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Reactivity and performance of blastfurnace slags of differing origin

A. Bougara [a,*], C. Lynsdale [b], N.B. Milestone [c]

[a] *Laboratory of Material Sciences and Environment, University of Hassiba Benbouali Chlef, Algeria*
[b] *Department of Civil and Structural Engineering, University of Sheffield, Sir Frederick Mappin Building, Sheffield S1 3JD, UK*
[c] *Department of Engineering Materials, University of Sheffield, Sir Frederick Mappin Building, Sheffield S1 3JD, UK*

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ABSTRACT

The performance of an Algerian blastfurnace slag has been assessed by examining the parameters influencing reactivity in a comparative study of two slags from different origins. These parameters include chemical composition, glass content, particle size distribution, heat of hydration and microstructural development. Three cement paste systems were investigated; OPC as a control, and two blended cements; 50% OPC-50% Algerian slag and 50% OPC-50% UK slag. All samples were made with a water/binder ratio of 0.4 and cured at 20 °C for up to 90 days. The specimens were tested using calorimetry, thermogravimetry, X-ray diffraction, selective dissolution, back-scattered electron microscopy and compressive strength. The chemical composition of the slag has a profound influence on strength development. The heat evolved appears to be proportional to the strength development and may be used as an important indicator of the reactivity of slag. A relationship was established between the amount of calcium silicate hydrate formed and compressive strength.

1. Introduction

There is general agreement among researchers that the properties of hydrated paste systems incorporating ground granulated blastfurnace slag (GGBS) such as strength, porosity and heat of hydration are influenced by slag properties such as chemical composition, glass content, fineness and particle size distribution [1–3]. The reactivity of the slag is considered to be an important parameter for assessing its suitability as a cement replacing material in concrete. Many studies have attempted to relate these properties to strength directly, or to develop a relationship which could explain or predict the observed strength in slag containing concrete. All attempts at such correlations have had limited success in being able to provide consistent predictions of compressive strength [4].

Douglas et al. [5] studied the influence of chemical composition, glass content and particle size distribution on the compressive strength development and heat of hydration for two blastfurnace slags; one from Canada and the other from the USA. The result for the total heat evolved at 3 days, determined by conduction calorimetry, was 97.4 J/g and 71.6 J/g for the Canadian and American slags respectively, whereas the compressive strength at 28 days was 36.2 and 47.7 MPa respectively. According to their work, the total heat evolved did not seem to be the best indicator of the slag's strength contribution. This could be attributed to the differences in the other parameters, i.e. chemical composition, glass content and fineness of these slags. Douglas et al. [5] also found that increasing the fineness had a positive effect on strength gain but an increase in the glass content did not necessarily result in higher strength. Escalante et al. [6] observed that slag with a higher glassy fraction (97.0%) displayed higher reactivity than one with a lower fraction (53.5%). The amount of the reacted slag in blended cements incorporating 30% of these two slags with different glass content was about 50% and 20% after 6 months of hydration at 50 °C respectively. Their study [6] also showed that these results were at odds with the slags hydraulic index of 1.84 and 1.94 respectively. On the other hand, Pal et al. [7] found the hydraulic index to be correlated strongly with most of the physical and chemical properties of the slags they studied and corresponded to the slag activity index. Wang et al. [8] studied the effect of particle size distribution on the heat evolution rate and strength development of a composite cement paste containing 79% slag. They found that the finest fraction, 0–20 μm, showed much greater rate of heat evolution after 40 h of hydration than the other fractions. The composite containing this fraction yielded a compressive strength of 64 MPa at 28 days, whereas the fractions with sizes >40 μm behaved almost as inert materials up to 28 days.

It is clear from the previous work, that the factors which have the most effect on the reactivity of the slag in cement paste systems are not well defined. The lack of good understanding of the correlation between strength development and underling materials' parameters may affect considerably the quality of concrete produced with blended cements. This paper attempts to assess

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[*] Corresponding author.
E-mail address: Aekbougara@hotmail.com (A. Bougara).

