



An investigation into the strength development of Wastepaper Sludge Ash blended with Ground Granulated Blastfurnace Slag

E. Mozaffari*, J.M. Kinuthia, J. Bai, S. Wild

Division of Civil and Mechanical Engineering, Department of Engineering, Faculty of Advanced Technology, the University of Glamorgan, Pontypridd, Wales, CF37 1DL, UK

ARTICLE INFO

Article history:

Received 6 February 2007

Accepted 2 July 2009

Keywords:

Wastepaper Sludge Ash

Slag

Lime

Setting

Strength

ABSTRACT

Wastepaper Sludge Ash (WSA) contains reactive components such as free lime (CaO), and less reactive and inert mineral species. When water is added to WSA some constituents hydrate faster than others, lime being the fastest giving high alkalinity to the solution. If the WSA is combined with Ground Granulated Blastfurnace Slag (GGBS) then the latter, activated by the raised pH, produces new minerals which will contribute further to the strength development of the paste. The kinetics of the hydration reactions and the possible ways of making lime a more effective contributor in activating other phases in the WSA–GGBS system are discussed.

Crown Copyright © 2009 Published by Elsevier Ltd. All rights reserved.

1. Introduction

The paper recycling process produces a waste ash which has potentially useful applications in construction [1–3]. The possible use of WSA as a construction material derives from its cementitious properties [1]. This cement-like behaviour is brought about by a series of chemical reactions occurring when water is added to WSA. Hydration is the most important mechanism when studying cementitious materials, as a number of chemical reactions take place. As a result of hydration new minerals (hydration products) are formed which can be crystalline or amorphous [4]. WSA exhibits different setting and hydration behaviour [5] in comparison with PC, as also does sewage sludge ash produced via an incineration process [6,7].

WSA contains considerable amounts of aluminosiliceous material, most of which appear to be combined with calcium [8]. It can facilitate the hydration of latently hydraulic materials as well as undergo its own hydration. For example, the hydration of GGBS is activated by the alkaline environment provided by calcium hydroxide in WSA in the presence of water, to form compounds possessing cementitious properties at room temperature, including calcium silicate hydrate gel (C–S–H) [9]. Most amorphous or glassy calcium aluminosilicates (e.g. GGBS) together with pozzolanic materials (e.g. PFA), when used with Portland cement (PC) reacts with calcium hydroxide in the cement paste and produces additional C–S–H gel resulting in increased concrete strength [4].

For WSA, on addition of water the reactions start with the rapid exothermic hydration of CaO in the WSA to produce portlandite, together with the hydration of α' -C₂S and bredigite [8] to produce cementitious components. Also, the elevated pH environment produced by the portlandite activates the hydration of amorphous calcium aluminosilicate glass in the WSA. Unfortunately, however, WSA alone is not very cementitious partly as a result of unsoundness from the CaO hydration, partly because it contains a significant proportion of non-hydraulic products including gehlenite, and also possibly because some hydraulic particles are inaccessible by water. It has been shown that an improvement in the formation of hydration products can be achieved by combining WSA with GGBS [1,2,8,10]. These paste samples achieve improved performance in setting and strength development. These improvements may be compared with those in the clay–lime system where the presence of GGBS produces more cementing agent (C–S–H). More importantly is the effect of partial substitution of lime with GGBS in altering the kinetics of hydration and in the formation of new minerals in this system, which has been studied by Wild et al. [9,11]. Pera and Amrouz [12] also studied the production of Metakaolin by calcining paper sludge in the temperature range of 700 °C to 800 °C. The chemistry and mineralogical composition was studied, and it was shown that Kaolinite mineral in the sludge converted to Metakaolin. However no Metakaolin is detected in WSA due to the much higher combustion temperatures.

Chaipanich et al. [10] reported that WSA paste at standard consistence (w/b:0.65) sets very rapidly (initial setting time 5.9 min) and is therefore totally unsuitable for use alone as a cement in conventional mortar and concrete. Whether this is due to the nature of particular constituents in the ash and/or the hydration characteristics of its active components needs to be established. The authors also observed that for WSA–GGBS blended pastes a marked increase in the time to initial set occurred as the GGBS:WSA ratio increased. The addition of the

* Corresponding author.

E-mail addresses: e.mozaffari@ntlworld.com, eazem101@yahoo.co.uk (E. Mozaffari).

second binder and the observed alteration in setting time is a good indication of possible changes in the rate at which the hydration products are created. Therefore, GGBS is found to reduce the proportion of expansive products by consumption of CaO when added to lime-bearing materials such as WSA or clay–lime systems.

Wet-milling of WSA prior to the addition of GGBS, also provides a greater degree of CaO hydration to occur before setting [5]. The objective of this paper is to further investigate the rate of the formation of the hydration products both for the milled and unmilled WSA samples by monitoring lime hydration (pH measurement), setting time, heat of hydration and strength development in a binary binder system.

2. Paper recycling at Aylesford Newsprint Ltd., UK

Paper recycling reduces the environmental impact of paper manufacture. At Aylesford Newsprint Ltd. UK, the wastepaper sludge is de-watered and pressed to approximately 63% solids with a potential ash content of between 55 and 60% prior to incineration in the combustor. The combustor is a bubbling fluidised bed boiler and is designed to burn approximately 200 tonnes of de-watered sludge per day producing 26 tonnes/hour of steam to generate electricity for use in the paper-making process. The furnace is designed to meet the requirements for dioxin destruction (850 °C–1200 °C for a 2-second residence) with rapid cooling in the range 200 °C to 400 °C to prevent dioxin reformation. About 100 tonnes of ash per day is discharged from the silos and conditioned with water to prevent dusting during disposal to landfill. The capital investment costs of incineration are estimated to be high [13], however, utilisation of the residual ash may compensate for the cost of landfill disposal and its long-term environmental impact. Moreover, waste heat recovered from the combustion gases, to generate electricity can in part compensate for the high capital costs, in that the burning of fossil fuel is replaced by a renewable resource.

