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Improving strength development of wastepaper sludge ash by wet-milling

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Abstract

Wastepaper sludge ash (WSA) requires relatively higher proportions of water than Portland cement (PC) when used as a single binder. This high water demand may be reduced by the addition of secondary binders such as ground granulated blastfurnace slag (GGBS), which improves the hydration properties of the mixes. Based on the already determined physico-chemical properties of WSA a new method of paste preparation is introduced which also enhances the cementitious properties of WSA. The method utilises a wet-grinding stage prior to mixing. Pre-treatment of WSA prior to the addition of GGBS enhances effectively the strength development of the blended binder. Higher compressive strengths are obtained for the paste cube samples made using the new method of paste preparation than those achieved by conventional dry mixing methods.

Keywords: Wastepaper sludge ash; Ground granulated blastfurnace slag; Wet milling; Strength development

1. Introduction

Incineration of wastepaper sludge produces ash, which when leached with alkali produces a material which has potential applications as binder [1,2]. Similar cement-like behaviour to that of wastepaper sludge ash was observed when sewage sludge was incinerated with lime [3]. Veerapan et al. [4] carried out research on residual waste ash produced by Aylesford Newsprint Ltd. in Kent, UK as to its use as a binder in the manufacture of concrete blocks. The performance and properties of the concrete blocks which were manufactured were shown to be acceptable for commercial applications. Previously published work had provided a closer insight into the raw material and its complex cementitious properties including high water demand and the hydration products [5]. WSA absorbs water faster and more extensively than other cementitious materials such as PC. When water is added to Portland cement (PC) all the discrete particles commence hydrating and this continues from the surface of individual particles inwards at a decreasing rate as the layers of reaction products build up. Unlike PC, WSA particles show a wide range of size and composition, and therefore do not behave in a similar manner. Some phases react more rapidly than others and produce a chemical environment appropriate for other phases to hydrate or possibly contribute to pozzolanic reactions, while some phases are wholly inert. Early observations suggest that two primary phenomena occur upon addition of water to WSA:

- dissolution of the free lime available and formation of "slaked" lime, and
- occurrence of soluble alumina and silica in solution subsequent to lime hydration.

First the hydroxyl ions released from the hydrated lime will make the solution alkaline, later the glassy phases begin dissociating and freeing alumina and silica into the system. It is the objective of this paper to investigate and develop

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possible methods of improving the very low strength observed for neat WSA paste and of minimising this problem by mechanical means such as wet-grinding of material prior to mixing.

Recent investigations do not recommend WSA to be used as a cement on its own due to the fact that it does not develop adequate strength [2,5]. This is mainly because of the relatively high water demand of WSA which is thought to be due to its porous nature and to the free lime that constitutes approximately 5% of material. The free lime removes a significant amount of water when it hydrates and produces unsoundness i.e. increase in volume on precipitation of hydrated lime results in disruption to the hardened paste. The addition of a second binder such as GGBS is found to be a possible solution for controlling the rapid setting and expansion of WSA. The role of GGBS is not only to reduce the proportion of expansive product by diluting the system but also to increase the effective water to WSA ratio which enables a greater degree of CaO hydration to occur before setting. It also provides a surface upon which lime can be absorbed and subsequently interact, thus activating slag hydration in the enhanced pH environment. This minimises the degree of disruption to the hardened fabric, reduces the overall expansion and contributes to strength development.

The reactivity of WSA is in part attributable to the presence of lime which is freely available and renders the WSA-water system very alkaline. The prevailing chemical conditions may be comparable to those of the lime-clay–GGBS system, in which slag activation and hydration bring about enhancement of the formation of the strength contributing silicates and aluminates [6]. The strength increase is attributed to the formation of additional C-S-H gel derived from GGBS hydration.

Apart from the free lime, which hydrates immediately on addition of water, the finely divided (~0.1 μm) α'-C_2S/bredigite is another key component that hydrates and produces calcium silicate hydrate (C-S-H) gel and calcium hydroxide (CH). Also present in WSA is calcium aluminosilicate glass which reacts with water slowly in an alkaline environment. In order to take full advantage of the hydration characteristics of the WSA–GGBS system the damaging effects of the lime hydration need to be minimised relative to the beneficial effects of the hydration of the glassy phase and the α'-C_2S/bredigite.

2. The material

The WSA material was provided by Aylesford Newsprint Ltd. In Kent, UK. The material comprises the principal crystalline components gehlenite, calcium oxide, bredigite and a α'-C_2S (stabilised with Al and Mg) together with small amounts of anorthite and calcium carbonate and traces of calcium hydroxide and quartz. WSA has been found to contain about 5% free lime (CaO) and also 5% calcium carbonate content. The existence of the amorphous glassy phase has been demonstrated by electron microscopy and accounts for approximately 20% of the material [5].

