

MA2012-9

**MARINE ACCIDENT
INVESTIGATION REPORT**

September 28, 2012



The objective of the investigation conducted by the Japan Transport Safety Board in accordance with the Act for Establishment of the Japan Transport Safety Board is to determine the causes of an accident and damage incidental to such an accident, thereby preventing future accidents and reducing damage. It is not the purpose of the investigation to apportion blame or liability.

Norihiro Goto
Chairman,
Japan Transport Safety Board

Note:

This report is a translation of the Japanese original investigation report. The text in Japanese shall prevail in the interpretation of the report.

MARINE ACCIDENT INVESTIGATION REPORT

Vessel type and name: Chemical tanker Nisshomaru

Vessel number: 137240

Gross tonnage: 499 tons

Accident Type: Fatality and injury of crew

Date and time: Around 11:27, June 28, 2011

Location: North Fairway in Port of Nagoya, Aichi Prefecture

173° true, 250m from Nagoya Port North Fairway Light Buoy
No.3, located east of the Nagoya Kinjo Signal Station, Nagoya
City

(approximately 35°02.0' N, 136°51.2'E)

September 6, 2012

Adopted by the Japan Transport Safety Board

Chairman Norihiro Goto

Member Tetsuo Yokoyama

Member Kuniaki Shoji

Member Toshiyuki Ishikawa

Member Mina Nemoto

SYNOPSIS

<Summary of the Accident>

The chemical tanker Nisshomaru was sailing in the North Fairway in Port of Nagoya with 5 crew members on board consisting of the master, chief engineer, chief officer, first engineer, and junior chief officer after leaving the quay of the cargo owner in Port of Nagoya where she unloaded sodium hydrogen sulfide. The chief officer, first engineer, and junior chief officer collapsed on the starboard side of the forecastle deck and the chief engineer became groggy on the stern side at approximately 11:27 on June 28, 2011 when the 4 crewmembers were attending to tank cleaning.

The chief officer and first engineer deceased, and the junior chief officer and chief engineer were injured.

<Probable Causes>

It is probable that this accident occurred when the chief officer, first engineer, and junior chief officer, who were attending to tank cleaning, inhaled the hydrogen sulfide gas that was sprayed out of the open manhole hatch of each slop tank (starboard/port) and when the chief engineer inhaled the hydrogen sulfide gas that was sprayed out of the exhaust pipe outlet for the slop tanks as well as the open manhole hatch of each slop tank (starboard/port) due to the fact that hydrogen sulfide gas was produced due to a chemical reaction of sodium hydrogen sulfide wash water and acrylic acid wash water when the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) was transferred to the slop tanks (starboard/port), in which acrylic acid wash water was stored, after finishing the cleaning of the No.2 cargo tanks (starboard/port), from which sodium hydrogen sulfide was unloaded, during tank cleaning while Nisshomaru was sailing in the Port of Nagoya.

It is probable that the reason Nisshomaru transferred the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) to the slop tanks (starboard/port), in which acrylic acid wash water was stored, was because Nisshomaru crew members did not know that dangerous substances can be produced due to chemical reactions when tank wash water is mixed nor were they aware of the contents of the dangerous goods handling manual due to the facts that Matsuda Kisen Co., Ltd. was not aware of the danger of mixing tank wash water, that they did not include the tank wash water transfer work in the tank cleaning work manual, and that they did not train crew members regarding the danger of tank wash water, which can cause chemical reactions when mixed, or the usage of slop tanks.

1 PROCESS AND PROGRESS OF THE INVESTIGATION

1.1 Summary of the Accident

The chemical tanker Nisshomaru was sailing in the North Fairway in Port of Nagoya with 5 crew members on board consisting of the master, chief engineer, chief officer, first engineer, and junior chief officer after leaving the quay of the cargo owner in Port of Nagoya where she unloaded sodium hydrogen sulfide. The chief officer, first engineer, and junior chief officer collapsed on the starboard side of the forecastle deck and the chief engineer became groggy on the stern side at approximately 11:27 on June 28, 2011 when the 4 crewmembers were attending to tank cleaning.

The chief officer and first engineer deceased, and the junior chief officer and chief engineer were injured.

1.2 Outline of the Accident Investigation

1.2.1 Setup of the Investigation

The Japan Transport Safety Board appointed an investigator-in-charge and 2 other investigators to investigate this accident on June 28, 2011.

1.2.2 Collection of Evidence

On-site investigation and interviews: June 29, 30, July 1, 2, 6, and 7 of 2011

Interviews: July 8, 26, 27, and December 13 of 2011

Collection of questionnaires: August 8, September 5, October 17, and November 28 of 2011 and June 4 of 2012

1.2.3 Tests and Research by Other Institutes

Regarding this accident, analysis of the produced substance within slop tanks and the substance production situation on Nisshomaru was commissioned to the Physical & Chemical Analysis Center of the Nippon Kaiji Kentei Kyokai, and analysis of the effects of the hydrogen sulfide gas, which was sprayed from the exhaust pipe outlet for the slop tanks, on the crew members was commissioned to the National Maritime Research Institute.

1.2.4 Information Provision

On August 4 of 2011, the JTSTB submitted the factual information to the Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism based on the facts found up to that date.

1.2.5 Comments from Parties Relevant to the Cause

Comments on the draft report were invited from parties relevant to the cause of the accident.

2 FACTUAL INFORMATION

2.1 Events Leading to the Accident

According to the statements of the master, chief engineer, and junior chief officer of Nisshomaru (hereinafter referred to as “the Vessel”) and the members of Nagoya Emergency Task Forces (hereinafter referred to as “Emergency Unit Members”) and the information from the Nagoya Coast Guard Office (hereinafter referred to as “the Nagoya Coast Guard”), the events leading to the accident were as follows.

The Vessel berthed at the quay of the cargo owner in Port of Nagoya at approximately 8:30 on June 28, 2011, with 5 crew members on board including the master and started unloading the 250m³ of sodium hydrogen sulfide, which was loaded in the No.2 cargo tanks, at approximately 8:55.

The Vessel finished unloading and left the quay of the cargo owner at approximately 11:10 and started to navigate toward Port of Wakayamashimotsu in Wakayama Prefecture, for loading.

The master was on the bridge duty alone after quay departure maneuvering and ordered the chief officer to start the tank cleaning work in order to have crew members attend to the tank cleaning work for the No.2 cargo tanks to prevent contamination^{*1} from the cargo to be loaded in Port of Wakayamashimotsu and the residual cargo after the master turned the main engine to slow ahead – half ahead so that the cargo pump revolutions per minute (rpm) for the main engine drive would be 270 – 280.

The chief engineer had opened the steam vent master valve for the boiler immediately after completing the port departure process and was sending the steam to the No.2 cargo tanks (starboard/port) through sounding pipes.

The junior chief officer was preparing the side Butterworth cleaners^{*2} in preparation for the tank cleaning work after organizing the tools, etc. used for unloading.

The chief officer communicated to the chief engineer, junior chief officer, and first engineer, who were preparing for the tank cleaning work on the expansion trunk^{*3}, that they were starting the tank cleaning work.

The chief officer operated the freshwater cleaning pump in the deck store and started the tank cleaning work by using the 4 Butterworth cleaners, which were installed in the No.2 cargo tanks (starboard/port), at approximately 11:17 when the Vessel was proceeding south-southwest in the North Fairway in Port of Nagoya.

Crew members on the expansion trunk prepared to transfer the ‘wash water used for tank cleaning’ (hereinafter referred to as “tank wash water”) in the No.2 cargo tanks (starboard/port) to slop tanks (starboard/port) after the chief officer stopped the freshwater cleaning pump and finished cleaning the No.2 cargo tanks (starboard/port) at approximately 11:22.

The chief engineer started the cargo pump with the control panel, which was installed on the starboard side of the poop deck above the cargo pump room in order to transfer the tank wash water in the No.2 cargo tanks (starboard/port) to the slop tanks (starboard/port) at approximately 11:25.

*1 “Contamination” refers to residual liquid, etc. of a different type of liquid cargo, which was loaded in the past navigation, mixing with the newly loaded cargo.

*2 “Butterworth cleaner” refers to a device, which is installed within cargo tanks, that cleans the inner wall of the tank by thoroughly spraying high pressure water while rotating.

*3 “Expansion trunk” refers to the space installed above cargo tanks in order to prevent danger from cargo expansion due to temperature increase and tank pressure increase due to gas production.

The master confirmed that the chief officer, first engineer, and junior chief officer were near the No.2 cargo tanks.

The chief engineer saw a whitish substance spray out of the exhaust pipe outlet with the noise of “boh” when he was about to climb down the stairs on the port side of the poop deck toward the bypass valve operation handle, which was above the No.4 cargo tank (port), in order to adjust the discharge pressure after starting the cargo pump.

The master saw a liquid-like substance spray out of the exhaust pipe outlet with the noise of “pang” at approximately 11:26 soon after he confirmed that the cargo pump was started from the bridge.

When the junior chief officer was waiting near the suction valve operation handle of the No.2 cargo tank (starboard) along with the first engineer and when the chief officer was waiting near the suction valve operation handle of the No.2 cargo tank (port) in order to operate the valves to transfer the tank wash water, the junior chief officer saw white smoke spray out of the exhaust pipe outlet of the slop tanks with the noise of “goh” soon after the cargo pump was operated. The junior chief officer could not immediately judge whether it was gas or liquid when he saw the white smoke, which was like exhaust gas from diesel engines, but he thought it was closer to gas due to the fact that it did not look like liquid got on the work suit.

When the chief officer, first engineer, and junior chief officer were evacuating toward the starboard side of the forecandle deck, which was on the windward side, the chief officer opened the manhole hatch lid for the port side slop tank, and one of the evacuating crew members opened the manhole hatch lid for the starboard side slop tank.

After seeing the substance spray out of the exhaust pipe outlet for several seconds, the chief engineer thought that he must close the master valve for the boiler. However, he became groggy when he started to proceed toward the stern and sat down in the mess room.

When the Vessel was sailing in the course of 213° (true bearing, the same hereinafter) in the vicinity of Nagoya Port North Fairway Light Buoy No.3 at the speed of approximately 8kn (speed over the ground, the same hereinafter) at approximately 11:27, the first engineer sat down in front of the bollard on the starboard side of the forecandle deck, the junior chief officer sat down near the freshwater faucet on the starboard side of the forecandle deck, and the chief officer sat down between the two. Soon after this, the first engineer collapsed. Seeing the first engineer collapse, the master ordered the chief officer and junior chief officer to “undress him and pour water on him” with the microphone.

Although the junior chief officer handed a nearby hose to the chief officer, the chief officer immediately collapsed.

Seeing that the junior chief officer also collapsed after the first engineer and chief officer collapsed, the master called 118 with the mobile phone on the Vessel at approximately 11:33. He communicated with Matsuda Kisen Co., Ltd. (hereinafter referred to as “Company A”) at approximately 11:37.

The Vessel let go anchor off the southern coast of the central breakwater of the high water breakwater in Port of Nagoya at approximately 12:05.

The master ordered the chief engineer, who had returned from letting go anchor and was sitting down in the mess room, to undress and pour water on the junior chief officer, who was in pain and struggling on the forecandle deck on the starboard side.

Due to the fact that the chief engineer was recovering consciousness, he followed the master’s order and proceeded toward the forecandle deck.

The chief engineer poured water on the chief officer and first engineer first, but there was no reaction. The chief engineer held the junior chief officer so that he would not fall from the forecastle deck and kept washing inside of his mouth and body with freshwater, due to the fact that he was moving slightly.

Officers of the Nagoya Coast Guard boarded the Vessel at approximately 12:35, moved the 3 people who had collapsed to the patrolling boat between 12:45 and 12:55, and started transferring them.

Emergency Unit Members met with the patrolling boat on water and transferred the injured people to the Garden Pier in Port of Nagoya while jointly performing life-saving measures on the injured people with officers of the Nagoya Coast Guard. The injured people were transferred to a hospital in Nagoya City on ambulances, which were waiting for them.

The date and time this accident occurred was approximately 11:27 on June 28, 2011, and the location it occurred was the vicinity of 173° 250 m from Nagoya Port North Fairway Light Buoy No.3.

(Refer to Attached figure 2: Accident Location)

2.2 Injuries to Persons

According to the statements of the chief engineer, junior chief officer, and the doctor in charge of the hospital, information by the Nagoya Coast Guard, postmortem certificate, and medical certificate, it was as follows.

The chief officer and first engineer who were in cardiac or respiratory arrest were rescued from the Vessel. Although they were transferred to the hospital while cardiopulmonary resuscitation was provided, they were confirmed dead. The cause of death was hydrogen sulfide poisoning. The junior chief officer was rescued from the Vessel with difficulty in walking. He was diagnosed with hydrogen sulfide poisoning after being transferred to the hospital and required hospitalization for treatment for 8 days.

The chief engineer went to the hospital on the day of this accident and was diagnosed with hydrogen sulfide poisoning as well as chemical pneumonia and required hospitalization for treatment for 7 days.

2.3 Damage to Vessel

There was no damage to the vessel.

2.4 Crew Information

(1) Gender, Age, and Certificate of Competence

The master Male 60 years old.

Fourth grade maritime officer (navigation)

Date of issue: February 10, 1984

Date of revalidation: May 9, 2008

Date of expiry: February 9, 2014

Class A Officer Responsible for Handling Dangerous and Other Substances for Tanker (oil, chemical)

Approval Stamp expiration date: October 13, 2016

Master that was replaced by the master (hereinafter referred to as “regular master”)
Male 57 years old.

Third grade maritime officer (navigation)

Date of issue: November 24, 1981

Date of revalidation: May 27, 2008

Date of expiry: October 20, 2013

Class A Officer Responsible for Handling Dangerous and Other Substances for
Tanker (oil, chemical)

Approval Stamp expiration date: September 29, 2016

Chief officer Male 64 years old.

Fourth grade maritime officer (navigation)

Date of issue: October 7, 1981

Date of revalidation: January 29, 2009

Date of expiry: September 7, 2014

Class A Officer Responsible for Handling Dangerous and Other Substances for
Tanker (oil, chemical)

Approval Stamp expiration date: June 26, 2014

Junior chief officer Male 42 years old.

Fifth grade maritime officer (navigation)

Date of issue: August 8, 1991

Date of revalidation: February 21, 2007

Date of expiry: July 22, 2012

Class A Officer Responsible for Handling Dangerous and Other Substances for
Tanker (oil, chemical)

Approval Stamp expiration date: August 11, 2013

Chief engineer Male 62 years old.

Fourth grade maritime officer (engineering)

Date of issue: October 22, 1976

Date of revalidation: December 9, 2008

Date of expiry: July 19, 2014

Class A Officer Responsible for Handling Dangerous and Other Substances for
Tanker (oil, chemical)

Approval Stamp expiration date: August 29, 2015

First engineer Male 62 years old.

Fifth grade maritime officer (engineering)

Date of issue: March 14, 1975

Date of revalidation: February 5, 2008

Date of expiry: September 15, 2013

Class A Officer Responsible for Handling Dangerous and Other Substances for
Tanker (oil, chemical)

Approval Stamp expiration date: April 1, 2012

(2) Manning Situation

According to the statements of the master and regular master and the reply to the questionnaires by the designated person of Takara Kaiun Co., Ltd. (hereinafter referred to as “Company B”), it was as follows.

Operation of the Vessel involved 5 regular crew members boarding the vessel for approximately 3 months, followed by approximately 25 days of break. When the regular crew members were on a break, replacement crew members were on board. The master was a replacement master, and the chief officer was a regular crew member.

(3) Main Seagoing Experience, etc.

The master

According to the statement of the master, it was as follows.

The master had approximately 40 years of seagoing experience, most of which time he was on board chemical tankers. He had boarded the Vessel 3 times as a replacement master since November of 2010. He had been on board the Vessel since June 22, 2011, at the time of this accident.

Chief officer

According to the reply to the questionnaires by Company B, the chief officer joined Company B in December of 2003 and was on board the Vessel as the chief officer and junior chief officer. He had been on board the Vessel since April 8, 2011, this time.

First engineer

According to the reply to the questionnaires by Company B, the first engineer joined Company B in May, 2011, and had been on board the Vessel as the first engineer since May 28 of the same year.

Regular master

According to the statement of the regular master, the regular master had approximately 37 years of seagoing experience, approximately 20 years of which time he was on board chemical tankers. He had been on board the Vessel as a regular master since November of 2003 and was on board from March 22 to June 22, 2011, immediately before this accident.

2.5 Vessel Information

2.5.1 Particulars of Vessel

Vessel number:	137240
Port of registry:	Osaka City, Osaka Prefecture
Owner:	Company A, Matsuda Marine Co., Ltd. (hereinafter referred to as “Company C”)
Operator:	Company A
Gross tonnage:	499 tons
L×B×D:	64.95m×10.00m×4.50m
Hull material:	Steel
Engine:	1 diesel engine
Output:	1,029kW
Propulsion:	1 Fixed pitch propeller

Date of launch: October 2003

2.5.2 Loading condition, etc.

(1) This Voyage

- 1) According to the statements of the master and the chief engineer, on the day of this accident, the Vessel left the quay in ballast with draught bow approximately 1.20m and draught stern approximately 3.20m after unloading all of the sodium hydrogen sulfide, which was loaded into the No.2 cargo tanks (starboard/port), at the quay of the cargo owner in Port of Nagoya, cleaned the tanks by using approximately 5m³ of freshwater while injecting steam in the No.2 cargo tanks (starboard/port), and left the produced sodium hydrogen sulfide wash water*⁴ in the No.2 cargo tanks (starboard/port).
- 2) According to the statements of the personnel in charge of Company A, the master, and the chief engineer, the amount of steam normally used to clean the No.2 cargo tanks (starboard/port) was approximately 1m³ (calculated into solidified water), and the amount of sodium hydrogen sulfide left in transfer pipes to slop tanks was approximately 0.1m³.
- 3) According to the Procedures and Arrangements (P&A) Manual, the total remaining stripping amount*⁵ for the No.2 cargo tanks (starboard/port) was approximately 0.102m³.

(2) Last Voyage

- 1) According to the statements of the master and the chief engineer, the tank cleaning work for the No.2 cargo tanks (starboard/port) and No.4 cargo tanks (starboard/port) of the Vessel was conducted after all of the acrylic acid was unloaded at the quay of the cargo owner in Port of Yokkaichi in Yokkaichi City, Mie Prefecture, on June 25, 2011, and the Vessel had stored approximately 4.9m³ of acrylic acid wash water*⁶, which was produced due to the cleaning work, in the slop tanks (starboard/port).
- 2) According to the P&A Manual, the total remaining stripping amount for the No.2 cargo tanks (starboard/port) and the No.4 cargo tanks (starboard/port) was approximately 0.205m³.

(3) Situation of the Slop Tanks and No.2 Cargo Tanks after the Accident

According to the statements of the master and the personnel in charge of Company A, it was as follows.

- 1) Slop tanks (starboard/port) contained acrylic acid wash water and sodium hydrogen sulfide wash water, and the total approximate amount was 6m³.
- 2) No.2 cargo tanks (starboard/port) contained a total of approximately 5m³ of sodium hydrogen sulfide wash water.
- 3) Slop tank (center) contained approximately 14.8m³ of the remaining freshwater.
- 4) The temperature of the tank wash water in the slop tanks was 29°C at approximately 10:00 on July 5, 2011.

(4) Past Tank Wash Water Mixture Situation, etc.

According to the statements of the master and the regular master and tank cleaning record book, it was as follows.

- 1) Acrylic acid wash water and sodium hydrogen sulfide wash water

*⁴ "Sodium hydrogen sulfide wash water" refers to mixed water, which is produced by cleaning residual sodium hydrogen sulfide within the tank after unloading by using freshwater.

*⁵ "Remaining stripping amount" refers to the remaining cargo amount after emptying tanks for unloading.

*⁶ "Acrylic acid wash water" refers to mixed water, which is produced by cleaning residual acrylic acid within the tank after unloading by using freshwater.

- a The Vessel transferred approximately 14m³ of acrylic acid wash water, which was stored in No.1 through No.4 cargo tanks, into the slop tanks (starboard/port) outside of Port of Nagoya on December 12, 2010.
- b The slop tanks contained mixed wash water when they transferred approximately 11m³ of sodium hydrogen sulfide wash water, which was produced after cleaning the No.2 cargo tanks (starboard/port), to slop tanks (starboard/port), while the Vessel was sailing in Ise Bay in the course of approximately 180° at the speed of approximately 12kn with acrylic acid wash water on board in the slop tanks (starboard/port) at approximately 11:25 on December 15.

