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Mechanistic modeling of colloidal rust particles deposition on coated optical surfaces in single-beam spectrophotometric systems

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Abstract

During the prolonged operation of optical systems used for liquid-consistency inspection, their surfaces inevitably become contaminated. Among the most persistent contaminants are micrometer-scale rust particles, colloidal in nature and inclined to agglomerate, which gradually accumulate on the optical elements. To elucidate the mechanisms governing this deposition, numerical modeling was conducted to evaluate particle adhesion on a functional coating, both with and without an additional protective layer. The analysis incorporates the principal forces shaping particle behavior: adhesion, Hertzian elastic response, electrostatic double-layer interactions, and the hydrodynamic drag imposed by the surrounding liquid. From these components, the total interaction force, particle velocity, displacement, and their temporal evolution were derived. Taken together, the results offer a coherent physical picture of how rust particles engage with coated optical surfaces and how protective layers may mitigate this persistent form of contamination.

Keywords: contaminants; rust; interaction; optical window; numerical simulation

1 Introduction

Monitoring the chemical consistency of liquids is critical across industries such as pharmaceuticals, environmental science, and food processing. Single-beam spectrophotometry has emerged as a widely used technique for this purpose due to its simplicity, cost-effectiveness, and non-destructive nature. This method measures the absorbance of light by a liquid at specific wavelengths, providing insights into the concentration of analytes present. Research (Agberien and Örmeci [1]) demonstrated the utility of single-beam spectrophotometry for environmental monitoring by detecting cyanobacteria in water, while Feng et al. [2] developed an open-source dual-beam spectrophotometer for citizen-science-based water quality monitoring. In microbiology, Montesinos-Cruz and Somerville [3] highlighted the technique's role in analyzing microbial content in liquids, and Bausch & Lomb (Spectronic 20 [4]) and Drawell Analytical [5] provided guidance on spectrophotometer design and optimization.

Despite its widespread use, challenges remain in ensuring measurement accuracy. Lab Manager [6] and Fisher Scientific [7] discussed factors such as light source stability, detector sensitivity, and sample turbidity, while Elite Scientific & Mediatech (Spectroscopy, [8]) and Ezilab (Scientific [9]) have worked on improving instrument performance and usability. Yang et al. [10] developed an in-situ analyzer for dissolved reactive phosphorus in natural waters, demonstrating the feasibility of real-time nutrient monitoring. Carreres-Prieto et al. [11] applied LED spectrophotometry for wastewater characterization and optimized measurement accuracy using regression and dimensionality reduction techniques. Hladová et al. [12] reviewed methods for determining formaldehyde in liquid samples, emphasizing the versatility of single-beam spectrophotometry for detecting low-concentration industrial contaminants.

Online and in-line spectrophotometric monitoring has become central to continuous process and water-quality surveillance. Shi et al. [13] highlighted that probe design, flow cell configuration, and fouling control strongly influence performance in field deployments. Single-beam spectrophotometers remain attractive for portable and low-cost monitoring due to mechanical simplicity, but they are more sensitive than double-beam systems to source fluctuations and mechanical drift. Ríos-Reina and Azcarate [14] emphasized that combining robust mechanical design with signal processing strategies such as baseline correction, reference replicates, and chemometric drift compensation is essential to achieve reliable results.

The choice of sample cells and cuvettes also affects measurement precision. Páscoa et al. [15] reviewed the advantages of liquid waveguide capillary cells for enhancing sensitivity in trace analyte detection, compared to traditional quartz or glass cuvettes. Whitehead et al. [16] and Yimkosol et al. [17] demonstrated that 3D-printed adapters and holder designs improve mechanical stability and minimize alignment drift. Dupont et al. [18] and Lee et al. [19] highlighted that portable LED-based systems benefit from bespoke holder designs, light isolation covers, and fixed geometries to ensure reproducibility. Integrating mechanical and computational strategies enables low-cost single-beam systems to achieve fit-for-purpose performance comparable to laboratory-grade instruments (Ríos-Reina and Azcarate [14]).

Matrix-specific factors can further complicate measurements. Logozzo et al. [20] showed that iron contamination from corrosion can distort UV-Vis absorbance, necessitating auxiliary iron measurements or spectral corrections. Wilding and Blanton [21] demonstrated that fertilizers such as urea ammonium nitrate (UAN) require careful calibration to avoid interference from turbidity, precipitation, or overlapping absorbance bands. El Bindary et al. [22] and Türkmen et al. [23] developed methods for detecting iron contamination in complex matrices, while Esfandiari and Aliofkhazraei [24] reviewed complementary electrochemical strategies for low-level iron quantification. Fay et al. [25] and Anelli et al. [26] showed that portable LED-based systems with mechanically stable cuvette holders can accurately monitor high-absorbance solutions such as Ad-Blue®.

Overall, single-beam spectrophotometry provides a rapid, non-destructive, and cost-effective approach for monitoring the chemical consistency of diverse liquids. While challenges such as mechanical instability, matrix complexity, turbidity, and light source fluctuations remain, advances in optical design, portable LED-based systems, and computational correction strategies continue to enhance the technique's robustness, confirming its role as a valuable tool in environmental, industrial, and agricultural applications.

The objective of this study is not to experimentally quantify deposit formation, but to develop and evaluate a mechanistic framework describing the interaction between rust particles and modified optical surfaces under representative UAN-32 operating conditions. The proposed modelling framework provides a scalable approach for industrial applications, demonstrating that surface modification is a viable strategy to enhance the durability and reliability of in situ spectroscopic sensing systems.

2 Problem formulation

In single-beam spectrophotometric systems, accurate light transmission through the cuvette's optical window is essential for reliable absorbance measurements. During operation and handling, however, contaminants such as dust particles, chemical residues, or microdroplets may accumulate on or adhere to the optical surface (Fig. 1). These surface deposits introduce additional scattering and absorption, distorting the transmitted light intensity and compromising both measurement accuracy and reproducibility.

This issue is particularly pronounced in single-beam configurations because these systems lack a reference beam to compensate for optical losses or drift caused by surface contamination. Even minor variations in the optical path arising from particle deposition, adsorption kinetics, or surface roughness changes-can produce significant systematic errors in absorbance readings.

Therefore, it is necessary to develop a model and experimental framework that quantifies contaminant deposition on cuvette windows and evaluates its effect on transmitted light intensity in single-beam spectrophotometric systems.

Key factors to consider include: Mechanisms of contamination - particle settling, vapor condensation, and chemical adsorption; Optical interactions - scattering, reflection, and absorption by the deposited layer; Temporal dynamics - evolution of contamination during measurement; Instrumental sensitivity - amplification of measurement errors inherent to single-beam systems.

In addition to these challenges, surface contamination of cuvette windows has been widely recognized as a source of error in single-beam spectrophotometry. Dust, chemical residues, or microdroplets adhering to the optical interface introduce scattering and absorption that distort transmitted light intensity, reducing measurement accuracy and reproducibility (Blaney et al. [27]; Esfandiari and Aliofkhazraei [24]; Mettler Toledo [28]). Turbid or particulate-containing samples further exacerbate this effect, as light scattering can result in falsely elevated absorbance readings (Blaney et al. [27]; Li et al. [29]).

While previous studies support the general principle that fouling or contamination can affect UV-Vis transmission, there is a lack of published work investigating the specific impact of rust particles, $\sim 1\ \mu\text{m}$ $\alpha\text{-FeO(OH)}$, adhering to fused-silica cuvette windows in high-ionic-strength fertilizer solutions such as UAN 32. This represents a novel source of error that this study seeks to quantify.

The objective of this work is to establish a quantitative relationship between the degree of particle adhesion on fused-silica cuvettes and the resulting optical signal deviation in single-beam spectrophotometric measurements of UAN 32 solutions. By examining particle deposition mechanisms, optical interactions, temporal dynamics, and instrumental sensitivity, this study aims to provide predictive and corrective strategies to mitigate measurement errors caused by surface contamination in single-beam systems.

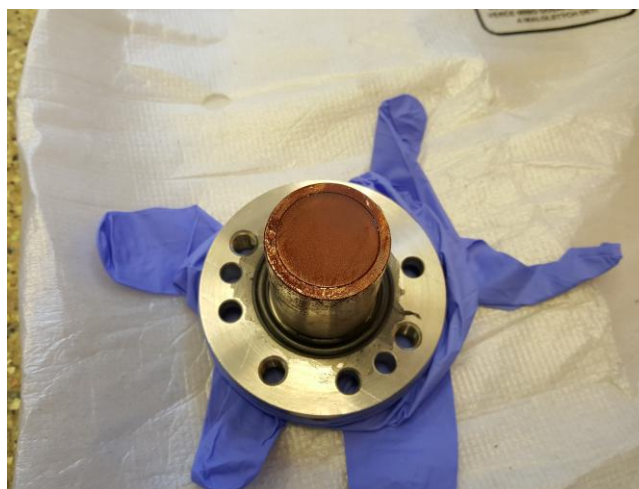


Fig. 1 An optical window that is covered with rust

2.1 Technical background of the use of silanes for coating technology

The silane category refers to chemical compounds of silicon and hydrogen, which are the silicon analogues of hydrocarbons. It is generally accepted that the general formula, analogous to the formula of alkanes, is $\text{Si}_n\text{H}_{2n+2}$ (Fig. 2).

The simplest form of silanes is monosilane SiH_4 (analogous to methane). There are also a number of disilanes (Si_2H_6), trisilanes (Si_3H_8), etc. with different valences.

The structure is usually tetrahedral, and silicon in silanes is usually sp^3 -hybridized. Unlike hydrocarbons, the bond between silicon is weaker, and the bond between silicon and hydrogen is more polar than in the carbon-hydrogen pair. For these reasons, silanes are more chemically reactive.

Silane acts as a reducing agent and is easily oxidized. In a substitution reaction, the reaction proceeds as shown, resulting in the formation of organosilanes $\text{Si-H} \rightarrow \text{Si-R}$ (where R is an organic group). From the point of view of chemical formation, silanes are a basic class of silicon hybrids and an intermediate link between inorganic chemistry in the form of SiH_4 and organic polymer chemistry in the form of silicones.

Silane is rarely used in its pure form, but its derivatives are widely used as organosilanes, siloxanes, and silicone polymers. The main form of organosilanes can be $\text{R}_n\text{SiH}_{4-n}$ or $\text{R}_n\text{SiX}_{4-n}$. These types are used for surface modification, and silanes act as cross-linking agents for both polymers and composites. Hydrolysis and condensation of silanes form siloxanes, which are converted into silicone polymers in production.

In terms of technology, silanes are used to form thin films and are widely used in construction chemistry and materials chemistry as water repellents, protective coatings, corrosion inhibitors for steel in concrete, and as components of composite coatings. They are capable of penetrating deep into porous materials, interacting with the hydroxyl groups of the cement matrix, and forming stable organosilicon bonds, giving the material water-repellent properties without significantly changing its vapor or visual permeability. They are also used in the manufacture of chips and solar panels to form protective films. To modify construction mixtures, such as concrete, silanes are used for impregnation, hydrophobization, and thus the formation of additional protection against moisture and salts. Scientific research pays great attention to the application and modification of silanes. Silanes are being studied in durability tests of 20-year-old concrete modifications, where they were used as penetrating water-repellent agents that reduce capillary water absorption (Christodoulou et al. [30]).

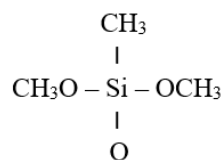


Fig. 2 Typical alkyl alkoxysilane molecular structure (Christodoulou et al. [30])

For porous materials, protection against aggressive marine environments containing ions or chlorides, as well as a reduction in the transfer of aggressive salts to metal surfaces, was achieved by coating with a silane emulsion. This modification reduced the permeability coefficient by up to 50% (Christodoulou et al. [30]).

Other studies (Zhang et al. [31]) have determined that water-based silane emulsion significantly reduces the water absorption of concrete, which is explained by the hydrophobization of capillary walls in hardened cement paste. A schematic diagram of chemical reactions involved in the silane-modified cementitious systems, R is C₈H₁₇, Et is C₂H₅ is presented (Zhang et al. [31]) (Fig. 3). At the same time, this coating slightly inhibits early cement hydration and slightly reduces the compressive strength of concrete. Studies also show that the hydrophobicity of the silane coating decreases with an increase in the amount of absorbed water, which is believed to be associated with the swelling of the CSH-type gel upon water absorption.

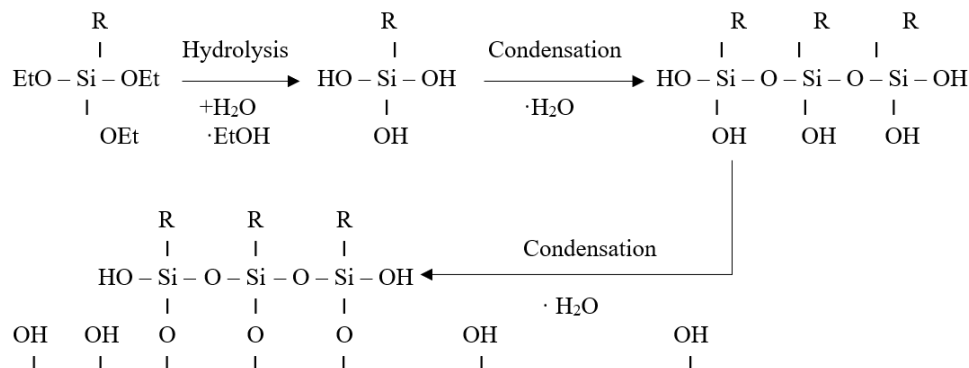


Fig. 3 Hydrolysis and condensation reactions of alkoxysilanes

Other studies have determined that silane organo-mineral coatings increase the adhesion and durability of polyurethane nanocoatings (Ghamarpour et al. [32]).

Compounds of octyltriethoxysilane (OTES) and vinyltriethoxysilane (VTES) improved the scratch resistance of the polyurethane coating by 25% when a coating containing 5 wt% OTES-modified nanoparticles was added, and by 37.5% when 1 wt% VTES-modified nanoparticles compared to coatings with unmodified nanoparticles. Organosilane coating with nanoparticles of CeO₂, SiO₂, or CeO₂·ZrO₂ types increased the corrosion resistance of metal substrates and enhanced the properties of the barrier layer by increasing the cross-linking of molecules in the film (Montemor et al. [33]).

The hydrophobic properties of silanes were confirmed by research using triethoxy(octyl)silane-based compounds (Fig. 4). This coating had a significant water-repellent effect (contact angle up to ~135°), which is important for protecting wood, paper, and textiles (Baranov et al. [34]).

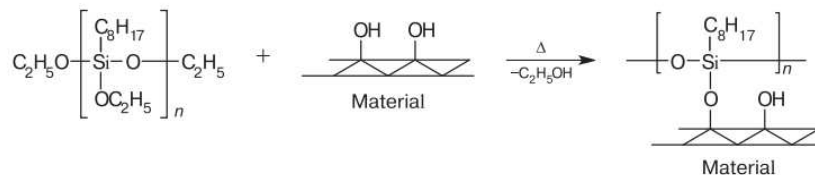


Fig. 4 Schematic representation of the interaction between compounds 1 and 2 and cellulosic material surfaces (Baranov et al. [34])

The use of a silane-containing layer has also been found to have antibacterial properties in combination with Ti_3C_2 nanoplates (Fig. 5). Chemical etching creates a rough surface that promotes superhydrophobicity. Silane molecules cross-link to form a film with low surface energy, which not only contributes to the superhydrophobicity of the surface, but also plays an important role in corrosion resistance (Nie et al. [35]).

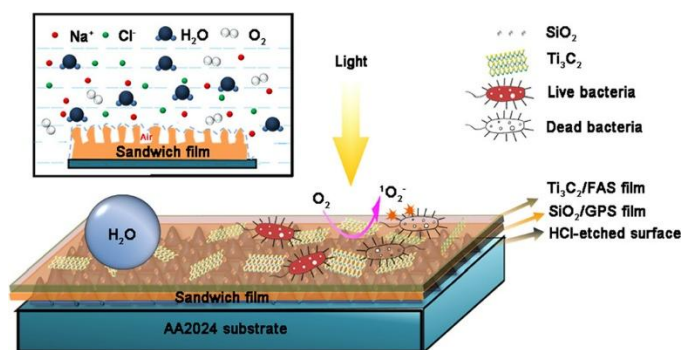


Fig. 5 Superhydrophobic silane-based surface coatings on metal surface with nanoparticles hybridization (Nie et al. [35])

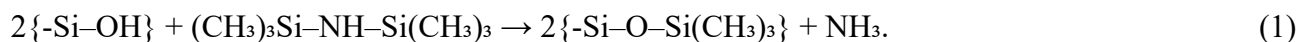
A silane coating as a modifier improves the adhesion between the organic and inorganic phases in composite coatings, increasing resistance to corrosion and mechanical stress. This effect has been confirmed by studies of the synthesis and characteristics of silane-bonded sodium silicate composite coatings. In this work (Liu et al. [36]), a silane coupling agent was used as a bridge between organic and inorganic interfaces through hydrolysis and condensation reactions of its bifunctional groups, forming an interphase layer bound by hydrogen and covalent bonds, thereby improving the compatibility between the organic resin and inorganic sodium silicate. The results showed that with a modified sodium silicate content of 60 wt%, the coating hardness reached 4H. In addition, electrochemical tests demonstrated that the coating has a higher impedance ($9.62 \times 10^4 \Omega/\text{cm}^2$) and a lower corrosion current density ($5.82 \times 10^{-7} \text{ A}/\text{cm}^2$).

To coat silicon surfaces, including chromatography analysis cuvettes, silane modifications from the categories hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS), octyltriethoxysilane (OTES), and others can be used.

HMDS is an organic silicon compound belonging to the silane group, with the chemical formula $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$. It is an amine derivative in which two hydrogen atoms of ammonia are replaced by trimethylsilyl (TMS) groups. HMDS is a colorless, volatile liquid with a boiling point of $\sim 125^\circ\text{C}$ and a density of $\sim 0.77 \text{ g}/\text{cm}^3$. Structurally, HMDS can be considered a silanazane: the central nitrogen atom is connected to two $\text{Si}(\text{CH}_3)_3$ groups, forming a Si–N–Si bridge. The Si–N bond length and Si–N–Si angle are close to the values of other disilazane compounds, which indicates that the molecular geometry is mainly determined by the properties of the electronic groups rather than steric factors alone.

Since HMDS is a strong donor of silyl groups, it reacts with compounds containing active protonic groups ($-\text{OH}$, $-\text{NH}$, $-\text{SH}$, $-\text{COOH}$), replacing them with trimethylsilyl (TMS) fragments. This process is called silylation and is widely used in organic synthesis and analytical chemistry. Silylated compounds (TMS derivatives) generally exhibit higher volatility and thermal stability, which is particularly important when preparing samples for gas chromatography.

HMDS is sensitive to moisture, so contact with water causes hydrolysis, which produces ammonia and trimethylsilanols. An example reaction with a silicon dioxide (SiO_2) surface, where the surface becomes less polar and hydrophobic:



Used to protect functional groups in the synthesis of complex molecules, especially when it is necessary to protect –OH or –NH groups from unwanted reactions. Used in sample preparation for gas or liquid chromatography to increase the volatility of polar compounds. Photolithography and microelectronics. HMDS is widely used as a surface activator (primer) in the treatment of silicon or glass surfaces. This makes the surface hydrophobic and improves the adhesion of photoresist in lithography processes. It is used for surface modification (e.g., hydrophobization of oxides) by reacting with silanol groups on the surface. HMDS belongs to the class of silanazanes, which are silane derivatives in which silicon hydrides are replaced by functional groups (in this case, an amino NH group). Unlike silanols or siloxanes, the chemical activity of HMDS is manifested in its ability to transfer trimethylsilyl groups to other molecules or surfaces. This property makes it an effective silanization reagent in organic chemistry and materials science.

TMCS is an organosilicon compound with the chemical formula $(\text{CH}_3)_3\text{SiCl}$. It belongs to the class of chlorosilanes – silane derivatives in which one of the substituents attached to the silicon atom is a chlorine atom. TMCS is a colorless, highly volatile liquid with a pungent odor and high chemical reactivity.

Structurally, the TMCS molecule consists of a tetrahedrally coordinated silicon atom bonded to three methyl groups and one chlorine atom. The Si–Cl bond is highly polar, making the silicon atom strongly electrophilic, which determines the high reactivity of TMCS towards nucleophiles (especially –OH and –NH groups). TMCS is a highly active silylation reagent and is therefore used for the modification of active protonic groups. It reacts with –OH, –NH, –SH, and –COOH groups, replacing the active hydrogen with a trimethylsilyl (TMS) group:



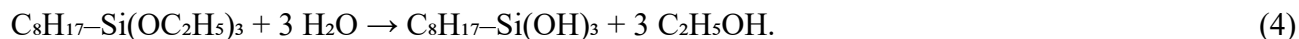
During the reaction, hydrogen chloride (HCl) is formed, which can catalyze side reactions or cause unwanted substrate decomposition, so basic additives (e.g., pyridine, imidazole) are often used. Due to its high reactivity, TMCS silylation proceeds rapidly and efficiently even at low temperatures. TMCS is particularly sensitive to water, and the following reaction occurs:



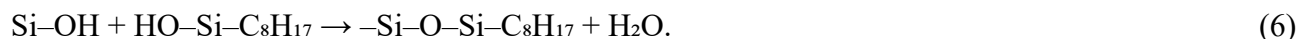
The resulting trimethylsilanol can further condense to form siloxanes. The release of HCl makes the reaction not only fast but also chemically aggressive, so TMCS must be stored and used under strictly dry conditions. Used to protect alcohol and amine groups during the formation of TMS compounds. Often used as an activator in combination with HMDS, as TMCS generates HCl and HCl activates HMDS and accelerates silylation reactions. Also used for the modification of enols, carboxylic acids, and heterocyclic compounds. Widely used for sample preparation for gas chromatography (GC): polar compounds are converted into volatile TMS derivatives, peak shape is improved, and column adsorption is reduced. Used for surface silanization, especially on a laboratory scale: reacts with surface silanol groups to form hydrophobic trimethylsilylated surfaces. Due to the release of HCl, milder silane reagents are more commonly used in industry, but TMCS remains important in scientific research. TMCS belongs to the class of chlorosilanes, which are silane derivatives in which a halogen (usually Cl) acts as a reactive leaving group. Unlike HMDS (which acts through silyl group transfer without the formation of strong acids), TMCS silylation occurs through a nucleophilic attack on an electrophilic silicon atom, with immediate release of HCl.

