P. RANACHOWSKI*, Z. RANACHOWSKI*#, K. WIECZOREK**,
M. JAROSZEWSKI**, S. KUDELA JR***

STUDY OF MODIFIED ALUMINOUS PORCELAIN SUBJECTED TO MECHANOACOUSTIC TESTS

The paper presents the microscopic and mechanoacoustic study of degradation processes of the porcelain material C 130 type. This kind of material is used in the production of the most durable and reliable electrotechnical elements. Raw material composition of the studied porcelain was modified. This had an impact on the inner properties, cohesion and – in consequence – on operational properties of the material.

Using mechanical-acoustic and microscopic methods of testing of small-size samples that were subjected to compression, it was possible to distinguish successive stages of degradation of the porcelain structure. These stages were generally typical of the porcelain materials. In the authors' opinion, they are connected to the ageing process happening over many years of work under operating conditions.

Optimization of composition and technological properties – important during technological processes – resulted in a slight decrease in inner cohesion of the porcelain. When compared to the reference material – typical domestic C 130 material, mechanical strength was somewhat lower. Carried out investigations proved that resistance of the investigated material to the ageing degradation process – during long term operation – also decreased. The improvement of technological parameters and the reduction in the number of defective elements occurred simultaneously with some decrease in the operational parameters of the material. To restore their initial high level, further work is needed to optimize the raw material composition of the porcelain.

Keywords: electrical porcelain materials, ageing processes, acoustic emission (AE), optical microscopy

1. Introduction

Aluminous high strength material C 130 type is at present widely applied in electrical engineering. It is mainly applied to produce insulators (line, station, apparatus) from medium to extra-high voltages [1-5]. This kind of porcelain is especially useful in case of hollow insulators of high dimensions. For all insulators high mechanical strength and long period of operation without breakdown is required. Nowadays the most important problem is to guarantee the reliability of power supply, which is determined by durability closely associated with resistance to ageing processes and long-term mechanical strength of the material.

Domestic porcelain C 130 type was developed in the 1990s and has only been slightly modified since. Both the raw material composition (kaolins, refractory plastic clays, feldspar fluxes and ceramic alumina) as well as the technology have been only insensibly changed. Although the material demonstrated very good operational parameters [5,6], during the production process, especially while firing the porcelain, numerous defective elements appeared. It raised the production costs and was burdensome for the producer, particularly in the case of high hollow insulators. For this reason measures were taken to improve the

technological properties of the porcelain, which in this paper, is the reference material. The modifications involved the raw material composition and concentrated mainly on the fluxes and to some extent, on the ceramic alumina. Silty components and production technology remained almost unchanged.

The modified material was used for a test batch of products of different dimensions and application. As expected, technological properties of the material improved and the number of defective items markedly decreased. The modified material was used for a big batch of products (pilot plant scale of production), especially long-rod high voltage insulators, to better evaluate the properties of the modified porcelain. The samples of this material were taken from long-rod high voltage insulators and were subjected to the tests described in this paper. Carried out electrical tests showed that a slight modification of the porcelain composition did not affect the electrical parameters of the material. They were the same as in the case of the reference porcelain. Unexpectedly, however 10% decrease in short-term mechanical strength of insulators as compared to the original material was found. Considering the big margin in the material strength as far as the norms are concerned [3], it seemed not to pose a problem. However, a decision was taken to investigate

*   INSTITUTE OF FUNDAMENTAL TECHNOLOGICAL RESEARCH POLISH ACADEMY OF SCIENCES, 5B PAWIŃSKIEGO STR., 02-106 WARSZAWA, POLAND
**   WROCŁAW UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF ELECTRICAL ENGINEERING, WYBRZEŻE WYSPIAŃSKIEGO 27, 50-370 WROCŁAW, POLAND
*** INSTITUTE OF MATERIALS AND MACHINE MECHANICS SAS, 9 DUBRAVSKA CESTA, 845 13 BRATISLAVA, SLOVAK REPUBLIC

\#   Corresponding author: zranach@ippt.pan.pl

thoroughly the microstructure of the modified porcelain and carry out mechanoacoustic tests. They allowed recognizing the effects of the material degradation processes, its resistance to progressing degradation and, to a large extent, enabled to assess service life of the ceramics [7]. The important objective of this paper was to evaluate in general the modified material.

