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On-Line and Bulk Analysis for the Resource Industries

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SUMMARY

Nuclear techniques are the basis of many CSIRO on-line and bulk analysis systems that are now widely used in the mineral and energy industries. The continuous analysis and rapid response of these systems have led to improved control of mining, processing and blending operations. This paper reviews recent developments in neutron, gamma-ray and X-ray techniques for on-line and bulk analysis by CSIRO Minerals including neutron techniques for the on-conveyor belt determination of the composition of cement raw meal, the on-line analysis of composition in pyrometallurgical applications, the on-conveyor belt determination of ash in coal, and the rapid and accurate determination of gold in bulk laboratory samples. The paper also discusses a new gamma-ray technique for the on-line determination of ash in coal and the application of X-ray diffraction techniques for the on-line determination of mineralogy in the cement industry.

1. INTRODUCTION

There is an increasing need in industry to reduce costs and improve product quality through the increased use of automation. The application of on-line analysis techniques in the mineral and energy industries opens up new possibilities for improved process control. The practice of manual sampling followed by laboratory analysis is slow, labour-intensive and has the potential to significantly increase sampling error. By contrast, on-line analysis systems improve control by providing rapid and accurate analyses in real time. As a result, there has been a rapid increase in the industrial application of on-line analysis instrumentation over the last 25 years, particularly in the mineral and coal industries. CSIRO Minerals has been actively involved in this field through the development, field testing and commercialisation of on-line analysis systems based on nuclear, microwave, ultrasonic and optical techniques (1). A number of Australian and overseas companies are marketing the systems worldwide.

The present paper reviews recent developments in neutron, gamma-ray and X-ray techniques for on-line and bulk analysis by CSIRO Minerals. The paper discusses neutron/gamma techniques for the on-conveyor belt determination of the composition of cement raw meal, the on-line analysis of composition in pyrometallurgical applications, the on-conveyor belt determination of ash in coal and the rapid and accurate determination of gold in bulk laboratory samples. In addition the paper reviews the development of a new gamma-ray method for on-line determination of ash in coal and the development and application of X-ray diffraction techniques for the on-line determination of mineralogy in dry powders.

2. NEUTRON TECHNIQUES

Elemental neutron/gamma analysers rely on neutrons interacting with atoms present in the target material and producing gamma rays with energies characteristic of the emitting nuclei. Subsequent detection of these gamma rays allows the elemental composition of the material to be inferred. The two most important nuclear interactions are thermal neutron capture (TNC) and neutron inelastic scattering (NIS). TNC occurs when a low energy neutron is absorbed by a nucleus. NIS takes place when a fast neutron collides with a nucleus.

Most commercial analysers use ^{252}Cf neutron sources together with sodium iodide (NaI(Tl)) detectors and are mainly sensitive to TNC reactions. The analysers developed by CSIRO Minerals use ^{241}Am-Be sources and bismuth germanate (BGO) detectors. The higher energy neutrons produced by the ^{241}Am-Be source allow both TNC and NIS reactions to be used for elemental detection. NIS reactions are particularly useful for elements such as C, O, Al and Si, which have a small neutron capture cross-section. BGO detectors, whilst having a lower resolution at room temperature than NaI, have a higher photopeak efficiency, particularly for high-energy gamma rays. Tests have shown that cooling can significantly improve the resolution of BGO detectors. For example, the FWHM resolution at 662 keV of one BGO detector improved from 10.3% at +15°C to 8.2% at -20°C (2).

2.1 On-Belt Elemental Analyser for the Cement Industry

In a cement plant, the various components in cement raw mill feed (limestone, shale, iron ore, etc.) are typically fed onto a conveyor belt in sequence prior to milling and subsequent firing in a kiln. The on-belt elemental analysis of this raw mill feed would enable improved control of raw mix chemistry in cement plants. Compared to sampling and subsequent laboratory analysis, plant control is improved as timely on-belt measurements allow real time control action. In the cement industry, plant control is based on parameters that are calculated from the proportions of calcium, silicon, aluminium and iron in the raw mill feed. Elements of secondary importance are magnesium, sulphur, chlorine, sodium, titanium and potassium.

In 1997 Fuel & Combustion Technology (FCT)[1] commenced work on *Mastermind*, a cement plant control system integrating a series of novel on-line analysers with sophisticated control software. As part of *Mastermind*, CSIRO Minerals developed a new and improved neutron/gamma on-belt elemental analyser XENA (X-belt Elemental Neutron Analyser) for cement raw mill feed, capable of accurately measuring key elements independently of both horizontal and vertical segregation and independently of changes in belt loading.

