

Table 1: Typical reproducibilities of ED-XRF cement analysis

Element	typical Concentration (%)	abs. Std. Dev. (n=15, %)
CaO	45	0.2
SiO ₂	12	0.1
Al ₂ O ₃	2	0.02
MgO	1	0.05
Fe ₂ O ₃	1	0.01
K ₂ O	0.5	0.03
SO ₃	0.3	0.01
Mn ₂ O ₃	0.1	0.001

neither compressed air, cooling water or detector gas (Figure 2).

If higher analytical speed and sample throughput is required, the high-power 4kW S4 PIONEER is the right choice. This spectrometry solution not only meets the demands for space saving, but also brings an efficient and economical solution to high-power excitation at 4kW by simply connecting it to an external cooling water system. Water consumption is automatically minimized based on

the generator power setting, and is typically one-third that of conventional X-ray spectrometer systems. Short-term variations in water flow and flow interruptions are compensated for. A further step was to improve the analytical capability and performance of ED-XRF. The goal was to

Figure 3: Benchtop size S2 RANGER spectrometer for at-line process and quality control

make operation and sample handling easier through an intuitive touch-screen interface, and more convenient based on an all-in-one instrument combined with revolutionary new evaluation methods for routine samples and totally unknown materials. The self-explaining touch-screen operation provides full analytical functionality without keyboard and mouse, enabling users without any experience in PC operation to get results from the very first day. The compact all-in-one design of modern bench-top spectrometers with integrated computer, touch-screen, printer and vacuum pump ensure minimum space requirements, single port connection, and fast installation and relocation (Figure 3). Modern high-performance energy-dispersive spectrometers such as the S2 RANGER are able to give enough accurate data to keep control of the process. Typical reproducibility data for raw meal analysis are shown in Table 1.

The principal reason for the use of a sequential X-ray spectrometer for production control is that the sequential

instrument is much more flexible, analytically, allowing measurement of additional elements and reliable trace element analysis based on peak/background measurements. This is because in sequential X-ray spectrometers all element lines are measured one after the other and the number of elements which can be analyzed is thus not limited. In multi-channel X-ray spectrometers the element lines are measured simultaneously by means of fixed spectrometer channels. The number of elements which can be analyzed is limited due to geometric reasons. In multi-channel spectrometers the total analysis time is determined by the longest analysis time required for an individual element. In sequential spectrometers the total analysis time is the sum of the individual analysis times for all elements measured.

XRF Analysis of alternative liquid and solid fuels and raw materials

The use of alternative raw materials and fuels is commonly established in modern cement plants. Examples for alternative raw materials are fly ashes, blast furnace slags, desulphurization gypsum, and foundry sands. Alternative liquid fuels include waste solvents and oils, glues, paints and even waste waters. Potential solid waste-derived alternative fuels – such as, used tyres, waste plastics, textiles and paper, rubber scrap, used wood and sewage sludges may be used.

Using alternative fuels and raw materials in the cement process leads to extended tasks in analytical process and quality control, which may range from determination of elements and their concentrations which have an influence on the burning process, or may cause corrosion and coagulation in the kiln, to elements which have to be controlled for environmental protection by the national authorities.

Conventional quantification routine in XRF analysis is based on setting up different calibrations for the individual elements and materials (such as raw meal, clinker and cements). When dealing with the large variety of alternative fuels, development of calibrations may fail because of the lack of available reference samples for the specific waste derived material or missing certified values for specific elements, such as specific heavy metals or halogens. This situation is resolved now by modern XRF systems offering precalibrated methods for universal 'standardless' or material specific multi-element analysis to easily extend the range of analytical cement routines. In XRF analysis modern fundamental parameter programs provide fast, easy calculation of appropriate correction coefficients ('variable alphas') to compensate for interelement influences (matrix effects). This allows definition of universal calibrations over a wide concentration range.

The usual requirements for such a 'standardless' XRF analysis range from classification into major and minor elements to 'nearly' quantitative results, even for traces. The price to pay for such an absolute universality, however, is the limited accuracy of the results; these results may vary between 'almost' quantitative results of massive and homogeneous samples and a more or less rough chemical characterization for extremely small, bulky or untreated samples. The 'standardless' XRF approach allows analysis



Table 2: 'Standardless' WD-XRF analysis of shredded rubber material used as alternative fuel

conc. in %	C	O	Mg	Si	P	S	Cl	K	Ca	Fe	Zn	Pb
rubber 1	88.1	3.0	0.021	0.86	0.006	5.25	0.013	0.007	0.71	0.016	1.98	0.011
rubber 2	87.6	3.9	0.025	0.91	0.005	4.90	0.015	0.007	0.74	0.016	1.92	0.009

of nearly all elements of the periodic table in any totally unknown sample which can enter an XRF process and quality control laboratory in the cement industry. Any sample – metal pieces, minerals, rocks, slurries, filter samples or even alternative liquid fuels or plastic cuttings – can be analyzed with this universal precalibrated program.

