Analytical Solutions

XRD & XRF

Cement

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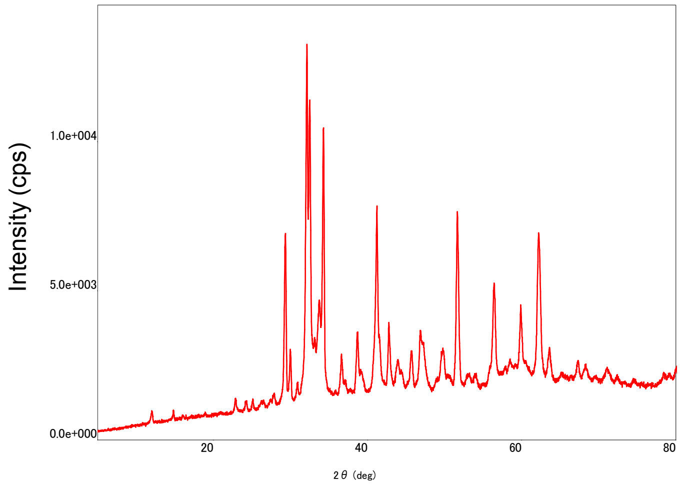
Quantitative Phase Analysis

Performance of the cement is largely influenced by constituent crystallographic phases. The clinker cement typically includes alite (Ca_3SiO_5), belite (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$), ferrite ($Ca_2(Al,Fe)O_5$), periclase (MgO) and free lime (CaO), expect phases in lesser quantities like alkali sulfates and calcium sulfates. Phase identification and quantitative analysis of identified phases are able to be done by X-ray diffraction (XRD). Especially, accuracy of quantitative analysis has been improved drastically by implementing a fast X-ray detector and software featuring a fully automated Rietveld analysis.

XRD How long does it take?

Thanks to the Rigaku original high-power X-ray sources, e.g. rotating anode generator (RAG) or 600W X-ray tube equipped by MiniFlex, and fast 1D strip detector *D/teX Ultra2*, measurement can be performed by around 3 to 5 minutes per sample. Data shown in the right was recorded by 3 minutes of data acquisition time by benchtop *MiniFlex*.

D/teX Ultra2: 1D fast strip detector

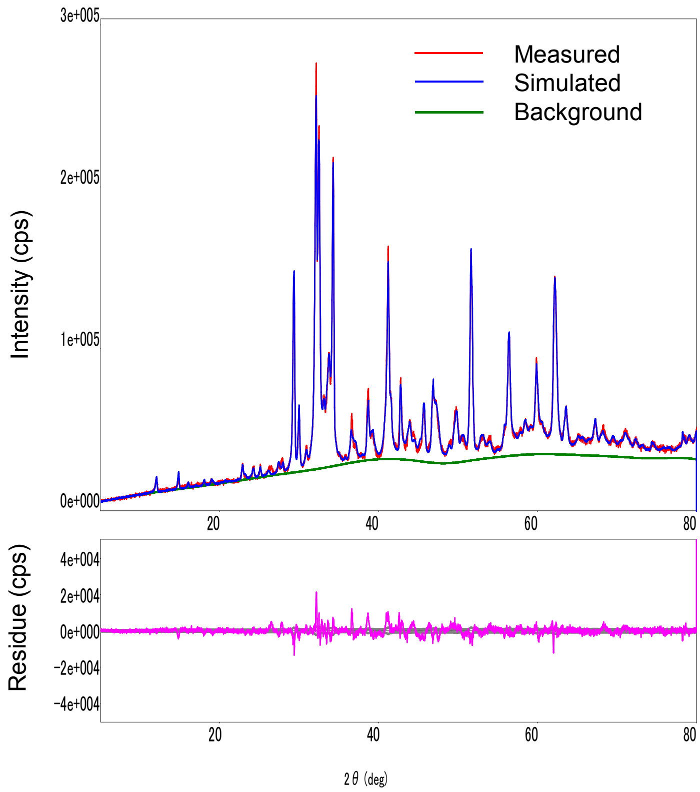


Typical XRD scan profile on clinker cement sample measured by MiniFlex 600

XRD "Phase ID" + "Rietveld quantitative analysis"

The *PDXL*® analysis software enables seamless analysis through phase identification (phase ID) to Rietveld quantitative analysis. One don't need to transfer phase ID result to Rietveld analysis separated software. Moreover, Rigaku is able to offer a cement database, which includes more than 50 possible phases in clinker cement. This makes phase ID easier than using conventional database. The right figure shows XRD pattern as well as Rietveld quantitative analysis done by *PDXL* on *NIST SRM 2686*. Table below shows obtained mass volume % of each phase indicating the *PDXL* gives fairly good agreement with certified numbers.

