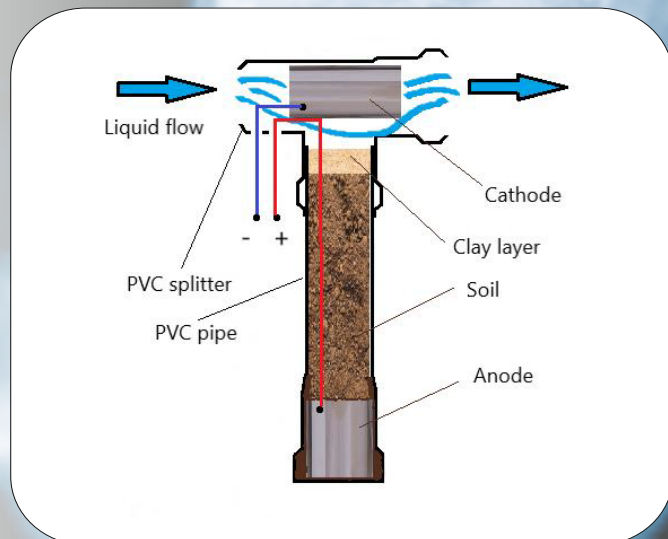


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Thermodynamic analysis of steam turbine and condenser from combined cycle power plant

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Abstract: Energy and exergy analyses results of steam turbine and steam condenser, which operate in commercial combined cycle power plant are presented in this paper. Energy analysis shows that steam turbine has high energy (isentropic) loss equal to 71.71 MW, and very low energy (isentropic) efficiency of 58.79% only. Simultaneously, steam condenser is an almost perfect component from the energy viewpoint. At the base ambient state, steam turbine has high exergy destruction of 61.80 MW and low exergy efficiency of 62.34%, so both used analyses show that steam turbine operation can and should be notably improved. Steam condenser has an exergy destruction of 17.12 MW and exergy efficiency of 55.17% at the base ambient state, what are acceptable results. Observed steam condenser is much more sensitive to the ambient temperature change than steam turbine. Increase in the ambient temperature from 5 °C to 35 °C decreases steam condenser exergy efficiency for 35.90%, while the same increase in the ambient temperature decreases steam turbine exergy efficiency for 2.39% only.

KEYWORDS: ENERGY ANALYSIS, EXERGY ANALYSIS, STEAM TURBINE, STEAM CONDENSER, THE AMBIENT TEMPERATURE CHANGE

1. Introduction

Due to the high efficiency, combined cycle power plants are standard and often used power systems in the entire energy sector [1, 2]. These plants offer many benefits, however, its shortcomings must always be considered and cannot be neglected [3].

Combined cycle power plants are composed of two parts – the first part is related to the gas turbine (or more of them) and the second part is related to the steam turbine (or more of them) [4]. Combustion gases from the gas turbine are not released to the atmosphere, they are used in HRSG (Heat Recovery Steam Generator) which produces steam for the steam turbine. Therefore, HRSG represents a connection between gas turbine and steam turbine parts of the combined cycle power plant [5]. As the heat from gas turbine exhaust is effectively used in HRSG (heat utilization for the steam production), efficiency of combined cycle power plant is notably higher in comparison to the individual gas turbine or steam turbine power plant [6, 7].

Steam turbines in combined cycle power plants can be composed of only one or several cylinders, they can be arranged in various configurations, but they always drive an electric generator for the electricity production [8, 9]. Steam after steam turbines in combined cycle power plants have low pressure and temperature and must be delivered to steam condenser for condensation [10, 11].

In this paper are performed energy and exergy analyses of the steam turbine and its corresponding steam condenser from the commercial combined cycle power plant. It is presented did both components show the expected performance. A statement from the available literature that energy analysis should be avoided for any heat exchanger is confirmed in the observed steam condenser. It is investigated and presented which component is more influenced by the ambient temperature change (from the exergy viewpoint).

2. Description and operating characteristics of the analyzed steam turbine and steam condenser

Simplified scheme of the analyzed steam turbine and steam condenser is presented in Fig. 1. Observed steam turbine and steam condenser are constituent components of the combined cycle power plant [12]. However, in this paper both steam turbine and steam condenser will be observed as independent components.

Steam turbine analyzed in this paper gets steam of the highest possible pressure and temperature inside combined cycle power plant from HRSG, operating point 1, Fig. 1. Steam turbine did not possess any steam extraction, so the entire steam mass flow rate delivered to the turbine inlet expands through the turbine until the outlet, operating point 2, Fig. 1. Mechanical power produced in the steam turbine stages is used for the electric generator drive and electricity production.

From the turbine outlet, entire steam mass flow rate is delivered to the steam condenser, Fig. 1. It should be highlighted that at the

turbine outlet steam is still superheated (operating point 2, Fig. 1), so the observed steam condenser has two functions: first function is steam cooling and after cooling when the steam is in the two-phase zone (wet steam) the second condenser function is steam condensing. Analyzed steam condenser is counter flow heat exchanger in which steam from the steam turbine transfer heat to the cooling water through the pipe wall (two convections and conduction through the pipe wall). After heat transfer, obtained condensate (operating point 3, Fig. 1) is delivered to the condensate pump. Steam condenser cooling is performed by using cooling water – colder cooling water is delivered to the condenser (operating point 4, Fig. 1) and warmer cooling water, after the heat transfer (operating point 5, Fig. 1) exits steam condenser. Analyzed steam condenser is similar to marine steam condensers which, in some operating regimes (at low plant loads), along with condensation must ensure steam cooling [13].

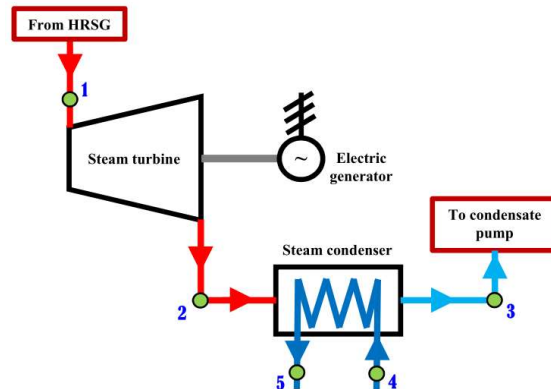


Fig. 1. General scheme of the analyzed steam turbine and steam condenser along with marked operating points required for the energy (isentropic) and exergy analyses

Exergy analysis of both steam turbine and steam condenser is performed by using data from the plant exploitation [12]. In the exergy analysis of any plant or a component, only data from the real exploitation conditions are required, there is no need for any comparison with ideal processes.

Energy analysis did not consider parameters of the ambient and therefore, it cannot be performed in a same manner as exergy analysis for any system or a component. For a steam condenser, energy analysis is performed in a standard way (steam condenser is considered as counter flow heat exchanger with two fluid flow streams). Temperatures of both fluid flow streams at the left and right condenser side (at the steam condenser input and output) are presented in Fig. 2 (b).

Considering steam turbine, energy analysis is actually isentropic analysis which shows a comparison between real (polytropic) and ideal (isentropic) steam expansion processes [14]. Regardless of the

observed steam expansion process in the turbine, performed energy (isentropic) analysis did not consider the ambient parameters in any way. Real (polytropic) steam expansion process in turbine (process between operating points 1 and 2, Fig. 2 (a)) is defined by the increase in steam specific entropy. Mentioned increase in steam specific entropy during expansion represents losses which occur in the turbine stages. In comparison to real expansion process, ideal (isentropic) steam expansion process (process between operating points 1 and 2_{is}, Fig. 2 (a)) did not consider any losses in the turbine, so steam specific entropy during ideal expansion remains always the same. For both ideal and real turbine expansion processes, inlet and outlet steam pressures are the same. Steam turbine is a mechanical power producer, so in the ideal (isentropic) expansion process, turbine will produce the highest possible mechanical power. The same steam turbine in the real (polytropic) expansion process will produce lower mechanical power in comparison to the ideal process (because real process involves all losses which occur during expansion) [15].

Operating points of the steam turbine and steam condenser presented in both Fig. 2 parts are consistent with operating points from Fig. 1.

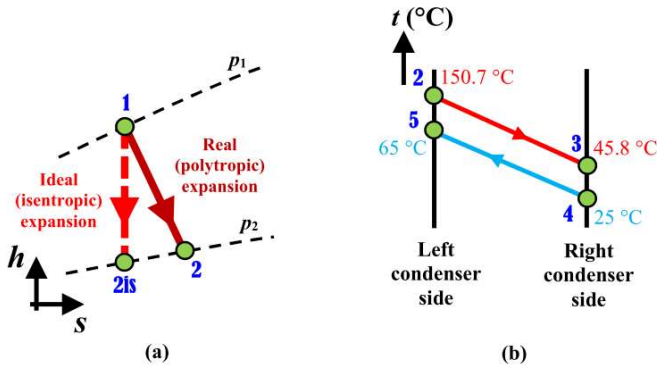


Fig. 2. Turbine and condenser processes: (a) Ideal and real expansion in the turbine for the energy (isentropic) analysis, (b) Fluid temperatures during the heat exchange in the condenser

3. Energy and exergy analyses equations

In the energy (isentropic) analysis of any system or component, the ambient parameters (ambient pressure and temperature) are not considered, what means that energy (isentropic) analysis is independent of the environment [16, 17]. In contrast to energy (isentropic) analysis, exergy analysis considers the ambient parameters, therefore, in exergy analysis are considered different kinds of losses in comparison to energy (isentropic) analysis [18, 19]. It should be highlighted that in real exploitation conditions the change in ambient pressure is small and it did not have a notable influence on any system or component exergy parameters, however, the ambient temperature change can be significant and it notably influences exergy parameters of any observed system or component [20]. Energy (isentropic) and exergy analyses equations of the observed steam turbine and steam condenser are defined according to recommendations from the literature [21, 22] as well as by using operating points numeration presented in Fig. 1 and Fig. 2.

3.1. Energy analysis equations of the steam turbine and steam condenser

Turbine:

- Real (polytropic) mechanical power:

$$P_{re,Turbine} = \dot{m}_1 \cdot (h_1 - h_2), \quad (1)$$

where P is mechanical power, re is an index of real (polytropic) steam expansion process, $\dot{m}$ is fluid (steam) mass flow rate and h is fluid specific enthalpy.

- Ideal (isentropic) mechanical power:

$$P_{id,Turbine} = \dot{m}_1 \cdot (h_1 - h_{2is}), \quad (2)$$

where id is an index of ideal (isentropic) expansion process.

- Energy (isentropic) loss:

$$En_{Loss,Turbine} = P_{id,Turbine} - P_{re,Turbine}, \quad (3)$$

where En is marking for the energy analysis.

- Energy (isentropic) efficiency:

$$\eta_{En,Turbine} = \frac{P_{re,Turbine}}{P_{id,Turbine}}, \quad (4)$$

where η is efficiency. Markings presented in the above four equations remain the same also in all other equations below.

Condenser:

- Total energy input:

$$En_{Input,Condenser} = \dot{m}_2 \cdot h_2 - \dot{m}_3 \cdot h_3. \quad (5)$$

- Total energy output:

$$En_{Output,Condenser} = \dot{m}_5 \cdot h_5 - \dot{m}_4 \cdot h_4. \quad (6)$$

- Energy loss:

$$En_{Loss,Condenser} = En_{Input,Condenser} - En_{Output,Condenser}. \quad (7)$$

- Energy efficiency:

$$\eta_{En,Condenser} = \frac{En_{Output,Condenser}}{En_{Input,Condenser}}. \quad (8)$$

3.2. Exergy analysis equations of the steam turbine and steam condenser

Turbine:

- Total exergy input:

$$Ex_{Input,Turbine} = \dot{m}_1 \cdot \epsilon_1, \quad (9)$$

where Ex is marking for the exergy analysis and ϵ is fluid specific exergy.

- Total exergy output:

$$Ex_{Output,Turbine} = \dot{m}_2 \cdot \epsilon_2 + P_{re,Turbine}. \quad (10)$$

- Exergy destruction:

$$Ex_{Destruction,Turbine} = Ex_{Input,Turbine} - Ex_{Output,Turbine}. \quad (11)$$

- Exergy efficiency:

$$\eta_{Ex,Turbine} = \frac{P_{re,Turbine}}{\dot{m}_1 \cdot \epsilon_1 - \dot{m}_2 \cdot \epsilon_2}. \quad (12)$$

Condenser:

- Total exergy input:

$$Ex_{Input,Condenser} = \dot{m}_2 \cdot \epsilon_2 - \dot{m}_3 \cdot \epsilon_3. \quad (13)$$

- Total exergy output:

$$Ex_{Output,Condenser} = \dot{m}_5 \cdot \epsilon_5 - \dot{m}_4 \cdot \epsilon_4. \quad (14)$$

- Exergy destruction:

$$Ex_{Destruction,Condenser} = Ex_{Input,Condenser} - Ex_{Output,Condenser}. \quad (15)$$

- Exergy efficiency:

$$\eta_{Ex,Condenser} = \frac{Ex_{Output,Condenser}}{Ex_{Input,Condenser}}. \quad (16)$$

4. Steam and condensate operating parameters for the energy (isentropic) and exergy analyses

Operating parameters of steam and condensate (water) in real exploitation process are found in [12] and presented in Table 1. Operating parameters which are not known from the literature in each operating point from Fig. 1 are calculated by using NIST-REFPROP 9.0 software [23]. It should be highlighted that at the end of ideal

(isentropic) steam expansion process in the turbine (operating point 2is, Fig. 2 (a)), steam specific enthalpy is equal to 2240 kJ/kg – this specific enthalpy is required for the turbine ideal mechanical power calculation.

The exergy analysis baseline for any system or component is the definition of the base ambient state [24]. In the exergy analysis performed in this paper, the base ambient state is defined by the ambient temperature of 25 °C and the ambient pressure of 1 bar.

Table 1. Steam operating parameters from turbine and condenser exploitation (real process)

O. P.*	Temp. (°C)	Press. (bar)	Mass flow rate (kg/s)	Specific enthalpy (kJ/kg)	Specific entropy (kJ/kg·K)	Quality (-)**	Specific exergy (kJ/kg)***
1	575.4	106.4	131.9	3559.20	6.8000	SH	1536.40
2	150.7	0.2	131.9	2783.70	8.3712	SH	292.37
3	45.8	0.1	131.9	191.78	0.6491	SC	2.81
4	25.0	3.0	2044.0	105.10	0.3672	SC	0.20
5	65.0	3.0	2044.0	272.34	0.8935	SC	10.51

* O. P. = Operating point (in accordance to Fig. 1)

** SH = Superheated steam; SC = Subcooled (condensate)

*** At the base ambient state

5. Results and discussion

Energy (isentropic) analysis results of the steam turbine are presented in Fig. 3.

Ideal (isentropic) steam expansion process in the turbine did not consider any losses, so the ideal mechanical power which can theoretically be developed in the turbine is always higher in comparison to the real mechanical power. Ideal mechanical power cannot be developed by the turbine in real exploitation conditions, but it can be a guideline for any turbine improvements and modifications. Real mechanical power is calculated from the real (polytropic) steam expansion process in the turbine which considers all losses during expansion. Observed steam turbine has high energy (isentropic) loss equal to 71.71 MW, and very low energy (isentropic) efficiency of 58.79% only. Considering the fact that observed turbine develop more than 100 MW of mechanical power in real exploitation conditions, obtained energy (isentropic) efficiency is too low for such turbine (it is in the range of low power auxiliary steam turbines [25]). Therefore, steam turbine energy (isentropic) analysis shows that its operation is far from optimal and that it can be notably improved.

Energy analysis results of the steam condenser are not presented. For heat exchangers in general, available literature suggests to avoid energy analysis because it is highly dependable on the accuracy and precision of measuring equipment which is used for obtaining operating parameters [26]. Moreover, any properly operating heat exchanger will always have extremely high energy efficiency (just slightly lower than 100%) and very low energy loss (which can almost be neglected). The same is obtained in the energy analysis of the observed steam condenser. For heat exchangers, only the exergy analysis can be recommended.

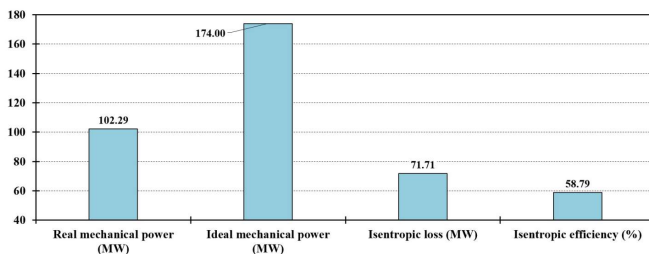


Fig. 3. Results of the steam turbine energy (isentropic) analysis

Exergy analysis results of the steam turbine and steam condenser at the base ambient state are presented in Fig. 4.

Comparison of steam turbine and steam condenser total exergy inputs and outputs show that steam condenser has notably lower both total exergy inputs and outputs. Steam turbine has high exergy destruction of 61.80 MW and low exergy efficiency of 62.34%. For a steam turbine which develops real (polytropic) mechanical power

higher than 100 MW, Fig. 3, also exergy analysis shows very high exergy destruction and too low exergy efficiency. Both energy and exergy analyses of the observed steam turbine show that its operation can and should be notably improved.

Steam condenser has exergy destruction of 17.12 MW and exergy efficiency of 55.17%, what is in the range of similar steam condensers from the literature [27].

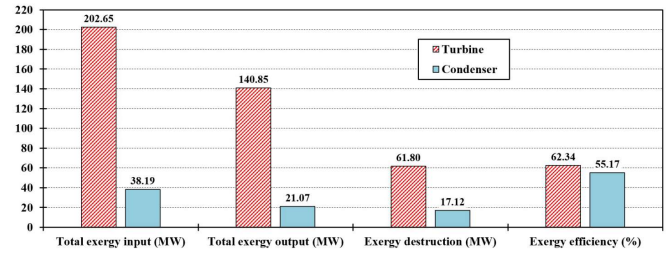


Fig. 4. Results of the steam turbine and steam condenser exergy analysis at the base ambient state

Observed steam turbine and steam condenser are also analyzed during the ambient temperature change. Both steam turbine and steam condenser are observed in the ambient temperature range from 5 °C up to 35 °C in steps of 10 °C, Fig. 5. Regardless of the ambient temperature, ambient pressure remains always the same and identical as at the base ambient state. In real exploitation, ambient pressure change is small and its influence on the observed steam turbine or steam condenser exergy parameters can be neglected.

For both steam turbine and steam condenser, increase in the ambient temperature simultaneously increases exergy destruction and decreases exergy efficiency, Fig. 5.

It is clear that steam condenser is much more sensitive to the ambient temperature change than steam turbine. At the ambient temperature of 5 °C steam condenser exergy efficiency is equal to 72.72% and it decreases to 36.82% at the ambient temperature of 35 °C (decrease in exergy efficiency of 35.90%), while in the same temperature range steam turbine exergy efficiency decreases for 2.39% only (from 63.95% up to 61.56%).

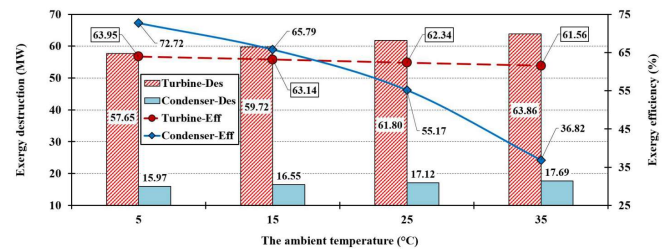


Fig. 5. Results of the steam turbine and steam condenser exergy analysis during the ambient temperature change

In further research related to the steam turbine and steam condenser analyzed in this paper will be applied various artificial intelligence procedures with the main aim to optimize performance of both components. As such procedures gives many beneficial results in improving various systems and components from the energy sector [28, 29], it can be expected that performance of the analyzed steam turbine and steam condenser will be notably improved.

6. Conclusions

In this paper are presented energy and exergy analyses results of steam turbine and steam condenser, which operate in commercial combined cycle power plant. For both steam turbine and steam condenser, exergy analysis is performed at the base ambient state and during the ambient temperature variation. The most important conclusions of the performed research are:

- Energy analysis shows that steam turbine has high energy (isentropic) loss equal to 71.71 MW, and very low energy (isentropic) efficiency of 58.79% only, which is in the range of low power auxiliary steam turbines.

- From the energy viewpoint, steam condenser is an almost perfect component. For the observed steam condenser, as well as for any other heat exchanger, only the exergy analysis can be recommended.
- At the base ambient state, steam turbine has high exergy destruction of 61.80 MW and low exergy efficiency of 62.34%. Therefore, both energy and exergy analyses show that steam turbine operation can and should be notably improved.
- Steam condenser has an exergy destruction of 17.12 MW and exergy efficiency of 55.17% at the base ambient state, what is in the range of similar steam condensers.
- For both steam turbine and steam condenser, increase in the ambient temperature simultaneously increases exergy destruction and decreases exergy efficiency.
- Steam condenser is much more sensitive to the ambient temperature change than steam turbine. Increase in the ambient temperature from 5 °C to 35 °C decreases steam condenser exergy efficiency for 35.90%, while the same increase in the ambient temperature decreases steam turbine exergy efficiency for 2.39% only.

