Engineering Properties of Ternary Cementless Blended Materials

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Abstract

This study combined three by-products to fully replace cement as cementless blended materials without the need for an alkali activator. The feasibility of the cementless materials was assessed in terms of workability, mechanical properties, permeability, and microscopic properties. An innovation cementless blended material is consisted of desulfurized gypsum, water-quenched blast-furnace slag, and co-fired fly ash, resulting in a ternary mixture. The results were shown to perform well in terms of compressive strength, absorption, and chloride ion penetration. Scanning electron microscopic micrographs revealed that desulfurized gypsum accelerated hardening and improved the compressive strength through the formation of C-S-H and C-A-S-H gels produced by Ca(OH)2, SiO2, and Al2O3. The improvements in permeability can be attributed to the coating of gypsum particles by hydration products. Overall, our results confirm the efficacy of combining 3% gypsum, 60% slag, and 37% fly ash as the cementless composites with excellent strength and permeability.

Keywords: non-cement binder, co-fired fly ash, GGBS, chloride migration, green materials

1. Introduction

The enormous quantity of CO2 produced in the manufacture of cement has prompted efforts to develop green alternatives [1]. Much of this work has focused on the use of fly ash, ground-granulated blast-furnace slag (ggbs), and/or silica fume as a partial replacement for cement, referred to as supplementary cementitious materials [2-4]. At present, construction regulations in many countries stipulate an upper limit on the use of these materials; however, researchers continue efforts to develop new materials that could completely replace cement in civil construction. Alkali-activated cementless composites (AAC) and geopolymers are currently the main focus of this research [5-7]. AAC and geopolymers use fly ash, ggbs, and other supplementary cementitious materials (or their by-products) presenting pozzolanic activity [8-9]. Cementless composites are combined with a sodium/silicate-based alkali activator to promote the activation of AAC or the geopolymer. AAC provides good mechanical properties and excellent durability [10-13]; however, the need for of alkali activator greatly increases the overall cost.

Researchers have shown that using fly ash and slag as a partial or full replacement for Portland cement can immobilize lead and other toxic elements [14-15]. In several materials, these materials have also been used to make bricks and other non-structural elements for construction [16-17]. Nonetheless, there is a pressing need to find other suitable uses for these materials to reduce the cost of reprocessing, avoid the construction of large landfills, and conserve raw materials [18-20].

Taiwan, Korea, and Japan have recently begun developing cementless construction materials which do not impose high energy consumption. Researchers have demonstrated that ggbs can be combined with supplementary cementitious materials to
create materials with compressive strength and durability sufficient for civil construction (30 MPa to 60 MPa) without the need for an added alkali activator [21-25]. Cementless blended materials containing ggbs and circulating-fluidized-bed (CFB) co-fired fly ash have been shown to form strong cementitious materials via hydration reactions without the addition of an alkali activator. These materials have been used to make CLSM, pervious concrete, and RCC [25-28]. The objective in this study was to combine ggbs and co-fired fly ash with desulfurized gypsum to create a novel cementless material for construction. Various combinations of desulfurized gypsum, water-quenched blast-furnace slag, and co-fired fly ash from circulation of fluidized bed combustion were assessed in terms of flowability, compressive strength, absorption, total charge-passed (rapid chloride permeability), chloride diffusion coefficient (accelerated chloride migration), and scanning electron microscopic (SEM) observations. A flowchart of the research methodology is presented in Fig. 1.

![Flowchart of research methodology](image)

**Fig. 1 Flowchart of research methodology**

### 2. Materials and Methods

#### 2.1. Materials

![SEM images of ggbs and CFB](image)

(a) ggbs  
(b) CFB  

**Fig. 2 SEM images of ggbs and co-fired fly ash**

The ternary cementless blended material introduced in this paper combined ggbs, CFB co-fired fly ash, and desulfurized gypsum as an alternative to Portland cement. The first step involved screening the above combined materials through a No. 100 sieve (150 μm). The ggbs (CHC Resources Corporation, Taiwan) had a fineness of 5860 cm$^2$/g and specific gravity of 2.88. The CFB co-fired fly ash (Yuen Foong Yu Corporation, Taiwan) had a fineness of 3000 cm$^2$/g and specific gravity of 2.73. The
desulfurized gypsum (Sing Da thermal power plant, Taiwan) had a fineness of 2300 cm²/g and specific gravity of 2.59. Figs. 2(a)-2(b) respectively present SEM images of the ggbs and CFB co-fired fly ash [27]. As shown in Table 1, the chemical composition of both materials met the requirements of ASTM C989.