OTES is an organosilicon compound with the chemical formula $\text{C}_{14}\text{H}_{32}\text{O}_3\text{Si}$, structurally it is $\text{C}_8\text{H}_{17}-\text{Si}(\text{OC}_2\text{H}_5)_3$. It belongs to the class of alkoxysilanes – silane derivatives in which hydrolyzable

alkoxy groups (–OR) are attached to the silicon atom. OTES is a colorless or slightly yellowish, low-viscosity liquid widely used for surface modification and hydrophobization. In the molecule, the silicon atom is tetrahedrally coordinated: it is attached to one long octyl (C₈H₁₇) hydrophobic chain and three ethoxy groups (–OC₂H₅), which can hydrolyze and participate in condensation reactions. This structure allows OTES to act as a molecular bridge between the inorganic surface and the organic hydrophobic coating. OTES first undergoes hydrolysis, during which the ethoxy groups are converted into silanol groups:



The resulting silantriol (Si–OH) is highly reactive and can participate in condensation reactions. Silanol groups can either condense with each other to form siloxane bonds or react with surface silanol groups (e.g., on SiO₂, glass, minerals):



This creates a chemically bonded monomolecular or polymeric layer with hydrophobic octyl chains on the outside. It is used to improve the water repellency of glass, silicon dioxide, ceramics, and mineral fillers. Octyl chains reduce surface energy, thereby increasing the contact angle and reducing water and salt penetration. It is used to impregnate concrete, stone, and plaster in order to reduce capillary water absorption and increase resistance to frost and salts. Unlike polymer coatings, OTES forms a chemically bonded, breathable layer that does not interfere with water vapor diffusion. Used as a bonding promoter between inorganic fillers (silicon dioxide, ash, mineral powders) and organic binders (polymers, bitumen).

2.2 Physical and chemical interaction of materials and coating into an area of UAN-32

To clarify the effect of the materials used on each other, it is necessary to consider the possible interactions between the contacting surfaces. Thus, an analysis of the physical and chemical bonds for the main pair, the silane coating with the surface of the fused silica spectrometry cuvette, is presented. Since the main technical problem is the deposition and formation of a layer of iron oxides on the cuvette, the object of optimization is the relationship between the silane coating layer and the iron oxides contained in the flowing liquid medium. A secondary but also important factor is the environment in which all processes take place, which means that the interaction between the silane coating and the liquid medium of urea (ammonium nitrate, UAN-32) is also important and may be relevant for the durability of the silane coating optimization.

2.3 Silane-Fused silica

Silane-based materials interact complexly with silica (SiO₂) surfaces, including fused silica, a form of amorphous silicon widely used in optics and composite materials. Organoalkoxysilanes in solution undergo hydrolysis and subsequent condensation, leading to the formation of active –Si–OH groups capable of reacting with the surface silanol groups of silica. A variety of structures of organosilanes is presented in Fig. 6.

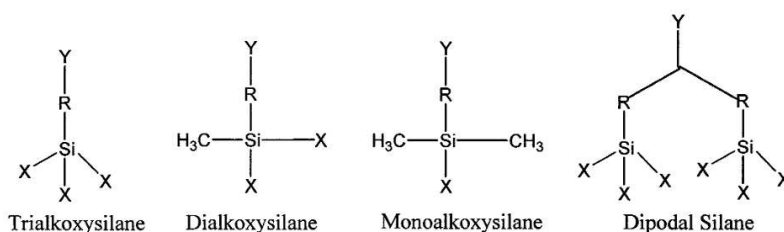


Fig. 6 Generic structures of functional organosilanes with varying numbers of hydrolyzable substituents on silicon (Dickens et al. [37])

The study (Dickens et al. [37]) determined that in dental practice, when using silanes for interphase bonding in polymer composites, organosilanes are capable of interacting with silanol groups on the surface of glass or ceramics through the functional group $-SiX_3$, forming strong $Si-O-Si$ bonds with the surface (Fig. 7).

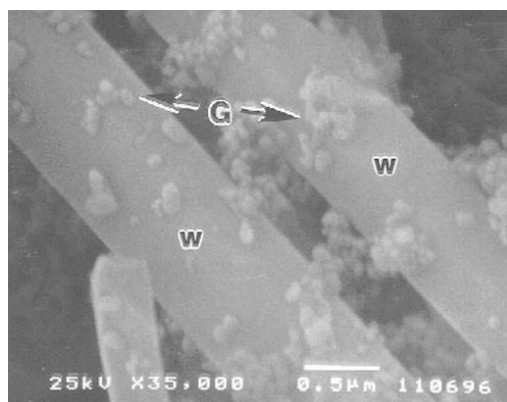


Fig. 7 SEM micrograph of nano-sized silica glass particles “G” fused onto the silicon nitride whiskers “w” by heating at a temperature of 800 °C. The purpose of the silica-whisker fusion was to facilitate the silanization of whiskers and roughen the whisker surfaces for enhanced retention in the resin matrix (Dickens et al., 2005 [37])

In another study (Söderholm and Shang [38]), also using silane coating in dental composites, the formation of two types of chemical bonds was confirmed during the treatment of colloidal silica with silanes: one of them is silicone bridges formed by the condensation of hydrolyzed silanes with surface $Si-OH$ groups, and the other is associated with the orientation of silane molecules parallel to the silica surface. It was also noted that during the reaction of siloxane bridge formation, water is formed, which immediately binds to silanol groups, and water molecules are no longer available for hydrolysis reactions of unhydrolyzed silane (Yamaguchi et al. [39]; Iijima et al. [40]). As a result, the intensity of isolated OH groups decrease, their availability for bonding disappears, and surface reactions do not occur (Fig. 8).

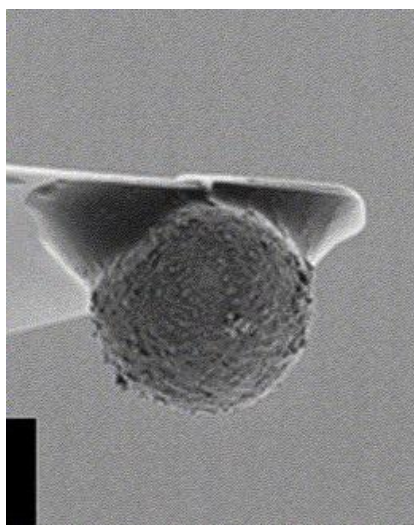


Fig. 8 Typical image of colloid probe with granular silica particle (bar = 4.5 μm) (Iijima et al. [40])

2.4 Silane-Iron oxide

In its typical form, rust is hydrated iron oxides ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ and $\text{FeO}(\text{OH})$). These compounds form on the surface of iron and steel during corrosion and are characterized by the presence of hydroxide groups.

The study (Al-Saadi and Singh Raman [41]) examined the corrosion resistance of low-carbon steel under conditions of enhanced corrosion, and organosilanes were used for pretreatment. When treating a metal surface with silanes, the alkoxy groups undergo hydrolysis to form reactive silanol groups $-\text{Si}-\text{OH}$, which can be adsorbed onto the surface of the oxide and hydroxide phases of iron by means of hydrogen bonds and subsequent condensation, forming $\text{Me}-\text{O}-\text{Si}$ bonds. It was determined that most types of silanes undergo acid-catalyzed hydrolysis, which is accompanied by slow gel formation. However, in an alkali-catalyzed reaction, the condensation reaction rate is higher and gel formation occurs faster. It has also been noted that silane coating is highly sensitive to the number of silanol groups formed as a result of hydrolysis, and only a sufficient number of them can form a protective layer of metal against corrosion. Such a coating can limit the access of oxygen and aggressive ions, the main factors of corrosion, by creating an intermediate phase. The possibility of combining silanes with organic components to form protective films, preventing further oxidation, as well as sealing the area of the coated material, is also mentioned.

The most important step to form the organofunctional group of silanes is the addition of silicon hybrids to substituted olefins and acetylenes according to the reaction (Al-Saadi and Singh Raman [41]):



Reactivity of silane(s) and silanols could be different. Silanols are most stable at pH around 3, and their reactivity increases when pH is lower than 1.5 or higher than 4.5. Effect of pH on alkoxysilane hydrolysis. The gross changes in silane condensation and polymerization in an acid vs. base condition Fig. 9) (Al-Saadi and Singh Raman [41]).

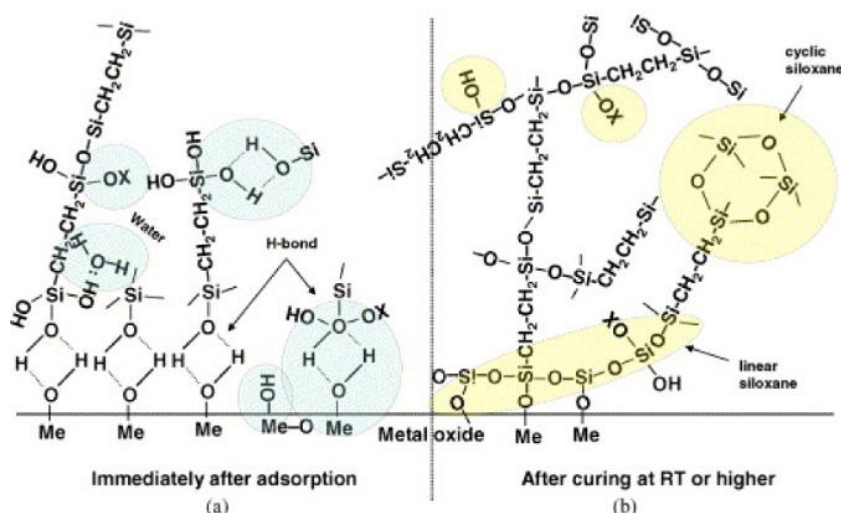


Fig. 9 Simplified schematic of bonding mechanism between silane molecules and metal surface hydroxide layer (a) before condensation: hydrogen-bonded interface and (b) after condensation with covalent-bonded interface (Al-Saadi and Singh Raman [41])

2.5 Silane-Urea fluid phase

UAN-32 solution consists of urea and nitrate in water and is a product of fertilizer production. The liquid has relatively low acidity and reactivity in corrosive reactions when in contact with metal surfaces. The interaction between this type of liquid and silane can be assumed based on the characteristics of these materials. The liquid contains large proportions of ammonium and nitrates, which are catalysts for electrochemical corrosion processes (Sundaram et al. [42]).

Part of the liquid composition contains water, so silanes can theoretically interact with it by forming protective organosiloxane layers on the substrate (e.g., on the metal surface), reducing the access of aggressive components of the solution (NO_3^- , NH_4^+ ions) to the substrate. This process was studied in a paper (Al-Saadi and Singh Raman [41]) that investigated the adsorption of hydrolyzed silanol groups and the subsequent formation of a dense Si-O-Si network structure that limits the diffusion of corrosion-active particles.

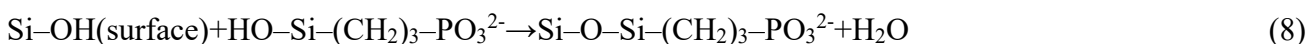
2.6 Technical background of the use of phosphonate-functional silanes for optical surface modification

The category of anionic silanes, specifically phosphonate-terminated silanes, refers to organosilicon compounds where the silicon atom is bonded to a functional phosphonate group (typically as a sodium salt). The general formula for such a molecule, which acts as a molecular bridge on optical surfaces, can be represented as $(\text{OH})_3\text{Si-R-PO}_3^{2-}$.

Unlike alkyl silanes such as OTES, which primarily provide hydrophobicity through long carbon chains, phosphonate silanes are engineered to provide high surface energy and a strong negative electrostatic potential (zeta potential). The structure typically consists of a trialkoxysilyl or trihydroxysilyl group at one end, which facilitates bonding to the substrate, and a phosphonate head-group at the other, which provides the anionic functionality.

2.6.1 Hydrolysis and bonding mechanism

Analogous to the reactions described for alkoxy silanes (Eq. 8 in previous sections), phosphonate silanes undergo hydrolysis to form reactive silanetriol intermediates. These silanols then participate in condensation reactions with the surface silanol groups ($-\text{Si-OH}$) of fused silica or glass:



This creates a chemically bonded, stable monolayer that is resistant to mechanical wear and chemical degradation. While OTES forms a non-polar barrier, phosphonate-functional silanes create a "charged shield."

2.6.2 Zeta potential and antifouling properties

Aqueous media such as UAN-32 promote dissociation of the phosphonate groups, resulting in the surface acquiring a pronounced negative charge. Scientific studies indicate that such modifications can achieve a zeta potential of approximately -50 mV. This is critical for the prevention of "fouling" caused by iron oxide microparticles (rust). According to the DLVO theory, the strong negative charge of the optical surface creates a repulsive electrostatic force that prevents neutral or slightly negatively charged iron oxide particles (Fe_2O_3) from adhering to the surface.

2.6.3 Stability in aggressive fluids (UAN-32)

The interaction between the phosphonate silane layer and the Urea Ammonium Nitrate (UAN-32) fluid is governed by the chemical stability of the Si–O–Si bond and the phosphonate group. Unlike simple carboxylic silanes, phosphonates exhibit superior resistance to hydrolysis in environments with high ionic strength and varying pH levels (typically pH 6.5–7.5 for UAN-32). The dense siloxane network formed after thermal curing (110°C) limits the diffusion of aggressive NO_3^- and NH_4^+ ions to the silica substrate, thereby acting as both a corrosion inhibitor and an antifouling agent.

2.6.4 Comparison with HMDS and OTES

While HMDS and TMCS are used for temporary protection or to increase volatility in chromatography, phosphonate silanes are permanent modifiers. Compared to OTES, which provides a water-repellent effect (contact angle $\sim 135^\circ$), phosphonate silanes are often more hydrophilic but offer superior protection against the deposition of inorganic micro-solids. For optical spectrometry cuvettes, this ensures that the light path remains clear of rust deposits, maintaining the accuracy of the measurements without altering the optical properties of the fused silica, as the coating thickness remains in the 1–5 nm range.

3 Methodology

3.1 Single rust particle interaction

When modeling using the discrete element method (DEM), it is important to first find out the interaction model, since it is difficult to predict the behavior of the interacting system (as an example, to know whether the particle will adhere or not) how the interaction of individual elements occurred. The interaction of rust particles is described considering Newton's second law, discrete element method (DEM):

$$m_i \mathbf{a}_i(t) = \mathbf{F}_i(t), \quad (9)$$

here m_i is the mass and $\mathbf{a}_i(t)$ is the acceleration of rust particle. Vector $\mathbf{F}_i(t) = \sum_j \mathbf{F}_{i,j}(t)$ corresponds to the resultants of forces added up and acting on the center of a rust particle i during a possible interaction. The calculation is performed in each time step Δt numerically by applying a fifth order Gear's predictor-corrector scheme used in the DEM.

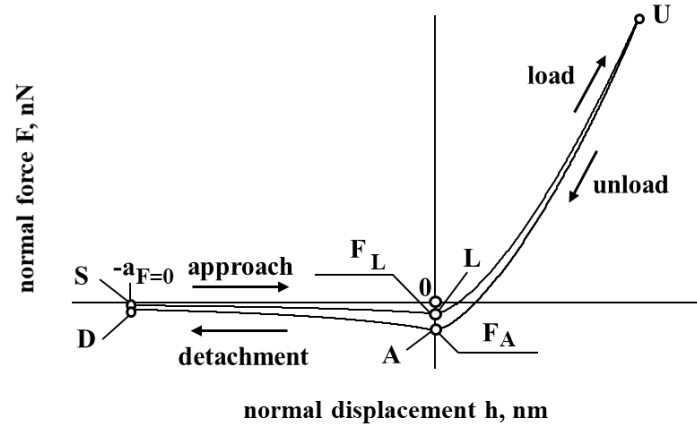


Fig. 10 Force versus displacement. Rust particle interaction

Fig. 10 shows a model of the interaction of rust particle. The interaction begins at point A, before contact, when the attractive forces acting on the surface of the particle are sufficient for their mutual attraction. Here SL is the approach of a rust particle to the surface of another particle. LU is the load upon contact of the particle, UA is the unloading upon contact, AD is the separation of the particle upon breaking the contact.

In the present work, the calculation of the mass is simplified and expressed as follows:

$$m_i = \frac{4}{3}\pi\rho_i R_i^3, \quad (10)$$

here ρ_i denotes the density of the particle.

The total force acting on the particles during interaction can be decomposed into individual components, each of which describes the combined effect of attractive and repulsive forces:

$$F(t) = F_{adh}(t) + F_{el} + F_{diss} + F_{dl}(t) + F_{drag}(t), \quad (11)$$

here $F_{adh}(t)$ is adhesion force; $F_{dl}(t)$ is electrostatic double layer force; $F_{drag}(t)$ is drag force; $F_{el}(t)$ is elastic force; $F_{diss}(t)$ is energy dissipation force.

As mentioned earlier, when considering particles interaction, it can be divided into separate segments (Fig. 10), including interactions at a distance (approach and detachment/separation) and interactions at contact (loading and unloading). Now let's consider the forces, considering each stage/segment separately.

3.1.1 Approach

The interaction begins at point A (Fig. 10) with the process of approach. When particle approach each other, the adhesion force, the electrostatic double layer force, and the liquid resistance force are estimated:

$$F(t) = F_{adh}(t) + F_{dl}(t) + F_{drag}(t), \quad (12)$$

here $F_{adh}(t)$ is adhesion force; $F_{dl}(t)$ is electrostatic double layer force; $F_{drag}(t)$ is drag force.

3.1.2 Calculation of adhesion force

The adhesion force F_{vdW} for a R_i radius having rust particle on glass in liquid at separation distance h is calculated as follows (sphere interaction with a flat surface, Israelachvili and Ruths [43]):

$$F_{vdW} = \frac{A_H \cdot R_i}{6h_{separation}^2}. \quad (13)$$

Separation $h_{separation}$ distance is considered as $h_{separation} = a_{F=0}$.

If the separation increases (e.g., due to surfaces roughness or hydration layers), the adhesion force decreases rapidly because $F \sim 1/h^2$. A_H is the Hamaker constant.

This uses the van der Waals force formula

$$F_{vdW} = \frac{A_H R}{6h^2}, \quad (14)$$

with a Hamaker constant $A_H = 30 \cdot 10^{-20}$ J.

If the separation increases (e.g., due to surface roughness or hydration layers), the adhesion force decreases rapidly because $F \sim 1/h^2$. The adhesion force of 1 μ m particle on fused glass in liquid at a 20 nm distance is $F_{vdW} = 1.5$ nN.

3.1.3 Loading

During loading, in the presence of contact, the deformation in the contact zone is additionally considered, and a new deformation describing member $F_{el}(t)$ is included:

$$F(t) = F_{adh}(t) + F_{el}(t) + F_{dl,L} + F_{drag}(t), \quad (15)$$

here $F_{adh}(t)$ is adhesion force; $F_{dl}(t)$ is electrostatic double layer force; $F_{drag}(t)$ is drag force; $F_{el}(t)$ is elastic force; $F_{diss}(t)$ is energy dissipation force.

3.1.4 Unloading

After loading the contact deformation is followed by unloading, which begins at point U (Fig. 10) and continues to point A, which describes the beginning of detachment/separation. Unloading is described similarly to loading, with the addition of the term $F_{diss}(t)$, which takes into account the change in attraction force during contact deformation. This term estimates the change in tension force necessary to assess the presence of rust particle adhesion.

$$F(t) = F_{adh}(t) + F_{dl}(t) + F_{drag}(t) + F_{el}(t) + F_{diss}(t), \quad (16)$$

here $F_{adh}(t)$ is adhesion force; $F_{dl}(t)$ is electrostatic double layer force; $F_{drag}(t)$ is drag force; $F_{el}(t)$ is elastic force; $F_{diss}(t)$ is energy dissipation force.

3.1.5 Detachment

The effect of the changed attraction force is also considered in the case where the particle is separated after contact, but since the contact is broken during detachment/separation, the deformation forces are not considered:

$$F(t) = F_{adh}(t) + F_{dl}(t) + F_{drag}(t) + F_{diss}(t), \quad (17)$$

here $F_{adh}(t)$ is adhesion force; $F_{dl}(t)$ is electrostatic double layer force; $F_{drag}(t)$ is drag force; F_{diss} is energy dissipation force.

$$v_{liquid\ flow}(h) = v_{max,liquid\ flow} \left(1 - \left(\frac{R_{pipe} - |h|}{R_{pipe}} \right)^\xi \right). \quad (18)$$

3.2 Development of longitudinal and transverse models of fluid and particle flows

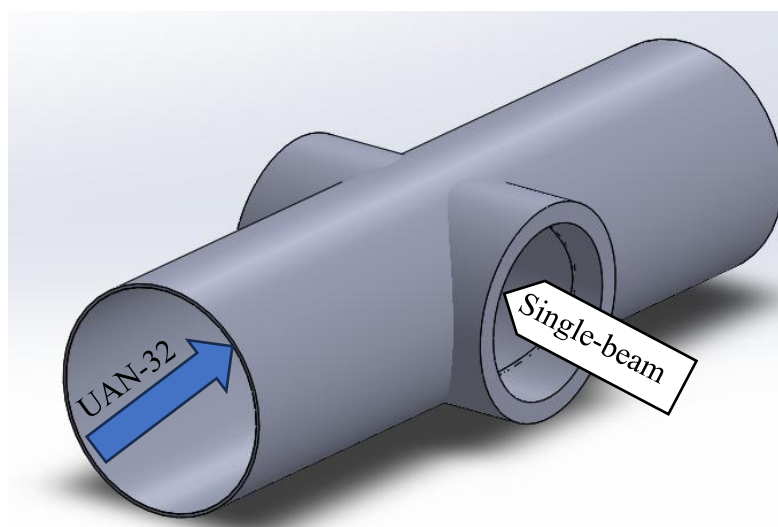
To create the numerical model, a physical model was employed consisting of a pipeline branch with a channel through which the investigated fluid flows. Within a segment of the channel, a spectral window is installed, bounded on both sides by cylindrical cuvettes. All geometric parameters of the numerical model fully replicate the real applied object. The geometry was developed using the parametric design software SolidWorks. Numerical simulations were carried out using the software package COMSOL Multiphysics.