2. Ultrasonic control and microstructure of the material samples

Four technological surpluses of long-rod insulators were used in the study. The samples were disk-shaped with the diameter of about 85 mm and thickness of 10 mm. Their side surfaces were coated with glaze.

The ultrasonic control of the homogeneity of the samples has confirmed the classification of the material as C 130 type porcelain. At the same time, however, the unexpected differences in acoustic waves propagation velocities were recorded. For example, the longitudinal wave propagation velocity c_L fluctuated between 6580 ÷ 6710 m/s. The mean value was 6670 ± 40 m/s. It may have indicated reduced homogeneity on macro and semi-macro scale – as in the case of the reference material the differences in parameters were much smaller. The measurements showed that despite similar density (2.64 ± 0.02 g/cm^3) – the investigated material had significantly lower acoustic and mechanical parameters than the reference porcelain. The calculated Young's modulus [8] decreased from 111 GPa in the reference material to 101 ± 2.8 GPa in the tested one.

Microscopic investigation of the material microstructure, especially of the specimens compressed during mechanoacoustic tests, required special surface preparation. The specimens were flooded in fast gelling epoxy resin. The surface intended for investigation was polished with abrasive paper grit 800. Then it was further polished with diamond paste of decreasing grit – 5, 1 and 0.25 μm, and finally with colloidal silica of 60 nm. Optical tests were carried out using *Clemex* microscope with a computer image analysis system. A 20× objective lens with 0.1 μm resolution was used. The Nomarski phase-interference contrast was used to interpret the phase composition of the porcelain and defects in the microstructure. Four specimens were prepared for microscopic tests – one for each technological surplus.

Figure 1 shows the microstructure after formatting and processing the picture with Photo Paint-Corel. In the middle of the image different phases were separated into different colours using binary masking. Yellow indicates corundum grains, red – chipped elements of the microstructure (cullet and quartz grains or their fragments), blue – sporadic pores. The green background included glassy matrix, mullite fragments and non-isolated in this image processing – quartz grains.

The material was well-fired aluminous porcelain and demonstrated big similarity to the reference material [6]. However, worse homogeneity was observed, especially in the distribution of mullite phase. There occurred slight – a few percent – differences in the amount of particular phases between tested samples.
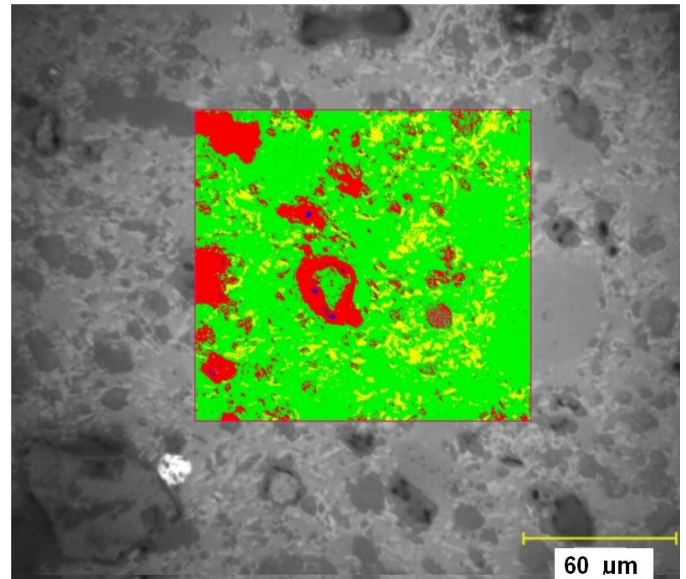

Fig. 1. Typical image of the microstructure of the investigated material, magnified × 500. In the middle particular phases are shown with different colours. Yellow indicates corundum grains, red – chipped elements of the microstructure (mainly cullet), blue – sporadic pores. The green background included glassy matrix, mullite fragments and quartz grains

The corundum contents changed within a few percent, its mean amount in different observation fields being equal to 15%. As in the reference material, corundum occurred in the form of elongated, a few micrometers long grains. However, its amount fell to about 4%, in a less homogeneous distribution in the matrix. Corundum grains were well bound with the glassy phase and their agglomeration was limited.

