Optimization of Silica Fume, Fly Ash and Cement Mixes for High Performance Concrete

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ABSTRACT

High performance concrete often consists of ternary mixes of silica fume, fly ash or other pozzolans, and Portland cement. However, the specification of the proportions of these components remains uncertain. One objective could be to add just enough of the pozzolans to consume all the excess calcium hydroxide produced during the hydration of the Portland cement. In terms of the cement chemistry ternary phase diagram, this means finding the intersection between the tie line connecting the cement composition and the fly ash composition and the boundary line of the calcium hydroxide stability field. The boundary line can be found by assuming that the final equilibrium mineral assemblage is a mixture of C-S-H gel and calcium aluminate hydrates. In order to determine the tie line it is necessary to know the composition of the fly ash and also of the Portland cement. Since not all of the fly ash is reactive, and the kinetics of the reactions proceed at a finite rate, it may be necessary to adjust the length of the lever arm based on a detailed analysis of the fly ash composition and measurement of its pozzolanicity.

INTRODUCTION

It is a common practice in specifying High Performance Concrete (HPC) to use binary or ternary mixes of Portland cement, fly ash or other pozzolan, and silica fume. . However, it is difficult to find a theoretical basis for these proportions, which are usually developed instead by trial and error. Each state DOT tends to use its own set of criteria among shrinkage, creep, early strength, permeability etc. for determining performance. There have been some advances in statistical experiment design for performing these tests[1], but these do not explicitly take into consideration the chemistry involved.

The approach proposed here adopts the equilibrium mineral assemblage concept of geochemical thermodynamics as a basis for establishing mix proportions. It also makes of chemographic methods developed in this field to visualize the reactions involved[2].

CEMENTITIOUS HYDRATION REACTIONS

This graphical approach begins by representing the reactions in an appropriate phase diagram. The key reactions are first, the hydration of Portland cement, here represented by its main component, tricalcium silicate[3]:

$$3CaO\cdot SiO_2 + zH_2O \rightarrow Ca_xSi(OH)_y\cdot nH_2O + (3-x)Ca(OH)_2 \qquad (1)$$

Thus the reaction produces a calcium-silicate-hydrate gel (C-S-H), with the C/S ratio, *x*, usually fixed at about 1.65.

Note that this reaction produces excess calcium hydroxide (CH). Pozzolanic materials can supply additional silicate ion (S) which reacts with the CH to form more C-S-H gel:

$$SiO_4^{4-} + xCa(OH)_2 + \left(y-2x\right)OH^- + nH_2O \rightarrow Ca_xSi(OH)_y\cdot nH_2O \qquad (2)$$

where SiO_4^{2-} stands for the entire collection of silicate species.

However, the aluminum (A) content in certain pozzolanic materials such as fly ash can also react with the CH to produce hydrogarnet phases:

$$2Al(OH)_4^- + 3Ca^{2+} + SiO_4^{4-} \rightarrow Ca_3Al_2Si(OH)_8O_4 \qquad (3)$$

Therefore the equilibrium mineral assemblage consists of a mixture of C-S-H, CH and hydrogarnet.

THE POZZOLANIC BOUNDARY LINE

Examination of Eqn (1-3) shows that the C3S hydration reaction produces excess CH while the pozzolanic reactions consume it. Thus, theoretically with the correct starting proportions of C3S and pozzolan, it is possible that these competing reactions end up with an equilibrium mineral assemblage that contains no CH.

