

Research to Develop Safety Assessment Measures of Alternative Fuel/New Cargo Transportation

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1. INTRODUCTION

This paper presents an overview of the lecture “Safety Assessment of Alternative Fuel and New Cargo Transportation” at the ClassNK R&D Forum held on January 28, 2025. In addition to proposals of various alternative fuels for realizing zero emissions in shipping, the cargos which are transported are also changing, beginning with mass transportation of liquefied hydrogen for decarbonization in industry and society. Ship safety has been achieved over the long history of ships. This is backed by the fact that, until now, rules specifying the design requirements for ships based on new concepts were not always established before those ships were designed, but rather, rules were developed by accumulating knowledge through the design and approval processes of ships with new concepts. Today, however, when we are attempting to quickly achieve systems that have little record of actual use on ships, or have not been used heretofore, formulation of safety requirements with a sense of speed is also necessary in order to accelerate social implementation of these new systems.

Therefore, in addition to the conventional approach of developing safety requirements in cooperation with the front runner who is, so to speak, the “first penguin,” ClassNK (hereinafter, the Society) has also adopted a proactive approach by strengthening its own research and development initiatives. As part of this, we are promoting research and development of “Advanced and quantitative risk assessment of alternative fuel ships” and “Integrity assessment techniques for cargo and fuel containment systems” as core techniques. As the reasons for selecting these two items, first, because risk assessments are required in the design of alternative fuel ships, quantification of risk assessments is necessary and indispensable for fostering a common recognition among diverse stakeholders, and secondly, although risk assessments consider the unlikely event of a leak, precisely for this reason, efforts to ensure that leaks do not occur in the first place were considered necessary. Research and development are being carried out based on these two approaches.

The research which the ClassNK Research Institute carries out based on the above-mentioned approaches spans a diverse range. However, due to the limited time available, we took up the following items in presentation at the R&D Forum.

Advanced and quantitative risk assessment of alternative fuel ships:

- Estimation of frequency of ammonia leaks in ammonia-fueled ships
- Ammonia gas diffusion tests
- Quantitative risk assessment methods and advanced risk assessment techniques for alternative fuel ships

Integrity assessment techniques for cargo and fuel storage facilities:

- Study of evaluation techniques for ammonia stress corrosion cracking sensitivity of materials
- Study of liquid oxygen (LOX) compatibility evaluation method for materials

In addition to these topics, in “Advanced and quantitative risk assessment of alternative fuel ships,” we are also promoting Verification & Validation (V&V) of analysis of hydrogen fine droplet leak and diffusion tests and gas diffusion analysis, and in “Integrity assessment techniques for cargo and fuel storage facilities,” we are conducting research on the fracture behavior of materials under cryogenic environments, evaluating the effects of post weld heat treatment (PWHT) on fracture toughness assuming liquefied CO₂ tanks, and studying the possibility of omitting large-scale tests by simulation of ductile fracture in materials for service at cryogenic temperature environments. The results will be incorporated successively in ClassNK Rules and Guidelines, and reports will be posted on the website of the ClassNK Research Institute. Persons with an interest in these issues are invited to refer to those sources.

This paper presents an outline of the research and development being carried out under “Advanced and quantitative risk assessment of alternative fuel ships” and “Integrity assessment techniques for cargo and fuel containment systems,” followed by an explanation of the results of the five above-mentioned research projects, which were discussed at the R&D Forum, and

the current condition of the projects.

2. ADVANCED/QUANTITATIVE RISK ASSESSMENT OF ALTERNATIVE FUEL SHIPS

As shown in Fig. 1, risk assessments are generally carried out by a flow that begins from identification of hazards. When a certain scenario has been selected, the risk can be found by evaluating the frequency of occurrence and the degree of effect, and then multiplying the effect of the hazard by its frequency. Therefore, for advanced and quantitative risk assessments, it is necessary to quantify the respective evaluations of the frequency of occurrence and degree of effect. Since quantitative risk assessments are not necessarily the general practice in the ship field, except in the case of HAZID, etc., it is also necessary to study an advanced and quantitative approach to the entire flow of risk assessments. For this reason, we are studying “Estimation of frequency of ammonia leaks in ammonia-fueled ships,” “Ammonia gas diffusion tests” and “Quantification of risk assessments and Application of the process safety concept to alternative fuel ships,” which will be explained in the next section.

