Peer Review

by competition

for the academic position "Associate Professor"

in Institute of Mineralogy and Crystallography-Bulgarian Academy of Sciences, scientific field 4.4 Earth Sciences (Applied Mineralogy, Innovative Building Materials) for the needs of department "Experimental Mineralogy and Crystallography" at IMC - BAS, published in the Newspaper of State p. 129, issue 56 of 19.07.2022.

with candidate Dr. Alexander Nikolaev Nikolov

Reviewer: Prof. Dr. Alexander Zhivkov Karamanov, IPC- BAS

Brief details of the applicant

In the announced competition as the only candidate participates chief assistant dr. eng. Alexander Nikolaev Nikolov, who currently works at the Institute of Mineralogy and Crystallography at the Bulgarian Academy of Sciences. The materials submitted by Dr. Nikolov are in accordance with the current Regulations for the Implementation of the Law on the Development of Academic Staff in the Republic of Bulgaria, with the Regulations for the Conditions and Procedure for the Acquisition of Scientific Degrees and for the Occupation of Academic Positions at the Bulgarian Academy of Sciences, as well as with the specific requirements added in the Regulations for the Conditions and Procedure for the Acquisition of Scientific Degrees and for the Occupation of Academic Positions at the Institute of Crystallography and Mineralogy, BAS.

The colleague Alexander Nikolov was born in 1987 in the town of Sofia. He finished the National Natural and Mathematical High School in Sofia in 2006. He graduated from the University of Architecture, Civil Engineering and Geodesy in Sofia in 2006, and in 2011 he obtained a Master's degree at the University of Architecture, Civil Engineering and Geodesy in Sofia, department "Construction of Buildings and Facilities", profile "Construction Technology and Management".

From 2012 to 2016 he was a PhD student at the University of Architecture, Civil Engineering and Geodesy, where he successfully defended his dissertation on "Natural zeolite-based geopolymers for application in construction, composition, structure, and properties".

In June 2017, Dr. Nikolov joined IMC-BAS as a technologist, while in 2018 he was appointed as a senior assistant professor. In the period from 03.2019 to 03.2021, he is a post-doctoral fellow under the awarded grant in the program "Young Scientists and

Postdoctoral Fellows of the Ministry of Education and Science". In 2022 he received the BAS Award "Professor Marin Drinov" for young scientists, up to 35 years, in the scientific field of "Nanosciences, new materials and technologies", competition 2021.

General description of the submitted materials

For the competition for associate professor, Dr. Nikolov has provided information on participation in 10 scientific publications, which were published after the defense of his dissertation at UASG. These publications, which are related to the competition's main indicator 'B', correspond to 227 points, which exceeds twice the required minimum of 100 points. Of these works, one is rated Q1 and four Q2, and he is first author on all five. In addition, 12 other works were submitted under criterion "D", corresponding to 271 points. These works were also published after his PhD thesis defense. In practice, Dr Nikolov is the sole author in half of the submitted works.

Impressive is the information on indicator "E", which is related to the citations on the scientific works of the colleague. With a required minimum of 60, more than 10 times as many points were reported. Practically all citations are from foreign authors, some of them in high rated journals (Construction and Building Materials - IF 7.7, Environmental Technology & Innovation - IF 7.8, Journal of Cleaner Production - IF 11, etc.). And here it can be noted that in the most cited publications “Nikolov, A, Rostovsky, I., Nugteren, H.. Geopolymer materials based on natural zeolite. Case Studies in Construction Materials, 6, Elsevier BV, 2017” (cited 85 times) and “Nikolov, A., Nugteren, H., Rostovsky, I.. Optimization of geopolymers based on natural zeolite clinoptilolite by calcination and use of aluminate activators. Construction and Building Materials, 243, Elsevier, 2020” (cited 34 times) the colleague is first author. The increase in citations in recent years should also be acknowledged: 2019 - 11, 2020 - 17, 2021 - 47, 2022 (to October) - 38. I would like to add that an up-to-date check in the Scopus system has revealed that the number of citations has increased from 126 citations used in the documents to 132.

All of the above data meet or exceed the quantitative indicators of the requirements of the IMC-BAS for the academic position of Associate Professor.

Positive evaluation should also be given for the activity of the colleague Nikolov, related to his participation in various research projects of IMH. Since 2017, he has participated in six projects, three of which (with a total value of about 80 000 BGN) he is the leader.

