The Application of X-Ray Fluorescence to Assess Proportions of Fresh Concrete

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Abstract

Any transportation infrastructure system is concerned with durability and performance issues. The proportioning and uniformity control of concrete mixtures are critical factors that directly affect the longevity and performance of concrete pavements. Currently, the only means available to monitor mix proportions of any batch are to track batch tickets created at the batch plant. This does not take into account potential errors in loading materials into storage silos, calibration errors, and addition of water after dispatch. Therefore, there is a need for a rapid, cost-effective, and reliable field test that estimates the proportions of as delivered concrete mixtures. In addition, performance based specifications will be more easily implemented if there were a way to readily demonstrate whether any given batch is similar to the proportions already accepted based on laboratory performance testing. This paper describes a preliminary investigation into the potential use of a portable x-ray fluorescence (XRF) technique to assess the proportions of concrete mixtures as they are delivered. Tests were conducted on the raw materials, paste and mortar samples using a portable XRF device. There is a reasonable correlation between the actual and calculated mix proportions of the paste samples, but data on mortar samples was less reliable.

Introduction

Performance based specifications need test methods that can prove that a mixture will perform as required. One approach would be to validate and characterize the mixtures before construction starts. All that is needed during construction then is to prove that the mixture delivered is similar to that tested and accepted in the lab.

X-ray fluorescence (XRF) is a method that is used to determine the element concentration of samples (EPA, 2007). This study used an XRF device that is a portable battery powered scanner to analyze elements of cementitious materials, and paste and mortar samples made with those materials. Ideally, using such a device will be cost-effective, especially given the fact that the cost of well-conducted testing and quality control is small when compared to the cost of removing and replacing failed concrete (Broton and Bhatty, 2004).

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Proportioning and uniformity of concrete mixtures are critical factors that can directly affect the longevity and performance of concrete pavements (Wang and Hu, 2005; Kropp and Hinsdorf, 1995). At present the only means available to monitor mix proportions of any given batch are to track batch tickets created at the batch plant or to submit hardened samples to a central laboratory for XRF analysis. However, batch tickets do not take into account potential errors in loading materials into storage silos, calibration errors, and addition of water after dispatch. Laboratory XRF analysis is expensive and time consuming. Therefore, there is a need for a rapid, cost-effective, and reliable field test that estimates the proportions of as delivered concrete mixtures.

The literature on applying the XRF technique to concrete samples is limited, particularly with the use of portable devices. Speed, accuracy, and precision are among the advantages of using the XRF technique in analyzing the chemical composition of samples, however the specimen preparation is challenging (Broton and Bhatty, 2004). Accurate quantitative XRF analysis requires a homogeneous and flat surface (Broton and Bhatty, 2004). Field studies have shown that the comparability of the obtained test results with confirmatory samples is mostly affected by the heterogeneity of the sample (EPA, 2007). This is achieved in a central laboratory by grinding and mixing the sample and embedding it in a glass matrix. However, this is not possible when using a portable device. In a field device, the aperture is considerably larger, leading to a reduction in precision but removing the need to prepare a special sample for analysis. It should be noted that concrete is heterogeneous at almost all scales from mm down to nm, including within individual aggregate particles. Obtaining a representative sample for micro analysis is therefore always a challenge.

This paper describes a preliminary investigation into the potential use of a portable XRF technique to assess the proportions of concrete mixtures as they are delivered. Tests were conducted on the raw materials, paste and mortar samples using a portable XRF device. There is a reasonable correlation between the actual and calculated mix proportions of the paste samples, but data on mortar samples was less reliable.

Methodology

Materials. The following materials were obtained:

- ASTM C150 Type I ordinary portland cement
- ASTM C618 Class F fly ash
- ASTM C618 Class C fly ash
- ASTM C989 ground granulated iron blast-furnace slag
- ASTM C1240 silica fume
- No 4 nominal maximum size concrete sand

Samples Tested. In order to determine the accuracy of the portable XRF device and establish whether there were reasonable correlations between the designed and tested values, the following samples were prepared:
Powder – 5 different types of cementitious materials (Type I portland cement, Class C fly ash, Class F fly ash, silica fume, slag cement) were tested to analyze the chemical compositions of the powder materials. 6-micron polypropylene sheets were used to cover the surface of the materials to minimize contamination (Figure 1).