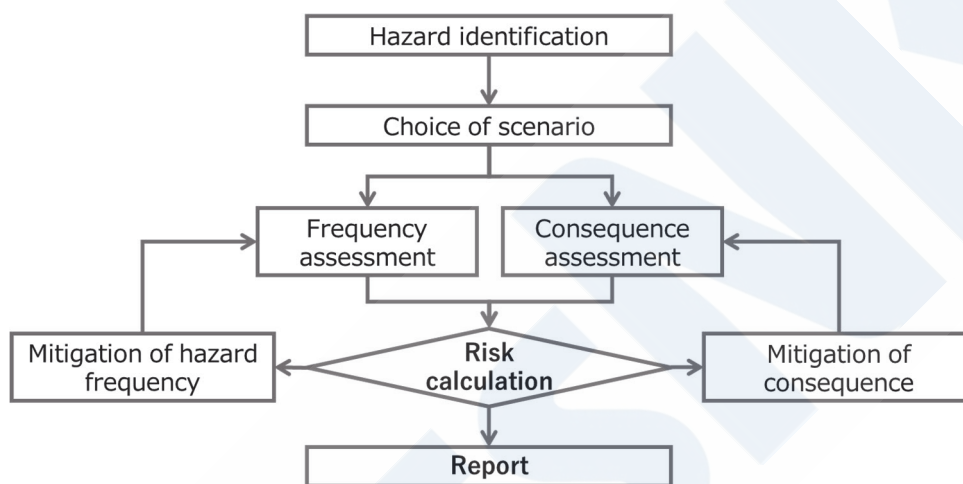


Fig. 1 Flow of risk assessment

2.1 Estimation of Frequency of Ammonia Leaks in Ammonia-Fueled Ships

The risk of alternative fuel ships originates from leaks of the fuel that is stored and used. Therefore, in performing a risk assessment of an alternative fuel ship, accurate estimation of the frequency of leaks is important. In hydrocarbon (petroleum, natural gas) plants, the scale and probability of leaks have been arranged based on an enormous amount of actual results to date, as seen, for example, in the IOGP Risk Assessment Directory¹⁾. Past research on ammonia-fueled ships includes an example of a risk assessment for ammonia-fueled ships using the statistical value of leaks at hydrocarbon plants²⁾ and an example that states to the effect that a conservative evaluation of the risk of ammonia-fueled ships is possible by using the IOGP frequency³⁾.

However, because the properties of ammonia are different from those of hydrocarbons, and the hazards that occur are also different, it would be preferable to apply the frequency of ammonia leaks in risk assessments of ammonia-fueled ships, but no statistical values are available for ammonia leaks. Therefore, we estimated the frequency of leaks from shipboard ammonia fuel equipment by using a limited database of ammonia leaks from land-based ammonia-using equipment by Bayesian updating, which is a technique that was used by the Sandia National Laboratories in the United States in a risk assessment of hydrogen stations⁴⁾. It may be noted that our research was carried out in cooperation with the Research Institute of Science for Safety and Sustainability of the National Institute of Advanced Industrial Science and Technology (hereinafter, AIST).

Since this research was presented at the Forum by Dr. Kojima of AIST, and submission of a peer-reviewed paper is still in the progress as of this writing (Feb. 2025), I will refrain from describing the details here. Although the results obtained in this research were based on various assumptions, because the results are the world's only estimated values for the frequency of leaks specifically for ammonia, this work is expected to be useful for securing the safety of ammonia fuel equipment, which still has a high degree of uncertainty.

2.2 Ammonia Gas Diffusion Test

In quantitatively evaluating the degree of effect in Fig. 1, evaluations of gas diffusion after a fuel leak are carried out on

alternative fuel ships. Since it is impossible to carry out experiments for all cases, a plume model or other diffusion equation, or computational fluid dynamics (CFD) is generally used. Of course, it is desirable to examine the validity of these evaluation methods from the viewpoint of V&V.

