Thermodynamic Investigation of Cementitious Mixtures Incorporating Off-Spec Fly Ashes

Deborah Glosser,1 Antara Choudhary1, Jason Ideker1, David Trejo1, W. Jason Weiss1, O. Burkan Isgor1

Oregon State University, School of Civil and Construction Engineering, 101 Kearney Hall, Corvallis Oregon, 97331

Keywords: Thermodynamic modeling, fly ash, reactivity, pozzolanic, concrete

Abstract

Current proportioning procedures for cementitious mixtures that contain fly ash do not currently explicitly consider the pozzolanic reactivity of fly ash. The authors believe that incorporating pozzolanic reactivity into mixture design can enable more predictable performance in terms of potential chemical reactions and porosity. Further, by considering fly ash reactivity, the utilization of fly ashes that do not currently meet ASTM C-618 (2017) (i.e., “off-spec” fly ashes) may be possible. In this research, Monte-Carlo based thermodynamic modeling was used to demonstrate that off-spec fly ash may be able to be used in concrete. In particular, the effect of fly ash mass by percent, chemical composition, and reactivity on calcium hydroxide content, C-S-H content, chemical shrinkage, and the pH and electrical conductivity of the pore solution were investigated. Simulations were based on statistical data for both in-spec and off-spec fly ash collected from literature. Roughly 300,000 simulations were conducted for each scenario to compare the performance of the mixtures prepared with in-spec and off-spec ashes. The results suggest that off-spec ashes can produce predictable reaction products and porosity provided that reactivity is incorporated into the GEMS simulation.

1. Introduction

As human population places increasing demands on both the natural and built environments, the need to develop sustainable infrastructure materials has become critical. Extending the use of coal combustion waste as a partial replacement for ordinary portland cement (OPC) by repurposing fly ash waste from coal combustion – as opposed to disposing of it in landfills and impoundments – is a beneficial strategy to satisfy multiple environmental, economic, and civil objectives (1). A major barrier to the development of mixtures using a wider range of ash sources than allowable under ASTM C-618 (2017) is an incomplete scientific understanding of the interactions between cement and fly ash, and how these interactions influence the structure and performance of the concrete mixtures (2). Once these fundamental knowledge gaps are addressed, there is practical potential to engineer infrastructure materials which meet the needs of industry and human and environmental health (3).
ASTM C-618 (2017) (4), the standard test method for testing fly ash for use in concrete, excludes a vast proportion of available fly ash from use as a partial replacement for OPC based. Roughly 110 million tons of fly ash produced in the United States annually; however, only 40% of the fly ash that is generated is beneficially used (5). This exclusion is based on the failure of the fly ash to meet certain chemical composition requirements. These parameters have been established largely based on the anecdotal reports of the performance of the fly ash for handling and its reaction with OPC.

The use of fly ash as a supplementary cementitious material (SCM) has several benefits including improved long term strength gain (6), pore solution alkalinity control, reduction of expansion caused by ASR (7), pore refinement, corrosion resistance (8), and minimization of damage by de-icing salts (9). However, the structural and chemical variability of fly ash can create challenges for designing mixtures with predictable performance, especially when chemical composition and reactivity of the ash are not appropriately considered (10). The range of fly ash chemical compositions and reactivity (both in-spec and off-spec) is quite wide, and depends in part on the parent coal properties (11) as well as combustion and processing techniques (12). The outcome of such variability is the challenge associated with the investigation of factors affecting performance and optimization of mixture proportioning approaches using purely experimental approaches. For this reason, computational modeling and advanced techniques such as Monte-Carlo based thermodynamic analysis are a powerful tool for addressing the variability of fly ashes with respect to chemical composition and reactivity, and evaluating the influence of this variability on mixture parameters.

