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The Application of Laser Element Online Analyzer MAYA for Extraction of Mineral Raw Materials and For Stabilization of Raw Mixtures in Nonferrous Metal Production

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The laser analyzers MAYA are successfully applied in industry in order to solve the tasks of crushed ore sorting and stabilization of the composition if raw material mixtures in metallurgy and in production of fireproof materials. The tests of non-ferrous ores such as Cu, Mo, Zn, Pb, Sn, Ti, Be, Sr and Ba confirm that the laser analyzers could be applied in this branch at different stages of the technological process: extraction of raw material, preparation of raw material mixture, check of technical composition, operative check of the finished products' quality.

Keywords: LIBS, online, industry, minerals, metals.

Introduction

During the process of mineral raw material extraction it is necessary to separate the raw materials by grades. Nowadays in most branches of industry dealing with extraction, processing of mineral raw materials and production of the most part of industrial materials including ferrous and nonferrous metal industry, production of fireproof and constructional materials, fertilizers, solid fuel the crude ore comes for processing with significant variations of chemical and mineralogical composition appearing just after extraction from open cast or mine and after storage as well. This decreases the stability of technological processes of concentration, processing, worsens the quality of finished products, and decreases in whole the efficiency of production. Therefore it is necessary to guarantee the stability of the raw material quality during realization of the specified technology for receiving the products with pre-assigned qualitative factors.

It is possible to solve these problems by separating the raw materials by grades including the rejection of the portions of material unsuitable for specific purpose application and by well-grounded regulation of the parameters of its processing based on operative information on chemical composition

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of raw material. This regulation could be applied at all the stages of production – from minerals survey, their extraction and concentration and up to preparation of raw mixtures with the specified composition and operative automatic regulation of the parameters of technological processes.

In most cases the information on chemical composition of raw material being extracted in open cast and moved along conveyers, on raw mixtures and their components becomes accessible for technologists who perform the control of processes of extraction, generation of averaging storages, batching of components of raw mixtures only in some hours after sampling. In case of large-tonnage production this information delays significantly not permitting to use it for the tasks of controlling these processes. Besides, the validity of the information received is also often rather low due to complexity of providing the representativeness of the samples taken and of preparing the samples for laboratory analyses.

The specified reasons stimulated the development of different flow element analyzers at the 20 century end. Their application permits to receive information on raw material composition in real-time mode directly at conveyers or in flow without sampling and gives a possibility to control the technological processes operatively, increases the degree of correspondence of analytical information to real composition of raw material moved [1-4]. But the majority of analyzers are based on activity of different sources of ionizing radiation – Roentgen, neutron or gamma – being rather dangerous for the personnel and for the environment pollution. Besides, their application requires to receive the permits from different state bodies dealing with radiation monitoring, is rather complicated from technological point of view and cost-based, all these reasons limit their application rather often.

For solving the same tasks of stabilizing the composition of ores, ore mixtures and quality of finished products in real-time mode by fully unsafe method, the Israeli firm Laser Distance Spectrometry (LDS) has developed the laser optic-emission element analyzer MAYA.

The operating principle of the analyzer MAYA is based on the method of laser optic-emission spectrometry (Laser Induced Breakdown Spectrometry, LIBS), where the solid-state pulsed Nd:YAG laser serves as an excitation source of the substance studied. The laser beam with a rate from 1 to 20 times per second is focused at the surface of material being analyzed where the temperature of more than 30000ºC is achieved immediately, and small amount of the substance turns into plasma state. The plasma is practically electric neutral but heavily ionized gas containg the molecules, atoms and ions of the chemical elements being in the material and the free electrons as well. The processes of recombination of positively and negatively charged particles begin in the plasma immediately and are accompanied by emission of photons – «glow» of the plasma occurs. The atom of every chemical element emits the photons with strictly defined wavelengths, and the lumonous intensity is connected in general case with the concentration of this element in the material analyzed (Fig. 1). Thus, the spectra received are the characteristics of the material analyzed, figuratively speaking their «fingerprints» [5-7].

The optical radiation of the plasma within wide optical range from 190 to 1000 nm is fixed by special spectrometers transferring the digital information on the spectrum composition to the analyzer computer (Fig. 2).

