Feasibility studies of the on-stream analysis of lead in mineral slurries

by S. K. KAWATRA*, P. Eng. (Canada), Ph.D. (Australia), M.Sc. (India) (Visitor)

SYNOPSIS

Instruments for the measurement of lead in mineral slurries by the use of isotopes can be based on the absorption of low-energy gamma rays, backscattering of beta particles, or X-ray fluorescence. The merits of each method are discussed, and the reasons for the selection of the beta-backscattering technique are given.

A system using this technique has been designed, constructed, and tested on samples of concentrates from an industrial concentrator.

SAMEVATTING

Instrumente om lood in mineraalflodders met gebruik van isotope te meet, kan op die absorpsie van lae-energie-gammastrale, terugverstrooiing van betadeeltjies, of X-straalfluoressensie gebaseer word. Die meriete van elke metode word bespreek en die redes vir die keuse van die betaterugverstrooiingstegniek word verstrek.

'n Stelsel wat van hierdie tegniek gebruik maak, is ontwerp, gebou en met konsentraatmonsters afkomstig van 'n industriële konsentreerder getoets.

INTRODUCTION

An instrument using isotopes for the measurement of lead in flotation slurries can be based on any of the following techniques: absorption of low-energy gamma rays, backscattering of beta particles, and X-ray fluorescence.

Absorption of Low-energy Gamma Rays

A system based on this technique has been developed at Zinc Corporation Limited and New Broken Hill Consolidated[1, 2]. The system uses the low-energy gamma rays close to the lead K-shell absorption edge (88keV), and is based on the fact that, as the radiation passes through a lead slurry, it is preferentially absorbed by lead. The system employs a gadolinium-153 source emitting principal gamma radiation energies at 42 and 100 keV. The 42 keV component is filtered with an aluminium filter 0,20 inch thick. The percentage solids in the slurry are measured with a density gauge incorporating a cobalt-60 source. Despite the reported success of the system in operating plants[2], it is considered probable that the entrained air will cause errors too large for the system to be successful in a plant. It has been shown[3, 4] that the optimum length of the flow cell, the specific gravity of the slurry, and its mass absorption coefficient are related by the expression

$$\rho.m.l = 2, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where ρ = specific gravity,

m = mass absorption coefficient, and

l = length of flow cell.

The average specific gravity of the concentrate slurry at the Zinc Corporation Limited is about 1,3, and its mass absorption coefficient can be calculated from the mass absorption coefficient of its constituent elements. The values of mass absorption coefficients and assays of constituent elements are listed in Table I.

The mass absorption coefficient of the solids listed in Table I can be shown to be 4,19 and, for a slurry containing 30 per cent solids, the mass absorption coefficient would be 1,38.

By substitution in equation (1) of the values for the absorption coefficient of the solids and the specific gravity of the slurry, the optimum length of the flow cell can be shown to be 1,1 cm. Even if the air content of such a small flow cell varies by a few per cent, large errors would occur in the measurement of the lead content of the slurry. This view was confirmed by the discussion on the paper by Cutten *et al.*[5] The authors commented: 'We are having difficulty in achieving reliable on-line measurement of lead in lead concentrates using gamma-absorption probes. The main problem appears to be variable amount of entrained air in the pulp'. They added further that 'the effect of entrained air is to modify the path length for absorption and, with the lead concentrate containing 76 per cent lead, minor changes in path length produce major fluctuations in observed count rates. It should be emphasised that this problem is confined to concentrates whose elements have a high absorption coefficient'.

TABLE I

MASS ABSORPTION COEFFICIENTS (AT 100 keV) AND THE CONSTITUENT ASSAYS OF A CONCENTRATE SAMPLE FROM ZINC CORPORATION LIMITED

	Assay	Mass absorption coefficient cm^2/g
Pb	76,4	5,4
Zn	3,2	0,49
Cu	0,9	0,461
SiO_2	1,6	0,169
S	14,3	0,19
Fe	3,6	0,38
H_2O	—	0,171

Beta-backscattering Technique

The complex behaviour of beta particles has been discussed extensively in the literature[6–9], from which the following conclusions can be drawn.

