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Investigation of Reactivity of Fly Ash and Its Effect on Mixture Properties

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The reactivity of fly ash can vary considerably when used as a supplementary cementitious material (SCM). This paper demonstrates a framework for a standard test method to quantify the maximum reactivity of fly ash. The test is based on mixing reagent-grade calcium hydroxide (CH) and fly ash in a 3:1 mass ratio and exposing the mixture to 0.5 M potassium hydroxide (KOH) solution. Isothermal calorimetry and thermogravimetric analysis (TGA) are used to measure heat release and CH consumption, respectively, which are done in conjunction with thermodynamic calculations, as a basis to characterize the maximum reactivity of the fly ash. Fifteen fly ashes were tested using the method, which revealed that the reactivities ranged from 33 to 75%. Thermodynamic modeling was used to demonstrate the effect of fly ash reactivity on the properties of blended OPC-fly ash mixtures with different fly ash replacement levels (0 to 80%) and at various reactivities (0 to 100%). It was shown that the reactivity of fly ash is a critical factor determining durability-related parameters of mixtures such as CH content, C-S-H type and content, and the pH of the pore solution.

Keywords: durability; fly ash; mixture proportioning; pozzolanicity; reactivity; supplementary cementitious material; thermodynamic modeling.

INTRODUCTION

The effect of supplementary cementitious materials (SCMs) on the chemical composition of concrete can be explained through three primary mechanisms.[1] First, the SCMs reduce the amount of ordinary portland cement (OPC) in the mixture (dilution effect). Second, the SCMs react with calcium hydroxide (CH) produced by OPC hydration to produce additional C-S-H (pozzolanic effect), which generally has a lower calcium-to-silica ratio (C/S) than typically obtained through the hydration of OPC. Third, the SCM can react hydraulically. Although the dilution effect is directly related to the replacement level of SCM in the mixture, numerous other factors influence the pozzolanic and hydraulic reactions such as chemical composition, particle fineness, and reactivity of SCM. It is well documented in literature that the chemical composition of SCMs can vary significantly.[2-11] Less documented is the variability in the reactivity of SCMs, specifically fly ash, used in concrete production. Several studies have demonstrated that reactivity of fly ash can be relatively low (typically ranging from 10 to 50%) and can vary considerably between different SCMs.[12-14]

It has also been demonstrated in previous works that fly ash reactivity influences the durability properties of concrete such as its alkalinity, CH content, C-S-H content and type, chemical shrinkage, and alkali content.[15,16] These properties are directly related to resistance of concrete to deteriorative processes such as alkali-aggregate reaction (AAR), sulfate attack, chloride ingress/binding, salt damage (for example, calcium oxychloride formation), and reinforcement corrosion.[15,17,18] Therefore, knowing the reactivity of SCMs is critically important for assessing the durability and proportioning of concrete mixtures.

Current concrete mixture proportioning procedures were developed to achieve specified fresh property, workability, strength, and durability requirements.[19] These procedures allow for the incorporation of fly ash as a partial replacement of OPC without consideration to its reactivity. However, this approach fails to capture many benefits of fly ash, resulting in non-optimized mixtures, which makes it difficult to proportion performance-engineered mixtures effectively.[20] Further, without consideration to the reactivity of fly ash, many existing fly ash specifications exclude the use of viable off-spec fly ashes, blending fly ashes, or using ponded ashes in concrete production.

A primary issue that needs to be addressed before fly ash reactivity can be incorporated into mixture proportioning procedures is the development of a standardized testing method for measuring SCM reactivity. Several methods have been proposed, including the Chapelle test, the Frattini test, the saturated lime test, the strength activity index (SAI) test, the SCM dissolution tests, and calorimetry-based tests.[21-25] While these tests provide information on mixture strength as compared to OPC, they are limited for use as a standard for quantifying fly ash reactivity and do not provide a simple numerical result for the maximum reactivity of the material.[23] A strength of the current test method is the ability to indirectly capture unseen structural influences of a fly ash that are known to affect its reactivity (for example, its particle size, crystalline versus amorphous content, and surface area and morphology).