Table 1
The chemical composition of WSA and GGBS

	Oxide composition of the WSA	Oxide composition of the GGBS
SiO_2	25.70	35.50
Al_2O_3	18.86	12.0
Fe_2O_3	0.87	0.40
CaO	43.51	42.0
MgO	5.15	8.0
Na_2O	1.56	–
K_2O	1.31	–
P_2O_5	0.52	Density (kg/m^3): 2800
TiO_2	0.68	Blaine specific surface (m^2/kg): 510
MnO	0.04	
BaO	0.04	
SrO	0.09	
SO_3	1.05	

Analytical data supplied by Southern Water for Aylesford Newsprint.

GGBS contains more than 90% glassy phase and is known to be a latently hydraulic material in a highly alkaline environment [5]. The GGBS material used contains approximately 42% CaO and 35% SiO_2, and is less dense but has higher specific surface than PC. Table 1 shows the chemical composition of WSA and GGBS used in this study.

3. Experimental

3.1. Mix design grinding and paste preparation

When used as a single binder, WSA shows inadequate strength development, but it does reach acceptable strength characteristics when blended with a second binder such as GGBS. Recent work has followed BS 1881-125:1986 i.e. dry mixing followed by the addition of mix water [5]. In fact it is common practice to prepare multi-binder pastes by dry mixing the various binders followed by the addition of water and wet mixing. In order to provide a more homogeneous mix in which GGBS particles could move more freely to be activated to stimulate the latent hydraulicity, the following procedure was adopted in the current work:

- addition of water to the WSA and grinding the mix,
- addition of the second binder followed by mixing the paste.

The new study of WSA paste preparation involves two stages, and is designed to comply with the high water requirement of the WSA, and to provide a more uniform environment in which the second binder activation could occur more easily. Both manual grinding and ball-mill grinding were used to provide a WSA slurry before the second binder was added.

Manual milling was done in a pestle and mortar for some of the paste samples prior to the addition of GGBS. The time of milling was between 5 and 10 min depending on the water binder (w/b) ratio used. It is notable that during grinding there was a sudden reduction in the viscosity of the mix which was most marked in the pastes of low w/b ratio. Suddenly the mixes which initially appeared dry and poorly workable became very fluid. It should be noted that this effect occurs as part of the mixing process prior to subsequent stiffening and setting.

The new paste preparation method gives rise to a change in mix density. As the milling process proceeds it has been observed that the volume of the mixes is reduced giving rise to an increase in the density of the resulting paste. This physical phenomenon which occurs suddenly during milling was examined by adopting the following procedure:

The unmilled sample: the WSA was mixed for a few minutes after adding the exact amount of water to give a mix of w/b:0.90; a cylindrical steel container (100 ml volume) was filled with the paste and weighed after levelling the surface of the paste.

The milled sample: the cylindrical steel container was filled with the WSA slurry (w/b:0.90) made via milling.

Wet ball milling was also applied for some of the samples to compare the influence of longer milling times namely 10, 15 and 20 min to those of manual milling. The ball-mill used is a porcelain type with balls of 10–20 mm diameter. It rotates at a constant rate of 25 rpm. The proportion of water and WSA was determined beforehand for various combinations of WSA/GGBS and w/b ratio. For example, if samples of 50/50 WSA/GGBS ratio were of interest the initial mixes were made with 100% water added to WSA. The ball-mill was charged with the correct quantity of water/WSA mixture and run for a specified period of time. The time of milling was varied while the w/b ratio was kept constant and vice versa. For manual milling a physical indicator of rheological change i.e. a decrease in mix volume or an increase in mix density, as described above was used as a signal to stop milling. For the ball-milling no simple indication of rheological change was possible although from observation of manual milling these changes would also be expected to occur. Thus, different periods of time were allocated for the ball-milling i.e. 10, 15 and 20 min milling times.

3.2. Preparation and testing of paste cubes

Paste cubes of dimensions 50 mm × 50 mm × 50 mm were manufactured from the binary WSA–GGBS mixes using both the conventional dry mixing method and the new paste preparation method. Three w/b ratios were used, 0.45, 0.50 and 0.55. Various combinations of WSA and GGBS were used, although a high proportion of the tests were carried out on the 50/50 WSA/GGBS blending ratio as this composition had been found previously to be the optimum combination for maximum strength [5]. The cube samples were demoulded after 24 h. The cubes were water cured at 20° ± 2 °C for periods of 7, 28 and 90 days. Cube densities were determined in accordance with BS 1881-114:1983.

Unconfined compressive strengths of the cube samples were determined in accordance with BS 1881-116:1983 using a constant load rate of 10 kN/min.

