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Självständigt arbete

# Liquefied Natural Gas Marine Fuel

## Naturally Occurring Radioactive Materials Contamination

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# Sammanfattning


Det verkar finnas tillräckligt med information tillgängligt om hur olika typer av strålning kan påverka människans hälsa. Det verkar också finnas adekvat forskning inom området för NORM och hur detta fenomen bör hanteras. Den bild som framhävs av denna undersökning visar att varken NORM eller andra strålningskällor inom andra industrier förekommer som överraskande eller ohanterliga. Tvärtom verkar det vara ett välkänt problem och säkerheten inom dessa områden har också anpassats därefter. Det framstår som att dessa problem har förbisetts då det gäller användandet av LNG som framdrivningsmedel på fartyg. Det saknas tillräckligt med data som kan påvisa huruvida förekomsten av NORM på fartyg är ett problem eller inte.

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# Abstract

There seems to be enough information available on how different types of radiation may affect human health. There also seems to be adequate research made about NORM and how to handle this phenomenon. The image put forth by this study shows that the appearance of NORM within affected industries do not appear surprising or difficult to deal with. On the contrary it seems to be a well-known issue and safety measures have been adapted accordingly. It appears as if these issues have been overlooked regarding the systems where LNG is being used as a marine fuel. There is not enough data to conclude whether NORM is an issue or not in such systems.

# Definitions

| | |
|---|---|
| NORM | Naturally Occurring Radioactive Materials |
| TENORM | Technologically Enhanced Naturally Occurring Radioactive Materials |
| LNG | Liquefied Natural Gas |
| CCTV | Closed Circuit Television |
| ESD | Emergency Shutdown |
| UPS | Uninterruptible Power Supply |
| FSGDS | Fire, Spill and Gas Detection System |
| SCS | Safety Control System |
| Cryogenic | Extremely low tempteratures (below -150°C) |
| MeV | Mega electron Voltage |
| NCMM | Norwegian Center for Molecular Medicine |

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# 1. Introduction

## 1.1 Background

As the awareness of our impact on the environment arises, an increasing number of ship owners are stepping up to the task of lowering their fuel emissions. Liquefied Natural Gas (LNG) has lately been considered a good alternative to the more commonly used marine fuels such as Heavy Fuel Oil (HFO) and Diesel Oil (DO) and thus more vessels are built to run on LNG. For example, such companies as Destination Gotland [1], Furetank [2]and Viking Line [3] all have new vessels running on LNG.
With all the good intentions of doing so, and with the added costs to these companies, there remain uncertainties regarding a safe work environment in its proximity. One of these being the possibility of hazardous levels of radiation from Naturally Occurring Radioactive Material (NORM) [13].

NORM is known to be present in the oil and gas industry during the extraction process. Although this will be removed as best possible before transported from the production plant, currently there's no information available concerning the presence of NORM build-up onboard vessels where LNG is used as a marine fuel.

LNG has just recently been introduced as a marine fuel in the global merchant fleet. Thus, little information is available regarding possible health risks affecting the crew operating and maintaining these systems. Questions arise whether residual NORM from the LNG manufacturing process and for example radon gas, are present in the fuel line systems in the engine room. Has all the radon gas been removed in the separation process? Does NORM appear in filters and tanks etc. and is it harmful to crewmembers working in its area of use?

Based on the review of the correspondence between the Swedish national authorities: Linnaeus University (LNU), The Transport Agency, The Radiation Safety Authority, The Maritime Administration and The Work Environment Authority, the present authors understood that the Swedish government have little, if any, knowledge about whether NORM is present in LNG fuel systems onboard vessels. The correspondence referred to herein can be found as embedded emails in separate PDF documents.
Note that there is seemingly also no information available regarding these issues from other countries. So, the lack of knowledge appears to be on a global scale. Thus, there is no information available which can conclude if this is a health risk or not.

## 1.2 Purpose

Considering the correspondence between the Swedish authorities, the present authors expect to find no conclusive information about the presence of NORM in systems where LNG is used as a marine fuel. However, this study aims to raise awareness of the lack of conclusive data from any such research. The oil, gas, coal, mineral and recycling industries are examples of those known to have issues with NORM.