3. The material

3.1. WSA, formation and characteristics

The heat treatment in the fluidised bed is a non-equilibrium treatment and the incineration process results in an ash material with various crystalline and non-crystalline components. The physico-chemical processes involved in the incinerator may be studied in the same way as volcanic ash deposition is done in geology [14]. The main factors influencing mineral formation in volcanic ash emissions are the temperature, the composition and the rate of cooling of the migrating fluids. Neville [4] pointed out that for PC the kinetics of the heating and cooling processes determine the formation of its main components, affecting the degree of crystallisation and the amount of amorphous material present in the cooled clinker. This is likely to be the case for WSA since a glassy phase is created and bredigite ($\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$) and α' - C_2S phases separate on cooling. The heating and cooling processes during the incineration provide an environment in which some mineral phases tend to bind others together.

The mineralogical compositions of WSA batches, over the period that research on WSA has been carried out at the University of Glamorgan, have been found to be fairly consistent. Bulk samples received from Aylesford Newsprint Ltd. have been characterised for crystalline phases using X-ray powder diffraction (XRD) analysis. Thermogravimetric (TG) analysis has been used to follow the hydration of WSA–GGBS blends [1,8,10]. The original sludge comprised about one-third kaolinite, one-third calcium carbonate and one-third cellulose fibre. The final material contains about 5% free lime (CaO), which was determined in accordance with BS EN 196-2 [15], a tiny amount of $\text{Ca}(\text{OH})_2$ from the effects of atmospheric moisture and also 5% calcium carbonate plus approximately 20% amorphous glassy phase [8], together with the hydraulic cementitious phases (α' - C_2S and bredigite) and the non-hydraulic phases gehlenite and anorthite.

There is also a trace of quartz from the fluidised bed. Changes in the composition of WSA, particularly the free lime content, can occur over time as reported by Aylesford Newsprint Ltd. The method of blending WSA with GGBS may however be regarded as a solution to this problem taking into account that the ratio of the binders can be adjusted to compensate for any possible alterations in the lime content in the mix.

3.2. WSA hydration

WSA absorbs water faster and more extensively than other typical cementitious materials such as PC. When water is added to PC all the discrete particles commence hydrating and this continues from the surface of the 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 other phases are wholly inert [8]. Immediately upon addition of water to WSA two primary phenomena occur: a) dissolution of the free lime available and formation of “slaked” lime, and b) dissolution of alumina and silica subsequent to the increase in pH.

First the hydroxyl ions released from the hydrated lime make the solution alkaline, the α' - C_2S and bredigite begin to hydrate, and subsequently the glassy phases begin dissociating, further freeing alumina and silica into the system. This all creates a suitable environment for the calcium ions to bind with Al_2O_3 and SiO_2 in solution to produce more C–S–H gel [9]. However rapidly or slowly the alumina/silica bearing phases dissociate, it may be possible to manipulate the reaction rates in order to affect the rate of setting and hardening. This in turn could provide improved performance of construction products manufactured using WSA–GGBS cement.

3.3. WSA, size analysis and textural properties

When sieved in wet conditions, 25% of WSA powder passes sieve No 120 mesh (125 μm) and 75% through 50 mesh (300 μm) indicating the coarseness of the material relative to PC. Fig. 1 shows the Malvern particle size analysis result for a WSA powder sample passing 125 μm sieve size. Fig. 2 shows the SEM images of WSA particles demonstrating the state of porosity and agglomeration of the material. The roughness at the surface of a single particle shown in Fig. 2a is thought to be a result of agglomeration of separate mineral grains produced during the incineration process. Fig. 2b is a close-up view, which also indicates that some mineral grains are bound together by others.

3.4. WSA, GGBS chemical and physical properties

Table 1 shows chemical analysis of WSA and GGBS. The density of GGBS was 2800 kg/m^3 and its Blaine specific surface was 510 m^2/kg .

4. pH tests

The initial slurry made from WSA–water is quite alkaline due to the reaction of free lime with water, which releases hydroxyl ions (OH^-) into solution. Also released immediately upon addition of water are calcium ions (Ca^{++}). The degree of alkalinity of the solution depends on the availability of the free lime to react with water and the interaction of lime with other mineral components within the WSA particles (see Fig. 2). To investigate these phenomena further a number of pH tests were carried out at various intervals subsequent to the addition of water. Two approaches were taken:

- pH testing of WSA solution relative to quicklime solution of equivalent concentration
- pH testing of wet-milled WSA solutions.

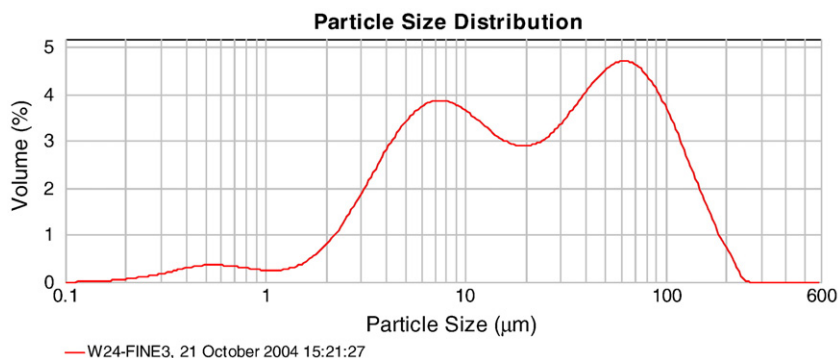


Fig. 1. Malvern particle size analysis of WSA material passing 120 mesh sieve ($\sim 125 \mu\text{m}$).