2) Tank wash water other than 1)

The Vessel had mixed more than 2 types of tank wash water in the slop tanks (starboard/port).

2.5.3 Information Regarding the Hull Structure

According to the statements of the master and the chief engineer and the general arrangement of the Vessel, it was as follows.

Below the upper deck was divided into the fore peak water tank, No.1 freshwater tank, slop tanks, No.1 through No.4 cargo tanks, void space, cargo pump room, No.1 fuel tank, engine room, and aft peak water tank, etc. from the bow side. The double-bottomed part and the sides between the slop tanks and the No.4 cargo tanks were divided into No.1 through No.3 freshwater tanks and No.1 through No.5 ballast water tanks.

There were forecandle and poop on the upper deck with boatswain's store and deck store in the forecandle. There were also the wheelhouse and upper engine room, etc. in the poop from the stern toward the bow, and the accommodation spaces were in the deck house above it. Furthermore, the navigation bridge was above it.

(Refer to Photo 1: The Vessel)

2.5.4 Information Regarding the Slop Tanks, Cargo Tanks, and Upper Deck Appliance

According to the statements of the master and the chief engineer and the capacity plan of the Vessel, it was as follows.

(1) Slop Tanks

Slop tanks of the Vessel were located towards the back of the forecandle, divided into 3 with longitudinal bulkheads, and were respectively called slop tank (starboard), (center), and (port).

The capacity of slop tank (starboard) and (port) were the same at approximately 15.3m³, and (center) was approximately 18.2m³. The total capacity was approximately 48.8m³.

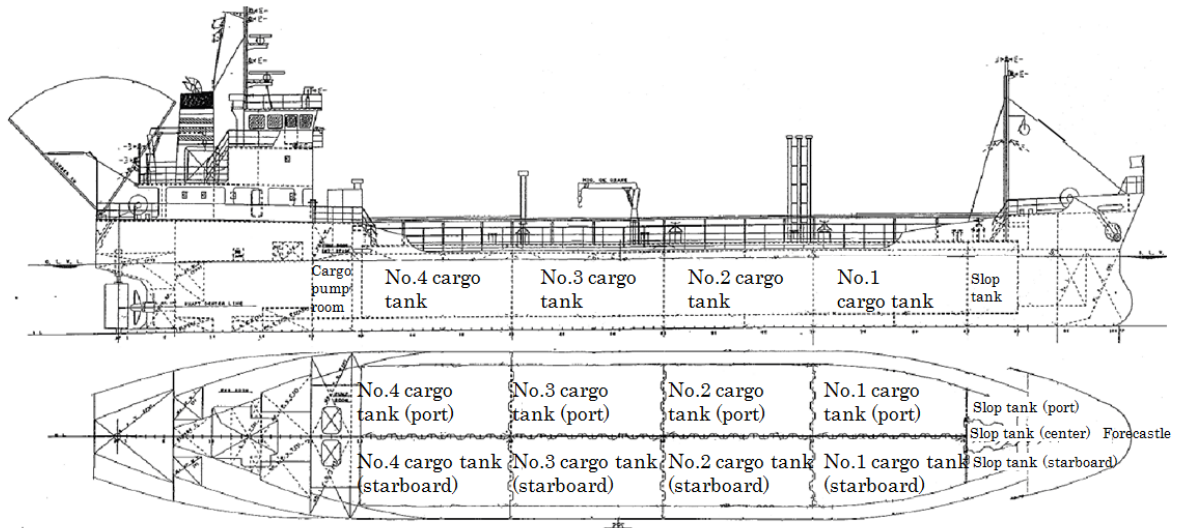
(2) Cargo Tanks

The cargo tanks of the Vessel were divided into 2 rows of port and starboard with a longitudinal bulkhead between the bow and the stern. In addition, they were also divided into 4 rows with transverse bulkheads between the bow and the stern into 8 tanks total. They were given the numbers 1 through 4 from the bow side and were respectively called No. X cargo tank (starboard) and (port).

The capacity of each cargo tank was as follows.

Cargo tank name	Volume (m ³)
No.1 cargo tank (port)	Approximately 133.7

No.1 cargo tank (starboard)	Approximately 133.6
No.2 cargo tank (port)	Approximately 161.3
No.2 cargo tank (starboard)	Approximately 161.0
No.3 cargo tank (port)	Approximately 161.5
No.3 cargo tank (starboard)	Approximately 161.4
No.4 cargo tank (port)	Approximately 158.7
No.4 cargo tank (starboard)	Approximately 158.8



(Figure 2.5-1 Arrangement of cargo tanks, etc.)

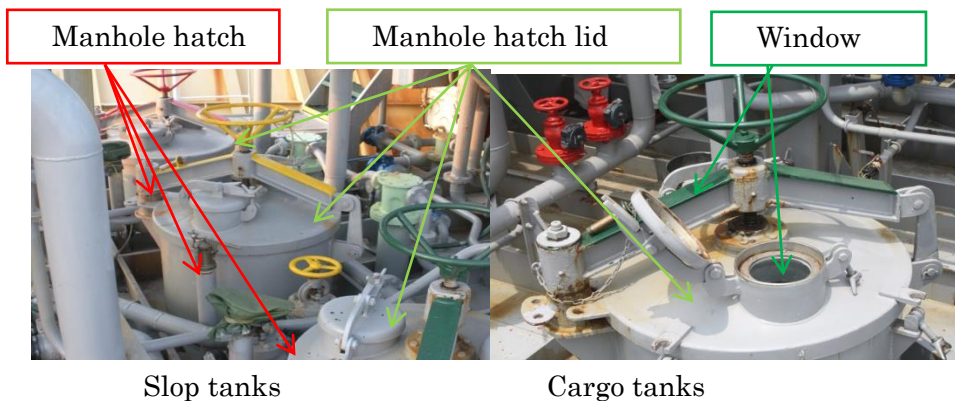
(3) Appliances on the Upper Deck

1) Manhole hatch

There was one manhole hatch on the stern side of each slop tank and each cargo tank. A vertical ladder was installed on the inside of the manhole hatch, connecting the hatch to the bottom.

The diameter of the manhole hatch was approximately 72cm for slop tanks and approximately 75cm for cargo tanks. The height of the manhole hatch opening from the expansion trunk was approximately 59cm for slop tanks and approximately 62cm for cargo tanks.

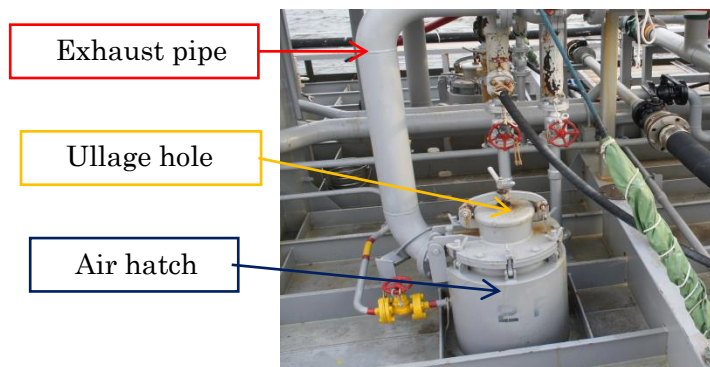
There were 2 windows with approximately 15cm diameter glass on the lid of the manhole hatches, enabling monitoring of cargo liquid surface, etc. within the tanks.



(Photo 2.5-1 Manhole hatches for slop tanks and cargo tanks)

2) Air hatch

There was an air hatch on the bow side of each cargo tank. An ullage hole*⁷ was installed on the lid of the same hatch, and an exhaust pipe*⁸ was connected to the side of the air hatch.

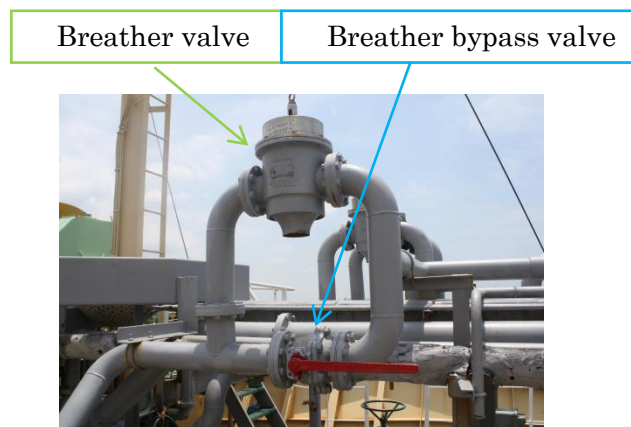
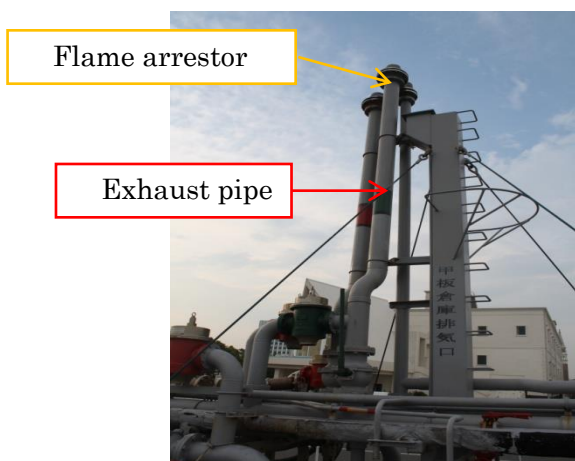


(Photo 2.5-2 Air hatch)

3) Exhaust pipe

Exhaust pipes were installed on slop tanks (starboard/center/port) as well as cargo tanks (starboard/port). Pipes coming out of the manhole hatch of each slop tank were integrated into one, pipes coming out of the air hatch of each of the No.1 and No.3 cargo tanks (starboard/port) were integrated into one, and pipes coming out of the air hatch of each of the No.2 and No.4 cargo tanks (starboard/port) were integrated into one. The tips were approximately 6.5m above the expansion trunk near the center of the No.2 cargo tanks toward the front.

A breather valve*⁹ and a breather bypass valve were installed on the exhaust pipe, and a flame arrestor*¹⁰ was installed at the tip as an outlet.



(Photo 2.5-3 Exhaust pipe, etc.) (Photo 2.5-4 Breather bypass valve , etc.)

4) Butterworth cleaner

2 Butterworth cleaners used for tank cleaning work of each cargo tank were installed for each cargo tank, hung from the tank top between the manhole hatch and air hatch.

5) Bypass valve operation handle

*⁷ “Ullage hole” refers to an opening used to measure the height of the reserve area above the cargo liquid surface within a cargo tank in order to measure the loaded amount of the liquid cargo.

*⁸ “Exhaust pipe” refers to a pipe installed to reduce excess pressure or negative pressure within the tank by releasing gas in the atmosphere when the pressure within the tank increases.

*⁹ “Breather valve” refers to a device used with exhaust pipes in order to automatically prevent excess pressure or negative pressure within the tank.

*¹⁰ “Flame arrestor” refers to a device used with exhaust pipes to prevent fire from entering enclosed spaces.

Bypass valve operation handles for the second and fourth cargo oil bypass pipes were on the bow side of the manhole hatch for the No.4 cargo tank (port). These handles were operated to adjust the flow volume when cargo and tank wash water were transferred to slop tanks.

Bypass valve operation handle



(Photo 2.5-5 Bypass valve operation handle)

6) Liquid Level Indicator

An electric liquid level indicator was installed on each tank, enabling the liquid level, pressure, and temperature, etc. within the tank to be monitored on the digital display in the wheelhouse and on the expansion trunk.

Cargo appliances used at the time of this accident had no defects or malfunction.

2.5.5 Situation of the Vessel after This Accident

- (1) According to the statement of the master, the manhole hatch lids of slop tanks were open, and the area around the manholes were blackened on the Vessel.
- (2) According to the statement of Emergency Unit Members, it was as follows.

Fireboat Konryu deployed at 15:07 on 28th and arrived in the vicinity of this accident location at 15:27 with Emergency Unit Members on board in order to promote the washing activities of the Vessel.

Emergency Unit Members held a discussion with officers of the Nagoya Coast Guard on Patrolling Boat Hidakaze, which was alongside the Vessel, and started spraying water for approximately 5 minutes twice in the range of approximately 10m from the bow toward the stern of the Vessel by using the fire hose of Fireboat Konryu at 15:37.

Afterwards, 4 of Emergency Unit Members and 3 officers of the Nagoya Coast Guard boarded the Vessel at 15:41 while measuring the hydrogen sulfide gas concentration.

Emergency Unit Members and officers of the Nagoya Coast Guard proceeded toward the bow while measuring the gas concentration in order to close the manhole hatch. The gas concentration was approximately 14ppm around 3m from the slop tank (port) manhole hatch toward the stern, approximately 60ppm around 1-2cm above the expansion trunk below the slop tank (port) manhole hatch, and over 100ppm at the root of the handle for the slop tank (port) manhole hatch lid. All of the manhole hatches for the starboard, center, and port slop tanks were open, and the port one was approximately 3cm uplifted from the closed position.

(Refer to Photo 1: the Vessel and Photo 2: Above the expansion trunk from the bridge)

2.6 Weather and Sea Conditions

2.6.1 Observed Values

- (1) The observed values of the wind direction and wind speed at 11:30 on June 28, 2011, according to the Eastern Signal Station of high water breakwater, Port of Nagoya, which is located

approximately 4.9km southwest of this accident location, were southwest for wind direction and 3.9m/s for wind speed.

- (2) According to the personnel in charge of the cargo owner in Tokai City, the observed values of the wind direction and wind speed at 11:45 on June 28, 2011, within a factory, which is located approximately 3.6km northeast of this accident location, were southwest for wind direction and 5.0m/s for wind speed.
- (3) The observed values according to the Tokai Region Meteorological Observation Station, which is located approximately 5.0km east of this accident location, were as follows.
11:30 Wind direction: East-southeast, Wind speed: 1.0m/s, Temperature: 32.5°C
- (4) The observed values according to the Kuwana Region Meteorological Observation Station, which is located approximately 14.0km west of this accident location, were as follows.
11:30 Wind direction: South, Wind speed: 3.1m/s, Temperature: 31.5°C
- (5) According to the Nationwide Ocean Wave information network for Ports and HARbourS (NOWPHAS), the significant waves*¹¹ on June 28, 2011, in Ise Bay were as follows.
11:20 Significant wave (Wave height: 0.29m Wave period: 4.8 seconds)
11:40 Significant wave (Wave height: 0.29m Wave period: 4.8 seconds)
- (6) The observed values according to the Chubu Aviation Weather Service Center, which is located 8.2km south of the Vessel, on December 15, 2010, when sodium hydrogen sulfide wash water was transferred into slop tanks (starboard/port) that contained acrylic acid wash water in the same manner as this accident, were as follows.
11:20 Wind direction: West, Wind speed: 12.9m/s, Temperature: 9.5°C
11:30 Wind direction: West, Wind speed: 12.7m/s, Temperature: 9.4°C

2.6.2 Observation by Crew

According to the statements of the master and the regular master and logbook, it was as follows.

- (1) The weather, wind direction, wind force, and wave height at the time of this accident were as follows. The weather was fine, wind direction was southwest, wind force was 2 (wind speed: Approximately 1.6-3.3m/s), and the wave height was less than 0.5m.
- (2) The wind direction and wind force at 12:00 on December 15, 2010, when sodium hydrogen sulfide wash water was transferred into slop tanks (starboard/port) that contained acrylic acid wash water in the same manner as this accident, were as follows. Wind direction was northwest, and wind force was 6 (wind speed: Approximately 11-14m/s).

2.7 Information Regarding the Cargo, etc.

2.7.1 Information Regarding Sodium Hydrogen Sulfide

According to the Material Safety Data Sheet*¹² of the Vessel, the physical and chemical properties of sodium hydrogen sulfide and required safety measures, etc. were as follows.

- (1) *Physical condition*
Form: Liquid (aqueous solution)

*¹¹ “Significant wave” refers to the average wave height and period of 1/3 of the highest waves among consecutive waves observed at a location.

*¹² “Material Safety Data Sheet” contains information regarding the physical/chemical properties, dangerous and harmful factors, and handling cautions, etc. of chemical substances or products containing chemical substances (notifiable substances). It is prepared by the party who transfers or provides notifiable substances to notify the other party to whom the notifiable substances are transferred or provided.

Color: Pale yellow – reddish brown

Odor: Unpleasant odor, hydrogen sulfide odor

pH: Strong alkaline over 11

(2) *Specific temperature/temperature range in which the physical condition changes*

Boiling point: 110°C (25% product)

Melting point: 5°C (25% product)

(3) *Flash point: None*

(4) *Ignition point: None*

(5) *Explosion property: Does not apply to a pyrophoric substance. However, it is as follows as hydrogen sulfide.*

Explosion limit of hydrogen sulfide: Upper limit: 46.0vol% Lower limit: 4.0vol%

(6) *Density: 1.18g/cm³ (25% product)*

(7) *Odor threshold (as hydrogen sulfide): 0.03ppm*

(8) *Combustibility: Non-combustible*

(9) *Molecular weight: 56.06 (as NaSH)*

(10) *Safety measures (excerpt)*

1) Due to the fact that hazardous hydrogen sulfide gas is produced when exposed to acid, be sure to avoid exposure to acid.

2) Due to the intense reaction when exposed to oxidizing agents, avoid exposure to oxidizing agents.

3) Leaving combustible materials, such as waste cloth and paper, etc., used to wipe off sodium hydrogen sulfide as is promotes heat generation due to oxidation. Due to the risk of combustibles catching fire from heat generation due to oxidation, dispose of the material after submerging in water once.

4) Due to the fact that hazardous hydrogen sulfide gas is produced due to pH reduction, avoid not only exposure to acid but also factors that reduce pH (such as exposure to air and mixture with substances with a pH buffering effect) as much as possible.

(11) *Emergency measures*

1) In case of inhalation

Immediately move the affected person to a location with fresh air. Thoroughly wash nostrils and mouth. If the person has stopped breathing or if the person's breathing is weak, perform artificial respiration. Immediately seek medical diagnosis.

2) In case of skin exposure

Immediately wash with a lot of freshwater for more than 15 minutes. Continue washing until there is no longer stimulation on skin or slimy feeling. Affected person must not be moved until washing is completed. Immediately seek medical attention.

2.7.2 Information Regarding Acrylic Acid

According to Material Safety Data Sheet of the Vessel, the physical and chemical properties of acrylic acid and required safety measures were as follows.

(1) *Physical condition, form, color, etc.: Clear, colorless liquid*

(2) *Odor: Strong acetic acid-like irritating odor*

(3) *pH: No data*

(4) *Melting point: 13.5°C*

(5) *Boiling point: 141°C*

- (6) *Flash point: 51.4°C*
- (7) *Range of explosion: Lower limit: 2vol%, upper limit: 17vol% (in air)*
- (8) *Steam pressure: 400Pa (20°C)*
- (9) *Steam density (air=1): 2.49*
- (10) *Specific gravity (density): 1.05*
- (11) *Solubility: Mixed with water*
- (12) *Spontaneous ignition temperature: 428°C*
- (13) *Odor threshold: 0.1ppm*
- (14) *Viscosity: 1.25mPa · s (25°C)*
- (15) *Conditions to avoid: Heating, light, oxygen*
- (16) *Reactive Hazardous substances: Avoid contact with oxidizing agent, strong base, amines, and iron salt, as it corrodes metal such as copper, nickel, iron, etc.*
- (17) *Hazardous degradation product: Harmful gas (carbon monoxide, carbon dioxide) is produced from combustion. Irritating or harmful fume or gas is produced in case of fire.*

2.7.3 Information Regarding Hydrogen Sulfide Gas

According to Material Safety Data Sheet, emergency measures in case of hydrogen sulfide gas inhalation, etc. were as follows.

- (1) *In case of inhalation*
 - 1) *Move the affected person to a location with fresh air and let the person rest in a comfortable position to breathe.*
 - 2) *Immediately contact a doctor.*
- (2) *In case of eye contact*
 - 1) *Carefully wash with water for few minutes. Next, if the person is wearing contact lenses and if the contact lenses can easily be removed, remove them. Continue washing afterwards.*
 - 2) *If eye irritation persists, seek medical diagnosis and medical attention.*
- (3) *In case of swallowing*
 - 1) *Wash the mouth.*
 - 2) *If feeling sick, contact a doctor.*

2.8 Information Regarding Tank Cleaning Work on the Vessel

According to the statements of the master, regular master, chief engineer, junior chief officer, and replacement chief officer and noxious liquid substance record book, it was as follows.

