RHEOLOGICAL BEHAVIOUR OF CEMENTS BLENDED WITH CONTAINING CERAMIC WASTES

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ABSTRACT

This research paper analyses the performance of new blended cements containing 10 and 20 % ceramic sanitary ware (SW) and construction and demolition waste (C&DW) to determine their suitability as future supplementary cementitious materials for commercial cement manufacture. The effect of these recycled materials on cement rheology was studied and an analysis of covariance was run to quantify the impact of each factor. The addition of ceramic waste reduced shear yield stress, whereas construction and demolition waste (C&DW) had the opposite effect, raising yield stress. These behavioural differences between the two types of industrial waste would have a direct effect on the final applications of the resulting blended cement.

Keywords: sanitary ware, construction and demolition wastes, supplementary cementitious materials, rheology

INTRODUCTION

The amount of waste attributable to productive activities such as construction, heavy industry or ceramic or automobile manufacture has risen steeply in the recent past, causing serious environmental damage as a direct result of its generation and subsequent dumped in landfill. This has heightened public sensitisation and led to the implementation of new sustainability-based environmental policies that encourage the recycling and re-use of such waste (1).
Essentially three strategies are deployed in the re-use of waste: valorisation in new materials, elimination and reduction of volume (2).

The versatility of the cement and concrete industry affords it huge potential (3) to absorb new materials of varying origin, either as supplementary cementitious materials (SCM) in cement or as a coarse or fine aggregate in mortar, concrete and road base and sub-base manufacture.

In this context, the use of supplementary cementitious material in blended cements helps to reduce clinker production (and hence CO₂ emissions), avoids landfill disposal needs, and can improve the performance of new building materials and thus prolong the service life of buildings; all of which contributes to sustainable development (4).

Over the last 10 year, research has pursued alternatives to the traditional materials used in commercial cement manufacture, with studies focusing on industrial waste such as ferroaluminous and manganese – siliceous slag, paper sludge, ceramic waste and agricultural research such rice husks and sugar cane.

The usage of ceramic waste from sanitary ware industry and construction and demolition waste as supplementary cementitious materials in cement manufacture is at present a novel research line at international level, as there are no standards applicable yet on its reuse. Nowadays, there are several papers (5-7) that study the possibility of using different ceramic waste (tiles, bricks, etc.) as active addition in the manufacturing of cement, taking advantage of their chemical composition to reach satisfactory results in respect of durability and mechanical properties. On the other hand, there are a series of works that analyse the possibility of introducing these kinds wastes (ceramic sanitary ware waste (3, 8-15) and C&DW (16)) in substitution of natural coarse aggregate (sand or gravel) when producing concrete or mortar for several uses.

The inclusion of new materials as supplementary cementitious materials in cements generally has an adverse effect on the workability of cement-based materials. Hence the importance of understanding the effect of their inclusion on material handling and on-site placement (17-19).

The aim of the present study was to investigate the effect of the partial replacement (10 or 20 wt. %) of ceramic sanitary ware (SW) and construction and demolition waste (C&DW) on the rheological properties of new blended cements. Analysis of covariance (ANCOVA) was also conducted to study the impact of the factors and co-variables on these results.
MATERIALS

The ceramic sanitary ware waste used in this research was provided by the Spanish ceramic sanitary ware industry, which manufactures over seven million units yearly. In this manufacturing process inevitably generates a percentage of products deemed unsuitable for sale, regardless of any improvements made to the process. The two principle reasons for the rejection of these items are breakage or defective shape, defects which do not affect the intrinsic properties of the ceramic material, or firing defects as a result of too much or too little heat, which in this case do affect the physical-chemical properties.

The second waste used was recycled sand supplied by a Spanish C&DW management plant. At this time, despite the decline in construction business, 23 million tonnes of C&DW are generated yearly in Spain, 17 % of which is re-used. This recycled fine aggregate contents different components, such as concrete, natural aggregates, ceramics (tile, bricks, sanitary ware, etc.), asphalt and other particles.

Figure 1 shows the chemical composition of the two types of waste by X-ray fluorescence. This shows that both comprised primarily silica (SiO₂), although the sum of the alumina (Al₂O₃) and lime (CaO) contents accounted for over 24 and 27 % of the total in SW and C&DW, respectively. While other oxides such as Fe₂O₃, MgO and sulphates (SO₃) were also present, their concentrations were under 2.70 %. The C&DW exhibited a much higher loss on ignition (12 %) than the SW (0.23 %), due primarily to decarbonation of the calcite present in the former.

Mineralogically speaking, ceramic sanitary ware waste contained quartz, feldspar, zircon and hematites, while quartz, calcite and feldspar were identified as the main mineralogical phases in the C&DW.
The percentage passing of the starting materials was analysed on a Sympatec HELOS 12A particle size analyser. The results obtained are shown in table 1. The percentage passing of the wastes (SW and C&DW) is similar. The cement has a percentage passing at 90% lesser than these wastes. This result is in consonance with the particle size distribution curves, where the main wastes peak was shown by 13.8 μm, while in the OPC was centred at 19.5 μm.