Mullite phase was well integrated into the glassy matrix. It occurred in dispersed form, but mainly in the form of precipitates several dozen micrometers big. As in the reference material, precipitates took up about 25% of the area. A further decrease in low homogeneity of this phase was seen. The combined contents of glassy-mullite matrix remained at almost unchanged level – about 70%.

The amount of quartz phase – about 7% – was slightly lower than in the reference material. The quartz grains were cracked, especially peripherally, they were not well integrated into the matrix and their distribution was not very homogeneous.

Chipped elements of microstructure took up slightly more space than in the reference material and made up about 5% of the total. They mostly included cullet fragments (5% of the material content) and cracked quartz grains, less integrated into the matrix. The cullet is not melted during sintering process and, as a rule, it is les connected to the matrix. Hence it undergoes crushing out easily even when gently polished.

As compared to the reference material, the investigated porcelain demonstrates slightly less advantageous microstructure, less homogeneous and with lower content of the strongest corundum phase, which constitutes the basic dispersion strengthening of the material. This led to lower mechanical stress resistance of the tested porcelain.

3. Experimental

Eight cuboid-shaped specimens were cut out of the technological surpluses of four different insulators, each 11×10×9.5 mm in size. Two opposite walls of the cuboids were polished to make them plane parallel, accurate to at least 0.1 mm. The cuboid specimens were subjected to mechanoacoustic measurements, using the method of acoustic emission (AE), on a specially set together two-channel measuring system. The samples were subjected to slowly increasing compressive stress with a simultaneous registration of the force in one channel (INSTRON 3382 machine), and AE descriptors in the second one (WD PAC broad band transducer). The arrangement of the measuring system and the method of investigations are described in detail in the paper [7]. The tests enabled the recording and description of correlation between the increasing external load and processes of structure degradation, which are reflected in the AE activity. There exists a serious analogy between the effects of years-long exploitation under operating load and ceramic material degradation during compressive stresses in a relatively short-lasting laboratory test. However, it is necessary to apply a quasi-static, very slow increase in stress and a precise registration of the AE descriptors. A typical mechanoacoustic test procedure was applied [7]. The velocity of the traverse of the testing machine, with quasi-static increase in compressive stress was 0.02 mm/min.

Compressive strength of three specimens (out of eight), that were subjected to compressive stress until they were destroyed, was equal to 582, 611 and 690 MPa. In the case of the reference material, the destructive compression for 11 specimens ranged from 522 to 933 MPa. The mean value was equal to 779 MPa. Hence, the investigated material demonstrated a significantly lower compressive strength.

Mechanoacoustic characteristics recorded for the specimens of the investigated material demonstrated a marked diversification. It is, however, typical of all ceramic aluminosilicate materials and is connected with a large spread of their compressive strength. The nature of degradation effects recorded for the investigated material is similar as in the reference material and consists of three well-defined stages: preliminary, subcritical and critical [6,7]. Microscopic examination of the effects of compressive stress was carried out on the specimens in which the application of compression was stopped at selected values: 275 MPa – after preliminary degradation, 504 and 582 MPa – in advanced subcritical stage and 690 MPa – where bigger fragments of the destroyed sample were examined (critical stage). Selected mechanoacoustic characteristics of the investigated material samples are presented in Figs. 2,3.

