Analysing AF Elements

Ravi Yellepeddi, Marc Dupayrat and Didier Bonvin, Thermo Fisher Scientific, Switzerland, provide an analysis of alternative fuels using XRF instrumentation.

Introduction

The use of alternative fuels in the cement industry has increased in recent years. In contrast to conventional fuels such as gas, fuel oil, coal and petcoke, alternative fuels are proving to be of significant advantage in terms of both economic and environmental impact. The cement industry is looking to reduce CO_2 emissions while also addressing the landfill issues of organic or inorganic waste and their combustion in dedicated incinerators.

One of the key factors that can influence the wider use of alternative fuels in cement kilns, apart from their calorific value and chemical interactions with the raw waste, is the concentration level of various elements, including toxic elements such as lead (Pb), cadmium (Cd), mercury (Hg) and thallium (Tl). In addition, chromium (Cr), cobalt (Co), nickel (Ni), vanadium (V), zinc (Zn), tin (Sn) and antimony (Sb) play an important role through their transfer mechanisms into the clinker and surroundings. Analysis and control of these elements in alternative fuels become imperative while the cement industry looks to benefit from their usage.

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Alternative fuels and their analysis issues

Alternative fuels can be organic or inorganic components in solid, liquid or high viscosity forms. Typical materials used as alternative 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.

Figure 1a. Thermo Scientific ARL OPTIM'X WDXRF.

Figure 1b. Thermo Scientific ARL QUANT'X EDXRF.

Very often they can be heterogeneous solids, pastes or liquids with an admixture of water and organic solvent. The sample taking, sample homogeneity and sample preparation are important factors for representative analysis.

X-ray fluorescence analysis (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. Depending on the accuracy and concentration limits needed to adhere to the environmental regulations or kiln equilibrium, it is possible to measure the samples using XRF without the need for sample preparation or dilution techniques. This technique is also used when controlling the transfer of some elements into clinker. XRF also covers a wide range of elements (from boron to uranium in solids and from sodium to uranium in liquids) and can detect their presence down to sub ppm levels depending on the analysis time and instrument conditions.

There are two types of XRF instruments: Wavelength Dispersive XRF (WDXFR) and Energy Dispersive XRF (EDXRF). While WDXRF instruments are used in central laboratories for more accurate and precise measurements across the periodic table, EDXRF instruments provide more flexible sample handling and quicker screening for medium to heavy elements. Generally, a vacuum environment is used for the analysis of solids, while helium flush is recommended for handling liquid samples. It is also possible to measure the samples under air in some cases.

However, it is very difficult to set up fully quantitative analysis programmes based on a set of reference materials. Since the nature of matrix, elements and their concentration range can vary significantly from sample to sample, it becomes a complicated and expensive task to set up specific calibration programmes in each case. Typical materials handled in the production of cement, such as limestone, clay, bauxite, iron ore, slags, gypsum, flyash, clinkers, cement and additives, can be analysed using well-established standards and matrix-specific programmes. Alternative fuels, on the other hand, do not always have matching standards or well-characterised type standards.

Such an analytical challenge can be overcome by the use of "standard-less" XRF analysis programmes. XRF, among all elemental analysis methods, has the distinct advantage of being able to handle any unknown material and quantify the elements present within the limits of sensitivity and standard errors. True calibration programmes offer more accurate analysis wherever possible, but the standard-less analysis approach breaks the barrier of matrix specific calibrations with well-prepared samples.

This article discusses the advancements in XRF instrumentation and analytical programmes designed to deal with alternative fuels to ensure simple and cost effective analyses.

Instrumentation

Figure 1a shows a WDXRF instrument (Thermo Scientific ARL OPTIM'X) with a direct loading

Contaminated sawdust.

Lignite.

Pips from grapes.

Organic solvents.

Figure 2. Typical samples of alternative fuels for analysis.

Figure 3. Disposable plastic cups used for the analysis of liquids or loose powders and preparation of pastes.

of sample in solid or liquid form with little or no peripheral dependence. No external water or gas is required depending on the configuration. The cost per analysis can be significantly low compared to other elemental analysis techniques. When equipped with a SmartGonio™, the instrument is capable of covering fluorine (F) to uranium (U) with increased sensitivity and lower limits of detection ranging from low to high atomic numbers.

Figure 1b shows a benchtop EDXRF instrument (Thermo Scientific ARL QUANT'X) that is transportable. Designed for flexible sample handling and easy operation, this instrument is equipped with a high performance Peltier cooled Si (Li) detector for reliable analysis.

Both the above systems can be programmed to handle alternative fuels via a Universal Quantitative Analysis package (Thermo Scientific UniQuant®). The UniQuant® programme uses unique XRF data processing methods and algorithms including matrix corrections for all types of samples. An "unknown" sample is measured with a pre-defined analysis programme covering most of the elements from F to U. The results are processed automatically to provide accurate quantitative analysis. The analysis time varies from 5 to 15 minutes, depending on the number of elements and their concentration levels. If only a few elements, such as toxic elements, are to be monitored, UniQuant® can be calibrated to reduce the analysis time down to a few minutes. The results can also be improved significantly by using one or two type standards, if available.