In result of statistical processing of a set of spectra for the period of time required for technologist in order to solve his task (usually from 20 s to several minutes) the concentrations of the elements being the components of the material analyzed are calculated [8]. The main advantages of the method

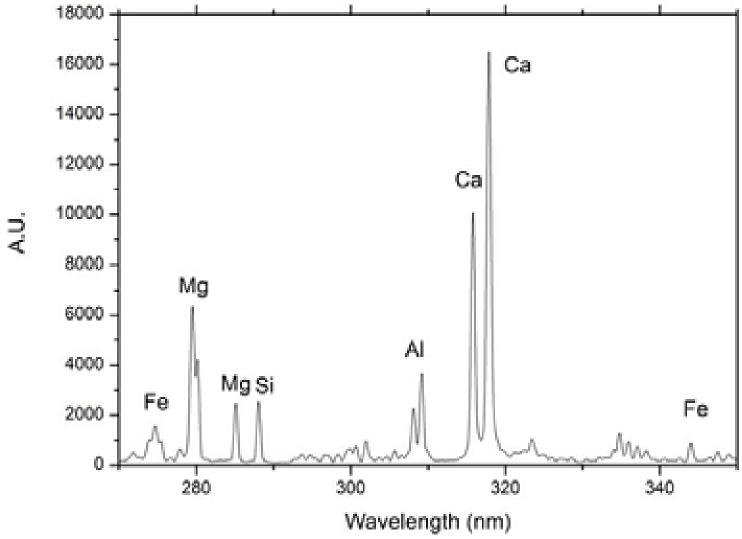

Fig. 1. Typical spectrum of limestone obtained by means of MAYA

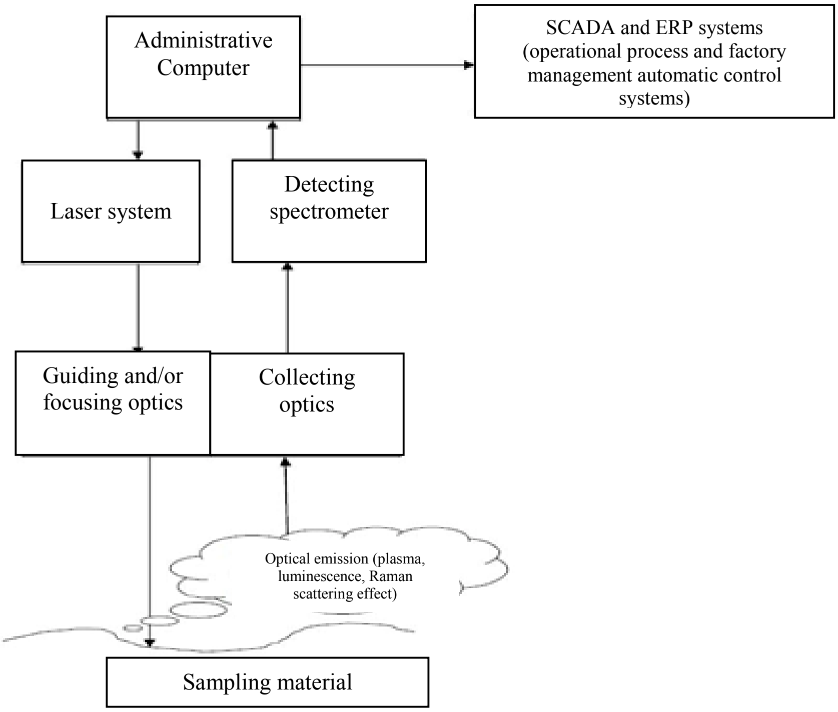

Fig. 2. Principal diagram of the laser analyzer MAYA operation

of laser-emission spectrometry in comparison with other analytical methods applied for analysis of the element composition in real-time mode are as follows:

- high sensitivity, low detection limits and high accuracy due to clear spectral lines of magority of the elements within wide optical range and to practical absence of thier interferences;

- ability to analyze simultaneously all required elements including light (C, Si, Mg, Al);
- absence of any types of ionizing radiation (neutron, gamma and Roentgen), absolute unsafety for the personnel, absence of necessity to get permits and permanent inspection of the state bodies dealing with atomic monitoring;
- independence of the analyses results from quality of the matrial surface, size of lumps an height of the matrial layer on conveyer;
- stability of calibration during long period of time;
- simplicity and safety of the analyzer's operation and maintenance.

