Corrosion and pressure action of the deep-sea on the NESTOR floor-detector

Deep sea water muon and neutrino detectors, like ANTARES, NEMO or NESTOR, use the Cherenkov light, produced by leptons (mainly muons) to detect the interaction of a neutrino. As a very complicated complex multipurpose arrays which are established deeply under water these detectors (deep under water neutrino telescopes) should be designed to provide continues operation within not less than 10 years for accumulation of necessary statistics of registered events. Presence of a high pressure and the aggressive seawater environment forces to approach with special carefulness to selecting the materials necessary for units and parts of deep-water neutrino telescopes.

The main "enemies" of the facilities working in deep sea water are corrosion and pressure. Process of corrosion is well studied and, basically, it is clear how to avoid significant corrosion of elements of deep-water neutrino telescopes. The major principle for prevention of electrochemical corrosion is manufacturing all metal details from the same kind of metal or even from different metals, but with almost equal electrochemical potentials [1,2]. For the deep-water devices, spending long time under water, Ti- alloys are the best materials. However in case of such complex systems as neutrino telescopes it is very difficult to make everything from titanium, especially the smallest details, because of its high price or the absence of prefabricated parts of the needed size. It is necessary to combine. First of all it concerns anchors and buoyancy, the elements distanced from the basic systems. Besides there always is a probability that at assembly of system among fixing elements there can occur a bolt or a nut made or others small things of inappropriate metal. Moreover, the proper combination could minimize material costs and simplify the technology for neutrino telescope production. Therefore any result of the analysis of processes of corrosion of devices, long time worked at the big depth in sea water, is very important and useful and experience should be generalized.

We started collecting data about influence of pressure and corrosion from first tests of elements of deep-water neutrino telescope NESTOR. In the given paper the results of the analysis of conditions of elements from the NESTOR test-detector which was exposed long time at the depth of 4000 m in the Mediterranean Sea are presented. This experience should be taken into account upon creation deep under water neutrino telescope.

Components in deep-sea

First long-term tests were started when in 2000. A 30 km-long deep sea cable with 18 mono mode optical fibers is laid from the shore to the deep-sea site (Fig.1). One copper conductor can deliver up D.C. power. The scientific payloads are attached at the end of cable. The sea end of cable is hoistable in order to change the deepwater equipment. The cable landing is terminated in the Terminal cable station in the village of Methoni (11 km from Pylos).

In January 2002 the end of the cable was brought to the surface by recovery rope and connected to the telescope bottom unit or “pyramid” constructed from corrosion resistant aluminum alloy (A14V2) tubes. (Fig 2). This pyramid structure is used for a attachment of environmental sensors and seawater electrode. The pyramid also houses the mass anchor and cylindrical junction box (JB) made from Ti-alloy. The mechanical part of the electro-optical cable is attached via a bend restrictor and a hang-off-terminator to the pyramid. The e/o cable is connected via GISMA hybrid connector to the JB. The off shore seawater electrode is also connected to the JB to provide the power. Many of these components are first-of-kind items and have had to be developed and tested for operation at a depth of 5000 m.

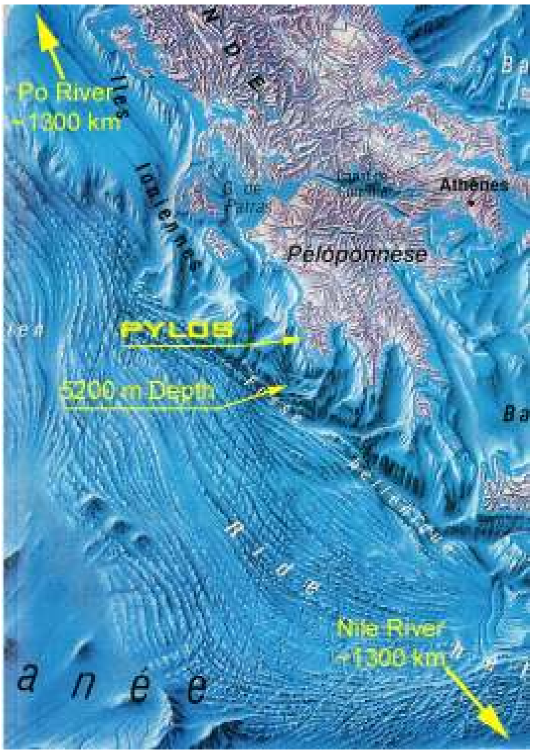


Fig.1. The NESTOR site.

