Appendix 12d

REPORT
to occupy the academic position:

"Professor"	
"Associate Professor"	X
	one of the academic positions indicated shall be marked with the sign "X"

Candidates to occupy the position:

1	Senior Assistant Professor	Ph. D	Vasil	Ivanov	Karastoyanov	UCTM
№	academic position	scientific degree	name	middle name	last name	workplace

Scientific area:

4.	Natural sciences, mathematics and informatics
code	name

Professional area:

4.2	Chemical Sciences
code	name

Scientific specialty:

Physical Chemistry

The competition has been announced:

23	19.03.2023	Department of Physical Chemistry	Faculty of Chemical Technology
in SG issue	date	for the needs of the Department	Faculty

The report was written by:

Professor	Ds.C	Evelina	Pavlova	Slavcheva	IEES - BAS
academic position	scientific degree	name	middle name	last name	workplace

1. Report for the candidate:

Senior Assist. Prof.	Ph. D.	Vasil	Ivanov	Karastoyanov

academic position	scientific degree	name	middle name	last name

1.1. Meeting the minimum requirements under the Regulations:

A) The candidate meets the minimum requirements	20 points	x
B) The candidate doesn’t meet the minimum requirements	0 points	
		one of the answers given is marked with the sign "X"

It must be filled in if answer B is marked. The publication activity of the candidate is analyzed. The response of the results achieved (quoted) is analyzed.
The candidate Dr. Vasil Karastoyanov participates in the competition with 16 publications, 6 of which 6 are submitted for habilitation work. Thematically, these publications are devoted to research on the corrosion of structural materials used in nuclear power plants. This area of scientific knowledge is extremely important from a practical point of view, since, among other things, it is related to the safe operation of this type of power plants. At the same time, there is significant scientific interest in the problem, since the mechanisms of formation and growth of oxide films on structural metal alloys with a complex chemical composition have not been studied in sufficient detail and unambiguously explained. The candidate's research is characterized by an in-depth study of the mechanism of the processes of formation and growth of oxide films on metal alloys used in the first and second circuits of WER-type nuclear power plants through an appropriate combination of electrochemical (mainly impedance studies), determination of the composition and the thickness of the formed oxide films by X-ray photoelectron spectroscopy (XPS analyses), and theoretical calculations based on the equations of non-stationary diffusion, by which the profiles of the metal components of the oxide during its growth on the main structural material are determined. The rate constants and diffusion coefficients of the individual components of the oxide are calculated, and a kinetic model for its formation and growth was proposed, based on which software for predictive diagnostics is developed. At the next stage, the kinetic model was further developed in order to quantitatively evaluate the effect of the water chemical regime in simulated operating conditions on the electrical and electrochemical properties of the passive film on a zirconium alloy containing Ni, Cr and Fe. It has been shown that increasing the concentration of LiOH leads to the formation of more defective films, while additions of H3BO3 have the opposite effect. Based on the conducted research, an optimal water chemical regime has been proposed, which leads to the growth of layers with higher corrosion resistance. Research has been continued by studying the corrosion of zirconium alloys used as claddings for pressurized water nuclear reactors (WWER type plants). The same approach of combining impedance studies and their theoretical interpretation is applied, as a result of which a quantitative corrosion model is proposed, taking into account the influence of internal stresses in the oxide and the spatial load of point defects and impurities of alloying elements on the values of diffusion coefficients and intensity of the electric field. The model is validated by continuous in-situ electrochemical measurements during the growth of the oxide layers in a purpose-built laboratory recirculation loop operating at temperatures up to 350 °C and pressures of 15 MPa. Based on the model, equations are derived for the

growth of the oxide thickness and the amount of introduced hydrogen, depending on time, temperature and water chemical regime.

Corrosion of carbon steel in secondary circuit coolant of pressurized water nuclear power plants is also studied. For this purpose, a flow cell has beens developed, which allows reaching the typical turbulent conditions for the process. Through hydrodynamic calculations, it has been shown that increasing temperature changes the stable corrosion product, FeOH+aq, and the corrosion rate is limited by charge transfer and the development of defects in the oxide. A quantitative kinetic model including oxide growth and dissolution is created, which is parameterized by a complex nonlinear regression of the experimental impedance spectra to the corresponding transfer function, depending on the temperature. Software was developed for the implementation of the model, which in 2021 was implemented in the Kozloduy NPP.

The presented publications for the candidate's habilitation work can be defined as fundamental with direct practical application, as evidenced by the application of the developed software products for practical purposes in the nuclear energy plant.

