

# MICROSTRUCTURAL DEVELOPMENTS IN PLAIN AND SLAG-BLENDED CEMENTS

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**Abstract:** The microstructures of cement systems such as pastes, mortars and concrete control other physical properties such as strength, transport properties and durability. The microstructure of cement changes with time and is made up of hydrated and anhydrous phases, including pores containing pore water. This study investigated changes in the microstructures of plain and slag-blended cement pastes from 7 to 28 days. These were achieved using scanning electron microscopes (SEM) – backscattered electron (BSE) images. Two slags (S1&S2) were blended with CEM I 52.5R at 30% and 70% replacement. These were compared with plain CEM I 42.5R for microstructural developments. X-ray diffraction (XRD) was used to follow patterns of hydration products. The results for plain cement pastes show more coarser microstructure at 7 days than 28 days, indicating refinement as hydration progressed. In the slag blends, unhydrated Portland cement clinker grains were scarcely present after 28 days of hydration. Less presence of calcium hydroxide and more outer products calcium silicate hydrate (C-S-H) were observed in the slag blends. Hydration of plain cement at 20 °C increased between 7 and 28 days, from 74% to 79% , while the weighted hydration of the slag-blends at 20 °C increased from 50% for 70% slag-blend, to 85% for 30% slag blend. Increasing curing temperature from 20 °C to 38 °C had a positive impact on the slag-blend.

**Keywords:** Cement, Hydration, Microstructure, Slag.

## 1.0 INTRODUCTION

The microstructure of cement paste comprises hydrated phases, anhydrous phases and pores with pore water. The hydrated phases are dominated by calcium silicate hydrate (C-S-H) gel and calcium hydroxide (CH), both products of tricalcium silicate (C<sub>3</sub>S) and dicalcium silicate (C<sub>2</sub>S) hydration, which are the most abundant phases, constituting about, 75-90% in normal cements. These phases are also known to be the main strength controlling phases at early and later ages respectively [1, 2]. In ground granulated blast-furnace slag (slag)-blended cements, these phases still occur but with the C-S-H modified to C-A-S-H and more reduced quantity of CH because of its consumption during slag's pozzolanic reaction [3, 4].

The porosity of cement systems affects the transport of aggressive substances with grave implications for durability. However, transport of fluids through cement systems is dependent on the number of

interconnected pores rather than total porosity. It has been shown in Power's model the volumetric changes that affect porosity due to continuous hydration of plain cement at 20°C. It showed how the gel spaces occupied by gel solid and gel water increased with time, while capillary spaces (pores, air and water) reduced with time [5]. Microstructures of mortars and concretes also include interfacial transition zone (ITZ), with potential to contribute to the pore network of the matrix [6-9]. ITZ can affect the transport of destructive chemicals significantly.

## 2.0 METHOD

Two slags (S1 and S2) of similar physical properties but different chemical properties were used to replace CEM I 52.5R at either 30 wt.% or 70 wt.% replacement. The particle size distribution of the slags and Portland cements (PC) as determined by laser diffraction, using a Malvern Mastersizer 2000, is shown in Fig. 1. The binder configurations and mix ratios are shown in Table 1, while the chemical oxide

compositions of the cementitious materials used are provided in Table 2.

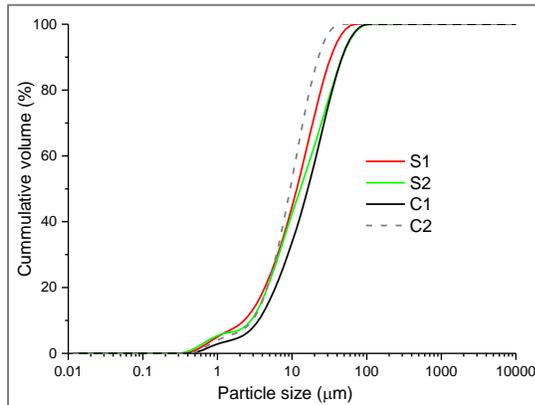


Figure 1: Particle Size Distribution Of Slags (S1 & S2) And Cem I (C1 & C2)

**TABLE 1**  
BINDER CONFIGURATION AND MIX RATIOS

No.	Binder	CEM I		GGBS		Added w/b ratio	Effective w/b ratio
		42.5R	52.5R	Slag 1	Slag 2		
1.	C1	1	0	0	0	0.5	0.493
2.	C2	0	1	0	0	0.5	0.493
3.	30S1	0	0.7	0.3	0	0.5	0.493
4.	30S2	0	0.7	0	0.3	0.5	0.493
5.	70S1	0	0.3	0.7	0	0.5	0.493
6.	70S2	0	0.3	0	0.7	0.5	0.493

**TABLE 2**  
CHEMICAL COMPOSITIONS (WT.%) OF CEMENTITIOUS MATERIALS

Component	CEM I 42.5R	CEM I 52.5R	Slag 1 (S1)	Slag 2 (S2)
SiO <sub>2</sub>	20.17	20.50	36.58	40.14
Al <sub>2</sub> O <sub>3</sub>	5.33	5.43	12.23	7.77
TiO <sub>2</sub>	0.29	0.29	0.83	0.30
MnO	0.05	0.05	0.64	0.64
Fe <sub>2</sub> O <sub>3</sub>	2.65	2.51	0.48	0.78
CaO	63.01	63.43	38.24	37.90
MgO	1.45	1.51	8.55	9.51
K <sub>2</sub> O	0.76	0.79	0.65	0.55
Na <sub>2</sub> O	0.14	0.17	0.27	0.36
SO <sub>3</sub>	3.33	3.43	1.00	1.47
P <sub>2</sub> O <sub>5</sub>	0.12	0.14	0.06	0.02

