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DEGREES OF REACTION OF THE SLAG IN SOME BLENDS WITH PORTLAND CEMENTS

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ABSTRACT

The degree of reaction of the slag in some blends with Portland cements has been studied at ages of 28 days to 2 years, using an EDTA extraction method. Potential sources of error in the method are discussed and, where possible, corrected for. At water/solids ratios (w/s) of 0.4–0.6 and 20°C, 30–55% of the slag reacts in 28 days and 45–75% in 1–2 years. The marked differences in reactivity of different slags are related, at least in part, to hydraulic modulus and fineness, but there was no apparent relation to glass content or whether the slag was granulated or pelletised. The degree of reaction decreases with the content of slag in the blend and with decrease in w/s. For blends with 92% slag and w/s = 0.3, it is probably limited to around 30%. Limited evidence showed no dependence on the composition of the Portland cement, but this may not be true at early ages, as the effects of cement composition and of slag composition probably then differ from those observed later.

Introduction

In 1968, Kondo and Ohsawa (1) briefly reviewed procedures that had been used for determining the slag contents of unhydrated Portland blastfurnace cements. They concluded that the experimental errors were large with all the methods known at that time and that none was suitable for determining unreacted slag in pastes. For this purpose, they described a modification of Takashima's (2) salicylic acid extraction method. They noted that the reagent used in this procedure did not dissolve all of the material other than unreacted slag, but applied a correction for this and concluded that the method gave satisfactory results. Several later investigators have used it; in a recent example (3), the degree of reaction of the slag in pastes made from a cement containing 60% of slag and having a water:solids (w/s) ratio of 0.5 was reported to vary between approximately 20% and 40% at 90 days, depending on the composition and fineness of the slag. However, Luke and Glasser (4), who made a comparative study of several extraction methods, showed that the method gave unacceptably high and variable quantities of residue from pastes of pure Portland cements, and the results of investigations using it, summarised by Taylor (5) show wide discrepancies.

Demoulian et al. (6) described a method based on extraction of the constituents other than unreacted slag with a reagent based on EDTA (ethylene diamine tetraacetic acid), and found it effective for determining the slag in either unhydrated slag cements or pastes. Several modifications of this method have been described (4,7–9), the last of which has formed the basis of a draft European standard (10). Luke and Glasser (4) found that the Demoulian method, in a slightly modified form, was much the most satisfactory of the methods they investigated. They found that it yielded small amounts of residue from pastes of pure Portland cements and used the data thus obtained to correct the results obtained for pastes of slag cements. They also corrected the results for small proportions of unreacted slag that were found to be dissolved by the reagent.

The EDTA residues from the pastes of pure Portland cements consisted largely of amorphous material high in silica, and also contained a hydrotalcite-type phase[1], which was shown to contain appreciable silica and iron. Blastfurnace slags are relatively high in MgO (7–12%), and the residues from the EDTA extractions of pastes of cements containing them are thus likely to contain, in addition to unreacted slag and the residue from the Portland cement component, hydrotalcite formed on hydration of the slag. Luke and Glasser (4,8) recognised that a correction should be made for this but did not find a way of determining the hydrotalcite.

Using the modified Demoulian method, Luke and Glasser (8) studied a blend having a w/s ratio of 0.6 and containing 30% of slag. At 25°C, the degree of reaction of the slag was around 40% at 1–6 months and 62% at 1–2 years. At 40°C or 55°C, some 60% had reacted in 6 months. Luke and Glasser recognised that their estimates of the degree of reaction were likely to be low because of the absence of a correction for the hydrotalcite produced by the slag.

Hinrichs and Odler (11) determined the quantities of slag remaining in several blends by differential thermal analysis (DTA), using the intensity of the exothermic peak at 880–950°C, which is due to devitrification of residual slag glass. They used the unreacted slag cement as standard. This method would not determine unreacted crystalline constituents of the slag, but no such phases were found by XRD in the slags used. For a number of pastes of w/s ratio 0.5, hydrated at 20°C, they found that detectable proportions of the slag had reacted by 2 days; typically, the degree of reaction was 40–60% at 28 days and 50–70% at 1 year. Reaction of the slag was accelerated by finer grinding of the blend or by curing under water rather than in air, but the degree of reaction was reported to be substantially unaffected by the percentage of slag in the blend over the range of 35–70% that was studied.