In the V&V mentioned here, the purpose of the first V (Verification) is to determine whether the created numerical calculation correctly implements the conceptual model, and the purpose of the second V (Validation) is to determine whether that numerical calculation can correctly reproduce the phenomenon ⁵⁾. Here, it can be pointed out that many diffusion evaluations assuming ammonia-fueled ships have been carried out at the research level, but validation of those evaluations has not been carried out adequately.

Particularly in the case of Validation, experimental data are necessary as an object of comparison. However, the reliable ammonia gas leak diffusion tests are limited to Tan et al. (2017) ⁶⁾, the RED SQUIRREL tests ⁷⁾ and the Fladis Field Experiments ⁸⁾, and in all cases, the object of those tests was diffusion behavior in an open space or in a wind tunnel. On the other hand, closed spaces where ammonia leaks may occur also exist in ammonia-fueled ships, for example, in the fuel preparation room, engine room, etc. Therefore, based on this background, ammonia leak and diffusion experiments were conducted in a closed space to contribute to validation of numerical analyses.

The experiment was carried out by releasing a mixed gas consisting of ammonia and nitrogen into an acrylic container with a volume of approximately 1 m³ from the container bottom, as shown in Fig. 2. Although omitted in Fig. 2, the ammonia was discharged from the top of the container via a hose, and was detoxified before final release. As an additional safety measure, the maximum ammonia concentration in the ammonia-nitrogen mixed gas was at maximum 5 vol%.

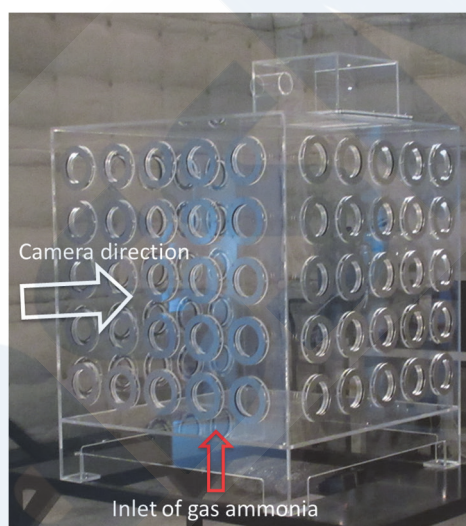


Fig. 2 Ammonia release space

The most important feature of this experiment was measurement of the ammonia concentration by 2-dimensional imaging by the Raman scattering method. For example, Tan et al. ⁶⁾ used a contact-type gas concentration meter in measurements of the ammonia concentration. However, in small-scale experiments, the possibility that this kind of concentration meter itself may affect the flow field is a concern. Moreover, commercially-available ammonia gas detectors are not suitable for application in this type of experiment due to their long response time. Therefore, we adopted a system that makes it possible to evaluate the ammonia concentration of their entire region, without influencing the flow field (flow distribution), by using a laser Raman spectroscopy technique developed by the Shikoku Research Institute Inc. This technique has an extensive record of results with hydrogen, as described in detail in Asahi et al. (2021) ⁹⁾. In our experiment, quartz glass windows were inserted into the numerous round holes in the acrylic container shown in Fig. 2. This system makes it possible to photograph the laser light and the scattered light of the gas molecules during laser Raman spectroscopy. Ideally, a photography surface made entirely of quartz glass would be desirable, but considering the difficulty of manufacturing large-scale quartz glass, quartz glass was installed in the observation windows.

In this experiment, the scattered Raman light was photographed with a CCD camera in the direction indicated by “Direction of photography” in Fig. 2. Fig. 3 shows an example of an image of the ammonia concentration. Because this is the condition

immediately after release of the ammonia started, high brightness (red contour) was observed near the release hole, and ammonia could not be detected in the upper part of the container, which is relatively far from the release hole. The measured luminescence here was converted to the concentration of ammonia by using the luminescence of a reference cell (compact vessel filled with ammonia of a known concentration). Fig. 4 shows an example of the transition of the measured ammonia concentration. It can be understood that the transition of the concentration accompanying the start and end of ammonia release was successfully measured.