For modeling fluid flow, two flow regimes were selected: laminar flow and the turbulent k- ϵ model. Boundary conditions for both models were intentionally set to be identical to enable a direct comparison between the cases. Both models were applied under steady-state conditions. The inlet velocity was defined using the “fully developed flow” condition, with an average velocity of 0.0021 m/s. The outlet boundary condition was specified as a free outflow, with the static pressure p_0 equal to 0 Pa.

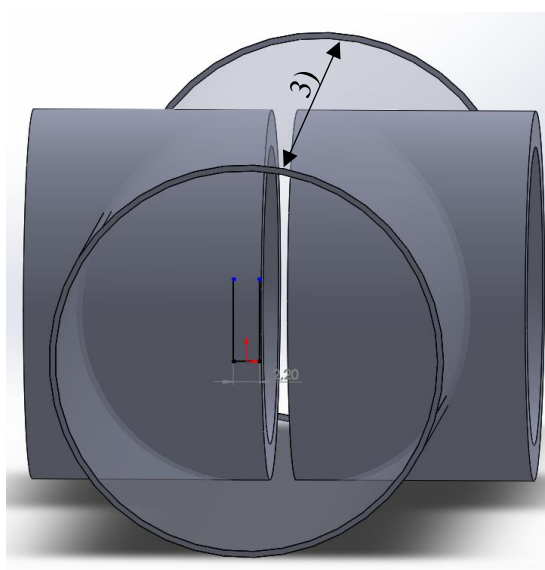
The fluid material properties were defined to accurately represent the physical model, with a density $\rho = 1310\text{ kg/m}^3$ and a dynamic viscosity $\mu = 0.005\text{ Pa}\cdot\text{s}$. Particle trajectories were computed using a time-dependent approach. The particles were assigned properties consistent with the physical model: particle density $\rho_p = 4000\text{ kg/m}^3$ and particle diameter of $1\text{ }\mu\text{m}$. At the inlet, particles were introduced with randomly distributed initial positions, with a total of 500 particles released. Particle velocity was coupled to the corresponding velocity field obtained from the fluid flow model. Additionally, a drag force acting on the particles was included in the simulation.

The computational mesh was generated using a physics-controlled meshing approach, consisting of approximately 190,000 elements (triangular, quadrilateral, tetrahedral, prismatic, and pyramidal elements). A physics-controlled solution method was selected for each flow regime. For particle tracking simulations, the total simulation time was set to 100 seconds to capture the full process from inlet to outlet.

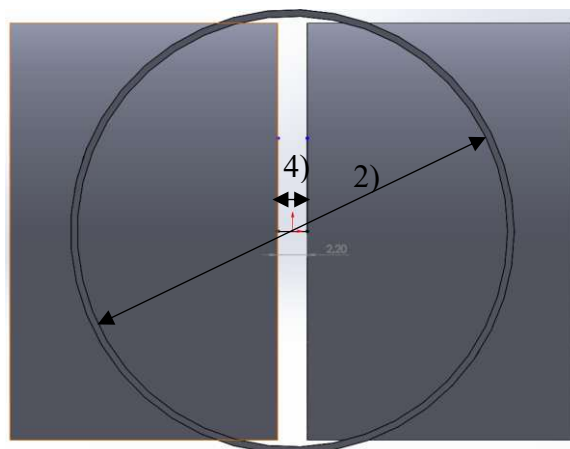
For visualization of solution, the following options were used: Streamline, Multislice, Surface, and Particle Trajectories. Additionally, Line Graphs were generated to represent transverse and longitudinal velocity profiles.



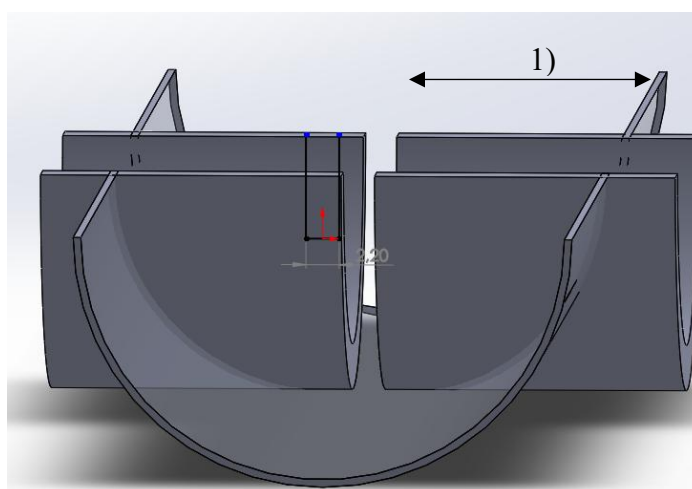
a)



b)



c)



d)

Fig. 11 Cross view a) isometric, b) from the inlet side, c) profile, d) a cross-section of fluid channel and single-beam cuvette with dimensions 1) 15 mm, 2) 32 mm, 3) 120 mm, 4) 2 mm, 5) 31 mm. 6) 25 mm

The trajectories of particles were analyzed using COMSOL Multiphysics 6.4. The model employed the following physics interfaces: Laminar Flow, Particle Tracing for Fluid Flow, and Fluid-Particle Interaction.

The boundary conditions for the laminar flow were set according to the first-stage simulation task, with an inlet velocity of 0.0021 m/s, corresponding to the *Fully developed flow* option.

For particle trajectory modeling, the Particle Tracing for Fluid Flow boundary conditions included Particle release specification set to *Specify mass flow rate*, with a maximum number of secondary particles (Maximum number of secondary particles) of 10,000. Additionally, the Particle size distribution was set to *Uniform size*.

Walls 1, which include all surfaces except the edge-parallel surfaces in the spectral window, were assigned the Wall condition: Bounce, with no other initial particle conditions specified. The particle density was set to 4000 kg/m³, particle diameter to 1 µm, and particle type was Solid particles, uncharged. The acting forces on the particles were defined as Drag force.

The inlet Mass flow rate was set to 1 µg/s with a random initial position, and the Number of particles per release was 5000. Walls 2, representing only the edge-parallel surfaces within the spectral window, were assigned the Wall condition: Stick. In the multiphysics settings, the Coupled Interfaces section defined the coupling from *Particle Tracing for Fluid Flow* to *Laminar Flow*.

The computational mesh was generated using the Element size: Finer option, resulting in 103,218 triangles, 552 quads, 1,643,771 tetrahedra, 190,572 prisms, and 4,332 pyramids.

Thus, the numerical model for particle trajectories was established following the above boundary conditions and model specifications.

3.2.1 Laminar flow

The default Laminar Flow reference pressure level is set to and equal to 0. For a steady-state process, the fluid properties are described by the following equations:

$$\rho(u \cdot \nabla)u = \nabla \cdot [-pl + K] + F; \quad (19)$$

$$\rho \nabla \cdot u = 0; \quad (20)$$

$$K = \mu(\nabla u + (\nabla u)^T), \quad (21)$$

here T is the temperature is taken from the common model input;

ρ and μ – are taken from fluid properties, density and specific dynamic viscosity.

The inlet is considered as fully developed flow and the model is set to a steady state, as described by the following equations:

$$u_w \cdot t = 0; \quad (22)$$

$$-\frac{1}{A} \int_{\partial\Omega_{in}} u \cdot ndS = U_{av}, A = \int_{\partial\Omega_{in}} dS. \quad (23)$$

For the outlet, the stationary process is described by the following equations:

$$[-pl + K]n = -\widehat{p_0}n \quad (24)$$

and

$$\widehat{p}_0 \leq p_0. \quad (25)$$

3.2.2 Particle tracing for fluid flow

For Particle Tracing for Fluid Flow is used Stationary study and equation is:

$$\frac{d}{dt} \left(m_v \frac{dq}{dt} \right) = F_t. \quad (26)$$

For Wall is set fixed and equation by default is:

$$v = v_c - 2(n \cdot v_c)n, \quad (27)$$

here v_c is the particle velocity when striking the wall. The Wall condition in model is bounce.

The physical characteristics of the rust particles were defined with a density of 4000 kg/m³ and a diameter of 1 μm. The particles were modeled as solid spheres. Charge is not used.

For drag force is using these equations

$$F_D = \frac{1}{\tau_p} m_p M(u - v); \quad (28)$$

$$\tau_p = \frac{\rho_p d_p^2}{18\mu}; \quad (29)$$

$$F_{vm} = \frac{1}{2} m_f \frac{d(u-v)}{dt}, \quad (30)$$

here

$$m_f = \frac{1}{6} \pi d_p^3 \rho; \quad (31)$$

$$\frac{d(u-v)}{dt} = \frac{\partial(u-v)}{\partial t} + v \cdot \nabla(u - v); \quad (32)$$

$$F_p = m_f \frac{Du}{Dt}; \quad (33)$$

$$\frac{Du}{Dt} = \frac{\partial u}{\partial t} + u \cdot \nabla u; \quad (34)$$

$$M = \frac{1}{1 - \frac{9}{16}\alpha + \frac{1}{8}\alpha^3 - \frac{45}{256}\alpha^4 - \frac{1}{16}\alpha^5} (1 - P(n)) + \frac{1}{1 - \frac{9}{8}\alpha + \frac{1}{2}\alpha^3} P(n); \quad (35)$$

$$\alpha = \frac{r_p}{L}, \quad (36)$$

here L is the distance to the nearest wall;

$P(n)$ is the projection onto the vector normal to the wall;

For inlet is set Stationary and by default is using:

$$q = q_0; \quad (37)$$

$$v = v_0. \quad (38)$$

Mass flow rate is set 1 µg/s. Initial position is random and number of particles per release (N) is 5000. As velocity (u) is used velocity field. For outlet is set Stationary and by default is using:

$$q = NaN. \quad (39)$$

For wall condition is set Disappear and Stick. Wall 2 is set Stationary and is described by the following equation:

$$v = 0. \quad (40)$$

3.3 Multiphysics model preparation. Movement of rust particles in the pipe

For a part of solution Multiphysics are used, Type is Fluid-Particle Interaction. Type is Stationary and described by the following equation:

$$\frac{\partial F_v}{\partial t} = - \sum_{i=1}^N \frac{f_{rel,i} F_D}{meshvol}, \quad (41)$$

here the sum is taken over particles in the mesh elements.

Coupled Interfaces is set as Source Particle Tracing for Fluid Flow and for Destination is Laminar Flow.

The numerical model was based on a physical setup consisting of a channel branching from a line, through which the test fluid flows. In the channel section, a spectral window is installed, bounded on both sides by cylindrical cuvettes. All geometrical dimensions of the numerical model precisely replicate the actual physical object. The geometry was created using the parametric design software SolidWorks.

For the numerical analysis, the COMSOL Multiphysics software package was employed. Two flow modules were selected for the fluid: laminar flow and turbulent $k-\epsilon$. The boundary conditions for both modules were deliberately set identically to enable comparison between the two cases. Both modules were applied under steady-state conditions. The inlet velocity was defined using the Fully developed flow option, with an average velocity of 0.0021 m/s. The outlet was set as a free outflow with static pressure p_0 is 0 Pa.

The fluid properties were defined to accurately represent the physical model, with a density $\rho = 1310 \text{ kg/m}^3$ and dynamic viscosity $\mu = 0.005 \text{ Pa}\cdot\text{s}$.

For particle trajectory simulations, a time-dependent approach was employed. Particle properties were defined according to the physical model, with particle density $\rho_p = 4000 \text{ kg/m}^3$ and a diameter of 1 µm. The inlet condition specified a random initial particle position, with 500 particles released per injection. Particle velocity was coupled to the corresponding velocity field computed in the fluid flow module. Additionally, drag force was included as the force acting on particle motion.

The computational mesh was generated using a Physics-controlled approach, consisting of approximately 190,000 elements (triangles, quadrilaterals, tetrahedra, prisms, and pyramids). For each flow case, a Physics-controlled solver was applied.

The duration of the particle motion simulations was set to 100 seconds, covering the complete process from inlet to outlet. For result visualization, Streamline, Multislice, Surface, and Particle Trajectories options were used, and additional Line Graphs were generated to display cross-sectional and longitudinal velocity profiles.

4. Results

4.1 Single particle interaction

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn. Initial data for numerical simulation is presented in Table 1. The parameter values summarized in Table 1 were selected to represent a physically realistic operating scenario for in-line spectrophotometric monitoring of UAN-32 fertilizer solutions contaminated with corrosion-derived iron oxide particles. The adopted particle diameter of 1 μm corresponds to the characteristic size range commonly reported for suspended iron oxyhydroxide particulates in industrial aqueous systems. This size range is particularly relevant because such particles are sufficiently large to influence optical transmission while remaining strongly affected by colloidal interaction forces.

Surface potentials, elastic properties, fluid characteristics, and electrochemical parameters were selected from experimentally reported literature values for fused silica, iron oxide particles, silane-based coatings, and concentrated aqueous electrolyte environments. The phosphonate-functional silane surface was represented by a strongly negative surface potential in order to evaluate the maximum achievable electrostatic repulsion and antifouling performance under realistic operating conditions.

The selected parameter set should be interpreted as a representative engineering configuration rather than a system-specific calibration. Consequently, the objective of the model is not to reproduce a particular experimental dataset, but to identify the dominant physical mechanisms governing particle transport, attachment, and detachment at the optical surface. This approach enables a mechanistic assessment of contamination processes and provides a physically grounded basis for evaluating the effectiveness of surface modification strategies.

Table 1 Initial data for simulation of pollutant rust, optical window, silan, Fluid Urea Ammonium Nitrate

Objects	Initial Parameters	Values	References, Source
Pollutant rust	Material (Goethite)	$\alpha - \text{FeO}(\text{OH})$	-
	Considered pollutant particle diameter (table 1), d	1 μm	Karim et al. [44]; Locsin et al. [45]
	Radius, R_i	0.5 μm	-
	Initial interaction distance, h_S ($h_S = a_{F=0}$)	20 nm	Hunter [46]; Israelachvili and Ruths [43]; Kosmulski [47]
	Initial velocity, v_0	-0.21 cm/s	Calculated from the flow rate.
	Tangential velocity, v_0^T	-0.0981 cm/s	-
	Normal velocity, v_0^N	-0.0981 cm/s	-
	mass, m_i	$\approx 2.094 \times 10^{-15} \text{ kg}$	Eq. (10)
	Density, ρ_i	$\approx 4000 - 4250 \text{ kg/m}^3$	Dana [48]
	Debit, Q	5 l/min	-

Optical window	Young's modulus, E_i	150 GPa	Tunega [49]; Wang and Huang [50]
	Poisson's ratio, ν_i	0.245	Tunega [49]; Wang and Huang [50]
	Surface potential, ψ_i	-10 mV	Sposito [51]
	The adhesion force (point L), $F_{L,adh}$	-1.5 nN	Eq. (13), Eq. (14)
	Material	Fused silica	
	Density, ρ_j	2.20 g/cm ³	Le Parc et al. [52]; Ollier et al. [53]; Root et al. [54]
	Young's modulus (Fused silica), E_j	74 GPa	Le Parc et al. [52]; Zha et al. [55]
	Poisson ratio, ν_j	0.17	Deschamps et al. [56]; Polian et al. [57]
	Surface potential, ψ_j	-10 mV	Hunter [46]; Israelachvili and Ruths [43]
Fluid Urea Ammonium Nitrate (UAN)	Type	UAN-32	-
	PH	≈ 7.0 (ranging between 6.5...7.5)	Ren et al. [58]; Wyszowski et al. [59]
	Temperature, T_{temp}	20 °C	-
	The permittivity of the free space, ϵ_0	$8.854 \cdot 10^{-12}$ C ² J ⁻¹ m ⁻¹	Leuchs et al. [60], [61]
	Debye length, λ_D	0.96 nm	Hua et al. [62]; Israelachvili and Ruths [43]; Patil and Keshri [63]; Wahab and Mahiuddin [64]
	Debye length, λ_D	0.106 nm	Gaddam and Ducker, [65]; Lee et al. [66]; Smith et al. [67]
	A dielectric constant of water, ϵ	74.5	
	Viscosity, η_f	≈ 0.005 Pa · s	
	Density	1.305–1.325 g/cm ³	
Cuvette	Diameter/width, $d_{cuvette}$	12 – 14 cm	Consistent with standard flow-through optical cell specifications (typical for spectrophotometric liquid analysis hardware; Sprana, 2026). www.sprana.eu
Silan	Surface potential, ψ_j	-50 mV	Parida et al. [68];

(phosphonate -functional)		Kosmulski and Kalbarczyk [69]; Hunter [46].
Density ρ_{silan}	0.9-1.3 g/cm ⁻³	Plueddemann [70]
Coating thickness	2–3 nm	Zhu et al. [71]

4.2 Fluid flow analysis

Now analytical calculations of the fluid flow rate will be performed. The flow rate (debit) can be calculated using following equation:

$$Q = \frac{v}{t}. \quad (44)$$

The debit in the system is $Q = 5.0$ l/min, which is expressed in m³/s:

$$Q = 5.0 \text{ l/min} = \frac{1}{12} \text{ l/s} \approx 0.08(3) \cdot 10^{-3} \text{ m}^3/\text{s};$$

$$\frac{1}{12} \text{ l/s} = 0.08(3) \text{ l/s} \approx 0.08(3) \cdot 10^{-3} \text{ m}^3/\text{s}.$$

Cross section area:

$$A = \frac{\pi(25 \cdot 10^{-3})^2}{4} - 5 \cdot 10^{-3} \cdot (25 \cdot 10^{-3} - 2 \cdot 10^{-3}) = 0.37587 \cdot 10^{-3} \text{ m}^2;$$

$$A = 0.49087 \cdot 10^{-3} - 0.115 \cdot 10^{-3} = 0.37587 \cdot 10^{-3} \text{ m}^2.$$

Liquid flow velocity:

$$v = \frac{Q}{A} = \frac{0.08(3) \cdot 10^{-3}}{0.37587 \cdot 10^{-3}} = 0.2128 \text{ m/s} \approx 0.21 \text{ m/s}.$$

4.3 Micro-mechanical analysis of 1 µm rust particle and modified surface interaction

Comprehensive Micro-mechanical Analysis of Particle-Surface Interaction and Energy Barrier Efficiency. A detailed investigation into the behavior of a 1 µm diameter rust particle, Goethite α -FeO(OH), within a Urea Ammonium Nitrate (UAN-32) solution reveals fundamental shifts in the energetic states between natural and chemically modified optical window surfaces. Based on the simulation parameters, where the particle mass is 2.094×10^{-15} kg and the initial normal velocity is precisely -0.0981 cm/s, the initial modeling of the uncoated glass surface indicates a dominant adhesive mechanism. In this context, the surface potential of the Goethite particle (-10 mV) and the negative potential of the fused silica glass (-10 mV) establish an sufficient electrostatic double layer force. When combined with van der Waals forces, this leads to irreversible heterocoagulation. The force-displacement curves (Fig. 12a) and (Fig. 12b) record a sharp escalation of force into the 24–25 nN range, which is scientifically interpreted as the particle falling into the primary adhesion minimum. The force history graphs (Fig. 12c) and (Fig. 12d) and displacement curves (Fig. 12e) show that the contact duration lasts only fractions of a microsecond, while the velocity history graph (Fig. 12f) definitively confirms that the particle's velocity stabilizes at zero post-interaction. This signifies that the adhesive dissipative energy (30×10^{-18} J) completely absorbs the particle's kinetic energy, preventing any elastic rebound. Electrostatic screening is extremely intense, with a Debye length of approximately 0.1-0.9 nm. Consequently, attractive forces become dominant at very short distances, yet their magnitude is sufficient for irreversible particle trapping.

