APPLICATION NOTE
XE-2015-3294

Quantitative Analysis of Fused and Pressed Cement Reference Samples.

Abstract

This report shows the result of the use of the simple, rapid and reliable Energy Dispersive X-ray Fluorescence method to determine the concentrations of the major components in cement to a high degree of accuracy and precision. It also shows the excellent performance of the advanced Xenemetrix X-Calibur SDD Benchtop System equipped with a high resolution SDD detector well suited for the light elements of cement.

Objective

The purpose of this study was demonstrate the efficient and reliable use of the Energy Dispersive X-ray Fluorescence method in the process control of the cement industry. This systematic and extensive study also had the objective of investigating the advantages of using differently prepared cement samples. For example, the use of pressed cement pellets allows for determination of volatile components such as SO_3 and K_2O which is not possible by using the conventional fused, at high temperature, cement discs.

Background

Controlling even relatively small changes in the composition of cement during the production process has become a high priority interest of progressive manufacturers worldwide. Timely and accurate analytical results during every stage of production are the keys to quality control. Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometers can play an important role in assuring that consistent quality is documented at every manufacturing step. Specifically EDXRF can play a critical role in resolving these challenges by providing the following benefits: 1) simple and rapid sample preparation, 2) automated analyses, via a multi-position sample carousel, couples with rapid data collection for high throughput without operator intervention, 3) high precision for major constituents, 4) minimal maintenance, and at-line operation for low-cost-per-analysis, and 5) non-technical operation.

In order to demonstrate the efficacy of EDXRF for this purpose, a set of customer supplied reference materials were used. The investigation examined the ability of EDXRF to quantify all the major components in a manner, useful for quality assurance in routine manufacturer operations.

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ANALYTICAL CONFIGURATION

Table 1: Analytical Configuration

Instrument	X-Calibur SDD
Excitation	Rh-Anode X-ray Tube. Direct excitation.
Detector	SDD with special light element optimized window
Analysis Time	500 second
Type of analysis	Regression analysis.
Environment	Vacuum
Sample Preparation	1. Cement reference samples fused in Platinum crucibles. 2. Cement reference samples fused in Carbon crucibles. 3. Pressed cement reference samples. Auxiliary: Sample Spinner

Experimental:

CALIBRATION OF X-CALIBUR SDD FOR OXIDES MgO, Al_2O_3, SiO_2, SO_3, K_2O, P_2O_5, CaO AND Fe_2O_3 IN FUSED AND IN PRESSED CEMENT REFERENCE SAMPLES AND EVALUATION OF PRECISION.

Calibration of X-Calibur SDD were done on three sets of differently prepared cement reference samples provided by the manufacturer.

The three sets were:
1. Reference cement samples prepared by fusion in Platinum crucibles.
2. Reference cement samples prepared by fusion in Carbon crucibles.
3. Reference cement samples prepared by pressing the cement into a pellet.

Volatile components such as SO_3 and K_2O cannot be measured in fused cement samples since the fusion occurs at high temperatures where these compounds evaporate. For these elements the technique of using pressed cement samples is then of major advantage.

Calibration curves for each element of cement was established using regression analysis and a model taking into account the different matrix effects. The analytical results of the regression analysis of the three sets of standard samples are shown in tables 2, 4, 6 and 7. Both the given and the calculated concentration of the different elements of each reference standard are tabulated. Standard Deviations and correlation data of the regression analysis are included for each element.

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Quantitative Analysis of Fused and Pressed Cement Reference Samples.

CALIBRATION DATA OF REFERENCE CEMENT SAMPLES FUSED IN PLATINUM CRUCIBLES

Table 2: Calibration data of fused samples in Platinum crucibles

	MgO		Al_2O_3		SiO_2		P_2O_5		CaO		Fe_2O_3	
	Std.Dev. 0.008%		Std.Dev. 0.038%		Std.Dev. 0.075		Std.Dev. 0.012%		Std.Dev. 0.068%		Std.Dev. 0.032%	
	Correlation: 0.994		Correlation: 0.999		Correlation: 1.000		Correlation: 0.998		Correlation: 1.000		Correlation: 0.999	
Ref. #	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc
RR1	0.66	0.66	3.32	3.27	14.20	14.19	0.08	0.06	43.10	43.25	1.93	1.99
RR2	0.46	0.45	1.44	1.44	6.08	6.07	0.00	0.02	50.18	50.16	0.78	0.82
RR3	0.49	0.48	1.87	1.88	8.04	7.98	0.01	0.02	48.61	48.59	1.04	1.04
RR4	0.73	0.71	3.78	3.82	16.50	16.77	0.05	0.00	41.25	41.20	2.21	2.25
RR5	0.55	0.56	2.73	2.76	11.44	11.43	0.03	0.01	46.63	45.62	1.46	1.43
RR6	0.71	0.71	4.13	4.14	16.73	16.59	0.07	0.06	41.22	41.13	2.02	2.03
RR7	0.68	0.68	3.28	3.23	14.11	13.91	0.41	0.38	43.18	43.74	1.60	1.55
RR8	0.61	0.61	2.67	2.61	11.37	11.36	0.41	0.43	45.68	45.68	1.30	1.20
RR9	0.57	0.58	2.35	2.42	9.81	9.93	0.41	0.42	46.98	47.00	1.10	1.08
RR10	0.72	0.73	3.74	3.76	16.05	16.15	0.39	0.39	41.44	41.78	1.92	1.90
RR11	0.67	0.67	3.36	3.34	11.20	11.26	1.32	1.33	44.00	44.06	2.61	2.61
RR12	0.56	0.56	2.27	2.18	7.71	7.66	0.97	0.96	47.10	47.01	2.65	2.63