The Vicat apparatus with a 10 mm diameter rod was used to assess the relative consistency of the pastes manufactured. The length of the penetration of the rod during the first 15 min was monitored using the 10 mm diameter rod. The higher the viscosity of the paste the shorter the length of rod penetration, and these data were utilised as a means of comparing consistency of pastes made with different w/b ratios.

4. Results

4.1. Particle size analysis

Early indications from particle size analysis suggested a wide range of particle sizes. The results of particle size analysis done by sieving are shown in Fig. 1.

4.2. Paste volume/density change due to wet-milling

The densities of the fresh paste made with WSA at w/b:0.90 unmilled and manually milled are 1360 kg/m^3 and 1420 kg/m^3 respectively, which shows an increase of about 4%.

4.3. Compressive strength

4.3.1. Manually milled samples

Fig. 2 shows the unconfined compressive strength analysis results for the cubes made via wet-milling and those

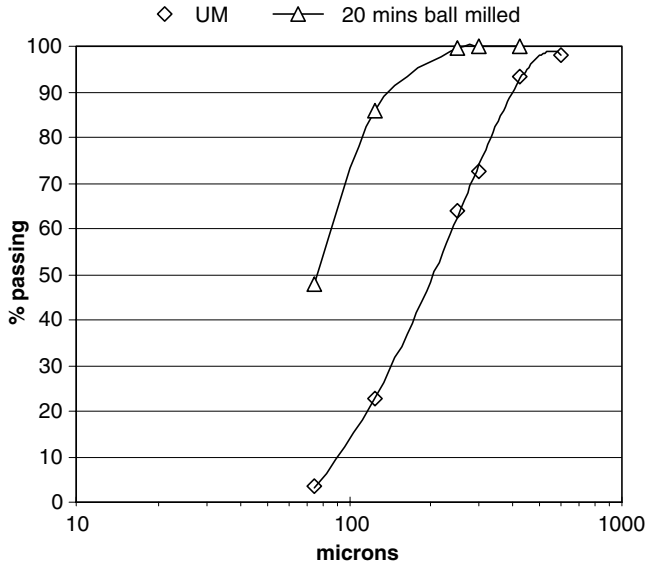

Fig. 1. Particle size analysis of unmilled (UM) and 20 min ball-milled WSA slurry.