A potential advantage of PGNAA in comparison with XRF and LIBS is its ability to measure the volume and not only the surface. The penetration depth of a laser beam is very shallow, so on a moving belt conveyer only the surface of the material is analyzed while we need to know the impurity concentrations of the volume. Moreover, only tiny spots on the particles' surface are analyzed. Thus the greatest challenge was to prove in ambient conditions of material transported on a conveyor that it is possible to transform LIBS data to quantitative elemental content evaluations, and that high-frequency sampling of surface chemistry is commensurate with the average of the total cross-section and length. It is clear that the LIBS analyzer has to be employed on a surface which statistically represents the whole volume of the material. For industrial control, you need the data for certain time periods, from 30 s to 5 min (approximately 60 to 600 m of conveyer belt run). For such large quantities of sample, the surface in most cases is statistically relevant, since bulk materials typically get to the conveyer belt after explosive/crushing processes that are random in nature. Its efficacy has been proven by many industrial installations of XRF, which is also of the surface analyzer type, and by our LIBS installations. According to our accumulated experience, to get the surface representative of the volume you need the following: get material to the conveyer belt via averaging storage; chose the installation point after the mixing drums; mix the material by inexpensive mechanical tools. The applicability of LIBS surface analysis has been practically confirmed by all current industrial installations.

Examples of industrial applications

Similarly to other existing today methods of online analysis, the applications of the laser analyzer MAYA in extraction, concentration and processing of the mineral raw materials could be divided into two basic groups – automatic sorting of the ore being extracted or crushed (Fig. 3) and automatic batching of components of the raw material mixtures for stabilizing the composition of the raw material mixtures.

For sorting of the crushed ore with fractions of up to 150 mm the analyzer MAYA is used, for example, at crushing-concentration factory of Magnesite Complex [9] (Fig. 4). Depending on the content of CaO and SiO_2 in portion of the material, passing along the conveyer during 60 s, the system SCADA, performing the control of automatic gate, determines a bunker where this portion of the material is to be directed on the basis of the operator's task and the data received from MAYA.

The accuracy and reliability of the analyzer's readings are well confirmed by the following example: : at setting as a task the threshold value of silicon oxide content equal to 1.45 % (at losses during burning for raw magnesite of about 50.6 % this corresponds to approximately 2.9 % of silicon dioxide in terms of the content in the material after burning) the raw magnesite was sorted into bunker, and burning of this raw magnesite gave a batch of fired periclase – fireproof powder with

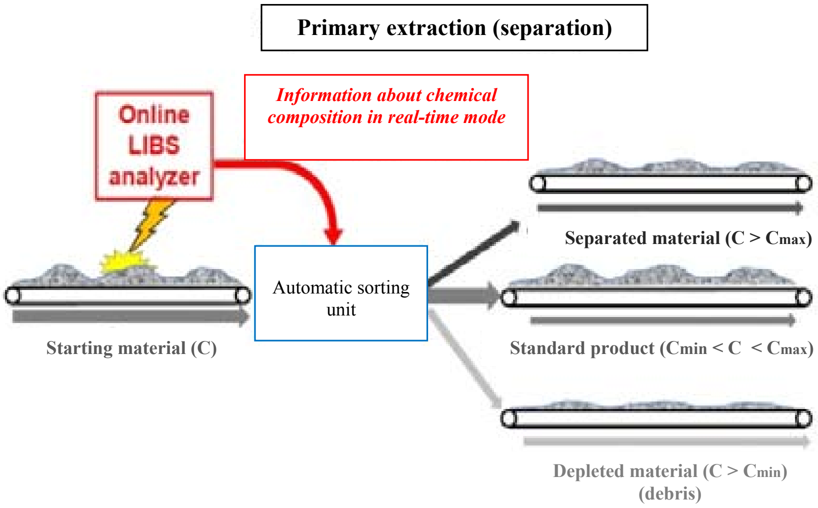

Fig. 3. Principal diagram of automatic sorting of crushed ore on the basis of data on its chemical composition coming in real-time mode

Fig. 4. The analyzer MAYA at crushing-concentration factory of Magnesite Complex

fraction of 0-150 mm with a level of silicon oxide of less than 3 %. Thus the relative deviation of the analyzer’s readings from the laboratory data is less than 5 % (Fig. 5), this is not worse than the reproducibility of the laboratory analyses. In the result of MAYA implementation the capability to reject the material with non-corresponding parameters (up to 10-15 %) from the flow of qualitative raw magnesite and to extract additional volume of high-quality raw material (10-30 %) from the flow of the medium grade crushed magnesite was realized. The estimated period of the cost recovery for the project was equal to not more than one year from the commissioning due to separation of more expensive high-quality products without damage to the mass production being realized and due to timely correction of quality of the fired magnesite used at subsequent production stages and for shipment to the consumers.

