Performance of high volume supplementary cementing materials for high density concrete at elevated temperature

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1. Abstract

Materials specifications for some applications of mass high density concrete, which may be subjected to elevated temperatures, require the use of either low heat of hydration (LH), moderate heat of hydration (MH) or high sulphate resistant (HS) Portland cement. With long term production and availability of LH, MH and HS cements uncertain, a comprehensive study was initiated to identify alternative cementing materials meeting specific cementing materials performance criteria. Slag blended cement was evaluated and determined to have acceptable plastic and hardened properties in high density concrete, meeting and often exceeding performance requirements. The current paper compares experimental results, including effects of aging and elevated temperature on mechanical and material properties, such as compressive strength, tensile strength, modulus of elasticity, mineralogy and porosity of high density concrete using HS and slag blended cement.

2. Background

The use of high density concrete in construction is a specialized field with limited published references on this topic. ACI 304.3R-96 [1] presents recommended methods and procedures for measuring, mixing, transporting and placing high density (HD) concrete. HD concrete is generally used for shielding structures, including structures for the nuclear industry or medical buildings (linear accelerators, high dose rate (H.D.R.) rooms, and all therapeutic modalities requiring shielding materials). It is also used as protective and weight coatings solutions for negative buoyancy and mechanical protection for pipelines in undersea and wet environments. For this purpose, high density materials such as iron bearing ores (magnetite, hematite, illmenite), barium sulphate, as well as scrap, scale, broken metal chips, and others are introduced into concrete as coarse aggregate. The fine aggregate fractions in such concretes are usually manufactured materials such as crushed iron ores, quartzite tailings or iron shot. Use of these coarse and fine aggregates, combined with special technological procedures make it possible to increase concrete density up to ~4,000 kg/m^3 at compressive strengths of ~79 MPa.

In Canada, currently approved cements for some applications of mass high density concrete, for which temperature rise in the concrete is of concern, will not be reliably available beyond the end of 2006. This is a result of the cement industry moving away from manufacturing these types of so-called 'special-use' Portland cements. These cements, Portland Types MH (moderate heat), LH (low heat) and HS (high sulphate resistance) are being replaced by blending varying amounts of supplementary cementing materials (SCMs) with 'general-use' Portland cement (Type GU) to provide 'Blended Cements'. In order to satisfy the current and future requirements of limiting temperature rise in concrete, and hence the potential for thermal cracking of the concrete, blended cements needed to be evaluated for use.

The work presented in this paper is part of a broad project having as its overall objective the technical evaluation of an alternative cement and high density concrete mix design to meet specific target properties. Two factors have been identified as essential for the cementing material to be used: heat of hydration, as it relates to potential concrete cracking, and protection of embedded steel components from corrosion. The project consisted of various stages including completion of preliminary assessments of candidate SCM blended cements, and identifying the most promising SCM blend, in this case blended cement based on the use of Type GU Portland cement replaced with 50% slag ('50% slag blended cement'). This was followed by detailed evaluation and testing of the slag blended cement HD concrete. The selection of a candidate SCM was based on a combination of technical and market factors, with slag providing the best combination of engineering performance, extensive performance history in the concrete industry, and long-term consistency and availability. The experimental program consisted of full laboratory and field experimental programs to assess and test fresh concrete properties and hardened concrete performance and durability at ambient and elevated temperatures. This paper focuses on the effect of aging and elevated temperature exposure on mechanical properties, such as compressive strength, tensile strength and modulus of elasticity, and on mineralogy and pore structure of high density concrete using HS and slag blended cement.

3. Experimental program

The effects of ambient (23°C) and elevated temperature (94°C) were evaluated both on hardened concrete and companion pastes produced using Type HS and slag blended cement. 94°C is the maximum temperature expected for the in-use HD concrete being evaluated. Concrete mix designs included the currently used 375 kg/m^3 Type HS reference high density mix at a water-to-cementing material ratio (w/cm) of 0.37, and a 325 kg/m^3 50% slag – GU cement at a w/cm of 0.42 for the slag blended cement concrete, which is the high density mix proposed in the current study. The w/cm ratio of 0.42 represents the maximum allowable water content. Both mixes used natural iron-ore based aggregates, air-entraining admixture as required to provide freeze-thaw resistance, and superplasticizer as required for suitable workability and placeability.

Companion paste samples were prepared to allow for testing of mineralogical composition of the solid phase and porosity. The pastes, which are more aptly described as micro-mortars (hereinafter referred to as ‘pastes’ throughout the paper), are composed of the cementing materials (Type HS cement and slag blended cement), the -75µm fraction of the aggregate from both the sand and the coarse aggregate, and admixtures and water at the same relative proportions as the concretes tested in this study. These paste samples effectively represent the concretes tested with all material coarser than 75µm removed. The pastes were cast into multiple 24mm diameter plastic vials, sealed using materials resistant to temperatures of 94°C and cured in the same manner as the concrete specimens. The sealed paste samples were then maintained at 23°C for 56 days. This represents the minimum time between placing the HD concrete and exposure to high temperatures in service. Following the 56 day ‘seal’-curing period, sealed samples were exposed to 94°C elevated temperature.