- (1) The chief officer held a pre-work meeting regarding tank cleaning work before leaving Port of Nagoya to inform crew members of the work plan and work procedures, etc. and gained approval of the master.
- (2) Crew members were in the usual positions on the day of this accident with the master on the bridge, chief engineer near the control panel installed on the starboard side of the poop deck, and the chief officer, first engineer, and junior chief officer opening and closing valves, etc. on the expansion trunk.
- (3) The bypass valve operation handle was half open after the unloading completion immediately before this accident.
- (4) The bypass valve operation handle was still half open when the tank wash water within the No.2 cargo tanks was transferred to slop tanks after the crew members started the tank

cleaning work after leaving Port of Nagoya.

- (5) The rpm of the cargo pump used to transfer the tank wash water at the time of this accident was approximately 280rpm and was within the range of 250 – 280rpm, which is normally used.
- (6) The Vessel transferred the sodium hydrogen sulfide wash water to slop tanks (starboard/port), which contained acrylic acid wash water, by using the cargo pump at the time of this accident.
- (7) The Vessel kept tank wash water in both sides of slop tanks when storing tank wash water so that the Vessel would not list.
- (8) In the past, crew members of the Vessel had prevented a leak from exhaust pipe outlets by opening the manhole hatch lids for slop tanks when tank wash water had leaked from slop tank exhaust pipe outlets while cleaning tanks using detergent because they recognized a patrolling boat traveling nearby. In addition, they had opened manhole hatch lids for slop tanks due to the risk of the leaked tank wash water irritating human bodies.
- (9) At the time of this accident, the Vessel stored freshwater in a slop tank (center) and heated it to approximately 60°C to use as wash water.
- (10) The master, chief engineer, regular master, and replacement chief officer were aware of the danger of sodium hydrogen sulfide itself, which was the cargo. However, they were not aware of the fact that mixing tank wash water of sodium hydrogen sulfide wash water and acrylic acid wash water, etc. could cause chemical reactions.

2.9 Usage Situation of Slop Tanks by Other Operators

When we conducted an investigation with 4 coastal shipping operators that operate chemical tankers regarding the usage situation of slop tanks and instructions for crew members regarding the usage method, we discovered that tank wash water was mixed in slop tanks by vessels managed by all of the coastal shipping operators.

In addition, half of the operators provided no instruction from the company on the usage of slop tanks. It was left up to the discretion of crew members.

2.10 Laws and Regulations Regarding Handling of Chemical Tanker Tank Wash Water

According to the Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism, it is as follows.

Regarding handling of tank wash water of chemical tankers, related laws and regulations and notifications for the Ship Safety Act specify (i) obligation to provide the master with a dangerous goods handling manual and obligation to comply with the items included in the manual and (ii) handling of tank wash water when substances that can cause dangerous interactions are simultaneously loaded as well as requirements on slop tanks to store bilge, etc.

Related laws and regulations and notifications are as follows.

- (1) THE REGULATIONS FOR THE CARRIAGE AND STORAGE OF DANGEROUS GOODS BY SHIPS (the Ministry of Transport ordinance No. 30 of 1957. Hereinafter referred to as “REGULATIONS FOR DANGEROUS GOODS”)

(Provision of dangerous goods handling manual)

Article 5-8 Owners of vessels transporting dangerous goods provided in each item of Article 111-1 and vessels (tankers, tank vessels, and lighter with tanks in case of transporting combustible liquid substances) transporting bulk liquid dangerous goods (excluding noxious liquid substances) shall prepare a dangerous goods handling manual that contains detailed

descriptions of properties of the said dangerous goods, work procedures, measures in case of disasters, and other cautions (hereinafter referred to as “cautions to prevent danger” and provide them to the master of the said vessel in order to prevent danger caused by transporting the said dangerous goods. However, if a manual for emergency measures against disasters, which is specified in the attached table No. 4, is provided, and if cautions to prevent danger are included in the said manual for emergency measures against disasters, the said items do not need to be included in the dangerous goods handling manual.

2 Master shall inform the crew members and workers attending to such work on the said vessel of the items included in the dangerous goods handling manual, which was mentioned in the previous paragraph, and make sure that the items are complied with.

(Cargo pump room)

Article 261

1-3 (omitted)

4 Measures shall be taken for internal bilge so that it can be processed in the bilge drainage facility, which is comprised of the following items.

a Bilge drainage pump that can be operated from outside

b Slop tanks to store drained bilge

c Appropriate connection to transport the bilge, which is stored in slop tanks, to shore

2-5 (omitted)

(2) Vessel inspection rules (notification by Director-General, Maritime Bureau)

(Cargo pump)

261.1.4

(C) Requirements for slop tanks are as follows.

(1)-(3) (omitted)

(4) When 2 or more types of substances that can cause dangerous interactions are simultaneously loaded, tank wash water and bilge containing these substances must not be loaded in the same slop tank. Therefore, there must be the same number of slop tanks as the number of the substances that can cause dangerous interactions that are simultaneously loaded.

(5) (omitted)

2.11 Information Regarding Safety Management, etc. of the Vessel

2.11.1 Owner of the Vessel, etc.

According to the statements of the safety manager of Company A and personnel in charge of Company B, it was as follows.

The Vessel was co-owned by Company A and Company C, and Company C was appointed as the vessel manager.

Company B was responsible for manning the Vessel, and Company A operated it.

Therefore, specific safety management for tank cleaning work, etc. on the Vessel was promoted by Company A, which was the operator.

2.11.2 Information Regarding Safety Management Manual

(1) The safety management manual by Company A stipulated training for crew members as

follows.

Safety manager and operation manager must periodically conduct specific safety training to and thoroughly notify operation manager assistant, owner, etc., crew members, those involved with safety management, and those who conduct internal audit of related laws and regulations, such as safety management manual, Mariners Act, and Act on Preventing Collision at Sea, etc., as well as other items deemed necessary to ensure safety in transportation.

(2) The safety management manual stipulated handling of dangerous goods, etc. as follows.

Dangerous goods and other objects that may harm crew members' safety must be handled as stipulated by laws and regulations.

2.11.3 Information Regarding Safety Management by Company A

According to the statement of safety manager, tank cleaning work manual, and safety training record, it was as follows.

- (1) Company A had prepared and provided the safety management manual on the Vessel in order to ensure transportation safety as a coastal shipping operator stipulated in the Marine Transportation Act.
- (2) Company A had prepared the tank cleaning work manual regarding the washing method, etc. of cargo tanks, cargo lines, and pumps, etc. in order to prevent accidents, such as oxygen deficiency, gas poisoning, fires, and explosions, etc. during tank cleaning work and provided it on the Vessel. However, the manual for the work did not include transfer work of tank wash water.
- (3) Company A had set up 8 basic policies, such as thorough promotion of safe cargo-handling and promotion of voluntary ISM, etc., prepared an annual plan for each, and had been implementing them.
- (4) Company A had conducted safety training on the Vessel at least once a year and at necessary timing. In the safety training conducted on January 31, 2011, they explained about the contents of the P&A Manual, entry method for the noxious liquid substance record book, discharge standard, division of discharge work, tank wash water transfer work into slop tanks, its division, and cautions (oxygen deficiency) on products filled with nitrogen as part of tank washing work. However, Company A had not conducted training on the danger of tank wash water, the fact that dangerous chemical reactions can occur by mixing tank wash water, nor the usage of slop tanks because they were not aware of the danger of mixing tank wash water.
- (5) The operation manager assistant of Company A visited the Vessel once a month in principle to conduct safety checking of the monthly key goals of Company A and provided instructions if necessary.
- (6) Company A had sent materials regarding examples of accidents that occurred at Company A or at other companies to the Vessel and raised awareness to prevent accidents.

2.11.4 Information Regarding Dangerous Goods Handling Manual, etc.

- (1) A dangerous goods handling manual stipulated in the REGULATIONS FOR DANGEROUS GOODS had been prepared and provided to the Vessel.
- (2) The dangerous goods handling manual of the Vessel contained cargo properties, chemical interaction table, and cargo handling, etc. It described tank wash water processes as follows.

5.9.3 Tank wash water process

(5) Slop of cargoes that can cause interactions

If the previously-loaded cargo can cause interactions, be careful not to leave its slop in slop tanks.

5.9.7 Other cautions

Do not work in the port. Turn the vessel to prevent the steam from entering the accommodation spaces at sea. Process tank wash water and slop tanks according to the items stipulated in 5.9.3.

2.11.5 Information Regarding Training, etc. to Crew Members by the Master

According to the statements of the master and regular master and on-board meeting records and record book by the personnel in charge of safety, it was as follows.

- (1) The master and regular master held one on-board meeting a month based on the annual plan to provide explanations, etc. as part of the duties as a master and personnel in charge of safety.
- (2) The master and regular master provided explanations on measures on static electricity, cargo-handling appliance, checking and maintenance of mooring equipment, etc., use of masks, etc., and thorough promotion of work standards, etc. in the on-board meetings. However, they were not aware of the contents of the dangerous goods handling manual regarding processing of tank wash water, which could cause chemical reactions when mixed, and usage of slop tanks, etc. and did not provide explanations.

2.12 Information Regarding Hydrogen Sulfide Gas Concentration and Its Effect on Human Body

“The Prevention of Anoxia, etc. – new edition” (issued by the Japan Industrial Safety & Health Association in 2007) describes as follows.

Hydrogen sulfide poisoning

<i>Concentration ppm</i>	<i>Poisoning/reaction by part</i>	
0.025	Odor <i>Sensitive people can detect the characteristic odor</i>	
0.3	<i>Anyone can detect the odor</i>	
3 - 5	<i>Medium-level strength of odor that feels unpleasant</i>	
10		<i>Acceptable concentration (Lowest limit of irritation in eye membrane)</i>
20 - 30	<i>It is bearable, but one no longer feels the strength of higher concentration by getting used to the odor (fatigue in the sense</i>	Respiratory organs <i>Lowest limit of irritation in lungs</i>

	<i>of smell)</i>		
<i>50</i>			Eyes
<i>100 - 300</i>	<i>In 2-15 minutes, one starts to actually feel that the unpleasant odor has decreased due to the paralysis in the sense of smell.</i>	<i>Continuous exposure for 8-48 hours causes bronchitis, pneumonia, and death by suffocation due to pulmonary edema</i>	<i>Conjunctivitis (“gas-damaged eye”), itchiness in eyes, pain, feeling of sand being in the eyes, dazzle, bloodshot eyes and swelling, opacity of cornea, cornea damage and separation, distorted vision and blur vision, and increased pain due to light</i>
<i>170 - 300</i>		<i>Burning pain in the respiratory tract membrane. Limit of not suffering from serious symptom as long as the exposure is within 1 hour</i>	
<i>350 - 400</i>		<i>Life-threatening with 1 hour of exposure</i>	
<i>600</i>		<i>Life-threatening with 30 minutes of exposure</i>	
<i>700</i>	Cranial nerves	<i>Respiratory paralysis immediately after overbreathing for a short period of time</i>	
<i>800 - 900</i>	<i>Loss of consciousness, respiratory arrest, death</i>		
<i>1000</i>	<i>Unconsciousness, respiratory arrest, death</i>		
<i>5000</i>	<i>Instant death</i>		

2.13 Information Regarding the Report to the Rescue Organization and Rescue

2.13.1 Report by the Master

According to the statement of the master and information from the Nagoya Coast Guard, the master called 118 with the mobile phone on the Vessel at approximately 11:33 on June 28, 2011, after seeing the first engineer, chief officer, and junior chief officer collapsing on the forecastle deck and communicated “3 people who inhaled sodium hydrogen sulfide collapsed while cleaning tanks on the vessel. They seem unconscious, and I request rescue. We are proceeding toward Port of Nagoya”.

2.13.2 Response by the Rescue Organization

(1) Response Situation by the Japan Coast Guard

According to the information from the Nagoya Coast Guard, it was as follows.

Fourth Regional Coast Guard Headquarters received the 118 call from the master at approximately 11:33 on June 28, 2011, and instructed the Nagoya Coast Guard and Yokkaichi Coast Guard Office (hereinafter referred to as “Yokkaichi Coast Guard”) to go for rescue. The Nagoya Coast Guard deployed Patrolling Boat Hidakaze at approximately 12:10 and Yokkaichi Coast Guard deployed Patrolling Boat Isegiku at approximately 12:28.

Patrolling Boat Hidakaze came alongside the Vessel at approximately 12:35, and officers of the Nagoya Coast Guard who boarded the Vessel confirmed the 3 crew members, who had collapsed on the starboard side of the bow.

2 out of the 3 collapsed crew members were in a state of cardiac or respiratory arrest, and the other crew member's consciousness level was 3 (unable to state his own name and date of birth), and he had difficulty walking on his own.

Officers of the Nagoya Coast Guard transferred the 3 crew members to Patrolling Boat Hidakaze at approximately 12:45 – 12:55 and proceeded toward Garden Pier in Port of Nagoya while performing life-saving measures.

Patrolling Boat Hidakaze arrived at Garden Pier in Port of Nagoya at approximately 13:26 and transferred the rescued crew members to the ambulances.

(2) Response Situation by the Nagoya Emergency Task Forces

According to the statements by Emergency Unit Members, it was as follows.

Fireboat Konryu deployed from South Fire Department Daido Substation with Emergency Unit Members on board and came alongside Patrolling Boat Hidakaze of the Japan Coast Guard at approximately 13:14. 4 members boarded Patrolling Boat Hidakaze.

When Emergency Unit Members boarded the boat, 2 out of the 3 rescued crew members were in a state of cardiac or respiratory arrest, and officers of the Nagoya Coast Guard were performing cardiopulmonary resuscitation, such as cardiac massage, etc. The other crew member, though he was conscious, was unable to speak due to impaired consciousness. Emergency Unit Members continued to perform cardiopulmonary resuscitation.

2.14 Investigation and Experiment Regarding the Substance Produced within Slop Tanks and the Substance Production Situation

Based on the statements of the master, chief engineer, and the personnel in charge of Company A, the P&A Manual, noxious liquid substance record book, tank cleaning record book, and the on-site investigation, we have specified the amount of the acrylic acid wash water within slop tanks and the amount of the sodium hydrogen sulfide wash water that was transferred from the No.2 cargo tanks on the day of this accident as follows, due to the fact that this accident occurred when the wash water, which was used to wash cargo tanks that contained 45% concentration sodium hydrogen sulfide, and acrylic acid were mixed in slop tanks on the Vessel. Based on these facts, we have commissioned the investigation and experiment regarding the substance produced within slop tanks and the substance production situation to the Physical & Chemical Analysis Center at the Nippon Kaiji Kentei Kyokai, Incorporated Association (hereinafter referred to as "NKKK Physical & Chemical Analysis Center").

2.14.1 Specification of the Amount of Acrylic Acid Wash Water within Slop Tanks and the Amount of Transferred Sodium Hydrogen Sulfide Wash Water, etc.

(1) Amount of Acrylic Acid Wash Water

On the Vessel, the tank cleaning work for the No.2 cargo tanks (starboard/port) and the No.4 cargo tanks (starboard/port), in which acrylic acid was loaded, was conducted, and the produced acrylic acid wash water was transferred to slop tanks (starboard/port) during the voyage before this accident.

1) Amount of acrylic acid

According to 2.5.2(2) 2), the residual amount of the acrylic acid was specified as approximately 0.205m³ total.

2) Amount of wash water

The amount of acrylic acid wash water was specified as 4.7m³ by excluding the residual

amount of the above acrylic acid from the amount of acrylic acid wash water mentioned in 2.5.2(2) 1). The water temperature was specified as 29°C according to 2.5.2(3) 4).

(2) Amount of Sodium Hydrogen Sulfide Wash Water within the Tanks

This accident occurred when part of the tank wash water in the No.2 cargo tanks (starboard/port) was transferred to slop tanks in the Vessel.

1) Amount of sodium hydrogen sulfide in the No.2 cargo tanks

The residual amount of the sodium hydrogen sulfide in the No.2 cargo tanks was specified as approximately 0.102m³ total according to 2.5.2(1) 3).

2) Amount of wash water in the No.2 cargo tanks

The amount of sodium hydrogen sulfide wash water was specified as 6.0m³ according to 2.5.2(1) 1) and 2).

(3) Amount of the Sodium Hydrogen Sulfide Wash Water Transferred to Slop Tanks

1) Amount of sodium hydrogen sulfide

According to 2.5.2(1) 2), the amount of the sodium hydrogen sulfide transferred to slop tanks (starboard/port) of the Vessel is the amount transferred to slop tanks (starboard/port) among the total amount of 0.102m³ including the residual amount of 0.1m³ within transfer pipes and the remaining stripping amount in the No.2 cargo tanks (starboard/port). In terms of the transferred amount from the No.2 cargo tanks (starboard/port) to slop tanks (starboard/port), the remaining amount of the tank wash water in the No.2 cargo tanks (starboard/port) before this accident was approximately 6.1m³ according to (2) 1) and 2), and the remaining tank wash water in No.2 cargo tanks (starboard/port) after this accident was approximately 5m³ according to 2.5.2(3) 2). Therefore, it is probable that approximately 1/6 of the tank wash water in the No.2 cargo tanks (starboard/port) was transferred to slop tanks (starboard/port), and the transferred amount of sodium hydrogen sulfide was specified as 0.017m³, which is approximately 1/6 of the amount mentioned in (2) 1). Therefore, the total amount (residual amount of 0.1m³ within the pipes and the transferred amount of 0.017m³ from the No.2 cargo tanks) of sodium hydrogen sulfide transferred to slop tanks (starboard/port) was specified as 0.117m³.

2) Amount of wash water

According to (3) 1), approximately 1/6 of the remaining wash water amount in the No.2 cargo tanks was transferred to slop tanks. Therefore, the amount of wash water transferred to slop tanks was specified as 1.0m³. According to 2.8(9), the wash water temperature was specified as 60°C.

(4) Setting of Additional Condition

Due to the fact that the residual amount for acrylic acid and sodium hydrogen sulfide used the water test value at the time when the Vessel was newly build for reference, approximately 1.2 times the above amount was specified as condition 2 and approximately 1.5 times the above amount was specified as condition 3. In addition, due to the statement that the amount of acrylic acid wash water was 5m³, we set condition 4 with 5m³ by increasing the acrylic acid wash water amount by 0.3m³.

2.14.2 Summary of the Investigation and Experiment

(1) Investigation Summary

We have investigated the substance produced by mixing acrylic acid, 45% sodium hydrogen sulfide, and each wash water.

The following examinations were conducted in order to identify the type of gas produced by mixing acrylic acid wash water and sodium hydrogen sulfide wash water as well as its volume.

1) Presumption of the produced substance

The chemical reaction formula for sodium hydrogen sulfide wash water and acrylic acid wash water is as follows.



This chemical reaction formula indicates a general chemical reaction for when weak acid salt and medium acid are mixed. In this case, hydrogen sulfide gas, which is volatile with weak acidity, is produced.

2) Calculation of the produced substance

Data (residual liquid amount and wash water amount within the tanks) used for calculation is shown in Table 2.14-1.

a Chemical reaction

As Table 2.14-1 shows, the number of moles for acrylic acid is greater when the numbers of moles for sodium hydrogen sulfide and acrylic acid are compared. Therefore, it is probable that all of the sodium hydrogen sulfide reacts and that the chemical reaction of (i) formula is completed toward the right side.

b Calculation of the produced amount

Due to the fact that (i) formula proceeds by 100% in all of the mixture conditions (Table 2.14-1), it is clear that the amount of the produced hydrogen sulfide gas depends on the amount of sodium hydrogen sulfide.

The amount of sodium hydrogen sulfide within the mixed liquid and the amount of produced hydrogen sulfide gas in each mixture condition are as shown in Table 2.14-1.