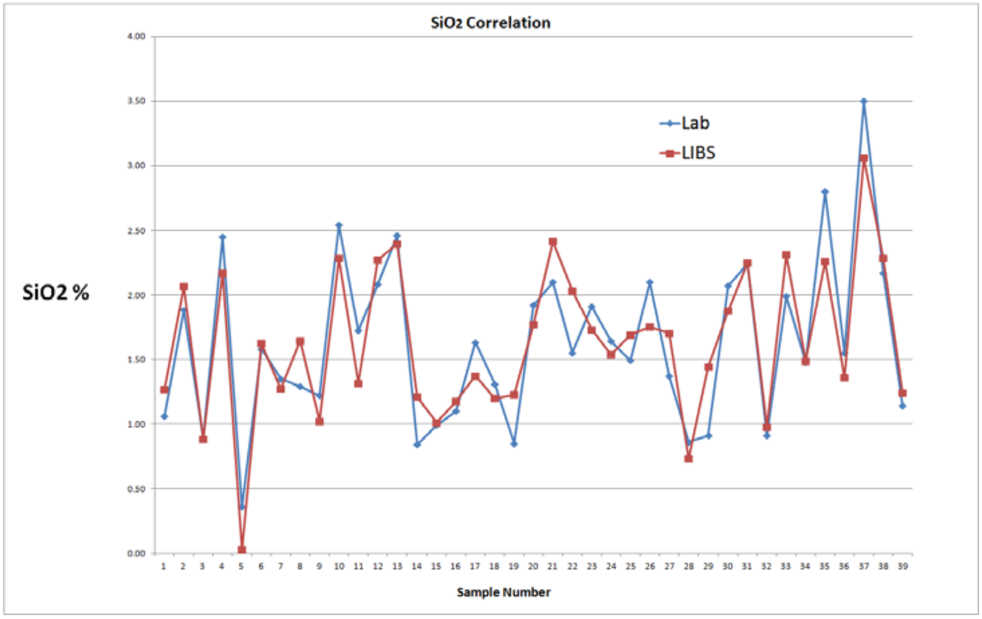

Fig. 5. Comparison of laboratory data and the analyzer MAYA data for SiO_2

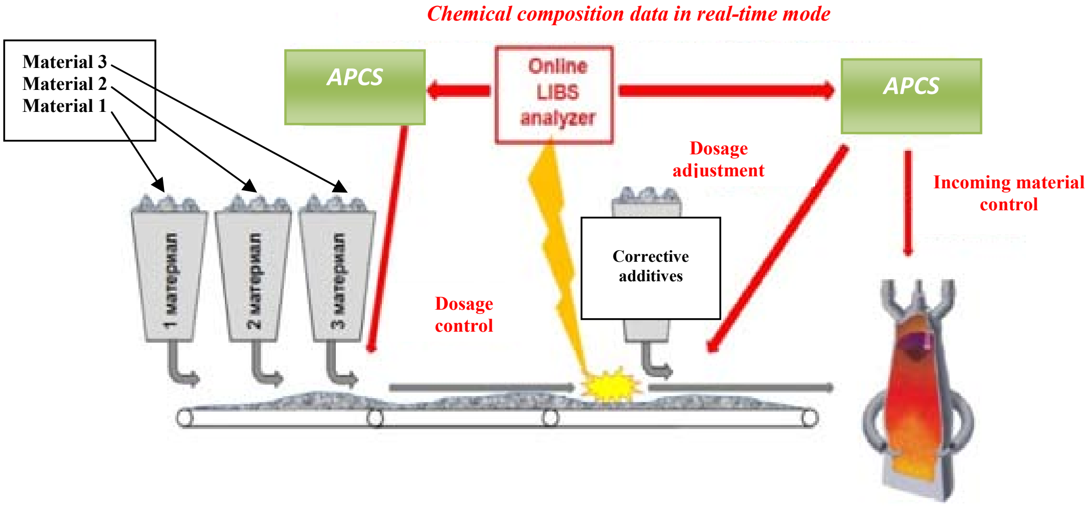

Fig. 6. Principal diagram of automatic batching of the raw material mixture components on the basis of information on its chemical composition coming in real-time mode

The operating experience of the analyzers demonstrates that they could be also used in the composition of crushing and sorting complexes directly at places of the ore extraction and the primary crushing of the ore materials and for technological operative inspection of the finished products quality as well.