Using the idealized ratios of C/S = 1.65 in C-S-H, and C/S = 3, with A/S = 1 in the hydrogarnet and zero CH, gives the set of mass balances:

$$\begin{aligned} S &= 1\cdot S_{csh} + 1\cdot S_{hyd} \\ C &= 1.65\cdot S_{csh} + 3\cdot S_{hyd} \\ A &= 0\cdot S_{csh} + 1\cdot S_{hyd} \end{aligned}$$

along with the constant sum constraint for the ternary system:

$$C + S + A = 1$$

These equations can be solved to give:

$$A = (1 - 2.65 \cdot S)/2.35$$

This plots as a straight line in the ternary diagram as seen in Fig. 1. Any starting mixture that plots to the left of this line would thus have excess calcium hydroxide, which is the normal condition for Portland cement hydration. The excess CH stabilizes the solution pH at 12.5, which maintains a high solubility of silicate ions and thus ensures the reaction continues. However, any mix plotting to the right of this line would be calcium hydroxide deficient, and unable to sustain the reaction, which is the definition of a pozzolanic material. Consequently, this line defines the boundary between pozzolanic and self-sustaining mixes.

This relationship is a line rather than a fixed point, because there are two phases present, which could be in any ratio. Thus this is a unvariant phase relationship.

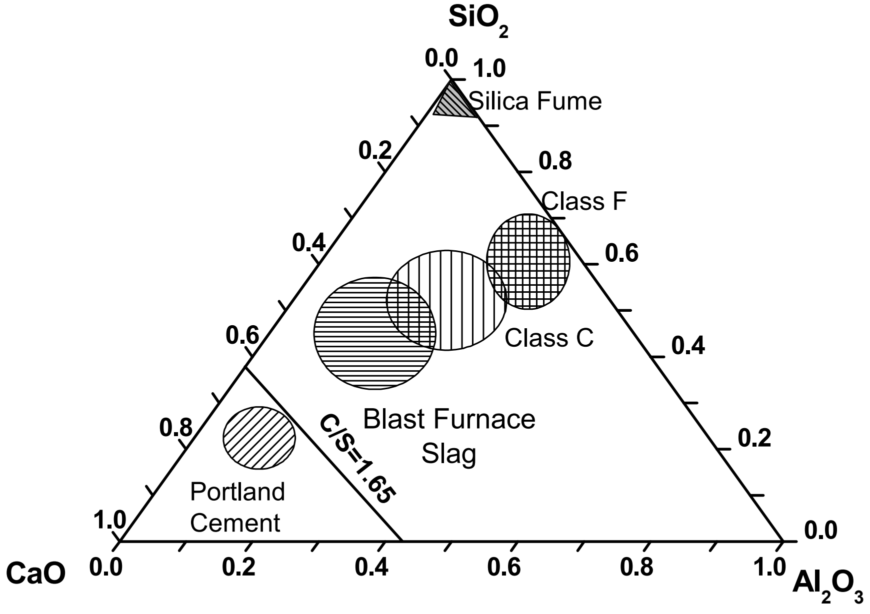

Figure 1: The phase diagram for the ternary system CaO-SiO_2-Al_20_3

BINARY CEMENT/POZZOLAN MIXES

A mixture of Portland cement and one type of pozzolan can also be plotted as a line in the phase diagram. The ends of the line are fixed by the chemical compositions of the pure Portland cement and the pure fly ash respectively, as shown in Fig 3. The chemical composition of a mixture of these two phases is a point somewhere along this line.

The position of the point on the line is determined by the proportions of the phases. If L is the length of the line, and the origin of the line is set at end point for pure Portland cement, then the distance to the point p is $(1-x)$ L, where i is the proportion Portland cement. This relationship is shown graphically in Fig 2. It is often referred to as the lever rule.

This point represents the chemical composition of the starting mixture. Since the cement hydration reaction takes place in a closed system, i.e. no reactants are added or subtracted during the reaction, the final equilibrium mineral assemblage will have the same composition.

