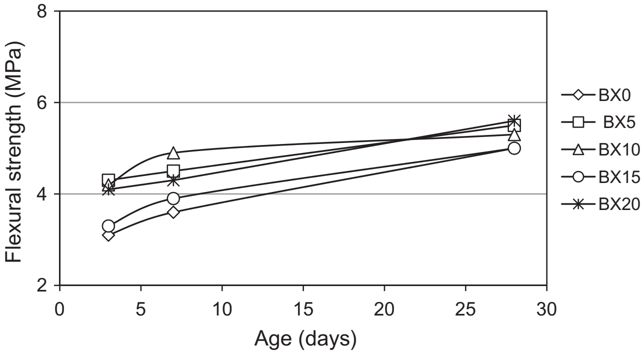

Fig. 6b. Flexural strength of concrete for Series B.

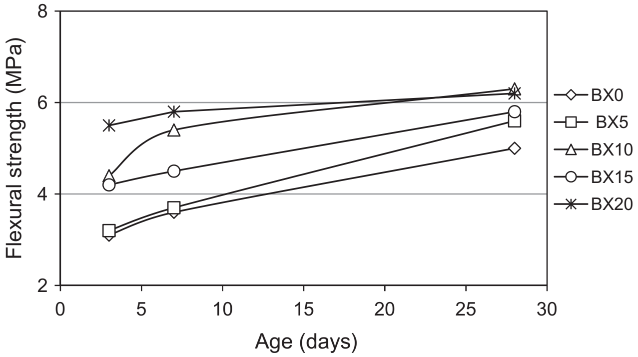

Fig. 6c. Flexural strength of concrete for Series C.

3.2.3. Drying shrinkage of concrete

The drying shrinkage data for Series A, B and C are presented in Figs. 7a, 7b and 7c. Fig. 8a shows that for series A (at a fixed W/C of 0.55), drying shrinkage values for all the seawater-neutralised BRR concretes were lower than that of the control concrete, whereas in series B (Fig. 7b), at the fixed slump the drying shrinkage of seawater-neutralised BRR concretes was higher than the control at all ages. The drying shrinkage behaviour for both Series A and B can be related to the W/C because it increases with the increase in W/C [40]. However, other published results show that the inclusion of mineral admixtures as SCMs do not cause any significant effect on the drying shrinkage of concrete [41,42]. For Series C, where both the slump and W/C were kept constant using a superplasticiser (Fig. 7c), the drying shrinkage increased with an increase in the seawater-neutralised BRR content, which could be related to the effect of superplasticer, as explained below.

It is reported [43] that concretes made with superplasticisers show higher drying shrinkage than the control because of the reduced surface tension of water. Therefore, the increase in the drying shrinkage for series C is likely to be from the increased dosage of superplasticiser. However, and more importantly, BS EN 1367-4:1998 [25], recommends that drying shrinkage values should not exceed 0.075%. Hence, for Series B (Fig. 7b), the drying shrinkage values are only acceptable for mixes containing up to 15% seawater-neutralised BRR and for both Series A and C (Figs. 7a and 7c) the values are within acceptable limits for all the mixes.

3.2.4. Transport properties of concrete

Figs. 8a and 8b present respectively the air permeability and sorptivity of concretes containing seawater-neutralised BRR. The

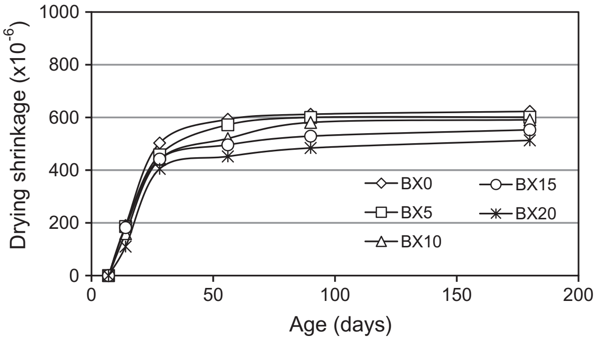

Fig. 7a. Drying shrinkage for Series A.

