



Effect of supplementary cementitious materials (binder type) on the pore solution chemistry and the corrosion of steel in alkaline environments



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ABSTRACT

The pore solution compositions of paste samples produced with Ordinary Portland Cement (PC), slag 25%, 50% and 75%, fly ash 30%, condensed silica fume (SF) 7%, and a ternary blend of 50% PC, 43% slag and 7% SF were determined. Not only are there significant variations in the concentration of the major cations and anions but also, and equally important from the perspective of development of the passivity of steel in solution, in the level of dissolved oxygen and redox potential.

Further, the impact of changes in the pore solution chemistry of cement pastes with SCMs on the passivation and corrosion of steel was investigated with mild steel in simulated pore solutions (SPS). Sulphides and thiosulphates, typically found in slag bearing pastes, appeared to reduce the chloride threshold concentration and increase the rate of corrosion in SPS, which has potential implication for the long term performance of reinforced concrete structures.

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1. Introduction

The investigation of pore solution composition of hardened mortar and paste has been the subject of considerable study since the development of the pore expression device (PED). A detailed description of the PED and its application is provided by Barneyback and Diamond [1]. The use of the PED permits the study of pore solutions of hardened concrete over time, allowing for the possible examination of age effects in the development of the pore solution chemistry. One area of concern has been that differences in the pressure at which the pore solution is extracted may lead to variations in the pore solution chemistry. Pressure effects on the alkali content however have been shown to be minimal [2,3,4] though some variation has been observed for sulphate ions at extremes of collection pressures. The collection of pore solution over the normal operating range (350 to 550 MPa) of most PEDs should not significantly affect the comparison of results.

1.1. Influence of binder type on the pore solution composition

Binder type is known to exercise a marked effect on pore solutions. Pore solution extraction has generally been conducted on cement pastes or mortars with water/cement (w/c) ratios in the range of 0.5 to 0.6, with the majority of work focused on the evaluation of hydroxyl ion concentration, and Na⁺ and K⁺ levels. The cement content in the w/c

ratio refers to the total cementitious material which includes all supplementary cementitious materials (SCM). The hydroxyl ion concentration of PC is typically in the range of 0.53 M to 0.71 M as shown in Table 1, drawn from a variety of literature.

The inclusion of SCMs significantly affects the alkali content of the pore solution with most SCMs binding more alkali than they release. Duchesne and Berube [2] state that the effects of SCMs are more than simply inert fillers as a 10% replacement by SF results in 60% or more decrease in alkali.

In addition to the major cations and hydroxides, there are a number of other minor ions which may be present in the pore solution. The results of Longuet [13] indicate a distinct difference in pore solution chemistry between the slag, at a replacement level of 76%, and non-slag bearing materials. The slag bearing samples all contained sulphides in the range of 10 to 85 mg/l, with one measurement of 201 mg/l, over two years of study, while no sulphides were detected in the non-slag bearing samples. The difference in pore solution chemistry is also highlighted by the more negative redox potential of the slag pore solution, typically >300 mV below the control which indicates a reducing environment in the pore solutions.

A relationship between redox potential and sulphide concentration has been demonstrated for various replacement levels of slag as shown in Table 2 [14]. Highly negative redox potentials are associated with sulphide concentrations in excess of 100 mg/l, which corresponds to a slag replacement level >75%. The results shown in Table 2 were determined after 25 days of hydration during which time only a fraction of the slag would have reacted, leaving a significant quantity of total S locked in the unhydrated portion of the slag [14].

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Table 1
Summary of chemical analysis of pore solutions.

	Concentration M				
	OH ⁻	Na ⁺	K ⁺	Ca ²⁺	SO ₄ ²⁻
Byfors et al. [5]					
3 months, 1% Cl added, w/c 0.6					
PC, Swedish	0.610				
FA (25%)	0.410				
SF (10%)	0.110				
Slag (30%) - Australian	0.600				
Duchensne and Berube [6]					
84 day, w/c 0.5					
PC	0.640				
Slag (35%)	0.416				
Slag (50%)	0.290				
FA-B (20%)	0.380				
FA-B (40%)	0.256				
SF-A (5%)	0.480				
SF-A (10%)	0.290				
Andrade and Page [7]					
28 day, 1% Cl added, w/c 0.5					
PC, U.K.	0.620				
Portland blastfurnace cem. Spanish	0.754				
Angst et al. [8]					
28 day, w/c 0.6, mortar					
PC, (CEM I 52.5)	0.335	0.204	0.164	0.002	0.0025
PC with 1.5% Cl added	0.48				
PC with 3.0% Cl added	0.46				
Diamond [9]					
30 day, w/c 0.4					
PC	0.3	0.141	0.223	0.0012	
FA-A (30%)	0.255	0.104	0.157	0.0007	
FA-B (30%)	0.219	0.084	0.143	0.0000	
Elsener et al. [10]					
PC paste, w/c 0.4	0.501	0.06	0.585	0.0006	0.0056
PC mortar, w/c 0.7	0.159	0.035	0.218	0.0001	0.0097
Constantiner and Diamond [3]					
2 year, w/c 0.5					
PC, low alkali	0.468	0.070	0.389	0.0035	0.0154
PC, mod-high alkali	0.523	0.181	0.358	0.0038	0.033
Hidalgo et al. [11]					
2 months, w/c 0.4					
PC (CEM I)	0.339 ^a	0.035	0.248	0.0006	0.0105
PC with 1.4% Cl added	0.275 ^a	0.663	0.277	0.0026	0.0105
PC with 7% Cl added	0.120 ^a	3.31	0.336	0.0031	0.0105
Page and Vennesland [12]					
84 day, w/c 0.5					
PC	0.713	0.323	0.639	0.0020	0.0270
PC/SF 10%	0.239	0.114	0.202	0.0010	0.0160
PC/SF 20%	0.078	0.051	0.069	0.0020	0.0250
PC/SF 30%	0.010	0.030	0.030	0.0070	0.0320
Longuet [13]					
3 months, w/c 0.5					
A 95.5% Clk, 4.5% gy	0.625	0.133	0.532	0.0030	0.0028 ^b
B 19.1% Clk, 4.5% gy, 76.4% slag A	0.142	0.050	0.086	0.0025	0.0008
C 19.1% Clk, 4.5% gy, 76.4% slag C ^c	0.225	0.078	0.160		0.0009