Battagin (12) also reported data obtained using a modified Demoulian method. The equation used to calculate the degree of reaction did not include corrections either for hydrotalcite or for the residue from the Portland cement. For pastes cured at 23°C, the degrees of reaction of the slag were reported to be around 17% at 3 days, 35% at 28 days and 52% at 1 year. Relatively little change was found between 1 and 3 months. The rate of reaction of the slag increased markedly with temperature, approximately 38% hydration being reached in 5 days at 40°C, 2 days at 60°C or 1 day at 80°C. The degree of reaction was reported to be unaffected by the content of slag in the blend over the 35–70% range studied. This conclusion agrees with that of Hinrichs and Odler (11), and the observation of a plateau in the degree of reaction is similar

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[1] Hydrotalcite is, strictly, the name of a natural mineral or equivalent synthetic phase of composition $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$. The CO_3^{2-} is present in interlayer sites, and many other anions can substitute for it. The Mg:Al ratio can vary between 2:1 and 3:1 and possibly higher, with equivalent change in the content of interlayer anion. Cation substitutions, e.g., of Al^{3+} by Fe^{3+}, are possible. We shall use the name hydrotalcite loosely, to denote any Mg-Al-OH-X phase of this structural type.

TABLE 1

Chemical Analyses (masses percent) and Other Data for Starting Materials

	Cements					Slags						
	A	B	C	D	E	N	L	T	P	X	Y	Z
SiO_2	19.3	20.6	19.8	19.9	20.3	36.1	33.0	35.0	35.4	36.8	33.6	31.0
Al_2O_3	5.7	5.0	5.8	6.4	3.8	9.9	11.8	12.3	12.7	11.2	13.4	16.0
Fe_2O_3	2.0	2.1	3.4	2.2	4.7	0.79	1.6	0.6	0.3	0.4	1.5	1.5
Mn_2O_3	0.04	0.05	0.12	0.04	0.21	0.51	0.64	0.43	0.89	0.83	0.85	0.83
P_2O_5	0.28	0.04	0.12	0.23	0.08	0.01	0.01	0.01	0.01	0.02	0.01	0.00
TiO_2	0.25	0.22	0.25	0.30	0.17	0.36	0.59	0.52	0.76	0.99	0.54	1.00
CaO	62.4	65.4	63.6	64.9	64.3	41.0	41.3	40.9	41.3	40.0	40.4	36.3
MgO	2.5	1.8	2.8	1.2	2.1	9.5	9.0	7.8	6.7	7.7	8.3	11.0
SO_3	4.0	2.4	2.3	2.9	2.4	0.3	0.13	0.30	0.14	0.13	0.05	0.16
S^{2-}						1.1	0.86	1.1	0.76	0.97	0.82	1.1
Ignition loss	1.4	1.0	1.1	1.5	0.90	0.6	0.8	0.2	0.6	0.6	0.40	0.4
K_2O	1.22	1.13	0.43	0.51	0.53	0.35	0.51	0.83	0.60	0.47	0.52	0.65
Na_2O	0.34	0.12	0.06	0.34	0.12	0.18	0.32	0.64	0.24	0.35	0.33	0.56
O≡S						−0.55	−0.43	−0.55	−0.38	−0.48	−0.41	−0.55
Total	99.4	99.9	99.8	100.4	99.6	100.2	100.1	100.1	100.0	100.0	100.3	100.0
Insol. res.	0.20	0.13	0.50	0.73	0.46	0.13	0.41	0.10	0.36	0.30	0.30	0.40
K_2O(w/sol)	1.18	0.98	0.31	0.28	0.44	0.01	0.01	0.01	0.01	n.d.	n.d.	n.d.
Na_2O(w/sol)	0.23	0.07	0.03	0.09	0.08	0.03	0.02	0.01	0.03	n.d.	n.d.	n.d.
Free lime	0.4	1.4	1.3	1.3	2.6	0.3	0.2	n.d.	0.2	<0.1	<0.1	n.d.
Glass						96	81	100	90	89	100	100
Merwinite						4	9	0	3	11	0	0
Melilite						0	0	0	7	0	0	0
MgO(glass)*						9.3	6.6	7.8	5.5	7.8	8.3	11.0
$(C+M+A)/S$						1.67	1.88	1.74	1.71	1.60	1.85	2.04
APD†	3110	3150	3150	3090	3200	2910	2950	2890	2920	2920	2930	2910
< 5 μm, %	22	21	25	18	24	35	31	28	27	19	20	21
<15 μm, %	57	50	50	44	53	79	65	62	60	47	49	48
SSA‡	401	362	390	333	400	561	498	437	451	397	395	384

w/sol = water soluble.

† Apparent particle density (kg m^{-3}).

* Calculated MgO content of glass, mass percent.

‡ Lea and Nurse specific surface area (m^2 kg^{-1}).

to that observed earlier by Luke and Glasser (4,8).

In the present work, the effects of varying some characteristics of the slag and, to a limited extent, of the Portland cement, the relative proportions of these constituents, the w/s ratio and the age of the paste were studied. An EDTA extraction method was used. For convenience, we shall refer to the Portland cement constituent as the cement and to its mixture with the slag as the blend.

