

A Figure of Merit for Fly Ash Replacement of Portland Cement

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ABSTRACT

The replacement of Portland cement by fly ash produces competing effects: it contributes C-S-H gel through the pozzolanic and alkali-activated reactions, but it also dilutes the contribution of the main Portland cement reaction. The relative importance of these individual effects depends on the chemical composition of the glassy phase of the fly ash. All of them must be taken into account in proportioning the fly ash/cement mix. Therefore a figure of merit (FOM) for fly ash replacement has been developed. Given a fly ash chemical composition, and a specified replacement factor, the algorithm for computing the individual C-S-H contributions has several steps modeling the consumption of the CaO, SiO₂ and Al₂O₃ contents of the fly ash. If the FOM is greater than unity, then the replacement should provide a beneficial effect, i.e. more C-S-H gel. If it is less than unity, then the fly ash replacement would degrade the performance of the concrete. This algorithm can be iterated using different replacement factors to find the optimum value. An example of this approach is presented using a typical lignitic-type (Class C) fly ash and a bituminous-type (Class F) one. In most cases the FOM was less than unity.

I. INTRODUCTION

In previous work a methodology was developed to calculate the optimum replacement factor fly ash based on the constraint of no excess CH at the completion of the hydration reaction ¹. However, that mixing line approach was based only on the pozzolanic reaction of the fly ash. It did not take into account the other effects of fly ash replacement: the dilution of the C-S-H produced by the main Portland cement reaction, and the possible additional C-S-H contribution from the calcium content of the fly ash itself, i.e. self-cementation or alkali-activation.

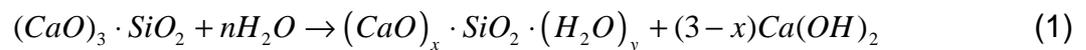
Adding the fly ash dilutes the amount of Portland cement and thereby the C-S-H contributed by the main cementitious reaction, and it also reduces the amount of CH required by the pozzolanic reaction. Thus the effect of adding too much fly ash may be a net reduction in performance in terms of the concrete's strength and durability.

There are also economic implications. Fly ash is usually regarded as a low-cost replacement for expensive Portland cement. However, if because of dilution, there is not enough excess CH to react with all of it, the remaining fly ash serves as only an inert additive, and thus becomes an expensive replacement for the fine aggregate. Therefore an algorithm has been developed that takes into account all three effects. The result is a figure of merit (FOM) for a given combination of fly ash and Portland cement and a specific replacement factor. The FOM can be used to assess whether the fly ash replacement would have an overall beneficial or detrimental effect on fly ash performance. It thus provides a way of comparing the performance of different fly ashes.

II CEMENT AND FLY ASH CHEMICAL REACTIONS

1. Portland Cement Hydration

The key reaction in the development of strength in concrete is the hydration of Portland cement which represented by its main component, tricalcium silicate (with formula: $(CaO)_3 \cdot SiO_2$, or C_3S in cement notation*) yields excess Ca:

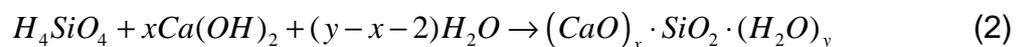


The factor x is the Ca/Si ratio, which is usually given as 1.65 to 1.70 for the porewater solution chemistries found in Portland cement concrete,

The hydration of fly ash in cement concrete can form products through several reactions. It contributes C-S-H by pozzolanic action and the self cementing action through the alkali activation reaction. However, it also produces a C-A-S-H gel and calcium aluminate hydrate gel.

2. Pozzolanic Reaction

The main reaction for fly ash is the pozzolanic reaction. At high pH, the silicate ion in the fly ash supplies becomes soluble to react with excess calcium in the pore solution from hydration of cement:

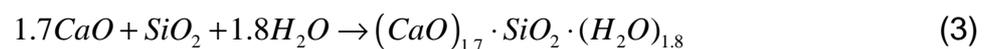


These will form calcium-silicate hydrate (C-S-H) gels similar to that produced by the Portland cement hydration reaction, but the C-S-H gel produced from fly ash may have a wider variation in composition, particularly the C/S ratio, which tends to be lower .

