REVIEW

on the competition for the academic position "Professor"
in the professional field 4.2. Chemical sciences (Inorganic chemistry),
announced in the State Gazette no. 47/04.06.2021
by the Institute of General and Inorganic Chemistry-BAS
for the Laboratory of Salt Systems and Natural Resources

Reviewer: Prof. Dr. Ekaterina Zhecheva from the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences

General Information and Brief Biography of the Applicant

One candidate - **Associate Professor Dr. Diana Todorova Rabadjieva** from IGIC-BAS - participates in the competition for the selection of a Professor in the professional field 4.2 Chemical sciences (Inorganic chemistry) announced by the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences (IGIC- BAS) in SG No. 47/04.06.2021 for the Laboratory of Salt Systems and Natural Resources at IGIC.

Associate Professor Dr. Rabadjieva graduated in the year 1986 from the University of Chemical Technology and Metallurgy in Sofia as a Chemical Engineer, majoring in Technology of Inorganic Substances. During 1986-1988 she worked at the Institute of Chemical Industry in Sofia, and during 1990-1993 – at the Department of Inorganic Chemistry of the Institute of Chemical Technology and Metallurgy – Sofia as a chemist. In 1994 she was appointed at the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences, initially as a chemist and since 1997 as an Assistant Professor. In 2003 she defended a PhD Thesis in the field of Inorganic Chemistry entitled "Crystallization in sea-type processes and some applications" under the supervision of Prof. Christo Balarew. In 2005 she was selected as an Associate Professor in Inorganic Chemistry at the same Institute.

The entire research activity of Diana Rabadjieva at the Institute of General and Inorganic Chemistry takes place in the Laboratory of Salt Systems and Natural Resources, and since 2017 she has been the head of this laboratory.

Description of the Submitted Documents

Assoc, Prof. Rabadjieva presented a list of her total scientific output: 76 scientific papers, 41 of which were in Impact Factor (IF) and Impact-Rank (SJR) journals. The candidate participates in the competition for Professor with 20 scientific papers, 6 of them are assigned to the papers of the habilitation work. All papers included in the habilitation work are published in specialized international journals with an impact factor. They are distributed in the quartiles (Q) as follows: Q1 – 4 papers (Desalination with impact factor IF_{2014}=3.756, Journal of Biomedicals Materials Research A with IF_{2019}=3.525, Pure and Applied Chemistry

with IF_{2014}= 2.492 and Journal of Trace Elements in Medicine and Biology with IF_{2020}=3.245); Q2 – 1 paper (Environmental Monitoring and Assessment with IF_{2018}=1.959); Q3 –1 paper (Journal of Solution Chemistry c IF_{2016}=1.342).

The papers that do not belong to the habilitation work are assigned to the following quartiles: in Q1- 5 papers (Journal of Trace Elements in Medicine and Biology, Dental Materials, Journal of Sol-Gel Science and Technology, International Journal of Mineral Processing, Pure and Applied Chemistry), in Q2 – 4 papers, in Q3 – 1 paper, in Q4 – 1 paper, in journals with SJR but without IF – 3 papers.

According to the candidate, a total of 275 citations have been noticed on her entire scientific output in the Web of Science, Scopus and Google Scholar databases, and their distribution determines a Hirsch factor of 10. After her habilitation, a total of 190 citations were noticed in the Web of Science and/or Scopus databases. The citations on the papers for this competition that are reflected in Web of Science and/or Scopus are 63.

Associate Professor Rabadjieva has participated in a large number of scientific forums in Bulgaria and abroad - the attached list includes a total of 170 titles of scientific reports for her overall scientific activity, and the number of reports relating to the period after the habilitation is 68. Summaries of the reports are also attached.