There is a clear need to extend the pool of available fly ash for beneficial use based on its performance in OPC-based mixtures. To do so requires an understanding of how fly ash of variable compositions and reactivity potentials influences mixture properties, as well as evidence that shows these mixtures can perform as well as the fly ashes that meet the requirements of ASTM C-618. This study is aimed at characterizing the reaction products and pore solution chemistry of OPC made with partial replacement of off spec fly ash, and comparing mixture properties to those produced using in spec ashes. Monte-Carlo based thermodynamic modeling was performed to generate a range of in-spec and off-spec fly ash compositions, and to evaluate the multiple variables (in particular, chemical composition, fly ash reactivity and replacement level), which can influence its reactions with OPC. This approach allows for parametric examination of how mixture properties develop (e.g. calcium hydroxide (CH) content, pore solution pH and conductivity, calcium silicate hydrate (C-S-H) content), and shows whether the performance of off-spec fly ashes is significantly different from in-spec ashes when reactivity is explicitly considered. The knowledge generated by this work can be used to develop performance-based alternatives to ASTM C-618, and to extend to pool of fly ash available for use as replacement for OPC.

2 Modeling
2.1 Analyzed Materials

Monte Carlo simulations were performed on Type I/II ordinary portland cement (OPC) based OPC/fly ash systems including in-class (class C and class F) and off-spec fly ash. The compositions of the cementitious materials were modeled as Gaussian (normal) distributions that are based on reported data from the literature. Tables 1, 2, and 3 respectively provide the statistical data on reported compositions of constituents of the Type I/II portland cement and in-and-off spec SCMs that are used in this investigation.

Table 1 Statistical data for normal distributions of Type I/II OPC

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Type I/II ordinary portland cement (% mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>C₃S</td>
<td>61.43</td>
</tr>
<tr>
<td>C₂S</td>
<td>14.20</td>
</tr>
<tr>
<td>C₃A</td>
<td>6.94</td>
</tr>
<tr>
<td>C₄AF</td>
<td>10.20</td>
</tr>
<tr>
<td>MgO</td>
<td>2.25</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.32</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.18</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.61</td>
</tr>
<tr>
<td>Blaine fineness, m²/kg (ft²/lb)</td>
<td>395 (1928.7)</td>
</tr>
</tbody>
</table>

Table 2 – Statistical data for normal distributions of the constituents of fly ash

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Class C fly ash (% mass)</th>
<th>Class F fly ash (% mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>39.04</td>
<td>6.13</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.79</td>
<td>2.47</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.67</td>
<td>1.02</td>
</tr>
<tr>
<td>CaO</td>
<td>21.43</td>
<td>5.19</td>
</tr>
<tr>
<td>MgO</td>
<td>4.63</td>
<td>1.49</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.65</td>
<td>0.98</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.53</td>
<td>2.92</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.72</td>
<td>0.39</td>
</tr>
<tr>
<td>Na₂O-equivalent</td>
<td>3.40</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Table 3 – Statistical data for normal distributions of off-spec fly ashes

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mean</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>29.16</td>
<td>10.97</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.07</td>
<td>7.68</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.98</td>
<td>3.71</td>
</tr>
<tr>
<td>CaO</td>
<td>17.08</td>
<td>11.31</td>
</tr>
<tr>
<td>MgO</td>
<td>2.74</td>
<td>2.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.08</td>
<td>1.38</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.16</td>
<td>1.09</td>
</tr>
<tr>
<td>SO₃</td>
<td>6.64</td>
<td>3.48</td>
</tr>
<tr>
<td>LOI</td>
<td>17.04</td>
<td>13.35</td>
</tr>
</tbody>
</table>
2.2 Thermodynamic Modeling

Thermodynamic modeling of the OPC-fly ash systems was performed using software developed by the authors (13) in conjunction with the open source GEMS3K software (14, 15), which is based on the Gibbs free energy minimization method (16), and the thermodynamic database for cement-based materials, CEMDATA (version 14.01) (17-29). The GEMS3K-CEMDATA framework can be used to solve for the concentrations of chemical species (both in the solid cementitious matrix and pore solution), their activity coefficients, chemical potentials of chemical elements, and other thermodynamic quantities such as pH, fugacities, and the redox states. The CEMDATA database allows the modeling of the evolution of the hydration products as well as the precipitation and dissolution of complex chloride compounds such as Friedel’s salt (30-32). All calculations in this study were performed at room temperature (23°C) and atmospheric pressure.

