

IAEA-TECDOC-459

NUCLEAR ANALYTICAL TECHNIQUES FOR ON-LINE ELEMENTAL ANALYSIS IN INDUSTRY

PROCEEDINGS OF AN ADVISORY GROUP MEETING
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN ESPOO, FINLAND, 1-5 JUNE 1987



**A TECHNICAL DOCUMENT ISSUED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1988**

**NUCLEAR ANALYTICAL TECHNIQUES FOR
ON-LINE ELEMENTAL ANALYSIS IN INDUSTRY
IAEA, VIENNA, 1988
IAEA-TECDOC-459**

Printed by the IAEA in Austria
June 1988

**PLEASE BE AWARE THAT
ALL OF THE MISSING PAGES IN THIS DOCUMENT
WERE ORIGINALLY BLANK**

The IAEA does not normally maintain stocks of reports in this series.
However, microfiche copies of these reports can be obtained from

INIS Clearinghouse
International Atomic Energy Agency
Wagramerstrasse 5
P.O. Box 100
A-1400 Vienna, Austria

Orders should be accompanied by prepayment of Austrian Schillings 100,—
in the form of a cheque or in the form of IAEA microfiche service coupons
which may be ordered separately from the INIS Clearinghouse.

FOREWORD

This report is the result of an advisory group meeting organized in Espoo, Finland, June 1 to 5, 1987. The meeting was hosted by the Reactor Laboratory of the Technical Research Centre of Finland and it was attended by 12 persons representing five countries: Australia, Federal Republic of Germany, Finland, Japan and United Kingdom.

The purpose of the meeting was to assess the present status and development trends of nuclear analytical techniques used for industrial process control. This document contains a report written by the participants during the meeting and summaries of the presentations.

The report gives an overview of the different nuclear techniques used for process control and the most important applications. It is expected to be useful for everybody dealing with different aspects of industrial production but especially for administrative personnel and engineers in developing countries, who plan and implement national development programmes to increase the quality and economies of industrial production.

The meeting was organized by Professor P. Hiismäki and Ms. L. Lamberg from the Technical Research Centre of Finland and Drs. R. Rosenberg and H. Vera Ruiz from the Agency. Dr. T.B. Pierce acted as chairman of the meeting.

EDITORIAL NOTE

In preparing this material for the press, staff of the International Atomic Energy Agency have mounted and paginated the original manuscripts as submitted by the authors and given some attention to the presentation.

The views expressed in the papers, the statements made and the general style adopted are the responsibility of the named authors. The views do not necessarily reflect those of the governments of the Member States or organizations under whose auspices the manuscripts were produced.

The use in this book of particular designations of countries or territories does not imply any judgement by the publisher, the IAEA, as to the legal status of such countries or territories, of their authorities and institutions or of the delimitation of their boundaries.

The mention of specific companies or of their products or brand names does not imply any endorsement or recommendation on the part of the IAEA.

Authors are themselves responsible for obtaining the necessary permission to reproduce copyright material from other sources.

CONTENTS

1. INTRODUCTION	7
2. NUCLEAR TECHNIQUES	9
2.1. Photon methods	9
2.1.1. X-ray fluorescence	9
2.1.2. X-ray diffraction	10
2.1.3. γ -ray and X-ray absorption and scattering	10
2.1.4. High-energy γ -ray interactions	11
2.1.5. Natural γ -rays	11
2.2. Neutron methods	12
2.2.1. Absorption and scattering	12
2.2.2. Prompt gamma-ray measurement	13
2.2.3. Neutron activation analysis	14
3. APPLICATIONS	16
3.1. Applications in mineral processing, metallurgical and industrial minerals industries	16
3.1.1. Coarse material	16
3.1.2. Ground material	16
3.1.3. Hydrometallurgical applications	17
3.1.4. Pyrometallurgical applications	18
3.2. Coal industry	18
3.2.1. Coal mining	18
3.2.2. Beneficiation plant	19
3.2.3. Power generation	20
3.2.4. Iron and steel industries	20
3.3. Petrochemicals	21
3.4. Coating	22
3.5. Paper	23
4. CONCLUSIONS	24
On-line analysis in mineral and coal industries	29
<i>J.S. Watt</i>	
Nuclear techniques for on-line analysis in mineral and coal processing	37
<i>N.G. Cutmore, R.J. Holmes, B.D. Sowerby, J.S. Watt</i>	
Applications and developments of X-ray fluorescence and neutron activation analyzers in the Finnish mining and metallurgical industry	47
<i>M. Hietala</i>	
Prompt gamma ray measurement (<i>Summary</i>)	57
<i>W. Herzog</i>	
Nuclear analytical techniques for industrial processes in Japan	63
<i>H. Tominaga</i>	

Value of neutron activation techniques for off-line industrial analysis (<i>Summary</i>)	69
<i>T.B. Pierce</i>	
Application of X-ray techniques for the determination of vertical paper filler distribution	73
<i>H. Kumpulainen</i>	
List of Participants	79

1. INTRODUCTION

On-line analysis of process streams in industrial plants has a number of advantages, e.g.:

- The plant can be better controlled based on the continuous analysis of input material flow and other process streams. If laboratory assay is used, a delay is inevitable with the potential consequence of waste of raw material and decreased quality of the product.
- Automation of the process is enabled. With the continuously increasing labor cost and requirement for high quality products, the need for automation is commonly acknowledged. In many cases automation is the only way to competitive manufacturing.
- Continuous control of waste releases can be effected. In many cases accidental releases can be decreased or prevented. If laboratory assay is used there is an inevitable delay between the commencement and discovery of the release.

Analysis information required is elemental or chemical concentrations. Some of these analyses can be measured by non-nuclear, and others by nuclear, methods. The on-line determination of elemental concentrations, however, is mainly done by nuclear methods. Analytical techniques based on the interaction of X-rays, γ -rays and neutrons with matter, are partly well established and in wide spread use, and partly in a vigorous development stage.

The Agency convened the Advisory Group Meeting to discuss the present status and development trends of nuclear methods in industry.

Special objectives of the meeting were:

- (1) To clarify the present level of applications of on-line elemental analysis using nuclear analytical techniques, such as activation analysis and X-ray fluorescence analysis.
- (2) To assess the future development in this field.

(3) To identify the main problem areas which prevent the applications becoming used more widely.

The known applications of on-line activation analysis are relatively few, and hence off-line on-site activation analysis applications is also considered. The major emphasis is, however, put on the on-line applications.

Nuclear techniques are already well-established for certain types of process measurement, for example for weighing, and for determination of thickness and bulk density. The similarity between these techniques and some of the methods used for measuring sample composition means that there is no sharp dividing line between methods for measuring gross characteristics of and those for measuring a component in, a sample. The Advisory Group considered only those techniques which could provide information about the concentration of some component of the sample. Borehole, logging, although having considerable similarity with some of the methods considered by the Advisory Group, was not considered, since the topic is being covered separately by the Agency.

No attempt was made in the discussion to give comprehensive or even coverage to the several methods reviewed. The wide range of techniques available and applications under investigation, world-wide, would have required extensive assessment and limitations imposed by time and by the areas of expertise of those present necessarily restricted the view taken. Conclusions were drawn and recommendations made on those topics covered during the meeting.

2. NUCLEAR TECHNIQUES

Various nuclear techniques are used for on-line analysis of materials. The most commonly used techniques are X-ray fluorescence, absorption and scattering; the γ -ray interactions of absorption, scattering and pair production; and the moderation of neutrons. The other neutron interactions of inelastic scatter, capture and activation are used much less frequently. This section briefly reviews the nuclear techniques used and the favourable areas for application of each technique.

2.1 Photon Methods

2.1.1 X-ray fluorescence

Two types of excitation are commonly used in XRF. These are radioisotope sources of X-rays, and X-ray tubes.

Lower flux from isotopes necessitates the use of energy dispersive techniques. The fluorescent X-rays of elements can be isolated by absorption edge filters or energy dispersive detectors like proportional counters or semiconductor detectors. Depending on the energy resolution needed to solve the specific problem, proportional counter or semiconductor detector is selected.

X-ray tube excitation makes possible the use of diffraction crystals for the analysis of the spectrum and gives highest peak-to-background ratio and best energy resolution.

A variety of instruments can be designed combining different excitation and detection methods.

Both X-ray tube excitation combined with crystal spectrometry, and radioisotope energy dispersive techniques, are widely used for on-line analysis in industry. Elements from P to U can be analyzed.

Very commonly probes where radioisotopes are used for excitation and detection are made by proportional counter or scintillation detector with or without absorption filters have been used. The advantages of

the method for low atomic number elements is a very compact measurement geometry which minimizes the X-ray absorption by air.

For a portable analyzer the solution based on radioactive source excitation and proportional counter with efficient use of microprocessor has been a growing trend. Several companies produce those equipments and total number of those analyzers in use is well over thousand.

2.1.2 X-ray diffraction

In on-line analysis of the mineral slurries direct information of the chemical form of minerals is sometimes required instead of elemental content. A natural solution for this is X-ray diffraction. By using this method it is also possible to measure light element containing minerals which are impossible to detect using X-ray fluorescence because of low penetration power of soft X-rays in slurries and air.

Compared to laboratory analysis, the on-stream XRD measurement has the considerable advantage of seeing the very large number of particles swept past the analyser by the moving slurry. This is even more important in XRD than XRF because only the particles which fulfils the Bragg conditions are counted.

X-ray diffraction eliminates any possible confusion related to amount of dissolved element and element concentration of the solids in the slurry.

Industrial analyzers have been designed and application studies made for apatite, sylvinite, fluorspar and talc slurries. In addition to diffraction, elemental information is available simultaneously in the X-ray fluorescence spectrum.

2.1.3 γ -ray and X-ray absorption and scattering

The absorption of γ -rays of energy > 300 keV depends mainly on the mass per unit area of material in the γ -ray beam. At lower energies, the absorption also depends on the atomic number and concentrations of various elements of the material. The absorption

measurements can be combined to determine the concentration of a higher atomic number (Z) component in a lower Z matrix, the technique being called dual energy γ -ray transmission (DET). Applications of this technique include the on-line determination of the ash content of coal, lead in ores and concentrates, uranium in solutions, tungsten in ore and concentrates, and manganese nodules in sea bed material and sea water (during sea bed hydraulic mining operations).

The scattering of low energy γ -rays, and the scattering of low and high energy γ -rays, can be used to determine the concentration of a high Z component in a lower Z matrix. The two energy scattering technique (DES) is analogous to the dual energy γ -ray absorption technique. Applications include the determination of ash in coal, ore sorting of individual lumps of ore, and determination of the iron content of high grade iron ores.

2.1.4 High energy γ -ray interactions

At high γ -ray energies (> 1.02 MeV), pair production interactions occur, with the instantaneous emission of 0.511 MeV annihilation γ -rays. The pair production interaction is Z-dependent. The ratio of annihilation γ -rays to Compton scattered γ -rays is used to determine the ash content of coal and the iron content of high grade iron ores.

Another high energy γ -ray interaction, γ -ray resonance scattering, is highly specific to a particular element, but can in practice only be used to determine a limited number of elements because of lack of appropriate radioisotope sources. The main applications are the determination of copper and nickel in ores and concentrates.

2.1.5 Natural γ -rays

Radioisotopes of potassium (^{40}K), and uranium and thorium and their daughter products, occur in nature in certain materials such as clay and shales. By measurement of the natural γ -ray activity, a qualitative and sometimes quantitative determination of the concentration of the component containing the natural radioactivity can be made. Applications include the determination of the potassium

content of potassium ores and in some cases the ash content of coal, and the discrimination between clay and brown coal, and shale and black coal, during mining operations.

2.2 Neutron Methods

2.2.1 Absorption and Scattering

An important feature of neutron applied measurements is that the energy of neutrons can be adjusted by moderation although the energies of neutrons emitted from a source are rather high. Therefore, measurement is made not only of fast neutrons but also of slowed down neutrons, namely intermediate neutrons, epithermal neutrons and thermal neutrons. Sometimes, moderation itself is also useful, in particular, in the measurement of the hydrogen content.

On the other hand, in the viewpoint of element selective measurement, the difference in neutron cross sections for elements must be utilized. The total cross sections of fast neutrons for atoms are not much different in all the elements, if averaged values or effective values are taken for the whole range of neutrons having a continuous spectrum. However, the mass attenuation coefficients of fast neutrons have a specially high value only for hydrogen, even when the averaged value for a continuous spectrum is considered. This can be used for measurement of hydrogen content or moisture in a bulk material by a transmission technique. Instead of such averaged measurement, if transmission measurement of fast neutrons are made spectrometrically by some means, some several elements of low atomic numbers, for example C, N, O and Si as well as H, can be determined because of their characteristic changes of cross sections against neutron energies. The spectrometry of fast neutrons can be made with an organic scintillator having the properties of pulse shape discrimination capability, by measuring the energy distribution of recoiled protons. In the case of pulsed neutrons generated by an accelerator, the time of flight technique will be more useful to obtain a better energy resolution. And the time of flight technique is more powerful in the measurement of resonance absorption in a region of epithermal neutrons, where prominent absorption peaks for many elements can be observed.

The thermal neutron measurement is the most well known, because of simplicity, although the measurement is not analytical and does not give any qualitative information. This technique is particularly useful to thermal neutron capture or scattering by such elements as Li, B, Cd, Gd and H.

The neutron slowing down or moderation also is very popular in the measurement of hydrogen as described above, and this technique is mainly employed in moisture measurement for coke and sintering material in iron making industry and soil in civil engineering and agricultural engineering.

2.2.2 Prompt gamma-ray measurement

PNAAs, i.e. the spectroscopy of the prompt γ -radiation following neutron capture, is well suited for the rapid analysis of major elements in different matrices. Using Cf-252 with a source strength of about 200 μg and a high-purity Ge-detector with 20% rel. efficiency, the determination of C, H, N, S, Al, Si, Ca, Ti, Fe, Na, K and Cl in coal or lignite is possible with high accuracy and precision within 15 min. The analysis of glass raw mix for Na, Si and Ca could be achieved within 6 min. The analysis of lime-stone, of cement raw-mix, the determination of lead, zinc and copper in the corresponding ores have also been demonstrated. Beside these above mentioned examples a series of other applications are possible, since almost each chemical element emits some characteristic γ -rays after neutron capture.

Using a transmission technique, neutron source and γ -detector can be mounted on both sides of a conveyor belt with the result, that the PNAAs-device can be operated in a real on-line mode. One of the main advantages of the PNAAs consists on the analysis of bulk materials on rapid moving conveyor belts without any sampling or sample division and preparation. This has potential to save the costs of the huge and sometimes unreliable sampling systems.

The first PNAAs systems have recently been introduced to the industry. A sulphur meter using a scintillation detector has been operating in a coal fired power plant at Monroe (USA) since the early eighties.

Since 1983 a multielement analyzer with Ge-detector is in use for coal analysis in the Paradise Plant (USA, Ky). Three further systems are operated in US coal fired electricity generating plants and one device for lime-stone analysis is being installation in Belgium.

The future of the PNAAs is strongly depending on the reliability, the operating costs and the results of these pilot plants and of the possibility to use the method in other industries. Despite of the advantages of the PNAAs as an on-line method, a series of problems have to be solved before the method can find a broader application. These problems are as follows:

- (1) Design and manufacture of a standardized source housing for 200 μg Cf-252 including a source transportation mechanism.
- (2) Experience in the maximum permissible fast neutron dose to a HPGe-detector and the total number of heating cycles possible in order to repair neutron damages of the detector.
- (3) Reducing the measurement time or increasing the precision respectively, by using much faster analog electronic circuits(ADC).

2.2.3 Neutron Activation Analysis

Off-line measurement of induced radioactivity is acceptable only if information on sample composition is available sufficiently rapidly for it to be of use to assist the production process. It is therefore likely to be of use only in monitoring of slowly changing industrial processes, and the entire determination will need to be carried out locally. Neutron generators or isotope sources are likely to be the preferred source of neutrons.

A primary requirement for a successful determination is that gamma-rays of measurable intensity are generated from the element or elements to be determined and that nuclear or other interferences do not degrade, unacceptably, the quality of the analytical results. While off-line application may offer some scope for optimizing the activation procedure, process measurements, particularly the need to produce results rapidly, may restrict the actual flexibility available.

The principles and capability of activation analyses with both neutron generators and isotope sources have been extensively discussed in the open literature. The technique must be regarded as mature and relatively stable with counting equipment and data processing techniques well developed. Isotope sources have the advantages of simplicity and reliability but are not able to provide neutron fluxes that are as high as those that are attainable with the large neutron generators. The high energy of the neutrons produced by generators making use of the reaction of deuterium with tritium may lead to several different reactions with some elements thus offering options for the determination, but the likelihood of interference is also greater.

The measurement of γ -radiation emitted as a consequence of neutron irradiation offers the opportunity of analysing the intact sample thus reducing the level of sample manipulation involved in the analyses, but some sample preparation is still likely to be required for the material analysed to be representative of what will certainly be a very much larger volume of material. Limitations are imposed by the neutron fluxes available and by the difficulty in producing unambiguous photon lines from all the elements to be determined in some cases. The cost of shielding high activity neutron sources also needs to be examined as does the in-service support needed by neutron generators.

On-line activation analysis of materials on conveyors, hoppers, pipes etc. is based on use of a radioisotope neutron source placed close to the moving material, and (usually) a scintillation detector mounted close to the moving material but downstream from the source. The radioactivity produced in the material must have a short-half, and in practice too little activity is produced in most cases for accurate elemental analysis on fast moving conveyors. .

3. APPLICATIONS

The main industries in which nuclear techniques for on-line analysis are used are the mineral processing, metallurgical, industrial minerals, coal, petrochemical, coating, and paper industries. The main applications are summarized in Table 1. This should be considered to be an incomplete list because the AGM panel members did not have a background in all industries. The application areas are discussed in more detail in the rest of this section.

3.1 Application in mineral processing, metallurgical and industrial minerals industries

3.1.1 Coarse material

After mining, the ores of metalliferous minerals are in a very coarse and heterogeneous form. Sampling for analysis purposes is difficult and expensive. The preferred analysis methods are those which give measurement information averaged over relative large volumes. This condition favours the use of neutron methods and gamma methods because of their penetrating radiation. In some cases also XRF methods can be considered.

There are applications like continuous measurements of iron ore on conveyor belt using pair production or dual energy scattering (DES) methods, or analysis for sorting and hence preconcentration of ore lumps by XRF or dual energy gamma scattering methods.

3.1.2 Ground material

The next stage of mineral processing is grinding and flotation. In flotation the material is handled in grain size typically smaller than 1 mm. This material is suitable for XRF methods and there are about 200 concentrators in the world using continuous on-line analyzers for approximately 1500 slurry streams. Typical number of elements measured per stream is 2-4. Elements analysed cover the atomic number range 20 to 92, and include all important metalliferous minerals such as nickel, copper, zinc, tin, lead and uranium. Several manufacturers make this type of analyzer.

XRF method can be used also for measuring dry fine powder on-line because there are suitable sampling systems available. The measurement of cement raw meal and smelter feed can for example be measured this way.

The drawback of continuous XRF analyzers for low atomic number elements is the poor penetration of their characteristic X-rays. In practice, elements lighter than aluminium are impossible to measure.

For low Z elements XRD (X-ray diffraction) or neutron techniques should be considered. The XRD and XRF methods combined in one instrument give good results for slurries-containing low Z minerals and also in cases where the liquid of the slurry contains the same elements as the solid particles, e.g. in salt flotation. The aim usually is to measure the content of solid material in the slurry. The XRD method gives valuable information also in cases where we have to assay continuously different minerals containing the same elements (for example, mixed sulphide and oxidised ores). There is now at least one on-stream analyzer on the market having XRD and XRF combined.