For stabilization of composition of the raw material mixture the analyzer MAYA is used, for exampleat public corporation «Novolipetsk metallurgical complex» [10-11] (Fig. 6).

The chemical composition of the iron-ore materials used in the agglomeration production of ferrous metallurgy is significantly varied, first of all by content of such elements as Fe, Ca, Si, Mg. The content of CaO and SiO_2 in the iron-ore mixture has significant variations connected with bad averaging and segregation of the materials in pile. The addition of lime into the iron-ore pile for moisture fixation causes considerable influence on variations. This is one of the main problems connected with obtaining of agglomerate being stable by content of Fe and by basicity factor (CaO/SiO_2). It is known that the quality of the iron-ore materials (agglomerate and pellet) has strong influence on efficiency of operation of blast furnaces. The stability of the chemical composition of agglomerate and its basicity is also such an important characteristic of the quality as reducibility, reactivity index and strength after reaction. The decrease of the agglomerate basicity variation permits to reduce the output of slag per ton of cast iron and to decrease the coke rate in blast furnaces.

The analyzer MAYA was installed at combined conveyer of aggloburden coming to agglomachine No.1 before place of flux batching. The system is based on receipt of information on content of Fe, CaO and SiO_2 in iron-ore mixture from the analyzer MAYA and performs the automatic continuous correction of the flux flow rate at subsequent batching, decreasing the agglomerate basicity variations. (Fig. 7, 8). Starting from February 2011 the laser analyzer *MAYA*, installed at agglomachine No.1 of Novolipetsk metallurgical complex, has been operated round-the-clock without failures in rigid conditions of high dust level, вvibrations and temperature variations from -10 to +40 °C.

In one year after the start of the analyzer's operation the check of the current calibration (correctness of its readings) was carried out, and it confirmed the stability of the analyzer's calibration during that period. The comparison of the analyzer's data for the content of Fe and CaO in iron-ore and the results of the laboratory analyses are given in Fig. 9. This compatibility of the data is the result of high stability of the laser radiation parameters and of the optical schemes used, and application of effective means of the analyzer's protection from industrial factors (dust, vibration, variations of temperature and humidity) during continuous operation.

In the result of this system implementation the portion of agglomerate, which basicity deviated from the value specified by the blast furnace shop by more than 0.05 was decreased by more than twice – from 8-10 % to 3-4 %, the saving of flux in the blast furnace shop was reduced by more than

	Текущие	Задание	час	мин	сек	Fe	CaO	SiO2	MgO	Состояние
КОНЦЕНТРАТ	0	0	15	2	55	63.49	2.65	6.58	0.76	Норма
Концентрат_1			15	0	54	63.26	2.67	6.59	0.78	
Концентрат_2			14	59	9	63.59	2.59	6.59	0.75	
		Расчет			9	*****	5.31	13.97	1.54	Сеть
ФЛЮС	0.0	0.0				Проба флюсов	48.0	0.00	0.00	ДА
Доля CaO смеси	0.2	0.1								
Уд.расход	0.0	11.4								

Fig. 7. The interface of automatic flux batching system to agglomerate furnace charge