7. Acknowledgment

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Bio-electrochemical system based electro-generative pipeline element

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Abstract: *In the context of a changing climate and the pursuit of sustainable development, any technology or device that produces green energy will help reduce dependence on fossil fuels. This work presents a prototype of an electro-generative pipeline element based on a bio-electrochemical system. The element is suitable for integration into pipelines carrying various liquids. The electro-generative element has shown high efficiency in laboratory conditions, and depending on the passing liquid, it can generate energy in the range of 0.5W - 1.5W. A different number of elements can be located in the pipeline system, depending on its length. Depending on the number of elements in the chain, enough energy can be obtained to power various devices.*

Keywords: GREEN ENERGY, SEDIMENT MICROBIAL FUEL CELL, BIO-ELECTROCHEMICAL SYSTEMS

1. Introduction

With the growth of the global population, the demand for natural resources and energy increases. Manufacturing companies expand their operations with new technologies and processes to meet their needs. Rapid development in resource use and energy consumption puts pressure on the environment, increasing pollution, greenhouse gas emissions, and waste generation. Energy and resources are two of the most crucial elements of economic progress. Economic progress is impossible without adequate resources and energy; therefore, resources and energy must be used wisely and efficiently. [4] Climate change and environmental pollution pose significant challenges to the global economy. This problem threatens not only people's health but also their finances and productivity. The urgency to address climate change and environmental pollution has led to significant advancements in renewable energy technologies. With growing global energy needs, developing sustainable and efficient energy solutions is critical. Renewable energy plays a multifaceted role in environmental conservation, providing solutions that generate clean energy and help restore ecosystems. [9]

The number of studies on green energy technologies published so far clearly shows a lack of fragmentation, as research often focuses on specifics such as solar or wind energy, without providing a comprehensive overview of the entire spectrum of available developments. This fragmentation narrows the field of research and hides the interconnectedness of multiple technologies that are critical for the functioning of sustainable energy systems. Green technology is already a branch of science that studies the creation, use, and application of technological tools, as well as how they interact with society, the environment, and human existence. Green inventions are those that benefit the environment and often include recycling, energy efficiency, renewable resources, safety, healthcare, and other areas. [14]

The construction industry is currently undergoing a radical shift towards sustainability, driven by the need to reduce the ecological footprint and improve energy efficiency. Green building is an innovative approach based on sustainable practices aimed at reducing the environmental impact of structures. It offers opportunities to mitigate the negative effects of buildings on the environment and the health of occupants. The water sector, as an integral part of the construction industry, also strives for higher energy efficiency and sustainability. [10] Water supply systems are crucial for providing safe, efficient, and sustainable water services in buildings. However, current design practices are based on outdated assumptions that contribute to stagnation, deterioration of water quality, and compromises between energy and health. Energy efficiency is one of five areas (including hydraulic design, water conservation, water quality, and socio-economic factors) where significant work needs to be done to achieve higher performance of water supply systems. Recognizing the problems of outdated methods of designing water supply and drainage systems, building regulators in developed countries have acknowledged that existing plumbing standards may no longer reflect how water is used in buildings. As a result, new tools and methods are being developed

to improve design accuracy. In addition to hydraulics, there is a need to integrate other key areas into the design, including energy efficiency and sustainable development. [2]

Water conservation is a fundamental aspect of the design of water supply and drainage systems, especially in the context of increasing pressure on drinking water resources due to climate variability and population growth. At the same time, energy efficiency has become a critical issue in the design of water supply and drainage systems. This highlights the importance of improving energy efficiency through effective design of water supply systems and integrating systems and devices for generating green energy. [8]

Socio-economic considerations are also crucial for the design, construction, and long-term operational efficiency of water supply systems. Factors such as rising construction costs and material accessibility significantly influence design decisions and project outcomes. Cost-effective solutions that enhance energy efficiency and sustainability are key to addressing this challenge. [4]

Green technologies encompass a wide range of systems and devices. Bio-electrochemical systems are such a technology that can directly convert the available biochemical energy in organic matter into electricity. A variation of bio-electrochemical systems is sediment microbial fuel cells. [6] Sediment microbial fuel cells are special types of microbial fuel cells where the anode is placed in anaerobic sediment, while the cathode is submerged in the surface layer of water. [15] Natural electroactive bacteria break down organic compounds in the sediment, producing electrons and protons. The electrons reach the cathode through an external electrical circuit, while the protons pass through the soil layer, acting as a makeshift membrane. [1]

Oxygen is often preferred as an electron acceptor due to its availability in the cathode region and its high potential. However, reduction reactions of dissolved oxygen are slow and limited due to the limited solubility and diffusion of oxygen. [13] On the cathode, heavy metal ions and other compounds can also be reduced, which will lead to increased generated energy. All this suggests the use of a different fluid in the cathode region. Additionally, the material and configuration of the electrodes are crucial for the efficiency of sediment microbial fuel cells. [3]

Although sediment microbial fuel cells are an interesting and rapidly developing technology, some critical issues need to be addressed before they can be used for more practical purposes. [5] The main limitation of sediment microbial fuel cells is their low output power, which typically ranges from tens to hundreds of milliwatts, insufficient for directly powering various devices requiring watt-level power. [7] The limited energy production in SMFCs results from multiple factors, including undesirable sediment and water characteristics, significant cathodic activation losses, and large ohmic resistance due to the large anode-cathode distance. [11] Another challenge for real-world applications is the materials used for constructing sediment microbial fuel cells. Using expensive electrode materials is not cost-effective given the relatively low generated power. [12]

The aim of the current research is to propose a working practical application of sediment microbial fuel cells. A prototype of an electrogenerative pipeline element based on a sediment microbial fuel cell has been developed. In constructing the prototype, solutions have been found for most challenges limiting the practical, long-term application of sediment microbial fuel cells as a green energy generation technology, as well as improving performance. Inexpensive construction materials with high resistance to environmental factors have been used. The prototype represents a connecting element in pipeline technological schemes, with standardized dimensions, easy to operate and install. Depending on the specific technological scheme and application, a varying number of electrogenerative elements can be included. Connected in a suitable electrical circuit (in parallel or series), they can provide sufficient energy for an extended period.

2. Materials and methods

Construction of electrogenerative pipeline element

The pipeline element represents a sediment microbial fuel cell, which includes anode and cathode parts. The anode part consists of a PVC pipe with a diameter of 110 mm and a length of 250 mm. The bottom of the pipe is closed with a PVC plug. The pipe is filled with river sediment. At the bottom of the pipe, there is a stainless steel electrode AISI 304 with an area of 471 cm², which acts as the anode. At the top of the pipe, a perforated rubber cap filled with clay is placed, serving as a membrane between the anode and cathode zones. The cathode part consists of a PVC branch Ø110/110x87°, in which a curved stainless steel electrode AISI 304 with an area of 407 cm² is located, acting as the cathode. The two structural elements are connected and form an electrogenerative connecting pipeline element based on SMFC. The cathode zone is filled with water with the following chemical characteristics: pH 6.83, Eh 109 mV, and EC 68 µS/cm².

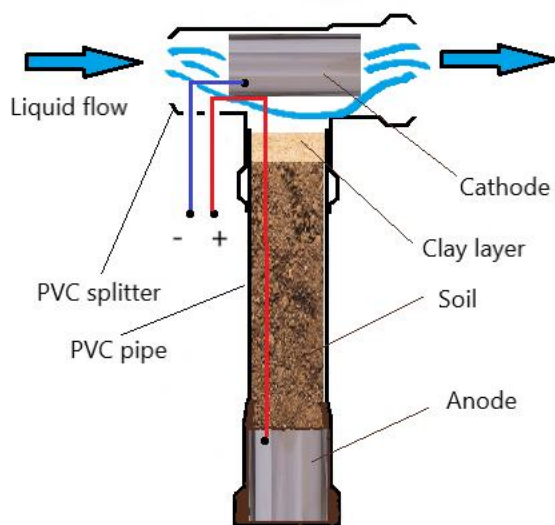


Fig. 1 The schematic diagram of electrogenerative pipeline element

Soil sampling

For the purpose of the study, riverside soil was taken from Ivanyanska river, Bulgaria (42°42'27.1"N 23°11'46.4"E), from a depth of 20-30 cm. After taking the river sediment, the larger pieces were removed by sieving through 2 mm. In order to carry out physicochemical analyses, part of the sieved soil was air-dried. The soil is characterized as alluvial-meadow with a high humus content of 6%. The soil has been classified as clay according to the Rutkowski method. Soil pH was measured by pH-meter HANNA HI-9021 determined at 1 : 2.5 (soil:water). Soil electrical conductivity (EC) was measured by WTW LF 197-S determined at 1:5 (soil:water). The main soil physicochemical properties were as

follow pH 6.42, EC 288.89 µS cm⁻¹. The Kjeldahl-N content were 0.59% and dissolved organic carbon 74.28 mg kg⁻¹. The amount of total nitrogen measured was 986.5 mg kg⁻¹, phosphorus – 20.2 mg kg⁻¹, potassium – 180.0 mg kg⁻¹. The abundance of exoelectrogenic microorganisms was quantified by 16S rRNA gene. In the sediment *Geobacter* and *Clostridium*, were the most abundant. *Anaeromyxobacter*, *Bacillus*, *Pseudomonas* and *Desulfolobus* were also detected. [18] All these indicators provide sufficient nutrients and substrate for degradation by exoelectrogenic microorganisms in the anode zone. This would ensure long-term and stable operation of the sensor. The soil thus prepared was then used to fill anode area of SMFC based biosensor. (Fig. 1).



Fig. 2 Photo of electrogenerative pipeline elements

Electrochemical analysis

To determine the operation and effectiveness of the composter polarization and power curves were obtained by varying external resistances sequentially from 10, 8, 6, 4, 2, 1.5, 1.3, 1, 0.7, 0.5, 0.3 to 0.1 KΩ using MCP lab electronics BXR-04 ResistorBox. The voltage dynamic were measured and recorded in real time with Vernier LabQuest Mini and Logger Lite software.

3. Results and discussion

In order to investigate and validate the operation of the electro-generative pipeline element under laboratory conditions, a series of chemical and electrochemical analyses were conducted. After constructing the element, the time it took to reach its optimal baseline voltage was recorded. The data from the study are presented in Figure 3.

The voltage of the element is directly dependent on the microbiological processes occurring in the soil (the anode zone). From the presented graph, it can be seen that it takes about 10 days for the microorganisms to adapt and initiate stable microbial processes. During this period, the voltage is relatively stable and ranges between 10 to 50 mV. After the tenth day, stable microbial processes have been established in the anode area, and anaerobic processes develop, leading to a significant increase in the potential difference between the soil and water (the cathode area). The voltage increases until the 21st to 22nd day, after which a stable baseline voltage of the electro-generative pipeline element is reached. The baseline voltage of the element when the cathode zone is filled with water is in the range of 425 ± 3 mV and remains so until the end of the experiment (day 31).

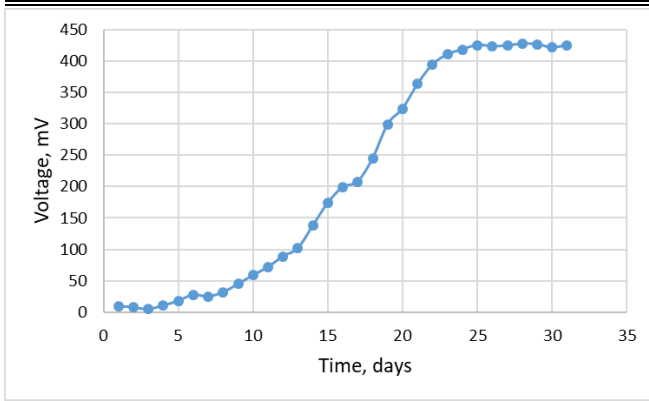


Fig. 3 Open circuit voltage of electro-generative pipeline element

The next experiment aimed to determine the dynamics of the open-circuit voltage of the electro-generative pipeline element over time before it was installed in a pipeline network. The data from the experiment are presented in Figure 4.

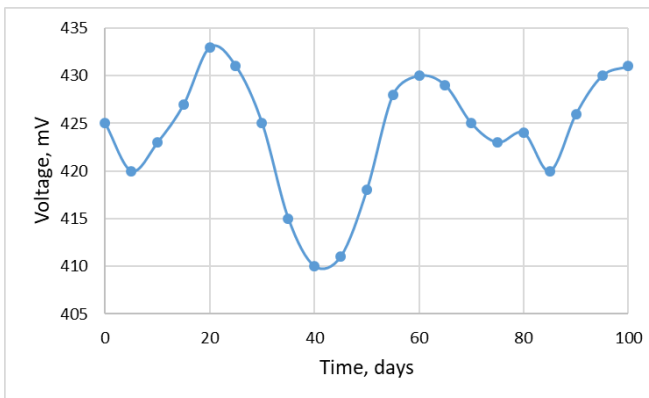


Fig. 4 Base open circuit voltage of electro-generative pipeline element

The experiment was conducted over 100 days, during which the open-circuit voltage was continuously monitored and recorded using Vernier LabQuest Mini and Logger Lite software. From the data, it can be seen that the open-circuit voltage remained relatively stable throughout the study period, ranging between 420 ± 15 mV. The slight fluctuations in the voltage of the electro-generative pipeline element can be attributed to temperature differences in the environment. Temperature is a factor that significantly influences microbiological activity in the anode zone, and consequently, the generated voltage of the element.

The next experiments were based on investigating the main electrical parameters of the electro-generative pipeline element. Data from the conducted analyses are presented in Figures 5 and 6.

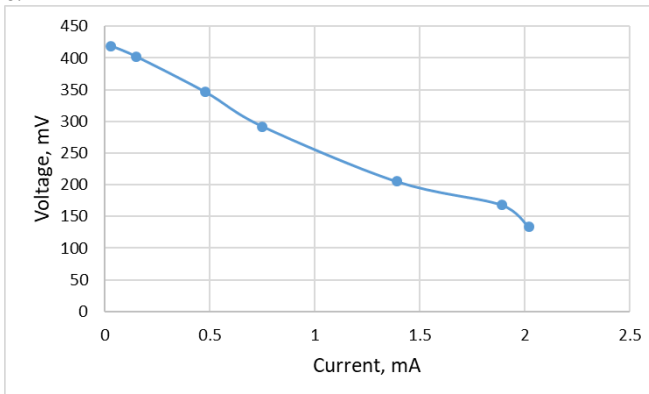


Fig. 5 V-A characteristic of the electro-generative pipeline element

Figure 5 shows the volt-ampere characteristic of the electro-generative pipeline element. From the graph, it can be seen that the element reaches a maximum current of 2.02 mA at a voltage of 133 mV and an applied resistance of 1.3 k Ω .

Figure 6 shows the polarization curve of the electro-generative pipeline element.

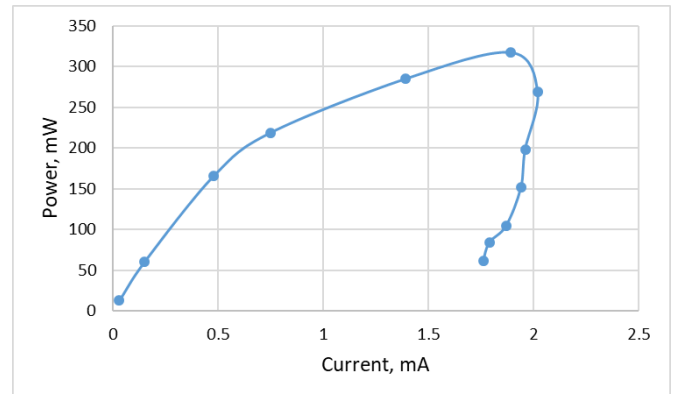


Fig. 6 Polarization curve of the electro-generative pipeline element

From the figure, it can be seen that the pipeline element reaches a maximum power of 317.52 mW at a current magnitude of 1.89 mA and a voltage of 168 mV.

It is important to note that the generated voltage and power of the electro-generative pipeline element are highly dependent on the redox potential of the fluid flowing through the cathode zone. The next experiment aimed to determine how the electrical parameters of the pipeline element would change when a solution with a higher redox potential flowed through the cathode zone. For this purpose, a copper solution with a concentration of 2 g/L was prepared, with a redox potential of 384 mV. After filling the cathode zone with this solution, the electrical parameters of the electro-generative pipeline element were measured again. The data from the experiment are presented in Figures 7 and 8.

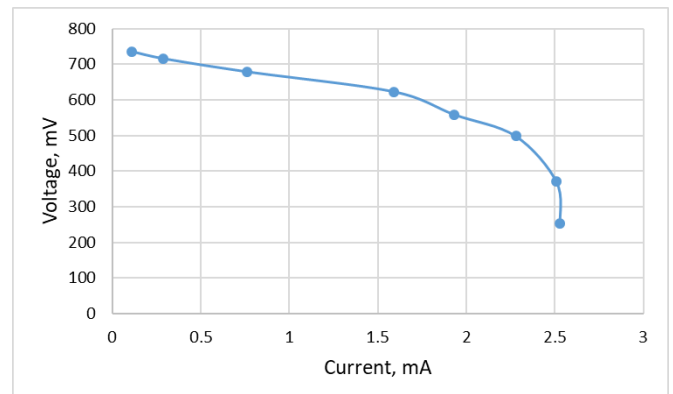


Fig. 7 V-A characteristic of the electrogenerative pipeline element with high ORP solution

From the volt-ampere characteristic, it can be seen that there is a significant increase in the open-circuit voltage, reaching up to 736 mV. The maximum current in this experiment reaches 2.53 mA.

From the polarization curve shown in the figure, it is determined that increasing the redox potential leads to a significant increase in the power of the electro-generative pipeline element. In this case, a maximum power of 1135.44 mW is reached at a current magnitude of 2.28 mA and an applied resistance of 1.5 Ω .

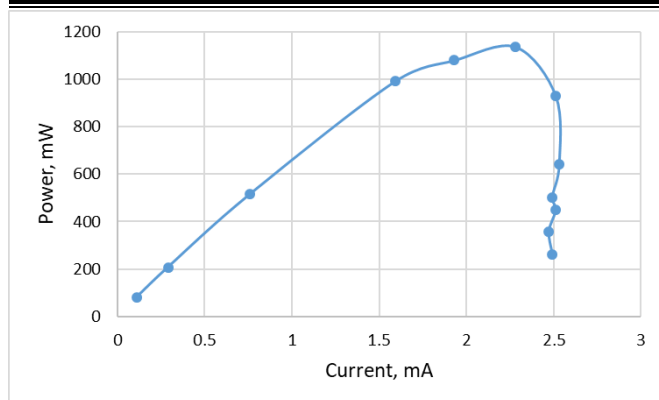


Fig. 8 Polarization curve of the electro-generative pipeline element with high ORP solution

4. Conclusion

Green technologies and their integration into practice are key factors for sustainable energy production and use. The article examined and proposed a practical application of bio-electrochemical systems technology for the production of green energy. The developed prototype of an SMG-based electro-generative pipeline element was investigated and validated under laboratory conditions. Analyses showed efficient and stable operation of the pipeline element. Laboratory studies established that the higher the oxidation-reduction potential of the fluid passing through the cathode zone, the higher the power generated by the pipeline element. From the electrical characteristics of the prototype, a maximum generated power of 1.135 W was determined.

Pipeline systems consist of interconnected pipes and pipeline elements with varying lengths. The proposed prototype represents a connecting pipeline element, and the longer the pipeline length, the more electro-generative elements can be incorporated. This will result in the production of greater amounts of energy and its utilization for various needs.

Acknowledgements

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Active damping in cable-stayed-bridge structures using hydraulic actuators

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Abstract: Cable-Stayed-Bridges are an important part of today's constructions in the traffic infrastructure. New materials and computational technology have led to the construction of longer and slender Cable-Stayed-Bridges are under the effect of dynamic loads as wind, traffic or earthquakes. Besides comfort restrictions, the vibrations of large amplitudes effects also the lifetime of the entire structure. Oscillations of Cable-Stayed-Bridges can be reduced significantly by active damping systems. In this paper is represented shortly an electro-hydraulic actuator concept for the active damping of Cable-Stayed-Bridges. This type of control is very efficient even in large bridges (up to 900 m span). Also, the tests on a large-scale bridge show the efficiency of active damping in Cable-Stayed-Bridges using electro-hydraulic actuators. The damping of deck and cables, has become crucial in the design of cable-supported structures. Because of the effectiveness of passive damping systems is limited, this new electro-hydraulic actuator concept is developed.

Keywords: CABLE-STAYED, BRIDGE, DAMPING SYSTEMS, OSCILLATIONS

1. Introduction

Cable-stayed bridges are continuously subjected to dynamic loads such as wind, traffic, and seismic excitations. Beyond issues related to user comfort, large-amplitude vibrations can significantly affect the structural integrity and long-term service life of the entire bridge system [1-3]. Therefore, effective vibration mitigation has become a critical aspect of modern bridge engineering.

Structural oscillations in cable-stayed bridges can be substantially reduced through the implementation of active damping systems. This paper briefly presents an electro-hydraulic actuator concept designed for the active vibration control of cable-stayed bridges. The proposed control approach demonstrates high efficiency, even for large-span bridges reaching up to 900 m. Experimental investigations conducted on a large-scale bridge model further confirm the effectiveness of active damping using electro-hydraulic actuators.

Consequently, the damping of both bridge decks and stay cables has become a crucial consideration in the design of cable-supported structures. Since the performance of traditional passive damping systems is inherently limited, the development of advanced active control solutions, such as the proposed electro-hydraulic actuator system, represents a promising alternative for improving structural performance and durability [4-7]. Figure 1 depict the Normandia bridge – example for a large cable-stayed bridge [8-11].



Fig. 1. Normandia bridge – example for a large cable-stayed bridge [8]

2. Damping Concept

Figure 2 illustrates the basic control concept based on the *Integral Force Feedback* (IFF) approach. In this configuration,

selected stay cables are equipped with actuators positioned between the stay cable and the bridge deck. The stay cable is modeled by the stiffness c_k , while the bridge deck is represented by the mass m_{st} . The combined structural stiffness of the deck and the stay cables is denoted by c_{st} . The actuator is connected to the stay cable through a force sensor, forming a collocated actuator-sensor pair, which ensures stable and efficient control performance.

For the purpose of explaining the damping concept, the effect of self-weight is neglected. The actuator displacement amplitude w is calculated from the dynamic component of the measured force F_D in the stay cable, see equation 1.

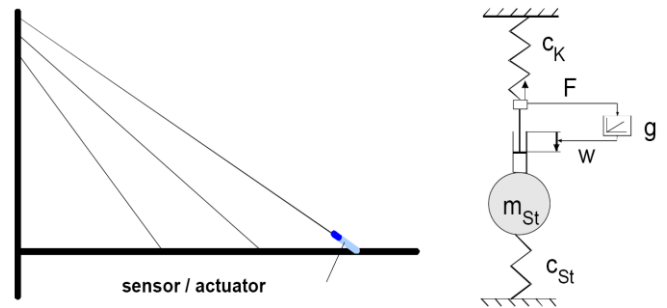


Fig. 2. Cable-stayed bridge mock-up and active damping model with "Integral Force Feedback"

$$w = g \cdot \int F_D \cdot dt \quad (1)$$

For an undamped system, the amplification factor approaches the limiting cases ($g \rightarrow 0$) and ($g \rightarrow \infty$). When $g = 0$, a rigid connection exists between the stay cable and the structure; consequently, no oscillation energy is absorbed. In contrast, when $g \rightarrow \infty$ the cable becomes effectively separated from the structure, causing the actuator forces and therefore the damping effect to vanish.