1. The number of beta particles backscattered from a material increases sharply with the thickness of the material, and then tends towards a limiting value that is reached at a certain thickness called the saturation thickness.
2. The ability of a material to backscatter beta rays is a function of the density of the interacting electrons per

*Canada Centre for Mineral and Energy Technology, Ottawa; formerly at Julius Kruttschnitt Mineral Research Centre, Brisbane (Australia).

unit volume, that is, the atomic number of the material. For compounds, Muller[7, 8] has introduced the concept of effective atomic number, $\overline{Z}$, defined by the relation

$$\overline{Z} = \frac{\mu \cdot A_b \cdot Z_b + \xi \cdot A_c \cdot Z_c}{\text{Molecular mass of } B\mu C_\xi}, \quad \ldots\ldots (2)$$

where

A_b and A_c are the atomic masses of elements B and C in the compound $B\mu C_\xi$, and Z_b and Z_c are the corresponding atomic numbers. Clayton and Cameron[9] have observed that 'the backscattered intensity of beta particles at saturation thickness is roughly proportional to the square root of the effective atomic number of the material', and also that 'the sensitivity of the beta backscatter technique depends on the backscattered energy spectrum. The spectra from a high $\overline{Z}$ material have a higher average energy than from a low $\overline{Z}$ material'.

From the foregoing discussion it can be concluded that, at saturation thickness, the backscattered intensity from a heterogeneous material is dependent upon the effective atomic number of the material. Now, suppose a material under investigation consists of a heavy element in a mixture of light elements. If the content of heavy element in such a material varies, the backscattered intensity from the material would also vary. In this manner, the backscattered intensity can be correlated with the content of heavy element in a matrix of light elements. This method of analysis has been used extensively for the analysis of ash in coal[10]. Coal consists essentially of elements of low atomic number (carbon, hydrogen, etc.), whereas ash contains elements of much higher atomic number (silicon, aluminium, iron, sulphur, etc.). The effective atomic number of ash is around 12, whereas that of coal is around 6. This method should be readily applicable to the determination of lead in a light matrix. For determination of the effective atomic number of a mixture of elements, equation (2) can be modified to

$$\overline{Z} = \sum_{i=1}^{n} w_i Z_i, \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where

n = number of elements in the sample,

Z_i = atomic number of the ith element, and

w_i = mass fractions of the ith element in the sample.

From equation (3), the effective atomic number of the sample presented in Table I can be seen to be 67,3.

The main source of error in this technique lies in the variation of zinc content in the slurry. For this purpose, it may be necessary to install an additional probe for the measurement of zinc. A zinc probe, involving the X-ray-fluorescence technique has been developed and successfully used at N.B.H.C./Zinc Corporation[1, 2].

X-ray Fluorescence

This technique, which has been described extensively in the literature[11–17], can be extended to the determination of lead, a plutonium-238 source being used for the excitation of Pb Lα X-rays. However, in a sample containing zinc, lead, and iron, the characteristic X-rays of lead would be excited along with zinc and copper characteristic X-rays, giving rise to matrix errors. These errors can be reduced either by the use of scattered radiation[11] or balanced filters[17].

If the accuracy of the method is not sufficient, Pb Kα instead of Pb Lα can be excited. Pb Kα has a greater range in matter and so gives better precision. For this purpose, an iridium-192 source can be used. The main disadvantage of iridium-192 is its short half-life of 74,2 days.

Comparison of the Three Techniques

The absorption of low-energy gamma rays has been previously used in industry because this technique is simple and hence does not require the use of sophisticated electronic equipment. However, the technique is not satisfactory for the determination of lead in concentrate slurries because of the variation of entrained air.

Backscattering of beta particles and X-ray fluorescence are equally competitive, and both are less affected by air than the gamma-ray transmission technique. This is because, in the gamma-ray transmission technique, air content significantly decreases the effective path length, whereas, in the backscatter techniques, if air voidage is present, radiation penetrates the slurry further than normal, thus resulting in some compensation.

