REVIEW

of the materials submitted for participation in the competition for the occupation of the academic position of "**Professor**" in the Professional area 4.2. "Chemical Sciences" (Thermochemistry of Natural and Synthetic Inorganic Substances), published in the State Gazette, No. 81/15.10.2019 for the needs of the Experimental Mineralogy and Crystallography Department at the Institute of Mineralogy and Crystallography (IMC-BAS)

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The only candidate in the present competition is **Assoc.Prof.Dr.Eng.Vilma Petkova Stoyanova**.

1. General Description of the Materials Presented. The set of materials, presented by Assoc. Prof. Dr. Vilma Stoyanova in the competition for occupation of the academic position (AP) "Professor" is in full compliance with the requirements of the Law for the development of the academic staff in Republic of Bulgaria and the Rules for its implementation, as well as with the Rules for the conditions and procedure for acquiring academic degrees and for occupying APs at IMC-BAS. The materials include many comprehensive documents describing the wide scientific activity of Assoc. Prof. Dr. Stoyanova, including numerous participation in scientific forums and research projects. All competition materials have been prepared very carefully, clearly and in detail, with relevant supporting materials and leave no doubt as to their authenticity. The report on the implementation of the *minimum national* requirements and the *specific ones of BAS and IMC* for acquiring academic degree "Doctor" and occupying APs „Associate Professor" and "Professor", shows that the candidate fulfills and in some of the indicators repeatedly exceeds the required minimum points. A comprehensive analysis is given below, in Section 2.

2. General Characteristics of the Applicant's Scientific Activity. The survey of the full list of publications of Assoc. Prof. Dr. Vilma Stoyanova shows that her main scientific interests and publications are in the field of inorganic material science. The list contains a total of 170 titles, 75 of which (44%) are published in impact factor journals or JCR and SJR journals with 448 citations noted on them. The H-factor according to Scopus and Web of science is 11. The scientific investigations of Dr. Stoyanova have been carried out properly, at a high scientific level with suitable methods and describe physicochemical studies of the structural and phase transformations of natural and synthetic minerals, salts and solid-phase waste materials. Part of the research is devoted to *environmental and biochemical applications* of modified natural mineral and technogenic Me-S-O systems (Me = Fe, Ca, Ba, Al). The substances of study were natural/synthetic and technogenic sulfur-containing materials such as energy and raw material resources - $FeSO_4.xH_2O$, FeS_2, $BaSO_4$, $CaSO_4.xH_2O$, $Al_2(SO_4)_3.xH_2O$. Another group of studies is dedicated to the *modeling of natural mineral and technogenic systems with applications in construction.*

The studied materials were cement minerals, solutions and composites, natural zeolites, inorganic mineral fillers - calcite, zeolites and river sand. Structural and thermal studies were carried out in natural and synthetic samples of the Ca-P-O system with the participation of SiO_2, $CaCO_3$, F-/OH- and others. Studied are natural phosphates, zeolites, technogenic wastes. The research methodology involves two groups of methods: for intensification and activation, and for identification. *The in-depth and wide-ranging studies of Assoc. Prof. Dr. Stoyanova have led to significant scientific contributions, among which, intensification of solid-phase transitions and reactions, increase of the reaction and chemical activity, study of different crystal-chemical, isomorphic transformations, determination of structural-phase and thermal characteristics (thermal decomposition temperatures and phase transformations, determination of mass losses in thermal decomposition/solid phase synthesis). Correlations are derived and possible reaction mechanisms in the natural and synthetic systems under consideration are predicted. Process control and management capabilities are evaluated.*

For participation in this competition, Assoc. Prof. Dr. Stoyanova has selected 26 scientific publications, which are on the topic of this competition and do not repeat the ones submitted for the educational and scientific degree "Doctor", and those used in the procedure for occupation of the AP "Associate Professor". With these publications, under the Indicators of “B” and “G” groups, the candidate achieved a total of 446 points, of which 115 from “B” (100 required) and 331 from “G” (220 required) points. In the group of Indicators "D" - citations of publications, 192 points were reached (120 required) and in group of Indicators "E" - 421.63 points at the required minimum of 150 points. Thus, in total for all groups of indicators, from scientific activity, Assoc. Prof. Dr. Stoyanova achieved 1109.63 points (required minimum 640), which significantly exceeded both the minimum national criteria and those of the IMC-BAS.

