

RAPID DETERMINATION OF CaO AND SO₃ IN LOOSE POWDER CEMENT BY ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF) TECHNIQUE

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ABSTRACT

Percentage CaO and SO₃ in loose powder cement were determined rapidly using the EDXRF spectrometer. Sample particle size was further reduced by grinding in a rotating disc gyratory mill for a period of 120 seconds. To avoid the absorption of secondary x-rays from the low atomic number elements (Ca and S), measurement was carried out in helium atmosphere instead of air. The results showed a high degree of accuracy and precision technically desired for process control in a cement factory. The method was found to be more efficient (less time consuming and cost saving) compared to the pressed pellet or the fused bead methods employed in the EDXRF spectrometry and the spectrophotometric and gravimetric methods often used by the industry.

INTRODUCTION

Stringent quality requirements are imposed on the production of cement to ensure that the correct mechanical strength is achieved after setting. Obviously, it is impracticable in production control to monitor this directly since the complex hydration process can take months and the full strength is not reached until they are complete (1). CaO and SO₃ have been found to have significant effect on the strength development of cement (2). There is an optimum SO₃ for good strength development (3). Effective monitoring of these compounds during production is therefore required to ensure that cement with the right strength development is produced.

Spectrophotometric, gravimetric and other wet analytical methods have been employed over the years for the determination of CaO and SO₃ in cement (4). However, the desire to obtain results within a short time and at lower cost, with ease of analysis required for effective quality control has led to development of other rapid methods of analysis (5,6).

X-ray fluorescence (XRF) analysis has been in use in the cement industry for over four decades for the determination of basic oxides in cement and cement raw materials (7). XRF analysis has shown itself to be a fast, reliable, simple and accurate method of analysis than other methods of analysis (8).

The fusion of sample into bead (prepared by taking 1 part by weight of sample with five parts

by weight of flux and fusing at 1200°C) and pressing into pellets in XRF analysis sample preparation is to overcome particle size variations. Variation in particle size will give differing secondary x-ray intensities and hence variation in results. In such cases, sample preparation takes longer time and is less economical. However in the method described here, sample preparation time is greatly reduced while at the same time particle size variations is minimized such that accurate and reproducible results are obtained at much shorter time and at lesser cost.

MATERIALS AND METHODS

Clinker and gypsum samples were obtained from the Ewekoro works of West African Portland Cement (WAPCO) Plc. The samples were collected using standard sampling method (9). Standard cement samples were prepared by grinding cement clinker and gypsum together in a laboratory scale ball mill. Percentage CaO and SO₃ were varied by varying the percentage of gypsum added.

CaO and SO₃ in the standard samples were determined by standard wet method (9). The standards have concentration range encompassing the range of interest for normal routine measurements.

Using the Oxford Lab-X³⁰⁰⁰ XRF spectrometer, a spectrum scan of the standards was carried out to ensure correct measurement conditions. The spectrometer was calibrated with the standards.

To overcome problem of particle size variation, 20g of loose powder cement sample was further pulverized in a gyratory disc mill for 120

seconds. The fine powder cement sample was poured into a sample cup fitted with 6µm thick poly carbonate film as the window material. The cup was gently tapped to ensure the sample in the cup have a flat surface. It was then placed in the sample port of the X-ray spectrometer and CaO and SO₃ measured over 100 seconds duration against the prepared calibration (which relates the intensities of the elemental spectra-lines and concentration).

Helium gas at a flow rate of 1.7 l/min and pressure of 1 bar was used to flush the air between the detector and the sample for optimum analytical performance.

RESULTS AND DISCUSSION

Figure 1 shows the change in intensity (counts per second, cps) against grinding time. CaO has a higher optimum grinding time than SO₃. The optimum grinding time for CaO was 120 seconds as against 30 seconds for SO₃. According to Robson, an optimum time is chosen which is the best for the most important element (7). The optimum time is the time corresponding to the maximum intensity peak for the most important element. CaO being the most abundant and hence most important component of cement, its grinding time of 120 seconds corresponding to the peak intensity is used as the optimum grinding time for the analysis.

