OPINION OF THE REVIEWER

by Prof. Dr. Daniela Georgieva Kovacheva

from the Institute of General and Inorganic Chemistry, BAS

For competition for occupying the academic position "Professor" in the professional field "Chemical Sciences", code 4.2 (Thermochemistry of Natural and Synthetic Inorganic Substances) for the Requirements of the "Experimental Mineralogy and Crystallography Department" at IMC-BAS, proclaimed in State Gazette, issue no. 81 / 15.10.2019

Documents for participation in the announced competition were submitted by only one applicant: Associate Professor Dr. Eng. Vilma Petkova Stoyanova from IMC-BAS

Brief biographical data for the candidate: Assosiate Professor Dr. Eng. Vilma Petkova Stoyanova obtained her Master's Degree from the University of Chemical Technology and Metallurgy in Sofia in 1985 in the field of Technology of Inorganic Substances. The doctoral dissertation on "Thermal Decomposition of $FeSO_4.H_2O$ and $Al_2SO_4.3H_2O$" she defended at UCTM -Sofia in 1993. In 2005 she was elected as Associate Professor at IMC-BAS and since 2013 is Associate Professor at New Bulgarian University. In the period 2010-2013 she was the head of the Thermal Analysis Laboratory at the IMC-BAS and in the period 2011-2013 she was the scientific secretary of the same institute. Since October 2019 she is a member of the Executive Board of NSF.

General description of the materials presented:

The total number of applicant's publications is 173, among them - 75 in impact factor journals and 98 in non-impact factor ones and conference materials. The number of citations on these papers is 448. The Hirsch index for the works of Assoc. Prof. Dr. Stoyanova is 13. She was the co-tutor of one successfully defended Ph.D student. The applicant participates in 11 national and international projects, in 4 of them she was a leader and in 2 - coordinator. The total amount of the attracted funds under the projects is over 830 thousand BGN. The works of Assoc. Prof. Stoyanova have been reported at a large number of international and national scientific forums.

Associate Professor Dr. Vilma Petkova Stoyanova participate in the present competition with 26 publications, 6 of them were presented as habilitation work (115 points according to the criteria of the Ministry of Education and Science and the rules of BAS and IMC) and 20 - outside it (331 points). Of these articles, 11 are in journals in the first and second quartiles for

the respective area (Q1, Q2). The citations on the articles submitted for the competition are 96.

With these indicators, the materials presented by Associate Professor Dr. Stoyanova exceeds significantly the national minimal requirements (according to Article 29b of the Law for the development of the academic staff in the Republic of Bulgaria), those of the Bulgarian Academy of Sciences (Article 2 of the Regulations on the Terms and Procedure for Acquisition of Academic Degrees and the Occupation of Academic Degrees in BAS) and the requirements of the Rules for the Conditions and Procedure for Acquisition of Academic Degrees and for Appointing Academic Positions in the IMC-BAS).

General characteristics of the Applicant's scientific activity:

Dr. Stoyanova's research is in the field of inorganic material science, and in particular the application of physicochemical methods for characterizing phase transformations in natural and synthetic minerals, salts and solid waste materials with potential new applications. They can be divided into the following topics:

• Modeling and modification of natural mineral and technogenic systems with applications in ecology, biochemistry and construction, including as objects natural, synthetic and technogenic sulfur-containing materials as energy and raw materials, cement minerals, solutions and composites, natural zeolites, inorganic mineral fillers and river sand.

• Crystalochemical and thermal studies of natural and synthetic samples from the Ca-P-O system with various additives. Natural phosphates, including those of Bulgarian origin, zeolites, and man-made wastes were studied.

• Application of physicochemical methods for characterization of different materials.

Basic scientific and/or applied scientific contributions:

Dr. Stoyanova's scientific contributions can be related to novelty in science (discovery of new facts and connections between phenomena) as well as enrichment of existing knowledge and can be summarized in the following main directions:

Related to the studies on modeling and modification of natural mineral and technogenic systems with applications in ecology, biochemistry and construction as habilitation work, 6 publications were selected.