Figure 1. Sampling of powder materials

Fine and coarse aggregates – In order to eliminate the effect of moisture, oven-dried fine and coarse aggregates were tested.

Paste - 15 paste mixes at w/b ratio of 0.45 were prepared in accordance with ASTM C305. Samples were molded in accordance with ASTM C109. Three cubes (2*2*2-in.) were prepared per mixture. 5 different cementitious materials (Type I portland cement, Class C fly ash, Class F fly ash, silica fume, slag cement) were tested. The supplementary cementitious materials (SCM) replacement levels were fixed at 0, 20, and 40% by mass.

Mortar - 15 different mortar mixes at w/b ratio of 0.45 were prepared in accordance with ASTM C305 and tested. Samples were also molded into three cubes (2*2*2-in.) per mixture. The cementitious blends used were the same as those in the paste mixtures. The cementitious to sand ratio was fixed at 1:3 by mass.

Test Procedure. A handheld XRF device (Niton XL3t900GOLDD+ analyzer) was obtained from Thermo Scientific to test and analyze elements. The weight of this portable device is less than 3 lbs. The dimensions are 9.60*9.05*3.75-in.

The device was equipped with a 50 kV x-ray tube with an 8-mm aperture. The measurement time is user-selectable. Up to 30 seconds of testing time is known to be adequate for initial screening whereas longer measurement times (up to 300 seconds) are needed to meet higher precision and accuracy requirements (EPA, 2007). Since the testing period affects the limit of detection, the testing was conducted for 15 minutes per sample to provide sufficient time for a reasonably repeatable analysis.

The electromagnetic radiation of wavelengths of x-rays ranges between 0.1 Å and 20 Å (Broton and Bhatty, 2004). The necessary wavelengths are produced by an x-ray tube in which the electrons are accelerated from an emitting source toward the target material (Broton and Bhatty, 2004). Under radiation from an x-ray source, a sample will emit characteristic X-ray intensities depending on characteristics of the beam, sample elemental concentration, powder particle size distribution, degree of compaction and the compounds in the matrix (Proverbio and Carassiti, 1997). A detector that collects and reports the intensities of the emitted x-rays, that in turn can be used in a calibrated system to determine the relative proportions of elements in the sample.

The tests were conducted on three samples per each mixture and the results were averaged. The prepared paste and mortar samples were tested 1 day after mixing in a hardened condition. The samples were not crushed or powdered prior to analyzing because grounding the samples would not reflect the field conditions.

Sample Placement. X-ray signal decreases as the distance from the source is increased. Therefore, in order to minimize the variations and maintain the same distance between sample and detector for each sample, the XRF device was attached to its portable test stand for all tests (Figure 2). A cover was used to protect operators during use.

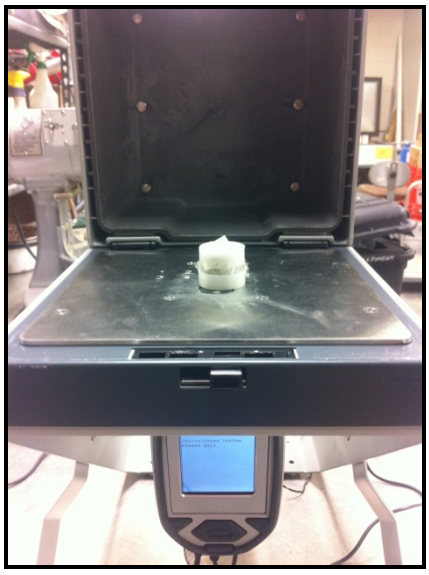


Figure 2. Portable test stand

Detecting Elements. The lighter the element, the more difficult it is to detect emitted x-rays. Table 1 presents the elemental limits of detection for a SiO_2 matrix of the portable XRF device. Those elements are the most common elements in cementitious materials that the device could detect.

According to the product specification sheet, the presented limits of detection (LOD) are dependent on the testing time, interferences and level of statistical confidence; and are calculated as three standard deviations (99.7% confidence interval) for each element, using 60-second analysis times per filter. No value was for silicon was provided by the manufacturer because the calibration was based on silicon being one of the major elements under test.