LOI 950°C	2.12	1.37	(+1.66)	(+0.40)*
Total at 950°C	99.42	99.62	99.88	99.43
Glass content	na	na	99.3	97.1

\* The sample was oxidized with HNO<sub>3</sub> before the determination of LOI

#### A. Degree of hydration by SEM/EDX image analysis (IA)

The degrees of clinker and slag hydration were investigated using scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX), image analysis of backscattered electron (BSE) images in conjunction with EDX magnesium maps. These were acquired using Zeiss EVO MA 15 SEM equipped with Oxford Instruments X-max SDD EDX detector. 30 BSE images and corresponding EDX maps were obtained per sample, at 800x magnification and working distances between 8 and 9mm, using an accelerating voltage of 20KeV. Image analysis was carried out using ImageJ software in line with previous studies [10, 11].

#### B. X-ray diffraction (XRD)

Crystalline hydration products were followed using a Bruker D2 phaser diffractometer with a Cu K $\alpha$  source, operating at 30 KV and 10 mA. Scanning was performed on back-loaded, powdered samples from 5° to 70°: 2 $\theta$ , at 0.034° increment with a scan time of 2 s and sample rotation of 15/min. Phases were identified using BRUKER XRD DIFFRAC.SUITE V3.0 software.

### 3.0 RESULTS AND DISCUSSION

Typical SEM-BSE images (Fig. 2 to Fig. 5), showing microstructural developments in the investigated pastes, from 7 to 28 days, reflecting early and later stages of hydration. At 7 days, the microstructure of the reference PC cured at 20°C (Fig. 2a), appear coarser with more pores than 28 days, reflecting the refining of microstructure as hydration advanced with time. Most of the fine-grained PC clinker had hydrated, leaving anhydrous grains of sizes ranging approximately 20 to 50 $\mu$ m.

The microstructures appeared a lot more refined for the slag blends, consistent with the literature [12, 13]. More presence of Op C-S-H and less of CH was observed at 28 days. Unhydrated PC clinker grains were scarcely present in the slag blends, even with the low 30 wt.% replacement, indicating the acceleration of PC hydration by the presence of slag in the paste. There were clear pore refinements as hydration progressed from 7 to 28 days.

At 38°C (Fig. 3), hydration was clearly accelerated for all the systems. However, micro cracks were observed at 28 days for the reference PC, which may be related to the disadvantage of curing PC systems at elevated temperatures. Many researchers have reported on the detrimental effects of elevated temperature curing [14-18]. These effects were less present in the microstructures of the slag-blended pastes, consistent with earlier findings concerning the robustness of slags to the detrimental effects of elevated temperatures.

The microstructural developments of 70 wt.% slag blends at 20 and 38°C curing temperatures are shown in Fig. 4 and Fig. 5 respectively. The changes in the microstructures between 7 and 28 days were similar to 30 wt.% slag blends discussed earlier, although more unreacted slag grains were seen. This is due to the high volume of slag in the paste compared with PC, and the consequent decrease in the weighted degree of hydration of the blend. Although the degree of slag hydration decreased only slightly (2-6%), the effect of increased slag content was more significant (>10%), considering the weighted degree of hydration of the blended paste as a whole. The large volume of unreacted slag grains explains the lower compressive strength observed at 28 days, for the 70 wt.% slag blends. The presence of limited quantity of CH was also observed. Increasing slag load to 70% had a significant positive effect on capillary porosity (Fig. 6).