The preliminary stage of acoustic activity took place in an approximate range from 10 MPa to 150 MPa of compressive stress. This initial period of degradation corresponded to destruc-
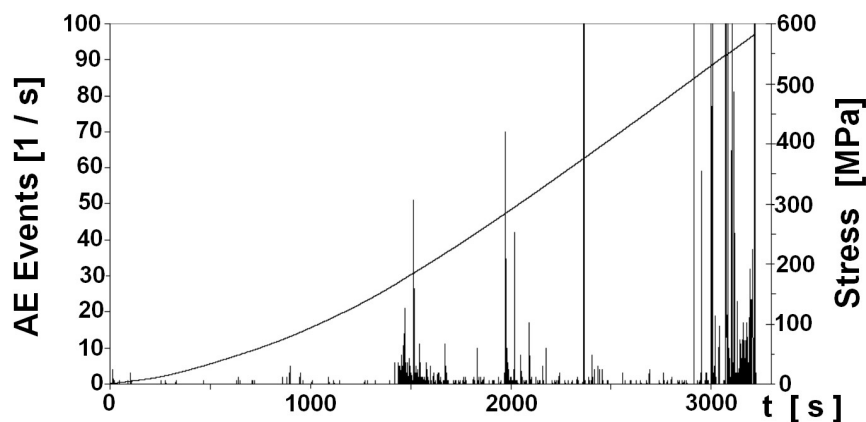

Fig. 2 Mechanoacoustic characteristics of the weaker specimen of the investigated material whose strength was equal to 582 MPa
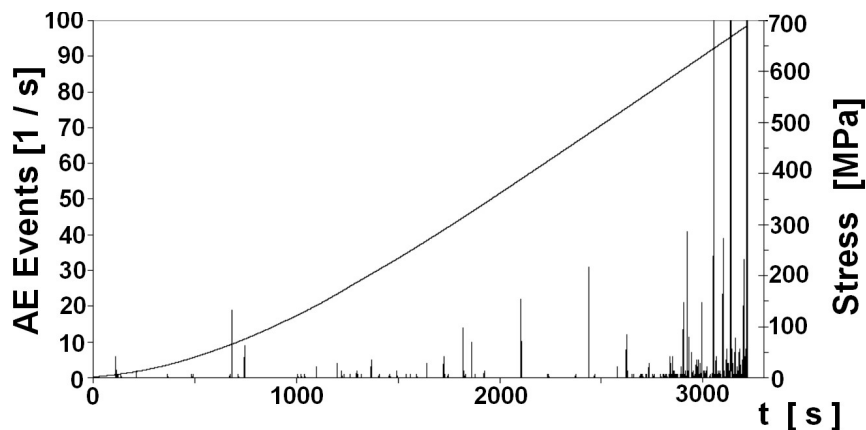

Fig. 3 Mechanoacoustic characteristics of the strongest specimen of the investigated material whose strength was equal to 690 MPa

tion of fragments of cullet, quartz grains and to the beginning of mullite phase damage. The last effect took place mainly in the central part of the specimens, where the highest concentration of compressive stresses occurred. Fragments of cullet, very poorly connected to the matrix, underwent a fracture and a separation from the porcelain body without any acoustic emission. Majority of quartz grains went through a similar process with or without very weak acoustic activity. However, in the case of the grains better connected to the matrix, without peripheral or internal cracks, this process required even much higher stresses and went together with acoustic signals. Slightly stronger EA effects were accompanied by the development of cracks in the periphery, and even in the middle of some mullite precipitates. The degradation of these quite numerous precipitates, with a large variation in size and shape, was the most important source of EA signals during the process of the samples compressing, and continued until their destruction.

Elements of the microstructure, destroyed and crushed out from the surface of the test specimens at the end of the preliminary stage, accounted for about 10% – Figure 4. This applied to almost all cullet particles, a large majority of quartz grains and few fragments of mullite precipitates. In the case of the reference material, the number of crushed out fragments was clearly lower, and the degradation of the mullite precipitates in the preliminary stage was hardly seen. The reference porcelain, presented in detail in [6], showed better homogeneity and also the cohesion of the microstructure, resulting from a stronger connection of the material building phases.

Subcritical stage of ceramic structure degradation is always closely connected with the homogeneity of the sample structure in micro and semi-macro scales. It started after the completion of the preliminary stage and lasted until the beginning of the development of critical defects in the microstructure. Due to the diversified strength of the material samples, the scope of development of subcritical effects was different for individual specimens – Figures 2 and 3. The recorded EA signals showed very varied intensity during the subcritical stage. However, weaker signals dominated and occurred individually or less frequently – Figure 2 – in longer ranges of continuous activity.

