A COMPARATIVE STUDY OF SELF-CONSOLIDATING CONCRETES INCORPORATING HIGH-VOLUME NATURAL POZZOLAN OR HIGH-VOLUME FLY ASH

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ABSTRACT

The purpose of this study is to compare the effects of Portland cement replacement on the strength and durability of self-consolidating concretes (SSC). The two replacement materials used are high-volume natural pozzolan (HVNP), a Saudi Arabian aluminum-silica rich basaltic glass and high-volume Class-F fly ash (HVFAF), from Jim Bridger Power Plant, Wyoming US. As an extension of the study, limestone (LS) is also used to replace Portland cement, alongside HVNP or HVFAF, forming ternary blends. Along with compressive strength tests, non-steady state chloride migration and gas permeability tests were performed, as durability indicators on SCC specimens. The results were compared to two reference concretes; 100% ordinary Portland cement (OPC) and 85% OPC – 15% LS by mass. The HVNP and HVFAF concrete mixes showed strength and durability results comparable to the reference concretes; identifying that both can effectively be used to produce of low-cost and environmental friendly SCC.

Keywords: Ternary blend, high volume fly ash, high volume natural pozzolan, limestone, durability
INTRODUCTION

As of 2012, more than 25 billion tonnes of Portland cement concrete is produced annually making it the world’s most widely used manufactured material (WBSCD, 2009). Even though the reasons for concrete’s dominance are diverse (Mehta and Monteiro, 2006), the massive production and consumption cycle of concrete have significant environmental impacts, making the concrete industry unsustainable (Mehta, 2001). Currently, Portland cement concrete production accounts for around 7% of anthropogenic carbon dioxide (CO₂) emissions annually (Mehta, 2001). Most of the emissions are attributable to the production of Portland cement clinker; the active ingredient in Portland cement ([IEA] and [WBCSD], 2009). Using an increased proportion of supplementary cementing materials (such as natural pozzolan (NP) and fly ash) provides a sustainable solution, while yielding concrete mixtures with high workability, high durability, and comparable ultimate strength. HVFAF mixtures have been utilized successfully in many projects with technical and environmental advantages and is a low-cost, sustainable alternative to conventional Portland cement concrete (Malhotra and Mehta, 2008). With growing field experience of fly ash and increasing demand for environment-friendly structural materials, fly ash consumption through the concrete sector is expected to rise (Mehta, 2009, Malhotra and Mehta, 2008). However, the global availability of fly ash is around 900 million tonnes annually (Mehta, 2010), and not all of it is suitable for use in blended cements or concrete mixtures. As a result, there is a need for other alternative materials, natural pozzolan and ground limestone, being two possibilities (Khan and Alhozaimy, 2011, Celik et al., 2012, Celik et al., 2013, Erdem et al., 2007, Uzal and Turanlı, 2012). Studies of Portland cement-based ternary and quaternary blends containing combinations of fly ash Class F (FAF), silica fume, blast furnace slag, ground limestone and natural pozzolans show that blended cements can be optimized to minimize the shortcomings of each component, resulting in synergetic properties of the cementing material (De Weerdt et al., 2011, Menéndez et al., 2003, Pipilikaki and Katsioti, 2009).

With the ongoing technological advances, the design and placement techniques of concrete are also changing. The ultimate target is the freedom in design while considering improved productivity, profitability, and sustainability. SCCs are highly engineered concrete mixtures obtained by optimizing normal concrete ingredients with a superplasticizer and a viscosity modifying agent (VMA). This study is based on the authors' previous work on SCCs (Celik et al., 2012, Celik et al., 2013), performed to analysis and compare the effect of NP/FAF as OPC replacement at 30 mass% and 50 mass% in SCC production without utilizing VMAs. The interaction of NP/FAF with LS is also studied in 30 mass%, 40 mass%, 50 mass% NP/FAF and 15 mass% LS in the ternary blended cements. The results are compared in terms of compressive strength development and durability performance with reference concrete mixes that have no mineral admixture and 15 mass% LS.