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the parameters most affecting the reactivity and strength development of an Algerian slag compared to a UK slag. The heat evolution of cement/slag paste systems were measured by means of an isothermal conduction calorimeter, the development of compressive strength by crushing of cubes, the formation of calcium hydroxide by thermogravimetric analysis (TGA), the amount of reacted slag by the selective dissolution method, and the development of microstructure by back-scattered electron imaging (BEI) of selected samples. The information obtained would provide a basis for the prediction of the performance of slag in cement/slag blends.

2. Experimental

2.1. Materials

An ordinary UK Portland cement (OPC), (Lafarge CEM I 52.5 N) with specific surface of 420 m^2/kg, an Algerian granulated blastfurnace slag provided by the El-Hadjar steel factory and a UK granulated blastfurnace slag supplied by the Appleby Group UK were employed. Both slags were ground in a ball mill to a specific surface area of 500 m^2/kg. In this work, three cement paste systems were investigated; OPC (as a control), and two blended cements, namely, 50% OPC:50% Algerian slag and 50% OPC:50% UK slag. The chemical composition of the OPC and slags is presented in Table 1.

Table 1
Chemical composition of the materials used.

Chemical composition (%)	OPC (CEM I 52.5 N)	Algerian slag	UK slag
SiO_2	22.81	38.20	35.80
Al_2O_3	7.68	7.96	13.19
Fe_2O_3	3.09	4.68	0.86
Mn_3O_4	0.07	2.04	0.69
MgO	1.14	3.82	8.55
CaO	58.13	42.18	39.72
Na_2O	0.32	0.20	0.28
K_2O	0.71	0.65	0.41
TiO_2	0.35	0.33	0.63
BaO	0.13	0.78	0.09
LOI	5.37	−1.06	−0.30
SO_3	–	0.47	0.56
Moisture	0.18	0.0	0.29
Hydraulic index [9] $(CaO + MgO + Al_2O_3)/SiO_2$	–	1.41	1.72
Glass content	–	97.9%	100%

2.2. Characterisation of unhydrated materials

The data presented in Table 1 indicates that the major differences between the two slags are in the contents of alumina, magnesia, iron and manganese oxides. Algerian slag has approximately half of the Al_2O_3 and MgO contents of the UK slag and much higher Mn_2O_3 and Fe_2O_3. The results of the hydraulic index derived from chemical composition analysis (shown at the bottom of Table 1) suggest that UK slag should exhibit higher reactivity than Algerian slag. The glassy fraction of the UK slag is slightly higher than that of Algerian slag, estimated at 100% and 97.9% respectively, according to BS6699 [9]. XRD traces of both the unhydrated slags shown in Fig. 1 indicated the presence of small amounts of crystalline phases such as gehlenite and hydrogarnet, which suggests that the glass content values have been slightly over-estimated. The glass content of both slags satisfies BS6699 [9] with respect to their acceptability as a cement replacement.

The particle size distribution determined using a laser diffraction particle size analyser (Coulter LS130) is presented in Fig. 2. The particle size distributions for the two slags were very similar with about 73% of the particles finer than 20 μm and about 10% coarser than 40 μm.

2.3. Sample preparation and testing methods

For heat evolution measurements, 15 g of OPC or the blended slag cements were weighed into a container and mixed by hand with distilled water at a water/binder ratio of 0.4 before inserting into the calorimeter cell. The cements were hydrated for 72 h at a constant temperature of 20 °C in an isothermal conduction calorimeter (JAF Wexham Developments) immersed in a silicone oil bath. Further details are described by Cembureau [10].

For compressive strength determination, OPC and blended slag cement pastes were prepared with a water/binder ratio of 0.4 and cast in 20 mm cube moulds. The samples were covered with wet hessian for 24 h and then de-moulded and cured in a water bath kept at 20 °C until tested for compressive strength. Four cubes were tested at 1, 3, 7, 28 and 90 days for each age using a Hounsfield compression machine with a capacity of 100 kN.