Phase	XRD result (mass%)	NIST certified (mass%)
C3S	55.0 ± 0.3	58.6 ± 4.0
C2S	25.9 ± 0.5	23.3 ± 2.8
C3A	3.1 ± 0.3	2.3 ± 2.1
C4AF	13.2 ± 0.4	14.1 ± 1.4
Periclase (MgO)	2.86 ± 0.05	3.3 ± 1.9



Rietveld quantitative analysis on *NIST SRM 2686*.

Quantitative Element Analysis

The X-ray fluorescence spectrometry (XRF) is widely used to analyze chemical compositions of cement materials. The XRF technique can be basically categorized into two, wavelength dispersive (WDXRF) and energy dispersive (EDXRF). Typically, WDXRF is employed in cement industries due to its high elemental resolution. Compared with other analysis like wet chemical analysis, XRF has advantages in 1. speed, 2. sample preparation and 3. reproducibility. Measurement takes less than 5 minutes with floor standing equipment and sample preparation requires just pulverization and pressing. In this application note, accuracy and reproducibility are discussed based on the results measured with ZSX PrimusIII+. Other products like Supermini, ZXS PrimusII and Simultix14 are also able to achieve similar level of accuracy and reproducibility.

XRF Hydraulic Cement analysis based on ASTM C114-11

The **ASTM C114-11** describes testing procedures as follows;

• Using the test method chosen, make single determinations for each analyte under consideration on at least seven CRM (Certified Reference Material) samples. Complete two rounds of tests on different days repeating all steps of sample preparations. Calculate the differences between values and averages of the values from the two rounds of tests.

• When seven CRMs are used in the qualification procedures, at least six of the seven differences between duplicates obtained of any single analytes shall not exceed the limits shown in Table 1 and the remaining differences by no more than twice that value

• For each analyte and each CRM, the average obtained shall be compared to the certified concentrations. When seven CRMs are used in the qualification procedure, at least six of the seven averages for each analytes shall not differ from the certified concentrations by more than the value shown in Table 1, and the remaining average by more than twice that value.

Table 1 Maximum permissible variation (in mass%)

Analyte	Maximum difference between duplicates	Maximum difference of the average of duplicates from the certificate values
SiO_2	0.16	±0.2
Al_2O_3	0.20	±0.2
Fe_2O_3	0.10	±0.10
CaO	0.20	±0.3
MgO	0.16	±0.2
SO_3	0.10	±0.1
Na_2O	0.03	±0.05
K_2O	0.03	±0.05
TiO_2	0.02	±0.03
P_2O_5	0.03	±0.03
ZnO	0.03	±0.03
Mn_2O_3	0.03	±0.03
Cl	0.003	N/A

A qualification test for “Rapid Test Method” in ASTM C114-11 was carried out. Pressed pellet specimens for the seven NIST CRMs (SRM1881a, 1884a, 1885a, 1886a, 1887a, 1888a and 1889a) were prepared and quantified with the calibration previously established. In a different day, the same procedure was repeated. The test results are summarized in Table 2, which shows only the maximum values for both the differences between the duplicates and the differences of the averages of the duplicates from the certificate values. The qualification test results shown in the table prove that the analysis meets the requirements described in the ASTM C114-11.

