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DEVELOPMENT AND APPLICATIONS OF AN ON-LINE THERMAL NEUTRON PROMPT-GAMMA ELEMENT ANALYSIS SYSTEM*

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ABSTRACT

This paper introduces the principles, instrumentation, implementation, and industrial applications of an on- line thermal neutron prompt- gamma element analysis system (using a ^{252}Cf neutron source, Am- Be neutron source, or neutron generator). The energy resolution of the system at the H prompt- gamma full- energy photopeak (2.22325 MeV) is 3.6 keV. The concentration measurement error of Al_2O_3, Fe_2O_3, CaO and SiO_2 is ±0.3%, ±0.1%, ±0.4% and ±0.4%, respectively.

The system has been tested on- site at both the Shandong and the Zhengzhou Aluminum Works. Our preliminary on- site measurements confirm that the stability, reliability, measurement range, and accuracy of the system can meet the requirements of the aluminum production process. Facilitation of this measurement at aluminum plants is expected to reduce plant costs by over 3 million dollars annually through reduced energy consumption, more rapid qualification of pulps being mixed during the production process, and in reduced labor costs.

Keywords: Prompt- gamma Neutron activation analysis On- line Aluminum Pulp

I . INTRODUCTION

The technique of prompt- gamma neutron activation analysis (PGNAA) has been reported by numerous investigators for both research and industrial applications[1-5]. In recent years, the technique of on- line analysis of elements in ore production process using a ^{252}Cf or Am- Be neutron source or neutron generator, a high- resolution large- efficiency HPGe detector, and a microcomputer multichannel spectrometer demonstrates the technique's many superiorities. In the U.S.A., J.H.McQuaid and others used a high- count- rate (150 kcps)spectroscopy analyzer and GeLi detector for on- line coal quantity analysis in power stations in 1981. They named the equipment NUCOALYZER[6]. At the Sixth Pacific Ocean Nuclear Energy Meeting held at Peking in September 1987, E.R.Karlashev[7] announced that USSR

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used 40 sets of neutron activation analyzers in industrial process control. To meet the requirements of the aluminum industry, a Sino- American cooperation group has recently jointly developed an on- line thermal Neutron Prompt- Gamma Analyzer. This group has carried out on- site comparison tests that confirm that the measurement accuracy, stability, and reliability of the system can meet the requirements of industrial production. This development represents a successful on- site application of a prompt- gamma neutron activation analysis technique.

Ⅱ. PRINCIPLES

During the analysis of a thermal neutron irradiated sample, neutrons are captured by the nucleus of atoms in the sample, and a prompt γ ray is emitted in the (n,γ) reaction. The prompt γ ray (2- 10 MeV) is released in about 10^{-14}s, and is detected by a high- resolution γ ray spectrometer; then, by the position of the characteristic peak and its net count, qualitative and quantitative analysis can be performed. This is called the "prompt gamma ray neutron activation analysis method" (PGNAA).

In quantitative analysis, the area of the characteristic peak of the element to be measured is represented by net count N (accumulated in the measurement period). The relationship between net counts N and the concentration of the element to be measured C is:

$$N=(CN_L/A)\sigma\ \varphi\ a\varepsilon\ jt \tag{1}$$

where N= net counts of a characteristic peak (in measurement period t), C= element concentration ($g \cdot l^{-1}$), N_L= Loschmidt number (Avogadro's number/standard volume for ideal gas $=N_A/V_o$), σ = thermal neutron capture cross section (in barns, $10^{-24} \cdot cm^2$), φ = neutron flux- density (in $n \cdot cm^{-2} \cdot s^{-1}$), a= isotopic abundance of the element, ε = detector efficiency, $j=\gamma$ quanta produced, A= atomic mass. In practice, σ , φ , ε , j, t, a, A and N_L are constant, so that the relation of N with C is