Future issues include improvement of measurement accuracy, installation of obstacles in the chamber, study of diverse methods of releasing the ammonia (e.g., pinhole release), and validation by comparison with a CFD analysis. Since no other attempts to measure the ammonia concentration in a closed space have been reported anywhere in the world, we plan to continue this research in cooperation with our joint research partners (Prof. Tomohiko Imamura of the Suwa University of Science and Prof. Emeritus Takeshi Shinoda of Kyushu University).

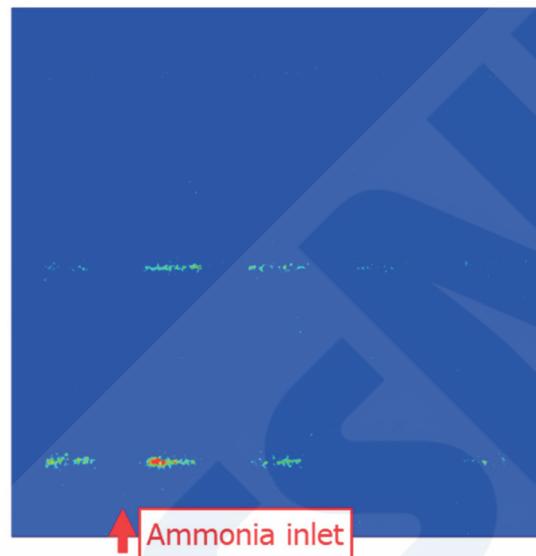


Fig. 3 Example of imaging of ammonia concentration

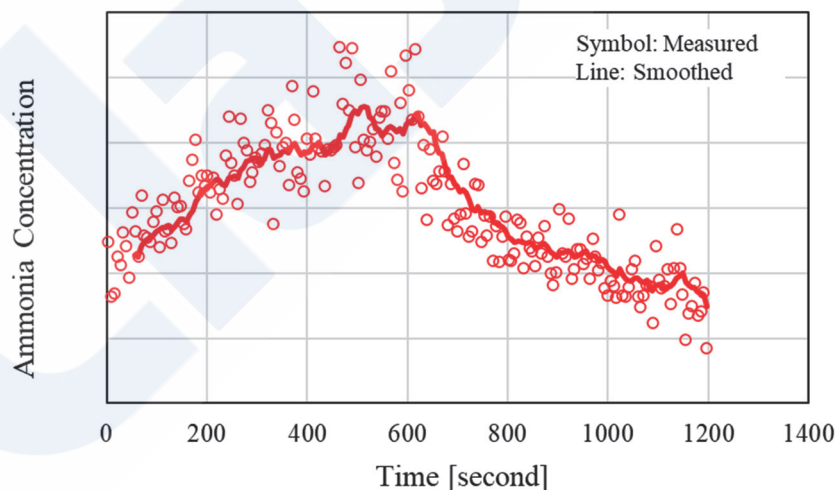


Fig. 4 Example of transition of ammonia concentration near ammonia jetting hole

2.3 Quantitative Risk Assessment and Advanced Risk Assessment Techniques for Alternative Fuel Ships

A risk assessment is required when designing an alternative fuel ship. Although HAZID or HAZOP is often conducted as the risk assessment, a risk assessment in the narrow sense (Quantitative Risk Assessment, QRA), like those carried out for hydrogen stations¹⁰⁾, is not the general practice in the maritime industry. Since visualization of the evaluated risk is simple with QRA, this approach easily fosters a common understanding among the stakeholders, and since quantitative evaluations of the effects of actions to reduce risks are possible, this approach is particularly suitable for risk assessments of systems with few actual

results of use until now. On the other hand, there are few results of application to alternative fuel ships. Therefore, in this research, research and development were carried out to perform a QRA of a hydrogen-fueled model ship. Up to the present, HAZID, HAZOP and bow-tie analysis have been carried out for the same model ship. An example of the results of a bow-tie analysis is shown in Fig. 5.