Prior to finalising the gauge design for plant testing, laboratory tests were performed to test design concepts and to compare results with Monte Carlo predictions. The laboratory tests were performed using 100 synthetic samples and 25 plant samples from the Adelaide Brighton Cement plant at Birkenhead, South Australia. The samples were measured over a range of depths between 80 and 200 mm. The results of the laboratory tests showed that the gauge was capable of accurately measuring the proportions of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, Cl, K_2O and TiO_2 in both the synthetic and plant samples (2).

XENA is in two halves, each containing a 370 GBq (10 Ci) ^{241}Am-Be neutron source and two 76 mm diameter x 76 mm long (BGO) detectors in a transmission configuration (Figure 1). The use of multiple detectors and sources provides much reduced sensitivity to non-uniformity of composition both vertically and across the conveyor belt. An additional BGO detector was positioned to estimate the material thickness by measuring the attenuation of the 4.43 MeV gamma rays produced by the source as they pass through the material on the belt. A Teflon slider plate supports the belt within the gauge. The detectors are mounted in two sealed cavities that are cooled using recirculating refrigerant systems to about -20°C to improve the detector resolution and thus signal-to-noise ratio.

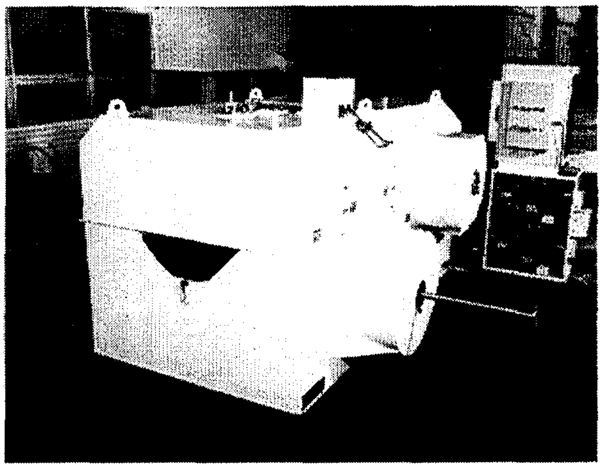

Figure 1. Photograph of XENA at CSIRO Minerals prior to being installed at Adelaide Brighton's Birkenhead cement plant in South Australia.

XENA was successfully installed on the cement raw mill feed belt at the Adelaide Brighton Cement plant at Birkenhead in March 1999. Material on the belt at the XENA location is segregated both horizontally and vertically. Dynamic tests in the plant on highly segregated material having depths in the range 100 to 200 mm have shown analyser total RMS (root mean square) errors of 0.49, 0.52, 0.38 and 0.23 wt.% (on a loss free basis) for CaO, SiO_2, Al_2O_3 and Fe_2O_3 respectively, when 10-minute counting periods are used (0). Since installation, the analyser has performed well during on-line tests. Stability has been excellent and the measurements from XENA have closely tracked the post-mill sampler XRF results.

In summary, XENA has the following features:

- The choice of both NIS and TNC gamma rays. Compared to instruments that use only TNC gamma rays, improved performance can be obtained for those elements such as Al, Si and Mg where NIS gives better results.
- Good spatial uniformity
- Calibration demonstrated over a wide depth range (at least 80-200 mm)
- Relatively low source costs and more stable neutron output over long periods due to the use of long life radioisotope sources.

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2.2 Bulk Elemental On-Line Analysers for Pyrometallurgy

On-line monitoring of pyrometallurgical processes is often difficult because measurements need to be made on hot materials (at 1000°C or higher) in circumstances where representative sample streams are not readily accessible. Most conventional monitoring techniques are based on the insertion of a probe into an environment so hostile that the probe can only be used once or twice. CSIRO Minerals has developed a non-intrusive nuclear analyser METRA (METallurgical Real-time Analyser) for continuous real-time measurement of elemental composition (3). METRA is based on the NIS technique, which allows many elements to be measured simultaneously and quantitatively, is independent of sample temperature and is capable of measurements through the walls of hot vessels.

There are three choices of location for METRA. The first is on the side of a hopper or large process vessel; the key requirement in this case is to ensure that the flow of ore adjacent to the gauge is representative of the total flow. A second option is to locate the analyser around a pipe. The third alternative is to automatically extract a bulk sample from the process, analyse the sample in METRA and then return the sample to the process stream. This approach has the advantage that the analyser can be located anywhere in the plant where there is a suitable exit point for the sample but the disadvantages of sample handling issues and the need for representative sampling from the process stream.