The subcritical stage was associated primarily with the degradation of quite many mullite precipitates. Cracks on the outskirts and inside precipitates were propagated. As a consequence, further fragments, or even entire precipitations and sometimes areas of concentration of corundum particles – placed in their vicinity – were separated and crushed out while polishing the surface of the tested samples. This effect was particularly related to the central part of the specimens, where the compressive stresses were accumulated. Crushed out fragments at the edge or in the middle of larger mullite precipitates are a characteristic element in the microstructure images of the tested material in the subcritical degradation stage. At stresses of about 200 MPa, the degradation of the corundum agglomerates began. As the load increased, more grains were separated until the entire agglomerates were destroyed.

For individual microscopic observation areas of samples loaded to an advanced subcritical level (504 and 582 MPa), crushed out elements of microstructure included quite a wide range – from 15% to even twenty-several percent, usually around 17%. Particularly many damaged elements were observed in the middle part of the samples – Figure 5. Figure 6 shows the size distribution of crushed out elements of microstructure in the samples of the tested material, which were loaded to 275, 504 and 582 MPa. Quantities of elements in the range of $5 \div 15$ µm were definitely predominant, with the average value equal to 11 µm. They came from particles of cullet and smaller grains of quartz or their fragments. Larger crushed out elements, in particular
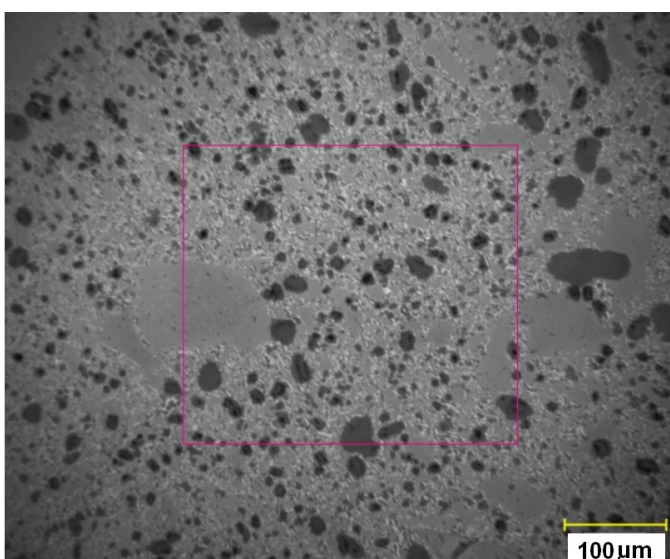

Fig. 4. Image of the tested material after the preliminary stage of degradation, ×200. The sample was loaded to 275 MPa. There are visible dark areas of crushed out cullet particles, quartz grains and to a small extent – fragments of mullite precipitates. They constitute about 10% of the surface area
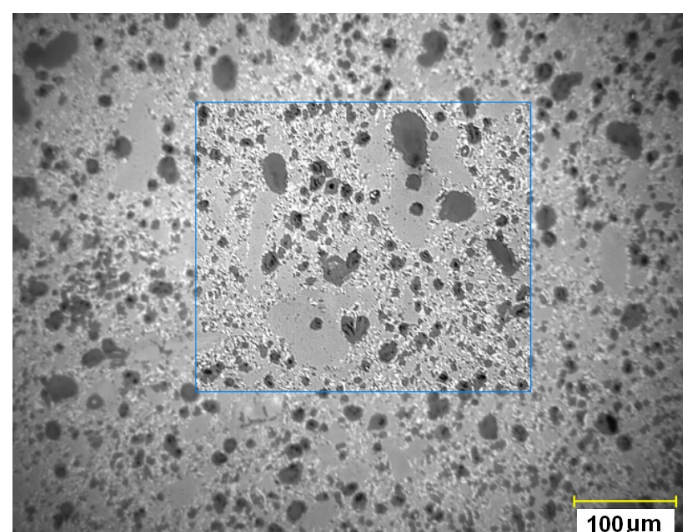