Experimental

Materials. Table 1 gives chemical analyses and other data for the Portland cements and slags used. Of the cements, one (E) was a sulfate resisting Portland cement (BS4027, SRPC Class 42.5) and the others normal Portland cements (BS12, PC Class 42.5). They varied widely in alkali content. The slags varied in composition, and thereby in hydraulic modulus, and in fineness. Two (P and X) were pelletised and the others granulated. The glass contents of the slags were estimated by XRD, using the areas of the broad bands produced by this constituent (13). The MgO contents of the slag glasses were calculated from those of the slags as a whole, using the proportions derived from XRD and assumed compositions for the merwinite (C_3MS_2) and melilite (C_4MAS_3, i.e, a solid solution of $C_2AS + C_2MS_2$).

Blends were made in a dry powder blender from various combinations of the cements and slags, together in one case with additional gypsum. This was a high purity commercial product containing approximately 96% of $CaSO_4 2H_2O$. Not all cements were blended with all slags: cement A was used only with slag N, cement B with slags L, T and P, and cements C, D and E with slags X, Y and Z.

Preparation and Hydration of Pastes. The pastes using cements A or B were made at w/s 0.4 from a wide range of blends and at w/s 0.6 and 0.8 from a narrower range. Each paste was mixed by hand in a beaker by stirring for 4 min. For each specimen, a polypropylene vial was filled to the top with cement paste, capped and made airtight with a wrapping of adhesive tape. The vials were stored at 20 ± 1°C until the time of test, and were then broken open and the hardened paste crushed to < 5 mm in a nitrogen-filled glove box to minimise carbonation. The pastes using cements C, D or E were made at w/s 0.3. They were hand-mixed as above and moulded into 25 mm cubes, which were cured in a fog room at 20°C and > 95% R.H. They were demoulded after 1, 3 or 4 days for those containing 0%, 65–69% and 92% of slag, respectively, and transferred to storage in deionized water at 20°C until the time of test. The sample for analysis was then taken from the interior of the cube. In all cases, the material was dried in a vacuum oven at 35 ± 2°C for 24 h and then ground with an agate mortar and pestle to < 90 μm. The loss on ignition was determined on a portion of this grind by heating in a tube furnace for 15 min at 900°C in a stream of nitrogen. Another portion was used for determining the degree of reaction of the slag as described below.

Determination of the Degree of Reaction of the Slag. The method used was essentially that described by Emtroy (9). 93.0 g of disodium $EDTA 2H_2O$ is dissolved in a mixture of 250 ml of triethanolamine and 500 ml of water. The solution is transferred to a volumetric flask, 173 ml of diethylamine added and the mixture made up to 1000 ml with water. This solution may be stored in a brown bottle for up to 3 months.

For the extraction, 50 ml of the above solution is pipetted into a beaker and diluted to approximately 800 ml with water. The solution is brought to a temperature of 20.0 ± 0.5°C and 0.5 g of the dried and powdered paste, weighed to the nearest 0.0001 g, sprinkled over its surface. The solution is stirred for 120 ± 5 min while maintaining the stated temperature and is then filtered under vacuum through a 90 mm diameter Whatman GF/C filter which had been previously washed with 100 ml of distilled water, dried and weighed. The residue is then washed 5 times with 10 ml lots of distilled water, dried at 105°C for 1 hour and weighed to the nearest 0.0001 g.

Following Luke and Glasser (4,8), EDTA extractions were also carried out on pastes of the pure cements cured under conditions similar to those used for the blend and on the untreated slags. Some additional experiments, described later, were carried out on slag L in order to examine the extents to which the quantity dissolved varied with the size fraction and the extraction time.

Calculation of the Degree of Reaction of the Slag. The dried residue from the EDTA extraction must be corrected for its contents of residues from the cement or its hydration products, for the hydrotalcite released from the slag and, if considered appropriate, for the dissolution of some of the unreacted slag in the reagent. It is assumed that (i) the quantity of residue from a given amount of the cement is unaffected by the presence of the slag, (ii) the crystalline phases in the slag do not hydrate, (iii) all the MgO from the reacted slag enters the hydrotalcite and (iv) the latter, after drying, has the composition $Mg_5Al_2(OH)_{14}(CO_3)$. The Mg/Al ratio of 2.5 assumed for the hydrotalcite was based on the values of 2.6 (14), 1.9–4.3 (15), ≈2.1 (16), 2.5 (17) and 2.0 (18) found for this product in pastes of slag blends. The correction for dissolution of unreacted slag is discussed later.