He has also successfully participated in conferences organized by IMC and other organizations. The presented information includes 25 contributions, 8 of which are presented personally.Some of them have been awarded.

General characteristics of the candidate's scientific, applied and pedagogical activities

The scientific activity of Dr. Alexander Nikolov after the defense of his dissertation is its logical extension. However, besides his work with natural zeolite, syntheses of geopolymers with other raw materials, with alternative activators and studies related to heat treatment of the basic raw material or the resulting material have been initiated. These problems, according to the correct self-assessment in the "author's statement of scientific contributions" can be grouped in the following directions:

➢Use of natural zeolite.

This topic follows the research by his dissertation "Geopolymers based on natural zeolite for application in construction, composition, structure, properties", which in addition is also formed as a monograph and can be used as a reference book.

The new research is related to the influence of the modulus of sodium metasilicate on the properties of the obtained geopolymers. It is shown that the use of higher modulus of the water glass (~3) results in a faster strength gain than the use of water glass with a modulus of 2. However, over time, geopolymers synthesized with water glass with modulus 2 reached higher strength after 90 days. The effect of adding polypropylene monofilament fibers was also investigated. The results show that these composites are suitable for plasters and screeds.

In order to improve the properties, the effect of addition of different amounts of metakaolin to the geopolymer zeolite compositions was investigated. It was shown that this replacement is effective if the addition is at least 30%. Additionally, the effect of adding aluminate activators such as sodium aluminate has been investigated. The resulting geopolymers are characterized by a 4-fold lower drying.

The effect of calcination of the zeolite at a temperature of 900 ^{o}C, on the properties of the geopolymer was also investigated. The use of the so-called amorphous "metaseolite" obtained after this treatment leads to an increase in compressive strength by more than 3 times and a reduction in drying by about two times.

➢ Use of fayalite waste

In the studies with the waste from copper production (with an annual production of 1 megaton for Aurubis in Pirdop), works were carried out in two directions - alkaline activation and acid-base reaction.

In alkaline activation, the influence of different concentrations of activating solution composed by sodium water glass and potassium was investigated. An optimum concentration at which the obtained geopolymer samples were characterized by a

compressive strength of 28 MPa was determined. In these compositions, the fayalite waste remains relatively inert and only the small amorphous fraction from the waste participating in the geopolymerization process. However, with the addition of 17-18% metakaolin, strength accumulation is greatly accelerated, allowing samples to be putted out from the form after one day.

Interesting positive results related to the oxidation and transformation of iron-containing phases were found during the heat treatment of obtained samples. High-strength geopolymers in which some Fe^{3+} ions are incorporation into the geopolymer net were obtained. In specimens thermally treated at 1150 °C, a strength of 140 MPa was reached and the water absorption was significantly reduced. Interesting differences in the oxy-reduction behavior in the surface and volume of the samples were also observed. But since I am a co-author in the publication related to these studies, I think it is not appropriate to go into details.

In experiments with mixing of fayalite waste with phosphoric acid solution (defined by Dr. Nikolov as an acid-base process), it has been shown that a rapid reaction takes place in which within minutes the material solidifies, subsequently reaching a compressive strength of 16 MPa. It has been shown that during the ongoing oxy-reduction processes about 15% of the iron (mainly from the initial fayalite phase) changes from Fe^{2+} to Fe^{3+}. The resulting structures differ significantly from the alkali-activated samples. Based on these results, a single-component cement was developed that can be used by traditional water addition.

➢ Use of fly ash

Geopolymerization experiments using fly ash from Maritsa East thermal power plant have been carried out and the optimum concentration of activation solution has been determined. Since the resulting geopolymers are characterized by relatively high water absorption, they form a porous structure. This feature was used to obtain lightweight materials, and the porosity was increased by adding hydrogen peroxide as a gas-forming agent. The resulting lightweight geopolymer has a density of 0.44 g/cm3 and 83% porosity. In the preliminary tests the samples showed good fire resistance. Investigations on the change of properties and phase composition with temperature change (at 400, 800 and 1150 oC) were also initiated.