Concrete mechanical properties such as compressive strength (ASTM C39), split tensile strength (ASTM C496), modulus of elasticity (ASTM C469) and hardened density (ASTM C642) were evaluated at ambient (23°C) and elevated temperature (94°C) over time up to 91 days exposure at 94°C. Samples at elevated temperatures were cooled at a rate not exceeding 20°C/hour and all physical testing was conducted at 23°C. In addition to the physical testing conducted on the concrete specimens, selected specimens were also subjected to concrete petrographic examination based on ASTM C856. Thin sections were prepared of Type HS and slag blended cement specimens subjected to ambient and elevated temperature curing conditions.

Paste samples were subjected to an array of tests evaluating mineralogy using X-ray diffraction (XRD) and connected porosity measured using mercury intrusion porosimetry (MIP). Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDXA) was used to provide evidence of differences between cementing materials at the microstructural level after 28 and 56 days exposure at 23°C and 94°C temperature conditions. These tests were conducted to assess the relative durability of the concrete, particularly related to corrosion resistance.

Connected pores together with cracks act as a pathway allowing chloride ions and water to penetrate the material, and potentially lead to corrosion. Permeability and diffusivity are controlled by the volume, size, distribution, shape, tortuosity and connectivity of pores. The pores relevant to permeability are capillary pores, with a diameter >0.12-0.16 µm [2]. Winslow and Liu [3] suggest that the pore structure of paste in concrete is more porous than pore structure of plain paste that is prepared without aggregate. The total volumes of pores in both paste in concrete and plain paste are reduced as hydration proceeds, but the later the stage of hydration, the greater the difference is seen. The paste in mortar has a pore structure that is more like that in concrete than in plain paste. Therefore, due to the fact that the ’paste’ prepared and used for MIP is actually a micro-mortar, which contains -75µm fraction of the aggregate (from both the sand and the stone), admixtures and water to the same relative proportions as the concretes tested, it is assumed that the porosity measured in this study is indicative of the connected porosity in concrete exposed to similar conditions.

4. Results and discussions

Figures 1-3 present the effect of material type and curing conditions on concrete compressive and tensile strength and modulus of elasticity (MOE) development over time. Concrete densities measured were 3644 and 3602 kg/m^3 for Type HS and slag blended cement concretes, respectively, which were within the target range of 3500-3700 kg/m^3. Although the total cementing materials content of the slag blended cement concrete was less than that of the Type HS cement concrete (325 vs. 375 kg/m^3) and the water-to-cementing material ratio was higher (0.42 vs. 0.37 respectively), both the compressive and split tensile strengths of slag blended cement concrete composition exceeded the target properties at ambient temperature. The MOE values measured were comparable for both mixes. No deleterious changes in the physical properties were observed following 56 days exposure to elevated temperature and both mixes experienced modest gains in compressive and tensile strength ranging from 2 to 11%.

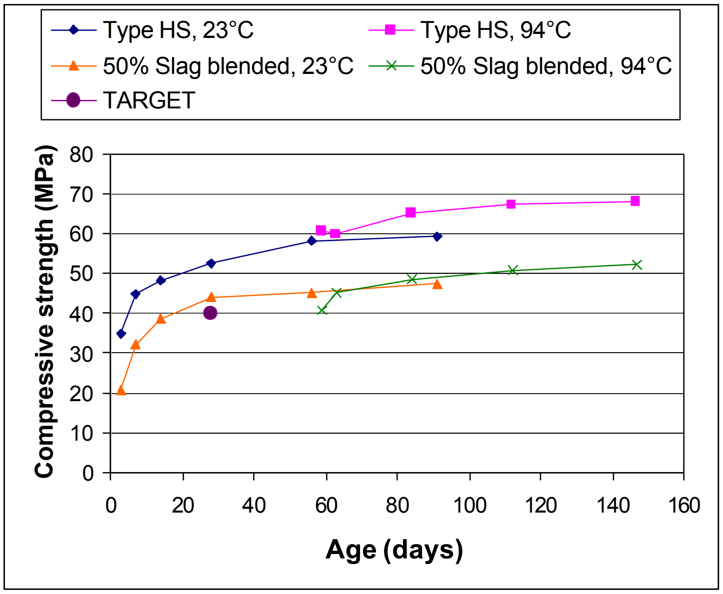


Figure 1. Effect of material type and curing conditions on compressive strength development.