* Cement notation: C \equiv CaO, S \equiv SiO₂, H \equiv H₂O, e.g., CH \equiv Ca(OH)₂

3. Alkali-Activation Reaction

The second possible reaction for fly ashes that contain calcium-rich glassy particles is the alkali activation reaction. In high pH solutions, the OH⁻ ion attacks the bonds of the silicate ion network. This permits the silicate ion to react with the Ca present in fly ash to form C-S-H. This self-cementing or alkali-activated reaction is the basis for high-volume fly ash concretes.² In these applications, alkali in the form of sodium or potassium hydroxide has to be intentionally added.³ However, in Portland cement there is typically some alkali already present as sulfates from impurities in the raw materials. During the hydration reaction the sulfate precipitates out as ettringite (CaO)₆.Al₂O₃.SO₄.H₂O, leaving behind a mixture of sodium and potassium hydroxide in the solution. Since concrete pore-water solutions, usually dominated by K⁺ ions, can reach pH > 13, alkali-activation is a definite possibility.⁴ This reaction is simply:



In the absence of any information on the actual values of x for the pozzolanic and alkali-activated C-S-H gels, the ideal value of 1.65 was used for consistency.

No excess CH is produced or consumed by this reaction. However, this applies only to the Ca in the glassy phase. Calcium can also be present in crystalline phases such as wollastonite, which would not be very reactive. This reaction can proceed more rapidly than the pozzolanic action since the chemical components are already intermixed. In contrast, in the pozzolanic action the excess calcium in the pore solution

has to diffuse to the site of the siliceous component in the glass network for the reaction to proceed.

4. Aluminate Reaction

The third possible reaction is C-A-S-H gel formation in fly ash that contains high alumina glassy particles. This aluminum content reacts with the silica content of the particle and excess calcium from cement hydration to produce C-A-S-H gel phases. Using the idealized ratios of C/S = 1.65 in C-S-H, and C/S = 3, with A/S = 1 in the C-A-S-H gel phases:



In the aluminate reaction, excess calcium from pore solution has to diffuse to the site of siliceous and aluminous components in the glass network to form C-A-S-H gel. This reaction proceeds more slowly than the alkali activation because it requires the transport of external Ca into the fly ash glass network. However, it can proceed more rapidly than the pozzolanic action because the alumina may not be as tightly bound in the glass network as the silica.

The pozzolanic reaction and C-A-S-H gel formation thus compete for the siliceous component in fly ash and the excess calcium in pore solution. Since only the pozzolanic action can contribute C-S-H to the system, the C-A-S-H gel formation would lower the C-S-H of the system indirectly. The C-A-S-H gel can be an unwanted product since it apparently does not act as a binder. So the use of a high percentage of high alumina fly ash can be suboptimal

III. THE FIGURE OF MERIT ALGORITHM

Several competing effects of fly ash in hydrating cement were identified in the previous section. To gain an idea of the relative significance of each of them to the performance of the fly ash/cement mix, an algorithm has been developed to calculate a Figure of Merit⁵. The algorithm is based on several assumptions:

1. The various reactions proceed until the available reactants are completely consumed
2. The CaO in the fly ash is consumed in the alkali activation reaction subject to availability of Si in fly ash.
3. The Al₂O₃ in the fly ash is consumed in the C-A-S-H gel formation subject to availability of both Si and Al in fly ash and excess Ca in pore solution.