The deployed package at the NESTOR site consisted of temperature sensors, pressure sensor, a compass, a light attenuation meter, a water current meter and an ocean-bottom seismometer (OBS). Useful data were transmitted to the shore from the pyramid and long-term variations in environmental parameters were obtained.

In March of 2003 the pyramid was brought back to the surface. The floor of the NESTOR test-detector, made out with Ti, was connected and deployed. The present detector floor structure measures only 12 m in diameter but consists of the usual 6 arms and is equipped with 12 OMs. The detector floor was mounted some 150 m above the anchor. There are LED calibration pulse modules installed 20 m above and 20 m below the center of the floor plane.


Fig.2. The NESTOR Ti-floor

The floor-detector has enough its own flotation and does not provided with additional buoy for underwater stability. The recovery buoy with its own mass anchor and release system was attached to the end of recovery rope and distanced from floor detector at about 5 km. The supporting frame of the buoy is made from mild steel structural shape. Two peaces of syntactic and 9 BENTHOS spheres are provide positive buoyancy of +215 kg which is enough to remove the end of the recovery rope on the sea surface. Buoy system is equipped with both auto light and auto radio beacons.

All deployment operations were made from a service vessel. All cable connections were made outside the water, on board of the vessel. This procedure does not require any robot or special submarine, it is cheap, quick and efficient

The purpose of this deployment was an engineering run with carrying out an overall system performance test under real conditions at full depth with the unavoidable ^{40}K decays and bioluminescence backgrounds, studying characteristics of the modules, testing the control and data acquisition system, the software, including its event reconstruction capability, and obtaining experience with the overall system operation.

Because of lack of coincidence between good weather and availability of a service vessel NESTOR test-detector stayed under water of 2.5 years. That provided very useful long-term examination for mechanical construction and all materials immersed at the big depth. Data about corrosion and pressure resistance are important for future large neutrino detecting array of KM3.

Pressure action

Housings for electronics and optical modules must resist against action of pressure which amount more than 400 atmospheres at 4000 m depth. All pressure housings were tested under 450 atm in the pressure tank before assembling of the NESTOR test-detector. However these tests cannot substitute long-term examinations *in situ*. First of all it concerns glass spheres that can loose strength in water because of leaching.

Practically all housing removed from 4000m depth do not have visible damages due to pressure action. Only one glass sphere lost visible chip about 5 cm in diameter and 1 mm at the maximum thickness from outward surface. There are no visible deformations of the titanium and bronze GISMA connectors. In the case of inappropriate construction the deformation under pressure could be so considerable that it did impossible to open connectors. In our case all connectors are opened easily. There is no water flowing through packing rings or from the side of cable penetration. This result looks like trivial, but it is very important result, because before that nobody had experience of so long maintenance glass spheres at the depth of 4000 m.

Corrosion action

Corrosion of the metal parts.

Corrosion is an electrochemical process in which a metal reacts with its environment to form an oxide or other compound. The cell which causes this corrosion process has three essential constituents: an anode, a cathode and an electrolyte (electrically conducting solution). The anode is the site at which the metal is corroded; the electrolyte is the corrosive medium; and the cathode (part of the same metal surface, or of another metal surface in contact with it) forms the other electrode in the cell and is not consumed in the corrosion process. At the anode the corroding metal passes into the electrolyte as positively charged ions, releasing electrons which participate in the cathode reaction. Hence the corrosion current between anode and the cathode consists of electrons flowing within the metal and ions flowing within the electrolyte. The surface of one component may become the anode, and the surface of another component in contact with it, the cathode. Usually, corrosion cells will be much smaller and more numerous, occurring at different points on the surface of the same component. Anodes and cathodes may arise from differences in the constituent phases of the metal itself, from variations in surface deposits or coatings on the metal, or from variations in the electrolyte. The rate of corrosion is influenced considerably by the electrical

conductivity of the electrolyte. Pure water has poor electrical conductivity and the corrosion rate will be much lower than, say, an acid or alkali solution of high conductivity. The ability of metals to resist corrosion is to some extent dependent upon their position in the electrochemical series (Table 1,[1,2]). Table 1 provides easy way to choose appropriate combinations of different metals for the underwater equipment production. The farther two metals are separated from one another in the electrochemical series, the more powerful is the electric current produced by their contact in the presence of an electrolyte. Also the more rapidly the metal towards the bottom of the table is attacked and the more will the metal towards the top of the table be protected. It must be remembered, however, that the order in the above series may vary under special corrosive conditions, and the galvanic series in service media, e.g. sea water, are often more useful from the corrosion aspect.