The test method proposed in this work overcomes an important limitation of earlier works aimed at characterizing reactivity insofar as it provides a numerical value that represents the maximum degree of reactivity (DoR) of a fly ash. The DoR of an ash is the measured percentage amount of the ash that has reacted with CH, and can be considered to be the maximum amount (%) of an ash that is available for the pozzolanic reaction.[26] The test method uses a combination of experimentally determined CH consumption and heat

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Table 1—Physical and chemical properties of all tested materials (mass %)

Fly ash	Na_2O_{eq}, %	MgO, %	Al_2O_3, %	SiO_2, %	SO_3, %	K_2O, %	CaO, %	Fe_2O_3, %	LOI, %
FA1	1.31	4.57	19.97	37.66	0.70	0.59	21.51	6.89	0.45
FA2	2.92	4.48	14.20	42.25	0.79	1.46	13.66	4.98	0.78
FA3	0.95	1.01	22.29	51.88	1.01	2.50	2.77	15.15	1.30
FA4	1.32	1.16	24.09	59.92	0.35	1.08	3.77	6.59	0.50
FA5	0.93	1.01	23.31	53.14	0.86	2.62	3.28	13.25	0.14
FA6	1.50	4.08	22.48	37.34	0.95	0.56	21.30	5.45	3.27
FA7	1.54	5.01	18.14	39.13	0.92	0.58	23.68	6.01	2.44
FA8	0.92	3.28	23.90	49.94	0.70	0.54	13.34	4.42	0.82
FA9	1.61	5.21	19.44	38.34	1.29	0.63	21.61	6.22	2.66
FA10	0.63	2.95	19.93	56.73	0.34	1.35	10.20	5.83	0.68
FA11	1.69	5.14	18.96	37.26	1.13	0.58	24.00	6.26	2.34
FA12	1.80	5.55	19.32	38.05	0.86	0.46	22.68	5.64	2.82
FA13	1.67	6.91	16.43	32.98	1.83	0.39	27.92	5.82	3.36
FA14	8.11	3.58	20.36	37.82	2.84	0.76	15.48	5.29	3.88
FA15	0.79	3.19	19.72	52.77	0.87	1.08	14.23	4.81	1.04

release values obtained from isothermal calorimetry, coupled with thermodynamic simulations of CH consumption and heat releases for reference SiO_2 and Al_2O_3 systems run to equilibrium at different theoretical maximum reactivities. When the results of the thermodynamic calculations for these reference systems are plotted, they provide reference lines from which reactivity values of the fly ashes can be determined. This paper discusses the details of the method. Furthermore, thermodynamic modeling was used to demonstrate the effect of fly ash reactivity obtained from the test method on the properties of blended OPC-fly ash mixtures with different fly ash replacement levels and at various reactivities.

RESEARCH SIGNIFICANCE

The reactivity of fly ash can vary considerably between sources. This can have a significant impact on the mechanical and durability properties that develop in fly ash concrete. Current concrete mixture proportioning procedures allow for the incorporation of fly ash as a partial replacement of OPC without any specific consideration as to its reactivity. As a result, this approach fails to account for specific features of the fly ash in tailoring the mixture proportions for specific mechanical or durability performance in concrete production. To incorporate fly ash reactivity into concrete mixture proportioning procedures, a reactivity testing procedure would be useful. This research interprets a recently proposed SCM reactivity test method that is also applicable for measuring the degree of reaction (DOR) fly ash using thermodynamic calculations. This test can provide significant insights into the DOR and type of reactions occurring with a given fly ash.

METHODS

Materials

A test method to determine the reactivity of 15 fly ashes is demonstrated in this research. The chemical compositions of the study fly ashes were determined using X-ray fluorescence (XRF) (Table 1). The loss on ignition (LOI) was measured in accordance with ASTM C114-18 by heating 3 g (0.11 oz) of each fly ash in a furnace up to 970°C (1778°F) for 3 hours and measuring the remaining mass after combustion.

Reactivity testing

The blends for measuring reactivity were made by dry mixing reagent grade calcium hydroxide (CH) and the fly ash in a 3:1 mass ratio. The powder was then mixed with 0.5 M potassium hydroxide (KOH) solution while keeping the liquid-to-powder ratio constant at 0.9. For each test, 40 g (1.41 oz) of materials were mixed for 4 minutes in a plastic container using a spatula. After mixing, approximately 7 g (0.25 oz) of the paste was immediately sealed in glass ampoule. The ampoules were transferred to an isothermal calorimeter that had been preconditioned at 50 ± 2°C (122 ± 3.6°F) for 24 hours. Following signal stabilization approximately 45 minutes after the ampoule was placed in the calorimeter and the heat flow was recorded for a total of 240 hours.

