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The influence of the Earth's exosphere on the micro-destruction of materials of space stations

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Research under the Test space experiment program on the physical and chemical properties of the resulting fine sediment on the surface of the International Space Station (ISS) has confirmed the possibility of its active participation in the aggressive influence of its own external atmosphere on the development of micro-degradation of ISS materials. An example of the effect of chemical elements with high electron affinity from volcanic gases reaching the surface of the ISS on the tightness of seals in portholes is given. The presence of graphite on the windows of portholes, samplers and cleaners indicates the degradation of the sealing materials, which can lead to leakage of the gaseous medium. The Test experiment showed that the natural contamination of the ISS surface by dispersed particles of the cosmosol requires consideration of the aging of station materials and their corrosion resistance, taking into account the external environment.

Keywords: international space station, fine deposition, exosphere.

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Introduction

One of the objectives of the "Test" space experiment during 2010–2024 was the collection of fine-dispersed sediment from the surface of the Russian Segment of the ISS using a special sampler for its physicochemical analysis in order to study the transfer of matter in space [1–5]. Sampling is performed by a cosmonaut during extravehicular activity into a container-monoblock (sampler), which is maintained sterile and hermetically sealed throughout the experiment, including during delivery to Earth. The objective of the ground-based phase is to conduct physicochemical, toxicological, microbiological, and molecular analysis of the samples.

Studies of the composition of the fine-dispersed sediment make it possible to assess the potential for micro-destruction of the pressurized hull, degradation of the transparency of portholes, and deterioration of the operational characteristics of solar panels and radiators under the influence of space factors, and to formulate requirements for advanced structural materials. Analysis of the physicochemical properties of the sediment allows determining its role in the aggressive impact on structural elements and, based on its elemental composition, identifying the source of its entry into the ISS's own external atmosphere, as well as refining data on the geochemical composition of cosmic dust at an altitude of 400 km above the Earth's surface and its sources.

Analysis of the possible influence of fine-dispersed sediment on materials of space objects

It has been established that the dispersed composition of cosmic dust on the ISS surface consists of three fractions: micron-sized ($1\text{ }\mu\text{m}$ and $5\text{ }\mu\text{m}$), submicron (the dominant fraction), and nanoparticles. Out of 46 studied samples, at least one element with high electron affinity was found in 27 samples, including chlorine (17 samples), fluorine (6 samples), and sulfur (17 samples), which are known to be constantly present in volcanic gases. Furthermore, the presence of traces of volcanic gases was confirmed by the simultaneous detection of the rare-earth element rhenium and radioactive elements (uranium, thorium, radium, cesium). Rhenium had not previously been detected in cosmic bodies; therefore, it can be assumed that this element is of terrestrial origin. The most probable source of rhenium reaching the ISS surface is the fumarolic gas-steam emissions of the Kudryavy volcano on Iturup Island. Kudryavy volcano represents a rare case of long-term, stationary, high-temperature magmatic degassing, in whose fumarolic gas-steam-dust emissions the amount of rhenium can reach 20–36 tons per year. It is the only open deposit of rhenium, the third largest in the world in terms of reserves of this metal; moreover, radioactive elements (uranium, thorium, radium, cesium) are also constantly present in the fumarolic gases of the Kudryavy volcano [3, 5].

Sulfur, chlorine, and fluorine particles, often detected in the composition of fine-dispersed sediment samples from the ISS surface, are not permanent elements of cosmic dust, but they are always present in volcanic gas emissions and are the main aggressive components of fumarolic gases. These elements actively participated in the formation of the Earth's primary atmosphere and still influence the climate. Ionized particles from gas-dust emissions enter the upper part of the ionosphere at the altitude of the ISS orbit via the ascending branch of the global electrical circuit connecting the stratosphere and the ionosphere. On their "crest", rapid injection of aerodispersed particles into the ionosphere with a change in the phase state "aerosol-cosmosol" is possible [6].

Thus, the detection of rhenium, sulfur, chlorine, and fluorine on the ISS surface based on the results of geological and mineralogical analysis is proof that during volcanic eruptions, gas-dust emissions can rise not only to the altitude of the stratosphere, but also much higher into space to an altitude of 400 km above the Earth. This fact poses an important materials science challenge: to investigate the impact of the deposition of constantly incoming elements with high electron affinity on the condition of materials of orbital objects, seals, porthole glasses, optical instruments, etc.

It should be noted that in the composition of 46 fine-dispersed sediment samples from the ISS surface, 65 chemical elements were found, and only in 5 fine-dispersed sediment samples from the RS ISS surface were no traces of iron detected [3]. In particles of volcanic gases rising beyond the atmosphere to orbital altitude, iron chloride, released from the magmatic melt at high temperatures, may be present. The presence of iron chloride particles in volcanic gases is associated with the reaction of magma with chlorine-containing compounds, which can also be released during an eruption. The volatile form of iron chloride is anhydrous iron chloride FeCl_3 , which transitions into a gaseous state upon strong heating, forming FeCl_3 monomers and Fe_2Cl_6 dimers [7, 8].

