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DETERMINATION OF CEMENT CONTENT OF CEMENT BLENDS USING GAMMA-RAY SPECTROSCOPY

C.G. Rowbottom,*[1] W.B. Gilboy,* and D.J. Hannant†
*Department of Physics and †Department of Civil Engineering, University of Surrey,
Surrey GU2 5XH, United Kingdom

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ABSTRACT

Samples of cement, ground granulated blast-furnace slag, and pulverised fuel-ash (PFA) were studied to determine their natural levels of radioactivity. A nondestructive test for the determination of the cement content of a PFA-cement blend was investigated with these samples using gamma-ray spectrometry. All tests were performed using a high-purity germanium detector. Several PFA-cement blends were sampled to establish the feasibility of the test and the linearity of the detector system used. Three blind tests were performed to independently evaluate the accuracy of the method. Two methods were used to calculate the blend proportions of the blind samples, and the cement content was consistently determined to within 5% of the actual content. © *1997 Elsevier Science Ltd*

Introduction

[1]Man has been exposed to radiation from the natural environment throughout history. This environmental, or, as it is often termed, "natural," radiation arises from three main sources: cosmic radiation, radiation from terrestrial sources, and radioactivity in the body itself.

The main source of terrestrial radiation comes from rocks and soil of the Earth's strata that contain small quantities of thorium, uranium, and potassium. These are all naturally radioactive elements with long decay chains for the two heavy elements that produce a large number of radioactive daughter products. The type of rock formation can greatly affect the concentration of these two elements; for example, sandstone and limestone regions contain much lower concentrations of these elements than granite regions (1).

Because each material may have a unique radiation spectrum, it is possible that such spectra can be exploited to solve some longstanding problems in the concrete industry. Typical problems are determining the quantities of the various constituents of a blended cement or even the cement content of concrete. Only the first problem is discussed herein, but the determination of the cement content of concrete is the subject of a continuing research study using a similar approach.

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[1] To whom correspondence should be addressed.

This paper, therefore, describes the techniques required to enable the radiation of materials to provide quantitative data of value to the concrete industry. Possible advantages over traditional approaches are that accuracy may be greater and that the origins of the various materials could also be established due to the distinctive radiation signatures of nominally similar materials from different sources.

Theory

Pakou and Assimakopolous (2) proposed a method for determining the cement content of a concrete mix via measurements of their natural radioactivity using gamma-ray spectroscopy. They found that the activity of cement was significantly higher than the activities of the other constituents of concrete, and this enabled the cement content to be ascertained. The samples of cement, aggregate, and concrete, were crushed, sieved, and dried before measuring the activity using a germanium detector with an efficiency of 22% at 1333 keV relative to a standard 76 mm × 76 mm thallium-activated sodium iodide, NaI(Tl), scintillation crystal. This enabled them to determine cement content with an accuracy in the range 5–8%.

The fraction by weight of cement in a concrete mix, R, can be deduced from a knowledge of the absolute activity per unit mass (specific activity) of concrete, cement, and aggregate, A_{con}, A_{cem}, A_{agg}, respectively, from the equation:

$$A_{con} = R \cdot \mathrm{A}_{cem} + (1 - R) \cdot A_{agg} \tag{1}$$

Hence,

$$R = \frac{A_{con} - A_{agg}}{A_{cem} - A_{agg}} \tag{2}$$

We have found (3) that PFA and GGBS have a substantially higher radioactive content than cement, so that Eqs. 1 and 2 can also be used to measure the fractional cement content, R_{cem}, of a PFA-cement blend, for example, using a similar equation:

$$R_{cem} = \frac{A_{blend} - A_{pfa}}{A_{cem} - A_{pfa}} \tag{3}$$

where A_{blend}, A_{cem}, and A_{pfa} represent the specific activities of the blend, cement, and PFA, respectively.

