Cement Quality Control by using Modern Radiation Methods of Chemical Analysis in the Process of its Production

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An essential part of modern quality management system in cement production is state-of-the-art radiation measurement technologies based on methods of neutron activation, X-ray fluorescence and X-ray diffraction chemical analysis of substance. The high speed and accuracy of measuring the characteristics of raw materials and finished products can be achieved by their complex application, thereby ensuring an improving in the level of automation of cement production and the quality of cement in general. The main stages of the portlandcement production process by dry method are considered, including the keypoints of quality control of their implementation by applying mentioned radiation methods of chemical analysis of raw materials and completed product. The metrological problems of their practical implementation in continuous cement production are analyzed, in particular problems of uncertainty assessment, static and dynamic calibration and increase of accuracy of measuring systems that implement neutron activation analysis methods. Shown the directions of their improvement by the use of alternative neutron sources, methods of Monte Carlo N-Particle Transport Code for neutron activation analysis physical processes simulation and machine learning for the efficient processing of spectral characteristics of investigated substances.

Keywords: cement, neutron activation analysis, PGNAA, PFTNAA, XRF, uncertainty

Контроль якості цементу за допомогою сучасних радіаційних методів хімічного аналізу у процесі його виробництва

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Невід'ємною складовою сучасної системи управління якістю продукції у цементному виробництві є передові вимірювальні технології, які базуються на радіаційних методах нейтронно-активаційного, рентгенофлуоресцентного та рентгенодифракційного хімічного аналізу складу речовини. Висока швидкодія та точність вимірювання характеристик сировини та готової продукції досягається саме комплексним їх застосуванням, тим самим забезпечуючи зростання рівня автоматизації цементного виробництва та якості цементної продукції в цілому. Було розглянуто основні етапи процесу виробництва портландцементу сухим способом, в т.ч. ключові моменти контролю якості їх проведення шляхом застосування згаданих радіаційних методів хімічного аналізу сировини та готового продукту. Проаналізовані метрологічні проблеми їх практичного впровадження у неперервному цементному виробництві, зокрема оцінки невизначеності, статичного та динамічного калібрування, а також підвищення точності вимірювальних систем, що реалізують методи нейтронно-активаційного аналізу. Показані напрями їх подальшого удосконалення шляхом застосування альтернативних нейтронних джерел, використання методів Монте-Карло для моделювання фізичних процесів нейтронно-активаційного аналізу та машинного навчання для ефективної обробки спектральних характеристик досліджуваних речовин.

Ключові слова: цемент, нейтронно-активаційний аналіз, PGNAA, PFTNAA, XRF, невизначеність

Ensuring the high competitiveness of enterprises in a highly competitive and complex world market of cement products requires a constant increase in productivity and quality control of cement production. To this end, considerable attention is paid to increasing the speed and accuracy of the quality management systems for raw materials and finished products at every stage of cement production. The main stages of the technological process of production of Portland cement by the dry method and its quality control can be described as follows (Fig.1). At the initial stage, with the help of specialized drilling rigs (1), the extraction of raw materials in the quarry (2) is carried out, depending on the predefined conditions of its occurrence and properties. So, before the start of extraction, the opening, alternation and thickness of various layers of raw materials, the angle of inclination of these layers, the length, shape and internal structure of the deposits, the level of groundwater, and the like are estimated. Moreover, important parameters are both the chemical composition and the physical properties of the raw materials. The latter include: rock hardness, angle of repose (the angle that can form a slope of free-flowing bulk material in a state of equilibrium with a horizontal plane), moisture capacity, water permeability, expansion (degree of volume increase after extraction compared to the rock mass), weight, rock strength at its compression and impact. Drilling machines (screw, roller cone, pneumatic, hydraulic, and combined), excavators, self-propelled combines based on rotary excavators (for soft rocks (chalk, clay)) and others are used as installations for the extraction of raw materials. To control the quality of raw materials coming from career, it is periodically sampled (ex situ method) and there is made a XRF/XRD chemical analysis [1, 2].