Table 1 Chemical composition of by-products

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂ (%)</td>
</tr>
<tr>
<td>ggbs</td>
<td>33.68</td>
</tr>
<tr>
<td>co-fired fly ash</td>
<td>29.47</td>
</tr>
<tr>
<td>desulfurized gypsum</td>
<td>3.44</td>
</tr>
</tbody>
</table>

2.2. Mix design and test methods

Table 2 Mix design (kg/m³)

<table>
<thead>
<tr>
<th>Mix no.</th>
<th>ggbs</th>
<th>desulfurized gypsum</th>
<th>CFB co-fired fly ash</th>
<th>fine aggregates</th>
<th>water</th>
<th>superplasticizers</th>
</tr>
</thead>
<tbody>
<tr>
<td>G50D1</td>
<td>262</td>
<td>3.3</td>
<td>257</td>
<td>1456</td>
<td>280.7</td>
<td>10.6</td>
</tr>
<tr>
<td>G50D3</td>
<td>262</td>
<td>15.9</td>
<td>246</td>
<td></td>
<td>283.3</td>
<td>8.0</td>
</tr>
<tr>
<td>G50D5</td>
<td>262</td>
<td>26.4</td>
<td>236</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G60D1</td>
<td>318</td>
<td>5.3</td>
<td>206</td>
<td>1456</td>
<td></td>
<td>10.6</td>
</tr>
<tr>
<td>G60D3</td>
<td>318</td>
<td>15.9</td>
<td>196</td>
<td>283.3</td>
<td></td>
<td>8.0</td>
</tr>
<tr>
<td>G60D5</td>
<td>318</td>
<td>26.4</td>
<td>185</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In accordance with ASTM C109 specifications, the water/blender ratio (w/b) of the mortar specimens was maintained at 0.55, and the mass ratio of the blender/fine aggregates was 1:2.75. Table 2 lists all of the mix designs used in this study. Superplasticizers were used in accordance with ASTM C494 standards for Type F mixes. The specimens were numbered using letters and numbers to indicate the composition of the blended materials, where G indicates ggbs, D indicates desulfurized gypsum, and the following number indicates the percentage in the mix. For example, G50 denotes 50% ggbs and D1 denotes 1% gypsum. Note however that ternary cementless blended materials also included a large quantity of fly ash. Thus, specimens labeled G50D3 included 50% ggbs and 3% desulfurized gypsum with the remaining 47% made up of CFB co-fired fly ash.

Table 3 Test methods

<table>
<thead>
<tr>
<th>Test methods</th>
<th>Specimen dimensions (mm)</th>
<th>Referenced standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Setting time test</td>
<td>-</td>
<td>ASTM C191</td>
</tr>
<tr>
<td>Flow test</td>
<td>-</td>
<td>ASTM C1437</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressive strength test</td>
<td>50x50x50</td>
<td>ASTM C109</td>
</tr>
<tr>
<td>Absorption</td>
<td>50x50x50</td>
<td>ASTM C642</td>
</tr>
<tr>
<td>Permeability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-steady-state chloride migration test</td>
<td>100x50</td>
<td>NT Build 492</td>
</tr>
<tr>
<td>Micro-structure observation</td>
<td>SEM observation</td>
<td>10x10x1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ASTM C1723</td>
</tr>
</tbody>
</table>

Fig. 3 Device used for non-steady-state chloride migration test
3. Results and Discussion

3.1. Fresh properties

The fresh properties of the ternary cementless blended materials were evaluated in terms of setting time and flowability. Note that setting time included the initial setting time and final setting time, as summarized in Table 4. Under fixed dosage of slag (60% of the cementless blended materials), the addition of desulfurized gypsum greatly decreased the setting time. The lowest setting time (30 min) was observed in the G60D10 specimens. The dosage of desulfurized gypsum was proportional to the formation of C-S-H gel, and the mixes containing desulfurized gypsum also produced larger quantities of ettringite. Note that the ettringite and C₃A dissolved to form monosulfoaluminate and/or hydroxy-AFm phases immediately after the depletion of the gypsum [29-30].