Table 2.14-1 Experiment conditions and the amount of produced gas

Residual liquid and wash water within vessel tanks		Condition in actual mixture			
		Condition 1	Condition 2	Condition 3	Condition 4
Sodium hydrogen sulfide (45% concentration)	Tank residual liquid (i)	0.117m ³	0.120 m ³	0.123 m ³	0.117 m ³
	Wash water (ii)	1.0 m ³	1.0 m ³	0.9 m ³	1.0 m ³
	(i)+(ii)	1.117 m ³	1.120 m ³	1.023 m ³	1.117 m ³
	Solute concentration	6.3wt%	6.5wt%	7.3wt%	6.3wt%
	Solute weight	1220mol/g	1252mol/g	1283mol/g	1220mol/g
Acrylic acid	Tank residual liquid (iii)	68445g	70200g	71955g	68445g
	Wash water (iv)	0.205 m ³	0.246 m ³	0.308 m ³	0.205 m ³
	(iii)+(iv)	4.7 m ³	4.946 m ³	5.008 m ³	5.205 m ³

	Solute concentration	4.4wt%	5.2wt%	6.6wt%	4.4wt%
		2989mol/g	3587mol/g	4492mol/g	2989mol/g
	Solute weight	215455g	258546g	323708g	215455g
Hydrogen sulfide gas production value	Calculated value	27.3 m ³	28.0 m ³	28.7 m ³	27.3 m ³

Note 1): In the calculation for the solute concentration, we specified the hydrogen sulfide concentration as 45wt%, specific gravity as 1.3, and acrylic acid purity as 100wt%. Wash water for each was considered to be pure water.

Note 2): The calculated value for the amount of the produced hydrogen sulfide gas is the amount of sodium hydrogen sulfide (m³) × 1000 × specific gravity × 0.45/56.063 (molar mass) × 1000 × 22.4 (standard condition: Absolute 0°, 1 pressure)/1000

Note 3): Tank residual liquid refers to the total amount of the residual amount within transfer pipes to slop tanks and the remaining amount of stripping, which has been transferred to slop tanks, within cargo tanks.

(2) Experiment summary

We have conducted a confirmation experiment for the presumed produced substance and the concentration of the produced gas. However, due to the fact that we are unable to make the entire amount react in conditions in Table 2.14-1 to measure the concentration of the produced gas, we have reduced the mixed amount by approximately 1/20,000 to measure. The reduction scale and amount of liquid in each condition are shown in Table 2.14-2.

Table 2.14-2 Reduction scale and amount of liquid in each condition

Condition	Reduction scale	Sodium hydrogen sulfide (ml)	Wash water (60°C) (ml)	Acrylic acid (ml)	Wash water (29°C) (ml)
Condition 1	1/20893	5.6	48	10	225
Condition 2	1/21426	5.6	47	12	219
Condition 3	1/21964	5.6	41	14	214
Condition 4	1/20893	5.6	48	10	239

(3) Mixture Condition

- 1) Mixture ratio: Sodium hydrogen sulfide wash water and acrylic acid wash water were mixed using the ratio of the conditions indicated in Table 2.14-1.
- 2) Solution temperature at the time of mixture: Sodium hydrogen sulfide wash water was 60°C, and acrylic acid wash water was 29°C.
- 3) Reactor: We produced hydrogen sulfide gas by injecting the solution into a glass reactor bottle (580ml).
- 4) Collecting the produced gas: After mixing each solution, we discarded the first several hundred ml of the gas that was produced approximately 5 minutes later. We measured the concentration of the following gas. This is due to the fact that the first several hundred ml of the produced gas contain a lot of remaining air in the gas flow route.
- 5) Measurement of produced gas concentration: We used a vacuum gas sampler to sample gas and measured the concentration of hydrogen sulfide gas using KITAGAWA Gas Detector Tube 120SH (Measurement range: 0.1-4%) (hereinafter referred to as "Gas Detector Tube").

2.14.3 Results of the Investigation and Experiment

(1) Investigation Results

1) Amount of the hydrogen sulfide gas

The amount of sodium hydrogen sulfide within the mixed liquid and the amount of produced hydrogen sulfide gas in each mixture condition are as shown in Table 2.14-1.

2) Comparison between the amount of produced hydrogen sulfide and the remaining capacity*¹³ of exhaust pipes, etc.

We have compared the amount of the produced hydrogen sulfide gas, which was calculated in 2.14.2(1) 2), and the remaining capacity.

With condition 1, the remaining capacity was approximately 25.3m³ (slop tanks: approximately 24.6m³, manhole hatch: approximately 0.5m³, exhaust pipe: approximately 0.2m³). Since the produced gas is 27.3m³, the produced amount is increased by approximately 2.0m³.

Therefore, if all of the sodium hydrogen sulfide within the sodium hydrogen sulfide wash water reacted and produced hydrogen sulfide gas, the amount of the produced hydrogen sulfide gas exceeds the remaining capacity of slop tanks (starboard/port). Therefore, part of the hydrogen sulfide gas may be discharged into the atmosphere from the slop tank exhaust pipe outlet. It is possible that part of the hydrogen sulfide gas produced in the same manner is discharged into the atmosphere from the exhaust pipe outlet under other conditions.

(2) Result of the Experiment

Although sodium hydrogen sulfide wash water and acrylic acid wash water are both clear liquid, they reacted and became cloudy when mixed. The produced gas is clear and had an odor of rotten eggs. Gas started to be produced immediately after mixing. When we took a sample of the gas, the Gas Detector Tube turned its color, indicating that hydrogen sulfide gas had been produced. Table 2.14-3 shows the hydrogen sulfide gas measurement results. In addition, due to the fact that the results of this experiment would largely exceed the measurement range of the Gas Detector Tube, the sample collection amount was set at 12.5 ml and the measurement results were calculated with 100ml.

Table 2.14-3 Measurement result for hydrogen sulfide gas

Condition	H ₂ S measured value (Collection amount: 12.5ml)(%)	H ₂ S measured value (collection amount: 100ml calculation)(%)
Condition 1	2.8	22.4
Condition 2	3.0	24.0
Condition 3	3.2	25.6
Condition 4	2.7	21.6

(3) Conclusion

The following items were discovered by this investigation.

1) Presumption of the produced substance

*¹³ "Remaining capacity" refers to the sum of the space excluding the volume of the stored tank wash water within the entire capacity of slop tanks, capacity of slop tank hatches, and capacity of exhaust pipes.

Mixing acrylic acid ($\text{CH}_2=\text{CHCOOH}$) and sodium hydrogen sulfide (NaSH) produces “hydrogen sulfide gas”.

2) Calculation of the amount of the produced substance

It is possible that all of the sodium hydrogen sulfide within the sodium hydrogen sulfide wash water reacted and produced hydrogen sulfide gas, that the produced amount of hydrogen sulfide gas was larger than the remaining capacity of slop tanks, etc., and that the produced hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet.

3) Confirmation experiment for the produced substance

We have confirmed that hydrogen sulfide gas is produced. In addition, we have measured the hydrogen sulfide gas concentration within the gas produced by mixing the wash water. High concentration hydrogen sulfide gas was detected.

(Refer to Attachment 1: Commissioned investigation regarding the substance produced within slop tanks and the substance production situation)

2.15 Investigation on the Effect of Hydrogen Sulfide Gas, which Sprayed out of the Slop Tank Exhaust Pipe Outlet, on Crew Members

According to the statements of the master, junior chief officer, and chief engineer, commissioned investigation results by the NKKK Physical & Chemical Analysis Center, and the general arrangement, etc., positions of the crew members, sprayed amount, relative wind direction, and wind force, etc. when hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet were identified as follows. Based on this data, we commissioned the National Maritime Research Institute to investigate the effect of hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet, on crew members.

2.15.1 Identification of Positions of Crew Members, Sprayed Amount of Hydrogen Sulfide Gas from the Slop Tank Exhaust Pipe Outlet, and Relative Wind Speed, etc.

(1) Positions of Crew Members

The chief officer, first engineer, and junior chief officer were positioned approximately 7.5m and the chief engineer was positioned approximately 27.5m from the slop tank exhaust pipe outlet toward the stern. The chief officer, first engineer, and junior chief officer were standing on the expansion trunk, and the chief engineer was standing on the poop deck, which is approximately 1.3m above the expansion trunk.

Positions of the above crew members in the horizontal direction from the center line of the vessel were; approximately 2.5m toward the port side for the chief officer, approximately 2.3m toward the starboard side for the first engineer, approximately 3.0m toward the starboard side for the junior chief officer, and approximately 2.5m toward the port side for the chief engineer.

(2) Sprayed Amount of Hydrogen Sulfide Gas from the Slop Tank Exhaust Pipe Outlet and Spraying Time

1) Sprayed amount: 2.0m^3 (refer to 2.14.3(1) 2))

2) Time for the entire amount to be sprayed: Approximately 3 seconds according to the statements of crew members

(3) Height of the slop tank exhaust pipe outlet above the expansion trunk, opening area, and opening direction

1) Height above the expansion trunk: 6.5m

- 2) Opening area: 0.0095m²
- 3) Opening direction: Vertically above
- (4) Height of crew members: 170cm (average height of crew members excluding the master)
- (5) Relative wind direction, relative wind speed, weather, temperature
 - (i) Relative wind direction: Starboard bow 5° Relative wind speed: 7.4m/s
 - (ii) Weather: Fine Temperature: Approximately 32°C
- (6) Specific gravity of hydrogen sulfide gas: 1.18
- (7) Concentration of leaking hydrogen sulfide gas: 100%
- (8) Draught: Bow approximately 1.25m, stern approximately 3.30m

2.15.2 Investigation Summary

(1) Investigation Summary

Using the data in 2.15.1, we used the numerical simulation method (so called “CFD analysis”) based on the fundamental equation for the flow field to calculate the diffusion situation of the hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet, in order to find out the temporal and spatial variation for the gas concentration.

In order to remove the initial value dependency from the calculation result, we calculated the flow field only for air for the first 15 seconds until the gas flow field completely developed for the calculation range, and we sprayed hydrogen sulfide gas from the outlet for 3 seconds from 15 to 18 seconds after the calculation start. We further calculated 7 more seconds in order to analyze the behavior of hydrogen sulfide gas after the spray completion. The overall simulation was for 25 seconds.

(2) Analysis Target

The numerical simulation method used in this analysis targeted part of the Vessel, as shown in Figure 2.15-1. This included 6m toward the bow and 28m toward the stern from the slop tank exhaust pipe outlet in term of bow-stern direction, and 20m in the port-starboard direction, including the sea surface. Due to the fact that the draught at the time of this accident was approximately 1.25m at the bow and approximately 3.30m at the stern, we postulated the draught for the target range to be 2.3m and constant, and the range from the sea surface to 20m above it was included in the calculation target in terms of vertical direction. In order to simplify the calculation target, the equipment/appliances on the deck were ignored, and it was postulated to be a flat surface. However, one of the slop tank exhaust pipes, from which hydrogen sulfide gas leaked, was included in the calculation model. In addition, considering the part of the poop deck where the chief engineer was standing before this accident (1m toward the stern), we included only its height (1.3m) in the calculation model. The model of the calculation target used in this analysis is shown in Figure 2.15-2.

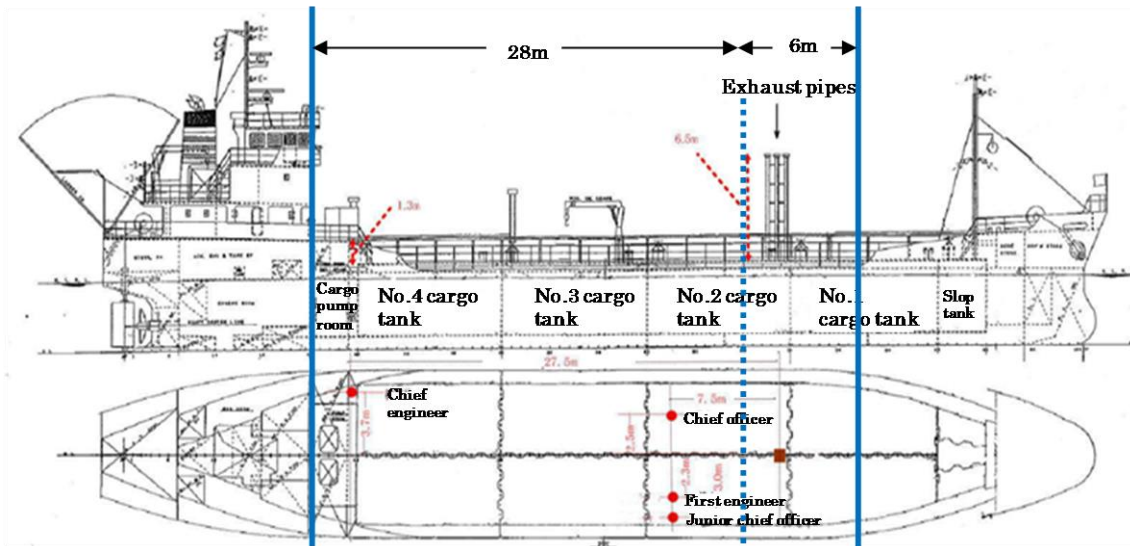


Figure 2.15-1 Calculation target range in the bow-stern direction (range indicated with solid blue lines)

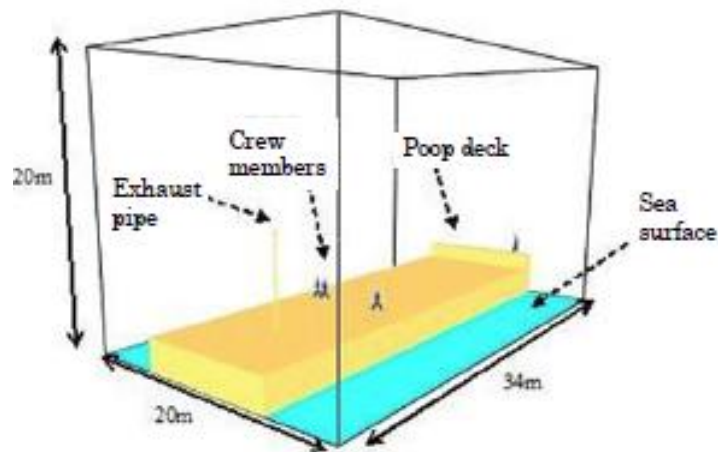


Figure 2.15-2 Calculation target model figure

2.15.3 Investigation Results

(1) Concentration Distribution in Horizontal Cross-section

Hydrogen sulfide gas concentration distribution in horizontal cross-section, including the slop tank exhaust pipe outlet, is shown in Figure 2.15-3. This shows the concentration distribution of every second up to 7 seconds after the beginning of the leak of hydrogen sulfide gas, excluding the result from 3 seconds after the leak. We have utilized the controlled concentration of 10ppm, which is regulated by the Industrial Safety and Health Law, as one of the indexes to determine the effect of hydrogen sulfide gas on people. The entire high concentration area with over 10ppm is shown in red. We can observe that the distribution form is disrupted due to mixture with surrounding air as the leaked hydrogen sulfide gas proceeds towards the stern and that the range of the high concentration area (red) increases.

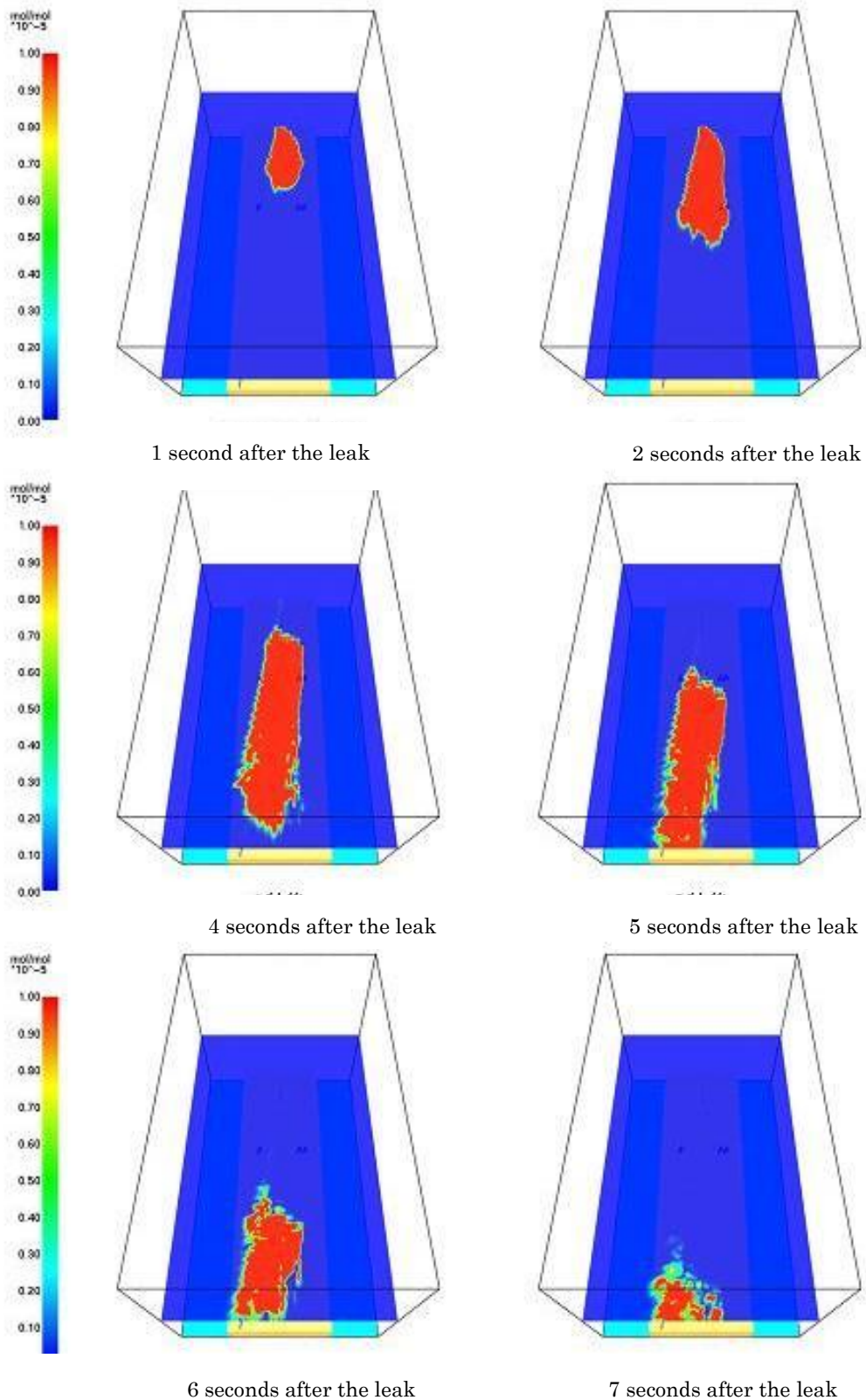


Figure 2.15-3 Hydrogen sulfide gas concentration distribution in horizontal cross-section, including the slop tank exhaust pipe outlet

(2) Change in the Isosurface with 10ppm Concentration Hydrogen Sulfide Gas over Time

Change in the isosurface with the controlled concentration of 10ppm over time is shown in Figure 2.15-4 in order to confirm the spatial range of high concentration hydrogen sulfide gas in a three-dimensional manner. This shows that the hydrogen sulfide gas, which sprayed out

of the slop tank exhaust pipe outlet, is carried toward the leeward side, where the navigation bridge, etc. is located, while making a thin and long gas cloud. A bore*¹⁴ has been formed at the tip of this gas cloud, and it matches the phenomenon generally seen in gravity flows*¹⁵ of high density gas, which is heavier than air.