## 1.3 Questions

To conclude whether LNG onboard vessels leave NORM build-up in bunker tanks and whether the levels of such build-up could be hazardous to human beings, this must be investigated on location and confirmed from measured radiation levels.

To achieve the purpose of this study, following questions have been formulated:

1. Have any research concluded the status of NORM in marine fuel systems and is there enough knowledge for the operating crew about the health risks involved?

2. Have routines been developed regarding the health risks that may be applicable, during maintenance of LNG systems onboard?

## 1.4 Method and Limitations

The literature-based method has been used, gathering information primarily from websites containing the relevance needed on each subject. This information has then been used for making logical assumptions to answer the questions in this study. Although there are verified issues with NORM at other facilities such as early in the LNG extraction process, this does not necessarily point to the presence of NORM in fuel systems onboard vessels. However, since NORM build-ups may be caused from the decay of Radon-222 (Rn-222) [14], and this gas can be found as part of LNG, it must be assumed that there is a probability of NORM build-up being present in consumer systems as well.

# 2. Theoretical framework

## 2.1 Naturally Occurring Radioactive Materials (NORM)

NORM as an expression, are radioactive materials found in environments where human intervention has enhanced the potential of exposure that may pose a hazard to human health. Radioactivity can be found naturally all around us and is generally not of harmful levels where humans reside. The natural occurrence of radioactivity itself is not something considered dangerous or abnormal. This is also known as the earths background radiation. Examples of what can be expressed as NORM are enhanced levels of radon in water wells when this water is used by humans. Another could be from Industry where the gathering of radioactive material poses a risk to human health. When radiation levels are low they may still be harmful to humans if either ingested or inhaled. One example is radioactive dust particles that may damage the lungs [13].

## 2.2 Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM)

Radionuclides are present in the earth's crust at different concentrations. As different industrial steps are being used in the recovery of gas and oil from deposits to the refining process, radionuclides may enhance as the concentration is increased. This may be caused when the material is being redistributed or as the result of industrial processing. This is an elevated form of NORM and may potentially be a higher risk to human health [13].

## 2.3 Radionuclides

Radioactive elements, of which some occur naturally while others are man-made, are called radionuclides. Each radionuclide emits radiation, although at different rates. The rate is determined based on the time required to decay half of the atoms present. This is called the half-life period. This process will cause radiation to be emitted. The half-life periods of different radionuclides may vary from a few seconds up to several billion years [16].

## 2.4 Radiation types

There are different types of radiation, where some are less harmful. Alpha ($\alpha$) radiation quickly loses its energy in a material although it is considered hazardous if the source is inhaled or ingested. Beta ($\beta$) radiation is also considered less harmful unless its source is inhaled or ingested. Gamma ($\gamma$) radiation though, is considered harmful and may enter and damage human tissues (organs etc) from an exterior source [19].

## 2.5 Radon

Rn-222, from Uranium-238 (U-238), is the most significant, since this type emits radiation that may cause biological damage to humans. Radium-226 (Ra-226) decays into Rn-222 and has a half-life of 1620 years and emits alfa radiation.

As seen in *figure 1*, after all the decaying steps of uranium and Thorium-232 (Th-232) have been done, the final product is lead (Pb). Th-232 and U-238 will end up as Pb-208 and Pb-206 respectively and become stable, which means no longer being radioactive [13]. The figure shows the decaying steps for the thorium and uranium series and which products are the so-called *Radon Daughter's*. The color of the pointers indicate which type of radiation is emitted in each step.