3.1.3 Hydrometallurgical applications

Hydrometallurgical samples are often liquids or slurries containing very fine size solid particles. The problem is often to analyse clear solutions. For this application reliable sampling techniques are available and the analysis can be done by XRF method. XRF is also useful for measuring the total content of metals in the slurry. It is also possible to separate the solid from the solution, and thus measure the solid directly, but automation of this sampling system is more difficult than the other mentioned cases. In hydrometallurgy the samples are often homogeneous which enables us to take only small volumes to the analyzer and keep sampling system simple.

There are about ten hydrometallurgical plants where XRF method is in on-line use. Present analyzers will tolerate the corrosive environment often present in hydrometallurgical plants.

3.1.4 Pyrometallurgical applications

In this case the continuous assay of the feed, for example to blast furnace, is important. PNA methods have potential for these applications but few analysers are yet in routine use. XRF methods are used in some applications. The representative sampling of large volumes of dry powder feed has been a major problem as well as often also the measurement of light elements. Partial help has been obtained by gamma-ray scattering and transmission methods in some cases.

3.2 Coal Industry

The on-line applications in the coal industry were covered well in the Summary and Conclusions of the 1984 IAEA Advisory Group Meeting "Gamma, X-ray and Neutron Techniques for the Coal Industry"^[1]. The following summarizes these on-line applications, and updates those applications which have developed more since this 1984 meeting.

3.2.1 Coal mining

Natural γ -ray techniques are used to assist in the seam delineation of cutting machines, hence minimizing the undesirable inclusion of adjacent shale strata in the product. Further development work is required to delineate when the adjacent strata is sandstone which usually contains little radioactivity, with γ -ray backscatter techniques being the most promising approach.

In continuous mining of brown coal, interseam sediments can be difficult to distinguish from good quality coal especially at night and when it is raining. Natural γ -ray techniques are in routine use to detect the presence of sediments or overburden on the boom conveyor of coal dredges. Natural γ -ray techniques are also being investigated for the on-line determination of ash in coal.

In some mining operations, both stone and coal are sent to the surface on the same conveyor belt. Dual energy γ -ray transmission techniques are used as the fast response detection of stone to avoid inappropriate material being sent to the beneficiation plant.

3.2.2 Beneficiation plant

Coal is usually beneficiated to reduce the waste material ash. The coarse coal fraction is beneficiated by heavy medium cyclones and baths, and jigs and the fine coal (< 0.5 mm) by froth flotation.

Dual energy γ -ray transmission (DET) techniques are routinely used to assess on-line the low ash coal which can bypass the beneficiation plant. Both DET and pair production techniques are routinely used to determine the ash content of product coal from the beneficiation plant. This ash information is used for feedback control of the heavy medium (magnetite) density in the cyclones and baths which determines the ash content of the product stream.

Both DET and pair production ash gauges determine ash content based on γ -ray interactions which are atomic energy dependent. The pair production technique measures ash content more accurately when there are large variations in composition of the ash, mainly due to Fe_2O_3 , and hence is in this case the preferred technique. The DET technique has the advantage of being used directly on coal on the conveyor, its response to ash is more rapid and it is less expensive. It is thus the preferred approach unless there are large variations in composition of the ash. Other techniques successfully used in industry for determination of ash in coal include γ -ray and X-ray backscatter, but the trend is more towards the use of DET techniques directly on-line or pair production techniques on a high flow sample by-line.

Fine coal (< 0.5 mm) is usually beneficiated by froth flotation. For control purposes, on-line information of solids weight fraction and ash content of coal in the feed, concentrate and tailings slurries is required. Conventional γ -ray transmission techniques cannot be used to determine accurately the density and hence the solids weight fraction, because of the variations in voidage due to air entrained in the slurries. Two techniques have been developed to overcome this problem of variable voidage. The first is based on neutron and γ -ray transmission to determine solids content, and these measurements are combined with radioisotope X-ray backscatter and iron K shell excitation to determine ash content. The first commercial

unit based on this technique has worked successfully for one year since installation. The second technique depends on continuously taking slurry in a sample by-line operating under high pressure, hence collapsing the voidage, and use of a DET technique to determine solids and ash. This technique has developed to the stage of use of prototype equipment in a coal beneficiation plant.

On-line conveyor determination of the moisture content of coal can be achieved by microwave transmission techniques, or by capacitance techniques compensated by γ -ray backscatter. The former approach is preferred when the moisture content of coal varies with the height of the coal on the belt. Further industrial experience in the use of these techniques is required before a full assessment can be made of their on-line accuracy.

3.2.3 Power generation

Apart from the ash and moisture measurements discussed in Section 4.2, on-line determination of calorific value, sulphur, volatile matter, aluminium and silicon in coal are becoming more important. The calorific value can be approximated by combining ash and moisture measurements, or combining various elemental abundance measurements based on neutron techniques. Sulphur in feed coal is required to control sulphur gas emissions, the preventative measures reducing pollution being adding of limestone or dolomite to the feed coal, or increased sulphur gas filtering in the stack. Knowledge of elemental abundances (eg. aluminium and silicon) gives information of boiler fouling, and of sodium, potassium, calcium, silicon and iron the fusion temperature of the ash. Neutron techniques have been developed to give the above information, but even for on-line sulphur determination there is little information available on long-term use of the neutron sample by-line techniques, in spite of the seven gauges installed in the USA. Most of the techniques developed are fairly complex and expensive, and further work is required to simplify them.

3.2.4 Iron and steel industries

Continuous determination of the moisture content of coke is required for two main applications in the steel industry. Moisture in lump

coke fed to blast furnaces is required to control the proportions of coke and iron ore fed to the furnace, and moisture in coke breeze is required in iron ore sinter plants to control the full ratio. The most promising technique for the application area is the combination of fast neutron and γ -ray transmission which has been in routine industrial use for three years.

3.3 Petrochemicals

Because of increasing attention to the environment pollution caused by combustion of fossil fuels, legal regulations to control the sulphur dioxide concentration in the air are in force in many countries. To cope with this situation, accurate measurement and control of the sulphur content of oil is required. On-line continuous determination is required in such processes as follows:

in petroleum refineries

- automated in-line blending process for shipping of heavy oil products directly from stored tanks
- fluid catalytic cracking process.

in electric power stations

- thermal power plants which are forced to use fuel oils under tight control of blending.

in petrochemical and steel industries

- fuel oil combustion process

etc.

For this demand, radioisotope X-ray fluorescence or X-ray transmission techniques are most advantageous because of simplicity, compactness of its measuring probe, ease of attaining explosion proof safety and ease of maintenance. A sufficiently high accuracy is usually obtained. Measurements are made with a by-line sampling system because a thin window must be used because of low energy X-rays.

In a typical sulphur meter based on the X-ray fluorescence method, an ^{55}Fe X-ray source of 50 mCi and a proportional counter are used. Corrections can be made for the potential errors resulting from changes in the C/H ratio in oil by a simultaneous measurement of Compton scatter peak. This technique is little affected by changes in concentration of heavy metals in oil. The technique is capable of determining the combustion heat of oil by a combination of three measurements of S, C/H and density (with an additional density gauge).

In a typical X-ray transmission sulphur meter, a γ -ray excited X-ray source yielding 22 keV X-rays generated by a combination of an ^{241}Am γ -ray source of 550 mCi and a silver target, is used. The X-rays transmitted through oil are detected with an ionization chamber. As the mass attenuation coefficients of X-rays for carbon and hydrogen are equal at 22 keV, changes in C/H ratio do not affect the accuracy of sulphur determination. A disadvantage of this technique is the necessity for manual correction in the case of oil containing significant amounts of heavy metals.

3.4 Coating

On-line coating thickness or mass per unit area determination is required in many industries, the most important being tinplate, galvanised iron, and magnetic tape. The techniques depend on X-ray fluorescence, either of the base material or of the coating material. Nucleonic coating gauges are widely used, and savings through closer tolerance to specified coating thickness are large. Reported savings in Australia in 1978 were US\$ 1 million per line per year for galvanising lines, and US\$ 3 millions for tinplate lines.

On-line determination of the thickness of more than one coating is also being determined routinely on-line. For example, in Japan, there are X-ray tube gauges with analyzing crystals determining coatings of both tin and chromium on steel, and tin and nickel on steel. Also for on-line control of double alloy coatings of different component ratios, for instance, different Fe-Zn alloys of steel, X-ray tube gauges are being in use, measuring in two different angles.

3.5 Paper

On-line ash meters based on beta and X-ray absorption are widely used in paper industry to determine the total content of mineral paper fillers, but also there are instruments for the determination of individual paper filler component contents (china clay, talc, CaCO_3 , TiO_2 and others) separately. Mass per unit area of paper coatings determinations are usually determined by means of differential beta or X-ray absorption and moisture measurements. The application of X-ray fluorescence techniques for this purpose has been claimed to bring some advantages for example insensitivity to moisture. A novel method is the determination of paper filler distribution perpendicular to paper sheet by means of combined X-ray fluorescence and absorption techniques.

4. CONCLUSIONS

4.1 The applications of nuclear on-line analysis techniques are listed in Tables I-IV. This includes the number of plant or gauge installations for those currently in routine use. Also listed are techniques which have reached an advanced stage of development but are not yet in use in industry. The industrially mature applications are on-stream analysis of metalliferous mineral slurries, coating mass per unit area determinations, analysis for sulphur in oil, determination of ash in coal and determination of the moisture content of coke and of sinter material being fed to blast furnaces.

TABLE I. ON-LINE ANALYSIS APPLICATIONS OF NUCLEAR TECHNIQUES
IN THE METALLIFEROUS MINERAL INDUSTRY

APPLICATION: DETERMINATION OF	TECHNIQUE	PLANT** INSTALLATIONS
Metal content of mineral slurries	XRF (X-ray tube)	74
	XRF, XRA (radioisotope source)	59
Metal content of hydro-metallurgical solutions	XRF (X-ray tube)	6
Metal content of clay mineral powders	XRF (radioisotope source)	5
		<u>NUMBER OF GAUGES</u>
Iron in high-grade iron ore on conveyors	Pair production	1
Sulphur, lead and zinc in sinter feed	Neutron inelastic scatter	*
Iron and chromium in ore on conveyors	Dual energy γ -ray scatter	4
Shale content of iron ore on conveyors	Natural γ -rays	-
Silica in taconite ore slurries	Neutron activation	3
Ore sorter	Dual energy γ -ray backscatter	
Manganese nodules in water and sediment	Dual energy γ -ray transmission	1

* Installation planned: late 1987.

** Plant installations usually determine the metal contents of between 3 and 14 streams.

TABLE II. ON-LINE ANALYSIS APPLICATIONS OF NUCLEAR
TECHNIQUES IN THE COAL INDUSTRY

APPLICATION: DETERMINATION OF	TECHNIQUE	NUMBER OF GAUGES
Ash in coal on conveyor	Dual energy γ -ray transmission (on-line)	31
	Pair production (sample by-line)	14
	Low-energy γ -ray backscatter (on-line)	20
	Low-energy γ -ray backscatter (sample-by-line)	35
	X-ray scatter and iron K X-ray excitation (sample by-line)	30
Ash in coal on reciprocating plate feeder	Natural γ -rays	1
Coal/clay discriminator	Natural γ -rays	2
Solids weight fraction and ash in coal in slurries	Neutron and γ -ray transmission, X-ray scatter and iron K X-ray excitation	1
	Dual energy γ -ray transmission in high pressure sample by-line	1
Moisture content of coal and other materials	Capacitance and γ -ray backscatter	10#
Sulphur in coal	Neutron capture γ -rays	1
Multielement analysis of coal	Neutron capture γ -rays	4
Moisture content of coke and of sinter feed	Neutron thermalisation	184*
	Fast neutron and γ -ray transmission	3

Commercial equipment installed on trial in coal, coke, brick and timber industries.

* Gauges in Japan. Many more gauges world-wide.

TABLE III. ON-LINE ANALYSIS APPLICATIONS IN THE CEMENT,
COATING, PAPER, AND OIL AND PETROCHEMICAL INDUSTRIES

APPLICATION: DETERMINATION OF	TECHNIQUE	NUMBER OF GAUGES
Tin content of galvanising solutions	XRF (radioisotope source)	7
Calcium in cement raw mix	XRF (radioisotope source)	10#
Ca, Si, Al and Fe in cement raw mix	XRF (X-ray tube)	9*
Coating weight of Zn, Sn and Sn-Pb alloy on steel	XRF (radioisotope source)	29**
Coating weight of Zn, Sn/Cr, Sn/Ni and Zn-Fe alloys on steel	XRF (X-ray tube)	58*
Coating weight of magnetic layer on films (memory tapes and disks)	XRF (X-ray tube)	28*
Sulphur in oil	XRF and β -ray transmission (radioisotope sources, sample by-line)	71*
	XRA (radioisotope source) and non-nuclear density gauge (sample by-line)	339*
Mineral filler material in paper	XRA (radioisotope source)	1000
	XRF (radioisotope source)	20

* Gauges in Japan. Many more gauges world-wide.

** Gauges in Japan and Australia. Many more gauges world-wide.

Gauges in Japan and Finland.

TABLE IV. ON-LINE ANALYSIS APPLICATIONS OF NUCLEAR TECHNIQUES

Industry	Application of determination	Technique	Plant installations
Paper manufacturing	Ash content of paper	β A and XRA	> 550
--	Ash component contents of paper	β A and XRA or β A and XRA/XRF	> 10

4.2 The nuclear techniques which have found most widespread use in on-line analysis are the X-ray techniques based on fluorescence, absorption and scattering; the γ -ray techniques depending on absorption and scattering particularly when two γ -ray energies are used; the γ -ray technique depending on pair production where the intensities of annihilation and Compton scattered γ -rays are compared; and neutron moderation techniques to determine moisture content. Other neutron techniques have found only limited use for on-line analysis, probably because of the complexity of the techniques and the shielding requirements for use in industry.

4.3 The use of nuclear methods is now very well established in many industries such as basic metal, coal, paper and petrochemical industries. Future trends will be the expansion of those methods to other industries.

One trend has been the increasing number of simple low-cost radioisotope on-line XRF analyzers with improved data processing capability. These analysers are now supplied by several companies and will seed the knowledge of nuclear methods to completely new areas.

A new method for on-line analysis of mineral slurries X-ray diffraction/X-ray fluorescence has recently been introduced for industrial use. Its need has been clearly identified for some low atomic number material applications, but further research work is still required to clarify the real potential of this method. The main applications so far have been in the fertilizer industrial minerals industries.

4.4 The Advisory Group considered that the application of nuclear techniques to on-line, elemental analysis is often limited by the difficulty of transferring the technology of established systems from expert to potential users. Lack of specificity (for example of some absorption and scattering techniques) may also restrict the use of the methods to certain types of applications and inadequate sensitivity may also be a limitation. Cost is also a major factor in determining whether an on-line analytical method can be economically justified and is competitive with alternative techniques. Some of the more elaborate nuclear methods are expensive and require careful

justification. Adoption of radiation-based techniques is also influenced by the perception of hazard associated with the use of nuclear radiation.

Reference:

- [1] Gamma, X-ray and neutron techniques in the coal industry, Proceedings of an advisory group meeting, Vienna, 4-7 December 1984, STI/PUB/707.

ON-LINE ANALYSIS IN MINERAL AND COAL INDUSTRIES

J.S. WATT

Division of Mineral Engineering,
Commonwealth Scientific and Industrial
Research Organization,
Sutherland, New South Wales,
Australia

Abstract

Australian developments in on-line nuclear gauges are reviewed briefly. The systems are grouped in three categories; those well established, those recently commercialized and those not yet commercialized.

This paper briefly reviews Australian-developed nuclear systems for on-line analysis in the metalliferous mineral and coal industries. The on-line analysis systems are grouped into three categories: those well-established in industry, those commercialised but not yet extensively used in industry, and those not yet commercialised. Table 1 summarises the current status of systems developed in Australia.

Well-established applications

a) On-stream analysis of metalliferous mineral slurries

Both radioisotope [1,2] and X-ray tube [3] techniques are widely used in mineral concentrators for the on-stream analysis of metalliferous mineral slurries. The radioisotope systems are based on both X-ray fluorescence (XRF) and preferential adsorption techniques, while the X-ray tube systems are based only on XRF techniques.

These on-stream analysis systems are used mainly in mineral concentrators based on froth flotation. Elements determined include lead, zinc, silver, copper, nickel, tin, iron and tungsten. In small plants, measurements may be made only in three process streams. In large plants, measurements may be made in many streams.

TABLE 1 ON-LINE ANALYSIS APPLICATIONS

Application: Determination of	Technique	Equipment supplier	Gauges installed
Metal content of metalliferous mineral slurries	XRF and XRA techniques, and gamma-ray transmission	Amdel	40
Ash in coal on conveyor	Dual energy gamma-ray transmission	MCI	22
	Pair production	MCI	13
Ash in coal on reciprocating plate feeder	Natural gamma-rays	-	1
Coal/clay discriminator	Natural gamma-rays	-	2
Solids weight fraction and ash in coal in slurries	Neutron and gamma-ray transmission, X-ray scatter and Fe K X-ray excitation	Amdel	1
Moisture content of coal and many other materials	Capacitance and gamma-ray backscatter	MCI	6*
Moisture content of coke	Fast neutron and gamma-ray transmission	-	#
Iron in iron ore on conveyors	Pair production	MCI	1
Ore on conveyors:			
--lead	Dual energy gamma-ray transmission	-	**
--copper	Gamma-ray resonance	-	**
--nickel	scattering	-	**
Sulphur, lead, and zinc in sinter feed	Neutron inelastic scatter	-	-

* Commercial equipment installed on trial in coal, coke, brick and timber industries.

Plant trial planned, 1987.

** On-line techniques possible with developed techniques, but no application requirement yet in industry.

The on-line analysis information is used for the better control of the concentrator[4]. Some reported increases in recovery of valuable minerals are shown in Figure 1. The main savings result from increased metal recovery and increased throughput of ore through the plant, but significant savings also result from reduced reagent consumption, redeployment of staff from sampling and chemical assay, and higher and more stable grade of concentrates. The savings resulting from use of the on-stream analysis information usually pays back the cost of the system in three to nine months.

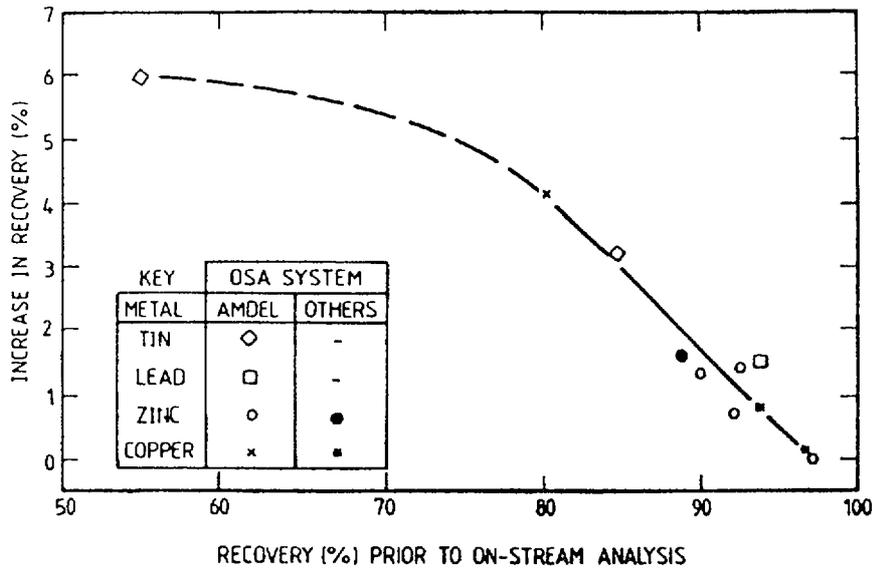


FIG.1. Improvements in recovery of mineral concentrates after installation of on-stream analysis systems.

b) On-line determination of the ash content of coal on conveyors

Various techniques have been used for the on-line determination of the ash content of coal: dual energy gamma-ray transmission[5,6], pair production[5,7], low-energy gamma-ray backscatter[8,9], and X-ray backscatter compensated by iron K shell XRF[10]. Each of these techniques has been routinely used in industry.