Clayton and Cameron[9] have cited both techniques for the measurement of tungsten in the tool industry. Their paper makes the important distinction between X-ray-fluorescence techniques for measurements of low concentrations and beta-backscatter techniques for measurements of high concentrations.

In view of the above, it was decided to carry out feasibility studies to determine if the beta-backscatter technique can be used for the determination of lead in concentrates.

It can be noted that, in addition to the three techniques described above, techniques based on the principle of absorption of bremsstrahlung, gamma backscattering, and so on could be used. These techniques are not expected to offer any more advantages than the three described. For example, the technique of absorption of bremsstrahlung would have disadvantages similar to those of absorption of low-energy photons described in the previous sections.

EXPERIMENTAL SYSTEM

The experimental system (Fig. 1) consisted of a radiation source and its shield, a cell for presenting the specimen to the beta particles, and a radiation detector.

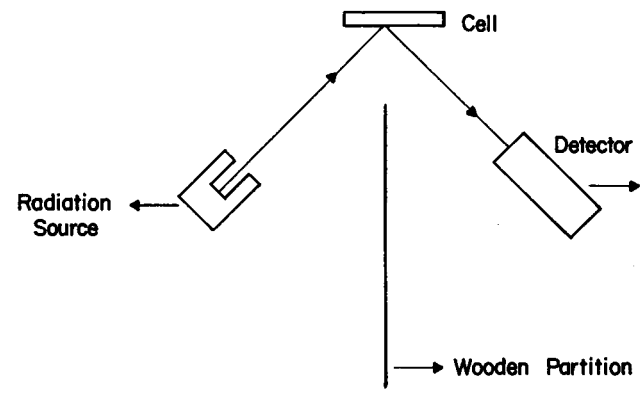

Fig. 1—Plan of the beta-backscatter system

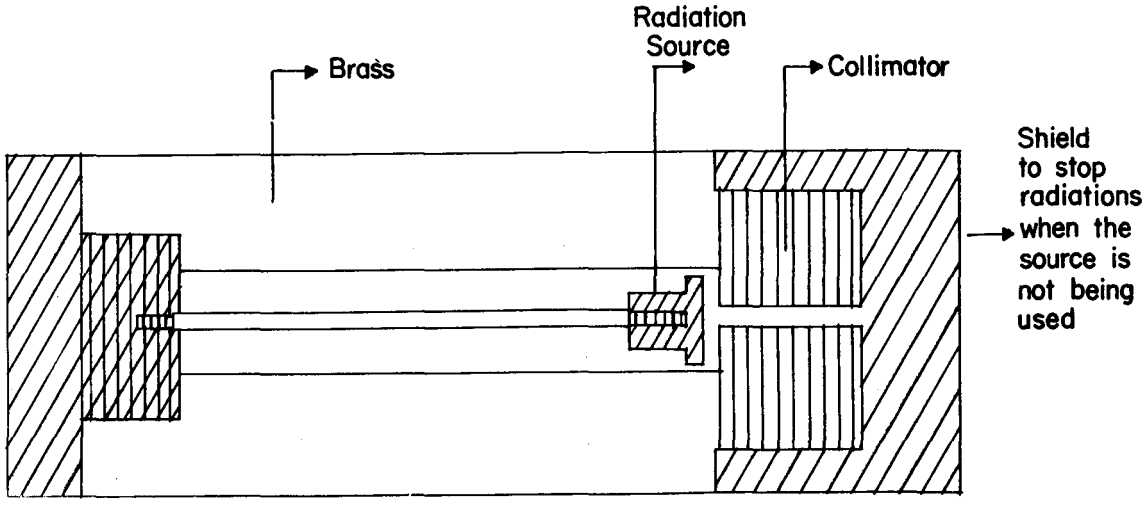

Fig. 2—Details of the strontium-90 source and its brass shield

Radiation Source

A 5 millicurie strontium-90 source was used, the source being enclosed in a brass shield as shown in Fig. 2. Brass was chosen for the shielding material as a compromise between a heavy metal such as lead, which gives rise to high background caused by beta-excited X-rays, and light material such as timber, which must be used in large volumes for successful shielding.