Table 1. Percentage passing of the materials

<table>
<thead>
<tr>
<th>Percentage passing (%)</th>
<th>Size particle of the materials (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
</tr>
<tr>
<td>10</td>
<td>1.31</td>
</tr>
<tr>
<td>50</td>
<td>9.96</td>
</tr>
<tr>
<td>90</td>
<td>29.77</td>
</tr>
</tbody>
</table>

Specific surface data were obtained by measuring N₂ adsorption isotherms on a Micrometrics ASAP 2000 analyser. The result shows that the surface area of the C&DW (6.58 m²/g) was much higher than the found for the SW (1.36 m²/g).

The chemical composition of the ordinary Portland cement used (CEM I 52.5 R), supplied by Lafarge, a cement manufacturer at Toledo, Spain.

The water-based modified polycarboxylate (SIKA ViscoCrete®-5920) superplasticiser added was supplied by SIKA, Madrid, Spain.

**EXPERIMENTAL PART**

Rheological measurements were taken on a TA Instruments CS500² rheometer fitted with a specially developed interrupted helical impeller, rotating in a stationary cylinder and operating in controlled shear rate mode. These test conditions have been used in previous studies on high flowability grouts and pastes (17). The shear rate and stress at a series of pre-established shear rates were logged with Navigator® software, after calibration with known liquids to define these two parameters in absolute units. The software provided sufficient flexibility to vary the shear rate suitably over time to ensure that any structure in the paste would be broken down to equilibrium before measurements were taken. The temperature was held at a constant 20 ºC by circulating water through a jacket surrounding the outer cylinder.

The pastes were mixed by hand for 2 min using 100 g of the blended powder (cement, cement plus SW or cement plus C&DW) and the amount of water (containing dissolved superplasticiser as appropriate) required for water/binder ratios of 0.35, 0.375, 0.40, 0.45 and 0.50, and immediately poured into the cylinder, which was mounted on the
rheometer. With the Navigator® software running, shear measurements were taken as soon as the impeller was automatically inserted and started up.

Table 2. Programme of experimental mixes with SW and C&DW

<table>
<thead>
<tr>
<th>Superplasticiser</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>water/binder ratio</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>0.35</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>0.40</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>0.45</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>0.50</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Tables 2 list the material combinations used in the experimental programme, where the w/b ratio was 0.35 and the superplasticiser 0 %, fluidity was insufficient to run the test in the pastes containing either of the supplementary cementitious materials (SW or C&DW). Consequently, at that w/b ratio, assessment of paste rheology was only possible after the inclusion of the admixture. At the other extreme, pastes at 0.45 and 0.50 w/b ratio were too unstable to test because of sedimentation. The dosages of superplasticiser added were 0.1, 0.2 and 0.3 wt. % of the binder.

Finally, the statistical analysis was carried out with the analysis of covariance (ANCOVA). This analysis was used to assess the findings and simultaneously study the effect of all the factors (water/cement ratio, superplasticiser content and measuring time), as well as their interactions, by eliminating the variability generated by the presence of co-variables (type of waste and replacement ratio). The differences between the levels of a given factor were found using the Bonferroni multiple comparison tests.

As the statistical study was conducted with a significance level of $\alpha = 0.05$, only those factors or co-variables whose p-value was less than 0.05 were regarded to have a significant effect on the results obtained. IBM SPSS Statistics 20 software was used for the statistical analysis.

RESULTS AND DISCUSSION

Rheology

The flow curves (Figure 4) were analysed with the standard Bingham model (Eq. 1) (20) used to study the rheological properties of non-Newtonian fluids such as cement pastes, mortars and concretes:
\[ \tau = \tau_0 + \mu \dot{\gamma} \]  

(1)

where \( \tau \) is shear stress; \( \tau_0 \) is yield stress, \( \mu \) is plastic viscosity and \( \dot{\gamma} \) is shear rate.

Figure 3a-e shows the effect of the superplasticiser content and water/binder ratio on yield stress in all the pastes studied (OPC, SW10, SW20, C&DW10 and C&DW20). Note that yield stress declined with increasing SW or C&DW content (19) and water/binder ratio, regardless of the type of supplementary cementitious materials used, revealing the impact of these factors on rheological behaviour.

Figure 3. Effect of the water/binder ratio and superplasticiser content on yield stress by type and percentage of waste: a) OPC, b) SW10, c) SW20, d) C&DW10 and e) C&DW20

Moreover, depending on the type of waste and, to a lesser extent, the replacement ratio, yield stress reacted differently. The inclusion of SW had a favourable effect on
rheological properties, lowering the yield stress, whereas C&DW increased the yield stress for a given water/binder ratio and superplasticiser dosage. This behaviour is probably due to the effect of binder specific surface on water demand, which rose with increasing BET and consequently raised yield stress.