Radioactivity is defined as the number of nuclear disintegrations per unit time, and, in SI units, 1 disintegration per second (dps) = 1 Bq, hence specific activity is in Bq/kg. Radioactivity levels can be assessed in principle by measuring any of the characteristic radiations (alpha, beta, or gamma), but, in practice, gamma-rays are the most convenient because they suffer very little self-absorption compared to alpha- or beta-rays that enables large samples to be employed with minimal sample preparation. The gamma-ray detection efficiency generally falls well short of 100%, but for a specified sample-detector geometry and the same degree of self-attenuation at a given gamma-energy, the gamma counting rate is directly proportional to the activity of the sample. Thus, in Eqs. 2 and 3 above, only the relative specific activities need to be known and Eq. 3 becomes:

$$R_{cem} = \frac{C_{blend} - C_{pfa}}{C_{cem} - C_{pfa}} \tag{4}$$

TABLE 1
The More Intense Gamma-Rays Emitted by Daughter Products in The ^{238}U and ^{232}Th Decay Chains

^{238}U Decay Chain			^{232}Th Decay Chain		
Nuclide	E_γ (keV)	Yield (%)	Nuclide	E_γ (keV)	Yield (%)
Ra-226	186	4.0	Ac-228	339	9.3
Pb-214	242	7.6		911	22.0
	295	18.8		968	13.3
	352	36.6	Ra-224	241	4.2
Bi-214	609	41.2	Pb-212	239	43.1
	769	4.2	Bi-212	727	6.5
	935	3.2	Tl-208	511	8.1
	1120	13.6		583	31.0
	1238	4.3		861	4.3
	1378	4.7			

The percentage yield gives the number of gamma-rays emitted per 100 disintegrations.

It should be noted that both long decay chains pass through a step involving isotopes of radon, which is a noble gas; if this escapes from a sample to any appreciable extent, radioactive equilibrium is disturbed, which alters the ratio of the number of gamma-rays emitted from radionuclides above and below radon.

where C_{blend}, C_{cem}, and C_{pfa} are the measured counting rates per kilogramme at a specified gamma-energy for the blend, cement, and PFA samples, respectively.

Thus far, we have followed the method described by Pakou and Assimakopolous, in which any appropriate gamma-ray can be chosen from the decay chains available. In principle, the long decay chains headed by ^{238}U, ^{235}U, and ^{232}Th provide a profusion of gamma-rays plus the prominent 1460 keV gamma from ^{40}K, but in practice only ^{238}U, ^{232}Th-232, and ^{40}K gammas are sufficiently intense to be practical. Clearly, the most suitable radiations are those for which the differences are most pronounced. Table 1 lists the more energetic gamma-rays (above 100 keV to reduce self-attenuation) with yields per disintegration greater than 1% from the daughter products of ^{238}U and ^{232}Th; the 1460 keV gamma from ^{40}K has a relative yield of 10.7%.

It should be noted that both long decay chains pass through a step involving isotopes of radon, which is a noble gas; if this escapes from a sample to any appreciable extent, radioactive equilibrium is disturbed, which alters the ratio of the number of gamma-rays emitted from radionuclides above and below radon. The extent of radon escape and its effect on the gamma-ray spectrum can be gauged by comparison with a sealed source in which radioactive equilibrium is maintained. In practice, the effects of disequilibrium were found to be small. If necessary, radon escape can be ignored completely by choosing gamma-rays from radionuclides that precede radon in the decay chains; this restricts the choice to ^{228}Ac or ^{224}Ra in the ^{232}Th decay chain, and to ^{234}Th, ^{230}Th, and ^{226}Ra in the chain headed by ^{238}U.

The three decay series of ^{238}U, ^{232}Th, and ^{40}K are all completely independent of each other, so a second method for determining the relative amounts of up to three components in a mixture involves solving simultaneous equations. For example, in the case of a two-component blend, such as cement and PFA, for a given counting time we have:

$$X = aA + bB \tag{5}$$

$$Y = cA + dB \tag{6}$$

where X is the net count in gamma peak 1 (from decay series 1) for the mixture, Y is the net count in gamma peak 2 (from decay series 2) for the mixture, a and c are net counts per kilogramme for the cement sample for peaks 1 and 2, b and d are net counts per kilogramme for the PFA sample for peaks 1 and 2, and A and B are the respective cement and PFA contents (kilogramme) of the sample.

Solving this pair of simultaneous equations we find:

$$A = \frac{dx - bY}{ad - bc} \tag{7}$$

$$B = \frac{aY - cX}{ad - bc} \tag{8}$$

This analysis assumes that self-attenuation factors are the same for the two components.