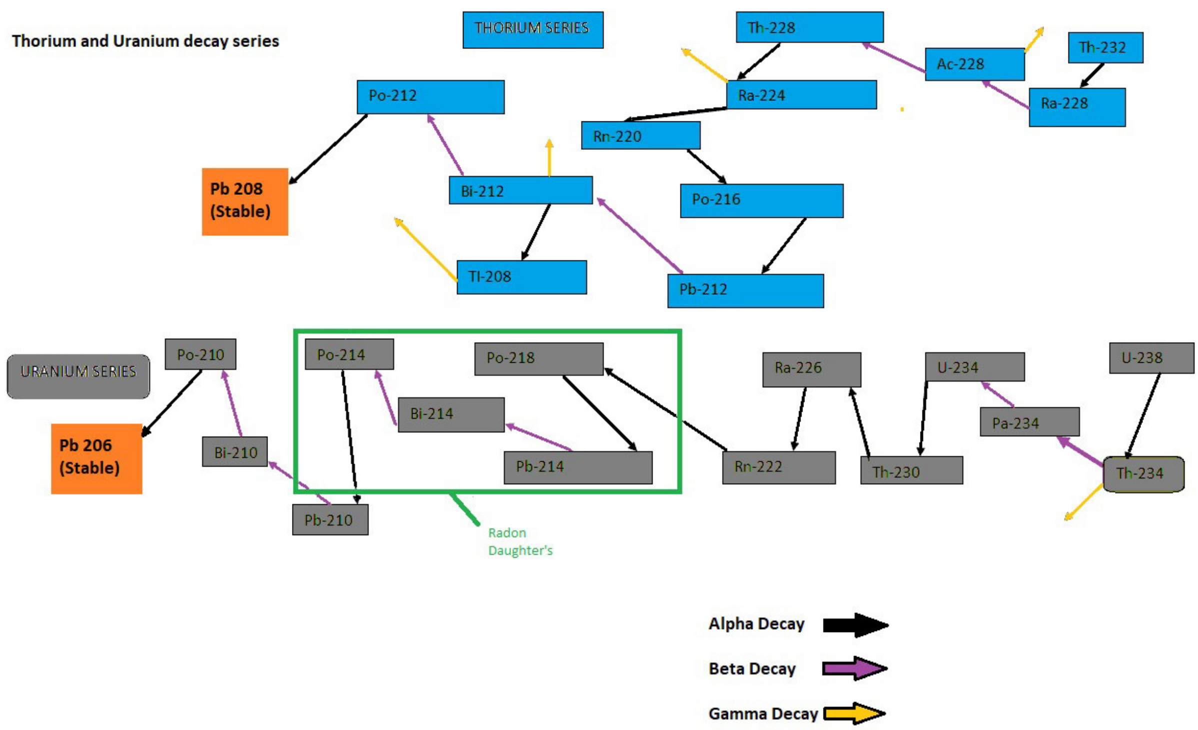


*Figure 1. The thorium and uranium decaying steps are shown in the figure with pointers in different colors where each color is representative of a type of radiation. Each series decays into the final product being stable, meaning it is no longer emitting radioactive radiation. Shown is also the so-called Radon Daughter's.*

## 2.6 Radon decay

Radon gas decays into so called daughter products. These are radioactive isotopes with relatively short half-life periods and have changed form from gas into particles. The first radioactive daughter product is Polonium (Po) followed by lead and Bismuth (Bi). Depending on whether the decay started from thorium or uranium, these daughter products will have different properties as seen in the decay series illustrated in *figure 1*. These daughter products emit alpha radiation (α) or beta radiation (β) or both as they decay [13].

## 2.7 The LNG process – from discovery to product

### Extraction

The extraction of LNG from subsea wells and onshore facilities is a costly process. It is time consuming and it requires a lot of resources to locate a potential well. The process faces many challenges. One of them being the risk of finding a so-called *dry well* where no LNG can be profited from. With this follows the legal procedures to extract the gas as another challenging part of the process [5].

### Exploration of LNG

To find and locate LNG underground, scientists use advanced technology. Although in the past, this was not the case, where actual physical evidence of oil or gas had to be found to determine a source. Today Geophysicists use seismology in their work. Thus, making use of the same technology as that of earthquake detection. Detecting earthquakes means measuring vibrations from the ground. When mapping or determining the composition of the different layers of the earth's crust, seismic waves are sent into the ground where the reflection of these vibrations will be measured. Each of these layers have their own properties and the seismic waves interact according to these. Depending on the different layers it travels across, different types of vibrations will bounce back to the surface where they can be measured. This way the properties of the crust may be determined. This data will then be used to determine whether LNG deposits are potentially present or not.

