

Time Dependent Changes in the Internal Chemical Evolution of Blended OPC Cements over a 20 Year Period

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Abstract

Changes in the composition of ordinary Portland cement blended with either Class F fly ash or blast furnace slag at 30% replacement of cement have been investigated from 1 hour to 20 years. A nearly “steady state” aqueous phase composition is achieved during the initial 6 hours with respect to Ca, Na, K and SO₄. Renewed activity, 6-24 hours, showed a rapid decrease in Ca and SO₄ while Na and K increased gradually. Over the 20 year span the internal chemical composition continued to evolve finally reaching some degree of equilibrium. Changes in mineralogy were determined by XRD and Ca(OH)₂ determination, while aqueous phase composition was determined from pore solutions extracted under pressure. Aqueous composition showed minor changes over the long term whereas mineralogy showed variable reactivity particularly between fly ashes. The significance of the results is discussed in relation to durability.

1. Introduction

The cement matrix in concrete is a reactive chemical system that can be influenced by internal chemical attack such as alkali-silica reaction, or environmental changes due to carbonation, sulfate or chlorides. Matrix changes in mineralogy, microstructure and aqueous phase chemistry occur continuously with time and temperature and it is assumed that ultimately a “steady state” is approached in terms of the solid and aqueous phases. Normally studies are performed on laboratory-aged samples cured for 2 years or less, with the data used to develop models for prediction of cement matrix and engineering parameters such as strength and durability over the long term [1, 2]. This time interval may be sufficient for ordinary Portland cements to approach a “steady state” [3] and can be regarded as a base-line from which internal or environmental effects can be measured and impact on durability determined.

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Addition of pozzolanic materials such as fly ash, slag and silica fume is considered in most cases to be beneficial in providing improved durability [4-7]. Blended cements differ significantly in their performance, possibly approaching a “steady state” more slowly than ordinary Portland cements [8], and it is not evident at what age the “steady state” is achieved. Actual investigations on aged blended cements tend to provide minimal early age data [9] or have an undefined history [10]. Compositions of pozzolanic materials tend to vary both chemically and physically, by particle size distribution, shape, apparent specific gravity, nature and morphology of the glass and crystalline mineral components, and impurities. Furthermore characteristics and their effect on the “steady state” can differ from particle to particle even within batches. Compositional variations in slag glasses, while large relative to those in bulk cement, are small in comparison to the chemical and mineralogical variations in fly ashes.

This study determines the aqueous and solid phase compositions over a time period from 1 hour to 20 years at ~25°C for ordinary Portland cement and blended cements that include two different Class F fly ashes, differing principally in their alkali and sulfate content, and a blast furnace slag. The results give a good indication of potential time scales required to obtain a reasonably “steady state” balance between aqueous and solid phases for blended cements and also provides a baseline from which environmental exchanges and durability aspects can be considered.

2. Experimental

2.1 Materials

The ordinary Portland cement conformed to BS 12 and is comparable to ASTM Type 1 cement. The alkali content was moderately low, with Na_2O_e of 0.51 wt.%. Mineralogical compositions were determined through quantitative X-ray diffraction by Dr. Gutteridge of the Cement and Concrete Association, Wexham Springs, England. Blending agents were two commercial fly ashes categorized as low lime Class F fly ashes and a blast furnace slag. The fly ashes, chosen for their differing alkali contents were obtained from British base-load power stations, Longannet and Eggborough. Their crystalline mineral content, as determined by X-Ray diffraction and optical microscopy, included quartz, mullite, spinel close to magnetite and unburnt carbon. The blast furnace slag was shown by petrographic analysis to have a glass content of ~ 97% and was supplied by Clyde Cement Ltd., Strathclyde, Scotland. Physical and chemical characterisation data for the raw materials are given in Table 1. Table 2 gives the water-soluble contents of the fly ashes obtained following the extraction of 1g of fly ash in 100 mL of distilled water for a period of 10 min

at 25°C: the Δ value is the difference between the total weight loss and the sum of the components found.