For review, I accept all the 26 scientific publications presented by the applicant for participation in this competition. Assoc. Prof. Dr. Stoyanova is the first author in 15 of these scientific publications (57.7%). In the 6 articles of the Habilitation work, the candidate is the first author in 2 publications (33%); in the other 20 publications (Group Indicators “G”), she is the first author in 13 (65%). The distribution of the publications by quartiles of the journals in which they are published, is as follows. From the 6 publications of the Habilitation work, one is in a Q1 journal, three are in Q2 journals and two are in Q3 journals. From the 20 publications in Group Indicators “G”, one publication is in Q1 journal, six are in Q2 journals, ten are in Q3 journals and three are in Q4 journals.

An integral part of the scientific biography of Assoc. Prof. Dr. Vilma Stoyanova is her active participation in a large number of scientific projects and scientific forums. Data are given on 96 participations in conferences, symposia and congresses, presented in details in a separate document. Assoc. Prof. Dr. Stoyanova was the leader of 4 projects (4x20=80 points), one funded by the National Scientific Fund (NSF) (2014) and three - within the framework of the Bilateral Cooperation between BAS and Estonian Academy of Sciences (EAS) (through CLMC-BAS) and Tallinn Technical University (2004-2006), (2007-2009), (2010-2012). Assoc. Prof. Stoyanova

was the project manager of the European Territorial Cooperation Program "Greece-Bulgaria (2007-2013)", co-financed by the European Regional Development Fund (ERDF) and the head of the Bulgarian team of a project co-financed by the ERDF (2007-2013) (2x50=100 points). Data were presented for participation in 4 projects funded by the National Research Fund (2004, 2008, 2009, 2011) and in 1 project on Bilateral Cooperation between BAS, EAS (through CLMC-BAS) and the Tallinn Technical University (2018-2020) (5x10=50 points). With the funds raised under the projects, the candidate has accumulated 166.63 points. Assoc. Prof. Dr. Stoyanova presented data and evidence for co-supervision of a PhD student at the University of Chemical Technology and Metallurgy, Ekaterina Stoyanova Serafimova, who successfully defended in 2013 a dissertation on the topic: “Waste utilization from poultry farms", under the supervision of Prof. Dr. Yoncho. G. Pelovski and Assoc. Prof. Dr. Vilma P. Stoyanova (50/2=25 points). Thus, by group of Indicators "E", the candidate achieved 421.63 points and has repeatedly exceeded the required minimum of 150 points.

3. Major Scientific Contributions in the Habilitation Work. The habilitation work is based on 6 scientific articles (*publ. B4.1-B4.6*) united by one theme: "*Modeling of natural mineral and technogenic systems with application for construction*". Four scientific articles have been published in the *Journal of Thermal Analysis and Calorimetry*, one in *Clay Minerals* and one in *Construction and Building Materials*. The publications include in-depth and comprehensive research in the field of building materials conducted to solve environmental raw materials and energy problems in the use of traditional raw materials. The specific research objectives include: optimizing cement compositions using cement substituents; determining the type and amount of additives to increase the physicochemical performance of construction compositions (strength, density, hardness); enhancement of chemical activity and binding properties of fillers and additives by activation methods (milling, thermal treatment); analysis of microstructure and phase formation by crystal-chemical, spectroscopic, microscopic and thermal methods. Some of the studies are related to the application of thermal methods for evaluating the modification of the building materials and the studies for determination the thermogravimetric and temperature dependencies of the compositions are supplemented by direct analysis data on the composition of the exhaust gases. The joint effect of fillers, additives and quantitative ratios in the systems under consideration as well as the formation of many and close in composition crystalline hydrate phases with low crystalline phase intensity, were studied. Valuable information was obtained on the formation of crystalline and amorphous hydrate phases and on the intermediate and final products in the thermal decomposition, respectively on the state of the solid phase microstructure. These data are very important and were used by Assoc. Prof. Dr. Stoyanova to clarify the chemistry of the thermal reactions in the solid phase.

Specific Scientific Contributions in the Habilitation Work, Some Results and More Important Results. Comprehensive studies have shown that thermal reactions in the range of 450-690°C, are dehydration-decarbonisation reactions for separation of carbonate ions from isomorphically-substituted positions and/or hydrogen-carbonate phases formed in the initial minutes of hydration of cement minerals. These phases are meta-stable and decarbonise at lower temperatures as

compared to $CaCO_3$, which explained the presence of low-intensity peaks in the major decarbonisation peak of the composite materials. It has been found that in the temperature range 650-850ºC there is a basic decomposition of stable carbonate phases. DTG/DTA assays indicated the presence of two carbonate-containing phases, which may be a mixture of carbonates or a mixture of $CaCO_3$ and a carbonate-containing silicate phase. The denser and more robust structure makes it difficult to decompose the carbonate-containing phases and this leads to increased decarbonisation temperatures. -Replacement of a portion of gray/white cement with natural zeolite has been shown to reduce the density of solidified solutions, but increase the amount and variety of new crystalline products, resulting in higher compressive strength and low water absorption. It has been found that the presence of natural zeolite in mortar influences the depth of the surface carbonate layer formed, the thickness of which depends on the time of contact with CO_2 from the air and the rate of diffusion through the layer formed.