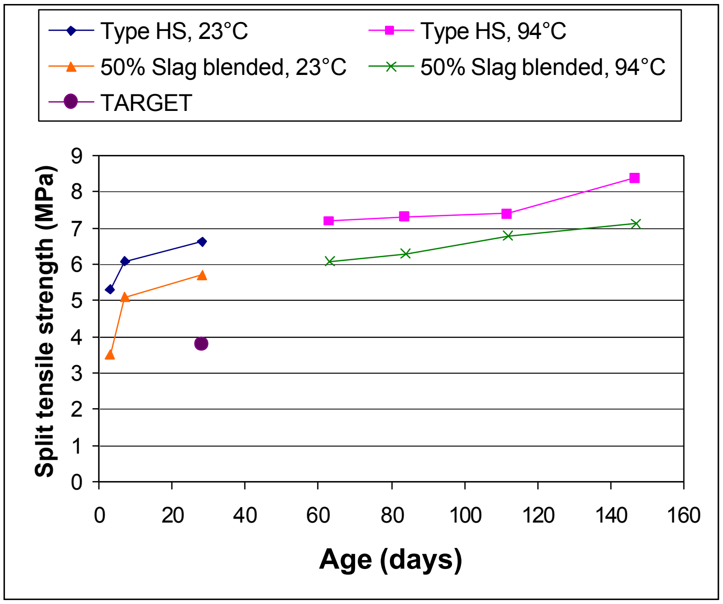


Figure 2. Effect of material type and curing conditions on split tensile strength development.

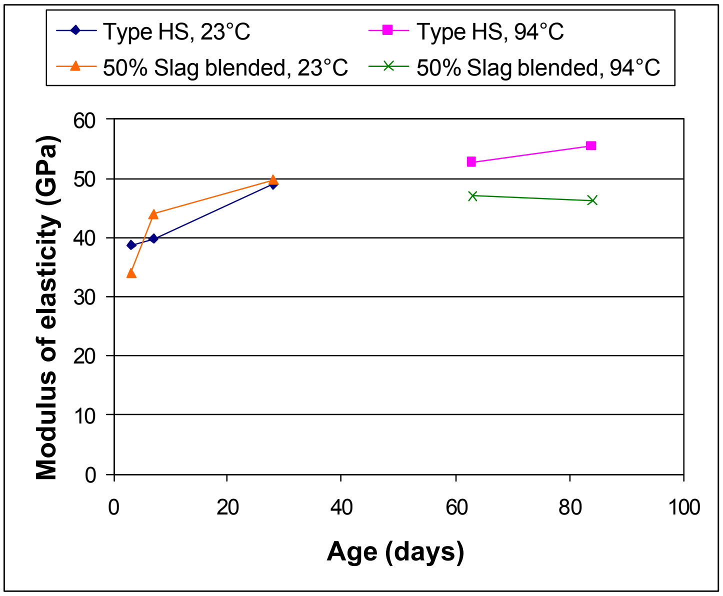
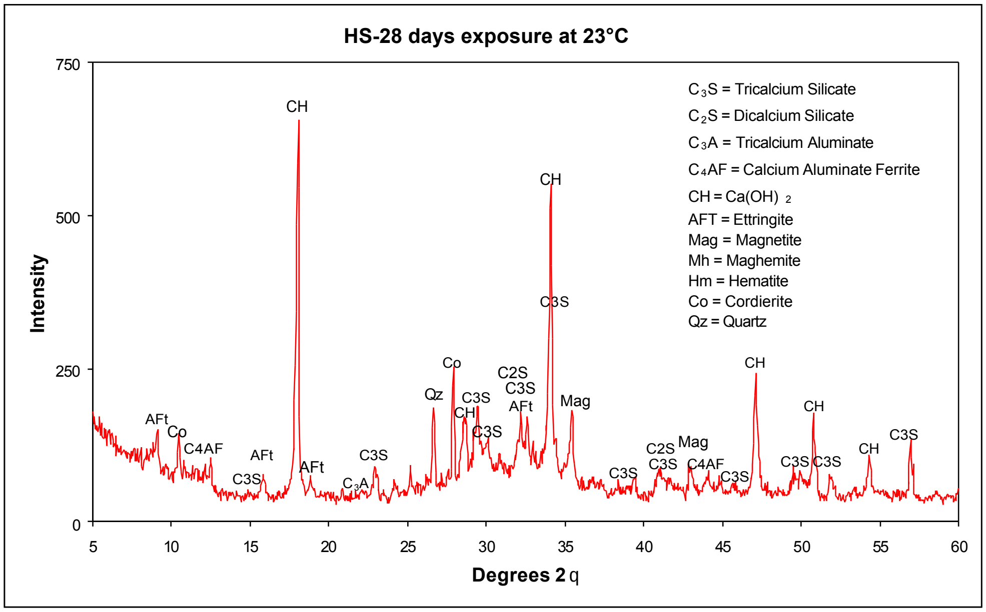
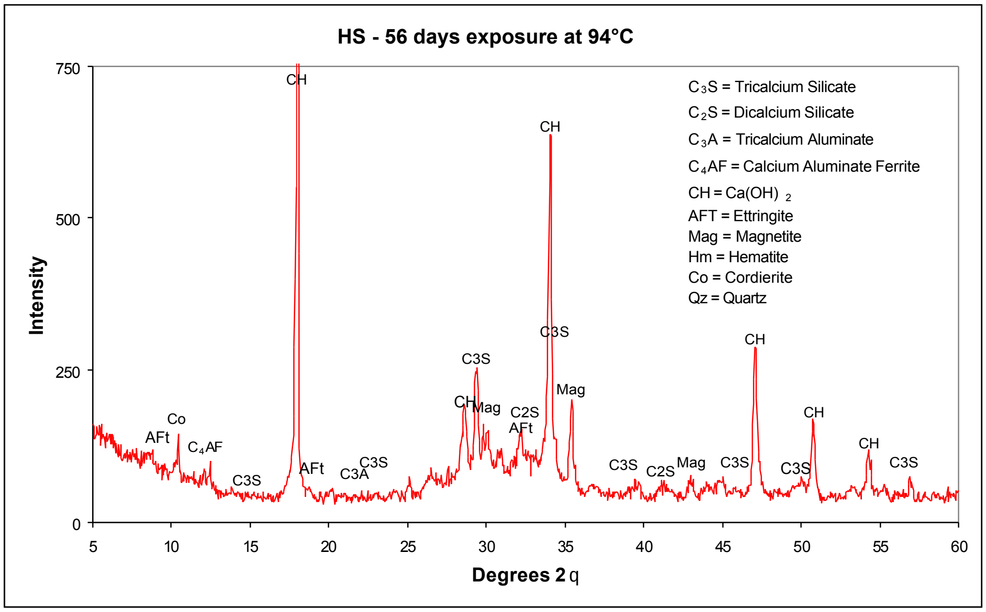