Among the elements listed in Table 1, the percentage of calcium oxide, silica and alumina describe the primary compounds in the cement and significantly affect the hydrated cement properties (Kosmatka et al. 2002).

Table 1. Elemental limits of detection of the Niton XL3t900GOLDD+ analyzer for a SiO_2 matrix

Element	Limit of Detection (ppm)
Ba	35
Sr	3
Fe	35
Mn	60
Ti	10
Ca	50
K	40
S	70
P	250
Al	500
Mg	3500

It was reported that the device does not detect elements lighter than Mg therefore interpretation of the data will have to compensate for the fact that the device is not able to detect hydrogen and oxygen (and so water).

Results and Discussion

Analysis of Raw Materials. The portable XRF device reported the test results as elemental mass percentage. Data was converted into oxides using their atomic weights. Some of the total values add up to more than 100%, and the variance from 100% is an indication of the error of the device. This is normal practice even though compounds in the cement are rarely in oxide form (Kosmatka et al. 2002). The summarized data are shown in Table 2. Only the elements showing non-zero results were utilized in the analyses.

Table 2. Test Results of Raw Materials, %

Oxides	Cement	Std. dev.*	C Ash	Std. dev.*	F Ash	Std. dev.*	Slag	Std. dev.*	Fine Agg.	Std. dev.*	Coarse Agg.	Std. dev.*
CaO	62.95	0.118	26.35	0.059	15.03	0.039	40.86	0.078	10.96	0.014	60.67	0.109
SiO_2	18.21	0.107	30.88	0.113	49.51	0.128	34.37	0.122	56.75	0.135	4.51	0.062
Al_2O_3	3.67	0.191	15.23	0.234	12.08	0.185	9.93	0.225	3	0.064	1.76	0.136
Fe_2O_3	4.63	0.016	9.4	0.023	11.17	0.024	0.79	0.006	1.42	0.009	0.74	0.006
MgO	3.12	1.169	2.64	1.383	1.29	0.595	8.47	0.909	3.34	0.595	0	1.902
K_2O	0.77	0.011	0.42	0.007	2.11	0.014	0.41	0.007	0.61	0.006	0.47	0.008
SO_3	8.55	0.042	5.14	0.030	2.52	0.020	4.69	0.032	0.35	0.010	0.94	0.020
TiO_2	0.16	0.003	1.57	0.008	0.8	0.005	0.41	0.003	0.06	0.002	0.07	0.002
BaO	0.03	0.002	0.57	0.003	0.47	0.003	0.05	0.002	0.04	0.001	0.02	0.002
SrO	0.03	0.032	0.28	0.001	0.21	0.001	0.03	0.001	0.02	0.001	0.02	0.001
Mn_2O_3	0.48	0.009	0.06	0.004	0.11	0.006	0.38	0.007	0.16	0.006	0.02	0.004
Total	102.61		92.53		95.3		100.4		76.7		69.23	

The tested cementitious materials were in the form of powder. The aggregates were oven-dried, but not ground, prior to testing.

The analytical results of the portland cement obtained from the portable XRF were compared with the requirements of ASTM C 150 for Type I portland cement as shown in Table 3.

Table 3. The comparison of the test results obtained from the portable XRF and the ASTM C150 recommended chemical composition range

Chemical Composition, %	ASTM C150 min- max	XRF Portable Device
SiO_2	18.7-22.0	18.21
Al_2O_3	4.7-6.3	3.67
Fe_2O_3	1.6-4.4	4.63
CaO	60.6-66.3	62.95
MgO	0.7-4.2	3.12
SO_3	1.8-4.6	8.55

Comparison of the results between the portable device and the standard shows that the obtained test results are mostly within the expected range. However, the observed SO_3 content reported by the portable device at 8.55% is well above expected levels. In addition, the observed Al_2O_3 and Fe_2O_3 content are slightly higher than the expected levels. The observed SiO_2 is slightly lower than the expected level. This difference may be due to the uniformity of the sample as tested.

Analysis of Fine Aggregate. The oven-dried fine aggregate was tested in a plastic sample cup covered with a 6-micron polypropylene sheet. For comparison, a sample of the fine aggregate sample was obtained using a riffle splitter and ground to less than 50 micron. This sample was then tested using a laboratory XRF. The results are presented in Table 4.