Assoc. Prof. Rabadjieva also has a pronounced project activity. She participated in 5 projects for supporting international research networking and in 14 research and infrastructure projects funded by the National Science Fund and the Ministry of Education and Science in Bulgaria, 2 of them being the project-leader. She was the team member in a COST – action and in international projects of BAS, as well as in applied research projects funded by private companies. During the period 2014-2021 she participated in the research and development project of IGIC "Chemistry of water-salt systems for the utilization of natural mineral resources and waste products, in particular marine chemical resources."

The candidate has participated in applied research activities, the most important being the technologies for production of $Mg(OH)_2$ and $MgCO_3.3H_2O$ from waste brines of marine malting and the products technologies and small-scale production of the series "Solilug" and "Sea Stars".

Assoc. Prof. Rabadjieva was supervisor of a PhD student who successively defended his PhD thesis at IGIC in 2019. Currently she is co-supervisor of a PhD student at IGIC.

All documents presented by Assoc. Prof. Rabadjieva fit the topic of the competition.

A check up is presented for the compliance of the scientific asset of the applicant with the requirements of the Institute of General and Inorganic Chemistry – BAS specified in its Regulations for the Terms and Conditions for Acquiring Academic Degrees and Occupying Academic Positions. Scientometric data of Asoc. Prof. Diana Rabadjieva exceed significantly the requirements of the Institute for occupying the academic position “Professor”.

General Characteristics of the Research Activity

The main scientific interests of Associate Professor Rabadjieva are in chemistry of water-salt systems and in particular in stable and metastable phase equilibria and in chemical speciation in multicomponent water-salt systems. Research can be attributed to inorganic materials science and ecology, as their ultimate goal is to develop methods and technologies for obtaining inorganic materials with desired properties or to assess the ecological behavior of natural surface water systems. A distinctive feature in the candidate's publications is the simultaneous application of thermodynamic modeling and experimental studies to predict the systems behavior.

The publications from the habilitation work of Associate Professor Rabadjieva fall also in this scientific field. They contain studies on three different multicomponent water-salt systems: (i) marine-type water-salt systems; (ii) calcium phosphates in simulated body fluids; and (iii) surface waters, water soil solutions and vegetation ecosystems. These publications do not fit thematically, but demonstrate the effectiveness of the research approach of the candidate, and namely combination of thermodynamic and experimental research to study multicomponent water-salt systems.

Some of the non-habilitation publications are thematically related to those of the habilitation work, namely synthesis and characterization of calcium-phosphate biomaterials (5 publications) and dynamics of transition metals in natural waters and soils (2 publications). The other non-habilitation publications are also associated with the chemistry of salt-water systems: synthesis and structure of glycine double salts (2 publications); crystallization kinetics of highly soluble salts (1 publication); spontaneous decomposition of metastable sulphate and selenate hydrates (1 publication). An exception present 3 publication devoted to metallurgical slag recycling. The latter studies were performed within a research project with a project-leader from another institute of BAS, but in the attached author's reference the candidate correctly indicated her personal contributions on the topic. Typical of these studies of Assoc. Prof. Rabadjieva is the search to clarify the relationships between composition, structure and properties for the systems studied.

Major Scientific Contributions of Publications of Habilitation Work

The stable and metastable phase equilibria in marine type carbonate systems were thermodynamically modeled by the Pitzer method for ionic interaction and the fields of crystallization of the formed simple and double salts were determined. It was found that due to kinetic factors $MgCO_3.3H_2O$ crystallizes as a metastable phase, which has been confirmed experimentally. A low-energy technology has been developed for the production of large-crystal $MgCO_3.3H_2O$ with pharmacopeia purity and good filtration characteristics from waste brines from marine malting.

Precipitation and transformations of calcium phosphates in simulated body fluids were thermodynamically modeled by the ionic association model. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ was found to have the highest thermodynamic stability and the conditions for metastable crystallization of $CaHPO_4.2H_2O$ and amorphous calcium phosphate $Ca_3(PO_4)_3$ (am) were predicted. Amorphous calcium phosphates were experimentally obtained, which

after maturation in a simulated body fluids recrystallized into weakly crystalline bone-like carbonate apatite. It has been shown that in simulated body fluids amorphous calcium phosphates with ion additives close to those in bone tissue and with an increased content of the biologically active elements Mg and Zn can be obtained.