Fragments were taken from the crushed cubes for X-ray diffraction (at 90 days), thermogravimetry (at 1, 7, 28 and 90 days) and scanning electron microscopy (at 28 days). These fragments were submerged in acetone to arrest hydration and prevent carbonation, before drying in a desiccator using a rotary vacuum pump. The fragments used for X-ray diffraction and thermogravimetry were ground to pass a 63 μm sieve. X-ray diffraction analysis was performed using a Philips PW1710 diffractometer using Cu Kα radia-

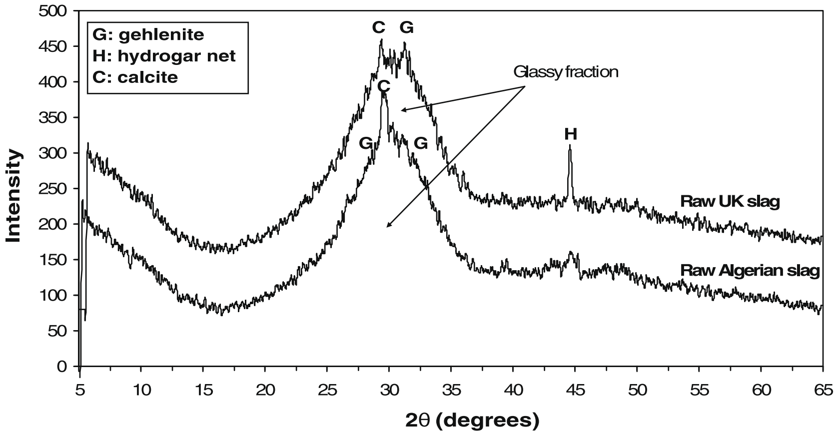


Fig. 1. XRD traces of unhydrated Algeria n and UK slags.

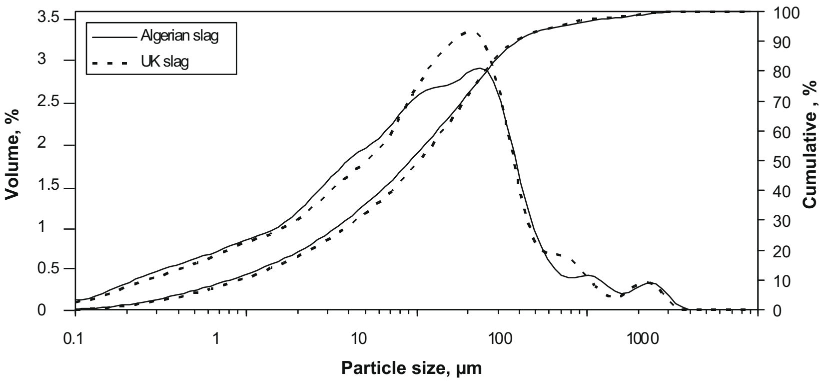


Fig. 2. Particle size distribution of Algerian and UK slags.

tion running at 30 kV and 40 mA with step size of 0.02°2θ and a scanning speed of 2°2θ /min between 5° and 65°2θ. Thermogravimetry curves were obtained, using a Perkin Elmer Pyris 1 TGA, with samples heated from ambient temperature to 1000 °C at a rate of 10 °C/min in nitrogen gas flowing at a rate of 15 ml/min. For electron microscopy, the sample fragments were mounted in epoxy resin cured under vacuum, then ground with grinding paper and polished using diamond paste with iso-propane as lubricant. The specimens were carbon coated before being analysed by back-scattered electron imaging (model CamScan) using an acceleration voltage of 20 kV.

3. Results and discussion

3.1. Compressive strength

Fig. 3 shows that at 28 days, all pastes achieved similar compressive strengths. This is to be expected for a UK slag complying with BS6699 at this level of cement replacement. It is interesting to note, however, that this high level of strength was also achieved with the Algerian slag, despite its lower hydraulic index (Table 1). However, this difference in hydraulic index probably contributed to the lower rate of strength development for the Algerian slag compared with the UK slag, at both ends of the strength development spectrum. At 1 and 3 days, Algerian slag contributed very little to strength as the strength of the 50% slag blend was approximately 50% of the OPC control strength. This is in contrast to the strength contribution evident for the UK slag. This difference between the two slags may be attributed to the higher alumina content in UK slag, and to higher manganese and iron oxide contents in the Algerian slag which were found to lead to lower strength [11]. Furthermore, it is probable that the hydrated iron and manganese oxides formed around the Algerian slag particles during hydration form a barrier which prevents ongoing attack of hydroxyl and alkali cations, resulting in retardation of reactions, evident at early ages. The gain in strength between 28 and 90 days clearly demonstrates the slag's contribution to strength which in the case of Algerian slag paste strength gain at 22%, was only half that of the UK slag paste at 41%. From the results seen, it appears that the chemical composition of slag plays an important role in slag reactivity and contribution to strength. Increased MgO [12] and Al_2O_3 and the hydraulic index $(CaO + MgO + Al_2O_3)/SiO_2$ [13] in the UK slag give rise to the differences in the strength development of the two slags studied.