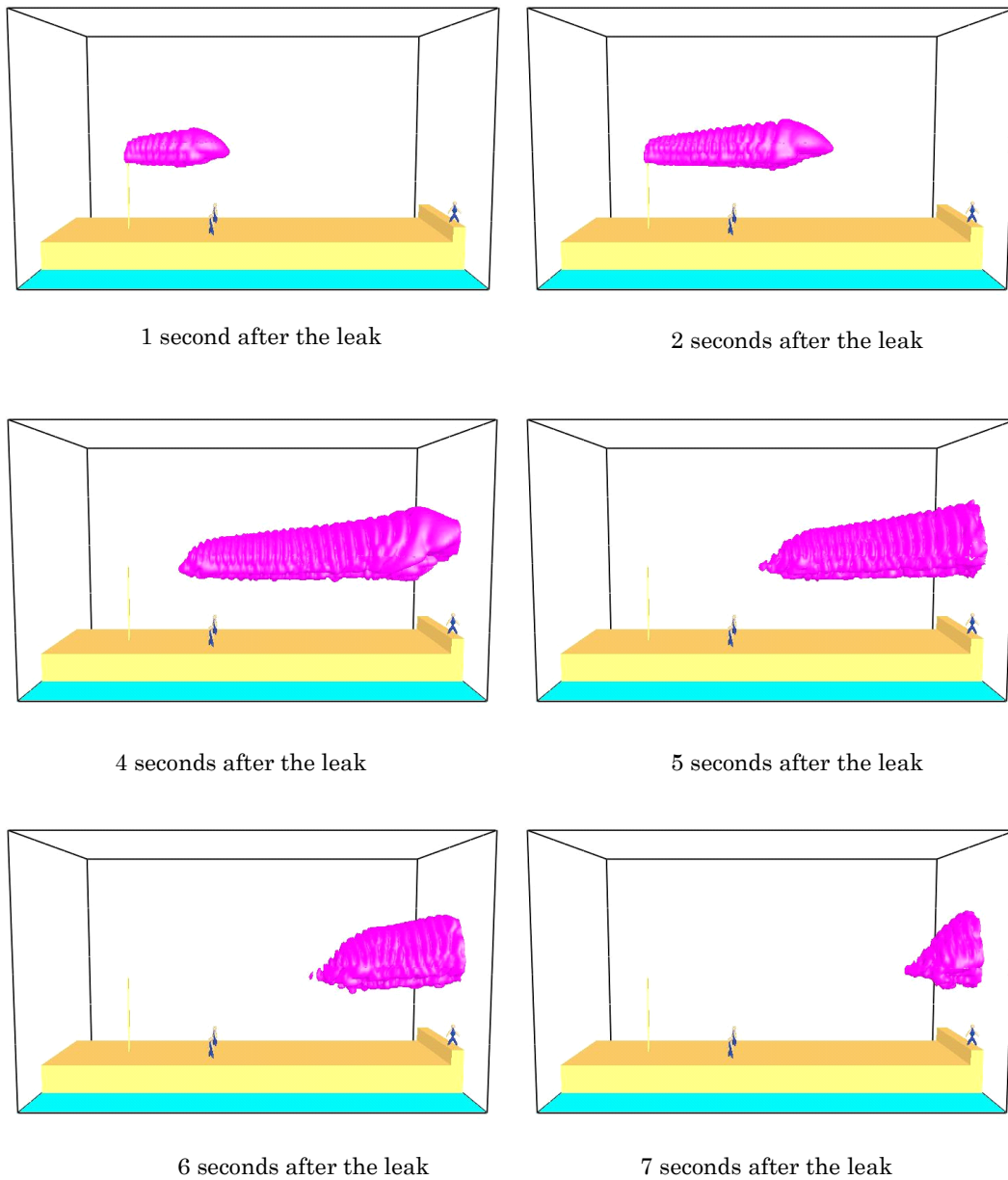


Figure 2.15-4 Change in the isosurface with the 10ppm concentration hydrogen sulfide gas over time

(3) Summary

The phenomenon of advection diffusion of the sprayed hydrogen sulfide gas toward the windward side, where the forecastle deck is located, was not reproduced. In addition, we have discovered that the phenomenon in which high concentration hydrogen sulfide gas of over

*¹⁴ “Bore” refers to a type of shock wave created along a density interface and a phenomenon in which it continues to move while maintaining a great density difference (discontinuous surface).

*¹⁵ “Gravity flow” refers to the flow created when heavy flow proceeds under a light flow.

10ppm diffuses as far as the deck vicinity is not reproduced. Even if we consider that the numerical simulation in this analysis investigation is based on many hypotheses, it is extremely unlikely that the 3 crew members, who were located relatively close to the slop tank exhaust pipe outlet, would have been affected even if each of these people remained in the same position without evacuating. Therefore, it is valid to consider that this accident involving death and injury was due to a different cause. However, regarding the one crew member toward the stern from the slop tank exhaust pipe outlet, due to the facts that the disturbance effect is increased toward the back of the vessel, that he was positioned higher than the 3 crew members toward the front, and the fact that there were structures with complex forms around such as the cargo pump room companion, we cannot completely deny the possibility that part of the hydrogen sulfide gas that sprayed out of the slop tank exhaust pipe outlet had reached him.

(Refer to Attachment 2: Commissioned investigation on the effect of hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet, on crew members)

3 ANALYSIS

3.1 Situation of the Accident Occurrence

3.1.1 Course of the Events

According to 2.1, 2.2, 2.5.2(2) and 2.13.2, it is probable that it was as follows.

- (1) On June 25, the Vessel left the quay of the cargo owner in Port of Yokkaichi after unloading all of the acrylic acid and stored the acrylic acid wash water produced during the tank cleaning work in the slop tanks (starboard/port).
- (2) On June 28, the chief officer received an order to start the tank cleaning work by the master while the Vessel was sailing in Port of Nagoya after leaving the quay of the cargo owner in Port of Nagoya after unloading all of the sodium hydrogen sulfide. The chief officer operated the freshwater cleaning pump with the chief engineer, first engineer, and junior chief officer and started the tank cleaning work for the No.2 cargo tanks (starboard/port) by using 4 Butterworth cleaners.
- (3) The chief engineer operated the cargo pump in order to transfer the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) to slop tanks (starboard/port) because the cleaning of the No.2 cargo tanks (starboard/port) was finished. Hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet when he was about to climb down the stairs on the port side of the poop deck in order to proceed toward the bypass valve operation handle, which was above the No.4 cargo tank (port), at approximately 11:26 in order to adjust the discharge pressure due to the fact that the sodium hydrogen sulfide wash water began being transferred to slop tanks (starboard/port).
- (4) When the chief officer, first engineer, and junior chief officer were evacuating toward the starboard side of the forecastle deck, which was on the windward side, the chief officer opened the manhole hatch lid for the slop tanks (port), and one of the evacuating crew members opened the manhole hatch lid for the slop tank (starboard).
- (5) The chief officer, first engineer, and junior chief officer collapsed on the starboard side of the forecastle deck at approximately 11:27, and the chief engineer was groggy for some time in

the mess room.

- (6) The chief officer, first engineer, and junior chief officer were rescued by the officers of the Nagoya Coast Guard, etc. who had come for rescue and were transferred to a hospital, but the chief officer and first engineer were confirmed dead. The junior chief officer suffered from hydrogen sulfide poisoning, and the chief engineer who was diagnosed in the hospital on the day of this accident suffered from hydrogen sulfide poisoning as well as chemical pneumonia, and both required hospitalization.

3.1.2 Date, Time, and Location of the Accident

According to 2.1, it is probable that the date and time this accident occurred was approximately 11:27 on June 28, 2011, and the place it occurred was the vicinity of 173° 250m from Nagoya Port North Fairway Light Buoy No.3.

3.1.3 Situation of Dead and Injured Personnel

According to 2.1, 2.2, 2.14.2, 2.14.3, and 2.15, it is probable that it was as follows.

- (1) When the chief engineer, chief officer, first engineer, and junior chief officer were attending to the tank cleaning work, hydrogen sulfide gas was produced due to the fact that sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) was transferred to slop tanks (starboard/port) which contained acrylic acid wash water. The chief officer, first engineer, and junior chief officer inhaled the hydrogen sulfide gas that sprayed out of the open manhole hatch of each slop tank (starboard/port) and collapsed on the deck. The chief engineer inhaled the hydrogen sulfide gas that sprayed out of the slop tank exhaust pipe outlet and the open manhole hatch of each slop tank (starboard/port), became groggy, and sat down in the mess room.
- (2) The chief officer and first engineer, who were in a state of cardiac or respiratory arrest, were rescued from the Vessel and were confirmed dead in the hospital, to which they were transferred. The cause of death was hydrogen sulfide poisoning. The junior chief officer had difficulty walking and was rescued from the Vessel and transferred to the hospital. He was hospitalized for hydrogen sulfide poisoning. The chief engineer went to the hospital on the day of this accident and was diagnosed with hydrogen sulfide poisoning as well as chemical pneumonia and was hospitalized. Both crewmembers were in serious conditions.

3.2 Causal Factors of the Accident

3.2.1 Analyses of Crew Member Situation

According to 2.4(1), crew members and regular master of the Vessel possessed legal and valid certificates of seamen's competence and qualifications

3.2.2 Situation of the Vessel

According to 2.5.3 and 2.5.4, it is probable that the used cargo appliances and the hull of the Vessel had no defects or malfunction at the time of this accident.

3.2.3 Weather and Sea Conditions

According to 2.6, it is probable that it was as follows.

- (1) At the time of this accident, the weather was fine, the wind direction was southwest, the wind speed was approximately 3.3m/s, the temperature was approximately 32.0°C, and the

wave height was approximately 0.3m.

- (2) The wind direction and wind speed at 12:00 on December 15, 2010, when the same procedure as this accident (sodium hydrogen sulfide wash water was transferred to slop tanks (starboard/port) that had stored acrylic acid wash water) was taken, were as follows. Wind direction was northwest, and the wind speed was approximately 13m/s.

3.2.4 Analyses of the Usage of Slop Tanks

According to 2.1, 2.5.2, 2.8, and 2.14.1, it was as follows.

- (1) It is probable that tank wash water had regularly been stored in slop tanks (starboard/port).
- (2) It is probable that the Vessel had regularly stored more than 2 different types of wash water in slop tanks.
- (3) It is probable that the Vessel was storing approximately 4.9m³ of the acrylic acid wash water, which was produced during the tank cleaning work after unloading acrylic acid on the 25th, in slop tanks (starboard/port) and that the sodium hydrogen sulfide wash water, that was produced during the tank cleaning work of the No.2 cargo tanks (starboard/port), from which sodium hydrogen sulfide was unloaded, was transferred to slop tanks (starboard/port) at the time of this accident.

It is probable that the acrylic acid wash water and sodium hydrogen sulfide wash water were mixed in the slop tanks (starboard/port). In addition, it is probable that approximately 6.1m³ of sodium hydrogen sulfide wash water was stored in the No.2 cargo tanks (starboard/port) and that the stored amount in slop tanks (starboard/port) after this accident was approximately 6m³.

- (4) It is somewhat likely that the amount of the sodium hydrogen sulfide wash water transferred to slop tanks (starboard/port) on the Vessel was approximately 1.1m³.
- (5) It is probable that the Vessel crew members transferred sodium hydrogen sulfide wash water to slop tanks (starboard/port), which had stored acrylic acid wash water, due to the facts that they did not know that dangerous substances can be produced due to chemical reactions when tank wash water was mixed and that they were not aware of the contents of the dangerous goods handling manual, as is described in 3.2.10 and 3.2.11.
- (6) It is probable that the Vessel crew members usually opened the manhole hatch lids for slop tanks in case tank wash water leaked from the slop tank exhaust pipe outlet in order to stop the leak because they were concerned about the effect of tank wash water on the human body.
- (7) It is probable that 3 crew members including the junior chief officer opened the manhole hatch lid for the slop tanks (starboard/port) while evacuating toward the starboard side of the forecandle deck, which was on the windward side, in order to stop the spraying when hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet while they were attending to the tank cleaning work on the Vessel in Port of Nagoya at the time of this accident.

3.2.5 Analyses of Tank Cleaning Work and Situation at the Time of Hydrogen Sulfide Gas Production

According to 2.1, 2.6, 2.8, and 3.2.3, it was as follows.

- (1) It is probable that they started the tank cleaning work for the No.2 cargo tanks

(starboard/port) while the Vessel was sailing in Port of Nagoya.

- (2) It is probable that the chief officer attended to the tank cleaning work by using Butterworth cleaners with hot water that was stored in slop tank (center).
- (3) It is probable that hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet on the Vessel when the chief engineer was about to climb down the stairs on the port side of the poop deck in order to proceed toward the bypass valve operation handle, which was above the No.4 cargo tank (port), in order to adjust the discharge pressure due to the fact that the sodium hydrogen sulfide wash water began being transferred to slop tanks (starboard/port) after he operated the cargo pump in order to transfer the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) to slop tanks (starboard/port) after finishing the cleaning of the No.2 cargo tanks (starboard/port).
- (4) It is somewhat likely that the Vessel was receiving approximately 7.4m/s wind from the direction of approximately 5° to the starboard side of the bow when the hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet as a result of the estimation from the course, speed, wind direction, and wind speed at the time of this accident.
- (5) It is probable that the master was near the bridge, the chief engineer was near the stairs on the port side of the poop deck, the junior chief officer and first engineer were near the suction valve operation handle for the No.2 cargo tank (starboard), and the chief officer was near the suction valve operation handle for the No.2 cargo tank (port) on the Vessel when the hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet and that the distances between the crew members and the slop tank exhaust pipe outlet were approximately 27.5m toward the stern with the chief engineer and approximately 7.5m toward the stern with the chief officer, first engineer, and junior chief officer.

3.2.6 Analyses of the Hydrogen Sulfide Gas Production and the Spraying Condition of the Gas from the Slop Tank Exhaust Pipe Outlet, etc.

According to 2.1, 2.8, and 2.14, it was as follows.

- (1) It is highly probable that acrylic acid wash water and sodium hydrogen sulfide wash water were mixed in slop tanks (starboard/port) and that hydrogen sulfide gas was produced due to the chemical reaction.
- (2) Due to the fact that the amount of the hydrogen sulfide gas produced within slop tanks (starboard/port) was more than the remaining capacity of slop tanks (starboard/port) and exhaust pipes, etc., it is probable that hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet.
- (3) It is probable that hydrogen sulfide gas sprayed out of each manhole hatch due to the fact that 3 crew members including the junior chief officer opened the manhole hatch lid for the slop tanks (starboard/port) while evacuating toward the starboard side of the forecastle deck in order to stop the spraying from the slop tank exhaust pipe outlet.

3.2.7 Effect of Hydrogen Sulfide Gas that Sprayed out of the Slop Tank Exhaust Pipe Outlet and Manhole Hatches

According to 2.15, it is probable that the chief officer, first engineer, and junior chief officer were not affected by the sprayed hydrogen sulfide gas in the vicinity of the slop tank exhaust pipe outlet. Therefore, it is probable that they inhaled the hydrogen sulfide gas that sprayed out of the open manhole hatch of each slop tank (starboard/port) and suffered from hydrogen sulfide

poisoning. In addition, it is probable that the chief engineer inhaled the hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet and was bounced off the cargo pump room companion, accommodation spaces, and wall in front of the bridge, etc., as well as the hydrogen sulfide gas that sprayed out of slop tank manhole hatches and suffered from hydrogen sulfide poisoning.

3.2.8 Past Mixture Situation, etc. for Acrylic Acid Wash Water and Sodium Hydrogen Sulfide Wash Water

- (1) According to 2.5.2(4), it is probable that approximately 14m³ of acrylic acid wash water, which was stored in the No.1, No.2, No.3, and No.4 cargo tanks, was transferred to slop tanks (starboard/port) on the Vessel outside of Port of Nagoya on December 12, 2010.
- (2) According to 2.5.2(4) and 2.14, it is probable that hydrogen sulfide gas was produced within slop tanks due to the chemical reaction of tank wash water due to the fact that they transferred approximately 11m³ of sodium hydrogen sulfide wash water, which was produced after cleaning the No.2 cargo tanks (starboard/port), to slop tanks (starboard/port) while the Vessel was sailing in Ise Bay in the course of approximately 180° at the speed of approximately 12kn at approximately 11:25 on December 15.
- (3) According to 2.5.2(4), 2.6, and 3.2.3 and according to the estimation from the course, speed, wind direction, and wind speed at approximately 11:25 on December 15, it is somewhat likely that the Vessel was receiving approximately 9.7m/s wind from the direction of approximately 18° abaft the starboard beam. It is somewhat likely that the hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet, diffused outside of the vessel within a short period due to this wind direction and wind speed and that the working crew members did not notice the production of the hydrogen sulfide gas and did not open the manhole hatch lids for slop tanks.

3.2.9 Situation of the Awareness Regarding Tank Wash Water by Crew Members, including the master

According to 2.8, it is probable that crew members, including the master, as well as regular master were aware of the danger of the cargo by itself but were not aware that mixing tank wash water could cause dangerous chemical reactions.

3.2.10 Analysis on the Safety Management of the Vessel

According to 2.11.3, it is probable that it was as follows.

- (1) Company A had prepared the tank cleaning work manual regarding the washing method, etc. of cargo tanks, cargo lines, and pumps, etc. in order to prevent accidents, such as oxygen deficiency, gas poisoning, fires, and explosions, etc. during tank cleaning work and provided it on the Vessel. However, the manual for the work did not include transfer work of tank wash water after tank cleaning.
- (2) Company A had set up 8 basic policies, such as thorough promotion of safe cargo-handling and promotion of voluntary ISM, etc., prepared an annual plan for each, and had been implementing them.
- (3) Company A had conducted safety training on the Vessel at least once a year and at necessary timing.

In the safety training conducted by Company A on January 31, 2011, they explained about

the contents of the P&A Manual involving tank cleaning, entry method for the noxious liquid substance record book, discharge standard, and division of discharge work, etc. However, regarding the danger of tank wash water, which can cause chemical reactions when mixed, and the usage of slop tanks, they were not aware of the danger of mixing tank wash water; therefore, they did not conduct the training. Therefore, it is probable that the Vessel crew members, including the master, etc., transferred sodium hydrogen sulfide wash water to slop tanks (starboard/port), which had stored acrylic acid wash water, and resulted in this accident due to the facts that they did not know that dangerous substances can be produced due to chemical reactions when tank wash water was mixed and that they were not aware of the contents of the dangerous goods handling manual.

- (4) The operation manager assistant of Company A visited the Vessel once a month in principle to conduct safety checking of the monthly key goals of Company A and provided instructions if necessary.
- (5) Company A had sent materials regarding examples of accidents that occurred at Company A or at other companies to the Vessel and raised awareness to prevent accidents.

3.2.11 Situation Regarding Training, etc. to Crew Members by the Master, etc.

According to 2.7.3 and 2.11.5, it is probable that it was as follows.

- (1) The master and regular master held one on-board meeting a month based on the annual plan to provide explanations, etc. as part of the duties as masters and personnel in charge of safety.
- (2) The master and regular master provided explanations on measures against static electricity, cargo-handling appliance, checking and maintenance of mooring equipment, etc., use of masks, etc., and thorough promotion of work standards, etc. in the on-board meetings. However, they were not aware of the contents of the dangerous goods handling manual regarding processing of tank wash water, which could cause chemical reactions when mixed, and usage of slop tanks, etc. and did not provide explanations.

3.2.12 Situation of Emergency Measures Ordered by the Master

According to 2.7.1 and 2.7.3, it is somewhat likely that the emergency measures ordered by the master to the chief engineer were measures in case of inhalation of or exposure to sodium hydrogen sulfide.

3.2.13 Analysis of the Accident Occurrence

According to 2.1, 2.5.2, 2.5.5, 2.8, 2.11, 2.14.3, 2.15.1, 2.15.3, 3.1.1, 3.1.2, and 3.2, it was as follows.

- (1) It is probable that the chief engineer, chief officer, first engineer, and junior chief officer attended to the tank cleaning work of the No.2 cargo tanks (starboard/port), from which sodium hydrogen sulfide was unloaded, finished cleaning the No.2 cargo tanks (starboard/port), and transferred the produced sodium hydrogen sulfide wash water to slop tanks (starboard/port) while the Vessel was sailing in Port of Nagoya.
- (2) It is probable that the slop tanks (starboard/port) of the Vessel had stored acrylic acid wash water.
- (3) It is highly probable that hydrogen sulfide gas was produced on the Vessel due to a chemical reaction when the acrylic acid wash water and sodium hydrogen sulfide wash

- water were mixed in the slop tanks (starboard/port).
- (4) It is probable that the produced amount of the hydrogen sulfide gas, which was produced in the slop tanks (starboard/port), was larger than the remaining capacity of slop tank (starboard/port) and exhaust pipes, etc., causing it to spray out of the slop tank exhaust pipe outlet.
 - (5) In terms of the Vessel crew members, it is probable that the master was near the bridge, the chief engineer was near the stairs on the port side of the poop deck, the junior chief officer and first engineer were near the suction valve operation handle for the No.2 cargo tank (starboard), and the chief officer was near the suction valve operation handle for the No.2 cargo tank (port) when the hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet and that the distances between the crew members and the slop tank exhaust pipe outlet were approximately 7.5m toward the stern with the chief officer, first engineer, and junior chief officer and approximately 27.5m toward the stern with the chief engineer.
 - (6) It is probable that the Vessel was receiving approximately 7.4m/s wind from the direction of approximately 5° to the starboard side of the bow at the time of this accident.
 - (7) It is probable that hydrogen sulfide gas sprayed out of each manhole hatch due to the fact that the chief officer, first engineer, and junior chief officer opened the manhole hatch lid of each slop tank (starboard/port) while evacuating toward the starboard side of the forecandle deck, which was on the windward side, in order to stop the spraying from the slop tank exhaust pipe outlet when hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet.
 - (8) It is probable that the chief officer, junior chief officer, and first engineer inhaled the hydrogen sulfide gas that sprayed out of the manhole hatch of each slop tank (starboard/port) and suffered from hydrogen sulfide poisoning. In addition, it is probable that the chief engineer inhaled the hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet, as well as the manhole hatch of each slop tank (starboard/port) and suffered from hydrogen sulfide poisoning, etc.
 - (9) It is probable that the Vessel crew members transferred sodium hydrogen sulfide wash water to slop tanks (starboard/port), which had stored acrylic acid wash water, due to the facts that they did not know that dangerous substances can be produced due to chemical reactions when tank wash water was mixed and that they were not aware of the contents of the dangerous goods handling manual, as is described in the later mentioned (11).
 - (10) It is probable that crew members did not know that dangerous substances can be produced due to chemical reactions when tank wash water is mixed due to the facts that the master and regular master were not aware of the contents of the dangerous goods handling manual regarding processing of tank wash water, which can cause chemical reactions when mixed, and usage of slop tanks, etc. and did not provide explanations to the crew members.
 - (11) It is probable that the Vessel crew members did not know that dangerous substances can be produced due to chemical reactions when tank wash water is mixed nor were they aware of the contents of the dangerous goods handling manual due to the facts that Company A was not aware of the danger of mixing tank wash water, that they did not include the tank wash water transfer work in the tank cleaning work manual, and that they did not train crew members regarding the danger of tank wash water, which can cause chemical reactions when mixed, or the usage of slop tanks.

