

Effects of the Replacement of Industrial By-Products as Fine Aggregate in Concrete on Chloride Penetration

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ABSTRACT

The aim of this work is to investigate how the replacement of by-products such as bottom ash (BA) or granulated blast-furnace slag (GBFS) as fine aggregate in concrete affects the chloride permeability of concrete. And so to have an opinion about the effect on the corrosion risk in reinforced concrete. Thus, rapid chloride permeability test and capillarity tests are conducted on the GBFS and BA concretes by replacing 10, 20, 30, 40 and 50% of fine aggregate by weight. Recently, there are researches related with replacement of aggregate as non-ground form of GBFS and/or BA. GBFS and BA can be substituted as fine aggregate in concrete production because of their positive effects on concrete durability. Three different groups of concrete are produced by replacing GBFS and BA single or mutual. Test results show that these types of concretes have sufficient durability for the structures exposed to chloride ion penetration.

INTRODUCTION

Chloride ions are generally known as the most harmful materials for embedded steel in concrete [Baradan et al. 2002]. A universal recognition is said that corrosion reinforcement due to chloride penetration is the most significant threat to the existing reinforced concrete infrastructure of developed countries [Richardson 2002]. Road bridges, marine structures, tunnels, buildings car parks and precast structures can be deteriorated by the corrosion of reinforcement due to chloride ingress. Chloride ions have so many negative effects on corrosion such as solving the passive layer which prevents development of corrosion. The existence of carbonation also influences the impermeability of layer negatively. Chlorides can be introduced into concrete in aggregates, water, cement and admixtures but low level of chloride ions can be tolerated in durable concrete. Excessive chloride levels may occur over the service life by reason of external chloride sources. Chloride ions increase the electrolytic property and decrease the electrical resistance of concrete media. Thus, corrosion rate also increases due to the increment of current. Because of having acid characters they simultaneously decrease pH value of media. Due to the low pH value of media, corrosion rate also increases. The anode reaction occurs easily by the behavior of chloride ions as a catalyst. Because of the existence of (OH⁻) ions and iron amply in media, chloride ions are continuously restored after reaction and deterioration of reinforcement attends without cease. Corrosion due to

chloride ingress generally focuses on a small area and forms a pit surrounded by not corroded reinforcement. This may cause a rapid loss of cross-section and reduce the load-bearing capacity of the reinforced concrete member. Chlorides present in three states as free chloride ions in the pore solution, chlorides strongly and loosely bound. The free chloride ions are the most dangerous ions for the corrosion risk. The aluminates can combine with free chlorides up to a certain concentration and reduce the corrosion risk. It is known that the critical chloride threshold level is dependent on several factors such as C_3A content of the binder, the free chlorides/total chlorides, chloride ion/hydroxyl ion and water/cement ratios, the hydroxyl ion concentration, temperature and relative humidity of concrete media and electrical potential of the reinforcement [Richardson, 2002]. The chloride ingress depend on the sorptivity and chloride diffusivity of concrete, ability of concrete to bind chlorides, water/cement ratio, chloride diffusivity of aggregates, degree of exposure to chloride source, temperature, carbonation, hydrostatic head. It is possible that salt water can be absorbed when especially the concrete surface is dry [Broomfield, 1997]. pH and aluminate varies with type of cement so the chloride level and corrosion rate also depend on the type of cement [Broomfield, 1997]. Corrosion can be observed if the concrete quality is poor and water and oxygen are available. High strength concrete has a low porosity and a more uniform microstructure compared to normal strength concrete, so this gives an advantage to high strength concrete as a high resistance to carbon dioxide and chloride penetration into concrete [Shah and Ahmad, 1994]. Addition of mineral admixtures such as silica fume, slag or fly ash also increases the resistance chloride penetration by the high capacity of chloride binding at the same time [Shah and Ahmad, 1994]. Fineness of mineral admixtures improves the chloride binding capacity but if concrete becomes carbonated in question binding capacity reduces. When an electrical current passes through the concrete in the form of charged ions, it is possible to say that there is a close relationship between electrical resistivity, ion concentration and porosity [Shah and Ahmad, 1994]. It can be said that the way to produce denser concrete is the way of producing both high performance concrete having high chloride resistant and durable concrete.