3.2. Calorimetric study

Fig. 4 shows the rate of heat evolution and total heat output for the OPC and blended cements hydrated at 20 °C. The initial peak, which occurs immediately after contact with water, is not shown here. The peak shown in Fig. 4 for OPC is a single peak, while in slag cements it is broad and can be resolved into two peaks; the first is due to the OPC component and occurs at the same time as that for the OPC sample; while the second peak is contributed mainly by the slag component, as accepted in many publications [14–16]. This peak in the Algerian slag blend, was delayed by approximately 3 h compared to that of the UK slag blend and its height was also less pronounced, so it only appears as a shoulder. The low amount of heat evolved is related to the reactivity of slag and appears to be related to the hydraulic index. The computed total heat evolved

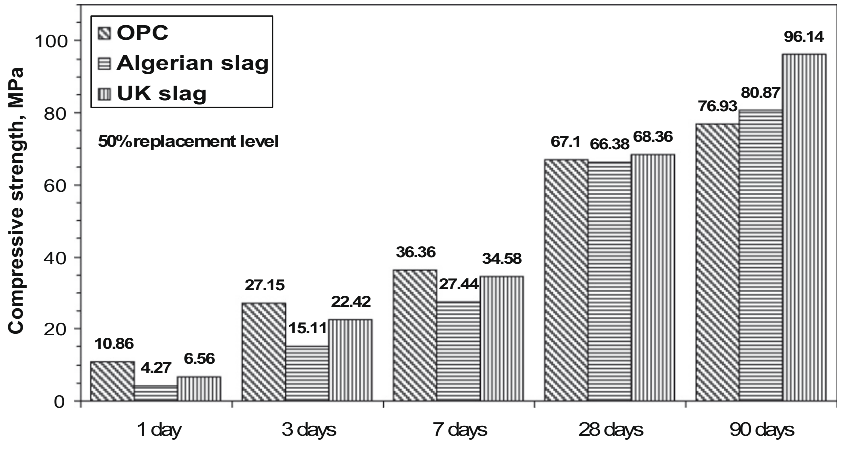


Fig. 3. Compressive strength of the three paste systems at different ages.

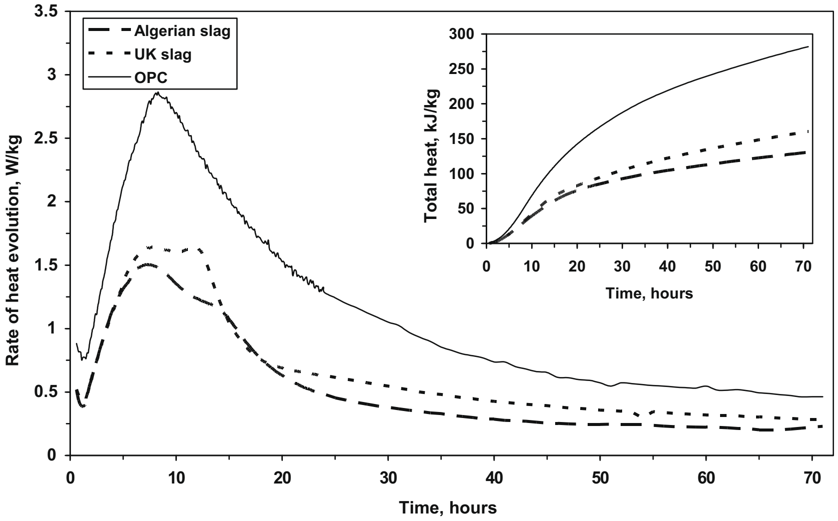


Fig. 4. Rate of heat evolution and total heat for the three paste systems hydrated at 20 °C.