Figure 3. Effect of material type and curing conditions on modulus of elasticity development.

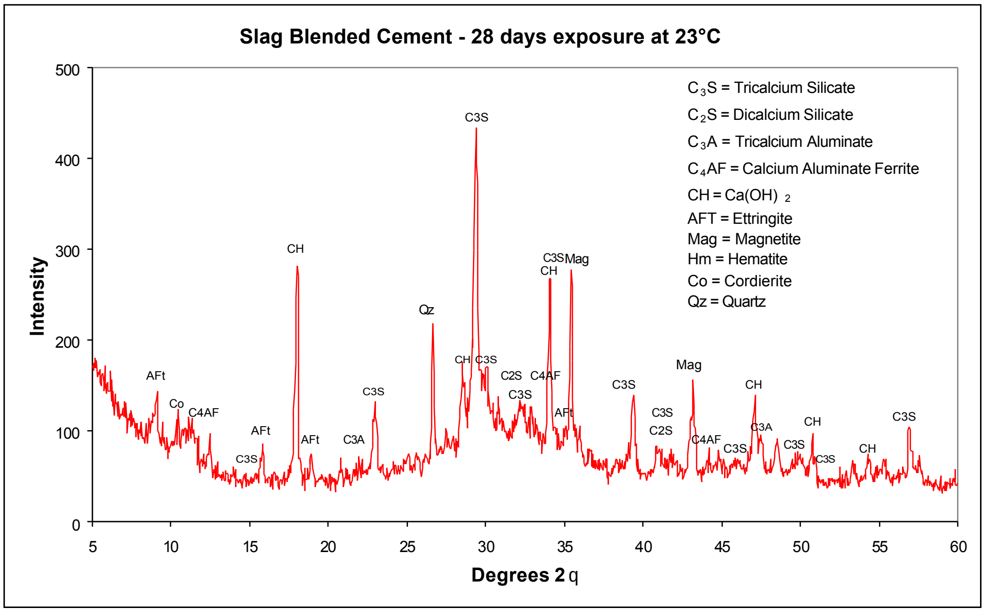
Figures 4 and 5 present XRD patterns of the cement paste mixes studied at 28-day ambient (23°C) and 56-day elevated temperature (94°C) exposure. After 28 and 56 days exposure to 94°C of the paste samples, there has not been any significant alteration of the mineralogy, with the exception of a reduction in ettringite and tricalcium silicate for both paste compositions, and an increase in calcium hydroxide for the 56-day elevated temperature HS paste. The overall calcium hydroxide was lower for the slag blended cement pastes at all ages compared to the Type HS, as expected. Notably, there was no reduction in the relative amounts of calcium hydroxide at these ages, indicating the continued saturation of the pore fluid with respect to calcium hydroxide. The continued presence of calcium hydroxide indicates that the environment in the paste will maintain a pH in excess of 11.5, thus continuing to passivate embedded steel.