Table 2 Qualification test result (unit: mass%)

Analyte	Calibration range			Difference between duplicates		Difference of the average of duplicate from the certificate values	
				Limit	Result*	Limit	Result*
SiO_2	18.637	–	22.38	0.16	0.10	0.2	0.2
Al_2O_3	3.85	–	7.06	0.20	0.04	0.2	0.1
Fe_2O_3	0.152	–	3.09	0.10	0.00_3	0.10	0.04
CaO	57.58	–	67.87	0.20	0.12	0.3	0.1
MgO	0.814	–	4.475	0.16	0.04	0.2	0.1
SO_3	2.086	–	4.622	0.10	0.05	0.1	0.1
Na_2O	0.021	–	1.068	0.03	0.02	0.05	0.01
K_2O	0.093	–	1.228	0.03	0.00_3	0.05	0.01
TiO_2	0.084	–	0.366	0.02	0.01	0.03	0.01
P_2O_5	0.022	–	0.306	0.03	0.01	0.03	0.00_4
ZnO	0.001	–	0.107	0.03	0.00_1	0.03	0.00_2
Mn_2O_3	0.007	–	0.259	0.03	0.00_1	0.03	0.00_2
Cl	0.0019	–	0.013	0.003	0.005**	N/A***	0.006

* In the columns of “Result”, only the maximum values among the analysis results of the seven NIST CRMs are listed.

** The maximum difference for Cl is 0.005 mass%, which exceeds the limit 0.003 mass% while the differences of all the other CRMs are less than 0.003 mass%. The value 0.005 mass% is less than the double of the limit, 0.006 mass%.

*** No value is given.

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Quantitative Element Analysis

XRF Repeatability of Hydraulic Cement analysis

The specimens of NIST SRM1889a were measured consecutively ten times. This repeatability test results are summarized in Table 3. In the table, average and standard deviation of ten-time measurement for each specimen together with limits of the qualification test for ASTM C114-11 are summarized. It shows that the standard deviation is much smaller than that defined and required in the ASTM C114-11.

Table 3 Repeatability test result using SRM1889a (unit: mass%)

Analyte	Certified value	Ten-time measurement result				Maximum difference of averages between duplicates	Maximum difference of the average of duplicate from the certificate values
		1st specimen		2nd specimen			
		Average	Std. dev.	Average	Std. dev.		
SiO_2	20.66	20.74	0.040	20.78	0.024	0.16	0.2
Al_2O_3	3.89	3.85	0.008	3.86	0.005	0.20	0.2
Fe_2O_3	1.937	1.912	0.0026	1.910	0.0019	0.10	0.10
CaO	65.34	65.41	0.048	65.42	0.031	0.20	0.3
MgO	0.814	0.864	0.0031	0.864	0.0027	0.16	0.2
SO_3	2.69	2.68	0.006	2.69	0.002	0.10	0.1
Na_2O	0.195	0.201	0.0022	0.199	0.0025	0.03	0.05
K_2O	0.605	0.610	0.0010	0.612	0.0008	0.03	0.05
TiO_2	0.227	0.225	0.0012	0.223	0.0013	0.02	0.03
P_2O_5	0.11	0.11	0.002	0.11	0.002	0.03	0.03
ZnO	0.0048	0.0042	0.0001	0.0040	0.0001	0.03	0.03
Mn_2O_3	0.2588	0.259	0.0005	0.259	0.0009	0.03	0.03
Cl	0.0019	0.0030	0.0001	0.0020	0.0001	0.003	N/A

XRF Cement Raw Meal analysis

A series of reference materials of cement raw meal certified by CSBTS were used for calibration. Cement raw meal powders, previously pulverized, were pressed into aluminum rings at 120 kN and was measured consecutively 10 times to demonstrate short-term stability. The test results, tabulated in Table 4, prove that it is possible to analyze pressed pellet specimens of cement raw meal with high repeatability.

Table 4 Repeatability test results on cement raw meal. (unit: mass%)

Analyte	Std. value	Average	Std. dev.	RSD%
SiO_2	12.76	12.78	0.016	0.12
Al_2O_3	3.56	3.56	0.0048	0.14
Fe_2O_3	2.94	2.92	0.0047	0.16
CaO	41.74	41.70	0.012	0.029
MgO	1.87	1.85	0.0078	0.42
SO_3	0.17	0.18	0.0016	0.86
Na_2O	0.07	0.07	0.0008	1.1
K_2O	0.24	0.24	0.0003	0.13
TiO_2	0.22	0.21	0.0009	0.44
Cl	0.179	0.205	0.0008	0.38

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Instrumentation (XRD)