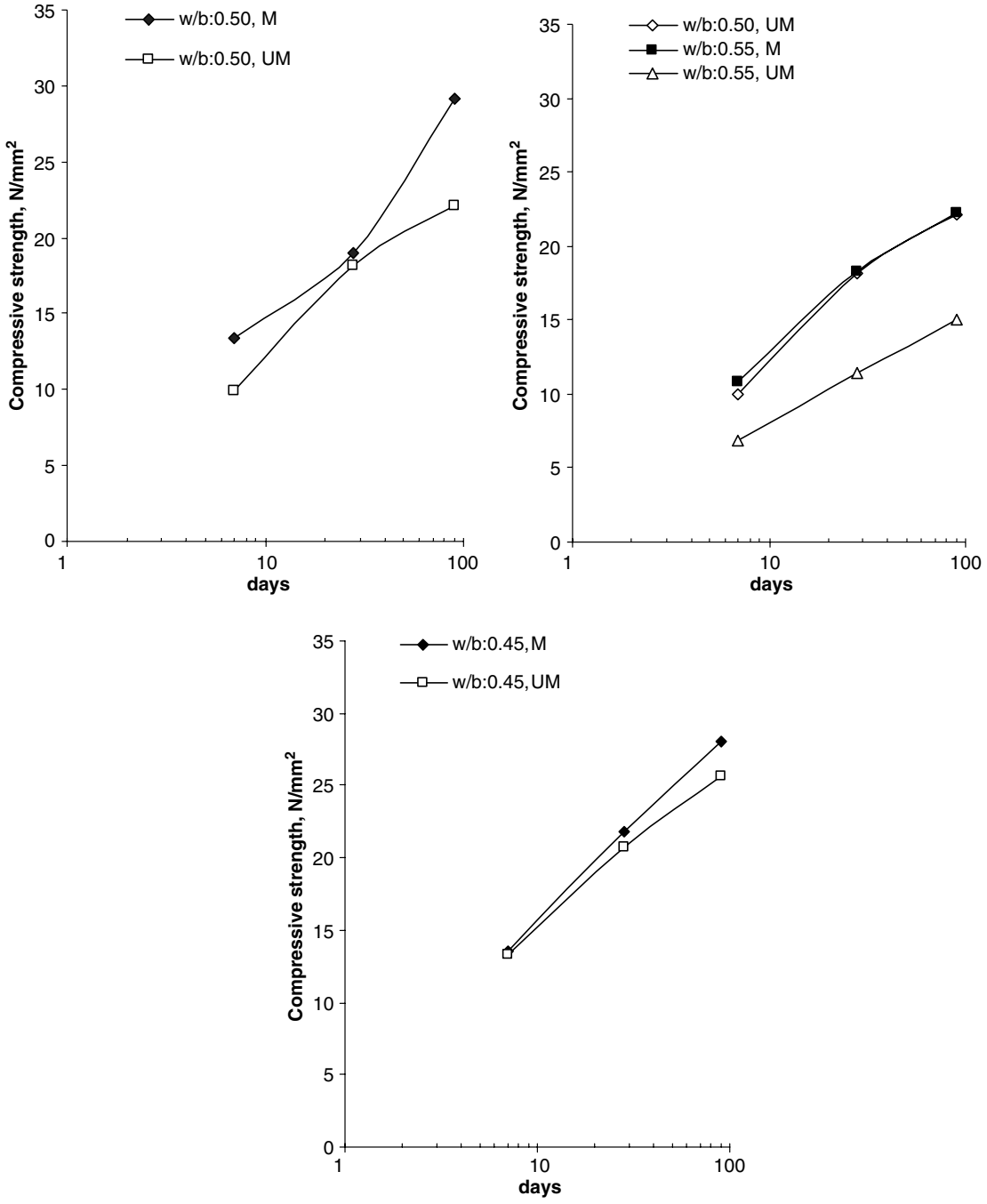

Fig. 2. Compressive strength versus curing time for WSA paste cubes (both manually wet-milled and unmilled) at various w/b ratios.

made without milling. The milled (M) cubes show higher strengths than do the unmilled (UM) cubes at all the w/b ratios tested. The graphs are designed to demonstrate the strength differences achieved during 7, 28 and 90 days. Samples made at the lower w/b ratio (w/b ratio: 0.45) show an increase in strength of about 15% at 90 days for the milled samples compared to the unmilled ones. For w/b ratio 0.50 the milled cubes show about 30% higher 7-day strength than those unmilled. The milled sample (w/b ratio: 0.50) demonstrates a slightly lower rate of strength development between 7 and 28 days relative to the unmilled sample, but it improves considerably between 28 and 90 days showing 28% higher strength after 90 days curing. The strength results for the unmilled cubes of w/b ratio 0.50 resemble those of the milled cubes of w/b ratio 0.55.

Fig. 3 shows the densities of the pastes together with the 28 day strength results for comparison. It is evident that the milled samples have developed higher densities than those of unmilled samples. Also, as would be expected, strength increases with increase in density. This indicates that wet-milling enables greater mix densification and hence greater strength development.

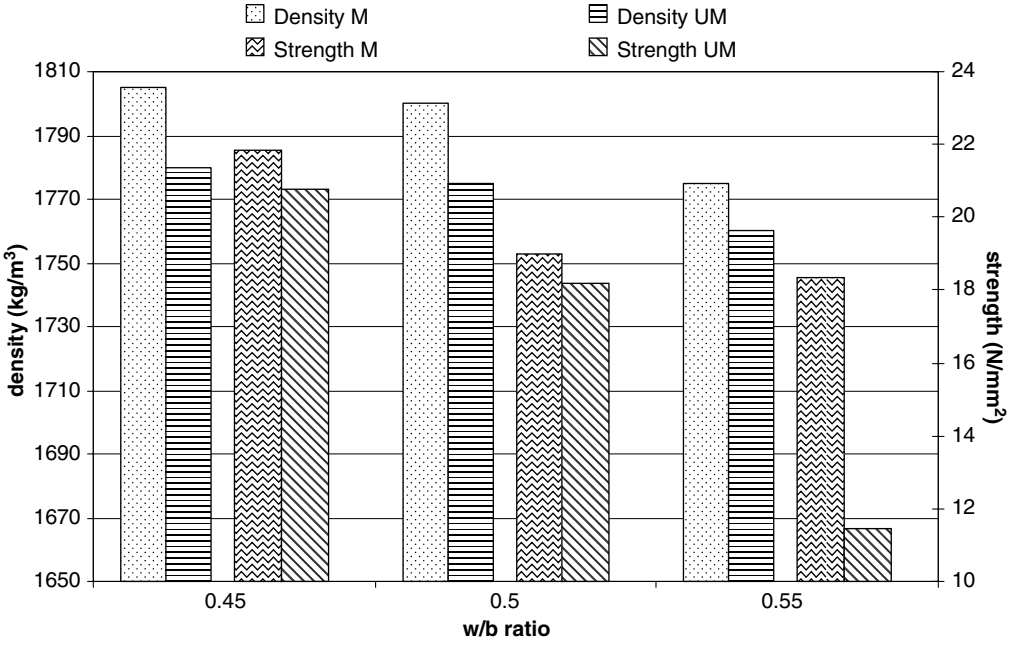

Fig. 3. Density and 28 days compressive strength of WSA hardened paste (manually wet-milled and unmilled) at various w/b ratios.

