Analysis of Cement and ASTM C114 Qualification

EDXRF APPLICATION NOTE #3051 REV1

NEX CG II

- **Model**
  NEX CG II
- **X-ray tube**
  50 W Pd-anode
- **Excitation**
  Indirect with polarization EDXRF
- **Detector**
  Large-area SDD
- **Autosampler**
  15-position sample tray
- **Sample type**
  Hydraulically pressed pellets
- **Analysis Time**
  1200* sec
- **Environment**
  Vacuum
- **Aperture Safety Film**
  Ultra-Polyester® 1.5 µm

SCOPE

Cartesian Geometry EDXRF performance is demonstrated for the analysis of finished Portland cement and ASTM C114-16 qualification.

BACKGROUND

EDXRF is a simple analysis technique used in cement plants around the world. The technique is ideal for QA/QC throughout the cement production process. EDXRF can be used as a screening tool and a QA/QC analyzer to ensure proper quality of incoming feedstocks, raw meal mixture balances, the addition of gypsum, and throughout the manufacturing process, including analyzing alternative fuels and ULSD used for firing the kilns.

Rigaku NEX CG II complies with the performance required in ASTM C114 and makes an excellent backup analyzer to WDXRF or as the main analyzer when producing Portland cement.

SAMPLE PREPARATION

Each sample is prepared by grinding to a fine, dry, homogeneous powder of approximately 200 mesh (<75 µm particle size) using a ball mixer/mill or ring-and-puck mill. For measurement, a sample is prepared by weighing 8 grams of sample and making a hydraulically pressed pellet using 20 tons of pressure for 30 seconds.

INTERNATIONAL STANDARD TEST METHODS

NEX CG II can be used to comply with the following international testing norms.

Designation	Title
ASTM C114-16	Standard Test Methods for Chemical Analysis of Hydraulic Cement
ISO 29581 – 2 : 2010	Cement -- Test methods -- Part 2: Chemical analysis by X-ray fluorescence

* Shorter measurement times can be used if the precision and ultra-low detection limits demonstrated are not required.

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CALIBRATION

Empirical calibrations were built using a set of eight NIST SRM certified standards: 1880b, 1881b, 1884b, 1885b, 1886b, 1887b, 1888b, 1889b. Using the empirical approach, X-ray absorption/enhancement "alpha corrections" are then employed to automatically compensate for variations in X-ray absorption and enhancement effects within the sample due to the independent variations in element concentration, thus yielding a very accurate model characterizing the cement type. A separate calibration method should be set up for raw meal, clinker and finished cements. For producing cement at a cement plant, it is recommended to augment the NIST standards with additional standards to further optimize the model.

A summary of the finished Portland cement empirical calibration is shown here using the eight NIST SRM certified standards.

Component	Concentration Range (mass%)	RMS Deviation	R^2 Confidence
SiO_2	18.39 – 29.05	0.055	0.99988
Al_2O_3	3.903 – 8.812	0.057	0.99940
Fe_2O_3	0.297 – 3.681	0.010	0.99989
CaO	49.27 – 66.05	0.187	0.99981
MgO	1.562 – 4.740	0.033	0.99967
SO_3	2.634 – 4.599	0.024	0.99994
Na_2O	0.017 – 0.790	0.002	0.99998
K_2O	0.016 – 1.115	0.015	0.99917
TiO_2	0.2034 – 0.3011	0.0068	0.99052
P_2O_5	0.0510 – 0.2970	0.0021	0.99993
ZnO	0.0042 – 0.1198	0.0002	0.99999
Mn_2O_3	0.0264 – 0.1981	0.0027	0.99882
Cl	0.0021 – 0.0183	0.0015	0.97742
SrO	0.0258 – 0.2840	0.0010	0.99996

PRECISION

To demonstrate repeatability (precision), NIST SRM 1887b was chosen from the set of calibration standards. The sample was measured in static position for ten repeat analyses using a total analysis time of 1200 sec per measurement, with typical results shown below.