Symbols.

r_p = Mass of dried EDTA residue (g) given by 100 g of the dried paste of the pure Portland cement.
r_b = Mass of dried EDTA residue (g) given by 100 g of the dried paste of the blend.
w_p = Ignition loss (g) on 100 g of the dried paste of the pure Portland cement.
w_b = Ignition loss (g) on 100 g of the dried paste of the blend.
R_p = Mass of dried EDTA residue (g) given by the dried paste made from 100 g of the pure Portland cement.
R_b = Mass of dried EDTA residue (g) given by the dried paste made from 100 g of the blend.
f = Mass fraction of slag in the unhydrated blend.
h = Mass of dried hydrotalcite (g) formed from 1 g of MgO in the slag glass.
p = Mass fraction of the unreacted slag that does not dissolve in the EDTA reagent.
x = Mass fraction of the slag that has reacted.
M_s = MgO content of the slag glass, mass percent.

From the formula masses of the dried hydrotalcite (473.7) and of MgO (40.3), it follows that h is equal to 2.35 g.

Calculation. Refer the masses of dried EDTA residue to the ignited masses of blend and cement:

$$R_p = 100\, r_p/(100 - w_p) \tag{1}$$

$$R_b = 100\, r_b/(100 - w_b) \tag{2}$$

The residue from the paste produced by 100 g ignited mass of the blend contains:

100 f p (1 - x) grams of unreacted slag
R_p (1 - f) grams of residue from the cement
f h x M_s grams of dried hydrotalcite from the reacted slag

Thus,

$$R_b = 100 f\, p(1 - x) + R_p(1 - f) + f\, x\, h\, M_s \tag{3}$$

whence

$$x = \frac{100\, fp - R + R(1 - f)}{f(100\, p - hM)} \tag{4}$$

If no correction is to be made for the dissolution of slag in the EDTA reagent, p = 1.

TABLE 2
Dissolution of Untreated Slags in the EDTA Reagent (fractions by mass)

Slag	N	L	L (<5μm)	L (5–18 μm)	L (>18 μm)	L (>18 μm)*	T	P	X	Y	Z
Fraction Dissolved	0.16	0.13	0.18, 0.19	0.13, 0.13	0.08, 0.08, 0.11	0.17	0.02	0.03	0.05	0.04	0.04

* Extraction time 24 hours. In all other cases, the standard time of 120 minutes was used.

Errors, Assumptions and Corrections

In those cases in which a significant fraction of the unreacted slag dissolved in the EDTA reagent, uncertainty as to the appropriate correction is probably the largest source of potential error. As the slag reacts in the paste, its particle size distribution changes and the proportion of crystalline material increases. The correction to be applied in any particular case should be that corresponding in particle size distribution and proportion of crystalline material to the slag that remains unreacted in the paste. The untreated slags that dissolved significantly in the EDTA reagent were N and L, which were the most finely ground (Tables 1 and 2). The data in Table 2 show that the finer fractions of the slag dissolve in the EDTA reagent more quickly than the coarser fractions. If the fraction of the slag that dissolved in the reagent had all reacted in a paste of the age under consideration, no correction would be required. On the other hand, if the rate of dissolution was independent of particle size, the correction would be that found for the untreated slag, decreased by a factor related to the glass content, since the crystalline phases may be assumed to remain undissolved. The quantity p in equation (4) was taken to be (1–0.67D), where D is the value given in Table 2 for the appropriate, unfractionated slag and 0.67 is a semi empirical factor derived from the amounts of the different particle size fractions of slag L that were dissolved by the reagent. The values of p thus obtained ranged from 0.89 for slag N to 0.98 for slag P and 0.99 for slag T. For slag N, omission of this correction increased the result for the percentage of slag reacting by up to 8% absolute.

Typically, the mass (r_b) and ignition loss (w_b) of the dried residue were in the region of 15–35 g and 20 g per 100 g of blend, respectively. The corresponding quantities for the pastes of pure Portland cements, r_p and w_p, were typically around 3 g and 20 g, respectively. XRD showed that the EDTA residues from the pastes of slag cements contained unreacted glassy and, where present, crystalline phases in the slag together with hydrotalcite and with minor amounts of periclase and quartz derived from the Portland cement. The relative importance of the corrections for the residue from the cement and for the hydrotalcite from the slag depends chiefly on the degree of reaction of the slag. Unreacted slag typically constituted over 90% by mass of the dried EDTA residue at 30% reaction of the slag, falling to around 40% at 80% reaction. Any errors resulting from inaccuracies in these corrections are thus likely to be greatest at high degrees of reaction, and especially where this is more than about 70%.

The formula $Mg_5Al_2(OH)_{14}(CO_3)$ may not correctly represent the hydrotalcite composition. The value of the constant, h, in equation (4) changes to 2.0 if Mg/Al = 4 or to 2.6 if Mg/Al = 2. Changes in assumptions regarding the anion have only a small effect; assuming Mg/Al = 2.5, h becomes 2.21 if the anion is hydroxyl and 2.53 if it is sulfate. Decrease in the value assumed for h to 2.0 typically lowers the result for the degree of reaction by 1–2%, and increase to 2.6 raises it by a comparable amount.