Table 1. Characterization data of raw materials

Composition (wt. %)	Ordinary Portland Cement	Longannet Fly Ash	Eggborough Fly Ash	Blast Furnace Slag
SiO ₂	20.31	47.29	50.78	34.22
CaO	60.23	2.53	0.95	38.12
Al ₂ O ₃	4.75	34.23	27.45	12.38
Fe ₂ O ₃	1.81	5.66	9.69	0.78
MnO	0.05	0.05	0.05	0.68
MgO	1.93	1.53	1.34	8.08
Na ₂ O	0.19	0.28	1.14	0
K ₂ O	0.48	1.39	3.73	0.31
TiO ₂	0.16	1.52	0.96	0.79
P ₂ O ₅	0.01	0.75	0.15	0
SO ₃	2.30	-	-	-
S	-	-	0.03	0.93
LOI (1000°C)	1.20	1.41	0.92	0
Physical Data				
Density g/cm ³	3.15			2.92
Specific Area m ² /g	432			524

2.2 Sample Preparation

Samples of cement and cement with blending agent at 70/30 weight ratio were prepared as described previously [8] and stored at ~25°C for up to 20 years.

Table 2. Fly ash water soluble component

Water soluble fraction (wt. %)	Longannet Fly Ash	Eggborough Fly Ash
K	0	0.038
Na	0.010	0.060
Ca	0.221	0.262
SO ₄	0.368	0.570
Cl	0	0.050
Δ	0.290	0.270

Excess bleed water observed in most cases was quantitatively measured and a correction factor applied such that practical w/s ratios lay between 0.54 and 0.60. Samples taken at predetermined curing times were subjected to pore fluid extraction [11], yielding between 2 and 15 mL, depending on the degree of hydration and the pressure exerted.

Ca and Mg contents of the pore fluid were determined by atomic absorption spectroscopy and Na and K by atomic emission spectroscopy using a Pye Unicam SP9 spectrophotometer. SO_4^{2-} and Cl^- contents were obtained using a Dionex 2010i anion chromatograph. Spectrophotometry, using catechol violet [12] and molybdenum blue [13] reagents, was used to measure Al and Si respectively. pH was measured with a Russell type CMAWL electrode, by titrimetric methods using HCl with bromothymol blue as indicator and by calculation from $\Sigma(\text{Na} + \text{K} + \text{Ca})$ assuming these to be present as fully dissociated ions.

Solid phase studies were made on 2g sections taken prior to pore fluid extraction on selected samples obtained from cylinders taken at 0.5 month to 20 years. Sections were quenched in acetone to stop hydration, then oven-dried at 60°C and ground to $< 53\mu\text{m}$. X-ray data were obtained using a Hågg Guinier camera for 2 year old samples and a Rigaku DMAXB diffractometer with CuK_α radiation and Ni filter for the 6 and 20 year old samples. Fresh fractures for electron microscopic investigation were coated in gold and examined in a JEOL 2000X EX Temscan operating at 20 kV in the SEM mode and a Hitachi S-520 SEM at 15kV. A sample of each section, not quenched in acetone, was analysed for $\text{Ca}(\text{OH})_2$ content by thermogravimetry using a Seiko 320 SSC 5200 DTA-TGA thermoanalyser.

3. Results

3.1 Aqueous Phase

The composition of the aqueous phase for OPC and OPC blended cements is shown in Figs. 1-4. Ca^{2+} concentrations, Fig. 1, are dominated by four distinct regions; a) an initial plateau from 1-6 hours, b) a rapid decrease in concentration up to 24 hours, c) a slower decrease from 24 hours to about 1 month and d) a “semi-steady state” equilibrium after 1 month. Initial Ca^{2+} concentrations are high, in the range of 20 to 25 mM, and are notably higher for the blended systems than for the neat OPC. Values for all samples drop to around 5 to 7 mM in 24 hours and then decrease further to between 1 and 3 mM at 6 months, after which Ca^{2+} concentrations remain fairly constant. The slight increase in $[\text{Ca}^{2+}]$ from 6 to 20 years may not be significant.

