

MA2012-4

**MARINE ACCIDENT  
INVESTIGATION REPORT**

*April 27, 2012*

**Japan Transport Safety Board**

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 | Cargo ship  | SINGAPORE GRACE |
| IMO number           | 9224099   |                 |
| Gross tonnage        | 15,071 tons   |                 |
| Accident type        | fatality of workers   |                 |
| Date and time        | June 13, 2009, about 08:30 (local time, UTC+9 hours)  |                 |
| Location             | Hiroura A wharf, Raw Material Acceptance Wharf,<br>Nikko Smelting & Refining Co., Ltd. , Saganoseki Smelter and Refinery,<br>wharf of port of Saganoseki, Oita City, Oita Prefecture, Japan<br>(approximately 33° 15.4'N 131° 52.1'E) |                 |

March 15, 2012

Adopted by the Japan Transport Safety Board

Chairman Norihiro Goto

Member Tetsuo Yokoyama

Member Kuniaki Shoji

Member Toshiyuki Ishikawa

Member Mina Nemoto

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# 1 PROCESS AND PROGRESS OF THE INVESTIGATION

## 1.1 Summary of the Accident

While the cargo ship “SINGAPORE GRACE” was berthed at the wharf of port of Saganoseki for discharging cargo work of copper sulfide concentrate, at about 08:30 (local time, UTC+9), June 13, 2009, one of the workers fell while descending a ladder in for cargo work at No. 3 cargo hold. Two of the three other workers who went to rescue him also collapsed in the cargo hold.

The all three workers were rescued from No. 3 cargo hold, but later they were confirmed dead.

## 1.2 Outline of the Accident Investigation

### 1.2.1 Set up of the Investigation

The Japan Transport Safety Board (JTSB) appointed an investigator-in-charge, two other investigators, and a regional investigator from the Moji Office participated to this investigation on June 13, 2009.

### 1.2.2 Collection of Evidence

June 13, June 14 and November 28, 2009

—— on-site investigations and interviews

June 15, June 16, June 25, September 10, September 11, October 2, November 26, November 27, November 30, 2009 and January 28, February 5, November 26, 2010

—— interviews

June 19, October 7, October 13, October 28, November 6, November 16, November 17, December 14, 2009 and January 25, March 1, March 18, July 19, October 22, 2010

—— collection of written replies of questionnaires

September 12, 2009 and March 30, March 31, 2010

—— on-site investigations

February 25, May 17, June 9, 2010

—— collection of sample (floatation reagents) for analysis

### 1.2.3 Tests and Research by Other Institutes

For investigation and analysis of the accident, JTSB entrusted investigation of the properties of the copper concentrate in the ship and its influence on the environment (atmosphere) of enclosed spaces such as the cargo hold to Nippon Kaiji Kentei Kyokai (Physical and Chemical Analysis Center).

### 1.2.4 Cooperation towards the Investigation

JTSB requested the Australian Transport Safety Bureau (ATSB) to forward the sample of floatation reagents.

### 1.2.5 Interim Report

On July 30, 2010, the JTSB submitted an interim report to the Minister of Land, Infrastructure, Transport and Tourism based on the facts found up to that date and made it available to the public.

### 1.2.6 Comments from Parties Relevant to the Cause of the Accident

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

### 1.2.7 Comments from Flag State/Cooperating States

#### (1) Flag State

Comments were invited from the Government of the Hong Kong Special Administrative Region, People's Republic of China (the Maritime Accident Investigation Section, the Maritime Department).

#### (2) Cooperating State

Comments were invited from the ATSB.

## 2 FACTUAL INFORMATION

### 2.1 Events Leading to the Accident

According to the statements of the master, chief officer, third officer and three of the deck ratings of SINGAPORE GRACE (hereinafter referred to as "the ship" except chapters 5 and 6), two executives, one manager and five workers of Nissho Koun Co., Ltd. (hereinafter referred to as "the stevedoring company" except chapter 5), three members of Nikko Smelting & Refining Co., Ltd. (hereinafter referred to as "the smelter" except chapters 5 and 6) and two members of Nippon Marine Co., Ltd. (hereinafter referred to as "the agent"), questionnaires received, the cargo work logbook, reports at loading port (hereinafter referred to as "the place of loading"), and others (charter party, logbook, crew list, cargo plan, communication records, etc), events leading up to the accident were as follows.

All times referred to this report are local times (Japan:UTC+9, Papua New Guinea: UTC+8).

#### 2.1.1 Navigation History of the ship

##### (1) Process for Transport of Copper Sulfide Concentrates (hereinafter referred to as "copper concentrates" except chapters 5 to 7) by the Ship

On May 15, 2009, the master received the voyage instructions from the charterer that instructed him to load 21,600 metric tons (mt)<sup>1</sup> of copper concentrate<sup>2</sup> in Port Moresby Harbour, Independent State of Papua New Guinea and unload 10,800 mt in port of Saganoseki, Japan and port of Onsan, Republic of Korea, respectively.

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<sup>1</sup> "Metric Ton (mt, MT)" is a unit of mass defined based on the kilo-gram (kg). It defines 1 metric ton as 1000 kilo-grams (1 mega-gram).

<sup>2</sup> "Copper concentrates" are refined ores in which the valuable components have been enriched by eliminating the bulk of waste material and in general the particle size is small. The methods of processing ore are floatation, gravity separation, manual separation as well as others. Floatation is the standard method for copper concentrate.



On May 19, the master notified the outline of the voyage to the management company and inquired about the properties of copper concentrates and important notes on carriage safety.

The management company instructed the master to request a Material Safety Data Sheet<sup>3</sup> (hereinafter referred to as “MSDS”) from the shipper<sup>4</sup> Ok Tedi Mining Limited (hereinafter referred to as “the shipper” except chapter 6) and refer to the Code of Safety Practice for Solid Bulk Cargo<sup>5</sup> (hereinafter referred to as “BC CODE”) , and moreover, instructed the following:

- [1] Ensure that seams of hatch covers<sup>6</sup> are watertight.
- [2] Seal seams of hatch covers with tapes, etc. if necessary.
- [3] Keep a careful check to ensure that cargoes are not liquefied.
- [4] The cargo holds should not be ventilated.

The master made the unloading plans for cargo holds No. 1 and No. 3 to be emptied in port of Saganoseki and cargo holds No. 2 and No. 4 to be emptied in port of Onsan.

## (2) Hold Conditions before Loading

During the voyage to Port Moresby Harbour, in preparation for loading at port, the crew of the ship swept all holds (No. 1 ~ No. 4), washed them with sea water and then fresh water, and then dried them before cleaning the inside of the bilge well<sup>7</sup> near the both sides of the rear bulkhead of the hold and attached burlap<sup>8</sup> to avoid possible mixing with any remnants of the iron ore carried on the previous voyage.

## (3) Conditions of Loading Cargoes

The ship, with a master and twenty one (21) crew members, arrived at the Port Moresby Harbour in ballast condition and moored alongside the copper concentrates storage vessel “ERAWAN.”

After the hold-inspection and ensuring good condition by a surveyor<sup>9</sup>, the ship commenced loading at 23:18, May 28.

ERAWAN’s copper concentrates were loaded into the ship’s cargo holds (in the following order) No. 4, No. 2, No. 3, No. 1 by her two cranes before moving the other cargo into the

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<sup>3</sup> “Material Safety Data Sheet” is the document that has necessary information on handling chemical substances or raw materials containing chemical substances safely.

<sup>4</sup> “Shipper” is the owner and consignor of cargo and also means the exporter in oversea transportation.

<sup>5</sup> “Code of Safe Practice for Solid Bulk Cargo” is a non-binding code adopted by International Maritime Organization (IMO) that provides requirements for transportation of ore concentrated by floating and other minute cargo that may be liquefied during voyage, bulk solid cargo of chemical hazard (dangerous goods), MHB (Material Hazardous only in Bulk) and materials that shift with ease by hull inclination. On January 1, 2011, the code became mandatory for enhancement of safety in marine transport of bulk cargo as “The International Maritime Solid Bulk Cargoes Code ; IMSBC CODE).

<sup>6</sup> “Hatch Cover” is a cover made of steel that covers the opening to load/unload cargo into/out of hold.

<sup>7</sup> “Bilge Well (near the both sides of the rear bulkhead of the hold)” is a compartment to collect the water in the hold (hold bilge : bilge water, moisture from cargo, etc.).

<sup>8</sup> “Burlap” is hemp cloth placed over the cover of the bilge well to avoid clogging of bilge intake by cargo powder entering from the bilge well cover.

<sup>9</sup> “Surveyor” is a person who checks the stowage condition of cargo, assesses cargo damage (decay, sea water damage, etc.), surveys draft measuring to determine the amount of loaded/discharge cargo by calculation from draft as well as other duties.

ship's cargo holds according to the planned departure conditions (draft, trim, hull strength).

Weather during the loading operations was either fine or cloudy without rain and the loaded copper concentrates were not wet.

On May 31, loading operations cargo work finished with 21,600 mt of copper concentrates. The following day at 11:39 June 1, the ship departed Port Moresby Harbour for port of Saganoseki, as the first calling port, nearly full load condition.

(4) Sea Conditions Encountered during the Voyage

The ship navigated using weather-adjusted Optimum Ship Routing Service<sup>10</sup>.

Just after departure, the ship encountered continuous windy conditions with wind force 6-7, ESE. To reduce pitching and rolling, the ship adjusted speed and course to face the swells almost directly head on.

The conditions when the deck was exposed to splash were as follows.

At about 19:25, on June 1, when the ship proceeded in wind force 7, ESE, the upper deck was constantly washed by waves and exposed to splash.

During the voyage, her upper deck had been washed by waves and exposed to splash continuously until 04:00, on June 3.

From 04:00 to 08:00, June 8, forecastle deck, upper deck and the hatch covers of cargo holds of No. 1-3 were sometimes washed by waves and exposed to splash.

From 08:00 to 12:00, June 11, the port side of the forecastle deck and the hatch cover of cargo hold No. 1 were sometimes exposed to splash.

From 12:00 to 16:00, June 11, the starboard side of the forecastle and upper deck were sometimes exposed to splash.

From 20:00 to 24:00, June 11, the port side of the forecastle deck, the vicinity of cargo holds No. 1 and No. 2 were sometimes exposed to splash.

Between 04:00 and 08:00, June 12, the port side of the upper deck and the hatch cover of No. 1 cargo hold were sometimes washed by waves and exposed to splash.

(5) Condition of Arrival at port of Saganoseki

At 15:36, on June 12, the hours propelling<sup>11</sup> ended and the ship was put in stand-by engine<sup>12</sup>, at 17:25 a pilot boarded; at 19:06 the ship dropped anchors in quarantine anchorage and stood-by.

At about 06:50, on the following day, June 13, a pilot boarded, weighed anchors and proceeded to Raw Material Acceptance Wharf (hereinafter referred to as "private wharf" except chapters 5 and 6) of the smelter; at 07:30, the first mooring line was sent to private wharf; at 07:48 mooring operation was finished.

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<sup>10</sup> "Optimum Ship Routing Service" is a business that selects an optimum route based on forecasted weather, sea conditions (wave, wind on sea, etc.) and movement of ship information and provides it to the ship, management company, etc.

<sup>11</sup> "Hours Propelling" is usually the time between starting of proceeding for destination after departure and stand-by engine or initial change of engine motion at the destination. Definition depends on shipping company or operation contract.

<sup>12</sup> "Stand-by engine" means to let main engine be controllable (stopping, running ahead/astern, etc.) when desired.

## (6) Conditions at Time of Discharging Preparations

After mooring operation, about a little after 07:50, the chief officer read out the draft of the ship with the surveyor then, by the previous agreement of Discharging Plan with the foreman<sup>13</sup>, he ordered the crew to open the hatch covers of cargo holds No. 1 and No. 3 which were scheduled to discharge cargoes at this port.

The hatch cover of cargo hold No. 1 was opened first and 3-5 minutes later, at about 08:05, the hatch cover of cargo hold No. 3 was opened.

The hatch covers had been kept closed from the completion of loading operation in Port Moresby Harbour to arrival. When initially opened, the back of the hatch cover of cargo hold No. 1 had no dew condensation water but from the back of the hatch cover of cargo hold No. 3 a large flow of dew condensation water poured down.

There was no sea water damage<sup>14</sup> of cargo in cargoes holds No. 1 and No. 3.

### 2.1.2 Condition of Unloading Operation

#### (1) Discharging Procedure

The stevedoring company intended to discharge cargo in following manner.

- [1] Foreman makes crew of the ship open hatch covers.
- [2] Foreman measures Oxygen (hereinafter referred to as "O<sub>2</sub>") concentration in the holds.
- [3] Foreman opens entrance hatches of holds to be discharged and closes other hatches.
- [4] Foreman sets notice boards on entrance hatch. (See 2.1.2(4))
- [5] The ship's crane hoists the backhoe (heavy vehicle) and carries it into hold.
- [6] Heavy vehicle gathers cargo (copper concentrates) in the center of hold.
- [7] Grab bucket<sup>15</sup> of the on-shore crane grabs cargo and drops it into hopper.
- [8] Repeat [6] and [7] as necessary.
- [9] Discharge the remaining cargo that the grab bucket cannot grab and collect using scoops and brooms.

(See following pictures and schematic, "Discharging Condition of Another Ship", "Heavy Vehicle" "Arrangement of Shore Crane (excerpt)" and "Grab Bucket and Hopper")

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<sup>13</sup> "The foreman" is a person who discusses the time of arrival/departure and operation schedule with the shipping company, agent and shipper, and cargo work procedure, safety operations, etc. with chief officer, as well as supervising cargo work.

<sup>14</sup> "Sea water damage" is cargo damage resulting from sea water that entered the cargo hold. If recognized as cargo damage, processing cost will be claimed on insurance or other measures will be taken.

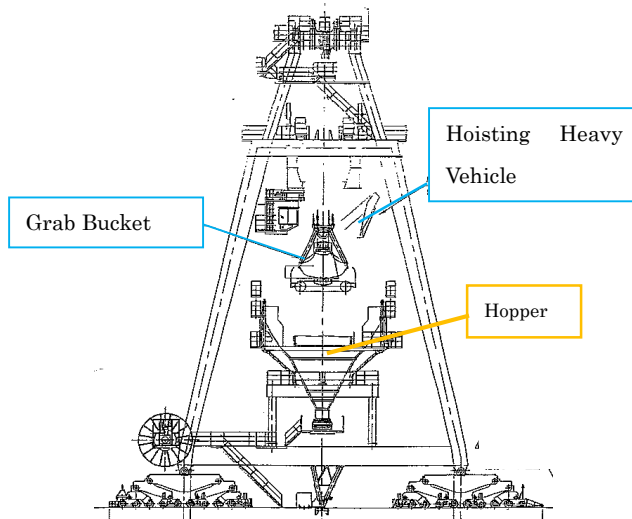
<sup>15</sup> "Grab Bucket" is equipment attached to end of crane arm that is able to open and close like clam to grab bulk cargo such as coal, ore and so on in cargo work.



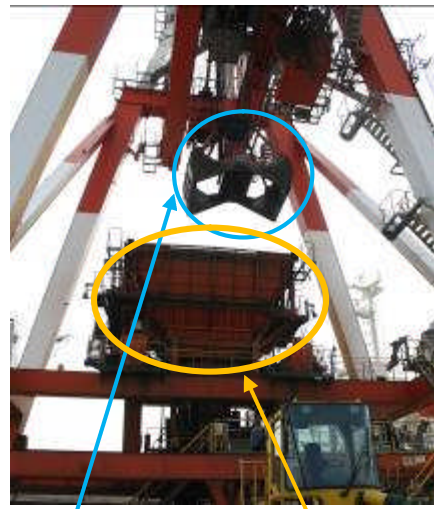
“Discharging Condition of Another Ship”



“Heavy Vehicle”



“Arrangement of Shore Crane (excerpt)”



“Grab Bucket and Hopper”

## (2) Members of Operation Team

Seven workers of the stevedoring company set up an operation team (hereinafter referred to as “the team”) from 07:00 to 15:00 to discharge cargo from the ship.

- [1] The foreman (victim, supervisor of unloading operation)
- [2] Driver of heavy vehicle in cargo hold No. 3 (victim, hereinafter referred to as “Driver B”)
- [3] Senior operator of on-shore crane (victim, hereinafter referred to as “Operator C”)
- [4] Ship crane operator (hereinafter referred to as “Operator D”)
- [5] Driver of heavy vehicle in hold No. 1 (hereinafter referred to as “Driver E”)
- [6] Operator of on-shore crane (hereinafter referred to as “Operator F”)
- [7] Worker in charge of the heavy vehicle’s slinging work<sup>16</sup> etc. (hereinafter referred to as “Worker G”)

## (3) Meeting for Unloading Operation

At about 07:00 the team had a meeting in the cargo handling office near the private wharf.

<sup>16</sup> “Sling Work” is work that connects a wire sling (worked into an “eye” on both ends) to the load (such as the heavy vehicle) and the crane wire. For a heavy vehicle, generally its eye plate and wire sling are connected by shackle.

The foreman assigned works to each member and explained the discharging. And all workers confirmed to be aware of the movement of the heavy vehicle and cranes, to do sling work carefully, communicate accurately and not to work under the grab bucket.

(4) Mooring Operation and Opening the Hatch Covers

About 07:10-07:30, before discharging, the team changed the grab bucket of the on-shore crane to one of high capacity (900 ton/hour, bridge type un-loader) and about 07:30-07:50, engaged in the mooring of the ship.

About 07:50-08:10, the team, with the exception of the foreman, waited near the cargo handling office for the hatch to be opened.

At little past 07:50, the foreman boarded the ship and the chief officer ordered crew to open the hatch covers of cargo holds No. 1 and No. 3.

There were notice boards placed on cargo holds No. 1 and No. 3 entrance hatches' (opened) that indicated “*Working Now, stevedores are permitted to enter.*” (hereinafter referred to as “entrance permitted notice board”) and on cargo holds No. 2 and No. 4 (closed) that indicated “*Keep out, stevedores are not permitted to enter.*”

(See following pictures, “Entrance Hatch” and “Notice Boards”)



“Entrance Hatch”



“Notice Boards”



(Left: entrance permitted notice board)

(5) Measuring of O<sub>2</sub> Concentration before Cargo Operation

Foreman went back to the office and entered the O<sub>2</sub> concentration measured data before cargo operation in O<sub>2</sub> concentration measuring record book (hereinafter referred to as “record book ”)

Data entered in the record book was as follows,

[1] cargo hold No. 1

O<sub>2</sub> concentration of near the walls in lower level of the hatch coaming<sup>17</sup>'s four corners in hold.

O<sub>2</sub> concentration in upper and lower points of fore entrance hatch.

O<sub>2</sub> concentration in lower point of aft entrance hatch. (Seven points in total)

<sup>17</sup> “Hatch Coaming” is vertical steel wall surrounding the hatch to prevent sea water from entering and supports the weight of the hatch cover. Additionally the hatch is an opening for carrying cargo into or out of the hold.

[2] cargo hold No. 3

O<sub>2</sub> concentration of near the walls in lower level of the hatch coaming's four corners in hold.

O<sub>2</sub> concentration in upper and lower points of fore entrance hatch.

O<sub>2</sub> concentration in lower point of aft entrance hatch. (Seven points in total)

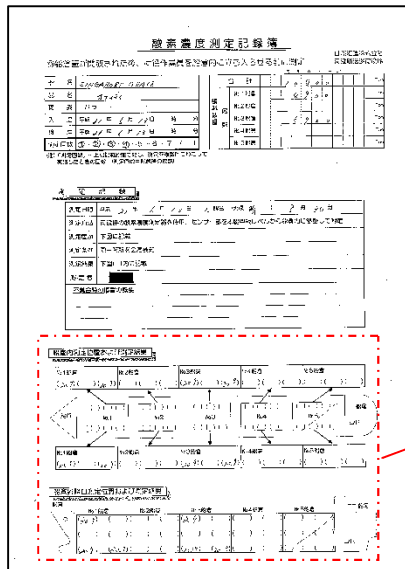
[3] The Measured O<sub>2</sub> concentration data were 20.9% in all points (equal to the O<sub>2</sub> concentration of ordinary air)

[4] Date and time of measuring : 08:30, June 13, 2009

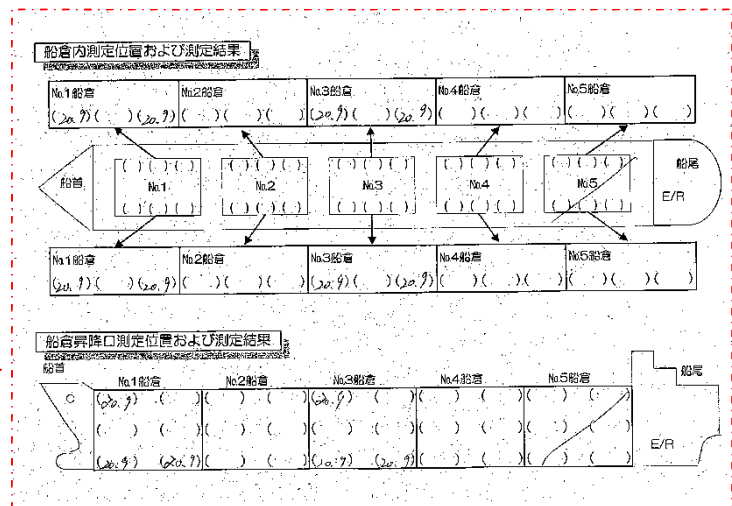
[5] Signature of measurer (foreman)

However workers had measured O<sub>2</sub> concentration at other points instead of entrance-hatch due to difficulties of measuring by change of structure beside with increased size of vessels (adoption of slanting ladder, landing and others) without the stevedoring company's noticing it. The stevedoring company perceived it after the accident.

(See following "Copy of Record Book" and "Record Book (excerpt)")



"Copy of Record Book"



"Record Book (enlarged)"

#### (6) Conditions Leading to Primary Accident

At about 08:05, Operator D boarded the ship according to the foreman's instructions and was told that it was possible to lower the heavy vehicle onto the ship, and then he got in the cockpit of the ship's crane No. 2 (Second crane from bow, hereinafter referred to as "crane No. 1-No. 4 counting from the from bow") and waited for the sling work that connects wire from the crane's boom<sup>18</sup> end, swung to the wharf, to the heavy vehicle with a shackle to be finished.

Driver B boarded in advance and stood-by on the upper deck near cargo hold No. 3.

<sup>18</sup> "Boom" is the arm or pole of a crane, etc. On the far end hoisting equipment is attached to allow a load to be moved in both horizontal and vertical directions.

The decision of the meeting in the cargo handling office was to open the hatch cover of cargo hold No. 3 first and then open the hatch cover of cargo hold No. 1 in turn and lower the heavy vehicle into the hold at the same time.

Driver E stood-by on the wharf to board after the lowering of the heavy vehicle into cargo hold No. 3.

Driver E, boarded and entered the cargo hold No. 1 through the entrance hatch, because contrary to the decision, cargo hold No. 1's hatch cover was opened first and it was possible to lower the heavy vehicle into hold by crane No. 2.