<table>
<thead>
<tr>
<th>Mix no.</th>
<th>Initial setting time (min)</th>
<th>Final setting time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G60</td>
<td>723</td>
<td>976</td>
</tr>
<tr>
<td>G60D2</td>
<td>200</td>
<td>575</td>
</tr>
<tr>
<td>G60D5</td>
<td>52</td>
<td>80</td>
</tr>
<tr>
<td>G60D7</td>
<td>34</td>
<td>53</td>
</tr>
<tr>
<td>G60D10</td>
<td>15</td>
<td>30</td>
</tr>
</tbody>
</table>

The G60 specimens easily met the 110% flowability standard; however, the G50 specimens were unable to do so without a larger quantity of added superplasticizer. Table 5 lists the flowability results obtained for the three G60 specimens. The addition of desulphurized gypsum was shown not to have significant effect on the fluidity of the mix.

<table>
<thead>
<tr>
<th>Testing no.</th>
<th>Mix no.</th>
<th>G60D1</th>
<th>G60D2</th>
<th>G60D3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.5</td>
<td>21.5</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>21.3</td>
<td>21.0</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>21.8</td>
<td>20.6</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>21.5</td>
<td>21.3</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>Ave.</td>
<td>21.5</td>
<td>21.1</td>
<td>21.7</td>
<td></td>
</tr>
</tbody>
</table>

Flowability (%) 115 111 117

3.2. Compressive strength

Fig. 4 presents the compressive strength development curves of G60 specimens containing various quantities of desulphurized gypsum. Compressive strength was shown to increase proportionally with curing age and inversely to the proportion of desulphurized gypsum. At a curing age of 7 days, the strength of all three specimens was similar; however, at 28
days, the compressive strength of the G60D3 specimens was slightly (5%) higher than that of the other specimens. At 91 days, the G60D1 specimens presented the highest compressive strength. These results indicate that the desulfurized gypsum was weaker than co-fired fly ash in terms of its ability to blend with ggbs.

The compressive strength of all cementless specimens approached the target strength of 30 MPa at 7 days, reaching 40 MPa at 28 days. At 91 days, the maximum strength in G60D1 specimens reached 48.5 MPa (a 22% increase from 28 days). This is an indication that in these specimens, the co-fired fly ash and desulfurized gypsum can be regarded as an alkaline excitation material. Following the addition of ggbs, the cementless blended specimens reached the target strength for ternary cementless blended materials. This can be attributed to the reaction of Ca(OH)$_2$ and other hydrated components with water after CaO hydration. Note that ggbs must be mixed with strongly alkaline materials (e.g., co-fired fly ash) to achieve an activated hydration reaction and corresponding hardening.

Fig. 5 presents compressive strength histograms of G50 specimens containing various quantities of desulfurized gypsum. The compressive strength of specimens with 3% desulfurized gypsum exceeded that of the other samples at 7, 14, 28, and 56 days. Note that the G50D3 sample achieved compressive strength of 47.4 MPa at 56 days, which far exceeds the typical target strength of conventional Portland (35 MPa) [24, 31-33].

![Fig. 5 Compressive strength histograms of G50 specimens](image)

![Fig. 6 Compressive strength histograms comparing G50D3 and G60D3 specimens](image)

Fig. 6 presents compressive strength histograms of specimens with a fixed quantity of gypsum (3%) and either 50% or 60% ggbs (G50D3 and G60D3). The compressive strength of G50D3 exceeded that of G60D3 specimens at 7 to 28 days, due to the high proportion of co-fired fly ash. Like conventional fly ash, specimens containing higher proportions of co-fired fly ash achieved the majority of their strength between 28 and 90 days. The retarded hydration reaction associated with the co-fired fly ash caused the molecules to react with water and gain strength at a later stage. Note that the compressive strength of G60D3 specimens exceeded that of G50D3 specimens at 56 days. Thus, engineers should consider the late strength development of composites containing co-fired fly ash and apply them accordingly.

### 3.3. Absorption

Absorption testing is an indirect approach to the evaluation of pore structure and compactness in cementitious materials. The main active components in co-fired fly ash, desulfurized gypsum, and ggbs include CaO, SiO$_2$, Al$_2$O$_3$, MgO. As shown in Fig. 7, the absorption of all specimens decreased with curing age. The absorption of G60D1 and G60D3 dropped off significantly at 91 days, whereas the absorption of G60D5 began slowing after just 14 days. Increasing the proportion of desulfurized gypsum was shown to reduce the density of the cementless materials through the formation of pores via the expansive formation of ettringite. The formation of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) can be attributed to reactions
between gypsum and calcium aluminate hydrates (e.g., 4CaO·Al₂O₃·13H₂O) [34]. However, the different proportions in each group of G50 specimens produced similar results, and the effect of desulfurized gypsum on absorption was not significant, as shown in Fig. 8.