3.2.14 Analyses of the Damage

It is probable that the chief officer, first engineer, and junior chief officer inhaled the hydrogen sulfide gas that sprayed out of manhole hatches and suffered from hydrogen sulfide poisoning due to the fact that they recognized white smoke from the slop tank exhaust pipe outlet and opened the manhole hatch lid for each slop tank (starboard/port) while evacuating toward the starboard side of the forecastle deck, which was on the windward side, in order to stop the spraying due to the fact that they were concerned about the effect of tank wash water on the human body. However, it is probable that they could have avoided suffering from the poisoning if they had not opened the lid for each manhole hatch due to the fact that the gas would not have diffused toward the windward side of the slop tank exhaust pipe outlet.

Therefore, it is probable that it is necessary for one to quickly evacuate to the windward side of the slop tank exhaust pipe outlet and not to open manhole hatch lids for slop tanks (starboard/port) if one is near the slop tank exhaust pipe outlet in case of hydrogen sulfide gas production.

In addition, although the chief engineer entered the mess room, it is probable that it is necessary for one to quickly evacuate to the enclosed accommodation spaces if the person is near the accommodation spaces.

4 CONCLUSIONS

4.1 Findings

(1) Course of the Events

- 1) It is probable that they attended to the tank cleaning work of the No.2 cargo tanks (starboard/port), from which sodium hydrogen sulfide was unloaded, and transferred the sodium hydrogen sulfide wash water, which was produced in the tanks, to slop tanks (starboard/port), in which acrylic acid wash water was stored, while the Vessel was sailing in Port of Nagoya. (3.1.1)*¹⁶
- 2) It is probable that hydrogen sulfide gas was produced when the sodium hydrogen sulfide wash water was transferred to slop tanks (starboard/port) due to the chemical reaction of both wash water, making hydrogen sulfide gas spray out of the slop tank exhaust pipe outlet. (3.2.6)
- 3) It is probable that the chief officer, first engineer, and junior chief officer opened the manhole hatch lid for each slop tank (starboard/port) while evacuating toward the starboard side of the forecastle deck, which was on the windward side. (3.1.1(4))
- 4) It is probable that the chief officer, first engineer, and junior chief officer collapsed on the starboard side of the forecastle deck and that the chief engineer was groggy for some time in the mess room. (3.1.1(5))

(2) Situation of the Accident Occurrence

- 1) It is probable that Company A was not aware of the danger of mixing tank wash water, that they did not include the tank wash water transfer work in the tank cleaning work

*¹⁶ Number at the end of each sentence in this clause indicate the number of the main clause related to the description in "3 ANALYSIS" and clauses following "5 SAFETY ACTIONS".

manual, and that they did not train crew members regarding the danger of tank wash water, which can cause chemical reactions when mixed, or the usage of slop tanks.

Due to this, it is probable that the Vessel crew members transferred sodium hydrogen sulfide wash water to slop tanks (starboard/port), which had stored acrylic acid wash water, due to the facts that they did not know that dangerous substances can be produced due to chemical reactions when tank wash water was mixed and that they were not aware of the contents of the dangerous goods handling manual. (3.2.13(11))

2) It is probable that the chief officer, first engineer, and junior chief officer were positioned on the deck approximately 7.5m toward the stern and the chief engineer was positioned on the deck approximately 27.5m toward the stern from the slop tank exhaust pipe outlet when the hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet while the chief engineer, chief officer, first engineer, and junior chief officer were attending to the tank cleaning work on the Vessel. (3.2.5(5))

(3) Causal Factors for this Accident

1) It is probable that the chief officer and first engineer deceased from hydrogen sulfide poisoning, the chief engineer suffered from hydrogen sulfide poisoning, etc., and the junior chief officer suffered from hydrogen sulfide poisoning when the chief officer, first engineer, and junior chief officer, who were attending to tank cleaning, inhaled the hydrogen sulfide gas that sprayed out of the open manhole hatch of each slop tank (starboard/port) and when the chief engineer inhaled the hydrogen sulfide gas that sprayed out of the slop tank exhaust pipe outlet as well as the open manhole hatch of each slop tank (starboard/port) due to the fact that hydrogen sulfide gas was produced due to a chemical reaction of sodium hydrogen sulfide wash water and acrylic acid wash water when the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) was transferred to the slop tanks (starboard/port), in which acrylic acid was stored, after finishing the cleaning of the No.2 cargo tanks (starboard/port), from which sodium hydrogen sulfide was unloaded, during tank cleaning work while the Vessel was sailing in the Port of Nagoya. (3.2.13(1) - (4), (8))

2) It is probable that hydrogen sulfide gas sprayed out of each manhole hatch due to the fact that the chief officer, first engineer, and junior chief officer opened the manhole hatch lid for the slop tanks (starboard/port) while evacuating toward the starboard side of the forecastle deck, which was on the windward side, in order to stop the spraying from the slop tank exhaust pipe outlet when hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet. (3.2.13(7))

3) It is probable that the reason the Vessel crew members transferred the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) to the slop tanks (starboard/port), in which acrylic acid wash water was stored, was because they did not know that dangerous substances can be produced due to chemical reactions when tank wash water is mixed nor were they aware of the contents of the dangerous goods handling manual due to the facts that Company A was not aware of the danger of mixing tank wash water, that they did not include the tank wash water transfer work in the tank cleaning work manual, and that they did not train crew members regarding the danger of tank wash water, which can cause chemical reactions when mixed, or the usage of slop tanks. (3.2.13(9), (11), 5)

4.2 Probable Causes

It is probable that this accident occurred when the chief officer, first engineer, and junior chief officer, who were attending to the tank cleaning work, inhaled the hydrogen sulfide gas that sprayed out of the open manhole hatch of each slop tank (starboard/port) and when the chief engineer inhaled the hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet as well as the open manhole hatch of each slop tank (starboard/port) due to the fact that hydrogen sulfide gas was produced due to a chemical reaction of sodium hydrogen sulfide wash water and acrylic acid wash water when the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) was transferred to the slop tanks (starboard/port), in which acrylic acid wash water was stored, after finishing the cleaning of the No.2 cargo tanks (starboard/port), from which sodium hydrogen sulfide was unloaded, during tank cleaning work while the Vessel was sailing in the Port of Nagoya.

It is probable that the reason the sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) on the Vessel was transferred to the slop tanks (starboard/port), in which acrylic acid wash water was stored, was because the Vessel crew members did not know that dangerous substances can be produced due to chemical reactions when tank wash water is mixed nor were they aware of the contents of the dangerous goods handling manual due to the facts that Company A was not aware of the danger of mixing tank wash water, that they did not include the tank wash water transfer work in the tank cleaning work manual, and that they did not train crew members regarding the danger of tank wash water, which can cause chemical reactions when mixed, or the usage of slop tanks.

4.3 Other Identified Safety Issues

It is probable that the chief officer, first engineer, and junior chief officer inhaled the hydrogen sulfide gas that sprayed out of manhole hatches and suffered from hydrogen sulfide poisoning due to the fact that they recognized white smoke from the slop tank exhaust pipe outlet and opened the each manhole hatch lid for the slop tanks (starboard/port) while evacuating toward the starboard side of the forecastle deck, which was on the windward side, in order to stop the leak due to the fact that they were concerned about the effect of tank wash water on the human body. However, it is probable that they could have avoided suffering from the poisoning if they had not opened the lid for each manhole hatch due to the fact that the gas would not have diffused toward the windward side of the slop tank exhaust pipe outlet.

Therefore, it is probable that it is necessary for one to quickly evacuate to the windward side of slop tank exhaust pipe outlet and not to open manhole hatch lid for the slop tanks (starboard/port) in case of hydrogen sulfide gas production if the person is near slop tank exhaust pipe outlets.

In addition, although the chief engineer entered the mess room, it is probable that it is necessary for one to quickly evacuate to the enclosed accommodation spaces if the person is near the accommodation spaces.

5 SAFETY ACTIONS

It is probable that this accident occurred when sodium hydrogen sulfide wash water and

acrylic acid wash water had a chemical reaction to produce hydrogen sulfide gas and when 2 crew members, who inhaled the gas, deceased and 2 other crew members suffered from hydrogen sulfide poisoning due to the fact that sodium hydrogen sulfide wash water in the No.2 cargo tanks (starboard/port) was transferred to the slop tanks (starboard/port), in which acrylic acid wash water was stored, after they finished cleaning the No.2 cargo tanks (starboard/port), in which sodium hydrogen sulfide had been stored, on the Vessel.

It is probable that the Vessel crew members transferred the sodium hydrogen sulfide wash water to the slop tanks (starboard/port), in which acrylic acid wash water was stored, due to the facts that Company A was not aware of the danger of mixing tank wash water, that they did not include the tank wash water transfer work in the tank cleaning work manual, and that they did not train crew members regarding the danger of tank wash water, which can cause chemical reactions when mixed, or the usage of slop tanks.

In addition, considering the fact that we did not confirm the phenomenon for hydrogen sulfide gas to diffuse toward the windward side in the investigation of this accident, it is probable that in case of such emergency it is necessary for one to quickly evacuate to the windward side of slop tank exhaust pipe outlet if one is near the slop tank exhaust pipe outlet or quickly evacuate to enclosed accommodation spaces if one is near the accommodation spaces and not open the manhole hatch lids for slop tanks.

5.1 Information Provision by the Japan Transport Safety Board

Due to the concern for similar accidents recurring in the future, the Japan Transport Safety Board provided the information included in the Annex to the Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism in order to raise awareness among operators and owners on August 4, 2011.

5.2 Safety Actions Taken after the Accident

5.2.1 Safety Actions Taken by the Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism in Response to the Information Provision

In response to the information provision by the Japan Transport Safety Board, the Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism (Safety and Environment Policy Division, Safety Management and Seafarers Labour Division, and Inspection and Measurement Division) issued a notification with the following contents to the Japan Federation of Coastal Shipping Associations on September 26, 2011, in order to raise awareness regarding handling of tank cleaning wash water on chemical tankers.

If wash water of different types of cargo are stored in slop tanks, it is necessary to note that substances that are harmful to the human body can be produced due to mixing wash water and conduct appropriate management/operation.

Therefore, thoroughly notify operators/owners of chemical tankers belonging to the association that appropriate management/operation must be conducted by keeping the following items in mind regarding wash water storage, etc. on chemical tankers.

- Appropriately manage properties of wash water so that “what kinds of substances are contained in wash water, which is stored within slop tanks” can be comprehended in an accurate manner.
- Provide vessels with information regarding substance reactivity with “dangerous goods

handling manual” and “Material Safety Data Sheet (MSDS)”, etc. so that they can confirm the danger of harmful substance production.

- Confirm “if there is any danger of harmful substances being produced when new wash water is added to the already stored wash water” by using “dangerous goods handling manual” and “Material Safety Data Sheet (MSDS)”, etc.
- Frequently discharge wash water when it may be discharged to the sea.
- In case of any reaction within tanks, cautiously respond to the matter by keeping risks to human lives in mind.

5.2.2 Safety Actions Taken by Company A

After this accident, Company A held a safety training meeting with attendance of a total of 8 people including crew members and shore auditors, etc. on July 11, 2011, and informed them of points to note regarding tank cleaning work, such as the transfer method of sodium hydrogen sulfide wash water, prohibition of opening manhole lids for cargo tanks and slop tanks during tank cleaning work, and emergency measures in case of gas spraying from slop tank exhaust pipe outlets, etc., as well as properties of cargo containing sodium hydrogen sulfide by using Material Safety Data Sheet for cargo.

They also included those items such as the transfer method of sodium hydrogen sulfide wash water, prohibition of opening manhole lids for cargo tanks and slop tanks during tank cleaning work, and emergency measures in case of gas spraying from slop tank exhaust pipe outlets, etc., which were informed in the above safety training meeting, in the tank cleaning work manual on September 1, 2011. Furthermore, they informed the above items to shore staff of Company A and crew members of chemical tankers operated by Company A.

5.3 Safety Actions Required

Although safety actions were taken as the above, it is necessary for coastal shipping operators, owners, and masters to continue informing crew members about the following items to be complied with in order to prevent recurrence of accidents.

(1) Understanding of the Danger of Tank Wash Water and Its Handling Method

Be aware that tank wash water contains the loaded cargo and possesses similar properties as the cargo, understand dangerous tank wash water by preparing an interaction table for cargos that are dangerous to mix by using the contents of dangerous goods handling manual and Material Safety Data Sheet for reference to avoid mixing tank wash water that can cause dangerous chemical reactions, and inform crew members. At the same time, prepare a manual, etc. for tank wash water processing method and usage of slop tanks in order to avoid mixing such wash water and inform crew members about it to be complied with.

(2) Thorough Evacuation

If tank wash water was transferred without confirming the status inside of slop tanks, resulting in the production of substances such as hydrogen sulfide gas, etc. due to a chemical reaction, do not open slop tank manhole hatch lids. Crew members near slop tank exhaust pipe outlets must quickly evacuate toward the windward side of the exhaust pipe outlets, and crew members near the accommodation spaces must quickly evacuate to the enclosed accommodation spaces.

Japan Transport Safety Board Marine No. 59

August 4, 2011

To Director, Safety and Environmental Policy Division

The Maritime Bureau of the Ministry of Land, Infrastructure, Transport and Tourism

Japan Transport Safety Board Secretariat

Investigator-General for Marine Accident

Provision of Information Gained through Factual Investigation

Although the cause of the accident involving death and injury of crew members of chemical tanker Nisshomaru, which is operated by Matsuda Kisen Co., Ltd., on June 28, 2011, is currently under investigation, we hereby inform you of the following items which we have confirmed in the course of the factual investigation.

1. Summary of the Accident

Nisshomaru (hereinafter referred to as “the Vessel”) left the port toward Port of Wakayama with 5 crew members on board including the master at approximately 11:10 on June 28, 2011, after unloading sodium hydrogen sulfide at Quay C4 of Toray Industries, Inc. Tokai Plant of Tokai City, Aichi Prefecture.

On the Vessel, the tank cleaning work started using freshwater at approximately 11:17 and finished at approximately 11:22. White smoke-like substance sprayed out of the exhaust pipe when they operated the cargo pump in order to transfer the wash water within the tanks to slop tanks.

3 crew members (the chief officer, first engineer, and junior chief officer) out of the 4 crew members who were attending to the work evacuated toward the bow but collapsed near the bollard on the starboard side of the forecastle deck.

The chief officer and first engineer deceased from hydrogen sulfide poisoning, and the junior chief officer and chief engineer, who was near the pump room, were injured due to hydrogen sulfide poisoning.

2. Facts

Although facts will be confirmed in the following investigations, investigations up to this point have discovered the fact that wash water containing sodium hydrogen sulfide was transferred into slop tanks, which contained wash water containing acrylic acid. It is somewhat likely that hydrogen sulfide gas was produced due to this. In addition, the Vessel had stored different types of wash water in slop tanks even before the accident, and similar facts were confirmed with chemical tankers of other operators.

Figure 1 Factors leading to death and injury of crew members (summary)