At about 08:10-08:15, Driver E got into the heavy vehicle in the cargo hold after disconnecting the sling and proceeded to gather the cargo loaded at forward area of the hold in center area of the hold.

At about 08:15-08:20, Operator D got out of No. 2 crane and got in the cockpit of crane No. 3 and waited for the crane wire to be connected to the shackle of another heavy vehicle on the wharf.

At this time, four workers including Operator C and F were engaged in sling work around the heavy vehicle on the wharf.

Worker D received instructions by walkie-talkie from driver B, who was waiting on the upper deck for the heavy vehicle to be lowered, that he would not go in the hold because of the strong odor of the cargo but to go ahead and put the heavy vehicle in.

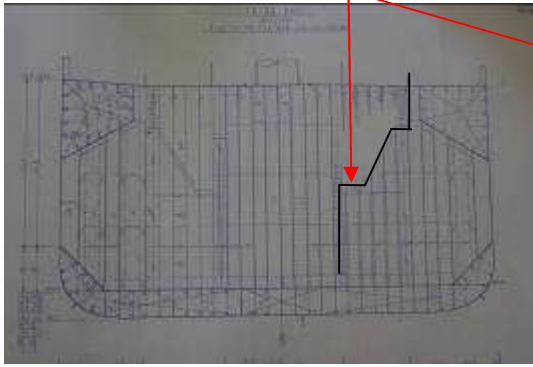
At about 08:25, when Operator D was lowering heavy vehicle into cargo hold No. 3 by crane No. 3, he witnessed Driver B going down the slanting ladder leading from the entrance hatch to the bottom of the hold although he was supposed to stand-by on the upper deck.

Driver B entered entrance hatch(0.8m length×0.8m width) located on the upper deck, aft-left side of cargo hold No. 3 and went down a straight ladder (about 2.5m length), landing, and slanting ladder (about 4.7m passage length, about 4m vertical), and at about 08:30, when he moved to the second landing, he fell feet-first, landed on his behind, and remained motionless.

(See following pictures "Section of Hold (excerpt)" and "Slanting Ladder on Bulkhead of Cargo Hold No. 3")



## Second Landing



“Section of Hold (excerpt)”



“Slanting Ladder on Aft-Bulkhead of Cargo Hold No. 3”

Operator D put the heavy vehicle down on the cargo, lashed the control lever, shut down the power of crane No. 3 so it would not move, and notified the office by walkie-talkie that Driver B had collapsed.

Operator D notified Operator C through the cockpit window of crane No. 3 that B had collapsed, Operator D then got off the crane and ran to the entrance hatch of cargo hold No. 3.

Operator C and F, who were waiting under the shore crane, went to the office after hearing that driver B had fallen.

### (7) Conditions Leading to Secondary Accident

Staff from the agent involved (hereinafter referred to as “staff of the agent”) boarded at about 08:00, finished clearance procedures at about 08:30, disembarked and entered name of the ship, ship’s registry, time of arrival, etc. on the white board in the cargo handling office.

While discussing the completion time of discharging and the time of departure with the foreman, Operators C and F rushed into the office and reported that Driver B collapsed in cargo hold No. 3.

The foreman and Operator C rushed to the scene, operator F quickly followed them to the ship after taking out the Self-contained Breathing Apparatus (SCBA)<sup>19</sup> equipped in the office. Additionally the staff of the agent followed them.

The three workers arrived at the hatch of cargo hold No. 3 and the foreman and Operator C in turn entered the cargo hold through the entrance hatch leaving the SCBA on the upper deck.

Because the foreman and Operator C entered the cargo hold without SCBA, Operator F followed them to prevent them from going down.

When he climbed halfway down the slanting ladder and felt breathless he saw a signal from Operator C to “Back.”

<sup>19</sup> “Self-contained Breathing Apparatus (SCBA)” is protective equipment for breathing that reduces the pressure of compressed air in a tank and supplies it to the equipper to prevent the intake of gas in a harmful environment. It consists of a mask, regulator (including hose, alarm, pressure indicator, etc. ), tank and a harness. Refer to 2.13.2.



Operator C and F then returned back to the upper deck from halfway down the ladder.

When the staff of the agent and Operator D arrived at cargo hold No. 3, they did not see the foreman and asked where he was, but then recognized that the foreman was the one of the two men collapsed in the cargo hold.

On the way to the cargo handling office to call ambulance and rescue team, Operator D met the older worker and he reported that Driver B and the foreman had collapsed in the cargo hold. The older worker asked a guard in the guardroom of the smelter to call ambulance, and then Operator D back to the ship.

(8) Conditions Leading to Tertiary Accident

When Operators C and F were catching their breath, crew of the ship provided them with gas masks<sup>20</sup>. On the canister attached to the gas mask “INORGANIC GASES & VAPOROUS” was written.

(See following pictures of “Gas Mask and Canister”, and “Canister”)



“Gas Mask and Canister”



“Canister”

Operator C equipped with a gas mask and, carrying the SCBA, headed for the hatch of cargo hold No. 3.

The chief officer, who was calculating draft with a surveyor in the deck office, heard about the unusual event from the third officer and went to hatch of cargo hold No. 3.

The chief officer advised Operators C and F, who had equipped with the gas masks and were going to enter the cargo hold No. 3, that they should equip SCBA and that going into the hold with only gas masks on is dangerous.

Operator C equipped with the gas mask, carried the SCBA on his back and entered cargo hold No. 3 through the hatch again.

At the time, Operator F could not understand the chief officer’s advice due to spoken by English, and the mask received from the ship was bigger than the gas mask, so he thought the mask might an oxygen supply mask .

Because Operator F had a idea that the mask made him safe and followed Operator C into the hold.

When he climbed halfway down the slanting ladder he felt breathless and when he arrived at the second landing from entrance he felt faint and that it was dangerous to

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<sup>20</sup> “Gas Mask” eliminates poisonous gas in air by forcing it through a filter (canister) to detoxify it. It is unusable when the concentration of poisonous gas is too high or there is a lack of oxygen. There are various kinds of canisters – i.e. for organic gas, halogen, hydrocyanic acid, hydrogen sulfide, ammonia, etc.

continue, he tried to turn back to upper deck and used his all strength to crawl up the ladder.

When operator F arrived near the hatch, ship's crew rescued him by pulling him up to upper deck by his arms.

Operator C began to climb up the final ladder but fell into the hold after climbing one or two rungs.

(9) Actions Taken to Prevent Subsequent Accidents

The third officer, who was on his way to get SCBA, informed the master about the situation that occurred in cargo hold No. 3 as the third officer passed the master on the upper deck near the crews quarters.

The master understood the situation and instructed the third officer to prepare stretchers and Emergency Escape Breathing Devices (EEBD)<sup>21</sup> as well.

And third officer and staff of the agent instructed the crew to prepare a fan for ventilate cargo hold No. 3 from the entrance hatch.

The master went to cargo hold No. 3 and discussed measures to rescue the fallen workers in the hold with the chief officer.

The third officer began to equip with the SCBA and proposed to the master that he, equipped with it, would enter the hold to rescue the workers.

When the master saw workers of the stevedoring company going to enter the hold, he asked the staff of the agent to stop them.

The staff of the agent also thought it dangerous to enter cargo hold, and stopped workers of the stevedoring company from entering cargo hold No. 3.

(10) O<sub>2</sub> Concentration Measured after Accident

Operator D knew that Operator C had also collapsed in the cargo hold and he went back to the cargo handling office and reported it to his boss.

At about 08:40, Operator D was instructed by his boss to measure the O<sub>2</sub> concentration in the cargo hold and went to the ship with an O<sub>2</sub> concentration meter.

Because it was the first time operator D had used an O<sub>2</sub> concentration meter, when he met a senior worker on the way to the ship, he asked for assistance to set the meter can be measured by just putting it in the cargo hold.

At about 08:50, Operator D put the sensor of the O<sub>2</sub> concentration meter in the cargo hold from the aft-left-side of cargo hold No. 3's hatch coaming. The moment he lowered it 4-5m, the sensor's alarm began to sound, warning that O<sub>2</sub> concentration had reduced to 18%. As he continued to lower the sensor, the O<sub>2</sub> concentration reduced. At about 10cm above the cargo surface where the foreman, Driver B and Operator C had collapsed, (where below the second landing) the O<sub>2</sub> concentration was about 1.5-2%.

Operator D reported the measured O<sub>2</sub> concentration to his boss. And then Operator D went to the cockpit of crane No. 3, because he was instructed to remove the heavy vehicle from the cargo hold so it did not disturb the rescue operation.

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<sup>21</sup> "Emergency Escape Breathing Device (EEBD)" is a breathing apparatus consisting of a tank which supplies compressed oxygen or air and a face piece which prevents the wearer from breathing in harmful gas.

It should be noted that the horizontal length from the aft end of the left side of the hatch coaming to the point below the second landing was 5-6m (as indicated in “Section of Hold (excerpt)” (2.1.6. (6))).

(11) Rescue Work

Staff of the agent contacted the guard in the smelter guard office by mobile phone to arrange an ambulance and rescue team.

Operator D returned to the cockpit of crane No. 3 and moved the heavy vehicle back to the wharf and waited for it to be disconnected the sling of the crane by another worker.

Then, at the request of the rescue team that had just arrived, operator D used crane No. 3 to lower the rescue team into cargo hold No. 3 in a cage(1.3m length, 2m width, 1.5m depth) normally used for carrying materials and equipment.

2.1.3 Rescue Operation Information

According to a written reply from the Fire Chief of Oita-city’s East Fire Station and the statements of rescue team members, the main details were as follows.

(1) Rescue Conditions from Cargo Hold

[1] The rescue team began by confirming the condition of the scene - such as the hatch entrance, number of victims, etc.

[2] Although they could not determine the cause of the three victims collapsing, because there were multiple victims the team first suspected gas-poisoning and measured the concentration of oxygen, hydrogen sulfide and flammable gas.

[3] O<sub>2</sub> concentration measured on the upper deck near the cargo hold was 19.3%.

[4] The team considered the risk that O<sub>2</sub> concentration in the bottom of cargo hold was lower than the upper deck, and they lowered several opened compressed air tanks by rope to supply fresh air to the bottom of the cargo hold where the victims had collapsed.

[5] Two team members (with three air tanks) equipped with air breathing apparatus and got in the cage for carrying material and equipment, and the ship’s crane hoisted it down into the cargo hold.

[6] The members put victims into the cage in the cargo hold.

[7] Because of the difficulty of moving in sandy cargo, when they put the two victims into the cage, the air capacity in the equipped tanks reduced to the lower limits for action, so they went back to the wharf in the cage and other members rescued the remaining one victim.

(2) Explore the Rescue Method

Because of the following conditions, they adopted the entrance method by using the crane of the ship and a cage.

[1] Entrance through hatch

They considered that it was difficult for the rescue team members equipped with air breathing apparatus to perform the rescue using the slanting and vertical ladders.

[2] Entrance using three-partite ladder

Because the full length of a three-partite ladder is about 8m it could not reach the bottom of the cargo hold and the team could not rescue the victims.

[3] Entrance using rescue rope

Considering the time of rescue and risk of secondary accident involving the rescue team members, it was not an appropriate method.

[4] Entrance using crane of the ship and cage

Because they recognized the victims were oxygen deficiency, it was necessary to rescue them in short amount of time. They judged that using the cage they could rescue two or more victims at one time and the risk of a secondary accident was reduced.

(3) Equipment Used by the Rescue Team Members

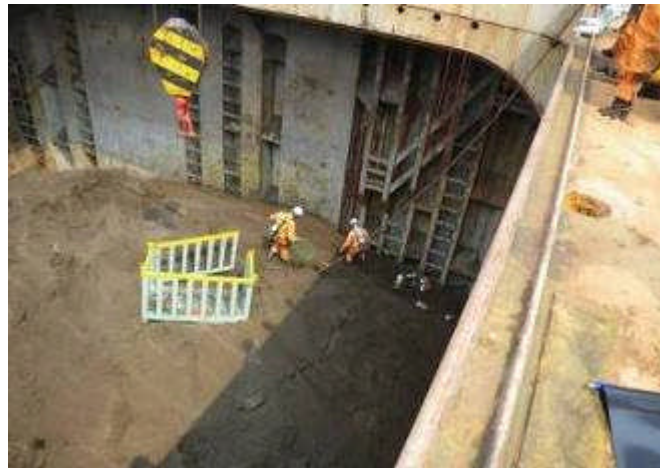
The rescue team member equipped with pressure demand type air breathing apparatus<sup>22</sup>. The following formula indicates usable time (h).

$$h = \text{capacity of bottle (}\ell\text{)} \times \{ \text{tank air pressure (15MPa)} - 3\text{MPa} \} / \text{consumption (}\ell\text{/minute)}$$

The alarm pressure setting<sup>23</sup> is set to 3MPa.

Consumption per minute of air is 40 ( $\ell$ /min.) for light work, 60 ( $\ell$ /min.) for medium work and 80 ( $\ell$ /min.) for heavy work. The actions of the rescue team are always regarded as heavy work, hence the calculated usable time is 12 minutes.

(See following picture “Rescue Conditions”)



“Rescue Conditions”

#### 2.1.4 Information Regarding the Accident Report and Rescue Measures

According to a written reply from the Fire Chief of Oita-city’s East Fire Station and the statements of rescue team members, the main details were as follows.

(1) Report Time

The time receipt of the call to 119 (emergency phone number) from the guard was 08:50:34, finishing at 08:53:59.

(2) Time of departure of the ambulance and arrival at the scene of the accident were as follows.

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<sup>22</sup> “Pressure Demand Type Air Breathing Apparatus” is a breathing apparatus that supplies higher pressure air than outside into the mask to prevent inhalation of oxygen deprived air and poisonous gases.

<sup>23</sup> “Alarm Pressure Setting” is setting the apparatus’ alarm to sound when a certain amount of air is remaining in the tank.

- [1] Oozai Paramedic Team                      Departure: 08:52    Arrival: 09:07
- [2] East Station Rescue Team                Departure: 08:54    Arrival: 09:20
- [3] Saganoseki Paramedic Team             Departure: 09:08    Arrival: 09:23

(3) The times the victims were loaded into an ambulance and carried into medical institutions were as follows. Victims were taken to three different medical institutions in Oita city.

- [1] Driver B                                      Loading Time: 09:39    Transporting in Time: 09:46
- [2] Foreman                                      Loading Time: 09:44    Transporting in Time: 10:06
- [3] Operator C                                  Loading Time: 09:49    Transporting in Time: 10:05

(4) Condition of victims and medical measures taken in ambulance were as follows.

[1] Driver B

| Time<br>Condition<br>Measures         | 09:39                                   | 09:42                   | 09:46                   |
|---------------------------------------|---|-------------------------|-------------------------|
| JCS <sup>24</sup> / GCS <sup>25</sup> | 300/3                                   | 300/3                   | 300/3                   |
| Breathing/ Pulse                      | 0/0                                     | 0/0                     | 0/0                     |
| Pupil                                 | Left, Right :<br>Dilation <sup>26</sup> | Left, Right :<br>5mm(-) | Left, Right :<br>5mm(-) |
| O <sup>2</sup> Inhalation ℓ/min       | 10                                      | 10                      | 10                      |
| Heart-lung Massage                    | Implemented                             | Implemented             | Implemented             |

[2] Foreman

| Time<br>Condition<br>Measures   | 09:44                     | 09:46                     | 09:50                     | 10:06                     |
|---------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| JCS / GCS                       | 300/3                     | 300/3                     | 300/3                     | 300/3                     |
| Breathing/ Pulse                | 0/0                       | 0/0                       | 0/0                       | 0/0                       |
| Electro Cardiogram              | —                         | Cardiac<br>Standstill     | Cardiac<br>Standstill     | Cardiac<br>Standstill     |
| Pupil                           | Left, Right :<br>Dilation | Left, Right :<br>Dilation | Left, Right :<br>Dilation | Left, Right :<br>Dilation |
| O <sup>2</sup> Inhalation ℓ/min | 10                        | 10                        | 10                        | 10                        |
| Blood Oxygenation<br>Level      | —                         | —                         | 74%                       | 97%                       |
| Heart-lung Massage              | Implemented               | Implemented               | Implemented               | Implemented               |
| Nasal Airway <sup>27</sup>      | —                         | —                         | 7 mm                      | 7 mm                      |

<sup>24</sup> “JCS: Japan Coma Scale” is a classification of the depth of the disturbance of consciousness used mainly in Japan. JCS300 indicates the victim does not respond to pain stimulation.

<sup>25</sup> “GCS (Glasgow Coma Scale)” is a classification for the assessment of the disturbance of consciousness used worldwide. Full (15) points for normal condition, 3 points for deep coma.

<sup>26</sup> “Dilation (of pupil) Left and Right” indicates that the diameter of left and right pupil is 5mm or more. Normal diameter is 2.5~4mm.

<sup>27</sup> “Nasal Airway” is an instrument inserted through the nose to maintain an airway.

[3] Operator C

| Time<br>Condition<br>Measures   | 09:49       | 09:51                 | 10:00                     | 10:05                     |
|---------------------------------|-------------|-----------------------|---------------------------|---------------------------|
| JCS / GCS                       | 300/3       | 300/3                 | 300/3                     | 300/3                     |
| Breathing/ Pulse                | 0/0         | 0/0                   | 0/0                       | 0/0                       |
| Electro Cardiogram              | —           | Cardiac<br>Standstill | Cardiac<br>Standstill     | Cardiac<br>Standstill     |
| Pupil                           | —           | Left, Right :<br>5mm  | —                         | —                         |
| O <sup>2</sup> Inhalation ℓ/min | 10          | 10                    | Artificial<br>Respiration | Artificial<br>Respiration |
| Heart-lung Massage              | Implemented | Implemented           | Implemented               | Implemented               |
| LT <sup>28</sup>                | —           | —                     | No. 4                     | No. 4                     |
| Reserve Vein Road <sup>29</sup> | —           | —                     | —                         | 20G                       |
| Administration<br>of Adrenaline | —           | —                     | —                         | Three Times               |

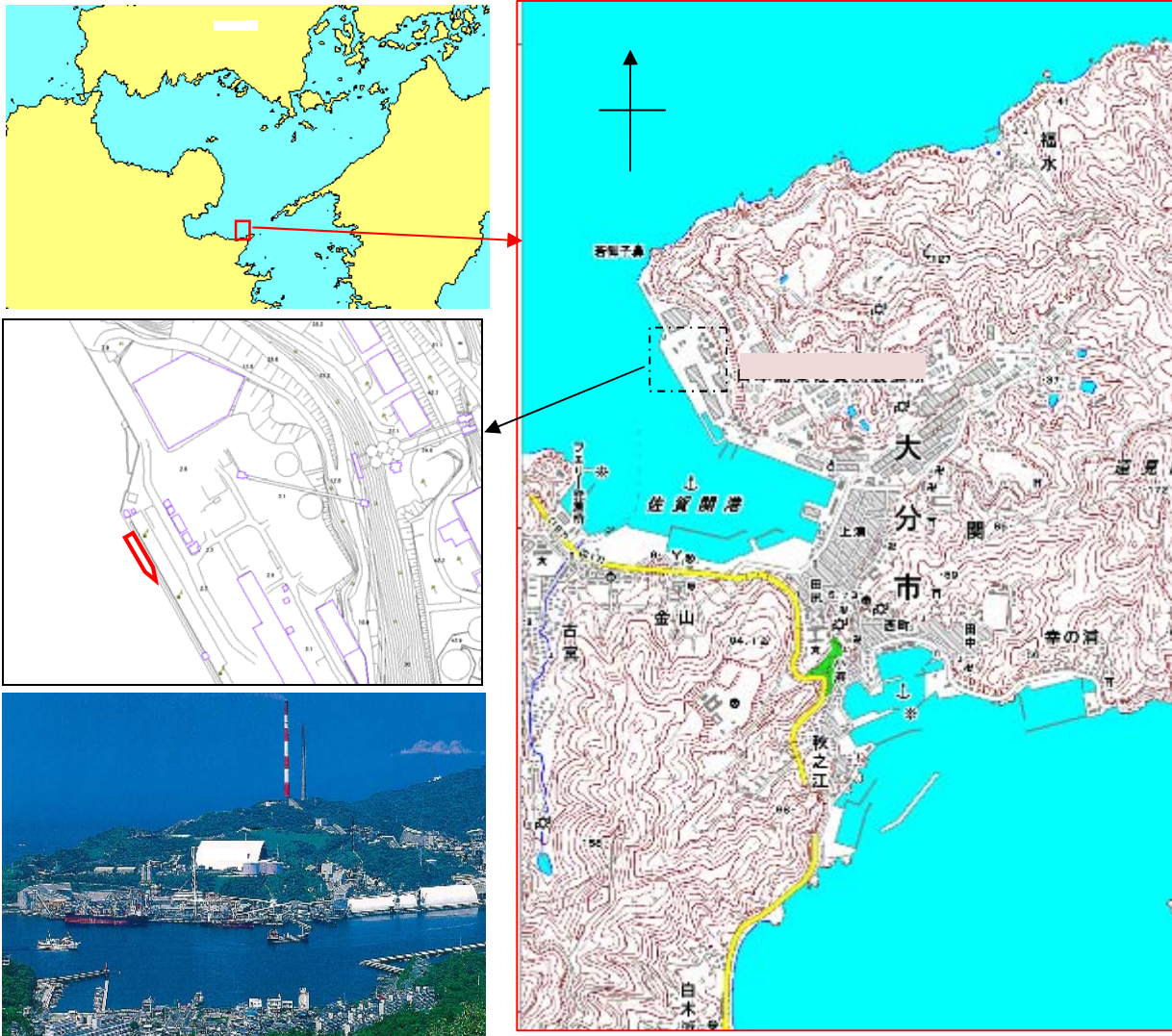
The date and time of the occurrence of the primary accident were at about 08:30, on June 13, 2009 and located inside of cargo hold No. 3 of the ship berthed at the private wharf of port of Saganoseki.

Further, the second and tertiary accidents occurred at between 08:30 and 08:40 in the same location as the primary accident.

(See following maps and picture “Map of Seto Inland Sea (Setonaikai) (excerpt)” “Map of Saganoseki, Oita Prefecture” “The Schematic of Mooring Position of the Ship” “The Smelter (excerpt from pamphlet)”

<sup>28</sup> “LT” is a Laryngeal Tube, which is an apparatus to keep artificial respiration for victims. It is used to prevent to enter the air to esophageal and help to enter the air to respiratory tract.

<sup>29</sup> “Reserve Vein Road” is measures to set a needle or tube in the vein and keep transfusion road.



Left upper “Map of Seto Inland Sea(Setonaikai) (excerpt)”

Left middle “The Schematic of Mooring Position of the Ship”

Left lower “The Smelter (excerpt from pamphlet)”

Right “Map of Saganoseki, Oita Prefecture”

## 2.2 Information Regarding the Death of the Victims

### 2.2.1 Condition in Medical Institute

According to the written reply from the medical institutes, the conditions of the victims in medical institutes where they were taken were as follows.