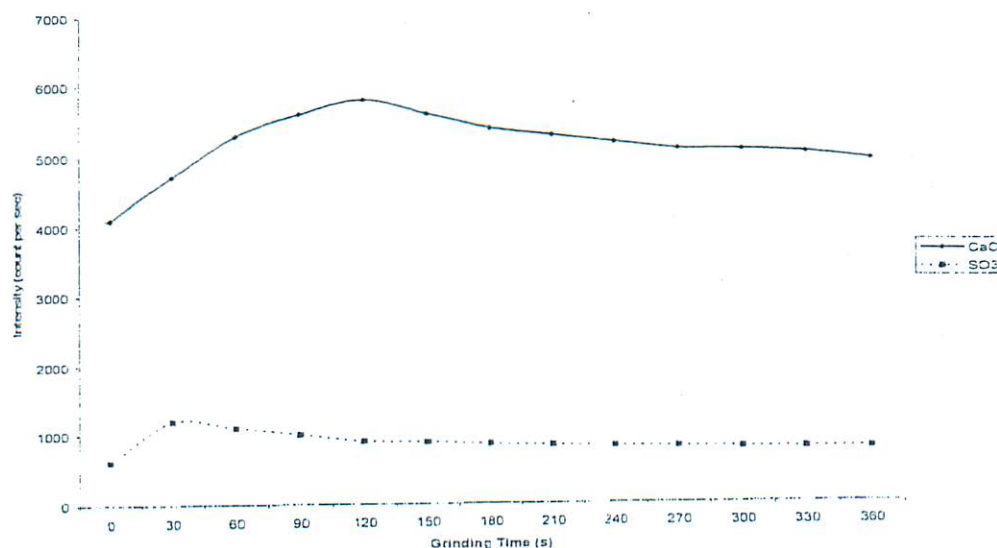


Fig 1: Optimum grinding time for CaO and SO₃

The spectrum scan of loose powder cement (for both CaO and SO₃) used to identify the channel number(s) required for calibration on the spectrometer is shown in figure 2. The calcium signals dominate spectrum because of the abundance of CaO in Ordinary Portland Cement (OPC), usually in the range of 60-64% and for SO₃, usually ≤ 3%. This is in agreement with the report of Oxford Instruments Industrial Analysis Group

which shows that when a cement sample is excited by a radioactive source, the calcium dominate the spectrum making it difficult to measure the much weaker sulfur signals (10). The channel number for CaO is between 40 – 70 with the peak at 60. SO₃ has channel number between 80-110 with the peak at 90. The calibration for both CaO and SO₃ has a linear relationship between concentration and intensity.

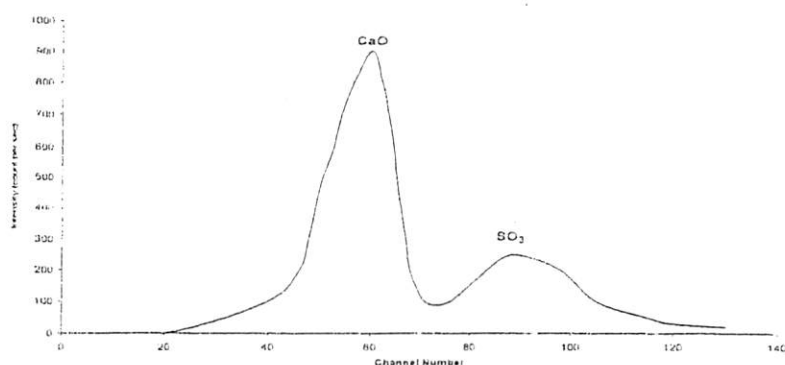


Fig 2: Spectrum Scan of loose powder cement.

Table 1 shows the result of measurement of CaO and SO₃ % in cement determined using wet, fused bead, pressed pellet and loose powder methods. The result is the mean of the three measurements for each of the sample. From the table, the results by the loose powder, pressed pellet, fused bead and wet method are quite in agreement. This indicates that any of the four methods could be used for monitoring CaO and SO₃ in cement. However, the wet method is time consuming taking at least four hours for completion. This is in agreement with the findings of Abdulrahman, (5). In the cement industry, this method may not be good enough for

effective quality control. The fused bead and the pressed pellet methods are faster than the wet method but much costly requiring additional equipment (Press mill, Claisse fluxy fusion machine). The loose powder method is however easier, faster and less costly than the other three, thus facilitating effective monitoring of production as more samples can be analysed frequently. A maximum difference of 0.08% and 0.03% between duplicates for CaO and SO₃ respectively was recorded using the loose powder method. This is in agreement with the maximum of 0.20% and 0.10% allowable in XRF method of cement analysis recommended by ASTM (11).