$$N=kC+b \tag{2}$$

Here, k and b are empirical constants determined by experiment using pure reagents or from standards characterized by chemical anlysis. In ore pulp containing some moisture, the specific element concentration in the whole sample is represented by C. In moisture- free pulp, the concentration is presented by C_g. The relation between C and C_g is as follows:

$$C=C_g \cdot (1-C_{H_2O}) \cdot \rho \cdot 1000 \tag{3}$$

where C_{H_2O} is moisture (percent by weight) and ρ is the density of the pulp ($g \cdot cm^{-3}$). Therefore, equation (2) can be written as:

$$N= kC_g(1-C_{H_2O})\rho + b \tag{4}$$

That is,

$$C_g=(N-b)/k(1-C_{H_2O})\rho \tag{5}$$

The relationship of C_{H_2O} and N_{H_2O} is

$$N_{H_2O}= k_{H_2O}C_{H_2O}\rho + b_{H_2O} \tag{6}$$

where k_{H_2O} and b_{H_2O} are empirical constants and are determined in the sample with free water, so that C_{H_2O} represents only the concentration of adsorbed water. If there are other organic compounds in the sample, the result needs to be corrected. C_{H_2O} is calibrated by the loss- on- ignition method.

Ⅲ. INSTRUMENTATION

This measurement system consists of the sample irradiation and detector assembly comprising the front- end device of the analyzer (see Fig.1). The detector output is then presented to pulse processing electronics consisting of the Model 673 Gated Integrator Amplifier, Model 918A Multichannel Buffer, Model 990 Digital Stabilizer, and an IBM① ,PS/2 Computer, all of which comprise a multichannel spectrometer (Fig.2). The front- end equipment and the multichannel analysis system are connected by a 100m special cable using common- mode rejection methods to reduce noise resulting from the long cable lengths.

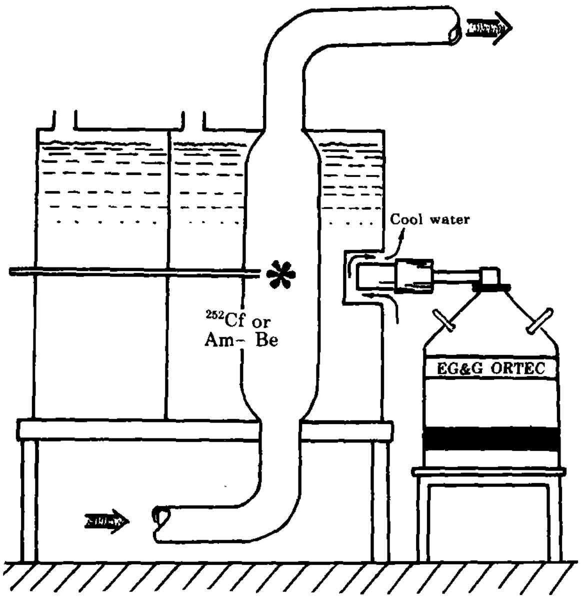

Fig.1 Diagram of on−line measurement assembly

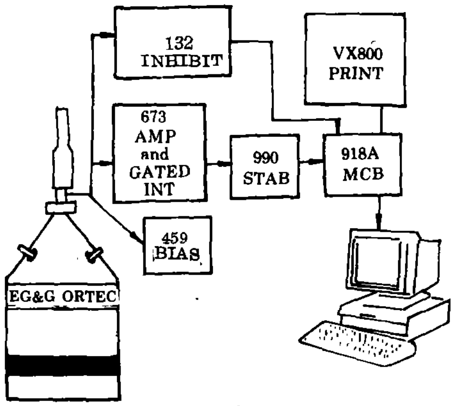

Fig.2 Diagram of spectrometer system

The analysis system was developed jointly by a Sino- American cooperation program. EG&G ORTEC (USA) provided a high- count- rate, high- resolution gamma- ray spectroscopy analysis system. The Henan Joint Center provided the ^{252}Cf isotopic neutron source, source shielding, sampling apparatus, and application software.