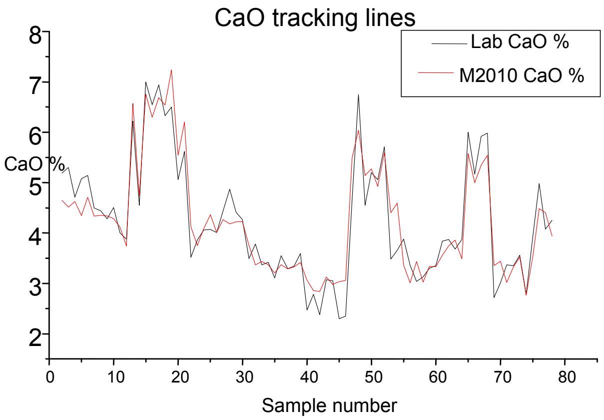

Fig. 8. Comparison of laboratory data and MAYA data

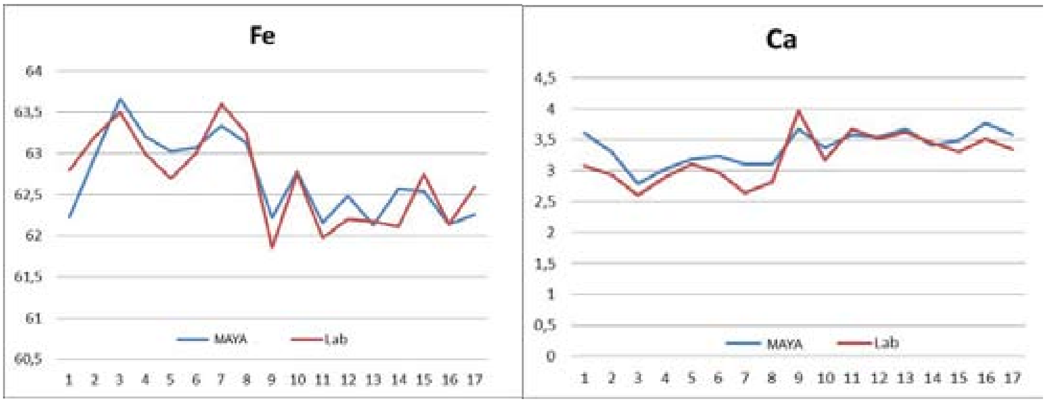

Fig. 9. Comparison of the analyzer's data and laboratory data for the content of Fe and CaO

0.6-0.8 kg per ton of cast iron; the period of cost recovery for the project was equal to less than 6 months.

Applications proven feasible by laboratory scale LIBS analyzer Cu and Ni

Copper ores quality control is usually needed for several tasks, for example online control of Cu, S, Ca and Si and laboratory scale tests gave very satisfactory correlations for all these elements (Fig. 10). Another important task is online control of Mo impurity in copper-bearing ore. Molybdenum impurities are confidently detected even with Mo concentrations in the hundreds of ppm range and correlation with laboratory data of Cu, Mo and Fe are quite satisfactory (Fig. 11), promising good results in industrial online LIBS application.

Nickel- and copper-bearing ore requires online control of both elements' contents. Correlation between laboratory data on Cu and Ni and laboratory-scale LIBS tests for two different fractions are quite satisfactory (Fig. 12), promising good results in an industrial online LIBS application. In another task, Fe/Ni concentration ratio and MgO content were the aims of online analyses, and the correlation between laboratory data and laboratory-scale LIBS conveyer tests was very satisfactory (Fig. 13).

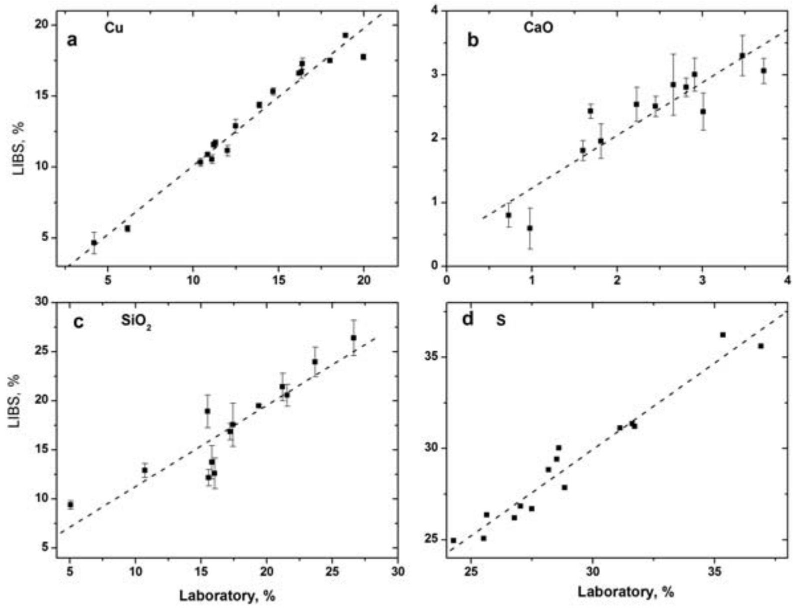

Fig. 10. Correlation between online LIBS and traditional laboratory data on Cu (a), CaO (b), SiO2 (c) and S (d) for copper bearing ore