A new combined model for the calculation of the inorganic chemical species in salt and hyper-salt waters has been developed, according to which the behavior of the macro- and micro-components is described by means of the Pitzer model and the ionic association model, respectively. The combined model is applied to natural waters with a wide range of salinity and it is shown that for high ionic strength it allows more accurate calculation of the inorganic chemical species compared to the ionic association model.

The possibility to assess the ecological status of waters and soils on the basis on total analytical content of the elements and thermodynamic calculations of the inorganic and organic chemical species of the transition metals Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb is shown. The inorganic and organic complexation as well as self-purification of water by proceeding of spontaneous crystallization were evaluated. The effect of the chemical species on their phytoaccumulation is demonstrated.

Major Scientific Contributions of Non-habilitation Publications

The synthesis methods of calcium-phosphate biomaterials are optimized. The presence of biodegradable polymer matrices as modifiers of the biomimetic reaction medium has been shown to be an effective way to decrease the calcium phosphates particle sizes. A method for the preparation of finely dispersed ion-modified calcium phosphate powders and composites based on them has been developed and the biocompatibility has been proven.

New analytical data for the concentration dynamics of transition metals in waters, soils and vegetation in agro-industrial zones are obtained. A higher exchange mobility of the transition metal ions in soils compared to their water-soluble mobility is shown. The chemical species of the transition metals in the water-soil solutions have been calculated and it has been established that metal-organic complexes accumulate in the vegetation to the greatest extent. The order for preferential phytoaccumulation of the different complex forms has been determined.

The impact of the solution structure on the crystallization kinetics of highly soluble magnesium salts was studied. A direct correlation was found between the formation of different magnesium sulphate associates in the saturated solutions and the crystallization rate of the corresponding salts.

New double salts of glycine with zinc bromide and zinc iodide were obtained as products of equilibrium and nonequilibrium crystallization and their crystal structure was determined.

The influence of the presence of moisture on the mechanism of spontaneous decomposition of metastable sodium sulfate and selenate heptahydrates was proven.

The interaction of complex silicates from metallurgical slag with alkaline solutions was studied. New data on the oxidation of copper pyrometallurgical slag as the first stage of

its utilization process have been obtained and the ongoing structural transformations have been established. The influence between the composition of the oxidized pyrometallurgical slag and the pH of the gel formation is shown.

Recommendations and Personal Impressions

I have no general objections to the documents presented.

The candidate's publications are collective, but the multidisciplinary research in materials science and ecology requires the involvement of scientists with different fields of competence. The role of Associate Professor Rabadjieva in these studies and her contributions are clearly outlined.

I have known Assoc. Prof. Rabadjieva since she started work at IGIC-BAS and I have witnessed her academic progress. She impresses with her in-depth professional knowledge, responsibility, collegiality and teamwork skills, which makes her a desirable partner for joint research.

CONCLUSION

Associate Professor Dr. Diana Rabadjieva participates in the competition with an asset that fulfills the requirements for occupying the academic position of Professor at the Institute of General and Inorganic Chemistry - BAS. The scientific topic is well defined and relevant, and her scientific works contain a large volume of new results and generalizations having significant scientific contributions. From the presented materials it is clear that the applicant is an established scientist in the field of inorganic chemistry who is able to plan and lead systematic studies. I believe that her selection for "Professor" will contribute to progress further the research in the Laboratory of Salt Systems and Natural Resources at IGIC, for whose needs the competition was announced.

I evaluate the application positively and strongly recommend Assoc.Prof. Dr. Diana Todorova Rabadjieva to be appointed at the academic position of Professor in the professional field 4.2. Chemical Sciences (Inorganic Chemistry) at the Institute of General and Inorganic Chemistry - BAS.

Reviewer:

Prof. Dr. Ekaterina Zhecheva

Sofia, 19.09.2021