The Model PG- 8901 Neutron Irradiation and Measurement Assembly consists of 100- 200 μ g of ^{252}Cf·source, shield containment, and measurement piping. The neutron source is filled in a firm metal tube, which is inserted into the measurement piping during the measurement period. The tube can be lifted up to the center of the shield container while no measurement is required. Between the neutron source and the detector, there is a Bi plug, neutron moderator, and Cd layer, in order to prevent the γ rays and neutrons of the source from directly exposing the detector. All geometries are determined by requirements of both measurement accuracy and personnel safety.

The data acquisition and analysis system consists of a large- volume (40% relative efficiency) n- type HPGe detector and preamplifier capable of throughput rates in excess of 800 GeV/s and an EG&G ORTEC Model 673 Gated Integrator Amplifier with a shaping time of 0.25 μ s, providing maximum throughput with minimal pile- up.

Most pulse pile- up resulted from the 2.22325 MeV prompt- gamma of hydrogen from the water matrix of the sample. Pulse pile- up results in a distortion of the spectrum at higher energies and is the chief limitation to sensitivity for this measurement. Using this system, energy resolution at the 2.22325 MeV prompt- gamma of hydrogen is 3.6 keV (at a gross counting rate of 100 kcps). The peak shape is Gaussian.

The amplifier output is then presented to a Model 918A Multichannel Buffer, which contains a 10μ s- fixed- conversion time ADC and an 8000- channel data memory. A Model 990 Digital Stabilizer is interposed between the Model 673 and Model 918A, ensuring the stability of the analysis system with both varying counting rates and varying operating temperatures.

Recent improvements by EG&G ORTEC in high- count- rate pulse processing has resulted in the next generation of instrumentation. These new systems are capable of double the system throughput compared with that of the present system. Future developments include a completely computer- controlled ultra- high- count- rate system capable of totally automated data acquisition and analysis.

Ⅳ. MAIN TECHNIQUE PERFORMANCE INDEX

1.Analysis error for main elements in raw alumina pulp

Oxide	Al_2O_3	Fe_2O_3	CaO	SiO_2	Na_2O	TiO_2	H_2O
Concentration range (%)	10- 40	1- 10	10- 30	5- 20	10- 30	<5.5	10- 100
Measurement error (%)	±0.3	±0.1	±0.4	±0.4	±0.4	±0.2	±0.5

2. Longtime stability = ±1 channel/8 hours (8000 channels, at 25±5°C)

3. Dose at 0.5 m around measurement assembly less than state permissible dose

Ⅴ. MEASUREMENT METHODS

1. Calibration of the system

The coefficients of determination used in the calculations are determined by mixing samples of varied concentration (using the pulp on- site flow process) with special equipment [8 9]. The accuracy of sampling by chemical analysis must meet requirements, usually one order of magnitude higher than the measurement error of the equipment. To obtain the coefficient of determination with enough accuracy, the group data calculation method was used. In practical data processing, about 200 experimental points were utilized.

To account for spectral interference between elements, multivariate linear regression equations are used to find each element's coefficient of determination. To find the relationship of $N_{Al_2O_3}$ to $C_{Al_2O_3}$, considering the interference of other elements, the following equation is employed:

$$\begin{aligned} C_{Al_2O_3} = {} & k_{Al_2O_3}N_{Al_2O_3} + k_{Fe_2O_3}N_{Fe_2O_3} + k_{Na_2O}N_{Na_2O} \\ & + k_{SiO_2}N_{SiO_2} + \ldots + b_{Al_2O_3} \end{aligned} \qquad (7)$$

where $k_{Al_2O_3}$, $k_{Fe_2O_3}$, k_{Na_2O}, k_{SiO_2} and $b_{Al_2O_3}$ are coefficients of determination; $N_{Al_2O_3}$, $N_{Fe_2O_3}$ and N_{Na_2O} are peak area counts of every element.