4.1. pH, WSA versus quicklime

In this series of tests, two 500 ml flasks were filled with deionised water; 8 g WSA powder was added to one flask and to the other 0.4 g quicklime powder was added. The 0.4 g quicklime was chosen to replicate the 5% free lime concentration in WSA. The pH and temperature probes were then put into the solution making sure that the flasks were completely sealed on top. pH readings were recorded at various intervals while continuously stirring the solutions in the flasks at a temperature of $23 \pm 0.5^\circ\text{C}$ (monitored by placing a temperature probe

in the flasks). On two other occasions WSA was initially milled in a pestle and mortar for 2 and 4 min separately and the above procedure was again followed.

4.2. pH, samples wet-milled

4.2.1. Mortar and pestle milling

For the second approach the WSA was treated in a similar manner to the way ore minerals are treated during mineral processing. Here, the raw materials are ground to liberate valuable constituent minerals [16]. Sink–float analysis is also often used for analysing the concentrate and tailing samples. Froth flotation, which is a method of separating coal particles from mineral constituents, is also used for analysis of milled samples. The flotation tests produce concentrate and tailing samples, and the tailings from the first flotation stage become the feed for the next flotation stage and so on. This method is called “Release Analysis” and was first introduced in the UK in the early 1960s for the beneficiation of coal powder [17]. In the current work, a grinding–sieving method was adopted and used on the WSA where the ground slurry was sieved and the coarse fraction ($+75 \mu\text{m}$) recycled for further milling, a procedure that was continued for 6 cycles (Fig. 3). For each cycle the milling process took about 5 min after which the pH of the milled samples was measured at a temperature of $23 \pm 0.5^\circ\text{C}$ after diluting the samples (5% by weight). The diagram shown in Fig. 3 illustrates the procedure adopted in the present work with WSA.

4.2.2. Drum and pebble milling

Tests were also carried out on a larger scale using a rotational drum and pebble mixer charged with silica pebbles as grinding media for the WSA powder. The silica pebbles of 1 in. mean diameter and over 99% silica content were supplied by Whitfield and Son Limited in

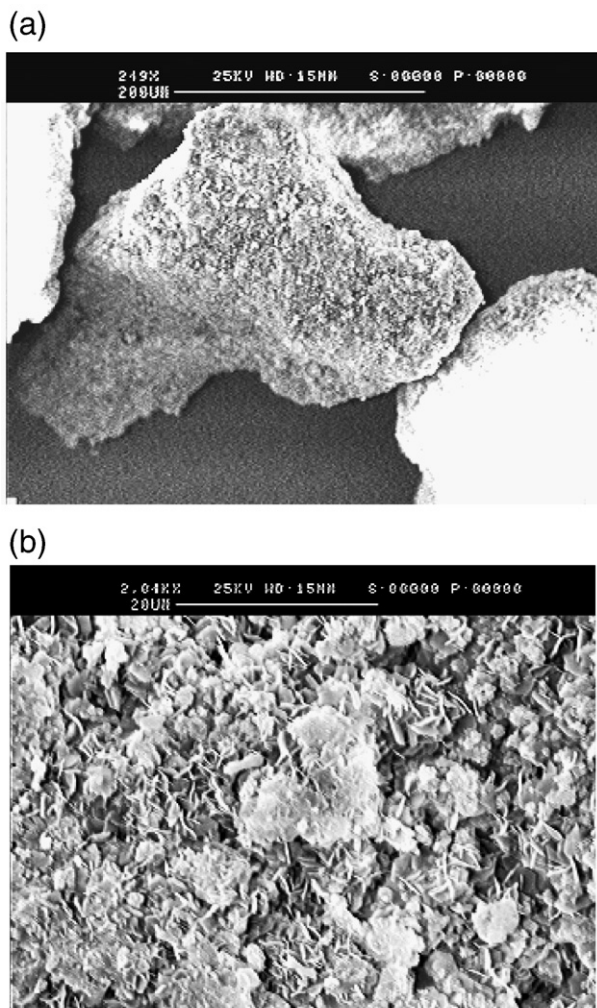


Fig. 2. SEM micrographs of WSA powder.

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 ₂ O ₃	18.86	12.0
Fe ₂ O ₃	0.87	0.40
CaO	43.51	42.0
MgO	5.15	8.0
Na ₂ O	1.56	–
K ₂ O	1.31	–
P ₂ O ₅	0.52	
TiO ₂	0.68	
MnO	0.04	
BaO	0.04	
SrO	0.09	
SO ₃	1.05	

Analytical data supplied by Southern Water for Aylesford Newsprint.

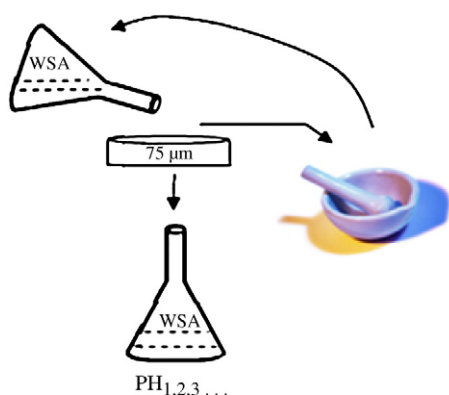


Fig. 3. The grinding-sieving for sequential pH measurement.