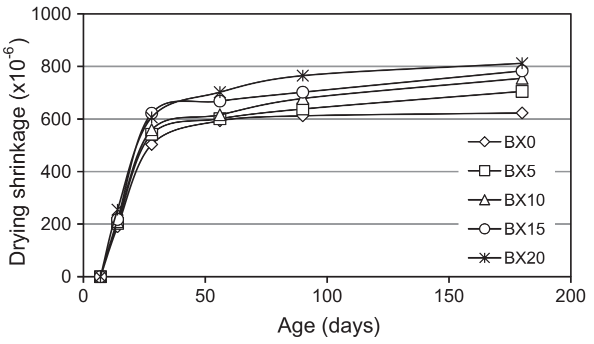

Fig. 7b. Drying shrinkage for Series B.

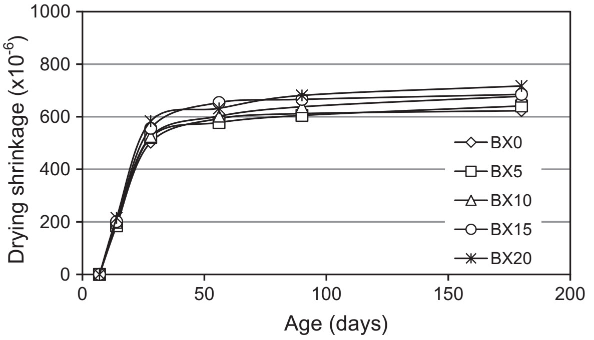

Fig. 7c. Drying shrinkage for Series C.

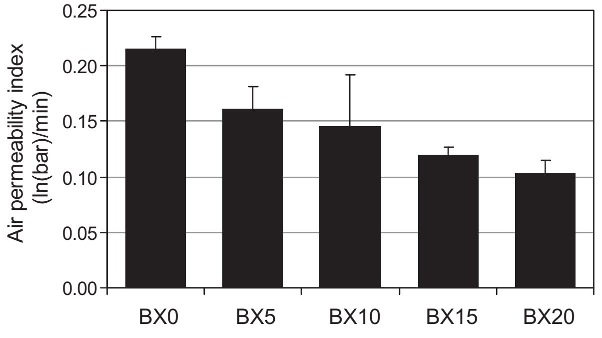

Fig. 8a. Air permeability index of concrete containing seawater-neutralised BRR.

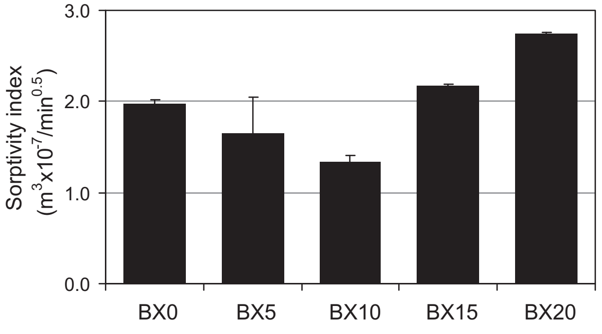

Fig. 8b. Sorptivity index of concrete containing seawater-neutralised BRR.

air permeability index decreased with the increased seawater-neutralised BRR content (Fig. 8a), but the sorptivity index decreased for concrete containing up to 10% seawater-neutralised BRR and then, steadily increased at higher contents (Fig. 8b). This apparent contradiction in behaviour can be explained in relation to the microstructure of concrete.

It is known that air permeability of concrete depends on the volume, size and continuity of the pores [44]. The reduction in the air permeability with increased seawater-neutralised BRR content may be the result of improved particle packing due to its fine-grained nature compared to that of the natural sand (Fig. 1). In addition, very fine seawater-neutralised BRR particles may also act as pore blockers and help to reduce interconnectivity of pores, thereby, reducing air permeability. Similar improvement in the air permeability has been noted previously with the incorporation of FA, SF and MK in concrete [45,46].