The algorithm for computing the individual contributions requires as input the chemical compositions of the fly ash and the cement, along with the replacement factor. The steps in the algorithm are then (see flow chart, Fig 1):

1. Use all CaO in the fly ash to produce C-S-H by alkali-activation (Eqn. 3).
2. Compare the remaining SiO₂ with Al₂O₃ in fly ash.
 - a. SiO₂ > Al₂O₃: use Al₂O₃ from fly ash as a key factor to determine SiO₂ and excess Ca to make C-A-S-H gel (Eqn. 4).
 - b. SiO₂ < Al₂O₃: use remaining SiO₂, Al₂O₃, and excess Ca to make C-A-S-H gel (Eqn. 4).
3. Reduce the C-S-H produced by the main cementitious reaction by the dilution factor
4. Reduce the excess CH by the main cementitious reaction by the dilution factor.
5. Use any remaining SiO₂ and the available excess CH to make C-S-H by the pozzolanic reaction (Eqn.2).

6. Sum the individual C-S-H contributions
7. Divide the sum by the C-S-H contribution of the undiluted cement reaction to yield the figure of merit (FOM)

This algorithm can be iterated using different replacement factors to find the optimum value. An example of this approach is presented below using a typical lignitic-type (Class C) fly ash and a bituminous-type (Class F) one.

Table 1: Subscripts used in Flow Chart, Fig. 1

Subscript	Name
ext	External porewater
fa	Fly ash
aa	Alkali-activated
pz	Pozzolanic
hg	Hydrogarnet or C-A-S-H
dil	Diluted