Another method is the use of magnetometers where changes in the earth's magnetic field is measured and used to determine the properties of the crust below the ground or the seafloor. Different underground formations have different magnetic properties, which will be used to generate geological and geophysical data.
Once the data has proven to be evident of a potential gas deposit, the next step in the process is to make an *Exploratory Well*. This is costly and will only be made where the data shows a high probability of finding a deposit. When drilled, geologists will study the composition of the different layers looking for gas and petroleum deposits. They will also examine the properties of these layers to determine the geologic features of the area.
As the well is being drilled, different types of logs are made. Logging means that different tests are performed during and after the drilling process, where geologists can further analyze data and other members of the crew can monitor the progress of the process. This allows for a broader and clearer picture of the formations below the surface. These logs help ensure that the correct equipment is being used and that the drilling moves forward accordingly [7].

**Production**

As natural gas has been verified as profitable, the production process starts. This means lifting the gas from the deposit and processing it prior to transportation. The gas, being mostly methane gas, when lifted, contains traces of many other components. Such could be traces of other gases, oil and water which needs to be removed before taking the next step, especially when transported via pipelines. This filtering process mostly occurs at the production site. The presence of NORM at the production site will cause contamination of the equipment used [11]. NORM build-ups in this process will be referred to as TENORM rather than NORM and the radiation levels will increase with time as equipment is being further exposed. NORM build-up may be found at different locations in the oil and gas extraction process. For example, wellheads, pumps, pipes, tanks and other processing equipment may become contaminated. NORM may accumulate as scaling and sludge from the process and for example pipes with scaling will eventually need to be decontaminated before being disposed of [9]. NORM/ TENORM is a known problem in the oil and gas industry and safety measures are being taken to prevent risks to human health.

Natural gas comes from different types of deposits. Aside from being a well containing gas only, it can be found in oil wells, as either mixed with the oil or as separate gas known as *free gas*. It can also be found in condensate wells where both *free gas* and condensate gas are found. This condensate is referred to as a semi-liquid hydrocarbon condensate. Condensate wells contains little or no oil at all. The gas not only comprises methane, although this counts for 70-90% [10]of its composition, but may also contain radon, ethane, propane, butane and pentanes. It may also contain water vapor, hydrogen sulphide, carbon dioxide, helium and nitrogen.

When processing the raw natural gas, these fluids and contaminants are separated from the methane, leaving a product known as a *pipeline quality* dry natural gas. Although the gas has been refined already at the production site and contains mostly methane, it must still be transported to a processing plant for further refining before being ready for use. From here it will be transported to the end user [11]. To know if any contaminants such as radon gas is present in the finished product, the gas must be analyzed. For example, SGS Group offer gas testing for radon in gas product supply lines and testing for other contaminants [12].

## 2.8 Radioactivity in LNG and Petroleum

The origins of radiation and NORM in the earth's crust started already when it was formed. Such materials as uranium and thorium, both being radioactive, were part of the crust causing rock formations to contain certain concentrations of radioactivity. When these decays, they produce other radionuclides that may follow the oil and gas from the underground deposits to the surface. In doing so, NORM may accumulate in the different steps of the process as it flows with the oil and gas, including interior surfaces of tanks. From here, the radioactive gases and material may follow all the way to the LNG user system unless completely

separated. There are two nuclides of concern linked to the oil and gas production. These are Radium-226 (Ra-226) and Radium-228 (Ra-228). Ra-226 comes from the decay of uranium.
Ra-228 comes from the decay of thorium. As radium decays it forms Radon (Rn), which is a radioactive gas that can be found following other gases from the underground natural gas deposits.
Rn-222, the daughter of Ra-226, decays to alpha (α) and beta (β) emitting daughter products which in turn may be harmful to human health either when ingested or inhaled.
Looking at the presence of NORM from the production process raises a concern whether NORM could be present as dust particles in fuel systems onboard vessels. When maintenance is carried out there may be a risk of inhalation of these particles which is then harmful to humans regardless of radiation type. This could be a risk when cleaning filters and/or changing affected parts of the system [17].

## 2.9 LNG systems onboard

**LNG guidelines**

LNG is cooled to -163°C where it gets liquefied under atmospheric pressure. At higher temperatures it will remain as a gas. The volume of the gas is approximately 600 times greater than that of a liquefied state. This means that the systems onboard needs to be adapted so they can handle the low temperatures and changes in volume and especially so if any system doesn't work properly.
LNG, because of the low temperatures involved, exposes a risk for personnel and system materials. The tank volumes need to be twice as big for LNG compared to DO due to the lower density of LNG. There's also a need for specially designed bunker stations, storage tanks, piping and isolations, which leads to complex system structures.
The European standard EN 1473:2007 which has the status of the British standard, gives a functional guideline when installing LNG marine fuel systems on a vessel. Practices and procedures are recommended and will result in an environmentally acceptable design and safety plan. Furthermore, it will have recommendations for the construction and operation of the plant. For ship owners who consider building new LNG fueled ships, this guideline is a good beginning [15].