The sorptivity of concrete depends not only on the microstructure, but also on the water absorption characteristics of the ingredients in concrete. The reduction in sorptivity index of concrete containing seawater-neutralised BRR up to a content of 10% is believed to be because of a denser microstructure, which is thought to be due to the improved particle packing provided by the very fine-grained material of seawater-neutralised BRR (Fig. 1). However, even though the pore filling effect existed at all contents (Fig. 8a), the increase in sorptivity beyond 10% (Fig. 8b) suggest that un-reacted seawater-neutralised BRR might have absorbed water and that this absorption became dominant at beyond 10%.

3.3. Durability properties of concrete

3.3.1. Alkali–silica reactivity

The expansion data from the alkali–silica reactivity in seawater-neutralised BRR concrete is shown in Fig. 9. This shows that the total expansion of concrete due to alkali–silica reactivity at the end of the 14 days soaking period was within the limit of 0.20% specified by ASTM C 1260-94 [21] for all concretes up to 15% replacement level. However, the expansion exceeded the limit of 0.20% for the mix containing seawater-neutralised BRR at 20%, which is considered to be due to the large quantity of alkalis from this material providing the ideal conditions for the alkali–silica reactivity.

The use of various SCMs such as PFA, GGBS, MS and MK in concrete, are reported to minimise or eliminate the risk of alkali-aggregate reaction [47–49]. It is thought that these materials react with the $Ca(OH)_2$ liberated due to hydration of PC to form secondary C–S–H and this reduction in $Ca(OH)_2$, leads to a lowering of the pH and a lower risk of reaction due to high alkali contents. In addition, during the formation of the secondary C–S–H, the K^+ and the Na^+ ions are bound in the matrix and cannot react with any potentially siliceous aggregates. In the case of seawater-neutralised BRR, however, there is no such pozzolanic reaction and, hence, the phenomena associated with other mineral admixtures are less likely to

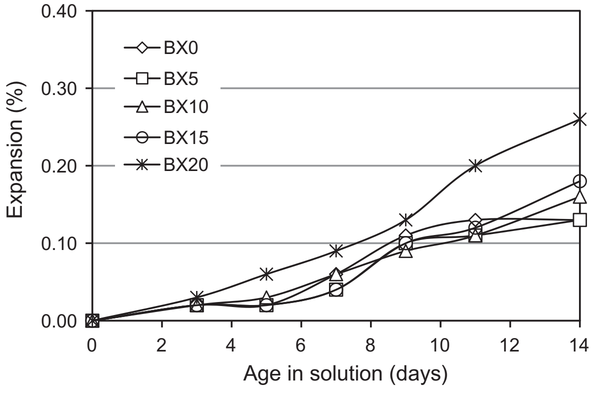

Fig. 9. Expansion due to alkali–silica reactivity.

occur in concrete containing this material. However, for alkali-aggregate reaction to occur the aggregates must be reactive. Consequently, as long as the aggregates are non-reactive the reaction cannot occur even if seawater-neutralised BRR contains high amount of alkalis. Nevertheless, at up to 15% seawater-neutralised BRR contents, concrete can be made without the concern of alkali–silica reactions affecting the durability properties.

3.3.2. Carbonation resistance

The carbonation depths after 6 and 9 weeks of the accelerated carbonation test are shown in Fig. 10. This shows that the carbonation depth decreased with increasing seawater-neutralised BRR content and the decrease is related to the addition rate. This decrease is possibly attributed to the fact that its increase decreases the free water content by absorbing water from it, which in turn reduces the porosity and permeability [16]. However, the observations could also be due to its micro-filler effect, because of the very fine grained nature of the material (Fig. 1). More importantly, a 20% substitution shows a 40% reduction in carbonation depth, whereas a 10% addition rate provides a reduction in carbonation depth of about 25%, which are quite substantial. The addition of seawater-neutralised BRR has an opposite effect compared to examples in the literature [50–53], which in general, indicates that concretes containing SCMs are less resistant to carbonation.