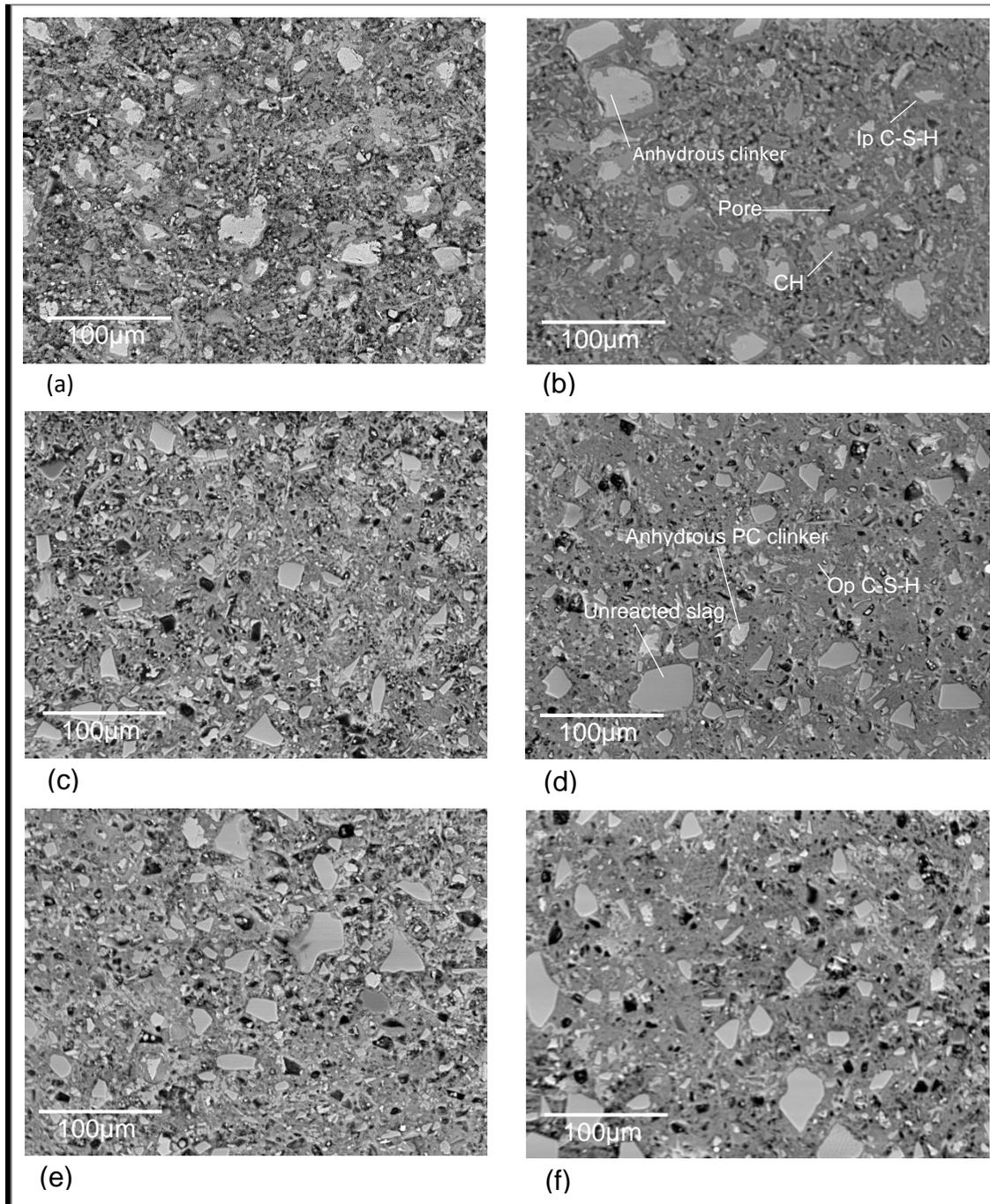


FIG. 2: SEM-BSE IMAGES OF PASTE SAMPLES CURED AT 20°C: (A) C1-7DAY, (B) C1-28DAY, (C) 30S1-7DAY, (D) 30S1-28DAY, (E) 30S2-7DAY, (F) 30S2-28DAY