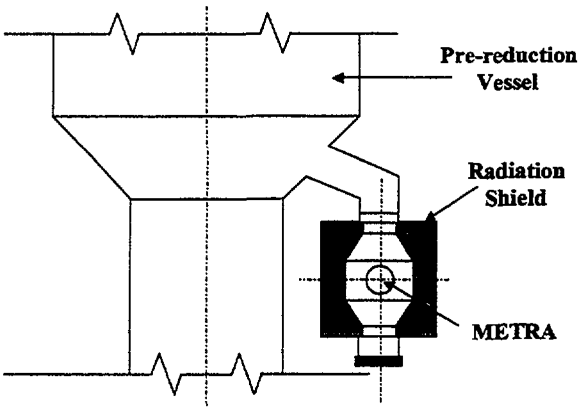

Figure 2. Schematic diagram of the NIS gauge METRA installed on a plant in Western Australia.

New technologies such as direct reduction and smelting reduction processes are increasingly being used in iron-and steel-making in addition to conventional blast furnace technology. Critical parameters for control of these processes include the degree of metallisation, degree of pre-reduction, and carbon and silica levels. The first plant prototype of METRA was tested on a new iron-making direct reduction and smelting process. A bulk sample of hot (~1000°C) pre-reduced feed to the smelting vessel was automatically extracted from the process and analysed in METRA (Figure 2). Accuracies of 1% relative, 0.5 wt.% and 1.0 wt.% were obtained for the degree of pre-reduction (a key parameter related to the ratio of Fe to O), carbon and silica respectively (4).

2.3 On-Belt Analysis of Coal

The accurate on-belt determination of ash in coal is required in a wide range of applications in the coal industry, including mine grade control, raw coal monitoring, coal sorting, coal preparation plant control, product blending, stockpile management, power station feed, monitoring and blending, and monitoring at coal shipping ports (1). A number of independent studies have estimated the benefits of on-line ash analysis to average more than $500,000 per year per installed gauge. Commercial analysers currently available include those based on dual energy gamma-ray transmission (DUET), pair production (PP) and Prompt Gamma-ray Neutron Activation Analysis (PGNAA) analysers. However, all these analysers have limitations. The DUET gauges are sensitive to changes in ash composition and only measure a relatively small proportion of the coal on the belt. The PGNAA and PP gauges primarily operate on sample by-lines and are therefore expensive and subject to sampling error.

CSIRO is developing a new and relatively simple neutron-and-gamma-ray analysis system for the direct on-conveyor belt bulk analysis of ash in coal (5). The analyser simultaneously measures NIS and TNC gamma rays from bulk coal samples on conveyor belts and incorporates a method for ash measurement that is independent of changes in segregation or belt loading. As a result, the new system provides greater accuracy than on-belt DUET gauges at a much lower cost than by-line PGNAA analysers.

A laboratory prototype gauge has been developed comprising an ^{241}Am-Be neutron source and multiple BGO detectors. Measurements on 25 bulk (about 70 kg each) coal samples of ash content from 8 to 31 wt.% and thickness from 100 to 300 mm have shown that the gauge can achieve calibration and cross-validation RMS errors of between 0.46 and 0.55 wt.% ash using spectral window count rates and either multiple linear regression or artificial neural net techniques. However, the standard deviation of the chemically measured ash values from which the gauge is calibrated has been estimated to be 0.5 wt.%; application of the Grubbs Estimator method (6) indicates that the gauge errors are actually about 0.40 wt.% ash (5). For comparison, the calculated accuracy of the DUET technique for the same 25 samples is 1.8 wt.%. A full scale industrial prototype based on this work has been designed and is currently being tested under industrial conditions in the laboratory using 50 bulk coal samples with ash ranging from 6% to 55%.

In summary, the new neutron/gamma ash analysers have the following characteristics:

- reduced analysis errors due to new and improved analysis techniques,
- reduced sampling errors compared to DUET gauges because of the much larger sample volume measured by the neutron/gamma gauge,
- improved accuracy of analysis compared to by-line PGNAA gauges due to significant sampling errors in taking a side stream from a moving belt,
- a relatively low installation cost compared to by-line PGNAA gauges, primarily because of the deletion of the by-line sampling equipment to supply coal to the analyser.
- improved availability, as a sample by-line is not required.