The interaction of iron chloride with compact aluminum leads to the accumulation of iron ions, culminating in the deposition of iron in a free state and the appearance of ferrimagnetic particles found on the surface of the fluoroplastic housings of the "Test" instruments. Chloride ions migrate through the oxide film to the metal primarily at defect sites, increasing the corrosion rate [7, 8].

Analysis of the chemical composition of contaminants on porthole glazing revealed a predominance of zinc oxide, which suggests the dispersion of coatings from radiators and other structural elements painted with enamels containing zinc. Silicon, aluminum, potassium, chlorine, fluorine, and sulfur are present as impurities. The presence of carbon was established, with a predominantly tabular particle shape. When sampling from portholes on the glass and at the interface with the frame, and during subsequent cleaning of the glass with special devices, black traces of tabular graphite were always found (Fig. 1).

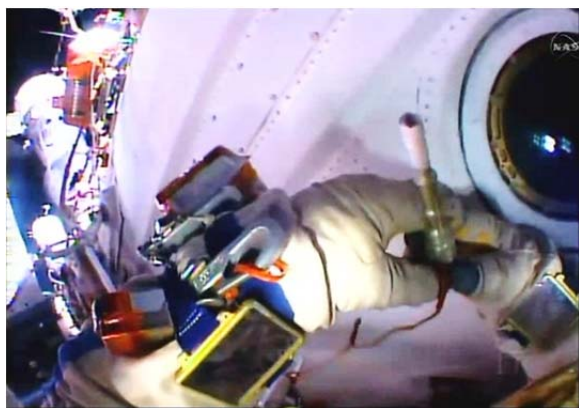


Fig. 1. Sampling from the porthole glass of the ISS service module (left) and view of the black sediment on the sampler swab delivered to the laboratory (right)

The presence of noticeable traces of tabular graphite on porthole glasses, samplers, and cleaning devices indicates ongoing processes of material degradation. Paronite, used as a sealant for porthole frames, contains more than 10 % graphite, including the tabular variety. It is known that under the influence of chlorine, interacting with other chemical components of paronite, the graphite is liberated. This circumstance could affect the tightness of seals in the porthole structures of orbital objects during their long-term operation. It should be noted that it is difficult to pinpoint the location of air leakage due to seal damage using instrumental means.

During the ISS-71 expedition (2024), cosmonauts O. Kononenko and N. Chub discovered the presence of condensate on the inner glass of porthole No. 1 of the small laboratory module MLM-U, indicating a leak in the frame seal. Earlier, on June 12, 2022, a photo of a crescent-shaped frost patch was taken by cosmonaut S. Korsakov on the inner side of the outer glass of this same porthole (Fig. 2). This indicates that a small air leak process has been occurring in the structure of porthole No. 1 of the MLM-U for two years. The formation of ice can be explained by the fact that in 2022, as a result of air leakage into the space between the porthole panes, thermodynamic conditions corresponding to the triple point of water were established: pressure 4.6 Torr (0.006 atm) and temperature 0.01 °C on the inner side of the outer glass. Due to the continued air leak into the inter-pane space, the pressure exceeded 4.6 Torr, and condensate droplets appeared.



Fig. 2. Photo of frost on the inner side of the outer porthole glass

Since the temperature of the outer glass decreases from the frame (at the temperature of the external structural elements of the ISS) towards the center of the glass (reaching temperatures near or below zero), the zone of maximum deposited frost layer and subsequently the location of droplets may indicate the location of the frame seal leak. One possible cause could be the degradation of the paronite seal tightness.

In 2021, to study the long-term survival of microorganisms in open space, two "Test-Exhibit" devices were installed on the handrails of the Poisk module for 3.5 years. The surface areas of the fluoroplastic sealed units were of interest for research, as a coating of fine-dispersed matter from the cosmosol composition formed on their surface. After the "Test-Exhibit" devices were delivered to Earth in 2024,

a scraping was taken from the fluoroplastic unit, and a conditionally clean area was cut from inside the unit for physicochemical analysis of the fine-dispersed substance. Analysis showed that the housing was covered with a reddish-colored sediment, which adhered quite firmly to the fluoroplastic surface, did not transfer to gloves, and was practically not removable with a cotton swab (Fig. 3).



Fig. 3. Sediment on the surface of the "Test" housing

Elemental analysis of the samples was performed using inductively coupled plasma optical emission spectrometry. The results obtained generally repeat the findings of previous papers. The ratio of elements may resemble both the composition of stony meteorites and that of ordinary mineral dust on Earth, as these are the most common elements on Earth. The data for iron and nickel allow for an analysis of the iron's origin. The iron/nickel ratio in the studied sample is 335; consequently, these iron particles are not of meteoritic origin, as for meteorites this ratio does not exceed 14.