From the quarry (2), the roughly crushed raw materials are transported to the main crusher (3), where they are ground into small fractions. Three main groups of crushers are used for this purpose: impact hammer crushers; jaw, cone crushers; roll and gear roll crushers. The principle of their work is based on the physical methods of crushing and cutting the rock. The choice of a specific type of crusher is based on the optimal combination of requirements for its cost, wear resistance, energy efficiency, the maximum allowable size of the input and output particles, hardness, tensile strength, and the moisture capacity of the raw material. The crusher system can include one or several crushers to gradually achieve the required particle size of the raw materials. The quality control of the crushing process is ensured by the design of the crushers, which are equipped with special output grids that let through only raw material particles whose size does not exceed the allowable value.

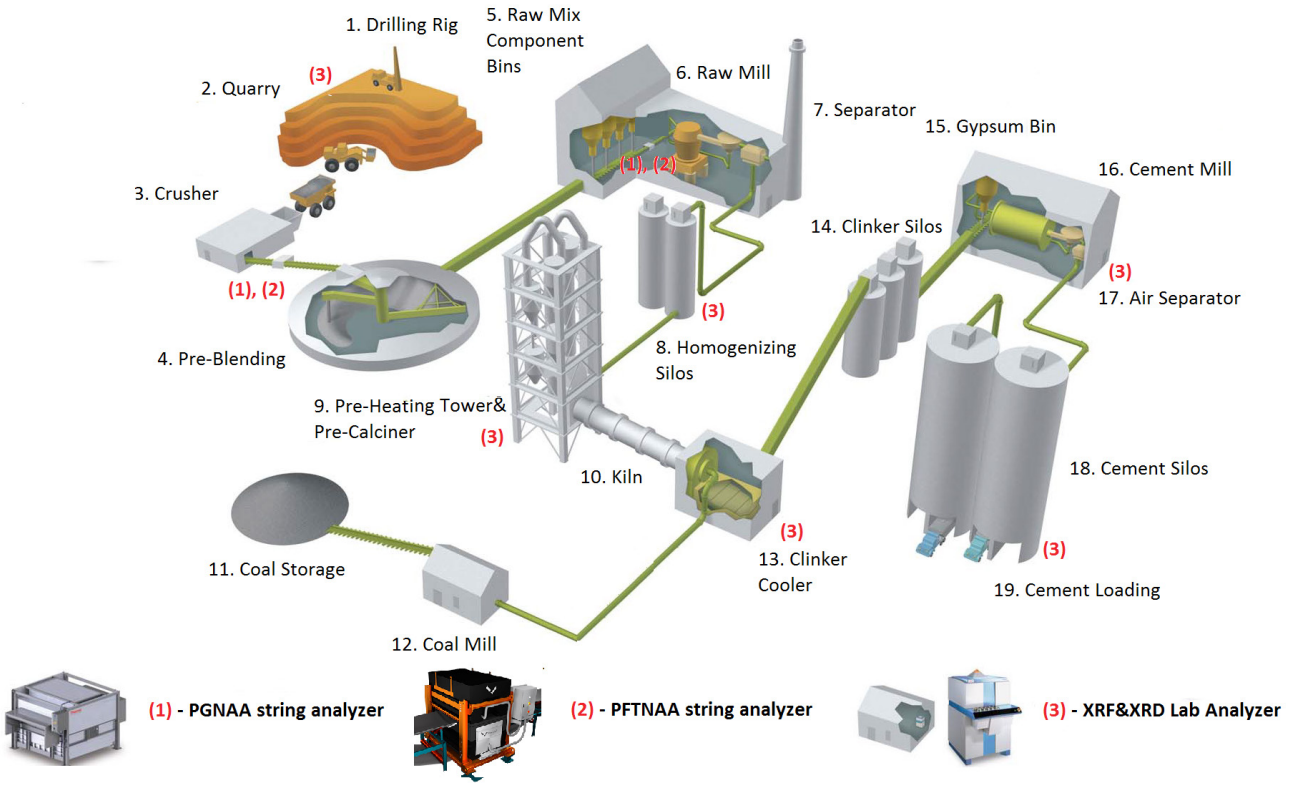

Fig.1. Quality control of raw materials and finished products in cement production.