The size of the cathode relative to the anode is important, e.g. small copper rivet (cathode) in a large steel plate (anode), is quickly polarised and corrosion on the plate is small. On the other hand, a large cathode coupled to a small anode has the opposite effect, with rapid attack of the anode. Electrochemical corrosion can be stimulated by not only differences in the metal surface, but also by variations in the electrolyte, [3, 4]. The presence of dissolve oxygen in the sea water accelerates the cathodic reaction; and consequently the corrosion rate increases in proportion to the amount of oxygen available for diffusion to the cathode. Cavities in metal surfaces and metal surfaces partially covered by another material are prone to this type of attack. The diffusion of oxygen into cavities or crevices is impeded and results in these areas becoming anodic to the surrounding metal which oxygen can easily reach (oxidation-concentration cell). The metal ions formed in the cavity migrate outwards and react with the hydroxide ions flowing in the opposite direction to form a corrosion product (rust) at the mouth of the cavity or crevice. This position of the corrosion product accentuates the corrosion by making the diffusion of oxygen to the anode more difficult, and if the cathode area is large severe pitting (Fig.3) may occur [5,6].

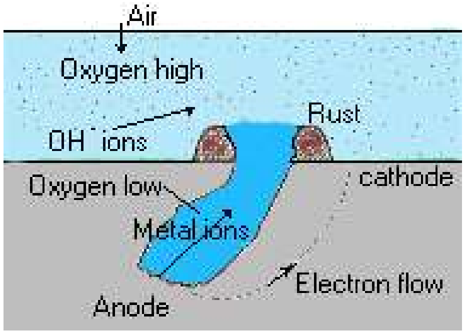


Fig.3. Pitting corrosion

Normally corrosion resistant materials which rely on thin oxide films for protection, such as stainless steel, can suffer from this type of corrosion attack [6,7]. These materials rely on oxygen being present, so that they can maintain their oxide films (passive state). When oxygen is excluded and the oxide films break down, the whole surface becomes active and corrodes readily (Fig.4).

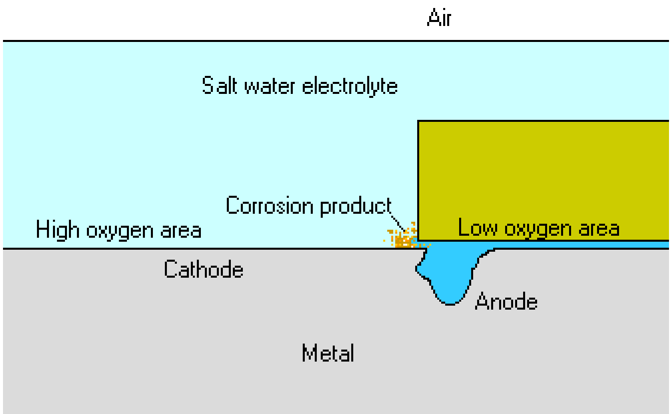
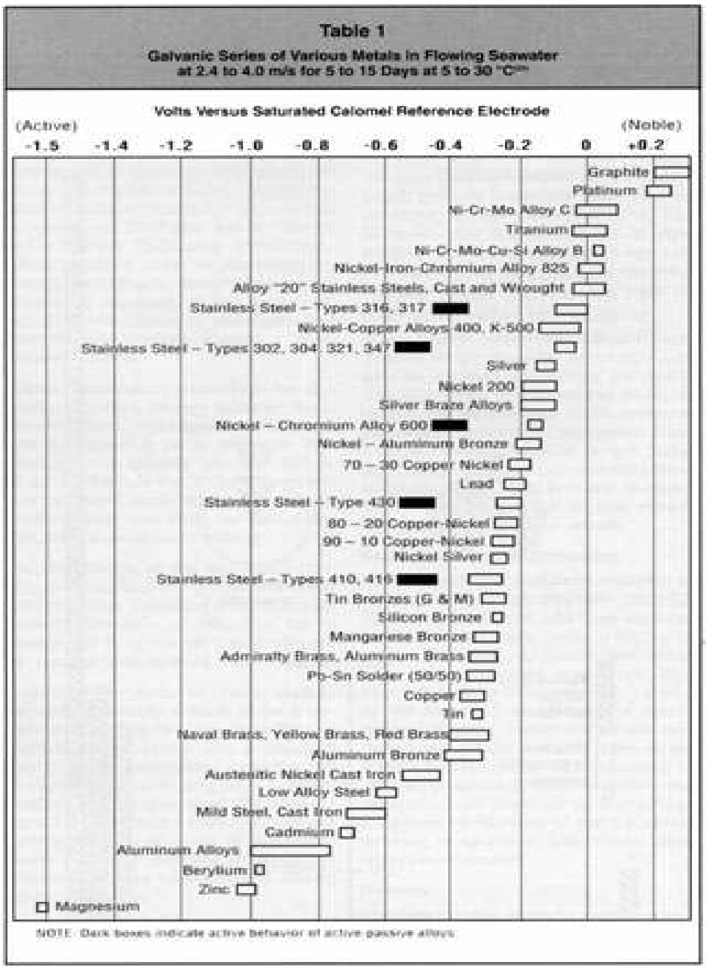