The hydrotalcite formed from the cement is accommodated in the correction for the cement residue. The presence in this material of other elements, such as Si or Fe, would thus not affect the calculation. On the other hand, their presence in the hydrotalcite formed from the slag would be relevant; e.g, if intergrown layers of talc were present, as suggested by Feng and Glasser (16), the value assumed for h should be increased. The proportion of such layers appears to be small.

The assumption that the degree of hydration of the cement is unaffected by the presence of the slag is probably reasonably accurate at the later ages, but less so at early ages, when the slag is known to have an accelerating effect (17). Calculations assuming increased contents of cement residue suggested that errors arising from this cause are unlikely to exceed 1% in the cases studied. At early ages, there is more likelihood that the content of cement residue has been underestimated, but the proportion of this constituent in the dried EDTA residue is small. At later ages, this proportion of cement residue is higher, but the error in estimating the amount is probably less. In the present work, the values of r_p and w_p for the pastes of pure cement were obtained at the same w/s ratios as those of the blends except where the latter had w/s = 0.6 or 0.8, for which the data obtained at w/s = 0.4 were used. The accuracy in these cases might have been improved by using values of r_p and w_p obtained at the same values of w/s as in the blends.

The derivation of equation (4) implicitly assumes that the ignition losses of the untreated cement and slag are zero. Tentative calculations suggested that errors from this cause were small. Duplicate determinations were made for 7 of the pastes. The average difference between the results for the degree of reaction of the slag was 3.0%. The absolute accuracy is possibly similar in cases where the unreacted slag is substantially insoluble in the EDTA reagent, but may be poorer if a significant proportion dissolves or at degrees of reaction higher than about 70%.

Results

Figs. 1–4 give the results. The blends brought together on each plot were selected to show the effect of a particular variable most clearly. Additional evidence concerning these effects may be obtained by comparing the results for blends that appear on different plots. For a few of the pastes cured for 1–2 years, anomalously low results were obtained; these are included in the plots. The cause of these anomalies was not found.

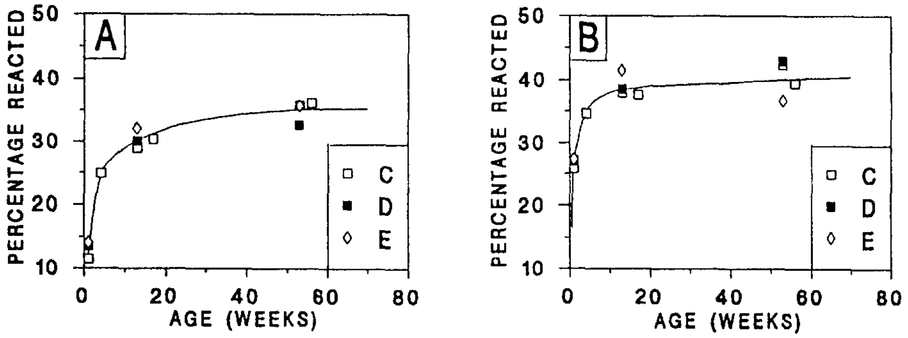

FIG. 1.

Percentages of the slag reacting: effect of varying the cement. A: Slag X; B: Slag Y. In both cases the blends contained 69% of slag with cement C, D or E, and the w/s ratio was 0.3.

Effect of Varying the Cement. Only limited data were obtained for the effects of varying the cement. Fig. 1 shows that, for blends of w/s = 0.3 and containing 69% of slag, the rate of reaction of the slag did not vary significantly with the cement used. This was true for combinations of 2 different slags with 3 cements, one of which (E) was a sulfate resisting Portland cement. All 3 cements were of low or moderate alkali content. The cement highest in alkalis, A, was only used in conjunction with slag N. However, the results for this blend did not show any differences from those made with other cements that could not be attributed to differences in the ratio of slag to cement, w/s ratio or properties of the slag. It is shown later that incorporation of additional gypsum did not have any significant effect on the rate of reaction of the slag.

Effect of Varying the Slag. The results show that the slags differ considerably in reactivity. This was the case at differing w/s ratios and differing proportions of slag. For slags L, T and P, the reactivity decreases in the sequence L > T > P (Figs. 2 A–C). This sequence corresponds to that of the hydraulic moduli; in addition, slag L was more finely ground than slag T or P. Comparison of slag N with the others is less reliable because a different cement was used; it appears to be similar in reactivity to slag T. The higher reactivity of slag Y as compared with slag X (Fig. 2 D) is also consistent with its higher hydraulic modulus. Slag Z had an even higher hydraulic modulus than slag Y, and the observation that less had reacted at 13 weeks was unexpected. The pelletised slags (P and X) were less reactive than the granulated slags for which reliable comparisons were possible, but this could have been due to their lower hydraulic moduli. The data show no clear relations between reactivity and glass content. If the reaction rate is expressed as the percentage of slag glass that has reacted, the difference between slag L and slags T and P would be increased, while that between slags X and Y would be lessened.