Staffordshire, UK. The mixer was charged with 20 kg silica pebbles and 5 kg WSA powder; then 5 l of deionised water was added and the drum and pebble mixer run for 5 min. Samples of the slurry were taken at time intervals of 30 s, for a period of up to 5 min. The slurry samples, (~20 g) each, were diluted to 500 ml, and the pH was determined at a controlled temperature of 23 ± 0.5 °C. Fig. 4 shows a photograph of the milling process carried out in a 90 litre capacity drum.

5. Setting

BS EN 196-3 [18] requires a standard consistency to be realised for the pastes before setting time is measured by Vicat needle (1 mm dia.) method. The setting time of WSA pastes were found to vary widely and were more dependent on changes in w/b ratio than is ordinary PC paste. The implementation of milling prior to addition of second binder (GGBS) was also found to result in more variation in consistency of the pastes [5]. It was expected that when working with these pastes the time of setting might vary over a wide range, particularly when using three different w/b ratios (w/b: 0.45, 0.50 and 0.55). Therefore, an apparent setting time was defined to be the period of time between when the needle penetrates $25 \text{ mm} \pm 1$ and the period where the needle leaves no scar on the paste surface ($t_f - t_i$); here, t_i may be regarded as apparent initial setting time and t_f as apparent final setting time. This way, the difference in setting property of both manually milled (M) and unmilled (UM) pastes of the same composition and w/b ratio can be found.

6. Thermal history

To follow the heat evolution during hydration BS EN 196-9:2003 [19] recommends a semi-adiabatic method as an alternative to calorimetry. Bai and Wild [20] used such a semi-adiabatic method for mortar mixes incorporating Metakaolin – Portland cement and fly ash, cast into 150 mm cube moulds. Thermocouples were mounted inside the cubes to record temperature. In the current work temperature – time profiles of the WSA and WSA – GGBS pastes were determined using a similar semi-adiabatic system; further information about the set up and procedure can be found in [20]. A cement mixer charged with silica pebbles as grinding media was used to produce the milled pastes. The time period after adding water to the WSA or WSA–GGBS and either milling or mixing was kept the same for both the milled and unmilled pastes prior to them being placed. The pastes were placed in 150 mm wooden cubes which were fitted within a larger polystyrene box (400 mm cube) to thermally isolate them from the surroundings. Thermocouples were embedded in the centre of each cube and linked to a computer. Immediately after casting temperature readings were recorded at 1 minute intervals over a period of up to

72 h. The efficiency of the boxes in providing a well insulated environment was tested by recording the variation of temperature inside the box against room temperature.

7. Production of WSA–GGBS paste cubes and concrete cubes

7.1. Paste cubes

Paste cubes of dimensions $50 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$ were manufactured from the binary WSA–GGBS mixes using both the conventional dry-mixing method and the new paste preparation method i.e. wet ball milling of WSA followed by addition of the second binder and mixing. Further details of w/b ratios and WSA/GGBS combinations can be found in Mozaffari et al. [5]. The cubes (referred to as milled: M) were water cured at 20 ± 2 °C for periods of 7, 28 and 90 days. Cubes were also made by dry-mixing of the two binders followed by adding water and hand mixing (these samples were referred to as unmilled: UM). Unconfined compressive strengths of the cube samples were determined in accordance with BS 1881-116:1983 [21].

7.2. Concrete cubes

7.2.1. Concrete cubes via wet-milling

Concrete cubes of 100 mm dimensions were manufactured using the following procedure:

- The powder mixer was charged with 20 kg of 20 mm coarse aggregate and 5 kg of WSA plus 6.5 l of tap water. The drum and pebble mixer was run for 15 min.
- The GGBS powder, 5 kg, was then added to the mixer along with 10 kg of sand (received from Bristol Channel) and the mixer was run for 5 more minutes.

The resultant concrete mix was fluent and easy to pour into 100 mm steel moulds. After casting, the cubes were covered with cling film and left to set for 24 h. The cubes were then de-moulded and put in the curing tank at 20 °C for 7, 28 and 90 days before testing for compressive strength. For each curing stage three cubes were tested and the average was taken according to BS 1881-116:1983 [21].

7.2.2. Concrete cubes via normal mixing

Cubes of the same size were also produced from the same ingredients with all the constituting materials (the binders: WSA and GGBS, the aggregates, the sand and water) being added together at the same time and mixed for 5 min to follow BS EN 206: Part 1 [22].



Fig. 4. WSA milling process using silica pebbles as grinding media in a drum and pebble mixer.