(1) Driver B

After arrival, various measures to revive the victim were taken but at 10:30, on June 13, his death was confirmed.

(2) Foreman

After arrival, various measures to revive the victim were taken but at 10:59, on June 13, his death was confirmed.

(3) Operator C

After arrival, various measures to revive the victim were taken but at 11:10, on June 13, his death was confirmed.



### 2.2.2 Information Regarding on Cause of Death

(1) The causes of death of workers stated in the death certificates were as follows.

- [1] Driver B Acute suffocation (suspected)
- [2] Foreman Suffocation by lack of O<sub>2</sub>
- [3] Operator C Brain anoxia

(2) Blood Gas Analysis<sup>30</sup> Value

According to the written reply from the medical institutes and the professor of the medical department who perform a judicial autopsy on Driver B were as follows.

|            | Carbon Dioxide (mmHg) | Oxygen (mmHg) |
|------------|-----------------------|---------------|
| Normal     | 35.0~45.0             | 75.0~100.0    |
| Driver B   | 60.1                  | 72.6          |
| Foreman    | 137.6                 | 51.1          |
| Operator C | 171.4                 | 18.5          |

(3) According to the statement of the doctor of the medical institute where driver B was taken, the main details were as follows.

- [1] There was no indication that the cause of death of driver B was anoxia<sup>31</sup> or poisoning of another gas (carbon monoxide, hydrogen sulfide, etc.).

If a victim arrives in a state of cardiopulmonary arrest, because they are in a non-respiratory state, the results of the examination indicate the same as anoxia.

- [2] As for Driver B it is difficult to determine the time to death, it is presumed that he died in several minutes. This was assumed because even with a lack of oxygen the heart and lungs function and blood circulation continue for some time, and therefore post mortal brain edema could be expected, but it did not show up in the results of the CT-scan.

(4) According to statement of the professor of medical department charged with the judicial autopsy, the main details were as follows.

- [1] Reason for judicial autopsy of Driver B is that the results of the blood gas analysis was unlike those expected for anoxia
- [2] Because death by anoxia has no distinctive postmortem appearance, it is possible only to presume cause was anoxia.
- [3] If there is proof of low O<sub>2</sub> concentration at the scene, and it can be determined that the two other workers died of anoxia, it is reasonable to assume that, although the blood gas analysis results differed, Driver B also died of anoxia.
- [4] It is conceivable that the reason for the difference in blood gas analysis results

<sup>30</sup> "Blood Gas Analysis" is an examination that measures O<sub>2</sub> concentration, quantity of CO<sub>2</sub>, etc. to judge the function of the lungs by extracting arterial blood and examining the quantity of O<sub>2</sub> and CO<sub>2</sub>

<sup>31</sup> "Anoxia" caused by inhaling air lacking in oxygen and is provided for in the Regulations on the Prevention of Anoxia etc (Ministry of Labor Regulation No. 42, 1972) . The ordinance defines lack of oxygen as having a concentration of O<sub>2</sub> less than 18%.

Furthermore, "anoxia and other" in the Regulations on the Prevention of Anoxia etc is anoxia or hydrogen sulfide poisoning.



between Driver B and the other workers is possibility due to the increasing level of O<sub>2</sub> as result of emergency measures, etc.

- [5] Driver B's cause of death is judged to be suffocation, which includes anoxia.
- [6] In case of death by poisoning of hydrogen sulfide, the color of livor mortis<sup>32</sup> is deep purple from hemoglobin sulfide generated in the blood which is different from the color of anoxia. However the color of Driver B was reddish-brown, as same as suffocation, therefore it is possible to rule out poisoning by hydrogen sulfide.
- [7] In case of death by carbon monoxide poisoning, the color of blood changes to vermilion and the color of livor mortis seen through the skin is pink. Therefore it is possible to rule out carbon monoxide poisoning.

### 2.3 Information Regarding Primary Workers

According to the original directory on the members of the stevedoring company, the workers' details were as follows.

#### (1) Gender, Age, Primary Qualification and Training Attended

##### [1] Driver B

Male 63 years old

Mobile crane operator, loading & discharging work conductor safety training, special training for hazardous work including oxygen-deficient environments (the second class)<sup>33</sup>

##### [2] Foreman

Male 48 years old

Skill training course for sling work, crane operator, special training for hazardous work including oxygen-deficient environments (the second class), ship-board lifting apparatus operator, skill training course for operations chief of stevedoring, foreman training, skill training course for operations chief of hazardous work in oxygen-deficient environments and with hydrogen sulfide.

##### [3] Operator C

Male 52 years old

Skill training course for sling work, crane operator, special training for hazardous work including oxygen-deficient environments (the second class),

##### [4] Operator D

Male 27 years old

Special training for hazardous work including oxygen-deficient environments (the second class), crane/derrick operator, loading & discharging work conductor safety training, ship-board lifting apparatus operator

##### [5] Operator F

Male 28 years old

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<sup>32</sup> "Livor mortis" is a purplish-red spot on the underside of a corpse caused by congestion of blood in capillary vessels.

<sup>33</sup> "Special training for hazardous work including oxygen-deficient environments (2nd class)" is special training that is provided for in the Regulations on Prevention of Anoxia etc and is to be conducted when business operators have employees do to work falling under the definition of hazardous work in oxygen-deficient environments. Its subjects include "Cause of Oxygen-Deficiency" "Symptoms of Anoxia" "Usage of Air Breathing Apparatus" "Requirements for the Prevention of Anoxia"

Skill training course for sling work, crane operator, special training for hazardous work including oxygen-deficient environments (the second class), ship-board lifting apparatus operator

(2) Primary Personal History in Company

[1] Driver B

On January 21, 1982, he joined the stevedoring company and engaged in cargo working, on February 28, 2006, mandatory at the age limit retired and on the next day was reemployed for a fixed period. About 27 years of service.

[2] Foreman

On April 1, 1980, he joined the stevedoring company, from July 1 of the year, engaged in cargo working and on April 1, 2005, was promoted chief of stevedoring.

He also acted as instructor of special training for specified dust work.

In December, 2003, he received a commendation as a man of merit of the year.

About 29 years of service.

[3] Operator C

On April 1, 2006, he joined the stevedoring company and engaged in cargo working.

About 3 years of service.

[4] Operator D

On January 1, 2006, he joined the stevedoring company and engaged in cargo working.

About 3 years of service.

[5] Operator F

On February 1, 2006, he joined the stevedoring company and engaged in cargo working.

About 3 years of service.

2.4 Crew Information

(1) Gender, Age and Seamen's Certificate of Competency

[1] Master

Male 51years old

Nationality Commonwealth of Australia

Endorsement attesting the recognition of certificate under STCW regulation I/10

First grade maritime officer (navigation) (Issued in the Hong Kong Special

Administrative Region, the People's Republic of China (hereinafter referred to as "Hong Kong" )

Date of Issue November 1, 2005

Date of Expiry March 30, 2010

[2] Chief officer

Male 41years old

Nationality Russian

Endorsement attesting the recognition of certificate under STCW regulation I/10

Second grade maritime officer (navigation) (Issued in Hong Kong)

Date of Issue January 5, 2009

Date of Expiry August 19, 2009

[3] Third Officer

Male 29 years old

Nationality India

Endorsement attesting the recognition of certificate under STCW regulation I/10

Third grade maritime officer (navigation) (Issued in Hong Kong)

Date of Issue February 4, 2009

Date of Expiry September 8, 2013

(2) Major Sea Going Experience etc.

[1] Master

According to the statement of the master, he embarked as an apprentice ordinary seaman in 1977 and was promoted to master in 1998.

He embarked on the ship on November 26 or 27, 2008.

[2] Chief officer

According to the statement of chief officer, he received mariner training at the Far East Marine School from 1983 to 1989 and embarked as fourth officer, he was promoted to chief officer in 2005.

He embarked on the ship on December 11, 2008.

[3] Third officer

According to the statement of third officer, after study and basic training he embarked as an ordinary seaman. He passed the duty officer examination in the United Kingdom (the United Kingdom of Great Britain and Northern Ireland) and was promoted to third officer in 2008.

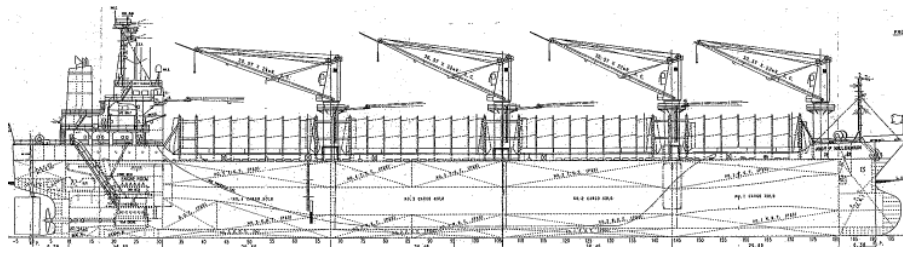
He embarked on the ship on January 7, 2009.

## 2.5 Vessel Information

### 2.5.1 Particulars of Vessel

|                    |  |
|--------------------|--|
| IMO                | 9224099                                      |
| Port of registry   | Hong Kong                                    |
| Owner              | SINGAPORE GRACE SHIPPING LIMITED (Hong Kong) |
| Management company | FLEET MANAGEMENT LIMITED (Hong Kong)         |
| Class              | Nippon Kaiji Kyokai (Class NK)               |
| Gross ton          | 15,071 tons                                  |
| L×B×D              | 159.94m×26.00m×13.50m                        |
| Hull material      | Steel  |
| Engine             | One diesel engine                            |
| Output             | 6,156kW (maximum continuous)                 |
| Propulsion         | One fixed pitch propeller                    |
| Date of launch     | December, 1999                               |

(See following drawing and picture “General Arrangement (excerpt)” “Picture of the Ship”)



“General Arrangement (excerpt)”



“Picture of the Ship”

#### 2.5.2 Other Relevant Vessel Information

Cargo-loading particulars of the ship were as follows.

|                         |  |  |
|-------------------------|--|--|
| Number of holds         | 4 Hatches,   | 4 Cargo Holds  |
| Hatch openings          | Cargo Hold No. 1   | 18.4m × 16.0m  |
|                         | Cargo Holds No. 2-4                                      | 22.4m × 17.6m  |
| Depth of hold etc.      | Double bottom top plate <sup>34</sup> -Top of upper deck | approx. 12.0m  |
|                         | Top of upper deck-Top of hatch coaming                   | approx. 1.35m  |
|                         | Top of Upper Deck-Second landing                         | approx. 6m   |
| Capacity of cargo holds | No. 1 Hold   | 6,845.76m <sup>3</sup>   |
|                         | No. 2 Hold   | 8,886.69 m <sup>3</sup>  |
| Closing Brackets        | No. 3 Hold   | 8,910.42 m <sup>3</sup>  |
|                         | No. 4 Hold   | 8,053.01 m <sup>3</sup>  |
|                         | King bolts <sup>35</sup> ,                               | 4 in port and starboard side, 2 in fore and aft side respectively. |

To keep watertight, tightening the king bolts makes the hatch cover, attached rubber packing, and the hatch coaming stick to each other.

Furthermore, the looseness of the king bolts when arriving at port of Saganoseki was not clear.

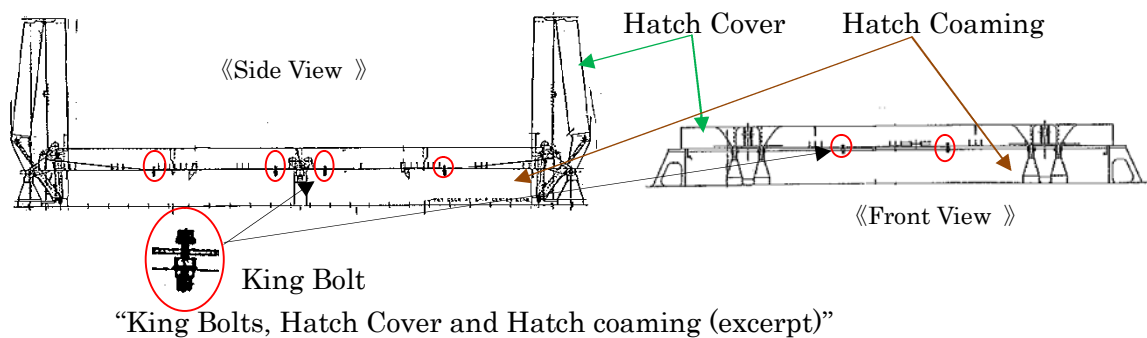
According to the written reply from the management company, the details were as follows.

On May 24, 2009, results of a water spray test before loading in Port Moresby showed no leakage into hold.

(See following schematic “King Bolts, Hatch Cover and Hatch coaming (excerpt)”

<sup>34</sup> “Double Bottom Top Plate” is plate that constitutes the top of the double bottom structure. It can also be called the “Inner Bottom Plating” or the “Tank Top”. It serves as both the top of the bottom tank and the bottom of the hold.

<sup>35</sup> “King Bolt” is a general term for the bolt and nut that secures the hatch cover and hatch coaming.



### 2.5.3 Cargo and Cargo Loaded Conditions

According to the MSDS for copper concentrates, bill of lading<sup>36</sup>, stowage plan, calculation sheet of loading condition, the written reply from the master and the statement of the chief officer, the details were as follows.

(1) Name of Cargo

- [1] The name of the cargo on the bill of lading was COPPER CONCENTRATE IN BULK.
- [2] The name of the cargo in the MSDS was COPPER SULPHIDE CONCENTRATE.

(2) Consignee

In consignee column of bill of lading was “To Order” and in the consignee’s address column were the name and address of the parent company of the smelter.

(3) Weight of Cargoes

|                  |          |                  |         |
|------------------|----------|------------------|---------|
| cargo hold No. 1 | 4,900mt  | cargo hold No. 2 | 5,600mt |
| cargo hold No. 3 | 5,900mt  | cargo hold No. 4 | 5,200mt |
| Total            | 21,600mt |                  |         |

(4) Cargo Volume and Bulk Ratio<sup>37</sup>

|                  |                             |            |             |
|------------------|-----------------------------|------------|-------------|
| cargo hold No. 1 | approx. 2,048m <sup>3</sup> | Bulk ratio | approx. 30% |
| cargo hold No. 2 | approx. 2,341m <sup>3</sup> | Bulk ratio | approx. 26% |
| cargo hold No. 3 | approx. 2,466m <sup>3</sup> | Bulk ratio | approx. 28% |
| cargo hold No. 4 | approx. 2,174m <sup>3</sup> | Bulk ratio | approx. 27% |

15 ft<sup>3</sup>/LT was used as a stowage factor<sup>38</sup> for copper concentrates.

(5) Draft and Trim<sup>39</sup>

- [1] Departure from Port Moresby Harbour

Fore draft 8.56m, Aft draft 9.65m, Trim 1.09mB/S

- [2] Arrival at port of Saganoseki

Fore draft 8.93m, Aft draft 9.34m, Trim 0.41mB/S

(6) Opening and Shutting of the Hatch Covers in Voyage

From departure of Port Moresby Harbour to arrival at port of Saganoseki, the hatch covers remained unopened and the cargoes were not ventilated. After berthing at the private wharf of port of Saganoseki, by instruction of the chief officer, ship’s crew opened

<sup>36</sup> “Bill of Lading” is a certificate that certifies loading or cargo for loading of cargo and promises to give shipped cargo in exchange for it.

<sup>37</sup> “Bulk Ratio” is the ratio of the volume of the cargo to the volume of the entire hold.

<sup>38</sup> “Stowage Factor (S/F)” is a volume value (ft<sup>3</sup>) indicating the amount of volume 1 long ton (LT, L/T, British ton and 1 L/T=1016.0469008 kg, a unit based on the yard and pound system) of cargo requires in the hold. A small S/F means heavy cargo and a large S/F means light cargo.

<sup>39</sup> “Trim” is the difference between the fore and aft draft, “trim by the stern (B/S)” is when the aft draft is larger than the fore draft and “trim by the head (B/H)” is the opposite.

cargo holds No. 1 and No. 3 hatch cover for the first time after loading in Port Moresby Harbour.

(7) Conditions of the Double Bottom under the cargo hold

Under cargo hold No. 1 was a ballast tank (W.B.T No. 1) and under cargo hold No. 3 was a fuel oil tank (F.O.T No. 2).

From departing Port Moresby Harbour to arrival at port of Saganoseki, W.B.T No. 1 was empty and the fuel oil volume in F.O.T No. 2 was as follows. Additionally, sea water and air temperature were recorded at noon.

[1] Fuel oil volume in F.O.T No. 2

| F.O.T No.2 | Volume in left side tank m <sup>3</sup><br>(Volume %) | Volume in right side tank m <sup>3</sup><br>(Volume %) | Sea water temperature °C | Air temperature °C |
|------------|---|--|--------------------------|--------------------|
| June 1     | 41.814 (14%)  | 41.509 (14%)   | 29                       | 30                 |
| June 2     | 30.807 (10%)  | 31.369 (11%)   | 30                       | 28                 |
| June 3     | 20.660 (7%)   | 20.461 (7%)  | 30                       | 29                 |
| June 4     | 9.567 (3%)  | 9.464 (3%)   | 31                       | 27                 |
| June 5     | 0.0   | 1.86 (0.1%)  | 32                       | 28                 |
| June 6     | 0.0   | 1.86 (0.1%)  | 32                       | 28                 |
| June 7     | 0.0   | 1.86 (0.1%)  | 31                       | 26                 |
| June 8     | 0.0   | 1.86 (0.1%)  | 31                       | 29                 |
| June 9     | 0.0   | 1.86 (0.1%)  | 31                       | 30                 |
| June 10    | 0.0   | 1.86 (0.1%)  | 30                       | 30                 |
| June 11    | 0.0   | 1.86 (0.1%)  | 27                       | 26                 |
| June 12    | 0.0   | 1.86 (0.1%)  | 25                       | 27                 |
| June 13    | 0.0   | 1.86 (0.1%)  | 21                       | 26                 |

[2] Bunkering

| Date of bunkering | Place                      | Bunkering oil temperature | Bunkering tanks  |
|-------------------|----------------------------|---------------------------|------------------|
| May 15, 2009      | People's Republic of China | Non-recorded              | FOT No. 1<br>P&S |
| March 27, 2009    | Republic of South Africa   | 20°C                      | FOT No. 2<br>P&S |
| February 15, 2009 | Republic of South Africa   | 20°C                      | FOT No. 3 C      |

[3] There is no monitoring system in the fuel oil tanks. It is noted that the fuel oil temperature was 23°C, nearly equal to the sea water temperature at the time of the accident.

## 2.6 Information Regarding Cargo etc.

### 2.6.1 Cargo on the Ship

According to the MSDS of copper concentrates, the details were as follows.

- (1) The cargo loaded on the ship was copper concentrate produced from copper ore, mined in the Independent State of Papua New Guinea, processed by floatation.
- (2) Components of the Copper Concentrate
  - [1] Chemical formula  $\text{CuFeS}_2$
  - [2] Composition ratio (%) of copper concentrates that the smelter obtained by analysis were as follows. Note : components less than 1% were omitted.

*Iron 26.6, Ceopper 27.7, Sulfur 29.8, Silicon 5.96, Magnesium 1.9, Zinc 1.32*
- (3) Description of the MSDS, etc.

The ship received the MSDS for the copper concentrates from the shipper in Port Moresby Harbour.

In the MSDS the following were written: name of the product, its composition, information on its components, precautions concerning handling, protection measures, emergency measures in case of entering the eye, danger of mild oxidization in air, mild heating by wetting, ignition generates “sulfur dioxide and sulfur trioxide gas”(hereinafter referred to as “sulfur gases.” Additionally, there was no information on the floatation reagent.

In the meantime, the shipper submitted a document titled “NOTICE OF ENTRY INTO CARGO HOLD” to the captain.

The document stated that “It is advised that unless ventilated sufficiently, no person is permitted to enter the hold loaded with copper concentrates.”

### 2.6.2 Description in the BC Code

In the BC Code (1998 version), copper concentrate are listed as “Copper Concentrates” in “Appendix A Bulk Materials which may Liquefy” and “Metal Sulfide Concentrates” in “List of Bulk Materials possessing Chemical Hazard.” According to the list, the details are as follows.

#### (1) Metal Sulfide Concentrates

##### [1] *Properties*

*Solid, finely divided sulfide concentrates of copper suliferrous ores, iron, lead, nickel, zinc or other metalliferous ores.*

*Some sulfide concentrates are liable to oxidation and may have a tendency to self-heat, with associated oxygen depletion and emission of toxic fumes.*

*Some materials may present corrosion problems.*

##### [2] *Observations*

*Prior to loading, the shipper or the competent authority should provide detailed information concerning any specific hazards and precautions to be followed, based on the history of carriage of the materials to be loaded.*

##### [3] *Special requirements*

*Loading and discharging operations should be closely supervised to minimize the exposure to dust.*

*Depending upon the advice of the shipper or the competent authority the following precautions should be followed.*

*1 oxygen stimulates the process of oxidation and self-heating, and thus ventilation of the materials should be avoided. Oxidation may also be inhibited by compaction<sup>40</sup> of the material or restricting the flow of air by carefully covering with plastic sheeting.*

### 2.6.3 Description in the International Maritime Solid Bulk Cargoes Code

In the International Maritime Solid Bulk Cargoes Code<sup>41</sup>, copper concentrates fall under “Metal Sulfide Concentrates” and “Mineral Concentrates.”

According to the code, the details were as follows.

#### (1) Description

##### [1] Metal Sulfide Concentrates

*Metal sulfide concentrates are refined ores in which valuable components have been enriched by eliminating the bulk of waste materials.*

*Generally the particle size is small although agglomerates sometimes exist in concentrates which have not been freshly produced.*

*The most common concentrates in this category are : zinc concentrates, lead concentrates, copper concentrates and low grade middling<sup>42</sup> concentrates.*

##### [2] Mineral Concentrates

*Mineral concentrates are refined ores in which valuable components have been enriched by eliminating the bulk of waste materials.*

#### (2) Hazards

##### [1] Metal Sulfide Concentrates

###### **HAZARD**

*Some copper sulfide concentrates are liable to oxidation and may have a tendency to self-heat, with associated oxygen depletion and emission of toxic fumes. Some materials may present corrosion problems. (omit after words)*

##### [2] Mineral Concentrates

###### **HAZARD**

*The above materials may liquefy if shipped at moisture content in excess of their transportable moisture limit (TML). (omit after words)*

#### (3) Precautions etc for Metal Sulfide Concentrates (including Copper Concentrates)

##### [1] Precautions

*Entry into the cargo space for this cargo shall not be permitted until the cargo space has been ventilated and atmosphere tested for concentration of oxygen. (omit after words)*

##### [2] Ventilation

###### **VENTILATION**

*The cargo space carrying this cargo shall not be ventilated during voyage.*

---

<sup>40</sup> “Compaction” is compacting soil, etc. with roller, etc.