An optimal amplification value g_{opt} exists at which the total system damping reaches its maximum. For this optimal value, a force oscillation with amplitude F_D produces an actuator displacement amplitude given by

$$\hat{w}(g_{opt}) = \frac{\hat{F}_D}{c_K} \quad (2)$$

This relationship links the structural parameters directly to the optimal dimensioning of the damping actuator. When the actuator is designed according to this criterion, the *Integral Force Feedback* (IFF) approach guarantees continuous energy dissipation within the system. The corresponding energy flow can be expressed as equation (3).

$$\dot{W} = -F_D \cdot \dot{x}_r = -g \cdot F_D^2 \leq 0 \quad (3)$$

$\dot{x}_r$ - frequency of the actuator stroke

This damping law enables stable operation for all observable and controllable state variables. However, practical actuators possess limitations related to response time and achievable amplification, which influence the effective feedback gain g and, consequently, the overall damping performance. For effective control, the actuator should have a natural frequency significantly higher than that of the controlled structural system.

Furthermore, actuator placement plays an important role in system efficiency. Positioning actuators on the main (longest) cable is particularly effective, as it both mitigates vibrations of the individual cable and increases the global damping of the entire bridge structure.

3. Electro-Hydraulic Actuator Concept

The primary design objective of active control systems is to ensure minimal energy consumption while maintaining a compact actuator size. To achieve a long service life for cable-supported structures, additional dynamic loads must be minimized through effective active damping. During periods of increased excitation caused by adverse weather or heavy traffic conditions, structural loads should remain below predefined limit values.

In active damping applications, the required dynamic control force is typically less than one-tenth of the corresponding static force. Considering the magnitude of static loads, several design approaches incorporate a separate passive device to sustain static demands, thereby reducing the power consumption of the actuator system. Static load compensation is achieved through the hydraulic component of the actuator. This passive device consists of a hydraulic plunger cylinder connected to a hydraulic accumulator. The passive subsystem can be combined with an additional hydraulic cylinder responsible for generating the active control force.

Compared with purely mechanical solutions, such an actuator configuration offers several advantages:

- The force level of the passive subsystem can be adapted to variations in static loads caused by wind or traffic, enabling variable spring characteristics.
- When combined with a mechanical system, hydraulic pressure can be unloaded during non-active structural periods, improving energy efficiency and reducing component wear over time.

Figure 3 presents different design options for active hydraulic actuators with passive compensation of tension loads. These concepts are classified according to the number of pressure chambers and the actuator control strategy. The number of pressure chambers corresponds to the number of hydraulic oil springs; consequently, a double-acting cylinder provides the highest actuator natural frequency.

Control of a hydraulic cylinder using a variable-displacement pump (displacement control) generally achieves higher efficiency than valve-controlled systems. Nevertheless, a valve-controlled configuration is adopted in this study due to its superior controllability for oscillations characterized by small amplitudes and high frequencies. For large cable-stayed bridges, displacement-controlled systems may offer additional advantages.

To minimize power consumption and extend system lifetime, the control power unit can be switched off during periods when structural oscillations remain within acceptable limits under normal operating conditions.

The experimental investigation focuses on evaluating the effectiveness of the proposed damping concept. For this purpose, a collocated actuator-sensor pair incorporating a valve-controlled

double-acting hydraulic cylinder was developed. Figure 4 illustrates the actuator system configuration. A key feature of this design is the integration of passive and active subsystems within a single unit. The passive component combines a hydropneumatics accumulator with a dedicated pressure chamber, enabling the actuator to sustain high tensile forces (cable pre-tensioning) without continuous power flow control during actuator motion. The active subsystem consists of two pressure chambers with nearly identical cross-sectional areas connected to the control ports of a servo valve.

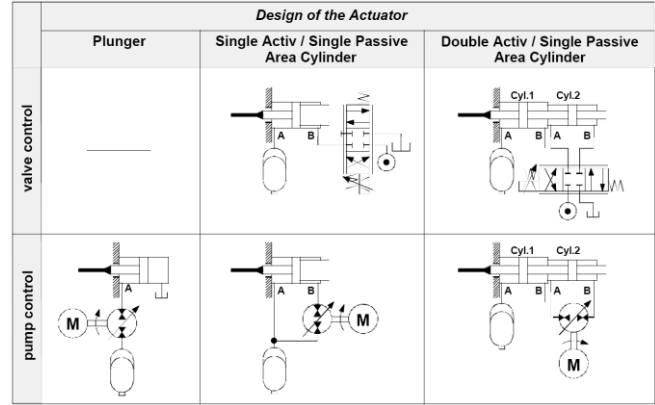


Fig. 3. Systematic of hydraulic actuators with passive load compensation

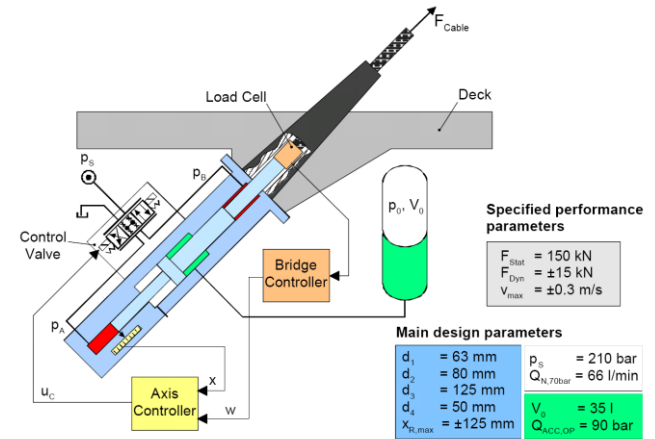


Fig. 4. Principle design of the prototype actuator and performance requirements

4. Static and Dynamic Characteristics of The Damping System

The effectiveness of active damping largely depends on the performance capabilities of the actuator. To satisfy both static and dynamic requirements, the actuator must be dimensioned based on an appropriate mathematical model. In addition to accurately describing the actuator dynamics, the model should also represent the complex nonlinear behavior of the bridge structure particularly that of the stay cables — through a suitably linearized system formulation.

4.1 Static and dynamic actuator characteristics

The mathematical model describes the interaction between the actuator and the bridge structure, as well as the internal power characteristics of the actuator, within a frequency range that is not lower than the fundamental frequency of the structure. The actuator dynamics are represented through inertial, stiffness, and damping effects. Damping arises primarily from mechanical friction and hydraulic flow losses, whereas stiffness results from the compressibility of the hydraulic fluid filling the pressure chambers.

The inertial effects are associated with the moving masses, particularly the cylinder rod.

The motion of the piston rod induces an exchange of hydraulic oil between the actuator and the accumulator. A specific characteristic of this actuator is that the dynamic effects associated with oil flow through the connecting pipe cannot be neglected. The oil volume within the pipe is not modeled as a distributed continuous oscillator but rather as a lumped parameter element. Consequently, the model exhibits two degrees of freedom. The inertial effect of the pipe flow can be represented by an equivalent mass, which is greater than the actual mass of the oil contained in the pipe.

Figure 5 illustrates the dynamic characteristics of the actuator model. The formulation accounts for the stiffness contributions of the hydraulic oil volumes in the three pressure chambers, as well as the inertial effects of both the cylinder rod and the hydraulic pipe flow. When the external load is neglected, the system behaves as a two-degree-of-freedom system with two natural frequencies. The model further describes the dynamic interaction between the actuator and the stay cable.

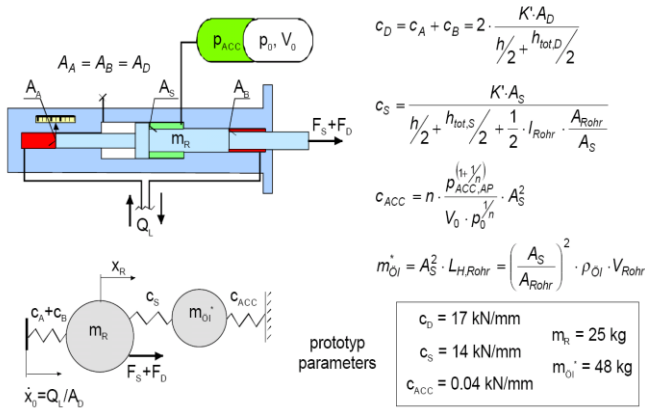


Fig. 5 Dynamic parameters of the actuator

4.2 Load Influence on Dynamic Actuator Characteristics

The theory of active damping in cable-stayed bridges must account for various nonlinear effects of the stay cables, including geometric extension and slackening phenomena.

A stay cable can be modeled as a continuous oscillator exhibiting complex dynamic behavior, capable of vibrating in both transverse and longitudinal modes. Since the actuator operates along the longitudinal axis of the cable, only longitudinal forces contribute directly to actuator motion.

The natural frequencies of a restrained cable primarily depend on its length and material properties.

Figure 6 presents the dynamic characteristics of the actuator under loading conditions, illustrating its response within the coupled actuator–cable system.

The most important is, that the stiffness c_D of the actively controlled pressure chambers will be higher than the cable stiffness c_K . So, the influence of the cable stiffness on the dynamic's actuator characteristics is negligible. The influence of the cable mass on the actuator performance is characterized by: cable mass and stiffness are distributed over the length far from the actuator and do not influence the actuator. Only mass shares nearby the actuator delay the actuator. It can be shown, that the inertial effect of the cable on the control behavior of the actuator can take into account, if a share of the total cable mass is added to the actuator rod mass.

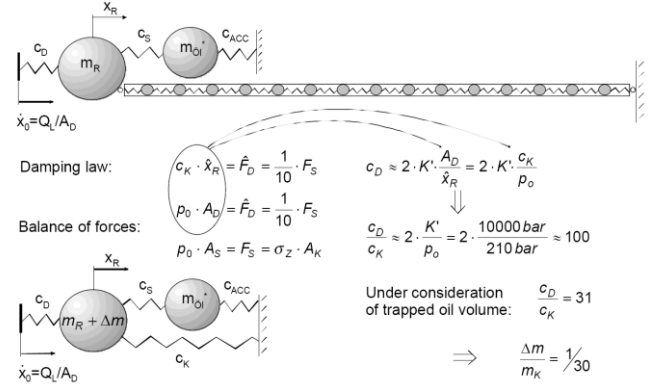


Fig. 6 Influence of cable mass and stiffness on dynamic actuator characteristics

5. Summary and Conclusions

Cable-stayed bridges are highly sensitive to dynamic oscillations caused by environmental and operational loads. The proposed Integral Force Feedback (IFF) concept enhances structural damping through collocated sensor–actuator pairs installed between the stay cables and the bridge deck. This approach enables efficient vibration reduction while requiring only minimal external power input under normal operating conditions.

Static loads are compensated by hydraulic accumulators operating without continuous power supply, thereby improving energy efficiency and reducing operational demands. For optimal performance, the actuator system must be designed such that its natural frequency is at least ten times higher than the dominant structural frequencies to be controlled, typically ranging between 0.5 and 3 Hz. This requirement ensures effective damping even under high loading conditions and for long stay cables.

Overall, the integration of active damping with passive hydraulic compensation provides a reliable and energy-efficient solution for mitigating vibrations in cable-stayed bridges, contributing to improved structural durability, operational safety, and extended service life.

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Kinetic investigation of copper ions adsorption onto corn stalks

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Abstract: Corn stalk was used as a biosorbent for the adsorption of copper ions from synthetic solutions. To examine the mechanism of the adsorption process and identify the potential rate-determining step, the following kinetic models were used in this study: the pseudo-first order kinetic model, the pseudo-second order kinetic model, the Elovich kinetic model, and the interparticle diffusion model. Kinetic studies show that copper ions adsorption followed the pseudo-second order kinetic model. The maximum adsorption capacity was 5.5 mg g^{-1} . The results indicate that corn stalk can be successfully used as a biosorbent for the adsorption of copper ions from synthetic solutions.

Keywords: CORN STALK, COPPER IONS, ADSORPTION, KINETIC INVESTIGATION

1. Introduction

The increasing discharge of heavy metals into aquatic environments poses a serious threat to ecosystems and public health, necessitating the development of efficient and sustainable wastewater treatment methods. Agricultural by-products, such as corn stalks, represent a promising class of low-cost, environmentally friendly adsorbents for removing metal ions from contaminated water.

Owing to their lignocellulosic composition and abundance of functional groups, modified or untreated corn stalks can effectively capture heavy metal ions through adsorption processes. To better understand the mechanisms and efficiency of these systems, kinetic modelling plays a crucial role. The application of kinetic models – such as pseudo-first-order, pseudo-second-order, and Elovich kinetic model – provides insights into the rate-controlling steps and adsorption dynamics, contributing to the optimisation of treatment parameters for practical applications.

2. Materials and methods

Corn stalks collected from agricultural fields near Bor were used as the adsorbent. The material was first ground and sieved, and the sieve fraction ($-1 + 0.4$) mm was used for adsorption experiments.

2.1. Adsorption of Cu^{2+} ions onto corn stalks – experimental procedure

Adsorption experiments of Cu^{2+} ions onto corn stalks were carried out in a stirred batch reactor with a magnetic stirrer operating at 300 rpm. Before the experiments, the adsorbent was washed with distilled water, and pH and conductivity were monitored.

A synthetic Cu^{2+} solution (0.2 g dm^{-3}) served as the aqueous phase, with 0.5 g of adsorbent mixed with 50 mL of solution. After a specified contact time, the suspension was filtered, and the filtrate was analysed for residual copper, alkali metals, and alkaline earth metals. The amount of adsorbed copper and the adsorption capacity were determined by mass balance, and pH variation was monitored during adsorption. All experiments were conducted at room temperature.

The adsorption capacity, defined as the amount of metal adsorbed per unit mass of adsorbent, was calculated using the following equation:

$$q_{(t)} = \frac{c_i - c_{(t)}}{m} V \quad (1)$$

where: $q_{(t)}$ is the adsorption capacity (mg g^{-1}); c_i and $c_{(t)}$ are the initial and time-dependent metal concentrations in solution (mg dm^{-3}); V is the solution volume (dm^3); m is the mass of adsorbent (g).

3. Results and discussion

3.1 Kinetics of the adsorption process

To investigate the adsorption mechanism and identify the rate-limiting step, the following kinetic models were applied: pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models, commonly used for liquid–solid adsorption systems [1,2].

Adsorption experiments were conducted at an initial Cu^{2+} concentration of 200 mg dm^{-3} and stopped after 90 minutes, assumed sufficient to reach equilibrium [3].

The adsorption capacity increased rapidly during the first 10 minutes, reflecting abundant active sites on the corn stalks. Thereafter, the rate slowed as available sites decreased and Cu^{2+} concentration in solution declined, approaching equilibrium after ~ 60 minutes, when the amount of adsorbed copper remained constant.

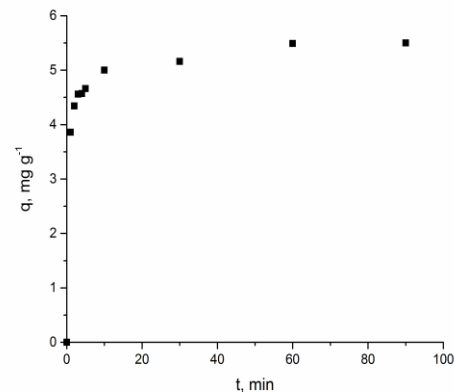


Fig. 1 Change of copper ion adsorption capacity with time on corn stalks.

3.1.1. Pseudo-first-order kinetic model (Lagergren model)

The pseudo-first-order kinetic model was proposed by Lagergren and is often referred to as the Lagergren model. This model assumes that the adsorption kinetics occur as a reversible process based on the adsorption capacity [4]. In differential form, the pseudo-first-order model can be expressed by equation (2):

$$\frac{dq_{(t)}}{dt} = k_1 (q_e - q_{(t)}) \quad (2)$$

where: $q_{(t)}$ is the adsorbent capacity defined as the mass of metal adsorbed per unit mass of adsorbent at time t (mg g^{-1}); q_e is the equilibrium adsorption capacity (mg g^{-1}); k_1 is the rate constant for the pseudo-first-order kinetic model (min^{-1}).

For practical application, the following equation can be used:

$$\log(q_e - q_{(t)}) = \log(q_e) - \frac{k_1}{2,303} \cdot t \quad (3)$$

A plot of $\log(q_e - q_{(t)})$ versus t provides a linear relationship, from which k_1 and q_e can be determined from the slope and intercept, respectively. Results are shown in Table 1.

As shown in Table 1, the pseudo-first-order model exhibits a correlation coefficient $R^2 = 0.89$, indicating a moderate fit. The calculated and experimental adsorption capacities differ significantly, suggesting limited applicability of this model.

Table 1: Pseudo-first-order kinetic parameters for Cu^{2+} adsorption.

Parameter/Ion	k_1 (min^{-1})	$q_{e,\text{exp}}$ (mg g^{-1})	$q_{e,\text{cal}}$ (mg g^{-1})	R^2
Cu^{2+}	0.082	5.5	1.76	0.89

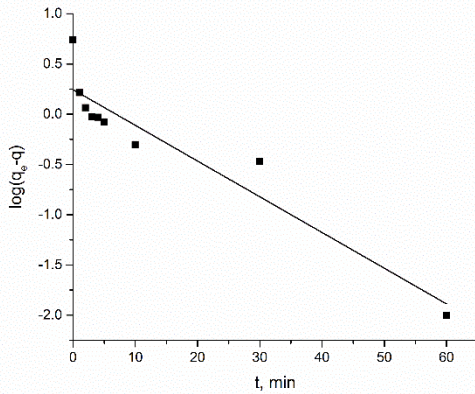


Fig. 2 Pseudo-first-order kinetic model for copper ion adsorption on corn stalks.

3.1.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetic model assumes that both adsorption and ion exchange occur at the adsorbent surface, with chemisorption controlling the binding of the adsorbate [5]. The nonlinear form of the pseudo-second-order model is expressed as [6]:

$$\frac{dq_{(t)}}{dt} = k_2 (q_e - q_{(t)})^2 \quad (4)$$

where: $q_{(t)}$ is the adsorbent capacity defined as the mass of metal adsorbed per unit mass of adsorbent at time t (mg g^{-1}); q_e is the equilibrium adsorption capacity (mg g^{-1}); k_2 is the rate constant for the pseudo-second-order kinetic model ($\text{g mg}^{-1} \text{min}^{-1}$).

For practical application, the following equation can be used:

$$\frac{t}{q_{(t)}} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Values of k_2 and q_e were determined from the intercept and slope of the $t/q_{(t)}$ vs. t plot. The results are shown in Table 2.

Table 2: Pseudo-second-order kinetic parameters for Cu^{2+} adsorption

Parameter/Ion	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{e,\text{exp}}$ (mg g^{-1})	$q_{e,\text{cal}}$ (mg g^{-1})	R^2
Cu^{2+}	0.205	5.5	5.5	1

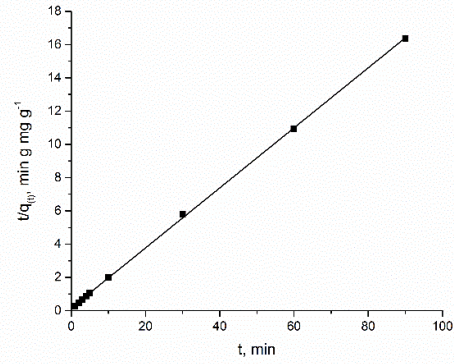


Fig. 3 Pseudo-second-order kinetic model for copper ion adsorption on corn stalks.

The perfect correlation ($R^2 = 1$) indicates excellent agreement between the experimental data and the pseudo-second-order model, confirming that chemisorption and ion exchange govern Cu^{2+} adsorption on corn stalks.

3.1.3. Elovich kinetic model

Originally developed for gas chemisorption on heterogeneous solid surfaces, the Elovich model is widely used for solution-phase adsorption [6]. It assumes that the adsorption rate decreases exponentially with increasing adsorbate coverage. In the literature, it is most commonly presented in the following form [7]:

$$\frac{dq_{(t)}}{dt} = \alpha e^{-\beta q_{(t)}} \quad (6)$$

where: α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$); β is a parameter related to surface coverage and activation energy (g mg^{-1}); $q_{(t)}$ is the adsorbent capacity (mg g^{-1}).

For practical application, the following equation can be used:

$$q_{(t)} = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

The values of the parameters α and β were determined from the intercept and slope of the $q_{(t)}$ vs. $\ln t$ plot (Figure 4), and are presented in Table 3 together with the correlation coefficient R^2 for copper ions.

Table 3: Elovich kinetic parameters for Cu^{2+} adsorption.

Parameter/Ion	α ($\text{mg g}^{-1} \text{min}^{-1}$)	β (g mg^{-1})	R^2
Cu^{2+}	4.073	0.4	0.958

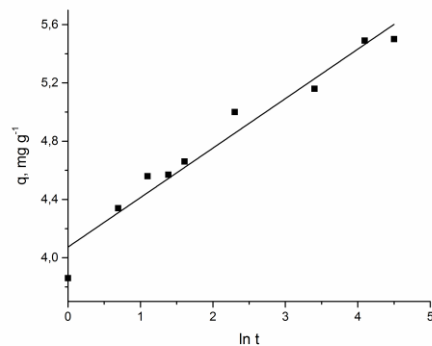


Fig. 4 Elovich kinetic model for copper ion adsorption on corn stalks.

From Table 3, based on the obtained value of the correlation coefficient $R^2 = 0.958$, it can be observed that the Elovich kinetic model describes very well the kinetics of copper ion adsorption onto corn stalks, indicating that copper ions bind to the adsorbent predominantly through chemisorption.

