



SAMPLE PREPARATION AND ANALYSIS TECHNIQUES

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Introduction

Cement has become one of the most thoroughly characterised commodities, with the product and its ingredients analysed before, during, and after its manufacture. Elemental analysis is critical at all stages of cement manufacturing, particularly when monitoring the raw materials, such as limestone and chalk, for a desirable balance of Ca, Mg, and Si, as well as unwanted elements like Fe, Na, and S that

can rapidly degrade concrete. The many types of cement have specific ranges and limits for elemental composition, as attested by ASTM methods, and seen in NIST and European analytical standards. Additives like slag, and flyash must also be screened for elements harmful in the finished product. The composition of cement products also affects their short-term and long-term performance, environmental compatibility and risk. This raises questions that must be answered.



Muffle furnace.



The K1-Prime

dissolving the samples in molten lithium borate flux. Borate fusions rapidly dissolve almost all samples associated with cement and concrete (silicates, oxides, phosphates and sulfates) and the resulting glass disks are, in effect, solid solutions with the analyte elements dispersed evenly throughout. Particle size effects, mineralogical effects and other handicaps of pressed powder disks are absent. In general, if a sample can be prepared with borate fusion, analytical accuracy and consistency are both improved. The fusion process is effective and rapid, taking only about 6 minutes to dissolve one sample; modern fusion systems can simultaneously fuse several samples.

Innovations in analytical chemistry and geochemistry

Borate fusion using lithium-based fluxes was first established in the early 1960s as a means of fusing natural and industrial materials. The technique allows a wide range of sample matrices (e.g. cement, ores and minerals, sludges, slags and soils) to be prepared for downstream elemental analysis in testing labs.

The rapid expansion of geochemistry from the 1960s onward was linked to advances in wavelength dispersive X-ray fluorescence spectrometry (WDXRF). In the 1970s, researchers pioneered the application of borate fusion to rapidly dissolve geological samples to produce homogeneous fused beads or glass disks by casting the melt into a platinum alloy dish. The WDXRF method was ideally suited to measure 50 or more elements on the glass disks produced.

With the advent of inductively coupled plasma spectrometry (ICP-OES and ICP-MS), analysts used lithium borate fusions in a number of ways.

They sometimes poured the melt into water to rapidly quench and fragment the glass. This fragmentation enhanced the speed of subsequent acid dissolution of the borate glass and allowed diluted solutions to be measured on the ICP instruments.

In its early days, the borate fusion of materials was largely achieved using manual handling and gas burners or electric muffle furnaces. Current systems still employ gas or electrical heating but are considerably more sophisticated and enable a high degree of automation. Electrical heating systems are considerably more attractive than gas-based systems for hazardous environments such as nuclear sites.

Innovations in radioactivity analysis for concretes and other materials

Given the beneficial characteristics of borate fusions, Professor Ian Croudace, Head of GAU-Radioanalytical Laboratories, recognised its potential and pioneered

How long will concrete last in specific environments? As concrete degrades, what does it release into the local ecosystem? Also, when concrete has been exposed to industrial contaminants, or nuclear radiation (particularly neutrons and charged particles), how should it be tested before being returned to the earth as landfill?

The chief method of elemental analysis for cement and cement products, from their beginning to their end, is XRF. Sample preparation is critical for accurate, quantitative XRF analysis. The recommended particle size for most powdered samples is 10 µm or less, which improves results for lighter elements. However the optimum particle size range for most samples is determined empirically.

Though many kinds of samples are still pressed as powders, cement and cement-related materials are increasingly being prepared as glass disks, made by

its application for the rapid dissolution of radioactive samples. This recognition came from a crossover insight from more than 25 years of research experience in geochemistry, XRF analysis and radioanalytical chemistry.

The first reported application of borate fusion in radioanalytical sample preparation related to a 1996 GAU research contract that required the rapid isotopic analysis of Uranium (U) and Plutonium (Pu) in 650 soil samples within a tightly defined three month deadline. This complex and high profile study focused on investigating ground contamination from alleged damage to a nuclear weapon at the former USAF airbase at Greenham Common, near Newbury in the UK. Prior to this work, radioanalytical specialists would traditionally have used one or more

sample digestion approaches to extract U and Pu (and other elements with radioactive species) from soils. The traditional methods were slow and often potentially hazardous, using hydrofluoric acid attacks or fusions with alkali fluorides, carbonates and peroxides.

Following on from the 1996 study, Professor Ian Croudace along with colleague Professor Phil Warwick, who manage GAU-Radioanalytical Laboratories, continue to use borate fusion for sample dissolution procedures. As a major provider of waste characterisation services to the nuclear decommissioning sector, GAU has continued to spearhead the application of borate fusion technology, including the use of automatic Katanax fluxers. Fusion is used in several of its accredited (ISO17025) procedures and serves to enable safe and effective extraction of many radionuclides from complex nuclear site sample matrices.

In addition to the long list of traditional applications within the cement, glass and ceramic industries, borate fusion fluxer devices have been shown to be effective in rapidly dissolving radioactive materials. Nuclear sites currently undergoing decommissioning have significant volumes of construction materials (including concrete) that may have become contaminated with radionuclides. Borate fusions have sped up the time to effectively dissolve complex materials, even where large samples are required to be digested. After dissolution and analysis, radioactive contamination data is used to guide the appropriate disposal route.

Fusion fluxers in the modern cement production QC lab

Katanax®, a SPEX® SamplePrep company, offers a range of instruments, designed for efficient borate



The X-600

fusion, including the K1 Prime, which uses electric heating elements to control temperature. The instrument is simple to use and fully automated, allowing the operator to walk away and collect samples once the cycle is complete. Katanax has also recently introduced a six position X-Fluxer®, the X-600, which is designed for higher throughput applications in cement production labs. The system utilises durable, ceramic components that are easy to clean, with heating achieved using robust sealed elements that are impervious to flux. The system is controlled by a graphic interface that is fully programmable and customisable.

Bryan Liston, Quality Manager of Irish Cement Limerick, which is part of the global buildings material group CRH, explains that “for the past 20 years Irish Cement has used the fused bead method of sample preparation for XRF technology to control its chemical process. This method of sample preparation forms part of the XRF Analysis Policy in all the CRH cement plants worldwide. This is due to its ability to eliminate the mineralogical effects that are a source of XRF analysis error.”

“To improve efficiency in its chemical Laboratory, Irish Cement Limerick had been on the lookout for an electric, multi-position fused bead machine. A machine that would be safe to operate, give an accurate and stable temperature, have the ability to make up to six fused beads at a time and, unlike enclosed furnaces, will not suffer internal chemical attack from the use of anti-wetting agents, like KI and LiBr”.

“We believe the X-600 Electric Fluxer will satisfy all these conditions and, very importantly due to its unique Halide venting system (positioned over each of the fusion stations), will not suffer breakdown due to chemical attack.”

Note: Examples of radioanalytical applications

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