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The raw materials of a career field can be quite heterogeneous (non-homogenized), especially if it comes from different fields. Therefore, to homogenize it, the crushed raw material is transported by conveyor to the pre-blending (4). It includes the stacker reclaimer system and homogenization composition. The stacker reclaimer mixes the raw materials by placing them in piles and by gradual selection according to the Chevron or Windrow methods [3]. The effect of mixing H is usually determined by the ratio of the standard deviation of one of the significant chemical parameters of the incoming raw materials Sin to the standard deviation of this parameter of the raw material Sout, that is: $H = Sin/Sout$. After mixing and achieving the desired effect of *H,* the raw material is accumulated in the homogenizing storage.

It should be noted that during transportation from the crusher (3) to the pre-blending (4), all raw material undergoes chemical analysis (in situ method) using a PGNAA or PFTNAA string analyzer [4, 5], which determines its elemental composition with high accuracy and in real time (every 1-2 min). The obtained information on the chemical composition of the raw material allows not only determining the standard deviation of the concentration of any of its chemical elements *Sin* and, thus, setting requirements for the process of its further homogenization, but also taking into account the real chemical composition when mixing its various components. As a result of mixing, the raw material becomes more homogenized, and the parameters of its chemical composition are averaged. To control the quality of the raw material mixing process, its periodic sampling and chemical XRF/XRD analysis can be carried out, which allows determining the standard deviation *Sout* and, accordingly, the *H* value and thereby evaluating the quality of the preliminary homogenization process. The raw materials from the composition of homogenization, depending on their type (marl, limestone, etc.), are transported to the appropriate raw mix component bins (5). The dosage of each type of raw material passes automatically by regulating the speed of conveyor strings from the output of the corresponding raw mix component bin to the mixer. Determination of the concentration of all components of the raw material in the mixture and its quality control is carried out every 1-2 minutes using a PGNAA/PFTNAA analyzer. To ensure the stability of dosing, the obtained values are averaged over a certain period of time (usually at least 5 values within 5-10 minutes) and serve as the basis of calculations for adjusting the raw mix component bin in real time.

The raw mix obtained after dosing is ground in a raw mill (6). Three types of mills [3] can be used: ball, vertical roller (VRM) and hydraulic roll presses (often in combination with ball mills). Together with the raw mill (6), there is a separator (7), which serves to separate the non-solid product and return it to the grinding mills. Quality control of the finished raw mix is carried out every 1-2 hours using the technology of XRF/XRD chemical analysis. It should be noted that the results of XRF analysis also serve to automatically correct (every 1–2 hours) shows of the aforementioned PGNAA/PFTNAA analyzer to ensure maximum accuracy of dosing of raw materials components. Periodically, in order to improve the accuracy of dosing, an additional dynamic calibration of the PGNAA/PFTNAA analyzer is carried out, based on the average value of its shows and XRF measurements. For temporary buffer storage and additional mixing (in order to achieve the highest degree of homogenization), the raw meal is transported to the Homogenizing Silos (8). To control the quality of the homogenization process, a sampling and XRF/XRD chemical analysis of raw meal is carried out every 1-2 hours at the silos outlet. After that, it is fed for heat treatment to a pre-heating tower and pre-calcining based on a cyclone heat exchanger system (9). To control the quality of raw meal after preliminary heat treatment and calcination (decarbonization), its regular sampling and XRF/XRD analysis are carried out. Next, the raw meal is transported to the rotary kiln for clinker burning (10). To create a high temperature (1700 - 1900 ° C) in a rotary kiln there can be used traditional types of fuel (coal or natural gas) as well as alternative sources [6], primarily industrial and utility wastes (waste tires, solvents, plastic, impregnated sawdust, wood, paper, cardboard, etc.). Coal comes from a separate composition (11) for grinding in a coal mill (12) and enters the rotary kiln (10) already in the pulverized state. The quality control of coal is also provided by the of XRF/XRD analysis. After heat treatment, the clinker enters the clinker cooler (13) for its quick cooling to a temperature of 50-60° C. At its outlet (every 1 – 2 hours), XRF/XRD analysis and quality control of the clinker burning process is carried out, and then it goes to the clinker silos (14) for temporary storage. It should be noted that the air heated in the kiln (10) is used in the process of preparing the raw meal in the system of cyclone heat exchangers of the pre-heating tower (9), as well as for its drying in the mill (6). Gypsum (from a gypsum bin (15)) and other additives (zeolite, slag, etc.) are added to the clinker, which comes from silos (14), in predetermined proportions, depending on the type of cement. Therefore, the mixture obtained is ground in a cement mill (16) using an air separator (17), which serves to return non-bulk cement to the mill for grinding. Every 2–4 hours, there is carried out the quality control of the finished cement at the outlet of the cement mill, and the cement is supplied for temporary storage in cement silos (18) for further packaging or loading to consumers in bulk form (19). Before shipment or packaging, final quality control of cement is carried out at the outlet of cement silos, which includes its full XRF/XRD chemical analysis and evaluation of all parameters in accordance with national and international criteria for the quality of cement products.