After 240 hours, the ampoules were removed from the calorimeter. Approximately 20 mg was taken from the removed sample for thermogravimetric analysis (TGA). The TGA involved heating the sample from 23 to 1000°C (73 to 1832°F) in a nitrogen-purged atmosphere at a rate of 10°C/min (18°F/min). TGA was performed within 12 hours of removing the samples from the isothermal calorimeter. The mass loss in the sample between 350 and 450°C (662 and 842°F) corresponds to the decomposition of CH present in the system that was used to calculate the amount of CH remaining in the system after 240 hours.[27] TGA data are generally reported in terms of temperature and change in temperature, with the peak properties (that is, temperature range, peak width, peak amplitude) used to determine the type of reaction (exothermic versus endothermic). Additionally, the characteristic peak of the decomposition of compounds can be used in quantitative analysis. In the case of CH, decomposition typically occurs between 350 and 450°C (662 and 842°F).[27,28]

Because simulated pore solution (KOH) does not include sulfates, some of the reactions that might take place with fly ash are not considered in the reactivity test. Fly ash samples rich in active alumina can undergo rapid hydration in presence of water to form hydrogarnet.[29] In typical cementitious systems, this reaction is slowed down by the presence of sulfates (for example, from gypsum added to OPC clinkers) to form ettringite (Aft) and monosulphate (Afm) phases. Although the test has been designed to capture the total heat released by complete reaction of the fly ash in a cementitious system, further work is needed to better understand the heat release associated with the Aft and Afm phases.[30]

Thermodynamic modeling

GEMS3K software[31,32] and the CemData v.14.01 database[33-45] were used to obtain internally consistent thermodynamic data and to model thermodynamic processes. GEMS computes equilibrium phase assemblages and speciation based on the total bulk chemical composition of the system and has been validated extensively for use in cementitious systems in prior works.[33-45] GEMS simulations are based on a Gibbs Free Energy Minimization algorithm and, therefore, reactions proceed to theoretically infinite time, or, the time when the free energy of the system is minimized. Therefore, kinetic effects need to be included separately. OPC hydration kinetics were accounted for using the Parrot and Killoh method,[35,46] and all simulations on blended systems assumed that OPC degree of hydration (DoH) was 90%. Hydrogarnet phases were blocked in the thermodynamic simulations, as these phases do not generally form during the service life of concrete structures.[18] All reactive fly ash was assumed to be available in thermodynamic calculations. Each oxide mass of fly ash, as given in Table 1, was multiplied by the reactivity of the fly ash to determine the fly ash oxide amounts that are used as input in thermodynamic calculations.

To produce the reference ranges for fly ash reactivity used in this test method, thermodynamic modeling was performed to determine the reference CH consumption versus heat release data for SiO_2 and Al_2O_3 reactions with 0.5 M KOH at 50°C (122°F). Thermodynamic modeling was further used to demonstrate the effect of fly ash reactivity on the properties of blended OPC-fly ash systems. For this purpose, FA-15, which is a low-calcium fly ash as shown in Table 1, was used. OPC-fly ash mixtures with different fly ash replacement levels (0 to 80%) and at various reactivities (0 to 100%) were investigated. A typical Type I/II OPC composition, as shown in Table 2, was used in thermodynamic calculations.

Table 2—Chemical compositions of OPC used in thermodynamic calculations (mass %)

C_3S	C_2S	C_3A	C_4AF	SO_3	Na_2O_{eq}	MgO
52.2	21.6	8.1	10.20	3.0	0.2	2.3

The experimental measurements for CH consumption and heat release for several of the fly ashes were adjusted mathematically to determine the additional amount of heat release that is expected when the system reaches equilibrium. The experimental data for these ashes were fitted to a logarithmic function and the fitted model was used to predict maximum heat release beyond the experimentally measured 240 hours. The additional heat release was used to calculate the total heat release expected after the reactions are complete (defined as the point where instantaneous heat change per unit time approaches zero), which is also shown in Table 3. For the high-calcium fly ashes (although no hard limit for "high calcium" exists in the literature,[26] it is defined herein as ashes with a CaO composition of >15% by mass), CH consumption values were calculated based on the percentage change in heat release. No CH correction was applied to low-calcium ashes (because low-calcium ashes are not likely to have hydraulic properties), or to ashes that were not corrected for heat, on the basis that these ashes had reached equilibrium under experimental conditions. These CH consumption versus heat release data were plotted for each fly ash. The reactivity of each fly ash was read from the plot with respect to the thermodynamically calculated reference lines for CH consumption versus heat release for SiO_2 and Al_2O_3 reactions with 0.5 M KOH at 50°C (122°F).