3.4. Penetration depth of chloride ions and SEM observations

Fig. 9 presents the results of accelerated chloride ion migration tests of G60 specimens under non-steady-state conditions. All three test mixtures presented low diffusion behavior (penetration depth), and the depth of penetration decreased significantly with an increase in curing age. The initial current measurement of 22 mA revealed that the inclusion of pozzolanic materials affected electron ionization. The penetration depth of G60D1 specimens was the lowest at 91 days and presented a linear relationship with compressive strength (see Fig. 10). Desulfurized gypsum, co-fired fly ash, and ggbs contain large quantities of aluminum and iron oxides, such as Al₂O₃ and Fe₂O₃, which react easily with CaO in the hydration products to form CaO·Al₂O₃·Fe₂O₃. Likewise, reactions of CaO with Al₂O₃, Fe₂O₃, and H₂O in the hydration products form hydration reactants such as 3CaO·Al₂O₃·4H₂O or 3CaO·Fe₂O₃·10H₂O, which are key factors in the development of strength in cementitious materials [35-36]. This is likely the main issue reducing the transmission of chloride ions. Fig. 9 presents regression analysis of compressive strength tests and chloride migration tests, showing that chloride ion permeability was negatively correlated with compressive strength and that the relationship was linear.

The SEM images in Figs. 11-12 show that few of the particles in the G50D1 and G60D1 specimens presented the polygonal shape characteristic of ggbs, indicating that there was insufficient fly ash and ggbs to participate in the hydration
reaction. The low absorption of the G60D3 and G60D1 specimens can be attributed to the fact that the ggbs particles were covered and most of the pores were filled with C-S-H colloids. The G50D1 specimens presented a small number of needle-shaped ettringite (Af) and hexagonal flake-shaped or rose petal-shaped monosulfide calcium aluminate (AFm) hydration products. G60D1 specimens presented a large number of needle-shaped ettringite (Af) and flake-shaped (AFm) hydration products. This is an indication that there was a sufficient quantity of co-fired fly ash and ggbs to produce a complete hydration reaction, which may explain the high compressive strength. Note however, that the large quantities of Af and AFm had a swelling effect, which left the specimens somewhat porous (i.e., susceptible to absorption and greater penetration depth). The SEM images also revealed needle-like C-S-H particles stacked irregularly on the surface of the gypsum, slag, and co-fired fly ash particles. These results are consistent with those reported in previous studies [23, 26, 31, 37], in which the main hydration products were C-S-H and C-A-S-H gels with high strength development in later curing stages (56 to 91 days).

4. Conclusions

This study examined ternary cementless blended materials without an alkali activator. The engineered properties of the proposed cementless materials meet or exceed those of conventional concrete based on Portland cement. The compressive strength of the G60D1 specimens reached 48.5 MPa at 91 days. The addition of desulfurized gypsum increased the setting time due to the formation of monosulfoaluminate and hydroxy-AFm phase.

It has previously been demonstrated that cementless materials containing ggbs are capable of self-hydration when combined with industrial by-products even in the absence of an alkali activator. It appears that the large quantities of calcium oxide and calcium oxide in co-fired fly ash and desulfurized gypsum met water as hydrogen, resulting in the rupturing and dissolution the glassy ggbs particles. The consumption of calcium hydroxide to produce C-S-H colloid as a hydration product increased the compactness and hardness of the specimens, resulting in strength values comparable to those of cementitious materials. All of the specimens demonstrated extended pozzolanic reactions, which reduced the number of capillary or gel pores as well as the connectivity between pores. The G60D3 specimens presented the highest compressive strength and highest resistance to absorption and chloride ion penetration. An excessive quantity of desulfurized gypsum tended to hinder hydration, which had negative effects on the engineering properties and durability of the resulting cementless materials. These cementless materials could help to reduce carbon dioxide emissions and conserve the consumption of raw materials.

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Conflicts of Interest

The authors declare no conflict of interest.

References


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