<sup>41</sup> “The International Maritime Solid Bulk Cargoes Code (IMSBC)” is a set of regulations created by the Maritime Safety Committee of International Maritime Organization (IMO), which changed the recommendations listed in the BC Code to mandatory regulations in the ISMBC Code and obligated the shipper to provide detailed information on carriage of specific solid bulk cargo to captains as well as providing information on the handling of cargo not described in the IMSBC (approval of loading country, negotiation between discharging country and flag state of the ship etc) and procedures to be taken when carrying solid bulk cargo, to promote safe loading and carriage of cargo.

<sup>42</sup> “Middling” is ore consisting of a desired mineral etc extracted in particle form through ore processing.



[3] 7.3.1.3 Provision for Liquefied Cargo, Section 7 of IMSBC Code

*7.3.1.3 Adequate measures shall be taken to prevent liquid entering the cargo space in which solid bulk cargoes are stowed during the voyage.*

2.6.4 Information Regarding Odor of Cargo Loaded on the Ship

(1) Information from the persons concerned cargo handling

According to the statements of the persons in 2.1.2(6), staff of the smelter, staff of the stevedoring company and other workers, the details were as follows.

[1] The copper concentrates had a relatively strong stench which could be detected on the deck.

When engaging in discharging work on copper concentrates in the past, there was a similar stench.

The ship's cargo was copper concentrates with a strong stench.

The stench prevented approaching the entrance hatch.

[2] The stench in cargo hold No. 3 at the first and second entrances were distinct and severe.

[3] When the hatch cover of cargo hold No. 1 was opened I was in the cockpit of the crane.

Even there I could smell the strong stench. I never have smelled one as bad as that one. The cargo the ship had loaded had strong stench previously.

I felt a warm, odorous gas exiting from the cargo hold several times.

[4] Cargo hold No. 1 smelled, too, but I thought that was just the normal odor from this mineral ore.

(2) Information Regarding cargo hold No. 4 from On-Site Investigation

At about 12:00, on June 14, 2009, the Marine Accident Investigators performed an on-site investigation. When cargo hold No. 4 was opened first time after loading, the conditions were as follows.

[1] Odorous gas

As soon as the hatch cover opened, warm gas with a chemical smell overflowed from the cargo hold to the upper deck.

[2] Measured O<sub>2</sub> concentration

As soon as the hatch cover opened, the portable O<sub>2</sub> concentration's alarm sounded, warning the O<sub>2</sub> concentration was less than 18%. The measured O<sub>2</sub> concentrations in the cargo hold were as follows.

| Time after opening (minutes) | O <sub>2</sub> concentration (%)       |                           |
|------------------------------|--|---------------------------|
|                              | 5m point below from aft entrance hatch | Near the surface of cargo |
| 0                            | 5.1                                    | 4.8                       |
| 0.5                          | 8.7                                    | 4.9                       |
| 1                            | 9.0                                    | 4.9                       |
| 2                            | 14.5                                   | 8.2                       |
| 3                            | 17.2                                   | 8.2                       |
| 4                            | 19.0                                   | 18.0                      |
| 5                            | 18.7                                   | 17.7                      |
| 6                            | 20.9                                   | 19.1                      |
| 7                            | 20.9                                   | 19.9                      |
| 8                            | 20.9                                   | 20.0                      |
| 9                            | 20.9                                   | 20.1                      |

#### 2.6.5 Information on Flootation and so forth

According to the MSDS of the floatation reagent, written reply from the shipper and the statement of staff from the smelter, the details were as follows.

##### (1) Description of Flootation

Flootation is one ore dressing method that processes copper ore with a low percentage content to obtain copper concentrates. Specifically, powdered crude ore is suspended<sup>43</sup> in water, an oil or floatation reagent stirred in and the copper concentrates float and attach to surface where they are collected.

##### (2) Information on Reagents used in Flootation

The shipper used two floatation reagents (hereinafter referred to as “reagent W” and “reagent X”) made in Commonwealth of the Bahamas by Company H.

Flootation reagent use was 17.0g for reagent W and 16.5g for reagent X per 1ton of crude ore respectively.

##### (3) Information on Flootation Reagents W and X

The MSDS of reagents W and X were as follows.

###### [1] Reagent W (Frother)

- a Principal Component                      Complex Oxygenated/Hydrocarbon mixture 60-85%  
2-Ethylhexanol 5-10%
- b Odor    Mixed alcohol and aldehydes
- c pH > 5.14, acidity
- d Vapor density > 1 (Air=1)
- e Precautions of Handling
  - (a) Do not heat above 49°C.
  - (b) Where this material is not used in a closed system, good enclosure and local exhaust ventilation should be provided to control exposure.

<sup>43</sup> “Suspension” is when the particles of a solid separate in liquid.

(c) If inhaled, recover to fresh air. If not breathing, give artificial respiration and seek medical attention immediately.

[2] Reagent X (Collector)

- a Principal Component Sodium diisobutyl / dithiophosphate 31.5-36%
- b Odor Slight sulfur odor
- c pH > 12, Alkaline
- d Vapor density Unknown
- e Precautions of Handling Nothing in particular

### 2.6.6 Information Related to Oxidation and Deoxidize of Copper Concentrate

According to the pamphlet introducing the smelter company, smelting copper concentrates take advantage of the ore's oxidizing characteristic. The main details were as follows.

(1) Copper concentrates, after being dried, are blown with highly oxidized air in condition of room-temperature through a concentrate burner into a flash furnace.

After exiting the burner, the copper concentrates begin oxidizing and, by the ore's own heat, melts and divides into a matte<sup>44</sup> of 68% copper with a slag<sup>45</sup> of iron oxide and silicic acid.

(2) The matte generated in the flash furnace is fed into a revolving furnace where additional highly oxidized air is blown in, oxidizing the metals in the matte except the copper, and creating crude copper with 99% copper content and a slag of iron oxide including silicic acid.

(3) The processes of oxidation and deoxidize in (1) and (2) can be expressed in the following chemical formulas.

- a  $4\text{CuFeS}_2$  (Copper Concentrates) +  $2\text{SiO}_2$  (Silicic Acid) +  $5\text{O}_2$  (Oxygen)  
→  $2\text{Cu}_2 \cdot \text{FeS}$  (Matte) +  $2\text{FeO} \cdot \text{Si O}_2$  (Slag) +  $4\text{S O}_2$  (Gas) + Heat of Reaction
- b  $2\text{Cu}_2\text{S} \cdot \text{FeS}$  (Matte) +  $\text{SiO}_2$  (Silicic Acid) +  $5\text{O}_2$  (Oxygen)  
→  $4\text{Cu}$  (Crude Copper) +  $2\text{FeO} \cdot \text{Si O}_2$  (Slag) +  $4\text{S O}_2$  (Gas) + Heat of Reaction

## 2.7 Research of Copper Concentrates by Nippon Kaiji Kentei Kyokai ;Japan Marine Surveyors and Sworn Measurers' Association (Physical and Chemical Analysis Center)

A research into the properties of the copper concentrates loaded on the ship and their influence on the environment (atmosphere<sup>46</sup>) of enclosed space such as the cargo hold, was entrusted to Nippon Kaiji Kentei Kyokai (Physical and Chemical Analysis Center).

### 2.7.1 Samples used in the Research

(1) Copper Concentrates

- [1] Cargo loaded in the Independent State of Papua New Guinea : Ok Tedi Ore (hereinafter referred to as "sample A" )
- [2] Cargo loaded in the Republic of Peru : Cuajone Ore (hereinafter referred to as "sample B")
- [3] Cargo loaded in the Republic of Chile : Cerro Corona Ore (hereinafter referred to as

<sup>44</sup> "Matte" is the phase of a metal after separating and settling in the lower layer of the blast furnace and is the intermediate stage of copper or other metals between ore and metal.

<sup>45</sup> "Slag" is the dregs of ore floating on the surface during smelting while valuable components settle.

<sup>46</sup> "Atmosphere" is defined as the conditions of a particular gas or mixed gas.

“sample C”)

In the meantime, sample A is equivalent to the copper concentrates loaded on the ship from the accident.

(2) Flootation Reagents

In addition to reagents W and X, two flootation reagents made in Japan (hereinafter referred to as “reagent Y” and “reagent Z”) were used as samples.

(3) Odorous gases, Water Condensation and Temperature of Cargo

On March 30, 2010, odorous gases and water condensation were extracted from the cargo holds (cargo holds No.1 and No.3) scheduled discharging and the hatch covers (hold-side) of another cargo vessel loaded cargo same as sample A at port of Saganoseki. They were extracted at same time as the hatch covers were opened.

On the following day, March 31, the temperature of sample A extracted from No. 1 cargo hold was 42.6°C.

The meteorological conditions when sample A was extracted were as follows.

Weather Cloudy, Wind Direction South, Wind Scale 3, Air temperature 14°C, Temperature of sea water 12°C

## 2.7.2 Method of Research and Obtained Results

According to the research report from Nippon Kaiji Kentei Kyokai (Physical and Chemical Analysis Center) (hereinafter referred to as “document of analysis of copper concentrates”), the main details were as follows.

(1) Oxidation Condition of Copper Concentrates

[1] Methods of Research

a Put samples A-C into various containers (the capacity is approx 650ml) with 30% vacant space and 70% vacant space respectively, seal containers enclosed, then change the surrounding temperatures of the sealed container to 40°C, 60°C and 80°C and measure O<sub>2</sub> concentrations.

b Starting with the sample with 70% vacant space, liquid is added so that the sample’s fluid content is 15%, seal containers airtight then change the surrounding temperatures of the sealed container to 40°C, 60°C and 80°C and measure O<sub>2</sub> concentrations.

[2] Obtained Results

a Regardless of the environmental temperatures and vacant spaces in the sealed containers, the O<sub>2</sub> concentrations in the containers reduced linearly through time.

b O<sub>2</sub> consumption speeds by the oxidation reactions of the copper concentrates, represented by the slope of the straight line, were faster the higher the environmental temperature.

c Since the molecular compound conditions of copper concentrates and the used flotation reagent etc. varies by place of production, so to the O<sub>2</sub> consumption speeds varies.

Of the used samples, sample A had the fastest O<sub>2</sub> consumption speed. In the case where sample A was sealed in a container with 70% vacant space and an environmental temperature of 40°C, the O<sub>2</sub> concentration of the vacant space was 20.9% to start with and reduced to 6.8% 6 hours later. If the O<sub>2</sub> consumption speed were to be maintained, it is expected that it would be almost 0% after 9 hours from

the start of the experiment.

In the case where sample A was sealed in a container with 30%vacant space and an environmental temperature of 40°C, the O<sub>2</sub> concentration of the vacant space was 20.9% to start with but 10 hours later it was less than 3%.

- d In the case where sample A was sealed in a container with 70%vacant space and an environmental temperature of 60°C, the O<sub>2</sub> concentration of the vacant space reduced to 8% after 3 hours from the start of the experiment. If the O<sub>2</sub> consumption speed were to be maintained, it is expected that it would be almost 0% after 5 hours from the start of the experiment.

In the case where sample A was sealed in a container with 30%vacant space and an environmental temperature of 60°C, the O<sub>2</sub> concentration of the vacant space reduced to 4.5% after 3 hours from the start of the experiment. If the O<sub>2</sub> consumption speed were to be maintained, it is expected that it would be almost 0% after 4.5 hours from the start of the experiment (for the results for 80°C, see the attached Appendix: Analytical Data on Copper Concentrate Extracts).

- e In the cases where water was added to raise the moisture of the sample to 15%, in every sample, vacant space and environmental temperature, the O<sub>2</sub> consuming speed was slower.

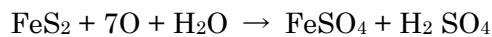
The result for sample A were as follows.

In the case with vacant space 70%, at 40°C, the O<sub>2</sub> concentration was 10.0%, 7 hours after measuring started.

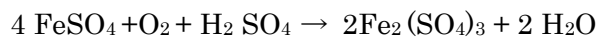
In the case with vacant space 70%, at 60°C, the O<sub>2</sub> concentration was 6.0%, 4 hours after measuring started, and expected to be almost 0%, after 5.5 hours.

- f Generally, oxidation of CuFeS<sub>2</sub> (Copper Pyrites : Copper Concentrates) is shown by the following reaction formula.

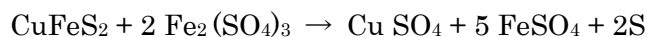
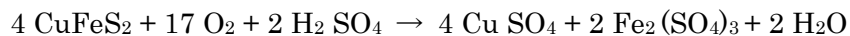
- (a) In the oxidation of copper pyrites, sulfuric acid and ferrous sulfate are generated.



- (b) From ferrous sulfate an oxidation reaction to ferric sulfate occurs.



- (c) Leading to the oxidation of copper pyrites (copper concentrates) and generation of copper sulfate.



## (2) Influence of the Flootation Reagents

### [1] Methods of investigation

- a Four samples, composed of sample A dried at 105°C and floatation reagents W-Z (5% the weight of sample A) respectively, were sealed into containers with 70% vacant space in an environmental temperature of 40°C.

The O<sub>2</sub> concentration in the upper and lower layer of the containers was measured after 24 hours.

- b Sample A (non-dried) and sample A (dried at 105°C) were sealed in containers with vacant space of 70%, in environmental temperature of 40°C without floatation reagents being added. The O<sub>2</sub> concentration in the upper and lower layer of the containers was measured after 24 hours.

c 300ml of pure water was added to 100g of sample A (dried at 105°C) and stirred by rotor for 5 minutes then filtered after 30 minutes.

After repeating the process four times, floatation reagent W-Z were added to the washed sample of A. 24 hours later, O<sub>2</sub> concentration in the upper and lower layer of the containers was measured in the same manner as experiment a.

[2] Obtained Results

a In every case of adding a floatation reagent, O<sub>2</sub> concentration in the lower layer was lower than the upper layer.

b In case of adding floatation reagent X, O<sub>2</sub> concentration was the lowest: upper layer 10.1% , lower layer 6.3%.

c O<sub>2</sub> concentration in containers of non-dried samples was lower than in containers of samples dried at 105°C.

See below.

Before drying : 5.4% in upper layer 3% and below in lower layer

After drying : 16.3% in upper layer 16.0% in lower layer

d In case of adding floatation reagents to washed and unwashed samples, for reagents W and X, the O<sub>2</sub> concentration in the containers with unwashed samples were lower than washed samples.

Additionally, depending on the added floatation reagents, the O<sub>2</sub> concentration varied as follows.

Unwashed sample : in increasing order of O<sub>2</sub> concentration reagents X, W, Z and Y

Washed sample : in increasing order of O<sub>2</sub> concentration reagents Z, X, Y and W

(3) Analysis of Odorous Gas

[1] Method of research

The odorous gases extracted from the cargo holds was sealed into tetra packs and the components were qualitatively analyzed.

[2] Obtained Results

The components of the odorous gases were toluene, xylene (both are aromatic hydrocarbons), diethylacetamide (ester compound) and phenol, all of which were harmful to the human body.

(4) Analysis of Generated Gas

[1] Method of research

a Four samples, composed of sample A dried at 105°C and floatation reagents W-Z (5% weight of sample A) were sealed into containers with 70% vacant space, in an environmental temperature of 40°C. Gases were then extracted after 24 hours.

b Samples of reagents W-Z were sealed into container with 70% vacant space, in an environmental temperature of 40°C, Gases were then extracted after 24 hours.

[2] Obtained Results

a In case of the pure sample of reagent W, ether (cs-1 butene, toxic) was detected while in case of adding agent W to sample A, ether was not detected but ester (2-methylpentylbutyrate) was detected.

b In both the components of agent X and the odorous gases extracted from the cargo holds, toluene and xylene were detected.

(5) Analysis of Water Condensation

[1] Method of investigation

- a pH was measured.
- b Qualitative analysis was conducted.

[2] Obtained Results

Since the detected value of sulfate ions ( $\text{SO}_4^{2-}$ ) were low, it is suspected that the possibility of hydrogen sulfide being generated in high concentration in the cargo holds is low.

(6) Summary

$\text{O}_2$  concentrations in the vacant space decreased linearly as the copper concentrates consumed oxygen. It was confirmed that the slopes of the straight line (i.e.  $\text{O}_2$  consumption speed) varies by the origin of the copper concentrates due to differences in the molecular compound form of the copper concentrates and used floatation reagent, etc.

2.8 Symptoms of Anoxia and Hydrogen Sulfide Poisoning

According to material from the Ministry of Health, Labour and Welfare (Website “Eliminate! Anoxia · Hydrogen Sulfide Poisoning ”

[www.mnhlw.go.jp/new-info/kobetu/roudou/gyousei/anzen/040325-3.html](http://www.mnhlw.go.jp/new-info/kobetu/roudou/gyousei/anzen/040325-3.html)), the details are as follows.

(1) Anoxia

*Oxygen deficiency is the reduction of  $\text{O}_2$  concentration in air, and can cause anoxia if inhaled. Anoxia causes dizziness, loss of consciousness and even death.*

(2) Symptoms of Anoxia

| $\text{O}_2$ concentration | Symptoms etc                               |
|----------------------------|--|
| 21 %                       | Ordinary air condition                     |
| 18 %                       | Within Safety limit but need ventilation   |
| 16 %                       | Headache, nausea                           |
| 12 %                       | Dizziness, muscle weakness                 |
| 8 %                        | Faint, death in 7,8 minutes                |
| 6 %                        | Immediate Faint, respiratory arrest, death |

(3) Hydrogen Sulfide Poisoning

*Hydrogen sulfide generates in various conditions in nature. Stirring of sludge, chemical reactions, etc. may scatter hydrogen sulfide in high concentrations into the atmosphere.*

*Hydrogen sulfide causes the loss of the sense of smell, eye damage, respiration impairment and pulmonary edema that may be fatal.*

(4) Symptoms of Hydrogen Sulfide Poisoning

| <i>Concentration of hydrogen sulfide</i>                 | <i>Symptoms etc.</i>   |
|--|--|
| <i>About 5ppm</i>  | <i>Unpleasant odor</i>   |
| <i>10ppm</i>   | <i>Permissible concentration (Lower limit of stimulation to mucous membrane of the eye )</i>   |
| <i>20ppm</i><br>↓<br><i>350ppm</i><br>↓<br><i>700ppm</i> | <i>Bronchitis, pneumonia, pulmonary edema</i><br>↓<br><i>Threat to life</i><br>↓<br><i>Respiratory paralysis, unconsciousness, respiratory arrest, death</i> |

2.9 Labour Management of the Stevedoring Company

The following details were from documents concerning the labor management of the stevedoring company.

(1) Occupational Safety Management System

The stevedoring company was following the guidelines established in the Occupational Safety Management System in the Occupational Health and Safety (OHS) manual, version 4 (enacted on April 1, 2008 and revised on December 1, 2008) aiming to establish, and maintain and improve occupational health and safety performance.

The management system applied to the smelter and the offices of affiliated companies including the premises of the stevedoring company.

The OHS manual, after examination of the person responsible for preparation ,etc. and OHS affairs on behalf of the chief person of the smelter, was applied under the approval of chief of the smelter through the deliberation of the Committee for the Promotion of Safety and Health Management, of which the chief of the smelter was the chairman.

As part of Occupational Safety Management System, the stevedoring company created operation standards that provided procedures, division of roles, rules of compliance, etc. for mooring, measuring O<sub>2</sub> concentration, discharging, etc.

(2) Rule of Compliance for Hazardous Work Environments Including Oxygen Deficient Environments

The stevedoring company provided the following under “Rules of Compliance for Hazardous Work Environments Including Oxygen Deficient Environments” in the original OHS Management System (enacted on February 1, 2008).

*Each section should determine if there is the possibility of hazardous work environments or hazardous work exists, including the risk of anoxia, etc. and appoint an operations chief for these operations.*

*The appointed operations chief should carry out his duties and ensure the prevention of anoxia, etc.*

(3) Standard for Measuring O<sub>2</sub> Concentration

The stevedoring company stipulated the followings in the “Standard for Measuring O<sub>2</sub> Concentration (On-board work)” section of the Operation Standards Book.



1. *Scope of Application*

*The purpose of this standard is the prevention of employee injury by Oxygen deficiency during ship's hold work by measuring O<sub>2</sub> concentration before operations commence.*

*Further, this standard also prohibits the operations chief of hazardous work in Oxygen deficient, operations chief of stevedoring, and on-board workers from entering Oxygen deficient environments.*

2. *Covered Workers*

*On-board workers (after completing special trainings for hazardous work in Oxygen deficient-and dust work)*

3. *Protective Equipment*

*Anti-dust mask, Uniform work clothes, Helmet, Safety shoes, Vinystar gloves, Goggles (as necessary)*

4. *Tools/Equipment to be Used*

*O<sub>2</sub> concentration meter*

5. *Operation Procedures*

1. *Measurer of O<sub>2</sub> concentration on vessel*

- 1) *O<sub>2</sub> concentration is to be measured by the operations chief of hazardous work in Oxygen deficient.*
- 2) *A person appointed by supervisor of the operation from among qualified person (operations chief of oxygen deficient danger), may also measure the O<sub>2</sub> concentration.*

2. *Role of the Operations Chief of Oxygen Deficient Danger*

- 1) *The operations chief of oxygen deficient danger takes charge of following matters.*
  - [1] *After the mooring of a vessel and opening the hatches and before the workers board, he measures the O<sub>2</sub> concentration.*
  - [2] *He confirms that the O<sub>2</sub> concentrations in cargo holds are 18% or more and reports the results to the operations chief of stevedoring.*
  - [3] *He enters the results into the daily report and reports the presence of any abnormalities to the supervisor of the operation.*
    - *He measures several minutes after opening the hatch cover because of the possibility of non-oxygen gas flowing over.*
    - *Measurements are taken in three designated points under the hatch.*
    - *Enter the results into the record book.*

3. *Rule of Compliance on Operation Oxygen Deficient Danger for Operations Chief of Stevedoring*

- 1) *The operations chief of stevedoring should not allow workers into the cargo hold unless O<sub>2</sub> concentration is 18% or more, after the chief received the report.*

4. *Rules of Compliance for Stevedoring Workers*

- 1) *Stevedoring workers do not enter the hold without permission of the operations chief of stevedoring.*
- 2) *Stevedoring workers should have completed special trainings for operations in oxygen deficient danger.*

## 5. Previous Accident

On June 26, 2005, a worker entered unopened hold by his carelessness, and died of anoxia.

### (4) Previous Accident

According to the record of employee injury, the main features were as follows.

- [1] Date and Time of Occurrence about 12:30, on June 26 (Sun), 2005
- [2] Place of Occurrence vessel (hereinafter referred to as “Vessel A”) mooring to the private wharf of the smelter
- [3] Conditions of Occurrence

A worker who was ordered to collect the remainder of the cargo with the heavy vehicle, shovel and broom was found collapsed on the landing under the entrance hatch of cargo hold No. 2 which was not to be unloaded.

O<sub>2</sub> concentration near the landing was 14%.

He was taken to the hospital where he was confirmed dead.

- [4] Cause of Death Death from suffocation by oxygen deficiency

### (5) Measures Taken after Past Accident

According to the statement of the staff of the stevedoring company and the measures to prevent employment injury and the implementation plan, following measures were taken.