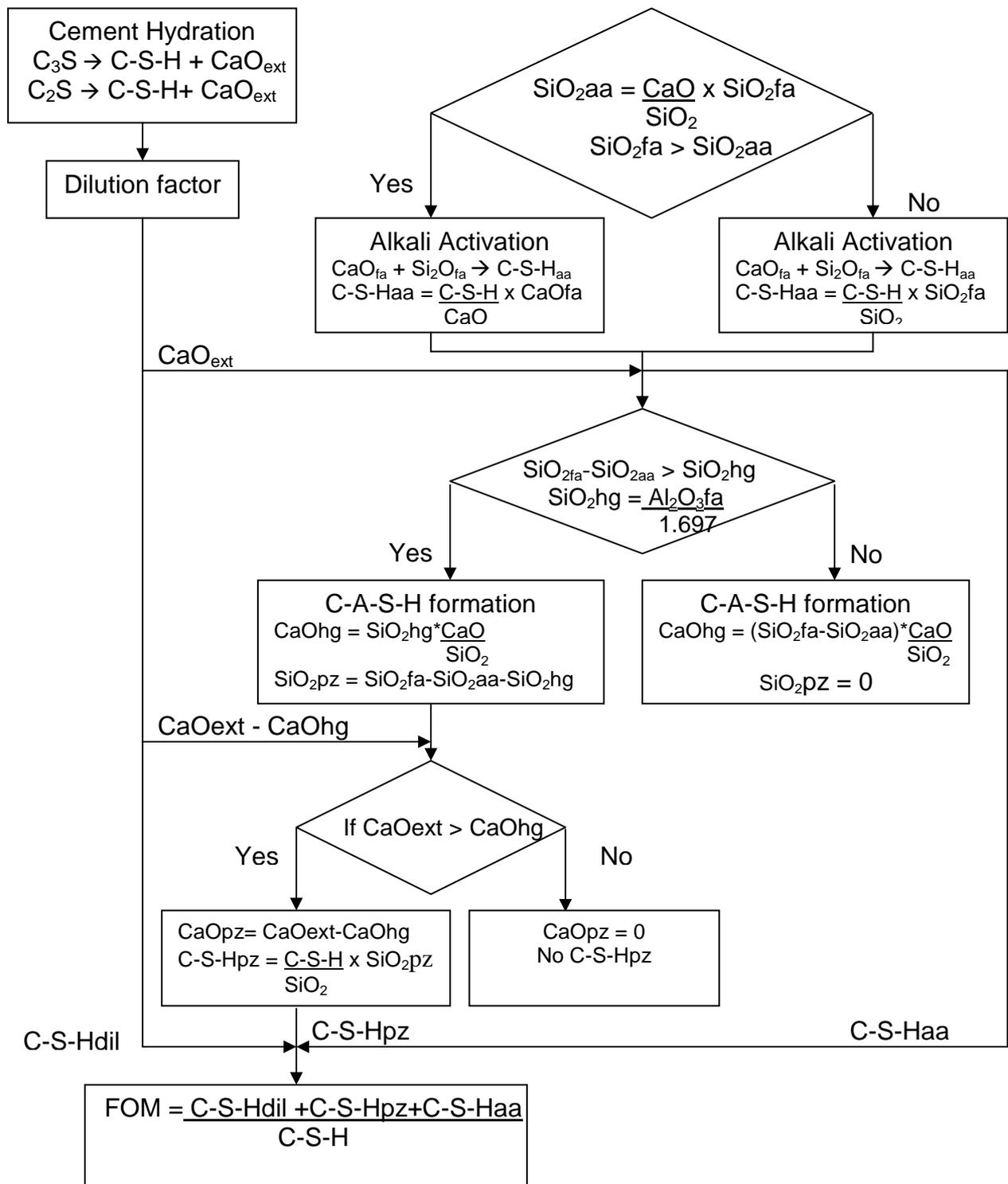


Fig. 1 Schematic diagram for FOM calculation

IV. FLY ASH CASE STUDIES

To illustrate the FOM approach, the compositions of some fractionated fly ashes have been used to calculate the FOM. Two different fly ash sources were used. One is from the Brayton Point Power Plant in Somerset, MA and represents an Eastern bituminous coal-type fly ash. The exact coal deposit is proprietary. The second one, Ottumwa, Marshalltown IA, is from a Wyoming Powder River Basin lignite coal deposit. On the basis of bulk chemical composition, the Brayton Point ash is Class F, and the Ottumwa is Class C.

1. Fractionation process

The fly ashes were first fractionated into sets of particles of given density by centrifuging in a high-density liquid. Primarily, this had the effect of defining a relatively narrow range of glass compositions within each set, but the particle size distribution was also affected in some cases, as discussed below. The multiple sink/float centrifugal technique was used to give six effective density fractions, designated by BP for the Brayton Pt fly ash and by OT for the Ottumwa fly ash. Six density fractions were selected ranging from $< 1.0 \text{ g cm}^{-3}$ to $> 2.85 \text{ g cm}^{-3}$ in intervals of 0.5 g cm^{-3} and numbered 1 to 6 respectively. This range of densities is typical of calcium silicate glasses⁶ which are the main reaction phases in fly ash.

2. Fly Ash Fraction Chemical Composition

The chemical composition of the glass particles was determined for each of the fly ash fractions by energy dispersive X-ray fluorescence analysis in a computer-

controlled scanning electron microscope (CCSEM).⁷ The analysis included 10 elements: Al, Si, Fe, Ti, Ca, Mg, Na, K, P & S and 8 particle diameters. Approximately 1000