2. Measurement

Table 1

Report of the instrument's on—line analysis

Date: Feb.6,1989 Time: 13:10:11- 13:25:11

H_2O (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	Na_2O (%)	Σ C(%)	A/S	N/S	C/S
41.0	9.02	2.34	26.25	10.20	15.27	63.08	2.910	0.906	1.212

Date: Feb.6,1989 Time: 13:25:13- 13:40:13

H_2O (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	Na_2O (%)	Σ C(%)	A/S	N/S	C/S
37.91	9.04	2.42	27.63	12.99	14.56	66.64	3.056	0.821	1.540

Date: Feb.6,1989 Time: 13:40:14- 13:55:14

H_2O (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	Na_2O (%)	Σ C(%)	A/S	N/S	C/S
38.13	8.55	2.23	25.99	12.63	14.87	64.27	3.040	0.892	1.583

Date: Feb.6,1989 Time: 13:55:16- 14:10:16

H_2O (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	Na_2O (%)	Σ C(%)	A/S	N/S	C/S
39.65	7.98	2.13	24.36	12.01	15.55	62.03	3.053	0.955	1.613

Date: Feb.6,1989 Time: 13:10:18- 14:10:18

H_2O (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	Na_2O (%)	Σ C(%)	A/S	N/S	C/S
39.20	8.65	2.98	26.06	11.96	15.06	64.01	3.015	0.904	1.487

To analyze an unknown sample with this equipment, the coefficient of determination for each element is entered into the computer. The concentration of each oxide can then be calculated automatically with multivariate linear regression equations for each element as in equation (7). With equation (5), C_g can be determined for Al_2O_3, Fe_2O_3, Na_2O and CaO. From these data (Table 1), calculation of the Al- Si ratio (A/S), the Na- Si ratio (N/S), and the Ca- Si ratio (C/S) can be calculated. In addition, the total weight fraction (Σ C%) of analyzed elements can be determined.

Unlike previous PGNAA applications, the system described here uses comparative techniques to reduce or eliminate the uncertainties in system efficiency, irradiation parameters, and nuclear cross section. This comparative technique also permits use of single and double escape peaks in addition to full- energy photopeaks, without the need to characterize the system response for each type of peak. The multivariate regression corrects for water content variability between unknowns and the calibration standards and for spectral effects based on compositional variability. The flow of data through the system is shown in Fig.3.

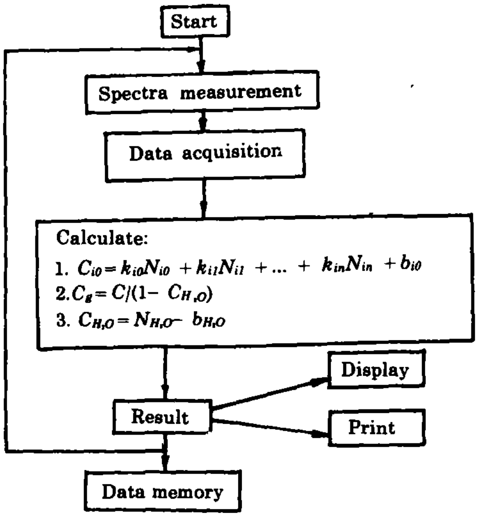

Fig.3 Diagram of application software

VI. RESULT OF ON-SITE TESTING

This system has been tested on- site for more than six months from December 1988 to February 1989, and from June 1989 to December 1989. Although working continuously, the system remained trouble free. The peakshift was about 1 channel during 24 hours. Part of the experiment record can be seen in Table 1. The results have been compared with the results of sampling by chemical analysis (see Table 2).