MATERIALS AND METHODS

Materials
Khan and Alhozaimy (Khan and Alhozaimy, 2011) reported that NP used in the present work complies with the requirements of ASTM C618 for Class N; there are several studies describing its pozzolanic properties (Khan and Alhozaimy, 2005, MR Moufti et al., 2000). The mean particle sizes of the powder materials used in this study were determined by laser light scattering
as 10.4μm, 17.4μm, 22.3μm, and 48.1μm for OPC (ASTM Type I/II), NP from Saudi Arabia, FAF from Jim Bridger Power Plant, Wyoming, US, and LS respectively. The chemical composition of the powder materials used is given in Table 1. Aggregates used include quartzitic sand with fineness modulus of 3.1, pea gravel with maximum size of 12.7mm (½”) and basalt with maximum size of 19.0mm (¾”). The entry-level carboxylated polyether-based high-range water reducer (ADVA-140) with a specific gravity of 1.04 kg/l was also used.

Table 1. Chemical composition of powder materials (oxides, % by mass)

<table>
<thead>
<tr>
<th></th>
<th>OPC</th>
<th>NP</th>
<th>FAF</th>
<th>LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.44</td>
<td>46.48</td>
<td>62.0</td>
<td>0.70</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.97</td>
<td>14.74</td>
<td>18.90</td>
<td>0.50</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.07</td>
<td>12.16</td>
<td>4.90</td>
<td>0.12</td>
</tr>
<tr>
<td>CaO</td>
<td>62.90</td>
<td>8.78</td>
<td>5.98</td>
<td>47.40</td>
</tr>
<tr>
<td>MgO</td>
<td>2.42</td>
<td>8.73</td>
<td>1.99</td>
<td>6.80</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.37</td>
<td>3.39</td>
<td>2.41</td>
<td>--</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.43</td>
<td>1.27</td>
<td>1.14</td>
<td>--</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.16</td>
<td>0.629</td>
<td>0.26</td>
<td>--</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.23</td>
<td>2.31</td>
<td>1.09</td>
<td>--</td>
</tr>
<tr>
<td>MnO</td>
<td>0.32</td>
<td>0.19</td>
<td>0.04</td>
<td>--</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>4.69</td>
<td>1.324</td>
<td>1.30</td>
<td>44.48</td>
</tr>
</tbody>
</table>

Concrete Mixture Proportions
Concrete mixture proportions are given in Table 2. The water/ cementitious material (W/CM) ratio was held constant at 0.35 for all mixes and the amount of superplasticizer (SP) was added to provide a slump flow diameter between 635-690mm, and a diameter of 50mm flow time, T₅₀, between 3 to 5 seconds. In order to reduce cement content compared to typical SCCs, the total aggregate to fines ratio was fixed at 4:1, and the cement replacement (CR) ratio ranging from 30 mass% to 65 mass%. For the ternary blends, the LS content was set as 15 mass%, and the ratio of NP/FAF was varied between 30 mass% and 50 mass%. The ratio between coarse aggregates (CA) and fine aggregates (FA) was kept at 1:1. The CA consists of 30 mass% pea gravel and 70 mass% basalt.