Apart from these publications, Dr. Karastoyanov has presented 10 more papers, in the majority of which, the work on researching the growth kinetics of oxide films on various metals (niobium, tungsten, titanium, titanium alloys) has been continued. Based on experimental steady-state current-potential curves and impedance spectra of W and Nb over a wide range of potentials and pH, a kinetic model for the growth of barrier films on these metals is established, according to which parallel processes of oxide growth and metal dissolution through it occur. Combining the created model with the theoretical concepts of the effect of stress and strain on the anodic oxidation of metals in film-dissolving electrolytes, a concept of the process of nanopore initiation, deepening, separation and nanotube formation is presented. Through DFT simulations, the processes occurring at the Ti/H2O interface were modeled. The adsorption energy of the water molecule was estimated depending on its orientation on the metal surface. Dissociative adsorption of water molecules with formation of Had and OH- and gradual oxidation of the surface layer of titanium atoms due to successive adsorption of OH- and Oad is established.

The formation of oxide films on titanium in fluoride-containing electrolytes has also been studied in detail. Based on a wide range of electrochemical data obtained from the recording of polarization curves and impedance spectra, combined with photocurrent energy spectroscopy and ex-situ X-ray photoelectron spectroscopy data on the composition of the oxide surface, a deterministic model of oxide film growth is proposed. The growth of the oxide thickness with time is evaluated depending on the main oxidation parameters – applied potential and concentration of fluoride ions. The rate constants and transport coefficients that characterize the processes of oxide growth, dissolution and pore formation at the oxide/electrolyte interface have been calculated. The main processes at the titanium oxide-solution interface (adsorption of water molecules and fluoride anions) are modeled by DFT+U simulations. The established model is extended to quantitatively describe the growth and dissolution of anodic films on Mo in concentrated phosphoric acid.

Research on the corrosion of structural materials used in nuclear power plants is also progressing through simulations of the online NobleChem technology to reduce stress corrosion cracking of core materials in fluidized bed nuclear reactors, where a technology in the feed water during reactor operation is dosed solutions of salts of noble metals, in order to reduce the corrosion potential. To investigate the deposition and distribution of Pt particles, a laboratory loop was developed to simulate a high-temperature steam-water cycle in which samples could be exposed to a simulated Pt-containing coolant. By inductively coupled plasma and laser sputtering mass spectrometry (LA-ICP-MS) it was found that using a higher injection rate of the same amount of Pt, a faster and more pronounced decrease in corrosion potential and therefore to better protection against stress corrosion cracking.

A new direction in Dr. Karastoyanov's work is the research devoted to the synthesis and modification of steel and titanium oxides formed by various methods, as photocatalysts for water decomposition - an extremely up to date topic, especially considered in the light of the transition to a climate-neutral economy. The formation mechanism and photocatalytic properties of the oxides have been studied in detail by a combination of electrochemical, photo-electrochemical and spectroscopic methods. It is shown that the surface oxides formed on steel have a two-layer structure: an inner layer enriched with the alloying elements Cr, Mo and Mn and an outer layer containing mainly Fe, with a maximum concentration of Ni observed at the film/alloy boundary. The captured photocurrent energy spectra show that the oxides absorb light throughout the visible spectrum, with an approximate indirect band gap of about 1.8-2.0 eV. Based on the obtained results, a high catalytic activity for photo-assisted electrolysis of water is predicted by additional modification of the formed oxide films.

The dynamics of photoinduced current carriers in porous anodic TiO2 modified with Cu2O by pulse electrodeposition is also studied. The modulated photocurrent and quantum yield are measured in a wide range of experimental conditions. The measured photocurrent spectra with light intensity modulation in 0.1 M KOH over a wide potential range are consistent with a generalized model of charge transfer and recombination. The formal rate constants of charge transfer and recombination depending on the potential and energy of the light are evaluated and the experimental conditions for the formation of the films, under which the highest photocatalytic activity is recorded, are determined.

The candidate's research work, reflected in the presented scientific works, is distinguished by high quality, a thorough theoretical approach, originality, qualitative and quantitative interpretation of the obtained results and, in most cases, proven practical application. Undoubtedly, these studies make a significant contribution to the development of knowledge in the relevant field.

1.2. Relevance of scientific and / or applied research:

A) The research is relevant. Part of the research is pioneering (no results are known on the topic by other authors)	8 points	x

B) Research is relevant. Results from other authors are known for each of the topics and / or applications studied.	6 points	
C) Most of the research is relevant, but also some results are presented that have no scientific and / or applied value	4 points	
D) The smaller part of the research is relevant	2 points	
E) Research is not relevant	0 points	
		one of the answers given is marked with the sign "X"

The evaluation of the relevance of the research must be substantiated.
The research presented is distinguished by its actuality, which is evidenced by the numerous citations of the presented publications in the specialized literature. The articles presented for the habilitation thesis (1-6) have been cited a total of 152 times, as the foundational paper (1) has been cited in 80 other authors' works. The total number of citations of the candidate's works up to the time of submission of the documents is 158, which testifies for a significant interest of the scientific community to the reported studies, their high quality, their clear and attractive presentation.