- [1] “Safety instruction for operation when a worker is entering the cargo hold” was newly added to the Book of Operational Standards and trained every stevedores and let them understand.
- [2] Making and Exhibition of an “entrance permitted notice board” (See 2.1.2 (4)).
- [3] Making and Exhibition of a “Plot Plan of Entrance hatches”, expressing the positions of permitted entrances clearly, in the briefing room and gangway.

(See following pictures, “Plot Plan of Entrance Hatches”)



“Plot Plan of Entrance Hatches”

- [4] Instructions to concerned manager to inspect the whole operation for oxygen deficient danger.
- [5] Education of Regulations on the Prevention of Anoxia for every manager and supervisor of the operation.
- [6] Video training on anoxia for all members.
- [7] Periodical education on anoxia.
- [8] Special education on operations of oxygen deficient danger.
- [9] Skill training for the operations chief of oxygen deficient danger.
- [10] Monthly training with KY (Kiken Yochi : Predicting Risks) sheet and video.
- [11] Education during every morning assembly.

- [12] Establishment of a system to improve mutual communication.
  - [13] Review of the inspection tour by the supervisor of operation immediately after the start of operation.
- (6) Training for Employees
- According to the operation records of special training for operations of oxygen deficiency danger etc. the details were as follows.
- [1] The stevedoring company, in conformity with Ordinance of Industrial Safety and Health, appointed instructors from qualified employees and made employees attend the lecture of “Special Training for Operation of Oxygen Deficient Danger.”
  - [2] The subjects were “Causes of Oxygen Deficiency”, “Symptoms of Anoxia”, “Usage of Air Breathing Apparatus”, “Evacuation and Method of Resuscitation”, “Matters about Prevention of Oxygen Deficiency, etc.” and “Related Laws and Regulations” – cumulative lecture time was approximately 4.5 hours.
  - [3] The stevedoring company issued a completion certificate to participants.

## 2.10 Actual Conditions etc. of O<sub>2</sub> Concentration Measurements

- (1) Form of the Record Book
- [1] The record book of the stevedoring company had a column named “Measuring Points in Ship’s Holds and Results of Measuring” to enter the O<sub>2</sub> concentration at each measuring point.
  - [2] The record had 12 blank spaces to record the O<sub>2</sub> concentration per hold i.e. 6 blanks for lower layer measuring points under fore, center and aft hatch coamings of both sides and 6 blanks for upper, middle, lower measuring points under fore and aft entrance hatches.
- (See “Copy of Record Book” and “Record Book (enlarged)” in 2.1.2(5))
- (2) Record book of the Past
- According to record book of the past, 157 vessels berthed in the period from January 3, 2007 to December 29, 2008, with details as follows.
- [1] Measuring points per 1 cargo hold and number of vessel of meeting the criteria.  
 12 points : 64 vessels, 10 points : 60 vessels, 8 points : 1 vessel, 7 points : 1 vessel, 6 points: 20 vessels, 5 points: 1 vessel, 4 points: 9 vessels, 0 point (not recorded): 1 vessel
  - [2] From April 7, 2008, the omission of measuring the central lower layer of both sides of the hatch coaming began and the records of 10 points measuring increased.
  - [3] In some cases of discharging from multiple cargo holds, each hold had a different measuring point. The following are included.
    - Example 1 on February 21, 2007
      - cargo hold No.1 : Two points, lower layer under fore starboard and aft port points of hatch coaming
      - cargo hold No. 2 : Two points, lower layer under fore port and aft starboard points of hatch coaming
      - (as for the entrance hatch, the lower layer under the fore side and the upper layer under the aft side in both holds)
    - Example 2 on December 6, 2007
      - cargo hold No. 1 : Two points, lower layer under fore left and right points of hatch coaming

Two points, upper layer under fore and lower layer under aft entrance hatch.

cargo hold No. 2 : Two points, lower layer under aft left and right points of hatch coaming

Two points, lower layer under fore and upper layer under aft entrance hatch.

Example 3 June 16, 2008

cargo hold No. 2 : Four points, lower layer under fore left and right and aft left and right points of hatch coaming

Two points, upper layer under fore and lower layer under aft entrance hatch.

cargo hold No. 4: Three points, lower layer under fore left and right, and aft starboard point of hatch coaming

Two points, lower layer under fore and upper layer under aft entrance hatch.

[4] According to the signature columns for the measurers, in the above period, supervisors of cargo work, including at least six foremen, engaged in measuring the O<sub>2</sub> concentration.

In the meantime, the records of three vessels among 157 had no signature in the measurer column.

[5] All O<sub>2</sub> concentrations in the record book were 20.9%.

[6] The time needed to measure was unknown because there were no records of start or finished time although the book had columns for date and time of measuring.

### (3) Actual Conditions of O<sub>2</sub> Concentration Measurements

According to the statements of the investigation staff and the workers from the stevedoring company, the actual conditions of measuring the O<sub>2</sub> concentration before this accident were as follows.

[1] Another cargo work supervisor took measurements by lowering an O<sub>2</sub> concentration meter from three points on the left and right side of the hatch coaming to the upper, middle and lower layers under each lowering point.

He did not measure O<sub>2</sub> concentration at the entrance hatch.

The measuring method of another cargo work supervisor was the same as that of the foreman.

[2] A worker measured 12 points by lowering a sensor from four corners of the hatch coaming to the upper, middle and lower layers under the four corners.

[3] Another worker measured near the fore entrance hatch adding to the above four corners.

[4] Measurements of the O<sub>2</sub> concentration in entrance hatch was not provided.

[5] The stevedoring company did not understand the actual conditions of measuring O<sub>2</sub> concentration

[6] If the measured O<sub>2</sub> concentration was less than 20.9%, measuring continued until it returned to 20.9%, hence it is not strange that all values in the record book were 20.9%.

[7] If entrance permitted notice board was exhibited on entrance hatch, workers of the stevedoring company entered the cargo hold even without permission of the cargo work supervisor.

[8] The measurer of the O<sub>2</sub> concentration did not inform the O<sub>2</sub> concentration to the workers, but the workers they entered cargo hold relying on the smell of the cargo and the entrance permitted notice board being displayed.

[9] Usually, a worker was not very aware of the O<sub>2</sub> concentration, but trusted the smell of the hold and his intuition.

[10] Depending on circumstance, sometimes the foreman displayed the “entrance permitted notice board”, measured the O<sub>2</sub> concentration and then met with the crew of the vessel and sometimes measured the O<sub>2</sub> concentration while the “entrance permitted notice board” was being displayed.

The order of work was at the discretion of the measurer (he is cargo work supervisor and the operations chief of oxygen deficient danger).

[11] A foreman was seen in the past measuring O<sub>2</sub> concentration with around his navel nearly touching the hatch coaming, lowering sensor of O<sub>2</sub> concentration meter into hold.

The number of measuring points was unknown.

[12] Operators D and F had never used an O<sub>2</sub> concentration meter.

(4) Conditions of O<sub>2</sub> Concentration Measurement at the time of the Accident

According to the statements of staff members and workers of the stevedoring company and the crew of the ship, the details were as follows.

They saw the foreman bringing O<sub>2</sub> concentration meter and putting up the “entrance permitted notice board”, but not actually measuring O<sub>2</sub> concentration because every person was already engaged in their own work.

(5) O<sub>2</sub> Concentration Recognized by Operator F before Entering Cargo Hold

According to the statements of operator F, the main details were as follows.

When he heard driver B had collapsed in the cargo hold, he suspected it was anoxia.

Although he was trained by the company on the symptoms of anoxia, places susceptible to anoxia, accident examples of the past, difficulty of a rescue, etc. when the accident occurred he was impatient and thought “What should I do? What should I do?”

If he was alone on the site, he would not have entered the hold, but because other workers entered the hold, he followed them to rescue the worker.

## 2.11 Information on O<sub>2</sub> Concentration etc. of Other Vessels

(1) Measuring method of O<sub>2</sub> concentration after this accident

According to the record book and so on obtained from staff of the smelter, the details were as follows.

After this accident, the measuring method changed so that, as a pair, the O<sub>2</sub> concentration measurers (the operations chief of Oxygen Deficient Danger) and an assistant (who has completed Special Training for Hazardous Work in Oxygen Deficient) measures with one meter at 18 points per 1 cargo hold.

The method took 20 minutes to measure O<sub>2</sub> concentration at 36 points for two cargo holds of another cargo vessel (hereinafter referred to as “vessel B”), which arrived on November 28, 2009, after loading copper concentrates at Port Moresby Harbour.

(2) O<sub>2</sub> Concentration in the Cargo Hold of Vessel B

The conditions of vessel B when Marine Accident Investigator measured the O<sub>2</sub> concentration, were as follows.

[1] At 08:39, the hatch cover of cargo hold No. 1 was opened. At that time O<sub>2</sub>

concentration on the upper deck was 20.0%.

- [2] Change in the concentration of O<sub>2</sub> near the cargo surface under the aft left hatch coaming of No. 1 cargo hold, was as follows.

08:40 18.9%, 08:41 20.6%, 08:48 20.7%

- [3] After 08:50, O<sub>2</sub> concentrations, near the cargo surface under the aft starboard hatch coaming of cargo hold No. 1, changed as recorded in the following table.

| Measuring time (approx) | O <sub>2</sub> Concentration (%) |
|-------------------------|----------------------------------|
| 08:50                   | 16.7                             |
| 08:51                   | 18.0                             |
| 08:51.5                 | 15.8                             |
| 08:54                   | 19.4→18.9→19.8→18.8              |
| 08:55                   | 20.0→18.5→20.0                   |
| 08:56                   | 19.2                             |
| 08:59                   | 17.9→20.9                        |
| 09:00                   | Settled down to 20.9%            |

- [4] Meteorological observations on vessel B at the time of measuring of the O<sub>2</sub> concentration were as follows.

Weather : cloudy, Wind direction : NNW, Wind scale : 5 (wind velocity: about 10m/s), Temperature : 10°C

- (3) Vessels that had a Remarkably Low O<sub>2</sub> Concentration

According to the results record of past arrivals, submitted by the smelter, the details were as follows.

In the period from the arrival of the ship in question until November 28, 2009, of 45 vessels arriving at port of Saganoseki loaded with copper concentrates, including the ship in question, only one other ship had remarkably low O<sub>2</sub> concentration.

Above vessel had loaded 9,887tons of copper concentrates (Cuajone) in the Republic of Peru and the measured O<sub>2</sub> concentration was 1.3%.

## 2.12 Information on Discharging Cargo Work

### 2.12.1 Standards of Discharging Cargo Work

The following are from “Discharging Cargo Work” in the Book of Operation Standards.

#### 1. Scope of Application

*This standard is applied to the discharging cargo work of ore vessels berthed at Hiroura A/B wharf.*

*In the meantime, the following standards are related to this operation.*

[1] *Standard of Mooring/Unmooring Work*

[2] *Operation of Discharging Cargo Gears*

[3] *Raking cargo by Backhoe in Hold*

[4] *Crane Operation*

[5] *Cleaning of Holds by Large Brush*

The following is an excerpt from the work procedures.

*In cases likely to cause oxygen deficiency, check the O<sub>2</sub> concentration with a meter before entering.*

*Enter entrance hatches with notice boards. Never enter a place with a “Keep Out” Notice Board*

#### 2.12.2 Changes to Discharging Cargo Work Procedure

According to the statements of staff members of the smelter and the Book of Operation Standards, the details were as follows.

- (1) From about 2004, the discharging cargo work procedure changed to have the heavy vehicle lifted into the hold a short time after opening the hatch cover.
- (2) The reasons for the change were two points as follows.
  - [1] Improvement of cargo work efficiency by collecting cargo into center of the hold using the heavy vehicle.
  - [2] Avoidance of interruption to cargo work caused by the moving of the shore crane to carry the heavy vehicle into the hold during cargo work.
- (3) The procedure before the change was to unload as much cargo as possible with the crane before carrying the heavy vehicle into the hold.

#### 2.13 Information on Safety Protective Equipment etc.

##### 2.13.1 O<sub>2</sub> Concentration Meter

The stevedoring company equipped with one O<sub>2</sub> concentration meter in the cargo handling office.

The O<sub>2</sub> concentration meter was made in July, 2005, calibrated<sup>47</sup> on May 23, 2008, was flame-proof, had a measuring range of 0~50%, supplied with 10m of sensor cable and when O<sub>2</sub> concentration decreased to 18%, an alarm (“pi-pi-pi-pi”) sounded and a red lamp blinked. The O<sub>2</sub> concentration meter worked normally.

(See following pictures “O<sub>2</sub> Concentration Meter”)



“O<sub>2</sub> Concentration Meter”

##### 2.13.2 Self-contained Breathing Apparatus

The stevedoring company equipped with one self-contained breathing apparatus (See footnote 19) in the cargo handling office.

According to the instruction manual of the breathing apparatus obtained from the stevedoring company, the details were as follows.

---

<sup>47</sup> “Calibration” is setting equipment so that measured quantities are correct.

The self-contained breathing apparatus was a pressure demand type (air pressure inside of mask is higher than outside) and is used when oxygen deficient air is likely to be breathed.

Principal specifications are as follows.

- (1) Specification of gas: Air
- (2) Maximum filled pressure (Air-bottle): 14.7MPa
- (3) Alarm (Whistle type) sounding pressure: 3 MPa
- (4) Maximum flow: approx 500 ℓ/minutes:
- (5) Volume of air bottle: 8.4 ℓ
- (6) Maximum carrying air volume: 1,260 ℓ
- (7) Usable time: 31minutes (under 1 atmospheric pressure)

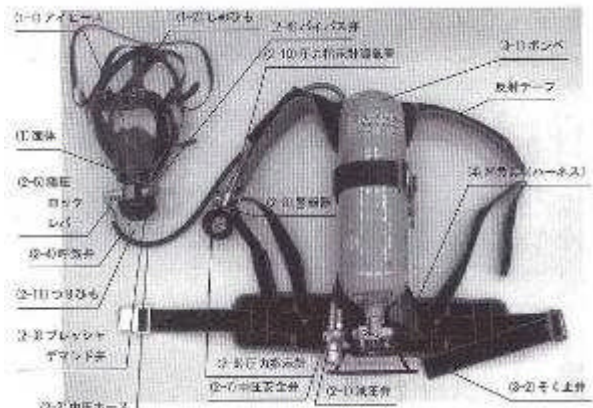
With the provision that usable time depends upon the level of proficiency and experience, mental and physical condition of equipper, difficulty of operation and filling pressure of bottle. The listed usable time is assuming maximum air volume and consumption of 40 ℓ /minute.

- (8) Gross weight: 4.8Kg
- (9) Size of air tank: External Diameter : 172mm, Length : 490mm

(See following pictures “Self-contained Breathing Apparatus” and “Instruction Manual (excerpt)”



“Self-contained Breathing Apparatus”



“Instruction Manual (excerpt)”

### 2.13.3 Training for Equipping with Self-contained Breathing Apparatus

- (1) The Stevedoring company etc.

According to the statements of staff of the stevedoring company, operator D, staff of the smelter and the record of employee injury, the details were as follows.

- [1] The stevedoring company put effort into equipment training but did not emphasize rescue operations by using the breathing apparatus in emergencies.
- [2] They thought that workers not trained practically could not perform a rescue even when equipping with a self-contained breathing apparatus.
- [3] The smelter thought that it was not impossible to go to the site to rescue the workers but very difficult.
- [4] Operator C received rescue training at another company in past time, but at this company he received a training for equipping with self-contained breathing apparatus but was not trained for rescue.



(2) The Ship

According to the statements of master, chief officer and third officer, the details were as follows.

- [1] Third officer seemed panicked by seeing the accident scene.
- [2] The ship was equipped with four or five self-contained breathing apparatuses (made by Unitor, Unipack Compressed Air Breathing Apparatus).
- [3] When the third officer was an able seaman, he had been a member of a rescue party and had equipped with self-contained breathing apparatus.

2.14 Information on Rescue by Persons concerned with Cargo Handling Works and Crew of the Ship

- (1) According to the written reply from the Fire Chief of Oita-city's East Fire Station regarding the above subject:

*Concerned person's finding victims of oxygen deprivation accidents going to rescue them quickly with air breathing apparatus before the arrival of a fire rescue team is desirable if a manual for such accidents is established and they have intimate knowledge of equipping with air breathing apparatus etc. It is very difficult to rescue victims at an accident scene, and even experts have a very high risk for a secondary accident.*

*Because of variable conditions of disaster scenes, it is important to assume the need for double and triple safety management for rescue activities.*

- (2) According to the written reply from the Fire Chief of Tokyo Fire Department regarding the above subject:

1 *Usage of Air Breathing Apparatus and Frequency and Subject of Equipment Training for Rescue Teams*

*After employment, fire fighters of Tokyo Fire Department learn basic matters such as usage of air breathing apparatus at Fire Academy. After graduation, firemen of and others who go to disaster scenes conduct pre-use inspection and equipment training every time they are on duty so they safely use the equipment at the scene.*

2 *Precautions for Rescue Operations in Compartments Expected to Contain Poisonous Gases or a Deficiency in Oxygen*

*If a fireman enters a compartment expected to contain poisonous gases or a deficiency in oxygen, he securely equips with an air breathing apparatus, as well as a pressurized hazmat suit as necessary, sets up a party of multiple members, and enters while measuring for oxygen deficiency and poisonous gases with a meter from a safe area.*

*If the measured value indicates danger, they choose to reject the risk or evacuate.*

*In the case of a disaster caused by a particular chemical substance, the chemical disaster special unit mobilizes and analyzes the concentration and danger of the substance.*

*By evaluation the measured results, we will set up a restricted area that prevents the entrance of ordinary people as well as a check-point that controls the entrance of members without proper equipment to prevent the possibility of secondary injury.*

*In the case where a victim has inhaled a poisonous gas, he or she is handed over to the ambulance crew after containment and decontamination of the affected area.*

3 *Regarding a person without training in the utilization of the appropriate equipment described above 2 entering a contaminated area to perform a rescue:*

*Members of Tokyo Fire Department without training in the equipping and utilization of air breathing apparatus do not go to the disaster scene.*

*Moreover, according to the regulations of the Tokyo Fire Department, entering a compartment such as the one described in the preceding paragraph by a person who is not a member of the Fire Department is restricted by the restrictive area.*

#### 2.15 Information on Ventilation of the Cargo Hold

According to the statements of the staff of the smelter and the stevedoring company as well as other workers, the main details were as follows.

- (1) After berthing, workers assumed the O<sub>2</sub> concentration in the vessel was already measured and they entered the cargo hold without thinking of danger.  
In case of an abnormality, the supervisor of cargo work informed them.
- (2) Before changes to discharging cargo operation procedure, they had not entered the cargo hold immediately after opening the hatch, and the cargo hold was almost completely ventilated by the time the worker entered.
- (3) Considering their past experiences of natural ventilation, they thought natural ventilation was possible in a short time, hence they were surprised by the accident.
- (4) They were under the impression that once the hatch-cover was opened the oxygen deficient air left the cargo hold immediately.
- (5) Until that point, the oxygen levels (less than 18%) had not been measured.
- (6) Serious accident as this one had not occurred from four years ago.

#### 2.16 Information on Weather and Sea Conditions

##### (1) Meteorological Observation

Meteorological observation by the Oita Meteorological Observatory around the time of occurrence of the accident was as follow.

08:00 Wind Direction NNW, Wind Velocity 1.2m/s , Temperature 22.5°C

08:30 Wind Direction NW, Wind Velocity 1.4m/s , Temperature 22.7°C

09:00 Cloudy, Wind Direction N, Wind Velocity 1.9m/s , Temperature 23.0°C

##### (2) According to the statements of the rescue team members, the details were as follows.

The weather information written on the command sent to the office to go into action with the mobilization order, observed at the operations center located in Maizuru Town, Oita City, was:

Wind NW, Wind Velocity 0.5m/s , Temperature 23.1°C.

## 3 ANALYSIS

### 3.1 Situation of the Accident Occurrence

#### 3.1.1 Course of the Events

According to 2.1 and 2.10, the events leading to the accident are as follows.

##### (1) Conditions Leading to Primary Accident

- [1] The ship, carrying copper concentrate in the airtight cargo hold No. 3, sailed from Port Moresby Harbour to port of Saganoseki, taking approximately 12 days. It is considered

probable that during the voyage, the copper concentrate oxidized, depleting the oxygen in No. 3 cargo hold. It is also considered probable that the atmosphere in cargo hold No. 3 became oxygen-deficient and an odorous gas, hazardous to humans, accumulated from two floatation reagents adhering to the copper concentrate.

- [2] The ship moored at a private berth in port of Saganoseki and opened the hatch cover of cargo hold No. 3 to discharge the copper concentrate.

However, it is considered probable that air in cargo hold No. 3 had not been replaced outside air, and the oxygen-deficient condition had remained.

- [3] After mooring operation, it is considered probable that about a little after 07:50, the chief officer read out the draft of the ship with the surveyor then, by the previous agreement of Discharging Plan with the foreman, he ordered the crew to open the hatch covers of cargo holds No. 1 and No. 3 were scheduled to discharge cargo at this port.

It is considered probable that the foreman posted an entrance permitted notice board at the entrance hatch from around 07:50 to around 08:05.

It is also considered somewhat likely that the foreman measured the O<sub>2</sub> concentration by himself from around 07:50 to around 08:05.

- [4] Driver B was on the upper deck near cargo hold No. 3 waiting for the cargo work.

It is considered probable that Driver B did not enter cargo hold No. 3 because of a strong odor from the cargo but contacted Operator D to load the heavy vehicle into cargo hold No. 3.

While Operator D was lowering the heavy vehicle into No. 3 cargo hold, Driver B entered the cargo hold and was moving toward the bottom when he inhaled oxygen-deficient air and developed anoxia. As a result, Driver B fell from the landing down to the surface of the cargo.

## (2) Conditions Leading to the Secondary Accident

- [1] While the foreman and other personnel were conducting a meeting in the cargo work office, they were informed by Operator C that Driver B had collapsed. They went to rescue him together with Operator F, who brought a self-contained breathing apparatus (SCBA). The foreman and Operator C entered into cargo hold No. 3 without wearing SCBA.

It is considered probable that the foreman inhaled oxygen-deficient air and developed anoxia and then fell down to the surface of the cargo.

- [2] Had Operator F known that Driver B fell down from developing anoxia, he would have deterred the foreman and Operator C.

However, it is considered probable that Operator F thought that he also had to go to rescue Driver B, and he entered into No. 3 cargo hold where he felt as though he was being choked.

It is also considered probable that Operator C signaled for Operator F to go back, hence Operator F returned to the upper deck together with Operator C.

## (3) Conditions Leading to the Tertiary Accident

- [1] The chief officer advised Operators C and F, who had equipped with the gas masks and were going to enter the cargo hold No. 3, that going into the hold with only a gas masks on is dangerous.

It is considered probable that although Operator F was advised by the chief officer, at the time, Operator F could not understand the chief officer's advice due to spoken by

English, so he thought the mask received from the ship might supply oxygen .