Method

To illustrate the principles outlined above, it is first necessary to select gamma peaks representing the two long decay chains (4) and ^{40}K (see Table 1). For the complex spectra emitted by the decay chains headed by ^{238}U and ^{232}Th there are many peaks to choose from, but on the basis of peak intensity and good signal to background ratio, peaks at 352 keV (from ^{214}Pb) and 609 keV (from ^{214}Bi) were chosen from the ^{238}U decay chain, and the ^{232}Th chain was represented by the peak at 239 keV (^{214}Bi). ^{40}K offers the prominent 1460 keV peak.

The requisite energy resolution was provided by a coaxial Canberra high-purity germanium (HPGe) detector; at the standard ^{60}Co energy of 1333 keV, this has an energy resolution of 2.3 keV, a peak to Compton ratio of 52.5:1, and a detection efficiency of 17.2% relative to a standard 76 mm × 76 mm NaI(Tl) scintillation detector. The HPGe crystal is surrounded by a 10-cm thick lead shield to reduce the ambient background. A Nuclear Data ND66C multichannel analyzer with 4096 channels was connected to the detector via a low noise-shaping amplifier to record the pulse-height spectra obtained. The gamma spectra were downloaded to a Unix computer network and the peak search program SAMPO (5) was employed to locate the gamma peaks. A typical spectrum is shown in Figure 1 where it can be seen that the full-energy peaks are situated on a slowly varying continuum that arises from Compton-scattered gamma-rays in and around the detector. SAMPO computes the net counts in each peak above this continuum. It is also necessary to correct for background counts registered by the detector in the absence of a radioactive sample; in this case a sample of deionised water was placed in the sample container and a background spectrum recorded (Fig. 2). This is particularly important because the general environmental gamma-ray background also consists mainly of gamma radiations from ^{238}U, ^{232}Th, and ^{40}K daughter products.

To optimise the absolute detection efficiency, samples were filled into a specially designed

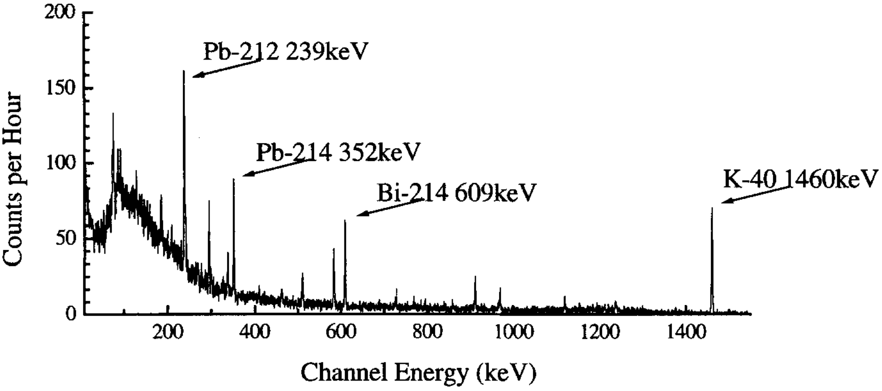

FIG. 1.
The gamma spectrum for the cement sample (4-h count).

Marinelli beaker that makes optimum use of the space available around the detector within the shield. It enables a large volume of material to be sampled (about 2 L) and so reduces the counting time to achieve a given statistical precision. The outside section of the beaker was made from Dural and the centre section surrounding the detector was formed from a thin-walled plastic pot to minimise the gamma-ray attenuation. Figure 3 shows the shape and dimensions of the Marinelli beaker; in some trial runs it was filled to increasing depths above the endcap of the HPGe detector and the integrated peak counts were found to level off above about the 12-cm fill depth due to the combined effects of self-attenuation and the inverse square law; if the self-attenuation does not vary much between the constituents these maximum counting rates are proportional to their specific activities and can be used in Eqs. 3, 5, and 6 above.

Samples of cement, PFA, and GGBS were sampled in turn on the detector to determine the counting rates in the chosen peaks for the standard 12-cm fill depth geometry and the counts