3.3.3. Sulphate attack resistance

Figs. 11 and 12 show the compressive strength of 100 mm concrete cubes immersed for both 56 and 180 days in 10% Na_2SO_4 and 10% $MgSO_4$ respectively. In both the cases, there was a decrease in compressive strength with a 5% inclusion of seawater-neutralised BRR, beyond which there was a consistent pattern of increase in compressive strength with its increase, which then deceased with further increase. It was found that the compressive strength was highest for the mixes containing 10% seawater-neutralised BRR content, although for the 10% $MgSO_4$ solution at 180 days this was marginal. In the case of cubes immersed in 10% Na_2SO_4 solution, the decrease in compressive strength after 56 days of immersion was marginal for concretes containing seawater-neutralised BRR content greater than 10% (Fig. 11). However, the decrease in compressive strength after 180 days of immersion was about one third of that of the control and the 10% seawater-neutralised BRR concretes. In the case of $MgSO_4$ solution, noticeable decrease in compressive strength was obtained only when the seawater-neutralised BRR content exceeded 15% at both 56 and 180 days of immersion (Fig. 12). In this case, the 20% seawater-neutralised BRR concrete shows about a 10% reduction in the compressive strength after 180 days of immersion. This improved behaviour may be from a combination of different effects, such as micro-filler effect due to its very fine-grains and/or chemical effects, which were not investigated thoroughly in this research.

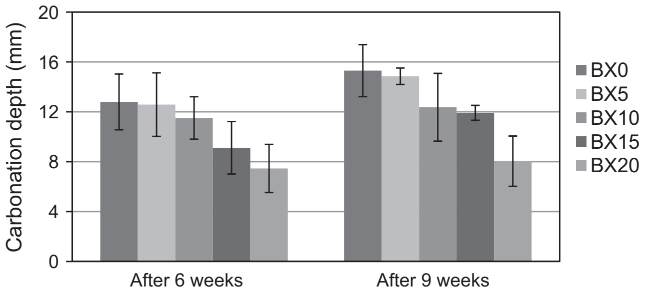

Fig. 10. Carbonation depth of concrete containing seawater-neutralised BRR.

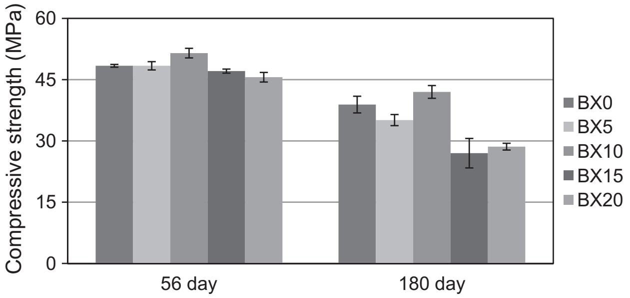

Fig. 11. Compressive strength of 100 mm concrete cubes immersed in 10% Na_2SO_4.

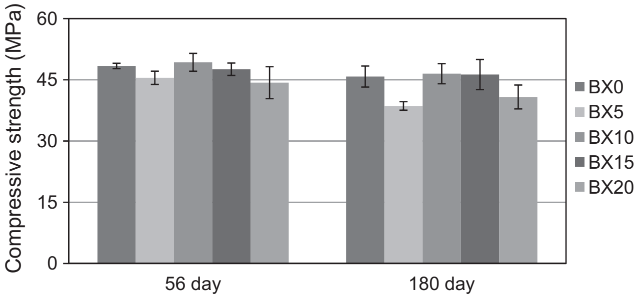

Fig. 12. Compressive strength of 100 mm concrete cubes immersed in 10% $MgSO_4$.

3.3.4. Chloride ingress resistance

The non-steady state migration coefficients are presented in Fig. 13, which shows that the non-steady state migration coefficient decreased with increasing seawater-neutralised BRR content. These data suggest that there is a distinct beneficial effect obtained from replacing natural sand with seawater-neutralised BRR as it provides improved resistance to chloride ingress. However, there are two important factors which affect the chloride transport in concrete, viz. the chloride ion diffusivity (which depends on the microstructure) and the binding capacity of the matrix. Diffusivity is a concentration driven phenomenon where chloride ions diffuse towards parts of the concrete that have lower chloride concentrations. Binding capacity is the capacity of the matrix to bind the chloride ions in mineral phases, which then reduces the amount of chlorides available in the pore solution. Different SCMs create varying effects on both the chloride diffusivity and chloride binding capacity of concrete. However, in general, the use of SCMs in concrete increases chloride ingress resistance [54–56].