Table 2 shows the results of 'standardless' XRF analysis of two shredded rubber samples used as alternate fuel with the S4 EXPLORER sequential X-ray spectrometer. Samples had been prepared as pressed pellets with wax as a binder and the C and O content was calculated as a matrix. With 'standardless' capability it is possible to check alternative fuels or additives as well to check 'strange deposits' on fan blades as well as the wear metal content in an oil to investigate machine failures. After 10 minutes of scanning time over the whole Periodic Table it is possible to automatically or interactively evaluate the obtained data.

Since there are almost no reference materials available for rubber materials, which applies too for plastic materials (PP and PE), a universal precalibrated program is the first step solution for reliable analytical control of such alternative fuels. To improve the analytical accuracy, however, it is important to qualify the sample matrix: this means the sample composition, and the sample preparation. For easy quality control of alternative liquid and solid fuels, such as used oils, paints and glues, as well as waste plastic materials, the precalibrated, fully quantitative OilQuant was developed.

OilQuant is an analytical package for full quantitative XRF analysis of solid and liquid fuels (coal, coke, oils, diesel, gasoline, etc.). Being optimized for liquid fuels it can also be applied to other light matrix materials such as coals, lignites and even polymers which also consist mainly of carbon. Twenty-six elements, from sodium to lead, are calibrated and this can be easily be extended by further element calibrations. Two different calibrations are available for sulfur and chlorine, one for trace contents each (up to 1,000 ppm) and one for contents in the percentage range each (0.1-5 %). Table 3 summarizes the most important calibration parameters for every element: concentration range, detection limit and standard repeating deviation for 500 ppm samples.

Sample handling

Sample preparation of liquid samples for the XRF spectrometer is quite simple. The liquid sample is directly poured into disposable plastic liquid cups with thin, high transmission foils (Figure 4). The same simple, fast sample preparation procedure applies to loose powders. Using disposable liquid cups, sequential XRF analysis (with Helium Flush and AXS Seal Technology) can assay a used oil sample in less than three minutes and imme-

diately after that go back and run solid clinker samples under vacuum mode. Smart vacuum sensors make it impossible to run liquids in vacuum: the AXS Seal Technology seals the spectrometer from the sample chamber, which gets purged with helium. The main part of the system remains under vacuum. Changeover times from vacuum to helium mode are therefore minimal, and so is the risk of spills. This can also be used to measure loose powders and raw-mix slurry.

The performance of the S4 EXPLORER is optimized for safe measurement of liquid samples. For example, when measuring liquid fuels (say S or Cl in waste oils) in helium or nitrogen atmosphere, the unique vacuum seal of the spectrometer closes the spectrometer chamber with the optics, and only the small volume of the sample chamber is flushed. This drastically reduces the consumption of helium or nitrogen. Besides preventing contamination of the

Table 3: Analytical specifications of the S4 EXPLORER and OilQuant optimized for alternative liquid and solid fuels

	concentration range	LLD		concentration	LLD
	[ppm]	(3s; 25s)		range	(3s; 25s)
		[ppm]		[ppm]	[ppm]
Na	LLD - 500	7	Cr	LLD - 500	1
Mg	LLD - 500	3	Mn	LLD - 500	1
Al	LLD - 500	2	Fe	LLD - 500	1
Si	LLD - 500	2	Ni	LLD - 500	1
P	LLD - 2,500	1	Cu	LLD - 500	1
S	LLD - 1,000	1	Zn	LLD - 2,500	1
S	LLD - 5.00%	2	Br	LLD - 1,000	1
Cl	LLD - 1,000	3	Mo	LLD - 500	2
Cl	LLD - 5.00%	6	Ag	LLD - 500	1
K	LLD - 300	1	Cd	LLD - 500	7
Ca	LLD - 6,000	1	Sn	LLD - 500	4
Ti	LLD - 500	1	Sb	LLD - 1,000	4
V	LLD - 500	1	Ba	LLD - 2,000	4
Zn	LLD - 2,500	1	Pb	LLD - 1,000	1

spectrometer chamber and reducing helium consumption when measuring liquids, this vacuum seal between sample chamber and spectrometer chamber, reduces the time when switching from one mode (helium) to another (vacuum, and *vice versa*) and again contributes to highest stability and reliability because the detectors remain under vacuum.