4. Conclusions

The kinetics of the copper ion adsorption process onto corn stalks were analyzed according to three theoretical kinetic models: the pseudo-first-order model, the pseudo-second-order model, and the Elovich model. Comparison of R^2 values for all models (Tables 1–3) demonstrates that the pseudo-second-order model provides the best fit ($R^2 = 1$), indicating that chemisorption is a possible mechanism of copper ion binding to the surface of corn stalks.

5. Acknowledgment

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Fiberglass casing string cementation operations in wellbore

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Abstract: Casing string is critical component in wellbore construction, defining wellbore diameter and providing structural integrity throughout drilling and production operations. Traditionally, steel casings are generally used due to their mechanical strength; however, problems connected with corrosion, particularly in environments containing hydrogen sulfide or saline formation water, presents significant operational and financial challenges. This paper explores the use of fiber-reinforced plastic (FRP) casing as a corrosion-resistant alternative, focusing on glass fiber-reinforced epoxy composites, especially concerning cementing operation. FRP casing properties depend on the fiber-matrix composition, fiber type, and manufacturing quality, which affect tensile and compressive strength, thermal stability, and resistance to environmental degradation. Laboratory and field studies, including pilot projects in Argentina, Oman, Brunei, and Kuwait, evaluated casing handling, rig down speed, anchoring, and cement bonding. Special attention was given to cementation procedures, fluid formulations for mud cake removal, and ultrasonic methods for assessing casing-to-cement bonding, adapted for the acoustic characteristics of FRP materials. Results indicate that while steel casings exhibit superior cement bonding, FRP casings can achieve adequate structural performance when mechanical stresses during handling and installation are carefully controlled and proper chemical compatibility between fluids and cement is ensured. Field data show that FRP casings can be deployed with only minor reductions in installation speed for smaller diameters and that optimized handling and cementation practices are crucial for operational success. These data demonstrate that FRP casings offer a technically feasible and economically advantageous alternative for wells in highly corrosive environments. However, their successful implementation requires tailored operational procedures, including modified handling equipment, optimized fluid systems, and specialized evaluation methods. Further field studies are needed to develop comprehensive guidelines for widespread adoption.

Keywords: CASING, FIBER-REINFORCED PLASTIC (FRP), CEMENTATION, CORROSION, CASING-TO-CEMENT BONDING

1. Introduction

Casing string is an extremely important part of the wellbore, as it defines the diameter of the wellbore and, among many other tasks, protects it from collapse. In order to ensure the long-term successful performance of the well, it is necessary to properly dimension casing string, which means that the appropriate inner and outer diameters should be selected along with the appropriate material and its quality and installation depth for each individual series of casing. The most commonly used casing is made of steel (of a certain quality), which remains the ideal material for most wells [1]. However, this material is prone to corrosion, which poses a major problem in certain locations during the production life of the well [2]. Corrosion is considered one of the most expensive problems in the oil and gas industry, even in modern times that offer various effective solutions to prevent its occurrence [3]. This phenomenon is defined as the deterioration of a metal or its properties and represents a major problem not only during drilling, but also throughout each subsequent phase of well operations. The process of corrosion occurs due to chemical reactions with substances containing oxygen, chlorine or hydrogen sulfide, which is a common occurrence during oil or gas production. Special emphasis should be placed here on hydrogen sulfide, a highly corrosive acid gas that causes major corrosion-related problems. In most oil wells around the world, formation (salt) water is produced along with oil and natural gas and is also a natural corrosive substance. With a longer production life, the proportion of formation water increases, which further worsens the situation in the well. Metals in the tubular tool oxidize and form their corresponding oxides and salts, which results in a decrease in the strength of the metal, i.e. the loss of the initial properties of the casing string. The ultimate consequence may be the replacement of the entire string to avoid production losses [4]. This problem, apart from the production phase, can also occur during special oilfield services, such as acid treatment of the underground formation, but also during the increasingly common enhanced oil recovery projects that involve injecting water or gases through existing or newly drilled wells.

Given all the important functions of casing, it is of utmost importance that the string can withstand high pressures, temperatures and forces that can lead to material failure over the long term. If the casing structure were to degrade, the worst consequence would be the collapse of the wellbore, making it almost impossible to replace the string in the well, especially if it is a small diameter wellbore. In that case, it would be necessary to start drilling and completion of a new well, which creates large

direct and indirect financial losses. In order to reduce, and possibly eliminate such consequences of corrosion on the casing string, the industry has begun to research cost-effective composite materials that could withstand the expected stresses in the wellbore conditions with better corrosion resistance than steel [5]. Composite materials are structurally heterogeneous materials consisting of two or more different phases that are chemically or mechanically bonded [6]. They can be produced by appropriate thermal and mechanical treatment, but many composites are produced by mixing individual components in such a way that they bind together. The properties of a composite depend not only on the intrinsic properties of the reinforcement (fibers) and the properties of the matrix, but also on the geometry (size and shape) of each component. In addition, the properties depend on the characteristics of the interface between the different components. Therefore, mechanical damage of composite material is associated not only with the breakage of the reinforcement and the matrix, but also with their separation at the interface [7]. This last characteristic depends on the bond between the two components. Surface roughness is also important, as it affects the degree of mechanical bonding of the components [6].

The introduction of composite materials into the oil and gas industry has provided many alternatives to expensive alloy steel, which, in addition to corrosion resistance and overall financial benefit, also has some other advantages such as easier handling of equipment since it is a material with a significantly lower unit mass. One of these materials is fiber-reinforced polymer, or so-called FRP. There are many types of fibers with which a polymer can be reinforced, such as aramid fibers, basalt fibers, carbon fibers or glass fibers. This type of composite is produced by mixing individual components in such a way that they bind, such as, for example, the incorporation of glass fibers into epoxy resin to produce fiberglass. Fiberglass consists of two different materials that together form a whole, namely a polymer and glass fibers. Epoxy resin is an example of a frequently used polymer resin, and in order for fiberglass to have satisfactory properties, it is reinforced with thin glass fibers. Epoxy resin has an excellent strength-to-density ratio, while glass provides additional strength under tensile and compressive stress. Thus, fiberglass equipment is lightweight due to the low density of epoxy resin, with significant strength due to the glass fibers in the structure [8]. The composition and proportions of epoxy resin and glass fibers primarily depend on the purpose of the fiberglass equipment, which means that the composition of the fiberglass material can vary significantly. For example, a pipe tool (such as a casing) made of fiberglass can be quite resistant to tensile and compressive stresses, but at the same

time it does not need to be designed to have good properties when subjected to torsion. It is also important to know that the matrix, in this case epoxy resin, defines the behavior of fiberglass with respect to environmental conditions, which is extremely important for downhole equipment.

Glass fibers are, along with carbon fibers, the most commonly used reinforcement for composites. A fiber can be described as an elongated, uniform material with a more or less uniform cross-section of less than 250 μm , with a length-to-diameter ratio that is typically greater than 100 [9]. The primary tasks of fibers are to absorb the load (in structural composites, fibers carry 70 to 90% of the load), provide strength, stiffness, and thermal stability, and to provide electrical conductivity or insulation, depending on the purpose of the composite [10]. The main component of glass fibers is SiO_2 , the proportion of which is usually above 50% [11]. The most commonly used glass fibers for fiberglass are E-glass fibers and S-glass fibers.

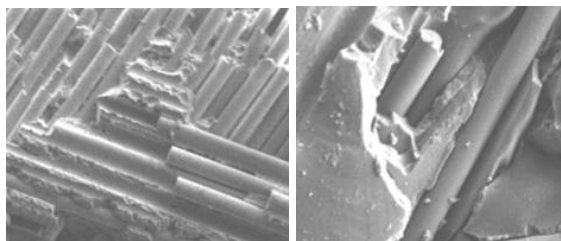


Fig. 1 A view of glass fibers in epoxy resin taken with a scanning electron microscope (SEM) [6]

In many composite materials, the main functions of the matrix are to transfer the load to the fibers and to maintain the structure and properties of the material under certain environmental conditions [12]. In addition, the matrix can affect the compressive strength, shear properties within the composite structure and the interaction of the matrix with the fibers [13]. The thermal stability of fiberglass is largely determined by the thermal resistance and stability of the polymer matrix. The heat resistance of polymeric materials is determined by their shape stability, which includes deformation when heated, and thermal stability is determined by the ability of the material to maintain chemical stability during heating [11].

2. Cementing operation

The cementation operation itself is carried out in a conventional manner, but it is necessary to pay attention to certain phases during cementation, which are considered critical when it comes to this type of material. It is necessary to adjust the cementation operational program in order to prevent breakage of fiberglass casing, given their weaker mechanical properties compared to steel casing, which primarily refers to resistance to burst and collapse, as well as axial loads [14]. Significant adjustments are required to properly handle the fiberglass casing at the rig floor and running in hole, and to ensure satisfactory bonding of the cement rock to the fiberglass after cementation. Conventional tools used for this purpose on drilling rigs are adapted to handle steel casing, including casing handling tools. Certain tools can be used for fiberglass casing without any modification, but the proportion of such equipment on site is insignificant. Accordingly, field reports show that improper handling on rig floor is a more common cause of damage to fiberglass casing than during casing running in hole, cementation, and post-cementation processes [15]. The solution to this problem lies either in modifying the equipment intended for handling fiberglass casing or in adding reinforcement to the contact surface of casing and handling tool. Handling equipment adapting most often involves tools that have a softer contact surface to minimize the possibility of damaging the outer wall of the fiberglass casing. The use of softer materials is particularly important for slips, rig tongs and elevators since each pipe is in contact with the aforementioned group of tools.

On the other hand, pipe adaptation is most often performed by coating a certain area of the pipe near the threaded joints (which are in contact with the handling tool) with a layer of appropriate material that prevents mechanical damage to the outer wall of the fiberglass casing. The described fiberglass casing have been successfully used on several projects in Argentina, Oman and Brunei [16]. In addition to all of the above, it is worth adding observations from Kuwait where fiberglass casing was handled on more than 20 wells [14]:

- when transferring casing to the rig site, only braided slings were used;
- for the initial manual tightening, special tightening tongs were used, made of a softer material that does not damage the outer surface of the fiberglass casing;
- to achieve the prescribed tightening torque for casing, an automatic pipe wrench (tongs) was used, but a significantly lower torque was used than for steel pipes, i.e. the tightening was performed to the torque prescribed by the manufacturer of fiberglass casing;
- pneumatic slips were used, instead of manual slips;
- only an annular preventer was used for well control.

If drilling rig has equipment adapted to handle fiberglass casing, it is possible to achieve a downhole speed that is close to that of a conventional steel string. For example, a project in Argentina has shown that the speed of fiberglass casing running in hole up to 0.0889 m (3 1/2 inches) in diameter is only 5.7% slower than that of an equivalent steel casing string [17]. The overall tripping time is somewhat worse, however, since the fiberglass casing is usually slightly shorter than the standard steel casing, which means that more time is spent overall due to the greater number of casing make-ups. When running in hole larger diameter casings, e.g. 0.2445 m (9 5/8 in), the difference in speed is still significant. The fiberglass casings were run in hole at an average speed of 0.3048 m/s (1 ft/s), which is three times slower than the 0.9144 m/s (3 ft/s) recorded for the steel string [14]. Fiberglass casings could withstand higher speeds of running in hole, but it is more important to avoid breakage caused by excessive axial load. Running in hole can be considered the riskiest part of the entire cementing process, since a significantly lower value of the tension is available in the event of string failure. In order to minimize such a possibility, the stability of open hole must be ensured by drilling. Therefore, the use of fiberglass casing string depends on the type of rock drilled, as well as on the level of quality of the drilled wellbore. Also, slightly larger ratios of the diameter of the wellbore to the outer diameter of the casing joints are taken into account, than is the case with steel casing.

Before cementing, due to the significantly lower total weight of the fiberglass casing, the string should be anchored to the borehole walls so that the lifting of the string, which is a direct consequence of buoyancy, does not cause critical pressure loads that can result in buckling or breakage. For this purpose, an anchor with stop rings without nuts is used in the open hole to prevent damage to the fiberglass casing, and the string thus manages to resist the compressive force. Also, this type of tool acts as a kind of centralizer, to enable uniform penetration of the cement slurry in the annular space between the string and the wellbore walls, and thus better cementing job. An alternative to casing anchoring is to use a lower density cement slurry [18], which in some cases is technically not feasible. Steel casing can also be used at the bottom of the string to provide additional weight and thereby reduce the negative buoyancy effect. Testing the quality of cement bonding behind fiberglass casing string (cement bonding) poses a significant challenge for conventional methods since there is a large difference in the acoustic properties of fiberglass compared to steel [19]. In wellbores lined with steel casing, methods based on measuring ultrasonic signals sent perpendicular to the casing have been successfully used for many decades. Pulse echo tool, which is

immersed in the fluid inside the casing, work by sending and receiving return signals with a frequency of 200 kHz to 400 kHz, which are used to calculate the acoustic impedance of the cement rock when the sound signal passes through the steel casing wall, the cement rock and the formation [20]. The parameters required for calculating the acoustic impedance of cement stone are shear velocity, compressional velocity and the acoustic impedance of steel and drilling fluid in the well, in which the ultrasonic probe is immersed. Among other things, the reliability of the method lies in the fact that the properties of steel are well known, and the changes in properties between different manufacturers of steel casings are insignificant. Due to the significant difference in the speed of sound and resonant frequency when passing through fiberglass compared to steel, the classic use of these tools is not possible, since the listed properties in the case of fiberglass are below the measurement range of typical ultrasonic scanning tools [21]. The cement bond log method, which measures the attenuation of the first return sound pulse, is also unusable in the case of cementation of fiberglass casing. The reason lies in the fact that waves passing through the cement stone and formation interfere with the slower return pulses from the fiberglass, making them almost impossible to isolate for the purpose of precise evaluation of the results.

Instead of conventional methods that calculate the boundary between steel and cement stone, the acoustic impedance of the cement stone located in the annular space between the fiberglass casing and the formation is calculated from the amplitudes between the first two pulses [20]. The first ultrasonic signal (echo) is from the boundary between the drilling fluid inside the casing and the inner wall of the fiberglass casing, while the second signal is a reflection from the boundary between the outer wall of the fiberglass casing and the cement stone, as shown in Fig. 2.

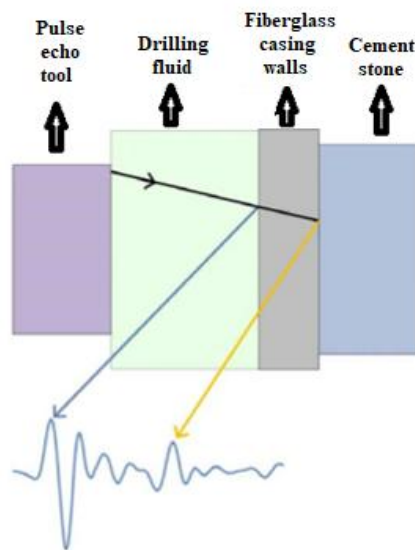


Fig. 2 View of the echoes from the boundary between the drilling fluid inside the casing and the inner wall of the fiberglass casing and from the boundary between the outer wall of the fiberglass casing and the cement stone [21]

This method of measurement can only give accurate results if the wall of the fiberglass casing is thick enough to keep the first and second signals separate. Also, the fiberglass casing must not have a structure that can significantly attenuate the signal as it passes through the wall, otherwise the second signal is unusable. The parameters needed to calculate the acoustic impedance of the cement stone and the wall thickness of the fiberglass casing are the compression rate, the acoustic impedance of the fiberglass, the attenuation factor of the signal as it passes through the fiberglass, and the acoustic impedance of the fluid inside the well. If the above parameters can be accurately determined by laboratory research, it is possible to determine the quality of the cement stone behind the fiberglass casing, as well as its wall thickness, with an ultrasonic probe. In addition to the above conditions that must be met,

differences in the composition of the fiberglass casing also pose a problem. There are several parameters that can affect the acoustic impedance of fiberglass [20]:

- a type of plastic polymer, primarily due to differences in density;
- glass fiber content (average content is about 70%);
- fiberglass casing production method;
- surface treatment method, surface smoothness;
- cavities in the wall of the fiberglass casing created during manufacturing.

Due to the lack of a database that includes different variants of fiberglass casings, the assessment of the possibility of using an ultrasonic probe (existing field equipment that does not involve additional investments) must be done separately for each well, which presents additional operational problems. Laboratory research and field results related to a project in Argentina, in which 70 wells were cased with fiberglass casings [16], provided an interesting insight into the level of casing to cement bonding of this material in relation to steel pipes. The experimental phase also included measurements of the quality of mud cake removal from the wellbore walls before cementing. An Intevap cell can be used to simulate the above process [22], and the mud cake is generated on Whatman #50 filter paper. Thus, with this device shown in Fig. 3, a quantitative evaluation of the effectiveness of a particular mud cake removal fluid formulation can be performed. Laboratory tests have shown that the best results were achieved with a water-based fluid portion containing 7% citric acid, 0.2% nonionic surfactant and 251 kg of calcium chloride (CaCl_2) per 1 m^3 of portion, followed by another water-based fluid feed containing 3% sodium carbonate (Na_2CO_3) and 2% anionic surfactant, which removed 80% of the mud cake [16].



Fig. 3 Device for laboratory testing of mud cake removal quality [22]

Also, laboratory tests were conducted to compare the bond quality of cement stone for fiberglass casing compared to steel ones. Before cementing the pipes, their outer surface is immersed in drilling fluid and then washed with a portion of fluid of the aforementioned composition, to remove the mud cake. The testing was carried out in such a way that segments of fiberglass pipe (smooth and rough surfaces) were cemented inside a larger diameter mold, and the cement slurry was dried for 48 hours at a temperature of 55°C [16]. The pipe is then axially loaded until a displacement in the opposite direction occurs, which indicates the force required to break the contact surface between the fiberglass pipe and the cement stone. The same procedure was performed with the steel pipe, so that the results could be compared. As expected, this study proved that steel protective pipes bond best to the cement stone, and a force of 23,350 N was required to move the cemented pipe, while the bond between the cement stone and the fiberglass protective pipe with a smooth (treated) surface was broken at an axial force of 13,900 N [16]. On the other hand, the bonding of the rough-surfaced fiberglass casing to the cement stone was extremely poor,

since this pipe surface remained saturated with the mud cake flushing fluid, which created poor bonding conditions at the interface due to the inefficient hydration process caused by the chemical incompatibility of the mud cake flushing fluid and the cement slurry. This is also evidence that in addition to the quality of mud cake removal, chemical compatibility between the different fluids is also extremely important. It should be noted that these results refer to a cement slurry with a density of 1649 kg/m³ (13.76 ppg), and similar results were obtained after cementing the pipes with a cement slurry with a density of 1849 kg/m³ (15.43 ppg), which proves that the change in density does not affect the quality of the bond. [16].

3. Conclusion

The use of fiberglass casing string represents a technically viable alternative to steel casings in corrosive environments. However, their successful implementation directly depends on a carefully designed and controlled cementation operation. Key success factors include limiting mechanical loads during handling and running in hole, ensuring string centering during running in hole, optimizing fluid systems and chemical compatibility, and adapted cement bond evaluation methods. However, for more accurate analyses of the cementation success of composite casings, significantly more projects of this type should be implemented in order to draw more detailed conclusions.

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Possibilities for accelerating chemical-thermal treatment

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Abstract: The intensification methods for carburizing and nitrocarburizing investigated in this study include the use of biochar, preliminary oxidation, and plastic deformation. The possibility of combining oxidation and plastic deformation was also examined.

KEYWORDS: INTENSIFICATION OF CHEMICAL–THERMAL TREATMENT, CARBURIZING, NITROCARBURIZING, BIOCARBON, OXIDATION, PLASTIC DEFORMATION, ACCELERATION OF DIFFUSION PROCESSES

1. Introduction

Chemical–thermal treatment (CTT) occupies an important place in mechanical engineering, being widely used to improve the properties of steel parts and tools. For example, in the automotive industry up to 70% of products are strengthened by carburizing, nitrocarburizing, and nitriding [1]. However, a common drawback of these technologies is the low rate of diffusion-layer formation [2]. Since the emergence of CTT as a scientific discipline, developments have followed two main paths: the creation of new CTT processes and the acceleration (intensification) of established ones. In this context, the search for and investigation of effective methods to accelerate CTT processes becomes particularly significant, as it directly contributes to resource-saving objectives [3]. A number of intensification approaches are known [4–14], and their combination is a promising direction.

The aim of this study is to investigate the feasibility of using biochars as a replacement for conventional carbon-containing components in saturating mixtures for pack carburizing and pack nitrocarburizing, as well as to evaluate the effect of combining oxidation and plastic deformation on subsequent gas nitrocarburizing.

2. Results and Discussion

Process acceleration was evaluated using the degree of intensification, defined as the relative increase in diffusion-layer thickness compared with the baseline regime:

$$\Delta = \left(\frac{h_i - h_0}{h_0} \right) \cdot 100\% \quad (1)$$

where h_i is the layer thickness after the corresponding intensification method, and h_0 is the layer thickness under the baseline regime without intensification.

The carburized layer thickness was taken as the distance from the surface to the point where the microhardness reached 550 HV. The nitrocarburized layer thickness was taken as the distance to the point where the microhardness exceeded the core hardness by 50 HV.

A promising direction for improving pack carburizing and pack nitrocarburizing is to modify the composition of saturating mixtures [12–14]. This topic has been successfully developed by the scientific school of L. G. Voroshinin at the Belarusian National Technical University, where positive results have been obtained [7, 9].

In the present study, the possibility of replacing traditional carbon-containing components with alternative ones—specifically, biochars—is considered. These materials are produced by pyrolysis of biologically derived wastes (e.g., from the food, agricultural, and other industries) [15]. It is known [16] that biochars possess a well-developed porous structure, which may potentially enhance the saturating capacity of CTT mixtures.

The relevance of this research is supported by the fact that hundreds of millions of tonnes of biological waste are generated worldwide every year [17]. The main disposal methods still remain landfilling and incineration. Incorporating this type of waste into industrial processes such as CTT is a pathway toward rational resource use and the development of secondary recycling.