RESULTS AND DISCUSSION

Reactivity test results

Table 3 presents data for CH consumption obtained from TGA and heat release obtained from isothermal calorimetry. Typical heat release versus time measurements using isothermal calorimetry are shown for two ashes (FA-4 and FA-8) in Fig. 1. The figure shows that the heat release from FA-4 at 240 hours plateaued, which implies that no additional reaction would take place between the fly ash and CH. On the other hand, the heat release from FA-8 at 240 hours had not plateaued, which implies that additional reactions would take place if the reactivity test were continued beyond 240 hours. Similar behavior was observed for some of the other ashes tested in this study (not shown in Fig. 1). As such, these ashes were adjusted in accordance with the methods described in the Methods section. The corrected heat release versus CH consumption data for each ash are plotted in Fig. 2. The reactivities of each ash were read from Fig. 2 and reported in Table 3.

As shown in Fig. 2, the reactivity test results indicate that for the fly ashes tested in this study, the reactivities range from 33% (FA-11) to 75% (FA-5). Several of the study ashes with initial CaO mass fraction of greater than 20% (for example, FA-6, FA-7, FA-9, and FA-12) fall to the left of the Al_2O_3 reference line on the plot. This is likely an effect of a combination of hydraulic effects of the ashes and the consequential production of CH during reaction and, in some cases, particle size effects of the ashes. However, the initial chemical composition of the ashes does not always directly correlate to the results of the reactivity test. For example, the low-calcium ashes (initial CaO mass fraction of less than 5%) show a wide range in reactivity, from 40% (FA-4) to 75% (FA-5), with FA-3 at 61%. It is known that fly ash reactivity can be highly variable, even for ashes with similar chemical compositions, and this is clearly seen in the results of the reactivity test. Differences in fly ash reactivity,

Table 3—Experimentally obtained and extrapolated CH consumption (b), (e) and heat release (c), (d), and measured reactivity (f) and d50 particle size (g) for all tested materials

(a) Fly ash	(b) CH consumed, g/100g SCM	(c) Heat released in 240 h, J/g (BTU/oz) SCM	(d) Calculated heat release after 240 h, J/g (BTU/oz) SCM	(e) Calculated CH change after 240 h, J/g (BTU/oz) SCM	(f) Measured reactivities, %	(g) d50, µm
FA-1	66.84	248.89 (6.69)	351.39 (9.44)	39.31 (1.06)	40	11.15
FA-2	56.83	262.05 (7.04)	327.84 (8.81)	42.56 (1.14)	40	9.62
FA-3	76.96	279.19 (7.50)	481.65 (12.94)	76.96 (2.07)	61	13.92
FA-4	72.17	210.89 (5.67)	210.89 (5.67)	72.17 (1.94)	40	17.42
FA-5	81.02	338.72 (9.10)	628.96 (16.90)	81.02 (2.18)	75	16.38
FA-6	68.51	336.13 (9.03)	469.62 (12.62)	41.30 (1.11)	50	10.12
FA-7	49.35	282.28 (7.58)	373.78 (10.04)	33.35 (0.90)	41	10.86
FA-8	71.51	316.83 (8.51)	511.85 (13.75)	71.51 (1.92)	62	NA
FA-9	54.73	301.52 (8.10)	388.73 (10.45)	38.90 (1.05)	42	5.62
FA-10	70.95	335.32 (9.01)	557.28 (14.97)	70.95 (1.91)	66	9.29
FA-11	50.82	191.76 (5.15)	191.76 (5.15)	50.82 (1.37)	33	N/A
FA-12	55.16	255.24 (6.86)	356.72 (9.59)	33.23 (0.89)	40	13.84
FA-13	43.00	200.68 (5.39)	200.68 (5.39)	43.00 (1.16)	35	9.42
FA-14	59.54	276.64 (7.43)	320.88 (8.62)	50.02 (1.34)	41	13.27
FA-15	57.45	315.86 (8.49)	497.58 (13.37)	57.45 (1.54)	58	13.45

*Indicates PSD not tested. Heat release values were obtained via isothermal calorimetry and CH consumption via TGA, and where applicable, extrapolated past 240 hours in accordance the methods described in relevant sections.