In addition to the analysis of alternative fuels, both these instruments can be used for routine analysis of oxides in cement materials either in a small cement plant or as backup in a big cement plant. They can also be used as backup instruments to a mainframe WDXRF instrument generally dedicated to process and quality control.

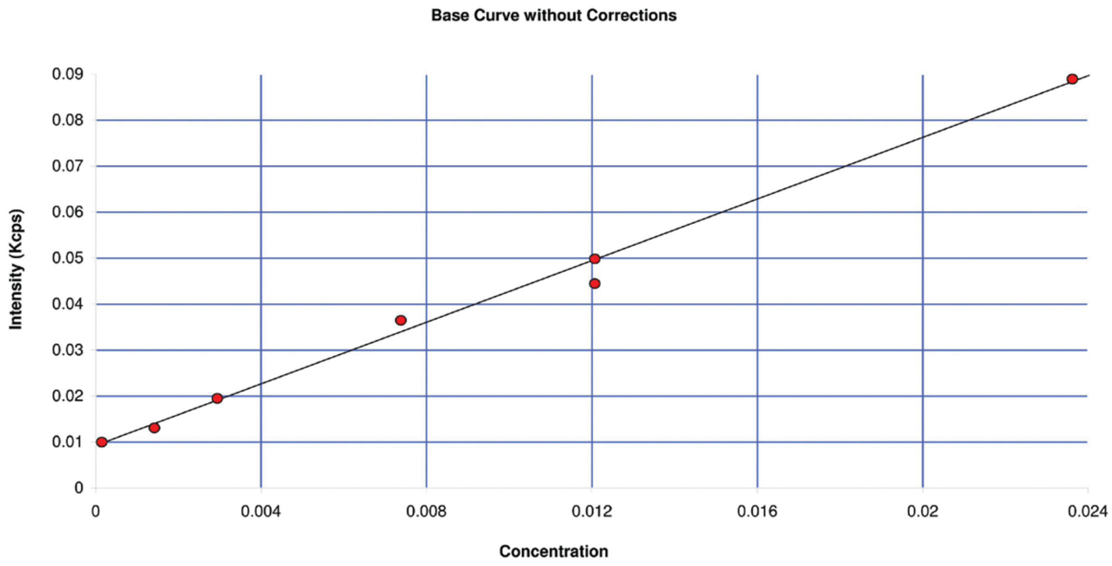

Figure 4. Calibration curve for Cl content using the ARL QUANT'X. 100 sec counting time. Range: 0 - 240 ppm. Residual error: 0.0015%.

Table 1. Analysis of chlorine in the same oil sample in five different cells using the ARL QUANT'X. 100 sec counting time

Sample X5: PCB in ppm	Cl level (ppm)
#1	119.5
#2	122.2
#3	120.5
#4	128.1
#5	126.5
Average (ppm)	123.4
Standard deviation (ppm)	3.8

Table 2. UniQuant® analysis on a wooden dust sample

Element	UniQuant®5
Cellulose	97.9
Ca	0.67
Si	0.72
Al	0.19
K	0.11
S	0.12
Fe	580 ppm
Ti	350 ppm
Mg	710 ppm
Cl	650 ppm
P	380 ppm
Zn	130 ppm
Ba	140 ppm
Pb	60 ppm
Mn	70 ppm
Sn	60 ppm
Ni	<10 ppm
Cr	<10 ppm
Sr	<10 ppm
V	<10 ppm

Results and discussion

Figure 2 shows typical samples for analysis. Liquids are analysed using disposable plastic cups as shown in Figure 3. However, the solvents will suffer from segregation and sedimentation with components of different density. This problem is avoided by using a coagulant powder to turn liquid into paste. The loose powders can be loaded directly using plastic cups with a polymer film underneath.

If the samples analysed are of the same matrix and fall within a given concentration range, it is possible to calibrate the instrument using suitable standards. One such example is shown in Figure 4 where chlorine from PCB of transformers is calibrated using the Thermo Scientific ARL OPTIM'X. Table 1 shows the repeatability of the same sample measured using five different cups. The results show excellent performance of the Thermo Scientific ARL QUANT'X for such samples and concentration levels.

Moreover, if the samples vary from one day to the next and the incoming materials for incineration in the kiln are of unknown origin, then programmes like UniQuant® provide an excellent method to analyse them.

Table 2 shows the typical analysis of a contaminated wooden dust sample analysed as an organic matrix. The UniQuant® programme produces quantitative results for all elements down to 10 ppm levels.

Most of the toxic and heavy elements can be detected down to a few ppm using the ARL QUANT'X. Table 3 shows typical limits of detection (LOD) obtained for various elements using ARL QUANT'X and measured under air.