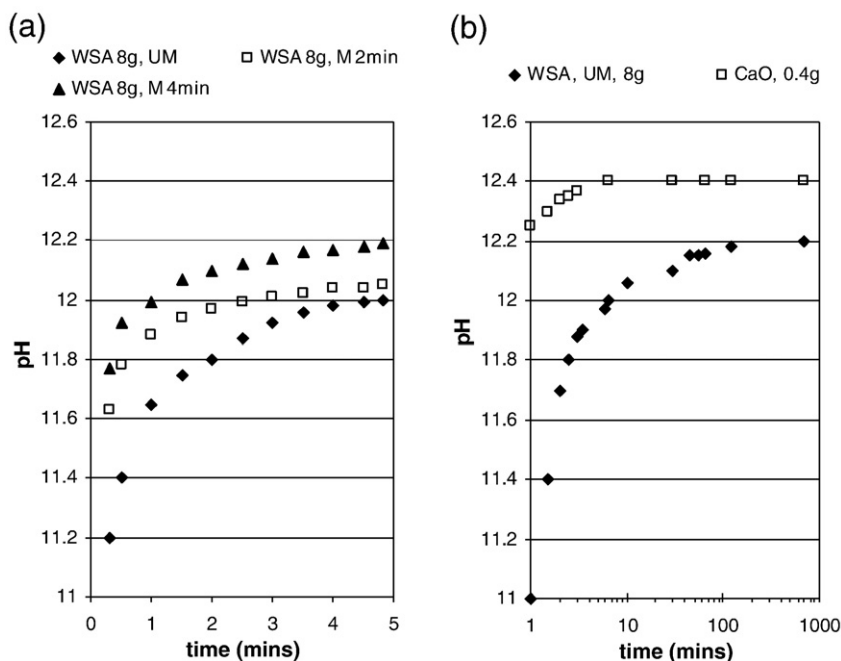


Fig. 5. (a) pH of dry milled (M) and unmilled (UM) WSA versus time; (b) pH of unmilled WSA versus time in comparison to quicklime (CaO) solution.

8. The results

8.1. pH

The results for comparative pH tests carried out for WSA and for quicklime are shown in Fig. 5(a) and (b). As the dry milling time is increased the pH is also increased (Fig. 5a). More interesting is the rate of pH increase which is much faster for the quicklime at the beginning. In fact, the quicklime solution reaches pH = 12.2 in less than 1 min while the WSA solution could not achieve pH = 12.2 after 100 min.

The results of pH tests for the manually (mortar and pestle) wet-milled samples are shown in Fig. 6. The residue from each milling stage (particles > 75 μm) was weighed and milled repeatedly and mixed with a sufficient amount of water to reach the same solid concentration (5%) before the pH measurement was made for that stage. The pH for the initial WSA solution is the highest: pH₁ = 12.3. Thus when the - 75 μm fraction which caused the highest pH at the start was separated and the coarse fraction (+ 75 μm) milled, pH₁ decreased to pH₂ = 12.1. The drop in pH continued gradually until pH₆ = 11.6. The pH readings indicate the degree of alkalinity of the milled solutions at each stage of milling resulting from the release and dispersion of free lime due to milling.

The results of the pH analysis of slurry samples produced using the drum and pebble milling are shown in Fig. 7. The pH of the solutions increase as the milling time is increased indicating more free lime is

present for hydration in the slurry that has been milled for a longer period of time.

8.2. Setting times

The results of setting properties of the pastes made via normal mixing and those of the pastes made by wet-milling are shown in Fig. 8. Fig. 8 compares the setting of pastes manually wet-milled with those made using the conventional mixing method at w/b ratios 0.45, 0.50 and 0.55. Wet-milling delays the final set, although as the w/b ratio increases the difference between the time of initial set and that of final set for the wet-milled pastes decreases substantially, and at w/b ratio 0.55 the time of final set is the same for both wet-milled and unmilled pastes.

In order to better understand the effect of milling on setting time a ratio has been defined as:

$$\alpha = \frac{(t_f - t_i)_{\text{UM}}}{(t_f - t_i)_{\text{M}}} \quad (1)$$

Fig. 9 shows the variation of α as w/b ratio is increased (Eq. (1)). The ratio α increases by a factor of 7 as the w/b ratio is increased from 0.45 to 0.55. This demonstrates a considerable drop in $(t_f - t_i)$ for the milled samples relative to that of unmilled samples as the w/b ratio is increased.

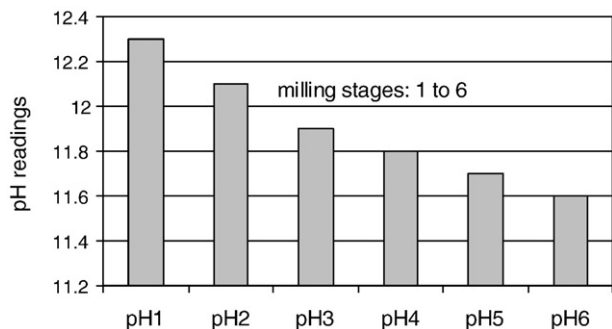


Fig. 6. pH of manually milled WSA samples.

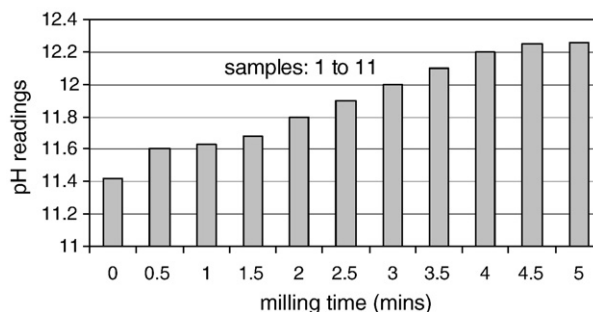


Fig. 7. pH of diluted samples taken from drum and pebble mixer (23 ± 0.5 °C).

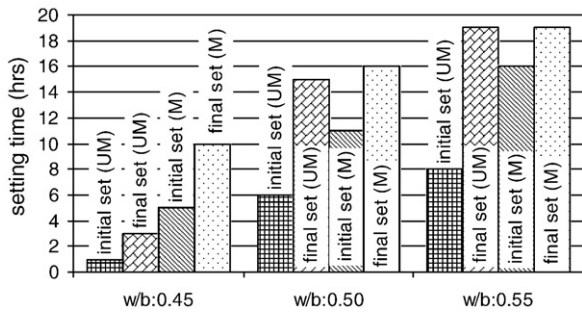


Fig. 8. Apparent initial and final setting times for the milled (M) and unmilled (UM) WSA/GGBS 50/50 pastes at w/b ratios: 0.45, 0.50 and 0.55.