The Parrot and Killoh hydration model was used to model the hydration of the OPC portion of the blended system (19, 33). This model can provide the approximate dissolution ratios of the main OPC phases (i.e., C\textsubscript{3}S, C\textsubscript{2}S, C\textsubscript{3}A and C\textsubscript{4}AF). The blended system was then analyzed based on assumptions of cement degree of hydration, fly ash degree of reactivity, and fly ash mass replacement. The dissolution rates of fly ash oxides were assumed to be uniform (however studies are underway to determine the suitability of this assumption). Formation of hydrogarnet-type phases was blocked in simulations (19, 20, 34). Additionally, an alkali uptake model by C-S-H phases was used for alkali modification in the pore solution (35).

2.3 Monte Carlo Analysis

Using the normal distributions of each constituent of the cementitious materials given in Tables 1-3, Monte Carlo simulations were performed though thermodynamic modeling on the blended systems containing OPC and different mass replacement levels of fly ash. For all cases, the water-to-cementitious materials ratio (w/b or w/cm), the degree of OPC hydration, and temperature were kept constant at 0.42, 0.90, and 23°C, respectively. Nine levels of SCM mass replacement (from 0 to 80%) and seven degrees of fly ash reactivity (from 0% to 80%) were analyzed.

For each scenario, random selections of OPC and fly ash chemical compositions were made using the statistical data provided in Tables 1-3. For each random selection, the hydration/reaction model was applied using the pre-assumed cement degree of hydration and SCM degree of reaction. The input data for each thermodynamic simulation was created for each random composition based on the SCM mass replacement level. Roughly 300,000 thermodynamic simulations were performed for each scenario representing a fly ash replacement level and fly ash reactivity.
3. Results and Discussion

3.1. Effect on calcium hydroxide (CH) content

The CH amounts (g/100g cement) are shown in Figure 1 for in-spec (A) and off-spec (B) fly ashes produced by Monte Carlo analysis for 7 assumed reactivities. Fly ashes consume CH through the pozzolanic reaction to form C-S-H, which is a desirable product for cement strength (36).

Because both the degree of reactivity and the replacement level of fly ash are important factors in the development of cement microstructure (and hence durability) (37-40), it is critical to examine the combined influences of SCM replacement level and reactivity on hydrated cement composition.

There are definite trends in the amount of paste CH in the paste as a function of reactivity, and the replacement amounts of fly ash in the paste. For both the in-spec (Figure 1A) and off-spec (Figure 1B) ashes, paste CH amounts are smaller at higher reactivities for all replacement levels. The trend of high reactivities corresponding to low paste CH amounts is exactly as expected: More reactive materials will consume more CH, hence paste CH amounts will be lower. The 0% reactivity cases show the effect of dilution only and are identical between the in-spec and off-spec ashes, as expected. In general, the differences between average values of the in-spec and off-spec ashes increase with the modeled reactivity. However, it is noteworthy that as the replacement amount increases from 0% to 80% the differences between the in-spec and off-spec ash CH amounts become smaller, irrespective of the modeled degree of reactivity. For example, at the 80% replacement level, all of the modeled pastes (both in-and off-spec) are entirely depleted of CH. In other words, there is no difference in CH amounts between in-spec and off-spec ashes at high replacement levels, regardless of the fly ash reactivity. Similarly, at the 60% and 70% replacement levels, the differences between in-spec and off-spec ashes are minimal, particularly for the ashes at the higher reactivities. The model results suggest that there is a physical threshold above which the amount of cement material replaced by the fly ash will result in the complete consumption of CH, irrespective of fly ash reactivity. At extremely high replacement levels, there is simply not enough OPC in the system to generate CH.