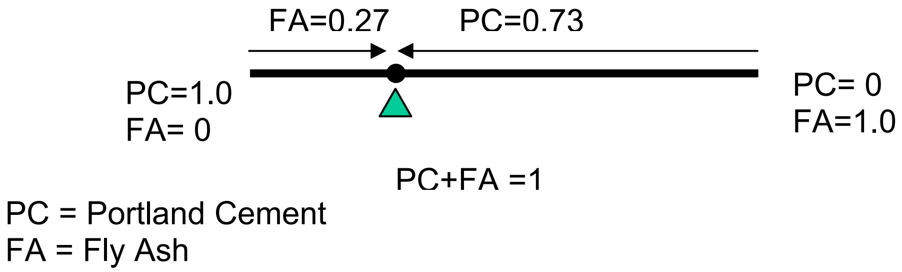

Figure 2: Schematic diagram of the lever rule

OPTIMIZATION OF THE BINARY MIX

The lever rule provides a method for optimizing a mix of Portland cement and pozzolanas. Optimization requires a set of one or more constraints. In this study it is proposed that the constraint should be the absence of CH in the final equilibrium mineral assemblage. This is based on the view that CH crystals form the interfacial transition zone around the aggregates, reducing the strength of the bond between the aggregates and cement paste. Moreover, eliminating the CH through the formation of additional C-S-H increases the amount of binder further adding strength and at the same time reducing permeability, which is regarded as an indicator of greater durability.

As shown in Fig.3, the mixing line between a Portland cement and a pozzolan will always cross the pozzolanic boundary line. The intersection point thus indicates the correct ratio of cement to pozzolan to achieve the optimum condition of zero CH.

FLY ASH EXAMPLES

To illustrate this approach, the compositions of two actual fly ashes have been plotted in the ternary diagram in Fig. 4. One was from the Ottumwa Power Plant in Fort Dodge Iowa, which burns a lignite-type coal. It is a Class C fly ash. The other was from Brighton Point, MA, which burns typical eastern bituminous coal, and is a Class F fly ash. The composition of the Portland cement, PC, is based on the analysis of an actual specimen.

A enlargement of the region around the pozzolanic boundary is shown in Fig. 5. Points representing arbitrary mix proportions are indicated along each mixing line. It can be seen that for the Brayton fly ash the 10% and 20% values straddle the pozzolanic boundary line.