8.3. Temperature rise

The results for the temperature rise with time for the unmilled and milled WSA pastes at w/b ratio 0.8 are given in Fig. 10 and those for the unmilled and milled WSA–GGBS pastes at w/b ratio 0.5 are given in Fig. 11. During the first few minutes the unmilled WSA paste produced the greatest temperature rise (32 °C), which is considerably greater than that produced by the unmilled WSA–GGBS paste (20 °C). This initial temperature rise is attributed principally to the hydration of free lime in the WSA which is of course much more dilute in the WSA–GGBS paste. From both graphs it is clear that wet-milling reduces the observed temperature rise, which would be expected as a result of heat dissipation during the milling process. Between the first couple of minutes and 120 min the initial temperature rise is maintained and even shows a small increase confirming continued heat evolution. This continued heat evolution is attributed to hydration of hydraulic components within the WSA (i.e. α' -C₂S and the latently hydraulic calcium aluminosilicate glass). However in the case of the WSA–GGBS pastes a clearly defined additional temperature rise occurs which reaches a maximum at about 900 min and then decreases gradually, producing a broad peak. This is indicative of further hydration associated with the GGBS.

8.4. Strength gain

The results for the compressive strength tests of 50 mm paste cubes are shown in Fig. 12. There is a systematic increase in strength from 7 to 28 and from 28 to 90 days of curing, but the milled samples show a significantly greater rate of strength gain leading to a substantially greater strength after 90 days.

The results for the compressive strength tests of concrete cubes are shown in Fig. 13. As for the paste cubes the compressive strength of the concrete cubes is also increased significantly for the milled samples for all curing ages. There is approximately 20%, 27% and 19% increased strength for the wet-milled concrete cubes cured at 7 days, 28 days and 90 days, respectively, relative to the conventionally produced (unmilled) concrete cubes.

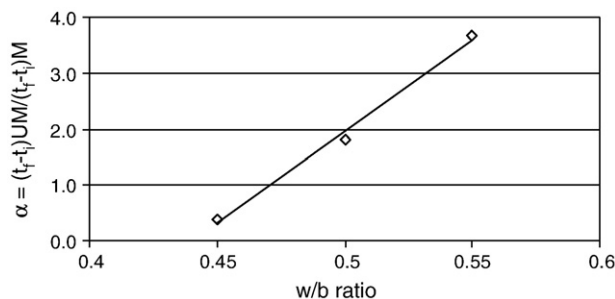


Fig. 9. The change of setting time ratio for the milled (M) and unmilled (UM) samples.

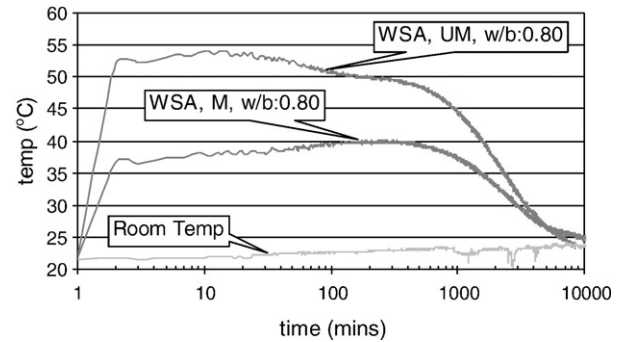


Fig. 10. The results for the temperature rise with time for the unmilled and milled WSA pastes at w/b ratio 0.8.

9. Discussion

The low strength of the hardened WSA paste has been shown to be partly due to its high porosity [8]. This high porosity is caused by continued hydration of free CaO after setting has occurred in that the hydration of CaO is expansive. The reason why the majority of CaO particles do not fully hydrate before setting and hardening is because access to water is inhibited due to the CaO particles being agglomerated with other minerals in the WSA. This explains why in the very early stages of hydration the rate of increase in pH of the unmilled WSA with time (Fig. 5b) is so much less than that of quicklime. If however the WSA is wet-milled this breaks up the agglomerates and releases and disperses the CaO, which can then more rapidly hydrate. Thus after setting there is very little, if any, free lime remaining. This is supported by Fig. 5a, which shows a much more rapid rise in pH for the milled WSA relative to the unmilled WSA. In fact, the WSA wet-milled for 4 min shows a pH versus time profile more closely approaching that for quicklime alone (Fig. 5b). The change in pH with time for WSA paste taken from the drum and pebble mixer (Fig. 7) also shows enhanced pH relative to unmilled WSA indicating that mixing the WSA with pebbles and water in a mixer has a similar effect to wet-milling, in breaking up agglomerates and dispersing the CaO.

The increase in the setting time ratio (α) which is defined in such a manner as to compare the setting property of the milled against the unmilled WSA/GGBS pastes indicates a change in the relative rate of chemical reactions during setting as w/b ratio is increased. This change can be attributed to the accelerating effect of lime which is more freely available in the milled samples. In particular, at higher w/b ratios the lime is likely to contribute more effectively in activating other hydrating species in the mix. It is also interesting to note that milling delays both the initial and the final set particularly at low w/b ratios, however, the delay is less pronounced for the final sets at high w/b ratios (Fig. 8). This may be attributed to greater particle dispersion allowing more uniform

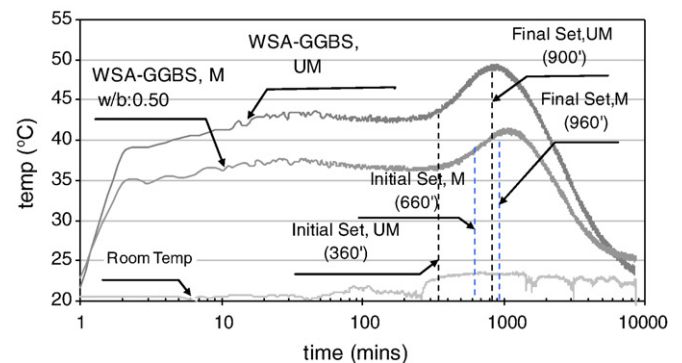


Fig. 11. The results for the temperature rise with time for the unmilled and milled WSA–GGBS pastes at w/b ratio 0.5.