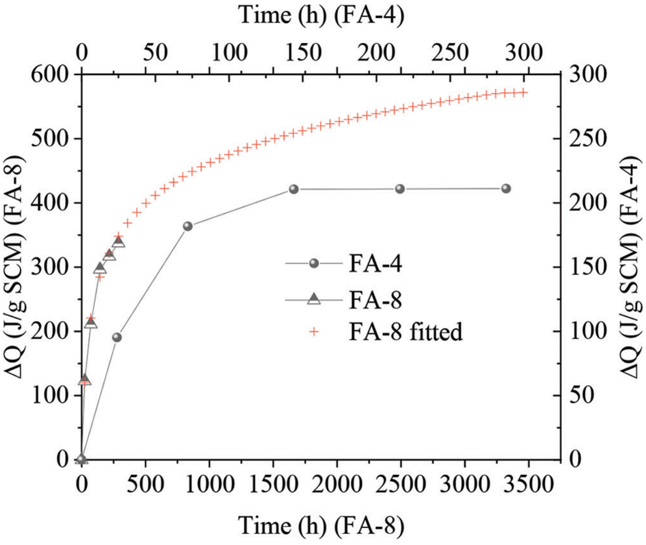

Fig. 1—Heat release curves determined by isothermal calorimetry for FA-4 and FA-8. Heat release data for FA-8 data was extrapolated to equilibrium to calculate heat release correction. FA-4 did not require any extrapolation because heat release did not change after 150 hours of testing. (Note: 1.0 J/g = 0.027 BTU/oz.)

for example, may also be partially due to the presence of crystalline versus amorphous phases with similar chemistries but different thermodynamic properties resulting from their structure. Particle fineness and surface area also likely influence the amount of fly ash that can react and, hence, its maximum reactivity. While previous works show some relationship between particle size and reactivity,[47-49] considerable knowledge gaps still exist in understanding how factors such as particle size, surface morphology, crystalline/amorphous phase ratio, and parent coal petrophysics combine to influence the DoR and related kinetics in fly ash-containing systems. In the present study, the particle size of the ashes does not strongly correspond to the measured reactivities. While some of the moderately low reactivity ashes (for example, FA-4; DoR = 40%) have a large particle size relative to the other study ashes (d50 = 17.42 µm as shown in Table 3), the relationship between PSD and DoR is generally not strong. For five of the six ashes with a measured DoR of approximately 40%, the d50 values fall within a narrow range of 9.62 to 13.92 µm (standard deviation = 1.74 µm). FA-4 is the outlier in this case, having a d50 value of 17.42 µm. By way of contrast, the d50 values for the entire population of ashes (excluding the outlier, FA-4) spans 5.62 to 16.38 µm (standard deviation = 3.10 µm). These results demonstrate the importance of having a simple, rapid, performance-based test to quantify reactivity without the need

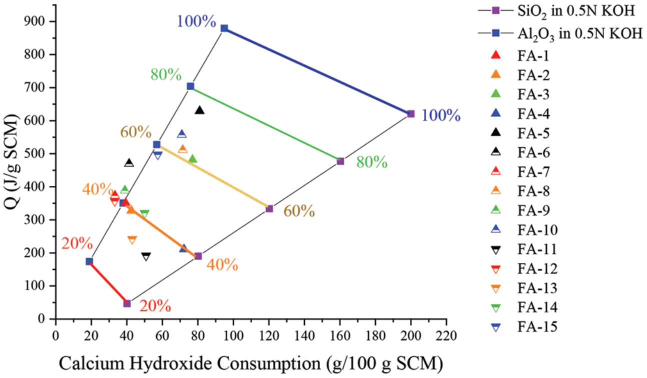

Fig. 2—Reactivity test results. (Note: 1.0 J/g = 0.027 BTU/oz.)

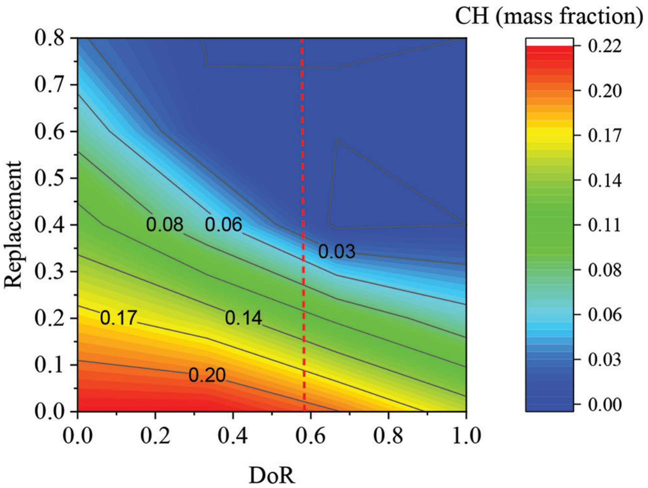

Fig. 3—Thermodynamic modeling of CH amounts (mass fraction) for mixtures of FA-15 and OPC at different replacement levels and fly ash reactivities: simulated DoR and replacement level from 0% to 100% and 0% to 80%, respectively. System w/b *= 0.42.*