The dual energy gamma-ray transmission techniques are used directly on-line on the conveyor, have fast response time and are essentially independent of the thickness of coal on the belt. This technique seems preferable to the low energy gamma-ray backscatter techniques used on-line or on a sample by-line. The errors in ash determination due to variations of composition of the ash are the same for the three gamma-ray techniques, and so the advantage of direct on-line use is the principal factor in selection of the dual energy technique.

In some applications the variations in composition of the ash results in unacceptable errors in ash determination in the techniques described in the last paragraph. The X-ray backscatter technique was introduced to overcome this source of error by correcting for the main cause of error, variations in iron concentration. However the more recently developed pair production gauge is relatively insensitive to variations in composition of the ash, and has the

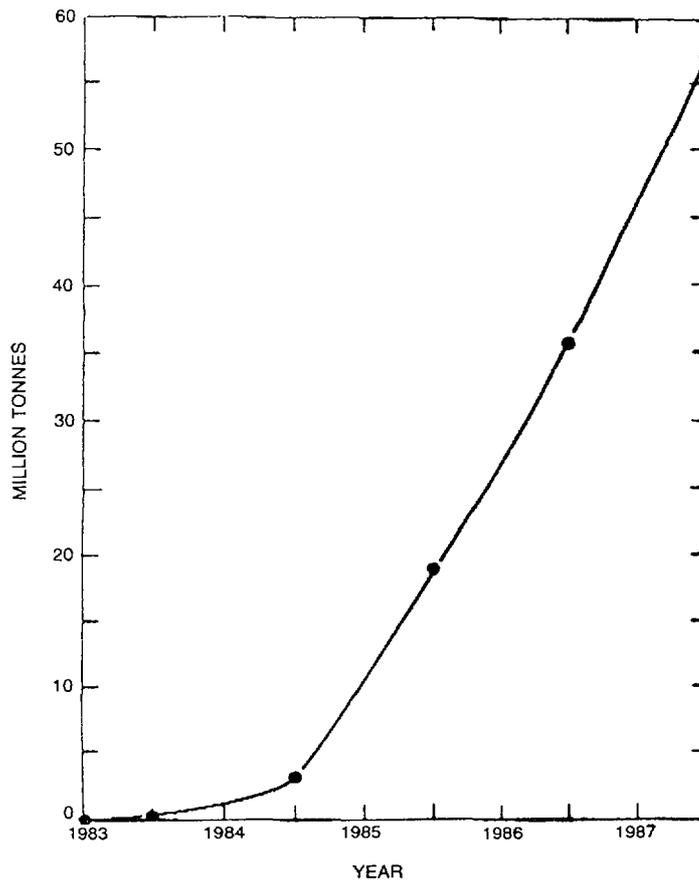


FIG.2. Australian coal monitored annually by Mineral Control Instrumentation Coalscan ash monitors.

advantage that measurements can be made on high flow rate sample by-lines. It is thus preferred to the X-ray backscatter technique.

The on-line ash monitors are used for mine grade and stockpile control, washery by-pass control, washplant control, monitoring of feed to power stations, and shipping grade control. About 50% of the Australian developed (Coalscan) monitors are used for the washplant control, and 25% for mine grade and stockpile control.

Applications recently introduced into use in industry

a) On-line detection of interseam sediments in brown coal

In continuous mining of brown coal, interseam sediments can be difficult to distinguish from good quality coal especially at night and when it is raining. Natural gamma-ray techniques are in routine use to detect the presence of sediment or overburden on the boom conveyor of coal dredges[11].

b) In-stream analysis of coal slurries

The first nuclear system for the in-stream determination of the solids weight fraction and ash content of coal in slurries was installed in a coal preparation plant in April 1986[12]. It continuously monitors the feed, concentrate and tailings streams about the flotation circuit, and this information is used for manual control of the circuit. The flotation banks in coal preparation plants are usually poorly controlled; potential increases in yield of more than 5% are anticipated[13].

c) On-line determination of moisture content of materials

A combined capacitance and gamma-ray backscatter gauge for the on-line conveyor determination of the moisture content of materials is currently installed for long-term testing in applications in the coal, timber, brick and iron ore industries[14]. The main applications in the coal industry are the control of the dewatering of coal in coal preparation plants and in the determination of the specific energy of coal (via ash and moisture) for power stations.

d) On-line determination of iron in high-grade iron ore

The iron content of iron ore is continuously determined by a gamma-ray backscatter technique based on the pair production interaction[15]. The on-line measurement is required for blending operations and for the determination of the average grade of ore being loaded onto ships.

e) Ash content of coal on reciprocating plate feeder

The ash content of coal is determined by detection of natural gamma-rays emitted by uranium, potassium and thorium and daughter products in the coal[16]. The reciprocating plate feeder provides a constant geometry of coal which is viewed by a large scintillation detector.

Potential applications not yet in industrial use

a) On-line determination of moisture in coke

Fast neutron and gamma-ray transmission techniques are well suited to the determination of moisture in coke[17,18]. Measurement of coke moisture has

two main applications in the steel industry: moisture in lump coke feed to blast furnaces is required to control the proportions of coke and iron feed to the furnace, and moisture in coke breeze is required in iron ore sinter plants to control the fuel ratio.

b) On-line determination of lead in ores and concentrates

Dual energy gamma-ray transmission techniques can be used to determine the concentration of lead in ores and concentrates on conveyors[19]. One potential application is to monitor the lead content of the tailings from heavy medium separation of high-and low-grade ore prior to the flotation process.

c) On-line determination to copper and nickel in ores and concentrates

Gamma-ray resonance scattering techniques are well suited to the determination of copper and nickel in materials on conveyors[20].

d) On-line determination of sulphur, lead, zinc and iron

The feasibility of use of neutron inelastic scatter techniques for analysis of sinter feed material has been demonstrated[21]. Before lead concentrate can be reduced to metallic lead in a blast furnace, it must be converted from the sulphide form to the oxide form, and the finely divided ore particles must be agglomerated into large lumps. This is achieved in a sinter plant, the optimisation of which requires on-line analysis of the sulphur in the sinter feed.

REFERENCES

- [1] WATT, J.S., "On-stream analysis of metalliferous ore slurries", Int.J.Appl.Radiat.Isotopes, 34 1 (1983), 309.
- [2] JENSON, H., TOOP, A., KORBEL, B., THOMAS, B., "Diversification of in-stream analysis instrumentation into new applications", to be presented at the XVI Int. Min.Proc. Congress, Stockholm, June 1988.
- [3] GROUNDSTROEM, L., BARKER, D.R., "Courier 30, A third generation on-stream analyser", Paper presented at: Sixth Australasian Conference and Schools on X-ray Analysis, Sydney, 10-14th February, 1986.

- [4] WATT, J.S., "On-line analysis in the metalliferous mineral and coal industries", Proc. Australas.Inst.Min.Metall., No. 290 (1985), 57.
- [5] WATT, J.S., SOWERBY, B.D., "On-line determination of ash in coal using SIROASH gauges", Proc. Second Australian Coal Preparation Conference (Whitmore, R.L., Ed.), Westminster Press, Brisbane (1983), 263.
- [6] GRAVITIS, V.L., WATT, J.S., MULDOON, L.J., COCHRANE, E.M. "Long-term trial of a dual energy gamma-ray transmission gauge determining the ash content of washed coking coal on a conveyor belt", Nucl. Geophys. (in press).
- [7] SOWERBY, B.D., "Determination of ash, moisture and specific energy of coal", In Gamma, X-ray and Neutron Techniques for the Coal Industry, (Proc. Advisory Group Meeting, Vienna, 1984), IAEA Vienna (1986), 131.
- [8] CIERPISZ, S., "Experiences with coal quality monitoring systems in Poland", In Gamma, X-ray and Neutron Techniques for the Coal Industry, (Proc. Advisory Group Meeting, Vienna, 1984), IAEA Vienna (1986) 149.
- [9] FAUTH, G., LEININGER, D., LUDKE, H., "Experience with nuclear instrumentation techniques in the preparation of hard coal", In Gamma, X-ray and Neutron Techniques for the Coal Industry, (Proc. Advisory Group Meeting, Vienna, 1984), IAEA Vienna (1986), 165.
- [10] BOYCE, I.S., CLAYTON, C.G., PAGE, D., "Some considerations relating to the accuracy of measuring the ash content of coal by X-ray scattering", Nuclear Techniques and Mineral Resources 1977 (Proc. Symp. Vienna, 1977), IAEA, Vienna (1977) 135.
- [11] AYLMER, J.A., HOLMES, R.J., BROCKWAY, D.J. "A gauge for the discrimination of overburden and sediments from low ash coal", Coal Power '87 (Ann. Conf. The AusIMM, Newcastle, Australia, May 1987).
- [12] DINNUZZO, P., GRAVITIS, V.L., TOOP, A., WATT, J.S., ZASTAWNY, H.W., "In-stream determination of solids weight fraction and ash content of coal in flotation circuit slurries of a coal preparation plant", Nucl. Geophys. (in press).
- [13] CLARKSON, C.J., HORNSBY, D.T., WALKER, D.J. "Automatic flotation control using on-stream ash analysis" Proc. Third Australian Coal Preparation Conf., Wollongong, (Ed. Bensley, C.N.) Westminster Press, Brisbane (1985), 238.
- [14] CUTMORE, N.G., ROCZNIOK, A.F., SOWERBY, B.D., "An under-belt capacitance and gamma-ray backscatter gauge for on-line determination of moisture in coal", Nucl. Geophys. (in press).

- [15] AYLNER, J.A., HOLMES, R.J., RUTHERFORD, L.C.. "Dynamic trial of an iron ore analyser based on pair production", Nucl. Geophys. (in press).
- [16] MATHEW, P.J. "On-stream ash analysis of coal based on its natural gamma-ray activity", Proc. Coal Research Conf. 15-17 October 1985, Wellington, New Zealand, Vol. 2, Paper No. 31.1.
- [17] TOMINAGA, H. et.al., "Simultaneous utilisation of neutrons and gamma-rays from californium-252 for measurement of moisture and density", Int.J.Appl.Radiat.Isot. 34 1 (1983) 429.
- [18] SOWERBY, B.D., MILLEN, M.J., RAFTER, P.T., "Fast neutron and gamma-ray transmission technique for the on-line determination of moisture in coal and coke", Nucl. Geophys. (in press).
- [19] WATT, J.S., STEFFNER, E.J., "Dual energy gamma-ray transmission techniques applied to on-line analysis in the coal and mineral industries", Int.J.Appl.Radiat.Isot. 36 11, (1985) 867.
- [20] SOWERBY, B.D., ELLIS, W.K., "Industrial on-stream analysis using gamma-ray resonance scattering", Nuclear Techniques in the Basic Metal Industries, (Proc. of a Symposium, Helsinki, 1972), IAEA Vienna, (1973), 479.
- [21] CUNNINGHAM, J.B., SOWERBY, B.D., RAFTER, P.T., GREENWOOD-SMITH, R., "Bulk analysis of sulphur, lead, zinc and iron in lead sinter feed using neutron inelastic scatter gamma-rays", Int.J.Appl.Radiat.Isot., 35 7, (1984) 635.

NUCLEAR TECHNIQUES FOR ON-LINE ANALYSIS IN MINERAL AND COAL PROCESSING*

N.G. CUTMORE⁺, R.J. HOLMES⁺⁺,
B.D. SOWERBY⁺, J.S. WATT⁺

⁺ Division of Mineral Engineering,
Commonwealth Scientific and Industrial
Research Organization,
Sutherland, New South Wales

⁺⁺ Division of Mineral Engineering,
Commonwealth Scientific and Industrial
Research Organization,
Port Melbourne, Victoria

Australia

Abstract

Major improvements have taken place in mineral and coal processing in the last decade. The development of nuclear on-line sensors that continuously analyse the material being processed has led to better control of metalliferous mineral processing and increased recovery of valuable minerals. The recent development of on-line techniques for analysis of coal is expected to be of similar importance.

Australian developments in on-line nuclear gauges are reviewed. These include systems for in-stream analysis of mineral slurries with comments on plant operating experience; on-line determination of ash in coal using low energy γ -ray transmission and pair production techniques; in-stream determination of solids weight fraction and ash content of coal in slurries with variable voidage; and on-line determination of moisture in coal, iron in high grade iron ores and sulphur in lead sinter.

The washed coal produced per year in Australia is valued at more than \$A4,000 million, and more than \$1,500 million of metalliferous mineral concentrates are produced per year. The value of a one per cent increase in recovery of coal and metalliferous mineral concentrates would thus be more than \$55 million per year. As a result of better plant control based on information supplied by the in-stream analysis a one percent increase in recovery of mineral concentrates is already being achieved. There is good potential for a one per cent increase in recovery of washed coal when gauges for on-line ash determination are better integrated into washery control.

This paper reviews Australian developments in on-line gauges based on nuclear techniques and their impact on the control of processing operations in the metalliferous ore and coal industries.

IN-STREAM ANALYSIS OF METALLIFEROUS MINERAL SLURRIES

INTRODUCTION

On-line nuclear gauges give information on the process variables in mineral and coal processing operations. These gauges determine, for example, the concentration of valuable minerals in concentrator process streams, and the ash content of coal in coal preparation plants. Such information leads quickly to a better understanding of the processing operation, which in turn leads to an increased recovery of valuable minerals. The cost of the gauge installation in metalliferous mineral concentrators is usually being recovered in a few months.

In a froth flotation concentrator, minerals are selectively floated from the ore to yield concentrates of each valuable mineral. The flotation process is complex. On-stream analysers provide information on concentrations of valuable minerals which is used to improve control of the concentrator. This increases recovery of valuable minerals, decreases consumption of reagents, and reduces requirement for shift samplers.

Research into radioisotope X-ray and γ -ray techniques for on-stream analysis of mineral slurries commenced in Australia in 1962. Two first generation analysers were installed in concentrators at Broken Hill, NSW, in 1968. Further developments led in 1973 to

* This paper is reproduced by permission of The Australasian Institute of Mining and Metallurgy. It was presented at the 13th Congress of the Council of Mining and Metallurgical Institution, Singapore, 11-16 May 1986.

the second generation of gauges based on radioisotope probes which are immersed directly into the plant process streams. There are now 34 of these Australian Mineral Development Laboratories (Amdel) on-stream analysis systems installed in concentrators in Australia and overseas, and three in pilot plants.

PLANT ANALYSIS SYSTEM

The plant analysis system (Watt, 1983) determines the concentrations of valuable minerals in the solids of process slurries. This is achieved by combining measurements of γ -ray transmission, which determines solids weight fraction, with either X-ray fluorescence (XRF) or γ -ray preferential absorption measurements. The XRF measurement is based on use of a radioisotope X-ray source and a scintillation detector. This detector cannot resolve K X-rays of the elements iron, nickel, copper and zinc, a problem which is overcome by the use of three complementary techniques based on filters, radiators, and the selection of the energy of γ -rays incident on the slurry. With these and preferential absorption techniques, concentrations of the common elements iron,

nickel, copper, zinc, tin, lead and uranium can be determined at all but very low concentrations. Solid state detector probes are used only for very low concentrations, for example, porphyry copper residues where analysis is required to ± 0.005 wt% copper in the slurry solids.

The plant analysis system, manufactured and marketed internationally by Amdel, is shown schematically in Fig. 1. Probes (Fig. 2) containing radioisotope source and detector are immersed directly into plant process streams. Electrical signals from these probes are processed in a signal analyser box mounted in the plant close to the probes. The processed signals are routed to a centrally located microcomputer which combines signals from the different probes in the same stream to give solids weight fraction and concentrations of elements in the slurry solids.

In small concentrators, probes are usually installed in three to six process streams. They have been installed in up to fourteen streams in large concentrators. The original on-stream analysis system for a few streams was later extended, in eleven mineral concentrators, to a larger number of streams.

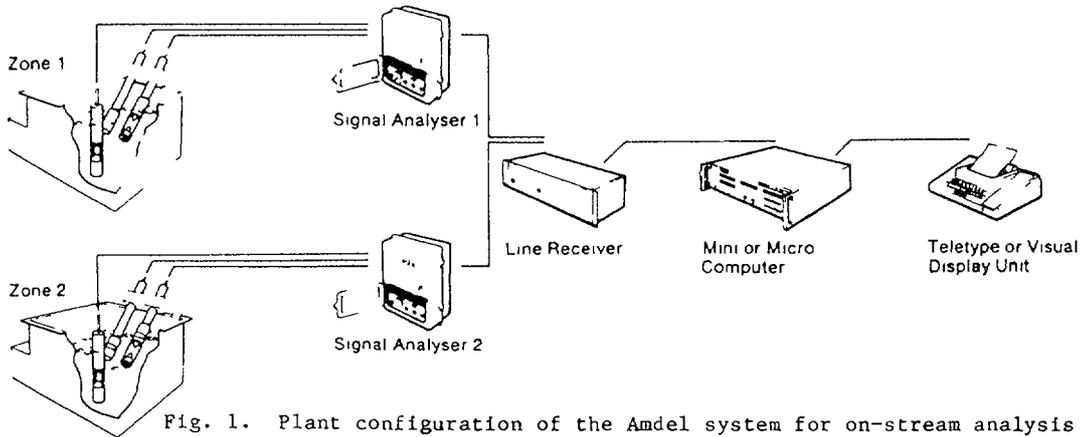


Fig. 1. Plant configuration of the Amdel system for on-stream analysis of metalliferous mineral slurries.

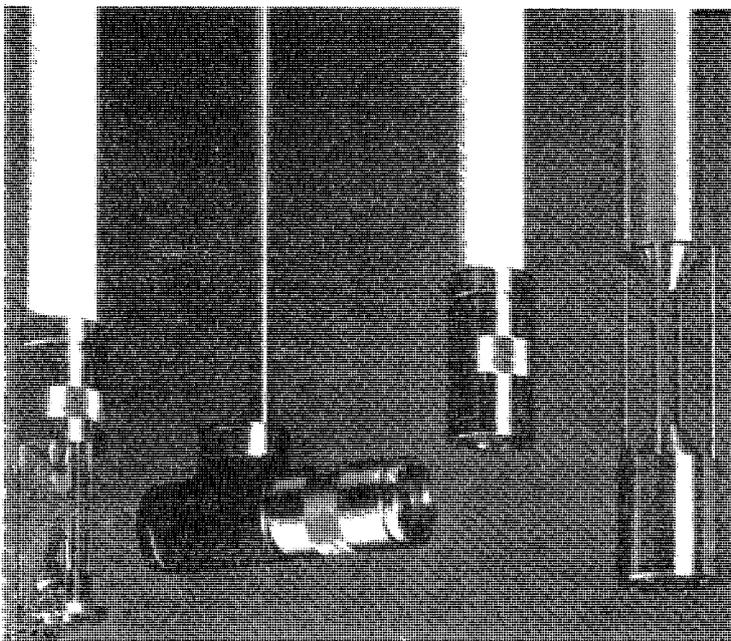


Fig. 2. The immersion probes of the Amdel on-stream system are from left to right, an X-ray preferential absorption probe, two XRF probes, and a density probe based on γ -ray transmission.

BENEFITS FROM ON-STREAM ANALYSIS

Soon after installation of an on-stream analysis system, plant operators experiment with varying plant parameters such as reagent addition rates and levels of slurry in flotation cells to determine the effect of these variations on concentrations of valuable minerals in process streams. Better understanding of the plant processes soon leads to better manual control of the concentrator. Often within weeks or a few months of installation of the analysis system, there is a significant increase in the recovery of valuable minerals (Orrock, Watters and Slattery, 1978; Jowett, Selby and Sutherland, 1980; Wells, 1983) or a substantial increase of ore tonnage processed at constant recovery.