According to Polden and Peelen [2002] concretes made with blast furnace cements or slag and fly ash cements show lower chloride penetration so these concrete types have higher electrical resistivity. Oh et. al. [2002] defines high performance concrete as the concrete having high resistance to chloride penetration as well as high strength. They have approved the positive effects of silica fume, fly ash (FA) or slag cement concretes on the property of chloride resistance. It is reported that water-binder ratio, maximum size aggregates, aggregate particle distribution and aggregate- paste volume ratio also affects the chloride ingress [Oh et al., 2002]. In another study, it is reported that the inclusion of fibers into mortars decreases the resistance to chloride penetration although the pozzolans such as silica fume, fly ash, granulated blast furnace slag that decrease the chloride diffusion into concrete, are also used to produce these mortars [de Gutierrez et al., 2005]. Hooton and Titherington also found out that usage of supplementary cementing materials e.g. slag to produce high performance concrete for both accelerated and ambient curing conditions provide high chloride resistance to chloride penetration [Hooton and Titherington, 2004; Aldea et al., 2000]. Accelerated curing increases the chloride permeability compared to ambient curing [Hooton and Titherington, 2004]. It is also possible to use concrete containing % 8 silica fumes and % 25 slag in precast operations employing accelerated curing [Hooton and Titherington, 2004]. Yüksel et. al. [2006] used granulated blast furnace GBFS as fine aggregate replacement and observed that it improves the chloride resistance of concrete. In some studies, bottom ash is used as fine aggregate replacement, too. BA increases the chloride permeability due to its high water absorption rate but decreases the chloride transport coefficient because of high binding capacity of chlorides [Ghafoori and Bucholc, 1996; Basheer and Bai, 2003]. It is also determined that if a low dosage of super plasticizer or chemical admixtures reducing water requirement are used with BA it is possible to produce concrete types which have

low permeability and increase the chloride resistance of concrete [Ghafoori and Bucholc, 1996; Basheer and Bai, 2003].

In this study, GBFS and BA single or mutual are used as fine aggregate and the effect to chloride penetration into concrete is investigated. In Zonguldak region, the production of GBFS is about 4 million tones and the production of BA is about 57.000 tones a year. It is aimed to increase the usage amounts and types of these by-products. The by-products can be used without any processes. It is also pointed out for many times by too many researchers that the utilizations or usages of by-products and wastes such as GBFS, silica fumes, fly ash, BA, waste concrete aggregates, waste glass, waste rubber etc. are very important to produce durable concrete [Yüksel et al., 2006; Mehta, 2002; Yüksel and Bilir, 2007; Topçu and Canbaz, 2004; Topçu and Şengel, 2004; Ghafoori and Diawara, 2000]. In recent time, determining methods of producing durable concrete is a critical issue in order to gain economical, ecological and technical advantages for the future of the concrete industry, humanity and world.

MATERIALS AND METHOD

Materials

In this study, CEM-I type Portland cement used corresponding to the Turkish Standard TS EN 197-1 [2002] which the marketing name is as PÇ 42.5 and has a 42.5 MPa value of 28-day compressive strength. Physical and chemical properties of this type of Portland cement are reported in Table 1.

Two types of aggregates which have diameter at the ranges of 0-4 mm and 4-7 mm sizes were also used. The sieve analysis of these aggregate types and by-products used in the scope of this study (GBFS and BA) are noted in Table 2 and Table 3. Physical properties of GBFS and BA are shown in Table 4.

Table 1. Properties of Portland Cement

| Chemical composition (by weight, %) | | Physical properties | |
|--------------------------------------|-------|--|---------|
| SiO ₂ | 20.52 | Specific gravity | 3.16 |
| Al ₂ O ₃ | 5.11 | Specific surface area (cm ² /g) | 3300 |
| Fe ₂ O ₃ | 2.84 | 32 µm sieve residue (by weight. %) | 21 |
| CaO | 63.62 | 90 µm sieve residue (by weight. %) | 0.8 |
| MgO | 1.9 | 200 µm sieve residue (by weight. %) | 0.1 |
| SO ₃ | 3.00 | Setting time(h:min) | 190/225 |
| C ₃ S | 53.13 | Expansion (mm) | 1 |
| C ₃ A | 8.74 | | |
| Cl | 0.72 | | |
| LOI | 1.96 | | |