In particular, when plastic or organic materials are analysed mainly for toxic elements, the ARL QUANT'X is capable of measuring them, as shown in Table 4.

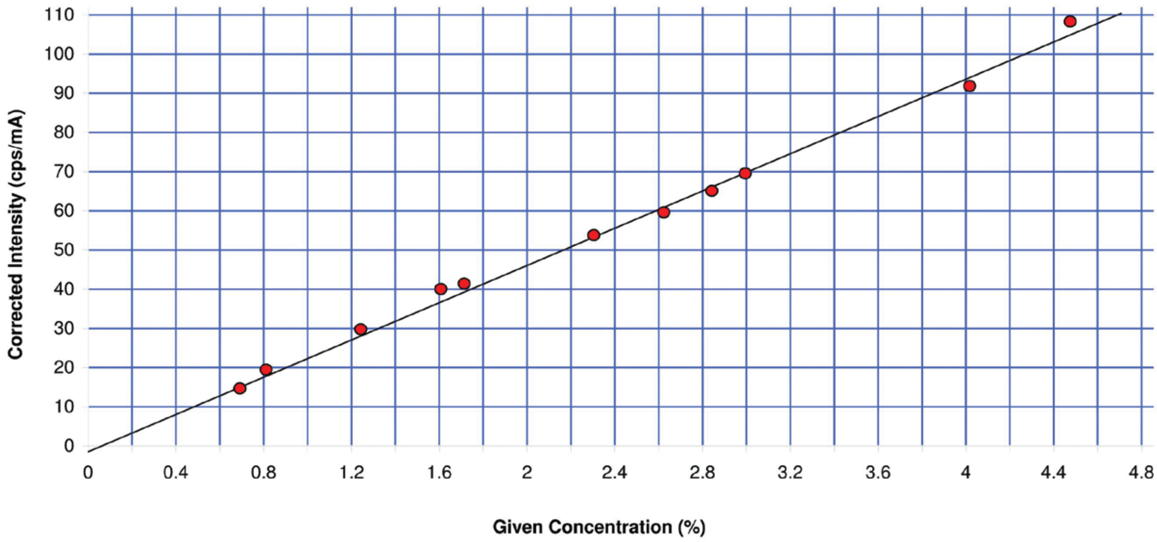

Figure 5. Calibration curve for Mg using the ARL QUANT'X in a series of cement samples.

As already mentioned, both ARL QUANT'X and ARL OPTIM'X can be used for routine analysis of oxides in cement materials either in a small cement plant or as a backup in a big cement plant, in addition to the analysis of alternative fuels. As an example, typical results for key oxides in cement materials are given here.

Figure 5 shows the calibration curve for Mg using ARL QUANT'X in a series of cement samples. Typical performances of ARL OPTIM'X are shown in Table 5 versus the required performance in terms of standard deviation.

Conclusion

Cost-effective XRF solutions have been presented to analyse alternative fuels incinerated in cement kilns. Both WDXRF and EDXRF instruments are designed to handle such a variety of samples in a simple and direct way.

Standard-less analysis programmes are developed to provide quantitative analysis on any unknown sample without the need for matrix-specific calibrations and standards. This alternative analytical technique has been shown to reduce time and effort in a cement plant compared to wet chemical and other elemental analysis methods. In addition, the same instrument can be used for the routine analysis of major and minor oxides, as backup to the cement process and for quality control.

Table 3. Limits of detection using ARL QUANT'X in organic liquids under air

Element	Limit of detection (ppm)
S, Cl	15
Ti, V, Cr, Mn, Co, Ni, Fe, Cu, Zn, As, Se. Ga, Ge, Br	<1
Hg, Tl, Bi, Pb, U	<1
Cd, Sn, Sb. Cd, I, Ba	<1

Table 4. Limits of detection for heavy and toxic elements in plastics using the ARL QUANT'X (500 s live time)

Element	Limit of detection (ppm)
Cr	2
Br	1
Cd	1.5
Hg	1.3
Pb	1.3

Table 5. Typical performance of the ARL OPTIM'X vs the required performance of standard deviation in cement related materials

Element/oxide	Concentration level	Required standard deviation	Analysis time (s)	Standard deviation
CaO	63.8	0.03 - 0.035	30	0.033
SiO_2	20.3	0.02	40	0.02
Al_2C_3	5.2	0.02	20	0.016
Fe_2O_3	2.8	0.01 - 0.02	10	0.014
MgO	1.7	0.02	30	0.024
Na_2O	0.2	0.015	10	0.007
K_2O	0.9	0.02	6	0.01
SO_3	3.2	0.01 - 0.015	20	0.013
P_2O_5	0.2	0.01 - 0.015	10	0.013
TiO_2	0.2	0.015	10	0.005
Mn_2O_3	0.1	0.015	10	0.003
			Total analysis time: 196 s	