1. Introduction

Self-compacting concrete (SCC) and self-compacting mortar (SCM) are innovative building materials that flow under their own weight, filling forms or restricted areas and achieving full compaction (EFNARC, 2005). In an SCC/SCM, the amount of powder materials that are fine particles or fillers, including Portland cement (PC) is higher than that of traditional concrete (TC). Usually, the paste volume of the SCC/SCM ranges from 34% to 40%. Changing the PC/powder materials ratio and keeping the amount of water constant change the pore amount of the cement paste. The degradation mechanisms of the hardened paste of an SCC/SCM exposed to potentially aggressive liquids are greatly influenced by the permeability of the material (Rilem Committee, 2008). The hardened paste of an SCC/SCM is more vulnerable to the harmful chemical effects surrounding it. One of the most important harmful chemical effects is the leaching of Ca\(^{2+}\) in the hardened paste.

Leaching of PC paste is important for the hydraulic structures and bridges constructed by an SCC or repaired by an SCM. The powder materials used in an SCC/SCM can change the leaching resistance of the PC paste. Leaching in PC paste refers to the dissolving of the components of hardened cement paste due to the influence of the surrounding waters. It is not usually a problem in the normal SCC structures because the degradation of the SCC by leaching is very slow. However, it is necessary to evaluate the durability of an SCC by testing the leaching of Ca\(^{2+}\) ions in hydraulic structures, such as dams and canals, which remain in the water for a long time (Ryu et al., 2002). In the hardened PC paste, the calcium silicate hydrate (C – S – H), calcium hydroxide (CH), and calcium aluminate silicate hydrate (C – A – S – H), which are in insoluble states, are in a stable equilibrium with the pore fluid of the PC paste with the high pH level that varies between 12.5 and 13.5 depending on the Na\(^+\), K\(^+\), and OH\(^-\) values. The chemical balance in the hardened PC paste deteriorates when the pH level goes low, that is theoretically less than 12.5. Therefore, the vast majority of industrial and natural waters are detrimental for PC concrete. The pH level of the harmful liquid and permeability of the concrete determines the rate of the chemical attack. The CO\(_2\) in soft water, sulfate and chloride ions in seawater and underground waters, and hydrogen ions in industrial wastewaters reduce the pH level of water to a level less than 6, which is quite detrimental to the concrete (Mehta and Gerwick, 1982). The pure waters coming from the fog or the vapor condensation or the soft waters coming from
the ice and rain contain little or no Ca²⁺ ions. If the hardened PC paste contacts such waters, the Ca²⁺ ions will dissolve or decompose. In this respect, leaching is a process which takes place when the concrete is exposed to poorly mineralized or acidic water. The phenomenon consists of the dissolution of Ca²⁺ and OH⁻ ions out of the hardened PC paste, which increases its porosity and causes the other changes in the material (Carde and François, 1999; Kamali et al., 2003). The process of dissolving and transporting the substances out of concrete is called leaching. When the water changes the dissolved ions to solid phases, the ions flow away by convection and diffusion from the solid phases. The shorter the flow paths are, the less the flow of water is and more ions flow by diffusion. The OH⁻ ions in the hardened PC paste get diffused by the aggressive water due to the gradient of concentration when the hardened PC paste gets into contact with water having a pH level lower than 13. When the pH level of the aggressive water is lower and the concentration gradient is higher, the diffusion of OH⁻ ions becomes significant (Kamali et al., 2003).

One of the main hydration products of the hydrated PC paste is CH, CH which has a high solubility in pure water (1230 mg/L), is highly susceptible to decomposition. Theoretically, the decomposition of the hardened PC paste continues until most of the CH is leached. In this case, the other components of the hardened PC paste are also subjected to chemical decomposition. The leaching of Ca²⁺ ions in the hardened PC paste causes a decrease in strength. It is believed that if one-quarter of the original Ca²⁺ ions in the hardened PC paste is released, its original strength decreases by half. The concrete pipes and the concrete structures having thin sections suffer the maximum damage from the waters with a low pH level. Furthermore, the acidic waters, which flow through the concrete structure due to the pressure gradient in its outside surfaces, are much more harmful to the hardened PC paste. This problem usually occurs in the dam structures exposed to pure water. In the dam constructions, the release of CH in the concrete with pores or cracks is very fast. It is reported that this release amount in the hardened PC paste reaches up to 50% of the total amount of lime (Hewlett, 2003).

Leaching behaviors of PC pastes containing some powder materials were investigated by different researchers. Some researchers reported that silica fume increased the leaching resistance of concrete against the aggressive environment, having low pH values (Mehta, 1985; Kawai et al., 2008; Jain and Neithalath, 2009; Matte and Morvanville, 1999; Lin et al., 2011; van Eijk and Brouwers, 1998; Bentz and Garboczi, 1992; Roziere et al., 2009) but Monteny et al. (2003) reported a decrease in leaching resistance. Some researchers argued that the class F fly ash effectively increased the leaching resistance in the PC system (van Eijk and Brouwers, 1998; Jain and Neithalath, 2009; Kawai et al., 2008; Novais et al., 2016). Phung et al. (2016) reported that limestone powder replacement gave a larger rate of leaching propagation in the PC paste system. In the literature, there is no study which is related leaching in the PC system containing the class C fly ash.