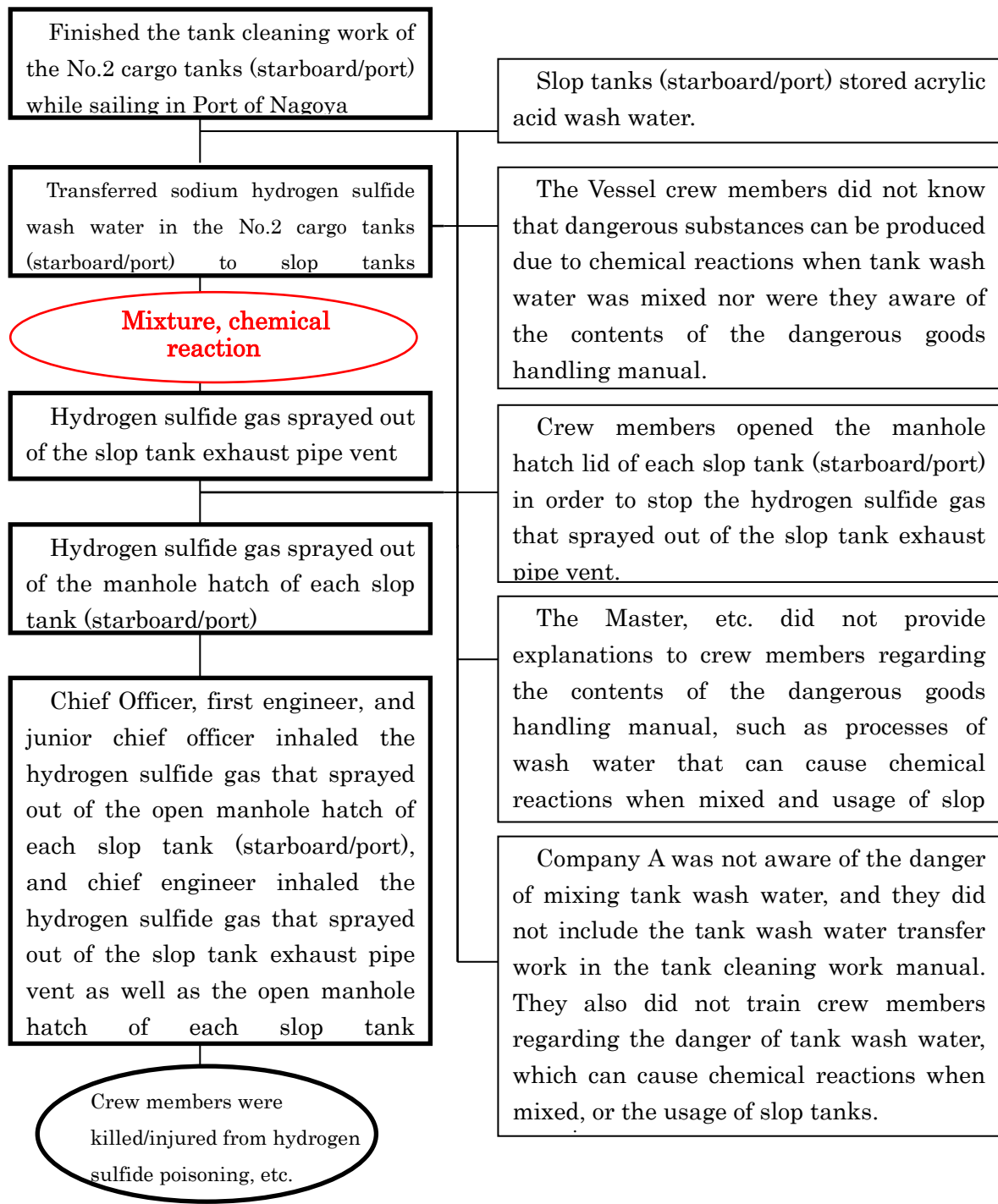


Figure 2 Location of the accident

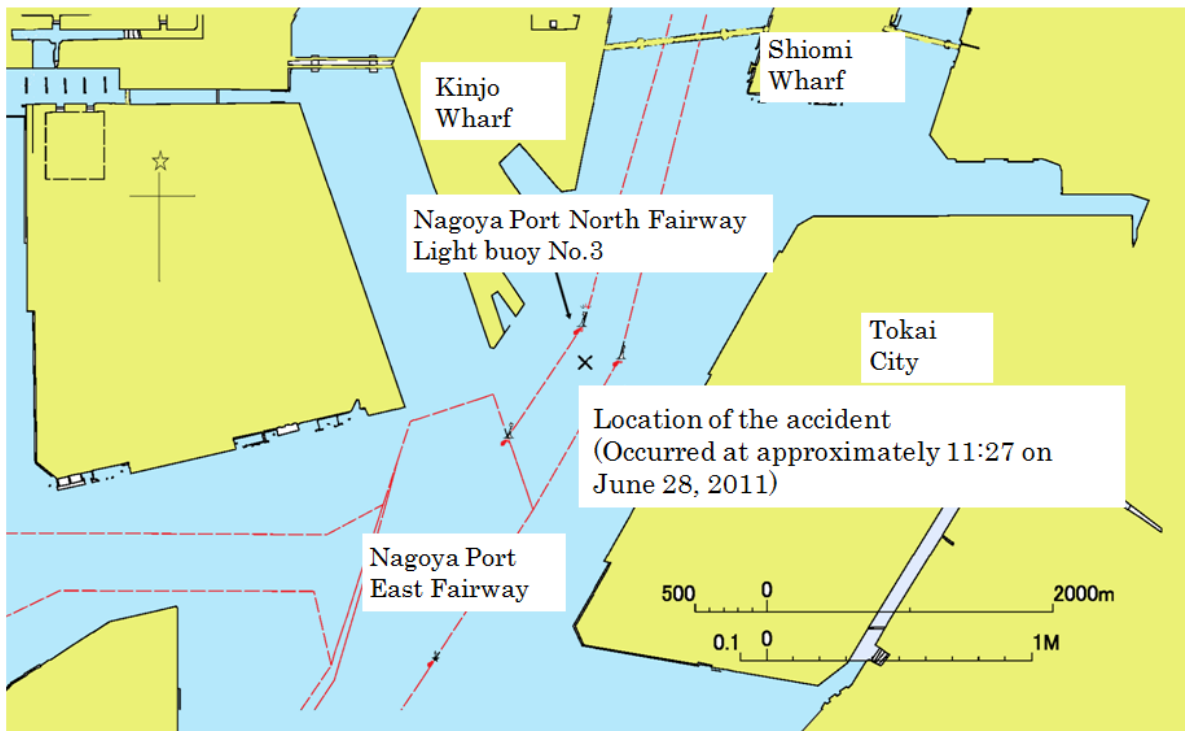


Figure 3 Crew member positions, etc. at the time of this accident

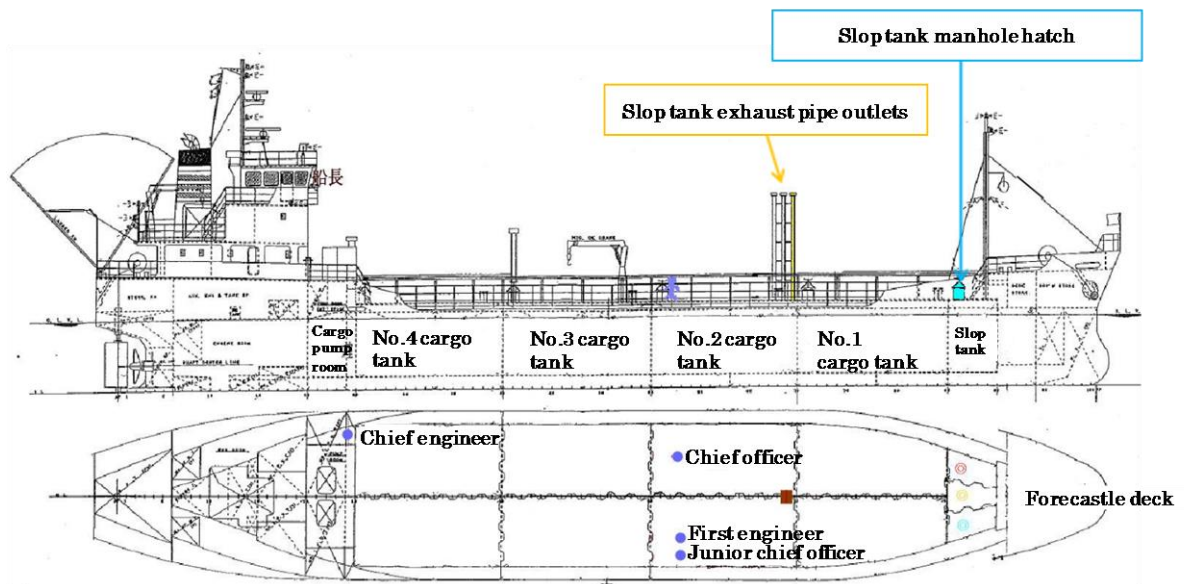


Photo 1 The Vessel



Photo 2 Above the expansion trunk viewed from the bridge



Attachment 1 Commissioned investigation regarding the substance produced within slop tanks and the substance production situation

1. Subject

Analytical investigation on the accident involving death/injury of chemical tanker crew members

2. Objective

To investigate the following contents regarding the substances produced by mixing acrylic acid ($\text{CH}_2=\text{CHCOOH}$), 45% sodium hydrogen sulfide (NaSH), and wash water of each.

- (1) Presumption of the produced substance
- (2) Calculation of the amount of the produced substance
- (3) Confirmation experiment for the produced substance

3. Investigation Method and Results

The following examinations were conducted in order to identify the type of gas produced by mixing the 2 target liquids as well as its volume.

3.1 Presumption of the Produced Substance

The chemical reaction formula for sodium hydrogen sulfide wash water and acrylic acid wash water is as follows.



This chemical reaction formula indicates the general chemical reaction for when weak acid salt and medium acid are mixed. In this case, hydrogen sulfide gas, which is volatile with weak acidity, is produced.

3.2 Calculation of the Amount of the Produced Substance

Data (residual liquid amount and wash water amount within the tanks) used for calculation is shown in Appendix 1-1.

(1) Chemical Reaction

As Appendix 1-1 shows, the number of moles for acrylic acid is greater when the numbers of moles for sodium hydrogen sulfide and acrylic acid are compared. Therefore, it is probable that all of the sodium hydrogen sulfide reacts and that the chemical reaction of (i) formula is completed toward the right side.

(2) Calculation of the Produced Amount

Due to the fact that (i) formula proceeds by 100% in all of the mixture conditions (Appendix 1-1), it is clear that the amount of the produced hydrogen sulfide gas depends on the amount of sodium hydrogen sulfide.

The amount of sodium hydrogen sulfide within the mixed liquid and the amount of produced hydrogen sulfide gas in each mixture condition are as shown in Appendix 1-1.

Appendix 1-1 Experiment conditions and the amount of produced gas

Residual liquid and wash water within vessel tanks		Condition in actual mixture			
		Condition 1	Condition 2	Condition 3	Condition 4
Sodium hydrogen sulfide (45% concentration)	Tank residual liquid (i)	0.117m ³	0.120 m ³	0.123 m ³	0.117 m ³
	Wash water (ii)	1.0 m ³	1.0 m ³	0.9 m ³	1.0 m ³
	(i)+(ii)	1.117 m ³	1.120 m ³	1.023 m ³	1.117 m ³
	Solute concentration	6.3wt%	6.5wt%	7.3wt%	6.3wt%
		1220mol/g	1252mol/g	1283mol/g	1220mol/g
	Solute weight	68445g	70200g	71955g	68445g
Acrylic acid	Tank residual liquid (iii)	0.205 m ³	0.246 m ³	0.308 m ³	0.205 m ³
	Wash water (iv)	4.7 m ³	4.7 m ³	4.7 m ³	5.0 m ³
	(iii)+(iv)	4.905 m ³	4.946 m ³	5.008 m ³	5.205 m ³
	Solute concentration	4.4wt%	5.2wt%	6.6wt%	4.4wt%
		2989mol/g	3587mol/g	4492mol/g	2989mol/g
	Solute weight	215455g	258546g	323708g	215455g
Hydrogen sulfide gas production value	Calculated value	27.3 m ³	28.0 m ³	28.7 m ³	27.3 m ³

Note 1): In the calculation for the solute concentration, we specified the hydrogen sulfide concentration as 45wt%, specific gravity as 1.3, and acrylic acid purity as 100wt%. Wash water for each was considered to be pure water.

Note 2): The calculated value for the amount of the produced hydrogen sulfide gas is the amount of sodium hydrogen sulfide (m³) × 1000 × specific gravity × 0.45/56.063 (molar mass) × 1000 × 22.4 (standard condition: Absolute 0°, 1 pressure)/1000

Note 3): Tank residual liquid refers to the total amount of the residual amount within transfer pipes to slop tanks and the remaining amount of stripping, which has been transferred to slop tanks, within cargo tanks.

(3) Comparison between the Produced Amount and the Remaining Capacity of Slop Tanks (Starboard/Port), etc.

We have compared the amount of the produced hydrogen sulfide gas, which was calculated in (2), and the remaining capacity. With condition 1, the remaining capacity was approximately 25.3m³ (slop tanks: approximately 24.6m³, manhole hatch: approximately 0.5m³, exhaust pipe: approximately 0.2m³), therefore the produced amount exceeds by approximately 2.0m³. If all of the sodium hydrogen sulfide gas is produced, there is a possibility that it is discharged to the atmosphere from exhaust pipe outlets. In the same manner, it is somewhat likely that produced hydrogen sulfide gas is discharged from

exhaust pipe outlets in other conditions.

3.3 Confirmation Experiment for the Produced Substance

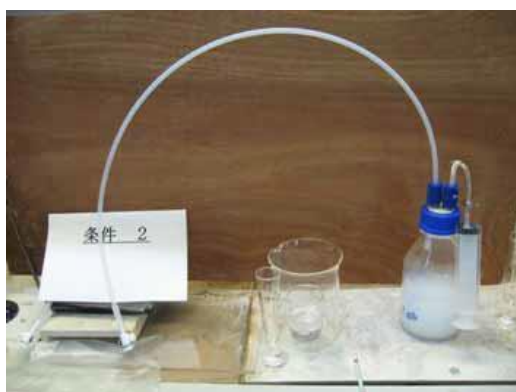
We have conducted a confirmation experiment for the presumed produced substance and the concentration of the produced gas. However, due to the fact that we are unable to make the entire amount react in conditions in Appendix 1-1 to measure the concentration of the produced gas, we have reduced the mixed amount by approximately 1/20,000 to measure. The reduction scale and amount of liquid in each condition are shown in Appendix 1-2. Scenes from the experiment are shown in Attached Figure 1-1 and Attached Figure 1-2.

(1) Mixture Condition

- 1) Mixture ratio: Sodium hydrogen sulfide wash water and acrylic acid wash water were mixed using the ratio of the conditions indicated in Appendix 1-1.
- 2) Solution temperature at the time of mixture: Sodium hydrogen sulfide wash water was 60°C, and acrylic acid wash water was 29°C.
- 3) Reactor: We produced hydrogen sulfide gas by injecting the solution into a glass reactor bottle (580ml).
- 4) Collecting the produced gas: After mixing each solution, we discarded the first several hundred ml of the gas that was produced approximately 5 minutes later. We measured the concentration of the following gas. This is due to the fact that the first several hundred ml of the produced gas contain a lot of remaining air in the gas flow route.
- 5) Measurement of produced gas concentration: We used a vacuum gas sampler to sample gas and measured the concentration of hydrogen sulfide gas by using KITAGAWA Gas Detector Tube 120SH.
- 6) KITAGAWA Gas Detector Tube 120SH: Specifications are as shown in Attached Figure 1-3.

Appendix 1-2 Reduction scale and amount of liquid in each condition

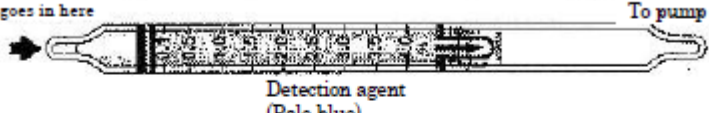
Condition	Reduction scale	Sodium hydrogen sulfide (ml)	Wash water (60°C) (ml)	Acrylic acid (ml)	Wash water (29°C) (ml)
Condition 1	1/20893	5.6	48	10	225
Condition 2	1/21426	5.6	47	12	219
Condition 3	1/21964	5.6	41	14	214
Condition 4	1/20893	5.6	48	10	239



Attached Figure 1-1 Experiment equipment



Attached Figure 1-2 Reactor bottle

Specifications	
	
Measuring range	0.1 - 4.0%
Sampling amount	100ml%
Measurement time	1 minute/100ml
Discoloration of detection agent	Pale blue -> Black
Detection limit	50ppm
Operating temperature	0 - 40° C
Humidity effect	None
Reaction principle	Produces copper sulfide by reacting with copper sulfate. $H_2S + CuSO_4 \rightarrow CuS$

Attached Figure 1-3 Specifications of KITAGAWA Gas Detector Tube

(2) Result of the Experiment

Although sodium hydrogen sulfide wash water and acrylic acid wash water are both clear liquid, they react and become cloudy when mixed. (Refer to Attached Figure 1-2) The produced gas is clear and had an odor of rotten eggs. Gas started to be produced immediately after mixing. When we took a sample of the gas, the Gas Detector Tube changed its color, indicating that hydrogen sulfide gas had been produced. Attached Figure 1-4 shows the image.

Next, Appendix 1-3 shows the hydrogen sulfide gas measurement results. In addition, due to the fact that the results of this experiment would largely exceed the measurement range of the Gas Detector Tube, the sample collection amount was set at 12.5 ml and the measurement results were calculated with 100ml.

Appendix 1-3 Measurement result for hydrogen sulfide gas

Condition	H ₂ S measured value (Collection amount: 12.5ml)(%)	H ₂ S measured value (Collection amount: 100ml calculation)(%)
Condition 1	2.8	22.4
Condition 2	3.0	24.0
Condition 3	3.2	25.6
Condition 4	2.7	21.6



Attached Figure 1-4 Gas Detector Tube (Image of discoloration)

4. Conclusion

The following items were discovered by this investigation.

(1) Presumption of the produced substance

Mixing acrylic acid ($\text{CH}_2=\text{CHCOOH}$) and sodium hydrogen sulfide (NaSH) produces “hydrogen sulfide gas”.

(2) Calculation of the amount of the produced substance

It is somewhat likely that all of the sodium hydrogen sulfide wash water reacted and produced hydrogen sulfide gas, that the produced amount of hydrogen sulfide gas was larger than the remaining capacity of slop tanks (starboard/port), etc., and that the produced hydrogen sulfide gas sprayed out of the slop tank exhaust pipe outlet.

(3) Confirmation experiment for the produced substance

We have confirmed that hydrogen sulfide gas is produced. In addition, we have measured the hydrogen sulfide gas concentration within the gas produced by mixing the wash water. High concentration hydrogen sulfide gas was detected.

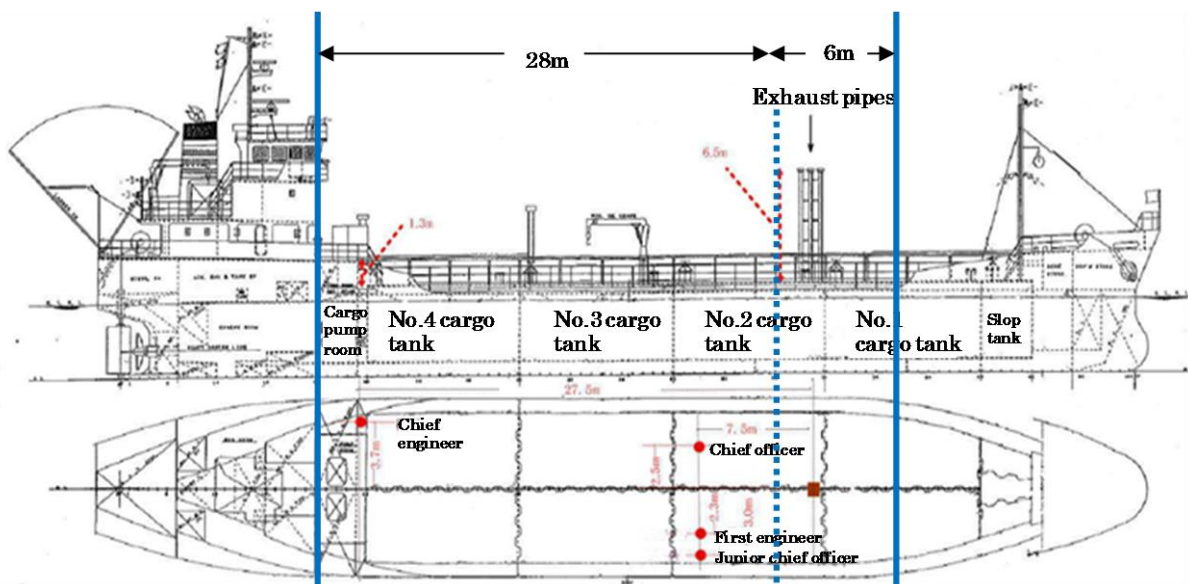
Attachment 2 Commissioned investigation on the effect of hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet, on crew members

1. Investigation Summary

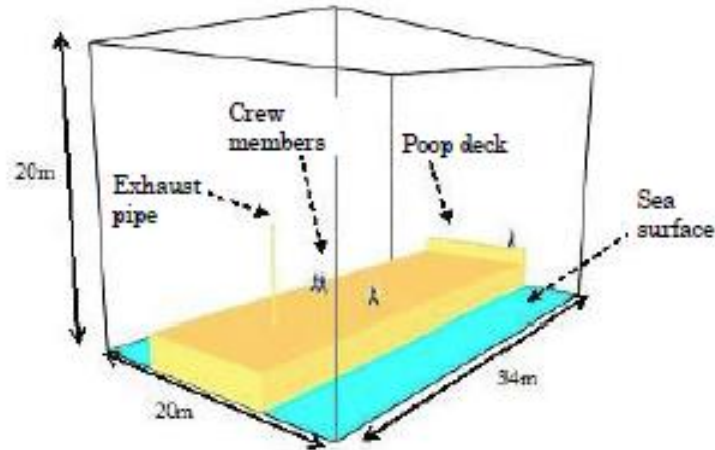
We calculated the diffusion situation of the hydrogen sulfide gas, which sprayed out of the exhaust pipe outlet, in order to find out the temporal and spatial variation for the gas concentration by using the numerical simulation method (so called “CFD analysis”) based on the fundamental equation for the flow field.

2. Analysis Target

Due to the fact that the numerical simulation method used in this analysis generally has a heavy computation load, we targeted part of the hull, which is shown in Attached Figure 2-1, rather than targeting the overall vessel as well as the surrounding area of water. This included 6m toward the bow and 28m toward the stern from the slop tank exhaust pipe outlet in term of bow-stern direction, and 20m in the port-starboard direction, including the sea surface. Due to the fact that the draught at the time of this accident was approximately 1.25m at the bow and approximately 3.30m at the stern, we postulated the draught for the target range to be 2.3m and constant, and the range from the sea surface to 20m above it was included in the calculation target in terms of vertical direction. In order to simplify the calculation target, the equipment/appliances, etc. on the deck were ignored, and it was postulated to be a flat surface. However, one of the slop tank exhaust pipes, from which hydrogen sulfide gas leaked, was included in the calculation model. In addition, considering the part of the poop deck where the chief engineer was standing before this accident (1m toward the stern), we included only its height (1.3m) in the calculation model. The model of the calculation target used in this analysis is shown in Attached Figure 2-2.



Attached Figure 2-1 Calculation target range in the bow-stern direction (range indicated with solid blue lines)



Attached Figure 2-2 Calculation target model figure

3. Value Calculation Method

The CFD (Computational Fluid Dynamics) code used in this calculation is Fire Dynamics Simulator (FDS)^{[1],[2]}, which was developed by the National Institute of Standards and Technology (NIST) of the United States Department of Commerce. The main characteristics are as follows.