4.3.2. The ball-milled samples

Fig. 4 shows the strength results of cubes with a w/b ratio of 0.50 manufactured from mixes prepared via wet ball-milling. As Fig. 4 demonstrates the cubes manufactured after 15 min milling gave generally higher strengths than did those that had been milled for 10 min or 20 min. The 7-day old pastes made using a 20 min milling time show slightly higher strength than those with a 15 minute milling time, however, the 15 minute milled samples achieve higher strength in the longer term i.e. 28 days. In general there is a systematic increase in strength with curing time between 7 and 28 days. For water binder ratio 0.50 the binder composition WSA/GGBS 60/40 was used instead of that of 50/50 because it was observed that at extended milling times the initially fluid slurry became more viscous. In particular, when WSA/GGBS pastes of w/b ratio <0.50 were made, less water needed to be used in the initial WSA slurry resulting in a drop in consistency of the final paste at extended milling times.

Figs. 5 and 6 present the strength results for the more flowable pastes (i.e. w/b ratio: 0.55 and 0.60). A systematic increase in strength occurs between 7 and 28 days with 15 min of milling time being the optimum milling time to achieve the maximum strength (Fig. 5). Fig. 6 shows the compressive strengths of WSA/GGBS 50/50 hardened pastes cured at 7, 14, 28 and 90 days employing 20 min wet ball-milling time at w/b ratios 0.55 and 0.60. As might be expected the lowest strength values are associated with

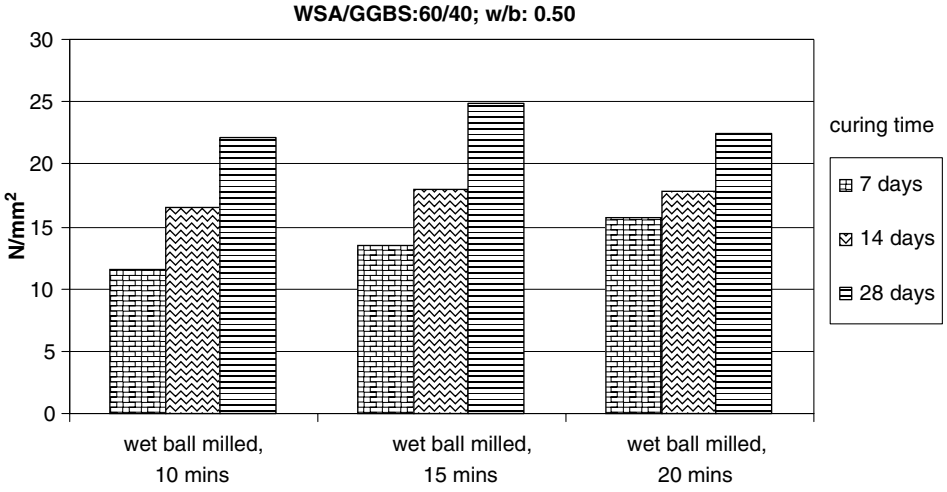

Fig. 4. Compressive strength WSA/GGBS hardened paste at w/b ratio: 0.50 and various curing times employing different wet ball-milling times.

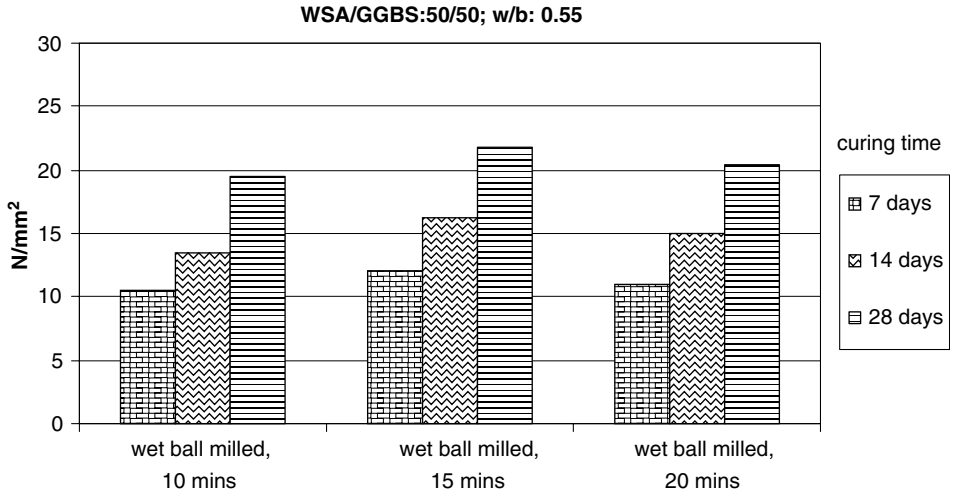

Fig. 5. Compressive strength of WSA/GGBS 50/50 hardened paste of various curing times employing different wet ball-milling times at w/b ratio: 0.55.