Seawater-neutralised BRR has high sodacity, with as much as 3% by mass as NaCl [11], and the presence of NaCl in the pores may well lower the concentration gradient in the non-steady state test, thereby reducing migration coefficients. However, what is more likely is that because of its fine-grained nature, this acts as a micro-filler, which earlier was considered to be the reason for the decrease in air permeability. In addition, as this material has a high Al_2O_3 (Table 2) content, the decreased chloride ingress of seawater-neutralised BRR concretes could also be due to the increase in the chloride-binding capacity of concrete through the formation Friedel's salt, similar to that found with other SCMs [57].

3.3.5. Salt-scaling resistance

The cumulative scaled mass data, measured after every four freeze–thaw cycles are presented in Fig. 14. This figure shows that the scaled mass from all the seawater-neutralised BRR concretes are less than that of the control concrete. This would suggest that its introduction in concrete is beneficial to improving the resistance to the salt-scaling. The scaled mass per unit area is shown

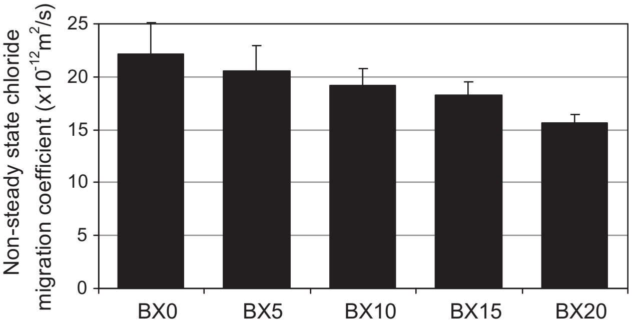

Fig. 13. Chloride ingress resistance of concrete containing seawater-neutralised BRR.

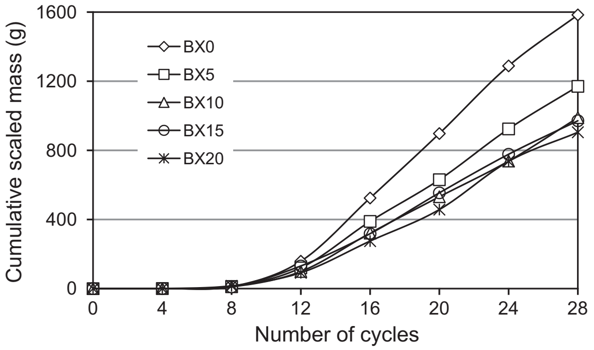

Fig. 14. Salt-scaling resistance of concrete containing seawater-neutralised BRR.

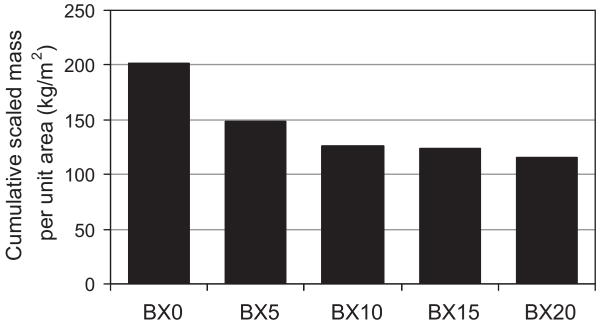

Fig. 15. Cumulative scaled mass of concrete containing seawater-neutralised BRR after 28 cycles.