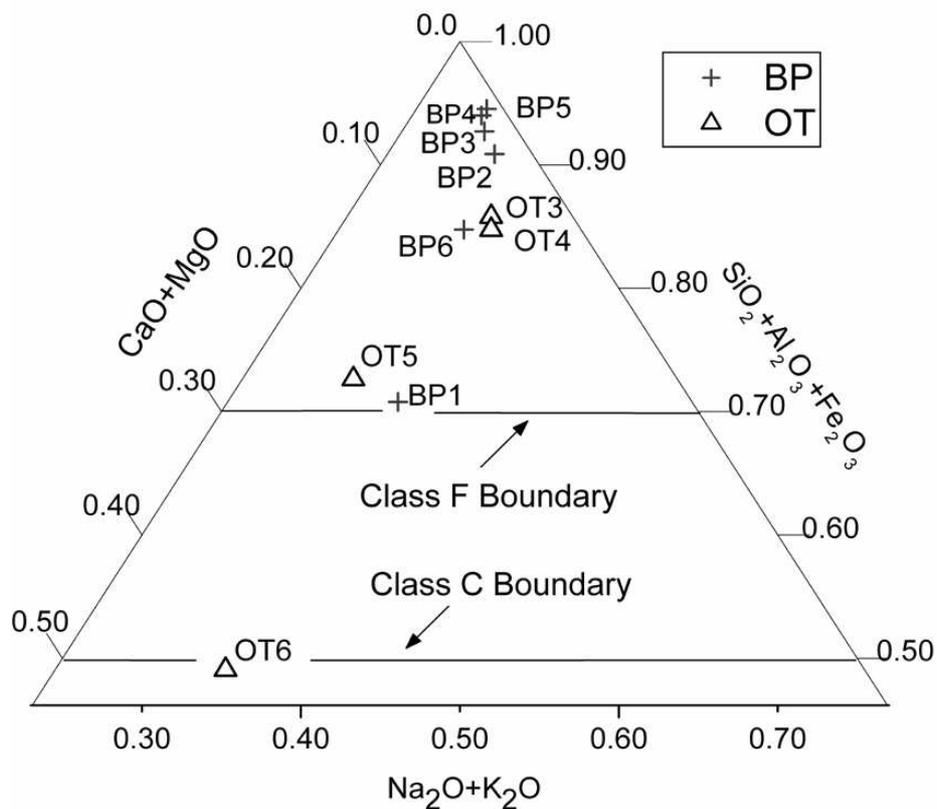


Fig. 2: Chemical compositions of fly ash glass fractions

particles from each fraction were analyzed. The mean chemical compositions of the fractions are presented in Fig. 2

3. Relative C-S-H contributions

In the calculations of the relative C-S-H contributions or FOM, the typical industry practice of 20 % mass replacement was used. The values calculated for Table 2 assume complete reaction of all components. Since they do not take into account

kinetics, they should be used only as a guide. In Table 1, columns *b*, *c* and *d* are the relevant oxide data for each fraction.

Column *e* is the amount of C-S-H formed in solid mixture (g/100g) that could theoretically be produced by alkali-activated reaction. This is by assuming that all CaO in fly ash is used to form C-S-H gel and $C-S-H/CaO = 3.34$. Column *f* is the amount of C-S-H (g/100g) that produced by pozzolanic action. It is formed from the SiO_2 remaining from the alkali-activated reaction and C-A-S-H gel formation in which $C-S-H/SiO_2 = 3.13$. Column *g* is the amount of C-S-H contributed by the diluted Portland cement. The C-S-H produced by the main cement reaction (C_2S and C_3S) is reduced by the dilution factor of 0.2. Column *h* is the sum of these contributions, and *i* is column *h* normalized by the C-S-H produced by the undiluted Portland cement. Column *i* is thus a figure of merit for the fly ash replacement. If this is greater than unity, then the replacement should provide a beneficial effect (more C-S-H). If it is less than unity, then the fly ash replacement degrades the performance of the concrete (less C-S-H).

Table 2: Theoretical C-S-H contributions of the various fly ash reactions as a function of chemical composition at 20% replacement

Sample (a)	CaO content of fly ash (mass %) (b)	SiO ₂ content of fly ash (mass %) (c)	Al ₂ O ₃ content of fly ash (mass %) (d)	Calculated C-S-H fraction in cement paste (mass g/100 g solid matrix)				Total C-S-H normalized to CCRL value (i)
				Alkali- activated C-S-H (e)	Pozzolanic reaction C-S-H (f)	C-S-H from hydration of C ₃ S, C ₂ S (g)	Total C-S-H (h)	
CCRL				-	-	60.87	60.87	1
OT3	3.56	42.39	47.52	2.38	6.64	48.70	57.71	0.95
OT4	4.75	60.54	27.54	3.18	24.60	48.70	76.48	1.26
OT5	17.09	30.77	36.48	11.43	0.00	48.70	60.13	0.99
OT6	25.73	11.52	18.67	7.23	0.00	48.70	55.92	0.92
BP1	9.31	19.19	28.70	6.23	0.00	48.70	54.93	0.90
BP2	0.21	38.53	53.38	0.14	4.29	48.70	53.13	0.87
BP3	0.17	38.63	55.66	0.12	3.54	48.70	52.35	0.86
BP4	0.55	45.59	47.13	0.37	10.80	48.70	59.87	0.98
BP5	0.78	59.99	32.54	0.52	25.07	48.70	74.28	1.22
BP6	2.02	29.54	43.56	1.35	1.08	48.70	51.13	0.84