Table 2. Concrete mix proportions

<table>
<thead>
<tr>
<th>OPC-LS-NP/FAF (mass%)</th>
<th>OPC</th>
<th>NP/FAF</th>
<th>LS</th>
<th>FA</th>
<th>CA</th>
<th>W/CM</th>
<th>SP (NP/FAF) (mass%)</th>
<th>CM (kg/m³)</th>
<th>OPC (kg/m³)</th>
<th>CR (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control mixes</td>
<td>100-0-0</td>
<td>1.00</td>
<td>--</td>
<td>--</td>
<td>2</td>
<td>2</td>
<td>0.35</td>
<td>1.43</td>
<td>461</td>
<td>461</td>
</tr>
<tr>
<td></td>
<td>85-15-0</td>
<td>0.85</td>
<td>--</td>
<td>0.15</td>
<td>2</td>
<td>2</td>
<td>0.35</td>
<td>1.43</td>
<td>458</td>
<td>389</td>
</tr>
<tr>
<td>Binary</td>
<td>70-0-30</td>
<td>0.70</td>
<td>0.30</td>
<td>--</td>
<td>2</td>
<td>2</td>
<td>0.35</td>
<td>1.08/1.39</td>
<td>453</td>
<td>317</td>
</tr>
<tr>
<td>HVNP/FAF blends</td>
<td>50-0-50</td>
<td>0.50</td>
<td>0.50</td>
<td>--</td>
<td>2</td>
<td>2</td>
<td>0.35</td>
<td>1.03/1.14</td>
<td>449</td>
<td>224</td>
</tr>
<tr>
<td>Ternary</td>
<td>55-15-30</td>
<td>0.55</td>
<td>0.30</td>
<td>0.15</td>
<td>2</td>
<td>2</td>
<td>0.35</td>
<td>1.22/1.14</td>
<td>451</td>
<td>248</td>
</tr>
<tr>
<td>HVNP/FAF-LS blends</td>
<td>45-15-40</td>
<td>0.45</td>
<td>0.40</td>
<td>0.15</td>
<td>2</td>
<td>2</td>
<td>0.35</td>
<td>1.22/1.03</td>
<td>448</td>
<td>202</td>
</tr>
<tr>
<td></td>
<td>35-15-50</td>
<td>0.35</td>
<td>0.50</td>
<td>0.15</td>
<td>2</td>
<td>2</td>
<td>0.35</td>
<td>1.12/1.00</td>
<td>446</td>
<td>156</td>
</tr>
</tbody>
</table>

* The chemical admixture used was an entry-level carboxylated polyether-based high-range water reducer (ADVA 140) with a specific gravity of 1.010-1.120.

Sample Preparation
For the each mixture, a total volume of 22L of concrete was prepared in a pan planetary-type mixer. The mixing procedure was as follows; CA and a small amount of water were mixed for 30 seconds. OPC, NP/FAF and more water were added and mixed for one minute. LS and the rest of the water were added and mixed for a further minute before the superplasticizer was
added and again mixed for one minute. Fine aggregate was then added and mixed for three minutes. During that time, the mixer was stopped and the bottom scraped to remove fine particles. Then, the slump flow test was performed. If the concrete was satisfactory, it was then returned to the mixer and mixed for an additional minute before casting. If the slump flow was too low or flow time too high, the concrete was returned to the mixer, mixed for an additional minute and additional water reducer added until consistency looks sufficient. The slump flow test was again performed. If the concrete was then satisfactory, it was remixed for an additional minute before casting. Otherwise, it was discarded and the mix attempted again with more or less water reducer.

The material was cast into eighteen 75x150mm cylinders and three 100x200mm cylinders in two lifts without mechanical vibration. Light shaking was allowed as the only method of consolidation for the SCC specimens. Cylinders were immediately covered with plastic wrap and remained undisturbed for 24 hours in lab conditions. After 24 hours, cylinders were demolded and placed in an environmental chamber (100% relative humidity at room temperature) to cure until testing in accordance with ASTM C192 (ASTM, 2007).

**Experimental procedures**

Each mixture was evaluated based on slump flow, compressive strength, chloride penetration coefficient, and gas permeability testing. These were selected as indicators of consistency, mechanical strength and durability properties.

**Slump flow test**

Freshly mixed samples were subjected to the slump flow of SCC test (ASTM C1611) (ASTM, 2009); performed to determine fresh state properties of each mix. The flow diameter and T$_{50}$ time was recorded. To test for SCC criteria, flow diameter and T$_{50}$ are checked to be between 635mm and 690mm, and 3 to 5 seconds, respectively. In addition, the stability of SCC was observed visually by examining the concrete mass in terms of segregation, bleeding and the mortar halo near the slump flow perimeter.