It is considered probable that Operators C and F again entered into cargo hold No. 3 wearing gas-masks from the ship and Operator C inhaled oxygen-deficient air and developed anoxia and then fell down to the surface of the cargo.

- [2] It is considered probable that Operator F sensed danger and came back to near the entrance hatch and the crew of the ship pulled Operator F up to safety.

### 3.1.2 Date and Location of the Accident

According to 2.1, it is considered probable that the date and the place of the accident occurred are as follows:

The date of the primary accident occurred was at around 08:30 on June 13, 2009 and the place in cargo hold No. 3 of the ship moored at a private berth in port of Saganoseki.

And the date of the secondary and tertiary accident occurred between around 08:30 to 08:40 on the same day. The place was the same of the primary accident in the same cargo hold.

### 3.1.3 Casual Factors on Death Occurred

According to 2.1.2(6)-(10), 2.2.2, 2.7 and 2.8, it is considered probable as the following:

- (1) The O<sub>2</sub> concentration had been lower around the surface of the cargo in cargo hold No. 3.
- (2) Life-threatening levels of hydrogen sulfide gas and carbon monoxide gas were not generated in cargo hold No. 3.

Considering the above, it is considered probable that Driver B, the foreman and Operator C inhaled oxygen-deficient air and developed anoxia causing death.

## 3.2 Causal Factors of the Accident

### 3.2.1 Causal factors related to the navigation status of the ship

The description in 2.1.1, 2.5.2, 2.5.3, 2.6.2 and 2.7.1(3) indicates as the following:

- (1) It is considered probable that the ship conducted the transportation, the stowage of the cargoes and the cleaning inside the cargo holds according to the voyage instructions.

It is also considered probable that the ship shut the hatch cover of cargo hold No. 3 tight in order to avoid cargo damage according to the instructions of the shipper, as the BC code and IMSBC code, state that in order not to move over by liquefaction of copper concentrate caused by an immersion into the cargo holds and not to be wetted by seawater and not get copper concentrate oxidized by reaching to air.

- (2) It is considered probable that the cargo was not wet from rain when loaded into the ship.
- (3) The Effect of Splashing
  - [1] It is considered probable that there were six (6) days when the upper deck of the ship was washed by waves or exposed to splashing from the loading port to the port of Saganoseki (anchorage).
  - [2] It is considered probable that the frequencies of cooling by waves and splashing of cargo hold No. 1, located, near the bow, was higher than that of cargo hold No. 3.
- (4) It is considered probable that the cargoes remained watertight during the voyage and is thought to have not been wetted by sea water.
- (5) Airtightness of Cargo Holds No. 1 and No. 3

It is considered probable that from the following, cargo hold No. 3 remained airtight in addition to watertight.

However, it is considered probable that cargo hold No. 1 remained watertight but airtightness was not maintained and the hold did not become oxygen-deficient.

- [1] When the hatch covers were opened, there was no dew condensation water seen on the hatch cover of cargo hold No. 1, however, a large flow of dew condensation water poured down from the back of the hatch cover of cargo hold No. 3.
- [2] Although it could not be determined whether or not the kingbolts of the ship were loose, it is considered somewhat likely that the king bolts of cargo hold No. 1, which was easily influenced by a rough sea passage, gradually loosened.

(6) Environmental Temperature in cargo hold No. 3

It is considered probable that from the following, the temperature (ambient temperature) in cargo hold No. 3 loaded copper concentrate was determined to be about 40°C~60°C at the time of the accident happened:

- [1] During the voyage, the average sea temperatures at noon was about 29°C and the average outer air temperature was about 28°C.
- [2] The temperature of sample A, which was taken from another cargo ship berthing at the port of Saganoseki on March 31, 2010, was 42.6°C.
- [3] The recorded outer air temperature while taking sample A from another cargo ship was about 14°C lower than that of [1], and the recorded sea water temperature was about 17°C lower than that of [1].
- [4] From [1] to [3], the ambient temperature in cargo hold No. 3 was at least around the temperature of sample A (42.6°C), plus the difference of the outside air temperature (approximately 14°C) and the difference of temperature of 42.6°C plus the seawater temperature (approximately 17°C).

3.2.2 Probable Atmospheric Conditions in cargo hold No. 3 based on Entrusted Research Results

According to 2.1.1(1), 2.5.3, 2.6, 2.7 and 3.2.1, it is considered probable as follows:

(1) A model indicating the atmosphere in cargo hold No. 3

From research entrusted to Nippon Kaiji Kentei Kyokai (Physical and Chemical Analysis Center), the results for the measured oxygen consumption rates in conditions with 70% vacant space and an ambient temperature of 40°C-60°C corresponds to a model of the atmosphere in cargo hold No. 3.

(2) The atmosphere in cargo hold No. 3 when the ship was moored at the private berth

- [1] O<sub>2</sub> in cargo hold No. 3 was consumed by the copper concentrate oxidizing, leading to the atmosphere in cargo hold No. 3 becoming oxygen-deficient.
- [2] When copper concentrate with two floatation reagents were closed tight in the cargo hold, O<sub>2</sub> concentrations became lower in the lower layers.

Therefore, O<sub>2</sub> concentrations in cargo hold No. 3, which had become oxygen-deficient from the copper concentrate oxidizing, were different depending on the measuring points.

- [3] The molecular state of copper concentrate compound and applied floatation reagents are different depending on the sources of production.

Therefore, the oxygen consumption rates differ.

[4] The accumulated odorous hazardous gases, which were heavier than air, were generated by the floatation reagents adhering to the copper concentrate.

(3) Review

The ship departed Port Moresby Harbour to port of Saganoseki.

During the voyage, copper concentrate loaded in cargo hold No. 3 oxidized, and the oxygen in the airtight hold was consumed.

Along with the atmosphere in cargo hold No. 3 becoming oxygen-deficient, odorous hazardous gases, which were heavier than air, were generated by the floatation reagents adhering to the copper concentrate and accumulated in the cargo hold.

3.2.3 Atmosphere in cargo hold No. 3 after opening the hatch cover

According to 2.1, 2.5.3(6), 2.6, 2.7, 2.8 and 3.2.2, it is considered probable as follows:

(1) O<sub>2</sub> concentration

[1] According to the measurements taken by rescue team, the O<sub>2</sub> concentration around the upper deck at around 09:07 was approximately 19%.

[2] Judging from symptoms and anoxia which Operator F developed when he entered into No. 3 cargo hold, the O<sub>2</sub> concentration at middle layers of the hold from around 08:30 to 08:40 was approximately 12-16%.

[3] According to the measurement by Operator D, the O<sub>2</sub> concentration at lower layers of the hold was approximately 1.5-2% at about 08:50.

[4] The O<sub>2</sub> concentration of the lower layers of the hold was lower than that of the upper layers.

(2) Atmosphere

[1] From around 08:30 when the accident occurred to 08:50 when Operator D measured O<sub>2</sub> concentrations in cargo hold No. 3, the cargo hold had remained on in an oxygen-deficient condition for at least 20 minutes.

[2] Regarding the O<sub>2</sub> concentration distribution in cargo hold No. 3, the results of the analytical experiment, where a copper concentrate with two floatation reagents was sealed in a container, showed that the O<sub>2</sub> concentrations was lower nearer the lower layers of the hold.

Thus the air in the hold was stable situation ( not flowing ).

[3] Odorous hazardous gases, which were heavier than air, which were generated by the floatation reagents were not replaced by fresh air and accumulated in the lower layer of the cargo hold.

[4] It was difficult for the air in cargo hold No. 3 to be replaced by outside air through natural ventilation with the wind velocity under 0-1.4m/s.

[5] The smelter and the stevedoring company did not understand the necessity of forced ventilation because, in the past, the O<sub>2</sub> concentration increased to 20.9% by natural ventilation as time passed.

[6] From the above, air in the hold was not replaced by outside air after opening the hatch cover, and the oxygen-deficient atmosphere remained.

(3) Reason why O<sub>2</sub> concentration decreased in the lower layer of the hold:

[1] Air around the surface of copper concentrate oxidized and consumed oxygen.

[2] Odorous hazardous gases, which were heavier than air, stayed in the lower layer of

the cargo hold and pushed the air of the lower layer up higher.

### 3.2.4 Analyses of the discharging cargo operation and the accident occurred

The description in 2.1 indicates the following:

- (1) It is considered probable that seven personnel including the foreman, Driver B, Operator C, Operator D, and Operator F were organized in the team to begin discharging cargo handling in the ship at around 07:00 on the day of the accident occurred.
- (2) It is considered probable as follows:
  - The foreman assigned work to each member. He measured the O<sub>2</sub> concentrations in the cargo hold and posted the access permit notice board
  - Driver B took charge of driving the heavy vehicle in cargo hold No. 3
  - Operator D took charge of operating the crane

- (3) It is considered probable that the foreman boarded the ship at around 07:50 and he instructed Operator D at around 08:05 as mentioned below (5).

Therefore, it is considered probable that the foreman posted the access permit notice board at the entrance hatch of cargo holds No. 1 and No. 3 from around 07:50 to around 08:05, according to a rule which had been created after the fatal accident occurred due to oxygen deficiency in a cargo hold four years ago.

- (4) It is considered somewhat likely that the foreman measured the O<sub>2</sub> concentration before giving instructions to Operator D, who is mentioned below (5). And it is considered probable that the foreman then returned back to the cargo work office and wrote down the O<sub>2</sub> concentrations of cargo holds No. 1 and No. 3 in the cargo record book as 20.9%.

Based on the cargo record book, the measuring points for cargo hold No. 3 were: four points of the lower layers of the fore and aft hatch coamings of both side of the ship, two points of the upper and the lower layers of the fore entrance hatch, and one point of the lower layers of the aft entrance hatch.

It is also recorded that the measurer was the foreman and the measuring time was 08:30.

- (5) It is considered probable that Operator D was called by the foreman to get on the ship at around 08:05 and got inside cockpit of crane No. 3 after lowering a heavy vehicle into cargo hold No. 1 with crane No. 2 as instructed by the foreman.

- (6) Concerning Driver B and Operator D, it is considered probable as follows:
  - Driver B was waiting on the upper deck around the entrance hatch of cargo hold No. 3 but did not enter the cargo hold because of a strong smell from the cargo.  
However, Driver B contacted Operator D to lower the heavy vehicle into cargo hold No. 3.
  - As Operator D was lowering the heavy vehicle into cargo hold No. 3 with the crane, Driver B was entering cargo hold No. 3 from the aft entrance hatch.
  - Driver B collapsed to the surface of the cargo while he was descending to the bottom of the cargo hold.

- (7) Concerning the foreman, Operator C and Operator F, it is considered probable as follows:
  - While the foreman and other personnel were holding a meeting, Operator C and others reported to them that Driver B fell down in cargo hold No. 3.  
The foreman, Operator C and Operator F went to rescue Driver B.
  - Operator F brought a SCBA. However, the foreman and Operator C entered cargo hold No. 3 without wearing SCBA, accordingly Operator F also entered into the hold

without wearing a SCBA.

- The foreman fell down to the surface of the cargo.  
Operator C and Operator F returned back to the upper deck.  
Operator F felt like he was choking in the cargo hold No. 3.
- (8) Concerning Operator C and Operator F, it is considered probable as follows:
- Although the chief officer advised Operator C and Operator F that going into the hold with only gas masks on are dangerous, Operator C and Operator F put on gas masks from the ship and again entered into cargo hold No. 3 to rescue the foreman.
  - Operator C then fell down to the surface of the cargo.
  - Operator F could not understand the chief officer's advice due to spoken by English, so he thought the mask received from the ship might supply oxygen and would be fine if he was wearing the gas mask.
- (9) Concerning Operator F, it is considered probable as follows:
- Operator F felt it was dangerous to continue with entering into the hold and then returned back to the entrance hatch and was pulled up to the deck by the ship's crew.
- (10) Concerning Fire Department, it is considered probable as follows:
- The fire department, which received an accident report from the smelter, sent out a rescue team, accordingly, rescued the three workers including the foreman from cargo hold No. 3 with using the ship's crane and a cage.  
The rescue team sent the three workers to medical facilities by ambulances.

### 3.2.5 Analyses of the measurement of O<sub>2</sub> concentration in cargo hold No. 3

The descriptions in 2.1.1(1), (4)-(10), 2.3, 2.10, 2.11, 2.12.2, 2.13.1 and 2.15 indicates the following:

(1) The measurer of the O<sub>2</sub> concentration

It is considered probable that the foreman measured the O<sub>2</sub> concentration by himself before discharging cargo operation.

And also it is considered probable that there are no personnel who know how the foreman measured the O<sub>2</sub> concentrations.

(2) Measurement of O<sub>2</sub> concentrations before the primary accident

It is considered somewhat likely as follows:

- At around 07:50, the foreman boarded the ship.
- Operator D was called by the foreman to get on the ship at around 08:05 and instructed to lower the heavy vehicle into the cargo hold.
- The foreman measured the O<sub>2</sub> concentration between around 07:50 and 08:05.

It can not be determined the points measured and the procedures used (the hold, the points of coamings, the depth of the sensor cable, etc) since:

- The foreman is dead.
- No one knows how the O<sub>2</sub> concentration was measured.

(3) Measurement of the O<sub>2</sub> concentration after the primary accident occurred

[1] After the primary accident occurred

It is considered probable that at the time the foreman entered into cargo hold No. 3 to rescue Driver B, he did not measure the O<sub>2</sub> concentration.

[2] After the secondary accident occurred

It is considered probable that at the time Operator C and Operator F entered into



cargo hold No. 3 to rescue the foreman and Driver B, they did not measure the O<sub>2</sub> concentration.

[3] After the tertiary accident occurred

It is considered probable as follows:

- At around 08:50, Operator D lowered a sensor from the hatch coaming of the aft port, and when the sensor was lowered to approximately 4-5m, he found that the O<sub>2</sub> concentration had decreased to 18%
- Operator D lowered the sensor further and discovered that the O<sub>2</sub> concentration around the point where the foreman, Driver B and Operator C had collapsed (below the second landing) was approximately 1.5%-2%.

It is considered additionally, it is improbable that such a big difference in O<sub>2</sub> concentrations could have occurred at the above mentioned points for the following reason:

- A horizontal distance from the hatch coaming of a back port corner, where the foreman might have measured the O<sub>2</sub> concentration, to the bottom of second landing, where Driver B collapsed, was approximately 5m-6m.

[4] Relationship between the method the O<sub>2</sub> concentration was measured at the time of the secondary accident and instructions etc.

It is considered somewhat likely that:

- If the foreman had measured the O<sub>2</sub> concentration when he entered into cargo hold No. 3, the secondary and the tertiary accidents could have been prevented.
- Although the stevedoring company provided training on wearing SCBA, it put no weight on rescue training while using them.
- Although fatal accidents had occurred in cargo holds in the past, the stevedoring company did not provide operators with appropriate education and training for accidents.

It is considered probable that the foreman entered into cargo hold No. 3 without measuring the O<sub>2</sub> concentration, and this led to the secondary accident and the tertiary accident.

- Therefore, it is considered probable that a lack of appropriate education and training for operators on countermeasures in case of the fatal accident occurring in the cargo hold is, as mentioned later in 3.2.7(4), responsible for the secondary accident and the tertiary accident.

(4) Current status of the methods for measuring and recording O<sub>2</sub> concentrations

According to the record books of 157 ships berthed from January 3, 2007 to December 29, 2008, 93 of the 157 ships ( $93/157 \doteq 60\%$ ) did not have O<sub>2</sub> concentrations listed completely in the record books.

Moreover, the measuring points used differed depending on the measurer, including the foremen of the stevedoring company.

Thus, it is considered that:

- Supervisors of cargo operation, including the foreman, of the stevedoring company were accustomed to measuring O<sub>2</sub> concentrations by individual discretion. Thus, measurements had been taken at different points and depths. The measurements had not been done according to the procedures outlined by the stevedoring company.
- The smelter and the stevedoring company did not take corrective measures of method

for the measuring mentioned above because they did not know current status.

(5) Probability that the oxygen-deficient condition could have been detected

It is considered probable that:

- About 20 minutes after the accident occurred, Operator D put the sensor of O<sub>2</sub> concentration meter into the hold from the hatch coaming of cargo hold No. 3's aft port.
- As soon as the sensor reached a depth of 4-5m, the warning sound was set off.
- As the sensor was lowered, the O<sub>2</sub> concentration decreased.

Therefore, it is considered somewhat likely that the foreman was not aware of the oxygen-deficient condition in cargo hold No. 3 from doing habitual practices for the measurement, and the foreman posted the access permit notice board for the reasons mentioned above (4).

Thus it is considered somewhat likely that if the smelter and the stevedoring company had realized that the foremen and supervisors of cargo work were taking measurements habitually and had corrected by them, the foreman would have known the true atmosphere of cargo hold No. 3 and thus the primary accident could have been avoided.

The smelter and the stevedoring company did not grasp the measuring practices mentioned accordingly, they did not warn the measurers to follow procedures.

It is considered probable that they were contributed in the primary accident occurred.

(6) Handling of O<sub>2</sub> concentration meters

It is considered probable that Operator D and Operator F had no experience in using O<sub>2</sub> concentration meters.

3.2.6 Knowledge on anoxia and so forth

The description in 2.3, (3), (5) and (6) indicates the following.

Operator B, the foreman and Operator C took "special training for hazardous work including oxygen-deficient environments (the second class)". And it is considered probable that the foreman had knowledge on recognizing the oxygen-deficient condition in cargo hold No. 3 because the foreman also took "skill training course for operations, and chief of hazardous work in oxygen-deficient environments and with hydrogen sulfide" and was an instructor for safety education.

3.2.7 Grasp of the atmosphere in cargo hold No. 3 and factors for entering

The description in 2.1.2, 2.10, 2.12 and 2.15 indicates the following.

(1) Driver B (at the time of the primary accident happened)

It is considered probable that Driver B was not aware of the oxygen-deficient atmosphere in cargo hold No. 3 and thought that it was possible to enter into the cargo hold and start working based on the following:

- Access permit notice board was posted at the entrance hatch of cargo hold No. 3
- Another Operator had start driving the heavy vehicle in cargo hold No. 1

(2) The foreman, Operator C and Operator F (at the time of the secondary accident occurred)

It is considered probable that since the foreman, Operator C left the equipment on the upper deck of the ship, which Operator F had brought the self-contained breathing apparatus with him, and entered into cargo hold No. 3, felt impatient and responsible to rescue Driver B, lost their sense of composure and were not aware of the oxygen-deficient condition in cargo hold No. 3.

And also it is considered somewhat likely that the following were contributed that the foreman and Operator C were not aware of the oxygen-deficient condition in cargo hold No. 3.

[1] There were workers who had a misunderstanding that oxygen-deficient conditions in cargo holds were resolved by natural ventilation as time passed after opening the hatch covers.

[2] Measurements for checking oxygen-deficient condition had not been done by the time when this case occurred and also there were no accidents causing injury or death since the fatal accident by developing anoxia in the cargo hold occurred four years ago.

Reasons why Operator F entered into cargo hold No. 3 following the foreman, it is considered somewhat likely as follows:

- Operator F recognized that Driver B collapsed by developing anoxia, thought of stopping the foreman and Operator C.

However, Operator F thought that he also had to join the rescue.

- Operator F felt impatient and responsible to rescue Driver B and lost his sense of composure.

(3) Operator C and Operator F (At the time of the tertiary accident occurred)

It is considered likely that Operator C perceived that the atmosphere in cargo hold No. 3 became oxygen-deficient by the following:

- Soon after Operator C entered into cargo hold No. 3, Operator C sent a signal to Operator F to go back and then Operator C also went back to the upper deck.

Operator C equipped with the gas mask, carry the SCBA on his back and entered cargo hold No. 3 again.

It is considered probable that Operator F came to the realization that the atmosphere in cargo hold No. 3 had become oxygen-deficient as follows:

- Operator F recognized that Driver B fell down by developing anoxia, and additionally Operator F felt a choking sensation when he entered into cargo hold No. 3.

It is considered probable that Operator C and Operator F entered into cargo hold No. 3 again as follows:

- Operator C and Operator F went back to the upper deck and equipped with gas masks rigged with the ship and they entered into cargo hold No. 3 once again.

According to the above and (2), it is considered somewhat likely that Operator C and Operator F entered into cargo hold No.3 once again for the following reasons:

- Operator C thought that he could act in an oxygen-deficient atmosphere when equipping with just gas masks.
- Operator F thought the mask received from the ship might supply oxygen .
- Operator C and Operator F felt impatient and responsible to rescue Driver B and lost their sense of composure.
- As Operator C and Operator F had already developed anoxia when they had gone to rescue Driver B at the time of the primary accident occurred, they lost their sense of reason.

It is considered somewhat likely that Operator F could not distinguish a gas mask from an oxygen mask because he thought that he could take action in an oxygen-deficient atmosphere without problems if he equipped with the gas mask, which he thought it was oxygen mask.

It is considered somewhat likely that Operator C also thought that he could take

action in an oxygen-deficient atmosphere without problems if he equipped with a gas mask. However, since Operator C died, it could not determine the reason why he thought like that.

(4) Review

It is considered probable that the foreman and the operators C and F had not taken appropriate education and training on coping behavior in case of fatal accidents occurring in cargo holds where copper concentrate was loaded.

It is considered somewhat likely that the stevedoring company was contributed to occurrences of the secondary and the tertiary accidents for the following reasons.

- The stevedoring company did not give appropriate education and training about coping behavior to the foreman, Operator C and Operator F in case of accidents causing injury or death in cargo holds which copper concentrates were loaded with topics such as: Safety check in cargo hold by the measurement of the O<sub>2</sub> concentration, the possibility for operators to enter into cargo holds in state of oxygen-deficient and appropriate apparatus at the time of entering into cargo holds

3.2.8 Causal factors on outbreak of the Accident

The description from 3.2.1 to 3.2.6 indicates the followings.

(1) It is considered probable as follows:

The ship, carrying copper concentrate in the airtight cargo hold No. 3, sailed from Port Moresby Harbour to port of Saganoseki.

During the voyage, the copper concentrate oxidized, depleting the oxygen in cargo hold No. 3. The atmosphere in cargo hold No. 3 became oxygen-deficient and an odorous gas, hazardous to humans, generated by the floatation reagents adhering to the copper concentrate and accumulated in the cargo hold.

(2) It is considered probable as follows:

The ship was moored at a private berth in port of Saganoseki and the hatch cover of cargo hold No.3 was opened to discharge the copper concentrate.

However, the air in No. 3 cargo hold had not been replaced by outside air and the oxygen-deficient condition remained.

(3) It is considered probable that the foreman assigned work operations to each worker and measured O<sub>2</sub> concentrations in the cargo hold by himself between 07:50 and 08:50.

However, since the foreman is dead and no one knows how the foreman measured the O<sub>2</sub> concentration, the method remains unclear.