An SCC/SCM is a flowing material used in both construction and repair works. The flowing property of the mixes is provided by a high amount of powder materials and superplasticizer. While an SCC is widely used in the production of building elements, construction of hydraulic structures, and concrete roads, an SCM is used to repair cracked concrete in restricted areas or to investigate some properties of the PC systems in a laboratory. Powder materials used in an SCC/SCM are fly ash, silica fume, rice husk ash, granulated blast furnace slag, metakaolin, limestone powder, and various kinds of stone powders (Parisot et al., 2016; Sua-Iam and Makul, 2015). Powder materials used in an SCC/SCM can vary from region to region. Fly ash has been widely used in an SCC/SCM because it is abundant and cheap (Sua-Iam and Makul, 2015; Hemalatha and Ramaswamy, 2017).

The chemical composition of fly ash obtained as a by-product in thermal power plants varies according to the type of coal burned. Therefore, fly ashes produced in thermal power plants are classified according to their chemical composition. The classifications of fly ash, according to the ASTM (ASTM C 618, 2017) and TS EN 197-1 (2012) standards, are given in Table 1. Some fly ashes, as powder materials, are not used in the concrete industry because their chemical compositions do not satisfy the ASTM (ASTM C 618, 2017) or TS EN 197-1 (2012) standards. Therefore, they are sent to landfills. One of the major problems of thermal power plants is the disposed fly ash in landfills. The disposed fly ash causes environmental problems by air pollution and groundwater contamination due to the leaching of metals from fly ash. The amount of disposed fly ash at landfills has been drastically increasing due to industrial development and urbanization. Therefore, it is very important to make efforts to convert the disposed fly ash to a useful product in the concrete industry.

In this paper, the use of disposed fly ash in SCM has been investigated as an alternative to other powder materials. Although previous researches have provided significant insights on the use of any kind of fly ashes in SCM, there has been a lack of research on the use of disposed fly ash at the landfill. In this work, some physical-mechanical and durability properties of SCM containing disposed fly ash are investigated and compared with those of original fly ash. The optimum amount of disposed fly ash to be used in SCM is determined by taking into account leaching of Ca²⁺, compressive strength, water absorption, sorptivity and drying shrinkage values of samples.

2. Materials and methods

2.1. Properties of materials used

In this study, the fly ash from the Kangal Thermal Power plant in Turkey was taken into consideration. The chemical compositions of the powder materials were determined by XRF method. The samples of powder materials were prepared as a pellet of pressed powder. A cylindrical sample die and a hydraulic machine were used to obtain a pellet. The die was filled with powdered material which was then compressed by the hydraulic machine to give the pellet. The prepared pellet was analyzed in the XRF device (DIN EN ISO 29581-2, 2007). The fly ash taken from precipitator of this thermal power plant was called as original fly ash (OFA). The chemical composition of the OFA was given in Table 2.

The percentage of CaO in the OFA was 32.7 while the total amount of SiO₂, Al₂O₃, and Fe₂O₃ was 44.5%. The total of SiO₂, Al₂O₃, and Fe₂O₃ was less than 50%, while CaO was satisfied as it was greater than 10%. The SO₃ amount in the OFA was 12.1%, and this value was greater than the 5% value given in the ASTM (ASTM C 618, 2017). Although the OFA did not conform to the classes given in the ASTM (ASTM C 618, 2017), it was close to the class C fly ash due to its cementing properties (Turgut, 2012).

Because amounts of the CaO and SiO₂ were greater than 10% and 25% values, respectively, they complied with the TS EN standards (TS EN 197-1, 2012; TS EN 450-1, 2013). The amounts of MgO, free CaO, and SO₃ were greater than 4%, 1%, and 3% values, respectively, in the TS EN standards (TS EN 197-1, 2012; TS EN 450-1, 2013). Therefore, the OFA did not conform to the TS EN standards (TS EN 197-1, 2012; TS EN 450-1, 2013) but it was close to the fly ash with calcareous.

Because the OFA does not comply with the relevant standards, it has not been used in the concrete industry. The OFA humidified with water (water/fly ash ratio: 1/3 by weight) has been carried to the landfill by the belt conveyors. The conveying and landfilling of
the MgO in the OFA decreased to 3.6% (Table 2).

The densities of the PC, OFA, and HFA were 3.10, 2.35, and 2.33 g/cm³, respectively. The natural river sand was used with a maximum size of 2.36 mm in the SCMs. The density and water absorption of sand were 2.65 g/cm³ and 1% by weight, respectively. The poly-carboxylates type new HRWRA, having a specific surface area of 3702, 2047, and 2437 cm²/g, respectively. The grinding process was quite easy and fast due to the loose agglomerated nature of the HFA. The SEM micrographs of the OFA and HFA were shown in Fig. 1. Some hydration products like CaCO₃/C₃A and Ca(OH)₂ were identified in the SEM micrographs of the HFA.

Classifications of fly ashes and limit values.

<table>
<thead>
<tr>
<th>Classes</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>SO₃</th>
<th>MgO</th>
<th>LOI</th>
<th>free CaO</th>
<th>Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>&lt;10</td>
<td>&gt;70</td>
<td></td>
<td></td>
<td>&lt;5</td>
<td>–</td>
<td>&lt;5</td>
<td>–</td>
<td>(ASTM C 618, 2017)</td>
</tr>
<tr>
<td>C</td>
<td>&gt;10</td>
<td>&gt;50</td>
<td></td>
<td></td>
<td>&lt;5</td>
<td>–</td>
<td>&lt;6</td>
<td>–</td>
<td>(TS EN 197-1, 2012)</td>
</tr>
<tr>
<td>Calcareous</td>
<td>&gt;10</td>
<td>&gt;25</td>
<td></td>
<td></td>
<td>&lt;3</td>
<td>&lt;4</td>
<td>&lt;5</td>
<td>&lt;1</td>
<td>(TS EN 450-1, 2013)</td>
</tr>
<tr>
<td>Siliceous</td>
<td>&lt;10</td>
<td>&gt;25</td>
<td></td>
<td></td>
<td>&lt;3</td>
<td>&lt;4</td>
<td>&lt;5</td>
<td>&lt;1</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