By analyzing this process of cement production,

we can conclude that its integral component is a quality management system based on the integrated application of advanced XRF and PGNAA/PFTNAA methods for chemical analysis of cement at the main stages of its production. Thus, the quality of cement products largely depends on the accuracy and speed of measuring systems that implement these methods. At the same time, the practical introduction of XRF/XRD and PGNAA/PFTNAA methods in the cement industry is accompanied by a number of complex metrological issues. These include, first of all, the problem of assessing the accuracy of the results of PGNAA/PFTNAA and XRF/XRD chemical analysis of raw materials under continuous production conditions [2, 7, 8]. The main components of the uncertainty of measurement results by these methods include:

- the uncertainty component associated with the in situ measuring methods (PGNAA/PFTNAA) and ex situ (XRF) in the continuous motion of the raw material, in particular the difference in the averaged value of PGNAA/PFTNAA analysis measurements for a certain time interval from the mean value of the XRF sampling analysis for the same period of time;

- the uncertainty component due to the natural inhomogeneity of the material being studied in the stream, as well as the influence of the processing procedures of the sample for conducting laboratory chemical analysis (XRF/XRD);

- analytical uncertainty determined by the metrological characteristics of the measuring system itself (including the uncertainty of its static and dynamic calibration), which implements an appropriate method of chemical analysis (PGNAA, PFTNAA or XRF), as well as additional equipment that provides it with the necessary input parameters for the correct processing and interpretation of the measured data, in particular the speed and productivity of the string conveyor, the temperature of the detecting unit for the implementation of PGNAA/PFTNAA analysis or equipment parameters for sampling preparation of material for its XRF analysis.

- component of the uncertainty that occurs when comparing the results of PGNAA/PFTNAA and XRF analysis during the dynamic calibration of PGNAA/PFTNAA systems based on the results of XRF analysis, due to the fundamental difference between their physical principles.

In addition to estimating the uncertainty and comparing the results of PGNAA/PFTNAA and XRF analysis under the production conditions, there is equally important scientific problem, i.e. to increase its accuracy and speed, which influences the quality of raw materials and finished cement products. To this end, today the most advanced methods of machine learning, including artificial neural networks (ANNs), [9-10] are being actively implemented. The result of their application depends to a large extent on the quality and quantity of the data set for the study of ANN. Given the complexity of obtaining a large number of experimental data for this purpose, there are applied mathematical modeling algorithms, in particular, the Monte Carlo-Library Least-Squares, MCLLS [9] and the family of programs for modeling the transfer of ionizing radiation (neutrons, photons, electrons) in material systems (Monte Carlo N-Particle Transport Code, MCNP) [10]. To improve the quality of the measured signal, advanced digital processing methods are applied based on Kalman filters (with XRF analysis [11]), Fourier methods [12] and wavelet transforms [13], and also empirical modular decomposition (EMD) for nonstationary processes (PGNAA/PFTNAA) [14].

