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A method for fast and contactless control of raw materials

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Abstract

A technique for quality control of ceramic materials is proposed based on the surface photo-charge effect. The method is demonstrated and studied in the case of controlling the chemical composition of bricks. Presented experimental results show that samples with different compositions invoke distinctly different electronic signals specific to sample's composition. In particular, it is revealed that the response signal is a function of the percentage of coal slurries added to the brick raw material for energy efficiency. The quality measurements using the proposed technique are express and contactless, and can be performed under the production conditions of brick firing. The obtained results indicate that the described technology could be extended to control the production quality of other raw materials.

Keywords: B. Impurities; D. Traditional ceramics; E. Sensors; Quality control

1. Introduction

In many industries, there is a need for constant monitoring of the chemical composition of the feedstock material from which a product is made. This is necessitated by the technological requirements for maintaining a high-quality product, and for preventing possible sabotage attempts, possibly by disgruntled employees or competitors. In our research, a technology was developed that can implement control during production. This report is focused on the mechanism to monitor the chemical composition of materials for the manufacture of ceramics and, in particular, bricks. This production has huge energy consumption. To reduce the energy consumption of the product, combustible waste materials such as coal slurries are added to the raw material. When bricks are inserted in the furnace, the coal slurries ignite and burn. This way, the bricks are self-baked and a serious environmental problem is solved since there are large quantities of coal sludge requiring specific storage measures. A constant monitoring of the quantities of combustible additives is needed; otherwise the quality of the bricks will deteriorate.

Different methods exist for control of the chemical composition of such materials. For example, X-ray diffraction and mass spectrometry were used by Andrés et al. [1] for physicochemical characterization of bricks. Laser-induced breakdown spectroscopy is an effective method for studying powdered samples, in particularly for the production of materials for bricks and tiles [2,3]. Neutron activation analysis [4] often finds its place in materials science and manufacturing technology. Alia et al. [5] have applied Fourier-transformation Raman spectroscopy and X-ray fluorescence spectrometry for quality control of clays. Belozerova [6] has examined the soil mineral component by X-ray electron probe. The X-ray diffraction, photoacoustic spectroscopy and electron paramagnetic resonance can also be used for soil characterization [7]. Dielectric permittivity measurements have also been successfully applied in studying clay minerals, granular samples and soil–water mixtures studies [8,9]. These methods exhibit certain disadvantages. They are either too slow and complicated or too expensive, being in general not suitable for continuous monitoring under production conditions.

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Our research has shown that for monitoring of the chemical composition of the material the so-called surface photo charge effect (SPCE) can be used. The essence of SPCE consists in the finding that the interaction of any solid with electromagnetic field results in occurrence of induced alternating electric signal with the same frequency as that of the incident field [10]. The SPCE represents generation of an alternating voltage when a solid interacts with a modulated electromagnetic field. The potential difference between the irradiated sample and the common ground of the system is measurable and is dependent upon many factors. The measurement of the voltage is rapid, contactless, and can be performed in-situ under production conditions with rather inexpensive equipment. The name surface photo charge effect has been kept for historical reasons.

Possible mechanisms causing SPCE are proposed and analyzed [10,11]. A detailed theoretical interpretation of the SPCE has not been developed yet. Several hypotheses, regarding the mechanism of the SPCE in various types of solids, were proposed:

- for conductors, the incident radiation, decaying in the medium depth leads to the generation of a force directed perpendicularly to the illuminated surface and redistributing the charges in the conducting medium;
- for non-conducting media, the incident radiation leads to redistribution of the charges, accumulated into surface energy states;
- the incident light redistributes dipole molecules absorbed on the surface of the dielectrics;
- photo desorption or surface sputtering induced by the incident radiation.

The above hypotheses cannot be regarded as complete or determinative. The explanation of the SPCE will probably require further investigation. It is possible to seek an explanation, within a theory dealing with field–matter interactions. The approach can involve quantum-mechanical, semi-classical and statistical considerations on the interaction of an electromagnetic field with the surface of a material, which may be a metal, a semiconductor or an insulator. Density functional theory (DFT) including external electromagnetic fields effect is one of the possible approaches considered at present as capable to offer reliable description of SPCE physical mechanisms.