Pack carburizing and pack nitrocarburizing in powder media based on biochar and charcoal were studied experimentally. The

results showed that biochar-containing mixtures provide a higher degree of process intensification compared with charcoal-based mixtures. The increase reached 21% (Fig. 1a).

At the next stage, the effect of preliminary oxidation and plastic deformation on subsequent gas nitrocarburizing was investigated. Previously, the school of Professor L. G. Voroshinin (Department of Materials Science in Mechanical Engineering, Belarusian National Technical University) reported positive results when applying these intensification methods. In particular, studies [3, 10] examined the effect of preliminary oxidation on accelerating carburizing and boriding of micro-objects, while studies [8, 11] demonstrated a positive effect of plastic deformation on accelerating boriding of micro-objects.

In the present study, an extremal dependence of the degree of intensification on preliminary oxidation temperature was identified, leading to an increase in intensification up to 38% (Fig. 1b). It was also established that the deformation degree affects the intensification nonlinearly, resulting in an increase up to 52% (Fig. 1c). These experimental findings are consistent with earlier results reported by Professor Voroshinin's school [3, 8, 10, 11].

When oxidation and plastic deformation are combined, one might expect an intensification degree of 90% as the additive sum of the individual effects (38% + 52%). However, the experimentally determined intensification degree for the combined treatment was 118%. Thus, the non-additive increment amounted to 28% (Fig. 1d).

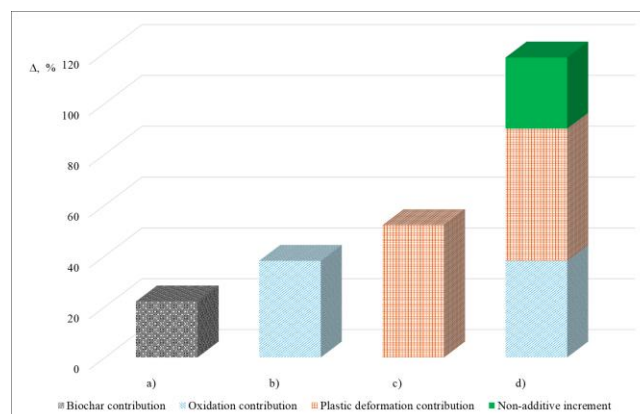


Fig. 1. Degree of intensification of carburizing and nitrocarburizing as a function of intensification methods: (a) use of biochar; (b) oxidation; (c) plastic deformation; (d) combined oxidation and plastic deformation.

3. Conclusions

1. The use of biochar as a carbon-containing component in powder saturating mixtures for pack carburizing and pack nitrocarburizing provides higher process intensification than conventional charcoal-based mixtures; the maximum increase in diffusion-layer thickness reached 21%.

2. Preliminary oxidation prior to gas nitrocarburizing exhibits an extremal dependence on oxidation temperature and can increase the degree of intensification up to 38%.

3. Preliminary plastic deformation affects the degree of intensification nonlinearly, with the maximum increase reaching 52%.

4. Combining preliminary oxidation and plastic deformation results in an intensification degree of 118%, exceeding the additive expectation ($38\% + 52\% = 90\%$); the non-additive increment is 28%.

5. The investigated intensification approaches (biochar application, preliminary oxidation, preliminary plastic deformation, and their combination) demonstrate practical potential for industrial implementation and contribute to resource-saving by involving bio-waste-derived materials in CTT processes.

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Rolling element bearing fault detection using accelerometer and laser displacement measurements

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Abstract: Rolling element bearing fault detection is of significant importance due to the widespread use of bearings across numerous industrial applications. In this study, vibration measurements using an accelerometer and a laser displacement sensor are carried out on a laboratory bearing test rig under different operating conditions, including a healthy state and bearings with localized inner- and outer-ring faults. Measurements are conducted at a constant rotational speed of 1700 rpm and the acquired signals are analysed to extract characteristic features associated with potential bearing faults. The results demonstrate that the applied methodology enables indicative bearing fault detection using both measurement approaches.

Keywords: ROLLING ELEMENT BEARINGS, FAULT DETECTION, ACCELEROMETER, LASER DISPLACEMENT SENSOR

1. Introduction

Rolling element bearings are critical components in rotating machinery, and their reliable operation is essential for the safety and efficiency of numerous industrial systems. Defects in the inner race, outer race, rolling elements, or cage are among the most common causes of mechanical failure and can lead to increased vibration levels, noise, and eventual catastrophic breakdowns if not detected at an early stage. Localized bearing defects generate impulsive vibration responses that excite structural resonances; however, these responses are often masked by background noise and other machine-related vibrations, making bearing fault diagnosis particularly challenging. Consequently, vibration-based condition monitoring has become a central topic in rolling element bearing diagnostics.

Envelope analysis is a well-established technique for detecting localized bearing faults, as it enables the demodulation of high-frequency resonance responses and reveals characteristic fault frequencies related to bearing geometry and rotational speed [1,2]. Randall and Antoni demonstrated that envelope analysis can effectively extract these fault-related features, provided that appropriate band-pass filtering is applied prior to demodulation [2]. To further enhance fault detection under noisy operating conditions, Antoni introduced spectral kurtosis as a frequency-dependent indicator capable of identifying impulsive, non-Gaussian signal components associated with bearing defects [3]. Based on this concept, the kurtogram was proposed as a systematic tool for selecting the optimal frequency band for envelope analysis in rotating machinery diagnostics [4]. This method was later refined into a fast, multi-resolution implementation, significantly improving its computational efficiency and practical applicability [5].

In recent years, the increasing implementation of data-driven and machine learning-based diagnostic techniques has intensified the need for high-quality, well-labeled experimental datasets. Antunovic et al. [6] evaluated machine learning performance using the CWRU bearing dataset, based on accelerometer measurements on the roller element bearing (REB) housing, directly connected to the REB outer ring. In simulation models, the primary degree of freedom is the radial displacement of the sleeve, directly connected to the inner ring. Since measurements focused on the inner ring are generally rare or unavailable, this study was motivated to perform vibration measurements using both an accelerometer and a laser displacement sensor on a laboratory test rig under different operating conditions, including a healthy state and bearings with localized inner- and outer-ring faults. The signals measured at a constant rotational speed of 1700 rpm were processed to extract fault-related features, enabling comparison of the two diagnostic approaches. Accelerometer data were processed using envelope spectrum analysis, while laser displacement signals were evaluated in the order domain to isolate defect-related components.

2. Experimental setup

The experimental setup is based on the DyLab Bearing Test Simulator (BTS-100) and is shown in Fig. 1. Sensor locations are indicated as follows: (1) accelerometer, (2) laser displacement sensor and (3) integrated single-pulse-per-revolution (1 PPR) analog tachometer reference sensor. A PCB 352C34 piezoelectric accelerometer is mounted vertically on the bearing housing to capture high-frequency vibration responses and has a nominal sensitivity of 100 mV/g. A Micro-Epsilon ILD2300-50LL laser displacement sensor is used to measure radial shaft displacements, providing a maximum sampling rate of 49.13 kHz with a reduced measuring range of 25 mm.

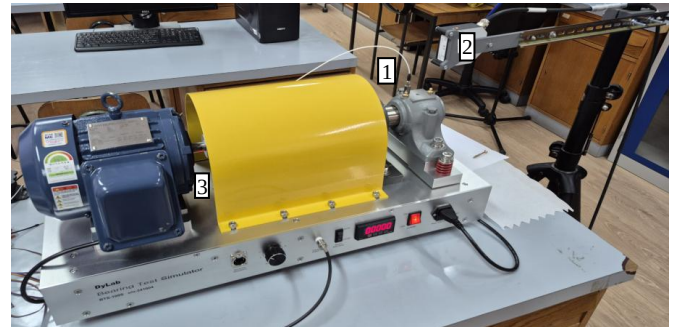


Fig. 1 Laboratory bearing test rig with sensors (1 – accelerometer, 2 – laser displacement sensor, 3 – phase reference sensor)

A relatively rigid shaft is supported by two healthy REBs, with the faulty deep groove REB mounted on an overhung section of the shaft. The drive unit consist of a 0.75 kW electric motor, capable of operating at rotational speeds up to 1800 rpm. Data acquisition is carried out using a DEWESoft SIRIUS Modular system, which offers eight simultaneously sampled analog input channels suitable for vibration and acoustic measurements.

3. Characteristic bearing fault frequencies

The characteristic defect frequencies of rolling element bearings are determined by the bearing geometry and the shaft rotational speed. The ball pass frequency outer race (BPFO) corresponds to defects on the outer ring and is calculated as:

$$BPFO = \frac{n}{2} f_r \left(1 - \frac{d}{D} \cos \theta \right), \quad (1)$$

while the ball pass frequency inner race (BPFI) corresponds to defects on the inner ring and is given by:

$$BPFI = \frac{n}{2} f_r \left(1 + \frac{d}{D} \cos \theta \right). \quad (2)$$

Here, n is the number of rolling elements, d is the rolling element diameter, D is the pitch diameter, θ is the contact angle, and f_r is the rotational frequency. These frequencies are critical for bearing fault

diagnosis, as they determine the locations of spectral peaks associated with inner and outer race defects.

4. Time-domain signals

The tested faulty REB (NTN 6307) consists of 8 balls, with harmonics $BPFO = 3.06 \times$ and $BPFI = 4.94 \times$. A sampling frequency of 50 kHz is employed for all measurement channels. Experimental results obtained at a constant rotational speed of 1700 rpm are presented.

Figs. 2–4 illustrate time-domain signals from accelerometer and laser sensors, comparing responses for a healthy bearing against bearings with localized faults on the outer and inner rings. These visualizations typically show lower-amplitude waveforms for healthy bearings, while those with damage exhibit periodic impulses or elevated vibration levels due to fault impacts. Healthy bearing produces steady, low-variance signals in the time domain from both sensors, reflecting uniform rolling without defects. Accelerometer data often appears as baseline noise, and laser measurements indicate minimal displacement variations.

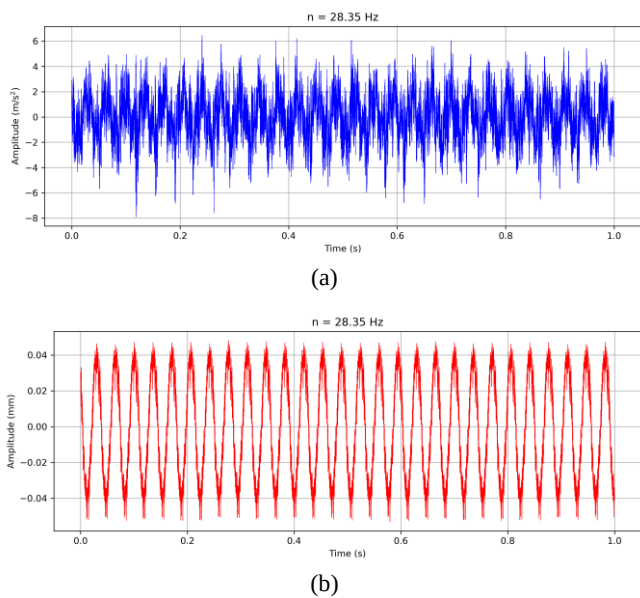


Fig. 2 Time-domain signal of a healthy bearing: (a) accelerometer, (b) laser sensor

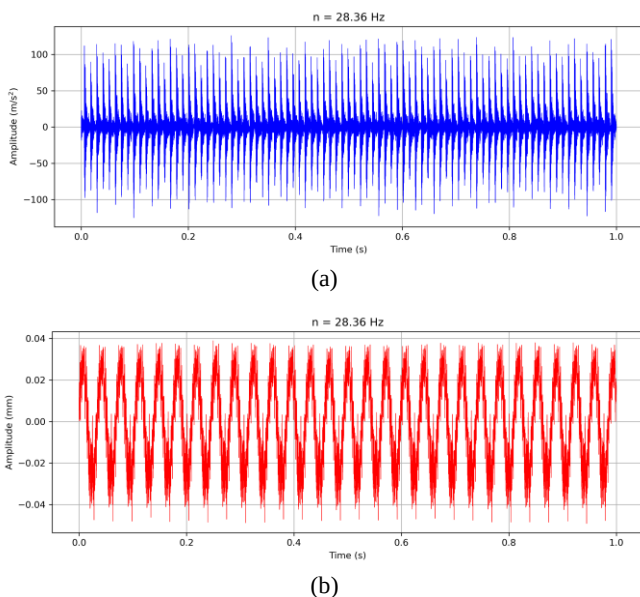


Fig. 3 Time-domain signal of a bearing with localized fault on the outer ring: (a) accelerometer, (b) laser sensor

Figures corresponding to outer ring faults display repetitive high-amplitude peaks in accelerometer signals, caused by rolling elements repeatedly striking the defect. Laser sensor data may show correlated displacement spikes, with periods matching ball-pass frequency. Inner ring defects produce less periodic but higher-frequency impulses in time-domain plots, as the defect rotates with the shaft. Accelerometers capture sharper transients compared to outer race faults, while laser sensors detect subtler positional shifts.

Figures 5–7 illustrate the time-domain signals obtained from the accelerometer and laser sensors over a shortened time interval of 0.1 s, allowing clearer visualization of the signal features and transient vibration responses.

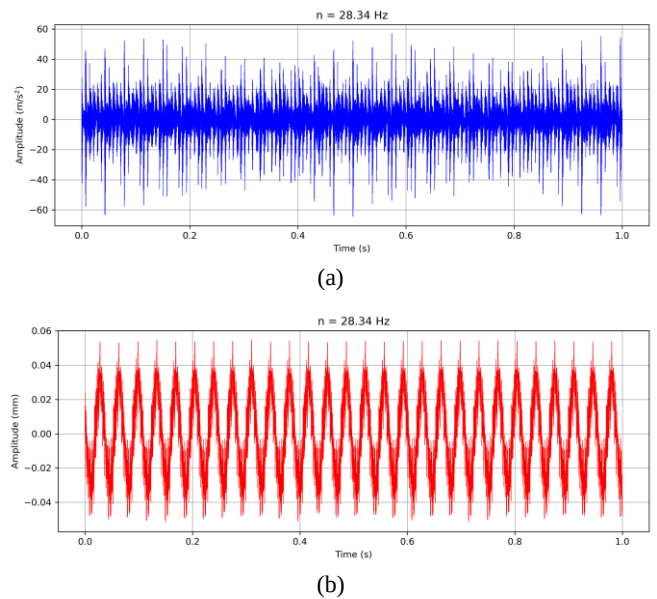


Fig. 4 Time-domain signal of a bearing with localized fault on the inner ring: (a) accelerometer, (b) laser sensor

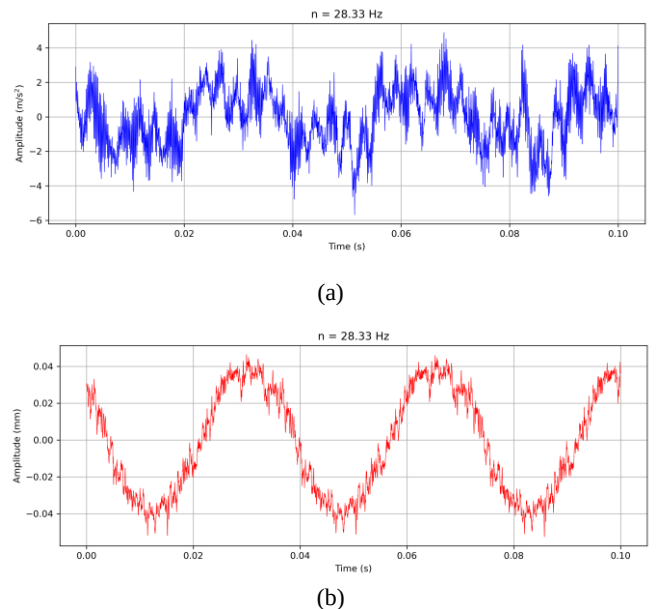


Fig. 5 Time-domain signal (0.1 s) – healthy bearing: (a) accelerometer, (b) laser sensor

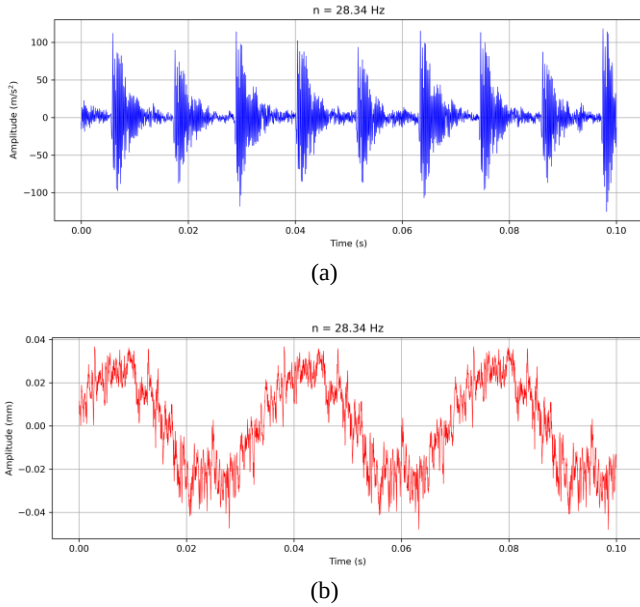


Fig. 6 Time-domain signal (0.1 s) – bearing with localized fault on the outer ring: (a) accelerometer, (b) laser sensor

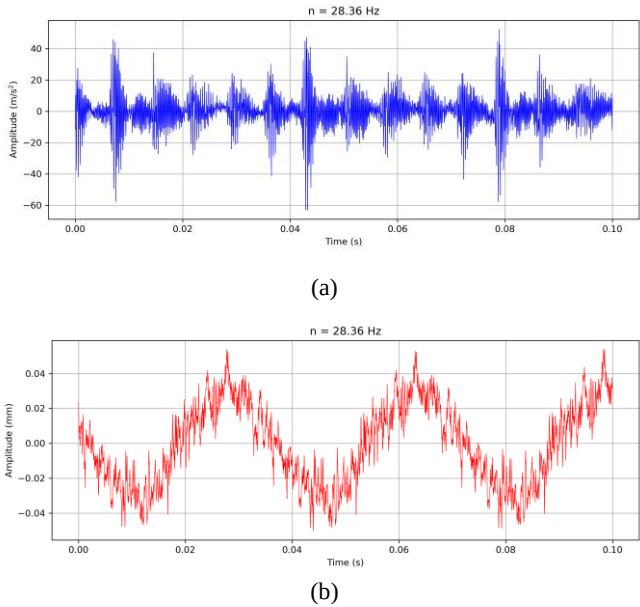


Fig. 7 Time-domain signal (0.1 s) – bearing with localized fault on the inner ring: (a) accelerometer, (b) laser sensor

5. Acceleration signal processing

Figs. 8–10 display the envelope spectra obtained from the accelerometer for a healthy bearing and for bearings exhibiting localized defects on the outer and inner rings. The spectra highlight the harmonic frequencies of BPFO and BPFI associated with bearing faults.

The envelope spectra were obtained using a Hilbert transform-based demodulation procedure applied to the acceleration signal. First, the mean value was removed to eliminate signal offset and improve numerical stability. Next, the analytic signal was computed using the Hilbert transform. The envelope was obtained as the magnitude of the analytic signal. This step removes the high-frequency carrier component and retains the amplitude modulation caused by repetitive bearing impacts. No band-pass filtering is applied prior to demodulation. Finally, the Fast Fourier Transform

(FFT) of the envelope signal was calculated, and only the positive frequency components were retained and properly normalized. The resulting envelope spectrum reveals characteristic defect frequencies (BPFI and BPFO) and their harmonics, which are not directly visible in the conventional vibration spectrum.

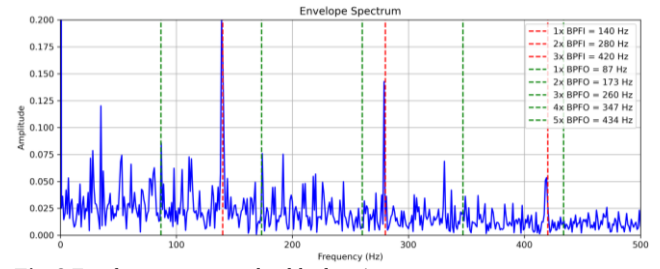


Fig. 8 Envelope spectrum – healthy bearing

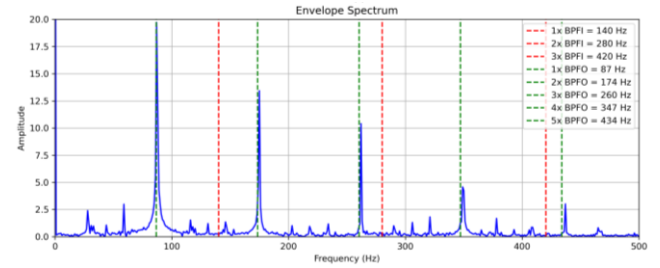


Fig. 9 Envelope spectrum – bearing with localized fault on the outer ring

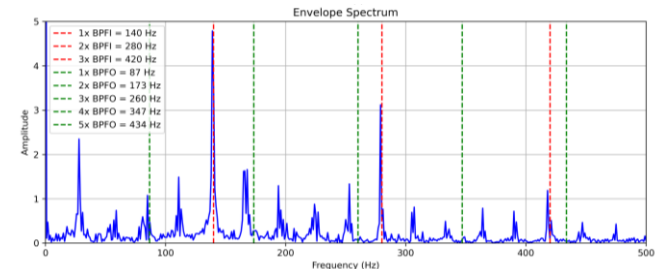


Fig. 10 Envelope spectrum – bearing with localized fault on the inner ring

6. Laser displacement signal processing

Since the laser sensor measures displacement rather than acceleration, the impact impulses generated by bearing faults are often insufficiently pronounced for effective envelope spectrum analysis. Therefore, the vibration signal acquired using the laser displacement sensor was processed in the order domain to enable detection of characteristic bearing defect frequencies. First, the laser displacement signal was transformed from the time domain to the angular domain and the mean value was removed to eliminate signal offset. The signal was subsequently resampled into the angular domain using tachometer-based angle synchronization, thereby ensuring constant angular resolution per revolution. To suppress low-order components associated with rotational effects, a high-pass Butterworth filter (HP) with a cutoff at the first two orders (Fig. 11) is applied. Figure 12 presents the tested and filtered signals for the bearing with an outer ring defect, while Figs. 13–15 show the corresponding order-tracked power spectral densities (PSDs) for the healthy bearing and for bearings with outer- and inner-ring defects.