NIST SRM 1887b	Standard Value	Average Value	Std. Dev
SiO_2	19.59	19.69	0.01
Al_2O_3	4.911	4.993	0.009
Fe_2O_3	2.471	2.453	0.002
CaO	61.15	61.22	0.02
MgO	3.624	3.630	0.039
SO_3	4.599	4.581	0.010
Na_2O	0.288	0.230	0.014
K_2O	0.961	0.955	0.002
TiO_2	0.203	0.208	0.001
P_2O_5	0.1540	0.1587	0.0006
ZnO	0.0156	0.0158	0.0001
Mn_2O_3	0.0957	0.0943	0.0003
Cl	0.0100	0.0179	0.0002
SrO	0.2625	0.2612	0.0002

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DETECTION LIMIT

To determine the lower limit of detection (LLD) using the empirical method, ten repeat analyses of a sample pellet of $CaCO_3$ were measured and the standard deviation calculated. $CaCO_3$ represents a high calcium "blank" cement matrix. The LLD is then defined as three times the standard deviation. This approach ensures that analyses above the determined LLD are measuring signal above background in a cement matrix. The following LLDs were determined using the same analysis times employed for calibration and repeatability. Actual detection limits may vary based on analysis time used, combinations of elements present, and elemental concentration levels.

Component	LLD (mass%)
SiO_2	0.002
Al_2O_3	0.012
Fe_2O_3	0.0003
MgO	0.013
SO_3	0.0006
Na_2O	0.041
K_2O	0.002
TiO_2	0.0018
P_2O_5	0.0009
ZnO	<0.0001
Mn_2O_3	0.0006
Cl	0.0003
SrO	0.0003

The LLDs shown here represent real-life detection limits in a matrix containing very high calcium using an analysis time of 1200 sec. Reducing the analysis time to 600 sec results in an increase in each LLD by a factor of 1.4.

ASTM C114

ASTM C114 and is a performance-based method. The analytical technique and operators must meet the qualification requirements given in C114 3.3.2 and not exceed limits given in C114 Table 1. Requirements for rounding figures are given in C114 4.5.6 and Table 3.

SAMPLES

NIST Portland Cement SRMs were used in the qualification: 1880b, 1884b, 1885b, 1886b, 1887b, 1888b and 1889b. To prepare a sample, approximately 8 grams of cement powder was made into a pellet using a hydraulic press and pressed to 20 tons for approximately 30 seconds.

C114 QUALIFICATION REQUIREMENTS

- Calibrate the analyzer using manufacaturer's guidelines.
- Measure at least seven hydraulic cement CRM* (Certified Reference Material) standards in one day.
- On a second day prepare and measure a second aliquot of each CRM.
- The difference between duplicates, and the difference between the average of each duplicate and the CRM ceritified value, cannot exceed limits given in C114 Table 1.

*The term SRM (Standard Reference Material) is used by NIST.

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Component	C114 Maximum Difference Between Dupplicates[1]	NEX CG II Maximum Difference Between Duplicates	C114 Maximum Difference of the Average of Duplicates from the SRM Certificate Value[2]	NEX CG II Maximum Difference of the Average of Duplicates from the SRM Certificate Value
SiO_2	0.16	0.10	0.2	0.13
Al_2O_3	0.20	0.09	0.2	0.10
Fe_2O_3	0.10	0.05	0.10	0.04
CaO	0.20	0.09	0.3	0.23
MgO	0.16	0.09	0.2	0.10
SO_3	0.10	0.08	0.2	0.08
Na_2O	0.03	0.02	0.05	0.03
K_2O	0.03	0.01	0.05	0.03
TiO_2	0.02	0.01	0.03	0.01
P_2O_5	0.03	0.01	0.03	0.01
ZnO	0.03	0.003	0.03	0.002
Mn_2O_3	0.03	<0.01	0.03	<0.01
Cl	0.003	0.001	0.005	0.002

[1] Reproducibility
[2] Accuracy

CONCLUSION

The Rigaku NEX CG II combines Cartesian Geometry indirect excitation with secondary targets, polarization targets, and a high-performance large area SDD detector to yield the optimum performance for elemental analysis of cement. NEX CG II can be used to comply with ASTM C114-16 and ISO 29581-2:2010.

During the entire production and processing cycle, oxide composition of the cement material must be reliably monitored to ensure optimal process control, physical characteristics of the cement, as well as profitability. The Rigaku NEX CG II analyzer is an ideal tool throughout the quality control process as the main instrument or as a backup to WDXRF systems. The system can also be used for verifying raw materials and clinkers, as well as testing various alternative fuels used at cement plants. By adding Rigaku RPF-SQX Fundamental Parameters, the NEX CG II is also an excellent analyzer for use in R&D to examine and compare formulations and for failure analysis. Powerful but simple to use, the NEX CG II is an excellent tool for non-technical operators and researchers alike.

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