2. Material and methods

The SPCE is a very fast effect: for example, an irradiation with 20 ns laser pulse results in a signal response which reproduces precisely the waveform of the incident pulse. As the experiments have shown, the arising of a signal from a solid after electromagnetic irradiation is a universal feature of solids. SPCE has been measured in the frequency range from1 Hz to 1 GHz, infrared, visible and the beginning of ultraviolet. Our hypothesis is that the effect exists in the whole frequency range of the electromagnetic radiation. SPCE can be induced only by modulated incident radiation. The lack of response upon non-modulated field is an evidence that the detected signal is induced by the SCPE. Since the electron properties of the solid are influenced by the incident electromagnetic radiation, one can expect that excited changes will provoke measurable SPCE signals. In this way, with all other conditions fixed, it is possible to detect changes in the solid properties. Experimental studies show that the sensitivity of the proposed method is high. An important feature of SPCE is its significant dependence on the specific properties of the irradiated samples. This fact reveals opportunities for a fast and contactless analysis, not only of solids, but also of liquids and gases e.g. foods [10,12].

As mentioned above, one of the features of SPCE, which is discussed in this article, is that every solid generates a specific electric signal. The amplitude and the phase of this signal depend on the chemical composition of the solid. In this study we monitor the amplitude. This means that we could quickly and without any physical contact, monitor the composition of a variety of samples. Quality control is carried out by checking whether a set of samples of interest always generate the same signal.

A schematic diagram of the experimental setup for SPCE observation we have used in our research is shown in Fig. 1. Here (L) is a source of incident radiation. The radiation was modulated by using a modulator (M). We have constructed these two details using standard modules and elements. The studied sample is placed in the measuring arrangement (S). In this particular setup the latter represents a small vessel in which two electrodes are mounted. The vessel was placed in a shielded chamber which had an optical window. For this purpose a transparent conducting film of SnO_2 was deposited on the glass plate. The film of SnO_2 was used for electromagnetic interference prevention. Mechanical device always fixes the samples in the same position to avoid errors caused by displacements. The signals measured are in the nano- and micro-volt scale and were 20 dB amplified by the preamplifier (A). The preamplifier type 233-7 manufactured by Unipan Scientific Instruments is usually used in our experiments. The detected signal had very low amplitude,

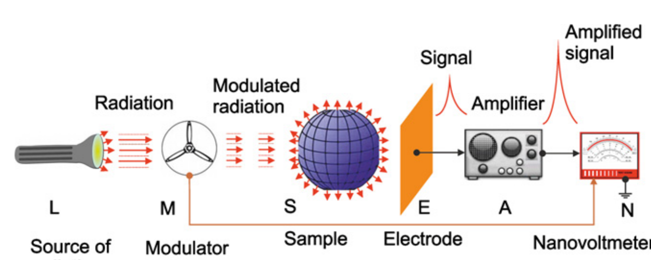

Fig. 1. Experimental setup for SPCE observation: L—source of radiation; M—opto-mechanical modulator; S—measuring structure; E—electrode; A—high impedance amplifier; N—lock-in nanovoltmeter.

thus a lock-in nanovoltmeter (N), capable of extracting the signal from the background noise, was utilized. The lock-in nanovoltmeter (N), (type: 232, manufacturer: Unipan Scientific Instruments, measurement range: 30 nV–30 mV) has output for inclusion of a recording device. We attach a special voltmeter (type V543, manufacturer: Meratronik, measurement range: 0.01 mV–1000 V) to this output for more accurate measurement of signals. Therefore the results described below are given in relative units. Using relative units is also correct in view of the fact that the measured electrical signals depend on many factors: the measuring structure, the way of shaping and positioning the holder of the samples, parameters of radiation exposure, equipment settings, etc. The key point is not to change anything other than research sample during series of experiments, making it possible to draw correct conclusions. The configuration was described in detail elsewhere [11].

For our study we used samples of clay, coal and coal slurries, and mixtures of clay and coal slurries. All the samples had the same weight—150 g. We analyzed them in ground form. They were placed in special holders ensuring that the upper surface of the sample has the same composition as its entire volume. The holders enabled easy mixing of samples by exchange of material between the surface and the volume. Special care was taken to avoid sample contamination. The samples were characterized by measuring the amplitude of the generated electric potential difference.

The quality control for possible chemical composition changes in a series of samples requires pre-calibration. For the purpose we need a sample which we are sure has the necessary chemical composition and is identical in size and weight with the currently studied series of samples. It is important that all samples in a series are of the same size and weight. We measure the signal generated by the standard sample in our experimental setup and compare it with the signals generated by the studied samples. If there is a deviation, the sample is taken out and if necessary sent to a laboratory for additional quantitative evaluation of the changes. If only one parameter in the series varies, calibration for quantitative analysis by SPCE is possible. Such analysis requires the relation between the generated signal and the controlled parameter changes, to be experimentally identified beforehand.