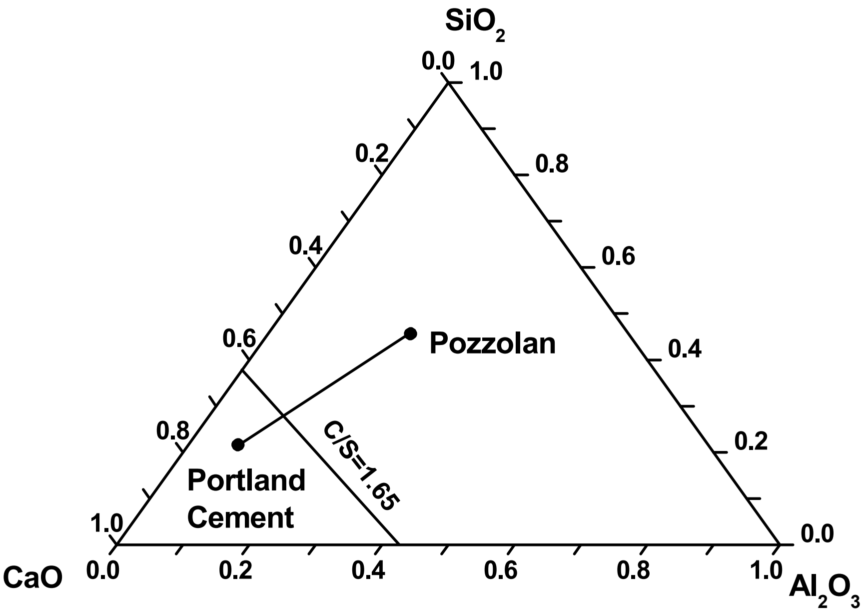

Figure 3: Illustration of mixing line

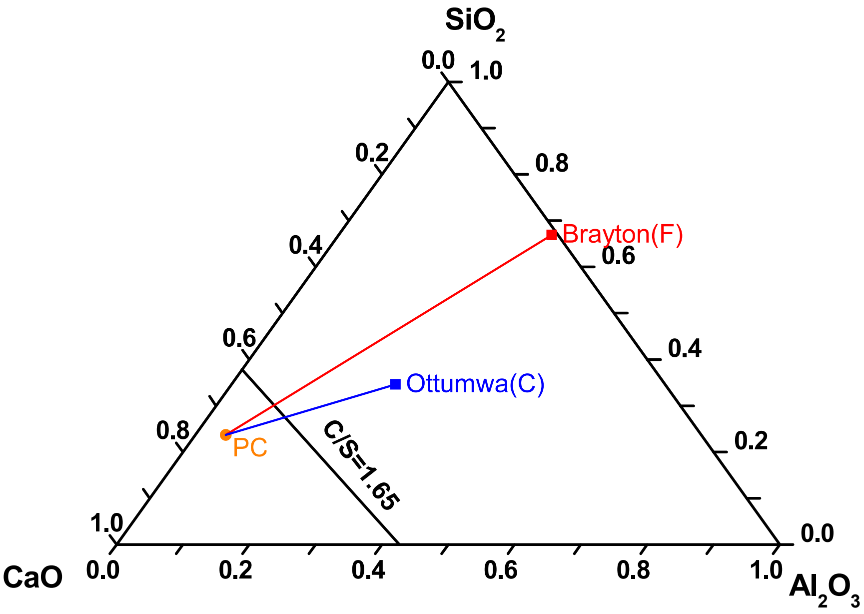

Figure 4: Plots of two fly ash samples

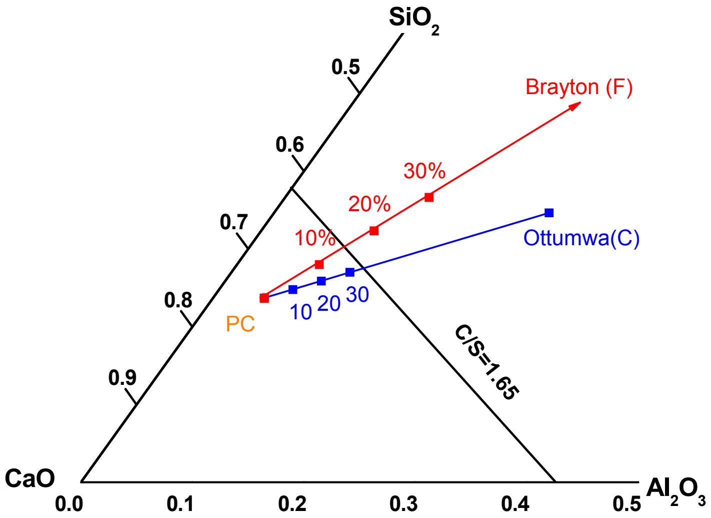

Figure 5: Enlargement of Fig. 5 showing effect of different arbitrary mix proportions.

However, for the Ottumwa fly ash, even a 30% mix does not cross the boundary. The optimum mix values are presented in Fig. 6 as 15% and 32% respectively.

These results illustrate the drawback of applying the same arbitrary mix proportions, i.e. 20%, to

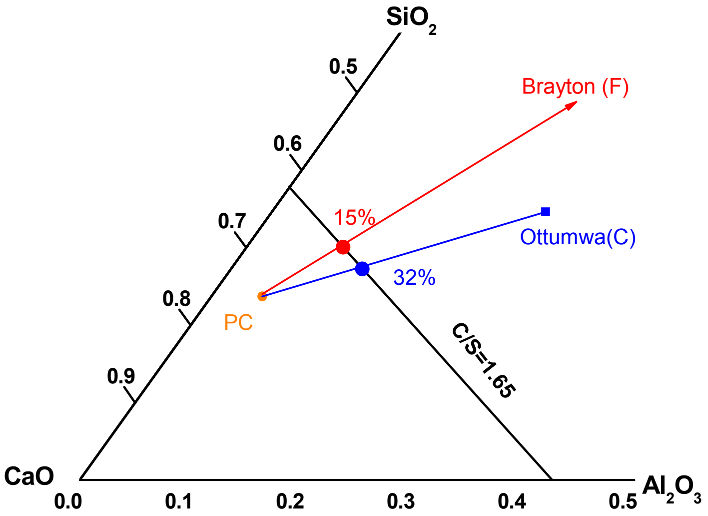

Figure 6: Optimum mix proportion based on zero CH

all fly ash /cement mixes. The optimum value is specific to each particular pair of fly ash and PC chemical compositions. Note that it is not just the fly ash composition that must be known.