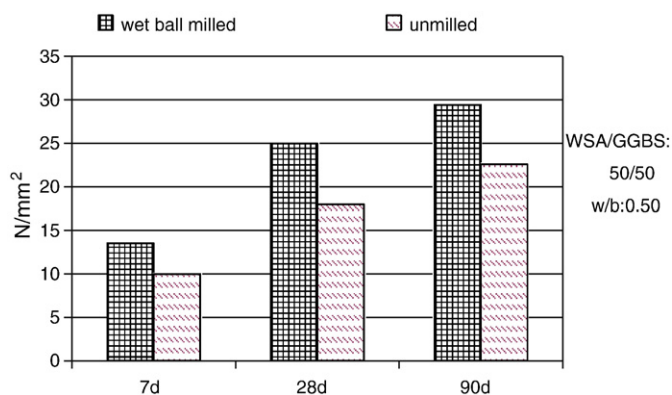


Fig. 12. Compressive strength of WSA/GGBS 50/50 hardened paste at water binder ratio:0.50, using binder that was (i) unmillied and (ii) wet ball-milled for 15 min.

separation of hydrating particles and thus increasing the time period for an interlocking network of hydration products to develop.

When WSA is first mixed with the coarse aggregate and water in the mixer, the WSA particle agglomerates will be first rapidly broken down, releasing and dispersing the CaO. This allows the bulk of the CaO to fully hydrate and the pH to approach its ultimate value prior to setting (and prior to the addition of GGBS) thus eliminating any future unsoundness. In addition, the GGBS is added at a time of enhanced pH which will itself accelerate the hydration of the GGBS. Thus, a significant enhancement in strength of concrete cubes is achieved by following this initial procedure of wet-milling the WSA during the mixing process (Figs. 12 and 13).

The blending of WSA with GGBS reduces the initial temperature rise as a result of the diluting effect of the GGBS, the particles of which will also increase the separation distance between hydrating WSA particles and thus increase setting times. Wet-milling (M) as opposed to normal mixing (UM) also reduces the observed temperature rise as a result of heat dissipation by the grinding media.

The immediate hydration of free lime, which is shown to be facilitated by wet-milling [5] is followed by the hydration of other key components such as α' -C₂S/bredigite and calcium aluminosilicate glass. The α' -C₂S phase which is finely divided ($\sim 0.1 \mu\text{m}$) hydrates and produces (C-S-H) gel and calcium hydroxide. The glassy phase in WSA also reacts with water in an alkaline environment. The wide range of Ca-Si-Al phases in WSA complicates the kinetics of the hydration reactions, and it is likely that some components hydrate over different periods. The rate of hydration of lime in WSA may be altered by either adding new material to the system or by pre-treatment of WSA. One optimal way of combining these two routes is by combining a sequential milling process with subsequent addition of GGBS. This results in accelerating lime hydration, greater particle dispersion, rapid increase in pH and creation of more cementing products. There

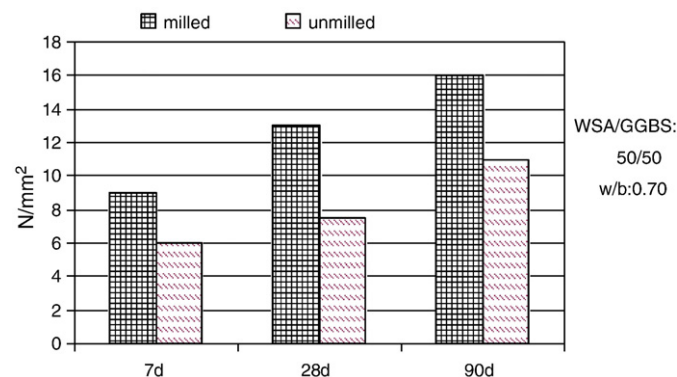


Fig. 13. Compressive strength of hardened concrete cubes made with WSA/GGBS 50:50 at water binder ratio 0.70 in a cement mixer.

will be an intimate interaction between individual particulates and the surrounding chemical solution (the pore fluids). These hydraulic particles with maximum exposure to other potentially reactive components and to the surrounding environment are likely to hydrate more rapidly. Lime particles of nano-scale size provide high specific surface as reactive components in a more homogenised and dispersed mix enabling them to interact with other latently hydraulic/pozzolanic particles available (i.e. the glassy phase and the added GGBS). Wet-milling of WSA, which has been shown to contribute to the development of stronger hardened pastes [5] has also been shown to bring about improved homogeneity by dispersing more lime into the hydrating environment, thus contributing to this improved performance.

10. Conclusions

WSA is a cementitious material in which some constituents hydrate faster than others. The free lime in the WSA reacts with water immediately upon soaking and provides a highly alkaline pore solution, which then results in the release of more reactive phases such as Al_2O_3 and SiO_2 into the system. To enhance this phenomenon a second by-product material GGBS may be added to WSA. An initial wet-grinding stage prior to the addition of GGBS has been found to further accelerate the hydrating effect of lime. Using this combination of techniques releases more lime, which is made available for hydration, and results in more cementing agents (including C-S-H gel) being produced, which in turn brings about higher strength to the hardened paste and concrete samples.