MiniFlex — Benchtop high-power XRD

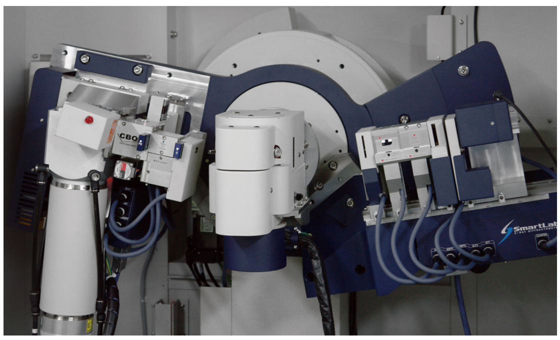
The MiniFlex 600 is equipped with the world's highest power 600W X-ray source. Together with innovative variable divergence slit and knife edge, X-ray intensity in the measurement is more than 7 times higher compared with conventional benchtop instrument equipping with a 300W X-ray source.
The MiniFlex 300 is equips with built in cooling device for X-ray generation. It saves space and cost for external cooling water chiller typically required for a floor standing XRD instrument.
Both types have sample magazine (changer) as an option. Combined with unique software package "PDXL for Cement", fully automated characterization is achieved. The MiniFlex fits to the demands in satellite labs, back-up instrument and on-site analysis where utilities and space are limited.

Ultima-IV — Multipurpose fully automated XRD

The Ultima-IV equips with a 3kW X-ray generator and a fast 1D silicon strip detector, *D/teX Ultra 2*, which enables to measure cement sample 100 times or more faster than a conventional point detector. It is able to be combined with high- and low-temperature chamber for non-ambient measurement as well as sample changer for automated measurement on multiple samples. The Ultima-IV fits to the demands in quality control and research & development.

SmartLab — High-resolution & high-power XRD

The SmartLab has a unique 9kW rotating anode X-ray generator[1)] and a direct optical encoding high-precision goniometer. The 9kW generator enables to carry out measurement about 10 times faster than the a 3kW generator and also it enables to evaluate impurity or minor phase having relative volume fraction less than 0.1 wt%. The measurement time can be more faster by a factor of 100 when a fast 1D silicon strip detector *D/teX Ultra 2* is integrated. It also can be combined with high- and low temperature chamber for non-ambient measurement as well as sample change for automated measurement on multiple samples. The SmartLab fits to the demands in research & development.



1) option

Instrumentation (XRF)

Supermini — Benchtop high-power WDXRF

The Supermini is equipped with the world largest 50kV, 200W X-ray source among the benchtop X-ray fluorescence spectrometers. The WDXRF gives higher energy resolution the EDXRF, therefore, the EDXRF is the best to analyze complicated matrix sample. The Supermini is equipped with 12 sample changer. Combined with the *EZ scan* software, it enabled to carry out fully automated analysis based on calibration line method, FP method and standardless SQX method for fused bead or pressed powder cement sample. The Supermini fits to the demands in back-up instrument, quality control and research & development.

Primus — WDXRF with tube above or below

The ZSX Primus series is a WDXRF instrument having both tube above and below configuration. User can select the type depending on the requirement. For cement analysis, tube above configuration has advantages in having less chance of damaging spectrometer by dropped powder from the sample. As a result, user may not need to add a binder material. In addition to the unique tube above configuration, the Primus has following advantages as well. 1. high-power 4kW X-ray tube with 30μm Be window offering higher sensitivity for light elements, from calcium (Ca) to fluorine (F), 2. Specially designed multilayer analyzer for magnesium (Mg) and fluorine (F) and 3. two vacuum lines for high throughput. The ZSX Primus series fits to the demands in quality control and research & development.

Simultix 14 — Simultaneous WDXRF

The Simultix14 is a multi-channel WDXRF instrument equipped with maximum 40 channels and a 4kW X-ray tube. A log-spiral optics with a curved crystal gives more than x2 intensity[1)] compared with other optics. Combined with vacuum pressure control system and optimized fundamental parameters (FP) algorithm implemented in the *Simultix* software, it achieves quite high sensitivity and stability for cement analysis. The Simultix14 fits to the demands in quality control and research & development.

1) Depends on element