SO_4^{2-} concentrations, Fig. 2, follow the same trend as the Ca^{2+} , concentrations, with an initial plateau extending to 6 hours after which they decline rapidly up to 24 hours and thereafter attain a relatively low constant level with a slight increase again between 2 and 6 years. Sulfate values of OPC initially around 37 mM are higher than in the Longannet and Eggborough fly ash blended cements, which are lower by about 10

mM and 5 mM, respectively. This most likely relates to the fact that the sulfate contribution comes primarily from the alkali sulfates and added gypsum in the cement, with a smaller percentage coming from the blending component. The higher SO_4^{2-} content of the Eggborough fly ash in comparison to the Longannet is due to its higher soluble alkali sulfates content, Table 2. At 24 hours the levels of sulfate decrease to around 1 to 3 mM for all systems and remain relatively constant until around 6 years, when there is a slight increase.

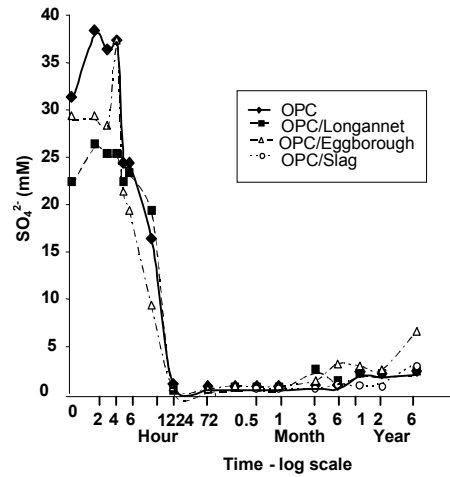
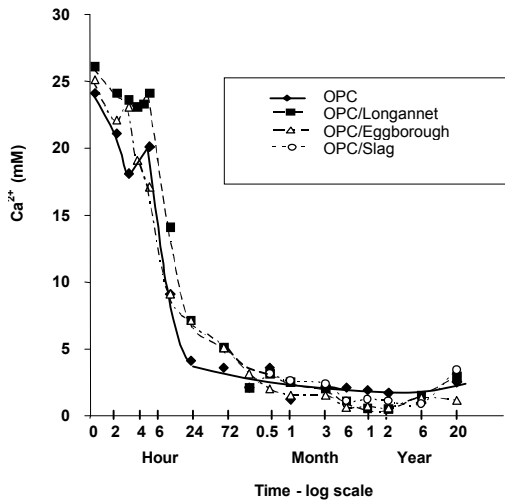


Figure 1 – aqueous $[\text{Ca}^{2+}]$

Figure 2 – aqueous $[\text{SO}_4^{2-}]$

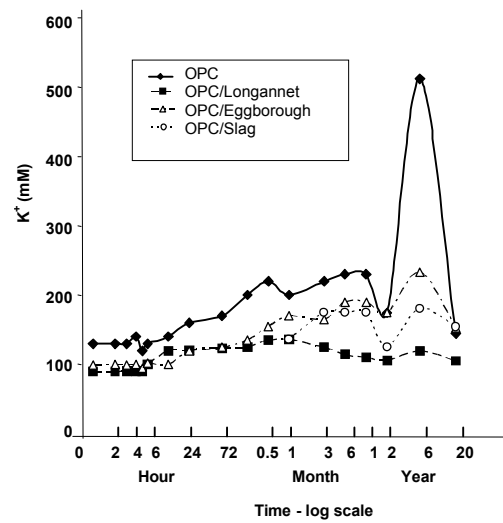
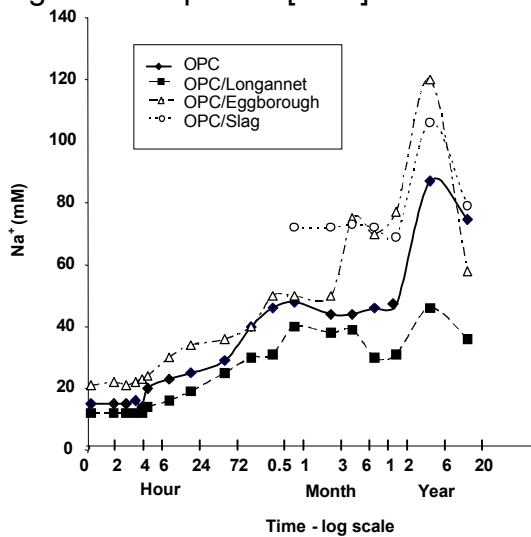