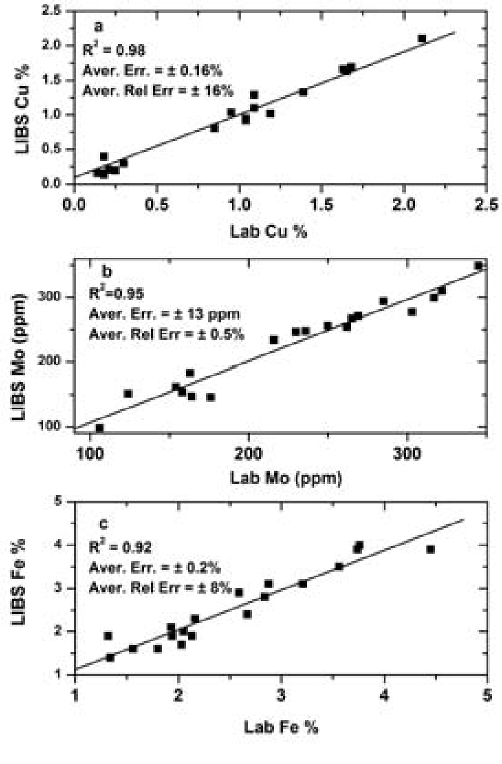

Fig. 11. Correlation between online LIBS and traditional laboratory data on Cu (a), Mo (b), and Fe (c) for copper bearing ore

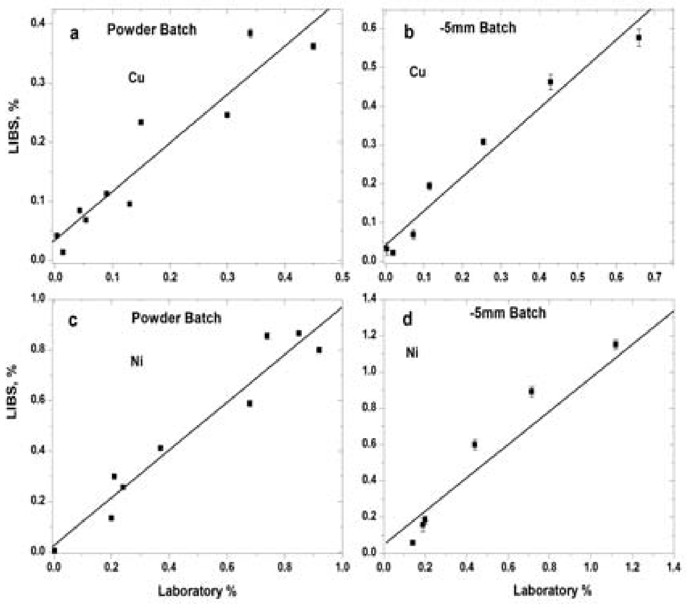

Fig. 12. Correlation between online LIBS and traditional laboratory data on Cu (a, b) and Ni (c, d) for different batches of Ni bearing ore

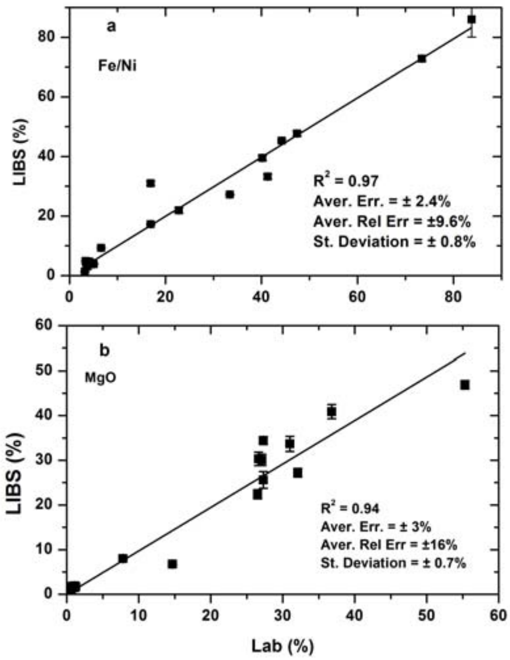

Fig. 13. Correlation between online LIBS and traditional laboratory data on Fe/Ni ratio (a) and MgO (b) for Ni bearing ore

Good analytical results have been received also for Zn-, Pb-, Sn-, Ti-, Be-, Sr- and Ba-bearing ores.