2.4 Fast Neutron Activation Analysis of Gold in Ore Samples

Conventional laboratory methods for gold analysis involve performing a pre-concentration procedure (fire assay) on an approximately 50 g sample of gold ore before measurement. The sample of gold ore is mixed with flux materials and a nickel or lead sulphide blank, then heated to extract the gold. The gold-containing material is then treated and analysed using atomic absorption spectroscopy, inductively coupled plasma mass spectroscopy or, for higher gold content samples, direct weighing of the extracted gold. The main drawbacks of this procedure are: (a) the small sample size means that careful sample preparation is necessary, and sampling errors are often considerable, (b) the pre-concentration and analysis procedures are very complex, involving several steps; and (c) the take up of gold by the metal bead depends on the mineralogy of the sample and particle size.

There is therefore an opportunity to develop a rapid (>100 samples per hour) and automated laboratory analysis system for the routine accurate analysis of gold down to 0.1ppm in bulk ore samples. CSIRO Minerals is developing a novel method of gold analysis using fast neutron activation (FNA). In the FNA technique, neutrons of energy above about 0.5 MeV can scatter from ^{197}Au nuclei, pushing them into an excited meta-state. This state decays with a half-life of 7.7 seconds, producing characteristic 279 keV gamma rays. The short-half life of the meta-state means that neutron fluxes 10^4-10^5 times lower than those used for the thermal neutron activation can be used. The measurement procedure then consists of irradiating the sample for about 15 seconds, followed by a 15-sec measurement period when the gamma rays are detected. Repeated irradiation/measurement cycles can be used to improve the accuracy of the method.

The energy of the neutrons used to excite the gold nuclei must be chosen to minimise interferences from excitation of other elements in the sample; this can now be achieved in conjunction with the required neutron fluxes using recently developed compact linear accelerators. After a suitable irradiation period, the sample is transferred to the measurement station, where gamma rays are detected using semiconductor (germanium) or scintillation detectors. Modelling of the gauge indicates that with a source producing 4-5$\times10^9$ neutrons per second, a gold concentration of 1 ppm can be determined with an accuracy (standard error) of 0.10-0.15 ppm in two irradiation/measurement cycles (approximately 1 minute). As the irradiation and measurement processes take place at different locations, two samples can be processed simultaneously, leading to a sample throughput in excess of 100 samples per hour. Currently the technique is being evaluated using as a neutron source a deuteron beam, from the ANSTO 3 MV Van de Graaff accelerator, incident on a deuterium gas target (7).

In summary, the fast neutron activation technique being developed by CSIRO has the following characteristics:

- large samples (up to 300-500 g) can be measured;
- sample preparation is straightforward and the analysis involves a two step procedure performed automatically by the analyser;
- analysis times of about 1 minute; and
- the method is independent of the chemical form of the gold and the composition and form of the sample.

3. GAMMA-RAY & X-RAY TECHNIQUES

3.1 Compton Profile Technique

CSIRO has recently patented a new method for the on-line measurement of ash in coal (8). This method, termed Compton profile analysis (CPA), relies on measuring the energy spectrum of gamma-ray photons that have been inelastically or Compton scattered from the coal under study (9). The shape of this spectrum carries information about the momentum distribution of atomic electrons in the sample, which in turn can be used to infer the ash content of the coal. CPA uses a low energy X-ray or gamma-ray source such as ^{241}Am together with a high-resolution gamma-ray detector in a backscatter geometry. The method offers good discrimination between light elements (H, C and O) and heavy elements (Al, Si, Ca and Fe), but is relatively insensitive to *which* of the heavy elements are present. CPA is typically 7-8 times less sensitive than DUET and 2-4 times less sensitive than PP to changes in ash composition.

The CPA technique has been tested in the laboratory on a series of 50 synthetic coal samples with "ash" contents in the range 5-15% and widely varying "ash" and organic compositions. Scattered gamma-ray spectra were collected using a low energy ^{241}Am source and a high-resolution detector. For these samples, the RMS error for ash determination was found to be 0.58 wt.% for a 20-minute measurement time. Inclusion of on-line coal moisture measurements and the use of faster detection electronics should reduce this error to below 0.4 wt.%. For comparison, the theoretical DUET error for these samples was calculated to be 1.4 wt.%. A new round of experimental measurements using real coal samples and an optimised analyser design is planned.