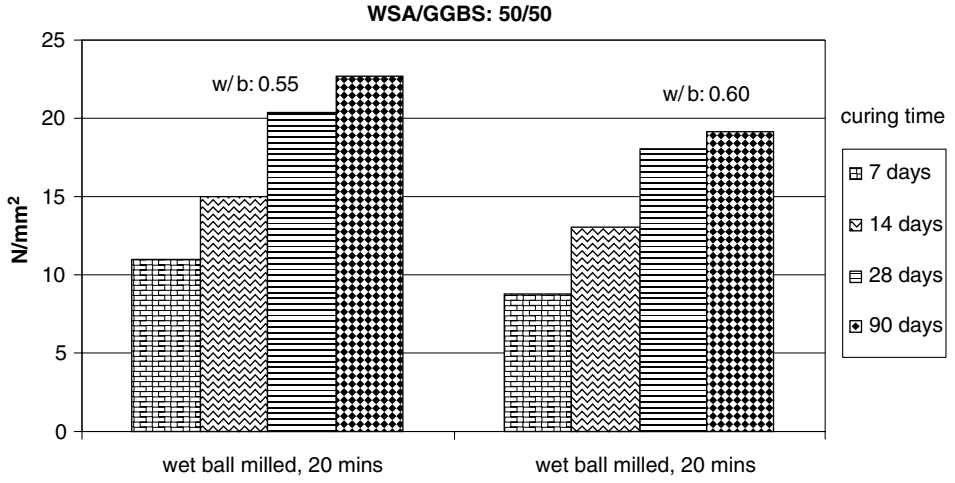

Fig. 6. Compressive strength of WSA/GGBS 50/50 hardened paste cured at 7–90 days employing different wet ball-milling times at w/b ratio: 0.55 and 0.60.

the highest w/b ratio and there is an average drop in strength of 15% for all curing times as the w/b ratio is increased from 0.55 to 0.60.

Fig. 7 shows the density results of WSA/GGBS hardened paste wet-milled for 10, 15 and 20 min at various curing times. The graphs indicate that 15 min is the optimum milling time to give maximum density. Also, as might be expected density decreases with increase in w/b ratio.

4.4. The setting analysis

Fig. 8 plots rod depth (10 mm) versus age for milled (manually) and unmilled fresh pastes of composition 50WSA.50GGBS at four different w/b ratios (0.45, 0.47, 0.50 and 0.55). This indicates how the consistency of the milled and unmilled pastes differs at various w/b ratios and at various ages. Also, the following remarks can be made:

(i) penetration is consistently higher for the unmilled pastes than for the wet-milled pastes, irrespective of the w/b ratio or the age of the paste,
(ii) at low w/b ratios (0.45 and 0.47) the rate of stiffening of the unmilled paste is greater than that of the wet-milled pastes resulting in convergence of the two curves to give a common time of set,
(iii) at high w/b ratios (0.50 and 0.55) the rate of stiffening of the unmilled pastes is slower than that of the wet-milled pastes which means that the two curves diverge and the time of set of the unmilled pastes is greater than that of the milled pastes.

5. Discussion

WSA develops a degree of unsoundness due to the expansion caused by CaO hydration after setting. Bai