The densities of the PC, OFA, and HFA were 3.10, 2.35, and 2.33 g/cm³, respectively. The natural river sand was used with a maximum size of 2.36 mm in the SCMs. The density and water absorption of sand were 2.65 g/cm³ and 1% by weight, respectively. The poly-carboxylates type new HRWRA, having a specific surface area of 3702, 2047, and 2437 cm²/g, respectively. The grinding process was quite easy and fast due to the loose agglomerated nature of the HFA. The SEM micrographs of the OFA and HFA were shown in Fig. 1. Some hydration products like CaCO₃/C₃A and Ca(OH)₂ were identified in the SEM micrographs of the HFA.

Classifications of fly ashes and limit values.

<table>
<thead>
<tr>
<th>%</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MgO</th>
<th>SO₃</th>
<th>Free CaO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>62.2</td>
<td>20.0</td>
<td>5.2</td>
<td>3.5</td>
<td>0.9</td>
<td>0.5</td>
<td>1.8</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>OFA</td>
<td>32.7</td>
<td>26.8</td>
<td>12.0</td>
<td>5.7</td>
<td>1.6</td>
<td>0.8</td>
<td>4.3</td>
<td>12.1</td>
<td>3.46</td>
<td>9.7</td>
</tr>
<tr>
<td>HFA</td>
<td>28.8</td>
<td>21.2</td>
<td>8.9</td>
<td>5.0</td>
<td>1.2</td>
<td>0.6</td>
<td>3.6</td>
<td>9.7</td>
<td>0.48</td>
<td>19.75</td>
</tr>
</tbody>
</table>

Table 2

The disposed OFA in these landfills is hydrated fly ash (HFA) because it is humidified in the plant before being conveyed. The hydration of the OFA in the landfill has been continuously caused by the rain and snow waters. Thus, the amounts of MgO, SO₃, and free CaO in the OFA decrease due to its long-term hydration. The free CaO amount in the OFA was about 3.46% by weight, while that of HFA at the landfill area decreased to 0.48%. The SO₃ amount decreased to 9.67% in the OFA from 12.06% in the HFA, while 4.3% of the MgO in the OFA decreased to 3.6% (Table 2).

The HFA was taken from different regions at the landfill. The HFA was milled, and then sieved through a 150 μm mesh. The grinding process was quite easy and fast due to the loose agglomerated nature of the HFA. The SEM micrographs of the OFA and HFA were shown in Fig. 1. Some hydration products like CaCO₃/C₃A and CH₂ were shown in the SEM micrographs of the HFA.

CEM I 42.5N Portland cement (PC) was used in all SCM mixtures. The densities of the PC, OFA, and HFA were 3.10, 2.35, and 2.33 g/cm³, respectively. The natural river sand was used with a maximum size of 2.36 mm in the SCMs. The density and water absorption of sand were 2.65 g/cm³ and 1% by weight, respectively. The poly-carboxylates type new HRWRA, having a specific gravity of 1.06 conforming to the ASTM (ASTM C 494, 2017), were used to achieve the desired workability in all SCM mixtures.

2.2. Preparation of the paste and SCM samples

The Paste and the SCM mixtures were produced by using the OFA and HFA. In both the paste and SCM mixtures, the replacements of PC with the OFA or HFA were 10, 20, and 30% by weight. Three groups of samples were prepared in both the paste and SCM mixtures. The control samples of the paste and SCM contained the only PC. The paste mixtures containing the OFA were called OFAp10, OFAp20, and OFAp30, while those containing the HFA were named HFAp10, HFAp20, and HFAp30. The numbers after the letter p indicated the paste. The SCM mixtures containing the OFA were called OFAm10, OFAm20, and OFAm30, while those containing the HFA were named HFAm10, HFAm20, and HFAm30. The letter m indicated the SCM mixture.

To prepare paste mixtures, 650 g of binder material (PC or PC-OFA or PC-HFA) were mixed with a measured quantity of water in accordance with the ASTM standards (ASTM C 305, 2014). The paste mixture was of normal consistency when the Vicat apparatus rod with 10 mm diameter settled to a point 10 ± 1 mm below the original surface within 30 s after being released. Trial paste mixtures with varying percentages of water were produced until the normal consistency was satisfied.

The SCM mixtures were designed as a water/binder ratio 0.43. The total binder material amount was 640 kg/m³. The SCM mixture proportions are given in Table 3. First, in the mixing process, the binder material and the sand were mixed as dry for 1 min as described by the ASTM standards (ASTM C 109, 2008). Then, the HRWRA chemical admixture and the water were added and mixed for an additional 4 min.

After being conform to the EFNARC guidelines (EFNARC, 2005), the prepared SCM mixtures were poured into the moulds. The samples were demoulded after 24 h, and all samples were cured in the lime-saturated water at 23 ± 2 °C. The 50 mm cube samples were used to determine the compressive strengths at 7th, 28th, and 56th days. The Ca²⁺ ion leaching tests, dry unit weight, water absorption, and sorptivity tests were performed on the 50 mm cube samples on the 56th day. The SCM samples with dimensions of 25 × 25 × 285 mm were used for the drying shrinkage test.