➢ Other studies

The colleague Nikolov has been involved in various other IMC studies. For example, he was a member of the team that characterised samples containing turquoise from the Chala deposit, Eastern Rhodopes. He has participated in studies on the ion exchange properties of natural zeolite from the Beli Plast deposit with bication solutions containing

Cs^{+} and Sr^{2+}. He was also a member of a group investigating thermal alteration of natural quartz materials.

Main scientific and/or applied contributions

The main contributions in the candidate's research can be categorically defined as scientific and applied ones, which are related to proving confirmed facts and obtaining and proving new facts.

In Dr Nikolov's work there is a clear tendency to seek quick applied results. It is obvious that he is at the heart of experiments planning and their scientific explanation. In his initial works he used traditional methods such as compressive strength determination, XRD, optical microscopy, SEM and DTA-TG, and the interpretations of the results were brief, clear and logical. Subsequently, methods such as FTIR, Mössbauer spectroscopy, computed tomography, HSM and SEM-EDS began to be used and some of the explanations became more thorough and professional. A very good impression is also made by the up-to-date literature review of the candidate's key publications, which shows that he is closely following the rapid development of this modern subject.

In my opinion it is very important to mention that unfortunately in Bulgaria there are no traditions in the research and application of geopolymer materials, therefore our scientific community is seriously lagging behind in the development of this interesting, very promising and rapidly developing field of materials science. Certainly this has not helped our colleague Nikolov.

Therefore, I believe that the successful syntheses he has carried out, his enthusiasm and his ambition to promote geopolymers and their applications should be considered as a prerequisite for the future serious development of this subject in our country. It is clear that this can only happen with determined, well-intentioned collaborations between different groups, where our colleague should play a key role. Personally, I would be happy to help for the development of such a collaboration.

Notwithstanding the applied nature of the research, some of the results obtained are also of a certain fundamental nature. As an example, I would give the study of phase transformations of the obtained materials during high-temperature processing (especially when using fayalite waste) and the positive initial results for the preparation of foam-geopolymers.

I am obliged to conclude with the fact that a large part of Nikolov's research is related to the study of the possibilities of using various industrial wastes (ashes from thermal power plants and flotation waste from copper production), which enables the search for economically viable ways of utilization of inorganic wastes. It is no coincidence that this field of geopolymer synthesis is developing very rapidly worldwide. It is likely that in the present decade a considerable part of cements and concretes will be replaced by geopolymers based on industrial wastes.

Critical comments and recommendations

I met Dr. Nikolov during the defense of his dissertation. Subsequently, we have had several meetings on different occasions, while since this year we have started a more serious scientific collaboration within the framework of Project BG05M2OP001-1.002-0019: "Clean Technologies for a Sustainable Environment - Water, Waste, Energy for a Circular Economy". Therefore, I would like to make some comments and recommendations.

I am pleased to note his good over-all culture, very quick reaction when learning new knowledge, combinative and willingness to communicate openly with colleagues with whom he works.

Nevertheless, or rather precisely for this, I would like to recommend that in the future he should try to reduce the number of more popular presentations of his results (which inevitably also involves some "duplication" of some of them and would cause problems for publication in high ranking journals) and to concentrate his time on studies to establish the relationships between the evolution of the structure of the resulting materials (as the time of geopolymerization and/or temperature changes) and their properties. From my point of view, his resent experience and the opportunities for more serious research contracts are a prerequisite for such an approach. This would also allow the search for future fruitful collaborations and the establishment of positive contacts with industry in Bulgaria.

CONCLUSION

The documents, presented by Assistant Professor Dr. Alexander Nikolov are in accordance with the Rules for the Implementation of the Law on the Development of the Academic Staff in the Republic of Bulgaria, with the Rules on the Terms and Conditions for Acquisition of Academic Degrees and Occupation of Academic Positions in the Bulgarian Academy of Sciences and with the specific requirements added to the Rules for the Terms and Conditions for Acquisition of Academic Degrees and for Occupation of Academic Positions at IMC - BAS.

The candidate presented an appropriate number of scientific papers, published after his Ph.D. degree defense. The supporting materials meet points, which exceeds significantly the minimum requirements of BAS and the additional requirements of IMC.

As a result, I declare my positive valuation and recommend to the Scientific Jury to propose Dr. Alexander Nikolaev Nikolov in the Scientific Council of IMC - BAS for the position “Associate Professor”.

Sofia, 4.11.2022 Prof. Alexander Karamanov