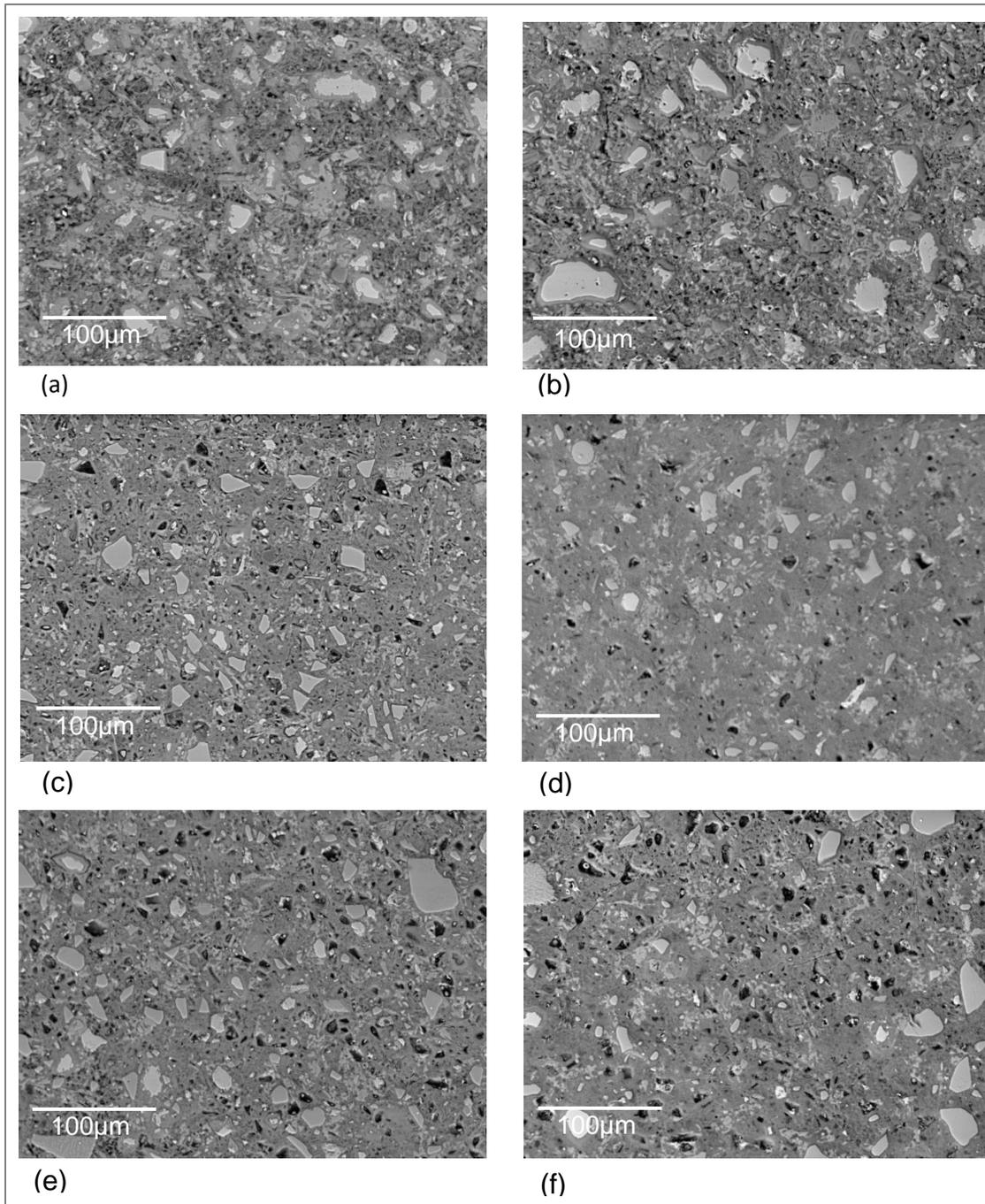


FIG. 3: SEM-BSE IMAGES OF PASTE SAMPLES CURED AT 38°C: (A) C1-7DAY, (B) C1-28DAY, (C) 30S1-7DAY, (D) 30S1-28DAY, (E) 30S2-7DAY, (F) 30S2-28DAY