2.3. Fresh paste and SCM mixture tests

2.3.1. Initial and final setting times of pastes

The initial and final setting times of the pastes were determined by using the Vicat apparatus described in the ASTM (ASTM C 191, 2018) standards. In this test, the pastes used were proportioned and mixed to the normal consistency. The initial setting time was the elapsed time required to achieve a penetration of 25 mm to the paste, while the final setting time was less than 1 mm.

2.3.2. Compatibility tests of fresh SCMs

The compatibility of fresh SCM mixtures was investigated by using the mini-slump and V-funnel tests in conformity with the EFNARC guidelines (EFNARC, 2005). As described by the EFNARC, the mini-slump test device was a truncated cone mould. It was placed on a plate and filled with the SCM mixture. Then, it was lifted upwards. The diameters of the SCM spread were measured in two perpendicular dimensions. The average value of the final diameter was calculated. The mini V-funnel flow test for the SCM was also described by the EFNARC (EFNARC, 2005). In this test, the V-funnel was completely filled with the SCM mixture. The bottom outlet was opened by allowing the SCM mixture to flow out. The elapsed flow time (t), measured in seconds, was between the opening of the bottom outlet and the time when the light became visible from the bottom. The deformability and the viscosity of the mixtures were evaluated through the measurement of the mini slump-flow diameter and the mini V-funnel flow time. There were not any segregation and bleeding that were visually observed in the slump flow test. All the SCM mixtures were designed to give a slump flow diameter of 25 ± 1 cm, which was obtained by adjusting the dosage of the HRWR chemical admixture used. Thus, all of the fresh SCMs had the slump flow diameter conforming to the EFNARC guidelines (EFNARC, 2005).
2.4. Hardened paste and SCM tests of samples

2.4.1. Soundness test of paste samples

The test was performed in accordance with BS EN 196-3 guidelines (2016). The test procedure was started by filling up two Le-Chatelier moulds with the fresh mixed paste, closing the cement surface with the two glass plates and fastening the arrangement with a suitable clamp. The moulds were kept in water at 20°C for 24 h. Then, the moulds were introduced into the thermostatic bath for performing the thermal cycle. The water contained in the bath was warmed up following a continuous heating ramp of temperature from 20°C to the boiling temperature in 30 min and maintaining a smooth boiling temperature for 3 h. After that, the samples were taken, even moulded, and the separation between the tips and ends of the mould were measured. This separation was compared with the measured separation between the tips once the sample was allowed to cool to 20°C.

2.4.2. Ca²⁺ ion leaching tests of SCM samples

At the end of the 56 days of curing, the SCM samples were dried in the oven for 48 h at 60°C. The oven was turned off after 48 h, and the samples were allowed to cool to the room temperature in the oven. The liquids with pH levels of 3.5, 7.0, and 10.5 were prepared in glass jars. First, all the jars were filled with an equal volume of pure water with a pH level of 7.0. H₂SO₄ and NaOH were used as pH modifiers to adjust the pH levels of 3.5 and 10.5 in the test environment, respectively. The test samples were left in the liquids in the jar and 5 ml of liquid sample was taken every 24 h. After the liquid samples were taken for every 24 h, the pure water was poured into the jar to complete the liquid volume reduced in the jar. The pH levels of the liquids were then adjusted using the pH modifiers. For the pH level of 7, the liquid in the jar was emptied and the pure water was poured into it. To determine the dissolved Ca²⁺ ions of samples, the 5 ml test solutions were each taken at different sampling times and put into the small glass bottles. Then, these solutions were left overnight in a cooler to allow any remaining insoluble particles to settle. The same process continued for six days. All samples were analyzed for Ca⁻² ions by using a PerkinElmer Optima 5300DV ICPOES type instrument (Demir et al., 2015).

Table 3

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>W/B</th>
<th>W</th>
<th>PC</th>
<th>OFA</th>
<th>HFA</th>
<th>B</th>
<th>HRWR</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.43</td>
<td>275</td>
<td>640</td>
<td>–</td>
<td>–</td>
<td>640</td>
<td>7.68</td>
<td>1328</td>
</tr>
<tr>
<td>OFAm10</td>
<td>0.43</td>
<td>275</td>
<td>576</td>
<td>64</td>
<td>–</td>
<td>640</td>
<td>7.68</td>
<td>1311</td>
</tr>
<tr>
<td>OFAm20</td>
<td>0.43</td>
<td>275</td>
<td>512</td>
<td>128</td>
<td>–</td>
<td>640</td>
<td>9.60</td>
<td>1289</td>
</tr>
<tr>
<td>OFAm30</td>
<td>0.43</td>
<td>275</td>
<td>448</td>
<td>192</td>
<td>–</td>
<td>640</td>
<td>10.88</td>
<td>1268</td>
</tr>
<tr>
<td>HFAm10</td>
<td>0.43</td>
<td>275</td>
<td>576</td>
<td>–</td>
<td>64</td>
<td>640</td>
<td>10.24</td>
<td>1303</td>
</tr>
<tr>
<td>HFAm20</td>
<td>0.43</td>
<td>275</td>
<td>512</td>
<td>–</td>
<td>128</td>
<td>640</td>
<td>10.88</td>
<td>1284</td>
</tr>
<tr>
<td>HFAm30</td>
<td>0.43</td>
<td>275</td>
<td>448</td>
<td>–</td>
<td>192</td>
<td>640</td>
<td>11.52</td>
<td>1264</td>
</tr>
</tbody>
</table>

W: Water; B: Binder; HRWR: High Range Water Reducer.