Table 2 presents an estimate of the relative contribution of C-S-H provided by each fraction based on its chemical composition. It can be seen that there is significant variation in the total C-S-H and in the individual contributions among the fractions. With 20% replacement, most of the fractions show a value in column *i* less than one, except for OT4 and BP5. OT4 and BP5 have high enough SiO₂ contents to provide for alkali activation, C-A-S-H gel formation and pozzolanic action, while they also have such low Al₂O₃ contents that not all the SiO₂ and CaO are consumed in C-A-S-H. OT5 has high CaO and enough SiO₂ to enable alkali activation.

The key factor that causes the difference among samples is the C-S-H contribution by pozzolanic action which depends on the SiO₂ in fly ash. OT6 has the lowest SiO₂ available for alkali activation and pozzolanic action so it has the lowest FOM in the series. In some fractions, all the SiO₂ is used up in alkali activation and C-A-S-H gel formation, hence there would be no pozzolanic reaction. All of the Ottumwa fractions show some significant (> 3 %) potential contribution of C-S-H by the alkali-activation (AA) reaction. In particular, OT5 has the potential of contributing more than 11 % by AA. However, the high CaO content comes with a corresponding reduction in SiO₂, so its pozzolanic contribution is much less than OT3 and OT4. The SiO₂ content of OT6 is so low that it cannot produce any pozzolanic C-S-H.

4. Replacement Factor Variation

The FOMs calculated in Table 2 are for a single fixed value of replacement factor. However, this is actually a variable in the concrete mix design. To investigate the effect of its variation, FOMs were calculated for the fly ash fractions for selected

values that spanned the typical range of replacement factors. Figures 3 and 4 show the plots of the FOM as a function of the replacement factor for the OT and BP series respectively. Most of the curves decrease monotonically, indicating that because of low SiO_2 contents, the fly ash replacement does not provide enough C-S-H to compensate for dilution.

However, there are peaks in the FOM curves for OT4 and BP5. These indicate optimum values for the replacement factor. Moreover, the peak values are greater than unity, which implies that a fly ash/cement mix would be more beneficial than Portland cement alone. It is interesting that in both cases the optimum replacement factor is around 22%, which is close to the 20% usually specified. The FOM of OT5 is close to 1 and is not varied with the replacement %. This is because its C-S-H contribution from alkali activation is close to that of cement.

For the others there is no optimum defined by a peak in the FOM curve. However, a maximum replacement factor can be specified as that for which the excess CH would be all consumed¹. This is indicated by vertical dashed lines in each plot. The value is different for each fly ash fraction because of variations in chemical composition. The maximum replacement factors can be as high as 56%. This would represent a significant cost saving. However, this would also come with a degradation in the performance of the concrete, as indicated by the reduced FOM. In the case of OT6 the excess CH would not be totally consumed because all the SiO_2 is used up in the alkali activation reaction.

