ARL OPTIM'X performance

D Bonvin, R Yellepeddi and A Kohler, Thermo Fisher Scientific SARL, Switzerland

X-ray fluorescence (XRF) has been an essential part of the process and quality control of cement plants for more than 60 years thanks to its ease of use and fast response. After sample preparation consisting of grinding and pressing the material determination of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, SO_3, K_2O, Na_2O, chlorine and fluorine among others is obtained within a few minutes in raw meal, clinker and cement.

Thermo Fisher Scientific™ ARL™ OPTIM'X analyser

Table 1: concentration ranges and typical performance using the SmartGonio

Element	*Range (%)*	*Limits of detection (ppm) 100s*	*Typical SEE (%)*
CaO	57.5 - 67.4	nr	0.4
SiO_2	20.0 - 22.5	nr	0.22
Al_2O_3	3.9 - 7.1	16.0	0.17
Fe_2O_3	0.3 - 3.1	9.0	0.06
SO_3	2.1 - 4.6	6.4	0.21
MgO	0.81 - 4.5	24	0.09
K_2O	0.16 - 1.27	4.3	0.025
Na_2O	0.02 - 1.07	42.0	0.028
Cl	0.004 - 0.013	9.0	0.001

SEE = Standard error of estimation
LOD = limit of detection (3 sigma)
nr = not relevant in view of the high concentration ranges

Wavelength-dispersive XRF (WDXRF) is generally selected over energy-dispersive XRF (EDXRF) due to its better resolution, its good capacity for analysis of light elements like Na and F and its excellent long-term stability. The role of an EDXRF system is usually as a back-up instrument for the main WDXRF or dedicated to alternative fuels analysis because EDX excels in the analysis of heavy metals in carbonate matrices that are typical of alternative fuels.

Instrumentation and performance

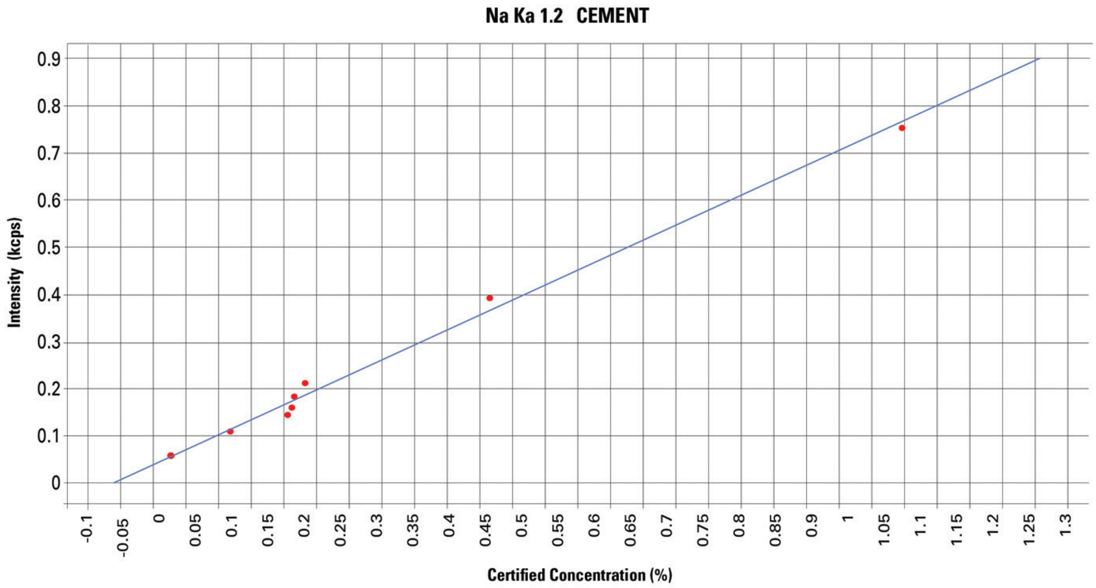
Generally, WDXRF instruments have existed either as high-performance systems with power levels from 1000W to 4200W or as low power systems below 200W. These latter systems have some advantages because they do not require external dependence on water cooling or compressed air, can operate on 220V (or 110V) and do not generate much heat in the laboratory. But they are either simultaneous instruments dedicated only to the analysis of a pre-defined fixed number of elements (usually 8 to 10), hence lacking analytical flexibility, or they are sequential instruments that can cover most of the elements of the periodic table but with a response time of 6-10 minutes, too slow to satisfy most cement laboratories.