And during this time it is considered probable that the foreman posted access permit notice board at the entrance hatch of cargo hold No. 3 according to a rule which had been created after the fatal accident occurred due to a lack of oxygen in a cargo hold four years ago. At this time, it is considered somewhat likely that the foreman was not aware of the oxygen-deficient condition in cargo hold No.3.

(4) Measurement Practices, it is considered probable as follows:

Cargo work supervisors including the foreman of the stevedoring company were accustomed to measure O<sub>2</sub> concentrations at their own discretion; that is measurements made at different positions and depths.

The measurements were not done according to the ways determined by the stevedoring

company.

It is considered probable that Foreman was not aware of oxygen-deficient atmosphere in cargo hold No. 3 because of poor habitual measuring practices.

- (5) It is considered probable that if the smelter and the stevedoring company, knowing that habitual practices were used in measurements of the O<sub>2</sub> concentration in cargo holds that the foreman and other supervisors of cargo operation had been doing and corrected it, the foreman would have properly known the atmosphere of cargo hold No. 3 and avoided the primary accident.

Therefore it is considered somewhat likely that the smelter and the stevedoring company were not aware of the habitual practices being used in the measurements of O<sub>2</sub> concentrations by the supervisors of cargo operation including the foreman and did not give instructions to supervisors of cargo operation and the foreman to do the measurements by the determined methods, which was a factor that invited the primary accident.

- (6) It is considered probable as follows:

Driver B was waiting on the upper deck near cargo hold No. 3 preparing for the cargo work.

Driver B didn't enter into cargo hold No. 3 because of a strong smell from the cargo but instructed Operator D to lower the heavy vehicle into cargo hold No. 3.

While Operator D was lowering the heavy vehicle into cargo hold No. 3, Driver B entered into cargo hold No. 3 and was descending to the bottom.

At that moment, Driver B inhaled oxygen-deficient air and developed anoxia.

As a result, Driver B fell down to the surface of the cargo.

- (7) It is considered probable that Driver B was not aware of oxygen-deficient atmosphere in cargo hold No. 3 and thought that it was possible to enter into the cargo hold to start working because:

- Access permit notice board was posted at the entrance hatch of cargo hold No. 3
- Another Operator had started driving the heavy vehicle in cargo hold No. 1

- (8) It is considered probable as follows:

While the foreman and other personnel were conducting a meeting in the cargo work office, they were informed by Operator D that Driver B had collapsed.

They went to rescue him together with Operator F who brought a SCBA.

The foreman and Operator C entered into No. 3 cargo hold without wearing SCBA.

The foreman inhaled oxygen-deficient air, developing anoxia, and then fell down.

- (9) It is considered somewhat likely as follows:

Operator F felt that Driver B collapsed under developing anoxia, and thought of deterring the foreman and Operator C. However, Operator F thought that he also had to join the rescue and entering into cargo hold No. 3 and felt choked. Operator C gave Operator F a signal to go back, so Operator F went back to the upper deck with Operator C.

- (10) Since the foreman and Operator C left the SCBA, which Operator F had brought, on the upper deck and entered into cargo hold No.3, it is considered somewhat likely that the foreman and Operator C felt impatient and responsibility to rescue Driver B and lost their sense of composure and not aware of the oxygen-deficient condition in cargo hold No.3.

And also it is considered somewhat likely that the following factors were reasons why the foreman and Operator C were not aware of the oxygen deficient atmosphere in cargo hold

No.3.

[1] There were workers who had a misunderstanding that oxygen-deficient conditions in cargo holds were removed by natural ventilation as time passed after opening the hatch covers.

[2] Measurements for checking oxygen-deficient condition had not been done by the time when this case occurred and also there were no accidents causing injury or death since the fatal accident by developing anoxia in the hold happened four years ago.

(11) It is considered probable that Operator C realized that the atmosphere in cargo hold No. 3 became oxygen-deficient for the following reasons:

- Soon after Operator C entered into cargo hold No. 3, Operator C sent a signal to Operator F to go back, and himself went back to the upper deck.
- Operator C equipped with the gas mask, carry the SCBA on his back and entered cargo hold No. 3 again.

And it is considered probable that Operator F realized that the atmosphere of cargo hold No. 3 was oxygen-deficient for the following reasons:

- Operator F recognized that Driver B collapsed after developing anoxia when he felt a choking after his entering into cargo hold No. 3.

(12) It is considered probable that Operator C fell down onto the surface of the cargo for the following reasons:

- Operator C and Operator F went back to the upper deck and put on gas masks from the ship and they entered into cargo hold No. 3 once again.
- Operator C inhaled oxygen-deficient air and developed anoxia.

(13) From the above descriptions, (9) to (12), it is considered somewhat likely that Operator C entered into No.3 cargo hold once again for the following reasons:

- Operator C thought that he could take action in an oxygen-deficient atmosphere when wearing just gas masks.
- Operator F thought the mask received from the ship might supply oxygen.
- Operator C and Operator F felt impatient and responsible to rescue Driver B and lost their sense of composure.
- As Operators C and F had already developed anoxia when they went to rescue at the time of the primary accident, they lost their sense of reason when they entered into cargo hold No. 3 once again.

It is considered somewhat likely that Operator F could not distinguish a gas mask from an oxygen mask because he thought that he could take action in an oxygen-deficient atmosphere without problems if he wore a gas mask.

(14) It is considered somewhat likely that the stevedoring company was responsible for the secondary accident and the tertiary accident for the following reasons.

- The foreman, Operator C and Operator F did not check the atmosphere when they entered into cargo hold No. 3.
- Operator C and Operator F learned that the atmosphere in cargo hold No. 3 had become oxygen-deficient. Despite this, they wore gas masks and entered into the cargo hold once again.

Thus the stevedoring company did not give appropriate education and training to the foreman, Operator C and Operator F on coping behavior in case of fatal accidents occurring in cargo holds where copper concentrate are loaded

- (15) However the foreman, Driver B and Operator C were rescued from cargo hold No. 3 by the rescue team of the fire department and sent to medical institutes, it is considered probable that they all died of anoxia.

### 3.2.9 The Ship's Crew and Staff of the Agent knowledge of the Oxygen-Deficiency Situation

The description in 2.1.2(9) indicates the following

- (1) The crew of the ship

It is considered that when the master, chief officer and third officer were informed about the accident occurring, they realized that Driver B collapsed from developing anoxia.

- (2) Staff of the agent

It is considered that staff of the agent knew that the operators fell down from developing anoxia.

### 3.3 Analyses of actions to avoid subsequent accidents

The description in 2.1.2(9) and (10) indicate the following.

- (1) Response of the Master

It is considered probable that the master did not give permission to third officer, who said would join the rescue equipping with a SCBA, because the master judged that it was dangerous to enter into cargo hold No. 3.

It is considered probable that the master also saw operators of the stevedoring company attempting a rescue and gave instructions to staff of the agent to stop them.

- (2) Assistance of staff of the agent

It is considered probable that the person in charge of staff of the agent also thought that it was dangerous for him to enter into the cargo hold.

Therefore, staff of the agent understood the intentions of the master immediately and deterred operators who were trying to enter into the cargo hold for the rescue.

- (3) Review

It is considered probable that the master and staff of the agent judged that the atmosphere in cargo hold No. 3 was oxygen-deficient and avoided subsequent accidents.

### 3.4 Causal factors of Rescue by personnel who were engaged in cargo work and the crew of the ship

The descriptions in 2.1.4, 2.8, 2.13.3, and 2.14 indicate the following.

- (1) Training for equipping with SCBA

[1] It is considered probable that personnel who were engaged in the cargo work did not have adequate training for wearing SCBA.

[2] It is considered probable that the third officer had experience in equipping with SCBA, however, he could not gain his composure and take action to perform a rescue at the time.

- (2) Causal factors of Requiring training

It is considered probable that it is necessary for considerable training including handling SCBA, how to equip with them, appropriate ways to approach to accident scenes and timely rescue methods for personnel to perform rescues inside oxygen-deficient cargo holds because of the following restrictions.

[1] Air capacity of the SCBA is limited.

[2] As the accidents in this case happened in the cargo hold, it was difficult for personnel wearing SCBA to approach the personnel who needed help.

[3] Rescue in a short time is required. If it takes a long time for the rescue, rescuers may become victims of a secondary accident.

(3) Causal factors on attempted rescue

It is considered somewhat likely that there were the risks of attempted rescues are:

- Personnel who were engaged in the cargo operation and the crew of the ship did not have training to rescue the personnel who needed help from inside oxygen-deficient compartment.
- Personnel who were engaged in the cargo operation and the crew of the ship panicked and could not take action to perform a rescue at the time.
- The accident scene made it difficult for them to reach the personnel who needed help.
- Even if they had equipped with SCBA, it would have been difficult for them to rescue the personnel who need help in a short amount of time.

Therefore it is considered probable that in case of accidents where rescue operations are difficult, a specialized rescue agency should be contacted at once.

### 3.5 Causal factors for taking Measures in order to avoid the primary accident and similar accidents in future

#### 3.5.1 Avoidance of the primary accident

It is considered probable that the primary accident could have been prevented if the following measures were taken.

(1) Understanding the atmosphere in cargo holds

- The atmosphere in cargo holds loaded with copper concentrate have the risk of being fatal to humans because of possible oxygen-deficient conditions, odorous gases and sulfur gases
- An appropriate measurement of O<sub>2</sub> concentrations and the above gases should be conducted in order to know the atmosphere in the cargo hold

(2) Ventilation of cargo holds

If the atmosphere in a hold is not safe, it should be ventilated in until becoming safe (keep O<sub>2</sub> concentration 20.9% and eliminate toxic gases).

(3) Entering into holds

No one should enter into cargo holds until the atmosphere is verified to be safe.

(4) Education on cargo handling for workers

[1] To teach about the risks of oxygen-deficient conditions, anoxia and how to take precautions.

[2] To teach about the properties and the risks of copper concentrate and floatation reagents.

[3] To teach the necessity of enforced ventilation as sometimes oxygen-deficient conditions in holds are not solved by only natural ventilation.

(5) Education on the difficulties and risks of rescues by workers and crew members

When workers or crew member attempt a rescue operation in oxygen-deficient cargo holds, they should have enough training on the handling of SCBA and how to approach



accident scenes.

Moreover, they should be taught that it is difficult for them to rescue personnel who need help inside oxygen-deficient cargo holds in a short amount of time, and there is the risk of death if they themselves develop anoxia.

### 3.5.2 Avoidance of similar accidents in the future

The smelter and the stevedoring company in this case should teach the risks of oxygen-deficient conditions, anoxia to all employees who may engage in cargo operation, as well as provide them with training on how to take action in case of an emergency.

The lessons from the accident should be inherited for the future.

## 4 CONCLUSIONS

### 4.1 Findings

#### 4.1.1 Course of the events

It is considered probable that the course of the events was as follows:

##### (1) The atmosphere in cargo hold No. 3

###### [1] During the Voyage

The ship carrying copper concentrate in the airtight cargo hold No.3 sailed from Port Moresby Harbour to port of Saganoseki.

During the voyage, the copper concentrate oxidized, and oxygen in cargo hold No. 3 was consumed.

The atmosphere in cargo hold No. 3 became oxygen-deficient and an odorous gas, which was heavier than air and hazardous to humans, was generated by the floatation reagents adhering to the copper concentrate and accumulated in the cargo hold.

###### [2] After opening the hatch cover

After opening the hatch cover at port of Saganoseki, the air in cargo hold No. 3 was not replaced by outside air, which has an O<sub>2</sub> concentration of 20.9%, and the oxygen-deficient condition remained.

##### (2) Circumstances leading up to the primary accident

While the ship was berthed at the wharf of port of Saganoseki, and as the heavy vehicle was being lifted by crane No. 3 into cargo hold No. 3, Driver B entered cargo hold No. 3 and was descending toward the bottom, he inhaled oxygen-deficient air, developed anoxia and died.

##### (3) Circumstances leading up to the secondary accident

The foreman, Operator C and Operator F entered into cargo hold No. 3 in order to rescue Driver B.

The foreman inhaled oxygen-deficient air, developed anoxia and died.

Operator F thought of deterring the foreman and Operator C.

However, Operator F thought that he also had to join the rescue, felt impatient and responsible to rescue Driver B and lost his sense of composure. Although Operator F entered into cargo hold No. 3 following the foreman, he was able to return back to the

upper deck together with Operator C.

(4) Circumstances leading up to the tertiary accident

As Operators C and F entered into cargo hold No. 3 once again in order to rescue the foreman, Operator C inhaled oxygen-deficient air, developed anoxia and died.

When Operator F came back to near the entrance hatch, he was pulled up to the upper deck by the crew of the ship and was rescued.

4.1.2 Grasp of the atmosphere in cargo hold No. 3, and factors of entering into cargo hold No. 3

(1) Grasp of the atmosphere in cargo hold No. 3

[1] It is considered somewhat likely that the foreman measured O<sub>2</sub> concentrations by himself inbetween 07:50 and 08:05. However, since the foreman died, and there are no one who knows how the foreman measured the O<sub>2</sub> concentration, the procedures taken for the measurement of the O<sub>2</sub> concentration remain unclear.

[2] It is considered probable that cargo operation supervisors including the foreman of the stevedoring company were accustomed to measuring O<sub>2</sub> concentrations by their individual discretion. It is considered somewhat likely that the foreman was not aware of the oxygen-deficient condition in cargo hold No. 3 since he had been doing habitual practices for the measurement.

[3] It is considered somewhat likely that if the smelter and the stevedoring company had, knowing that habitual practices for measurements of O<sub>2</sub> concentration that the foreman and supervisors of cargo work had been doing, corrected them, the foreman would have known that the atmosphere of cargo hold No. 3 had become oxygen-deficient and therefore could have avoided the primary accident.

Thus it is considered somewhat likely that the followings contributed to occurrence of the primary accident:

- The smelter and the stevedoring company had not known the habitual practices on measurement of O<sub>2</sub> concentration by cargo operation supervisors including the foreman

- The smelter and the stevedoring company had not given instructions to superintendent including the foreman to do the measurement by the ways determined.

(2) Factors in the reason why Driver B entered into cargo hold No. 3 (at the time of the primary accident occurred)

It is considered probable that since the access permit notice board was posted at the entrance hatch of cargo hold No. 3 and another operator had started driving a heavy vehicle in cargo hold No. 1, Driver B was not able to aware of the oxygen-deficient atmosphere in cargo hold No. 3 and thought that there was no problem in entering and starting work.

(3) Factors in the reason why the foreman and Operator C, and Operator F entered into cargo hold No. 3 (at the time of the secondary accident occurred)

[1] It is considered somewhat likely that since the foreman and Operator C left the SCBA which Operator F carried with him on the upper deck of the ship, they felt impatient and responsible to rescue Driver B and lost their sense of composure, and, not aware of the oxygen-deficient condition in cargo hold No. 3, entered to rescue Driver B.

It is considered somewhat likely that the following factors were the reasons that the foreman and Operator C were unaware of the oxygen-deficient atmosphere in cargo

hold No. 3:

- a There were workers who had a misunderstanding that oxygen-deficient conditions in cargo holds were removed by natural ventilation as time passed after opening the hatch covers.
- b Measurements for checking oxygen-deficient condition had not been done by the time when this case occurred and also there were no accidents causing injury or death since the fatal accident by developing anoxia in the hold happened four years ago.

[2] It is considered somewhat likely that Operator F entered into cargo hold No. 3 for the following reasons:

Since Operator F had a feeling that Driver B had fallen down from developing anoxia, he had thought of deterring the foreman and Operator C.

However, Operator F thought that he also had to join the rescue and felt impatient and lost his sense of composure from a sense of responsibility.

(4) Factors in the reasons why Operator C and Operator F entered into cargo hold No. 3 (at the time of the tertiary accident happened)

It is considered probable that Operator C was aware of the oxygen-deficient condition in the atmosphere in cargo hold No. 3 for the following reasons:

- Operator C sent a signal to Operator F to go back and then Operator C also went back to the upper deck.
- Operator C carried the SCBA on his back and entered cargo hold No. 3 again.

And it is considered probable that Operator F became aware of the oxygen-deficient atmosphere in cargo hold No. 3 for the following reasons:

- Operator F recognized that Driver B collapsed by developing anoxia.
- Operator F felt choking sensation upon entering cargo hold No.3.

It is considered somewhat likely that Operator C and Operator F returned to the upper deck and they once again entered into cargo hold No. 3 for the following reasons:

- Operator C thought that they could act in an oxygen-deficient atmosphere by wearing gas masks.
- Operator F thought the mask received from the ship might supply oxygen.
- Operator C and Operator F felt impatient and responsible to rescue Driver B and lost their sense of composure.
- As Operators C and F had already developed anoxia when they had gone to rescue Driver B at the time of the primary accident, they had lost their sense of reason when they entered into cargo hold No. 3 once again.

It is considered somewhat likely that Operator F could not distinguish a gas mask from an oxygen mask because he thought that he could take action in an oxygen-deficient atmosphere without problems if he wore a gas mask.

(5) Coping behavior in case of fatal accidents occurring

It is considered somewhat likely that appropriate education and training on coping behavior in case of fatal accidents had not been given to personnel by the stevedoring company, which contributed to this case for the following reasons:

- The foreman, Operator C and Operator F did not check the atmosphere in cargo hold No. 3 when they entered.
- Operator C and Operator F knew that cargo hold No. 3 became oxygen-deficient,

however, they entered with gas masks only.

#### 4.1.3 Causal factors why the atmosphere in cargo hold No. 3 was not changed

It is considered probable why the air of cargo hold No. 3 was not replaced by outside air, which has an O<sub>2</sub> concentration of 20.9%, and the oxygen-deficient condition remained after opening the hatch cover at port of Saganoseki were the following:

- (1) Odorous gases, heavier than air, generated by the floatation reagents were not replaced by air and accumulated at the lower layer of the hold
- (2) It was difficult for air in cargo hold No. 3 to be replaced by outer air by natural ventilation with the wind velocity under 0 – 1.4m/s.
- (3) The smelter and the stevedoring company had no idea of the necessity for forced ventilation because in the past the O<sub>2</sub> concentration increased to 20.9% by natural ventilation as time passed.

#### 4.1.4 Causal factors of the accident occurred

##### (1) The primary accident

It is considered probable that Driver B entered into cargo hold No. 3, which was oxygen-deficient, inhaled oxygen-deficient air and developed anoxia.

It is considered probable that Driver B entered into cargo hold No.3 since the access permit notice board was posted at the entrance hatch of cargo hold No.3 and another operator had started driving a heavy vehicle in cargo hold No.1.

It is considered probable that the copper concentrate loaded had oxidized during transportation from Port Moresby Harbour to port of Saganoseki, and oxygen in the airtight cargo hold No.3 had been consumed, creating an oxygen-deficient environment.

It is considered probable that the foreman posted the access permit notice board at the entrance hatch of cargo hold No.3 between 07:50 and 08:50 based on a regulation which was created after the fatal accident which occurred four years ago.

However, it is considered somewhat likely that the foreman was not aware of the oxygen-deficient atmosphere in cargo hold No.3.

It is considered somewhat likely that supervisors of cargo operation including the foreman of the stevedoring company were accustomed to measuring O<sub>2</sub> concentrations not using the determined methods, and that the foreman was not aware of the oxygen-deficient atmosphere in cargo hold No.3 because of such habitual practices.

It is considered somewhat likely that the smelter and the stevedoring company were not aware of the habitual practices being used in the measurements of O<sub>2</sub> concentrations by the supervisors of cargo operation including the foreman and did not give instructions to supervisors of cargo operation and the foreman to do the measurements by the determined methods, which was a factor that contributed to occurrence of the primary accident.

##### (2) The secondary accident

It is considered probable that the foreman, who was informed that Driver B had collapsed, was not aware of the oxygen-deficient atmosphere in cargo hold No.3 and entered into the cargo hold to rescue Driver B together with Operator C and Operator F, and as a result, the foreman inhaled oxygen-deficient air and developed anoxia.

It is considered somewhat likely that the foreman felt impatient and responsible to

rescue Driver B and thus lost his sense of composure and did not become aware of oxygen-deficient condition in cargo hold No.3.

And also it is considered somewhat likely that the following factors are reasons why the Foreman was not aware of the oxygen-deficient atmosphere in cargo hold No.3:

- There were workers who had a misunderstanding that oxygen-deficient conditions in cargo holds were removed by natural ventilation as time passed after opening the hatch covers.
- Measurements for detecting oxygen-deficient atmosphere had not been done by the time when this case occurred, and also there were no accidents causing injury or death since the fatal accident from anoxia in a hold four years ago.

(3) The tertiary accident

It is considered probable that Operator C together with Operator F entered into cargo hold No.3 wearing gas masks to rescue the foreman and Driver B, and as a result, Operator C inhaled oxygen-deficient air and developed anoxia.

It is considered somewhat likely that the following factors led Operator C to enter cargo hold No.3 again:

- Operator C thought that he could rescue in an oxygen-deficient atmosphere with a gas mask only.
- Operator C lost his sense of composure.
- Since Operator C had already developed anoxia when he had gone to rescue Driver B at the time of the primary accident occurred, he had been unable to make proper judgment when he entered into cargo hold No.3 once again.

It is considered somewhat likely that appropriate instruction and training on coping behavior in case of fatal accidents had not been given to personnel by the stevedoring company, which contributed to occurrences of the secondary and the tertiary accidents.

4.2 Situation where the subsequent accidents were avoided

It is considered probable that the master and staff of the agent decided that the atmosphere in cargo hold No.3 was oxygen deficient and prevented subsequent accidents from occurring.

4.3 Measures to avoid this case

It is considered probable that this case would have been prevented if the following measures had been taken.

(1) Grasp of the atmosphere in the cargo hold

It should be well understood that the atmosphere in cargo holds loading copper concentrate has the risk of being fatal to humans because of the generation of oxygen-deficient conditions, odorous gases and sulfur gases.

Appropriate measurements of O<sub>2</sub> concentrations and such gases should be conducted in order to check the atmosphere in cargo holds.

(2) Ventilation of cargo holds

If the atmosphere in a cargo hold is not safe, it should be ventilated until it becomes safe (keep O<sub>2</sub> concentration 20.9% and eliminate toxic gases).

(3) Entering into holds

No one should enter into holds until the atmosphere is checked to be safe.

(4) Instruction on cargo operations for workers

- [1] To disseminate the risks of oxygen-deficient conditions, anoxia and necessary actions to be taken
  - [2] To instruct on the properties and the risks of copper concentrate and floatation reagents.
  - [3] To instruct on the necessity of forced draft, since sometimes oxygen-deficient conditions in cargo holds are not solved only by natural ventilation.
- (5) Instruction on the difficulties and risks of workers and crew members performing rescue operations

When workers and crew member attempt rescue operations in oxygen-deficient cargo holds, they shall have enough training on the handling of SCBA and how to approach accident scenes.

Moreover, they shall be instructed that it is not easy to rescue quickly the injured, and that once anoxia developed, it is difficult to return from the cargo hold alive

#### 4.4 Probable causes

Regarding the primary accident, it is considered probable that Driver B, who was engaged in discharging copper concentrate loaded in cargo hold No.3, entered into the cargo hold which had become oxygen-deficient, inhaled oxygen-deficient air and developed anoxia while the ship was berthed at a private berth in port of Saganoseki.