Cell

A cell of rectangular shape, 12,5 cm by 7,5 cm, made from Perspex was used, with a PVC sheet forming the window of the cell.

Detector

A beta-scintillation detector, the crystal of which consisted of polystyrene and p-terpheny tetraphenyl butadiene, was used.

All the components were enclosed in a box made of $\frac{1}{2}$-inch thick plywood and containing a partition to stop stray beta particles from entering the detector.

The Philips PW 4620 high-voltage supply, single-channel analyser and PW 4631 counter/timer/printer control were used for counting purposes. A single-channel analyser was used for the elimination of low-level noise.

EXPERIMENTAL METHOD

So that the effect of variation in the effective atomic number of the target on the scattered intensity could be determined, the cell was filled with different analytical reagents and the backscattered intensities for each were measured for 100 seconds. The results are summarized in Table II and depicted in Fig. 3.

The effective atomic numbers in Table II were calculated by use of equation (2). A regression analysis showed the relation between backscattered intensity I_b and the effective atomic number to be

$$I_b = 1255 \cdot \bar{Z}^{(0,493)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

One experiment was designed to show the effect of variation of lead in solution on the backscattered intensity. For this purpose, solutions with a wide range of lead nitrate concentrations were prepared.

When the backscattered intensities were measured, it was observed that the count rates were very low. To eradicate this problem, the old source was replaced with one of 40 millicurie strength. The results are given numerically in Table III and graphically in Fig. 4.

TABLE II

VARIATIONS OF BACKSCATTERED INTENSITY WITH EFFECTIVE ATOMIC NUMBER

Reagent	Effective atomic number	Intensity I_b
$Na_2B_4O_7,10H_2O$	7,6	3 405
$ZnSO_4,\ 7H_2O$	13,5	4 588
$CuSO_4,\ 5H_2O$	14,02	4 594
$BaCl_2,\ 2H_2O$	37,6	7 430
PbO	76,7	10 737

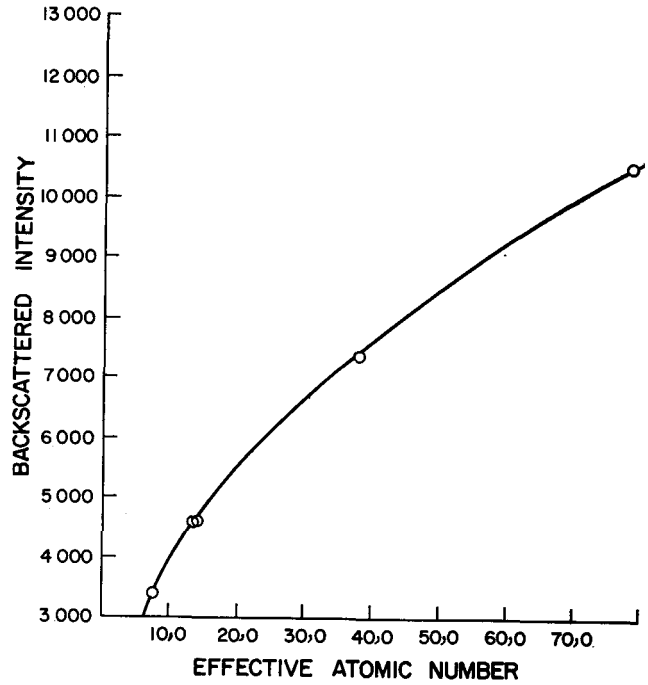

Fig. 3—Relation between backscattered intensity and effective atomic number

TABLE III

VARIATION OF BACKSCATTERED INTENSITY WITH LEAD CONTENT

Lead % (by mass)	Intensity I_b
0	201 818
4,76	207 930
9,09	213 777
13,04	217 833
16,67	221 219
20,00	223 674
23,07	228 654
25,93	231 594