Table 4. Fine aggregate test result comparison between portable device and XRF core scanner, %

Oxides	Desktop	Portable
CaO	8.91	10.96
SiO_2	65.24	56.75
Al_2O_3	7.26	3.00
Fe_2O_3	1.77	1.42
MgO	3.04	3.34
K_2O	1.47	0.61
Na_2O	1.95	
SO_3	0.21	0.35
TiO_2	0.11	0.06
BaO	0.02	0.04
SrO	0.03	0.02
Mn_2O_3	0.06	0.16
P_2O_5	0.07	0.00
LOI	9.30	
Balance	0.55	23.30
Total	99.45	76.70

There was a large difference between the Balance values (the percentage of undetected elements) from the handheld device and laboratory instrument. This difference is unlikely to be a result of the moisture content as both samples were oven-dried.

It should be noted that the fine aggregate sample was crushed to 50 micron before lab testing while the sample tested using the portable device was not ground. Sampling error may therefore account for differences between the two sets of data.

Analysis of Paste. The test results from paste mixtures are presented in Table 5. The percentage of detected elements was decreased in paste mixtures compared to the cementitious materials. The magnitude of the Balance is roughly equivalent to the percentage of water in the mixture.

Table 5. Test results of paste, %

Oxides	OPC	20 F	40 F	20 C	40 C	20 SL	40 SL	20F 20SL	10F 20SL
CaO	48.45	40.44	35.03	44.42	36.45	44.73	41.21	37.83	41.90
SiO_2	14.68	19.99	23.32	19.41	18.45	18.92	20.75	22.82	22.03
Al_2O_3	2.32	4.04	4.77	5.21	6.09	3.70	3.96	4.64	4.76
Fe_2O_3	3.29	4.19	5.21	4.14	4.60	2.73	2.17	3.69	3.26
MgO	0.00	0.00	0.00	2.71	1.71	2.46	2.21	1.79	2.46
K_2O	0.93	1.35	1.21	0.48	0.62	1.03	0.90	1.12	1.01
SO_3	6.96	5.37	5.00	4.69	6.00	4.81	4.96	4.65	4.50
TiO_2	0.12	0.21	0.30	0.36	0.55	0.16	0.19	0.25	0.21
BaO	0.03	0.09	0.15	0.11	0.17	0.03	0.03	0.09	0.06
SrO	0.02	0.05	0.07	0.06	0.09	0.02	0.02	0.05	0.03
Mn_2O_3	0.33	0.28	0.23	0.28	0.21	0.32	0.30	0.27	0.31
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Balance	22.87	24.00	24.69	18.14	25.06	21.09	23.30	22.78	19.48
Total	77.13	76.00	75.31	81.86	74.94	78.91	76.70	77.22	80.52

The solver function in Excel program was used to calculate the proportions of the cementitious materials based on a least differences approach. The solver varied the amount of SCM in each set, compared the calculated oxides with the measured. The total of the cementitious materials, aggregates and water (if considered in the calculation) was fixed as 1 and the SCM dosage was selected as variables. The solver function reported the SCM dosage that yielded the lowest error. The analysis of paste containing 20% F fly ash by using the solver function is presented in Table 6.

Table 6. Example of the solver function, %

	Cement	F ash	C ash	Slag cement	Total
Measured	0.8	0.2	0	0	1
Theory (solver)	0.81	0.19			1
	Oxides		**Theory**	**Measured**	**Delta**
	CaO		47.32	44.42	2.90
	SiO_2		13.69	19.41	5.72
	Al_2O_3		2.76	5.21	2.45
	Fe_2O_3		3.48	4.14	0.66
	MgO		2.34	2.71	0.37
	K_2O		0.58	0.48	0.10
	SO_3		6.42	4.69	1.74
	TiO_2		0.12	0.36	0.23
	BaO		0.02	0.11	0.08
	SrO		0.02	0.06	0.03
	Mn_2O_3		0.36	0.28	0.08
	P_2O_5		0.00	0.00	0.00
	Difference				14.36

Figure 3 presents the relationship between the cumulative error and the calculated SCM content and is a visual representation of the sensitivity of the approach. It is promising that for each of the mixtures there was a clear minimum error. The data sets shown in Figure 3 are for the 40% SCM mixtures.