Fig. 1. SEM image of OFA (Bar = 1 mm) and HFA (Bar = 10 mm).
2.4.3. Compressive strength, water absorption, sorptivity, and drying shrinkage tests of SCM samples

The ASTM standard (ASTM C 109, 2008) was followed in the compressive strength test of samples. For the compressive strength tests of the samples, a load-controlled press with a 900 kN capacity was used. The average loading speed was 1.8 kN/s. The load was applied to the surface of the cube sample with 50 mm side length. The compressive strength was found by dividing the fracture load to the surface area where the load was applied.

The unit weight and water absorption tests of the SCM samples with dimensions of $45 \times 90$ mm were carried out according to ASTM standards (ASTM C 642, 2006). The samples were dried in an oven at 110 °C for 24 h. After the samples were removed from the oven, they were cooled to room temperature and weighed. The weight of the sample was divided by its volume and the unit weight was found. Then, the samples were kept in water for 48 h at about 21 °C. After 48 h, the samples were removed from the water and weighed. The dry weight of the samples was subtracted from the absorbed weight, and the water absorption values were calculated.

The sorptivity tests of the samples with dimensions of $45 \times 90$ mm were carried out according to the ASTM standards (ASTM C 1585, 2013). The lateral curved surfaces of the samples were wrapped by waterproof plastic tape, but the lower and upper circular plane surfaces were not covered. The 5 mm portion of the

![Fig. 2](image)

Fig. 2. Concentration of Ca$^{2+}$ ions released from the SCM as a function of time at fixed pH 3.5 and different OFA and HFA percent replacement ratios.
bottom circular plane surface was retained in the water, and the weight increments of 5, 10, 30, 60, 240, and 1440 min were measured. The sorptivity values of the samples were calculated by weight differences according to the initial sample weights. The sorptivity values of the samples were calculated using the following relation:

\[
\frac{Q}{A} = k\sqrt{t}
\]  

(1)

In this equation, \(k\) was the sorptivity value \((\text{cm} \cdot \text{s}^{-0.5})\). The surface area of the sample in contact with the water was \(A\) \((\text{cm}^2)\). The contact time of the sample with the water was \(t\) \((\text{s})\). The amount of sucked water was \(Q\) \((\text{cm}^3)\). Using the least squares method, a linear relationship was established between the \(Q/A\) and \(t\) values, and the sorptivity values of samples were calculated.

Drying shrinkage tests of the SCM samples were performed in accordance with the ASTM standards (ASTM C 596, 2017). This test determined the change in the length on the drying of the mortar bar with the dimensions \(25 \times 25 \times 285\) mm. The moist cure of samples was made in the moulds for 48 h at 23°C. Then, the samples were removed from the moulds and cured in the lime-saturated water for 24 h. After 72 h, the samples were removed from the water, wiped with a damp cloth, and their length was immediately measured by a comparator. Then, the samples were placed in the air storage for 25 days. The length comparator readings for each sample were made after 4, 11, 18, and 25 days of air storage. Change the length of each sample at each age of air drying was calculated by subtracting the initial comparator reading, which was taken after removal from water storage, from the comparator reading taken at each age of air drying.

3. Results and discussion

3.1. Ca leaching test results of samples

At this stage of the research, the SCMs were obtained by adding the OFA and HFA to PC at different percent replacement ratio, and the calcium solubility behavior of the obtained structures in acidic \((\text{pH } 3.5)\), natural \((\text{pH } 7)\), and alkaline \((\text{pH } 10.5)\) mediums was investigated. The results obtained from the leaching experiment were presented in Fig. 2, Fig. 3, and Fig. 4. The release of \(\text{Ca}^{2+}\) ions showed a significant and continuous increase over the time interval of 0 and 10 days in all experimental conditions, and the dissolution reactions exhibited a second-order kinetics behavior for almost all of the SCM samples.

3.1.1. Effect of the pH modifiers on the Ca leaching

Leaching behaviors of the SCMs where the \(\text{pH}\) values were 3.5, 7, and 10.5 showed that the \(\text{Ca}^{2+}\) ions were highly influenced by the attack of \(\text{H}^+\) and \(\text{OH}^-\) ions and decreased significantly with increasing \(\text{pH}\) values. In the case of acid with a \(\text{pH}\) value of 3.5 as shown in Figs. 2 and 5, the addition of \(\text{H}_2\text{SO}_4\) acid or proton \((\text{H}^+)\) into the medium significantly affected the amount of potentially soluble calcium in the SCM. Because, when the acidic environment caused acidic corrosion, the \(CH\) formed as the hydration product of the cement given in Eq. (2), and the content of potentially soluble solid hydration products. The neutralization reaction did not occur, and the dissolution of \(\text{Ca}^{2+}\) ions in the medium significantly reduced when compared to the acidic medium as shown in Figs. 2 and 5. B

\[
\text{CaO} + \text{SiO}_2 + n\text{H}_2\text{O} \rightarrow 2\text{CaO}\cdot\text{SiO}_2 \cdot (n - 1)\text{H}_2\text{O} + \text{Ca(OH)}_2
\]  

(2)

Therefore, \(\text{Ca}^{2+}\) ions were not only dependent on the chemical reactions between the acid and solid hydration products, but also on the transport of ions in the pore system of the corrosive layer. The rate of the neutralization reaction depends on the proton concentration of the pore solution and the content of potentially soluble solid hydration products. The neutralization reaction proposed for the release of the \(\text{Ca}^{2+}\) ions in the acidic medium is as follows:

\[
\text{Ca(OH)}_2(s) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(l)
\]  

(3)