Although there is considerably more variability in off-spec ashes, the parity in CH amounts between the in-spec and off-spec ashes at higher replacement levels is of interest and suggests that off-spec ashes may be viable for use at high replacement levels (assuming other critical parameters, as discussed below) are not adversely affected by high off-spec replacement levels.
Figure 1 - Calcium Hydroxide (CH) amounts (g/100 g paste) for in-spec (A) and off-spec (B) fly ashes

3.2 Effect on pore solution pH

The alkaline nature of cement is protective against many forms of damaging attacks on cement (41, 42). Therefore, cements with higher pH are typically desirable, although in certain cases – such as mixtures designed for alkali silica reaction (ASR) prevention, low pH mixtures may be beneficial. Typically, partial replacement of OPC by fly ash results in a reduction of pH of cement pore solution (43).

There is a causal relationship between CH volumes in cement and pore solution pH: the reduction in CH levels and increase in C-S-H in the paste resulting from the pozzolanic reaction tends to reduce the alkalinity of the pore solution (41). The extent of the reduction in pore solution alkalinity from the pozzolanic reaction is due to several comingled factors, including the ash particle size, crystalline/amorphous phase ratio, and the initial alkali content of both the cement and fly ash (44). All of these factors are directly related to the reactivity of fly ash, and can influence uptake and binding of alkali by hydration products. Furthermore, at high pH levels, the solubility of CH decreases.
Relating fly ash reactivity to pore solution pH and its dynamic interactions with CH is important for performance-based mixture designs: Aqueous solutions of CH are medium strength bases, which can react with acid and cause passivation of certain metals (45), which is protective against corrosion of metals in cement structures (42).

Figure 2 shows the distribution of pH for in-spec (A) and off-spec (B) ashes. It can be seen that variability in the off-spec ashes is not considerably different than the in-spec ashes, however the average off-spec ashes tend to be more alkaline at any given reactivity. For both the in-spec and off-spec ashes, variability in pH values increase with both replacement level and reactivity. However, in off-spec ashes, on average, the mean pH values (Figure 2B) tend to fall in a narrower range than the in-spec ashes, and, on average, the pH of the off-spec ashes is more alkaline than the in-spec ashes, which suggests that either a higher proportion of alkali in the fly ash are being released, or that alkali binding in the hydration products is reduced. The difference is most noticeable in the higher replacement level cases.

The model results allow for separation of the chemical composition versus reactivity effects of the ashes: the pore solution pH of the 50% reactivity off-spec ash is roughly equivalent to the 25% reactivity in-spec ash at various replacement levels, each resulting in a minimum pore solution pH of approximately 12.5 at 90% hydration. This means that twice as much of the off-spec ash must react as the in-spec to achieve the reduction in pore solution alkalinity, indicating that the initial chemical composition and reaction products of the ashes is largely driving this difference. This is likely due to a combination of the initial alkali content of the off-spec ashes being on average higher than in-spec (a necessary condition when the SiO2+Al2O3+Fe2O3 content is fractionally lower by definition), and lower uptake of alkalis due to on average, lower total C-S-H and higher C/S C-S-H (see section 3.3). It is noteworthy however, that the same performance specification (here, pH) can be achieved with either ash, when reactivity is known.
3.3. Effect on calcium silicate hydroxide (C-S-H) content

C-S-H is responsible for much of the strength of a hydrated cement (10). It is well established that the replacement of OPC by fly ash results in an increase in C-S-H through the pozzolanic reaction (46). However, there are structural variations of C-S-H: The molar ratio of Ca/Si (C/S) of C-S-H is an important parameter insofar is it affects nonstructural characteristic of C-S-H (46, 47). The C/S and morphology of the C-S-H influence cement strength and cement density, and hence is an important property to quantify in OPC-SCM systems (48).