Fig.4. Crevice corrosion

The effects of corrosion can be accelerated or induced when operating in conjunction with stress and various wear mechanisms. Usually the mechanisms work by not allowing the corroded metal to become passive by continually removing protective films and setting up active/passive corrosion cells where the mechanism is not uniform applied [7]. The corrosion products formed may provide abrasive debris to make matters worse.



The best material for the mechanical construction of neutrino telescopes is a titanium alloy. Titanium resists corrosion by seawater at temperatures as high as 260^0 C, [2]. Titanium tubing which has been exposed to seawater for many years at depths of over a mile shows no measurable corrosion. It has provided over twenty-five years of trouble-free seawater service for the chemical, oil refining and desalination industries. Pitting and crevice corrosion are totally absent. The presence of sulphides in seawater does not affect the resistance of titanium to corrosion. Exposure of titanium to marine atmospheres or splash or tidal zones does not cause corrosion. However if Ti is chosen the use of Al details should be excluded completely. The combination Ti + Al is worst for the sea use (see Table 1.).

The main part of the test-detector, a Star, was made from Ti-alloy OT-4 (Russian Standard). This part of detector was not susceptible to corrosion. Only parts consisted of some details made from aluminum and mild- and stainless steel could provide a corrosion process: the anchor unit, the recovery buoy and LED units

We were surprised a little when found so slight corrosion on the parts which were taken out from the depth. Even made from mild steel the buoy's frame was slightly covered by spots of pitting corrosion. Of cause it was protected with Zn-anodes and painted by special protective vanish. In any

Fig.5. The buoy's frame from NESTOR test-detector is ready for new deployment

case the frame has returned from the depth in a very good condition and will be used again (see Fig.5). It should be mentioned also that after a long time of installation on the sear floor in 4000 m of water, there has been no visible indication of corrosion on the aluminum pyramid.

Even five fingers on the hand are too many for calculation of the details with evident corrosion. One can see at the Fig.6 a typical crevice corrosion between the stainless steel washer and "hard hat" of the BENTHOS sphere. We have to state, the corrosion was slow enough and has destroyed not more than a half of the thickness of washers. It's easy to see more of the same in Fig.7: neither bolts or nuts nor even the grovers were attacked. Only stainless steel washers had traces of crevice corrosion, but not all of them. Perhaps some washers and bolts (nuts and spring rings) were made of different kinds of stainless steel. The solution is simple, use plastic washers.

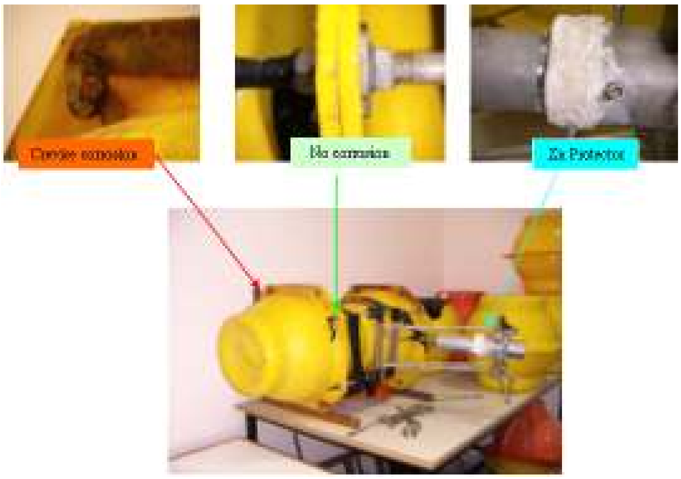


Fig.6. Manifestations of corrosion on the LED unit

One more corrosion attack took place on the stainless steel straps girdled BENTHOS spheres. Bolts on the buckles were completely destroyed by crevice corrosion (Fig.8). The weakening of the straps is not dangerous for BENTHOS spheres. However a settling of the rust on the BENTHOS's surface at the side of photo cathode can spoil sensitivity of the OM.