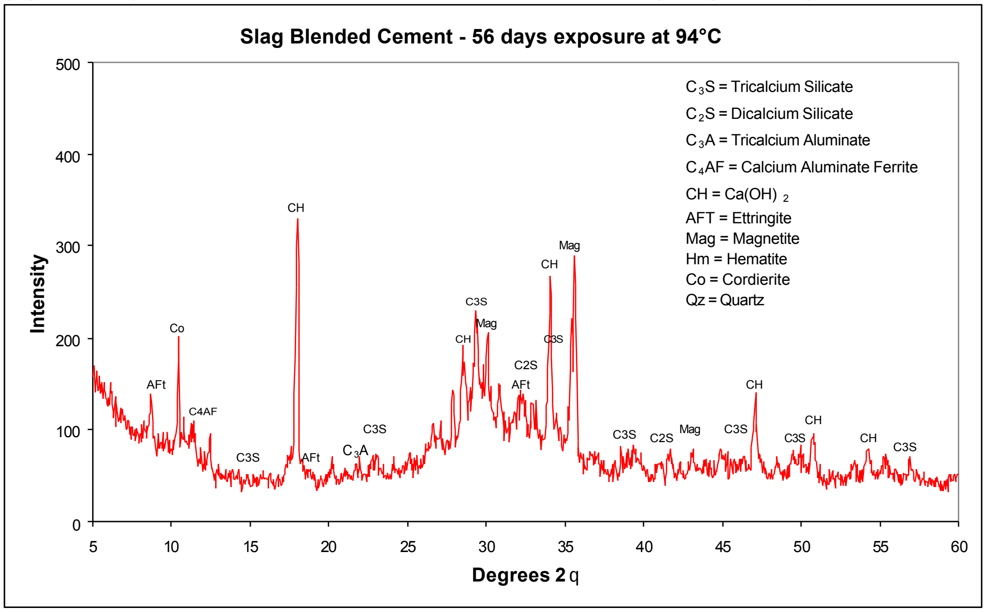
(a) 28-days exposure at ambient temperature (23°) curing conditions.



(b) 56-days exposure at elevated temperature (94°) curing conditions.
Figure 4. XRD patterns for Type HS cement paste samples.



(a) 28-days exposure at ambient temperature (23°) curing conditions.



(b) 56-days exposure at elevated temperature (94°) curing conditions.
Figure 5. XRD patterns for slag blended cement paste samples.

Thin section examinations of concrete specimens subjected to these exposure conditions revealed a notably higher proportion of calcium hydroxide in the Type HS cement concrete versus the slag blended cement (Figures 6 and 7). In the former, calcium hydroxide typically appeared as large anhedral masses along aggregate interfaces, the edges of air voids and randomly distributed throughout the cement paste. In contrast, the calcium hydroxide in the slag blended cement concrete was much smaller in size, as it formed discrete, anhedral shaped masses in similar locations. Although not readily evident from the XRD patterns, thin section examination revealed the proportion of calcium hydroxide was lower in the specimens exposed to 94°C versus ambient conditions for both the Type HS and slag blended cement specimens.

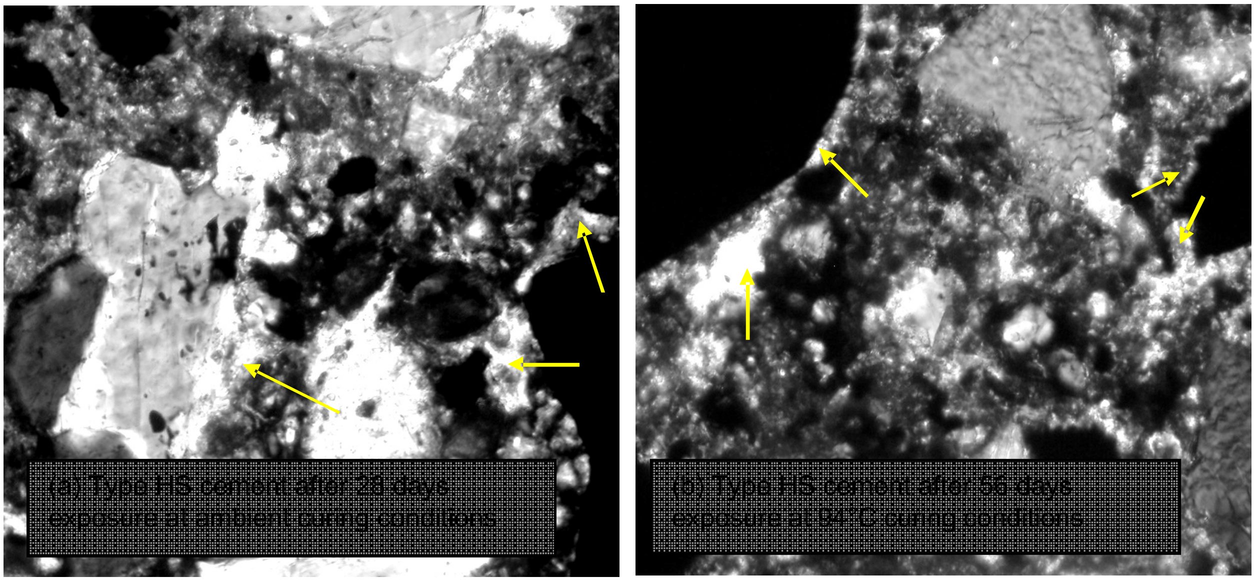


Figure 6. Photomicrographs of Type HS cement concrete. Width of photomicrograph is 0.3mm.