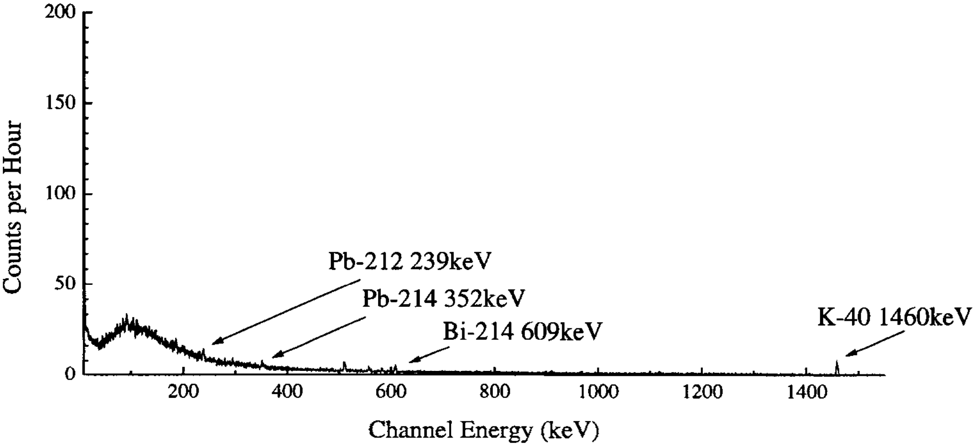

FIG. 2.
The background spectrum for the HPGe detector (8-h count).

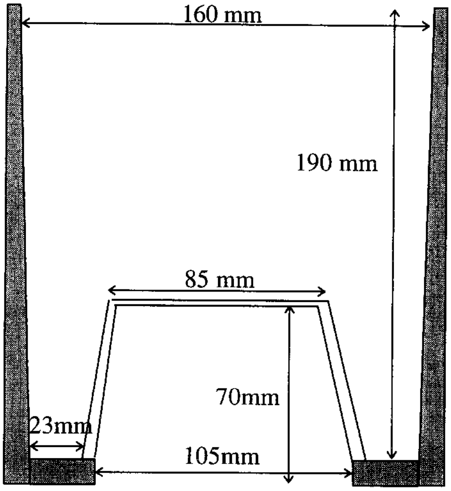

FIG. 3.
Dimensions of the Marinelli beaker.

per kilogramme per hour derived for each sample. To reduce the statistical error in the net peak areas to less than 5%, samples were counted for 4 h. Various blends were also sampled for 4 h in the standard geometry and a range of known PFA-cement ratios were studied to establish the linearity of the experimental system. The blends were prepared by weighing the cement and PFA required for a given blend separately and then mixing thoroughly in a large plastic bag to avoid dust emissions. The colour of the cement and PFA used were significantly different, and this helped to ensure the samples were mixed homogeneously by shaking the bag until the colour of the blend was uniform.

Two separate methods were used to determine the cement content of a PFA-cement blend. These methods are outlined below.

Method A uses the simple peaks ratio method described by Eq. 3 to determine the percentage of cement in the blend. For the HPGe detector, the 239 keV, 352 keV, 609 keV, and 1460 keV peaks were all used to calculate the percentage of cement for each individual peak and then a weighted average was taken to give a final result.

Method B uses Eqs. 7 and 8 to calculate the cement and PFA contents. Data for the 239 keV, 352 keV, 609 keV, and 1460 keV peaks were input to the equations in the following pairs: 239 keV and 352 keV, 239 keV and 609 keV, 239 keV and 1460 keV, 352 keV and 1460 keV, and 609 keV and 1460keV. This gives five independent peak pairs that yields five independent measurements for the amounts of cement and PFA. This method requires the values for the number of counts per kilogramme of each constituent at a particular peak energy (a, b, c, d) in Eqs. 5–8 to be ascertained. In practice, proportionate values were obtained by filling the Marinelli beaker to the standard depth as was used in the PFA-cement blends. From 2-h runs, the number of counts per kilogramme per hour for each peak and each mixture was calculated and then substituted into Eqs. 7 and 8.

Three additional "blind" samples were prepared by a colleague. The only prior information on these samples was that they contained PFA and cement, but the proportions of these constituents were not known. The same two methods as used previously were employed to