Table 2. Sieve Analysis of Aggregate Types

| Sieve size (mm) | Passing (%) | |
|-----------------|-------------|--------|
| | 0-4 mm | 4-7 mm |
| 8.00 | 100 | 99.57 |
| 6.70 | 100 | 93.68 |
| 4.75 | 100 | 66.99 |
| 4.00 | 66.47 | 66.47 |
| 3.35 | 60.12 | - |
| 2.36 | 32.05 | - |

| | | |
|------|-------|---|
| 1.70 | 21.52 | - |
| 1.18 | 11.78 | - |
| 0.60 | 6.31 | - |
| 0.30 | 4.14 | - |
| 0.10 | 0.00 | - |

Table 3. Sieve Analysis of GBFS and CBA

| Sieve size (mm) | Passing (%) | |
|-----------------|-------------|-------|
| | GBFS | CBA |
| 4.00 | 99.38 | 94.03 |
| 3.35 | 98.20 | 91.90 |
| 2.36 | 92.16 | 86.23 |
| 1.70 | 77.10 | 76.97 |
| 1.18 | 62.26 | 61.70 |
| 0.60 | 17.72 | 36.63 |
| 0.30 | 4.94 | - |
| 0.212 | 2.84 | - |
| 0.100 | 0.80 | 6.57 |
| 0.075 | 0.44 | 3.80 |
| 0.045 | 0.12 | 1.07 |

Table 4. Physical Properties of Aggregate, GBFS, CBA and FA

| Property | Unit | Aggregate (0-7 mm) | GBFS | CBA | FA |
|----------------------------------|-------------------|--------------------|--------------|-------|------|
| Loose unit weight | kg/m ³ | 1930 | 1052 | 620 | 870 |
| Compact unit weight | kg/m ³ | 1950 | 1236 | 660 | 1110 |
| Specific gravity | | 2.68 | 2.08 | 1.39 | 1.8 |
| Water absorption | % | 11.30 | 10.00 | 12.10 | - |
| Clay lumps and friable particles | % | 5.00 | - | 2.40 | - |
| Very fine particles | % | 4.00 | 3.00 | 7.00 | - |
| Organic impurities (NaOH sol.) | Colour | Light yellow | Light yellow | - | - |

GBFS was provided by a steel plant in Turkey which is called as Ereğli Steel Works Company and chemical composition of GBFS is given in Table 5.

Table 5. Chemical Composition of GBFS

| SiO ₂ (%) | CaO (%) | MgO (%) | Al ₂ O ₃ (%) | Na ₂ O (%) | S (%) | MnO (%) | TiO ₂ (%) | Fe (%) | P ₂ O ₃ (%) |
|----------------------|---------|---------|------------------------------------|-----------------------|-------|---------|----------------------|--------|-----------------------------------|
| 35.09 | 37.79 | 5.50 | 17.54 | 0.30 | 0.66 | 0.83 | 0.68 | 0.70 | 0.37 |

CBA and FA were provided by a power utility plant in Turkey. Chemical composition of FA is presented in Table 6. Reactive lime amount of FA is under % 10 and SiO₂+Al₂O₃+Fe₂O₃ value is above 70 % [Türker et al., 2003]. Thus FA used in this study can be classified as type V according to Turkish Standard TS EN 197-1 and F type according to ASTM C618 [Türker et al., 2003]. Some properties and chemical composition of CBA is given in Table 7 and Table 8, respectively.

Table 6. Chemical Composition of FA

| SiO ₂ (%) | Al ₂ O ₃ (%) | Fe ₂ O ₃ (%) | CaO (%) | MgO (%) | SO ₃ (%) | K ₂ O (%) | Na ₂ O (%) | KK (%) | Cl (%) |
|-------------------------|---------------------------------------|---------------------------------------|------------|------------|------------------------|-------------------------|--------------------------|-----------|-----------|
| 58.69 | 25.10 | 5.80 | 1.49 | 2.22 | 0.12 | 4.04 | 0.59 | 1.28 | 0.013 |

Table 7. Some Properties of CBA (Tests Achieved in TCMA Lab.)