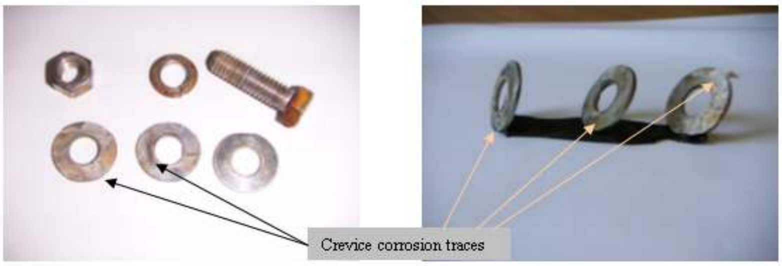


Fig.7. The bolts and washers of fig.6. Traces of the crevice corrosion on the stainless steel washers only. Bolts and nuts have no signs of corrosion

Glass spheres corrosion.

Corrosion of glass in sea water is a process of decomposition due to leaching (solving process)and diffusion of alkali ions, across a hydrated porous silica network. Factors effecting this decomposition are, [8]:

- the composition of the glass itself;
- the composition and pH of the attacking solution;
- the temperature of the attacking solution;
- time.

Fig.8 Result of corrosion attack to the buckle on stainless steel straps girdled around BENTHOS sphere.

The composition of the glass will determine its stability. Glass is composed of a network former – silica, and alkaline modifier such as sodium or

potassium oxide, and calcium oxide, the positively charged ions of which will stabilize the negative ions of the alkali. In our case borosilicate glass (Pyrex) with low rate of radioactivity is used for the BENTHOS.

The pH of the attacking solution is important [8]. For instance glass retrieved from an acid environment often had an iridescent layer of leached silica. If later that glass is immersed into fresh or sea water the alkali which diffuses out is neutralized by the acid and few hydroxyl ions are available to react with the silica. This reaction leaves a thick layer; the alkali leaks out and the silica remains as a hydrated network, in short, water is holding the glass together.

The composition of the attacking solution, in our case of marine environment, is rarely stable and can alternately increase or limit amount of leaching taking place. Being extremely saline, sea water contains many chlorides as well as oxygen and hydrogen sulphide generated through the activity of marine organisms and rotting vegetation. In such environment the reaction of exchanging alkali (mainly sodium) by hydroxyl (OH) ions proceeds at a constant rate throughout the glass [9]. A partially devitrified glass surface may change the appearance of the BENTHOS sphere. Particularly striking effects of iridescent colour may result from the interference of light by the thin film or flakes which compose the surface of the sphere.

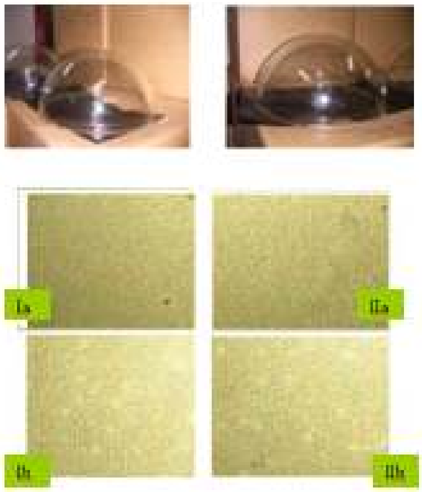


Fig.9 Condition of the BENTHOS exposed under water during 2.5 years (I) compare to one which never was under water (II)
Ia, IIa: outer surface's structure close to pole of the sphere
Ib, IIb: outer surface's structure at the back side of the sphere
Microscope magnification: 200

If many times glass sphere was immersed under water over time many of these iridescent layers may build up into an 'Onion Skin' laminar formation and eventually exfoliate or fall off the glass [9]. The similar event arises when glass sphere is getting old besides of the use under water. Even under variable humidity many of iridescent layers may build up too and sphere looses a mechanical strength.

Therefore, the leaching process may lead to a changing of the optical and mechanical properties of the BENTHOS sphere.