In laser-based radial displacement measurements, the spectral signatures of BPFO and BPFI harmonics are generally less pronounced than in acceleration-based measurements. The outer ring fault ($BPFO = 3.06 \times \text{shaft order}$), is dominantly characterized

by the $3\times$ and $4\times$ orders. On the other hand, the inner ring fault (BPFI = $4.94\times$ shaft order) exhibits a clear dominance of the $5\times$ order, which can be considered as a characteristic indication of an inner ring defect. Despite the reduced prominence of fault-related features in displacement-based measurements, the results demonstrate that laser measurements still exhibit characteristic spectral patterns associated with different types of bearing defects.

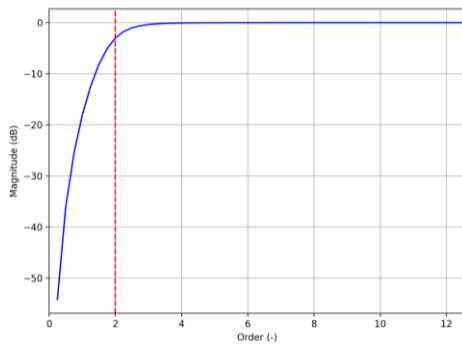


Fig. 11 Magnitude response of the Butterworth high-pass filter in the order domain

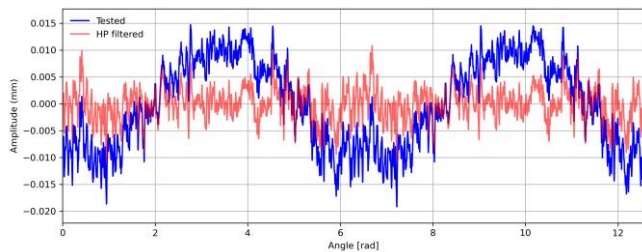


Fig. 12 Comparison of tested and filtered signals – bearing with localized fault on the outer ring

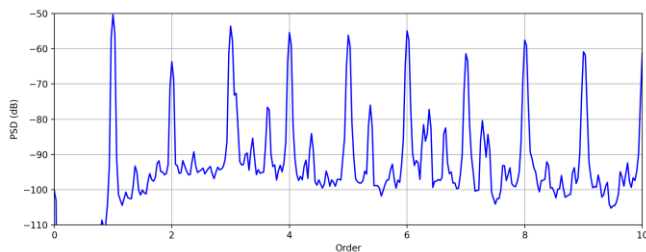


Fig. 13 Order-tracked power spectral density – healthy bearing

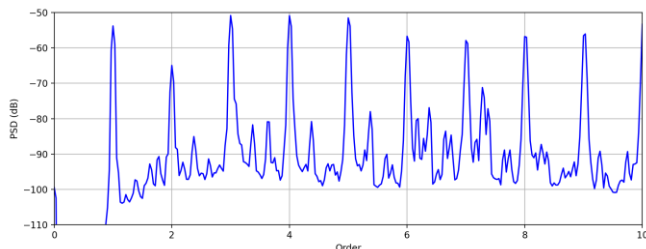


Fig. 14 Order-tracked power spectral density – bearing with localized fault on the outer ring

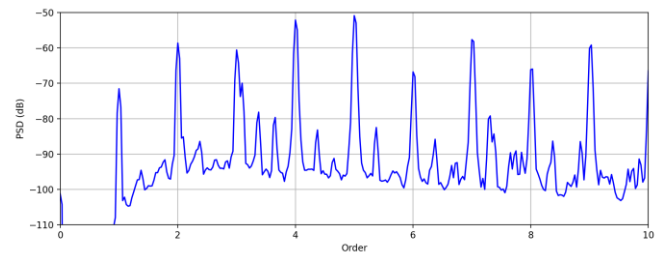


Fig. 15 Order-tracked power spectral density – bearing with localized fault on the inner ring

7. Conclusion

The study demonstrates that rolling element bearing faults can be reliably detected under laboratory conditions using vibration-based measurements. Accelerometer signals were analyzed in the time domain and further processed using envelope spectrum analysis, which enabled clear identification of characteristic inner-ring (BPFI) and outer-ring (BPFO) fault frequencies and their harmonics. Laser displacement measurements were evaluated in the order domain to extract defect-related components. A high-pass Butterworth filter was applied to suppress low-order contributions associated with shaft-related effects. Although fault-related orders were detectable, their amplitudes were less pronounced compared to the acceleration-based results, reflecting the lower sensitivity of displacement measurements to high-frequency impulsive events. Overall, the accelerometer combined with envelope analysis provided superior fault detectability and clearer diagnostic indications, whereas the laser displacement sensor represents a valuable non-contact alternative with complementary capabilities and specific practical considerations.

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Development of an All-Optical Platform for Real-Time Monitoring of Hypoxia Dynamics

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Abstract: Oxygen levels in the cellular microenvironment, particularly under hypoxic conditions, play an active regulatory role in modulating cellular function, signaling pathways, and metabolic networks. A radically new concept for sensing the oxygen concentration at the extracellular liquid microenvironment was developed, based on nanoconfined upconversion optical sensors. The experimental achievements in developing technologically applicable strategies for minimally invasive monitoring of the oxygen concentration in cell microenvironment will be presented and discussed.

Introduction

Viral infections remain a significant global health challenge, with emerging and re-emerging pathogens posing persistent threats to public health, economic stability, and societal resilience. Rapid and accurate assessment of infection status at the cellular and tissue levels is crucial for monitoring disease progression and evaluating treatment efficacy. Traditional diagnostic approaches often fail to capture the complex, dynamic interplay between viral replication, host immune responses, and microenvironmental factors such as oxygen availability.

Hypoxia - an altered oxygen balance in the local microenvironment - is increasingly recognized as a key modulator of viral pathogenesis, influencing viral replication, immune evasion, and inflammatory responses. However, direct, real-time control and monitoring of hypoxia dynamics in the intercellular space remain largely unexplored, in part due to existing at the moment technological limitations.

At this research paper this critical gap project is addresses by integrating optical control technologies with advanced microenvironmental sensing to monitor viral infection status through the modulation and observation of hypoxia. This approach is timely due to:

- The increasing frequency of viral outbreaks (e.g., SARS-CoV-2, influenza, emerging zoonotic viruses) that demand innovative diagnostic and monitoring strategies;
- Advances in optical and photonic tools that now enable precise, non-invasive control of cellular microenvironments.

Prerequisites and means for solving the problem

The study of the oxygen content of water is an important area of research because of its central role in the biochemistry of life. The ability to quantify in real time both the spatial distribution and temporal dynamics of oxygen concentration in the intercellular aquatic microenvironment is necessary for a complete understanding of the mechanisms involved in both normal physiology and disease states. Oxygen content at the cell microenvironment, especially under hypoxic conditions, plays an active and regulatory role in modulating cellular function,

signaling pathways, and metabolic networks.

There is a broad consensus [1] in the literature, that optical methods for O₂-sensing are less invasive and able to provide time-resolved and 2-dimensional (2D) spatial evolution of the O₂ distribution [2, 3]. Optical-sensing approaches based on phosphorescence quenching enable the direct visualization and quantification of oxygen concentrations across the intercellular aquatic phase, even in tissues [4]. The recent development of the phosphorescent oxygen sensors are summarized in comprehensive reviews [5, 6] demonstrating the importance of the studied problem for the fields of chemistry, biophysics and medicine.

Nevertheless, the process of optical oxygen sensing - either via the phosphorescence quenching methods [6, 4] or via the process of triplet-triplet annihilation upconversion, leads to the unwanted (often uncontrolled) but very effective generation of singlet oxygen [7]. The singlet oxygen oxidases efficiently intra-

chain carbon double bonds [8] or terminal double bonds [9] even at physiologically relevant temperatures. Furthermore, the singlet oxygen, formed during the optical excitation, takes part in a Diels-Alder type process on a parent sensitizer molecule (in the case of TTA-UC or methods, based on phosphorescence quenching), which leads to a loss of conjugation in the π -system and to a real-time decrease of the Q-band absorption. A similar process is also involved in photo-bleaching of the fluorescent chromophores, e.g. anthracene- and perylene- derivatives, etc. [10]. The problem of unavoidably generated singlet oxygen is exacerbated when high excitation intensities (on the level of MW×cm⁻²) are used - stimulated photo-oxidation not only affects the sensing molecules (metallated macrocycles) but also the surrounding biological sample [11].

Optical sensing technologies and modalities, based on sacrificial colorimetric change of reporter molecules, immobilized in hydrogels [12, 13] are being used for determination of the oxygen content in vitro in cell cultures, exposed to external stimuli - such as medications, nutrient changes, hypoxia or infection - and also to internal alterations as gene knockout, knockdown or gene gain. Below we will describe the competitive advantages of the arising HypoVir technology compared to the current technologies used for oxygen sensing.

Solution of the examined problem

At this research paper a radically new concept for sensing the oxygen concentration at the extracellular liquid microenvironment is proposed. The process of Triplet-Triplet Annihilation Upconversion (TTA-UC) performed in nanoconfinement is used as a sensing tool.

TTA-UC takes place in a multi-chromophore system consisting of energetically optimized pairs of sensitizer and emitter molecules, well dissolved in hydrophobic matrix, Figure 1 [14]. Photon energy is absorbed (Figure 1, the dark orange arrow) in the Q-band of the sensitizer and stored in its triplet state, which is formed after the process of intersystem crossing (ISC). The excited sensitizer triplet state has three channels for relaxation: (i) - via emission of a strongly red-shifted photon, belonging to the process of residual phosphorescence (the dotted orange arrow, Figure 1, the process is marked with rPh); (ii) - via effective generation of singlet oxygen (Figure 1, the dark gray dotted arrow, the process is marked with ET, [15]); last but not least - (iii) via the process of triplet-triplet transfer (Figure 1, the dotted blue arrows, the process is marked with TTT). It is important to note, that both, the lifetime (τ^{rPh}) and the quantum yield ($Q.Y.^{rPh}$) of the residual phosphorescence are strongly reduced by the presence and concentration of the quenchers - either ground state oxygen molecules [16] or ground state emitter molecules [17]. The third relaxation channel is accelerated by the process of the triplet-triplet annihilation upconversion (TTA-UC), in which the excited triplet states of two emitter molecules undergo triplet-triplet annihilation (TTA), so that one emitter molecule returns to its singlet ground state and the other molecule gains the energy of both triplet states and is excited to the higher singlet state. As the singlet state emitter radiatively decays back to the ground state, a delayed fluorescence photon (the blue arrow, Figure 1, the process is denoted dF) of

higher energy than the excitation photon is emitted. Through the process of TTA-UC, both emitter molecules effectively return to the ground state and can again participate in the quenching of the excited sensitizer triplet state.

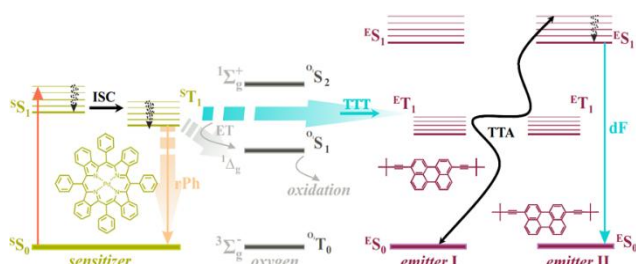


Figure 1. Simplified energetic scheme of the triplet-triplet annihilation upconversion (TTA-UC) process in an oxygen-saturated environment. **Insets:** structure of meso-tetraphenyl-tetrabenzoporphyrin palladium(II) (PdTBP) sensitizer (left), structure of 3,10-bis(3,5-dimethoxyphenyl)perylene (BDMP) emitter (right).

Results and discussion

An oxygen nanosensor **can be considered** minimally invasive **only if several** experimental criteria are simultaneously met:

(i) Confinement of the TTA-UC – O₂-sensing system in a hydrophobic microenvironment ensures 3D-localization of the permanently generated singlet oxygen, Figure 2a. The NC-core consist of a mixture of beeswax (BW, 40%wt.), squalene (SQ, 40% wt.) and rice bran oil (RBO, 20% wt.). We could not find oxygen solubility data for such complex mixture. On the one hand, the solubility of oxygen in ground state (³O₂) in the oil-phase of the NC-core is more than 10 times higher, than the solubility of oxygen in the surrounding water phase [18]. On the other hand, beeswax exhibits exceptionally high barrier properties against water vapor and molecular oxygen [19, 20]. We assume that not only the solubility of oxygen in the hydrophobic NC-core, but also the solubility of singlet oxygen is much lower, than the solubility of oxygen in the water microenvironment [21, 22]. Presence of large amounts of SSOS materials – SQ [23] and RBO [24], ensure effective and locally (within the NC-core) binding of the generated singlet oxygen; (ii) The excitation intensities required for the entire measurement process must be kept as low as possible to minimize the electromagnetic stress on the living entity, ideally below 10 W×cm⁻². The evolution of the living species occurred under light intensities equivalent to 1 Sun (i.e., 100 mW×cm⁻², AM 1.5). Therefore, light intensities up to 100 Suns may be considered acceptable. Often, the oxygen sensing experiments were performed at orders of magnitude higher intensities.

(iii) For stabilization of oil-in-water nanoconfined objects, surfactants with high HLB-value and high solubility in water are used [25]. For instance, non-ionic surfactant [26], such as Polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100, HLB = 13.4, defined following the Griffin's method), soluble in all proportions at 25 °C in water [27]. As well as ionic surfactant, for instance Sodium dodecyl sulfate (SDS, HLB = 40, defined following the Davies' method) soluble in water up to 20% wt. at 25 °C [28]. The use of highly water soluble surfactants has a major disadvantage: the molecular concentration of free surfactant in the extracellular water microenvironment is high, with a pronounced cell-toxic effect [29, 30].

Figure 2b shows the experimental set-up for all-optical sensing of intercellular water microenvironment. The diode laser beam pass through the spatial filter in order to reach nearly TEM₀₀ transversal intensity distribution. A defocusing achromatic lens (the violet lens) placed on an electronically controlled μ -positioning stage (DL125 Delay Line Stage, Newport Corp.) controls the excitation spot diameter. The luminescence emission generated by the sample was collected with the same apochromatic lens, thus the

excitation- and observation- spots are completely spatially overlapped. The used laser heads (TCLDM9, Thorlabs Inc.) allow current modulation *via* modulation input, depending on the maximal current supplied, the modulation frequency varies from 50 kHz up to 200 kHz. Therefore, the laser intensity was modulated by an arbitrary pulse generator (TGA1244, TTI Inc.) with caring frequency of 40 MHz. The obtained laser diode pulses have almost rectangular time-shape, with rise- and decay- slopes less than 2.5×10^{-6} s.

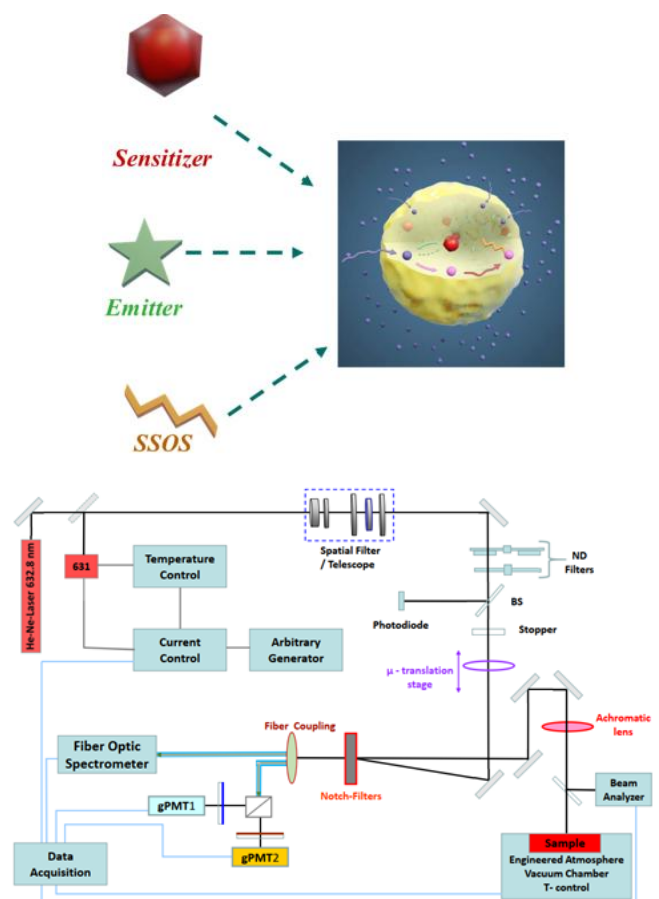


Figure 2: (a) - Scheme of the sensing nanocapsules (NC) proposed in this project; (b) - Set-up for registration of the dynamical parameters of the TTA-UC in engineered atmosphere with actively controlled oxygen content, active temperature control and temperature stabilization.

One edge-beam splitter (FF01-694/SP-25, Semrock Inc.) was used to spatially separate the sensitizer residual phosphorescence and delayed emitter UC-fluorescence, registered by gPMT1 and gPMT2, accordingly. Additional edge-filters, namely a short pass (SP01-633RS-25, Semrock Inc.) filter with cutting wavelength $\lambda_c = 650$ nm and long pass (HQ700LP, Chroma GmbH) filter with cutting wavelength $\lambda_c = 700$ nm, were installed in front of the registration opto-electronic devices at the delayed-fluorescence branch and phosphorescence branch, respectively. The normalized absorption spectra and normalized luminescence spectra of the sensitizer and emitter are shown in **Figure 3**.

The gPMT's are working in analogous mode with a rise- and decay-times less than 30×10^{-9} s. The gated photo-multiplier tubes are set in "Normally OFF" mode. The gating pulses should be with an amplitude of $3.5 \text{ V} \div 5 \text{ V}$ applied on 10 k Ω load, with maximal repetition rate of 10 kHz. The gPMT-operation delay is less than 0.2×10^{-6} s. Each gPMT is equipped with a wide bandwidth amplifier unit C9663 (DC up to 150MHz, Hamamatsu Photonics Inc.), where the current input signal from the photomultiplier tube is directly converted into a voltage output signal.

(1) Since the optical sensors are nanoconfined, and physically situated in a *close proximity* with sacrificial singlet oxygen materials, no singlet oxygen diffuses outside the sensors.
 (2) Instead monitoring of the dependence on oxygen concentration either of phosphorescent lifetime, or delayed fluorescence lifetime of the reporter molecules, or dependence on oxygen concentration of a colorimetric changes, we identify that the observation of loss of TTA-UC-luminosity delivers *significantly higher oxygen sensitivity*, **Figure 4**.

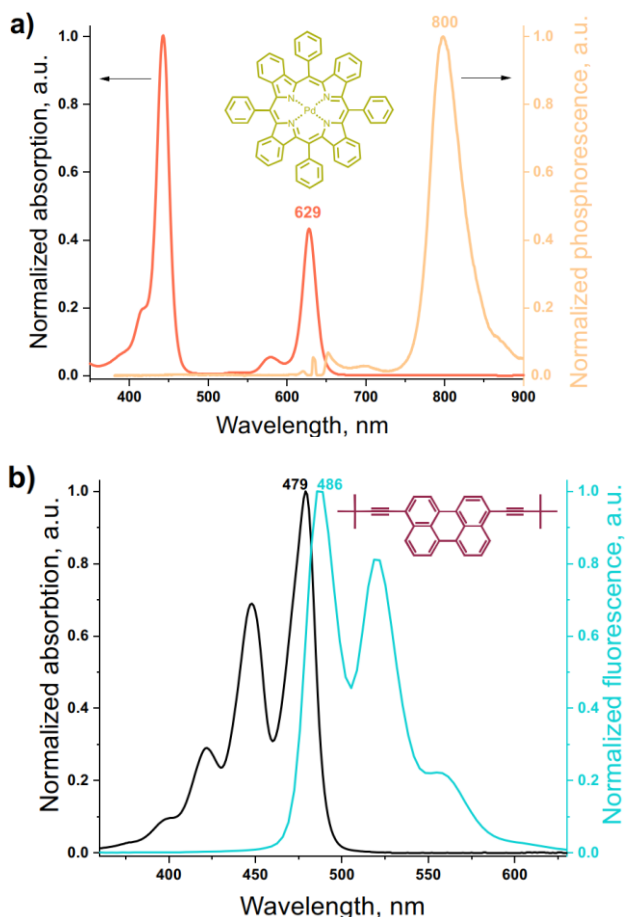


Figure 3: (a) Normalized absorption spectrum (red line) and normalized luminescence spectrum (brown line, excitation wavelength $\lambda = 635$ nm) of the sensitizer molecule in toluene solution; (b) Normalized absorption spectrum (violet line) and normalized fluorescence spectrum (blue line, excitation wavelength $\lambda = 459$ nm) of the emitter molecule in toluene solution. **Insets:** structure of meso-tetraphenyl-tetrabenzoporphyrin palladium (II) (PdTBP) – sensitizer (a), structure of 3,10-bis(3,5-dimethoxyphenyl)perylene (BDMP) – emitter (b).