Key Scientific Contributions in the Publications of Group "G" Indicators. 20 scientific papers (*publ. 7.1-7.20*) were selected to cover the requirements of Group „G" Indicators, mainly on the scientific topic: "Structural, crystallochemical and thermal studies in natural and synthetic samples of the Ca-P-O system, with participation of SiO_2, $CaCO_3$, F-/OH-". They are published in the Journal of Thermal Analysis and Calorimetry - 9, the Journal of the Balkan Tribological Association - 4, the Journal of Environmental Protection and Ecology - 3, Bulgarian Chemical Communications - 3 and Ceramics International - 1. *The main scientific contributions of Assoc. Prof. Dr. Stoyanova in this group of publications are in the study of thermochemistry of natural and synthetic minerals and activated natural and synthetic minerals from the apatite group, of composites of natural and activated minerals from apatite and synthetic/waste $(NH_4)_2SO_4$ and of composites of natural and activated apatite minerals and natural ion-exchange zeolite (clinoptilolite). The research was conducted at a high scientific level within a series of joint scientific projects, incl. those in the frame of bilateral cooperation between BAS and EAS.*

Specific Scientific Contributions in the Publications of Group "G" Indicators, *described within the four topics formulated by the candidate.* ***"Thermochemistry of Natural and Synthetic Minerals in the Apatite Group"*** *(publ. 7.1-7.12, 7.14-7.20).* Physicochemical methods have been applied to study the structure of natural apatites. Detailed studies have been carried out and a scheme of the reaction chemistry of the thermal decomposition process is proposed through a combination of mass spectroscopic and IR analysis of the exhaust gases. The subjects of study were natural apatites from North Africa (Tunisia and Syria) and Europe (Estonia). Fluor-hydroxylapatite (*publ. 7.18*) and hydroxylapatite (*publ. 7.19*) obtained in laboratory conditions have been investigated as representatives of the synthetic minerals in the apatite group. Mass-losses and thermal effects have shown that natural apatites from Tunisia, Syria and Estonia are carbonate-hydroxyl-apatite (COHFAp), type B. In the Estonian samples (*publ. 7.20*), where pyrite is also present in the sample, the reaction scheme includes the specific reactions reflecting its transformation to hematite, phosphates, aluminosilicates and calcium sulfate. By the thermal decomposition of synthetic hydroxylapatite minimal amounts of crystallization and bound water are obtained in the structure.

"Thermochemistry of Activated Natural and Synthetic Minerals from the Apatite Group" (*publ. 7.4-7.19*). Natural apatites from North Africa (Tunisia and Syria) and synthetic bi-phase hydroxylapatite mixed with $Ca_2(PO_4)_3$ were investigated. The activation of the natural apatites from Tunisia (*publ. 7.4, 7.5, 7.9, 7.11*) and Syria (*publ. 7.6, 7.7, 7.8, 7.12, 7.13, 7.14*) was carried out by varying the activation conditions. Powder X-ray diffraction was used to determine the structural and phase transitions (mineralogical composition) and the occurrence of an amorphous state. Structural defects were identified by IR spectroscopy. Thermal analyses (TG-DTG-DSC/DTA) were used to identify structural and phase transitions and to calculate mass-losses at different temperature intervals. Using the data from these methods, relationships between the conditions and the degree of modification as well as between the amount of the impurities, have been found. Correlations are derived on the degree of impact and the activation effect achieved when comparing the samples according to their origin and mineral composition, as well as on the impact of the different types and sizes of milling bodies and the duration of activation. The results and functional dependencies obtained can be used in determining the methodology for the production of modified apatite materials for practical use in organic farming, etc. An advantage of the proposed approach is that its implementation leads to the elimination of environmental and technological problems that traditional technologies create. *The scientific contributions in this group of publications consist in the proposed schemes, describing the chemistry of the solid-phase reactions depending on the experimental conditions, the origin of the samples and the conditions and duration of the HEM.*