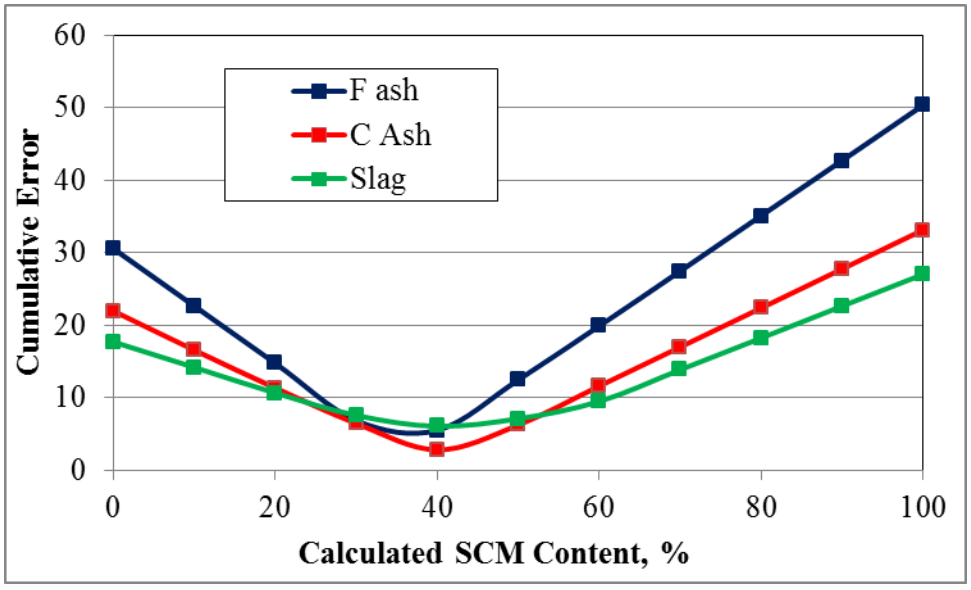


Figure 3. The relationship between cumulative error and calculated SCM content

Figure 4 presents the relationship between the tested and batched SCM contents. The calculated SCM content was based on analysis using only the reported oxides. This figure shows that the portable device provides an adequate correlation

between the real mix proportions for both binary and ternary paste mixtures as there is less than 10% of variation between the predicted values and the actual SCM content.

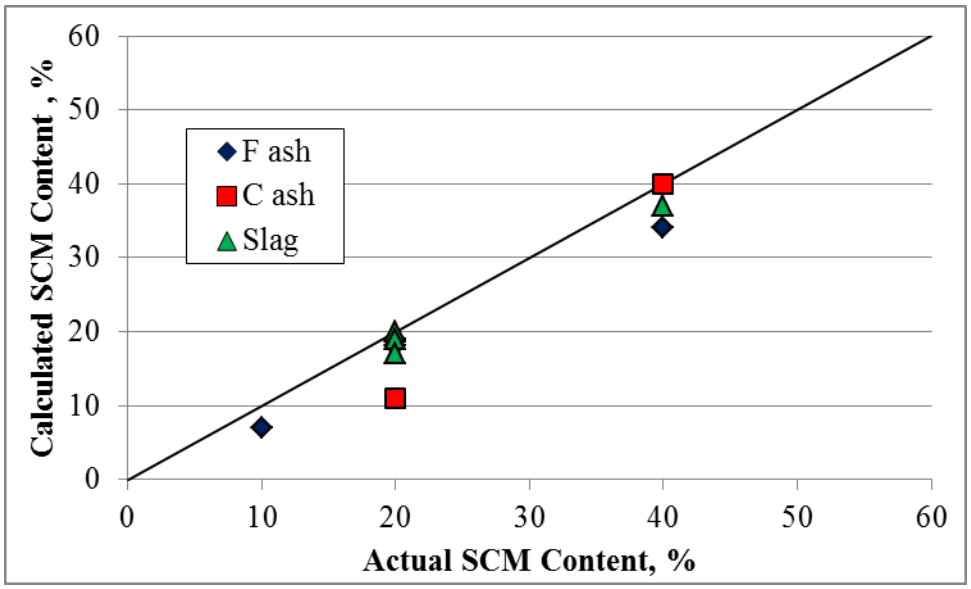


Figure 4. The relationship between tested and designed SCM content

Figure 5 presents the relationship between the tested and actual SCM contents when the presence of the water is included in the calculation. Water in the mixture is dealt with by assuming that the "Balance" in the reported results is a measure of water content. In this case, the results are less promising. When Figure 4 and Figure 5 are compared, it can be observed that the consideration of water increases the prediction error of the mix proportions.