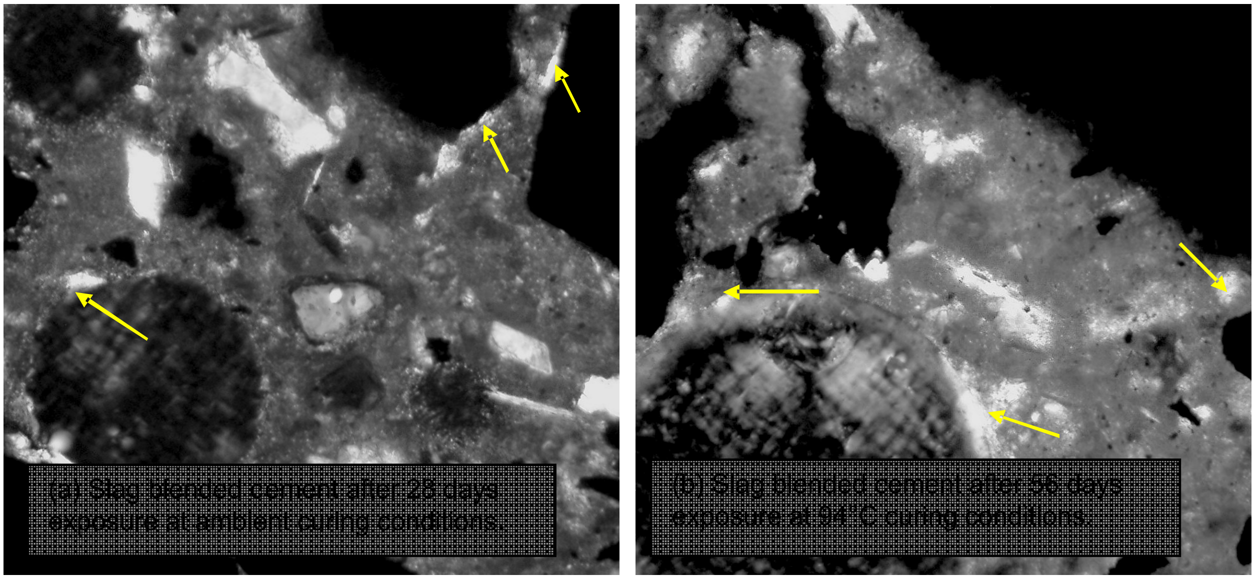


Figure 7. Photomicrographs of slag blended cement concrete. Width of photomicrograph is 0.3mm.

The MIP results presented in Table 1 suggest that the connected pore volume decreases over time regardless of the cementing material and curing conditions used. This is in agreement with results reported in the literature [3] and it is due to continued hydration of cementing materials. For Type HS cement paste, the change in pore volume after 56 days ambient curing is not significant and flattens regardless of the curing temperature used. This confirms formation of typical hydration products, which are visible in the SEM images in Figure 8. The pore volumes after 28 and 56 days ambient curing are lower for Type HS paste compared with the slag blended cement. For the slag blended cement paste there is a significant change in pore volume after 56 days ambient curing and the pore volume after 28 and 56 days elevated temperature curing is lower than that of the Type HS cement paste. The change in microstructure of the slag blended cement paste is visible in the SEM images in Figure 9. Thin section examination of slag blended cement concrete specimens reveals the presence of occasional, short, narrow (0.002mm) micro-cracks in the ambient cured specimens (Figure 10). These types of cracks however, are not present in the specimens subjected to the 94°C curing conditions. The decrease in continuous pore volume noted in the MIP results is likely due to continued formation of hydration products by pozzolanic reactions, which fill the pores and the occasional micro cracks. This is typical for slag blended cement, and is in agreement with other results in the literature [4].