**Compressive strength test**

Compressive strength tests were performed after seven, 28, and 91 days of hydration. In accordance with ASTM C1231 and ASTM C617 (ASTM, 2012b, ASTM, 2012a), rubber pads capped the seven-day-old samples; all others were capped with sulfur capping compound. The cylinders were compressed using a displacement rate-based machine until significant softening was observed in accordance with ASTM C39 (ASTM, 2010). The peak load value was taken as the compressive strength. In order to identify and remove outliers from data set, the coefficient of variation (ratio of standard deviation to mean) was kept less than 10% for each mix-curing period combination. The cylinder size was chosen for convenience and economy. The use of small specimens in compressive strength tests may result in lower strengths when compared with standard-size specimens (Issa et al., 2000, Tokyay, 1997). Therefore, the correction factor of 102.94% was applied.

**Non-steady state chloride migration test**

The chloride migration coefficients of the one-year-old concrete samples were determined according to NT BUILD 492 (NORDTEST, 1999), where the test duration and electrical potential were 24 hours and 30V, respectively. After sawing the samples 50 ± 2mm-thick
sections and brushing and washing away any burrs from the surfaces of the specimen, the samples were returned to the fog room until the testing date. The test steps were as follows: a) the specimens were vacuum soaked with a saturated Ca(OH)₂ solution, b) a 30V electrical potential was applied that forces chloride ions from a 10% NaCl solution (catholyte) to migrate into the specimen, and c) the initial current through each specimen was recorded. Three specimens were tested for each mixture. Each specimen was then split axially into two pieces, and a 0.1M AgNO₃ solution sprayed on the freshly split surfaces. The chloride penetration depth was precisely measured on photographic images of the specimens enlarged in image processing software at seven points over 70mm distance from the white silver chloride precipitation. From the mean penetration depth, the non-steady state chloride migration coefficient \( D_{nssm} \) was calculated, as described in NT BUILD 492 (NORDTEST, 1999), using equation (1):

\[
D_{nssm} = \frac{RT}{zFE} \cdot \frac{x_d - \alpha \sqrt{x_d}}{t} 
\]

(1)

where

\[
E = \frac{U - 2}{L} \quad (2) \quad \text{and} \quad \alpha = 2 \sqrt{\frac{RT}{zFE}} \cdot \text{erf}^{-1} \left( 1 - \frac{2c_d}{c_0} \right) \quad (3)
\]

where

- \( D_{nssm} \) is the non-steady-state migration coefficient (m²/s)
- \( z \) is the absolute value of ion valence for chloride (\( z = 1 \))
- \( F \) is the Faraday constant (\( F = 9.648 \times 10^4 \) J/(V·mol))
- \( U \) is the absolute value of the applied voltage (V)
- \( R \) is the gas constant (\( R = 8.314 \) J/(K·mol))
- \( T \) is the average value of the initial and final temperatures in the anolyte solution (°K)
- \( L \) is the specimen thickness (m)
- \( x_d \) is the average value of the penetration depths (m)
- \( t \) is the duration (s)
- \( \text{erf}^{-1} \) is the inverse of the error function
- \( c_d \) is the chloride concentration at which the color of the concrete changes for OPC concrete (\( \approx 0.07N \) where \( N \) is the molar concentration divided by an equivalence factor)
- \( c_0 \) is the chloride concentration in the catholyte solution (\( \approx 2N \))

Three specimens were tested for each mix, and the average result calculated.

**Gas permeability test**

The gas permeability of the one-year-old concrete specimens was measured with the CEMBUREAU method (RILEM, 1999) using nitrogen gas as the permeating medium. Five gas pressure stages varying from 0.5bar (0.05MPa) to 2.5 bar (0.25MPa) were applied to the dried specimens until the observed weight loss was less than 0.5g between two successive readings over a time interval of 24 hours. Flow times were read every 30 minutes until a steady-state flow was reached. If the difference between successive readings within five minutes was less than 3%, it was determined that the flow had reached a steady-state condition. For each gas pressure step, the gas permeability coefficient, \( K_g \), was calculated using the Hagen-Poiseuille relationship for laminar flow of a compressible fluid through a porous under steady-state conditions (Kollek, 1989), so that:
\[ K_g = \frac{2P_0QL\mu}{A(P^2 - P_a^2)} \]