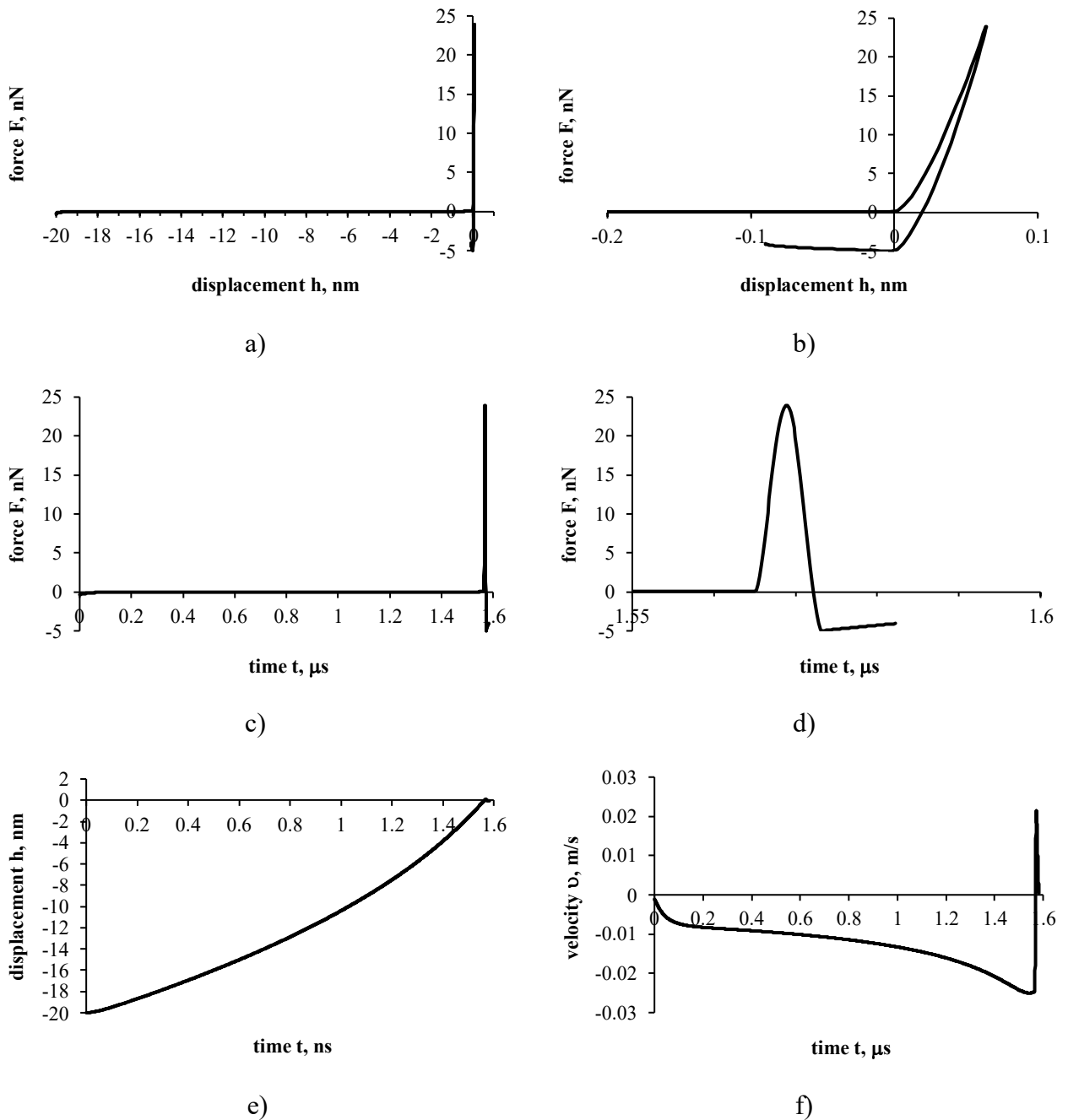


Fig. 12 Interaction of rust particles on the surface of an optical window without additional coating

In the silane-coated system, a significant alteration in the interaction process is observed, as consistently illustrated by all graphs in Fig. 13. Although the initial dynamic parameters of the particle remain identical, the silane layer forms a repulsive energy barrier, which, according to DLVO theory, creates a "positive energy wall." The surface potential of the negative potential of the silan layer (-50 mV) establish a strong influence of electrostatic double layer force. The force-displacement graphs (Fig. 13a) and (Fig. 13b) show that the maximum interaction force is drastically reduced to less than 0.6 nN, representing an approximately fifty-fold decrease compared to the uncoated glass. This repulsive effect manifests even during the particle's approach, preventing it from reaching the physical contact zone. The displacement history graph (Fig. 13c) indicates that the particle stops at a safe distance from the solid surface, and the ultimate proof of protection is visible in the velocity history

graphs (Fig. 12d), (Fig. 12e) and (Fig. 12f). Here, a positive rebound velocity of approximately 0.004 m/s is recorded. This phenomenon is scientifically classified as elastic repulsion, where the silane coating transforms the particle's kinetic energy into a repulsive impulse. Comparing these results to literature describing hydrophobic or charged silane layers, your findings confirm that the coating acts as an effective "soft" barrier that not only reduces adhesion but also ensures the particle remains suspended in the flow. Given that the particle remains detached from the surface after interaction, the hydrodynamic flow is expected to transport suspended particles away from the optical window. This behavior suggests a reduced likelihood of rust particle accumulation and deposit formation on the coated surface. This sequence of data scientifically substantiates that surface modification is an essential requirement for operating optical sensors in aggressive fertilizer media to shift the nature of interaction from static-adhesive to dynamic-repulsive, thereby minimizing measurement errors and extending equipment lifespan. This analysis aligns with the latest trends in surface engineering, which prioritize the creation of energy barriers as the most effective method for combating both organic and inorganic fouling.

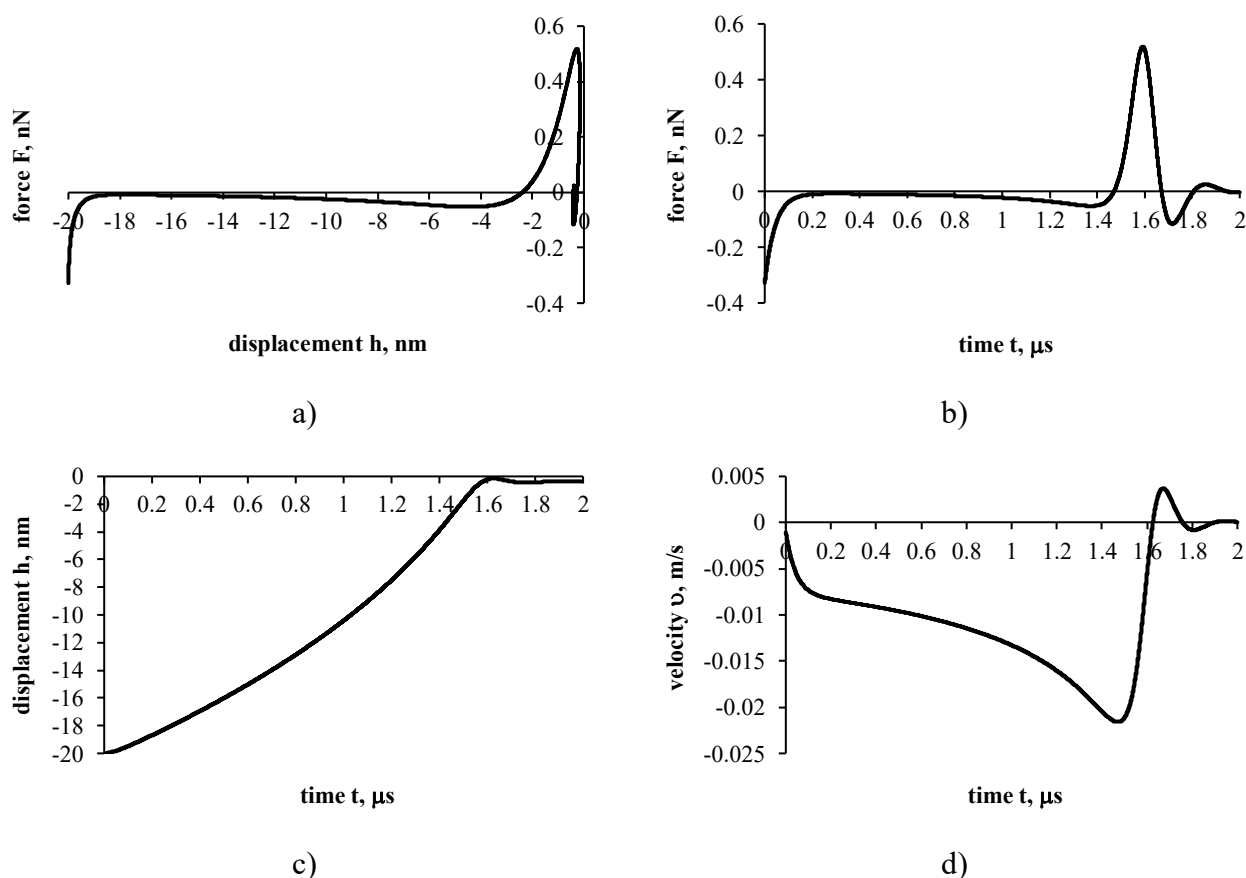


Fig. 13 Interaction of rust particles on the surface of an optical window with additional coating (Silan)

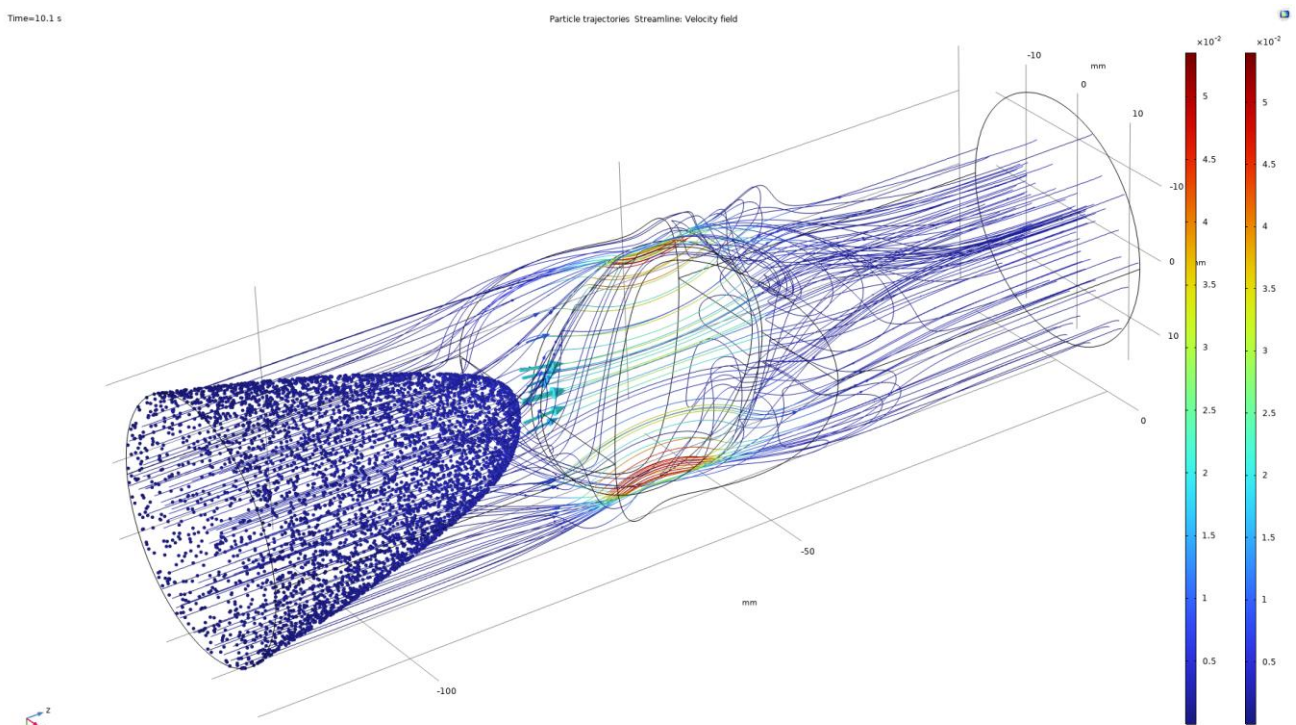
The presented analysis focuses on the interaction between a representative rust particle and fused silica surfaces, both in their pristine state and with silane-based modification, within UAN-32 media. The observed transition from adhesive to predominantly repulsive behavior demonstrates the potential of silane-based coatings to mitigate particle attachment under the investigated conditions. While particle deposition in practical systems may also be influenced by complex particle-particle interactions, local hydrodynamic disturbances, and the long-term evolution of surface chemistry, direct experimental quantification of these coupled effects remains challenging due to the combination of micrometer-scale particles, nanometer-scale interaction distances, and thin surface layers. Therefore,

the adopted modeling framework provides a physically based assessment of the dominant mechanisms governing particle attachment and detachment, establishing a foundation for future investigations of fouling mitigation strategies in optical sensing systems.

4.4 Particle motion using fluid-particle Multiphysics model

The calculated particle trajectories (streamlines) and the framing of particle motion are presented in Fig. 14.

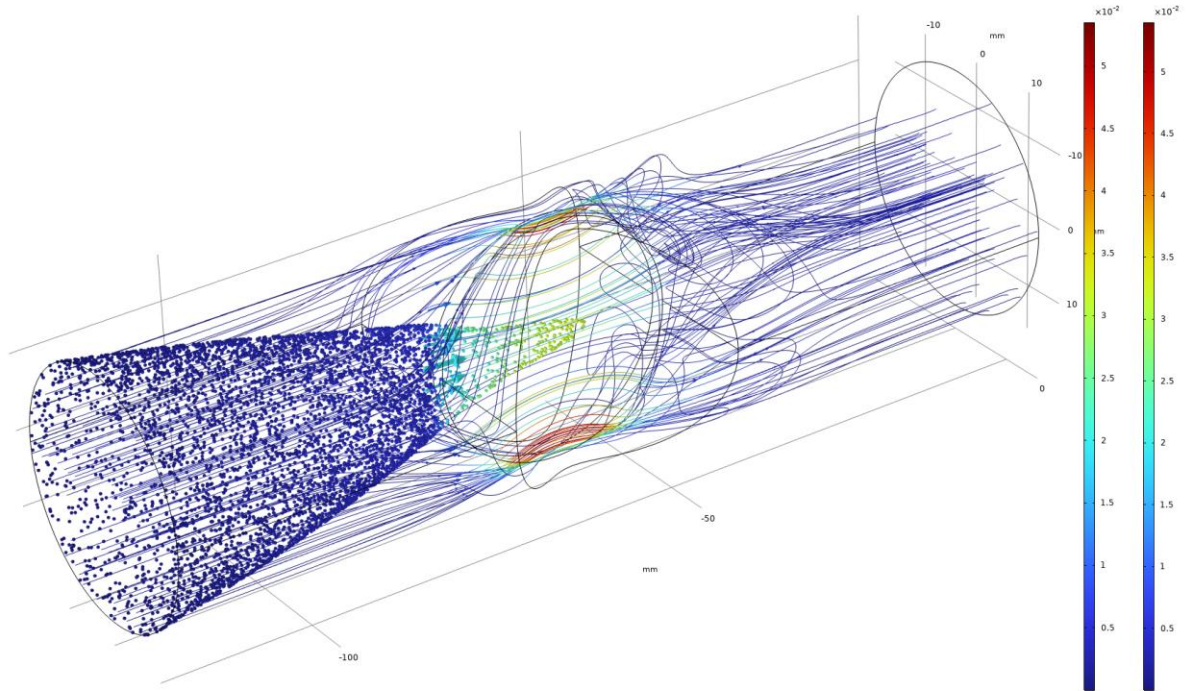
Model results indicated that the entire process, from entering to exiting the channel, occurs within 30 s. For result generation, 100 frames were captured, with each frame having a duration of 0.1 s. Fig. 14a illustrates the situation at the 10-second mark after particle injection. The shape of the particle cloud confirms the effect of the Fully developed flow setting. At 10 s, the particles approach the spectral window; the velocity remains unchanged, and the entire particle flow concentrates along the axis within a section comprising approximately 20% of the channel's transverse width.



a)

Time=11.1 s

Particle trajectories Streamline Velocity field

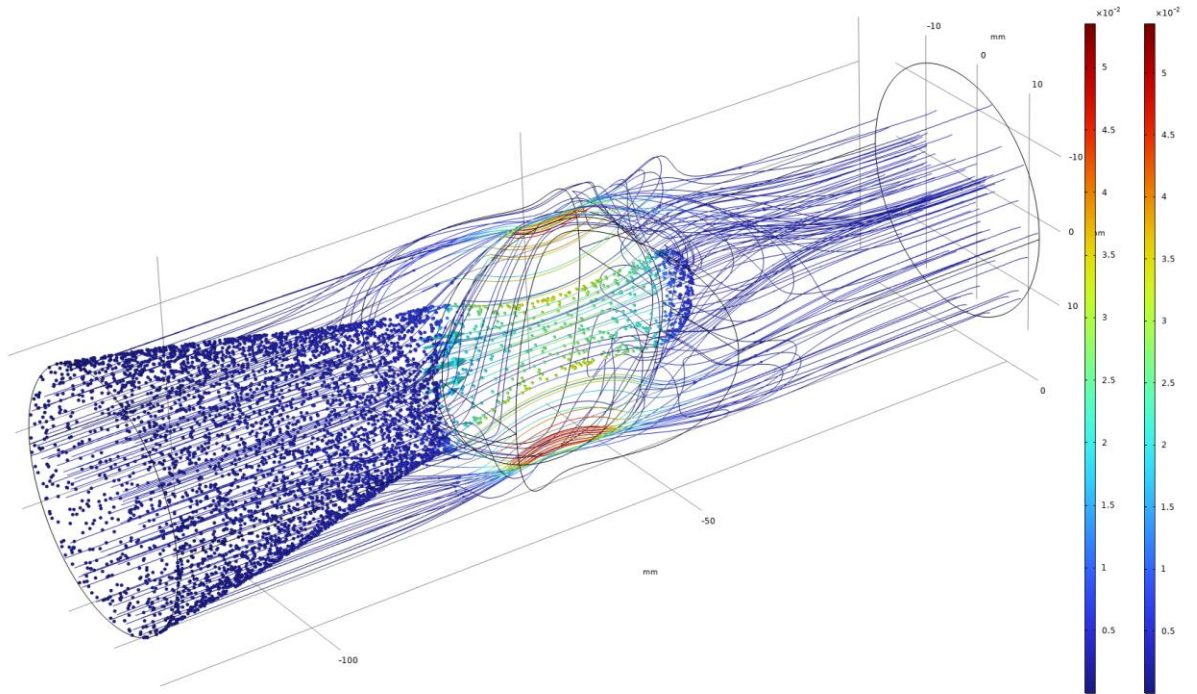


878
879

b)

Time=12.1 s

Particle trajectories Streamline Velocity field

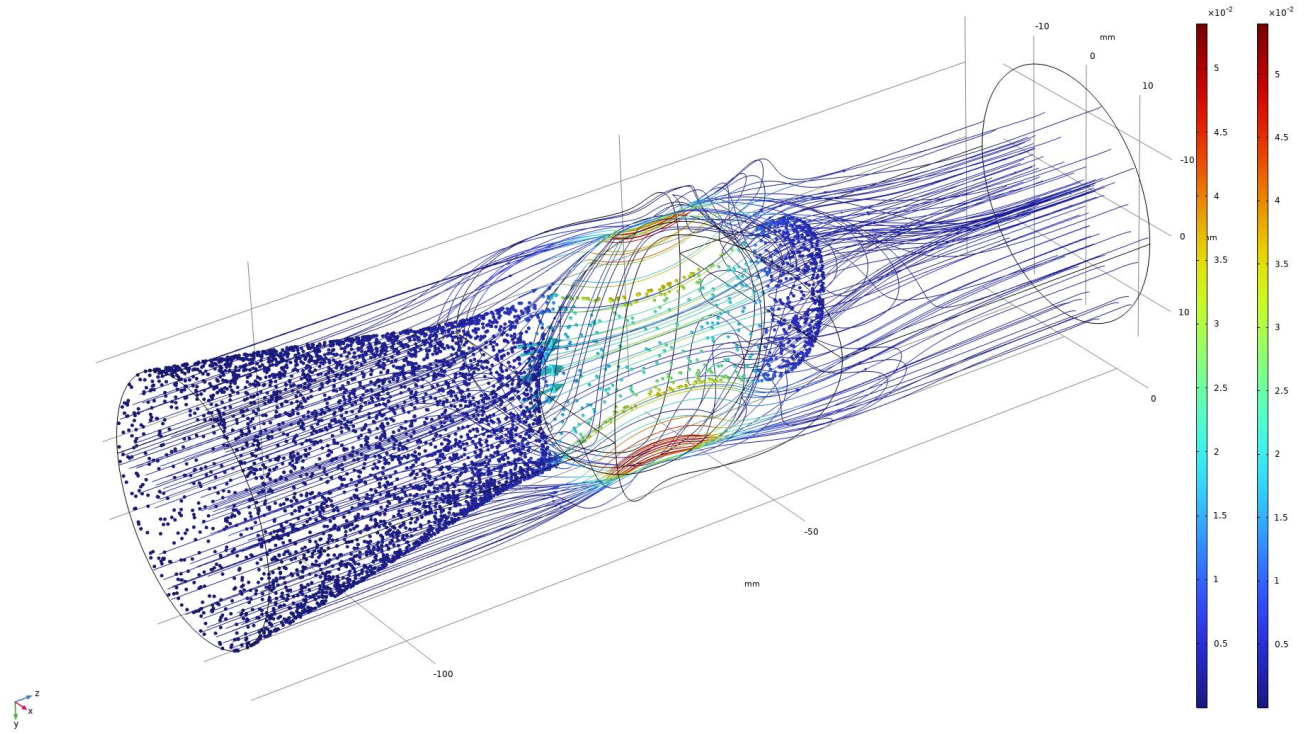


880
881

c)

Time=13.1 s

Particle trajectories Streamline: Velocity field

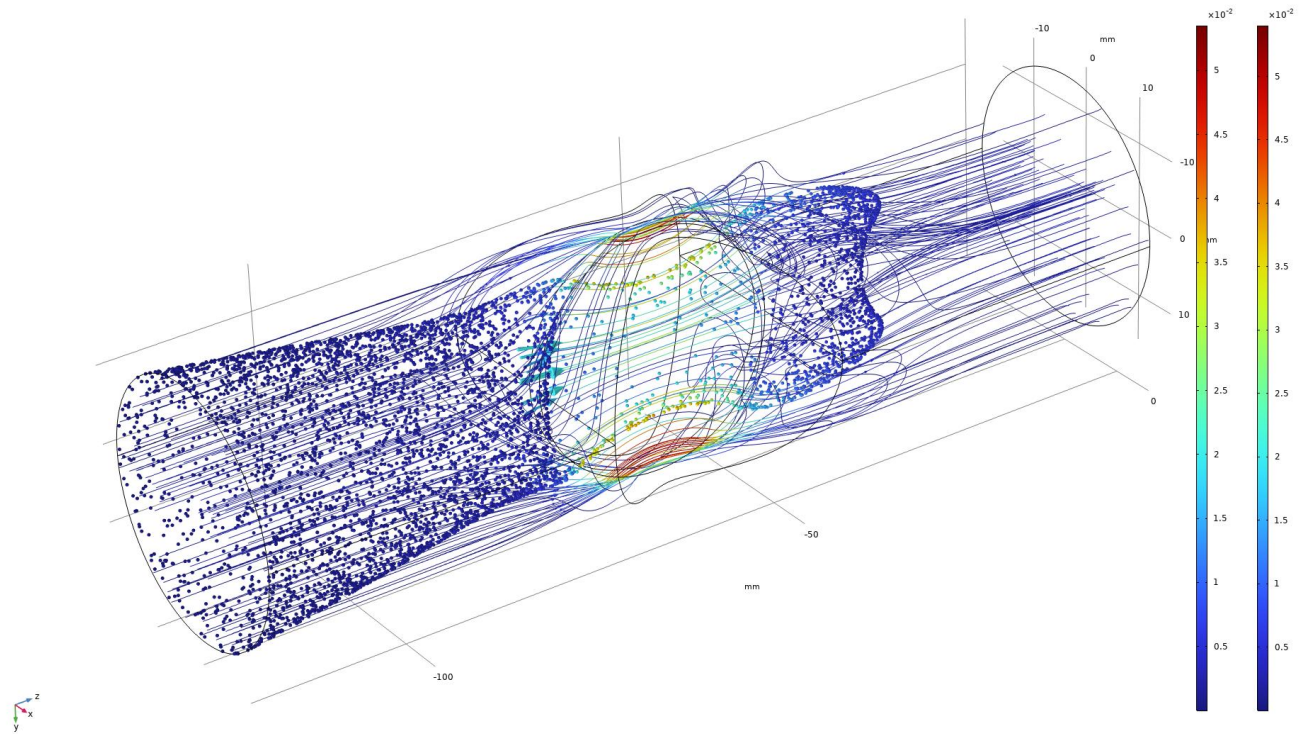


882
883
884

d)