The new Thermo Scientific™ ARL™ OPTIM'X (see Figure 1) is a WDXRF instrument designed with a new 200W X-ray tube and Ultra Closely Coupled Optics (UCCO™) to provide the highest possible performance within a short response time. To prove this a series of NIST cement-certified reference materials (CRM) are used for calibration of the ARL OPTIM'X. These standard samples cover the concentration ranges shown in Table 1. Samples are pressed at 20t in the form of flat ϕ40mm pellets and measured on the instrument to establish a calibration curve for each element. The Standard Error of Estimation (SEE) in Table 1 is a measure of the accuracy of analysis. It is the average error between the certified concentration of the standard samples and the calibration curve for a given oxide.

Light elements like Na and Mg can also be successfully analysed with the ARL OPTIM'X. As shown in Figure 1, a good calibration curve is obtained for Na_2O with a standard error of estimation of 0.028 per cent in a range from 0.02 to 1.1 per cent. The limits of detection are all sufficient for a typical analysis in the cement industry.

The short-term and long-term repetition of analysis (see Table 2 and 3) are excellent using only 10 seconds counting time per element. Therefore, the response time of the instrument is less than two minutes for a typical clinker or cement analysis. Typical standard

Figure 2: calibration curve for Na_2O in cement using NIST standard samples. Standard error of estimation is 0.028 per cent in a range from 0.02 to 1.1 per cent



deviations expected in cement industry are also shown. The ARL OPTIM'X does comply with these values for all elements/oxides.

Furthermore, the ARL OPTIM'X system can be linked automatically to the online PGNAA analyser that controls either the stockpile blending or the raw meal composition. AccuLINK software is used to bring lab accuracy online by regularly comparing the PGNAA results with the ARL OPTIM'X analysis and re-calibrating the online equipment seamlessly.[1]

Alternative fuels analysis

Thanks to its SmartGonio™ the ARL OPTIM'X has the flexibility to analyse elements from fluorine (^{9}F) to uranium (^{92}U) and therefore it can also be used for analysis of alternative fuels where major, minor and trace heavy metal elements must be controlled. Alternative fuels can be organic or inorganic components in solid, liquid or high-viscosity forms. Typical materials used as secondary fuels range from tyres, wood, plastics, used oils, paints, resins, adhesives, solvents, sludges, animal waste and other organic waste, resulting in a variety of matrices and concentration ranges in samples of 'unknown' nature.

XRF is one of the most universal techniques to deal with such a variety of samples. It is capable of handling solids, liquids, pastes, loose powders or granules with minimal or no sample preparation. Standardless software package such as UniQuant™ must be used for total elemental determination in alternative fuels because typical standard samples

Table 2: results of a repeatability test on a cement pressed pellet (10 consecutive runs) for a sequential configuration at 200W

Run	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	S	P_2O_5	TiO_2	MnO
1	62.27	20.79	4.43	2.66	4.60	1.02	0.254	2.78	0.139	0.191	0.085
2	62.21	20.81	4.44	2.63	4.59	1.01	0.264	2.77	0.136	0.187	0.086
3	62.28	20.79	4.42	2.65	4.62	1.01	0.248	2.77	0.134	0.191	0.084
4	62.25	20.83	4.44	2.65	4.57	1.01	0.234	2.76	0.131	0.189	0.085
5	62.28	20.80	4.44	2.64	4.60	1.01	0.242	2.77	0.129	0.190	0.084
6	62.25	20.80	4.43	2.65	4.62	1.02	0.247	2.76	0.140	0.185	0.086
7	62.23	20.81	4.42	2.63	4.60	1.02	0.246	2.78	0.134	0.185	0.082
8	62.25	20.81	4.42	2.63	4.59	1.01	0.252	2.76	0.136	0.186	0.086
9	62.27	20.83	4.43	2.64	4.60	1.02	0.251	2.76	0.139	0.188	0.083
10	62.29	20.83	4.43	2.64	4.56	1.02	0.236	2.77	0.141	0.187	0.086
Avg	62.26	20.81	4.43	2.64	4.60	1.01	0.248	2.77	0.136	0.188	0.085
Std Dev	0.025	0.015	0.009	0.01	0.020	0.003	0.009	0.008	0.004	0.002	0.001
Time (s)	10	10	10	10	10	10	10	10	10	10	10
Desired Std Dev	0.03	0.02	0.02	0.015	0.02	0.02	0.02	0.012	0.012	0.015	0.015