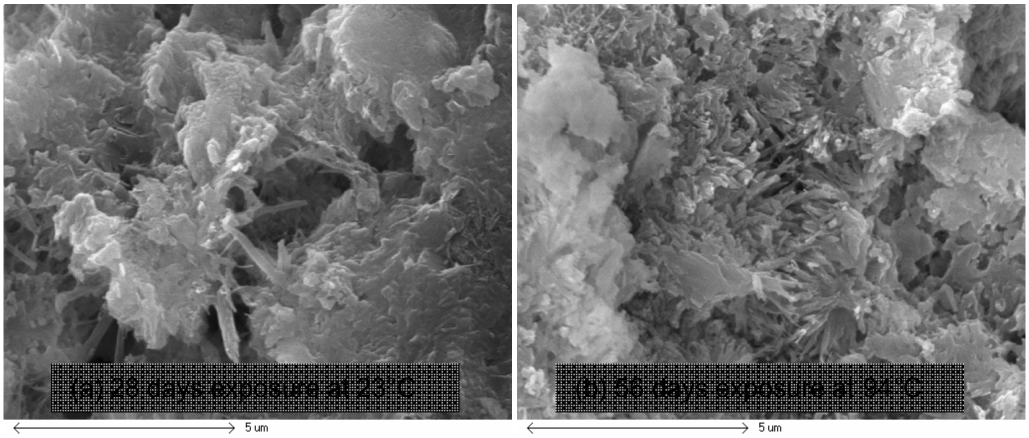


Figure 8. SEM images of Type HS cement pastes (20kV, 15 mm working distance).

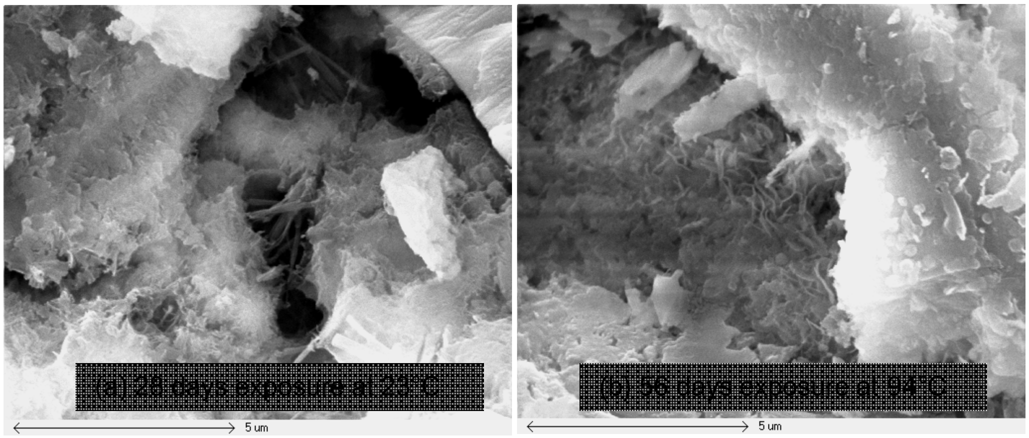


Figure 9. SEM images of slag blended cement pastes (20kV, 15 mm working distance).