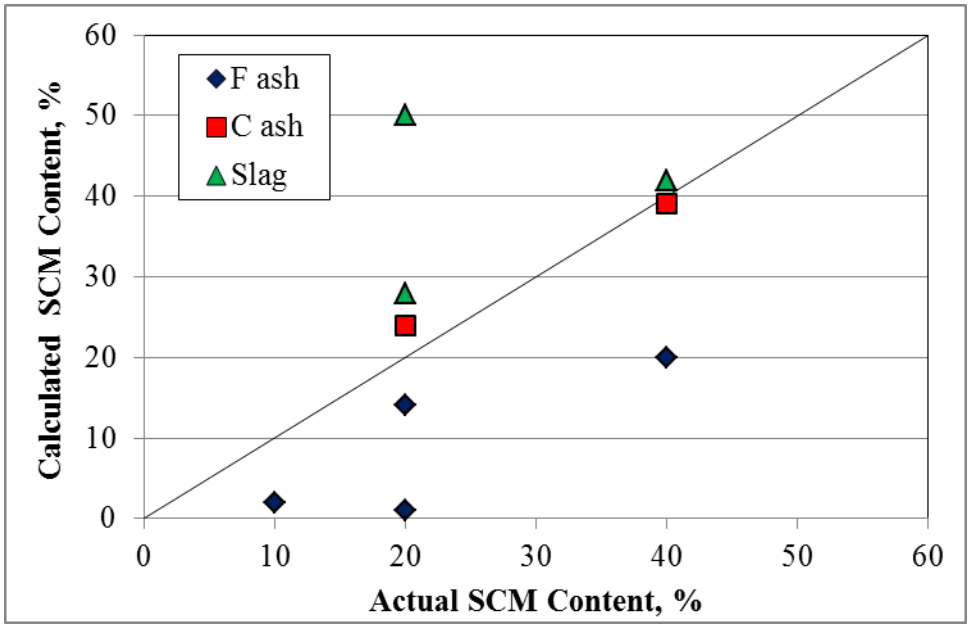


Figure 5. The relationship between tested and actual SCM content when the water presence is included

Analysis of Mortar. The test results of mortar mixtures are presented in Table 7. The undetected element percentage is significantly increased, likely due to the presence of

moisture, small detection area (8 mm in diameter) and heterogeneity of the tested samples. The XRF device provided sufficient accuracy for finely grounded homogenous powder samples. However, once the heterogeneity of the increased, the percentage of the total detected elements decreased.

Table 7. Test results of mortar mixtures, %

Oxides	OPC	20 F	40 F	20 C	40 C	20 SL	40 SL	20F20SL	10F20SL
CaO	35.57	31.40	27.75	32.94	29.33	33.68	32.55	29.72	32.25
SiO_2	13.44	17.07	20.56	15.79	17.87	16.16	17.41	19.69	17.86
Al_2O_3	1.66	2.54	3.25	3.18	4.63	2.44	2.87	3.18	2.90
Fe_2O_3	2.48	2.97	3.65	2.90	3.38	2.03	1.95	2.66	2.36
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K_2O	0.34	0.51	0.82	0.60	0.38	1.00	0.44	0.99	0.52
SO_3	4.96	4.59	3.80	4.75	4.62	4.22	3.98	3.22	3.89
TiO_2	0.09	0.16	0.22	0.24	0.41	0.11	0.14	0.18	0.15
BaO	0.04	0.07	0.08	0.07	0.09	0.04	0.04	0.06	0.05
SrO	0.02	0.03	0.04	0.03	0.05	0.02	0.02	0.03	0.02
Mn_2O_3	0.21	0.18	0.16	0.18	0.15	0.22	0.20	0.18	0.20
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Balance	41.17	40.49	39.67	39.33	39.09	40.08	40.39	40.08	39.80
Total	58.83	59.51	60.33	60.67	60.91	59.92	59.61	59.92	60.20

Similar to the analysis on paste mixes, the calculated SCM content was predicted by using the solver function, this time including the data from the sand analysis. The solver reported the percentage of sand content to be around 30% by mass which is close to the actual mix. Figure 6 demonstrates the relationship between the tested and actual SCM content. The inclusion of sand increased the error between the predicted and the actual percentages of SCMs.