Note: For Longuet Clk – clinker, gy – gypsum, sample C taken at 2 months.

^a Value calculated from pH.

^b Value taken at 6 months. The three month value was reported as zero.

^c Values reported for 2 months. Reported calcium concentration was zero.

Variations in redox potential (E_h) and, by association, sulphide concentration with time have been attributed to competition between the reduced species of the slag and the oxidized species of the cement [15]. Where the E_h is positive, the effectiveness of reduced species is insufficient to overcome the oxidized content and dissolved oxygen of the pore solution. Conversely, where E_h is negative, the reduced species (S^{2-} and $S_2O_3^{2-}$) are dominant. According to MacPhee and Cao [15] in the short term the reduced species of the slag are insufficient to overcome the oxidized species in the rapidly hydrating cement, thus the redox potential remains positive until such time as the oxidized species are consumed and a reducing environment dominates.

The effects of slag concentration on the redox potential with time are illustrated in Fig. 1. A reducing environment is established after

Table 2
Redox potential and S^{2-} concentration [14].

OPC	BFS	E_h (mV)	S^{2-} (mg/l)
100	0	+82	0
75	25	+79	NR
50	50	+68	12
25	75	+35	6
15	85	-240	120
10	90	-269	110
5	95 ^a	-330	1000
2.5	97.5 ^a	-259	1100

NR – no result.

^a 0.5% Ca(OH)₂ added to ensure setting.

approximately 28 days for an 85% slag content with a 75% slag content taking approximately 3 months to reach a similar state. The 50% slag cement is also expected to develop a reducing environment though at a later date.

An investigation of other sulphur species by Glasser et al. [16] revealed the presence of significant quantities of thiosulphate ($S_2O_3^{2-}$) in the pore solution derived from 85% slag, 15% cement samples. The results are provided in Table 3. Glasser et al. [16] note that the use of polythene plastic bags for curing of the paste samples would have inhibited though not totally prevented the ingress of oxygen. Thus, some oxidation of S^{2-} to $S_2O_3^{2-}$ would likely have taken place.

The general range of sulphide concentrations in pore solutions for slag replacement levels >75% and <90% appear to be in the range of 110 to 300 mg/l in addition to thiosulphate. As previously noted, the early work of Longuet [13] indicated sulphide levels in the range of 10 to 85 ppm, with one measurement of 201 ppm at a replacement level of 76%. Little or no sulphide has been reported at lower replacement levels of slag.

One of the difficulties in the measurement of sulphides in pore solution is the reaction rate and relative ease of oxidation of the sulphides. Great care must be taken when extracting the pore solution and determining the concentration of sulphides.

1.2. Role of sulphur species in the corrosion of steel in aqueous alkali environments

The study of corrosion of steel in the aqueous phase is valuable in investigating the chemical influences of the various materials, since the environment can be more precisely controlled compared to steel in mortars or concretes. The effects of specific variables can therefore be assessed with greater confidence. Gouda [17] investigated the influence

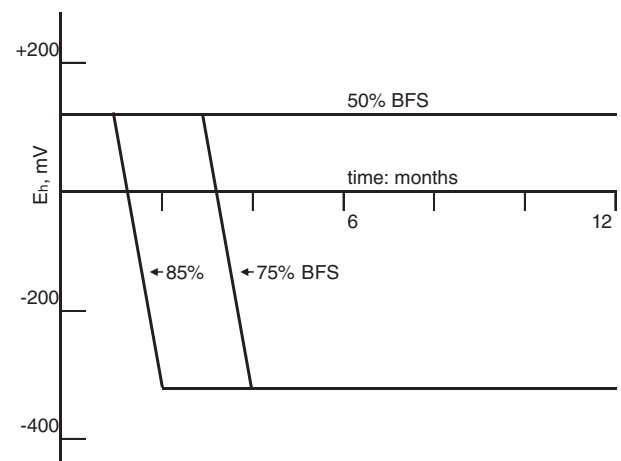


Fig. 1. Effect of slag replacement levels and time on the redox potential of the pore solution [15].

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