Using these risk assessment results, research was carried out with the aim of using the risk assessment results not only in the QRA, but also in operation. As characteristic features of ships, the designer, operator and owner are different, and the crews assigned to ships also change with comparatively high frequency. Used ship sales are also the general rule, and in many cases, the ships are operated by different owners. Therefore, it is thought that management using the results of the risk assessment at the time of ship design, that is, the types of risks that exist for the ship and the actions that should be taken, will contribute to improved safety of alternative fuel ships, for which few records of actual use are available.

These studies are being carried out jointly with Associate Professor Yuichiro Izato of Yokohama National University.

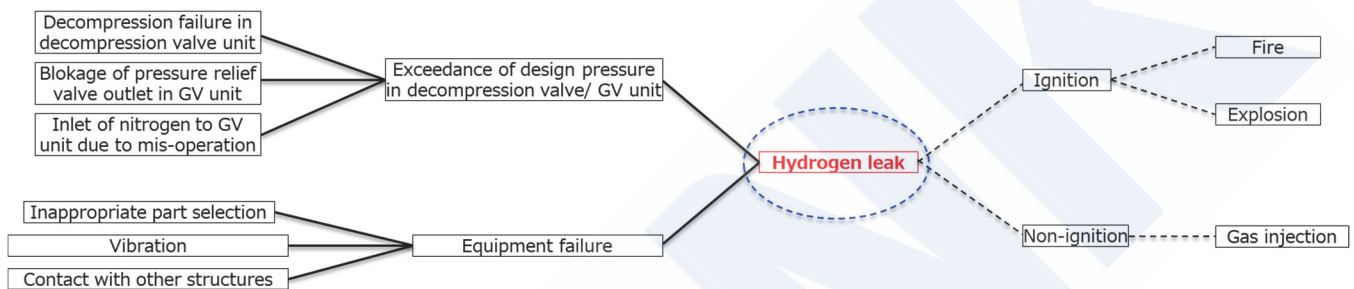


Fig. 5 Example of bow-tie analysis of hydrogen-fueled model ship

3. PREVENTION OF CARGO AND FUEL CONTAINMENT SYSTEM DAMAGE

Although risk assessment is necessary in order to prepare a design that ensures the safety of the system as a whole, considering the unlikely event of a leak. On the other hand, however, leaks and damage are only treated statistically. That is, in systems for which no actual results exist, there is naturally a possibility of damage which has not been experienced in the past, and this type of damage itself cannot be prevented simply by a design based on a risk assessment. Therefore, in order to prevent damage of the fuel and cargo containment equipment itself, it is necessary to study techniques for evaluating the integrity of this equipment and countermeasures for events that may threaten that integrity. Until now, rules had been created based on damage that actually occurred, but in an era of technological innovation, proactive research and development, like that mentioned in chapter 1, is needed. The Society carries out research and development from the viewpoints of “Structural integrity” and “Material compatibility.”

In an assessment of structural integrity, accurate evaluations of the driving force that causes failure and the force of the resistance against failure are required. The following are examples of research carried out by the Society. Among these, as an example of a driving force that causes failure, a study of an evaluation method for ammonia stress corrosion cracking (SCC) of materials was reported at the Forum. Together with this, research and development for material compatibility with liquid oxygen (LOX), which can become a source of fire, was also reported at the Forum. In this chapter, the content of these two topics is introduced in sections 3.1 and 3.2, respectively.

3.1 Study of Evaluation Method for Ammonia Stress Corrosion Cracking Sensitivity of Materials

In storage and use of liquefied ammonia tanks, ammonia SCC is a cause of damage. At present, the countermeasures against ammonia SCC include limitation of the strength of the steel materials used, addition of water to the ammonia, post weld heat treatment (PWHT), etc., as specified in the IGC Code 17.12. However, since these measures are based on the knowledge up to the 1970s, this may be an obstacle to upscaling of ammonia transport ships and the spread of ammonia-fueled ships in the future. Therefore, the Society is studying methods for evaluating the possibility of using materials in ammonia storage, considering ammonia SCC.