Potential for bauxite, alumina and aluminum industry

As the Al industry continues to grow the concentrations of impurities in raw materials are increasing with significant implications to meet customer chemical specifications. The mostly important impurities are Cr, Ti, Ni and V of the coke and Fe, Si, Ga, Zn of the alumina. These impurities must be removed in order to get good quality aluminum, because they make it brittle and liable to corrosion. In some smelters the concentration of these impurities is beginning to exceed customer cast product specifications. Rapid and automatic analysis allows industrial minerals producers to promptly detect changes in incoming raw materials, allowing them to take appropriate action in the process streams.

Specifically in Russia, the absence of high quality local bauxites, with silicon module (A/S) up to 10 with corresponding 50 % Al_2O_3 content, and strategic reasons led to creation of unique technologies to process domestic low grade bauxites with A/S in 3-6 range [12]. The term bauxite is used for naturally occurring mixtures of aluminum monohydrate (boehmite or diaspore) and trihydrate gibbsite $Al(OH)_3$, including impurities which are typically clay minerals, free silica, iron hydroxides and titania. Thus online bauxite control enables to detect bauxite parts with low aluminum contents and to remove them from the following beneficiation process. It may be done by the way used for crushed magnesite ore mechanical sorting.

The applicability of radiometric sorting by XRF technique of Russia bauxite rocks has been extensively studied [13]. It was proved that for -100+50 and -50+25 fractions of North Ural deposit it is possible to remove carbonate from bauxite using intensity lines of Ca and Fe. As a result, the CO_2 content was lowered from 18.0 to 4.1 %, while the A/S was increased from 10.2 to 14.1 %. For Timanskoe deposit, the main task was to improve the A/S of the low grade hematite-boehmite bauxite. It may be done by separation of minerals with high Fe and Si contents, mainly chlorites, using characteristic Fe emission. It was proved that A/S may be raised by 1.6.

Another source is non-bauxitic raw materials such as nepheline $Na_3K(AlSiO_4)_4$ and alunite $KAl_3(SO_4)_2(OH)_6$. At the moment 4 major bauxite mines and 2 nepheline sources/mines are in operation in Russia. The Al_2O_3 content is substantially lower than in bauxite ores and in order to produce 1 t of Al, usually 3-4 t of bauxite is enough, while 7-8 t of nepheline and alunite are needed. Nevertheless, nepheline ore is a part of apatite-nepheline, nepheline sienite and urtite deposits. It enables complex process with nepheline concentrate used for alumina and apatite concentrate for fertilizers production. Alunite is also complex source, containing alumina, sulfur anhydrite and alkali Na and K metals [14]. Once again, all those elements may be definitely detected and controlled by online LIBS technique. The applicability of XRF sorting of nepheline was studied on non-conditional rocks with the following composition: Al_2O_3 – 22 %; SiO_2 – 40,1 %; CaO – 11 %; MgO – 2,2 %; Fe_2O_3 – 5,6 %; Na_2O – 9,0 %; K_2O – 2,3 %. It was proved that 10-40 % of the rocks may be separated as tail while the remaining part is a suitable for further technological treatment. Good XRF radiometric sorting results prove that the corresponding rocks are very contrast and online process control may be very effective. The main potential advantages of LIBS technique compared with XRF are the following. XRF is not suitable for the light elements detection, usually with atomic number less than 20. If the energy of characteristic emission is less than 5 keV, the interference is very strong because of air absorption and water on the minerals surface [1]. Thus very relevant elements, such as Al and Si, may not be detected directly and all control may be accomplished using accessory elements analysis, such as Ca and Fe. LIBS can detect all elements relevant for online control, including Al, Si, Ca, Fe and Ti.

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Применение лазерного анализатора для сортировки минерального сырья и стабилизации сырьевых смесей в режиме реального времени в производстве цветных металлов

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Лазерные анализаторы MAYA успешно применяются в промышленности для решения задач сортировки дробленой руды и стабилизации состава сырьевых смесей в металлургии и производстве огнеупорных материалов. Испытания руд цветных металлов, таких как Cu, Mo, Zn, Pb, Sn, Ti, Be, Sr и Ba, свидетельствуют о том, что в данной отрасли лазерные анализаторы могут быть применены на самых разных стадиях технологического процесса: добыча сырья, подготовка сырьевой смеси, контроль технического состава, оперативный контроль качества готовой продукции.

Ключевые слова: LIBS, online, промышленность, минералы, металлургия.