Modern analytical X-ray systems fit the user's requirements of sample handling today and for the future by modular sample changer concepts with full access to process automation. This achieves an advantage in all industrial applications where a user-specific input of process samples is requested. Fully integrated large sam-

Figure 4: Disposable liquid cups for XRF analysis



Figure 5: Laboratory automation concept with full integration of XRF and XRD analysis



ple magazines (50 and more positions) and automatic, safe measurement routines of large sample measuring sets ensure a maximum (unattended) measuring capacity. At any time, longer routine measurements can easily be interrupted for priority samples for immediate process control. For similar-sized samples, e.g. pressed powder pellets, fused beads or metal disks, there exists an innovative approach to handle samples without sample holders. For laboratory automation the spectrometers can be equipped with a process automation sample magazine to handle powder samples pressed in steel rings without sample holders, to take over process samples from a conveyor belt or a robot, as well as to manually handle liquid samples (Figure 5).

The chemical analysis is performed by X-ray fluorescence (XRF) using a sequential wavelength-dispersive X-ray spectrometer S4 ONLINE. In many cement works however, knowledge about the absolute phase abundance in cement clinker, such as the quantification of free lime (CaO), is a requirement to control the cement process. In an automated laboratory, an X-ray diffractometer, such as the process diffractometer D4 ONLINE, can easily be integrated for quantitative phase analysis by X-ray diffraction (XRD). The advantages of dual-instrument configuration are firstly, the independent XRF and XRD operation without any restrictions concerning analytical versatility and functionality and, secondly, the simultaneous execution of all analytical tasks with highest sample throughput.

As stated at the introduction, the main reason for the use of a sequential X-ray spectrometer for quality and production control in the cement industry is that the sequential instrument offers the highest analytical flexibility. But, with an ever increasing demand for faster analytical turnaround times, can a sequential X-ray spectrometer meet the requirements on analytical speed?

To further improve the speed of analysis, a measurement method has been developed with the S4 EXPLORER which enables the determination of nine elements in less than three minutes. This time is inclusive of the sample loading and unloading, changing of instrumental parameters, actual analysis time and reporting of the result. Extreme care was taken to ensure that the improvements in speed did not compromise the quality of the analytical data produced.

A method was created for the analytes Na₂O, MgO, Al₂O₃, SiO₂, SO₃, Cl, K₂O, CaO and Fe₂O₃. The actual analysis time was distributed amongst the analytes to give maximum performance where required. The standards used to construct a calibration were finished cement samples prepared as pressed powder pellets. Wax was used as the binding aid. To test the precision of the new method, two cement samples were both measured fifty times. The samples were loaded alternately, to ensure that for each analysis, each of the instrumental parameters were changed including sample handling. The analytical data from these precision trials is shown in Table 4.

Conclusion

XRF instruments and software have become more flexible and powerful. Sequential systems are more flexible and scalable than before. The compact S4 EXPLORER X-ray spectrometer system offers full wavelength dispersive XRF performance with no need for P10 detector gas, compressed air or cooling water. With its exceptionally small footprint, full SPECTRAplus software and a process sample X-Y loader to take over samples from a conveyor belt or a robot, it fulfils every wish for flexible and reliable multi-element determination in cement process and quality control. Modern X-ray spectrometers also allow safe measurement of alternative liquid fuels and slurries and provide precalibrated universal ‘standardless’, as well as fully quantitative methods for multi-element analysis, easily extending the range of conventional analytical cement routines.

The need for fast, reliable, flexible, small and cost-effective systems, as well as for easy-to-use software and turnkey systems, have fuelled the advancements in XRF and in the X-ray diffraction (XRD) sector. Combining both techniques as a Total Cement Solution gives the user seamless control of two full instruments under one common interface. The S2 RANGER benchtop element ED-XRF analyzer is an ideal solution as a first step into element determination by XRF analysis, as backup system for the larger WD-XRF spectrometer, or as a flexible analyzer for non-routine samples, such as solid or liquid alternative fuels. ■

Sample A	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	Fe ₂ O ₃
Average (%)	0.358	4	3.08	21.1	0.097	2.26	0.827	62.11	4.4
abs. Std. Dev. (%)	0.004	0.01	0.02	0.02	0.002	0.005	0.003	0.04	0.005
Sample B	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	Fe ₂ O ₃
Average (%)	0.121	1.27	5	20.08	0.059	4.65	1.253	62.85	2.17
abs. Std. Dev. (%)	0.003	0.01	0.02	0.02	0.002	0.007	0.002	0.04	0.004