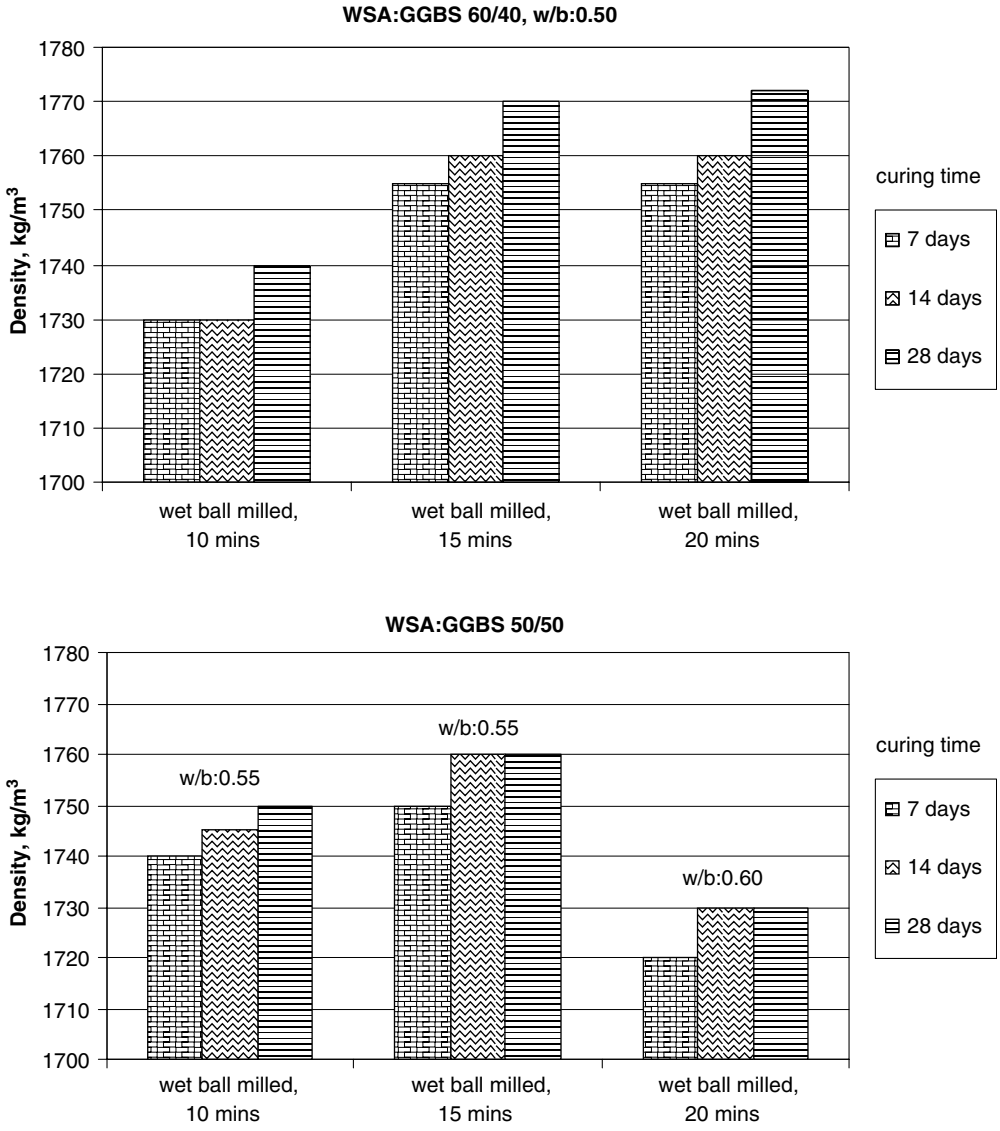

Fig. 7. Density of WSA/GGBS hardened paste at various curing times and w/b ratio, wet ball-milled for 10, 15 and 20 min.

et al. [5] attributed the low strength of cured WSA paste in part to this unsoundness and to the resulting pore structure of the paste. They pointed out that the role of slag in the WSA–GGBS system is twofold: (i) it dilutes the system and allows for more hydration of CaO to occur before setting and (ii) it provides a means for lime consumption (a lime sink) which also subsequently activates hydraulic reactions. Therefore, the replacement of WSA with GGBS alleviates the detrimental expansive effect of lime hydration resulting in strength increase over extended curing periods.

The new method of paste preparation i.e. two stages of milling and mixing contributes to the improved strengths by reducing the particle size and accelerating the lime hydration. The particle size distribution of milled samples is different from that of the unmilled samples in that a finer particle size distribution is present in the pre-treated slurry (i.e. milled slurry, see Fig. 1). Milling reduces particle size and increases the total surface area available for the hydration process and allows greater densification. Once milled the most reactive components in WSA: the free lime, the amorphous glassy phase (which was found to be in the size range 5–10 μm in diameter with a silica/alumina ratio of 1.46 [5]) and the α'-C_2S will be released in fine fractions. Thus, not only does milling render the fresh paste denser, as mentioned earlier with a sudden change of density of the mix as milling proceeds, but it also allows for more hydraulic particles to hydrate and occupy the originally water-filled spaces.

The lime hydration reaction suggests a great deal of water removal occurs at the beginning of hydration which is why WSA is observed to be a water-demanding cementitious material [2]. Finer, more dispersed and denser slurries are produced for the milled pastes. This brings about a greater degree of CaO hydration before the pastes start setting, hence reducing the degree of disruption to the hardened fabric and minimising the overall expansion.