Since ammonia SCC is a time-dependent fracture phenomenon, it is desirable to evaluate the ammonia SCC sensitivity of materials by an accelerated test. Since it is known that ammonia SCC sensitivity generally displays a correlation with the

hardness of the material, experiments focusing on high strength steel materials were carried out in past research. However, in many cases, steel materials without such high yield stress, such as those used in ship tanks, were not evaluated. Therefore, the Society set test conditions referring to the research by Nakai et al.¹¹⁾ in the 1980s, and verified whether cracking occurred or not in steel materials with a wide range of strength levels. These tests were conducted using the 4-point bending method.

Fig. 6 shows the condition of HT80 class steel after immersion for 2 weeks in ammonia with addition of 5% CO₂ and 1 000 ppm of oxygen, under the combined conditions of strain equivalent to the yield stress and application of a potential of 2.0 V vs Pt. It can be understood that remarkable cracking has occurred. In contrast, when the same test was carried out with steel having the lowest yield stress of 325 MPa under the standard, only fine cracks with a length of approximately 200 μm were observed. From these results, it was suggested that, under these test conditions, more significant results can be obtained in the ammonia SCC test with the steels currently in practical use, with the exception of mild steel.

On the other hand, Fig. 7 shows the result when the same HT80 class steel was immersed for 136 hours in the same experimental system. As this experiment shows, although cracks will still occur, they will be limited to minor length if the immersion time is short. In addition, no cracks occurred with the steel with the lowest yield stress of 325 MPa. Based on these facts, it can be said that setting an appropriate immersion period corresponding to the test conditions is necessary in order to evaluate the ammonia SCC sensitivity of materials.



Fig. 6 SCC fracture surface of HT80 (immersion time: 2 weeks)



Fig. 7 SCC fracture surface of HT80 (immersion time: 136 hours)

When conducting accelerated ammonia SCC tests, setting appropriate acceleration conditions is indispensable. While it is known that impurities, namely, oxygen, carbon dioxide and water, affect ammonia SCC, the mechanism responsible for changes in ammonia SCC behavior is not clear. In addition, corrosion reaction is also a contributing factor, and at present, the success rate in experiments is not necessarily high. Therefore, in the future, we plan to continue research with the aim of setting the conditions for stable experiments and confirming variations.

3.2 Study of Evaluation Method for Liquid Oxygen (LOX) Compatibility of Materials

Liquid hydrogen, which is expected to become an important zero-emission energy source in the future, is liquified under the cryogenic temperature of $-253\text{ }^{\circ}\text{C}$. Since this temperature is lower than the liquefaction temperature of oxygen, oxygen in the air may possibly liquefy, depending on the state of thermal insulation. Therefore, Guidelines for Liquefied Hydrogen Carriers¹²⁾ published by ClassNK requires consideration of ignition risk due to liquefied oxygen (LOX) when the air is cooled below its liquefaction temperature in single-failure scenarios. Specifically, it must be ensured that the generation of LOX does not pose a hazard, or that materials in contact with LOX are LOX compatible.

“LOX compatibility” refers to the ability of a material not to ignite upon mechanical impact when in contact with LOX. Although LOX compatibility assessment is specified in the ASTM code, until now, LOX compatibility assessments have mainly been used in the aerospace field, and have rarely become an issue in the maritime field. Therefore, the Society has accumulated

experience and knowledge on LOX compatibility through collaborative research with Japan Aerospace Exploration Agency (JAXA).

In LOX compatibility tests, the assessment specimen is immersed in LOX and struck by way of a striker pin, as shown in Fig. 8. When there is no ignition or sign of ignition in the specimen, the tested material is considered to be LOX compatible. On the other hand, when ignition similar to that in Fig. 9 is observed, the material is considered to be incompatible with LOX. The forms of ignition vary; it can be relatively mild, as shown in Fig. 9, or it can be explosive, as classified as “Explosion” by Guo et al.¹³⁾. Through the collaboration with JAXA, the Society has carried out experiments with six materials, carbon steel (SM400C), coated carbon steel, Al-Mg alloy (A5083-O), PEEK resin, insulation material (MLI) and an epoxy-based structural adhesive.