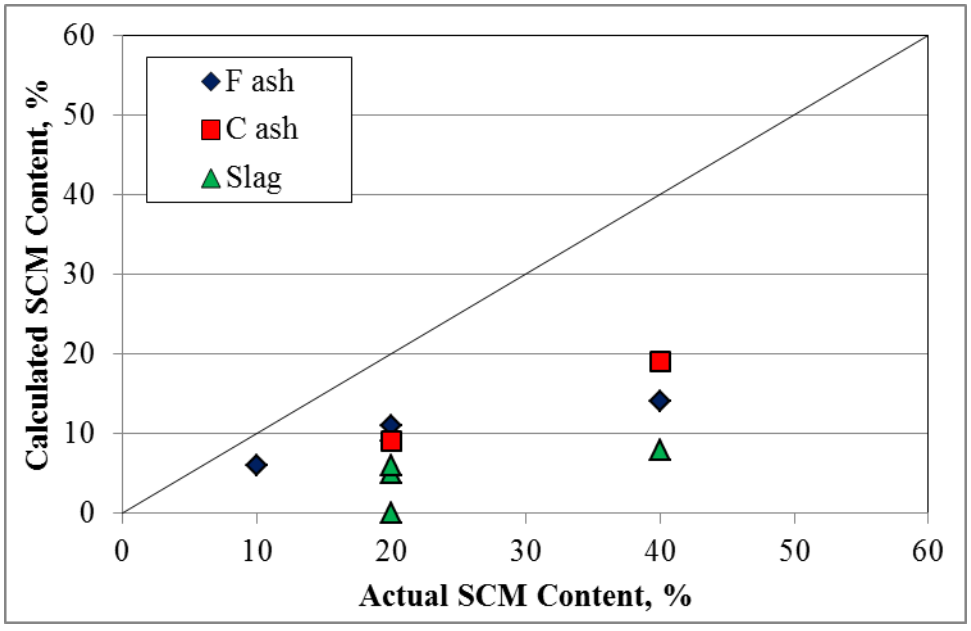


Figure 6. The relationship between tested and designed SCM content

To assess the effect of potential errors in detecting sand in the mortar sample because of the relatively small field of influence of the x-ray beam, the calculations were repeated with a range of fixed sand contents forced into the model for the 40% SCM mixtures. This relationship is presented in Figure 7. Based on this figure, when assumed sand content is between 12% and 18%, the predicted SCM content is the closest to the actual SCM content. This clearly illustrates a non-representative amount of sand was being detected by the beam.