**Storage tanks**

The storage tanks must meet the requirements and standards. The LNG tanks are designed to operate safely between the minimum and maximum design pressure, to safely contain the liquid at cryogenic temperatures and for safe filling and removal.
The structure design of the tank must be of cylindrical, vertical and flat-bottomed steel. The primary tank shall be secured by a continuously welded membrane, plate or cryogenic

concrete with cryogenic reinforcement. The outer or secondary case shall be secured by compacted sand or earth and a continuously welded plate.
The outer layer is exposed to the atmosphere and therefore the correct design is important. If the outer case is made of pre-stressed concrete, the cables need to remain compatible with the strength of the upper limit of the hydrostatic head. The shell needs to be of cryogenic grade if it is made of metal. Furthermore, it is important to have instruments to measure the temperature, pressure and density values.
A relief valve is also required in case of over pressure. The materials surrounding the tank needs to be of special character since materials and components will react differently when in contact with the cold liquid [15].

## 2.10 Piping systems

The piping and construction design need to be taken into consideration because of the temperatures it must handle. Two cases need to be considered and analyzed.
If the material and pipes on occasions will be subjected to liquefied natural gas, then the components must have cryogenic properties so that the risk of brittleness are minimized.
The second case is if there's an accident like spillage or leakage and liquefied natural gas meets the piping, then the design must to have proper insulation and cryogenic materials. All the piping's that liquefied natural gas will flow through should have a stress test for integrity. A pressure test is also recommended, and two options are available. One is pneumatic testing: as per accepted standard or as per Pressure Equipment Directive (PED). The second test is hydro testing the pipe where it will be pressurized to 150 percent of design pressure. Pneumatic tests are preferred over the hydro test for cryogenic systems. After approval from local authorities and safety measures are accepted to protect personnel, the pneumatic tests may be conducted. During a test an accident can happen and therefore safety precautions concerning distances must be analyzed. There's also a guideline to use regarding the safety distances during the testing [15].

## 2.11 Valves and vaporizers

The valves also need to be manufactured of special materials and the recommendation is to have butt welded ends if the valves are installed in cryogenic systems. The valves should be designed in a way that enables the maintenance of the internal components without removal of the body from the line. When deciding the number of valves needed, the demand for sectional depressurization of the system must be taken into consideration. Safe isolation of hazardous fluids or LNG need to be considered too. Compatibility between materials need to be thought of since open rack vaporizer tubes are made of aluminum alloy and the pipe work on LNG fueled ships are made of austenitic stainless steel. The vaporizer can be protected from physical and chemical attacks from the heating fluid by using a coating. Vaporizers that are coated by the manufacturer shall endue means for the coating to be replaced or repaired. The manufacturers must also give a properly detailed description of the maintenance of the coating [15].

## 2.12 Safety systems

When using LNG as a marine fuel, there needs to be safety systems installed. Where leaks are anticipated, a detection system shall be installed. High and low temperature detectors, flame detection and flammable gas detectors are also recommended onboard. Smoke and heat detection as well as Closed-circuit Television (CCTV) is also recommended.

These different types of safety systems shall be connected to the UPS-system. An Emergency Shutdown valve (ESD) needs to be in close proximity of the equipment. This valve may be either hydraulic or pneumatic, although the recommended ESD valve is the hydraulic actuators. To protect the piping, hoses and equipment from over pressure a thermal relief valve needs to be installed. The relief valve shall under normal circumstances be installed uninsulated.

The emergency shutdown consists of a fire, spill and gas detection system (FSGDS) and a safety control system (SCS). When a fire or spill is detected the SCR will perform the required automatic measures to take control of the situation. Besides taking some actions the SCR provides the personnel with detailed information on the type of hazard, status of protection systems, water pumps and system faults.