To make sure that it is possible to work with the materials of interest, we initially examined a wide range of samples of coal, coal sludge, clay, and a mixture of clay and coal sludge. To avoid random errors each measurement was repeated several times. We also constantly controlled the parasitic electrical signals (background noise). For the purpose, before placing each new sample, the indications of the lock-in nanovoltmeter (N) of Fig. 1 are recorded to verify that no significant signals without a sample are present and that the level of parasitic signals is always the same. The purpose of these inspections was to make it sure that the observed differences in the amplitudes of the signals generated by different samples are actually caused by differences in the composition of samples. Therefore, experimental conditions and in particular the settings of the apparatus within a series of measurements is maintained strictly in an unchanged manner.

3. Results

Table 1 shows the results of one of many measurements of a series of samples: coal, sludge with high content of coal, sludge with low-coal content, clay mixed with sludge and clay only. As mentioned above results are in relative units.

Note that various materials of the same type, such as clay taken from different locations, can generate different signals. As an example, in Table 2 we give the results of testing series of samples of coal. They were taken by drilling in the vicinity of Lom, Bulgaria. Samples are low-quality lignite coals. The samples are from boreholes: 50,417; 50,418; 50,419; 50,420, 50,421; 50,430. We chose this series of coal samples, because there are well-developed standard methodologies for coal testing and are also close to the materials that we are interested in. The first three columns of numbers after the drill, give sulfur, volatile, and ash. These are important indicators of environmental perspective. Sulfur is the dried sample. The data in the table show that the materials have different

Table 1
Results for a series of studied samples.

No	Compound	Measured signal U (a. u.)
1	Coal	0.55
2	Sludge with high-coal content	2.64
3	Sludge with low-coal content	2.82
4	Clay with sludge	3.72
5	Clay	2.8

Table 2
Results from testing with SPCE—a series of low quality lignite coal samples.

No	Probe No	Total S of dry fuel S_t^d (%)	Volatile compound in dry fuel V^d (%)	Ash in dry fuel A^d (%)	Measured signal U (a. u.)
1	50,417	2.08	33.38	36.08	2.718
2	50,418	0.85	18.38	70.02	2.658
3	50,419	0.43	16.93	74.52	2.506
4	50,420	1.19	21.93	67.58	5.562
5	50,421	1.36	26.09	57.83	2.688
6	50,430	1.02	30.92	50.48	2.866

Table 3
Signal generated by the SPCE at different percentages of sludge.

No	Compound	Measured signal U (a.u.)
1	Sludge	4.01
2	Clay	4.57
3	Clay with 50% sludge	4.12
4	Clay with 40% sludge	4.57
5	Clay with 30% sludge	4.74
6	Clay with 20% sludge	5.04
7	Clay with 10% sludge	5.29

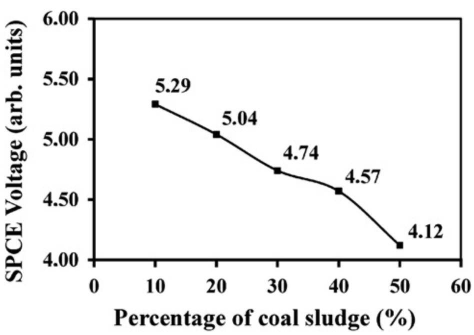

Fig. 2. Changes of the measured signal versus the quantity of coal sludge added.

compositions. The last column shows the signal measured by SPCE.

As mentioned above, the aim of our work is to verify that the electric signal generated by SPCE changes as a function of the chemical content of samples. In this respect, we present our results of studying the measured signal as a function of the percentage of sludge, as shown in Table 3. As can be seen, the signals of both the clay and sludge ingredients are shown separately, followed by results of samples representing a mixture of clay and sludge in reducing the rate of sludge added from 50% to 10%. Fig. 2 shows the graphic form variation of the amplitude of electrical signal changes as a function of the quantity of sludge.

4. Discussion

The data presented in Table 1 clearly demonstrates that each material generates its own specific signal. This result meets our expectations and opens the possibility for performing such kind of research. Interestingly, in sample 4, which is a mixture of clay and sludge, we see a significant increase in the signal compared to signals generated by the two components separately. Another point to note is that the signal tends to increase with decreasing percentage of carbon contained in the sample. A similar trend continued in the results of Table 3.

It should also be noted that sample 4 (Table 1) which is a mixture of clay and sludge, generated relatively heterogeneous signals in amplitude compared to other types of samples. They were taken at the same time from a brick factory and should have the same percentage of the two components. This probably means that the mixing of clay and sludge in the machinery of the plant is not sufficiently homogeneous.