Figure 3 – aqueous $[\text{Na}^+]$

Figure 4 – aqueous $[\text{K}^+]$

The Na^+ content of the aqueous phase, Fig. 3, remains on a plateau up to 6 hours and then increases in the interval between 6 – 168 hours. This is

followed by another relatively “steady state” plateau region occurring between 0.5 months to around 2 years, though data shows some scatter. It is noteworthy that the Eggborough fly ash blend shows a slight but significant increase in Na^+ concentration from 54 to 77 mM between 3 and 6 months. Slag cement shows a significantly higher plateau “steady state” between 0.5 months to 1 year at around 70mM. A substantial increase in Na^+ concentration occurs in all the systems from 2 to 6 years. It then decreases again to levels that at 20 years are still higher than previously obtained. Values for blended cements are typically 58 to 79 mM compared to 36 mM with OPC. Aqueous K^+ contents follow a similar trend to Na^+ . An initial plateau up to 6 hours is followed by an increase in K^+ up to 1 to 6 months depending on the blending agent. This increase is then followed by a slight decrease in K^+ concentration not observed with Na^+ . However there is a notable increase in K^+ concentration between 2 and 6 years followed by a decrease up to 20 years with values falling almost to those obtained initially, around 100 to 130 mM. In general, the relatively high soluble Na^+ content of the Eggborough fly ash raises the the aqueous concentration, whereas the lower soluble K^+ content of the fly ash relative to cement effectively dilutes the cement contribution. Both fly ashes are relatively rich in alkali, which is liable to release during hydration. Assuming complete reaction of the fly ash and release of the contained Na^+ and K^+ , mass balance calculations suggest Na^+ concentrations of 22.5 and 90 mM for Longannet and Eggborough respectively. Neither fly ash contributes high concentrations of these ions to the pore solution. The Longannet fly ash, for example, gives an aqueous Na^+ content comparable to that of OPC with 30% replacement by and inert material, whereas the Eggborough fly ash slightly increases Na^+ concentrations though not as much as it could potentially release.

Silica, aluminium, iron, magnesium and chloride concentrations were typically below detectable limits, but traces of silica, aluminium and magnesium, Table 3, were observed in samples cured for at least 2 years.

Table 3. Aqueous phase data for minor components

System	Ion concentration (mM)					
	Al^{3+}			Si^{4+}		Mg^{2+}
	2 years	6 years	20 years	6 years	20 years	6 years
OPC	< 0.3	< 0.3	0.30	0	0.39	< 0.02
OPC/Longannet	< 0.3	0.71	1.22	4.1	1.42	0.068
OPC/Eggborough	1.1	2.33	1.04	4.6	2.07	0.037
OPC/Slag	< 0.3	0.92	0.30	0.59	0.39	< 0.02

Initially, the chloride contents of the aqueous phase showed significant scatter with values of around 40 ppm in the first 6 hours, declining to

around 10 ppm or less at 24 hours and were barely detectable after 72 hours. The chloride arises from the cement and blending component since there was no chloride in the mixing water and none was added.

The different methods of pH determination showed reasonable agreement, considering the limited accuracy of the pH electrodes, titration methods and assumptions concerning the degree of ionization. Values typically ranged from pH 13.2 to 13.4 and were in general 13.4 for the OPC and 13.2 to 13.3 for the blended cements.