curve for OPC (see the inset in Fig. 4) at 72 h is obviously well above those of the blended cements; about 281, 160 and 130 kJ/kg for OPC, UK and Algerian slag respectively. These values indicate that at this age, the Algerian slag contributes little to heat evolution. The total heat generated from Algerian slag is less than half that of OPC, while that from UK slag is greater than half that of OPC. This trend is similar to that observed for strength development up to this age. Thus, it may be said that the heat evolved seems to correlate with early strength development.

3.3. Calcium hydroxide content

Fig. 5 presents the amount of calcium hydroxide in the various hydrating cement pastes estimated from the weight loss on heat-

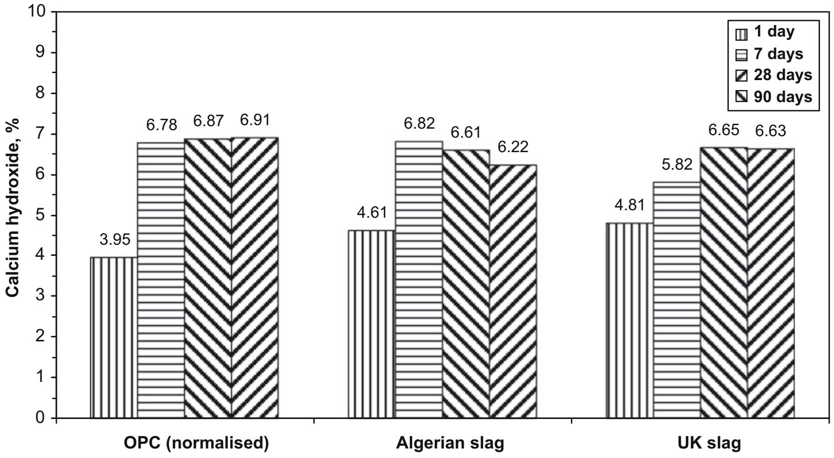


Fig. 5. Amount of calcium hydroxide for the three paste systems at different ages.

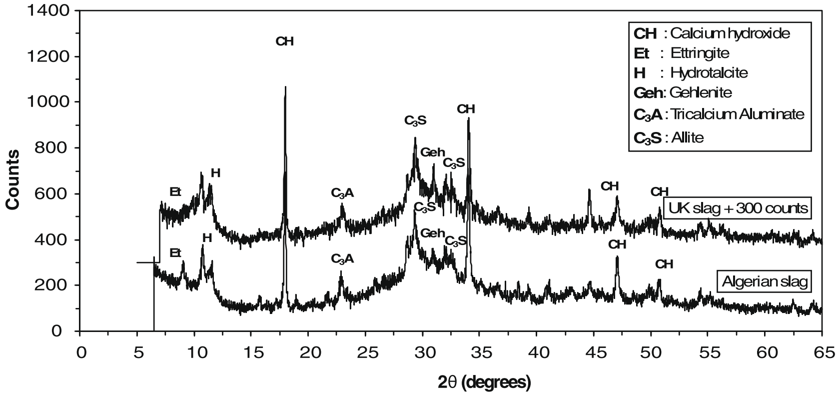


Fig. 6. XRD traces for Algerian and UK slag cement hydrated for 90 days.

ing between 425 °C and 580 °C in thermogravimetric analysis, due to the dehydroxylation of $Ca(OH)_2$ liberated during OPC hydration. It may be consumed with time as a result of carbonation or reaction with pozzolanic materials in the sample. For comparison purposes, the results for the OPC sample have been halved, as there is only 50% OPC in the blended samples. The amount of $Ca(OH)_2$ liberated as a result of hydration in the OPC paste system increased significantly in the first 7 days but the increase from then up to 90 days was small, suggesting a significant change in the rate of reaction, as found elsewhere for similar water/cement ratio pastes [17]. In the slag cement blends the $Ca(OH)_2$ levels at 1 day, were slightly higher than that for the OPC paste system, possibly due to the increase in water/cement ratio as a result of 50% dilution with slag. For later ages, on average, there was a slight drop in the level of $Ca(OH)_2$ in the blended pastes, which indicates a pozzolanic reaction, however, longer time span and the use of higher water/binder ratio might be needed to confirm this. The amount of $Ca(OH)_2$ present in the slag blends was surprisingly high suggesting the rate at which these slags reacted was low. There was little difference between the results for the two slags, to differentiate between them. The X-ray diffraction traces for the two slag cements, at 90 days, presented in Fig. 6, shows similar hydration phases for the two blends.