Effect of Varying the Ratio of Slag to Portland Cement. This is shown in Fig. 3. With one insignificant exception in Fig. 3 A, the results show a consistent decrease in reactivity with increased content of slag. The differences between the results in Figs. 3 A–C for slag contents of 30–60% and those in Figs. 3 D–E for contents of 65–92% are consistent with this conclusion but the comparison is rendered less reliable by the use of different cements and different ranges of w/s in the two cases. The incorporation of additional gypsum (Figs. 3 D–E) had no significant effect on the rate of reaction of the slag. The decreases in the degree of reaction on increasing the proportion of slag are more marked for the less reactive slags.

Effect of Varying the Water/Solids Ratio. This is shown in Fig. 4. There is a consistent decrease in reaction rate with decreasing w/s ratio, which was observed with 2 different slags and 2 different ratios of slag to cement.

Discussion

The results show that, over the age range of 4 to 104 weeks studied, granulated or pelletised blastfurnace slags in blends with Portland cement react to extents broadly similar to those typically reported for belite (19). For w/s ratios of 0.4–0.6, the degrees of reaction at 20°C were 30–55% at 28 days, increasing to 45–75% at 1–2 years. These results are broadly similar to those of Luke and Glasser (4,8), Hinrichs and Odler (11) and Battagin (12), but give no indication of the plateaux in the curves of degree of reaction against time that were reported by some of these investigators. The results demonstrate the importance of the corrections indicated by Luke and Glasser (4,8).

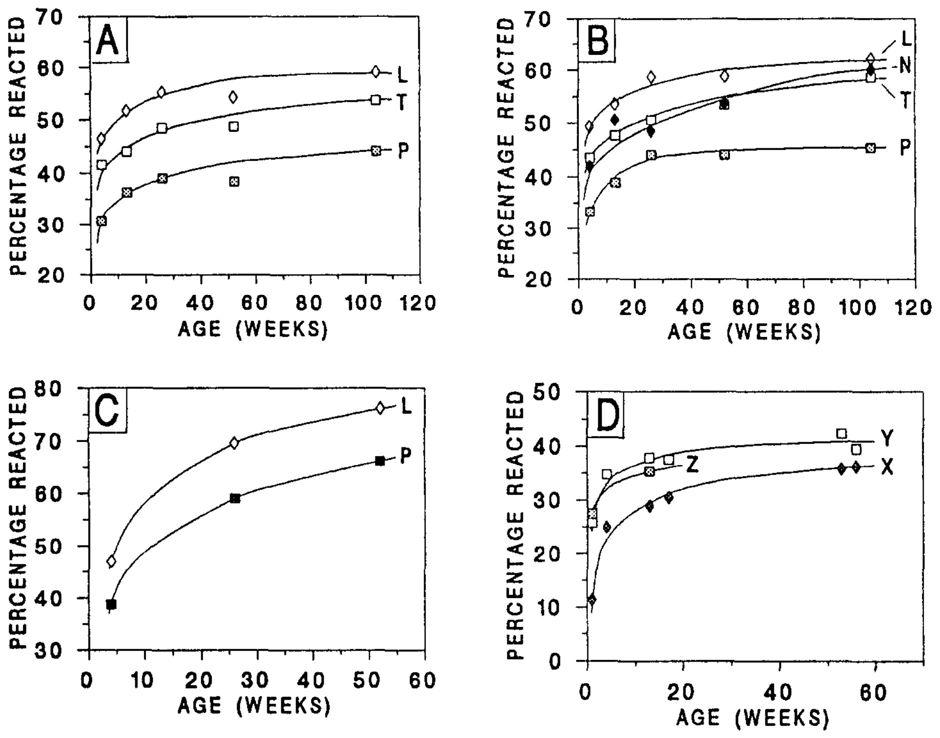

FIG. 2.

Percentages of the slag reacting: effect of varying the slag. A:Slags L, T and P in blends with cement B containing 60 % of slag; w/s ratio 0.4. B:Slags L, T and P in blends with cement B and slag N in a blend with cement A, all containing 50 % of slag; w/s ratio 0.4. C:Slags L and P in blends with cement B containing 30 % of slag; w/s ratio 0.6. D:Slags X, Y and Z in blends with cement C containing 69 % of slag; w/s ratio 0.3.

The results support earlier indications that the extent of reaction increases with fineness of grinding of the slag (3,11) and with quantities related to the hydraulic modulus (3,20). The observation that slag Z, which had the high hydraulic modulus of 2.04, showed a marginally lower degree of reaction at 13 weeks than slag Y, can be correlated with observations by Kollek and Lumley (21) on the strength development in mortars made with the same slags in conjunction with 3 different cements, of which one was cement C of the present work. Slag Z gave higher strengths than slag Y at ages up to 28 days in blends of varying proportions with cement C, but at later ages the position was reversed. It is emphasised that none of the present results provides data on the relative degrees of reaction of different slags at early ages, which probably differ from those at later ages.