This information provided aids the operator in selecting appropriate actions such as initiating emergency actions with mobile or portable fire extinguishers, isolation of the process system involved or a complete shutdown of the system [15].

## 2.13 Radon and NORM health hazards

### General description

Radon, which is a naturally occurring radioactive gas, may when exposed to higher doses, be fatal to humans. When radon decays it forms so called “daughter atoms”. In the decaying process alfa and beta particles are emitted. Depending on which element is decaying, different energy levels will be present. This energy is measured in Mega electron Voltage (MeV).

These daughter atoms attach to water aerosols and may be in the air we breathe. These daughter products gather in for example our nose and lungs and emits ionizing radiation. Radon daughters tend to attach to dust and smoke particles. This increases the risk for lung cancer when smoking.

The exposure to radon occurs via different sources such as water wells where the water is drawn from cracks in the rock formation. Another is areas where rock formations contain high contents of uranium and thorium which in turn causes high levels of radon gas leaking into the surrounding air, water and buildings.

Since radon has no color or taste and is odorless, it can only be detected if measured. Radon levels for drinking water and air, are measured in Becquerel/ litre (Bq/l) for water and Becquerel/ m3 (Bq/m3) for air. One Bq is one disintegration of atom per second [19].

## Radon health impact

According to The Environmental Protection Agency in the U.S.A. (EPA), radon is the number one cause of lung cancer among non-smokers. This type of cancer also has one of the highest mortality rates. Aside from smoking, radon is also the second leading cause of lung cancer. The figure below shows an estimated comparison of cancer mortality rates per type of cancer, where radon related cancer (lung cancer) has the third highest number of deaths as of 2010 [18].

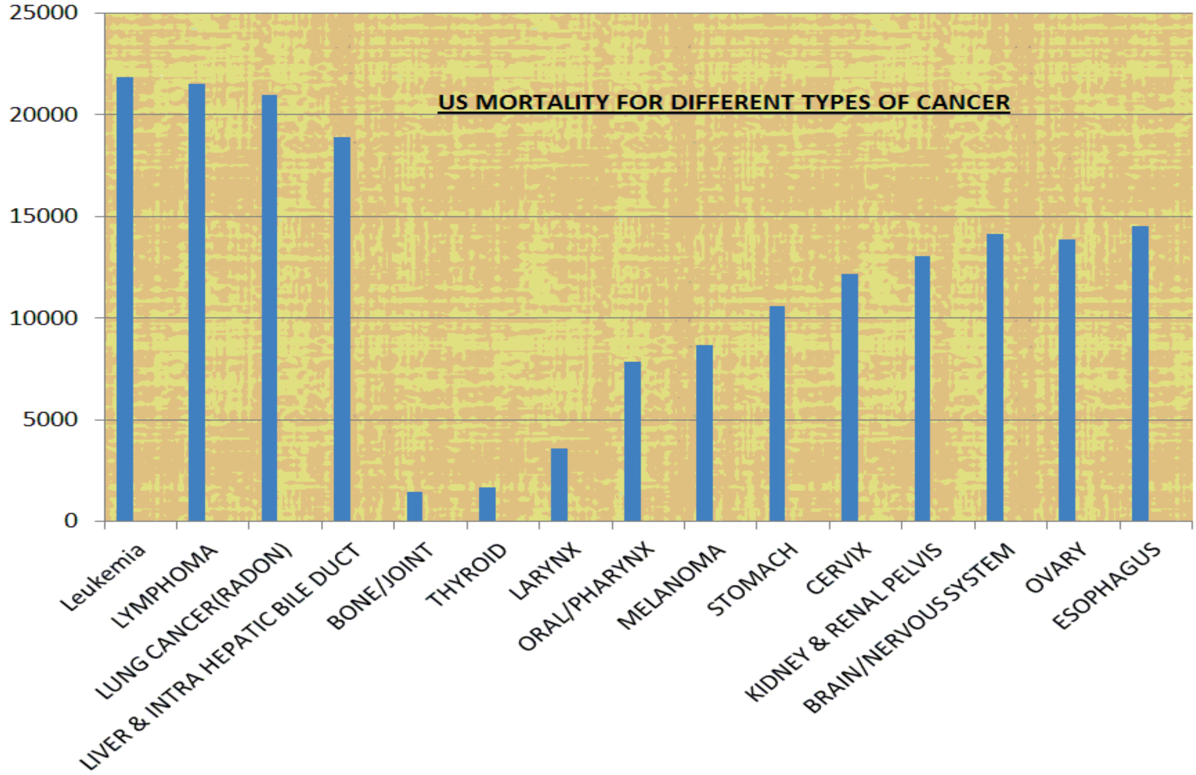


*Figure 2. Illustrated are different types of cancers and their number of mortalities in 2010, where lung cancer caused by radon has the third highest number of deaths.*