| Property | Unit | Results |
|---------------------------------|-----------------------|---------|
| Loss on ignition | (%) | 1.67 |
| SO ₃ ⁻ | (%) | 0.08 |
| Cl | (%) | 0.0064 |
| Free CaO | (%) | 0.00 |
| Density | (gr/cm ³) | 2.59 |
| 45 sieve residue (by weight. %) | (%) | 25.8 |
| 7 day strength activity index | (%) | 76.9 |
| 28 day strength activity index | (%) | 85.7 |
| 90 day strength activity index | (%) | 100 |

Table 8. Chemical Composition of CBA

| SiO ₂ (%) | CaO (%) | MgO (%) | Al ₂ O ₃ (%) | Na ₂ O (%) | K ₂ O (%) | SO ₃ (%) | TiO ₂ (%) | Fe ₂ O ₃ (%) |
|-------------------------|------------|------------|---------------------------------------|--------------------------|-------------------------|------------------------|-------------------------|---------------------------------------|
| 57.90 | 2.00 | 3.20 | 22.60 | 0.086 | 0.604 | - | - | 6.50 |

Mixing water which has pH 7.6 and hardness 12.8 was taken from city of Zonguldak. By-products used in the study (GBFS and CBA) increase water demand of concrete because of having higher specific surface areas than fine aggregate. Therefore, hyper-plasticizer chemical admixture was used at the amount of 0.7 % of cement in order to increase workability without increasing water demand. In addition, 19 mm length polypropylene fibers are used for mixture proportioning of some specimens with the 0.2% of cement weight. Some properties of fibers are reported in Table 9.

Table 9. Properties of Polypropylene Fibers

| Property | Polypropylene fibers |
|---------------------------------------|----------------------|
| Purity(%) | 100 PP |
| Cross section | Square |
| Length (mm) | 19 |
| Tensile strength (N/mm ₂) | 400-600 |
| Young modulus(N/mm ₂) | 1600-2400 |
| Change in length (%) | 25 |
| Specific density (kg/m ³) | 910 |
| Color | Transparent |

| | |
|------------------------|--|
| Softening (°C) | 150 |
| Melting (°C) | 160 |
| Acidic reaction | Stable |
| Oxalic reaction | Stable |
| Biologic reaction | Stable |
| Alkali reaction | Stable |
| Thermal shrinkage | Water 30 min. 100 °C = 0 % Air 30 min. 100 °C = 0 % Air 30 min. 100 °C = 0 % |
| Anti bacterial | Optional |
| Conformity with cement | Excellent |
| Abrasion resistance | Stable |

Method

In the study, 6 groups of mixtures which consist of fibers and no fibers were produced and coded by G, C and GC for each series. In G coded mixtures GBFS and in C coded mixtures BA has replaced the fine aggregate at the sizes of 0-4 mm by volume. The replacement ratios were chosen as 10 %, 20 %, 30 %, 40 % and 50 %, respectively. In GC coded mixtures GBFS and BA have replaced mutually together by being blended at the half of industrial by-product replacement ratio. The mutual industrial by-product replacements as half GBFS and half BA were made for fine aggregate at the sizes of 0-4 mm by volume at the ratios of 10 %, 20 %, 30 %, 40 % and 50 %. For instance, in GC5 coded mixtures which have % 10 by-product replacements, fine aggregate having the sizes of 0-4 mm was replaced with 5 % of its volume by GBFS and 5 % of its volume by BA. In this way, 3 groups of concrete specimens which consist of 0.2 % polypropylene fibers were produced by using these mix proportions. Finally, 18 series of mixtures were produced coded as G, C and GC. Mixture proportions of concrete specimens are given in Table 10. FA was used as mineral admixture at the ratio of 10 % cement by weight.