The results do not support findings that the extent of reaction is unaffected by the proportion of slag in the blend (11,12). For the cements studied, they show no significant dependence on cement composition. As with the relative reactivities of different slags, the situation at early ages may differ from that at later ages. Kollek and Lumley (21) found that at ages up to 28 days,

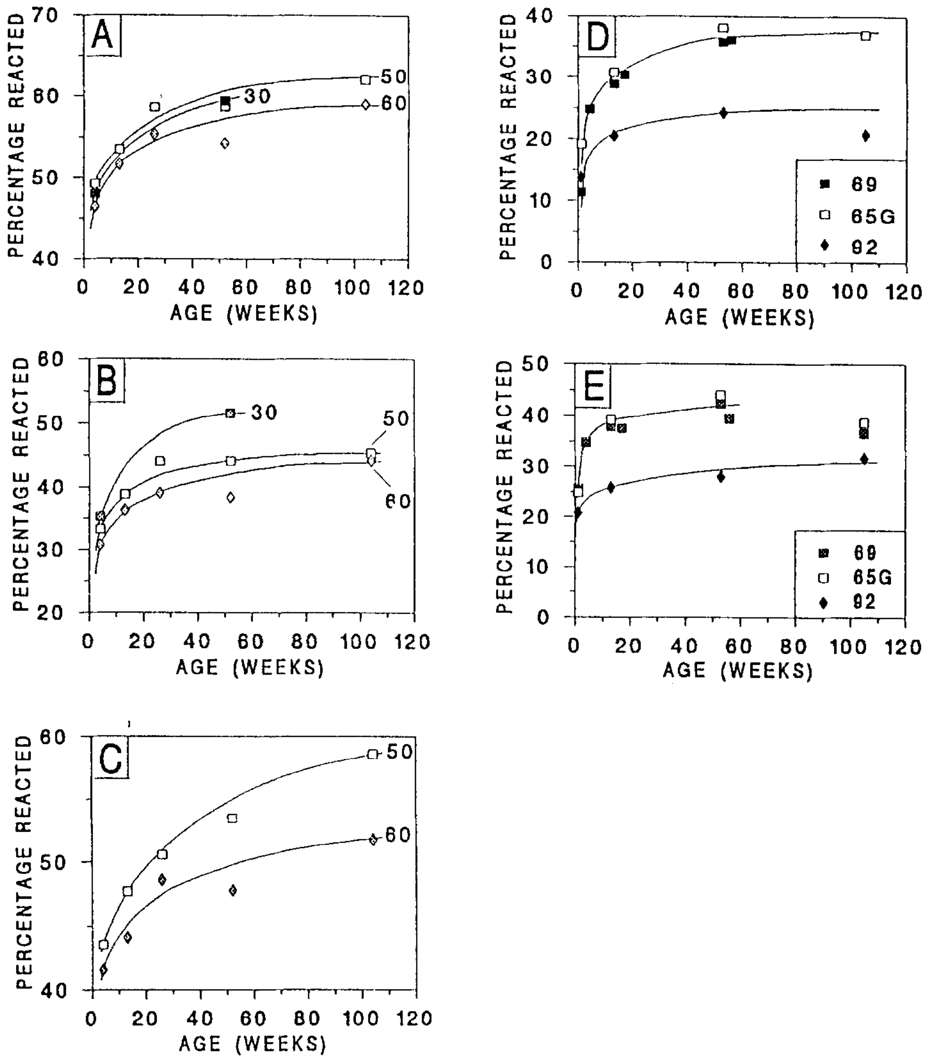

FIG. 3.

Percentages of the slag reacting: effect of varying the ratio of slag to Portland cement. A: Slag L in blends of cement B with 30, 50, or 60% of slag; w/s ratio 0.4 B: Slag P in blends of cement B with 30, 50 or 60% of slag; w/s ratio 0.4. C: Slag T in blends of cement B with 50 or 60% of slag; w/s ratio 0.4. D: Slag X in blends of cement C with 69 or 92% of slag, or 65% of slag and an additional 5% of gypsum (65G); w/s ratio 0.3. E: Slag Y in blends of cement C with 69 or 92% of slag, or 65% of slag and an additional 5% of gypsum (65G); w/s ratio 0.3.

strength development was usually more rapid with a cement high in alkalis than with cement C, but at later ages there was often either no significant difference or the position was reversed.