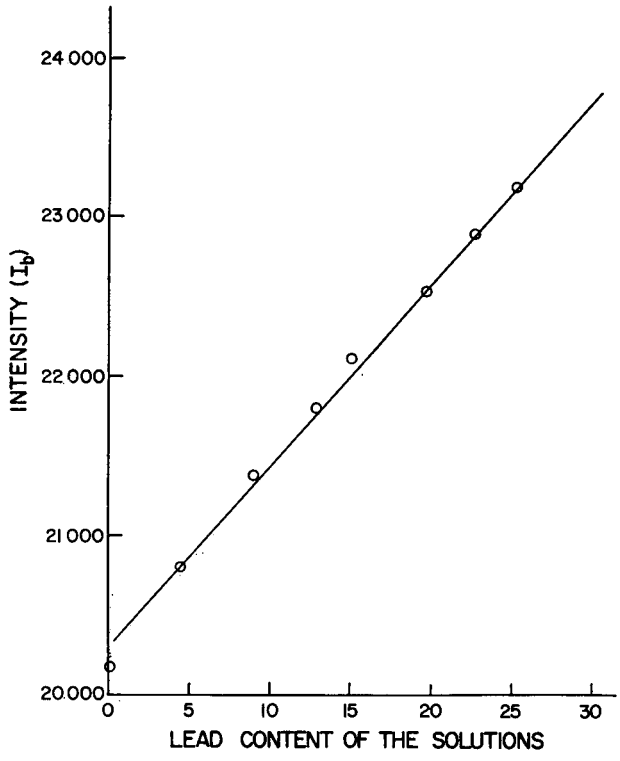

Fig. 4—Relation between backscattered intensity and lead content of the solutions

From these results, it can be observed that there is a significant change in concentration for fairly small changes of lead content.

Suitable briquettes of lead concentrates, kindly provided by Zinc Corporation Limited, were used in a study of solid samples. Each briquette was 7,5 cm in diameter and 1 cm in thickness, and contained 10 g of lead and 10 g of Kalodent powder. A pressure of 1 tonne at 190 °C was applied for 20 minutes in the briquetting process. A plastic holder was fabricated to position the briquettes accurately in the experimental set-up, and the count rates for each briquette were taken for 100 seconds. Fig. 5 shows the relation between backscattered intensity (I_b) and the lead content of the briquettes. The results, together with the assays of lead and zinc, are presented in Table IV. The count rates obtained with briquettes are much smaller in magnitude than those obtained with lead nitrate solutions.

A linear regression analysis relating lead content and backscattered intensity gave the relation

$$\% \text{ Pb} = -189{,}725 + 33{,}44.10^{-4}.I_b$$

with a standard deviation of 1,9.

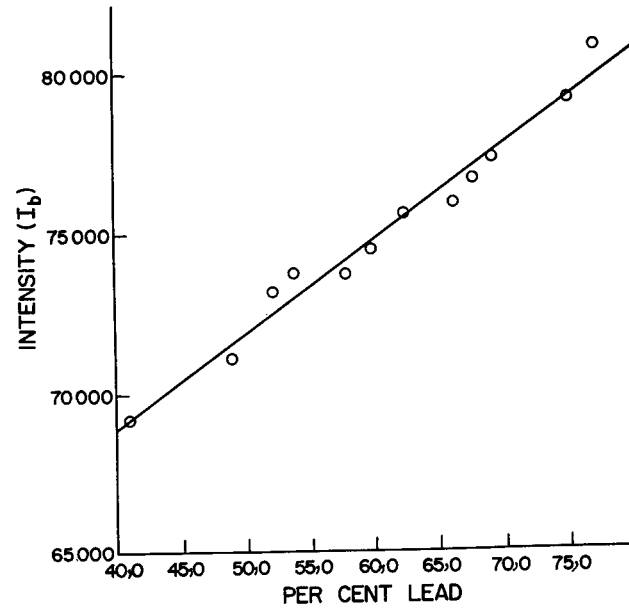

Fig. 5—Relation between backscattered intensity and lead content of the briquettes

TABLE IV

EXPERIMENTAL RESULTS FOR THE SAMPLES FROM ZINC CORPORATION LIMITED

(Mean lead content = 61,18 %)

Lead % (by mass)	Zinc % (by mass)	Intensity I_b
41,0	18,9	69 170
48,8	14,6	71 047
52,2	12,7	73 165
54,1	11,4	73 631
58,1	9,9	73 677
60,0	9,5	74 399
62,4	8,1	75 511
66,4	7,0	75 866
68,0	6,2	76 576
69,8	4,7	77 230
75,6	3,4	79 160
77,8	2,4	80 791

The effect of zinc on the accuracy is apparent from the relation between lead content as a function of zinc content and backscattered intensity, which can be expressed as

$$\% \text{ Pb} = -0{,}8 + 11{,}08.10^{-4}.I_b - 1{,}537.\text{Zn}$$

with a standard deviation of 1,22.