Time=15.1 s

Particle trajectories Streamline: Velocity field

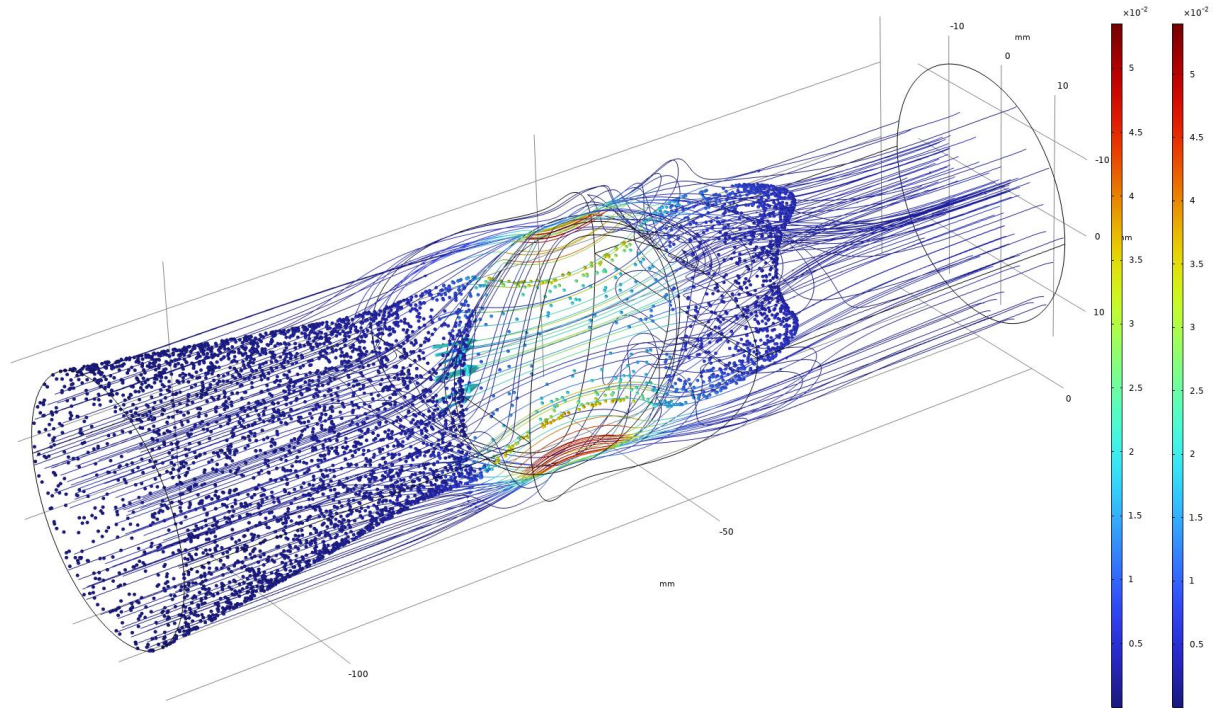


885
886

e)

Time=15.1 s

Particle trajectories Streamline: Velocity field

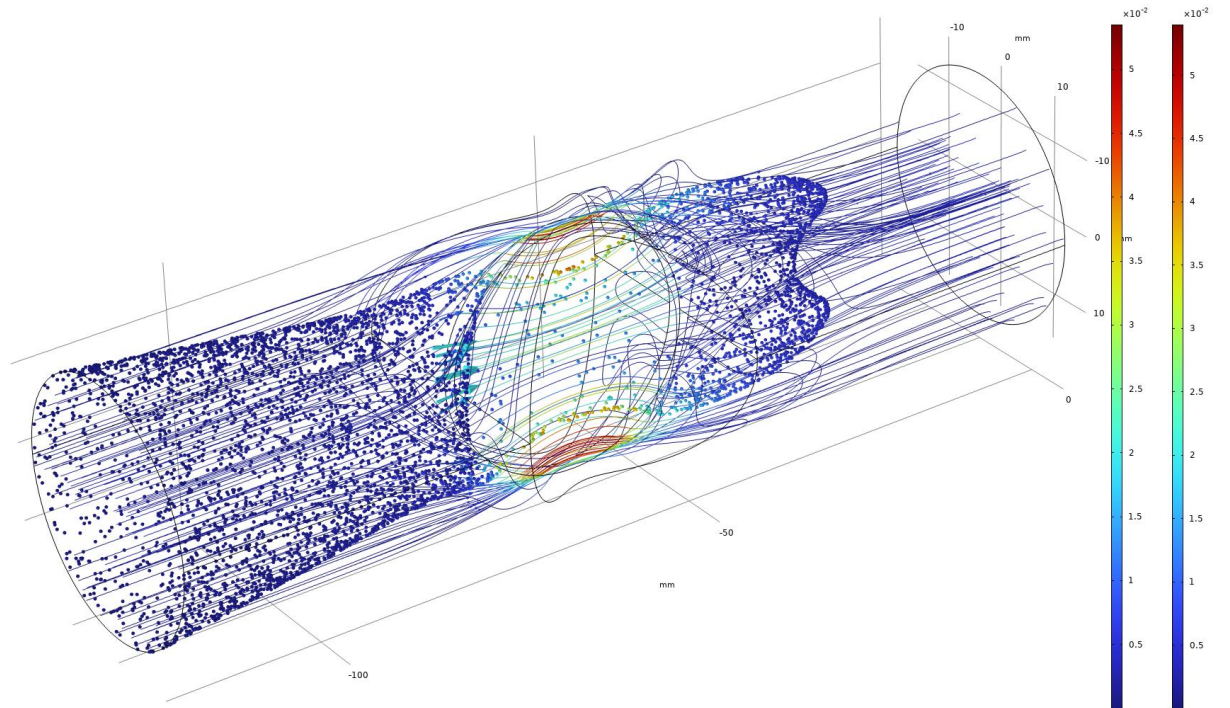


887
888



Time=16.1 s

Particle trajectories Streamline: Velocity field

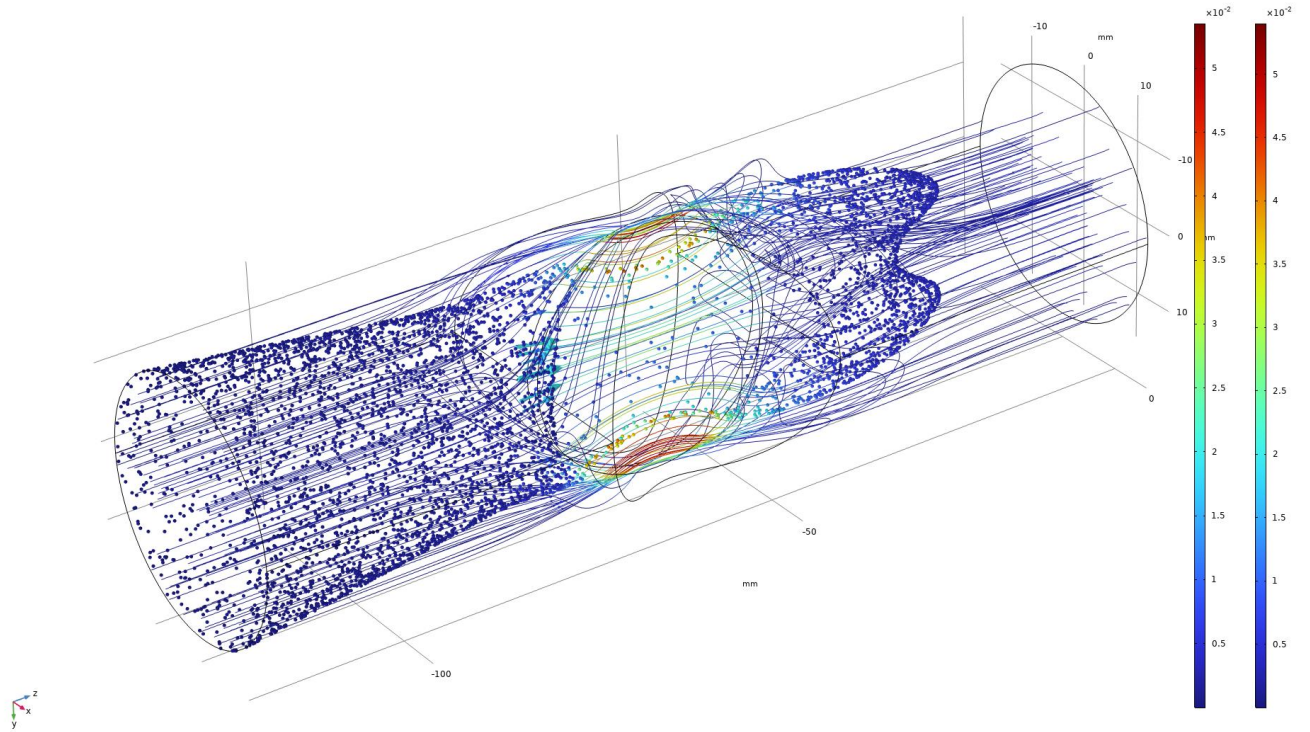


889
890



f)

g)



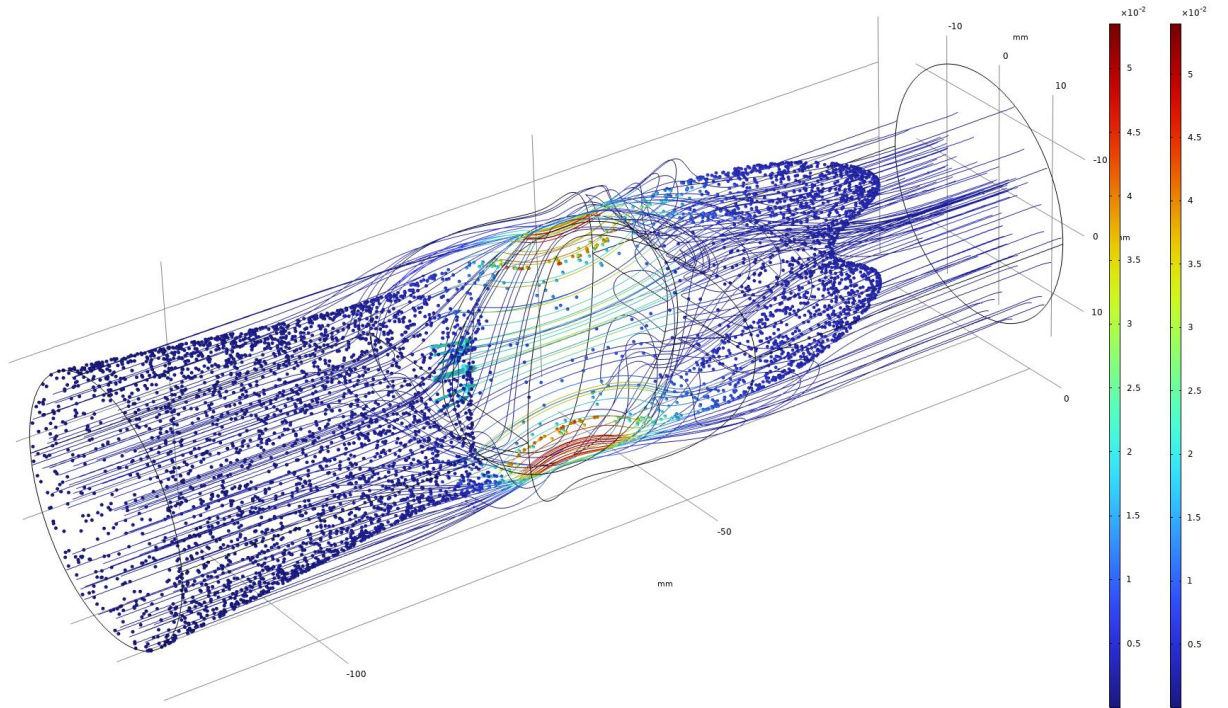
h)

Fig. 14 General view showing particles at a) 10 s, b) 12 s, c) 13 s, d) 14 s, e) 15 s, f) 16 s, g) 17 s, and h) 18 s after inlet, along with particle velocity streamlines under turbulent flow conditions

In Fig. 14b, the particle positions are shown at 12 s from injection. As can be observed, the particles have already entered the spectral window zone, where the transverse width is significantly smaller. This leads to an increase in particle velocity, reaching 0.02 m/s initially and up to 0.035 m/s at the center of the spectral window. The cross-sectional area occupied by the particle cloud decreases approximately threefold upon entering the spectral window zone, and the particles move in a nearly linear beam.

Time=18.1 s

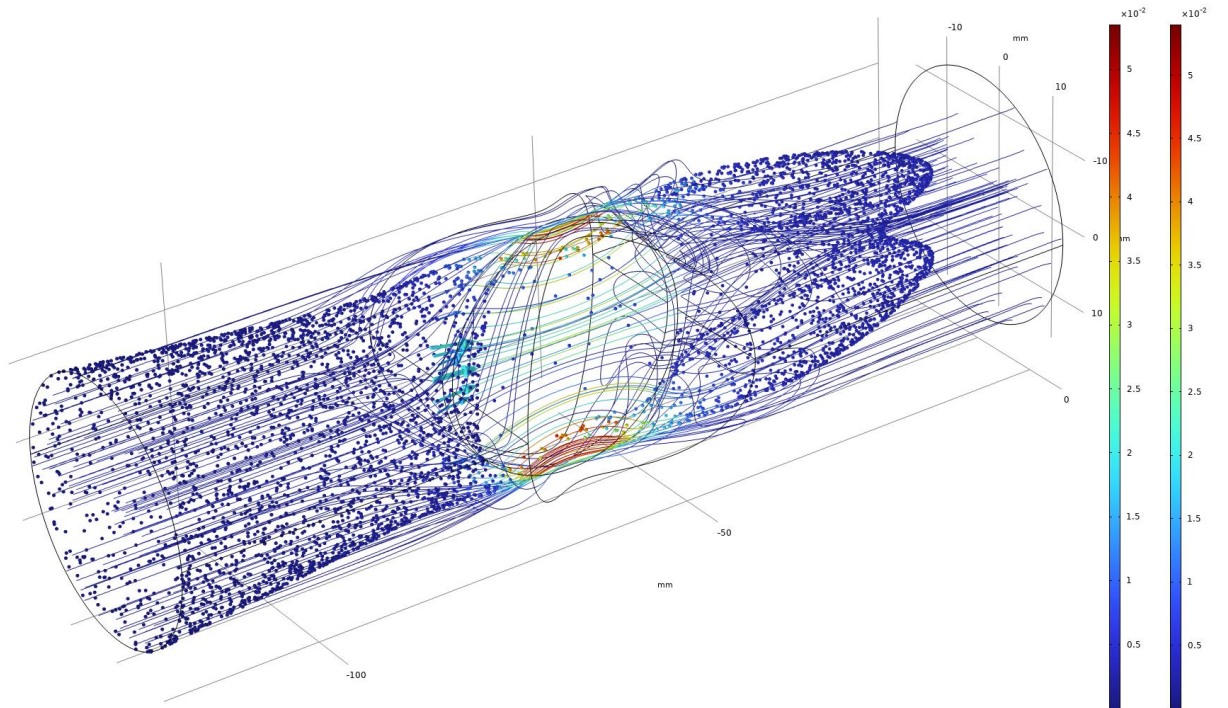
Particle trajectories Streamline: Velocity field



904
905

Time=20.2 s

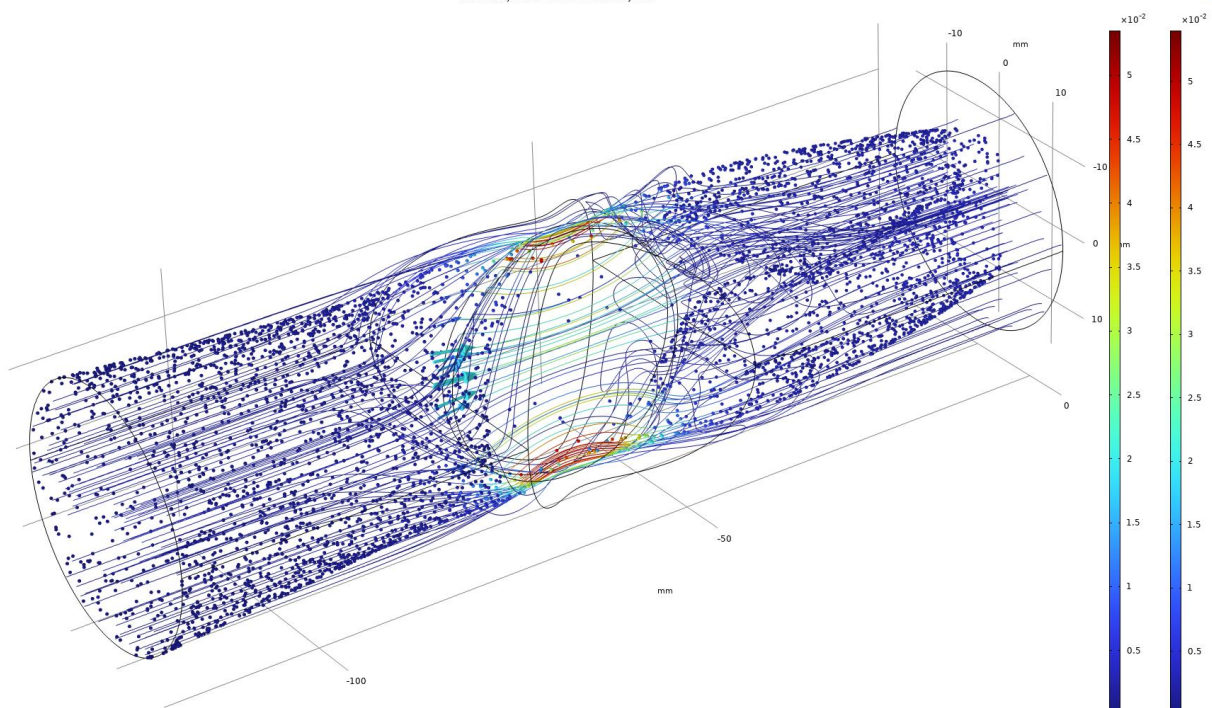
Particle trajectories Streamline: Velocity field



906
907
908

Time=25.2 s

Particle trajectories Streamline: Velocity field

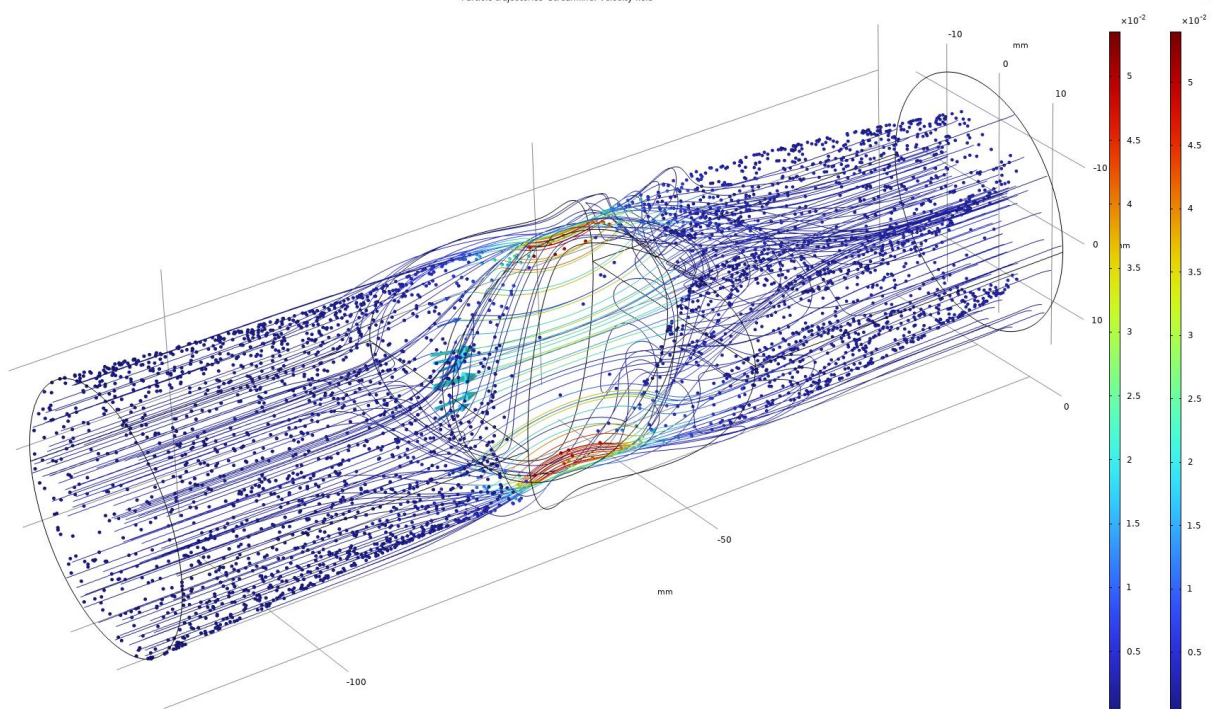


909
910

k)