Acknowledgements

The authors would like to thank the technical staff of the Faculty of Advanced Technology and Faculty of Applied Sciences at the University of Glamorgan for their support. The authors also thank ONYX Environmental Trust, Aylesford Newsprint Ltd and the Cementitious Slag Makers Association for funding the continuing research and for the supply of the materials used in the research.

References

- [1] J.M. Kinuthia, M. O'Farrell, B.B. Sabir, S. Wild, A preliminary study of the cementitious properties of wastepaper sludge ash – ground granulated blastfurnace slag (WSA-GGBS) blends, in: R.K. Dhir, M.C. Limbachiya, M.D. Newlands (Eds.), *Recovery and Recycling of Paper*, Proceedings of the International Symposium, University of Dundee, Thomas Telford, London, 2001, pp. 93–104.
- [2] G. Veerapan, J.M. Kinuthia, M. O'Farrell, B.B. Sabir, S. Wild, Compressive strength of concrete block manufactured using wastepaper sludge ash, *International Symposium: Advances in Waste Management and Recycling*, University of Dundee, 9–11th September, Symposium W2-Recycling and Reuse of Waste Materials, Theme W23 – Recycling and Reuse, 2003.
- [3] Hiroji Ishimoto, Takeshi Origuchi, Masahiro Yasuda, Use of papermaking sludge as new material, *J. Mater. Civ. Eng.* 12 (1) (2000) 310–313.
- [4] A.M. Neville, *Properties of Concrete*, 4th edn. Longman, Harlow, 1995.
- [5] E. Mozaffari, M. O'Farrell, J.M. Kinuthia, S. Wild, Improving strength development of wastepaper sludge ash by wet-milling, *Cem. Concr. Compos.* 28 (2) (2006) 144–152.
- [6] Joo-Hwa Tay, Kuan-Yeow Show, Manufacture of cement from sewage sludge, *J. Mater. Civ. Eng.* 5 (1) (1993) 19–29.
- [7] K.L. Lina, K.Y. Chiangb, C.Y. Linc, Hydration characteristics of waste sludge ash that is reused in eco-cement clinkers, *Cem. Concr. Res.* 35 (6) (2005) 1074–1081.
- [8] J. Bai, A. Chaipanich, J.M. Kinuthia, M. O'Farrell, B.B. Sabir, S. Wild, M.H. Lewis, Compressive strength and hydration of wastepaper sludge ash-ground granulated blastfurnace slag blended pastes, *Cem. Concr. Res.* 33 (8) (2003) 1189–1202.
- [9] S. Wild, J.M. Kinuthia, G.I. Jones, D.D. Higgins, Suppression of swelling associated with ettringite formation in lime stabilized sulphate bearing clay soils by partial substitution of lime with ground granulated blastfurnace slag (GGBS), *Eng. Geol.* 51 (4) (1999) 257–277.
- [10] A. Chaipanich, J. Bai, M. O'Farrell, J.M. Kinuthia, B.B. Sabir, S. Wild, Setting time and heat of hydration of wastepaper sludge ash-ground granulated blastfurnace slag blended pastes, 6th International Congress on Global Construction: Ultimate Concrete Opportunities, Cement Combinations for Durable Concrete, University of Dundee, 5–7 July, 2005.
- [11] S. Wild, J.M. Kinuthia, G.I. Jones, D.D. Higgins, Effects of partial substitution of lime with ground granulated blast furnace slag (GGBS) on the strength properties of lime-stabilised sulphate-bearing clay soils, *Eng. Geol.* 51 (1) (1998) 37–53.

- [12] J. Pera, A. Amrouz, Development of highly reactive Metakaolin from paper, *Adv. Cem. Based Mater.* 7 (2) (1998) 49–56.
- [13] J. Petts, Incineration as a waste management option, in: R.E. Hester, R.M. Harrison (Eds.), *Waste Incineration and the Environment*, the Royal Society of Chemistry, Bath, 1994.
- [14] A.M. Evans, *Ore Geology and Industrial Minerals*, 3rd edn. Blackwell Scientific, London, 1993.
- [15] BS EN 196-2, *Methods of Testing Cement: Part 2. Chemical Analysis of Cement*, BSI, European Committee for Standardization (CEN), Brussels, 1995.
- [16] B.A. Wills, *Mineral Processing Technology*, 5th edn. Paragon Press, Oxford, 1992.
- [17] D.W. Brown, S.T. Hall, Froth flotation: preparation of a laboratory standard, *Fuel* 78 (14) (1999) 1621–1629.
- [18] BS EN 196-3, *Methods of Testing Cement: Part 3. Determination of Setting Time and Soundness*, BSI, European Committee for Standardization (CEN), Brussels, 1995.
- [19] BS EN 196-9, *Methods of Testing Cement. Heat of Hydration. Semi-adiabatic Method*, British Standard Institution, London, 2004.
- [20] J. Bai and S. Wild, Investigation of the temperature change and heat evolution of mortar incorporating PFA and Metakaolin. *Cem. Concr. Compos.* 24 (2) (2002) 201–209.
- [21] BS 1881: Part 116, *Testing Concrete. Method for Determination of Compressive Strength of Concrete Cubes*, British Standard Institution, London, 1983.
- [22] BS EN 206, Part 1, *Concrete. Specification, Performance, Production and Conformity*, British Standard Institution, London, 2001.