- Targets flow fields in which low-mach-number approximation works
- Analysis of turbulent flow fields is done by Large Eddy Simulation (LES), and the Smagorinsky model is used as the SGS (Subgrid Scale) model.
- Material transportation is calculated using mixture fraction, and a turbulent diffusion combustion model, which combines an eddy dissipating model and the oxygen consumption calorimetry, is used as the flame source model.
- Impact of radiation heat transfer is evaluated by calculating a radiation transfer equation of non-diffusion gas according to the finite volume method.
- Second-order accurate central difference scheme is used for discretization for the spatial derivative term, and upwind difference scheme, which uses local Courant number as the parameter, is used for the convective term. The explicit method using the second-order accurate predictor-corrector method is used for time integration. The computational grid is a rectangular orthogonal grid, which also corresponds to multi-block grids.
- Parallel computation using the MPI (Message Passing Interface) library is possible

Since this calculation targets a material transportation phenomenon in an even temperature field without handling a combustion phenomenon, the governing equation for the flow field, which will be solved numerically, involves mass conservation equation, momentum conservation law equation, emission constraint conditions, and conservation equation and state equation of the mass fraction.

Analysis of the turbulent flow field was done with Large Eddy Simulation (LES), using the Smagorinsky model^[3], which is the basic SGS (Subgrid Scale) model. Although the Smagorinsky model is widely used for engineering for its simplicity and stability of the value calculation, it is difficult to ensure a sufficient number of calculation grids for the calculation range in practical analyses for targets, such as that of this analytical investigation. Therefore, we used a coherent structure Smagorinsky model (CSM)^[4], which is one of the SGS models that can determine the

[1] - [6] indicate the reference at the end of the document.

model constant in a local manner. Due to the fact that the coherent structure no longer exists in a layered flow field, the model coefficient automatically becomes zero, ensuring that the SGS model also correctly behaves near a wall. CSM implements performance evaluations for the flow field surrounding complex objects, including back step flow, diffuser flow, and staggered flow, etc. It has been confirmed that it also matches well with the experiment.^[5]

In this analytical investigation simulation, we used a FDS Ver.5.5 source program, in which we independently incorporated the above CSM.

4. Calculation Condition

We set the necessary conditions required for the calculation according to the specifications. However, vertical speed distribution is required as the boundary condition for the flow, so we calculated it from the power law described with the following formula.

$$u(z) = u_0 \left(\frac{z}{z_0} \right)^\alpha$$

In this calculation, z_0 stands for the height of the measurement point of the wind speed, and u_0 stands for the wind speed with $z = z_0$. Exponent α is a parameter that depends on the atmosphere stability, but the atmosphere stability is expected to be C (slightly unstable) or D (neutral), judging from the information regarding the weather at the time of the accident. Unlike the atmospheric diffusion phenomenon, for which the analysis target includes a wide spatial area, only a limited spatial range near the chemical tanker is the target in this analysis. Therefore, we used $\alpha = 0.15$ by assuming that the atmosphere stability was D (neutral) ^[6].

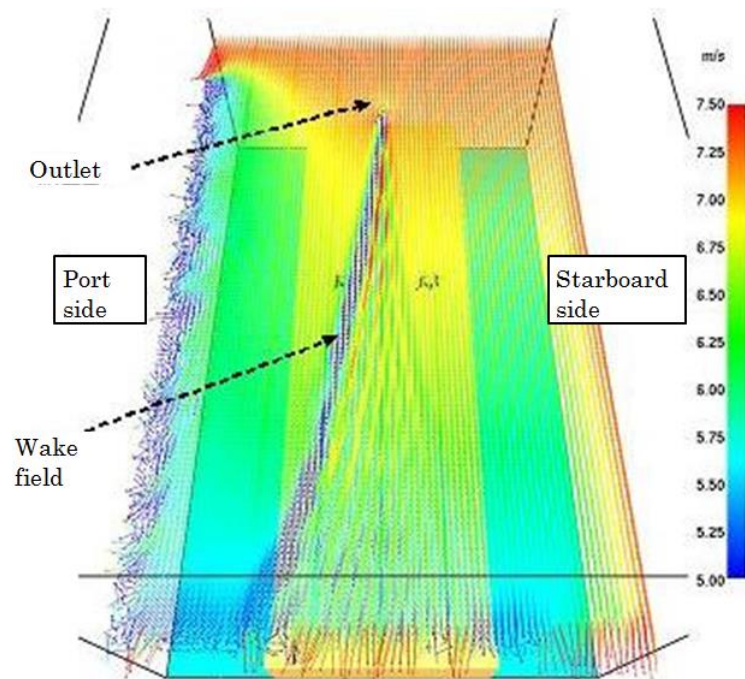
The computational grid used in this analysis was a rectangular orthogonal grid, and the grid width in the horizontal direction was set as 0.125m, and the grid width in the vertical direction was set as 0.25m. Therefore, the total number of used grids is $272 \times 160 \times 80 = 3,481,600$. In addition, 1 grid was allotted for the cross-section of the exhaust pipe, so the setting was approximately 65% larger than the actual cross-section of the exhaust pipe (0.0095m²). Therefore, it is probable that the actual flow speed of hydrogen sulfide gas was approximately 70m/s vertically upward. However, the flow speed reduced in this analysis for the amount of the increased cross-section. The calculation was done by setting the speed as approximately 42.7m/s. In terms of investigating the effect on crew members who were lower than the height of the outlet, the condition was set so that we would evaluate the safety aspect (maintenance aspect). It is necessary to use more detailed calculation grids in order to calculate according to the actual flow speed. However, we used the above calculation grids in this calculation due to the fact that we considered that it would not be preferable to increase the calculation time due to this.

In order to remove the initial value dependency from the calculation result, we calculated the flow field only for air for the first 15 seconds until the gas flow field completely developed for the calculation range, and we sprayed hydrogen sulfide gas from the outlet for 3 seconds from 15 to 18 seconds after the calculation start. We further calculated for 7 more seconds in order to analyze the behavior of hydrogen sulfide gas after the spray completion. The overall simulation was for 25 seconds.

5. Calculation Results and Observation

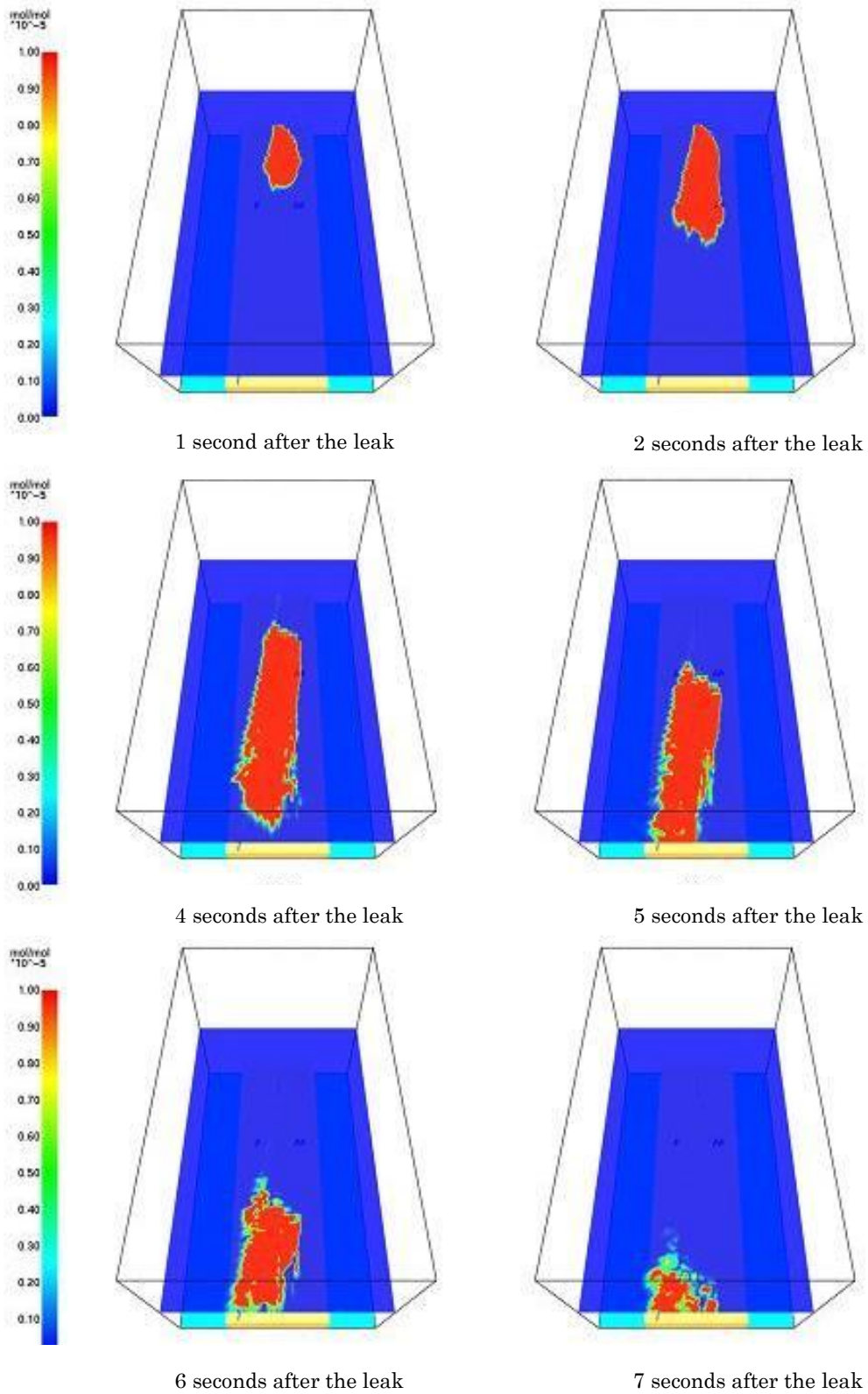
Attached Figure 2-3 shows the speed distribution in horizontal cross-section 8.5m above the sea surface as an example of a gas flow field within the calculation range. This shows the

fully-developed gas flow field (momentary value) 15 seconds after the start of the calculation. Since this is the speed distribution 0.3m below the exhaust pipe outlet, we can see that a low speed wake field is formed behind the exhaust pipe due to it affecting the gas flow field as an obstacle. Since the boundary condition is set with the wind direction of starboard bow 5°, we can observe that the wake is leaning toward the port side. In addition, the estimation for the flow speed in this cross-section according to the power law mentioned in the previous clause is $7.4 \times (8.5/9.5)^{0.15} \approx 7.28$ [m/s], indicating that the same level of flow speed is gained around the exhaust pipe outlet shown in Attached Figure 2-3. However, the speed is slower than the expected flow speed on the leeward side of the outlet speed due to the boundary condition effect. The advection diffusion analysis of leaked gas using this gas flow field would evaluate the safety aspect, so we conducted the following simulation based on the judgment that the necessary gas flow field for this analytical investigation is recreated for the most part.

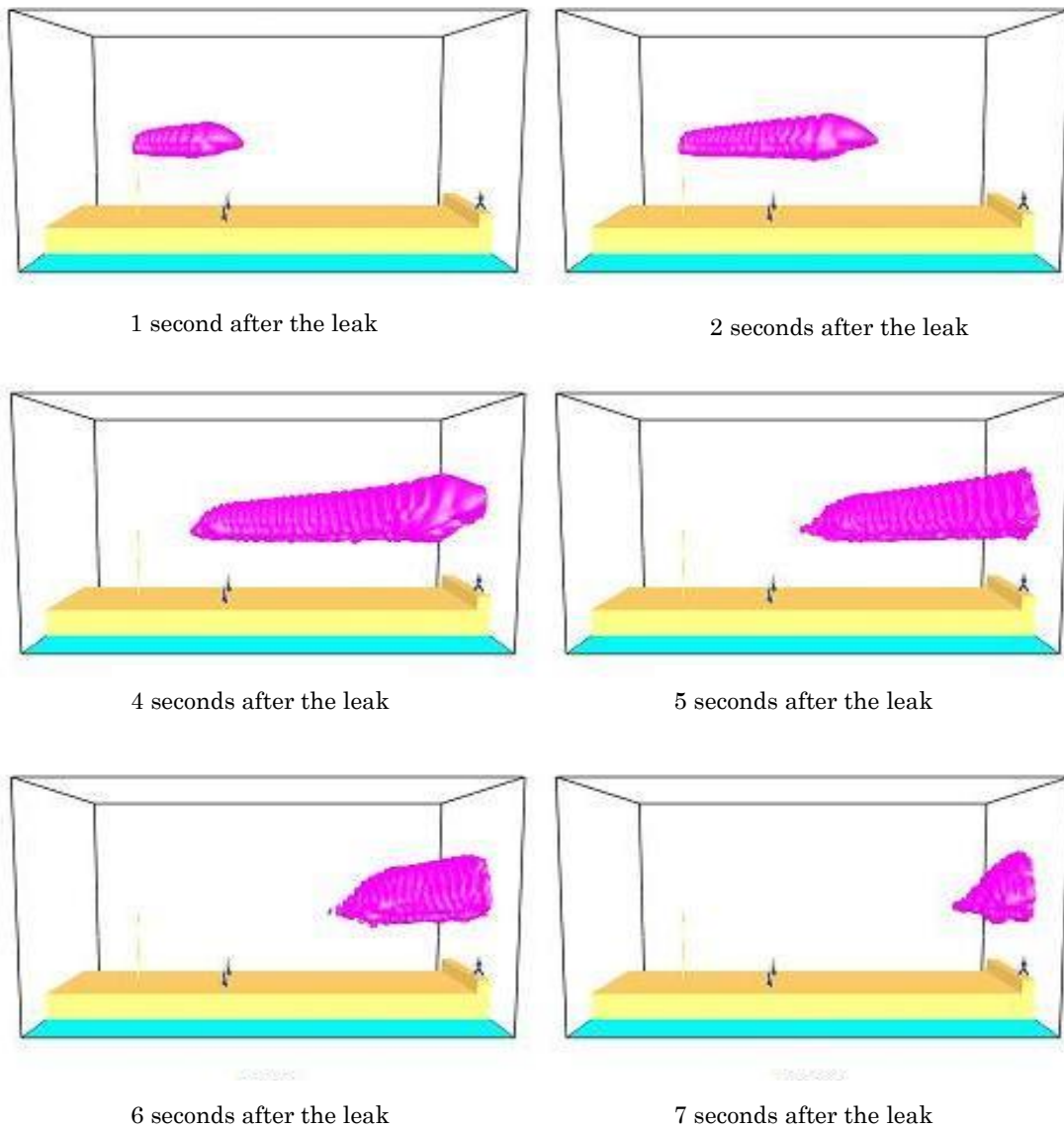


Attached Figure 2-3 Speed distribution in horizontal cross-section 8.5m above the sea surface (This shows the fully-developed gas flow field (momentary value) 15 seconds after the start of the calculation)

First, hydrogen sulfide gas concentration distribution in horizontal cross-section, including the slop tank exhaust pipe outlet, is shown in Attached Figure 2-4. This shows the concentration distribution of every second up to 7 seconds after the beginning of the leak of hydrogen sulfide gas, excluding the result from 3 seconds after the leak. We have utilized the controlled concentration of 10ppm, which is regulated by the Industrial Safety and Health Law, as one of the indexes to determine the effect of hydrogen sulfide gas on people. The entire high concentration area with over 10ppm is shown in red. We can observe that the distribution form is disrupted due to mixture with surrounding air as the leaked hydrogen sulfide gas proceeds towards the leeward side and that the width of the high concentration area (red) increases.



Attached Figure 2-4 Hydrogen sulfide gas concentration distribution in horizontal cross-section, including the exhaust pipe outlet



Attached Figure 2-5 Change in the isosurface with the 10ppm concentration hydrogen sulfide gas over time

Next, change in the isosurface with the controlled concentration of 10ppm over time is shown in Attached Figure 2-5 in order to confirm the spatial range of high concentration hydrogen sulfide gas in a three-dimensional manner. This shows that the hydrogen sulfide gas, which sprayed out of the slop tank exhaust pipe outlet, is carried toward the leeward side, where the navigation bridge, etc. is located, while making a thin and long gas cloud. A bore has been formed at the tip of this gas cloud, and it matches the phenomenon generally seen in gravity flows of high density gas, which is heavier than air. Therefore, it is probable that the concentration distribution indicated in Attached Figures 2-4 and 2-5 is a valid calculation result at least from a qualitative perspective.

In addition, the 4 crew members in the figure are positioned where they were standing before evacuation (3 crew members toward the front and 1 crew member toward the back). Their sizes are set as 1.7m high so that they would meet the measurement for the chemical tanker calculation model. Concentration distribution in Attached Figures 2-4 and 2-5 shows that the hydrogen sulfide gas, which leaked out of the exhaust pipe outlet, would have passed over all of the crew members without affecting them, even if they remained in the positions before the accident without evacuating. In fact, when we investigated the time history of concentration at the head positions of

4 crew members from the calculation results, it was 0ppm for everyone from the starting time for hydrogen sulfide gas leak ($t=15$ seconds) to the ending time of the simulation ($t=25$ seconds). However, the numerical simulation in this analytical investigation was based on many hypotheses, such as targeting only part of the vessel in the analysis and ignoring all of the equipment/appliances on the deck, etc. In reality, it is possible that the gas flow field on the vessel would be disrupted due to objects on the bow and deck of the hull. Due to the fact that the position of the 3 crew members toward the front was close to the slop tank exhaust pipe outlet, it is not probable that such disruption in the gas flow field would be big. Therefore, it is probably valid to directly apply the calculation results and to consider that the possibility of them receiving damage is extremely small. However, with the position of the other crew member, who was far from the slop tank exhaust pipe outlet, we cannot completely deny the possibility that part of the hydrogen sulfide gas, which has 1.18 times more specific gravity than air, had reached near him due to the fact that we cannot exclude the following reasons:

- (i) The disturbance (whirls, etc.) effect is increased toward the back of the vessel due to the distance from the bow and objects on the bow and deck
- (ii) He was positioned slightly higher than the 3 crew members toward the front, meaning that he would be closer to the height in which hydrogen sulfide gas flowed
- (iii) There were structures with complex forms around him, including the wall of the poop deck directly behind him and pump room companion next to him.

6. Conclusion

We have numerically recreated the diffusion situation of hydrogen sulfide gas that sprayed out of the exhaust pipe outlet by using a computational fluid dynamics method in order to investigate the effect of the hydrogen sulfide gas, which sprayed out of slop tank exhaust pipe outlet, on crew members by simulating the accident involving death and injury of “Chemical Tanker A-maru” crew members. As a result, the phenomenon of advection diffusion of the sprayed hydrogen sulfide gas toward the windward side, where the forecastle deck is located, was not reproduced. In addition, we have discovered that the phenomenon in which a high concentration hydrogen sulfide gas of over 10ppm diffuses as far as the deck vicinity is not reproduced. Even if we consider that the numerical simulation in this analytical investigation is based on many hypotheses, it is extremely unlikely that the 3 crew members, who were located relatively close to the slop tank exhaust pipe outlet, would have been affected even if each of these people remained in the same position without evacuating. Therefore, it is valid to consider that this accident involving death and injury was due to a different cause. However, regarding the one crew member toward the stern from the slop tank exhaust pipe outlet, due to the facts that the disturbance effect is increased toward the back of the vessel, that he was positioned higher than the 3 crew members toward the front, and the fact that there were structures with complex forms around him, etc., we cannot completely deny the possibility that part of the leaked hydrogen sulfide gas had reached him.

7. References

- 1) K. McGrattan, S. Hostikka, and J. Floyd, 'Fire Dynamics Simulator (Version 5) User's Guide', NIST Special Publication 1019-5, (2009).
- 2) K. McGrattan, et al., 'Fire Dynamics Simulator (Version 5) Technical Reference Guide, Volume 1: Mathematical Model', NIST Special Publication 1018-5, (2009).
- 3) J. Smagorinsky, 'General Circulation Experiments with the Primitive Equations', Monthly Weather Review, Vol.91, No.3, pp.99-164, (1963).
- 4) H. Kobayashi, 'The Subgrid-Scale Models based on Coherent Structures for Rotating Homogeneous Turbulence and Turbulent Channel Flow', Physics of Fluids, Vol.17, 045104, (2005).
- 5) H. Kobayashi, F. Ham, and X. Wu, 'Application of a Local SGS Model Based on Coherent Structures to Complex Geometries', International Journal of Heat and Fluid Flow, Vol.29, pp.640-653, (2008).
- 6) 'Guidelines for Consequence Analysis of Chemical Releases', Center for Chemical Process Safety of the American Institute of Chemical Engineers, (New York, 1999), ISBN:0-8169-0786-2.