Time=30.3 s

Particle trajectories Streamline: Velocity field

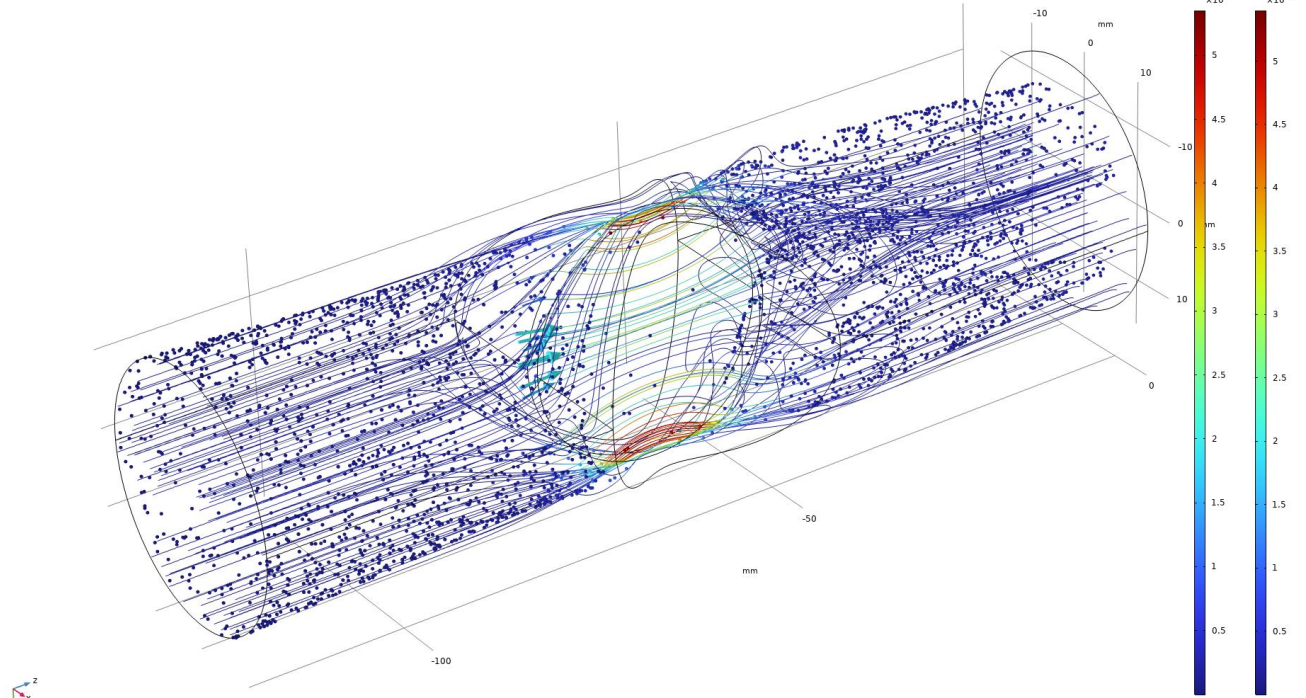


911
912
913

l)

Time=35.3 s

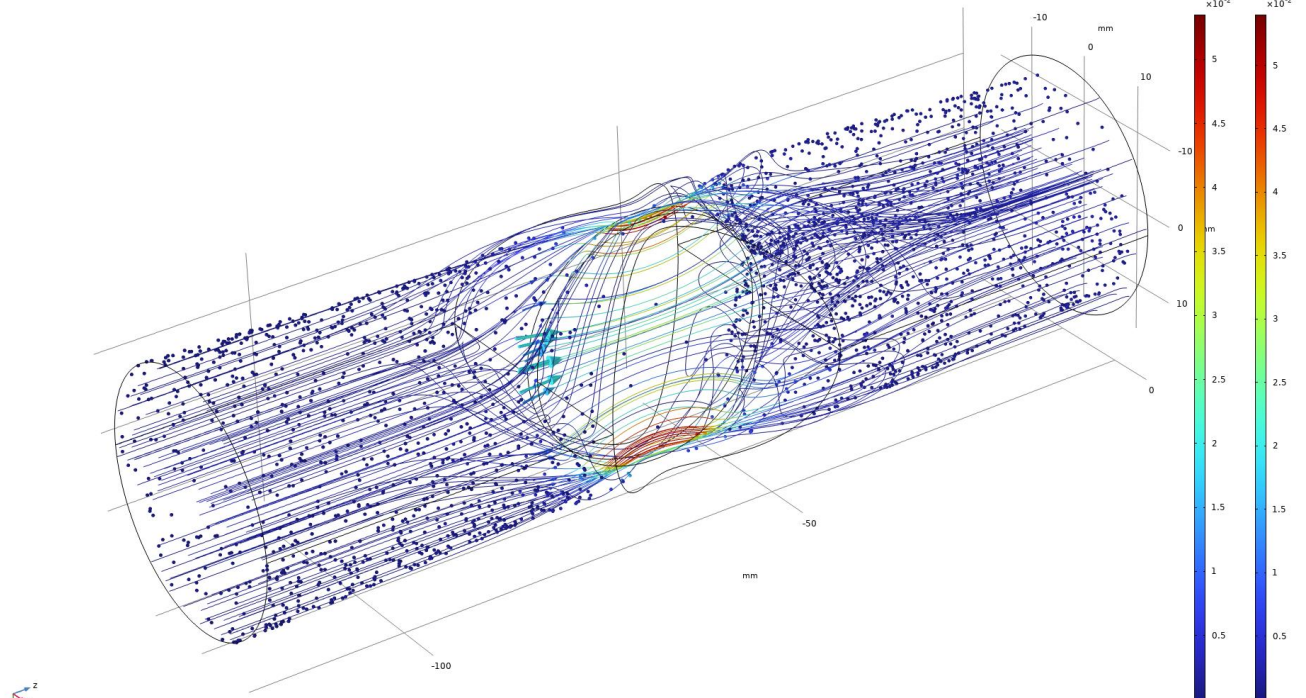
Particle trajectories Streamline: Velocity field



m)

Time=49.4 s

Particle trajectories Streamline: Velocity field



n)

Fig. 15 General view showing particles at i) 19 s, j) 20 s, k) 25 s, l) 30 s, m) 35 s, and n) 50 s after inlet, along with particle velocity streamlines under turbulent flow conditions

At 13 s from injection, the first particles introduced into the channel completely pass through the spectral window. Due to the sudden increase in cross-sectional area, the particle velocity decreases from 0.023 m/s to 0.01 m/s. Furthermore, as seen from the particle color scale, the particles attain maximum velocity at the center of the spectral window zone and in the section slightly downstream from the center. It is also noted that higher velocities, reaching up to 0.035-0.04 m/s, prevail among the particles furthest from the channel axis.

Once the particles have completely passed through the spectral window zone, the shape of the aggregate cloud reverts from a narrow beam to an expanding form, occupying approximately 25% of the total channel cross-sectional area. From 14 s (Fig. 14d), the consequences of the spectral window's influence on particle motion become evident. Due to high drag forces at the entrance of the spectral window, the particles shift vertically in both directions away from the axis. The sudden constriction of the cross-sectional area, from a 32 mm diameter channel to a zone 2 mm wide and 31 mm high between two cuvettes installed perpendicularly to the channel, creates pressure gradient. This causes the particles to deflect into zones above and below the parallel cuvette cylinders located within the spectral window. By 15 s, it is observed that almost no particles remain moving at the axial level, as they distribute toward the periphery. Particle velocity in the lower part of the spectral window reaches up to 0.045 m/s, while in the upper part, it is approximately 0.035 m/s. The particle trajectories maintain a meniscus shape, concave toward the channel axis. Downstream of the spectral window, the particles spread across the entire channel cross-section; however, in this case, the front particles do not travel along the centerline but rather along the periphery. Fig. 14e shows that immediately upon exiting the spectral zone, the particle velocities are higher (0.02 m/s) than the main flow in the central channel zone (0.01 m/s). Upon exiting the spectral zone, the particles concentrate more toward the periphery than the axis, though less intensely than within the spectral window zone itself.

In later stages, between 16-20 s, the situation remains similar; however, the particle streams exiting the spectral window zone increasingly divide into upper and lower sections, passing through the narrow gaps above and below the parallel cuvette cylinders, while the central portion remains undefined. Particle velocities at the periphery of the spectral window increasingly equalize, leaving only isolated particles along the axis.

After 25 s (Fig. 15k, l, m), the particles become fully mixed across individual trajectories, and the front particles reach the channel exit. From 30 s onward, an increasing accumulation of particles is observed at the entrance to the spectral window zone, along with vortex motion and particle recirculation immediately following the exit from this zone, particularly along the axis.

By 50 s (Fig. 15n), the trajectory lines indicate a uniform velocity distribution in the channel both before and after the spectral window, where the velocity changes insignificantly over the entire flow distance. Downstream of the spectral window, a slightly larger proportion of particles concentrates in the upper part of the channel. This asymmetric particle distribution is attributed to local secondary flow patterns and velocity field non-uniformities inherent to the flow geometry in this region.

Based on the ratio of incoming particles to those moving through the spectral window, it is evident that high resistance significantly delays the particles before they enter the spectral window zone. Furthermore, the formation of vortices and backward particle motion immediately after exiting the spectral window zone creates conditions not only for particle accumulation in this central part of the channel but also for sedimentation and strong adhesion to the surfaces of the elements in this zone.

Only the velocities at the periphery, which are approximately twice as high (reaching up to 0.04 m/s), allow dynamic forces to overcome the adhesion force and transport the particles without permanent sticking or with only temporary attachment and subsequent detachment from the surface. Although the velocities along the axis are similar to the inlet velocity, the cross-section of this zone is nearly 12 times smaller; therefore, the probability of both particle-to-particle sticking (forming agglomerates) and particle adhesion to surfaces increases significantly.

Based on the ratio of incoming particles to those moving through the spectral window, it can be clearly stated that high resistance significantly delays particles prior to their entry into the spectral window region. Furthermore, the formation of vortices and the reverse motion of particles immediately downstream of the spectral window create conditions not only for particle accumulation in this central part of the channel, but also for their deposition and strong adhesion to the surfaces of elements within this region.

Only in the peripheral zones, where velocities are approximately twice as high, reaching up to 0.04 m/s, do dynamic forces become sufficient to overcome adhesion forces, thereby enabling particles to be transported without complete attachment, or with only temporary adhesion followed by detachment from the surface.

Along the axis, velocities are comparable to the inlet velocity; however, given that the cross-sectional area of this region is nearly twelve times smaller, the probability of both interparticle agglomeration and adhesion to surfaces increases significantly.

Prediction of particle trajectories in the model revealed essential phenomena occurring due to flow continuity according to the continuity equation; since the volumetric flow rate in a closed system remains constant, the velocity of the particles and the fluid inevitably increases as the channel's cross-sectional area decreases. Conversely, upon exiting the constriction and as the channel cross-section expands again, the flow velocity decreases according to the same principle of continuity, and the particles begin to spread across a larger cross-sectional area.

The pressure gradient is considered another critical factor; due to the abrupt change in channel geometry between the cylindrical cuvette elements, local hydrodynamic resistance and a pressure drop in the flow direction are created. This pressure gradient forces the fluid flow to redistribute into zones where hydraulic resistance is lower; therefore, particles deflect from the channel axis and distribute into the upper and lower sections of the channel. In this manner, two main flow branches are formed, passing through the narrow gaps between the cylindrical elements and the channel walls. The simulation results also align with laminar flow theory. At low Reynolds numbers, a typical laminar velocity profile forms in the channel, where maximum velocity is reached at the center and decreases near the walls due to viscous friction forces. However, in the spectral window zone, this profile is distorted by complex geometry and local flow accelerations. Consequently, higher velocities may occur in peripheral zones, particularly where the flow is forced through narrower gaps. This shift in velocity distribution explains why particle trajectories downstream of the spectral window often deviate from the channel axis and form peripheral flow bundles.

An important practical aspect highlighted by the simulation results is the potential for particle accumulation and scale/deposit formation within the spectral window zone. This zone is characterized by two significant hydrodynamic features: high resistance at the inlet and recirculating flow structures immediately following the constriction. Due to the reduced flow velocity before entering the spectral window, particles begin to accumulate in the central part of the channel. Furthermore, local vortices and backward-moving trajectories at the exit of the spectral window create conditions for particles to remain in this area for longer durations. Such hydrodynamic conditions increase the likelihood of particles contacting structural surfaces and gradually forming a layer of deposits. The mechanism of deposit formation in this zone can be explained by particle transport and surface adhesion processes. At low local flow velocities, the hydrodynamic forces acting on the particles become similar to, or even smaller than, surface adhesion and intermolecular interaction forces. In this case, particles entering the recirculation zone may temporarily adhere to the surface. Subsequently, other particles may join them, forming agglomerates. Over time, this process can lead to the formation of a stable deposit layer on the surfaces of the cuvette cylinders or the channel walls within the spectral window zone.

Based on the simulated particle trajectory results, it can be hypothesized that the process of deposit formation may begin quite rapidly. Since particle accumulation before the spectral window is

observed just a few dozen seconds after the start of the flow, the first instances of temporary attachment to surfaces could theoretically occur within the first tens of seconds or minutes. If the particle concentration in the flow remains constant and sufficiently high, a deposit layer can begin to form within a relatively short period. In later stages of operation, this process may accelerate further due to already formed particle agglomerates, which create additional surface roughness zones and increase the probability of adhesion for new particles.

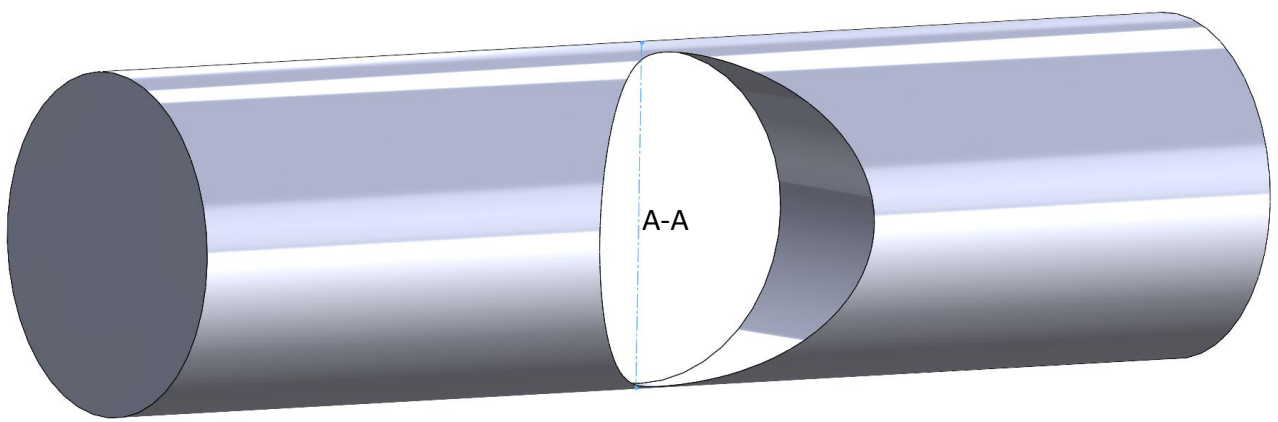
The analysis of particle motion in this study was performed using the trajectory framing method, where particle position and velocity are evaluated at sequential time intervals. This visualization technique allows for the observation of not only the instantaneous flow field but also the dynamics of particle motion along the entire length of the channel. By analyzing different moments in time, it is possible to determine zones of flow acceleration and deceleration, identify recirculating structures, and evaluate changes in particle concentration across the cross-section. This method provides an opportunity to investigate complex particle transport processes in detail and allows for a more reliable interpretation of the hydrodynamic phenomena occurring in the spectral window zone.

4.5 Transverse and longitudinal analysis of fluid flow. Particle streamlines. Pressure and velocity distribution

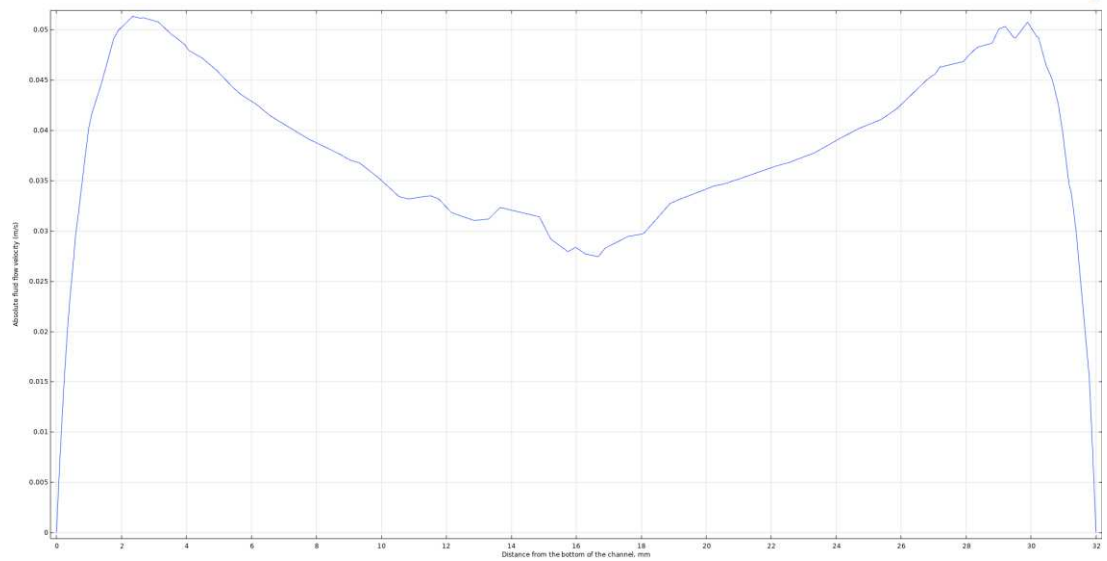
The conducted numerical model study revealed the fluid flow dynamics within the channel space and specifically in the zone adjacent to the spectral window. For the analysis, two profiles were established along the channel axes A-A and B-B, as presented in Fig. 16a and Fig. 17a.

The cross-sectional view (Fig. 16a) illustrates the velocity variation vertically from the bottom to the top of the channel. Under laminar flow conditions, the velocity variation is relatively symmetrical from the channel axis in both directions (Fig. 16b). With a constant inlet velocity of 0.0021 m/s, which was defined as fully developed, the absolute velocity at the channel periphery reaches 0.05 m/s. The velocity decreases steadily towards the channel axis with a gradient of approximately 0.005 m/s every 2 mm, exhibiting slightly higher fluctuations in the upper part of the spectral window compared to the area above the channel axis. At the axis, the velocity reaches 0.0027 m/s; however, the minimum value is attained immediately beyond the channel's transverse symmetry axis (at a distance of 16.7 mm from the bottom). Above the channel axis, the velocity varies with an almost linear dependence and reaches its maximum value at a distance of 29.8 mm from the bottom. On both sides of the spectral window, there is a free fluid flow zone extending to the circular boundary of the channel. Beyond this point, the flow cross-section of the channel decreases by a factor of 11.95 (becoming equal to 67.31 mm²).

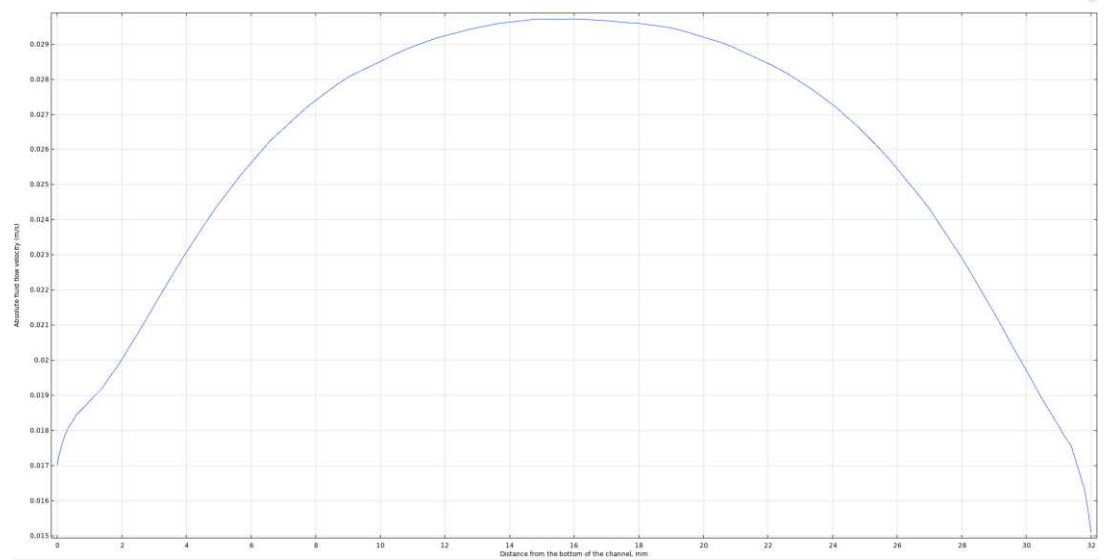
The results obtained using the turbulent flow module are depicted in the cross-section as the dependence of the absolute fluid flow velocity on the distance from the channel bottom (Fig. 16c). As observed, the turbulent flow exhibits minor disturbances in the boundary layers within the intervals of 0-2 mm and 30.5-32 mm from the bottom. However, in other sections, the velocity variation is a smooth parabolic curve, with the peak velocity exactly at the central point of the channel axis, reaching a value of 0.0031 m/s. A slight asymmetry was detected between the velocities of the lower and upper zones, indicating that the velocity at the bottom is somewhat lower. It can also be seen that the initial velocity directly at the bottom wall starts at 0.017 m/s, whereas at the upper wall, it decreases more significantly to 0.015 m/s. This can be attributed to the effect of the drag force, the value of which influences the distribution at low velocities within the channel.



a)



b)



c)

Fig. 16 Velocity distribution in a) the cross-sectional profile A–A for different types of fluid flow, b) laminar and c) turbulent ($k-\epsilon$), based on the steady-state module

In the longitudinal profile for laminar flow, the dependence of the absolute fluid velocity on the distance from the channel inlet toward the outlet illustrates the *throat effect* (Fig. 16b). The initial velocity along the axis at the inlet is 0.004 m/s and remains nearly constant over the first 40 mm, i.e., up to 20 mm before the center of the spectral window. At a distance of 40 mm from the inlet, the velocity sharply increases by approximately 0.0036 m/s per millimeter, reaching 45 mm from the inlet, where resistance and velocity damping effects occur. These effects are visible in the plot as kinks in the curve.