In 2019, All-Russian Scientific Research Institute for Physical-Engineering and Radiotechnical Metrology analyzed objects that had been exposed on the external surface of the ISS and contained fine-dispersed particles: a roll of cotton fabric material exposed for 10 years on

a bracket of the Zvezda module, and the fluoroplastic "Test-Exhibit" device on a bracket of the Pirs module after 1 year of exposure. Neutron activation analysis (NAA), a highly sensitive and accurate method used for the quantitative analysis of major, minor, and trace elements, was employed for sample analysis. The NAA technique is based on measuring the radiation emitted during the decay of radioactive nuclei formed as a result of irradiating the material with neutrons. The iron/nickel ratios in the studied samples were: for the fluoroplastic instrument housing in 2019–220 (in 2024–335); for the contaminated area of the cotton fabric – 280; and for the clean area – 236.

It is important to note the concentration of uranium and thorium [3] in the samples. Their quantities are small, but this method has excellent resolution for such heavy nuclei. Their amount increased by 3–4 times in the contaminated area. The appearance of these elements could be explained by ground-based testing, the operation of satellites with nuclear power sources, or traces of volcanic gases.

While working with the contaminated fabric areas, its low mechanical strength and increased brittleness were noted. When cutting, the surface fibers crumbled and scattered. This did not occur with the uncontaminated areas. Therefore, a comparative analysis of the contaminated and uncontaminated fabric areas was performed using a JEOS jsm-35CF scanning electron microscope. Several types of defects were found in the contaminated fabric that were absent in the clean fabric and are not characteristic of cotton. "Eroded" and "crumbling" fibers were identified in the contaminated area (Fig. 4).

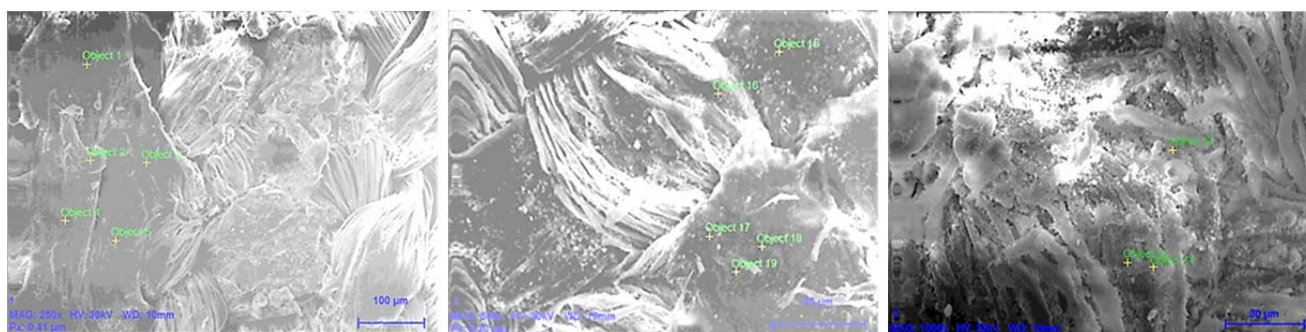


Fig. 4. Enlarged fabric fragments

Loops of fabric fibers were preserved only in a small area. Since the fabric fibers were destroyed, the mechanical properties of intact loops on both sides of the fabric were investigated. On the outer side (which had been exposed), the loops tear with almost no elongation, under a force approximately five times smaller. On the protected side, the minimum breaking force was 1.5 kgf, and the maximum was 2 kgf. On the outer side, in the brown areas, the maximum withstandable mass was 0.5 kg, the minimum about 0.25 kg; in the white areas, it was 1.5 kg and 0.75 kg, respectively.

Elements Al, Si, Ca, and Mg, which are most often found in cosmic dust and meteorites, were detected on both sides of the fabric. On the outer side, S, Cl, and F, which are present in volcanic gases, were also found. The detection of Zn confirms the dispersion of coatings from structural elements painted with zinc-containing enamels. The difference in composition may be a consequence of different velocities of dust particles. Sol particles are extremely small and, moving at high speed, become embedded in the fabric fibers. At high speed, they can pass through the material.

Thus, studies of the physicochemical properties of the fine-dispersed sediment forming on the ISS surface have confirmed its potential active role in the aggressive influence of the own external atmosphere on the development of

micro-destruction of structural elements made of various materials on the ISS. This circumstance creates new requirements for the surface materials of spacecraft, coatings, and protective elements, considering the adsorption and accumulation of particles of various origins.

Conclusion

The results of the "Test" space experiment have shown that orbital constellations and space debris act as collectors and carriers of aggressive chemical elements on their surfaces, which are not dispersed into space as previously assumed. It has been discovered that chemically active elements and iron particles can be a result of volcanic activity. The continuous influx of biogenic material, meteoroid stream particles, chemically active elements from volcanic gases, and, importantly, radioactive particles onto the ISS surface necessitates further study of the corrosion resistance of surfaces under conditions of long-term combined exposure to the aggressive near-Earth environment. This defines new hazardous factors of the Earth's exosphere's influence not only on the technical condition of orbital assets externally, but also internally after frequent crew extravehicular activities. Elements of the fine-dispersed sediment accumulated on the external surface of any object will fall to Earth upon the spacecraft's return, and this could pose a danger. Research on the transfer of matter in space is an important task, also necessary for planetary safety.

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