3.2 Solid Phase

The Ca(OH)_2 values for OPC and OPC blended systems from 0.5 months to 20 years hydration are shown in Fig. 5. Most of the C_3S and C_2S hydration occurs within the initial 0.5 month, with formation of at least 25 wt% Ca(OH)_2 . Hydration continues up to 2 years, after which solid Ca(OH)_2 and Ca^{2+} in solution attain a “steady state” equilibrium. In the case of the blends, the Ca(OH)_2 content decreases due to the pozzolanic reaction. Ca(OH)_2 consumption (difference between Ca(OH)_2 from the OPC corrected for 30% replacement by an inert material, Ca(OH)_2 “corr” in Fig.5, and that of the blending component), an indication of reactivity of the blending component, shows that both fly ashes appear to react continuously over time, whereas the slag blend remains reasonably constant irrespective of curing time. Both fly ashes consume most of the Ca(OH)_2 in pozzolanic reactions between 0.5 months and 1 year, with the Longannet fly ash consuming somewhat more Ca(OH)_2 than the Eggborough fly ash. The Longannet fly ash is thus either more reactive, or has a higher Ca(OH)_2 demand, or both. Continued variability in Ca(OH)_2 consumption for the fly ash blends in the following 1 to 6 years suggests the differences in reactivity still predominate. Decreased values in Ca(OH)_2 up to 20 years, with approximately 15 wt % consumption, shows that the fly ash blends have not yet attained equilibrium with regards to fly ash reaction. The slag blend differs considerably from the fly ashes and, after an initial consumption of about 5 wt% Ca(OH)_2 over 2 years, attains a steady state. This suggests the demand on Ca(OH)_2 of the hydrating slag is quite modest. Dissolution studies on the slag blend indicate that a high proportion, ~40%, has reacted during the first month [14], and possibly within a week [15]. It is also considered that the slag hydrates in stages with dormant periods occurring between times of rapid growth. It is estimated that ~60% of the slag has hydrated by 1 to 2 years.

X-ray studies on selected samples, Table 4, show most to give weak diffraction patterns, principally of C-S-H and Ca(OH)_2 with the Ca(OH)_2 being most prevalent in the OPC system. All samples showed some degree of carbonation, as calcite or its polymorph vaterite, although

conditions had been chosen to minimize this effect. Ettringite and AFm were observed in substantial amounts in both the OPC and OPC/fly ash blends, whereas only AFm was detected in the OPC/slag blend.

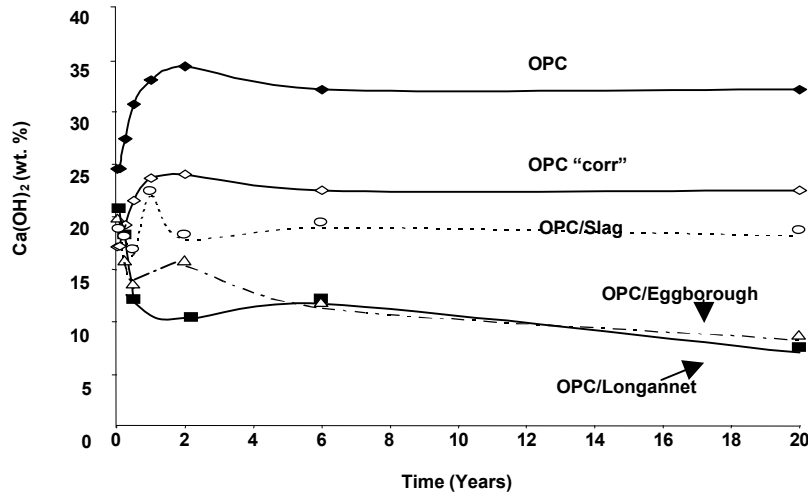


Figure 5. $\text{Ca}(\text{OH})_2$ content as a function of time

Crystalline phases associated with the blending agent were also detected, typically mullite, hematite and quartz in fly ash particles and gehlenite in the slag. Hydrotalcite as a hydration product of blended cements was clearly evident in OPC/slag blends and to a lesser extent in OPC/fly ash blends. Manasseite, a hitherto unknown phase, as yet not completely characterized, was also possibly detected in the OPC/Eggborough blends at the earlier ages. Weak, unidentified peaks were also observed both in the OPC and OPC blended systems.