The neutralization reaction at the different points of the SCM with \(\text{H}^+\) ions dissolved the soluble solid hydration products, which resulted in more \(\text{Ca}^{2+}\) ions entering the pore solution. More pores were formed when the \(\text{Ca}^{2+}\) ions were released, which increased the diffusion of ions in the pore system of the corroded surface (Demir et al., 2015). The results were consistent with the results of Beddoe and Dorner (2005) the simulation studies of corrosion of the concrete surface in an acidic environment (Yuan et al., 2013). In the alkaline environment with a \(\text{pH}\) of 10.5, the absence of \(\text{H}^+\) ions have caused low \(\text{Ca}^{2+}\) ions in the medium since the neutralization reaction did not occur, and the dissolution of \(CH\) was significantly reduced when compared to the acidic medium as shown in Fig. 3. Bérubé et al. (2004) explained the reason of the low...
solubility of calcium ions in the pore solution of concrete in an alkaline environment. They have claimed that different ionic species, such as Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), H\(_2\)SiO\(_4\)/C\(_0\), Al(OH)\(_4\)\(^-\), and so on, might get released into the concrete pore solution over time from the minerals present in the aggregates. However, in the presence of calcium ions, because the C\(_0\)/C\(_S\)/C\(_0\)H and C\(_0\)/C\(_A\)/C\(_S\)/C\(_0\)H products had a very low solubility product, they would easily precipitate even if a small amount of calcium was present in a solution like the concrete pore solution (Bérubé et al., 2004). The explanation confirmed the presence of low Ca\(^{2+}\) ions at high pHs in this study.

The Ca\(^{2+}\) ion concentration at the natural pH values in all the experimental conditions was lower than the concentration in the acidic medium and higher than the concentration in the basic medium due to the precipitation of C\(_0\)/C\(_S\)/C\(_0\)H and C\(_0\)/C\(_A\)/C\(_S\)/C\(_0\)H. Bérubé et al. (2004) reported that the Ca\(^{2+}\) ions required for this precipitation were readily provided by the CH of the solid cement part of the concrete, which allowed the precipitation of C\(_0\)/C\(_S\)/C\(_0\)H and C\(_0\)/C\(_A\)/C\(_S\)/C\(_0\)H.

### 3.1.2. Effect of aging on the Ca\(^{2+}\) leaching

The aging experiments were carried out to observe how the cumulative Ca\(^{2+}\) ions were changing with time under the different experimental conditions. The test results presented in Figs. 2, Fig. 3, and Fig. 4 showed that the Ca\(^{2+}\) ions continued to release from the SCM starting from the first day of the test to the 10th day. At fixed pH 7, as shown in Fig. 3, which was the natural pH value without pH adjustment, the Ca\(^{2+}\) ions slowly started to release from the SCM on the first day and then increased remarkably after the fifth and sixth days, exhibiting behavior between first and second-order reaction kinetics. The CH, C\(_0\)/C\(_S\)/C\(_0\)H, and C\(_0\)/C\(_A\)/C\(_S\)/C\(_0\)H solubility contributed to the increase in the initial Ca\(^{2+}\) ions on the first day, whereas the subsequent increase in the following days was probably the contribution of the dissolution of the SCM structure due to the increased surface area and pores where the dissolution occurred in the lower part of the SCM surface region. The more continuous the dissolution was over time, the greater the surface area and the more pores in the SCM structure was covered, and hence the more released Ca\(^{2+}\) ions. When the effect of aging on the leaching test of Ca\(^{2+}\) ions was examined for all test groups, the same tendency was observed in general. The difference between these test groups was only due to the amount of the cumulative Ca\(^{2+}\) ions released, which were significantly related to the different
pH values of the test mediums and the types and replacement ratios of the fly ashes used.

3.1.3. Effect of the OFA and HFA contents on the Ca\(^{2+}\) leaching

The results of the leaching tests when the OFA and HFA were used at different percent replacement ratios have revealed that the SCMs containing 10% and 20% OFA produced Ca\(^{2+}\) ions at higher amount compared to the control and HFA SCMs at the same percent replacement ratios within the time interval of 0 and 10 days. However, the SCM containing 30% HFA produced more Ca\(^{2+}\) ions than the other SCMs at all pH conditions, as shown in Figs. 2, Fig. 3, and Fig. 4. The results obtained are shown comparatively in Fig. 6 at different OFA and HFA percent replacement ratio and pH values.

As shown in Fig. 6, the increase in the OFA content in fixed pH values have caused more cumulative Ca\(^{2+}\) ions to be released, compared to the control sample except 10% OFA replacement at pH 3.5, which was also very close to the amount of the control sample. However, in the case of the HFA, the cumulative Ca\(^{2+}\) ions exhibited a different behavior than the OFA with the increasing HFA ratios.

**Fig. 4.** Concentration of Ca\(^{2+}\) ions released from the SCM as a function of time at fixed pH 10.5 and different OFA and HFA percent replacement ratios.

**Fig. 5.** Variation of cumulative Ca\(^{2+}\) ions with pH.
Fig. 6. Ca\textsuperscript{2+} ions released from the SCM on the tenth day.

For example, it has been determined that when the OFA was used in the SCM, the Ca\textsuperscript{2+} ions formed were always greater than those formed when the control SCM was used. However, unlike the OFA using HFA, it was observed that 10% and 20% HFA SCMs produced lower Ca\textsuperscript{2+} ions than the control and the OFA samples in the same replacement ratios, but 30% HFA formed more than all the other samples at fixed pH values.

As the fly ash was used and the replacement ratio was increased, it was expected that CH would be converted into a C–S–H gel according to Eq. (4) by a pozzolanic reaction and to bond to the concrete structure resulting in a more impermeable concrete, leading to less released Ca\textsuperscript{2+} ions than the control SCM.