Typically, the stronger the pozzolanic reaction, the lower the C/S of the cement (49). The reduction in C/S from fly ash replacement is a consequence of both the initial silica content of system, as well a reduction in pore solution alkalinity: the pozzolanic reaction releases more alkalis, which become bound to C-S-H with a lower C/S. These C–S–H phases take up more alkalis, which is beneficial for the hydrated paste insofar as the increased alkali binding reduces risk of deleterious processes such as sulfate attack and delayed ettringite formation (35).

Portland cement should have a C/S mole of 1.5 or less for optimal durability, although values of up to 1.7 are generally acceptable (50). At very high replacement levels, more alkalis should be bound due to the consumption of CH, and high levels of low C/S C-S-H. In addition to the reduction in alkali content of the pastes, low C/SC-S-H (those between 0.83 and 1.00) have been shown to have increased compressive strength (48).

Figure 3 shows the C/S of the C-S-H in in-spec (A) and off-spec (B) fly ash pastes. There is not a substantial difference in variability of C/S between the in-spec and off-spec ashes, although the average C/S values of the off-spec ashes are higher than in-spec. At very low replacement levels (up to 20%), the mean C/S is identical at all modeled reactivities for in-spec and off-spec pastes and range from 1.4 to 1.6. This is not surprising, given that the bulk of the cement paste is comprised of OPC at these replacement levels.
As fly ash replacement levels increase, the C/S decreases for both in-spec and off-spec ashes, which is consistent with expectations based on prior works (48). On average, the in-spec ashes have lower mean C/Ss at all modelled reactivities, although the difference between in-spec and off-spec pastes become more pronounced at higher reactivity levels. This is a direct consequence of the lower SiO₂ content of the off-spec ashes. Lower silica content of the ashes will result in higher C/Ss of the C-S-H.

For both types of fly ash, more reactive fly ashes result in lower C/Ss, which is a direct result of more silica from the ashes being available for the pozzolanic reaction at higher fly ash reactivities. This result is consistent with results of prior studies (20). Although the in-spec pastes have, on average, lower mean C/Ss than the off-spec pastes, the mean values for the off-spec pastes are well within the desirable range of 1.5 or lower for moderate to large (>45%) replacement levels at all modeled reactivities >37.5%. The relevance of this result to performance-based mixture design is that the reactivity of the ashes is influencing the development of C-S-H type, independent of the ash chemical composition. In other words – both in-spec and off-spec ashes can reduce the C/S of C-S-H beyond that of OPC, but the extent of this reduction depends on the ash reactivity as well as its initial composition.
3.4. Effect on chemical shrinkage

Chemical shrinkage of hydrated cement can be a result of many factors, including but not limited to, relative humidity (51, 52) w/b (47), and the replacement of OPC by pozzolans such as fly ash (51). Fly ash replacement can result in increased chemical shrinkage insofar as it tends to refine pore structure relative to plain OPC, as well as reducing pore humidity as a result of the pozzolanic reaction (53).

Figure 5 shows hydrated paste chemical shrinkage as a percent of the overall cement volume for in-spec (A) and off-spec (B) pastes. Although the variability in chemical shrinkage is higher in the off-spec ashes (particularly at high reactivity levels), the mean values are nearly identical for the in-spec and off-spec ashes and tend to fall between 5% and 12% of total normalized cement volume. As expected, ashes modeled at higher reactivities display greater chemical shrinkage. As with the other parameters discussed in this study, the 0% reactivity cases (dilution) are identical between the in-spec and off-spec pastes. SCM contribution to chemical shrinkage (Figure 5 C and D) is not substantially different between in-spec and off-spec pastes. Because chemical shrinkage tends to be increased in pastes containing fly ash due to the pozzolanic reaction and its effect on pore solution humidity and water availability, these results seem to suggest that the in-spec and off-spec ashes do not substantially differ in how the pozzolanic reaction and water availability proceeds during cement hydration.