Taking into account the manifestations of leaching described above, we carefully inspected BENTHOS spheres recovered from the 4000 m depth after 2.5 yeas from deployment. Neither iridescent layers nor 'Onion Skin' were found. The absence of any visual spots of mat, micro scratches or rainbow colours on the outer or inner surfaces of the BENTHOS spheres allowed us to state that leaching during 2.5 years is negligible. The view of the outer surface of the used BENTHOS compared with one never used under seawater is shown on the Fig.9. One can see the practically identical structure of outer surfaces of both spheres.

Summary.

Table2. Signatures of the corrosion			
Part of the detector	**Material**	**Type of corrosion**	**Comments**
Recovery buoy's bearing construction	Mild steel	Pitting corrosion	Frame was painted by special enamel and protected by Zn
Floor detector	Titanium alloy	No corrosion	Ti-alloy OT 4 (Russian)
LED encapsulations	Stainless steel	No corrosion	Protected by Zn
Bottom pyramid	Aluminium alloy	No corrosion	Al-alloy A14V2 (German) Protected by Zn
Junction box	Titanium alloy	No corrosion	Ti-alloy OT 4 (Russian)
Bolts Nuts Brads Washers	Stainless steel Stainless steel Stainless steel Stainless steel	No corrosion No corrosion No corrosion Crevice corrosion	Not all washers were corroded
Spring rings	Stainless steel	No corrosion	
Hardhats	Plastic	No corrosion	
Sheath of cables	Plastic	No corrosion	
GISMA connectors	Ti-alloy	No corrosion	
GISMA connectors	Sea bronze	minor Pitting corrosion (on the flange)	Bronze connectors were used at the OMs
Glass BENTHOS spheres	Borosilicate glass	No corrosion (leaching)	
Straps for BENTHOS	Stainless steel	Crevice corrosion	Maximum attack is on buckle bolts

All observations concerning corrosion we summarised in the Table 2. One can easy see there are only a small number of corroded elements of the detector's construction. At first, of cause, it is due to right choice of material. However the question still arises: why if the corrosion appears, it's rate is so slow? Indeed, buoy's frame has a slight pitting corrosion and washers lost only a half of their thickness due to crevice corrosion during 2.5 years under water. We suppose perhaps it results from low quantity of oxygen dissolved in deep sea water. It should be mentioned here also, there is low rate of sedimentation and overgrowing by marine organisms at the NESTOR site. We did not find visible signature of vital function of micro marine organisms on the surface of any part of the detector. One can argue that detector was washed during recovery procedure. This could be true however in Baikal project for instance, there are a lot of sediments fixed on the surface of neutrino detector with slime and it never was washed completely at the time of recovery.[*)]

The fact of low rate of sedimentation and overgrowing is very important for the future full neutrino telescope not only because they could brake sensitivity of optical modules, but could provoke corrosion and leaching also.

Low sedimentation rate, absence overgrowing, slow rate of corrosion all together with the excellent optical and hydrological characteristics of water render NESTOR site as most suitable for neutrino telescope accommodation

References:

1. *V.V.Novysh*. Brief hand book for underwater pressure housings design. Troitck, 1997, 40 p. (In Russin)
2. Titanium in sear water. www.azom.com/details.asp?ArticleID=1336. CODEWELD® Titanium Tubing www.stainless-steel-world.net/titanium/seawate.
3. Corrosion. Hand bock. www.metaltrade.ru/abc/k/korroziya.htm.(In Russian).
4. *E.Savinkina*. Corrosion of the metals. 83.222.31.122/articles/116/1011691/1011691a1.htm (In Russian).
5. *H. Rachev, S. Stephanov*. Hand book of corrosion. M., Mir, 1982, 523 p. (In Russian).
6. *A.I. Alcibeeva, S.Z.Levin*. Inhibitors of corrosion. (Hand book) M., Chemistry, 1968, 264 . (In Russian).
7. *I.L.Rosenfeld*.Corrosion and protection of metals. M., Mmetallurgy , 1969, 448 p. (In Russian).
   Corrosion. referat.niv.ru/referat/026/02600073.htm
8. *I.A.Kumalagaev.* Technology of glued multiple glass panes. Windows, Doors and stained-glass windows Magazine, № 2, 2004, glass, (In Russian).
9. *Jane Pannel*. Conservation of glass in Bodrum Museum of Underwater Archaeology. www.diveturkey.com/inaturkey/lab/pannell.htm
   Optical glass catalog 2005 ru. glassbank.ifmo.ru/eng/ (in Russian).