The experimental results obtained so far are presented in Table 1. The ASTM code stipulates an impact energy of 98 J, but in this study, 49 J and 25 J were also used to examine the sensitivity of LOX compatibility to impact energy, because the suitable impact energy for the maritime industry is still unclear. “Non-ignition” refers to a test condition in which ignition does not occur in 10 or more experiments. However, if even one trial in the multiple experiments results in ignition, that experimental condition is regarded as “Ignition.” Although some scattering of the results was found, Table 1 shows that the LOX compatibility of various material displays dependency on the amount of the impact energy. This finding suggests that it may be possible to assess LOX compatibility based on the degree of the ignition factor to which the material is subjected.

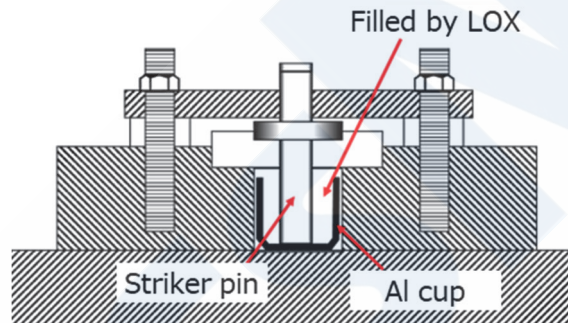


Fig. 8 LOX compatibility impact tester

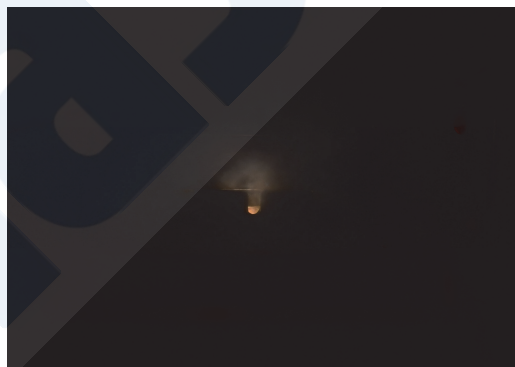


Fig. 9 Result of LOX test

Table 1 Status of LOX compatibility test

Specimen	Impact energy [J]		
	98	49	25
SM400C	Non-ignition		
Coated SM400C	Ignition	Ignition	Non-ignition
A5083-O	Non-ignition		
PEEK resin	Ignition	Non-ignition	
Insulation material (MLI)	Ignition	Ignition	
Epoxy-based structural adhesive*	Ignition	Ignition	Ignition

Because LOX compatibility has been assessed in the aerospace field, it is valuable to investigate the assessment methodology and criteria suitable for the maritime field for reasonable onboard liquid hydrogen operation. This study has been carried out under a partnership with JAXA, and we aim to deepen this collaboration to improve the safety of liquid hydrogen usage.

4. CONCLUSION

Decarbonization of the maritime industry is progressing rapidly, and design of alternative fuel ships and new cargo carriers is underway. On the other hand, safety requirements have been developed as an extension of the rules existing until now, or in a form that reflects the knowledge gained in the approval process of those designs. Depending on the case, there are also areas where design precedes the development of safety requirements. For this reason, proactive research and development is even more important. The Society promotes research and development by the two approaches of “Advanced and quantitative risk assessment of alternative fuel ships” and “Integrity assessment techniques for cargo and fuel containment systems,” and is accumulating the knowledge necessary to materialize and operate safe and efficient alternative fuel ships and new cargo carriers.

The Society carries out research and development in each of the stages of element technology research, establishment of safety requirements/rule development, and actual projects. ClassNK Research Institute is mainly involved in research and development in the stages of element technology research and establishment of safety requirements/rule development. However, together with providing advanced knowledge obtained through element technology research to actual projects, we are also building a research and development system based on organic cooperation by obtaining feedback on needs from actual projects. In addition, we are constructing cooperative systems with a diverse range of fields in order to acquire necessary knowledge, without being bound by the conventional field of naval architecture and ocean engineering, and with the aim of achieving timely research and development by maintaining and promoting these open innovation systems.

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