TABLE 1

SAMPLE	LOOSE POWDER		PRESSED PELLET		FUSED BEAD		WET METHOD	
	CaO %	SO ₃ %	CaO %	SO ₃ %	CaO %	SO ₃ %	CaO %	SO ₃ %
A	61.05	2.53	61.05	2.54	61.06	2.54	61.07	2.54
B	62.37	2.12	62.40	2.09	62.39	2.10	62.39	2.11
C	63.45	2.00	63.49	2.02	63.46	2.01	63.48	2.01
D	63.56	1.92	63.53	1.89	63.55	1.90	63.56	1.91
E	63.65	1.78	63.62	1.76	63.59	1.79	63.60	1.76
F	64.08	1.12	64.10	1.10	64.05	1.15	64.05	1.14

The effect of measurement of both CaO and SO₃ in air and in helium gas was studied. The result as contained in table II showed that the results of both pressed pellet and loose powder are in agreement as indicated by the figures for the concentration of CaO and SO₃. The percentage

concentration obtained for measurement in air are generally lower. This can be attributed to the absorption of radiations from both CaO and SO₃. Radiations from 'low' atomic number elements are absorbed by air (10). It is therefore desirable to measure in helium gas for better and desired accuracy.

TABLE II

PRESSED PELLET				LOOSE POWDER			
MEASUREMENT IN HELIUM GAS		MEASUREMENT IN AIR		MEASUREMENT IN HELIUM GAS		MEASUREMENT IN AIR	
CaO %	SO ₃ %	CaO %	SO ₃ %	CaO %	SO ₃ %	CaO %	SO ₃ %
63.63	1.24	61.60	0.98	63.60	1.22	61.32	0.93
62.30	2.05	60.67	1.73	62.50	2.01	60.60	1.70
64.10	1.10	63.05	0.86	64.08	1.12	63.02	0.85

SENSITIVITY

Sensitivity is defined as the intensity corresponding to 1% of the element in question. It is expressed as CPS / 1 %. The sensitivity of the X-ray analyzer for pressed pellet and loose powder cement in air and helium atmosphere was studied. The variation in helium gas flow pressure was found to have no significant effect on the sensitivity of the analyzer. The result as contained in table III showed that the sensitivity to each of

the analyte at both 1 bar and 2 bar helium gas flow pressure is high while in air, it is weak particularly for SO₃. This is because the radiations by 'low' atomic number sulphur are extensively absorbed by air. This further confirms the need to take measurement in helium gas for better accuracy. From the table, the sensitivity of the analyzer for loose powder in helium gas is lower than the sensitivity of the pressed pellet cement. This is in agreement with the findings of Field (1).

TABLE III

PRESSED PELLET			LOOSE POWDER		
SENSITIVITY IN HELIUM GAS		SENSITIVITY IN AIR	SENSITIVITY IN HELIUM GAS		SENSITIVITY IN AIR
CPS/1% CaO 138	139	100	136	135	125
	(1 bar) (2 bar)		(1 bar) (2 bar)		
Cps/1 % SO ₃ 4829	4836	545	4814	4818	521
	(1 bar) (2 bar)		(1 bar) (2 bar)		

CONCLUSION

From the foregoing, it can be concluded that loose powder cement results compare well with results of pressed pellet or fused bead used in EDXRF analysis. This new method is a faster, economical and reliable method for the determination of CaO and SO₃ in cement which makes effective quality control of cement possible. For better accuracy of results, it is desirable to measure in helium gas, and a flow pressure of 1 bar is adequate. Further pulverization of cement sample for a period of 120 seconds minimizes error likely to be introduced to the measurement due to variation in particle size.

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