The results in Table 2 are given to confirm the idea that each material generates a specific signal. Series of samples controlled through conventional methods were also explored. The examined samples were from the same material—coal mined in the same area but from different drills. The samples generate electrical signals that are very different. This fact indicates the existing deviations in the chemical composition and properties of the samples. These deviations have also been detected with tests based on conventional methods, as shown in Table 2. Thus is confirmed the idea that any material generates a specific signal and using SPCE it is possible to retrieve information on similar samples. The method is express, in-situ and contactless. This confirms the presumption that specific differences among samples in a series can be detected.

The most important information related to the aim of this work is derived from the results in Fig. 2. They show that the measured signal from the surface photo charge effect is proportional to the amount of coal sludge added to the clay. This gives a positive answer to the fundamental issue of our study: it is possible to control the percentage of this additive by the proposed method. Our previous experimental results with other materials show that this method, which is based on the SPCE, could also be applied to control processes occurring in ceramics [11].

It should be noted, however, that different batches of clay and sludge have numerous possible variations in chemical composition. It is therefore necessary to determine whether a new calibration is needed when new raw materials are introduced. Also, the control system of chemical composition could be applied to sludge and clay separately, and not only to their mixture. We can therefore, respond to changes in one of the two components. Random deviations are also possible within one batch of raw material. These deviations may be sifted out through the accumulation of a sufficient number of measurements.

From commercial standpoint, we were asked about the insertion point of this measurement, i.e. at which point of the technology line should the measurements be implemented to control the quantity of coal slurries in the material for the manufacture of ceramics. From general considerations, we propose that this should be done after the extruder (apparatus, which prepare for firing blanks). Further analysis shows some additional step to be taken in addition to the approach above.

- Bricks are produced in different sizes. This will require a change in the basic setup when varying the size of the bricks which is an additional problem and source of errors.
- The registration of standard brick composition deviations needs to be dispatched to the dosing devices for adequate adjustments. If the measurements are taken

after the extruder, the period during which the material goes to and through it will additionally delay these adjustments.

- Each brick must be positioned in a certain way on the conveyor band. This fact is also a disadvantage.
- For uniform performance, it is necessary to use calibration control samples. The preparation in the form after the extruder is more difficult than in bulk form.

These problems can be avoided when controlling the materials in bulk form before the extruder entry. Therefore, we have targeted monitoring of bulk materials.

The proposed method for controlling the chemical composition of incoming raw materials is relatively simple as compared to other methods used for this purpose. It could be applied under production conditions, including continuous measurements for automatic adjustment of the composition. In this case, a small part of the final mixture must pass through the sensor and then to be returned to the mainstream. The cost of our system is expected to be low. It is neither expensive nor difficult to maintain elements.

It must further be noted that the SPCE effect is very sensitive and the whole apparatus together with all of the necessary electronic sections must be placed in a dense metal shield for protection against electro-magnetic interference. We believe that the detector design could be made relatively simple and small in size, so it could be easily installed in any location where it is needed. The method, however, cannot be used to determine the exact amount of various chemical components present in any unknown sample. It can only be applied to detect whether the sample meets a certain standard. It is also possible to trace the change in a certain impurity in a series of samples provided that all other components are kept unchanged. This would require a preliminary calibration.

Theoretically, it is possible that a random combination of different materials which do not meet the standard, generate a signal coinciding with the signal generated from materials meeting the standards. However, such a coincidence is very unlike and is of no practical significance. But it is possible to further increase the reliability in this respect. Besides improving the technological working conditions, such a system also provides high degree of security against sabotage. Incoming raw materials are highly vulnerable and their properties can be strongly modified by intruders. In contrast, there are practically no easily applicable methods for continuous quality control of incoming raw materials. This work aims to fill this gap by simultaneously working along with other control methods that complement each other.

5. Conclusions

We proposed the surface photo charge effect to be used in various industrial applications for the control of incoming raw materials. This can affect positively the quality of manufactured products. The proposed method in the case of bricks not only improves product quality, but also saves energy and has an environmental impact. This follows from the fact that maintaining the right balance between coal sludge and clay slurries minimizes the need of adjusting the temperature in the furnace by adding fuel. It will also encourage the use of waste materials as fuel. It is possible to monitor expressly whether incoming plant materials are not subject to malicious action. It is also possible to control other parameters of incoming raw materials along with their chemical composition. It has been proven experimentally that surface photo charge effect is sensitive to different changes in the monitored samples. Our previous experimental results with other materials show that the method illustrated in this paper could also be applied to control processes occurring in ceramics [11]. The described method could be developed for other types of ceramics.

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