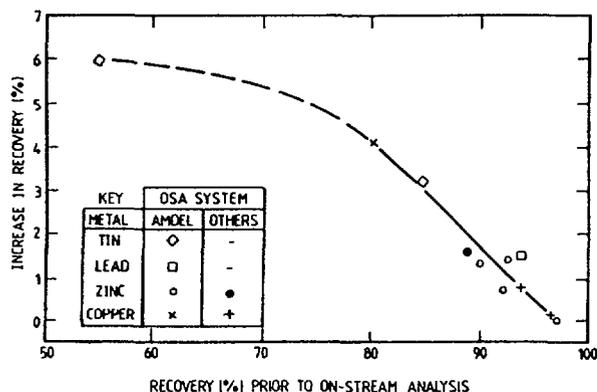


Fig. 3. Improvements in recovery of mineral concentrates after installation of on-stream analysis systems.

Additional information on plant processes can lead to the introduction of simple automatic control loops for such tasks as varying the reagent addition rate in proportion to mass flow of valuable mineral into the flotation circuit.

Figure 3 shows improvements in recovery of valuable minerals following introduction of on-stream analysis systems. Increases are greater for plants operating with lower recoveries. The value of increased recovery depends on ore throughput, but is usually in the range of hundreds of thousands to several million US dollars per year.

Other benefits arising from use of on-stream analysis are the reduction in reagent consumption by 10 to 40%, the occasional increase in concentrate grade, and a reduced need for plant personnel such as shift samplers.

ON-LINE ANALYSIS OF COAL

Coal is washed to reduce ash and obtain a product of the required ash specification. The washing operation is mostly based on separation of the higher and lower density coal particles using a heavy medium (magnetite/water slurry) in baths for the +25 mm particles and cyclones for the +0.5 to 25 mm particles. The small

(-0.5 mm) size fraction is usually processed by flotation. The density separation process is controlled manually by changing the density of the heavy medium which alters the ash content and yield of product. The flotation process can be controlled by varying the reagent addition rate or aeration of the flotation cells.

On-line analyses required in coal processing include the on-line conveyor determination of the ash content of coal; in-stream analysis of solids weight fraction and ash content of coal in slurries which, because of the flotation process, usually have variable voidage; and the determination of moisture content as the coal is dewatered after the washing operation. Rapid on-line determination of ash content of coal is required for coal blending operations. Determinations of ash, moisture and specific energy are required for improved control of power stations.

ASH IN COAL

Most nuclear techniques for ash determination are based on γ - or X-ray interactions which depend on atomic number (Z), and on the fact that ash has an effective Z greater than that of coal matter. The main Z-dependent γ -ray interactions are photoelectric absorption, coherent scatter, and pair production.

Two types of ash gauges are in routine use in Australian coal preparation plants (Watt and Sowerby 1983; Watt 1984; Sowerby, 1984): (a) gauges, based on photoelectric absorption, in which measurements are made directly on coal on-line on conveyors, producing accurate results for most low ash coals and an acceptable accuracy for some high ash coals; and (b) gauges, based on pair production γ -ray interactions, and high flow sample by-lines, resulting in accurate ash determinations in both low and high ash coals. Both are manufactured and marketed by Mineral Control Instrumentation Pty.Ltd. (MCI). The former gauge is called the SIROASH (an acronym for CSIRO ash) low energy γ -ray transmission (LET) gauge or the Coalscan through-belt ash monitor and the latter is called the SIROASH pair production gauge or the Coalscan sample by-line ash monitor.

Low energy γ -ray transmission

The LET gauge (Fookes et al., 1983; Watt and Sowerby, 1983; Watt, 1984) depends on the determination of intensities of narrow beam transmission of low and high energy γ -rays through coal on the conveyor (Fig. 4). Both intensities depend on the weight per unit area of coal in the γ -ray beam and the low energy also depends on the effective atomic number of the coal. The detected intensities are determined separately by pulse height analysis of output pulses from the scintillation detector, and then combined to give an ash content of coal which is independent of the thickness and vertical segregation of coal on the belt.

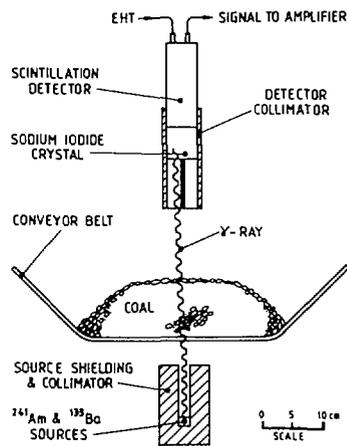


Fig. 4. Schematic of the SIROASH gauge showing transmission of narrow beams of ^{241}Am and ^{133}Ba γ -rays through coal on a conveyor.

The γ -ray sources and detector are mounted at opposite ends of the C frame about the conveyor (Fig. 5). The C frame is swung under computer control so that the γ -ray beam either traverses coal at the centre of the belt, or is beyond the edge of the belt during standardisation and calibration.

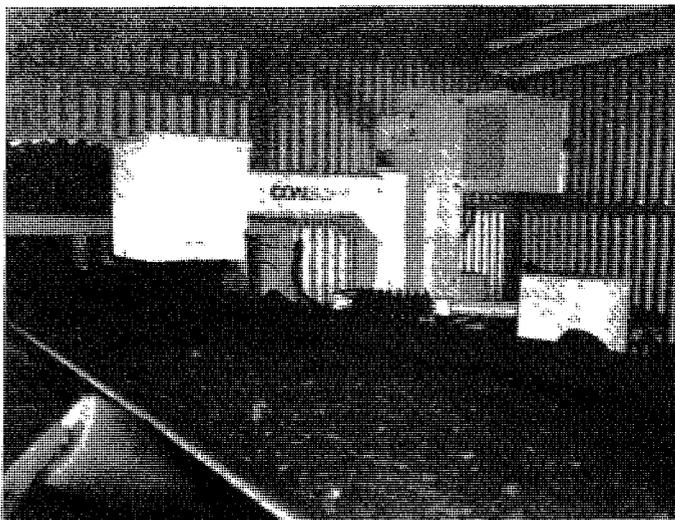


Fig. 5. The first commercial Coalscan through-belt ash gauge installed at the Swamp Creek mine of the Hebdon Mining Company.

Errors in determination of the ash content of high ash coals are caused mainly by variations in the concentration of constituents, particularly Fe_2O_3 , in the ash. This is also a significant source of error for low ash coals but, since the absolute error in ash is proportional to ash content, the magnitude of the error is much smaller than for high ash coals. The error in measurement of count rate can be a significant source of error when the weight per unit area of coal in the γ -ray beam is low, e.g. 5 g cm^{-2} . If it is frequently less than 5 g cm^{-2} , the conveyor speed should be reduced to allow the coal to be more deeply packed on the conveyor.

Errors in ash determination have been determined in a series of laboratory measurements on coal samples (Watt and Sowerby, 1983), and in plant trials (Fookes et al., 1983) and gauge installations. The r.m.s. difference for low ash coals was in the range 0.3 to 0.45 wt% ash and contained a significant error due to sampling and conventional assay. The r.m.s. error for intermediate and high ash coals varied in the wide range of 0.36 to 2.24 wt% ash. The lowest error corresponded to an intermediate ash content coal (12-20 wt% ash) with little variation in Fe_2O_3 in the ash. The highest error corresponded to coal with unusually wide variations in Fe_2O_3 in the ash (4.3 to 27 wt%). For high ash coals, the r.m.s. error in ash determination would normally be in the range 0.7 to 1.5 wt% ash.

Three LET gauges are in routine use in the Australian coal industry and four more have been ordered. The gauge on the coking coal product line of the coal preparation plant of Stockton Borehole Pty Ltd, near Newcastle, NSW, has had the most comprehensive tests of all LET installations. Gauge ash has been compared with chemical assay ash of the two hour composite samples taken with an automatic sampling system. The r.m.s. difference over about a year's operation was determined to be 0.33 wt% ash for ash in the range 6 to 9 wt% (Muldoon et al., 1985). This r.m.s. difference includes a significant error in the operation of the automatic sampler.

The advantages of the Coalscan LET gauge are that coal is measured directly on the conveyor, the measurement time is short, and its cost is only two thirds that of the Coalscan pair production gauge.

Pair production

The pair production (PP) ash gauge (Watt and Sowerby, 1983; Sowerby, 1984) depends on determinations of the intensities of γ -rays backscattered by the coal and resulting from pair production and Compton interactions. Both interactions depend on the bulk density of the coal; the pair production also depends on the effective atomic number of the coal. The intensities of the backscattered γ -rays resulting from the two interactions are separately determined by pulse height analysis of the output from the scintillation detector. The detected intensities are then combined to give the ash content. The main advantage of the PP gauge over the LET gauge is that it is less sensitive by about a factor of 4 to variations in ash composition.

The PP gauge views coal in a by-line stream taken from the main process line. Figure 6 shows schematically the PP gauge viewing coal passing through a cylindrical plastic tube in the by-line. The Coalscan PP gauge is calibrated by comparing the gauge signals with ash determined by the assay of samples of coal taken from the by-line output.

Errors in ash determination have been determined in a series of laboratory measurements on coal samples (Watt and Sowerby 1983) and in gauge installations (Smith et al., 1983; Sowerby, 1984). In the laboratory tests, the PP gauge was tested on 40 kg sub-samples of

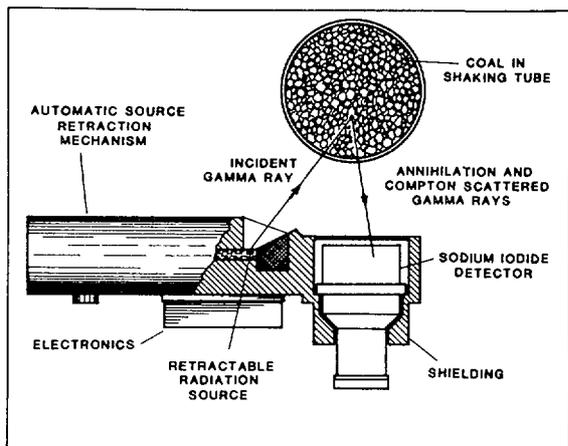


Fig. 6. Schematic diagram of the PP gauge which determines the ash content of coal in a sample by-line.

88 coal samples from four different Australian coal mining areas. Most of these were as-mined coal samples. The r.m.s. differences between chemical laboratory ash and PP gauge ash were in the range 0.46 to 1.3 wt%, compared to 1.0 to 2.2 wt% for the L&T gauge on the same samples.

The Coalscan sample by-line ash monitor incorporates the SIROASH PP gauge and a sample presentation system developed by the University of Queensland. This Coalscan ash monitor also incorporates a moisture monitor which uses a capacitance technique for moisture determination, with conducting plates built into the walls of the sample presentation system. Eight Coalscan PP gauge ash monitors have been installed in Australian coal washeries, and four more have been ordered.

The first Coalscan PP gauge system was installed at Ulan Coal Mines, New South Wales (Fig. 7) (Smith et al., 1983). This system has been operating on the product line of the 1200 tonnes/hour washplant since February, 1983. The mean ash content of the Ulan product coal is about 17.5 wt%. Two major studies have been made on the accuracy of the Ulan gauge. The r.m.s. deviations between Coalscan ash readings and assays of coal samples from a conventional automatic sampling system over 60 eight-hour and 51 twelve hour periods were 0.33 and 0.34 wt% ash respectively. Calibration data from three other Coalscan PP gauges has shown r.m.s. deviations from 0.21 to 0.35 wt% ash on low ash coal (< 11 wt% ash) (Sowerby, 1984).

IN-STREAM ANALYSIS OF COAL SLURRIES

The γ -ray transmission techniques widely used in the metalliferous mineral industry to determine solids weight fraction (W) via density of the slurry are inaccurate in coal slurries of variable voidage. A new technique has been developed to determine W (Watt, 1984). It depends on the correlation between W and the hydrogen concentration (wt/wt) of the slurry; coal has about 5 wt% hydrogen in the coal matter compared with 11.2 wt% hydrogen in water. Hence coal slurries with higher W have lower hydrogen concentrations.

The technique depends on measurements of neutron moderation and γ -ray transmission to

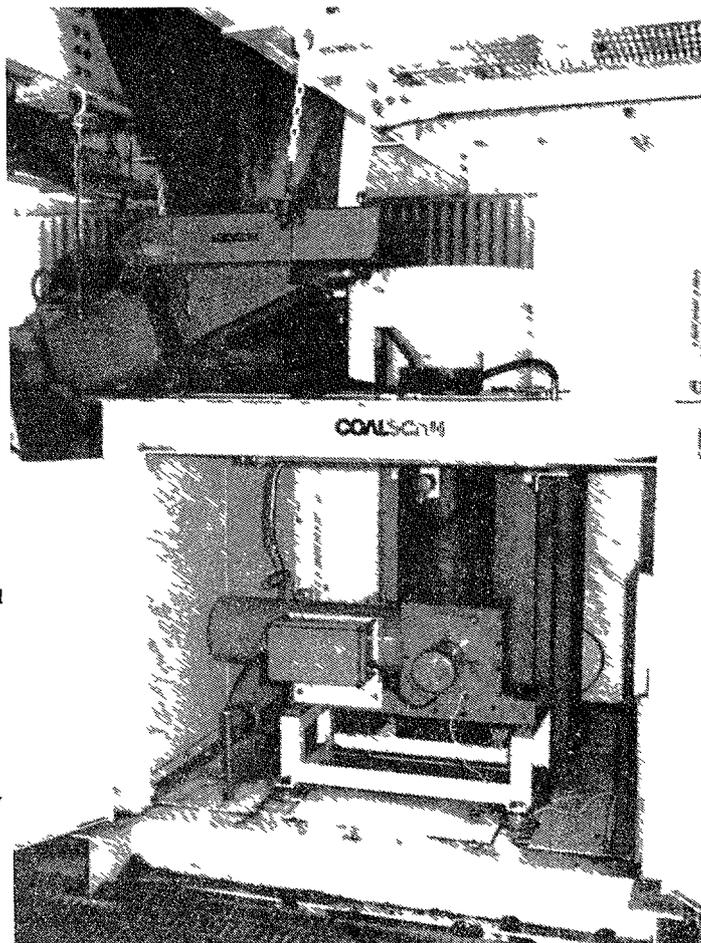


Fig. 7. The Coalscan sample by-line ash monitor, based on the PP technique, installed at the Ulan coal washery.

given hydrogen (wt/wt) in the slurry, and combining these with ash-sensitive measurements, e.g. X-ray backscatter and iron K X-ray excitation. Determination of both W and ash content is independent of voidage of the slurry.

The SIROASH coal slurry gauge to be used in coal preparation plants is based on probes immersed directly into plant process streams or into high flow rate sample by-lines. The main difference between this system and that used for metalliferous mineral slurries (Fig. 1) is that one of the probes for the coal slurries is based on neutron moderation techniques.

The new technique has been demonstrated in both laboratory (Gravitis, Watt and Zastawny, 1985) and plant trials (Muldoon et al., 1985). In the laboratory trials, measurements were made for slurries with solids weight fraction in the range 5 to 22 wt%, ash in the coal from 20.7 to 30 wt%, and voidage 0 to 4 vol%. The r.m.s. difference between probe and conventional determinations of W was 0.54 wt%, a factor of five better than that obtained by γ -ray transmission measurements. The r.m.s. difference for ash was 0.78 wt%, compared with 0.56 wt% for slurries without voidage.

The plant trial was undertaken at the BHP Steelworks coal preparation plant at Newcastle, NSW, with probes immersed in slurry in the feed box upstream of the bank of flotation cells.

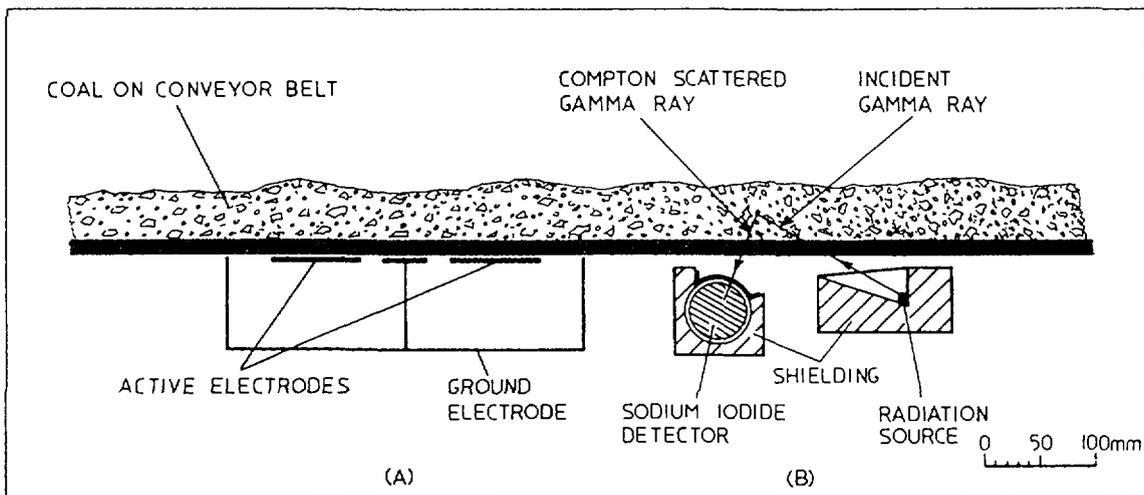


Fig. 8. Underbelt capacitance (A) and γ -ray backscatter density (B) gauges for on-conveyor determination of moisture in coal.

Solids weight fraction, ash and voidage varied respectively in the ranges 0 to 13 wt%, 26 to 41 wt%, and 0 to 4 vol.%. The r.m.s. differences in solids weight fraction and ash were respectively 0.52 wt% and 2 wt%. Better sampling techniques were used in the last half of the plant trial, improving r.m.s. differences to 0.35 wt% solids and 1.5 wt% ash.

The SIROASH coal slurry gauge is licensed to Amdel. The first plant demonstration of Amdel commercial equipment will be undertaken at the Oaky Creek coal preparation plant in Queensland late in 1985. The feed, concentrate and tailings streams will all be continuously monitored for solids and ash content.

Clarkson, Hornsby and Walker (1985) conclude from their work on on-line analysis and control of the flotation circuit at the Peak Downs plant that improvements in combustible recovery of approximately 10% can be achieved. If this improvement is typical, then a A\$2 million per year increase in value of coal product can be obtained from a plant with an annual throughput of 3 million tonnes of coal, if it is assumed that 15% of the coal entering the product flows from the flotation bank, and the coal product value is \$50 per tonne.

ON-LINE ANALYSIS OF MOISTURE

The CSIRO Division of Mineral Engineering is investigating both nuclear and non-nuclear techniques for the on-line determination of moisture. The techniques include capacitance, microwave transmission, nuclear magnetic resonance, infrared reflectance, neutron transmission and scattering, and neutron inelastic scatter (Sowerby, 1984). The most promising methods for the direct on-line determination of moisture in coal on conveyors are capacitance and microwave transmission. For coke the most promising method is neutron transmission.

In the capacitance technique, moisture is correlated with radiofrequency (100 kHz to 10

MHz) susceptance and conductance. A non-contacting under-belt capacitance sensor, in which a fringing electrical field interrogates a layer of material on the conveyor belt directly above the sensor, has been developed for direct on-belt measurement. Variation in the density or thickness of this layer is compensated for using an under-belt γ -ray backscatter density gauge (Fig. 8). Each gauge interrogates equivalent volumes of material, independent of variation in thickness, density or moisture content.

The capacitance technique has been proven under laboratory conditions, and shown to be capable of determining moisture to better than 0.5 wt% (1 σ) for a range of Australian product coals (0-15 wt% moisture) and filtercake (20-30 wt% moisture). A plant trial was undertaken at BHP Stockton Borehole Colliery at Teralba, New South Wales during late 1985, where underbelt capacitance and density gauges were installed on the coking product conveyor.