Table 10. Mix Proportions of Concrete Specimens

| Codes | Description | Cem. | Water | FA | Coarse agg. | Fine agg. | GBFS | CBA | Chem. Admix. | Fiber (19mm) |
|-------|-------------------|------|-------|----|----------------|--------------|------|-----|-----------------|-----------------|
| | | kg | lt | kg | (4-7) mm | (0-4) mm | kg | kg | kg | kg |
| G0 | Reference | 350 | 167 | 35 | 1120 | 720 | 0 | 0 | 2.45 | 0.7 |
| G10 | 10 % GBFS | 350 | 167 | 35 | 1120 | 648 | 72 | 0 | 2.45 | 0.7 |
| G20 | 20 % GBFS | 350 | 167 | 35 | 1120 | 576 | 144 | 0 | 2.45 | 0.7 |
| G30 | 30 % GBFS | 350 | 167 | 35 | 1120 | 504 | 216 | 0 | 2.45 | 0.7 |
| G40 | 40 % GBFS | 350 | 167 | 35 | 1120 | 432 | 288 | 0 | 2.45 | 0.7 |
| G50 | 50 % GBFS | 350 | 167 | 35 | 1120 | 360 | 360 | 0 | 2.45 | 0.7 |
| C10 | 10 % BA | 350 | 167 | 35 | 1120 | 648 | 0 | 72 | 2.45 | 0.7 |
| C20 | 20 % BA | 350 | 167 | 35 | 1120 | 576 | 0 | 144 | 2.45 | 0.7 |
| C30 | 30 % BA | 350 | 167 | 35 | 1120 | 504 | 0 | 216 | 2.45 | 0.7 |
| C40 | 40 % BA | 350 | 167 | 35 | 1120 | 432 | 0 | 288 | 2.45 | 0.7 |
| C50 | 50 % BA | 350 | 167 | 35 | 1120 | 360 | 0 | 360 | 2.45 | 0.7 |
| GC5 | 5 % GBFS 5 % BA | 350 | 167 | 35 | 1120 | 648 | 36 | 36 | 2.45 | 0.7 |
| GC10 | 10 % GBFS 10 % BA | 350 | 167 | 35 | 1120 | 576 | 72 | 72 | 2.45 | 0.7 |
| GC15 | 15 % GBFS 15 % BA | 350 | 167 | 35 | 1120 | 504 | 108 | 108 | 2.45 | 0.7 |
| GC20 | 20 % GBFS 20 % BA | 350 | 167 | 35 | 1120 | 432 | 144 | 144 | 2.45 | 0.7 |
| GC25 | 25 % GBFS 25 % BA | 350 | 167 | 35 | 1120 | 360 | 180 | 180 | 2.45 | 0.7 |

RESULTS AND DISCUSSION

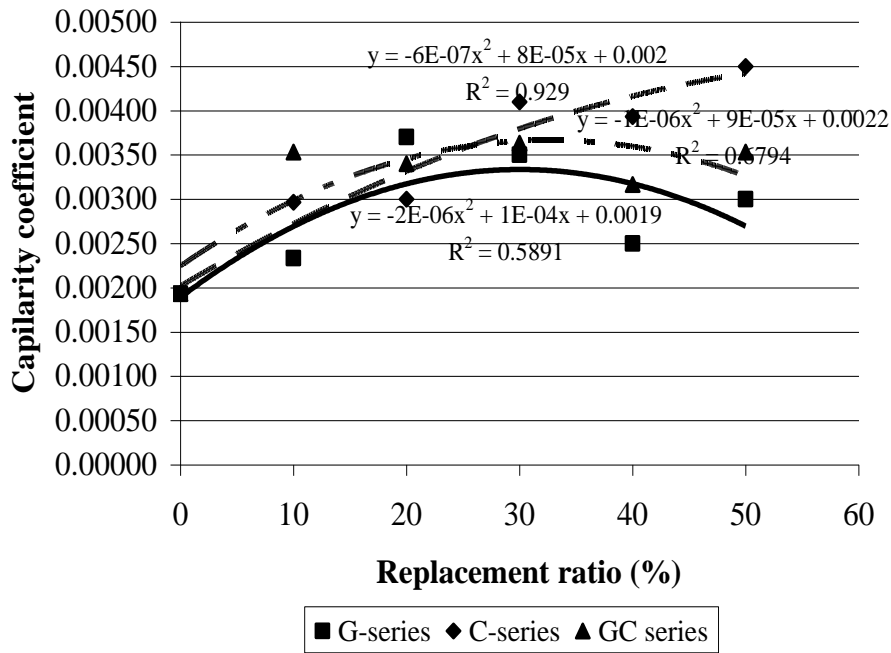


Fig. 1. Capillarity Test Results of Concrete with Fibers

Fig. 1. shows the capillarity of fiber concrete. It can easily be seen in Fig. 2. that fibers increase chloride penetration into concrete. Firstly, chloride resistance increases due to the increase in chloride binding capacity by the increment of replacement ratio. Then, chloride resistance decreases due to the increase in porosity. The fiber concrete produced by GBFS and BA fine aggregate is durable against chloride penetration.