where
- \( K_g \) is the gas permeability coefficient (m²)
- \( Q \) is the volume flow rate of the fluid (m³ s⁻¹)
- \( A \) is the cross-sectional area of the specimen (m²)
- \( L \) is the thickness of the specimen in the direction of flow (m)
- \( \mu \) is the dynamic viscosity of the nitrogen at test temperature (N s m⁻²)
- \( P \) is the inlet (applied) pressure (absolute) (N m⁻²)
- \( P_a \) is the outlet pressure assumed in this test to be equal to atmospheric pressure (N m⁻²)
- \( P_0 \) is the pressure at which the volume flow rate is determined, assumed in this test to be atmospheric pressure (N m⁻²).

RESULTS AND DISCUSSION

Flowability of fresh concrete

The slump flow diameter (\( d_s \)) and \( T_{50} \) times are presented in Figure 1. According to the slump flow results, all mixes produce with blended cements met the specified SCC requirements. The visual stability index (VSI) values of mixes were between zero (no evidence of segregation or bleeding) and one (no evidence of segregation and slight bleeding observed as a sheen on the concrete mass) in accordance with ASTM C611 (ASTM, 2009). Because of the constant water content and variable use of water reducing agent, the impact of SCM replacement amount on flowability was not obvious. However, it could be seen that increasing amount of FAF or NP had the effect of either decreasing the water reducer content or \( T_{50} \) times in binary mixes.

![Figure 1. The slump flow diameter (\( d_s \)) and \( T_{50} \) times of the cement blends.](image-url)
**Compressive Strength**

The effects of changing the mixture proportions of cementing materials on the rate of strength development of concrete are shown in Figure 2. The binary mix containing 30% FAF or NP by mass resulted in concrete with slightly lower strengths compared to the control concrete after seven days of curing. The concrete containing a cementing material mix with 50 mass% FAF or NP registered a much lower rate of strength development when compared with control specimens; however, the 28-day and 91-day strength values 41MPa and 55MPa for the FAF specimens and 34MPa and 42MPa for the NP specimens, which are adequate for most structural applications. Among the binary mixes, the specimens replaced with 30 mass% NP produced 6% higher strength than the one with 30% FAF at 28 days, while they had similar strength at 91 days. However, the specimens replaced with 50 mass% NP produced 18% and 23% lower strength than the one with 50 mass% FAF at 28 and 91 days, respectively. In the case of ternary blended cements containing 15 mass% limestone powder, the larger amount of NP/FAF addition led to reduced compressive strength compared to the control specimen that have only 15% LS addition. The comparison between FAF and NP among the ternary mixes in Figure 2 shows that 30 mass% NP replacement had higher strength than the 30 mass% FAF replacement, whereas 40% and 50 mass% NP replacement had lower strength than the corresponding FAF replacements.

![Figure 2. Compressive strength development over time (days).](image-url)
Durability Properties

Coefficient of chloride migration
The effect of changing the mixing ratio of FAF/NP, and FAF-LS/NP-LS as a Portland cement replacement on the chloride migration coefficient of concrete is shown in Figure 3. All mixes made with blended cements demonstrated higher resistance to the chloride migration compare to the control mixtures. Based on standard guidelines (Gjørv, 2009), the chloride penetration resistance of the binary and ternary mixes ranges from extremely high to high. This result suggests that hydration of FAF/NP and FAF/NP-LS impedes voids and pores, leading to pore size reduction and smaller effective chloride diffusivity. The concretes produced with FAF and FAF-LS demonstrated higher chloride migration resistance compared to the concrete produced with NP and NP-LS with the exception of 55OPC-30FAF-15LS which showed slightly lower resistance to chloride migration. The increased amount of FAF replacement increased the resistance to chloride migration in binary and ternary mixes with the exception of 35OPC-50FAF-15LS. However, the increased amount of NP in binary and ternary mixes decreased the chloride migration resistance. In general, the concrete mixes with ternary cement showed greater resistance to chloride migration compared to the mixes with binary cement for a similar cement replacement configuration for the mixes with NP.