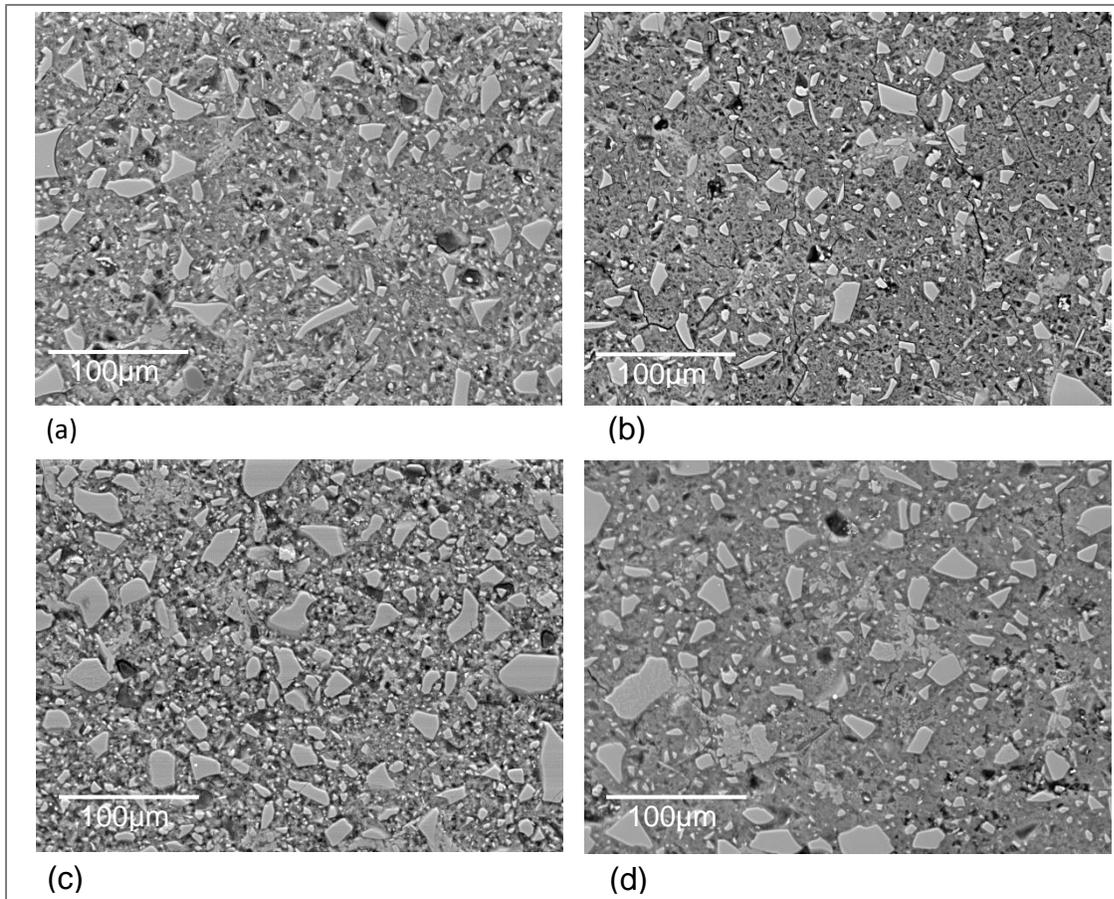


FIG. 4: SEM-BSE IMAGES OF PASTE SAMPLES CURED AT 20°C: (A) 70S1-7DAY, (B) 70S1-28DAY, (C) 70S2-7DAY, (D) 70S2-28DAY

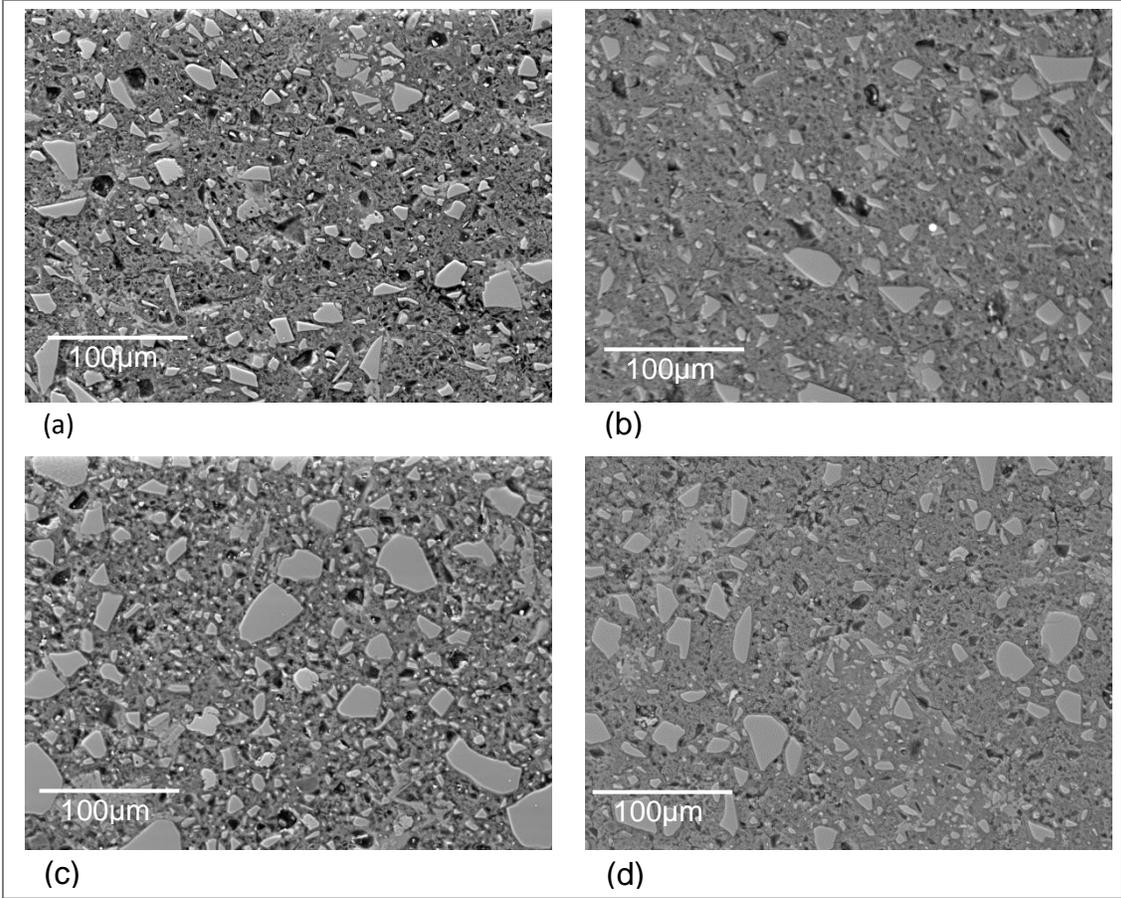


FIG. 5: SEM-BSE IMAGES OF PASTE SAMPLES CURED AT 38°C: (A) 70S1-7DAY, (B) 70S1-28DAY, (C) 70S2-7DAY, (D) 70S2-28DAY

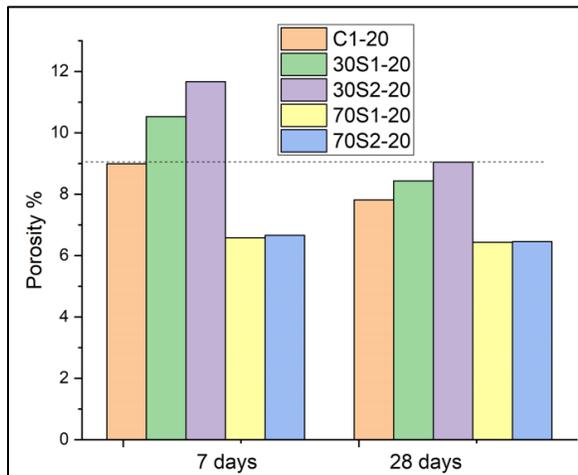


FIG. 6: CAPILLARY POROSITY FROM SEM-BSE IMAGES OF PASTES EXPOSED AT 20°C

A. *Degrees of slag and clinker hydration by SEM-EDX*

The weighted degrees of hydration of the slag blends obtained at 7 and 28 days, from image analysis of coupled SEM-BSE images with SEM-EDX magnesium maps are presented in

TABLE 3. This shows the combined effects of slag composition, slag loading, and exposure temperature. At 7 days, a higher temperature led to significant acceleration of slag hydration, with up to a 50% increase for 30% slag blends, and about a 30% increase for the 70% slag blends. This increased hydration however dropped to between 2 and 7% at 28 days, showing that the acceleration of slag hydration during early ages become diminished at later ages. This follows the hydration of neat PC shown by the precipitation of CH where at 38°, XRD analyses (Fig. 8) showed rapid increase in CH to approximately maximum levels up to 7 days, while only increasing gradually to maximum at 28 days, for samples cured at 20°C. This behaviour can be related to slag hydration which is activated by the presence of CH in a slag-PC blend. The more basic slag 1 showed higher rate of hydration, exceeding the mean value (Fig. 7) by 7 days for samples cured at 38°C. This agrees with Ogirigbo [11] who investigated the hydration of similar slags using 30 wt.% replacement in CEM I. Increasing slag content to 70% had a slight retardation effect on the degree of slag hydration. This may be due to decreased availability of CH (Fig. 8), which is a precursor for slag pozzolanic reaction. The consumption of portlandite is known to be associated with pozzolanic reaction [19-25].