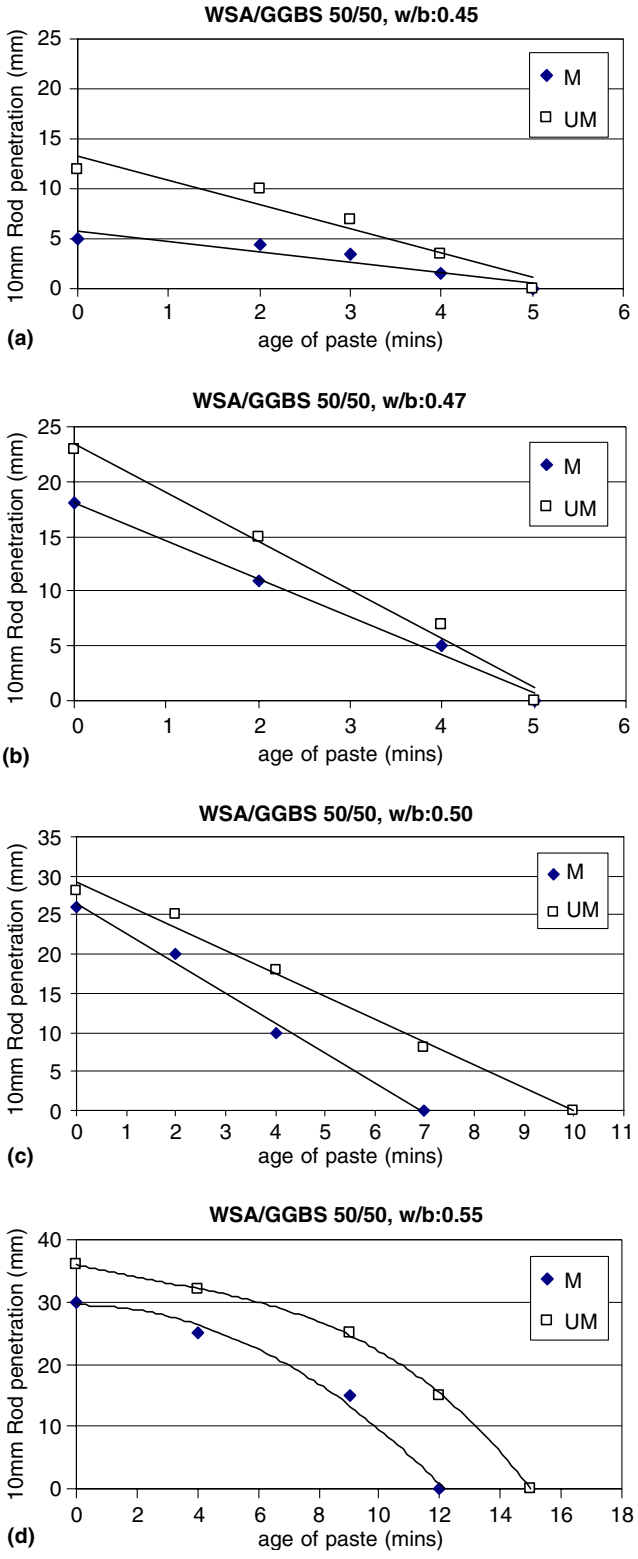

Fig. 8. The consistency of fresh pastes made from WSA/GGBS 50/50 at various w/b ratios.

Comparison of the compressive strength versus curing time plots for the milled and unmilled WSA pastes shown in Fig. 2 supports this explanation. Figs. 4–6 illustrate the results of further development of WSA slurry preparation from manual milling to ball-milling, which brings about even higher strengths.

Wet milling increases the density of the manufactured pastes (see Fig. 7) and improves the strength development (see Fig. 2). Among the manually milled pastes those with higher water content (0.50 and 0.55 w/b ratio) show improved long-term strength development. This is despite the lowest density observed in the pastes with w/b ratio: 0.55, indicating manual milling is more effective when sufficient water is available. In general, the density increase in the hardened paste made via wet-milling compared to those of unmilled paste may seem insignificant being of the order of 1–2%, however, this may be expected because relatively high w/b ratios are used. The employment of wet-milling as well as the addition of GGBS contributes to the refinement of pore volume in the hardened paste and is likely to account for the corresponding strength increase determined, although small in value.

The wet-milling process is an effective mechanical method for separating and dispersing the constituent particles in WSA. While manual milling is regarded as an appropriate technique for a laboratory study ball-milling is more efficient allowing for slurry production on a larger scale with a more controllable size reduction. Figs. 2, 4, 5 and 6 demonstrate the progress made in strength gain. Employing 15 min ball-milling time gave the highest 28 day strength at w/b ratios 0.55 (Fig. 5).

6. Conclusions

The wet-milling of WSA applied prior to addition of GGBS and mixing, improves the strength development of the hardened pastes. The milling process allows a more homogenous evenly dispersed mixture to be produced that forms a denser more active paste facilitating hydration of dicalcium silicate (α'-C_2S) and GGBS. The optimum ball-milling time is 15 min for the ball-milling system used. Above or below this the strength is lower (e.g. for 10 min grinding) or the consistency deteriorates (e.g. for 20 min grinding). When applied on a larger scale and under different conditions wet-milling may need further optimisation but the procedure for mix preparation (i.e. initial slurry and addition of second binder) will need to be maintained.

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