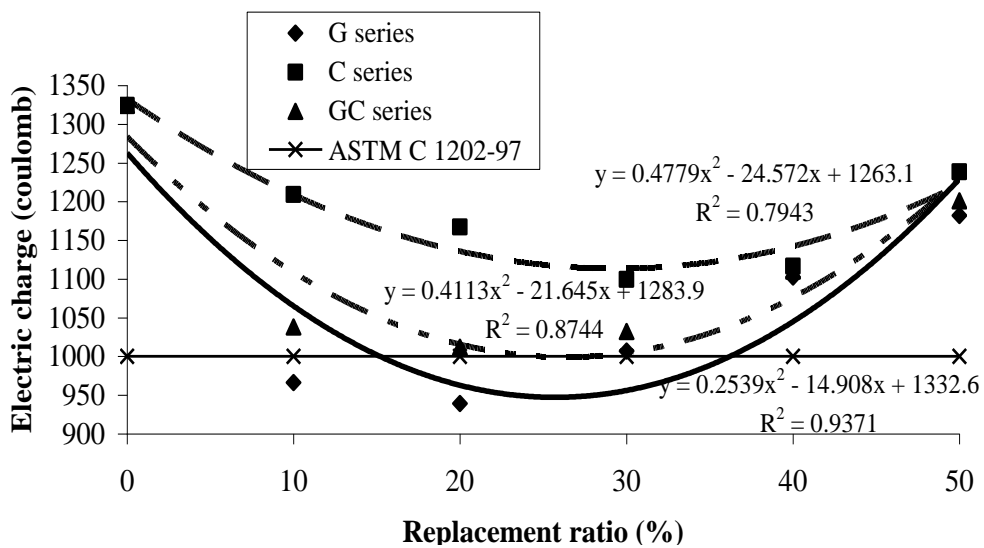


Fig. 2. RCPT Test Results of Concrete with Fibers

In G concrete chloride diffusion decreases up to 30 % replacement ratio. Between 30 % and 50 % ratios, it increases because of high porosity. C concrete has higher porosity compared to G concrete, especially between 25 % and 50 % replacements ratios according to capillarity test results, this result can be also seen from the Fig. 2. as the higher chloride ion penetration compared to G concrete between the ratios 15 % and 50 %. The reason of this result can also be connected with the differences between the chloride binding capacity of GBFS and BA. GBFS as fine aggregate may have higher chloride binding capacity, so the replacement ratio having lower chloride penetration decreases to 15 % comparing GBFS to BA. Both by-products as fine aggregate have low chloride permeability and high chloride binding capacity, although their finenesses and specific surfaces are not enough great to bind more chloride ions. 10 % replacement ratio has lower chloride ion penetration due to pozzolanic reaction of by-products causing low permeability except G concrete. The mechanism was mentioned in capillarity test results. This means that the rapid chloride permeability test results are connected with the capillarity test results. The reason of the lower chloride penetration into G concrete is thought as the higher chloride binding capacity of GBFS compared to BA. GC concrete has charge passed between G and C concrete because this type of concrete has lower amount of GBFS than G concrete and higher amount than C concrete.

The compressive strengths of the specimens at the dimensions of 70x70x70 mm for 28 and 90 day ages are given in Table 11. The compressive strength generally presents a tendency of decrease with the increase in replacement. However, the losses in compressive strengths for the lower GBFS replacement ratios such as 10 and 20 % are below 5%. The losses in compressive strength for the same replacement ratios of bottom ash are increasing up to 17%. Compressive strength is an important parameter for evaluating the durability of concrete. Even though the observed compressive strength losses for lower replacement ratios such as 10 and 20% seem not to have effects on rapid chloride permeability, these losses have negative effects increasing the rapid chloride permeability for higher replacement ratios. However, the decrease in rapid chloride permeability for lower replacement ratios can be reported as the positive effect of the usage of these industrial by-products.