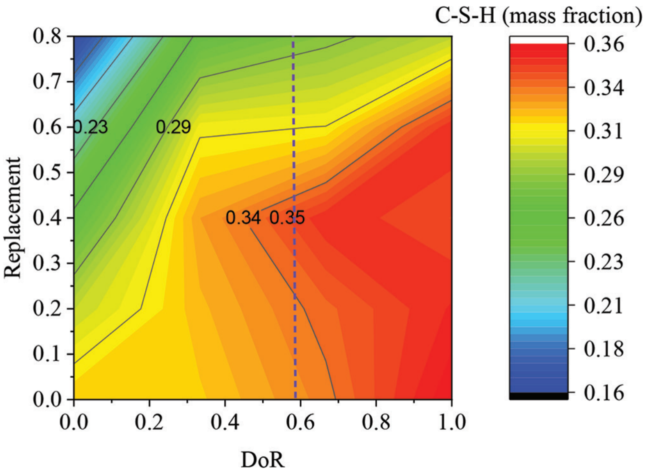

Fig. 4—Thermodynamic modeling of C-S-H amounts (mass fraction) for mixtures of FA-15 and OPC at different replacement levels and fly ash reactivities: simulated DoR and replacement level from 0% to 100% and 0% to 80%, respectively. System w/b *= 0.42.*

to directly measure or characterize the multiple structural parameters which can influence it, because these dynamics are not yet well understood or easily measurable.

Thermodynamic simulations

Thermodynamic simulations of an OPC-FA system were performed using GEMS3K thermodynamic software and CemData v 14.01 in conjunction with software developed by the authors to illustrate the importance of fly ash reactivity in the formation of reaction products and properties of concrete critical for durability. The GEMS3K thermodynamic software computes the molar amounts of molecules and ions, their activities, and the system chemical potentials, using a Gibbs Energy Minimization algorithm, and has been described and validated for use in cementitious systems extensively.[50-52] The water-binder ratio (*w*/*b*) of the mixtures was held constant at 0.42, and fly ash replacement levels were modeled at replacement levels from 0% to 80%. The chemical composition of the cement and the fly ashes are listed in Tables 1 and 2. Figures 3 and 4 show the mass percent values of CH and C-S-H, respectively, in simulated mixtures of OPC and FA-15 as a function of the fly ash the degree of reaction (DoR) and mass replacement level. Figure 4 shows the simulated pore solution pH, and Fig. 5 shows the simulated C-S-H variant. Vertical lines in the plots show the reactivity of FA-15 (58%) as determined using the reactivity test method.

As shown in Fig. 3, CH amounts of the system correlate strongly with fly ash replacement level and reactivity. As expected, CH values are higher at low fly ash replacement levels, and decrease as replacement levels increase, until the system becomes almost fully depleted of CH at and above the 40% to 70% replacement levels (depending on the DoR). Note that the lines in Fig. 3 are nearly horizontal at replacement levels less than 40% and reactivities less than 40%. This indicates that the amount of OPC replaced by the fly ash is the main control on CH within this range. However, at replacement levels and reactivities above these thresholds, the DoR of the ash becomes a factor. This is evidenced by the slope of the lines along the horizontal (replacement %) axis. Within this portion of the plot, as the modeled DoR of the ash increases, the CH values tend to decrease. This is most evident at replacement levels of <60%, because beyond that level, the system is almost completely devoid of CH, which is an expected outcome because it is known that the pozzolanic effect will be stronger in higher reactivity ashes. It is noteworthy that below the 40% replacement level, the system never becomes fully depleted of CH.