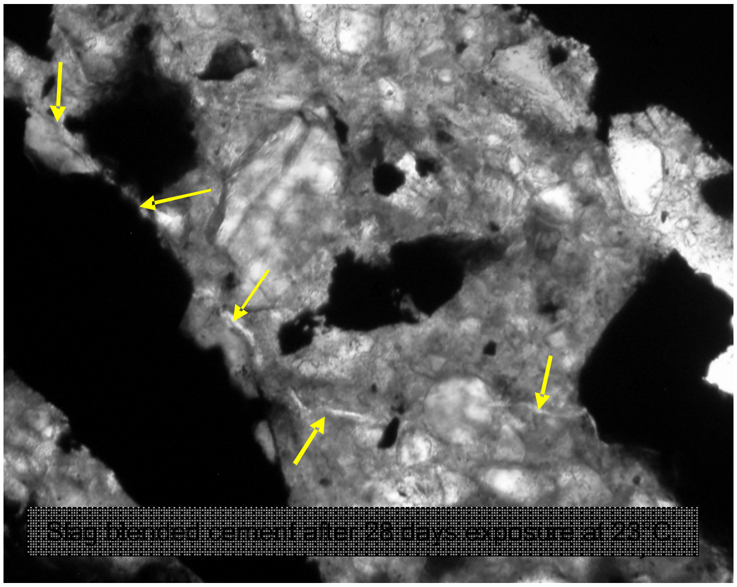


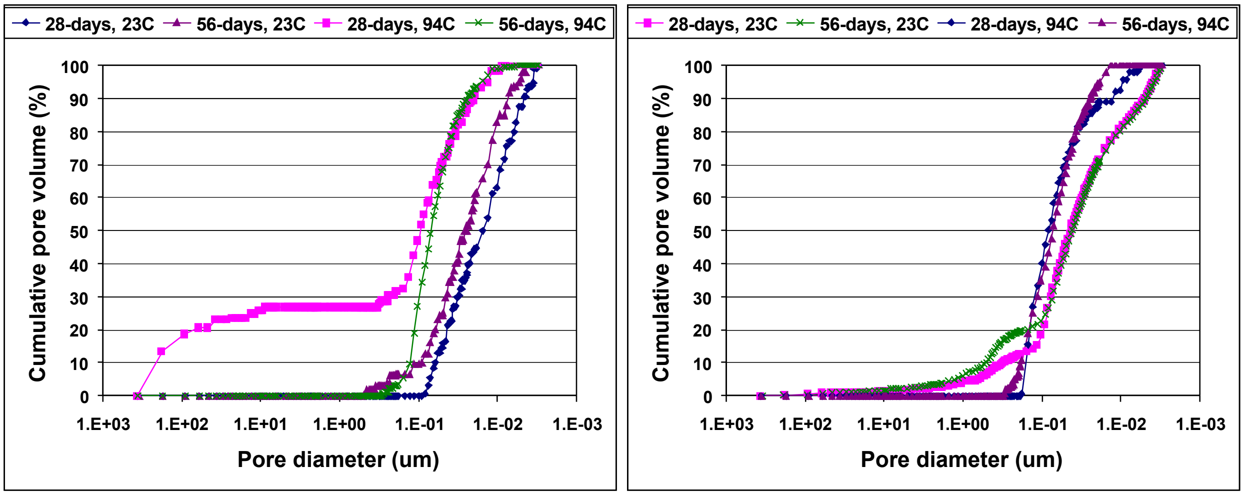
Figure 10. Photomicrograph of slag blended cement cured at ambient temperature, at 28 days. Arrows indicate crack intersecting cement paste. Width of photomicrograph is 0.3mm

Table 1. Cement paste porosity, MIP results.

Temperature (ºC)	**Age (days)**	**Porosity (%)**	
		Type HS cement paste mix	**Slag blended cement paste mix**
23	28	11.0	32.8
	56	6.2	12.7
94	28*	6.5	4.5
	56*	4.8	4.2

* After 56 days ambient curing at 23ºC

Figure 11 shows coarser porosity for slag blended cement paste compared with Type HS cement paste after 28 and 56 days ambient curing. This is expected due to slower formation of hydration products in slag blended cement compared to ordinary Portland cement. The higher percent of pores for slag blended cement compared to Type HS cement is not of concern due to the fact that only a small percentage of the pores is in the pore size range which is relevant to permeability and chloride diffusion (~15%). After 28 days elevated temperature curing, the pore distribution changed for both materials tested, when the Type HS cement paste showed about 30% coarser porosity for pore diameters above 0.2µm. These pores were not previously present, which may be due to changes in the existing hydration products due to the high temperature. This observation is in agreement with results in the literature, which suggest that higher curing temperatures have a detrimental effect on pore volume of ordinary Portland cement, whereas the effect is beneficial for slag blended cement [5]. The slag blended cement paste showed a porosity refinement at elevated temperature, resulting in no porosity above 0.2μm. The more compact pore structure is likely due to formation of finer hydration products and is in agreement with results in the literature [6]. Densification of the pore structure of both cement paste mixes continues after 56 days exposure at elevated temperature, with approximately 10% of the pores above the threshold relevant for permeability and chloride diffusion. The mechanical tests and porosity results in this study confirm that strength development of slag blended cement to a value equivalent to pure Portland cement is obtained more rapidly compared to pore structure refinement [6].



(a) Type HS cement paste (b) Slag blended cement paste

Figure 11. Effect of age and curing conditions on pore size distribution.

5. Conclusions

The objective of the project to identify an alternative low heat cement and to develop a high density concrete mix design to meet target properties was accomplished. The mechanical test results and micro-structural evaluations showed that the candidate proposed containing 50% slag blended with Type GU Portland cement at 325 kg/m^3 total cementing material and a w/cm of 0.42 meets and for some cases exceeds key target properties.

Specific conclusions are as follows:

- The 28-day physical properties after ambient temperature exposure exceeded the targets both for compressive and tensile strength, with MOE values comparable to the reference Type GU Portland cement concrete.

- Physical properties after 91-day elevated temperature exposure (94°C) showed modest gain in strength; most significantly no deleterious changes were observed.
- Hardened density was within target limits.
- No significant change in cement paste mineralogy has been observed after 28-day elevated temperature exposure.
- Fine micro-cracks observed in ambient cured slag blended cements were not present after 28-day elevated temperature exposure.
- MIP results suggest that total connected porosity and thus permeability decreases over time regardless of the cementing material and curing conditions used. Both age and elevated temperature independently affect the pore size distribution. After 56-day elevated temperature exposure, both Type HS and slag blended cement paste mixes have comparable porosity and pore size distribution. All the porosity results show that only a small percentage of the pores is in the pore size range which is relevant to permeability and chloride diffusion (~10-15% of the total connected porosity), therefore both Type HS cement and slag blended cement concrete are low permeability mixes.

6. References

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7. Acknowledgements

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