TABLE 3  
WEIGHTED DEGREES OF HYDRATION

Age (day)	Mix	Wt.% of slag	Degree of hydration (%) at 20°C				Degree of hydration (%) at 38°C			
			Slag	Clinker	Weighted	Std Error	Slag	Clinker	Weighted	Std Error
7	C1	0	0.00	74.91	74.91	0.74	0.00	75.76	75.76	1.02
	30S1	30	38.73	91.33	75.55	0.80	58.60	91.67	81.75	0.50
	30S2	30	31.32	90.83	72.98	0.99	47.60	89.87	77.19	0.79
	70S1	70	37.78	96.88	55.51	0.72	50.35	98.56	64.81	0.82
	70S2	70	30.86	96.99	50.70	0.79	37.70	95.43	55.02	0.77
28	C1	0	0.00	79.28	79.28	0.70	0.00	80.31	80.31	0.65
	30S1	30	63.22	94.53	85.14	0.60	67.57	96.02	87.49	0.52
	30S2	30	52.09	94.26	81.61	0.76	53.47	95.93	83.19	0.49
	70S1	70	62.11	98.47	73.02	0.77	63.32	99.84	74.28	0.60
	70S2	70	49.35	98.43	64.07	0.56	51.67	98.64	65.76	0.74

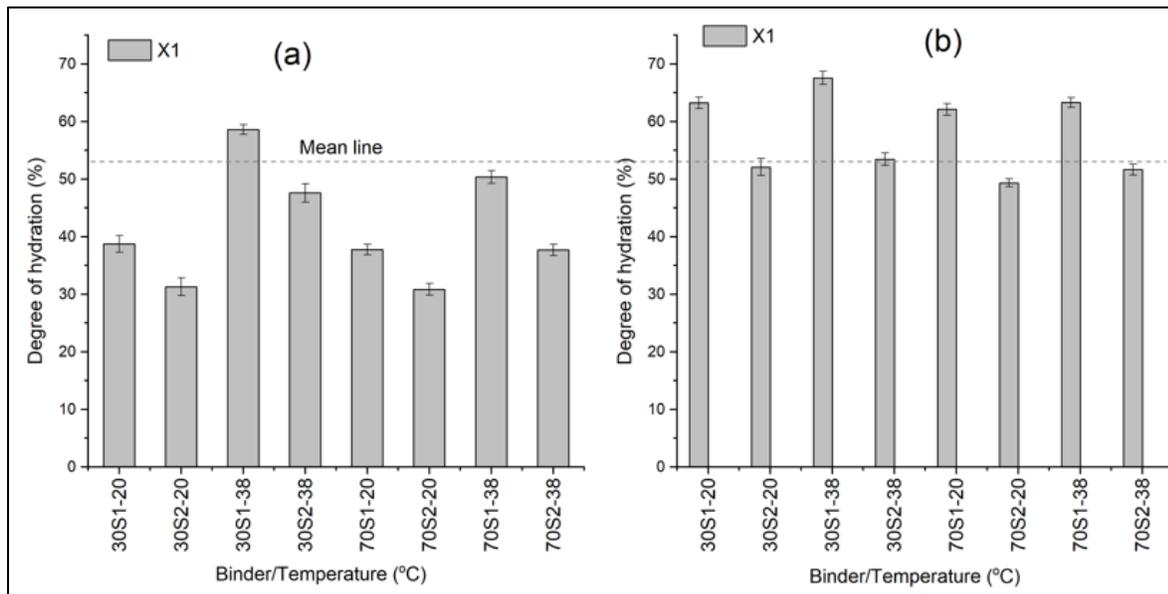


FIG. 7: DEGREE OF HYDRATION OF SLAG CEMENTS: (A) AT 7 DAYS. (B) AT 28 DAYS

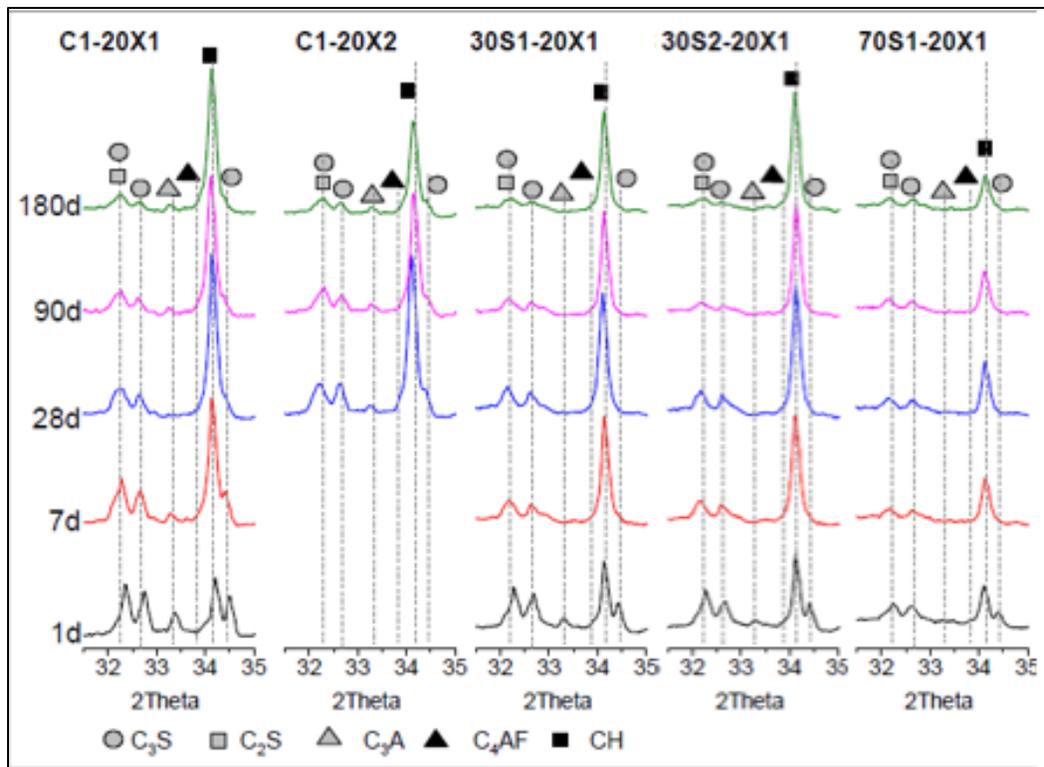


FIG. 8: XRD PATTERNS SHOWING OF HYDRATION OF CEM I AND SLAG CEMENTS FROM 1 TO 180 DAYS

#### 4.0 CONCLUSION

This study has shown that the more basic, alumina-rich slag 1 blend showed overall, more compact microstructure than slag 2 blend. This behaviour was more consistent at early age than later age and reflects the reactivities of the 2 slags. Slag 1 had higher degree of hydration and reacted more quickly at early age, leading to a considerably different microstructure. However, at later age when hydration had slowed down considerably, the performance of the 2 slag systems seems to be on a par. The 2 slag systems showed significantly more compact microstructures than that of the reference Portland cement.

##### *Effect of temperature*

Samples were investigated at 20 and 38°C simultaneously, to understand the influence of elevated temperature on the hydration and microstructural properties of pastes. Elevated temperature led to accelerated hydration. This was particularly detrimental to the reference PC. Elevated temperature was however, more beneficial for the slag blends as slag hydration was accelerated over longer periods than PC. The effect of temperature was more pronounced at early ages than later ages. The slag blends showed improved and more compact microstructures at elevated temperature, while the reference PC was more porous and more permeable. This difference in the porosity and consequently, permeability, due to