CH content of concrete can influence durability, particularly where a reaction between CH and chloride-based deicing salts forms calcium oxychloride (CAOXY),[53,54] which can cause expansive damage. Hence, the ability to predict CH based in part on fly ash reactivity can fundamentally improve the ability to design mixtures optimized to avoid such reactions. Concrete pavement joints provide an example of where the CH content of a concrete is an important durability consideration.[53-56] Over the last decade, these joints have shown premature deterioration, which has been attributed in part to the CAOXY formation as a result of the reaction between calcium hydroxide in the concrete and chloride-based deicing salts.

This reaction results in the formation of a phase known as calcium oxychloride which is expansive and damages pavement joints. From a practical perspective, CH, and therefore CAOXY amounts, can be lowered through the use of SCMs.[57] All of the tested SCMs show a decrease between CAOXY amounts and their volume replacement; however, determining the exact amount of SCMs to use depends on several factors. Using the GEMS modeling approach would enable the efficiency of each SCM in reducing CAOXY amounts to be quantified; however, this requires accurate information on the chemistry of the SCM as well as the reactivity that can be expected from the SCM.

The pH of concrete pore solution (Fig. 6) strongly influences the susceptibility of concrete to deleterious processes

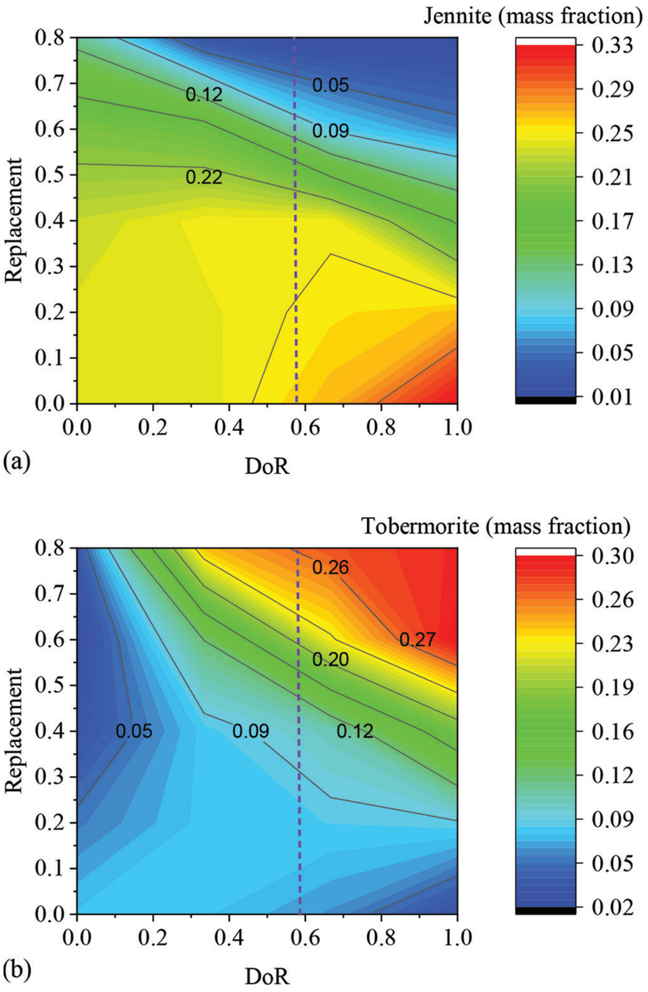

Fig. 5—Thermodynamic modeling of mixtures of FA-15 and OPC at different replacement levels and fly ash reactivities: (a) total Jennite (mass fraction); and (b) total Tobermorite (mass fraction). Vertical lines represent the measured reactivity of FA-15. Simulated DoR and replacement level from 0% to 100% and 0% to 80%, respectively. System w/b = *0.42.*

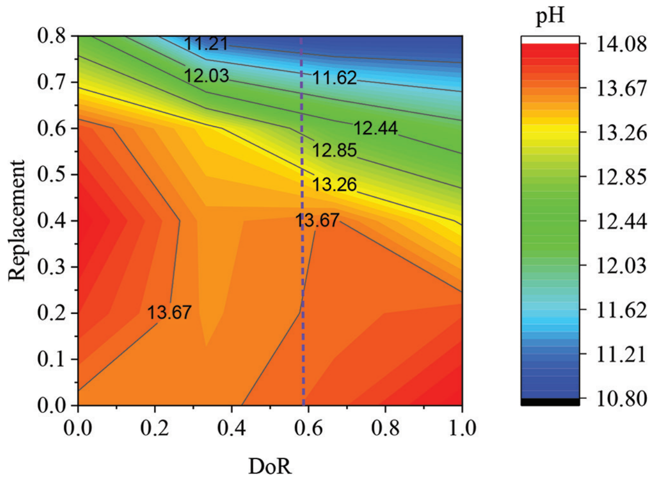

Fig. 6—Thermodynamic modeling of pore solution pH for mixtures of FA-15 and OPC at different replacement levels and fly ash reactivities: simulated DoR and replacement level from 0% to 100% and 0% to 80%, respectively. System w/b = *0.42.*