The significance of these results for a performance-based mixture standard incorporating fly ash is that the reactivity of the ashes is a primary driver of the SCM contribution to system chemical shrinkage. Mixture designs intended to minimize chemical shrinkage can be accomplished with off-spec fly ash based in part on knowledge about its degree of reactivity.
Figure 4 - Chemical shrinkage (%) of in-spec (A) and off-spec (B) fly ash pastes, and fly ash contribution in chemical shrinkage for in-spec (C) and off-spec (D) pastes.

3.5. Electrical conductivity of the pore solution

The electrical conductivity of pore solution is an important parameter in cement pastes, which can affect mechanical (e.g. strength) and durability (e.g. transport properties, ASR resistance) performance (56)(57)(58). Both the pore solution ionic concentrations and solid microstructure change as the cementitious system hydrates and reacts, and those reactions and reaction products are affected by the composition and amount of fly ash in the system. Indeed, past studies have found this to be the case (58).
Figure 5 shows the pore solution conductivity of in-spec (A) and off spec (B) at all modeled replacement and reactivity levels. Figure 6 (C) and (D) shows the distributions for just the 40% replacement case. Panels (A) and (B) demonstrate that the electrical conductivity of paste pore solution is not substantially different between hydrated in-spec and off-spec pastes. For both in-spec and off-spec pastes, conductivity is higher at higher modeled reactivities until the mass replacement level exceeds ~30%. At this point, the conductivity in the more reactive pastes become lower than the less reactive pastes. This effect becomes more pronounced as replacement levels increase and is especially apparent in the off-spec pastes (6B). This is likely a result of pore structure refinement, as well as C-S-H enrichment in the pastes at high reactivity levels. At low replacement values, the effect of the fly ash would be insubstantial, as OPC comprises the bulk of the material.
3.6. A note on outliers

As shown in sections 3.1-3.5, there is considerably more variability in the modeled results of off-spec fly ash than in-spec, as indicated by outliers in the plots. However, as shown in Figure 6, these outliers represent only a small fraction of the simulations (smaller than 1% of all simulations), and it is likely that some of these outliers have compositions that are not found in practice. The fact that a trivial fraction of the modeled off-spec ashes are contributing to the higher variability in the parameters of interest is a crucial point: in the absence of these outliers, the differences between paste properties of in-spec and off-spec ashes are often times insubstantial. The fact that in-spec and off-spec ashes pastes are not substantially different has implications for the durability and performance of hardened concrete made with off-spec fly ashes, since these factors are a function of the paste properties discussed in this report.
Figure 6: The percent of total simulated off-spec fly ash compositions that fall outside of 20% and 50% of the mean value for the component of interest. The overall number of outliers is very small – less than 1% of the total for each component.

4. Conclusions

This study has demonstrated that the following parameters of OPC-fly ash pastes can be determined using GEMS and reactivity for off-spec fly ashes:

- the amount of calcium hydroxide (CH),
- pH and electrical conductivity of the pore solution,
- C-S-H type (e.g., C/S) and amount, and
- chemical shrinkage.

This study has further shown that the maximum degree of fly ash reactivity exhibits at least as great of an impact on the aforementioned parameters of the OPC-fly ash mixtures as the chemical composition of the ashes. Further, many parameters that results in labeling ashes as “off-spec” using ASTM C-618 are arbitrary in terms of actual performance of fly ash containing cementitious mixtures, as determined from GEMS. For
these reasons, fly ash reactivity should be considered in future specifications to quantify the performance of the fly ash.

Acknowledgments

The authors gratefully acknowledge support of Electric Power Research Institute (EPRI) and the national pooled fund through TPR-5(368) Performance Engineered Concrete Paving Mixtures. The authors also wish to thank Vahid Jafari Azad for his vision and assistance in developing the Monte Carlo code used in this work.

REFERENCES