SEM micrographs typical of OPC hydrated at 6 and 20 years are shown in Figs. 6-7 while those for the OPC blended systems are shown in Figs. 8-13. Interestingly no significant difference was noted in morphology of the OPC between 6 and 20 years of hydration, Figs. 6-7. Morphologies show a somewhat open structure as expected for a w/s ratio of 0.6, with fibrous type C-S-H and platelets of $\text{Ca}(\text{OH})_2$ having various dimension well distributed throughout the specimen. As expected the morphology of the OPC/fly ash blends is somewhat different with less $\text{Ca}(\text{OH})_2$ and a more compact ill-defined C-S-H. The OPC/Longannet fly ash tends to be characterized by large micropores that become more evident on hydration, Figures 8-9. The structure remaining between the pores is considered most likely to be composed of mullite crystals present in the original fly ash particles. Reaction rims of fly ash hydration product also occur around some of the fly ash particles as seen in Fig. 9. The OPC/Eggborough fly ash morphology is somewhat different from that of the OPC/Longannet fly

ash system. Most notable is the high percentage of almost completely unreacted fly ash particles, at 6 years of cure and of which Fig. 10 is typical. At 20 years, however, most of the Eggborough fly ash particles have reacted to some extent showing either reaction rims or more typically surface coated particles as observed in Fig. 11. $\text{Ca}(\text{OH})_2$ crystals are

Table 4. Phases observed by XRD in OPC and OPC blended systems

Sample, curing time	Phases observed
OPC, 0.5 month	AF_m , CH, C-S-H, vaterite
OPC, 6 years	AF_m , AF_t , C-S-H, CH, calcite
OPC, 20 years	AF_m , AF_t , C-S-H, CH, calcite
OPC,/ Longannet, 6 years	AF_m , AF_t , C-S-H, CH, calcite, vaterite, hydrotalcite, mullite, quartz
OPC/Longannet, 20 years	AF_m , AF_t , C-S-H, CH, calcite, vaterite, mullite, quartz
OPC/Eggborough, 6 months	AF_m , CH, C-S-H, Q, unidentified phase
OPC/Eggborough, 2 years	C-S-H, vaterite, mullite, unidentified phase, (Tr)-CH
OPC/Eggborough, 6 years	AF_m , AF_t , C-S-H, calcite, vaterite, hydrotalcite, mullite, quartz, (Tr)-CH
OPC/Eggborough, 20 years	AF_t , C-S-H, calcite, vaterite, hydrotalcite, mullite, quartz, (Tr)-CH
OPC/Slag, 6 months	AF_m , C-S-H, CH, vaterite, hydrotalcite, gehlenite, (Tr)-manasseite
OPC/Slag, 2 years	AF_m , C-S-H, CH, hydrotalcite, gehlenite, (Tr)-manasseite
OPC/Slag, 6 years	AF_m , C-S-H, CH, hydrotalcite, calcite
OPC/Slag, 20 years	AF_m , AF_t , C-S-H, CH, hydrotalcite, calcite, vaterite

frequently observed in close contact with the fly ash spheres in the OPC/Eggborough fly ash system. The OPC/slag blend hydrated for 6 years shows a dense microstructure in which the $\text{Ca}(\text{OH})_2$ crystals are well less defined and unreacted slag grains persist, Fig 12. At 20 years the morphology of the OPC/slag system is significantly different showing non-descript C-S-H and, in areas where there appears to be greater porosity, fibrous C-S-H similar to that observed in the OPC system. The $\text{Ca}(\text{OH})_2$ crystals which at 6 years were ill-defined, at 20 years were clearly well defined, Fig. 13. A few unreacted slag particles were also observed with some in close proximity to $\text{Ca}(\text{OH})_2$ crystals.