Following the analysis of the regulatory framework and new trends in building materials science, several directions for the applicant's research are outlined:

1. Studies for the optimization of cement compositions by the use of fillers and by varying the water/dry powder ratio to provide optimal conditions for the pozzolanic reaction and to increase the physicochemical parameters of building compositions such as strength, density, hardness, etc. Papers (77, 88, 91, 135)

2. Studies to enhance the chemical activity and binding properties of the fillers and additives used by various activation methods such as grinding, thermal treatment, etc. Papers (23, 136)

3. Studies for evaluation the results obtained by the complex application of crystalochemical, spectroscopic, microscopic and thermal methods for the analysis of microstructure and phase formation in the investigated building materials compositions. (23, 77, 88, 91, 135, 136)

In Paper 23, the effects of parameters of the intensive energy activation (NEM) for a series of dolomite samples on their thermal decomposition was investigated with a view to increase their reactivity. Optimal conditions have been found to lower the decomposition temperature by about 200°C and to separate the decomposition steps of $MgCO_3$ and $CaCO_3$. The possibility of intensifying the decomposition of dolomite by its preliminary mechanochemical activation and dopping has been proved. The chemistry of solid state reactions influenced by mechanochemical activation has been clarified.

In Paper 77, the effect of various zeolites dopping on the hydration processes in cements is examined. The activity of the zeolites in the early stages of hydration is shown to be due to their high specific surface area, while in the later stages - to the chemical reaction between the products of hydration and soluble silica. The zeolite additive has been shown to suppress the formation of portlandite in cements, and the amount of hydrated phases in cement increases with the increase of the amount of zeolite additive.

Papers 88 and 91 investigate the effect of two additives that lead to a high dispersion of cement particles, allowing faster and better wetting and a correspondingly low water/cement ratio. Both the added marble aggregate and the zeolite have been found to contribute to the self-drying of the cement and the associated autogenous shrinkage. Despite the very dense structure, the resulting cements have an open and continuous porosity. The water penetrates through the capillaries, thus enabling the realization of the processes of delayed hydration and pozzolanic reactions. Increasing the temperatures of the dehydration and decomposition of the carbonate phases provides further evidence of the dense and hard structures of the investigated cements with high marble dust content.

I will not comment on Publication 135 which examines the carbonation processes of zeolite and silica fume cements with cementation.

In paper 136, a study was performed to evaluate the effect of mechanochemical activation on phase transformations and thermal behavior of samples of bio-waste material - egg shells. The effect was evaluated by changes in the specific surface area, changes in carbonate ion positions, and mainly by phase transitions in thermal decomposition. Partial phase transformation from calcite into aragonite under the influence of NEM, decrease in thermal decomposition temperature as a result of destabilization of the structure, reduction of energy costs due to accumulation of mechanical energy with subsequent relaxation during the decomposition period estimated by calorimetric dependencies, has been demonstrated. The results obtained are related to the potential application of this material as filler for mortars, a heavy metal sorbent in contaminated soils or as a soil conditioner in mixtures with minerals and suitable man-made wastes as carriers of biogenic elements, etc.

The conclusions presented in the Habilitation Summary are based on in-depth complex research as an attempt to solve the essential problems concerning raw materials, energy and environmental impact of modern building materials science. A substantial part of these studies is related to the application of thermal analysis methods for evaluating the modification of the mortar structure, as the traditional studies to determine the thermogravimetric and temperature dependencies of the test compositions are enhanced by direct analysis data on the composition of the exhaust gases. The use of thermal methods to the completeness of their functionality provides additional fundamental knowledge. These results are essential for clarifying the peculiarities of the formation of crystalline and amorphous hydrate phases, for the intermediate and final products in thermal decomposition, for the state of the microstructure of the solid phase, which is directly related to the elucidation of the mechanism of the thermal reactions in the solid phase.

The applicant's work outside the habilitation theme is mainly related to the crystalochemical and thermal studies of natural and synthetic samples of the Ca-P-O system with the participation of various additives.

The minerals in the apatite group have the general chemical formula $M_{10}(RO_4)_6X_2$, where M = Ca, RO_4 = PO_4, SiO_4, SO_4; X = F, Cl, OH. The high content of PO_4 in the minerals of the apatite group determines their widespread use in agriculture, medicine, cement composites, etc. The possibility of practical application also provokes scientific interest in this subject. Modern research on the minerals within the apatite group focuses entirely on modifying the properties of the natural minerals and creating their synthetic analogues. The modification of

the properties of natural apatite minerals aims at obtaining multifunctional new materials for use in agriculture and medical practice.

Applicant's research in this field is presented in 20 scientific articles, summarized in four areas:

1. Thermochemistry of natural and synthetic minerals from the apatite group. The publications include a complex of physicochemical methods for studying the structure of natural apatites, with scientific contributions related to the analysis and mechanism of the reaction of the thermal decomposition process with combined mass spectroscopic and infrared analyzes of the exhaust gases. Mass losses and thermal effects indicate that natural apatites from Tunisia, Syria and Estonia are carbonate-hydroxyl-apatites (COHFAp), type B. For the samples from Estonia, in which pyrite has been identified, specific reactions have been added to the reaction scheme, pointing its transformation to hematite, phosphates, aluminosilicates and calcium sulfate. The thermal decomposition of synthetic hydroxylapatite exudes minimal amounts of crystallization and bound water.