"Thermochemistry of Composites of Natural and Activated Apatite Minerals and Synthetic/Waste $(NH_4)_2SO_4$" (*publ. 7.1-7.3, 7.16*). In the publications on this topic, mixtures of Tunisian apatite and ammonium sulphate of different origin were investigated - pure for analysis, waste from a number of technological productions in a mass ratio of 1: 1. In the thermo-tribo-activation of mixtures of Tunisian phosphorite and ammonium sulphate in the temperature range of 20-1200^oC with an activation duration of 10 minutes to 50 hours, evidence was obtained to increase the reactivity of the Tunisian phosphorite and to perform solid-state reactions between the components of the system. In these reactions, the formation of ammonium calcium phosphates and pyrophosphates $NH_4Ca(PO_3)_3$, $(NH_4)_2CaH_4(P_2O_7)_2$, $(NH_4)_2Ca_3(P_2O_7)_2.6H_2O$, $CaH_2P_2O_7$ has been identified, which is an advantage over the pure thermal treatment of the investigated system. A significant decrease in the conversion temperature ranges has been demonstrated as compared to the inactivated mixture.

"Thermochemistry of Composites of Natural and Activated Apatite Minerals and Natural and Ion-Exchanged Zeolite (clinoptilolite)" (*Publ. 7.10, 7.11*) To increase the effect of triboactivation for the transformation of phosphate minerals into forms digestible for plants, natural and NH_4-exchanged clinoptilolite were used. For the purposes of the studies, activation of mixtures containing Tunisian phosphorite and natural and NH_4-exchanged clinoptilolite was performed in two modes: mixing and tribochemical activation. Thermal methods, infrared spectroscopy and XRD phase analysis have been applied to investigated the structural and phase transformations of the natural apatite - natural clinoptilolite system with an emphasis on the

changes occurring during the period of tribochemical activation. The results obtained were used to determine the optimal mixing and activation conditions, the thermal stability of the selected compositions, the effect of the impurities of clinoptilolite tuff and the natural apatite on the effect of their processing. Natural clinoptilolite (Beli Plast (Nat-Cpt)) and NH_4-exchanged, Bulgaria, and natural apatite (Ap) originating in Tunisia, were used. Three types of mixtures with different mass ratios of natural clinoptilolite (Nat-Cpt) and NH_4-clinoptilolite (NH_4-Cpt) to Tunisian apatite (Ap) were prepared. Tribochemical activation and tribochemical mixing were applied. Studies have shown that by mixing natural apatite with natural and NH_4-clinoptilolite, it is possible to increase the rate of conversion of non-absorbable forms into P_2O_5. It was suggested that the effect of tribo-activation is enhanced by the ion exchange between natural apatite and clinoptilolite (especially NH_4-clinoptilolite) and by defect and isomorphism in apatite.

4. Personal Scientific Contributions of the Applicant. *The original scientific contributions of Assoc. Prof. Dr. Eng. Stoyanova consist in the development of a research methodological approach for the accumulation, evaluation and interpretation of data from activation-, structural- and thermal methods. This approach successfully determined the stages of thermal decomposition and clarified the reaction mechanisms of the solid-phase reactions in the studied samples. The proposed reaction schemes logically, reliably, and in depth describe the ongoing chemical reactions, regardless of the systems' complex nature and the simultaneous processes. The analysis of the presented materials, as well as my excellent personal impressions of Assoc. Prof. Dr. Stoyanova, strongly support the claim that the main part of the conducted research and the data obtained from them, are result of her personal idea and implementation.*

5. Conclusion. The only candidate in this competition, Assoc. Prof. Dr. Eng. Vilma Stoyanova, fully complies with the requirements of the Law for the development of the academic staff in Republic of Bulgaria and the Rules for its implementation and the Rules of the IMC-BAS for occupying the academic position of "Professor". She has presented a sufficient number of scientific papers published in reputable international journals with an impact factor. The scientific output presented undoubtedly proves the applicant's competence to perform independently and to conduct valuable theoretical studies in the future. The results achieved in her research and teaching activities, as well as her participation in a number of scientific projects and scientific forums, outline the profile of an in-depth scientist with clearly defined research interests and achievements in the field of inorganic material science. *After analyzing the materials presented and based on my personal excellent impressions, I find it justifiable to give my positive assessment and convinced to vote "yes" for the election of Assoc. Prof. Dr. Vilma Petkova Stoyanova in the academic position of "Professor" in Professional are 4.2. "Chemical Sciences", scientific specialty "Thermochemistry of natural and synthetic inorganic substances".*

Sofia, 25.01.2020 Reviewer:
(Natasha Trendafilova, Prof. Dr. IGIC-BAS)