Potential applications of the CPA coal analyser include:

- The accurate determination of ash and coal matter in coal slurries. One particular application is for the on-line determination of coal losses in tailings from a coal preparation plant.
- The accurate on-belt determination of ash in product coal from coal preparation plants. Because of the 50-mm penetration depth of the CPA method, the coal would need to be well mixed on the belt.
- The accurate on-belt determination of ash for the control of blending.
- The accurate on-line determination of ash in coal from samplers.

Compared to existing on-line ash analysers on the market, the CPA technique offers higher accuracy than DUET and PP analysers when measuring coal streams from different sources with variable ash composition. However, the restrictions imposed by the CPA backscatter geometry and a depth penetration of around 50 mm mean that careful attention will need to be taken in presenting a representative sample stream to the analyser. Compared to the neutron/gamma gauges, the CPA technique offers considerably lower cost and reduced shielding; however CPA measures a much smaller sample volume and it does not have the ability to perform a full elemental analysis. The recent commercial availability of low-cost, room temperature, high-resolution gamma-ray detectors should enable a CPA gauge to be produced at similar cost to a conventional DUET instrument.

3.2 On-Line XRD of Dry Powders

In conjunction with FCT, CSIRO Minerals has developed an on-line, X-ray Diffraction (XRD) instrument capable of continuously monitoring mineral phase abundances in dry powders (10). As with XENA, this development was carried out as part of the *Mastermind* project. The on-line XRD analyser uses a position-sensitive detector to simultaneously collect data over a wide angular range (120° 2θ) and whole pattern analysis techniques using the Rietveld method. The analyser incorporates a continuous feed mechanism for sample presentation. The analyser (Figure 3) has been installed and commissioned in the Birkenhead cement plant in Adelaide, South Australia. This analyser has shown that XRD is a viable, robust technology for plant control. The new technology has enabled XRD to be taken from the laboratory into the plant where it can now be used to control the plant parameters 'on-line'. In its current configuration, the instrument is capable of returning the abundances of some 13 phases every minute. The accuracy of determination of the major phases in cement appears to vary from about 1 to 4% relative depending on the phase (10,11). FCT has recently received orders for the manufacture, supply and installation of two commercial instruments based on the CSIRO design.

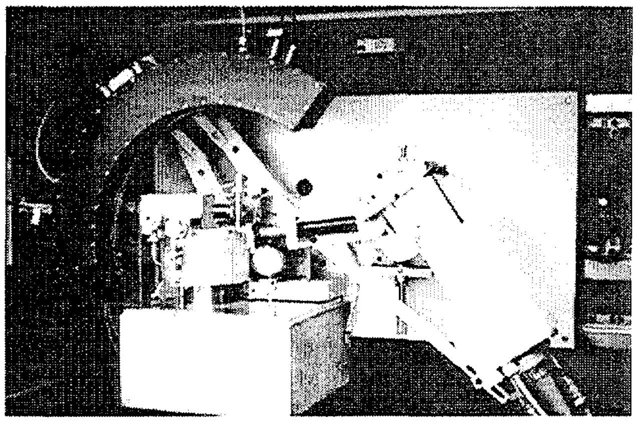

Figure 3. The upper cabinet of the on-line XRD instrument showing the position sensitive detector, continuous feed sample presenter and X-ray source.

The continuous nature of the sample feed significantly reduces the problems associated with obtaining a representative sample by more traditional methods of sampling. The sample feeder and presentation system is capable of handling up to 36 kg of sample per hour, compared with the 5 kg of material sampled over 2 to 4 hours for conventional XRF based methods. An additional benefit of the use of a moving sample is the increase in the total number of particles examined during the data collection. This leads to increased accuracy in the peak intensities and hence the quantitative phase analyses.

In its current configuration, this instrument can be used to analyse any multiphase system that is amenable to analysis by powder X-ray diffraction. The instrument can be rapidly reconfigured to allow a 'single sample' mode of operation for the periodic investigation of smaller samples for research purposes. Currently, the sample feed system is limited to dry feed materials but CSIRO work is in progress to allow for the continuous analysis of slurry samples.

4. DISCUSSION

Nuclear techniques are the basis of many on-line analysis systems that are now widely used in the mineral and energy industries. Some of the systems developed by the CSIRO depend entirely on nuclear techniques; others use a combination of nuclear techniques and microwave or ultrasonic techniques. The continuous analysis and rapid response of these systems has led to improved control of mining, processing and blending operations, with increased productivity valued at tens of millions of dollars per year.

The recently developed techniques for on-line and bulk analysis in the cement, pyrometallurgy, coal and gold industries have high potential for widespread applications with consequent significant savings in these industries.

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