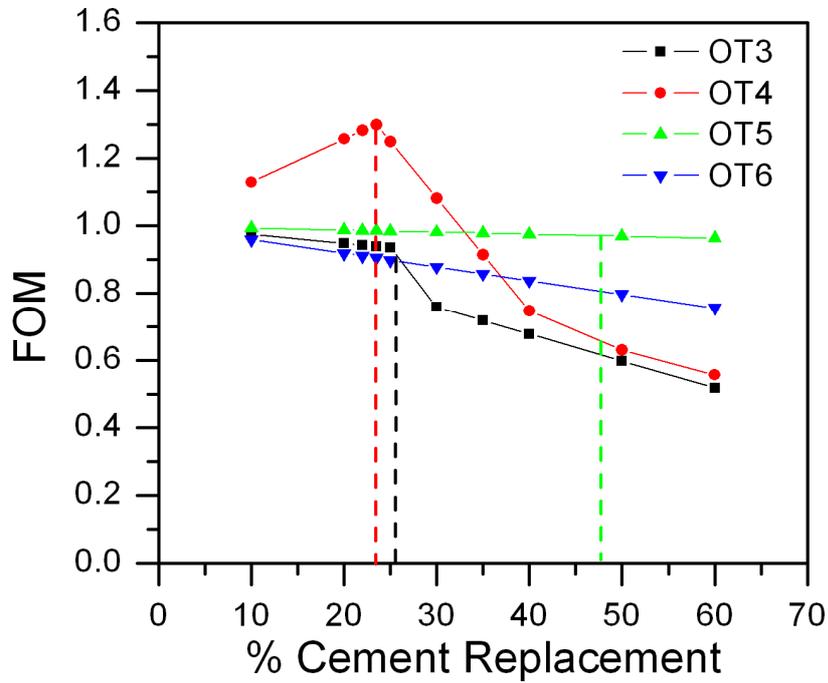


Fig. 3 FOM of OT Series as a function of cement replacement

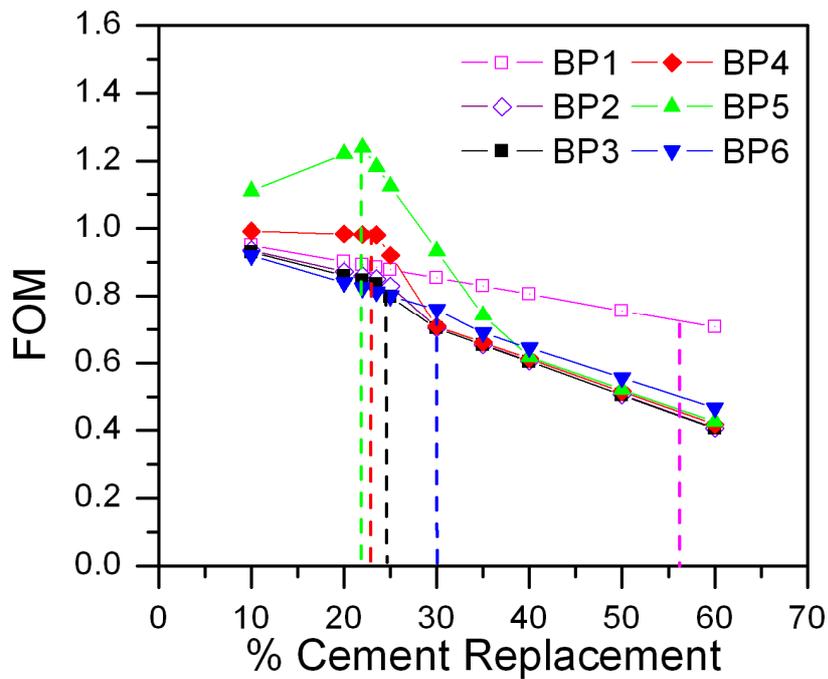


Fig.4 FOM of BP Series as a function of cement replacement

IV DISCUSSION

The concept of the FOM has been introduced as a way of sorting out the complexities of fly ash/cement mix hydration. In the process some simplifying assumptions had to be made. A major one was that the reactions involved go to completion. In reality, the reaction kinetics slow down with time as gel layers develop, Nevertheless, the results of the algorithm are still useful for a rough understanding of relative significance of dilution, pozzolanic action and alkali-activation for a given fly ash and cement combination.