3.4. Bound water

The amount of chemically bound water often referred to as the non-evaporable water, can be used to provide an indication of the degree of hydration. This would normally include $Ca(OH)_2$ but as these samples contain ground slag only the amount of water lost between 105 °C and 450 °C and expressed as the percentage of the ignited weight at 450 °C has been determined. This should account for most of the water in the calcium silicate hydrate, which is of particular interest due to its influence on strength development. It simplifies the calculation and avoids the need to correct for carbonation which may be responsible for part of the weight loss between 600 °C and 780 °C [17]. The water in C–S–H results at 90 days of hydration for Algerian and UK blended pastes (Fig. 7) were 9.3% and 11.4% respectively, i.e. the water estimated for UK slag was approximately 22% greater than for the Algerian slag, which is reflected in the higher strength for the UK slag at 90 days. The water results reported here are in agreement with those reported by other investigators [6,13].

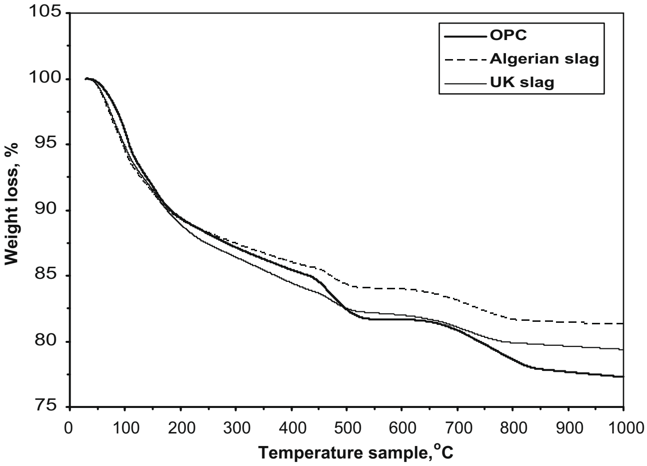
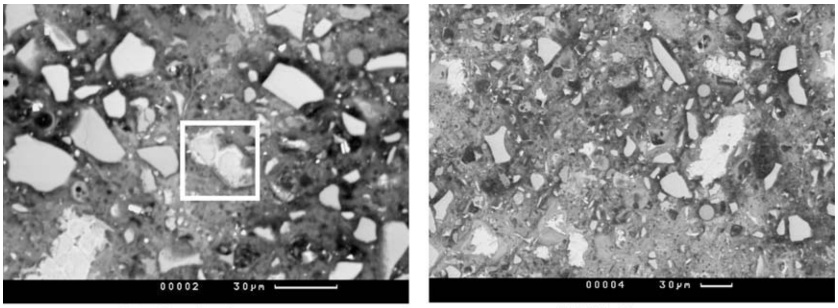


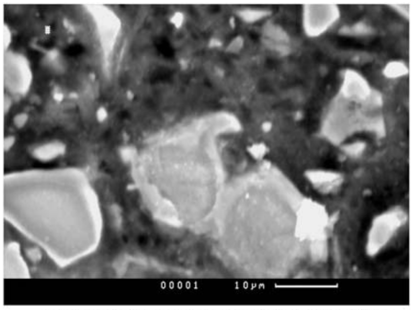
Fig. 7. TG curves for the three paste systems cured at 20 °C for 90 days.