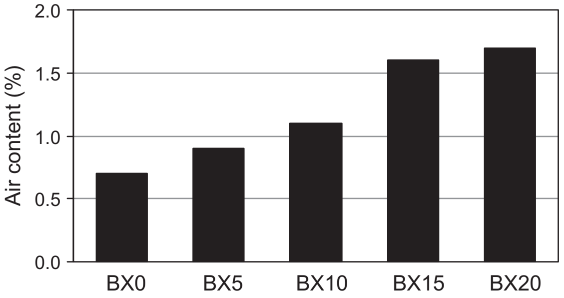

Fig. 16. Air content of mixes in Series A.

in Fig. 15 and from this figure, it can be seen that the benefit of seawater-neutralised BRR addition in concrete approaches an asymptotic limit at about 20% addition rates. This figure also shows that a 10% addition provides a 33% reduction in the scaled mass per unit area, but that a doubling to 20% reduces the scaled mass per unit area by 40% over the control. This means that for twice the material only a 20% improvement in the reduced scaled mass per unit area can be obtained.

Although the mechanisms related to the scaling of concrete surfaces due to freezing in the presence of de-icing salts are still not fully understood, the two most important factors are regarded to be the air-void structure and the W/C [19]. Therefore, the improvement in the salt-scaling resistance in the seawater-neutralised BRR concretes can be considered to be from the combined effects of a reduction in free water content and/or an increase in the air content (Fig. 16) through air entrainment in the fresh concrete [49].

4. Conclusions

On the basis of the data presented in this paper on the replacement of natural sand in concrete with seawater-neutralised bauxite refinery residue up to 20% by mass of Portland cement, the following conclusions have been drawn:

(i) The water demand of fresh concrete increased with an increase in the seawater-neutralised bauxite refinery residue content, but the required workability was possible with the addition of an appropriate superplasticiser instead of increasing the water content. It use as a sand replacement material up to 20% did not detrimentally affect the compressive and flexural strengths of concrete, rather there was some modest improvement in the compressive strength for concrete when the W/C was kept constant and a substantial improvement in the flexural strength of concrete up to an age of 28 days.

(ii) The drying shrinkage of concretes containing seawater-neutralised bauxite refinery residue was lower than that of the control concrete at all ages for a fixed water-cement ratio of 0.55. At a fixed slump of 90 mm, the drying shrinkage of seawater-neutralised bauxite refinery residue concretes was higher than that of the control at all ages, and this was outside an acceptable range of 0.075% for the 20% replacement level. However, when both the slump and the water-cement ratio were kept constant using a superplasticiser, although the drying shrinkage increased with the increase in the seawater-neutralised bauxite refinery residue content, the values were within the acceptable range of 0.075% for all the samples.

(iii) The air permeability deceased with an increase in the seawater-neutralised bauxite refinery residue content. There was also an associated decrease in the depth carbonation and improvement in the chloride ingress resistance of concrete. The sorptivity of concrete decreased up to a replacement level of 10% and, then it increased.

(iv) The total expansion due to alkali–silica reactivity of concrete containing up to 15% of seawater-neutralised bauxite refinery residue at the end of the test period was within the limit of 0.20% specified by ASTM C 1260-94, but at 20% replacement level, the expansion exceeded this limit.

(v) There was an improvement in compressive strength and mass loss of concrete in sodium and magnesium sulphate environments when seawater-neutralised bauxite refinery residue was used at 10% by mass of cement to replace natural sand at a fixed W/C. Beyond this level of addition, the compressive strength decreased, indicating that concrete deteriorated due to the sulphate attack. However, the effect of addition up to 20% at a fixed W/C was found to improve the salt scaling resistance of concrete.

Overall, it can be concluded that seawater-neutralised bauxite refinery residue may be used to replace the natural sand in concrete at levels up to 10% by Portland cement mass to improve all the durability properties studied, namely the resistance to carbonation, chloride ingress, sulphate attack and salt-scaling of concrete. These improvements in concrete properties are thought to be related to the micro-filler effect due to its fineness. Whilst combining these durability characteristics with the environmental benefits reported by McConchie et al. [11], concretes containing seawater-neutralised bauxite refinery residue could be a sustainable option for many application areas, such as concretes for environmental barriers.

Acknowledgements

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