The position and length of the mixing line also depends on the PC composition, and therefore this must be determined also.

The fact that the optimum mix values differ significantly is a reflection of the lever rule. The Brayton fly ash has very little CaO, and thus it plots at a much greater distance from the boundary line than the Ottumwa fly ash. This means that a relatively small addition of it will change the chemical composition of the mix significantly. In other words, it has a much longer lever arm than the Ottumwa.

Another factor is the angle at which the mixing line crosses the boundary line. In principle, this should be as close to perpendicular as possible, in order to minimize the distance between the PC point and the boundary line. This in turn would minimize the amount of fly ash needed to move the composition of the mix to the zero CH condition. Thus, because the Ottumwa mixing line crosses the boundary at an oblique angle, more of it is required.

However, the angle of the mixing line is determined by the A/S ratio of the fly ash. This ratio also determines the relative amounts of hydrogarnet and C-S-H that is formed in consuming the excess CH. Since hydrogarnet contributes little to the strength of the concrete, it is preferable that this ratio be as low as possible.

ADJUSTMENTS

This method of optimizing the binary Portland cement/fly ash mix is based simply on the stoichiometry of the equilibrium mineral assemblage. However, other factors have to be taken into account. One is that the bulk chemical composition of the fly ash by itself does not adequately represent the amount of the reactive glassy phases. For example, Table I is a mineralogical analysis of the Brayton fly ash. It can be seen that it is only 83% glass. The most significant mineral phases are mullite and quartz. These are essentially unreactive, and thus their constituents should not be included in the calculation of the optimum mix percentage.

Table I: Mineralogical Analysis of Brayton Fly Ash

Glass	83.4%
Mullite ($3Al_2O_3 \cdot 2SiO_2$)	10.7%
Quartz (SiO_2)	4.0%
Other Minerals	1.9%
TOTAL	100.0%

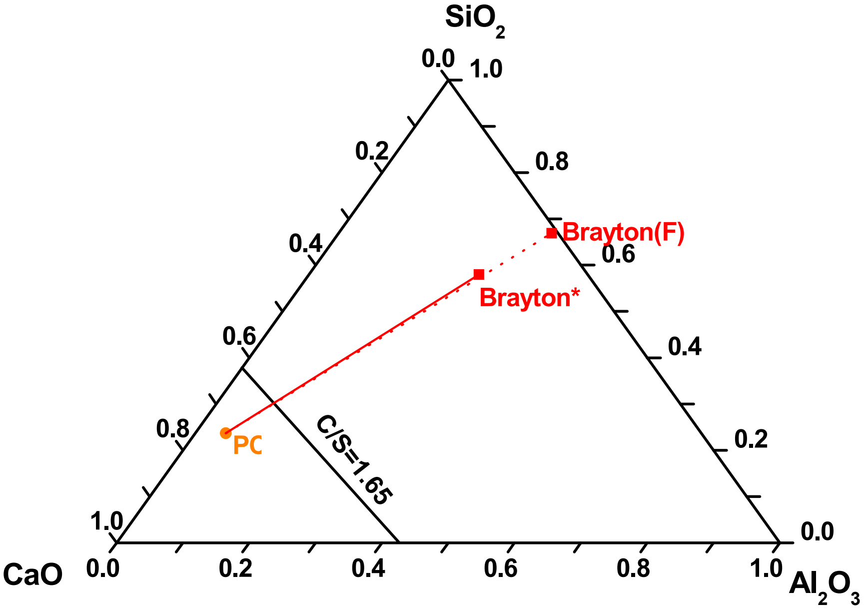

Figure 7: Effect of adjustment for nonglassy content

Figure 7 shows that the effect of this adjustment is to reduce the lever arm by 23%, and thus the optimum mix percentage is increased from 15% to about 20%.