2. Thermochemistry of activated natural and synthetic minerals from the apatite group. - As an alternative to the traditional methods of processing natural phosphates related to treatment with mineral acids, methods are required through intensive mechanochemical activation (NEM). In the candidate's work on this topic, studies were conducted on the activation of specimens of natural apatites from Tunisia and Syria, with varying conditions of activation (material and size of grinding bodies, duration of activation) when comparing the samples according to their origin and mineral composition, the impact of the different types and sizes of grinding bodies and the duration of activation. It has been suggested that the resulting final products should be used as slow acting balanced fertilizer components and soil improvers. On the basis of the obtained results, functional dependencies were found to determine the methodology for the production of modified apatite materials with practical application in organic farming and others. Applying the chosen approach eliminates the environmental and technological problems that traditional technologies create.

3. Thermochemistry of composites of natural and activated apatite minerals and synthetic / waste $(NH_4)\ 2SO_4$. - Blendes of Tunisian apatite and ammonium sulphate of different origin in a 1:1 mass ratio have been investigated in this field. In the thermo-triboactivation experiments of mixtures of Tunisian phosphorite and ammonium sulfate in the temperature range of 20-1200^{o}C with an activation duration of 10 minutes to 50 hours, an evidence for the increased reactivity of the Tunisian phosphorite and for solid-state reactions between the components of the system was obtained. The formation of ammonium-calcium phosphates and

pyrophosphates was found in these reactions, which is an advantage over the pure thermal treatment of the system under study. A significant decrease in the conversion temperature ranges has been demonstrated compared to the inactivated mixture. Under the selected experimental conditions, no nutrient retention was found in the products which are not absorbed by the plants.

4. Thermochemistry of composites of natural and activated apatite minerals and natural and ion-exchanged zeolite (clinoptilolite). The application of thermal methods in complex with infrared spectroscopy and XRD analysis have enabled the applicant to investigate the structural and phase transformations in the system natural apatite - natural clinoptilolite with emphasis on the changes that occur during the period of tribochemical activation. Structural and phase transformations, solid-phase synthesis reactions and decomposition in mixtures during thermal treatment were investigated. In addition to increased solubility of apatite, it has been found that intensification of the decomposition processes is also achieved by reducing the conversion temperatures. The results obtained were used to determine the optimal mixing and activation conditions, the thermal stability of the selected compositions, the influence of the impurities of clinoptilolite tuff and the natural apatite on the effect of their processing. The performed studies prove the possibility of increasing the degree of conversion of the non-absorbable into the digestible forms of P_2O_5 by mixing the natural apatite with the natural and NH_4-exchanged clinoptilolite.

Applicant papers outside the habilitation work related to the application of physicochemical methods for the study of different objects.

Papers 95, 131,138 and 159 deal with the development of methods for improving the utilization of agricultural waste biomass (poultry manure) by treatment with mineral acids. Other papers 55, 86, 117, 64, 96 are related to the application of thermal analysis methods in clarifying the phase transformations and mechanisms leading to the formation of the studied objects.

The documents presented show that the applicant's research work is subjected to a comprehensive approach for the evaluation and interpretation of structural and thermal analysis data. The interpretation of the results of the experiments seeks to clarify the causes and mechanisms of the phase changes leading to the production of materials with optimal characteristics and properties.

Associate Professor Dr. Vilma Stoyanova works very well in team and contributed significantly to the success of a number of multidisciplinary projects. Her recognition as a specialist is confirmed by the fact that she is a desired participant in the implementation of many projects (their number is mentioned above). Associate Professor Dr. Stoyanova has also a fruitful teaching activity as lecturer at the New Bulgarian University in the program Ecology and Environmental Protection. She is an active participant in the creation of the Chemistry Laboratory in NBU. Her contributions to the training of specialists is valuable also– she is a co-leader of successful PhD student.

I know the candidate personally and I have excellent impressions from her. Associate Professor Stoyanova is a wonderful experimenter with deep knowledge, scientist with high respect and responsibility.

Conclusion

All presented above describes Assoc. Prof. Dr. Vilma Petkova Stoyanova as a recognized researcher with established authority and contribution in the field of thermal analysis, unconventional methods for synthesis of inorganic materials and modification of inorganic natural materials with interesting properties. This gives me a strong reason to recommend to the Honorable Jury to elect Associate Prof. Dr. Vilma Petkova Stoyanova for the academic position of "Professor" in the professional field 4.2. Chemical Sciences.

Sofia 02/14/2020 Signature:

(Prof. Dr. Daniela Kovacheva)