PLANT CONTROL BASED ON ON-LINE COAL ANALYSIS

The above developments in the on-line analysis of coal are likely to lead in the mid and late 1980s to rapid improvements in the manual control of coal washing and blending operations, and to the installation of simple automatic control loops as the first step towards complete automatic control. Thus the stage is set in the coal industry to emulate the exciting period of the mid 1970s in the metalliferous mineral industry, where the introduction of on-stream analysis systems led to better manual control of concentrators and increased recoveries of valuable minerals.

ON-LINE ANALYSIS OF METALLIFEROUS MINERALS

Continuous on-line analysis of metalliferous ore and ore products is required in various operations in the mineral industry. Examples discussed include

determination of iron in iron ore on conveyors for better control of blending operations, and of sulphur, lead, zinc and iron concentration in lead sinter feed on a grate conveyor.

An application not discussed further in this paper is the use of dual γ -ray transmission techniques (Watt and Steffner, 1985) to determine lead in tailings rejects on a conveyor from a heavy medium separation process.

IRON IN IRON ORE

Quality control in the iron ore mining industry is based on measurements of the chemical constituents of the ore being mined or processed. Conventional analytical techniques rely on accurate sampling, sample preparation and chemical analysis in a well equipped laboratory. These procedures are time-consuming and rely on the final small sample of about 0.5 g being representative of the ore stream from which it was taken.

In order to overcome these difficulties, on-stream analysis techniques based on penetrating neutron and gamma radiation have been developed to continuously analyse the ore on a moving conveyor belt. Sampling and sample preparations are then eliminated, and information on ore grade is rapidly made available to plant operators.

Initially, a neutron method was developed, utilizing a well thermalized ^{252}Cf source, to simultaneously measure the iron and aluminium contents of the ore by thermal neutron capture and thermal neutron activation analysis respectively (Holmes, Messenger, Miles, 1980). Acceptable r.m.s. deviations of 0.6% Fe and 0.1% Al_2O_3 were obtained. However, it was found that the speed of the conveyor could not exceed about 0.05 m/s if good accuracy for Al_2O_3 was required. This is much less than typical conveyor speeds in iron ore plants, so an auxiliary analysis belt was required to avoid interfering with ore-processing. An accurate primary sampler was therefore required to feed the analyser and this substantially increased the installation cost.

The pair-production method of analysing iron ore, now being developed in collaboration with Hamersley Iron Pty.Ltd., overcomes this difficulty (Holmes et al., 1983). Although only iron content can be measured, the analyser is less expensive and can be installed directly on existing conveyor belts, without major modification. The method was originally developed to measure ash in coal (Sowerby, 1984), but can also be used to measure the iron content of iron ore.

The analyser is mounted underneath the conveyor belt (Fig. 9), and analyses the ore through the belt. The presence of steel cables in the belt does not affect the measurement or iron concentration once the analyser has been correctly calibrated. Both static and dynamic trials have shown that lump (-30+6 mm particle size) and fine (-6 mm particle size) ore can be analysed, provided the ore thickness exceeds about 15 cm. Typically, the r.m.s. deviation between pair production and chemical analyses is 0.6% Fe for a single 10 min measurement.

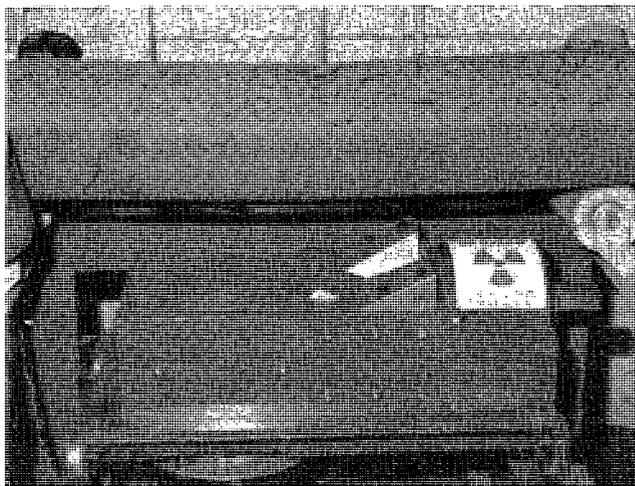


Fig. 9. Prototype pair production gauge mounted under the conveyor facility at Port Melbourne for dynamic trials with iron ore.

Plant trials to assess performance in an industrial environment are presently in progress and the initial results are encouraging.

An obvious application for the analyser is in grade control at a mine, where it would allow a mining company to more effectively use its ore resources by blending as much low-grade ore as possible with high-grade ore to achieve target grades. The analyser can also be used at the port to check grades before the ore is stockpiled or while it is being loaded onto ships.

ON-LINE ANALYSIS OF SULPHUR IN LEAD SINTER FEED

Before lead concentrate can be reduced to metallic lead in a blast furnace, it must be chemically converted from the sulphide form to the oxide form, and the finely divided ore particles must be agglomerated into large lumps. These steps are achieved by sintering, the optimization of which requires on-line analysis of the sulphur in the sinter feed. Analysis is preferably required to within 0.3 wt% sulphur, with an analysis time of less than 5 min. Techniques using penetrating radiation, such as neutrons or gamma rays, are needed if sampling and sample preparations are to be avoided.

The measurement of prompt gamma rays from neutron inelastic scattering is a promising technique for the bulk analysis of lead-sinter feed. Analyses of sulphur, lead, zinc, and iron are based on the measurement of such gamma rays at 2.23, 2.62, 1.00, and 0.85 MeV respectively. A collaborative research and development project between CSIRO and Mount Isa Mines Ltd is being carried out to develop the technique and apply it at the Mount Isa lead sinter plant.

Measurements made on bulk lead-sinter samples at Lucas Heights have shown that determinations of sulphur, lead, zinc, and iron in lead-sinter feed can be made to within about 0.3, 0.85, 0.15, and 0.45 wt% respectively (Cunningham et al., 1984). A sulphur bulk analyser developed at Lucas Heights was field-tested at Mount Isa in October and

November 1983 with static bulk samples of lead-sinter feed and return. The aims of this test were to calibrate the gauge off-line, to determine its accuracy for a wide range of lead-sinter samples, and to closely simulate plant conditions regarding moisture and lead variation. The analyser is expected to be installed on-line in the sinter plant in 1985/6.

INDUSTRIAL NUCLEONICS INDUSTRY

In the late 1960s, Australia had a very small industrial nucleonics industry manufacturing and marketing radioisotope level gauges. The widely used thickness and density gauges were imported from overseas and installed by local agents.

The development of on-stream analysis techniques by the Australian Atomic Energy Commission, with Zinc Corporation Ltd (Watt, 1983) supplying the important concept of the immersion probe, led to the licensing of Phillips Industries Pty.Ltd and Amdel to respectively manufacture and market this system. Phillips later withdrew and Amdel took over completely, introducing improvements to the technology of this system. By 1981, Amdel had installed about 50% of radioisotope on-stream analysis systems throughout the world, and 25% of all installations which included X-ray tube systems developed before the radioisotope systems (Watt, 1983). Amdel's share of the world market has probably increased since then as it has gained good access to the market for on-stream analysis systems in the USSR and has made a good start in development of a market in the People's Republic of China. Amdel has gained a spin-off from the development of on-stream analysis systems by using much of this and similar instrumentation for other applications such as γ -ray density gauges, bench X-ray analysers, uranium ore truck monitors and bulk analysers for copper and nickel. The sales value of these products is about two-thirds that for on-stream analysis systems.

The on-line ash gauge systems have been licensed by CSIRO to MCI. MCI are marketing the SIROASH gauges worldwide under the Coalscan trademark. The first Coalscan gauge was installed late in 1982 and nineteen have now been installed or ordered. The first overseas installation was made in August, 1985.

Australia now has a well-established and advanced industrial nucleonics industry supplying equipment to the metalliferous mineral and coal industries throughout the world. Two of the industrial nucleonic systems developed by Australian industry have won prestigious awards: the in-stream system for analysis of mineral slurries was awarded the Industrial Design Council of Australia's 1973 Prince Philip Prize for Australian Design, and the Coalscan pair production ash monitor won one of the 1984 IR*100 awards given by the U.S. magazine Research and Development for the 100 most significant technical products developed throughout the world and marketed for the first time in the preceding year.

ACKNOWLEDGEMENTS

The development of the on-line gauge systems discussed above, excluding the iron ore applications, have been initiated and developed in collaboration with Australian industry, by a group working firstly with the Australian Atomic Energy Commission and then, since transfer in 1982, with the Divisions of Mineral Physics and Mineral Engineering of the Commonwealth Scientific and Industrial Research Organization (CSIRO Australia). The development of the coal analysis systems has been supported, in part, under the National Energy Research, Development and Demonstration Program of the Australian Government.

REFERENCES

- Clarkson, C.J., Hornsby, D.T. and Walker D.J., 1985. Automatic flotation control using on-stream ash analysis, Third Australian Coal Preparation Conference, Wollongong, November, 1985.
- Cunningham, J.B., Sowerby, B.D., Rafter, P.T. and Greenwood-Smith, R., 1984. Bulk analysis of sulphur, lead, zinc and iron in lead sinter feed using neutron inelastic scatter gamma rays, Int. J. Appl. Radiat. Isot. 35, 635-643.
- Fookes, R.A. et al., 1983. On-line determination of the ash content of coal using a SIROASH gauge based on the transmission of low and high energy gamma-rays, Int. J. Appl. Radiat. Isot., 34 (1), 63.
- Gravitis, V.L., Watt, J.S. and Zastawny, H., 1985. Determination of solids weight fraction and ash content of coal in slurries of variable voidage: laboratory measurements, Int. J. Appl. Radiat. Isot. (in press).
- Holmes, R.J., Messenger, A.J. and Miles, J.G., 1980. Dynamic trial of an on-stream analyser for iron ore fines, Proc. Australas. Inst. Min. Metall., No. 274, 17-22.
- Holmes, R.J., Rocznik, A.F. Rafter, P.T. and Sowerby, B.D., 1983. Grade determination of iron ore using pair production, Anal. Chim. Acta, 152, 105-112.
- Jowett, A., Selby, W. and Sutherland, D., 1980. Preparation for computer control of a cassiterite flotation circuit, Automation in Mining, Mineral and Metal Processing, p. 219 (Pergamon Press: New York).
- Muldoon, L.J., Howells, E.M., Cochrane, E.E.M., Bull, D.M., McLennan, T.D., Sowerby, B.D., Watt, J.S. and Hooper, J., 1985. Ash control in coal preparation plants, Final Report, National Energy Research Development and Demonstration Council Project SD/0227.
- Orrock, G.I., Watters, T.J. and Slattery, T.E., 1978. Radioisotope on-stream analysis at North Broken Hill Limited, Proc. 11th Commonwealth Mining and Metallurgical Congr. (Institution of Mining and Metallurgy: London).

- Smith, K.G., Crowden, H., Sowerby, B.D., Lyman, G.J., Howarth, W.J., 1983. Performance of a Coalscan on-line ash measurement system at Ulan Coal Mines Ltd., Australia, Seminar on Application of Continuous Coal Analysis, Electric Power Research Institute, Nashville, Tennessee EPRI Report CS-989, vol. 13.
- Sowerby, B.D., 1984. Determination of ash, moisture and specific energy of coal, IAEA Advisory Group Meeting on Gamma, X-ray and Neutron Techniques in the Coal Industry, Vienna, 4-7th December, 1984.
- Watt, J.S., 1983. On-stream analysis of metalliferous ore slurries. Int. J. Appl. Radiat. Isot., 34, 309.
- Watt, J.S. and Sowerby, B.D., 1983. On-line determination of ash in coal using SIROASH gauges, Proc. 2nd Australian Coal Preparation Conference, p. 263 (Ed. R.L. Whitmore).
- Watt, J.S., 1984. Determination of ash content of coal on-line on conveyors and in-stream in coal slurries, IAEA Advisory Group Meeting on Gamma, X-ray and Neutron Techniques in the Coal Industry, Vienna, 4-7th December, 1984.
- Watt, J.S. and Steffner, E.J., 1985. Dual energy γ -ray transmission techniques applied to on-line analysis in the coal and mineral industries, Int. J. Appl. Radiat. Isot. (in press).
- Wells, A.P., 1983. On-stream analysis at Wheal Jane, Min. Mag., 148(2), 124.
-

APPLICATIONS AND DEVELOPMENTS OF X-RAY FLUORESCENCE AND NEUTRON ACTIVATION ANALYZERS IN THE FINNISH MINING AND METALLURGICAL INDUSTRY

M. HIETALA
Outokumpu Electronics,
Espoo, Finland

Abstract

Applications and developments of on-line nuclear gauges in the Finnish mining and metallurgical industry are reviewed. The analyzers discussed are X-ray fluorescence process analyzers, XRF portable analyzers, bulk material analyzers based on neutron and gamma sources, and analyzers based on measurement of natural radioactivity.

1 Introduction

In Finland process control and new measurement techniques have always been considered as a method to save scarce material and manpower resources in process industries. The use of X-ray and nuclear techniques has gained a strong position in the mining industry in Finland. Similar systems are in use also in the pulp and paper industry but this paper will concentrate mainly on equipment and applications used and developed for the Finnish mining industry.

2 The Mining industry's role in developing on stream process analyzers

The leading mining company in Finland is Outokumpu Oy, which is a base metal company making Cu, Ni, Zn, Co, Cr and precious metals from its own ore-bodies with processes mainly developed by the company itself. Technologically the company has been selfsupporting and ambitious and it began to develop process measuring techniques extensively in the sixties.

For this reason Outokumpu Oy formed the internal "Institute of Physics" which was organizationally under the head office. The director of this institute was Professor Pekka Rautala who in many ways was an innovative person.

Outokumpu company's first concern was the automation of mineral concentrators. The use of X-ray and nuclear techniques seemed to be suitable for on line analysis applications.

3 X-ray fluorescence process analyzers

The first analyzer developed was the COURIER 300 XRF analyzer based on 1.5 kW X-ray tube, fixed crystal spectrometers and scintillation counters. The first installation was in the year 1970 and since then about 50 units have been sold all over the world into concentrator applications.

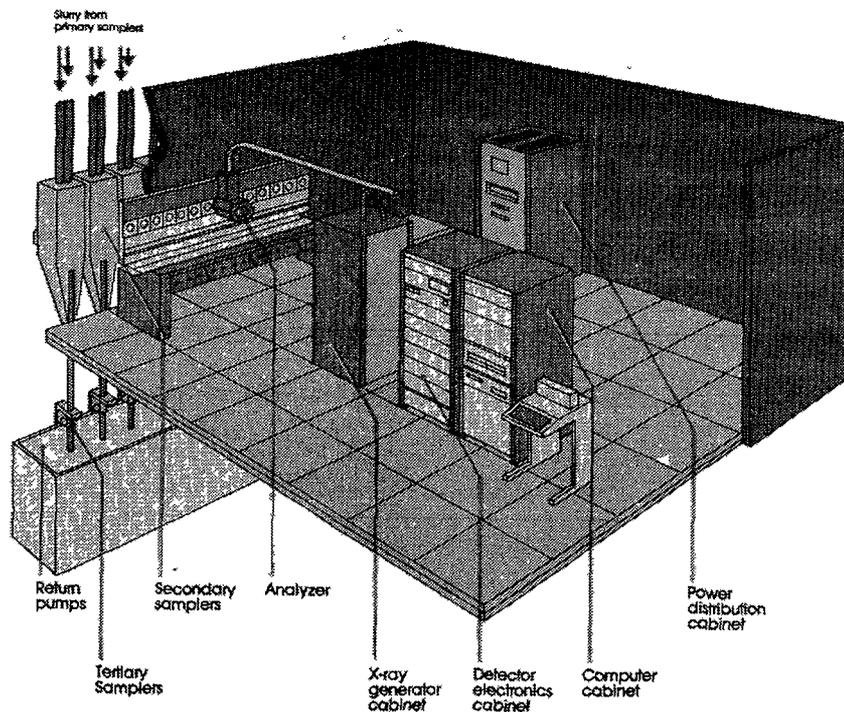


FIG.1. Schematic diagram of COURIER 300 analyzer capable of measuring 28 slurry lines.

The schematic diagram of the unit and installation is in figure 1.

It was very important to develop sampling systems in connection with the analyzer. If the sample was not representative the measurement would be of no practical value.

Mining slurries are practically a mixture of fine ground ore and water. The sample cell design is important for slurries because of the short penetration of X-ray fluorescence radiation in the sample itself. The sample just behind (< 1 mm) the sample cell window gives the information of the process streams. In immersible probes it is sometimes difficult to guarantee good sample representativeness just behind the window and sampling is not as easy to automatize as in by-line applications.

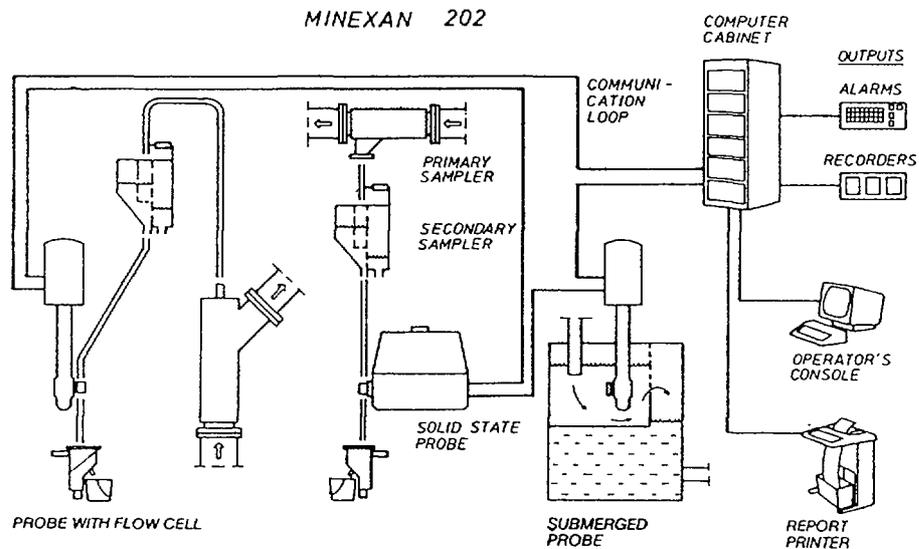
The development of XRF analyzer and sampling systems took quite a long time. To convince process and laboratory people that the system was reliable enough took some time as well. Since the first installation it took approximately four years for practically all Outokumpu concentrators to instal COURIER 300 analyzer. The first installation outside Finland was 1972 to Australia.

COURIER 300 was a centralized analyzer which was able to make measurement of up to 28 streams in sequence. The next stage was to develop a flexible analyzer with short slurry lines or even to be immersed in the process stream. For compact size we used radioisotope sources for excitation and proportional counters as detectors. The project led us to develop a high resolution proportional counter and spectrum stripping techniques based on deconvolution.

The first MINEXAN analyzer was installed in the year 1978. It was quite a successful concept which was used also for on-line measurements of dry powders in cement industry.

The resolution of the proportional counter was not in all cases good enough to separate neighboring elements, one with high concentrate and the other with low concentrate. For this reason a solid state MINEXAN was developed. This analyzer has now been developed into the COURIER 20. It has two measuring cells and to both of them many sample lines can be multiplexed.

Figure 2 shows MINEXAN analyzers and figure 3 COURIER 20 analyzer.



The MINEXAN 202 system offers a low cost solution for smaller applications

FIG.2. Schematic diagram of MINEXAN analyzer with different analyzer probes and samplers.