4. Discussion

Hydration of OPC and OPC blends is a continually evolving process that is controlled by the balances between a number of competing factors that

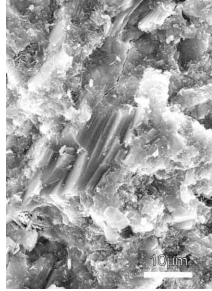


Figure. 6 – Micrograph of OPC cured for 6 years



Figure. 7 – Micrograph of OPC cured for 20 years

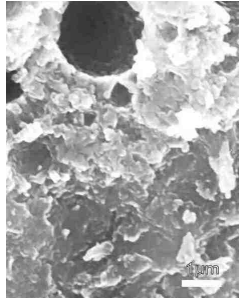


Figure 8 – Micrograph of OPC/Longannet fly ash cured for 6 years

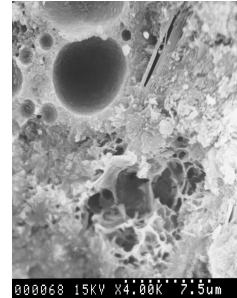


Figure 9 – Micrograph of OPC/Longannet fly ash cured for 20 years

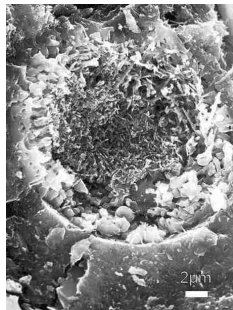


Figure 10 – Micrograph of OPC/Eggborough fly ash cured for 6 years

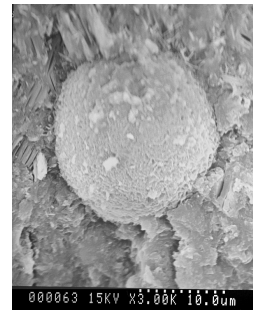


Figure 11 – Micrograph of OPC/Eggborough fly ash cured for 20 years

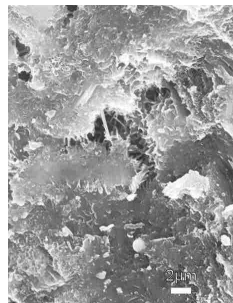


Figure 12 – Micrograph of OPC/Slag cured for 6 years

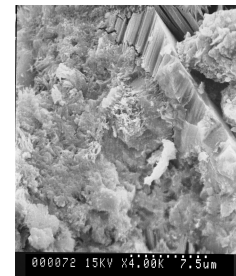


Figure 13 – Micrograph of OPC/Slag cured for 20 years

incorporate both the aqueous and solid phase chemistry. Simplistically the aqueous phase chemistry can be considered as a balance between dissolution of ions from the solid phase (cement, blending agent and/or hydration product) that increases the solution ion concentration and removal of ions to form hydration products that consequentially decrease the solution ion concentration. Some processes are continuous, such as liberation of alkali ions from cement or blending agent, and for which there is no distinct solubility limit, whereas other processes ultimately approach a “steady state” equilibrium and are dependent on the rate of dissolution and precipitation of hydrated phases. The time to reach a “steady state” is dependent on the rate of dissolution of the solid phases and that differs markedly whether it is OPC, fly ash or slag. In the present study, both solid and aqueous phase data show that the OPC appears to attain a “steady state” in 2 years, whereas the blended cements take more than 6 years.