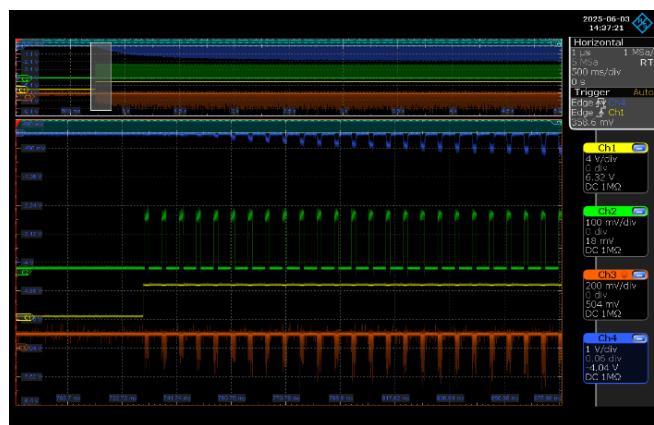


Figure 4: (up) - Time-resolved intensity of the optical signals of dF (the blue channel) and rPh (the orange channel) in oxygen saturated water macro-environment (160mm Hg); excitation pulses

(the green channel); enable pulse (the yellow channel); (down) - The temporal magnification of the first 25 excitation pulses clearly shows the intramolecular nature of the rPh signal: even at the first 5 excitation pulses, there is a non-zero residual phosphorescence intensity. Conversely, the intermolecular nature of the dF signal explains the complete suppression of upconversion during the first 5 excitation pulses

Conclusion

We demonstrate an original optical sensing technique for monitoring local oxygen concentration based on the observation of local quenching of nanocapsule (NC) luminescence. Rather than monitoring the oxygen dependence of either the phosphorescence lifetime or the delayed fluorescence lifetime of reporter molecules, we show that significantly higher oxygen sensitivity can be achieved by observing the local decrease in delayed fluorescence intensity. This experimental approach offers several advantages, particularly under hypoxic conditions: it directly reflects local oxygen concentration without the need for spatial or temporal averaging; it operates at low excitation intensities; and the photogenerated singlet oxygen is completely chemically bound within the sensing nano capsules, preventing diffusion into the surrounding aqueous microenvironment.

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Comparative Analysis of Natural Ruby and Synthetic Corundum Ceramics by UV-Vis and Raman Spectroscopy

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Abstract: This study presents a comparative spectroscopic investigation of natural Cr^{3+} -bearing ruby and multiphase Al_2O_3 -based ceramics derived from industrial waste. The natural corundum shows characteristic Cr^{3+} crystal-field absorption bands at ~ 405 and ~ 550 nm and sharp R-line emission near 693 nm, confirming a structurally ordered $\alpha\text{-Al}_2\text{O}_3$ lattice. In contrast, the waste-derived ceramics exhibit charge-transfer-dominated absorption associated mainly with V^{5+} and Fe^{3+} under oxidizing firing conditions. Strong UV absorption (220–300 nm) and the absence of vanadium crystal-field transitions indicate predominant V^{5+} stabilization, consistent with chemical and phase analysis. The ceramics display high lightness ($L^* \approx 93$) and a yellow hue ($b^* = 10\text{--}23$) governed by ligand-to-metal charge-transfer processes. The results demonstrate the effectiveness of combined UV-Vis and Raman spectroscopy for distinguishing crystal-field and charge-transfer mechanisms and for resolving dopant-related colour formation in alumina systems.

Keywords: $\alpha\text{-Al}_2\text{O}_3$; WASTE-DERIVED CERAMICS; VANADIUM OXIDATION STATE; CRYSTAL-FIELD TRANSITIONS; CHARGE-TRANSFER ABSORPTION; UV-VIS SPECTROSCOPY; RAMAN SPECTROSCOPY

1. Introduction

Corundum ($\alpha\text{-Al}_2\text{O}_3$) is a structurally robust and chemically stable oxide occurring both as a natural mineral and as an industrial ceramic material. Its exceptional mechanical strength, thermal resistance and chemical inertness make it essential for refractory, structural and optical applications. In its gem-quality form, ruby represents chromium-doped corundum, where Cr^{3+} substitutes for Al^{3+} in octahedral coordination, producing the characteristic red colour through spin-allowed d-d transitions and sharp R₁–R₂ luminescence lines near 693–694 nm. The crystal-field behaviour of Cr^{3+} in corundum has been extensively described within the framework of crystal-field theory and electronic spectroscopy [1–4].

In addition to chromium, minor transition metal ions such as Fe, Ti and V may significantly influence the optical absorption behaviour and hue of corundum. Vanadium is particularly important due to its multiple oxidation states (V^{3+} , V^{4+} , V^{5+}), each associated with distinct electronic and charge-transfer transitions. In natural systems, V^{3+} may contribute to absorption in the UV-blue region, whereas V^{4+} and especially V^{5+} are commonly linked to broad $\text{O}^{2-} \rightarrow \text{V}$ charge-transfer bands that modify colour saturation and absorption edge characteristics [5–7,10].

Natural Cr^{3+} -bearing corundum from the village of Mishevsko (Eastern Rhodopes, Bulgaria) was recently characterized using UV-Vis, Raman and photoluminescence spectroscopy [1]. The study revealed well-resolved Cr^{3+} absorption bands at ~ 405 and ~ 550 nm, sharp R₁–R₂ emission lines, and additional absorption features in the UV-blue region attributed to minor V and Ti admixtures. These results define a structurally ordered $\alpha\text{-Al}_2\text{O}_3$ reference system in which chromium is the principal chromophore and vanadium acts as a secondary modifier of the optical response.

In contrast, Al_2O_3 -based ceramics derived from industrial waste represent chemically complex multicomponent systems containing vanadium, iron, alkali elements and silica-rich phases. During high-temperature processing in an oxidizing atmosphere, vanadium is predominantly stabilized as V^{5+} , favouring intense ligand-to-metal charge-transfer transitions in the UV region. Moreover, the coexistence of multiple crystalline polymorphs of Al_2O_3 (α - and κ -phases), together with cristobalite (SiO_2) and residual amorphous material, results in heterogeneous optical behaviour governed by both crystal-field and charge-transfer mechanisms.

Consequently, colour formation in such engineered ceramics cannot be interpreted solely within the classical crystal-field framework typical of ruby, but must also consider oxidation-state equilibria, phase interactions and defect chemistry.

UV-Vis diffuse reflectance spectroscopy provides information on electronic transitions and oxidation states of transition metal ions, whereas Raman spectroscopy offers a structural fingerprint of $\alpha\text{-Al}_2\text{O}_3$ and related ceramic phases, as well as luminescent signatures of Cr^{3+} and other dopants [3,8]. The combination of these techniques enables differentiation between Cr^{3+} -controlled crystal-field coloration and vanadium- or iron-dominated charge-transfer absorption in complex Al_2O_3 -based systems.

The present study presents a comparative spectroscopic investigation of a natural Cr^{3+} -bearing ruby [1] and synthetic Al_2O_3 -based multiphase ceramics derived from industrial waste containing a wide range of impurities, including vanadium and iron. The objective is to correlate dopant chemistry and oxidation state with UV-Vis absorption behaviour, Raman structural features and Cr^{3+} luminescence characteristics, as well as CIELAB colour coordinates. By comparing a structurally ordered natural $\alpha\text{-Al}_2\text{O}_3$ reference with chemically complex waste-derived ceramics, the study highlights the capability of combined UV-Vis and Raman spectroscopy to distinguish crystal-field and charge-transfer mechanisms, detect oxidation-state variations, and resolve subtle differences in dopant environment and lattice structure.

2. Materials and Methods

2.1 Samples

Ruby: Natural corundum containing Cr^{3+} and traces $\text{V}^{3+}/\text{V}^{4+}$ and other transition metal ions (after Ref. [1]).

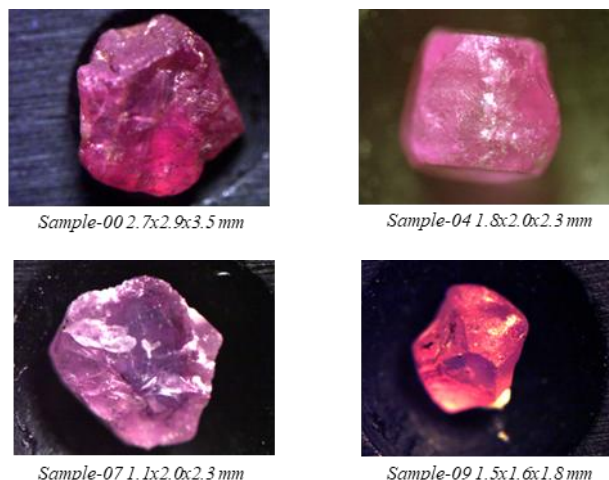


Figure. 1 Vanadium-bearing natural ruby crystals from the Eastern Rhodopes (Bulgaria). The colour variations reflect minor vanadium incorporation in Cr^{3+} -doped $\alpha\text{-Al}_2\text{O}_3$, where vanadium acts as a secondary chromophore modifying the UV-blue absorption region.

Synthetic ceramic: The spent catalyst with a complex chemical and phase composition is mixed with chemically pure reagents (Al_2O_3) for the production of multiphase ceramics by one-step solid-phase sintering method. The mixture was homogenized and sintered in a laboratory muffle furnace with a heating rate $500^\circ\text{C}/\text{h}$ in air with isothermal retention of 2 h at the final temperatures of 1200°C and 1300°C .

2.2 Analytical methods

Phase composition was analysed using a Bruker D8 Advance and Empyrean (Malvern Panalytical) powder X-ray diffractometers with $\text{Cu K}\alpha$ radiation operating at 40 kV and 30 mA, in the range $10 - 80^\circ 2\theta$. Pulse height distribution (PHD) optimization procedures have been applied in order to reduce the fluorescence-induced background and peak-to-background ratio.

Wavelength Dispersive X-ray Fluorescence Spectroscopy (WDXRF) was used to determine the chemical composition using Supermini 200 (Rigaku, Japan) spectrometer operating at 50 kV and 4.00 mA. The powder samples were pressed to obtain a tablet. The weight ratio of the amount of sample to the amount of glue (Acrawax C powder) was 5:1. A semi-quantitative method (SQX) was used to determine the elemental composition.

Diffuse reflectance spectra were recorded using a Cary 4000 (Agilent) UV-Vis spectrophotometer equipped with an internal DRA 900 integrating sphere accessory. Measurements were performed in the $200\text{--}800\text{ nm}$ spectral range with a spectral resolution of 1 nm. The reflectance data were baseline-corrected and transformed using the Kubelka-Munk function $F(R)$ to obtain absorption-related spectra suitable for comparison with the natural corundum reference. UV-Vis transmittance spectra of the natural ruby samples were collected in the same spectral range using a solid-sample transmission accessory.

Raman spectra and photoluminescence (PL) measurements were performed using a WiTec alpha300 R confocal Raman microscope with a 532 nm laser and $\times 50$ objective, producing a laser spot of $\sim 1\text{ }\mu\text{m}$. Each PL spectrum was recorded with an acquisition time of 0.05 s and averaged over 20 accumulations.

The colour of the ceramics was measured using a Lovibond Tintometer RT 100 and presented in the CIELAB colour space.

3. Results and Discussion

3.1. Phase composition of the studied samples

Rubies samples consist $\alpha\text{-Al}_2\text{O}_3$ with trace Ti, V, Cr and Fe [1].

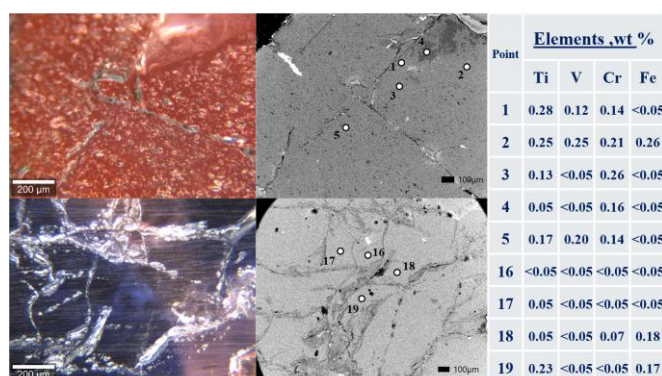


Figure 2. X-ray diffraction pattern of the natural ruby (after Ref. [1]) confirming single-phase $\alpha\text{-Al}_2\text{O}_3$ with trace substitution of transition metal ions (Cr, V, Ti, Fe) in the corundum lattice.

Synthetic ceramics were obtained from industrial waste with the following composition: SiO_2 (55.7 wt %), SO_3 (22.8 wt %), K_2O (11.95 wt %), V_2O_5 (4.36 wt %), Al_2O_3 (2.32 wt %), Na_2O (1.47 wt %), Fe_2O_3 (0.81 wt %), CaO (0.36 wt %), Cs_2O (0.13 wt %), As_2O_3 (0.1 wt %), P_2O_5 (0.05 wt %) and others (0.14 wt %) and addition of Al_2O_3 in an amount necessary to obtain a 1.5 molar ratio of

$\text{Al}_2\text{O}_3/\text{SiO}_2$. 100g waste+140 g Al_2O_3 The mixture was homogenized and sintered in a laboratory muffle furnace with a heating rate of $200^\circ\text{C}/\text{h}$ in an air atmosphere with an isothermal retention of 2 h at final temperatures of 1200°C and 1300°C .

The phase composition of the resulting ceramic sintered at 1100°C , 1200°C , and 1300°C determined based on the X-ray diffraction patterns (Figure 3), is presented in Table 1.

Table1. Quantitative phase composition (wt.%) of ceramics sintered at different temperatures, determined from XRD data.

Sample	$\alpha\text{-Al}_2\text{O}_3$	$\kappa\text{-Al}_2\text{O}_3$	cristobalite	amorphous
1100°C	55%	21%	24%	28%
1200°C	56%	30%	14%	23%
1300°C	43%	42%	16%	26%

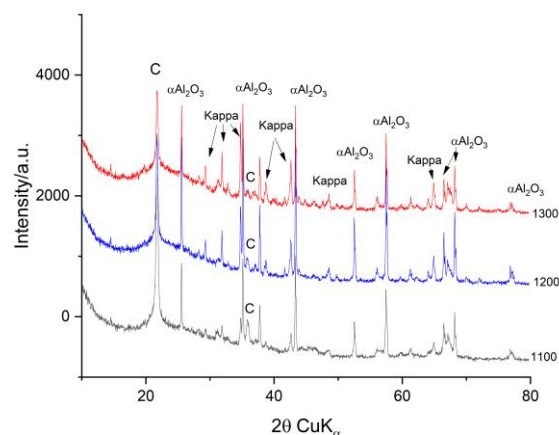


Figure 3. X-ray diffraction patterns of waste-derived ceramics sintered at 1100°C , 1200°C and 1300°C . Indexed reflections of $\alpha\text{-Al}_2\text{O}_3$, $\kappa\text{-Al}_2\text{O}_3$ and cristobalite illustrate temperature-dependent phase evolution under oxidizing firing conditions.

3.2. Chemical composition (XRF data)

The chemical composition of the ceramic sintered at 1100°C , 1200°C , and 1300°C expressed as weight percent oxides, is present in Table 2.

Table 2. Chemical composition of the sintered ceramics.

Oxides, wt%	1100°C	1200°C	1300°C
Na_2O	0.83	1.06	1.03
Al_2O_3	46.2	41.6	40.5
SiO_2	41.4	44.4	45.6
P_2O_5	0.022	0.02	-
SO_3	0.25	0.25	0.06
Cl	0.01	-	-
K_2O	6.41	7.35	7.6
CaO	0.18	0.18	0.21
TiO_2	0.08	0.12	-
V_2O_5	3.70	4.13	4.1
Fe_2O_3	0.85	0.90	0.93
CuO	0.021	0.02	0.03
As_2O_3	0.073	0.05	0.03
MoO_3	-	0.02	0.02

3.3. Optical absorption spectra

Natural ruby: The UV-Vis spectrum of the natural ruby exhibits well-resolved spin-allowed d-d transitions of Cr^{3+} centred at $\sim 550\text{ nm}$, together with higher-energy bands near 405 nm (Fig. 4). Weak absorption features in the 400 and 600 nm region indicate minor contributions from $\text{V}^{3+}/\text{V}^{4+}$, while an increase in absorption below 320 nm is attributed to ligand-to-metal charge-transfer transitions involving trace V^{5+} . The sharp R-line emission at $\sim 693\text{ nm}$ confirms the presence of structurally ordered Cr^{3+} in the $\alpha\text{-Al}_2\text{O}_3$ lattice [1,4,9].

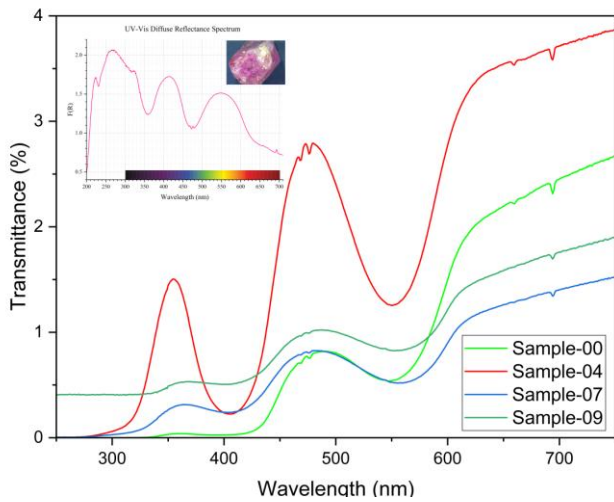


Figure 4. UV-Vis transmittance spectra of vanadium-bearing natural ruby samples showing characteristic Cr^{3+} crystal-field absorption bands at ~405 and ~550 nm together with enhanced UV-blue attenuation (below ~320–400 nm) attributed to $\text{V}^{3+}/\text{V}^{4+}$ crystal-field transitions and $\text{O}^{2-} \rightarrow \text{V}^{5+}$ charge-transfer processes. The spectra demonstrate the role of vanadium as a secondary chromophore modifying the absorption edge [5–7,9].

Synthetic corundum ceramic: In contrast, the synthetic ceramics exhibit strong and broad absorption in the 220–300 nm range, characteristic of $\text{O}^{2-} \rightarrow \text{V}^{5+}$ charge-transfer transitions (Fig.5). Crystal-field d–d transitions of vanadium are largely suppressed, indicating that vanadium is predominantly stabilized in its highest oxidation state under oxidizing firing conditions. A weak band near ~700 nm may suggest minor V^{4+} species associated with oxygen-deficient sites.

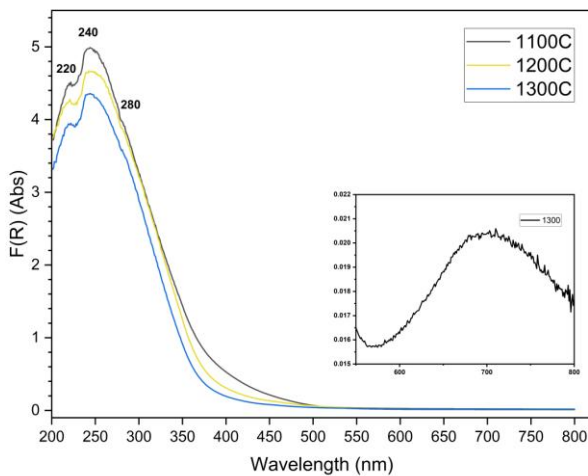


Figure 5. UV-Vis diffuse reflectance spectra of waste-derived alumina ceramics showing dominant $\text{O}^{2-} \rightarrow \text{V}^{5+}$ charge-transfer absorption in the 220–300 nm region and broad visible absorption associated with Fe^{3+} species, confirming charge-transfer-controlled colour formation [5–7].

The visible region is dominated by broad overlapping absorption features attributed to Fe^{3+} and vanadium-related charge-transfer processes. The absence of distinct Cr^{3+} -type transitions confirms a fundamentally different chromophore mechanism compared to natural ruby.

When Al_2O_3 reacts with vanadium-containing species in air atmosphere, the formation of AlVO_4 is thermodynamically favoured, further supporting stabilization of V^{5+} . This interpretation is consistent with XRF data showing significant V_2O_5 content and with the observed yellow colour coordinates.

3.4 Raman Spectroscopy

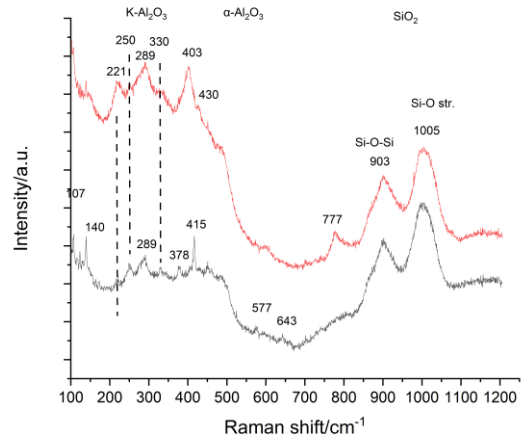


Figure 6. Raman spectra of waste-derived ceramics illustrating vibrational modes of $\alpha\text{-Al}_2\text{O}_3$, $\kappa\text{-Al}_2\text{O}_3$, cristobalite and amorphous silica, confirming the multiphase structure of the sintered system.

The natural ruby crystallizes in the trigonal $\alpha\text{-Al}_2\text{O}_3$ structure (space group $R\bar{3}c$), where Cr^{3+} substitutes for Al^{3+} in octahedral coordination without symmetry modification. Group theoretical analysis predicts seven Raman-active modes, and experimentally well-defined bands at 378, 415, 430, 577 and 643 cm^{-1} confirm a structurally ordered corundum lattice [3,4].

In contrast, the Raman spectra of the synthetic ceramics reveal multiphase composition. The presence of $\kappa\text{-Al}_2\text{O}_3$ (orthorhombic polymorph) introduces additional vibrational modes due to its lower symmetry and multiple non-equivalent Al sites, producing bands near ~ 250 , 300 and 500 cm^{-1} . Cristobalite contributes intense peaks at ~ 500 and 770 cm^{-1} , while the amorphous phase is characterized by broad bands in the $900\text{--}1100\text{ cm}^{-1}$ region (Fig.6) [8].

Under 532 nm excitation, luminescence lines associated with Cr^{3+} electronic transitions are also observed, indicating trace chromium incorporation despite the absence of ruby-type colouration (Fig. 7) [1,4,9].

