Suggested Method for X-Ray Emission Spectrometric Analysis of Portland Cement By the Energy-Dispersive Technique

Introduction

This is a standard pressed powder method using an X-ray tube for excitation in an energy dispersive X-ray spectrometer. Nuclear sources are also used with energy dispersive units. In an energy dispersive unit, wavelengths (energies) characteristic of all elements plus scattered radiation from the X-ray source are detected simultaneously by the same detector. Radiation characteristic of the various elements is then separated electronically and measured. The two previous methods used so-called wavelength dispersive optics, whereby the radiation characteristic of each element is physically separated by Bragg diffraction using separate crystals and detectors for each element.

This would appear to give a strong advantage to the energy dispersive approach in that much closer coupling of source-sample-detector can be achieved, resulting in much higher intensities for a given X-ray input than are available with wavelength dispersive optics. While this effect is real, it is not necessarily an advantage because of available detectors. These systems use solid-state lithium-drifted silicon detectors, most of which have to be cooled to liquid nitrogen temperature to operate with good resolution and low noise. Even so, the energy distribution resulting from the lightest elements of interest, specifically sodium through sulfur in the periodic table, overlap and must be mathematically separated based on assumed energy distributions. Another difficulty is that these detectors, as is the case with all detectors now available, saturate at count rates of 20 000 to 50 000 counts per second. That is, energy pulses are received faster than the detector can recover so as to accurately receive and measure the energy of the next pulse. This problem, again, is normally gotten around with a mathematical correction, based on assumed detector performance. A third difficulty is precision. The precision of a measurement in X-ray for a given element is, for large numbers of counts, equal to $\sqrt{1/n}$ where n is the number of counts collected from that element. Calcium oxide constitutes the vast majority, 60 to 70%, of portland cements and clinkers with the oxides of the other elements in lesser proportions. Calcium also has a high excitation potential in the system normally used and is readily detected. Consequently, some 75 to 85% of the total radiation from the sample seen by the detector

will be from calcium, with the remainder being from all other elements. In order to obtain adequate precision for minor and trace elements, one must either cut the intensity of the excitation radiation to stay within the optimum operating conditions of the detector and extend analysis time proportionately or provide another mathematical correction based on assumed conditions. A fourth correction to the data is then required to get final analytical results. These are the typical interelement corrections wherein the measured intensities or concentrations are corrected for each of the other elements and their quantities. Usually an iterative procedure will be used, repeating the calculations until the concentrations of each element "close" on a single value; that is, the change resulting from an iteration is negligible. All of these calculations are provided automatically by the analytical system.

This approach works quite well for a sufficiently narrow range of composition as, for example, a cement from a single source, and is highly applicable to routine quality control situations. Investigators have reported difficulties, however, with analysis of unknown samples. One can expect this situation to improve over the next several years with the rapid advances in solid-state technology. Improved detectors with better energy resolution and faster response eventually should eliminate the need for so many assumptions, each of which has a precision and a bias.

Editor