Another factor that needs to be considered is that from a practical viewpoint, the reaction must be effectively complete by some fixed time limit, for example 28 days. Thus the kinetics of reaction must be taken into account. Unfortunately, knowledge of the reaction rates of CH consumption by fly ash is still very limited. Nevertheless, a procedure for incorporating this information into the optimization of the mix can still be defined. Given that the fly ash reaction rate *dc/dt* can be determined by some test, then the amount reacted by time *t* can be found by simply integrating. This can be used to adjust the lever arm accordingly.

TERNARY MIXES

Some high-performance concretes are now being made using three cementitious components: Portland cement, fly ash and silica fume. When the compositions of these three materials are plotted in the phase diagram, the result is a triangular mixing region rather than a single mixing line (Fig. 8a). Consequently, the intersection with the pozzolanic boundary is a line segment rather than a point. In order to solve for an optimum mix, it is necessary to specify a ratio of fly ash to silica fume. This constraint then restricts the system to a single mixing line (Fig. 8b) and the optimum can be found as in the case of a binary mix.

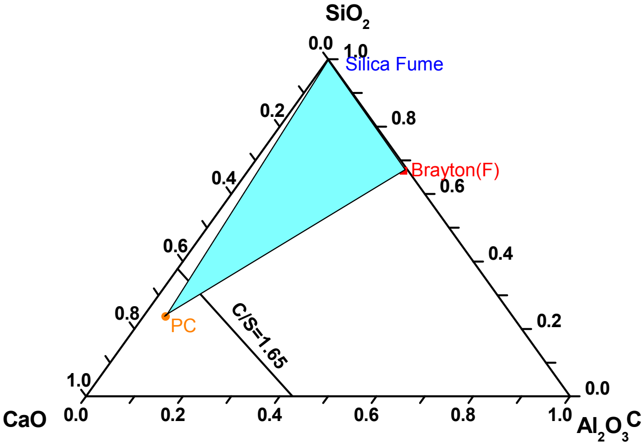

Figure 8a: Mixing region for ternary Portland cement, fly ash and silica fume mix

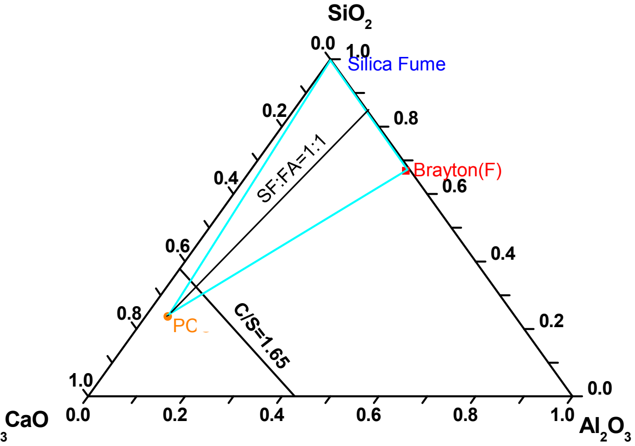

Figure 8b: Restriction to mixing line using a fixed fly ash/silica fume ratio

CONCLUSIONS

Chemographics can be a useful tool for visualizing the process of optimizing a binary or ternary mix of Portland cement, fly ash and silica fume. One possible constraint for the optimization is the elimination of calcium hydroxide from the final mineral assemblage. The practice of choosing an arbitrary value for the mix proportions does not ensure that this optimum condition will be achieved. In order to determine the optimum it is necessary to know chemical composition of both the fly ash and the specific Portland cement to be used. Adjustments to the lever arm may have to be made for nonglassy content and for the finite rate of reaction. To apply the optimization method to ternary mixes, it is necessary to specify a fly ash/silica fume ratio.

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