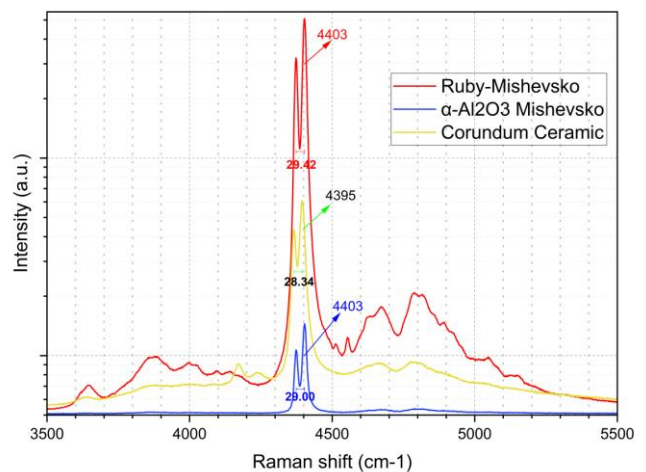


Figure 7. Raman spectra of natural ruby and synthetic ceramic under 532 nm excitation showing Cr^{3+} R_1 and R_2 luminescence lines. The R_1 peak is positioned at 4403 cm^{-1} Raman shift for natural ruby and 4395 cm^{-1} Raman shift for the synthetic ceramic, indicating lattice strain and structural differences.

The $R_2\text{--}R_1$ separation equals 29.00 cm^{-1} for weakly luminescent natural corundum, 29.42 cm^{-1} for strongly luminescent natural corundum ($\approx 30\times$ higher intensity), and 28.34 cm^{-1} for the ceramic.

Variations in peak position and splitting reflect differences in crystal-field strength, dopant environment and structural order between the natural α -Al₂O₃ reference and the multiphase waste-derived ceramic.

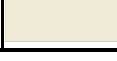
3.5. Colour

The optical neutrality of pure Al₂O₃ implies that colour in both systems originates exclusively from transition metal ions.

In ruby, the red colour arises from spin-allowed d–d transitions of Cr³⁺ in octahedral coordination, which selectively absorb blue and green light, resulting in red transmission and characteristic emission near 696 nm [2–4].

In the synthetic ceramics, however, the colour is yellow despite the presence of Cr³⁺ luminescence. CIELAB measurements show high lightness ($L^* \approx 92$ –93), negligible red-green contribution ($a^* \approx -1$), and pronounced yellow component ($b^* = 10$ –23) [12].

Table 3. CIELAB colour coordinates (L^* , a^* , b^*) of waste-derived ceramics.

Composition	T, °C	Colour	L^*	a^*	b^*
Ceramics: α -Al ₂ O ₃ , κ -Al ₂ O ₃ , cristobalite, amorphous	1100		92.2	-1.0	23.4
	1200		93.1	-1.0	15.0
	1300		93.2	-1.1	10.5

The high lightness is explained by the dominance of colourless high-band-gap phases (α -Al₂O₃, κ -Al₂O₃, cristobalite and amorphous silica) which efficiently scatter light. The yellow hue originates primarily from ligand-to-metal charge-transfer absorption of V⁵⁺ and Fe³⁺ in the blue spectral region. The absence of positive a^* values confirms that Fe³⁺ does not induce significant red coloration under the studied conditions [5–7,10,12].

4. Conclusion

This comparative study demonstrates that colour formation in alumina systems is governed by fundamentally different electronic mechanisms in natural and waste-derived materials.

In natural ruby, colour is controlled by Cr³⁺ crystal-field transitions within a structurally ordered α -Al₂O₃ lattice [2–4]. In contrast, the engineered multiphase ceramics exhibit charge-transfer-dominated absorption, primarily associated with V⁵⁺ and Fe³⁺ stabilized under oxidizing firing conditions [5–7,10].

The shift of the Cr³⁺ R₁ line (4403 → 4395 cm⁻¹) and variations in R-line splitting (29.42–28.34 cm⁻¹) confirm structural and crystal-field differences between natural and synthetic systems [1,4,9].

Vanadium oxidation-state stabilization emerges as a key technological parameter controlling optical response in alumina ceramics derived from secondary raw materials. The combined use of UV–Vis and Raman spectroscopy provides a reliable diagnostic tool for oxidation-state monitoring, phase verification and targeted colour engineering under sustainable processing conditions [3,8,11].

Industrial Relevance Statement

Control of vanadium oxidation state and phase composition enables predictable colour tuning in waste-derived alumina ceramics, supporting sustainable valorisation of industrial residues into functional ceramic materials.

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Effect of non-metallic inclusions on the grain structure of low-carbon steels under severe plastic deformation

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Abstract. The features of localization of severe plastic deformation in a steel matrix near non-metallic inclusions are studied. In the steel matrix, near inclusions and at the inclusion-matrix interphase boundaries, the nature of the stressed and deformed states changes, the strain increment is determined by the rotation angle of the inclusion during its movement in the plastic region. Processes of local structural transformations near non-metallic inclusions in steels exposing to intensive plastic deformation were investigated. The influence of non-metallic inclusions on the local refinement of the steel microstructure is an important effect during severe plastic deformation, which makes it possible to obtain additional nanostructural strengthening near the inclusions during the general refinement of grains to a submicrocrystalline state. It was shown the influence of non-metallic inclusions on mechanical properties of these steels.

KEYWORDS: SEVERE PLASTIC DEFORMATION, LOW-CARBON STEELS, NON-METALLIC INCLUSIONS, THE GRAIN STRUCTURE, SUBMICROCRYSTALLINE STATE, NANOSTRUCTURAL STRENGTHENING.

1. Introduction

Severe plastic deformation SPD is one of the promising methods for obtaining the Ultrafine-Grained structure of metallic materials, which makes it possible to obtain a high-strength state, as well as unique functional properties of these materials without changing the chemical composition [1 - 9]. Currently, many Ultrafine-Grained Materials are obtained by this method, in particular, non-ferrous metals and their alloys, steels have been studied to a lesser extent, in addition, the role of non-metallic inclusions in the formation of the Ultrafine-Grained structure has not been studied in the study of steels. **The goal** of this work was to study the local processes of plastic structure formation occurring in low-carbon steels near non-metallic inclusions during severe plastic deformation by the method of equal-channel angular pressing.

2. Materials and Procedures.

Samples of steels 08Al, 08Cr18Ni10T, 09Mn2Si, having dimensions of $\varnothing 20 \times 80$ mm, were subjected to plastic deformation by the ECAP method in four passes (one pass with a channel intersection angle of 90° and three passes with an angle of 120°), which corresponded to a true deformation of 3.2. Structural analysis was performed using an Olympus PME 3 optical microscope, as well as JEM 100CX and JXA-50F electron microscopes; the nanohardness of the steel matrix near and far from inclusions was measured on a Nano Indenter II setup at a load of 10 mN. Tensile tests of the samples of 08Al steel 08Al after severe plastic deformation were carried out.

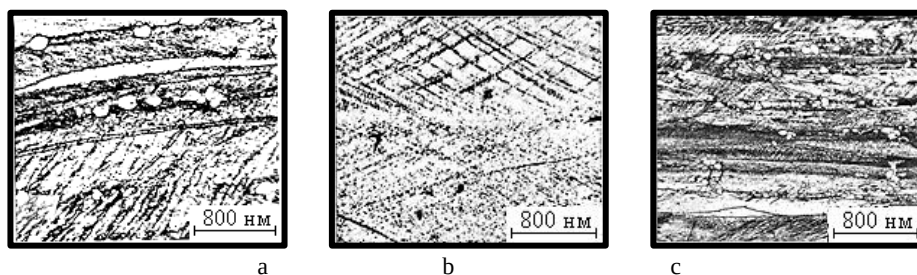
3. Results and discussion.

During severe plastic deformation SPD changes occurred in steels associated with the formation of oriented structural elements measuring 80...260 nm and separated by high-angle boundaries (Fig. 1, a - c), as evidenced by the presence of individual point reflections in the annular electron diffraction pattern. Such structural elements are characterized by the presence of dispersed curved mesobands of deformation, twins, elongated subgrains, and, in the case of 08Cr18Ni10T steel, also martensite plates [10]. With an increase in the number of passes, fragmentation of the mesobands of deformation occurred, leading to significant of grain

refining. In addition, individual equiaxed grains appeared, caused by the growth of subboundary misorientations in the developed cellular structure, which is associated with the development of cold dynamic recrystallization. The obtained structures are characterized by an increase in the dislocation density to $(3.2...5.6) \cdot 10^{12} \text{ cm}^{-2}$, which is three orders of magnitude higher compared to the initial state, as well as an increase in nanohardness with an increase in the number of passes from 2.5 to 4.2 kN/mm² for the different steels.

The effects that arise during structural changes in steels occur at the mesoscopic level and are associated with the transition from continuous plastic flow to localized flow in microshear bands during SPD. Such processes require repeated loading with changes in the direction of deformation, leading to the continuous evolution of the dislocation substructure, the transition to localization in shear bands and rotational localization, the introduction of high-angle boundaries, and the formation of junction disclinations. These processes lead to generate powerful internal stresses and facilitate the collective nature of the accommodative motion of dislocations, as well as fragmentation and rotation of fragments, which creates the conditions for refining the steel microstructure to the level of the substructure's cell size. The described general picture of grain refinement during SPD does not take into account the influence of non-metallic inclusions.

The synergetic methodology of physical mesomechanics requires determining the nature of possible stress concentrators, which are always present in a loaded solid, as well as the mechanisms of nonequilibrium structural transformations in localized zones of stress concentrators [11]. Such stress concentrators include non-metallic inclusions, as well as inclusion-matrix interphase boundaries separating two deforming phases with different elastic moduli. This contributes to the loss of shear stability and the emergence of various localized processes of structural and phase transformations in the steel matrix near the non-metallic inclusions and at the boundaries themselves during SPD. At the inclusion-matrix interface, oscillations of local stresses occur under loading, which can significantly exceed the average applied stresses. Obviously, it is necessary to consider the possible relaxation processes of these local stresses, which will improve the mechanical properties and reduce the risk of failure of steels subjected to equal channel angular extrusion.



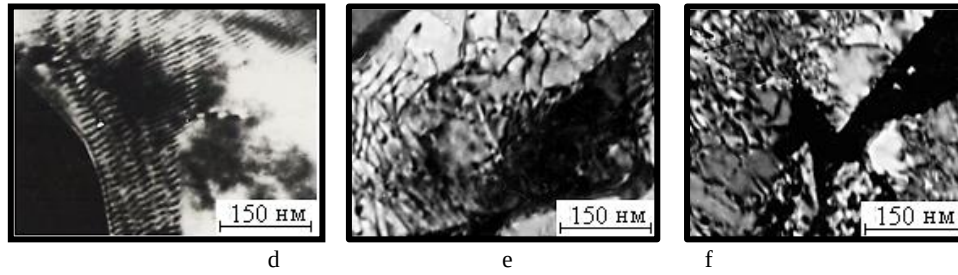


Fig. 1. Structure of steels 08Cr18Ni10Ti (a, e, g), 09Mn2Si (b, c), 08Al (d), deformed by equal channel angular extrusion.

Inclusion particles under equal channel angular extrusion conditions disrupt the homogeneity of deformation and facilitate its localization. The strain increment is determined by the inclusion's rotation angle as it moves through the plastic zone. Near the non-metallic inclusion, various spatial deformation patterns are realized by changing the position of the shear planes, the nature of which obviously depends on the inclusion's degree of plasticity. The presence of non-metallic inclusions should have a significant impact on the development of multiple shear deformation, used in fractional deformation along fixed planes with shear in mutually opposite directions, combined with uniform stress and strain states, as well as on the ultimate ductility of steels.

During SPD, plastic deformation gradients in the steel matrix lead to plastic rotation of non-metallic inclusions, which act as barriers to dislocation movement. Localized deformation zones (Fig. 1, d) form near the inclusions. These zones contain inhibited curved fragmented shear bands, broken subboundaries, microtwins, and vortex formations caused by rotational localization and the formation of discrete misorientations (Fig. 1, e). The cell sizes of the substructure are approximately 2...3 times smaller than those far from the non-metallic inclusions. Furthermore, several foci of rotational localization can be observed near a single inclusion (Fig. 1, f). Plastic deformation gradients in the steel matrix lead to plastic rotation of inclusions, which act as barriers to dislocation movement.

A defective layer, representing a complex dislocation-disclination system, develops near non-metallic inclusions, where accommodative collective motion of dislocations and dangling dislocation boundaries occurs. Since the density of point defects is always elevated near inclusions, it is in these zones of localized

deformation that diffusion accommodation within the system of dislocations and junction disclinations is most likely, which is the factor governing the limit of deformation-induced grain refinement in the steel matrix near inclusions. On average, nanograins sizes near inclusions are 2...3 times smaller than those farther away.

The nanohardness values of the steel matrix near non-metallic inclusions depended on the type of steel, but in all cases they exceeded similar values far from the inclusions by 20...35% (Table 1). Near plastic inclusions of sulfides and silicates, the nanohardness values are lower than near non-deformable oxides and carbonitrides of titanium, which is associated with a certain deformation relaxation of stresses in the plastic inclusion-matrix system [10 - 12]. In cases of localized dynamic cold recrystallization near inclusions, the nanohardness of the steel matrix decreased by approximately 10%. With developed deformations, most of the deformation energy is converted into heat due to the dissipation of mechanical energy, which can lead to heating of the metal to the recrystallization onset temperature. The probability of such heating increases with significant differences in the arrangement and vibrations of atoms located near non-metallic inclusions and at the inclusion-matrix boundaries, compared to atoms located within the grains. Cold recrystallization near inclusions occurs under conditions of a high concentration of defects in the crystalline structure, which do not have time to rearrange themselves to such a level as to ensure significant weakening of these areas. Recovery and recrystallization near inclusions can be significantly suppressed by limiting dislocation mobility by impurities present in these matrix zones in increased quantities.

Table 1. Nanohardness of the steel matrix near non-metallic inclusions and far from them (in brackets) after SPD in four passes (kN/mm²)

08Cr18Ni10Ti, TiCN	4,97 (3,8)
08Al, MnO·Al ₂ O ₃	4,49 (3,4)
08Al, (Fe,Mn)S	3,92 (3,4)
09Mn2Si, SiO ₂	5,38 (4,2)
09Mn2Si, MnO·SiO ₂	4,93 (4,2)

In steel 08Cr18Ni10Ti, rims of martensite phase were observed near non-metallic inclusions. This is associated with the redistribution of nonequilibrium defect flows during SPD, leading to concentration stratification of austenite and the formation of areas enriched in either nickel or iron and chromium. Electron microscopic studies allowed us to determine the basic reflections of fcc and bcc lattices with the presence of {111}_{fcc} and {211}_{bcc} deformation textures. Martensite grains have sizes of approximately 10...30 nm. Apparently, in localized areas of the austenite matrix near the non-metallic inclusions, a mechanism of concentration redistribution is realized, facilitating a local loss of nickel concentration, which leads to the formation of deformation-induced martensite. Far from the inclusions, the sizes of martensite grains reach 50...80 nm.

The relationship between the diffusion coefficients and the thermodynamic parameters in this steel during SPD should be taken into account. The diffusion coefficients of iron and chromium are approximately equal, while nickel has the maximum diffusion mobility. The appearance of nonequilibrium vacancies and the movement of impurity atoms toward non-metallic inclusions during SPD leads to the formation of

nonequilibrium segregations near the inclusions and at the inclusion-matrix boundaries, which disturb the thermodynamic state of the steel, as well as to the action of the inverse Kirkendall effect in the presence of inclusions and inclusion-matrix boundaries serving as sources and sinks of vacancies [10 - 12]. Iron and chromium atoms in this steel are "slow" impurities and, in the case of a vacancy sink directed toward the inclusions, will be localized in the sink areas, while the more mobile nickel atoms move toward the vacancy flow from the inclusions (inverse Kirkendall effect). A decrease in nickel concentration in localized matrix volumes near non-metallic inclusions leads to a transition of the lattice areas bordering the inclusions to the bcc phase - martensite. Thus, the presence of martensite grains near non-metallic inclusions indicates their participation in the transport of nonequilibrium vacancy flows during SPD, which can lead to concentration redistribution in localized areas of the steel's base components, which have different mobility.

The inverse Kirkendall effect in steel with non-metallic inclusions acting as localized sources and sinks for vacancies results in a spatial scale on the order of several grain sizes. This

mechanism is associated with the activation of rotational deformation modes near the inclusions, which was observed in all the steels studied, as well as the activation of slip along the inclusion-matrix boundaries. During SPD, the density of excess interphase defects (introduced dislocations and nonequilibrium vacancies) at the inclusion-matrix boundaries also increases, leading to an increase in the free volume of these boundaries and an increase in their diffusion permeability [4, 10-12]. Apparently, the presence of several rotational localization areas near the non-metallic inclusions contributes to the fact that deformation microvortices "sweep" lattice defects into the inclusion-matrix boundaries.

As the misorientation of inclusion-matrix boundaries increases during SPD, the flux of lattice dislocations entering them exceeds the flux of dislocations emitted by the boundaries. Deformation energy, previously dissipated within the grain bulk and propagated to an increase in internal energy and the formation of nonequilibrium point, linear, and surface defects, is localized at such interphase boundaries. The increase in distortions and stresses at nonequilibrium inclusion-matrix boundaries leads to a relaxational rearrangement of their structure and delocalization of dislocation cores within these boundaries. This results in cold slip along the inclusion-matrix boundaries, which can be accompanied by the generation of point defects within the grain. Accommodation of rotational displacements near inclusions is also a cause of cold slip along inclusion-matrix boundaries. It seems obvious that after SPD, inclusion-matrix interphase boundaries possess increased boundary energy, which ensures high diffusion rates within these boundaries.

Viscous microcracks and cavities associated with delamination or viscous decohesion of inclusion-matrix interphase boundaries were observed near inclusions in areas of localized deformation of the steel matrix. A study of the microcracks revealed that the type of nonmetallic inclusion influences on the mechanism

of their formation. Viscous microcracks were observed near silicate and titanium carbonitride inclusions (Fig. 2, a), while corundum and spinel inclusions typically formed cavities due to viscous decohesion of inclusion-matrix boundaries (Fig. 2, b). Clearly, under SPD conditions, the original structure of inclusion-matrix interphase boundaries retains its influence on their cohesive strength and the mechanism of microfracture formation [12]. It should be noted that SPD did not produce brittle microcracks in the steel matrix near inclusions, which is due to the high level of ductility under these conditions. The structure of the cavity surfaces indicates active plastic processes accompanying their formation and growth (Fig. 2, c).

Characteristic features of the tensile stress-strain curves of the specimens after SPD include the absence of the area of uniform elongation and also the onset of localized deformation with neck development immediately after reaching the yield point, which is close to the elastic limit and ultimate tensile strength, indicating a high-strength condition of the steel (Table 2). The elliptical cross-section of the neck in the specimens indicates significant anisotropy of steel deformed by simple shear. An increase in the content of non-metallic inclusions led to a significant reduction in both strength and ductility properties (Table 2). The fracture micromechanism in steel deformed by equal channel angular extrusion is predominantly dimpled (Fig. 2, d). However, fractures have a complex topography due to the formation of inhomogeneous deformation structures during SPD, as well as the presence of non-metallic inclusions. Large dimples are associated with non-metallic inclusions. Furthermore, areas resembling ductile intergranular fracture are found near the inclusions. This is due to the sharp localization of deformation in the steel matrix, as well as the development of cold slip along the inclusion-matrix boundaries. Therefore, the problem of non-metallic inclusions is also relevant for steels subjected to SPD.

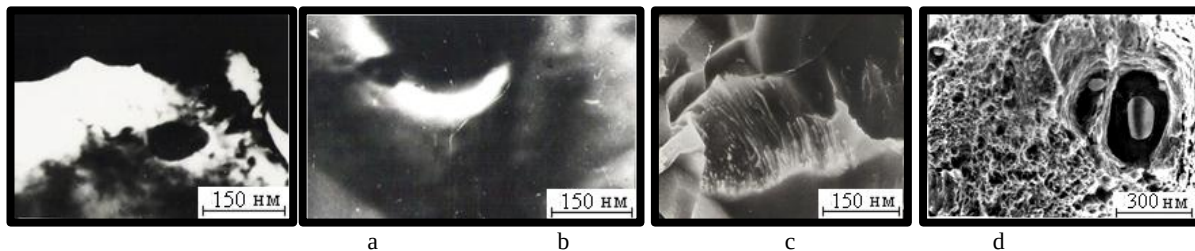


Fig. 2. Microcracks near inclusions that arose during the SPD process in steels 08Cr18Ni10Ti (a), 08Al (b, c) and fracture structure of 08Al steel, deformed by equal channel angular extrusion.

Table 2. Mechanical properties of steel 08Al with different non-metallic inclusion contents deformed by equal channel angular extrusion.

melt number	$\sigma_{0.2}$	σ_B	δ	ψ
	MPa		%	
1	654	643	12	32
2	533	521	7	24

4. Conclusions.

During SPD of steels subjected to equal channel angular extrusion, nonmetallic inclusions cause a number of effects: refinement of the nanograin structure, localized cold recrystallization and cold slipping along inclusion-matrix boundaries, as well as concentration redistribution in the matrix and martensite formation. Inclusions affect the mechanical properties of steels subjected to equal channel angular extrusion.

In the steels under study, structure formation during severe plastic deformation is associated with the formation of oriented structural elements that have dimensions of 100...260 nm and are separated by high-angle boundaries, which are characterized by the presence of dispersed curved mesobands of deformation, and in steel 08Kh18N10T also martensitic plates. With an increase in the number of passes, fragmentation of the mesobands of deformation occurred, which led to a significant fragmentation of

the grains. Near the inclusions, the grain sizes are significantly smaller than far from them and are 75...100 nm.

The nanohardness values of the steel matrix near the inclusions were 25...40% higher than the similar values far from the inclusions. Near plastic inclusions of sulfides and silicates, the values of nanohardness are lower than near non-deformable oxides and titanium carbonitrides, which is associated with a certain deformation relaxation of stresses in the plastic inclusion-matrix system. In cases of localization of dynamic cold recrystallization near inclusions, the nanohardness of the steel matrix decreased by about 10%.

The influence of non-metallic inclusions on the local refinement of the steel microstructure is an important effect during severe plastic deformation, which makes it possible to obtain additional nanostructural strengthening near the inclusions during the general refinement of grains to a submicrocrystalline state.

5. Literature.

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