increased temperature, was more pronounced at 7 days than 28 days. This study has shown that, while much higher temperatures from 60°C may cause adverse effects on microstructure of slag blends as reported in literature, exposure to moderately high temperatures such as 38°C did not show any adverse effects on paste and mortar microstructures up to 28 days.

##### *Effect of slag loading*

Increasing slag load from 30 to 70 wt.%, caused a retardation in the rate of hydration of the slag-blended pastes. However, this was beneficial with respect to the transport properties of the blended systems. All the tests indicated reduced porosity, indicating a significant decrease in penetrability by any attacking compound. This has great positive impact on the resistance of the paste and mortar or concrete systems to the ingress of destructive salt solution.

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#### References

- [1] H. F. W. Taylor, *Cement Chemistry*, 2nd ed. 1997.
- [2] P. K. Mehta and P. J. M. Monteiro, *Concrete: microstructure, properties, and materials*, 3rd ed. New York: McGraw-Hill, 2006.
- [3] C. Hu, Z. Li, Y. Gao, Y. Han, and Y. Zhang, "Investigation on microstructures of cementitious composites incorporating slag," *Adv. Cem. Res.*, vol. 26, pp. 222-232. [Online]. Available: <http://www.icevirtuallibrary.com/content/article/10.1680/adcr.13.00029>
- [4] I. G. Richardson and G. W. Groves, "Microstructure and microanalysis of hardened cement pastes involving ground granulated blast-furnace slag," *Journal of Materials Science*, journal article vol. 27, no. 22, pp. 6204-6212, November 01 1992, doi: 10.1007/bf01133772.
- [5] M. M. C. Canut, "Pore structure in blended cement pastes," PhD, Department of Civil Engineering, Technical University of Denmark, Denmark, R-268, 2011.
- [6] F. Li and X. Luo, "Interfacial zone effects of chloride penetrations in precast concrete member joints," *Adv. Cem. Res.*, vol. 0, no. 0, pp. 1-46, 2018, doi: 10.1680/jadcr.17.00211.
- [7] J. M. Gao, C. X. Qian, H. F. Liu, B. Wang, and L. Li, "ITZ microstructure of concrete containing GGBS," *Cem. Concr. Res.*, vol. 35, no. 7, pp. 1299-1304, 7// 2005, doi: <http://doi.org/10.1016/j.cemconres.2004.06.042>.
- [8] K. Wu, H. Shi, L. Xu, G. Ye, and G. De Schutter, "Microstructural characterization of ITZ in blended cement concretes and its