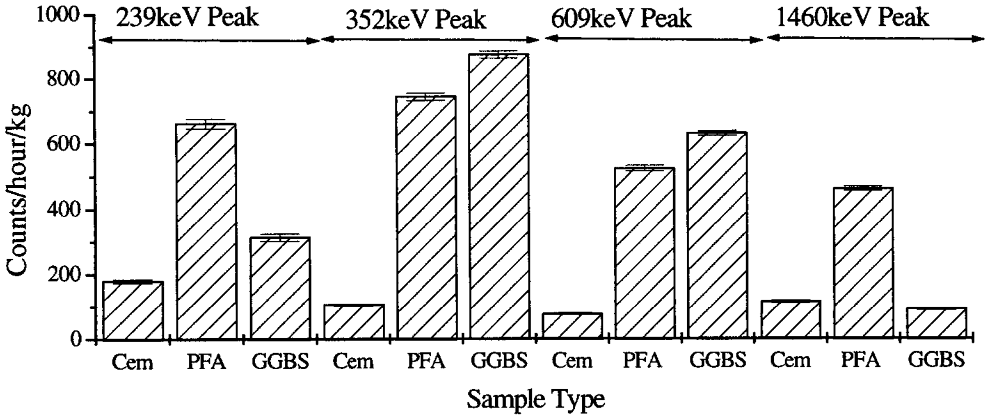

FIG. 4.
The number of counts per hour per kilogramme with the HPGe detector for the peaks at 239 keV, 352 kev, 609 keV, and 1460 keV.

calculate the blend proportions. The three samples were simply labelled "blind A," "blind B," and "blind C."

Results

Figure 1 is an example of the spectra obtained using the HPGe detector for the cement sample, with the ordinate giving the number of counts per hour per energy channel; the channel width was set at 0.377 keV. Figure 2 is a background spectrum and is included to give an impression of the quite measurable activity of the cement.

Figure 4 gives the counts per hour per kilogramme for peaks at 239 keV, 352 keV, 609 keV, and 1460 keV for the cement, PFA, and GGBS in the standard geometry. This shows the larger activity of the PFA and GGBS compared to the cement.

Figure 5 is a 3-D plot derived from the 1460 keV peak data. The range of PFA-cement blends sampled is plotted with the amount of PFA on the x axis, the amount of cement on

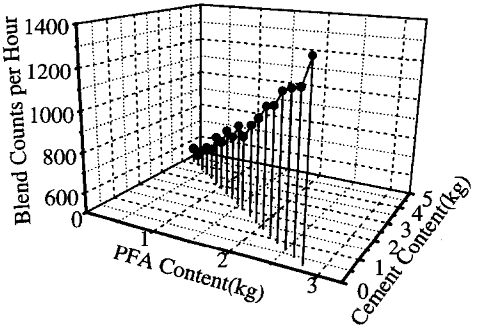

FIG. 5.
3-D plot of results based on the 1460 keV peak from ^{40}K.

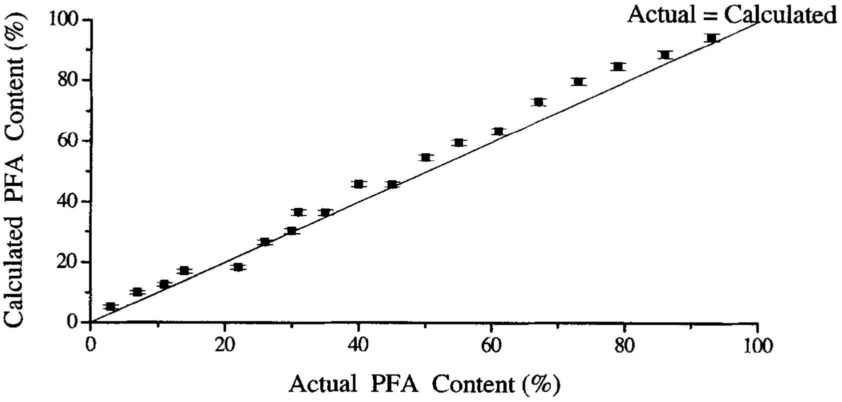

FIG. 6.
Actual PFA (%) vs. calculated PFA (%) by Method A.

the y axis, and the number of counts per hour for the PFA-cement blends on the z axis. It can be seen that the counts increase consistently with the increase in mass of the two constituents.

Figure 6 is a plot with the actual percentage mass of PFA in the blend as the abscissa and the calculated percentage mass of PFA from values derived from Method A as the ordinate. The full line indicates equality between the calculated and actual masses, and it can be seen that there is good general agreement, but the calculated PFA content tends to slightly exceed the actual content at higher PFA percentages.

Figure 7 is similar to Figure 6 for results derived from Method B, but in this case actual and calculated masses are plotted. Again, the line of equality is shown, but with Method B, there is a tendency for the calculated mass of PFA to be less than the actual mass. The small but systematic over- or underestimates shown in Figures 6 and 7 are probably related to small differences in self-attenuation in the two constituents.