## Ionizing radiation

Radiation with enough energy to remove electrons from the orbit of an atom is called *ionizing radiation*. Normally, atoms are electrically neutral since the total negative charge of the electrons are the same as the positive charge of the nucleus. When an atom has different numbers of neutrons it is called an isotope. An isotope is another form of one and same element, with the same atomic number, which in turn gives it identical biological and chemical properties. Different forms of an element can be either stable or unstable, where unstable means being radioactive. One example is hydrogen with atomic number one.

Hydrogen-2, also called deuterium, has one neutron and is stable and not radioactive, while hydrogen-3, also called tritium, with two neutrons is unstable and thus radioactive [19].

# 3. Results and conclusions

## 3.1 Results

1. *Have any research concluded the status of NORM in marine fuel systems and is there enough knowledge for the operating crew about the health risks involved?*
   - No research can be found showing analyzed data and conclusive results regarding the presence of NORM in marine LNG fuel systems and no guidelines were found for the operating crew regarding this matter.

2. *Have routines been developed regarding the health risks that may be applicable, during maintenance of LNG systems onboard?*
   - No routines have been found developed regarding the maintenance on marine LNG fuel systems where NORM could potentially be a risk.

This study reveals that there is reason to be concerned about the lack of information available about the presence of NORM in marine fuel systems onboard vessels. There is enough information about NORM and Rn-222 decay to raise questions about the safety of human health when working with these system components. There is also reason to further investigate whether NORM build-ups are present in such systems. If Rn-222 does make up part of the LNG used onboard, the gas itself is a contaminant and must be treated as such. An assumption of NORM build-up can be made with regards to the half-time period of radon and its daughter products if radon in fact is present. If radon and its daughter products are not completely separated from the methane gas at the LNG processing plant it will most likely cause NORM build-ups in the tanks and marine fuel systems onboard. Until enough data are available LNG must be treated as a contaminated product with risks to human health.

## 3.2 Conclusions

There appears to be too little information available to confidently disregard the appearance of NORM on vessels when used as a marine fuel. The conclusion from this must be that crew members maintaining the systems lack safety guidelines needed to perform such tasks and does not have enough information available to reduce potential health risks. No information could be found stating the exact contents of the LNG as a finished product. However, radon is verified as part of LNG products both on LNG Carriers and in methane gas user systems. Considering how NORM and TENORM are looked at in the oil and gas industry, this must be considered as potentially serious issues where LNG is used as a marine fuel too. Further investigation is needed where quantitive data can be used as a base for final conclusions.

## 4. Discussion

Depending on whether radon or other radioactive decay products are flowing with the LNG to the user system, times may vary before NORM can be found present at such levels considered hazardous to human health. Not knowing conclusively if there is NORM build-up or not onboard vessels in tanks and system components is reason enough to investigate this further. Looking at the issues with NORM in other Industry certainly raises a red flag and reasons to be concerned. The issue is well described by *Radiation Professionals* whom offers expert radiation advices to the industry affected by NORM [17].

Norwegian Center for Molecular Medicine (NCMM) describes that NORM can be found in LNG cargo vessel tanks and mentions how it can also build up in other system components onboard. NORM is here spoken of as a complicated contaminant which requires specialized equipment to detect and how a specially trained cleaning team is required before accessing the tanks or affected system components. It is also mentioned that radon may be entrained in the LNG product allowing it to follow all the way to the cargo tanks [22].

So, is there a difference between LNG cargo carriers and vessels storing LNG onboard as a marine fuel? The answer here is most likely no, there is not. Then, if the LNG for marine propulsion is the same as that being carried as a product on LNG tankers, there must be a risk of NORM build-ups in LNG fuel systems as well.

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