Fig. 5. Image of the microstructure of the central part of the tested sample loaded up to 504 MPa, ×200. There are visible smaller dark areas after crushed out particles of cullet and quartz, and larger – after fragments or even whole mullite precipitates. There are also numerous microcracks in the areas of concentration of small, bright corundum grains. Crushed out elements cover about 19% of the surface
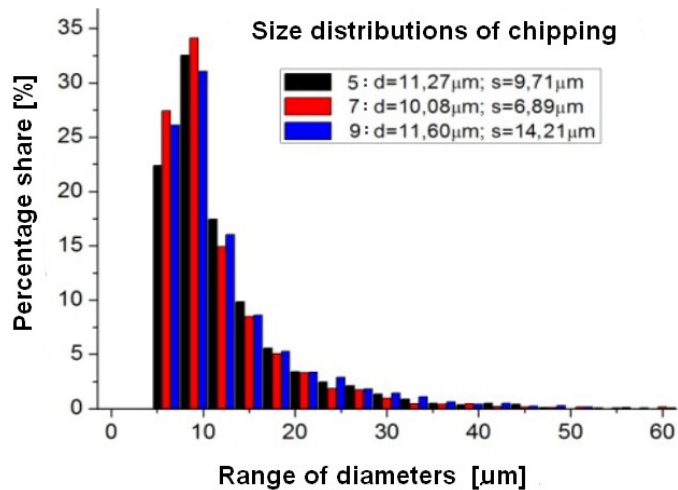
Fig. 6. The size distribution of the areas of crushed out elements of microstructure in the samples of the tested material, which were loaded up to 275, 504 and 582 MPa. The average value is equal to 11 μm (d denotes mean value, s – standard deviation for the particular sample)
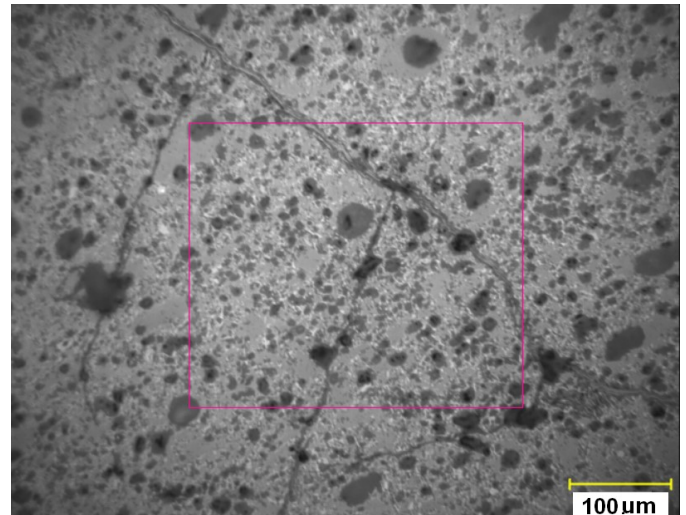

Fig. 7. The cracking system in the middle part of the sample of the tested material, subjected to destruction at 690 MPa, ×200. There are numerous dark areas after crushed out elements of the microstructure – particles of cullet, quartz, mullite precipitates and corundum agglomerates. They constitute a total of 22% of the surface area

over 30 μm, originated mainly from fractured and separated fragments of mullite precipitates and possibly accompanying them concentrations of corundum particles.

The nature of the subcritical stage confirms that the consistency of the material and the connection of crystalline phases – in particular the mullite precipitates – with the matrix were worse than in the reference material. Similar to homogeneity, especially on a semi-macro scale. For example – for the reference material the number of crushed out elements of the microstructure during advanced subcritical level did not exceed 14% and it included only a small part of mullite phase (a few percent). Damaged quartz grains were definitely dominant.

The last – critical stage, showing the highest level of acoustic activity, began at a load by dozens of megapascals smaller than the destructive stress.