DISCUSSION

From the experimental work discussed, it can be concluded that the beta-backscattering technique can be used successfully for the determination of lead in concentrate samples. For slurries, a simple portable beta-probe can be designed for use in plants. A possible design of such a probe is shown in Fig. 6.

In this system, the direct beam (ah) is stopped by a lead absorber. It is necessary to coat the lead absorber with Perspex to stop beta particles and also to reduce the production of beta-excited X-rays.

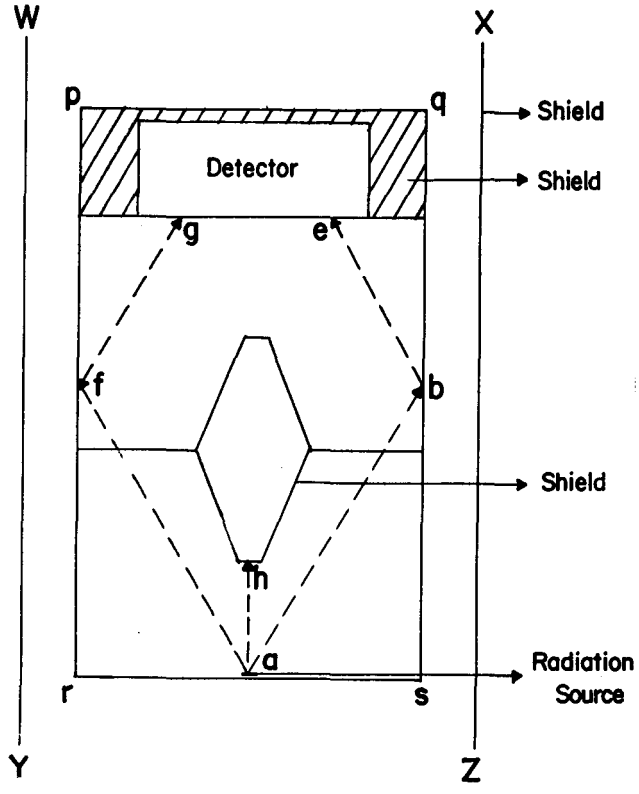

Fig. 6—Proposed design of a beta-backscatter probe

The whole assembly (pqrs) can be immersed in a slurry after the shield (wxyz) for the probe has been removed. The backscattered beta particles (beam afg and abe) would be detected.

It should be noted that a density gauge must be incorporated with the lead probe for determination of the percentage solids in the slurry.

ACKNOWLEDGEMENT

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Conference on shotcrete

The Engineering Foundation is to hold a conference on 'Shotcrete for Ground Support' at Easton, Maryland, U.S.A. from 2nd October to 8th October, 1976.

Aspects of the use of shotcrete to be discussed include the material itself; equipment and processes; field control; payment conditions and specifications; design, case histories, and performance, especially of structures that were built many years ago. Substantial contributions regarding foreign practices and experience are expected.

Further information is obtainable from Engineering Foundation Conferences, 345 East 47th Street, New York, NY 10017, U.S.A.

Mechanical properties of materials

A symposium on the above subject, organized by the South African Institute of Physics, is to be held at the University of the Witwatersrand from 29th November to 1st December, 1976. The topics include the following, the concept being to highlight recent developments in techniques, theory, and application:

— Recent advances in instrumentation
— Microstructural and theoretical considerations of deformation and fracture
— Application to engineering problems with special reference to those encountered in South Africa.

Further information is obtainable from Dr R. M. Mayer, Physical Metallurgy Division, Atomic Energy Board, Private Bag X256, Pretoria.