PRECISION DATA ON SAMPLE FUSED IN PLATINUM CRUCIBLE

Ten repeat measurements were performed on fused reference sample RR3 without moving the sample in between the runs. Results shown in Table 3.

Table 3: Static repeatability on fused reference sample RR3

Element	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	Fe_2O_3
Std. Dev.%	0.01	0.02	0.03	0.01	0.05	0.02
Mean	0.49	1.85	7.97	0.02	48.60	1.04
RSD %	2.0	1.1	0.38	5.0	0.1	1.9

CALIBRATION DATA OF REFERENCE CEMENT SAMPLES FUSED IN CARBON CRUCIBLES

Table 4: Calibration data on fused samples in Carbon crucibles

	MgO		Al_2O_3		SiO_2		P_2O_5		CaO		Fe_2O_3	
	Std.Dev. 0.008%		Std.Dev. 0.021%		Std.Dev. 0.044		Std.Dev. 0.051%		Std.Dev. 0.11%		Std.Dev. 0.016%	
	Correlation: 0.996		Correlation: 1.000		Correlation: 1.000		Correlation: 0.996		Correlation: 0.999		Correlation: 1.000	
Ref. #	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc
RR1	0.66	0.64	3.32	3.28	14.20	14.15	0.08	0.15	43.10	43.15	1.93	1.91
RR2	0.46	0.47	1.44	1.45	6.08	6.07	0.00	0.01	50.18	50.15	0.78	0.80
RR3	0.49	0.49	1.87	1.88	8.04	8.07	0.01	0.01	48.61	48.74	1.04	1.03
RR4	0.73	0.73	3.78	3.78	16.50	16.59	0.05	0.12	41.25	41.10	2.21	2.19
RR5	0.55	0.56	2.73	2.72	11.44	11.38	0.03	0.07	46.63	45.75	1.46	1.47
RR6	0.71	0.71	4.13	4.17	16.73	16.72	0.07	0.15	41.22	41.19	2.02	2.04
RR7	0.68	0.67	3.28	3.28	14.11	13.85	0.41	0.46	43.18	43.34	1.60	1.63
RR8	0.61	0.57	2.67	2.67	11.37	11.44	0.41	0.45	45.68	45.57	1.30	1.28
RR9	0.57	0.56	2.35	2.33	9.81	9.80	0.41	0.43	46.98	46.86	1.10	1.11
RR10	0.72	0.73	3.74	3.71	16.05	1601	0.39	0.47	41.44	41.54	1.92	1.93
RR11	0.67	0.66	3.36	3.37	11.20	11.17	1.32	1.30	44.00	44.00	2.61	2.60
RR12	0.56	0.57	2.27	2.29	7.71	7.73	0.97	0.90	47.10	46.46	2.65	2.65

PRECISION DATA ON SAMPLE FUSED IN CARBON CRUCIBLE

Ten repeat measurements were performed on fused reference sample RR6 without moving the sample in between the acquisitions. Results shown in Table 5.

Table 5: Static repeatability on fused reference sample RR6

Element	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	Fe_2O_3
Std.Dev. wt%	0.02	0.03	0.05	0.01	0.05	0.01
Mean wt%	0.69	4.07	16.7	0.15	41.3	2.02
RSD %	2.9	0.74	0.30	6.7	0.12	0.5

CALIBRATION DATA OF PRESSED PELLET REFERENCE CEMENT SAMPLES.