Ca(OH)\textsubscript{2} + Fly Ash + H\textsubscript{2}O → CaO·SiO\textsubscript{2}·H\textsubscript{2}O \hspace{1cm} (4)

However, no pozzolanic reaction has been observed due to the fact that the OFA and HFA used in the study had CaO>10% and were named as near high calcareous and class C fly ash and did not have enough siliceous or siliceous and alumino materials for a pozzolanic reaction. Otherwise, the SCMs consisting of the OFA and HFA would have formed less Ca\textsuperscript{2+} ions than the control SCM. Because a pozzolanic reaction is defined as a chemical reaction among the siliceous and/or siliceous-alumina components in the pozzolan, calcium hydroxide, and water, the fly ash used as pozzolan herein should have excess siliceous and/or siliceous-alumina components.

When the OFA was used and the percent replacement ratio was increased in the SCMs, no significant change in the released Ca\textsuperscript{2+} ions was observed. This result suggested that the OFA did not form a pozzolanic reaction, but created a cementation reaction like PC, resulting in the formation of C–S–H and CH. The cementation reaction of the OFA has yielded almost the same amount of CH production at different OFA ratios, and thus the amounts of Ca\textsuperscript{2+} ions released were not drastically changed. The cumulative Ca\textsuperscript{2+} ions determined in the leaching test were obtained from the dissolution of total CH produced by PC and the OFA.

In the case of the HFA, the SCMs containing 10% and 20% HFA replacements produced a lower amount of Ca\textsuperscript{2+} ions than the control SCM. But the 30% HFA replacement formed the highest amount of Ca\textsuperscript{2+} ions. These results have suggested that the HFA neither gave a pozzolanic reaction nor a cementation reaction like the OFA. Besides the lack of these reactions, i.e., the lack of binding properties, the fact that it was hydrated also caused it to be inert in the SCM without any interaction with the cement. Because if it were not so, the SCMs with the increasing HFA percent replacement ratio would either produce continuously less Ca\textsuperscript{2+} ions than the Ca\textsuperscript{2+} ions released by the control SCM or vice versa. The reason why the HFA at 10% and 20% replacement ratios caused much lower Ca\textsuperscript{2+} ions than the other SCMs was probably due to the fact that the HFA clogged the pores and cracks in the SCM, and thus reduced the surface area of the concrete in an inert way and prevented the CH release. When 30% HFA was used in SCM, the concrete might have lost their tight binding properties, and thus the CH release might have increased by increasing the surface area and pore size due to the excessive addition of the HFA in the SCM. Therefore, the SCMs containing 30% HFA might have produced more cumulative Ca\textsuperscript{2+} ions than the others.

The leaching test results of the HFA-containing SCMs were also supported by the compressive strength test results of this study, and it was determined that the SCMs showed similar compressive strength properties with control SCMs at 10% and 20% HFA replacement ratios, indicating that the structures had similar characteristics (Fig. 11). However, when a 30% HFA replacement ratio was used, the decrease in the compressive strength value indicated that the tight bonding of the SCM structure was deteriorated and most likely new regions had occurred in the SCM structure that would cause CH release. These results have also indicated that the HFA can be used up to 20% by weight and the resulting SCMs are feasible for a CH release and compressive strength properties.

3.2. The setting times and soundness of the pastes

The consistency water of the paste mixtures was shown in Fig. 7. The consistency water of the OFA and HFA paste mixtures were more than that of the control paste mixture. When the replacements of PC with the OFA and HFA were same, the consistency water of the paste mixtures was also the same. The test results related to the setting time of the OFA and HFA pastes were shown in Fig. 8. The initial and final setting times of pastes with the OFA increased were compared to the control and HFA pastes. The initial setting times of all the OFA pastes were the same at all replacements. The initial setting times of the OFA pastes were 1.44 times greater than that of the control paste while those of the HFA pastes at 10, 20, and 30% replacements of PC with the HFA were 1.16, 1.13, and 1.09 times greater than that of the control paste. In other words, the initial setting times of the OFA pastes were 1.24, 1.28, and 1.31 times greater than those of the HFA pastes at 10, 20, and 30% replacements of PC with them. The final setting times of the OFA at 10, 20, and 30% replacements of PC with the OFA were 1.33, 1.26, and 1.24 times greater than that of the control paste. In the case of the HFA, the final setting time of the HFA was the same with control paste at 30% replacement of PC with the HFA while the final setting times at 10 and 20% replacements of PC with the HFA were 1.07 and 1.02 times greater than that of the control paste. The final setting times of the OFA at 10, 20, and 30% replacements of PC with the OFA and HFA were 1.24, 1.23, and 1.24 times greater than those of the HFA pastes. From these test results, it could be said that the HFA effectively reduced the adverse effect of the OFA on the initial and final setting times. This might have been due to two reasons. First, the amount of SO\textsubscript{3} was 9.67% in the HFA while it was 12.06% in the OFA. Because SO\textsubscript{3} in the OFA paste slowed down the rate of hydration of C\textsubscript{3}A, which was one of the main compounds of PC, the setting times of the OFA paste increased when compared to the HFA paste having lower SO\textsubscript{3} than the OFA. Second, some amount of SO\textsubscript{3} was consumed in the hydration products of the HFA after long term hydration of the OFA at the landfill. Thus, because the rate of hydration of C\textsubscript{3}A increased in the HFA pastes, the setting times of the HFA pastes were decreased compared to those of the
OFA pastes. The initial setting times of the HFA pastes at 10 and 20% replacements of PC with the HFA were 1.16 and 1.13 times greater than that of the control paste. The European Standard (ILNAS EN 450–1, 2012) declared that the initial setting time of PC with fly ash should not be more than twice as long as the initial setting time of the test cement alone.

