Why Bogue Phase Estimates Are Not Applicable for Blended Cements

Introduction

The purpose of this paper is to explain why potential cement phase compositions (C_3S, C_2S, C_3A, and C_4AF) are not calculated and reported using the Bogue equations for ASTM C595/AASHTO M 240 blended hydraulic cements.

The Bogue equations were developed in the 1920s to provide estimates of the amounts of potential phases that may be present in portland cement clinker and cements based on the oxide chemistry of portland cement clinker, correcting for calcium sulfate additions, such as gypsum. In 2005, ASTM C150 and AASHTO M 85 added adjustments to the Bogue equations for the purpose of reporting phase compositions of portland cement, which can contain up to 5% each of limestone and/or an inorganic processing addition (IPA). ASTM C595 and AASHTO M 240 do not contain instructions for the use of Bogue equations for blended cements because the presence of limestone, gypsum, IPAs, and SCMs make those estimates irrelevant and inaccurate.

Bogue equations are formulas for estimating portland cement phase composition, using oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3) of elemental analysis. Because thermodynamic equilibrium may not be reached during clinkering in the kiln, and other assumptions inherent to these formulas, calculated phase compositions only approximately describe a portland cement. In blended cements, not all constituents are processed in a kiln. Applying Bogue equations to the oxide composition of a finished blended cement to calculate clinker phases is fundamentally incorrect. The oxides for limestone, pozzolans, and slag used in blended cements are significantly different from portland cement and that can lead to analytical interferences. These interferences distort the results obtained if attempting to apply the Bogue equations to these cements and will clearly yield unrealistic values for the mineral phases. The primary utility of reporting Bogue phase composition was to satisfy requirements for a portland cement to be moderate or high sulfate-resistant (Type II(MS) or Type V), or to have lower heat of hydration cement characteristics (Type II(MH) or Type IV). ASTM C595/AASHTO M 240 takes a fundamentally different approach to establishing heat of hydration (performance testing by isothermal calorimetry, ASTM C1702) and sulfate resistance (performance testing by ASTM C1012); Bogue phases are simply not applicable and less relevant for blended cements. Pozzolans and slag cement generally improve the sulfate resistance of blended cements and reduce the early heat of hydration, so even if Bogue phases were correctly determined, they would not adequately characterize these performance characteristics of the cement. As such, there are no requirements in ASTM C595/AASHTO M 240 for Bogue phase contents of any blended cement.

The performance of ASTM C595/AASHTO M 240 cements are evaluated for end-use using month-to-month uniformity of the product and compositional information that is reported by suppliers via mill test reports and other documentation.

A few examples of applying Bogue equations to blended cements are shown in Table 1. This table shows the calculated Bogue phase compositions using a single base portland cement combined with various components to make different blended cements. The simplified method in Annex A1 of ASTM C150/AASHTO M 85 is used to adjust for the limestone, pozzolan, or slag content of the cement. In these examples, the Type IL cement is calculated to have a negative C_2S, which is not possible, as the lowest value would be zero. The Type IP and Type IS cements have higher calculated C_3A values than the base portland cement, despite each containing less clinker. Type IP and Type IS cements would typically be expected to provide higher levels of sulfate resistance, but the calculated Bogue C_3A values would indicate lower sulfate resistance. All of the Type IP examples shown also have negative C_3S values, and several have C_2S above 100%, none of which makes sense. If a phase is not present, it should have a value of zero. If only a single phase is present, it would have a maximum value of 100%, not greater than 100%. These examples demonstrate that the Bogue calculations are not meaningful for blended cements.

Why Bogue Phase Estimates Are Not Applicable for Blended Cements

Table 1: Example chemical analyses and Bogue calculations of various cements
"Calculated phases" are calculated based on finished cement chemistry, with the exception of the base cement fraction of the Type II cement example.

	Base portland cement	Type II portland cement with 3.1% limestone	Type IL blended cement with 12% limestone	Type IS blended cement with 40% slag	Type IP blended cement with 25% Class C fly ash	Type IP blended cement with 25% Class F fly ash	Type IP blended cement with 25% natural pozzolan	Type IP blended cement with 25% natural pozzolan
Oxides Measured (Finished Cement)								
SiO_2 (%)	20.7	20.1	18.5	24.7	24.3	28.7	32.4	33.3
Al_2O_3 (%)	4.7	4.6	4.2	8.6	8.3	7.9	6.7	6.7
Fe_2O_3 (%)	3.5	3.4	3.1	2.5	4.2	5.3	3.0	2.9
CaO (%)	63.9	63.6	62.6	54.8	54.0	50.1	48.5	48.4
SO_3 (%)	3.1	3.1	2.8	2.8	2.7	3.0	2.4	2.4
Oxides Measured (Limestone or SCM)								
SiO_2 (%)	n/a	2.2	2.2	30.8	35.2	52.9	67.5	71.3
Al_2O_3 (%)	n/a	0.5	0.5	14.5	19.0	17.3	12.8	12.8
Fe_2O_3 (%)	n/a	0.3	0.3	1.1	6.3	10.6	1.5	10
CaO_3 (%)	n/a	52.6	52.6	41.1	24.2	8.5	2.1	2.0
SO_3 (%)	n/a	0.7	0.7	2.4	1.6	2.7	0.1	0.0
Calculated Phases								
C_3S (%)	58	56	65	**-21**	**-26**	**-63**	**-79**	**-84**
C_2S (%)	16	15	**-2**	58	72	**109**	**129**	**135**
C_3A (%)	7	6	5	**11**	**11**	**9**	**10**	**10**
C_4AF (%)	11	10	8	5	10	**12**	7	7

Notes: For any cement in Table 1, performing Bogue calculations using the chemistry of the base cement will yield the same results as in the "Base Cement" example. The base portland cement chemistry is the same for all blended cements. Calculated phases are adjusted using the simplified method in Annex A1 of ASTM C150/AASHTO M 85, which does not assume knowledge of the base cement chemistry, or that of the limestone, SCM, or any processing addition. Type II cement data is taken from *Chemical and Physical Characteristics of US Hydraulic Cements: 2014*, PCA SN3284, and base cement is calculated from that.

Conclusion

Although the Bogue equations may have provided reasonable estimates for portland cement phase compositions since the 1940s, they do not provide a means of doing so for blended cements. To do so would provide the user with information that is fundamentally incorrect, and which cannot be used to characterize any performance characteristics of the cement. The interferences introduced by slag cement, pozzolans, and/or limestone will produce misleading results, and for this reason, these calculations are neither required nor referenced by ASTM C595 or AASHTO M 240.

PCA America's Cement Manufacturers
500 New Jersey Ave NW, 7th Floor
Washington, DC 20001-2066
202.408.9494 Fax 202.408.0877
www.cement.org