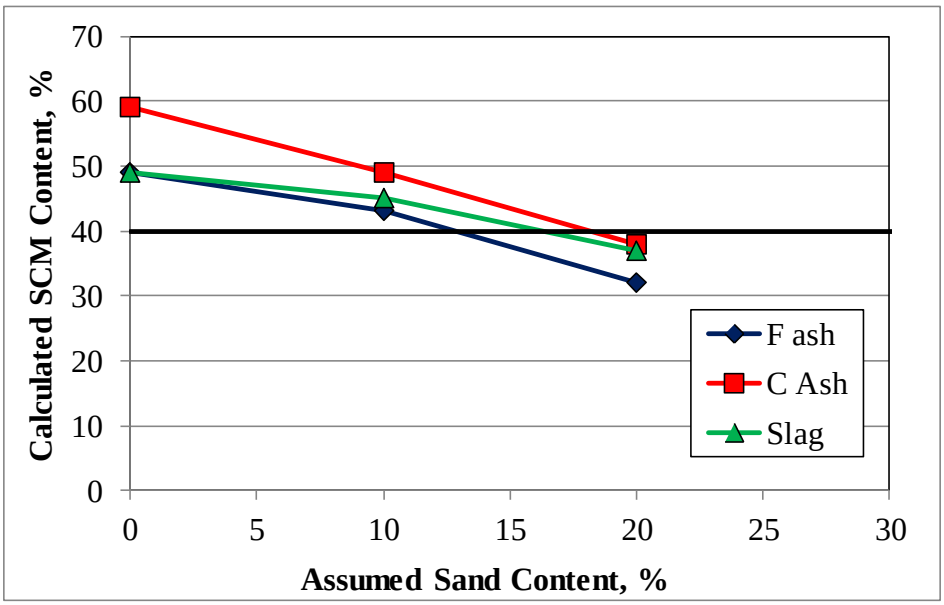


Figure 7. The calculated SCM content for varying sand contents forced into the model

Assuming a fixed 15% of sand the relationship between the actual and calculated SCM content was calculated as presented in Figure 8. The error between actual and predicted SCM content is lower than the variation when the sand content was not fixed, but is still unacceptably high.

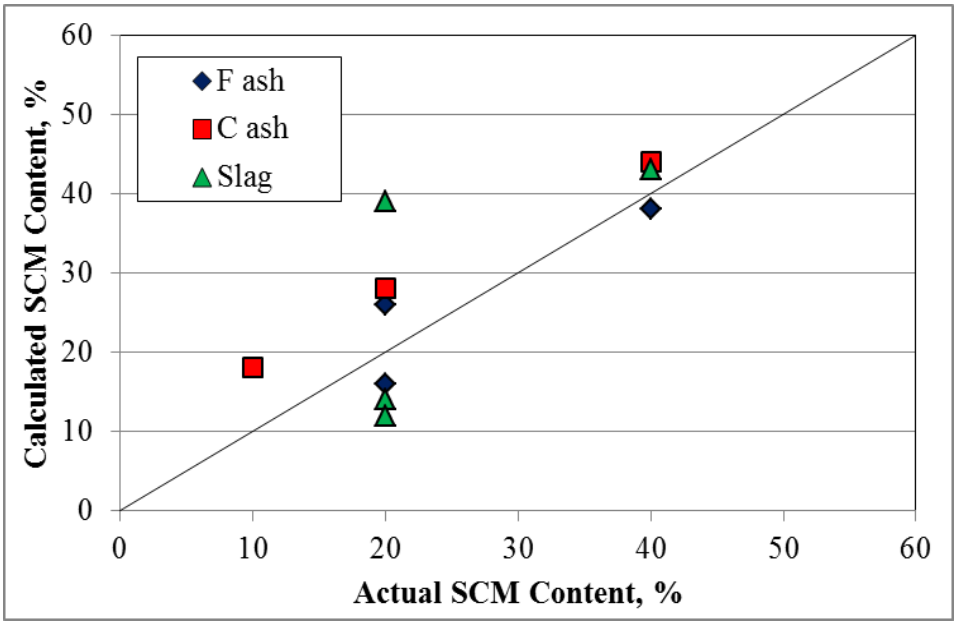


Figure 8. The relationship between tested and designed SCM content

Conclusions and Recommendations

When the paste was tested, the predicted SCM contents were close to the actual batched values. However, once the system was complicated with the addition of fine aggregates, Balance was significantly increased and the predictions did not match the batched values.

The following conclusions, which are limited to the materials used in this study, can be drawn:

1. When water is not included in the model, there is a reasonable correlation between the actual and calculated mix proportions of paste.
2. The percentage of the detected elements was decreased in mortar mixtures compared to the paste mixtures.
3. The accuracy of the approach decreased when the heterogeneity of the system increased.

This approach is not ready for prime time but shows promise if the technology and the models can be refined. More accurate results may be obtained if the model were to be calibrated for a given mix.

Acknowledgment

This study was funded by the Federal Highway Administration through Cooperative Agreement with the National Concrete Pavement Technology Center at Iowa State University. This study is a pooled fund project and Iowa Department of Transportation acts as the lead state. The authors also wish to acknowledge the Thermo Fisher Scientific for their support.

The opinions, findings, and conclusions presented here are those of the authors and do not necessarily reflect those of the research sponsors.

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