At the lower w/s ratios, the degree of reaction is possibly limited by available space, as in the case of the clinker phases. Because the slag is less reactive than the alite, its limiting degree of reaction in a given paste may be lower than that for the alite. The combination of high slag content and low w/s ratio in the pastes made from blends with 92% slag shown in Fig. 3 appears

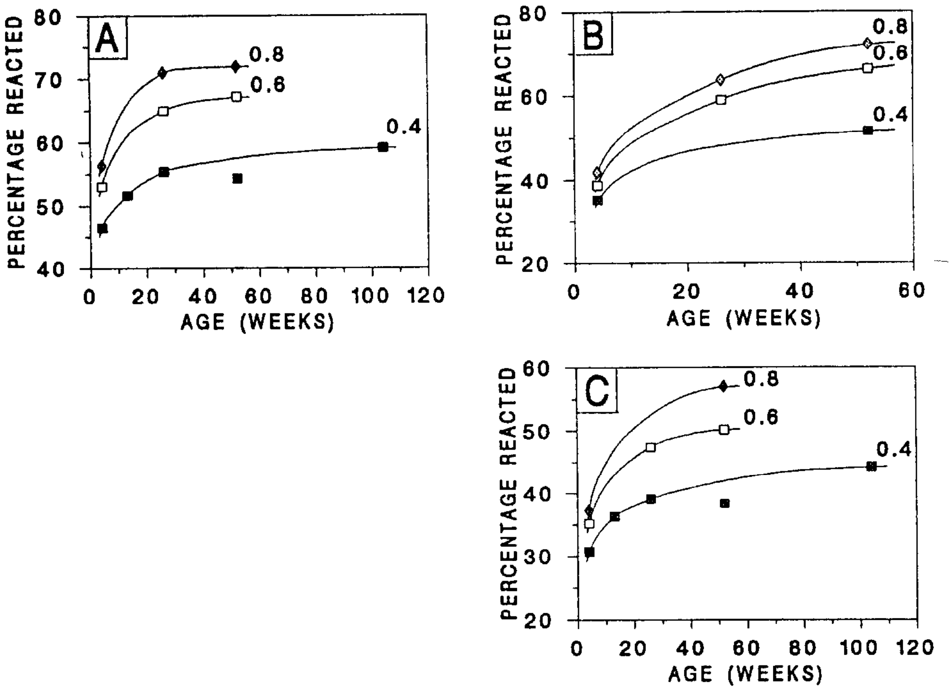

FIG. 4.

Percentages of the slag reacting: effect of water:solids ratio (w/s). A: Blends containing 60% of slag L. B: Blends containing 30% of slag P. C: Blends containing 60% of slag P. In all cases, cement B was used and the w/s ratios were 0.4, 0.6 and 0.8.

to limit the degree of reaction to around 30%.

From the standpoint of alkali silica reaction, and perhaps also of delayed ettringite formation, the fractions of the alkali released are important. The crystalline phases in the slag are virtually unreactive and the fractions of the glass that react are therefore higher than those of the slag as a whole. Since the alkali cations are almost entirely present in the glass, the fractions of them that are released are higher than those of the reacted slag as a whole, to an extent that depends on the glass content of the slag.

Conclusions

1. The EDTA extraction method described by Demoulian et al (1980), in a modified form, can be used to determine the percentage of a granulated or pelletised blastfurnace slag that has reacted in pastes made from blends with Portland cements. If certain corrections are applied, the absolute accuracy is possibly a few percent in favourable cases.
2. The accuracy is poorer at degrees of reaction above about 70% and in cases where a significant proportion of the unreacted slag dissolves in the reagent. This is the largest potential source of error in some cases. The fine fractions of the slag dissolve faster than the coarse fractions, but probably all the glassy material would dissolve given sufficient time.

3. For blends of granulated or pelletised blastfurnace slags with Portland cements, the percentage of the slag reacting in pastes of water:solids ratios of 0.4–0.6 and cured at 20°C is typically 30–55% at 28 days and 45–75% at 1–2 years. These values are broadly similar to those reported for the belite in Portland cements.
4. Limited data obtained at a water/solids ratio of 0.3 indicated that the composition of the Portland cement, or the inclusion of 5% of additional gypsum in the blend, has no significant effect on the extent of reaction of the slag at ages of 28 days to 1 year.
5. Different slags vary considerably in reactivity. For those examined in the present work, the main factors affecting reactivity appeared to be the hydraulic modulus, defined as (C+A+M)/S, and the fineness of grinding.
6. The rate of reaction of the slag decreases markedly with decreasing water/solids ratio and with increasing proportion of slag in the blend.
7. Comparison of the present results with those in the literature for strength development suggests that the extent of the reaction at ages of 28 days upwards is probably not simply related to that at earlier ages. A slag that gives relatively rapid increase in early strength may show lower degrees of reaction at later ages than one that gives slower strength development. Similarly, variations in the Portland cement can affect early strength development but have no significant effect on the extent of reaction at later ages.

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