1.3. Objectives of the research:

A) Realistic and of scientific and / or applied interest	8 points	x
B) Realistic, but not of scientific and / or applied interest	4 points	
C) Unattainable (unrealistic)	0 points	
		one of the answers given is marked with the sign "X"

Objectives must be specified. The type of the set objectives must be justified
The main goals of Dr. Karastoyanov's work could be formulated as follows: • Studying the mechanisms of growth of oxide films on structural materials used in nuclear power plants. • Theoretical interpretation of the obtained results and development of quantitative models representing the influence of various factors (temperature, chemical composition, hydrodynamics, etc.) on corrosion and/or corrosion-erosion processes • Creation of software products for control and diagnostics for direct practical application.

• Investigating the deposition and distribution of Pt particles in the feedwater during simulated operation of boiling water reactor conditionss on the stress corrosion cracking of in-shell materials. • Study of the growth kinetics of oxide films on different metals (niobium, tungsten, titanium, titanium alloys, alloyed steels). • Synthesis and modification of steel and titanium oxides as photocatalysts for water decomposition.

1.4. Candidate research contributions:

A) With lasting scientific and / or applied response, they form the basis for new research and applications	20 points	x
B) They are of significant scientific and / or applied interest, complete and / or summarize previous research	16 points	
C) They are of scientific and / or applied interest	12 points	
D) Lack of significant contributions	8 points	
E) Lack of contributions	0 points	
		one of the answers given is marked with the sign "X"

Contributions must be specified. The type of results achieved must be justified.
• The mechanism of growth of oxide films on zirconium alloys and corrosion-erosion processes of carbon steel, used as a structural material in the first and second circuit of nuclear power plants operating with pressurized water, has been clarified. • Parameterized quantitative models are proposed and equations are derived for the growth rate of oxides and the dissolution of corrosion products based on experimental results from impedance studies and analyzes of the chemical composition, thickness and structure of the formed products. • Software products have been developed for practical application in real working conditions at Kozluduy NPP. • Optimal experimental conditions for the targeted synthesis of materials with photocatalytic properties for photo-assisted electrolysis of water have been identified based on a complex quantitative analysis of electrochemical, photo-electrochemical and spectroscopic experimental data.

1.5. Participation of the candidate in the achievement of the presented results:

A) The candidate has at least an equal participation in the submitted papers	8 points	

B) The candidate has at least an equal participation in most of the submitted papers	7 points	x
C) The candidate has a secondary participation in most of the submitted papers	4 points	
D) The candidate participation is unnoticeable	0 points	
		one of the answers given is marked with the sign "X"

Critical notes must be provided if one of the items C or D is marked.

1.6 Pedagogical activity:

A) The candidate has effective and sufficient pedagogical activity at the university. The textbooks issued are modern and useful (they meet the requirements of the Regulations). The work with undergraduate and doctoral students is at a high professional level.	8 points	
B) The candidate has sufficient pedagogical activity at the university. The textbooks issued satisfy the requirements of the Regulations.	6 points	x
C) The pedagogical activity and / or textbooks issued are insufficient (do not meet the requirements of the Regulations)	0 points	
		one of the answers given is marked with the sign "X"

Critical notes must be provided if one of the items B or C is marked.
The candidate participates in the competition with asingle practical textbok for students - "Praktikum on fuel cell technology", in which an overview of the thermodynamics and kinetics of the processes taking place in fuel cells is made and the practical approaches to their research, testing and functioning in real conditions. I consider the publication of such an aid material to be very useful, especially since lecture courses and practical training on hydrogen technologies, in particular the theory and practice of fuel elements, are offered in a very small number of universities in Bulgaria. At the same time, the need for trained personnel in this field will be a reality in the near future.

1.7. Critical notes:

A) Lack of critical notes	8 points	x
B) Critical notes of a technical nature	7 points	
C) Critical notes that would partially improve the results achieved in a small part of the research	5 points	
D) Critical notes that would partially improve the results achieved in most of the research	3 points	
E) Significant critical notes	0 points	
		one of the answers given is marked with the sign "X"

Critical notes must be provided if one of the answers C, D or E is marked.

1.8. Conclusion

A) The evaluation of the candidate's activity is **POSITIVE**	This evaluation is assigned to a total number of at least 50 points	X (77 p.)
B) The evaluation of the candidate's activity is **NEGATIVE**	This evaluation is assigned to a total number below 50 points	
		one of the answers given is marked with the sign "X"

To be filled in if requested by the member of the scientific jury

	The report was written by:	
date		signature