Table 3: results of a 16h reproducibility test (178 runs) on a pressed cement pellet for a sequential configuration at 200W

Run	*CaO*	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*MgO*	*K_2O*	*Na_2O*	*S*	*P_2O_5*	*TiO_2*	*MnO*
1	65.60	20.57	3.86	1.90	0.861	0.641	0.149	3.02	0.111	0.223	0.257
2	65.73	20.57	3.86	1.90	0.881	0.639	0.175	3.02	0.108	0.222	0.259
3	65.68	20.56	3.87	1.91	0.881	0.640	0.174	3.01	0.112	0.220	0.256
4	65.73	20.60	3.87	1.91	0.890	0.642	0.166	3.02	0.108	0.220	0.258
5	65.67	20.60	3.89	1.90	0.872	0.643	0.170	3.01	0.111	0.227	0.257
6	65.62	20.57	3.88	1.90	0.882	0.641	0.169	3.01	0.122	0.221	0.260
	..	..	..	..	..	..	..	..	..	..	..
174	65.63	20.60	3.88	1.91	0.879	0.640	0.179	3.02	0.118	0.217	0.255
175	65.59	20.60	3.89	1.90	0.881	0.634	0.171	3.02	0.114	0.222	0.256
176	65.62	20.60	3.87	1.90	0.888	0.641	0.180	3.02	0.118	0.222	0.260
177	65.57	20.62	3.88	1.89	0.879	0.644	0.163	3.03	0.123	0.222	0.256
178	65.65	20.60	3.88	1.91	0.883	0.644	0.175	3.02	0.117	0.222	0.256
Avg	65.63	20.60	3.88	1.90	0.879	0.641	0.172	3.02	0.114	0.221	0.256
Std Dev	0.046	0.020	0.013	0.006	0.008	0.003	0.007	0.008	0.003	0.003	0.002
Time (s)	10	10	10	10	10	10	10	10	10	10	10

generally do not exist to establish a calibration.

Conclusion

The ARL OPTIM'X WD-XRF instrument permits successful analysis of various elements in cement and clinker in less than two minutes. Pressed pellet sample preparation is fast and simple and allows lower limits of detection and good precision. Good repeatability and reproducibility is obtained with the SmartGonio™ for all elements. If better results are required for any element the counting time for that particular element can be increased. But in view of the excellent standard deviations obtained the counting time for some elements could even be decreased, to four seconds for K_2O, P_2O_5, TiO_2 and MnO, therefore reducing the total counting time for 11 elements.

With the increase of alternative fuels in the cement industry in recent years looking to reduce CO_2 emissions while also addressing the landfill issues of organic or inorganic waste analysis of such highly variable materials can be addressed with WDXRF instruments such as the ARL OPTIM'X.

Analysis and control of these elements in alternative fuels become imperative while the cement industry looks to benefit from their usage.

Figure 3: typical sawdust sample

References

[1] WOODWARD, R: "The missing link is found" in: *ICR*

[2] YELLEPEDDI, R: "Analysis of AF elements" in: *WC*

Table 4. UniQuant standardless analysis results on a contaminated wood dust

Element	*UniQuant*
Cellulose	97.9
Si (%)	0.71
Ca (%)	0.65
Al (%)	0.2
K (%)	0.12
S (%)	0.11
Fe (ppm)	560
Ti (ppm)	360
Mg (ppm)	720
Cl (ppm)	640
P (ppm)	390
Zn (ppm)	130
Ba (ppm)	140
Pb (ppm)	60
Mn (ppm)	70
Sn (ppm)	60
Ni (ppm)	< 10
Cr (ppm)	< 10
Sr (ppm)	< 10
V (ppm)	< 10