It should also be noted that their precision calibration in production conditions is an integral part of ensuring the high accuracy of the systems implementing the PGNAA/PFTNAA chemical analysis methods. Such a process traditionally includes the preliminary calibration of the analyzer using standard samples at the factory, as well as calibration with the same samples in the production conditions [15]. Moreover, calibration in the production conditions requires a long stop of the conveyor line of the relevant process (in some cases up to 48 hours) and is carried out periodically when replacing radionuclide sources of neutron radiation (every 2.5 years when using Californium-252), or unscheduled at a substantial change in the geometry of measurement or detection unit. In any case, the component composition, the form of standard samples, the stationary mode of their calibration can not fully meet the real conditions of flow chemical analysis of raw materials in the production, which causes an additional component of the uncertainty of such analysis results. As noted above, for the partial solution of this problem, the averaged measurements of the PGNAA/PFTNAA systems (typically 30-60 values) are regularly (every 1-2 hours) corrected using the XRF analysis. However, the XRF method requires procedures for preliminary sampling, milling and pressing of the resulting powder of the test material on the appropriate equipment. Moreover, under real production conditions for the XRF analysis, samples of raw flour are taken after grinding in the mill (6) and this method only determines the composition of its surface layer, while PGNAA/PFTNAA chemical analysis is carried out for the entire volume of the raw material mixtures to the stage of its grinding. For this reason, dynamic calibration based on XRF measurements will have additional uncertainty in PGNAA/PFTNAA analysis results. In addition, such an approach naturally requires the joint use of PGNAA/PFTNAA and XRF analyzers, despite their high cost. In assessing the latter, it is necessary to take into account not only the initial cost of the measuring instruments themselves and their metrological characteristics, but also the high operating costs of them. The latter may include costs for the regular replacement of expensive fuel neutron sources (PGNAA/PFTNAA), periodic calibration and maintenance of analyzers, radiation

safety and physical protection during their operation in accordance with national and international standards.

In addition to improving the accuracy of chemical analysis of raw materials by applying the most advanced achievements of digital signal processing and high-speed electronic systems to implement them, scientists are actively working to improve PGNAA/PFTNAA analyzers using MCNP methods for modeling physical processes based on them [16-19]. In particular, the direction of using alternative sources of neutron radiation instead of classical Californium-252 [4, 16, 17], the newest materials and the design of the main blocks of PGNAA/PFTNAA analyzers [4, 18-20] is extremely promising. These works are aimed both at improving the accuracy and precision of measurement, as well as reducing capital and operating costs when introducing PGNAA/PFTNAA methods in production. In particular, in [16], modeling was carried out and there were shown practical advantages of replacing a short-lived (half-life 2.65 years) neutron source Cf-252 with a long-lived Am-Be (half-life 433 years) with a concomitant modernization of the neutron (moderator) of high-density polyethylene and with a lead sheath for radiation protection, which could ensure almost constant neutron flux throughout the lifetime of the PGNAA analyzer (20 years) and thereby increase its accuracy; while in [18, 19], MCNP simulations were performed on the effective choice of material and thickness of the reflector, absorber and moderator of the neutron flux in order to increase the reduced gamma radiation, and hence the sensitivity of the measurement using the PGNAA method with Cf-252; there is shown in [20] the use of the MCNP method for modeling a reflector and a moderator when using the D-T generator [4] as a neutron source, which is the basis of the PFTNAA technology to increase the neutron flux density on the sample under study and, as a consequence, increase the sensitivity of this method.

Thus, based on the above, we can conclude that the development of new and improvement of existing methods for estimating uncertainty, improving the accuracy of measurement, calibration and design of PGNAA/PFTNAA analyzers using modern methods of machine learning and mathematical modeling of the processes of ionizing radiation with substance is the actual scientific problem. Moreover, these studies should be aimed not only at improving the accuracy and precision of the above-mentioned methods and their integrated metrological support as part of quality management systems for cement products, but also at reducing capital and operating costs in order to increase the economic attractiveness of using such technologies in the cement industry.

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