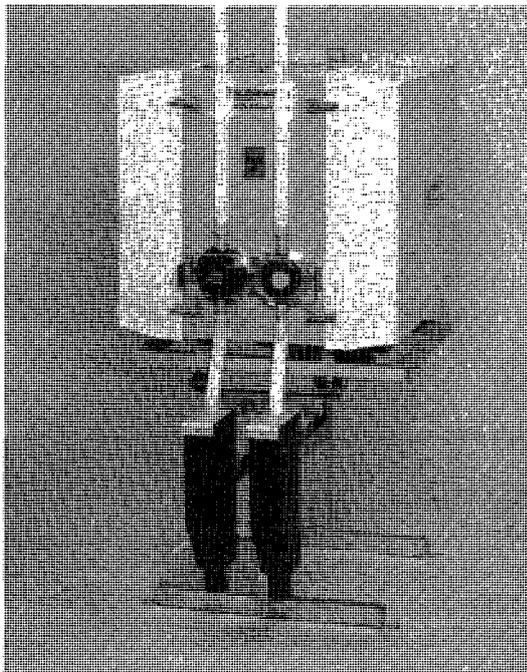


FIG.3. COURIER 20 analyzer with solid state detector and radio-isotope source.

With MINEXAN the concept of near stream or in stream probes was accepted. The benefit of shorter sample lines was smaller running costs. The capacity to use crystal spectrometers in special cases was missing. COURIER 30 was introduced to fill this need. COURIER 30 uses the same crystal spectrometers as COURIER 300 but the X-ray tube is of small endwindow type and the detectors are proportional counters.

The unit will tolerate a harsh process environment and it has been utilized not only in concentrators but as well in hydrometallurgical plants with very corrosive and quite hot liquids. One has been installed for tests in the liquid extraction process of nuclear fuel enrichment plant.

A new analyzer based on X-ray diffraction and XRF has been developed recently from COURIER 30. This will be suitable for mineral slurries for direct measurement of mineral contents. The applications seem to be good especially for minerals containing light elements only where the XRF method is not useful. Figure 4 shows the picture of COURIER 30 and figure 5 the principle of COURIER 40 analyzers.

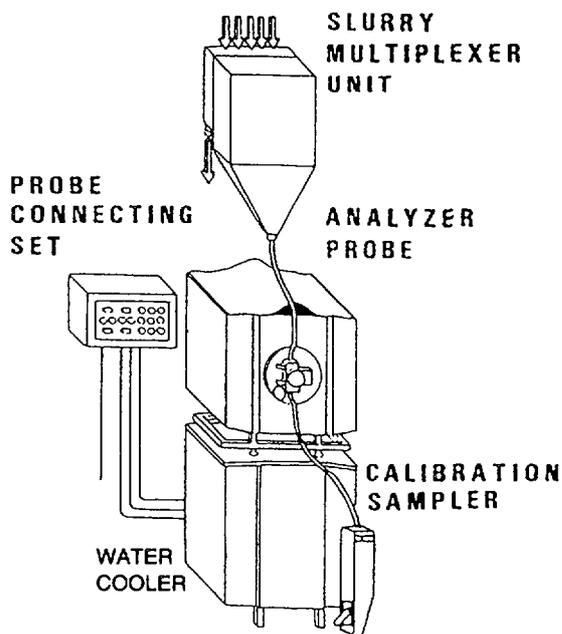


FIG.4. COURIER 30 analyzer equipped with X-ray tube and crystal spectrometers.

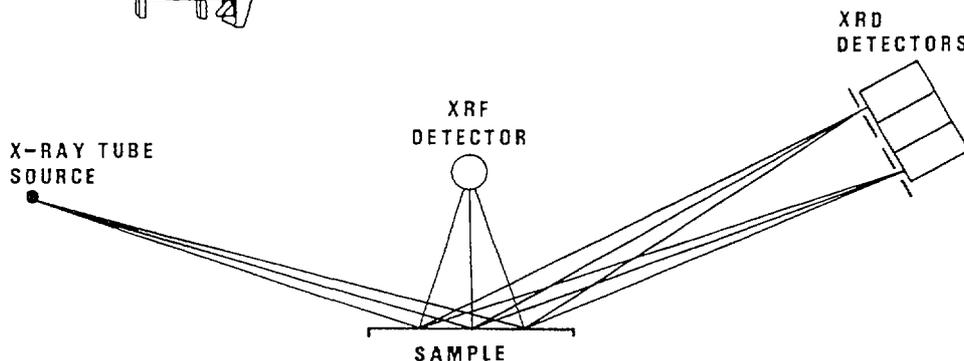


FIG.5. COURIER 40 looks like COURIER 30 but it contains diffraction tube and has detectors for measuring diffraction lines as well as fluorescence radiation.

A spin off of the MINEXAN analyzer was a portable bore hole logging analyzer based on proportional counter and the use of radioisotope source. This was also our first experiment in using microprocessor power built into the analyzer itself. From this analyzer we developed the present X-MET analyzer. The first prototypes were made more than ten years ago. The product and software have been further developed since its introduction and now it is a successful analyzer. Almost 500 units have been sold in 25 countries.

Figure 6 shows X-MET 840 with different probe types and figure 7 a bench top model X-MET 820.

The X-MET 840 analyzer has been used for various applications like: alloy analysis and identification, coating and pigment measurements, ore prospecting and as substitute of bigger laboratory X-ray analyzers. Some applications have been truly on-line measurements of the process.

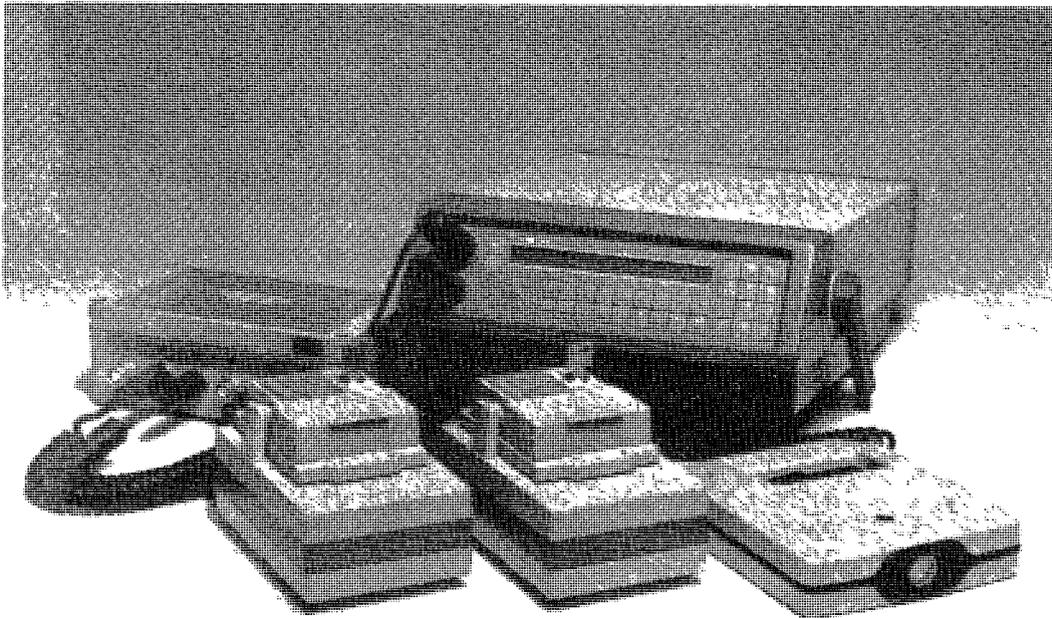


FIG.6. Portable X-MET 840 model with three measuring heads for different applications.

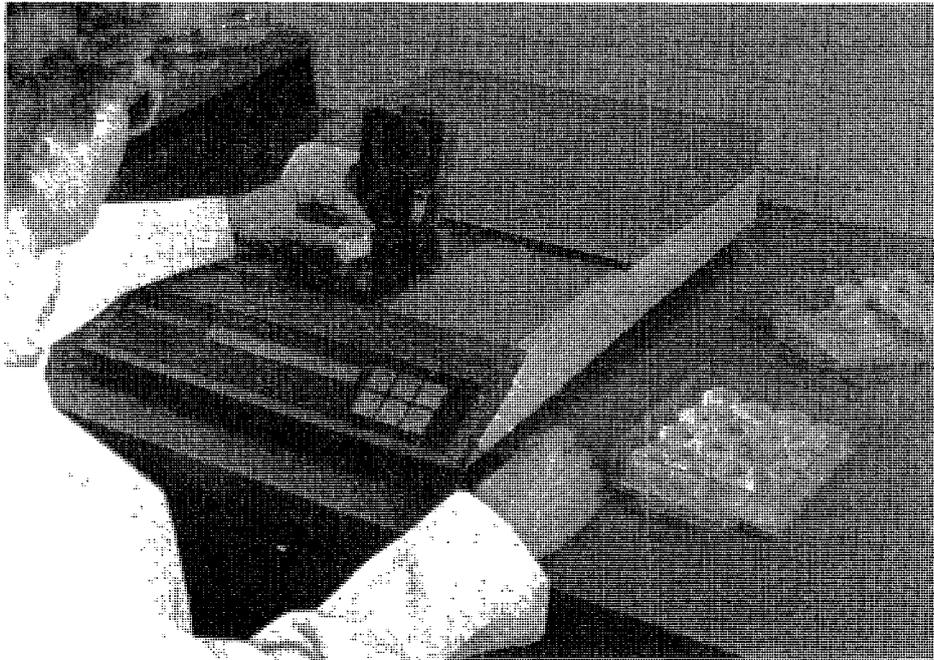


FIG.7. Bench top model X-MET 820.

5

Bulk material analyzers with neutron sources

Since the beginning of Outokumpu's Institute of Physics neutron activation analysis and prompt gamma measurements were considered as methods for the future in applications process industry. Compared to the XRF method much bigger volumes were contributing to the analysis and possible sampling devices were simple if needed at all.

Also, in the sixties the use of neutron sources were not considered as harmful as today. Outokumpu built a neutron activation analyzer called NACTAN which is shown in figure 8. The analyzer was first used to measure Si and Cr in Outokumpu Kemi concentrator. Later on more units were sold to the Finnish cement industry to measure Al and Si in raw meal.

Neutron methods were further studied to develop a prompt gamma analyzer for ore measurement purposes and for concentrate measurements for smelter feeds.

Much work was done to minimize background radiation from the Cf-252 source to the detector. One prototype was built and sensitivities for real samples were measured for conveyor type applications.

The project was set on hold because the accuracies for wanted elements, like sulphur, were not good enough with scintillation counter. The resistance to the use of a neutron source was increasing as time passed and the price of the system was estimated to be rather high and the stability of big germanium detectors unknown etc. We did never take this system into commercial use.

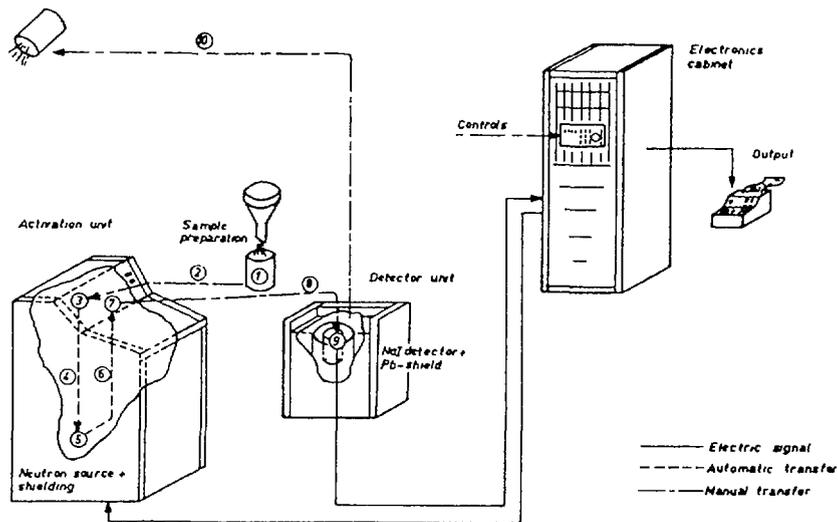


FIG.8. Schematic diagram of NACTAN NAA-analyzer used for cement raw meal measurements.

6
Bulk material analyzers with gamma sources

We did continue bulk material analysis by using gamma ray backscattering. The scattering coefficients depend on energy and on atomic number. By using Am 241 and Cs 137 gamma radiations backscattering ratio material containing light elements can be separated from material containing heavy elements.

The first device using this method was the ore sorter called PRECON. A schematic picture of it is in figure 9.

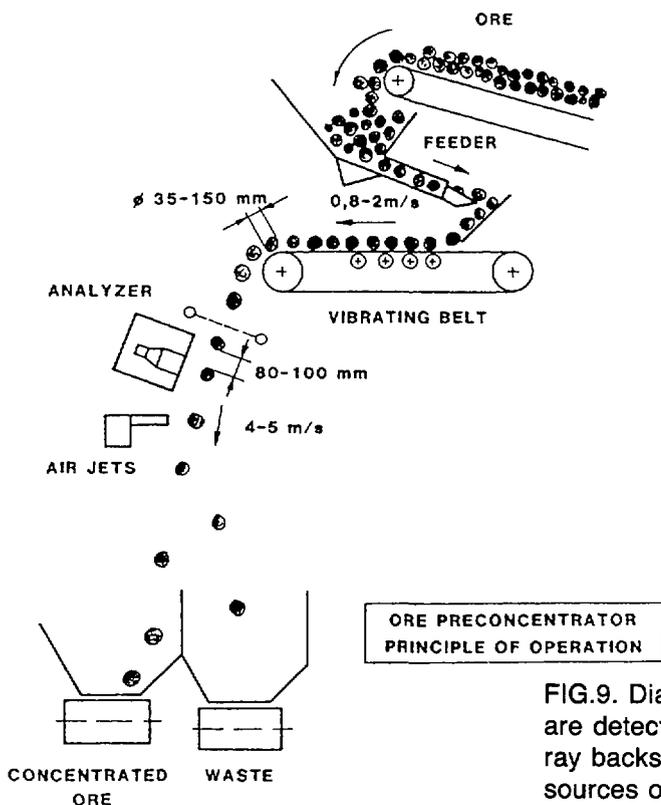


FIG.9. Diagram of PRECON ore sorter. The ore lumps are detected during free falling either by gamma ray backscattering of two different radioisotope sources or by X-ray fluorescence measurements.

In this unit the ore lumps were measured in free fall and were sorted to different bins by air blasts. This is a cost effective enrichment method when ore transport or grinding capacity is a bottle neck.

The measuring heads of PRECON can also be used to analyze the nature of material on a conveyor belt. This application has found many practical installations especially in iron ore concentrators. The unit is called BELTCON and its picture is in figure 10.

We have developed measuring heads for PRECON and BELTCON further based on XRF method with X-ray tube and filtering techniques.

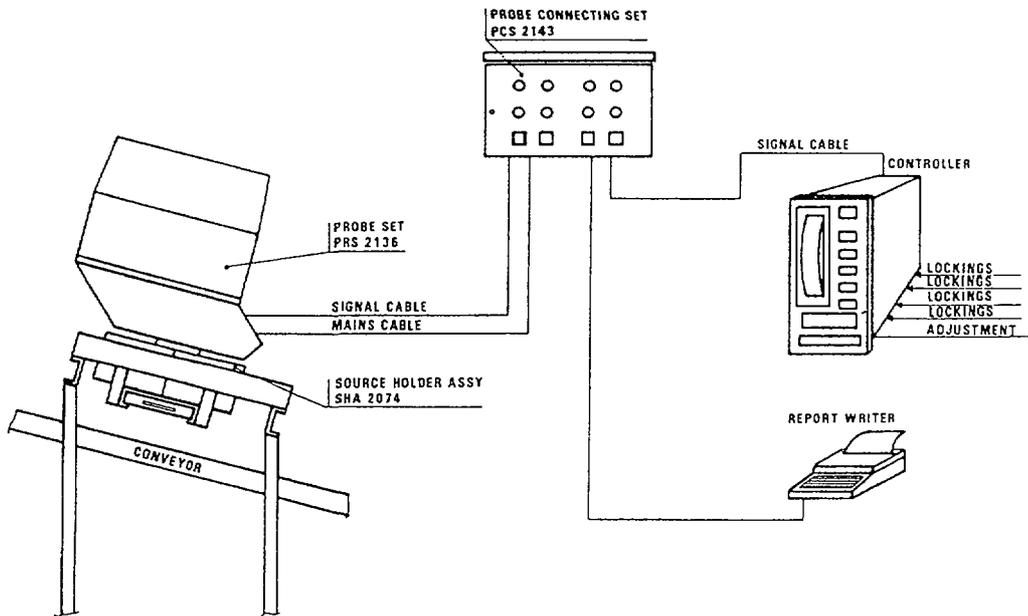


FIG.10. BELTCON measuring head for analysing material on conveyor belt. This measuring head is used also in PRECON.

7

Bulk material analysis based on natural radioactivity

Historically the first ore sorter designed by Outokumpu was based on uranium's natural radioactivity. This unit is not in use because we did not open an uranium mine in Finland.

Outokumpu has also designed and manufactured immersible probes for the potash industry based on K40 natural radioactivity.

8

Conclusions

The use of on stream analysis based on neutron and X-ray methods have quite a long history in Finland and they are intensively used for mining industry in base metals. Today the use of the above mentioned methods will increase also other applications in chemical industry.

Especially X-MET, COURIER and BELTCON analyzers have proven to be simple and reliable enough for use even in distant places and in developing countries.

REFERENCES

- 1 Leppälä, A., Koskinen, J., Leskinen, T., Vanninen, P., "COURIER 300 On-stream Analysis System", Trans. of SMC 250 (1971).
- 2 Hietala, M., Viitanen, J., "Advances in X-ray Analysis" (BARRETT, C.S., LEYDEN, D.E., NEWKIRK, J.B., RUUD, C.O., Eds) 21, Plenum, New York (1978) 193 - 205.
- 3 Rautala, P., Hietala, M., Sipilä, H., "Application and Economical Aspects of WDXRF and EDXRF Techniques in Industry", A Proceeding of an Advisory Group Meeting on Practical Aspects of Energy Dispersive X-ray Fluorescence Analysis Organized by the International Atomic Energy Agency and Held in Vienna, 29 May - 2 June 1978.
- 4 Hietala, M., Kiuru, E., "New Energy and Wavelength Dispersive On-stream XRF Probes", Third IFAC Symposium on Automation in Mining, Mineral and Metal Processing, Montreal, August 1980.
- 5 Rhodes, J. R., Rautala, P., "Application of a Microprocessor-based Portable XRF Analyzer in Minerals Analysis", Int. J. Appl. Radiat. Isot. Vol. 34. No. 1, pp. 333 - 343, 1983.
- 6 Lundán, A. I., Mattila, O. P., "Use of Radioisotope Neutron Activation and X-ray Fluorescence Analyzers in Process Control", Presented at the IAEA (International Atomic Energy Agency) Symposium on the Use of Nuclear Techniques in the Basic Metal Industries - Helsinki, Finland - 31 July - 4 August 1972.
- 7 Sipilä H., "Kaappausgammamenetelmän sovellutuksia", Vuoriteollisuus nro 2/1980 (in Finnish, English summary).

PROMPT GAMMA RAY MEASUREMENT

(Summary)

W. HERZOG

Staatliches Materialprüfungsamt,
Dortmund, Federal Republic of Germany

The Prompt Neutron Activation Analysis (PNAA), i.e. the measurement of prompt γ -rays after neutron capture as an analytical instrument, has been used by the Staatliches Materialprüfungsamt in Dortmund (FRG) for several years. The equipment consists of a source housing suited for up to 2 mg of Cf-252. The neutron source is mounted on a rod which can be moved mechanically in order to vary the neutron flux by different source to sample distances. The γ -ray detection system consists of a HPGE-Diode coupled by commercially available analog and digital electronics to a 8 k MCA and a DEC PDP 11/23 minicomputer. A detailed description of the instrumentation is given in refs. (1, 2). The samples are filled in cylindrical plastic containers which are positioned between source and detector. The sample size has been varied between 60 and 130 kg. In hard coal and lignite the following elements could be determined within 1000 sec irradiation and measuring time: hydrogen, carbon, nitrogen, sodium, aluminium, silicon, sulphur, chlorine, titanium and iron. For all these elements calibration curves as functions of the prompt γ -ray-yield vs. concentration have been established. In all cases a linear dependency resulted.