Table 11. The Compressive Strengths of the Groups

| Code | 28-day compressive strength (MPa) | 90-day compressive strength (MPa) |
|------|-----------------------------------|-----------------------------------|
| G0 | 48.51 | 56.19 |
| G10 | 47.53 | 55.45 |
| G20 | 44.83 | 53.19 |
| G30 | 42.32 | 51.30 |
| G40 | 40.41 | 49.83 |
| G50 | 39.07 | 47.66 |
| C10 | 39.79 | 55.99 |
| C20 | 38.56 | 53.61 |
| C30 | 33.84 | 49.02 |
| C40 | 37.26 | 41.46 |
| C50 | 36.53 | 40.74 |
| GC5 | 44.69 | 52.69 |
| GC10 | 43.29 | 48.05 |
| GC15 | 43.74 | 46.02 |
| GC20 | 43.30 | 44.94 |
| GC25 | 39.54 | 42.04 |

If the by-products used in this study were grounded and have higher finenesses, pozzolanic reaction would occur and permeability would be reduced. Thus, chloride permeability reduction would be greater. When the chloride binding capacities of these by-products were also taken into account, the resistance against chloride ion penetration would increase extremely. Consequently, it can be noticed that the chloride ion penetration of concrete depend on the properties and amount of replacing by-product.

Table 12. Chloride in Penetrability Based on Charge Passed [19]

| Charge passed (Coulomb) | Chloride ion penetrability |
|-------------------------|----------------------------|
| >4000 | High |
| 2000-4000 | Moderate |
| 1000-2000 | Low |
| 100-1000 | Very Low |
| <100 | Negligible |

Chloride ion penetrability based on charge passed according to ASTM C1202-97 [1997] is given in Table 12. Chloride ion penetration obtained in this study is shown in Table 13. It is seen that GBFS and/or BA as fine aggregate increases the resistance against chloride ingress. Even if the reference concrete has also low chloride ion penetration, the usage of GBFS and BA single or mutual as fine aggregate leads to lower charges passed through concrete till 40% replacement ratio. At 50% replacement ratios the charges passed are greater than reference concrete but include the same chloride ion permeability group. All values of the charges passed through concrete are very close to each other. All groups are in the group of “low” or “very low” chloride ion permeability.

Table 13. Chloride Ion Penetration of the Groups

| Codes | Description | Charge passed (Coulomb] | ASTM C 1202-97 |
|-------|-------------------|-------------------------|----------------|
| G0 | Reference | 1324 | Low |
| G10 | 10 % GBFS | 1209 | Low |
| G20 | 20 % GBFS | 1167 | Low |
| G30 | 30 % GBFS | 1100 | Low |
| G40 | 40 % GBFS | 1116 | Low |
| G50 | 50 % GBFS | 1238 | Low |
| C10 | 10 % BA | 1324 | Low |
| C20 | 20 % BA | 966 | Very Low |
| C30 | 30 % BA | 939 | Very Low |
| C40 | 40 % BA | 1007 | Low |
| C50 | 50 % BA | 1102 | Low |
| GC5 | 5 % GBFS 5 % BA | 1182 | Low |
| GC10 | 10 % GBFS 10 % BA | 1324 | Low |
| GC15 | 15 % GBFS 15 % BA | 1038 | Low |
| GC20 | 20 % GBFS 20 % BA | 1012 | Low |
| GC25 | 25 % GBFS 25 % BA | 1032 | Low |

CONCLUSIONS

1. All groups are durable against chloride permeability. Thus, these concrete types can be used to produce structures exposed to chloride ion. The reason is the high chloride binding capacity of the by-products. Fly ash as mineral admixture also takes part.
2. The usage amount of the by-products such as GBFS, BA and FA can be used as fine aggregate single or mutually. This is very important for the sustainable development to produce low cost, durable and environmental friendly concrete structures.
3. Additionally, it is observed that the usage of these industrial by-products decrease the compressive strength of the concrete with the increase in replacement ratio. However, it can provide some durability properties such as rapid chloride permeability resistance.

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