- relation to transport properties," *Cem. Concr. Res.*, vol. 79, pp. 243-256, 1// 2016, doi: <http://dx.doi.org/10.1016/j.cemconres.2015.09.018>.
- [9] K. L. Scrivener, A. K. Crumbie, and P. Laugesen, "The Interfacial Transition Zone (ITZ) Between Cement Paste and Aggregate in Concrete," *Interface Sci.*, journal article vol. 12, no. 4, pp. 411-421, October 01 2004, doi: 10.1023/B:INTS.0000042339.92990.4c.
- [10] V. Kocaba, E. Galluci, and K. L. Scrivener, "Methods for the determination of degree of reaction of slag in blended cement pastes," *Cement & Concrete Research*, vol. 42, pp. 511-525, 2012.
- [11] O. R. Ogirigbo, "Influence of Slag Composition and Temperature on the Hydration and Performance of Slag Blends in Chloride Environments," PhD, School of Civil Engineering, The University of Leeds, 2016.
- [12] J. Bijen, "Benefits of slag and fly ash," *Constr. Build. Mater.*, vol. 10, no. 5, pp. 309-314, 7// 1996, doi: [http://dx.doi.org/10.1016/0950-0618\(95\)00014-3](http://dx.doi.org/10.1016/0950-0618(95)00014-3).
- [13] S. Teng, T. Y. D. Lim, and B. Sabet Divsholi, "Durability and mechanical properties of high strength concrete incorporating ultra fine Ground Granulated Blast-furnace Slag," *Constr. Build. Mater.*, vol. 40, no. 0, pp. 875-881, 3// 2013, doi: <http://dx.doi.org/10.1016/j.conbuildmat.2012.11.052>.
- [14] J. I. Escalante-García and J. H. Sharp, "Effect of temperature on the hydration of the main clinker phases in portland cements: part i, neat cements," *Cem. Concr. Res.*, vol. 28, no. 9, pp. 1245-1257, 9// 1998, doi: [https://doi.org/10.1016/S0008-8846\(98\)00115-X](https://doi.org/10.1016/S0008-8846(98)00115-X).
- [15] K. O. Kjellsen and R. J. Detwiler, "Reaction kinetics of portland cement mortars hydrated at different temperatures," *Cem. Concr. Res.*, vol. 22, no. 1, pp. 112-120, 1992/01/01 1992, doi: [http://dx.doi.org/10.1016/0008-8846\(92\)90141-H](http://dx.doi.org/10.1016/0008-8846(92)90141-H).
- [16] K. O. Kjellsen, R. J. Detwiler, and O. E. Gjörv, "Backscattered electron imaging of cement pastes hydrated at different temperatures," *Cem. Concr. Res.*, vol. 20, no. 2, pp. 308-311, 1990/03/01 1990, doi: [http://dx.doi.org/10.1016/0008-8846\(90\)90085-C](http://dx.doi.org/10.1016/0008-8846(90)90085-C).
- [17] K. O. Kjellsen, R. J. Detwiler, and O. E. Gjörv, "Development of microstructures in plain cement pastes hydrated at different temperatures," *Cem. Concr. Res.*, vol. 21, no. 1, pp. 179-189, 1991/01/01 1991, doi: [http://dx.doi.org/10.1016/0008-8846\(91\)90044-I](http://dx.doi.org/10.1016/0008-8846(91)90044-I).
- [18] B. Lothenbach, F. Winnefeld, C. Alder, E. Wieland, and P. Lunk, "Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes," *Cem. Concr. Res.*, vol. 37, pp. 483-491, 2007.
- [19] M. J. Whittaker, "The Impact of Slag Composition on the Microstructure of Composite Slag Cements Exposed to Sulfate Attack," PhD, School of Civil Engineering, University of Leeds, Leeds, 2014.
- [20] O. R. Ogirigbo and L. Black, "Influence of slag composition and temperature on the hydration and microstructure of slag blended cements," *Constr. Build. Mater.*, vol. 126, pp. 496-507, 11/15/ 2016, doi: <http://dx.doi.org/10.1016/j.conbuildmat.2016.09.057>.
- [21] F. Bellmann and J. Stark, "Activation of blast furnace slag by a new method," *Cem. Concr. Res.*, vol. 39, no. 1, pp. 644-650, 2009.
- [22] A. Bougara, C. Lynsdale, and N. B. Milestone, "Reactivity and performance of blastfurnace slags of differing origin," *Cem. Concr. Compos.*, vol. 32, no. 4, pp. 319-324, 4// 2010, doi: <http://dx.doi.org/10.1016/j.cemconcomp.2009.12.002>.
- [23] R. Taylor, I. G. Richardson, and R. M. D. Brydson, "Composition and microstructure of 20-year-old ordinary Portland cement-ground granulated blast-furnace slag blends containing 0 to 100% slag," *Cem. Concr. Res.*, vol. 40, no. 7, pp. 971-983, 2010, doi: 10.1016/j.cemconres.2010.02.012.
- [24] A. Darquennes, B. Espion, and S. Staquet, "How to assess the hydration of slag cement concretes?," *Constr. Build. Mater.*, vol. 40, no. Supplement C, pp. 1012-1020, 2013/03/01/ 2013, doi: <https://doi.org/10.1016/j.conbuildmat.2012.09.087>.
- [25] J. I. Escalante, L. Y. Gomez, K. K. Johal, G. M. endoza, H. M. ancha, and J. M. endez, "Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions," *Cem. Concr. Res.*, vol. 31, pp. 1403-1409, 2001.