As examples, fig. 1 presents the calibration curves for silicon and carbon. To give an impression of the accuracy and reproducibility, table 1 contains results of ash building elements in a hard coal sample by the PNAA determination and two chemical laboratories. With the exception of the alkaline elements the reproducibility (standard dev.) of the PNAA is sufficient for process control purposes.

Using special experimental set ups, e.g. iron and bismuth shielding, it has been demonstrated on synthetic lead-, copper- and zinc-ores in the concentration range of 1-5 %, that the PNAA could be suited for the process analysis in the mineral industry. Furthermore the analysis of lime-stone for the elements calcium, silicon and iron was possible within several minutes.

Recently, the investigations had been concentrated to the rapid analysis of raw glass mixture with emphasis on the determination of sodium, silicon and calcium. Fig. 2 shows a prompt γ -ray spectrum of 60 kg of raw glass. In order to reach a sufficient reproducibility of the analyses the areas of more than one γ -peak of each element were summed up.

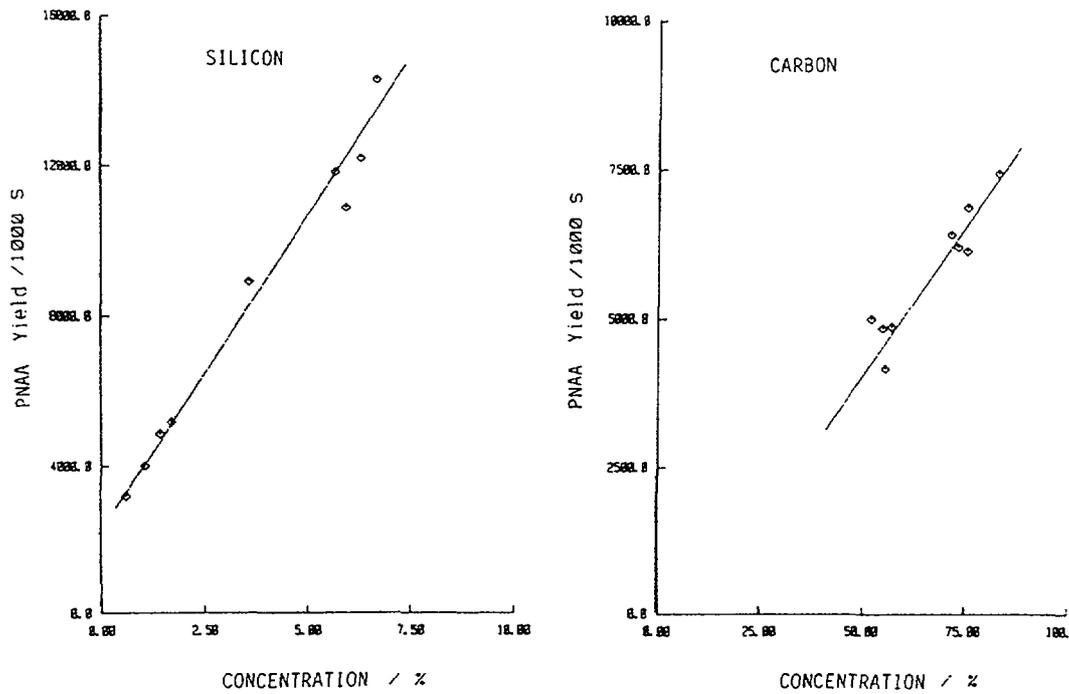


Fig. 1 : Calibration curves

TABLE 1. COMPARISON BETWEEN PNAA AND CHEMICAL ANALYSIS

Origin: Australia				
	Chem			
	Lab. 1	Lab. 2	PNAA	Error % rel.
Al	1.21	1.24	1.33	5.8
Si	4.55	5.28	5.18	1.8
Fe	0.88	0.83	0.86	1.5
Na	0.04	0.04	0.04	44.3
K	0.12	0.13	0.13	32.6
Ca	0.13	0.11	0.14	17.0
Ti	0.07	0.06	0.07	8.9
S	0.46	0.47	0.42	9.6
Cl	0.07	-	0.07	2.9

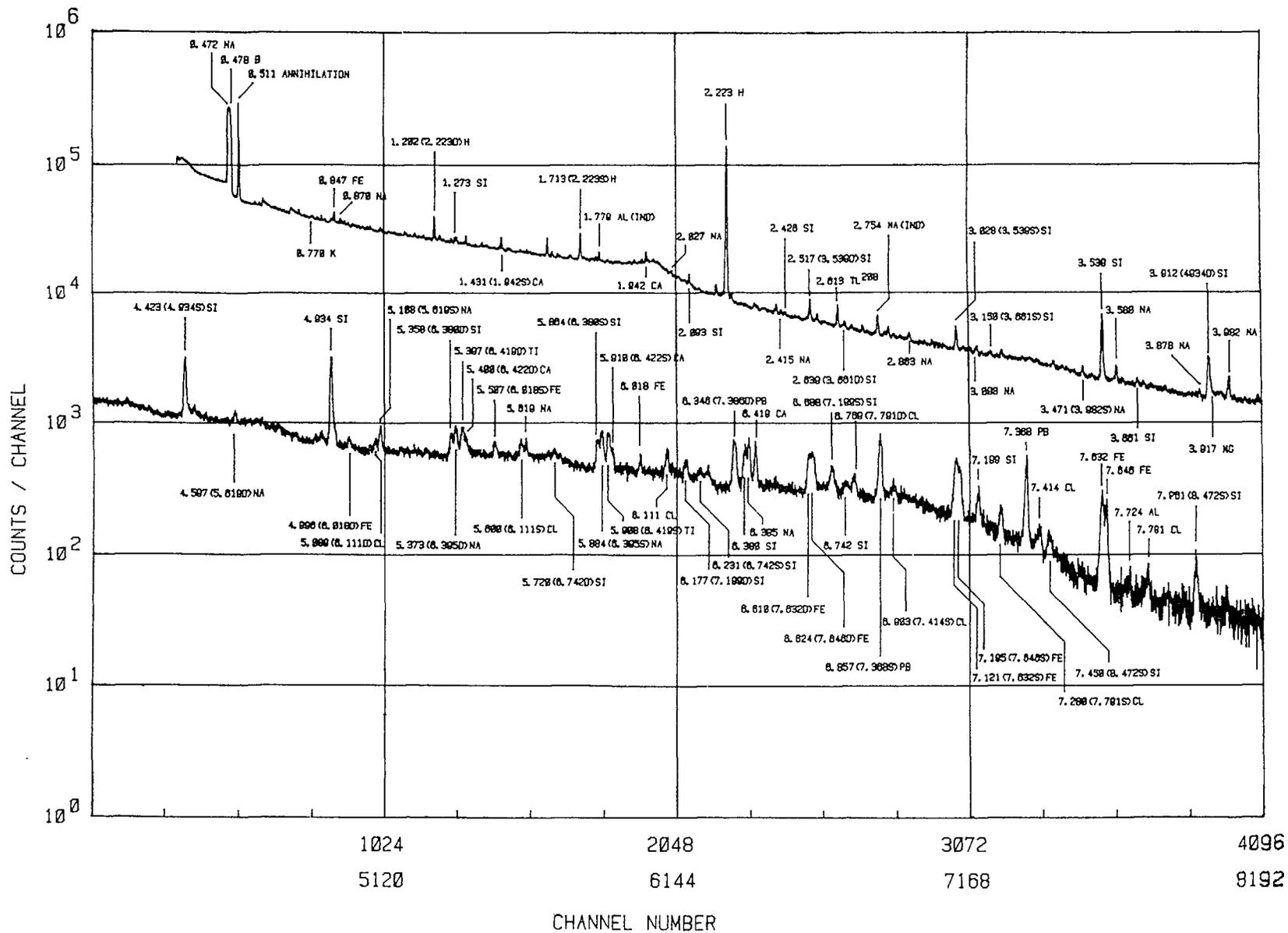


Fig. 2 : PNAASpectrum of raw glas mixture

TABLE 2. ANALYSIS OF RAW GLASS MIXTURE: COMPARISON OF RESULTS

Sample Nr.	SILICON DIOXIDE / %			SODIUM OXIDE / %			CALCIUM OXIDE / %		
	Chem. theor.	Chem. exp.	PNA A	Chem. theor.	Chem. exp.	PNA A	Chem. theor.	Chem. exp.	PNA A
1	58,8	58,3	58,9	11,3	11,5	11,5	7,8	7,6	7,7
2	60,3	60,4	60,5	10,9	10,3	11,0	7,5	7,5	7,5
3	61,8	62,3	61,7	10,5	10,6	10,3	7,2	6,9	7,3
4	56,3	56,4	55,9	12,1	11,9	12,1	8,6	8,5	8,3
5	54,0	53,1	54,2	12,9	12,9	12,8	9,3	9,3	9,5
$\sum \delta_{ij} $	-	2,1	1,0	-	1,1	0,6	-	0,6	0,7
F abs. / %	-	-	0,83	-	-	0,37	-	-	0,48

Explanations:

Chem. theor.: theoretical composition of the raw glass mixture

Chem. exp. : experimental chemical analysis (AAS, wet chemistry)

PNA A : calculated from calibration curves

$\sum |\delta_{ij}|$: Absolute sum of the deviation from theoretical value

F abs. / % : Absolute error of PNA A results calculated from standard deviation and the slope of the calibration curve.

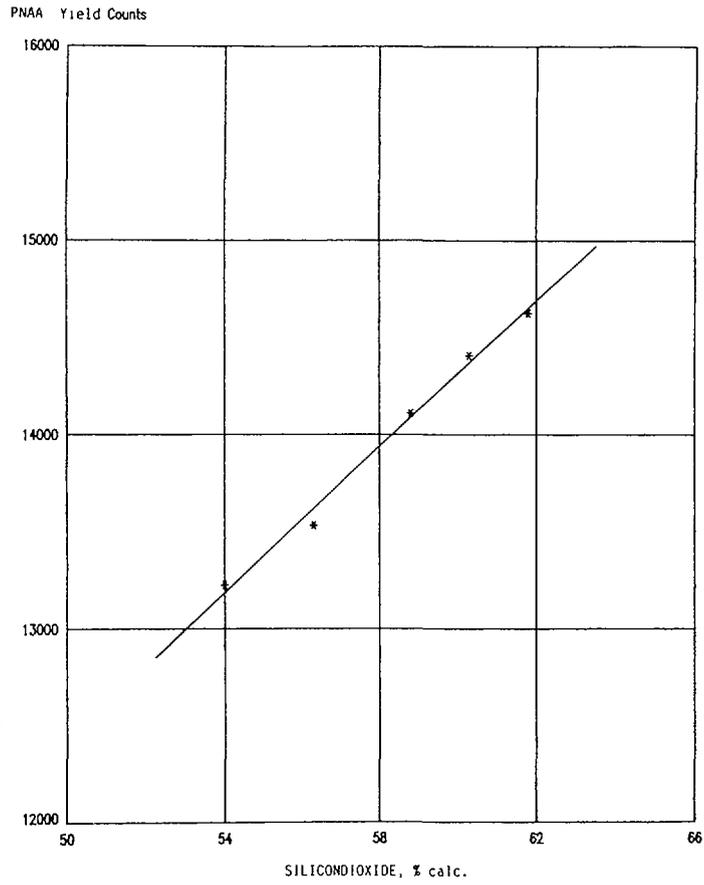


Fig. 3 : Calibration curve for silicon in raw glass mixture

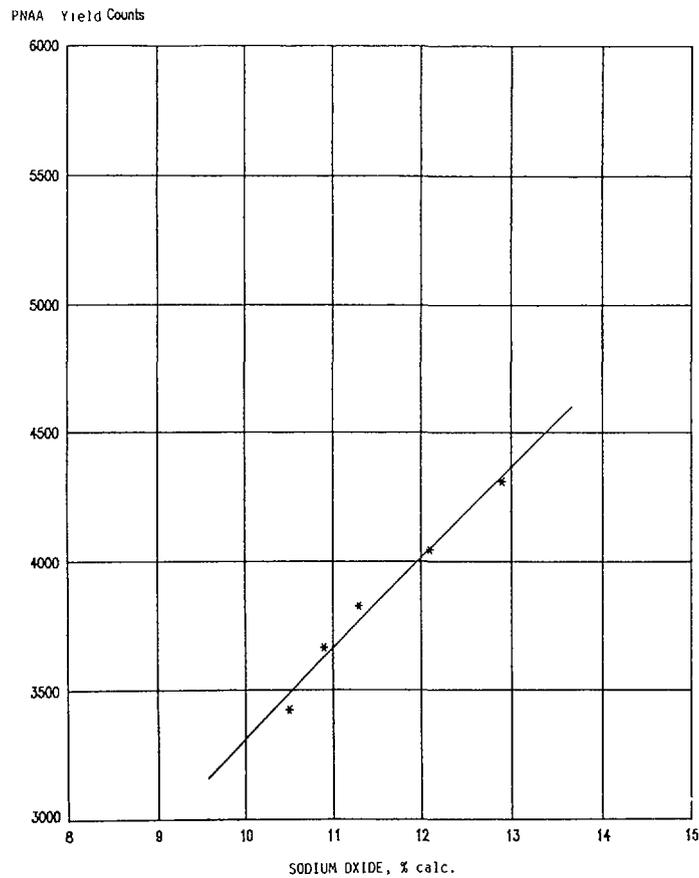


Fig. 4 : Calibration curve for sodium in raw glass mixture

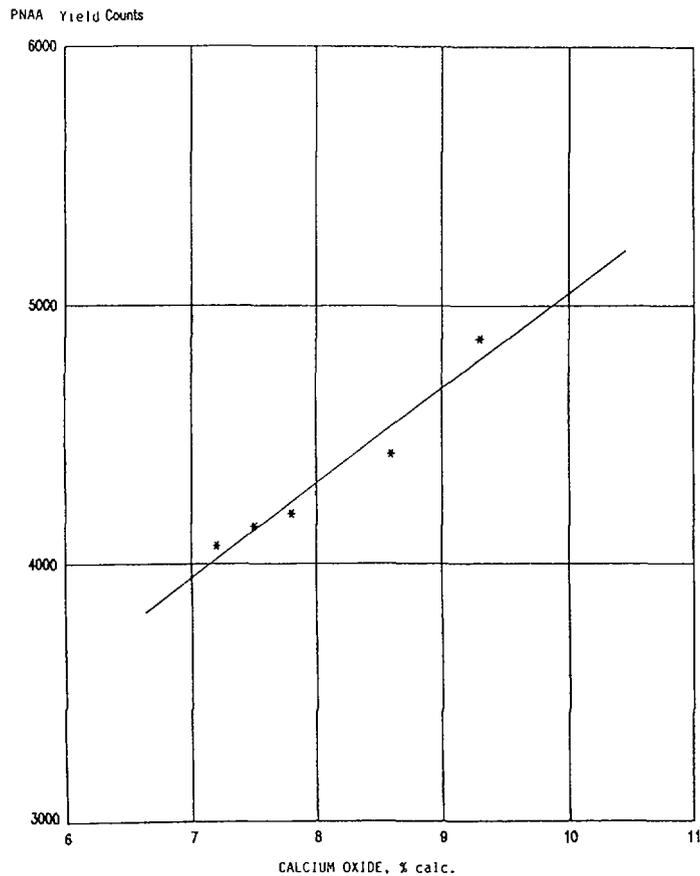


Fig. 5 : Calibration curve for calcium in raw glass mixture

The maximum irradiation and measuring time was limited to 360 sec. The figs. 3-5 show calibration curves for Na, Si and Ca in mixtures of known concentration. The table 2 shows a comparison of chemical analysis and PNAA results of these standard mixtures used for calibration.

As can be seen, the values of $\sum/\delta_{ij}/$ are smaller for the PNAA than for the chemical analysis. This indicates that the PNAA results in a higher accuracy than the chemical analysis.

However, further efforts will be made in order to achieve a greater reproducibility of the results, especially in the case of the silicon determination.

REFERENCES

- (1) H.R. Wilde, W. Herzog, On-line analysis of coal by neutron induced gamma spectrometry, J. Radioanal. Chem., 71 (1982), 253.
- (2) W. Herzog, H.R. Wilde, Kontinuierliche Analyse von Steinkohle, VGB Kraftwerkstechnik 64 (1984), 348.

NUCLEAR ANALYTICAL TECHNIQUES FOR INDUSTRIAL PROCESSES IN JAPAN

H. TOMINAGA

Japan Atomic Energy Research Institute,
Tokai-mura, Naka-gun, Ibaraki-ken,
Japan

Abstract

Nuclear analytical techniques used for process control in Japan are reviewed. The most common applications are determination of sulphur in oil, analysis of cement raw mix and determination of coating weight.

GENERAL

Japanese industry may be said, from the standpoint of natural resources, to be a typical manufacturing industry which has no domestic resources in significant quantities, except air, water and cement raw materials.

Radioisotope-equipped analytical instruments are therefore only in use in industrial processes for manufacturing where economical effects by use of the instruments are clearly evaluated or legal regulation forces industry to employ some instruments (the case of sulfur meters to control sulfur dioxide emission into the air). Recently, increase of production equipments in industries, in which radioisotopic instruments have been mainly used, almost stopped since the age of high economic growth was gone. The number of instruments in use, therefore, also seems not to increase in this several years.

Radiation-applied analytical instruments used actually on-line in industrial processes, even including tube X-ray generators and accelerators, are concentrated at the use of X-rays and γ -rays, while neutrons are not yet in routine use. Those are

- sulfur meters for oil
- cement raw mix analysers
- coating weight (or thickness) gauges including multi-elements- and multi-layers coating, and concentration gauges for galvanizing solutions.

Coal ash meters disappeared because of closing of coal mines.

Also in off-line uses of the analytical techniques for process control, the majority of them are X-ray instruments, and almost all of them use X-ray tube generators:

- sulfur meters
- analyzers for mineral ores including cement raw mixed materials and alloys etc.
- a portable X-ray fluorescence analyzer with radioisotopes being recently spreading for non-destructive alloy analysis etc.

As a typical nuclear technique in off-line use, reactor-neutron-induced α -particle autoradiography is now routinely used to control a trace amount of boron and its distribution in special steel plate production lines.

A 14 MeV neutron activation analysis technique was employed once about 20 years ago to determine the content of oxygen in steel in front of furnaces of a steel making process in several companies. However, it has been later replaced by a new non-nuclear technique, the electric cell technique, which is capable of measuring free oxygen separately from combined one.

In research and development of industrial production processes, analytical techniques using charged particles from accelerators are increasingly becoming of interest in recent years, in particular, for trace element analysis in semiconductor or other new materials.

DETAILS OF ON-LINE INSTRUMENTS

1 Sulfur meters for oil

- The largest in number of the instruments of all the radiation-applied analytical instruments for industrial process control.

1.1 Statistics

Radioisotopic - almost all in on-line use

Total: 413 in private industries
 32 in other organizations
 Σ 445
 (as of March 31, 1986)

Item of 413:

Main users

209 in petroleum refineries etc.
118 in electric power stations etc.

Methods

339 by X-ray transmission (γ -excited X-rays with
 ^{241}Am , YEW)
71 by X-ray fluorescence (with ^{55}Fe , Mitsubishi)

Tube X-ray - all in off-line use

The number is not clear.

Both methods of X-ray transmission and fluorescence.