The changes in aqueous phase chemistry occurring in the first 24 hours are consistent with the induction period and renewed onset of hydration so marked by calorimetry. The high SO_4^{2-} levels together with the high Ca^{2+} levels attained during ~6 hours, are consistent with formation of amorphous hydration products that are expected to have higher solubilities than the more stable crystalline phases containing Ca^{2+} and SO_4^{2-} . Hydration films coating the cement grain surface have been observed by microscopy and attributed as a factor relating to the induction period [16]. The drastic decrease in $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ with formation of $\text{Ca}(\text{OH})_2$ and AFt phases marks renewed hydration with the onset of setting. Subsequently, renewed hydration of C_3A with release of Na^+ increases aqueous $[\text{Na}^+]$, whereas the slower increase in $[\text{K}^+]$ arises from the renewed hydration of C_3S and C_3A . Na^+ and K^+ are not typically incorporated into the OPC hydration products and their concentrations increase as hydration proceeds. The use of fly ash and slag in blends has frequently been advocated as a means of controlling expansion due to alkali-aggregate reaction, but their effectiveness is questionable and it has proved difficult to produce a consensus on guidelines for their use. This work shows that only the Longannet fly ash decreases both $[\text{Na}^+]$ and $[\text{K}^+]$ consistently over the 20 years. Eggborough fly ash and slag both increase the Na^+ content with respect to OPC, but total alkali is lower, though at 20 years it actually equals that of the OPC. The notable increase in $[\text{Na}^+]$ and $[\text{K}^+]$ between 2 and 6 years again suggests continued hydration of C_3A and C_3S , releasing these ions into solution. Mass balance calculations based on OPC having 0.19 wt% Na_2O and 0.48 wt% K_2O and assuming complete hydration of OPC at w/c 0.36 would give, at an initial w/c of 0.6, aqueous $[\text{Na}^+]$ and $[\text{K}^+]$ of 225 mM and 425 mM respectively. Aqueous phase composition at 6 years is 87 mM in Na^+ and 512 mM in K^+ and, allowing for concentration effects due to removal of water of hydration, suggests that 32% of total Na^+ and 100% of total K^+ are released to the

aqueous phase. The subsequent decrease in alkalis from 6 to 20 years would indicate that ageing effects on the C-S-H make it more likely to incorporate Na^+ and K^+ . The pH of the solution remains relatively constant and it may be assumed that the partitioning of the alkalis between their release from the solid phase and the alkali composition of the aqueous phase are more important parameters in the beneficial properties of blended cements.

If the amount of $\text{Ca}(\text{OH})_2$ formed is indicative of degree of $\text{C}_3\text{S}/\text{C}_2\text{S}$ hydration, then for OPC this suggests that a “steady state” equilibrium is attained within 2 years. This is also consistent with the minimal changes noted in microstructure at longer cure times. Aqueous alkali concentrations, however, indicate reaction still occurs up to 6 years. In the blended cements the $\text{Ca}(\text{OH})_2$ is consumed in the pozzolanic reaction and the difference between the $\text{Ca}(\text{OH})_2$ formed from cement (corrected assuming a 30% decrease by addition of an inert material) gives an indication on the reactivity of the blending material. Consumption of $\text{Ca}(\text{OH})_2$ is greatest within the first 6 months to 1 year for all the blending materials. Slag differs in reactivity from the fly ashes in that it contains 38.12 wt% CaO and is activated by ~5 wt% $\text{Ca}(\text{OH})_2$. Based on $\text{Ca}(\text{OH})_2$ consumption, the slag appears to reach a “steady state” equilibrium within 2 years, but dissolution studies indicate only about 60% of the slag had hydrated and SEM showed unreacted slag particles and significant morphological changes occurring after 6 years. This suggests that $\text{Ca}(\text{OH})_2$ consumption may not be a valid means of establishing a “steady state” equilibrium for slags. In the case of the fly ashes the Longannet consumed ~60 wt% of $\text{Ca}(\text{OH})_2$ within the first 1 to 2 years whereas the Eggborough consumed ~40 wt% $\text{Ca}(\text{OH})_2$. At 20 years, consumption of $\text{Ca}(\text{OH})_2$ for both fly ashes was ~75%, indicating that the fly ash blended cements required more than 6 years to attain “steady state” equilibrium.

In order to determine the “steady state” equilibrium for OPC and OPC blended cements it is necessary to consider both solid and aqueous phase data. OPC attains a “steady state” equilibrium within 2 to 6 years whereas the blended cement systems take between 6 to 20 years to attain the same “steady state” equilibrium. Even so, at 20 years there are still changes taking place in both aqueous and solid phase.

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