such as ASR and reinforcement corrosion. An alkaline pH is also critical for C-S-H. Figure 6 shows the pH of the OPC-FA-15 mixture as a function of the fly ash the degree of reaction (DoR) and mass replacement level. It is known that partial replacement of OPC by fly ash tends to decrease the pore solution alkalinity of concrete. As expected, the pH of the mixture becomes less alkaline with increasing fly ash replacement levels, dipping below 11 at DoR greater than 40% and replacement levels greater than 75%. These results demonstrate the importance of obtaining an accurate fly ash reactivity.

Figure 4 shows the total C-S-H mass fraction of the system at 90% OPC hydration. The increase in C-S-H with the DoR of the ash, and particularly at replacement levels greater than 40%, becomes a driver of C-S-H content. Also noteworthy is that the 58% DoR obtained from the reactivity test represents a threshold in the plot: Fig. 6 shows that at 58% DoR and 40% replacement levels, C-S-H values comprise nearly 35% of the system by mass. This illustrates the importance of having a rapid, accurate way to quantify fly ash reactivity such as that as provided by the present reactivity test, so that mixture proportions can be optimized to promote durability.

GEMS3K's thermodynamic database recognizes four types of C-S-H variants based on the calcium-to-silica ratio (C/S): Jennite D (C/S = 2.27), Jennite H (C/S = 1.33), Tobermorite D (C/S = 0.45), and Tobermorite H (C/S = 0.667).[33] A typical cementitious system contains a combination of these C-S-H phases, and the average C-S-H composition varies from 0.7 to 2.0.[58] Because the C-S-H structure heavily influences cement density, strength, and, ultimately, resistance to deleterious processes such as chloride ingress, corrosion, and ASR, it is an important property of an OPC-SCM mixtures. Systems with high pozzolanic reactivity tend to produce C-S-H with low C/S.[59]

Figure 5 shows the mass fraction of the total Jennite (D and H) and Tobermorite (D and H) in simulated mixtures of OPC and FA-15 as a function of the fly ash the DoR and mass replacement level. At any point on Fig. 5(a) and 5(b), the sum of Jennite and Tobermorite will equal the value shown in the total C-S-H plot given in Fig. 4. As logically expected, where Tobermorite is high in this system, Jennite is low. However, interestingly, at fly ash replacement levels less than 40%, the mass fraction of Tobermorite of the system is lower than Jennite as DoR increases. Above the 40% replacement level, the shift is toward lower C/S. C-S-H, and Tobermorrite becomes the dominant C-S-H variant. The DoR of the ash is also an influence on C-S-H type, particularly at and above the 58% DoR obtained from the fly ash reactivity test. Above this DoR threshold, there tends to be a wide variation in C-S-H variant at any point along the y-axis, illustrating the importance of fly ash reactivity in the type of C-S-H produced. This effect is also noted at lower DoRs (below 20%).

CONCLUSIONS

An experimental testing protocol for evaluating fly ash degree of reactivity (DOR) is discussed. The data interpreted in this paper relate the measured reactivity of multiple fly ashes to thermodynamically calculated reference lines, providing a rapid, accurate, and standard method to assess the availability of fly ash for reaction. This testing protocol provides a simple characterization for the maximum proportion of a fly ash that is expected react. A numerical model is presented that simulates this testing protocol based on thermodynamic simulations that employ energy minimization. Thermodynamic calculations for heat release and CH consumption in model SiO_2 and Al_2O_3 systems at degrees of reactivity (DOR) ranging from 20% to 100% provide, for the first time, a reference range from which the reactivities of experimentally measured values for actual fly ashes. The results demonstrate that fly ash reactivity is highly variable and not strictly related its size or chemical composition. It was shown that the reactivity of fly ash is a critical factor determining durability-related parameters of mixtures such as CH content, C-S-H type (C/S) and content, and the pH of the pore solution. The results demonstrate the importance of accurately characterizing fly ash reactivity for computational simulations as well as for use in developing mixture proportioning procedures that can incorporate fly ashes to optimize for durability-related properties.

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