The rise in yield stress observed with the increasing percentage of C&DW waste was also found to be related to the greater hydration of cement components such as alite and aluminate, physically and chemically induced by calcite.

The effect of the superplasticiser on yield stress in pastes with a w/b ratio of 0.40 is depicted in Figure 4. Here also, increasing admixture content reduced yield stress regardless of the water/binder ratio used. The admixture dosage and type of waste were also observed to modify the effect of the superplasticiser, whose performance may have been impacted by the chemical composition (alkalis, sulfates, C₃A and so on) (21) and specific surface (22) of the waste. This effect should be investigated more thoroughly in future research.

![Figure 4. Variation in yield stress with superplasticiser in pastes with a w/b ratio of 0.40](image)

Figure 4. Variation in yield stress with superplasticiser in pastes with a w/b ratio of 0.40

Figure 5a–e shows the variations in yield stress over time in pastes with a w/b ratio of 0.40. According to this figure, the loss of paste fluidity was retarded with rising percentages of superplasticiser, since one of the effects of the admixture is to slow the hydration reaction in cement particles (20). At the same time, yield stress was observed to remain practically constant in pastes with 20 % SW or C&DW at superplasticiser contents of 0.2 and 0.3 %.
Figure 5. Variation in yield stress over time for pastes with a water/binder ratio of 0.40: a) OPC, b) SW10, c) SW20, d) C&DW10 and e) C&DW20

Finally, for lower percentages of admixture (0 and 0.1 %), all pastes were found to stiffen with time.

Statistical analysis

Table 3 shows the results of the ANCOVA on the effect of the factors (water/binder ratio, superplasticiser content and measuring time) and co-variables (type of waste and replacement ratio) on the yield stress of the pastes studied. The statistical model accounted for 70 % of the variability observed.
Table 3. Analysis of covariance data (ANCOVA)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Type III sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected model</td>
<td>82,452^a</td>
<td>7</td>
<td>11,778</td>
<td>169</td>
<td>0.000</td>
</tr>
<tr>
<td>Intersection</td>
<td>76,898</td>
<td>1</td>
<td>76,898</td>
<td>1,109</td>
<td>0.000</td>
</tr>
<tr>
<td>Mixing time</td>
<td>2,890</td>
<td>1</td>
<td>2,890</td>
<td>41.7</td>
<td>0.000</td>
</tr>
<tr>
<td>W/b ratio</td>
<td>44,281</td>
<td>1</td>
<td>44,281</td>
<td>638</td>
<td>0.000</td>
</tr>
<tr>
<td>Amount of superplasticiser</td>
<td>39,832</td>
<td>1</td>
<td>39,832</td>
<td>574</td>
<td>0.000</td>
</tr>
<tr>
<td>Percentage of waste</td>
<td>83.9</td>
<td>1</td>
<td>83.9</td>
<td>1.2</td>
<td>0.272</td>
</tr>
<tr>
<td>Type of waste</td>
<td>12,863</td>
<td>1</td>
<td>12,863</td>
<td>185</td>
<td>0.000</td>
</tr>
<tr>
<td>Interaction between percentage and type of waste</td>
<td>785</td>
<td>1</td>
<td>785</td>
<td>11.3</td>
<td>0.001</td>
</tr>
<tr>
<td>Error</td>
<td>35,204</td>
<td>508</td>
<td>69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>265,811</td>
<td>516</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected total</td>
<td>117,657</td>
<td>515</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a. R squared = 0.701 (corrected R squared = 0.697)

The data revealed that mixing time, amount of superplasticiser and the water/binder ratio all had a significant (p < 0.05) effect on paste yield stress, as observed in the findings discussed in section 3.1.

Of the two co-variables, type of waste had a significant effect (p < 0.05), whereas replacement ratio (p = 0.272 > 0.05) did not and this suggests that, although the two wastes have opposite effects on rheology, the difference between 10% and 20% replacement is not significant. That the interaction between type of waste and replacement ratio was significant (p = 0.001 < 0.05) confirms the results.

CONCLUSIONS

The following conclusions can be drawn from the results of the present study.

1) The addition of ceramic sanitary ware waste (SW) as a partial replacement for cement reduces yield stress, whereas the inclusions of construction and demolition waste (C&DW) increases yield stress.

2) Reducing the water/binder ratio reduces workability.
3) The type of waste plays an essential role in paste rheology, and while the replacement ratio has no significant effect, the interaction between these two variables affects yield stress significantly.

4) Based on their effects on paste rheology, low concentrations of sanitary ware and construction and demolition waste can be regarded as feasible new supplementary cementitious materials in concrete manufacture.

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References