Another assumption is that the hydrated aluminate phase is C-A-S-H with a fixed A/S ratio of 1 and C/S ratio of 3. Data from SEM analyses suggest that these ratios can vary from point to point in a fly ash/cement paste. However, it is not clear whether this represents an actual variability in the gel composition, or simply different proportions of C-S-H and C-A-S-H gel with fixed stoichiometries⁴. For lack of more detailed information, ideal values have to be assumed. More research is needed on the role of aluminates in the hydration of fly ash/cement mixes, possibly using synthetic fly ash glasses to reveal more clearly the reaction mechanisms⁸.

Finally, it is assumed that the performance of the mix can be defined in terms of C-S-H production. In practice the performance is usually measured as 28-day compressive strength (ASTM C-39) or total coulombs passed in the rapid chloride permeability test (ASTM C 1202). There is an overall positive correlation between gel volume and strength, and a number of models such as the Powers and Brownard gel/space ratio have been proposed⁴, However, these models are all empirical and differ significantly from each other in mathematical form and in the factors used.

Therefore, the FOM should be used as a guide for proportioning mixes rather than a precise number. Some physical testing would still be necessary for confirmation, but it is hoped that the amount of work could be reduced by using the FOM to narrow the range of mix designs that have to be tested.

V. CONCLUSIONS

The use of fly ash as a partial replacement for Portland cement introduces a number of competing effects. An algorithm has been developed that takes into account all three effects; pozzolanic action, alkali activation, and dilution. The result is a figure of merit (FOM) for a given combination of fly ash and Portland cement and a specific replacement factor. The FOM can be used to assess whether the fly ash replacement would have an overall beneficial or detrimental effect on fly ash performance. This algorithm can be iterated using different replacement factors to investigate the variation of the FOM. An example of the FOM approach is presented using fractions from a typical lignitic-type (Class C) fly ash and a bituminous-type (Class F) one.

VI. REFERENCES

1. R.A. Livingston and W. Bumrongjaroen: (2005) Optimization of silica fume, fly ash and cement mixes for high performance concrete, in Proc. of World of Coal Ash, (Lexington, KY, 2005) available from www.flyash.info/2005/79liv.pdf
2. V. Sivasundaram, G.G. Carrette and V.M. Malhotra, Properties of Concrete Incorporating Low Quantity of Cement and High Volumes of Low Calcium Fly Ash, in

- Fly Ash, Silica Fume, and Natural Pozzolans in Concrete, ACI SP-114, Edited by V.M. Malhotra , (American Concrete Institute, Detroit, MI, 1989)Vol. 1, pp.45-61
3. C. Shi, P.V. Krivenko and D. Roy: Alkali-Activated Cements and Concretes, (Taylor & Francis, London and New York, 2006).
 4. H.F.W Taylor: Cement Chemistry. (Thomas Telford, London, UK, 1997)
 5. W. Bumrongjaroen, R.A. Livingston , D.A. Neumann and A.J. Allen: Characterization of Fly Ash Reactivity in Hydrating Cement by Neutron Scattering, J. Mater. Res , in press (2009).
 6. C.I. Merzbacher and W.B. White: The structure of alkaline earth aluminosilicate glasses as determined by vibrational spectroscopy. J. Non-Cryst. Solids,130, 18 (1991).
 7. W. Bumrongjaroen and R.A. Livingston: Automated methods for fly ash particle characterization, in Proc. 8th CANMET/ACI Conf. on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, edited by V. M. Malhotra (American Concrete Institute, Detroit, MI, 2004), pp. 123-137
 8. W Bumrongjaroen,. and R.A Livingston: Synthetic Glass Models for Investigating Fly Ash Reactivity, in Ninth CANMET/ACI Conf. on Fly Ash, Silica Fune, Slag and Natural Pozzolans in Concrete, SP-242, edited by V.M. Malhotra,. 2007, (American Concrete Institute: Farmington Hills, MI 2007). pp. 227-242.