Table 2

Comparison of instrument analysis with chemical analysis

	H_2O	SiO_2	Fe_2O_3	Al_2O_3	CaO	Na_2O
1	44.80	7.69	2.84	22.22	15.38	16.31
	43.25	7.88	2.28	21.85	15.80	16.22
	+1.55	- 0.19	+0.56	+0.38	- 0.42	+0.19
2	44.47	7.29	2.89	22.72	15.68	15.48
	44.15	7.30	2.41	22.88	16.10	15.23
	+0.32	- 0.01	+0.48	- 0.16	- 0.42	0.25
3	43.17	7.51	2.48	22.62	17.99	15.00
	43.20	7.91	2.88	22.17	17.30	15.15
	- 0.03	- 0.4	- 0.40	0.45	+0.69	- 0.15
4	42.93	7.70	2.52	22.62	15.47	15.11
	44.20	8.06	2.80	23.00	15.40	15.23
	- 1.27	- 0.36	- 0.28	- 0.38	0.07	- 0.12
5	42.94	7.70	2.52	22.62	15.74	15.11
	43.07	7.84	2.74	22.80	15.95	15.04
	- 0.13	- 0.14	- 0.22	- 0.18	- 0.21	+0.07

To analyze the actual measurement error of the equipment, we used an on- site small loop system with pulp flowing to carry out a long- term repeated measurement of the accuracy of the equipment (Table 3).

Table 3

Experimental data from the on—site acquisition analysis

	H_2O	SiO_2	Fe_2O_3	Al_2O_3	CaO	Na_2O
1	40.37	7.73	1.60	23.08	11.84	14.97
2	39.73	8.07	1.57	23.24	12.31	14.61
3	39.65	8.11	1.63	23.81	12.19	14.55
4	39.40	8.46	1.58	23.72	11.85	14.47
5	39.40	7.98	1.50	23.09	11.86	14.46
6	39.44	8.17	1.46	22.85	11.35	14.53
7	39.45	8.58	1.50	23.27	10.38	14.69
8	39.55	8.14	1.50	23.26	12.01	14.29
9	39.44	8.53	1.45	22.96	11.73	14.29
10	39.19	8.30	1.29	22.77	11.54	14.35
11	39.50	8.68	1.41	22.71	12.42	14.03
12 σ	0.30	0.29	0.1	0.36	0.31	0.25
13 $\sigma/\overline{X}$(%)	0.77	3.5	6.48	1.54	2.61	1.69
14 X	39.56	8.25	1.50	23.16	11.77	14.48
15 Chem:	39.60	8.29	1.58	23.73	11.10	14.86
16 Error:	- 0.04	- 0.04	- 0.08	- 0.57	0.67	- 0.38

This six- month on- site test confirmed that the equipment can meet the main performance index (see Section 4).

Ⅶ. ERROR ANALYSIS

The element concentration error of the system results mainly from the peak area error (accumulated count N error). Other errors, such as peak position shift and interference of elements, can be minimized. For example, one channel shift during 24 hours has a petty effect on count N, and interference between elements can be eliminated by multivariate linear regression equation. Therefore, the measurement error is determined by the following expression:

$$\Delta C = \pm\sqrt{N}/S \qquad (8)$$

where S is sensitivity and the square root of N is counting statistical error. N generally is used as net count; that is, $N = N_{gross} - N_{bg}$. Here N_{gross} is gross count and N_{bg} is background count. When N is not large, we use N_{gross} instead of N ; that is, we set up a regression equation using N_{gross} and C.

Through such treatment, the measurement error of every element can fit in the following equation:

$$\Delta C = \pm\sqrt{N_g}/S' \qquad (9)$$

Note that since S' is less than S, the sensitivity of the measurement will also be slightly poorer.

By experimenting, it is confirmed that the above analysis conforms to real experiment.

VIII. CONCLUSION

About one year of on- site application research and test on the neutron prompt- gamma on- line element analyzer confirms that using this system for the analysis of alumina pulp produces fast, automatic, consecutive, widely representative, and reliable results. It can provide the basis of mixture for an operator in real time. Using this system in all plants in the P.R.China. is expected to reduce plants costs 3 million dollars yearly. The development of this analysis method makes modernization and scientific management possible in pulp mix for aluminum production.

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