QC OF ALTERNATIVE RAW MATERIAL AND FUEL

QUALITY CONTROL OF ALTERNATIVE RAW MATERIALS AND FUELS IN THE CEMENT INDUSTRY

STEFAN UHLIG & ARND BÜHLER, BRUKER AXS GMBH

Alternative raw materials and fuels present unique challenges to analysis from the fact that their matrix composition is often extremely variable, and thus analytical standards are difficult to select. New advances in 'standardless' analysis overcome these problems.

Les matières premières et carburants alternatifs sont extrêmement difficiles à analyser en raison de leur composition structurale souvent très variable. Il est ainsi difficile de sélectionner les normes analytiques. De récentes avancées dans l'analyse "sans normes" permettent de surmonter ces difficultés.

Alternative Roh- und Brennstoffe stellen für die Forschung eine einzigartige Herausforderung dar, da die Zusammensetzung der Grundmasse oft stark variiert. Deshalb sind die Forschungsstandards schwer zu bestimmen. Neue Fortschritte in der „standardlosen" Forschung stellen eine Lösung dieser Probleme dar.

El análisis de los combustibles y materias primas alternativos supone un auténtico reto, ya que su composición básica es a menudo muy variable y esto dificulta la selección de los criterios de análisis. Los últimos avances en la "estandarización" de análisis solucionan estos problemas.

Matérias-primas e combustíveis opcionais constituem um desafio à parte para a análise, já que a composição da matriz, em geral, é extremamente variável. Portanto, fica difícil selecionar padrões analíticos. Novos avanços obtidos com análises "sem padrão" dão conta desse problema.

X-ray fluorescence (XRF) analysis for determination of chemical composition of cements and raw materials is the most widely used analytical technique. The need for fast, reliable, flexible, small and cost effective systems as well as for easy-to-use software and turnkey systems have pushed the advancements in X-ray instrumentation over the last decade. New X-ray spectrometer generations had been designed to cover all modern analytical tasks in the cement industry. This includes that all the different materials can be analysed with one single instrument from natural and industrial waste recovery raw materials, S or Cl in alternative liquid or solid fuels, environmentally relevant control of filters, plants or sewage, to the traditional routine analysis of raw meal, clinker and cement. In case of laboratory automation, modern X-ray spectrometers can also be equipped with a process automation sample magazine to handle routine powder samples pressed in steel rings handed over from a conveyor belt or a robot, as well as manual loading of different sized samples such as alternative liquid fuels.

Alternative materials & fuel

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, desulphogypsum, and foundry sands. Liquid waste materials include waste solvents and oils, glues, paints and even waste waters. Solid waste-derived alternative fuels include, for example, used tyres, waste plastics, textiles, and paper, rubber scrap, used wood and sewage sludges.

Using alternative raw materials and fuels in the cement process lead 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 solved 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.

The usual requirements for such a

Table 1: 'Standardless' 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

'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 characterisation for extremely small, bulky or untreated samples. The 'standardless' XRF approach allows analysis 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 and plastic cuttings - can be analysed with this universal precalibrated program.

Table 1 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 binder and the C and O content was calculated as matrix. With 'standardless' capability it is possible to check alternative fuels or additives as well as to be able 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 fuels, such as used oils, paints and glues, but also solid plastic materials, the precalibrated, fully quantitative OilQuant was developed. OilQuant is a precalibrated program for carbon- and hydrogen-rich liquid and solid materials. In Table 2 the elements with concentration range and lower limit of detection are given for the OilQuant.

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. 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 3 minutes and immediately 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 also can be used to measure loose powders and raw-mix slurry.

Table 2: Analytical specifications of the OilQuant optimized for alternative fuels.

elements	concentration range [ppm]	LLD [ppm]
Na	0-500	5,4
Mg	0-500	2,6
Al	0-500	1,8
Si	0-500	1,9
P	0-2.500	1,5
S ppm level	0-500	1,2
S % level	0-5,5 %	2,4
Cl ppm level	0-500	2,6
Cl % level	0-2,5 %	5,7
K	0-300	1,5
Ca	0-6.000	1,2
Ti	0-500	0,9
V	0-500	0,8
Cr	0-500	0,8
Mn	0-500	0,5
Fe	0-500	1,2
Ni	0-900	0,6
Cu	0-500	0,6
Zn	0-500	0,7
Mo	0-500	1,6
Ag	0-500	6,3
Cd	0-500	6,6
Sn	0-500	3,3
Ba	0-500	3,7
Pb	0-500	0,8

The performance of the S4 EXPLORER is optimized for safe measurement of liquid samples. For example, when measuring liquid fuels (for example 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 spectrometer chamber and dropping 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 sample magazines (50 and more positions) and automatic, safe measurement routines of large sample measuring sets ensure a maximum of (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. **GCL**