In the soundness test performed with Le-Chatelier, the expansion value of the hardened control paste was zero. The expansion values of the hardened OFA pastes were 0.5, 2.5, and 3.25 mm while those of the hardened HFA pastes were 0.5, 0.5, and 0.6 mm at 10, 20, and 30% replacements of PC with the OFA or HFA. A decrease in free CaO of the HFA decreased the expansions of the hardened HFA pastes.

3.3. Fresh and hardened SCMs properties

The V-funnel flow time test was an important parameter related to the workability of the fresh SCM. The workability of the fresh SCM increased when the flow time decreased. The V-funnel flow times of control, OFAm10, and HFAm10 SCM mixtures were the same while that of HFAm30 was the highest (Fig. 9). The V-funnel flow time of the HFAm20 mixture was equal to that of the OFAm20 mixture. The flowability of the SCMs reduced with the increase of the HFA but their cohesiveness increased compared to the OFA mixtures. The increase in the V-funnel flow time of HFAm30 might have been resulted from the air entraining effect of the HFA. As seen in Fig. 7, compared to the control mixture, the amount of the HRWR increased in proportion to the amounts of the OFA and HFA in all mixtures except the OFAm10 mixture.

The unit weights of the control, OFAm10, OFAm20, and OFAm30 were 2271, 2242, 2211, and 2162 while those of HFAm10, HFAm20, and HFAm30 were 2269, 2191, and 2098 kg/m³, respectively. The unit weights of all SCM samples with the OFA or HFA were lower than that of the control sample. The unit weights of the HFA samples were also less than those of the OFA samples at the same levels of replacements of PC with the OFA or HFA, except for the OFAm20 sample.

Water absorption and the sorptivity values of samples were shown in Fig. 10. The water absorption value of the HFAm10 sample was the lowest and that of the HFAm30 sample was the highest in...
all SCM samples. At 10% replacement of PC with the HFA, water absorption was effectively decreased compared to the other SCM samples. The HFA increased water absorptions of the HFAm20 and HFAm30 samples. The sorptivity value of the HFAm20 sample was the highest and that of HFAm30 was the lowest in all samples. The compressive strength developments of control, OFA, and HFA samples for the 7th, 28th, and 56th days were shown in Fig. 11. The compressive strengths of the SCM samples with the OFA or HFA were lower than that of the control sample at all curing days. At the 7th, 28th, and 56th days, the HFAm10 sample showed the better compressive strength value than those of the other SCM samples with the OFA or HFA while those of HFAm30 were lowest at these time points. The compressive strength values of the control, OFAm10, and HFAm10 samples were 61.1, 53.2, and 59.2 MPa at 28 days while their values were 65.1, 58.7, and 59.9 MPa at 56 days, respectively. From these results, it could be said that the replacement of PC with 10% HFA did not have a negative influence on the compressive strength compared to the control sample. It was possible that the HFA behaved as an inert material like a fine aggregate in the sample. In other words, the HFA behaved like an inert material due to its hydrated nature, having no pozzolanic reactivity and cementing properties.

As seen in Fig. 12, the drying shrinkage values of the samples with OFA or HFA were higher than that of the control sample. At 20 and 30% HFA replacements, the drying shrinkage values were much higher than those of the other samples at all time points. The drying shrinkage values of the OFAm10 and HFAm10 samples were 1.08 and 1.13 times greater than that of the control sample at 25 days. Compared to the control sample containing the only PC, the drying shrinkage value of the OFAm10 sample was feasible.

4. Conclusions

The Ca leaching behaviors of the SCMs prepared using the OFA and HFA at different percent replacement ratios were investigated with the pH values of 3.5, 7, and 10.5 for 10 days. The results revealed that the leaching test was highly influenced by factors such as aging, pH modifiers, and the OFA and HFA percent replacement ratios. The leaching test results were summarized as follows.

- The addition of sulfuric acid to the medium led to chemical reactions between acids, solid hydration products and aggregates, and the transport of ions in the corrosive layer, and thus more Ca\(^{2+}\) ions were released. However, since the solubility product of the C–S–H of C-A-S–H phases in calcium presence was very low in the alkaline environment formed by the addition of NaOH, the Ca\(^{2+}\) ions were precipitated and appeared at low concentrations in the pore solution.

- The aging test showed that the Ca\(^{2+}\) ions were continually increased for 10 days, and the release of Ca ions over time behaved close to the reaction kinetics between the first and second order depending on the pH of the environment.

- No pozzolanic reaction was observed due to the fact that the selected OFA and HFA did not have a high fineness and enough siliceous or siliceous and aluminous materials for a pozzolanic reaction.

- The OFA showed a cementation reaction like PC, resulting in the formation of C–S–H and CH. However, the HFA neither gave a pozzolanic reaction nor a cementation reaction like the OFA. Besides the lack of these reactions, it has been as inert in the SCM without any interaction with the cement. At a low percent replacement ratio, the HFA probably clogged the pores and cracks in the SCM, thus reducing the surface area of the SCM in an inert way and prevented the CH release. At a high percent replacement ratio, i.e., 30% by weight, excessive addition of the HFA in the SCM might have led to the loss of the tight binding properties of the SCM, thus the CH release increased by increasing the surface area and pore size. Therefore, the SCMs containing the 30% HAF might have produced more cumulative Ca\(^{2+}\) ions than the others. These results suggested that the HFA could be used up to 20% replacement with cement by weight, and the resulting SCMs are feasible for CH release and compressive strength properties.

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