1.2 Main features

Radioisotopic

• Common for both methods, compared with tube X-ray instruments:

- 1) Ease of attaining explosion proof safety
- 2) Ease of maintenance (suitable to continuous on-line measurement)

• Transmission method

- 1) A long life radioisotope used (^{241}Am)
- 2) No influence by C/H ratio by using an X-ray energy (~ 20 keV) at which the magnitudes of mass attenuation coefficients of C and H come equal

- 3) (Disadvantage) manual correction required for significant contents of heavy metals

- Fluorescence method

- 1) Little effects by heavy metals
- 2) Correction incorporated for C/H ratio by measuring the Compton scatter peak at the same time
- 3) Capability of determining the combustion heat of oil by a combination of three measurements of S, C/H and density

Tube X-ray

- 1) No legal regulation concerning the use of radioisotopes
- 2) Short time measurement because of a high output intensity of X-rays

2 Coating weight (or thickness) gauges

- The most typical tube X-ray fluorescence gauges in on-line use, and radioisotopic X-ray fluorescence gauges in a complementary use.

2.1 Number of gauges (RIGAKU)

Radioisotopic

23 in Zn and Sn-Pb alloy coating on steel plates

Tube X-ray

58 in Zn, Zn-Fe alloys, Sn/Cr, and Sn/Ni coating on steel plates
28 in magnetic layer on films (memory tapes and disks)

2.2 Main features

Radioisotopic

- 1) Mainly used in Zn coating in a thicker range (200 - 400 g/m²) for a higher energy γ -ray from ²⁴¹Am (60 keV)

- 2) Lower cost (~ 30 MYen, a half of that of tube X-ray instruments)
- 3) Ease of maintenance
- 4) (Disadvantage) slower response time (4 s in the Zn coating weight gauge with an ^{241}Am source of 500 mCi x 2)

Tube X-ray

- 1) Capability of element-selective measurement by wave-length dispersion with analyzing crystals and goniometers
- 2) Therefore applicability to multi-layers of multi-component coating
for example:
an anti-corrosion steel plate for automobile
 - upper layer (5 g/m^2) = 80 % Fe, 20 % Zn,
 - lower layer (20 g/m^2) = 30 % Fe, 70 % Zn
 - the mean values of Fe/Zn ratio and coating weight of the two layers are obtained from the measurement with two sets of analyzing crystals and goniometers arranged at two different angles (30° and 80°)
- 3) High speed response (0.4 s in the Zn coating gauge)
- 4) (Disadvantage) a coating range of Zn thicker than 200 g/m^2 is difficult by the gauge with a 40 KV tube X-ray generator

3 Concentration gauges for galvanizing solutions

- A radioisotopic X-ray fluorescence gauge is in on-line use for measurement of Sn concentration.

7 sets (RIGAKU)

A slow response (80 s) is enough in this measurement.

4 Cement raw mix analyzers

- Only X-ray fluorescence analyzers are in use both in on-line and off-line analysis of raw mixed materials in cement factories.

On-line radioisotopic analyzers (6 sets by RIGAKU) with a 20 mCi ^{55}Fe source and a scintillation counter used to measure the concentration of lime (Ca) in mixed materials.

On-line tube X-ray analysis (9 sets by RIGAKU) used for analysis of the 4 components of Ca, Si, Al and Fe in by-pass sampling lines in mixing processes.

Both analyzers remain no shipping since 1983 perhaps because of bad business conditions.

VALUE OF NEUTRON ACTIVATION TECHNIQUES FOR OFF-LINE INDUSTRIAL ANALYSIS

(Summary)

T.B. PIERCE

Analytical Sciences Division,
United Kingdom Atomic Energy Authority,
Harwell, United Kingdom

INTRODUCTION

Neutron activation analysis is a well-established analytical technique which has been known for approximately half a century and which has benefitted from intense development in many major laboratories during the 1950's and the 1960's. Over that period of time, investigations not only covered development of the technique itself, but also the equipment and instrumentation needed for its widespread implementation. Development has continued over more recent years and an extensive literature has built-up covering a wide range of techniques and applications.

As sample irradiation is an intrinsic part of the analytical procedures, a wide range of irradiation facilities have been assessed, varying from small and relatively simple devices such as radioisotope sources to large and complex installations, for example linear accelerators and nuclear reactors. While neutrons have been most extensively used for sample irradiation, there has been considerable investigation and application of charged-particles and of gamma photons for sample irradiation. While the induced activity emitted as the result of radioactive decay provided the basis of the majority of determinations, prompt radiations, emitted during the irradiation process, have also provided the basis of specialised analytical measurements.

In spite of the range of measurements available, neutron irradiation has found widest acceptance and by far the largest number of determinations have been based upon the use of high-flux facilities. However, in considering the position of neutron activation analysis within the general family of analytical techniques, it is clear that other methods have been more widely adopted, particularly in industrial environments. Neutron activation analysis remains a technique of specialised rather than of general use, being exploited either in specialist centres which have made a particular feature of applying the technique, or for particular applications with requirements which match the characteristics of the technique itself.

INSTRUMENTATION

Instrumentation for the detection of nuclear radiation has been constantly improved and much advanced equipment is available. The digital nature of nucleonic information makes nuclear systems suitable candidates for computerisation and extensive use has been made of computer techniques in

the acquisition and processing of data. This has led to the development of sophisticated data processing techniques which can be applied cost-effectively to routine determinations in appropriate cases.

APPLICATIONS

The off-line application of neutron activation analysis to industrial problems tends to have centred on the exploitation of two separate features of the approach: (a) high sensitivity and (b) ease of determination.

(a) High Sensitivity

High sensitivity for activation analysis has been exploited from the earliest days of the technique, initially by making use of chemical separation but subsequently, with the increase in capability of intact methods of analysis based upon gamma-ray spectroscopy, moving to greater acceptance of instrumental techniques.

(b) Ease of Determination

The ability to measure the elemental content of intact samples has always been attractive when large numbers of determinations are required and the ability to carry out elemental determinations by gamma-ray spectroscopy on an intact, irradiated sample is particularly attractive for process-control type analyses where large numbers of similar samples are to be examined on a routine basis. A further advantage centres on the ability to obtain information from a relatively large sample, since a bulk figure can be obtained which can minimise the effect of inhomogeneities in the sample material.

RELATIVE STATE OF NEUTRON ACTIVATION ANALYSIS

The extent to which newer analytical techniques have been adopted in industrial laboratories in preference to activation analysis, over recent years raises the question why neutron activation analysis has not been more widely used. It is possible that three reasons have contributed.

(a) Availability of Sources

The neutron source is clearly an intrinsic part of neutron activation analysis and for most convenient use, the source should be situated locally to the application. Whilst it is, of course, quite feasible to carry out research and post-mortem analyses by irradiation at a relatively remote site, this is unlikely to be the preferred way forward for routine determinations. The limited availability of nuclear reactors at local sites has meant that applications requiring high-intensity irradiation have tended to be used more for research investigations and local determinations have centred on other types of neutron source, which are by their nature less intense, for example neutron generators and radioisotope sources.

(b) Incomplete Elemental Coverage

The analytical method must be chosen to match the requirements of the determination and clearly when the requirement is for a multi-element information, it is important that the chosen method offers as complete a coverage as possible since this reduces the complexity of the overall procedure. Further, the ease with which the total determination can be carried out is of importance since this also determines the time and cost. The dependence of activation analysis on the neutron cross-section which varies from one element to another and from one reaction to another often means that it is not always easy to get reliable determinations for combinations of elements thus reducing the acceptability of neutron activation analysis for that particular determination.

(c) The Perception of Hazards of Radioactivity

An additional factor in restricting the use of radiation-based techniques is the perception of the hazard associated with the use of radioactivity. Whilst, in many cases, this concern is out of proportion to the real hazard, it nevertheless, in many cases, does act as a deterrent to the use of the techniques.

In spite of the obvious limitations of and concerns with activation analysis as an industrial analytical tool, it still has found extensive application. Its value as a research tool is established and where the requirements for the determination match the capabilities of activation analysis, the technique can be very effective indeed, offering high-throughput determinations at low unit cost. For example, methods based upon isotope neutron sources have been applied very satisfactorily to various types of mineral analyses where alternative methods would be both more time-consuming and difficult. There may also be scope for exploiting the particular characteristics of activation analysis in providing information from solid samples by obtaining the information about elemental distributions in inhomogeneous materials, for example by using tomographic detection techniques.

APPLICATION OF X-RAY TECHNIQUES FOR THE DETERMINATION OF VERTICAL PAPER FILLER DISTRIBUTION

H. KUMPULAINEN

Reactor Laboratory,
Technical Research Centre of Finland,
Espoo, Finland

Abstract

This paper describes principles and feasibility studies of a method which enables even on-line determination and thus also control of vertical distribution and content of filler materials in paper using X-ray techniques. The method is much faster than the ones presently used in paper industry and offers potential for considerable technical and economical benefits.

1 INTRODUCTION

In the paper industry finely ground mineral filler materials are used to improve paper printability, opacity and brightness. Since fillers may also be cheaper than fibers, their optimal use will strongly affect both the product quality and the manufacturing economy. A good-quality printing paper should show the least possible two-sidedness, so that also the filler should be distributed as symmetrically as possible between the surfaces of the sheet.

Because most paper manufacturing processes produce two-sided papers, it is essential to have some method for determining the paper filler distribution. All the methods presently in use are destructive, slow and laborious. For example the sheet splitting method frequently used necessitates thorough soaking of the sheet in water and freezing in the nip of two rolling steel cylinders, in which the sheet is torn into two pieces, these are then once more torn into two pieces. Each piece of the split sheet has to be dried in an oven, cooled down in an exsiccator, weighed, incinerated in a crucible, again cooled down in an exsiccator, weighed, and once more incinerated in an oven at a still higher temperature to decompose calcium carbonate in case of the filler containing it, cooled down in an exsiccator and weighed. By performing a few X-ray measurements directly from the paper sheet the filler distribution perpendicular to the sheet surface can be determined rapidly and nondestructively. The method also provides a potential for on-line measurement. This paper will briefly describe the principles of the method. Furthermore, some practical viewpoints from the feasibility studies will be presented.

The construction of the experimental instrumentation and the feasibility studies were carried out mainly at the Reactor Laboratory of the Technical Research Centre of Finland within a joint project with Oy Kymi-Kymmene Ab Inc., Kemira Oy Inc. and Valmet Oy Inc. and later with Kymi-Strömberg Oy Inc. Research and Development Department, Kuusankoski,

and Kymi-Strömberg Oy Inc., Helsinki. The Ministry of Trade and Industry and the Technology Development Center have supported the project financially.

2 PAPER FILLER DISTRIBUTION

Mainly due to water removed only from one side of the paper web in most paper manufacturing processes, the filler particles are more enriched on one side of the web than on the other. Figure 1 shows a typical filler distribution in paper from a Fourdrinier-type paper-machine. The filler material content is much lower on the wire side than on the top side of the sheet.

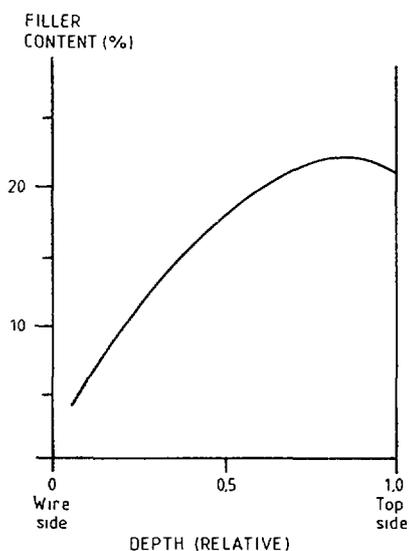


Figure 1. A typical paper filler distribution in a paper sheet manufactured by a Fourdrinier paper machine.

For calibration purposes many paper sheets from both Fourdrinier and twin-wire machines were analyzed for filler distribution by an independent destructive method. First a piece of paper sheet was fixed with cement on a levelled wood block and then cut in a sliding microtome with a microtome knife. The sheet was cut at different depths in a direction parallel to the surface. Thus the paper sheet was divided into about eight layers. The obtained cuts were then activated in a TRIGA-reactor and measured using a large Ge(Li)-detector.

The neutron activation analysis of the microtome cuts of paper -method was convenient in yielding the measuring results simultaneously for several filler components. In addition the measurements were sensitive and could be performed instrumentally. As to the measurement of calcium the analysis was useful, but could have been somewhat better, because the activation analysis sensitivity was relatively modest and the amount of calcium in several samples was of the order of only 30 μg .

Figure 2 illustrates one example of the obtained filler distributions.

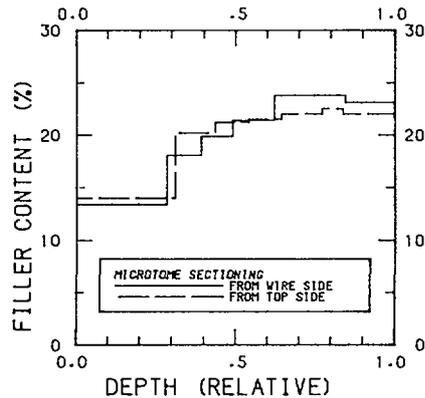


Figure 2. Paper filler distribution determined by the neutron activation analysis of microtome cuts of paper. The two curves represent the same paper sheet, but different sides of the beginning of cutting.

The two curves represent the same paper sheet, but one cut was started from the wire side, while the other was started from the top side of the paper sheet. All the obtained curves were analyzed by fitting with orthogonal polynomials of the third degree. In the sample sheets, which had been manufactured on Fourdrinier machines, the distributions could be described with adequate accuracy by three parameter polynomials of the second degree.

Another significant result from the analysis of the paper sheets was that the ratios of the different filler components across the cross section remained almost constant. This was indicated by the distributions of the filler component ratios as a function of depth, which were straight horizontal lines.

3 X-RAY TECHNIQUES

When characteristic X-rays are excited in a paper sheet by a radioisotope source or an X-ray tube the exciting and generated X-ray radiations are attenuated, while travelling through matter in the paper sheet. Consequently it is clear, that in the backscattering geometry the measurement will emphasize the region just near the surface of the sheet. Thus X-ray fluorescence measurements of a filler element carried out from both sides of the sheet will yield information of the paper filler distribution. In practical cases the measured intensities are functions of at least individual filler component distributions and the basis weight. Mass absorption coefficients are functions of separate filler component distributions and likewise functions of the depth.

Owing to too strong an attenuation in practice only characteristic X-ray fluorescence radiation of the heavier elements of fillers can effectively be measured, for example that of calcium from calcium carbonate or that of titanium from titanium dioxide. In order to be able to calculate the filler distribution of the specimen sheet one will need in addition X-ray absorption measurements and knowledge of the basis weight for example from the beta absorption measurement.

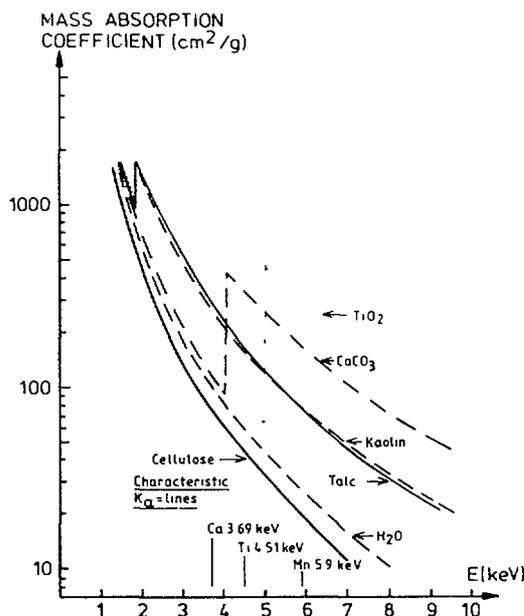


Figure 3 Mass absorption coefficients for a few typical paper filler materials and fibers and water as a function of X-ray energy.

Mass absorption coefficients for a few typical filler material components, fibers and water, are shown in Figure 3. The determination of the filler component ratios is performed by X-ray absorption measurements under the calcium absorption edge energy, above this edge but under the titanium absorption edge energy and above the titanium edge. Since the filler components kaolin or alternatively talc, calcium carbonate and titanium dioxide behave nonlinearly in the three measurements as one can discover from Figure 3, and the unknown effect of cellulose can also be taken into account by means of for example the beta absorption measurement, the ratios and the contents of these filler components can be calculated. The technique is described elsewhere more in detail /1/.

Five or six X-ray fluorescence and absorption measurements are necessary before the paper filler distribution can be solved by combined processing of the data.

4 MEASURING EQUIPMENT FOR THE DETERMINATION OF PAPER FILLER DISTRIBUTION

Based on the methods described a semiautomatic instrument for the determination of paper filler distribution was constructed. After one beta absorption, three X-ray absorption and two X-ray fluorescence measurements the microcomputer will calculate the paper basis weight, the kaolin (clay) + talc content, the calcium carbonate content as well as the titanium dioxide content and will plot the paper filler distribution. The measurements can be executed directly from the paper sheet and they take about fifteen minutes. This is remarkable, when comparing to the conventional destructive methods.

The instrument is composed of a measuring head, a 256-channel multichannel analyzer (Outokumpu X-met) and a Hewlett-Packard 9816 microcomputer with peripheral devices. The measuring head contains one beta and two ^{55}Fe -radioisotope sources. One ^{55}Fe -source is for the excitation of characteristic X-ray fluorescence radiation of fillers and the other for the generation of three different X-ray energies using secondary targets for X-ray absorption measurements. The proportional counter and its preamplifier (both made by Outokumpu) are components of the measuring head, as well.

The paper filler measuring instrument was in experimental use for a period of over one year at the Research and Development Department of Kymi-Strömberg Oy Inc., now Kymmene Oy Inc., in Kuusankoski, Finland, and the experience gained was favorable.

5 CONCLUSIONS

The method, the main principles of which have briefly been described above, for the nondestructive determination of paper filler distribution in the sheet's cross sectional direction, offers a new rapid possibility for e.g. paper quality control. It can be used for uncoated paper grades provided that the filler material contains some heavier element, for instance calcium from calcium carbonate or titanium from titanium dioxide. The measurements can be performed directly from paper sheets. The method provides a potential also for on-line measurement.

REFERENCE

- 1 Kuusi, J., Kumpulainen, H., On-line determination of vertical distribution of filler materials in paper using X-ray techniques. Acta Polytechn. Scand., Applied Physics Series no. 138, 90 - 96 (1983).

LIST OF PARTICIPANTS

J.S. Watt
Division of Mineral Physics
CSIRO, Lucas Heights
Private Mail Bag 7
Sutherland, NSW 2232
Australia

W. Herzog
Staatliches Materialprüfungsamt
Nordrhein-Westfalen
Postfach 410307
D-4600 Dortmund 41
Federal Republic of Germany

M. Hietala
Outokumpu Electronics
P.O. Box 85
SF-02201 Espoo
Finland

V. Kämäräinen
Technical Research Centre of
Finland
Reactor Laboratory
Otakaari 3 A
SF-02150 Espoo
Finland

H. Kumpulainen
Technical Research Centre of
Finland
Reactor Laboratory
Otakaari 3 A
SF-02150 Espoo
Finland

H. Sipilä
Outokumpu Electronics
P.O. Box 85
SF-02201 Espoo
Finland

H. Tominaga
Japan Atomic Energy Research Institute
Application and Development Division
Department of Radioisotopes
Oarai-Mura, Higashibaraki-Gun
Ibaraki-ken
Japan

T.B. Pierce
Analytical Sciences Division
AERE-Harwell
Oxfordshire OX11 0RA
United Kingdom

Chairman

R.J. Rosenberg
Scientific Secretary
IAEA
P.O. Box 100
A-1400 Vienna
Austria

Scientific Secretary

K. Anttila
Technical Research Centre of
Finland
Reactor Laboratory
Otakaari 3 A
SF-02150 Espoo
Finland

P. Hiismäki
Technical Research Centre of
Finland
Reactor Laboratory
Otakaari 3 A
SF-02150 Espoo
Finland

L. Lamberg
Technical Research Centre of
Finland
Reactor Laboratory
Otakaari 3 A
SF-02150 Espoo
Finland