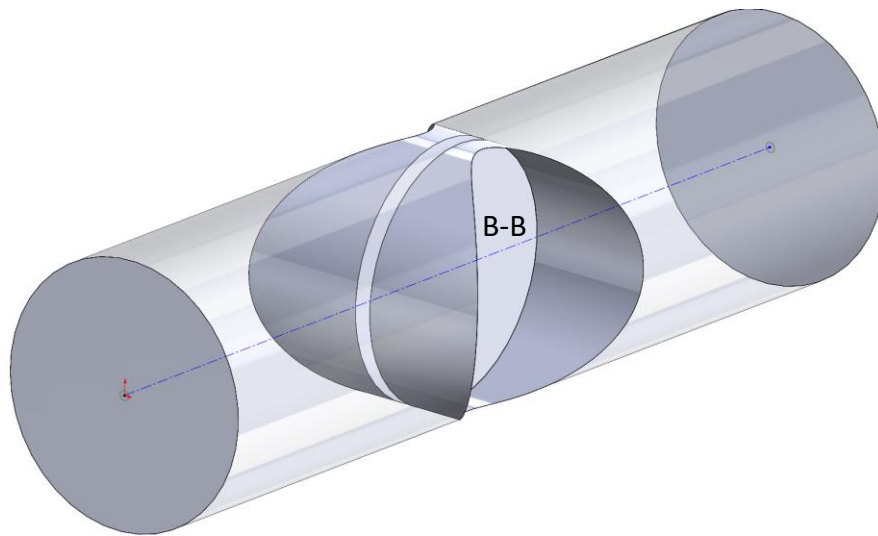
Subsequently, the flow stabilizes, and a plateau is reached 10 mm before the center of the spectral window. Approaching the center of the narrowest zone, at 60 mm from the inlet, irregular velocity fluctuations appear until the maximum velocity is reached at approximately 63 mm, i.e., 3 mm downstream of the spectral window center, where the velocity reaches 0.034 m/s. Beyond this point, flow relaxation occurs: within several steps, the velocity returns almost symmetrically to lower values, similar to the region before the spectral window. Additionally, prior to reaching the zone of nearly uniform velocity distribution, a local velocity drop occurs in the 80–100 mm region from the inlet.

This phenomenon can be attributed to the sudden entry of fluid into the full cross-section of the channel, where residual local resistances from the spectral window are no longer significant. Due to viscosity, the fluid decelerates slightly to stabilize, after which the velocity gradually normalizes. Absolute velocity stabilization occurs over a relatively long distance, and at 110 mm from the inlet (50 mm downstream of the spectral window center), the flow reaches a uniform velocity of 0.004 m/s, equal to the inlet value.

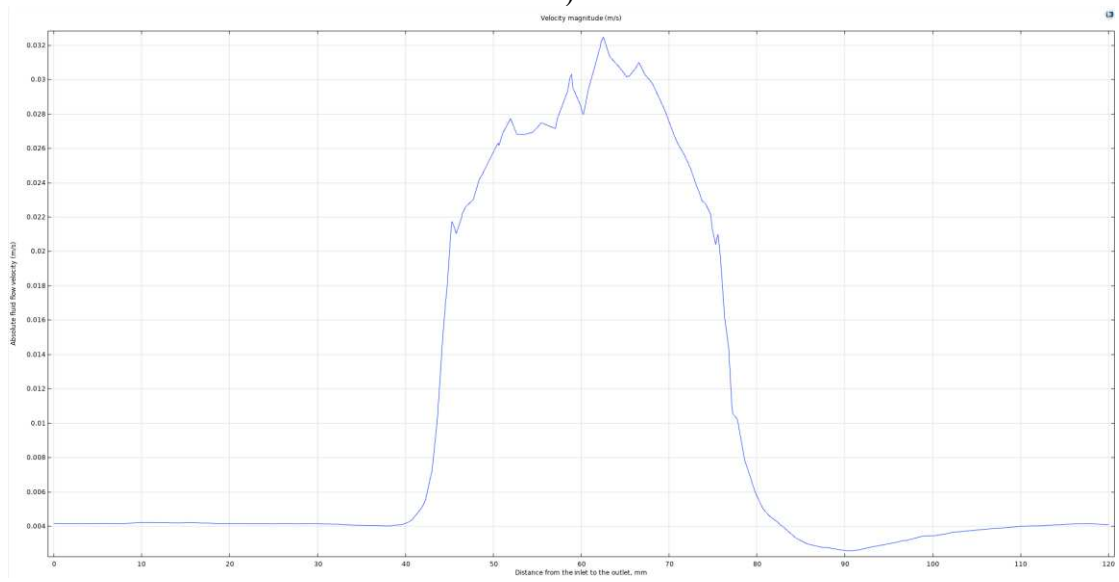
For turbulent flow, four distinct zones can be identified (Fig. 17b). At the inlet, the absolute velocity of the fluid increases steadily with very small acceleration. At 40 mm from the inlet, the acceleration sharply increases, reaching a peak velocity of 0.027 m/s. Due to the nature of turbulent flow, a sudden relaxation occurs, reducing the velocity by almost 15%. At 47 mm from the inlet, velocity begins to increase parabolically up to 62 mm, just beyond the center of the spectral window.

A subsequent symmetric velocity decrease occurs toward 75 mm from the inlet. Here, another abrupt velocity increase is observed due to flow relaxation, where the influence of the spectral window constriction as a local obstacle diminishes. Turbulent flow, being more sensitive, exhibits a more pronounced velocity increase, reaching approximately 0.035 m/s. After this peak, the absolute velocity decreases more sharply than the velocity rise before the spectral window.

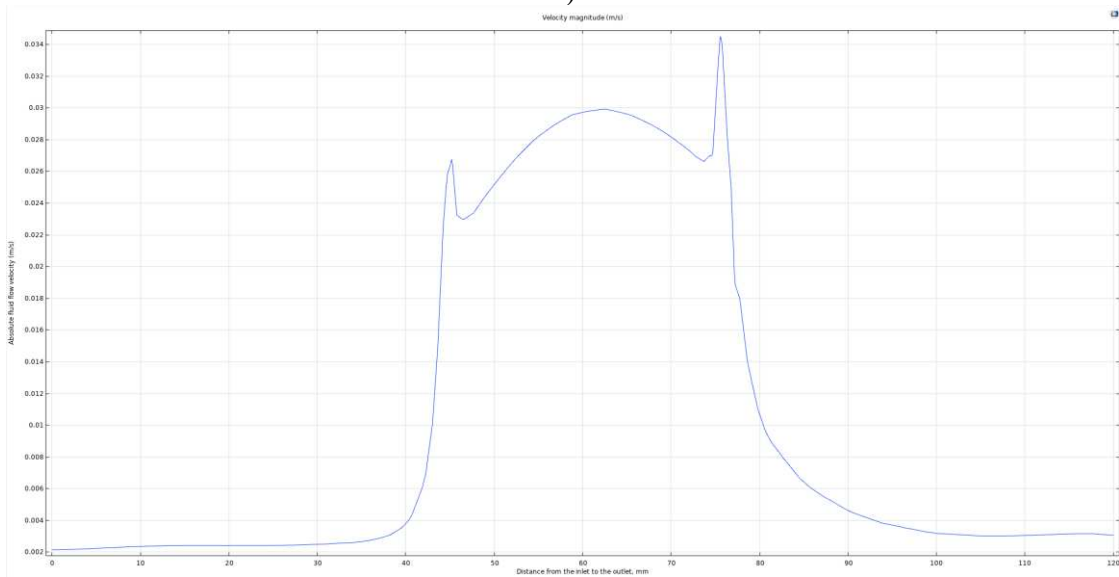
In turbulent flow, no significant fluctuations are observed. Beyond 100 mm from the inlet, the velocity profile gradually levels off and shows minimal oscillations until the outlet. The final velocity is slightly lower than in the laminar case but higher than in the region upstream of the spectral window, reaching approximately 0.035 m/s.



a)



b)



c)

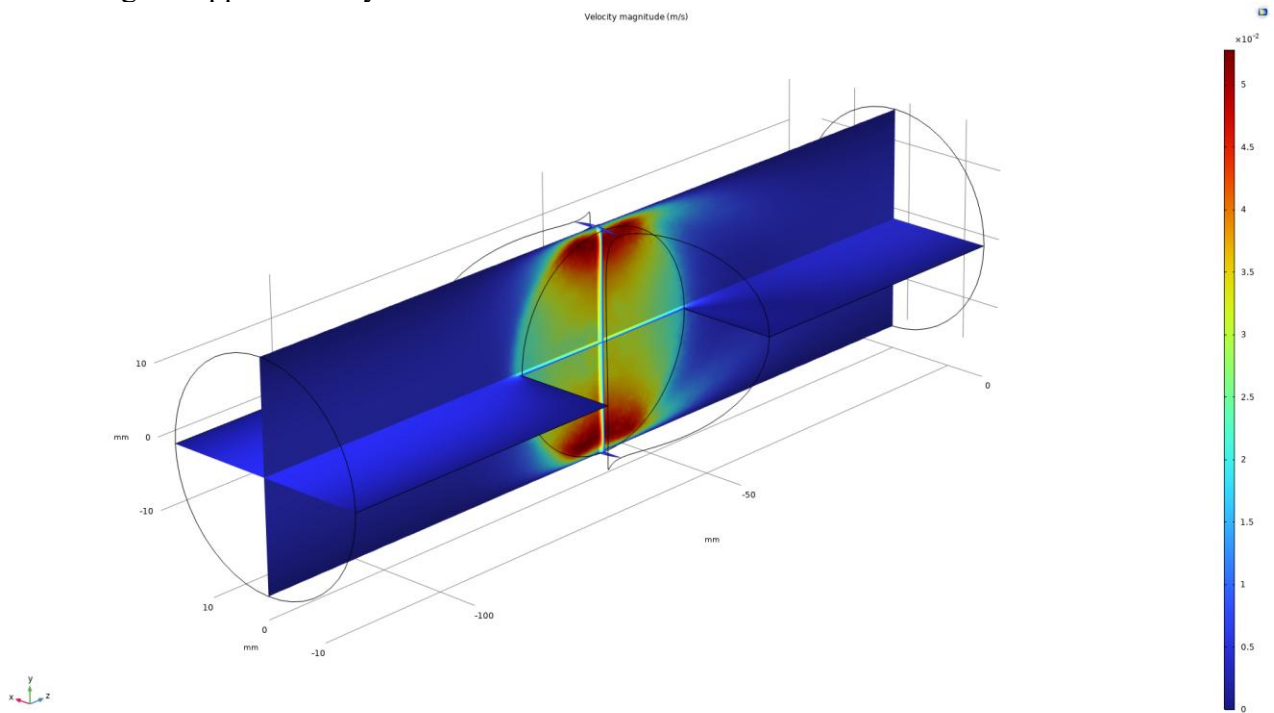
Fig. 17 Velocity distribution in a) the longitudinal profile B–B for different types of fluid flow b) laminar and c) turbulent ($k-\epsilon$), based on the steady-state module

Based on the results obtained from the spectral analysis of fluid flow velocity, the aim is to examine the spatial distribution of the highest velocity regions in the vicinity of the spectral window.

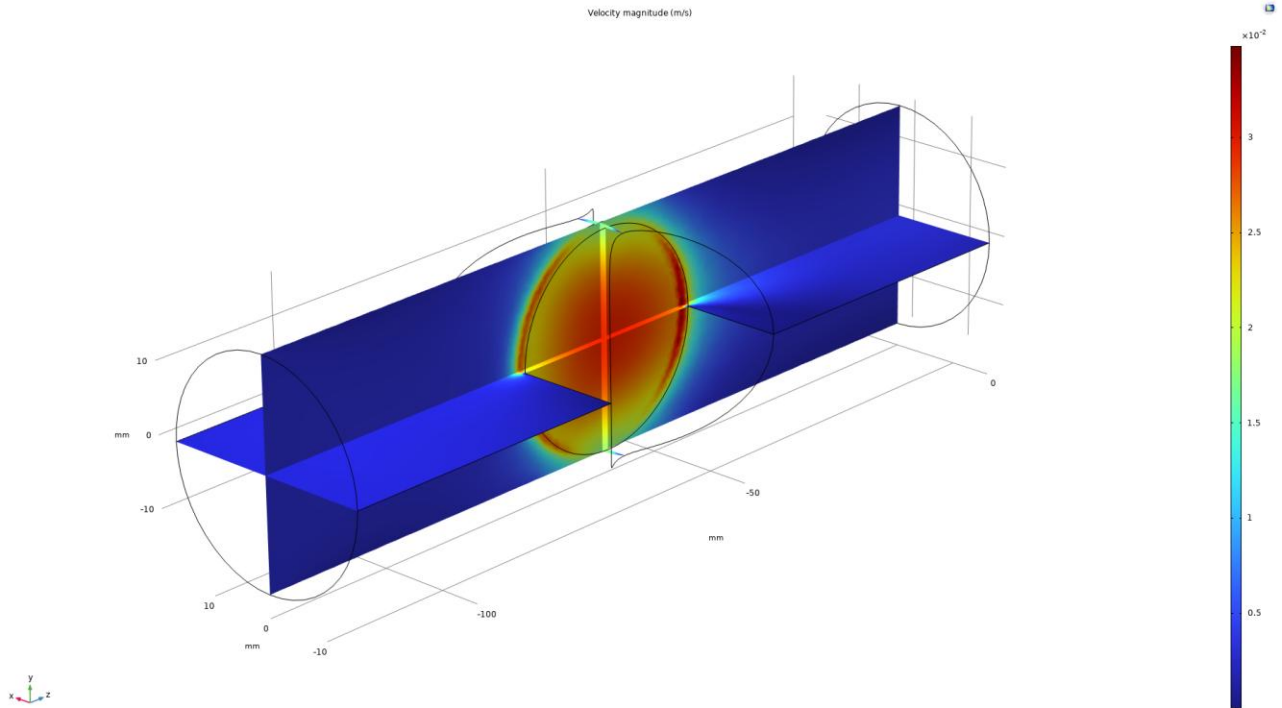
In the case of laminar flow (Fig. 18a), the maximum velocity values (in the range of 4–5.5 m/s) are distributed in the upper and lower zones of the channel, each occupying approximately one quarter of the total channel area. These peak velocities are confined to a narrow region extending no more than 10 mm on either side of the spectral window center.

In contrast, under turbulent flow conditions (Fig. 18b), the highest velocity values occupy nearly 80% of the total area within the spectral window region, expanding in both directions from the narrowest part of the throat. Additionally, a pronounced increase in velocity is observed at the inlet and outlet of the spectral window, where the fluid flow interacts with the cuvette walls and undergoes separation upon exiting at the rear edge of the cuvette.

Under these turbulent conditions, the highest velocities are concentrated along the central axis of the channel, whereas the upper and lower regions are dominated by moderate velocities, with values in the range of approximately 1.7–2.2 m/s.



a)



b)

Fig. 18 Fluid flow velocity field for a) laminar and b) turbulent ($k-\epsilon$) flow type, based on the steady-state module

By analyzing the fluid flow field and particle trajectories, corresponding visualizations were generated for both laminar and turbulent flow conditions (Fig. 19a and Fig. 19b).

The cases differ fundamentally in terms of the dominant flow patterns entering the spectral window. Under turbulent flow conditions, significantly larger flow contributions are observed along the channel axis. In contrast, for laminar flow, only a small fraction of the flow is distributed along the axis, while the majority is diverted toward the lower and upper regions of the channel, where free-flow zones exist and the spectral window does not significantly disturb the flow.

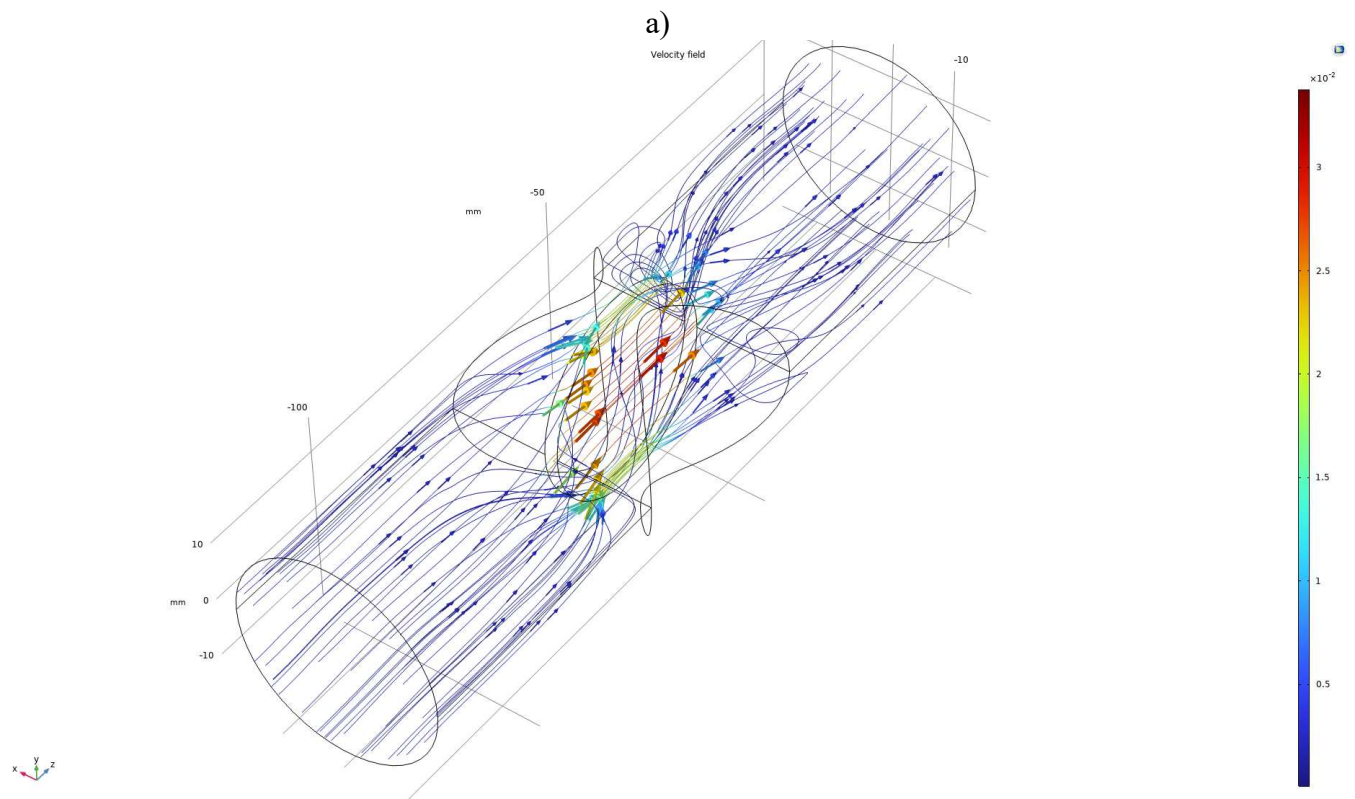
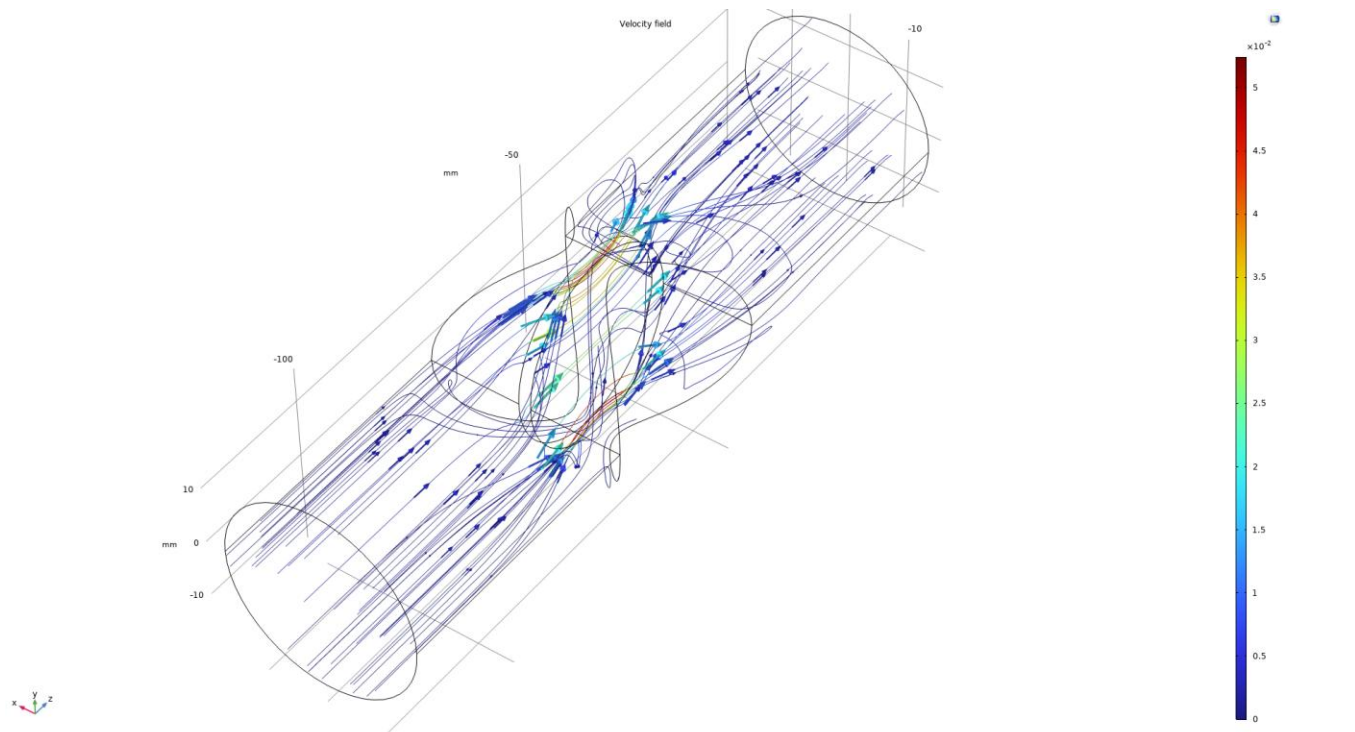