Figure 3. Non-steady state chloride migration coefficient as a function of cement replacement of the concrete mixes at 1 year. Zones 1, 2, 3 and 4 indicate extremely high, very high, high, moderate resistance to chloride penetration, respectively according to guidelines presented in (Gjørv, 2009)
**Gas permeability**

Figure 4 shows that FAF/NP and FAF/NP – LS mixes have a strong influence on the coefficient of gas permeability in the experimental concretes. Greater amounts of Portland cement replacement with FAF/NP lower the gas permeability in both the binary and ternary cement systems, with the exceptions of the 45OPC–40FAF–15LS and 45OPC–40NP–15LS. In general, addition of LS into the mix increased the gas permeability. The comparison of FAF and NP as a cement replacement in terms of gas permeability suggests that the mixes with NP exhibited lower resistance to gas permeability compared to FAF in binary cement system, whereas, NP-LS showed higher resistance to gas permeability compared to FAF-LS. It should be noted that the gas permeability is affected significantly by drying procedure (Sugiyama et al., 1996a, Hassan et al., 2000, Abbas et al., 2000, Abbas et al., 1999). While there is a correlation between gas permeability of concrete subjected air drying or short-term oven drying and chloride penetration of concrete, the correlation weakens with longer drying periods, as demonstrated for the specimens tested according to the CEMBEREU method. Sugiyama et al. (Sugiyama et al., 1996b) suggested that micro-cracks induced in concrete by longer drying periods result in higher gas permeability. The investigation of microstructure of the specimens is planned as a second phase of the project.

![Figure 4. Gas permeability coefficient in function of cement replacement of the concrete mixes at 1 year.](image-url)
CONCLUSIONS

This study focuses on comparing SCC mixes utilizing NP/FAF and LS. From the obtained results for NP or FAF incorporating mixes, the following observations can be made:

- In binary mixes, increasing the amount of NP/FAF used as OPC replacement resulted in either decreased superplasticizer content or $T_{50}$ times suggesting that both NP and FAF might increase the flowability of concrete mixes.
- Changing the OPC-NP/FAF-LS ratios utilized in the SCC allows designing for a desired strength.
- The 70 OPC-30 NP blend resulted in 12%, 6%, 2% higher strength than the 70 OPC-30 FAF mix at the age of seven-, 28- and 91-days, respectively. The 50 OPC-50 NP, however, showed 18% and 12% lower strength than the 50 OPC-50 FAF at 28- and 91-days, correspondingly.
- Among the ternary mixtures, 55OPC-30NP-15LS mix had higher strength, while 45OPC-40NP-15LS and 35OPC-50NP-15LS mixes had lower strength when compared to the corresponding mixes with FAF.
- All the binary and ternary mixes made with blended cements with either NP or FAF demonstrated higher resistance to the chloride migration compared to the control mixes. In general, the mixes with FAF or FAF-LS demonstrated higher chloride migration resistance compared to the ones with NP or NP-LS with the exception of 55 OPC-30 FAF-15 LS which showed slightly lower resistance to chloride migration at one year.
- In the binary mixes, the comparison of FAF and NP as a cement replacement in terms of gas permeability suggests that the mixes with NP exhibited lower resistance to gas permeability compared to FAF, whereas in the ternary mixes NP-LS showed higher resistance to gas permeability compared to FAF-LS.

Overall, FAF and NP (with or without LS) can be both used effectively in producing sustainable and durable SCC without utilizing VMA.

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REFERENCES


on Sustainable Construction Materials and Technologies, 2010 Italy. Coventry University and The University of Wisconsin Milwaukee Centre for By-products Utilization.


NORDTEST 1999. NT BUILD 492: Concrete, mortar and cement-based repair materials: chloride migration coefficient from non-steady-state migration experiments. Finland: Nordtest.