During the critical stage, further fragments or even whole precipitates of mullite as well as corundum agglomerates were damaged and crushed out, especially in the vicinity of the mullite phase. Therefore, the surface of damaged and broken elements of the microstructure increased to more than 20%, but with significant differences for individual microscopic observation areas. The most important and characteristic effect occurring during the critical stage was the formation and propagation of large, usually little branched cracks. Their development was facilitated by numerous damaged and separated from the matrix elements of the microstructure. Starting from loose fragments of cullet and quartz grains, through cracked mullite precipitates and finally – strongly fractured areas of corundum grains concentration. At sufficiently high stress, there took place a sudden increase of cracks and destruction of the entire specimen, which was accompanied by very strong but short-lasting acoustic activity. The effects of critical degradation of the microstructure of the tested material are presented in Figure 7.

Unfortunately, in the case of the reference material, the range of destructive stresses for the samples in the mechanoa-coustic test was clearly higher. This was a consequence of, above all, better homogeneity and stronger bonding of the elements of microstructure.

4. Summary

The investigated material was a modification of a typical domestic electrotechnical porcelain type C 130, characterized by very good durability and operational parameters. Modification of the raw material composition was initiated to limit the relatively high number of defective products. The modifications were not significant and were confined to little changes in the raw material composition – mainly fluxes and to some extent – ceramic alumina. Silty components and production technology remained almost unchanged. This led to a partial success. The number of defective elements fell considerably. Unexpectedly, however at the same time a 10% decrease in short-term mechanical strength of insulators as compared to the baseline status was seen.

Ultrasonic measurements showed a certain spread of the material parameters. It pointed to a decreased homogeneity of the investigated porcelain in the macro and semi-macro scale, which was confirmed by thorough microscopic examination. In addition corundum phase – the main dispersion strengthening factor in the material was a few percent less than in the reference material. The integration of crystalline phases and amorphous glassy matrix was weaker.

The overall compactness and cohesion of the material deteriorated. It was probably the result of using less effective fluxes than the ones in the reference material. It decreased the short-term mechanical strength. However, given the broad margin of the material strength, it seemed not to pose a big problem. Unfortunately, the above study demonstrated that the porcelain is less resistant to degradation and to the ageing processes.

1826

Compared to the reference material, the long-term mechanical strength of the porcelain decreased, and consequently, so did the durability and service life of the products. The improvement of technological parameters and reduction in the number of defective elements was accompanied by a certain deterioration of operational parameters of the product. This means that in order to restore their baseline level, more studies are needed to optimize the raw material composition of the porcelain. Probably slight changes in technological parameters – e.g. modification of the firing curve to better suit the modified raw materials will be needed.

REFERENCES

[1] IEC Publication 672-1:1995, Ceramic and glass-insulating materials, Part 1: Definitions and classification.

[2] IEC Publication 672-2:1999, Ceramic and glass-insulating materials, Part 2: Methods of test.

[3] IEC Publication 672-3:1997, Ceramic and glass-insulating materials, Part 3: Specifications for individual materials.

[4] D.W. Richerson, Modern Ceramic Engineering – Properties, Processing and Use in Design, Third Edition, Taylor and Francis, Boca Raton London New York 2006, Chapter 19.

[5] Z. Pohl, Overhead high voltage insulation in power engineering (Napowietrzna izolacja wysokonapięciowa w elektroenergetyce), Collective work edited by Pohl Z., Printing house of Wrocław University of Technology, Chapters 4 and 6, Wrocław 2003 (in Polish).

[6] P. Ranachowski, F. Rejmund, Z. Ranachowski, A. Pawełek, A. Piątkowski, Research of Degradation Processes of Insulator Porcelan C 130 Type, Archives of Acoustics, **33** 4 (Supplement), 117-122 (2008).

[7] P. Ranachowski, F. Rejmund, Z. Ranachowski, A. Pawełek, A. Piątkowski, S. Kudela Jr, Materials Degradation Research on the Basis of Mechanoacoustic and Microscopic Methods, Archives of Metallurgy and Materials **54** 4, 1035-1043 (2009).

[8] I. Malecki, Physical Foundations of Technical Acoustics, Pergamon Press, Oxford – Braunschweig, Chapter 3, 1969.