3.5. Amount of reacted slag

Selective dissolution in an alkaline ethylene-diamine tetraacetic acid (EDTA) solution [18] was employed to estimate the amount of slag that has reacted. The principal of this technique is all hydration products from a hydrated slag blend dissolve in the EDTA solution leaving only the unreacted slag undissolved. Samples of 100 mg of blended cement, were dried and crushed to pass 63 μm, and weighed on four figure balance and mixed with



(a) Algerian slag cement (b) UK slag cement



(c) Algerian slag cement at high magnification

Fig. 8. BEI micrographs for Algerian slag cement (a) and UK slag cement paste (b) and Algerian slag cement at high magnification (c).

50 ml of the EDTA solution on roller for 10 min. The solutions were then filtered on a Millipore filter with pore size of 0.45 μm, washed with distilled water and dried at 105 °C. The residue is the amount of slag that remained unreacted. The percentage of slag reacted was calculated as follows:

$$R_s(\%) = (50\% W_s - W_r)/50\% W_s \times 100$$

where R_s is the percentage of reacted slag, W_s is the weight of dried sample and W_r is the weight of dried residue. However, the percentage of reacted slag needs to be corrected by taking into account the amount of unreacted slag that dissolved in the EDTA solution. Samples of unhydrated slag were subjected to the same process to calculate the unreacted slag that dissolved.

The results obtained indicate that after 7 days of hydration at 20 °C, only 8% of slag had reacted in both slag cement systems. However, after 28 days of hydration, the percentage of Algerian slag that had reacted was 21%, whereas for UK slag it was only 19%. Although the difference is small, it does correlate well with the gain in strength observed; Algerian slag gained more strength between 7 and 28 days compared to the UK slag paste (Fig. 3). It is worth noting that the percentage of reacted slag found in this study, is nearly the same as that found by Escalante et al. [6].

3.6. Microstructure

The microstructure of the blended pastes hydrated to 28 days at 60 °C is shown in Fig. 8. Slag grains appear light in colour and angular in morphology with sharp edges while pores appear black in back-scattered electron imaging (BEI). There appeared to be more porosity in the microstructure of the Algerian slag cement paste than for UK slag cement paste which appeared more compact and continuous. Clean unreacted slag particles were present in both systems. The observations of increased porosity in Algerian paste system may help explain the reduced strength at later ages. High magnification of the highlighted area in Fig. 8a for the Algerian slag seen in Fig. 8c showed that the hydrating slag particles were surrounded by a bright rim which indicates heavy elements with higher atomic weight [19]. The heavy elements surrounding the slag particles are possibly hydrated iron and manganese oxides/hydroxides which have precipitated on release from the slag to form an insoluble barrier delaying early stage reaction. In a similar way Rha et al. [20] showed lead inhibited the hydration of slag by formation of insoluble precipitates. These hydroxides are likely to be soluble in the EDTA solution and so will be counted as part of the slag hydration products.

4. Conclusion

The reactivity and strength contribution of an Algerian slag have been assessed in comparison with the properties and performance of a known UK slag, and the main conclusions are drawn below. It should be emphasised, however, that these findings and the interrelationships between the various parameters studied should have general relevance and applicability to the performance of different slags in cement pastes and concrete.

- For slags of similar fineness and particle size distribution, 50% slag-50% OPC blends of both slag types achieved the strength of the 100% OPC control at 28 days. However, the rate of strength development for the Algerian slag blended paste lags behind that of UK slag paste at early ages and beyond 28 days.
- The amount of Algerian slag that reacted between 7 and 28 days was higher than that for UK slag, probably explaining the increase in strength gain for Algerian slag between these ages. The amount of bound water at 90 days of hydration also correlates with the strengths achieved.
- Both slags had similar glass content, fineness and particle size distribution yet the heat evolution and rate of strength development of their pastes were different, suggesting that the chemical composition plays a big role in affecting these properties. The delay in the Algerian slag's contribution to early strength may be related to precipitation of hydrated manganese and iron oxides formed by this slag.
- The work presented in this paper is in general agreement with the reported literature in that no one material parameter can fully predict slag performance in a cement/slag system. However, the heat evolved during the first 72 h correlates well with the early strength development of pastes of both slags. Both of these properties correlate well with the hydraulic index of the slags, suggesting that when all other properties are equal, the hydraulic index may be used to predict the performance of slag in cement/slag blends.

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