Fig. 19 Distribution of fluid flow velocity streamlines under a) laminar and b) turbulent ($k-\epsilon$) flow regimes, based on the steady-state module

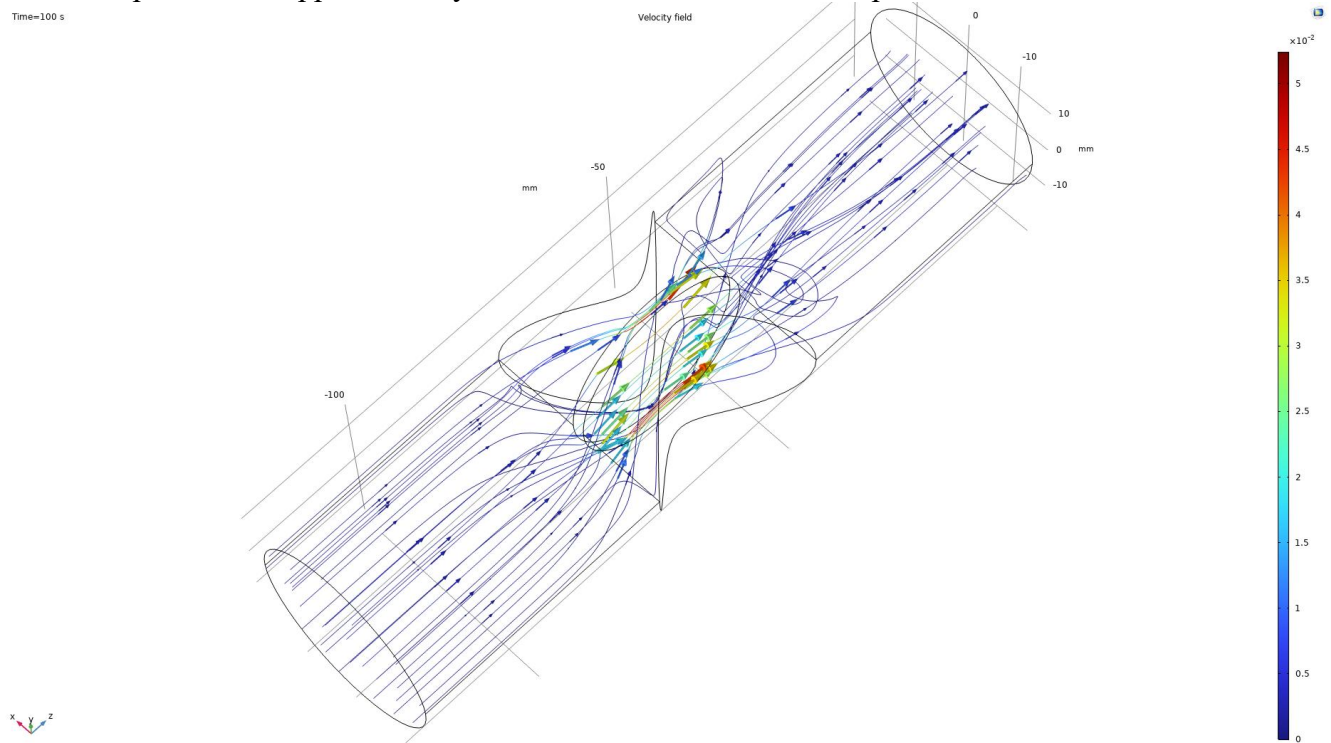
Differences are also evident in the trajectories upstream and downstream of the spectral window. In laminar flow, fluid trajectories remain essentially linear and change only in the immediate vicinity of the obstacle. Conversely, under turbulent conditions, trajectories upstream of the window

are nearly linear, whereas downstream they assume parabolic shapes and are oriented more toward the peripheral regions than toward the central axis of the channel.

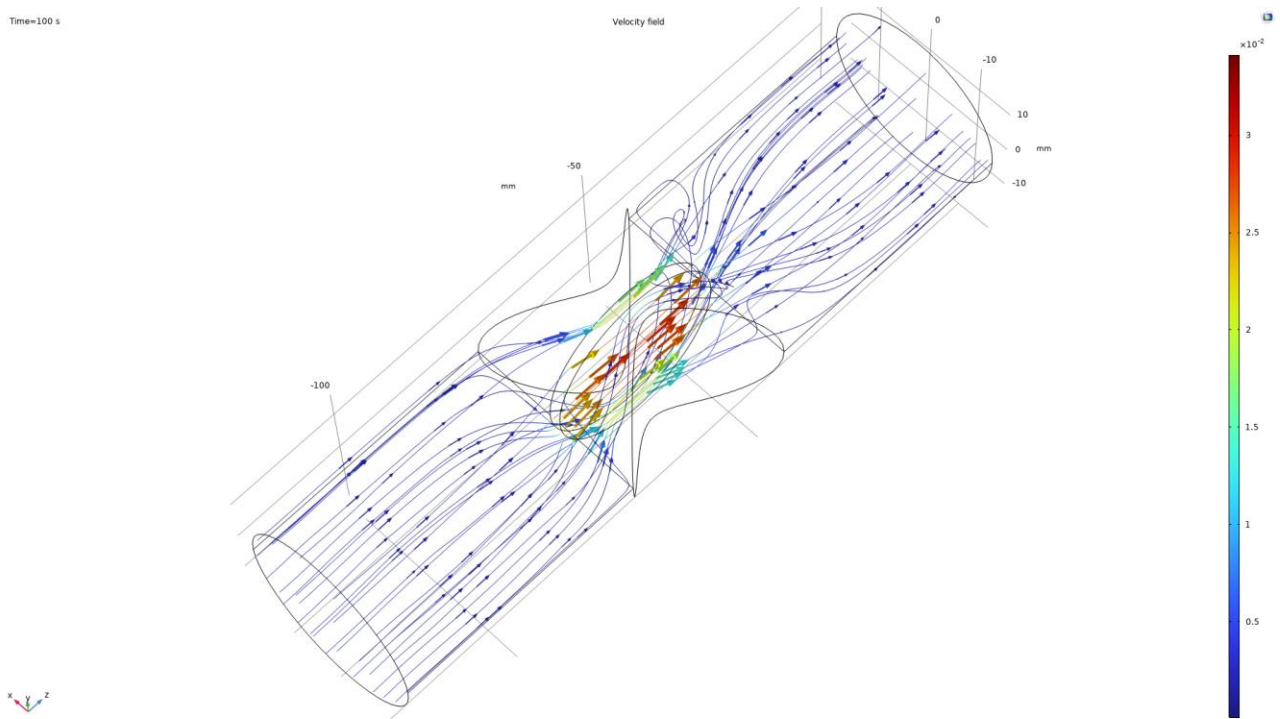
Particle trajectories in the fluid characterize their interaction with the surfaces of the spectral window. Higher particle velocities reduce the probability of particle accumulation on internal surfaces, thereby improving the operating conditions of the spectral window. As with other parameter visualizations, particle trajectory fields were obtained for both laminar and turbulent flow conditions (Fig. 20a and Fig. 20b).

In the case of laminar flow, the average particle velocity in the vicinity of the spectral window is approximately 0.03 m/s, with the highest values observed along the channel axis. Near the edges of the spectral window, the velocity increases by up to 30%, while slightly higher particle velocities are observed in the lower part of the channel. Upstream and downstream of the spectral window, velocities remain comparable to the bulk fluid flow and only begin to respond to the presence of the obstacle immediately before reaching the edge of the spectral window.

Under turbulent flow conditions (Fig. 20b), particle trajectories closely follow the fluid motion (Fig. 20b). The highest velocities, reaching 0.03-0.035 m/s, are concentrated along the channel axis. It is also observed that a larger proportion of particles with moderate velocities (approximately 0.015 m/s) move within the lower part of the channel. In the turbulent regime, more intense vortical structures are observed downstream of the spectral window, particularly in the upper part of the channel; however, these dissipate within approximately 20 mm from the center of the spectral window.



a)



b)

Fig. 20. Distribution of particle flow velocity streamlines under a) laminar and b) turbulent ($k-\epsilon$) flow regimes, based on the time-dependent step module.

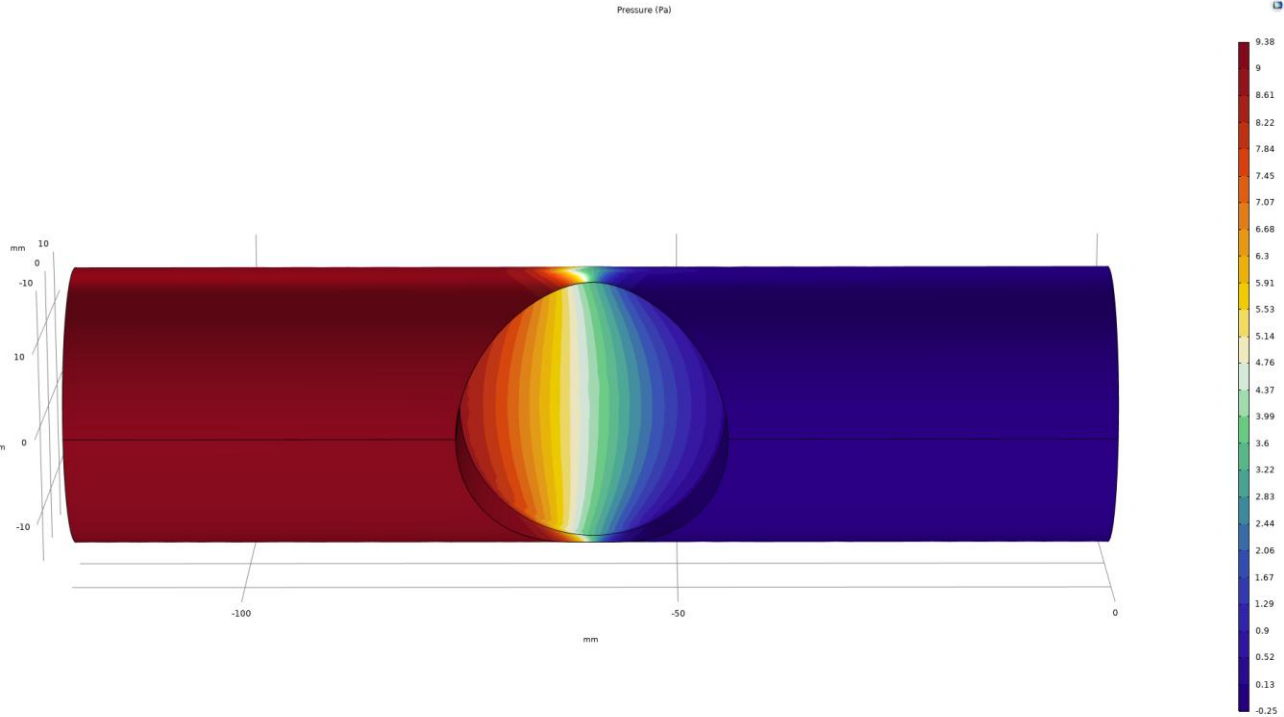
The only obstruction in the analyzed system is the spectral window, which causes a narrowing of the channel and corresponding pressure changes. Although the flow velocity is relatively low, clear differences are observed both between regions upstream and downstream of the spectral window and between pressure values under laminar and turbulent flow conditions (Fig. 21a and Fig. 21b).

Since the outlet of the channel is open, the highest pressures develop upstream of the spectral window. Under laminar flow conditions, the pressure reaches up to 9.4 Pa, whereas in turbulent flow it is approximately half that value, around 4.2 Pa. If absolute values are not considered, the overall distribution pattern is similar for both flow regimes. The main difference is observed in the cross-section of the spectral window itself: in laminar flow, the pressure symmetry line is located at approximately 4.5 Pa and is shifted slightly toward the inlet by about 2-3 mm.

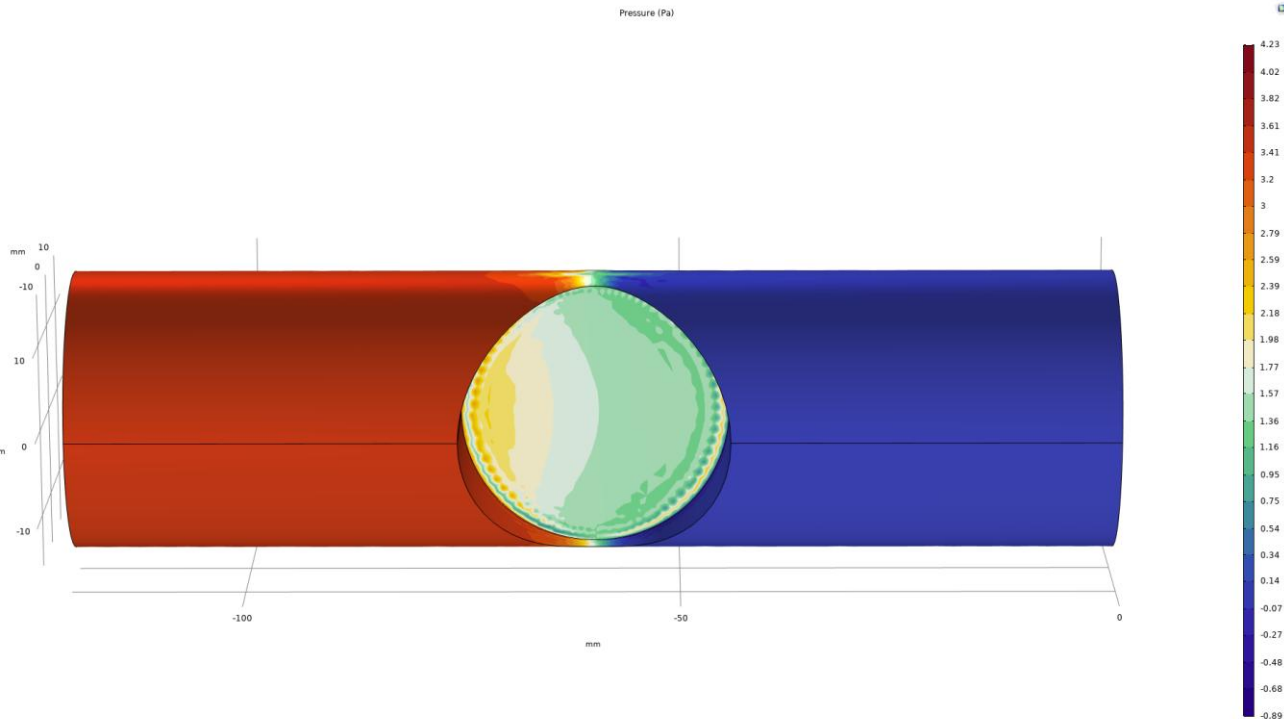
In turbulent flow, the pressure distribution does not exhibit clear symmetry; however, immediately downstream of the spectral window edge, the pressure drops to approximately 2.4 Pa. A narrow boundary layer region is observed, where pressure values are about twice as low, ranging from 0.9 to 1.3 Pa. Within the spectral window cross-section, pressure is distributed in a parabolic pattern, with values along the channel axis being about 0.3 Pa higher than in the peripheral regions.

At the end of the spectral window, pressure decreases to approximately 0.75 Pa, while within the boundary layer a pressure zone persists with values between 1.3 and 2.2 Pa. Immediately downstream of the spectral window, pressure further drops to about 0.14 Pa, and in the peripheral regions near the trailing edge of the spectral window slightly negative values (around -0.9 Pa) are

observed, indicating stronger local vacuum conditions compared to the laminar flow case.



a)



b)

Fig. 21. Surface pressure distribution of the fluid flow under a) laminar and (b) turbulent ($k-\epsilon$) flow regimes, based on the steady-state module.

5 Discussion

In the present study of UAN-32 flow in a channel equipped with integrated optical windows for spectroscopic monitoring, a key operational limitation affecting measurement reliability has been identified: progressive fouling of the embedded lens surfaces. Due to the real composition of UAN-32, which includes significant amounts of impurities such as iron oxide compounds, a persistent rust-like layer gradually forms on the optical windows, reducing their transparency and distorting the transmitted optical signal.

This fouling directly impacts the accuracy of spectroscopic measurements. Reduced optical transparency leads to lower signal intensity, increased scattering background, and baseline drift in recorded spectra. As a result, the error in concentration determination increases significantly, particularly in absorption-based spectroscopy. Recent studies indicate that even partial window fouling can introduce systematic measurement errors in the range of 5-20%, depending on fouling thickness and optical path length (Scheibelhofer et al. [72]; Spoor et al. [73]). In more severe cases, calibration stability is compromised, requiring frequent recalibration and reducing overall experimental reproducibility (Kang et al. [74]).

Maintaining optical window cleanliness is therefore critical for ensuring stable analytical performance. Fouling not only degrades signal-to-noise ratio but also alters the effective optical geometry of the measurement path, which is especially critical in high-precision flow diagnostics. Neglecting this factor can lead to cumulative errors and incorrect interpretation of flow-related physicochemical processes in UAN-32 systems.

Several engineering solutions can be proposed. First, anti-fouling and protective coatings such as titanium dioxide, diamond-like carbon (DLC), or fluoropolymer layers can reduce particle adhesion and surface deposition (Chae et al. [75]; Delgado et al. [76]; Mignani et al. [77]). Second, active self-cleaning approaches, including piezoelectric micro-vibration systems, can be implemented to prevent particle accumulation. Such systems have demonstrated fouling reduction efficiencies of up to 40–60% in flow environments (Kim et al. [78]; Piña-Díaz et al. [79]).

Additional approaches include hydrodynamic cleaning strategies such as pulsed flushing, flow reversal, or locally increased shear stress near the optical surface. Gas or liquid curtain systems forming a protective barrier between the main flow and the optical window have also shown promise in recent developments (Schuhmann et al. [80]). In combination, these methods can significantly enhance the stability and reliability of spectroscopic measurements in contaminated industrial fluids.

6 Model limitations and future validation

The present work was designed as a mechanistic investigation of the fundamental processes governing the interaction between colloidal rust particles and modified optical surfaces under representative UAN-32 operating conditions. Accordingly, the primary objective was not the reproduction of a specific experimental dataset, but rather the development of a physically consistent framework capable of resolving the dominant forces controlling particle attachment, detachment, and transport.

The proposed model integrates the principal interaction mechanisms expected to govern particle behavior at the solid–liquid interface, including van der Waals attraction, electrostatic double-layer interactions, elastic contact response, and hydrodynamic drag forces. The adopted material properties and physicochemical parameters were selected from experimentally established ranges reported in the literature for iron oxide particles, fused silica substrates, aqueous electrolyte environments, and silane-based surface modifications. Consequently, the obtained results should be interpreted as physically based predictions of the governing deposition mechanisms rather than as direct reproductions of a particular experimental configuration.

Despite the inherent simplifications associated with mechanistic modeling, the predicted transition from adhesive particle capture on unmodified fused silica to predominantly repulsive

interactions on phosphonate-functional silane surfaces is fully consistent with established colloidal interaction theory and the known antifouling behavior of highly charged surface coatings. The numerical results therefore provide a coherent theoretical explanation for the expected reduction in particle accumulation and surface fouling under practical operating conditions.

It should nevertheless be recognized that real industrial systems may involve additional complexities that were not explicitly considered in the present model, including particle size distributions, surface heterogeneity, coating aging, chemical transformation of corrosion products, and long-term hydrodynamic fluctuations. These factors may influence the quantitative rate of deposit formation while not necessarily altering the fundamental interaction mechanisms identified in this study.

Future work should focus on targeted experimental validation through controlled flow-loop investigations employing UAN-32 solutions containing representative iron oxide particulates. Such experiments, combined with optical transmission measurements and surface characterization techniques, would enable quantitative assessment of deposition kinetics and provide additional verification of the predictive capability of the proposed framework. Nevertheless, the present study establishes a rigorous theoretical basis for understanding contamination processes on optical windows and for the rational design of antifouling surface modifications for in-line spectrophotometric systems.

7 Conclusions

This study investigates the dynamics of a flow originating from a chemical industrial process and containing solid particulate impurities. The flow distribution within the channel and its passage through the spectral window are of particular importance for the accuracy and operational lifetime of in situ spectroscopic analysis due to particle deposition on the lens surfaces.

At identical inlet velocities, laminar and turbulent flow regimes exhibit differences in velocity distribution across the channel cross-section exceeding 10%, while their velocity profiles undergo significant changes along the streamwise direction. For the in situ spectroscopic system under consideration, the installed cuvette elements introduce parabolic obstacles that reduce pressure by at least 20% and generate a gradient from the channel axis toward its periphery.

An analysis of particle transport within the flow shows that particles traverse the spectral window and reach the channel outlet within approximately 15 seconds. Starting from the fourth second after entering the channel, particles increasingly deviate from the axial direction toward the periphery, where flow velocities increase by more than a factor of 15, with even higher accelerations observed in the lower region of the channel.

A substantial pressure drop caused by abrupt changes in cross-sectional geometry creates conditions conducive to particle accumulation at the entrance to the spectral window. This effect may further intensify lens fouling in the cuvette, in addition to primary contributing factors such as low flow velocity, high concentrations of suspended solids, and the large surface area of optical elements installed within the spectroscopic channel.

From a practical engineering perspective, the developed model demonstrates that silane-based surface modification offers a viable pathway for mitigating these fouling effects. By creating a barrier against particle adhesion, such coatings can substantially reduce the frequency of signal degradation, thereby extending the operational lifecycle of optical components and optimizing maintenance strategies in challenging industrial environments.

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Declarations

Ethics approval and consent to participate Not applicable.

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