Table 6: Calibration data of pressed pellet samples

	MgO		Al_2O_3		SiO_2		P_2O_5		CaO		Fe_2O_3	
	Std.Dev. 0.008%		Std.Dev. 0.055%		Std.Dev. 0.30%		Std.Dev. 0.016%		Std.Dev. 0.23%		Std.Dev. 0.074%	
	Correlation: 0.996		Correlation: 0.997		Correlation: 0.996		Correlation: 0.999		Correlation: 0.997		Correlation: 0.991	
Ref. #	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc
RR1	0.66	0.66	3.32	3.40	14.20	14.39	0.08	0.0	43.10	43.14	1.93	1.91
RR2	0.46	0.45	1.44	148	6.08	6.27	0.00	0.0	50.18	50.55	0.78	0.85
RR3	0.49	0.50	1.87	1.85	8.04	8.20	0.01	0.0	48.61	48.25	1.04	0.94
RR4	0.73	0.73	3.78	3.73	16.50	16.21	0.05	0.0	41.25	41.36	2.21	2.29
RR5	0.55	0.56	2.73	2.72	11.44	10.95	0.03	0.0	46.63	46.40	1.46	1.48
RR6	0.71	0.71	4.13	4.16	16.73	17.15	0.07	0.0	41.22	41.21	2.02	1.91
RR7	0.68	0.69	3.28	3.25	14.11	14.02	0.41	0.41	43.18	43.06	1.60	1.72
RR8	0.61	0.59	2.67	2.66	11.37	10.92	0.41	0.42	45.68	46.09	1.30	1.26
RR9	0.57	0.57	2.35	2.47	9.81	10.03	0.41	0.39	46.98	46.80	1.10	1.13
RR10	0.72	0.72	3.74	3.69	16.05	14.91	0.39	0.40	41.44	43.25	1.92	1.89
RR11	0.67	0.67	3.36	2.66	11.20	11.33	1.32	1.30	44.00	44.10	2.61	2.57
RR12	0.56	0.65	2.27	2.22	7.71	9.46	0.97	1.00	47.10	46.92	2.65	2.40

Table 7: Calibration data continued

	SO_3		K_2O	
	Std.Dev. 0.006%		Std.Dev. 0.006%	
	Correlation: 0.985		Correlation: 0.989	
Ref. #	Given Conc	Calc'd Conc	Given Conc	Calc'd Conc
RR1	0.09	0.08	0.24	0.25
RR2	0.03	0.03	0.14	0.14
RR3	0.03	0.03	0.18	0.18
RR4	0.06	0.07	0.28	0.27
RR5	0.04	0.05	0.18	0.18
RR6	0.05	0.05	0.27	0.27
RR7	0.09	0.08	0.23	0.24
RR8	0.10	0.10	0.21	0.21
RR9	0.10	0.11	0.20	0.20
RR10	0.14	0.14	0.27	0.27
RR11	0.24	0.13	0.19	0.19
RR12	0.27	0.13	0.15	0.18

PRECISION DATA ON PRESSED PELLET SAMPLE

Ten repeat measurements were performed on pressed reference sample RR3 without moving the sample in between the acquisitions. The repeatability is shown in Table 8.

Table 8: Static repeatability on pressed reference sample RR3

Element	MgO	Al_2O_3	SiO_2	P_2O_5*	CaO	Fe_2O_3	SO_3	K_2O
Std.Dev.%	0.01	0.02	0.13	0	0.08	0.06	0.003	0.004
Mean	0.50	1.87	8.33	0.01	48.6	0.97	0.03	0.17

* All ten measurements on RR3 gave the same result for P_2O_5.

DISCUSSION

The results presented in this report show the excellent performance of the Xenemetrix EDXRF analyzer X-Calibur SDD Benchtop system. In most cases the experimentally determined concentrations meet the severe accuracy requirements. In a few cases problems of non homogenous sample preparation forced the removal of a sample from the regression analysis due to deviations in SiO_2 and/or CaO.

Regarding the samples, it should be noted that the physical appearance of the samples fused in Carbon crucibels was non homogenous with large "bubbles", sometimes even holes in the fused discs. In addition, the surface facing the X-ray beam was not always planar. The samples fused in Platinum crucibles had a planar surface but showed many small air bubbles. The use of a sample spinner, i.e. rotating the sample during the acquisition improves on the results but the results would improve more by using a more proper sample preparation technique.

Results of the measurements on pressed cement samples show the outstanding opportunity presented by EDXRF to measure SO_3 and K_2O in cement. The concentration results of these components are in very good agreement with the given concentration values. This is also true for the results of the concentrations of MgO, Al_2O_3, P_2O_5, and Fe_2O_3. Deviations in the results of Ca and Si can be expected due to the "particle size effect", a known phenomena in XRF. High degree of polishing of the surface of the pressed pellets would improve the results largely.

Regarding the measurements on Phosphor, the samples in the three sets could be divided into two groups, one of "low" concentration and one of "high" concentration. The lack of samples with concentration in the middle range made it difficult to establish a good calibration curve. To get reliable results, the regression calibration curve was built on six samples only (RR7-RR12).

In short, the Energy Dispersive method is simple and rapid. It allows for reliable determination of the different components in cement, to meet the very stringent requirements of the cement industry. In addition to the simple use of the advanced, top of the line technology, offered by Xenemetrix X-Calibur SDD EDXRF Benchtop Spectrometer system, it also presents an instrument that is easy to calibrate and maintain without any complicated moving mechanical parts.

Figure 1: Typical spectra of a cement reference sample (fused in Platinum crucible).