This is also shown in Table 2, which gives both the cement and PFA contents of the three

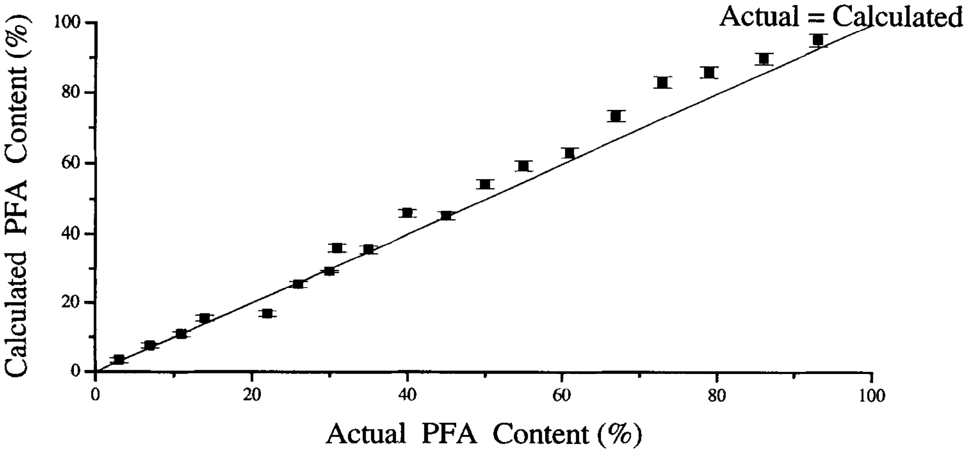

FIG. 7.
Actual PFA (kg) vs. calculated PFA (kg) by Method B.

TABLE 2
Percentage by Mass of Cement and PFA in Three Blind Samples Derived by Two Independent Methods

	Actual Constituents		Method A		Method B	
Sample	Cement %	PFA %	Cement	PFA %	Cement %	PFA %
Blind A	56.1	43.9	51.1 ± 1.6	47.5 ± 1.2	67.1 ± 4.3	32.9 ± 2.6
Blind B	82.1	17.9	79.8 ± 1.7	18.0 ± 0.8	89.5 ± 6.1	10.5 ± 1.2
Blind C	42.6	57.4	38.1 ± 1.6	60.9 ± 1.3	46.4 ± 9.1	53.6 ± 5.9

blind samples and the independently calculated values derived from both methods of calculation. All values are percentage by mass.

Conclusions

The activities of cement, GGBS, and PFA are all significantly above the general background level, with PFA and GGBS having higher activities than cement. GGBS has a comparable amount of ^{40}K to cement, whereas PFA is substantially higher, providing a simple method for determining whether a blend contains GGBS or PFA. These experiments have shown that there is a unique specific activity signature for a PFA-cement blend and that the system linearity is good. This provides a method for determining the PFA and cement content from such a blend by the use of gamma-ray spectroscopy. Figures 6 and 7 show that both methods are capable of determining the cement content of a PFA-cement blend over a wide range of cement content. From Table 2, it can be seen that Method A is more accurate than Method B, however, in determining both PFA and cement contents. Both methods used to calculate the blend proportions have smaller errors when finding the PFA content of the blend than the cement content. This is due to the higher activity of the PFA compared to the cement sample, so there is a higher sensitivity to changes in the PFA content. It would therefore seem sensible to determine the PFA content and infer the cement content. The current methodology would also be effective at predicting the contents of any other cement blend containing up to three components, as long as the proportions of the three radioactive constituents are sufficiently distinctive.

The techniques described here rely on self-attenuation factors for various constituents being equal, which is not always the case. It is possible to correct for differences in attenuation, which should reduce systematic errors; further work is in progress along these lines. With a sampling time of 4 h, the current HPGe detector system can adequately determine the cement and PFA contents of the PFA-cement blends to within 5% of the actual contents using Method A. By employing a more efficient detector, this time could be greatly reduced without loss of statistical accuracy, which could be achieved by employing a larger HPGe detector; crystals up to 10 times the sensitive volume of the detector used here are now commercially available. A lead shield with a larger internal diameter would also improve the geometric efficiency. With such an optimised system measurement, times of a few minutes are in prospect, which would be a considerable advantage if the technique can be extended to check the cement content of concrete as it arrives on site and before it is placed.

Measurement time is of less significance for testing blended cements where the material may be stored for several days before use.

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