It is considered probable that Driver B entered into cargo hold No.3 since the access permit notice board was posted at the entrance hatch of the hold and another operator had already started driving a heavy vehicle in cargo hold No.1.

It is considered probable that the copper concentrate had oxidized during transportation from Port Moresby Harbour to port of Saganoseki, and the oxygen in airtight cargo hold No.3 had been consumed creating an oxygen-deficient environment.

It is considered probable that the foreman instructed the chief officer to open the hatch cover and then he posted the access permit notice board at the entrance hatch of cargo hold No.3 based on a regulation which was created after the fatal accident occurred four years ago. However, it is considered somewhat likely that the foreman was not aware of oxygen-deficient atmosphere in cargo hold No.3.

It is considered somewhat likely that since supervisors of cargo operation including the foreman of the stevedoring company were accustomed to measuring O<sub>2</sub> concentrations not using the determined methods.

The foreman was not aware of the oxygen-deficient atmosphere in cargo hold No.3 because of such habitual practices.

It is considered somewhat likely that the smelter and the stevedoring company were not aware of these habitual practices used in the measurements of O<sub>2</sub> concentrations by supervisors of cargo operation including the foreman but did not give instructions to supervisors of cargo operation and the foreman to do the measurements in accordance with the regulations, which is determined to be a factor inviting the primary accident.

Regarding the secondary accident, it is considered probable that the foreman, who was informed that Driver B had collapsed, was not aware of oxygen-deficient atmosphere in cargo hold No.3 and entered into the hold to rescue Driver B together with Operator C and Operator F, and as a result, the foreman inhaled oxygen-deficient air and developed anoxia.

It also is considered somewhat likely that the foreman was not aware of oxygen-deficient atmosphere in cargo hold No.3 for the following reasons:

- He felt impatient and responsible to rescue Driver B, and he lost his sense of composure.
- There were workers who had a misunderstanding that oxygen-deficient condition in cargo holds were removed by natural ventilation as time passed after opening the hatch covers.
- Measurements for detecting an oxygen-deficient atmosphere had not been done by the time when this case occurred.

Additionally there had been no accidents causing injury or death since the fatal accident due to anoxia in a hold four years ago

Regarding the tertiary accident, it is considered probable that Operator C together with Operator F entered into cargo hold No.3 wearing gas masks to rescue the foreman and Driver B, inhaled oxygen-deficient air and developed anoxia.

It is considered somewhat likely that Operator C entered into cargo hold No.3 once again for the following reasons:

- Operator C thought that he could enter an oxygen-deficient atmosphere by equipping with gas masks.
- Operator C lost his sense of composure.
- Since Operator C had already developed anoxia when he had gone to rescue driver B at the time of the primary accident, he could not make appropriate decisions when he entered into cargo hold No.3 once again.

It is considered somewhat likely that appropriate education and training on coping behavior in case of fatal accidents had not been provided to personnel by the stevedoring company, which contributed to the secondary and the tertiary accident.

## 5 RECOMMENDATIONS

### 5.1 Recommendations to the Saganoseki Smelter & Refinery, Pan Pacific Copper Co.,Ltd.

It is considered probable that this accident (the primary, the secondary and the tertiary accidents) occurred, because while the cargo ship "SINGAPORE GRACE" was berthed at the Raw Material Acceptance Wharf of the Saganoseki Smelter and Refinery, Nikko Smelting & Refining Co., Ltd. for discharging copper sulfide concentrate loaded in cargo hold No.3, one of the workers entered into the cargo hold which had become oxygen-deficient and developed anoxia fell. Afterwards other workers who went to rescue him also developed anoxia fell.

It is considered somewhat likely that Nikko Smelting & Refining Co., Ltd. did not give instructions for workers to measure O<sub>2</sub> concentrations in accordance with the regulations, which contributed to occurrence of the accident.

In view of the results of this accident investigation, the Japan Transport Safety Board recommends the Saganoseki Smelter & Refinery of Pan Pacific Copper Co.,Ltd. which took over the project from the Nikko Smelting & Refining Co., Ltd. to implement the following measures pursuant to paragraph (1) of Article 27 of the Act for Establishment of the Japan Transport Safety

Board for the purpose of prevention of the accident caused by oxygen-deficient in cargo hold.

- (1) To train all employees who have the possibility of being engaged in cargo work to understand the properties and risks of copper sulfide concentrate.
- (2) To train all employees, who have the possibility of being engaged in cargo work, with the handling of O<sub>2</sub> meters in order to measure O<sub>2</sub> concentrations as necessary
- (3) To request the MSDS of floatation reagents from shippers.
- (4) To inform employees who have the possibility of being engaged in cargo operation on the following:
  - [1] Depending upon the properties of the floatation reagent adhered to copper sulfide concentrate, it may generate toxic gas.
  - [2] Since the generated toxic gas is heavier than air, it stagnates in cargo hold; hence, there is a danger of not being replaced by air.
- (5) To make the risks of oxygen-deficient conditions and anoxia known to all personnel who have the possibility of being engaged in cargo operation and to familiarize them with appropriate coping behavior in case of fatal accidents occurring in cargo holds loading copper sulfide concentrate

## 5.2 Recommendation to the Nissho Koun Co., Ltd.

It is considered probable that this accident (the primary, the secondary and the tertiary accidents) occurred, while the cargo ship "SINGAPORE GRACE" was berthed at the private wharf for discharging copper sulfide concentrate loaded in cargo hold No.3, one of the workers entered into the cargo hold which had become oxygen-deficient and he developed anoxia fell. Afterwards other workers who went to rescue him also developed anoxia fell.

It is considered somewhat likely that appropriate education and training on coping behavior in case of fatal accidents had not been given to personnel by the Nissho Koun Co., Ltd., which contributed to the accidents.

In view of the results of this accident investigation, the Japan Transport Safety Board recommends the Nissho Koun Co., Ltd. to implement the following measures pursuant to paragraph (1) of Article 27 of the Act for Establishment of the Japan Transport Safety Board for the purpose of prevention of accident caused by oxygen-deficient in cargo hold.

- (1) To train all employees who have the possibility of being engaged in cargo operation to understand the properties and risks of copper sulfide concentrate
- (2) To train all employees, who have the possibility of being engaged in cargo work, with the handling of O<sub>2</sub> meters in order to measure O<sub>2</sub> concentrations as necessary
- (3) To make the risks of oxygen-deficient conditions and anoxia known to all employees who have the possibility of being engaged in cargo operation and to familiarize them with appropriate coping behavior in case of fatal accidents occurring in cargo holds loading copper sulfide concentrate



## 6 SAFETY RECOMMENDATIONS

It is considered probable that this accident (the primary, the secondary and the tertiary accidents) occurred, because while the cargo ship “SINGAPORE GRACE” was berthed at the private wharf for discharging copper sulfide concentrate loaded into cargo hold No.3, one of the workers entered into the cargo hold which had become oxygen-deficient and developed anoxia fell.

Afterwards other workers who went to rescue him also developed anoxia fell in the cargo hold.

It is considered probable that reason why the air of cargo hold No. 3 was not replaced by outside air and the oxygen-deficient condition remained after opening the hatch cover was the following:

- Odorous gases, heavier than air, generated by the floatation reagent were not replaced by air and accumulated at the lower layer of the hold

In view of the results of this accident investigation (the primary, the secondary and the tertiary accidents), the Japan Transport Safety Board recommends the Ok Tedi Mining Limited as the shipper to take the following measure for the purpose of making known to the person that the properties of floatation reagents adhering to copper sulfide concentrate for safe transportation and cargo operation:

In case of the possibility of the existence of floatation reagents adhering to copper sulfide concentrate, it is recommended to the Ok Tedi Mining Limited as the shipper to submit information (Material Safety Data Sheet, etc.) on floatation reagents in addition to information of copper sulfide concentrate (Material Safety Data Sheet, etc.) to ships and consignees in order to make the properties and the risks of copper sulfide concentrate and floatation reagents known to ships and consignees.

## 7 OPINIONS

While the discharging operation from the cargo ship loaded copper sulfide concentrate, one of the workers entered into the cargo hold and he developed anoxia fell. And other workers who went to rescue him also collapsed in the cargo hold and developed anoxia fell.

Copper sulfide concentrates were beneficiated from copper ore by floatation method using reagents. Depending upon the properties of the floatation reagent adhered to copper sulfide concentrate, it may generate toxic gas. The toxic gas is heavier than air; therefore, it stagnates in cargo holds. As a result, the danger of the toxic gas not being replaced by air and an atmosphere of the cargo holds becoming oxygen deficient conditions exists.

In view of the results of this accident investigation, the Board expresses its opinions as follows to the Minister of Land, Infrastructure, Transport and Tourism to pursuant to Article 28 of the Act for Establishment of the Japan Transport Safety Board in order to prevent the recurrence of similar casualties.

The Board requests the Minister of Land, Infrastructure, Transport and Tourism to widely

disseminate following information regarding the risks of the use of floatation reagents through the International Maritime Organization (IMO).

- (1) Depending upon the properties of the floatation reagent adhered to copper sulfide concentrate, it may generate toxic gas.
- (2) Since the generated toxic gas is heavier than air, it stagnates in cargo hold; hence, there is a danger of not being replaced by air.

## 8 REMARKS

In view of the results of this accident investigation (the primary, the secondary and the tertiary accidents), the Japan Transport Safety Board expresses its remarks in order to contribute to the prevention of recurrence of similar accidents as follows:

8.1 To personnel who are engaged in the transport and the cargo operation of copper concentrate  
The Japan Transport Safety Board requests to the personnel who are engaged in the transport and the cargo operation of copper concentrate to pay further attention to the followings:

- (1) In order to know the atmosphere of enclosed space, it is necessary that the O<sub>2</sub> concentration and gases to be measured dproperly.
- (2) It is necessary that personnel should understand the atmosphere of enclosed space. No personnel should enter into enclosed space until the atmosphere becomes safe by forced draft, etc.
- (3) It is necessary that personnel should keep in mind that it is not easy to enter the cargo hold and rescue quickly the injured, and that once anoxia developed, it is difficult to return from the cargo hold alive.

8.2 To the industry involved in the transport and the cargo operation of copper concentrate

Due to the risks in dealing with copper concentrates, the Japan Transport Safety Board urges the Japan Mining Industry Association, the Japanese Ship Owners' Association, All Japan Seamen's Union, Japan Port Transport Industry Safety & Health Association, Japan Federation Dockworkers Unions and Japanese Confederation of Port and Transport Workers Unions to make this report known to those whom it may concern.

## 9 ACTIONS TAKEN

The smelter and the stevedoring company have implemented the following measures after the accident.

9.1 Changes to operating procedures

9.1.1 Changes to discharging cargo procedures

- (1) Personnel should not enter into cargo holds until at least 1 hour has passed after the

opening of hatch covers, and discharging cargo should be done by cranes not by workers entering into cargo hold.

- (2) O<sub>2</sub> concentrations in cargo holds are measured 1 hour after the opening of hatch covers. Prior to giving permission for workers to enter into cargo holds, O<sub>2</sub> concentration should be measured and confirmed to be 20% or more.

#### 9.1.2 Forced draft

- (1) 10 minutes after the hatch covers are opened, spiral ducts connected with forced draft fans (see pictures below) should be put into cargo holds from entrance hatches, and air should continuously be sent into the cargo hold.
- (2) Air should be sent continuously from entrance hatch for at least 1 hour.  
While cargo operation, air should be sent continuously from entrance hatch which is not in use.

(The photos below: “forced draft by forced draft fans and spiral ducts” “spiral ducts in hatch entrance”)



“forced draft by forced draft fans and spiral ducts”



“spiral ducts in hatch entrance”

#### 9.1.3 The measurement of O<sub>2</sub> concentrations

- (1) Double checking system was introduced.  
Chief of oxygen-deficient hazardous work should check O<sub>2</sub> concentrations and one assistant (those who finished the special training for hazardous work including oxygen-deficient environment) should record it.
- (2) The times for checking O<sub>2</sub> concentrations should be determined to be 5 minutes after, and 1 hour after the hatch covers have been opened.
- (3) Points for measurements were changed as follows:
  - [1] The points for 5 minutes after the hatch covers have been opened:  
total 18 points: Lower, middle and upper layers of the hold from the fore, the middle and the aft of both sides of ships
  - [2] The points for 1 hour after the hatch covers have been opened:  
In addition to the points mentioned above [1] 5 points inside hatch entrance: The upper landing, middle of the slanting ladder, the lower landing, the surface of the cargo (2 points of the corrugation – indented and outer)
- (4) Result of measurement of the lowest O<sub>2</sub> concentration should be entered onto “the Access Permit Notice Board” instead of the entrance permitted notice board.  
(See following “Access Permit Notice Board”)

“Access Permit Notice Board”(surface)

“Access Permit Notice Board”(back)

#### 9.1.4 Entrance and exit management of cargo holds

- (1) It was determined that personnel who entered into cargo holds should check the lowest level of oxygen entered onto the access permit notice board and fill in the time of entry and respective names.

It was also determined that personnel who exited from cargo holds should fill in the time of exit for confirmation.

- (2) It was determined that the person in charge of the stevedoring company should give permission to enter into cargo holds after checking the safety inside the cargo holds.

#### 9.1.5 Compact Portable Oxygen Meter

It was determined that all personnel who enter into the cargo hold should carry a compact portable oxygen meter.

#### 9.1.6 Monitoring working condition in cargo holds

It was determined that one watchman should be located at each hold during cargo operation hours in cargo holds.

#### 9.1.7 Replenishment safety protective device

In addition to one set of Self-contained Breathing Apparatus (SCBA) as was equipped with before, three sets of SCBA were purchased.

And it was determined to equip the cargo hold always with the Oxygen Mask for Emergency Evacuation during cargo operation hours.

#### 9.1.8 A manual for standard operating procedures

A manual for standard operating procedures was revised following the changes for operating procedures mentioned above in 8.1.1-8.1.7.

## 9.2 Management and supervision

- (1) It was determined that supervisor in the cargo operation department should perform on-site checks to confirm that cargo operations should be conducted based on the standard operating procedures and give instructions as required.
- (2) It was determined that the management ranks of the stevedoring company should regularly confirm that the above mentioned procedures should be kept.

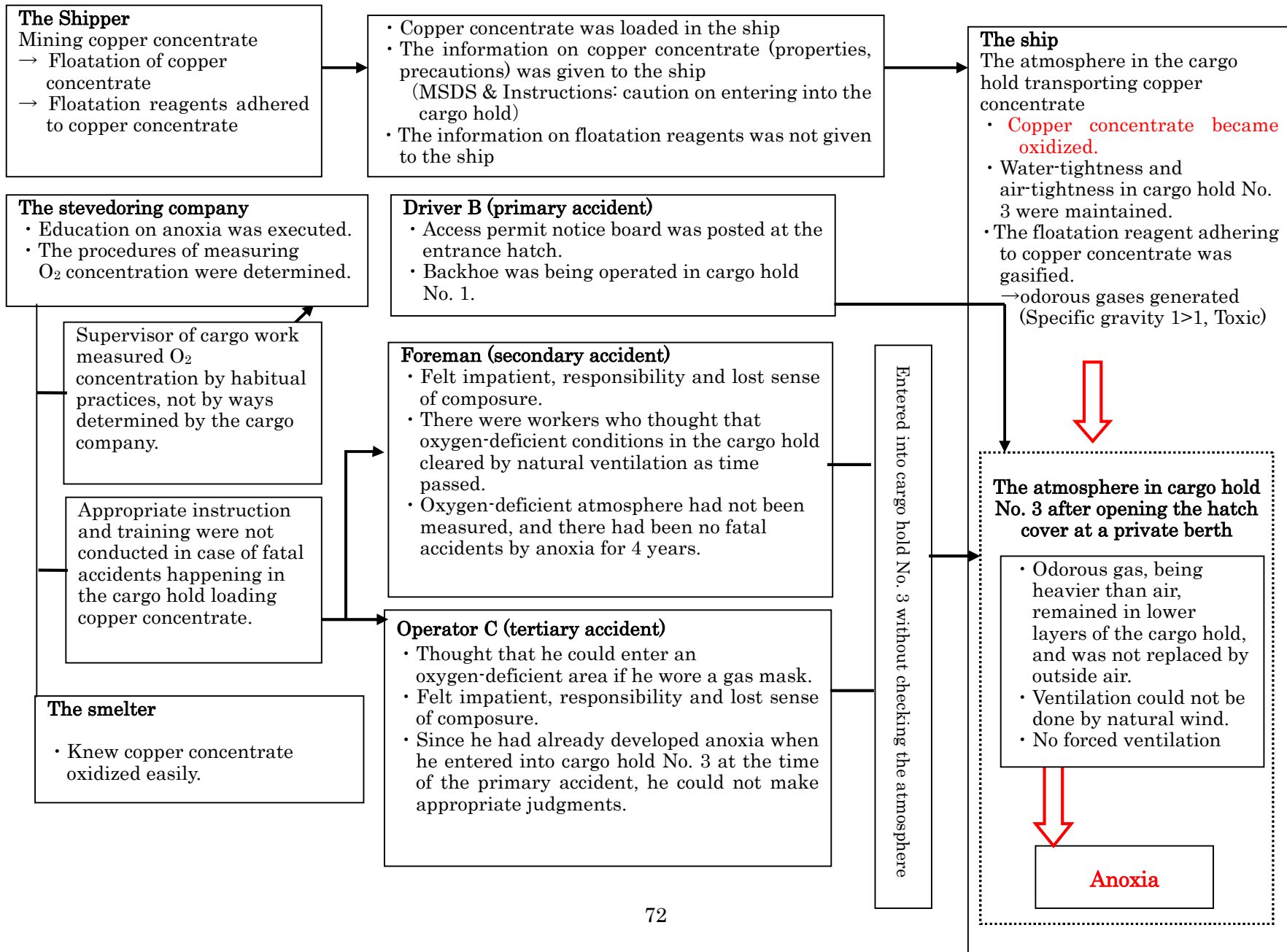
## 9.3 Training

- (1) The revision of instruction materials on oxygen deficiency  
The risks of oxygen deficiency were indicated to be more easily understood, and a postscript regarding inspection points for daily checking of SCBA and evacuation behavior in case of emergency was added.
- (2) Training  
Annual training including an introductory training program should be done repeatedly, not only for newly employed personnel but also for skilled personnel.
- (3) A rescue-manual was published to avoid the secondary accident and its training of all the staff of company was conducted.  
The followings were determined in the manual;
  - Even if personnel intends to rescue, the personnel must not enter the cargo holds which have the risk of being oxygen-deficient
  - Contact the specialized rescue agency immediately to mobilize etc.
- (4) The following was carried out in the training by the companies
  - On the vessel where the entrance hatch is located in an enclosed space such as deck house or crane room, there are risks of inhaling oxygen-deficient air when the personnel enters into these spaces

## 9.4 To avoid serious accidents in the future

- (1) Activities for learning from past serious accidents  
It was determined that “June 13” is “the day considering safety” for all the staff of the smelter company group to learn serious accidents occurred at the past.
- (2) Review of OHS management system  
It was determined to record the risk of accident in addition to level of the risk in the table of accident investigation to extract and evaluate causes of all accidents so that the risk of accident in the smelter should be reduce.
- (3) Training of superintendents for improvement of leadership qualities
  - [1] It was determined that Industrial Safety Consultant patrol the site and give direction superintendents based on Industrial Safety and Health Act. from Oct.,2009.
  - [2] It was determined to deal with the training of superintendents for their improvement of sensitivity to danger by conducting patrol of the site by retired persons (experts).

Appended figure: A correlation diagram of factors



# Appendix: Analytical Data on Copper Concentrate Extracts

## Research Report

### 1. Subject

An analytical investigation on the imported copper concentrate loaded in an ore carrier

### 2. Purpose

Study the variation of oxygen concentration according to the properties of copper concentrates under different conditions (Temperature • Moisture • Floatation reagent)

Sample A: Copper concentrate Ok Tedi (hereinafter referred to as Sample A)

Sample B: Copper concentrate Cuajone (hereinafter referred to as Sample B)

Sample C: Copper concentrate Cerro Corona (hereinafter referred to as Sample C)

### 3. Contents of the investigation

#### (1) Measurements of oxygen consumption rates

- [1] Measuring oxygen consumption rates in each ambient temperature (40°C, 60°C, 80°C) under the condition of the void ratio of Sample A being 70% (empty space ratio when the sample is put in an airtight container. Hereinafter referred to as void). (see 4-1-1)
- [2] Measuring oxygen consumption rates of Sample A in each ambient temperature (40°C, 60°C, 80°C) under a void of 30%. (see 4-1-2)
- [3] Comparing the results of the measurements of oxygen concentrations of Sample A in a void of 30% with that in a void of 70%. (see 4-1-3)
- [4] Adjusting moisture values of Sample A to 15% and measure oxygen consumption rate in each ambient temperature (40°C, 60°C, 80°C) under a void of 70%. (see 4-1-4)
- [5] Comparing oxygen consumption rates of Sample A in the case of adding moisture and no moisture under a void of 70%. (see 4-1-5)
- [6] Measuring oxygen consumption rates of each type of copper concentrate (Sample A, B, C) in each ambient temperature (40°C, 60°C, 80°C) under a void of 70%. (see 4-1-6)

#### (2) Investigations on effects by floatation reagents

Reagent W Used for Sample A

Reagent X Used for Sample A

Reagent Y

Reagent Z

- [1] Measuring oxygen concentrations after adding each floatation reagent in Sample A. (see 4-2-1)
- [2] Measuring oxygen concentrations without floatation reagent in Sample A. (see 4-2-2)
- [3] Measuring oxygen concentrations for each floatation reagent. (see 4-2-3)
- [4] Measuring oxygen concentrations by adding each floatation reagent after cleaning Sample A. (see 4-2-4-2)
- [5] Measuring components of generated odorous gases. (see 4-2-5)

- (3) Doing Qualitative analysis of the components of the odorous gas from a hold of a cargo ship, in which Sample A was loaded (see 4-3)

Odorous gas and water condensation adhering to a hatch cover were taken from the cargo hold of one of the cargo ships, which had been at port of Saganoseki. They were taken at almost the same time as the hatch cover was opened.

The next day, Sample A was taken from No. 1 cargo hold just after discharging.

The cargo temperature was 42.6°C. At that time, the outer air temperature of Oita city was between 10.7°C and 13.3°C.

- (4) Measuring the pH value of the water condensation adhering to the hatch cover of ship, from which Sample A was loaded and performed qualitative analysis by ICP emission spectrophotometric analyzer and ION chromatographs. (see 4-3-2)

- (5) X-ray diffraction on the different types of copper concentrate

[1] X-ray diffraction on the different types of copper concentrate (Sample A, B, C) (see 4-4-1)

[2] X-ray diffraction of Sample A after heating (100°C, 200°C, 300°C) (see 4-4-2)

- (6) Supplementary testing

Cleaning tests on the different types of copper concentrates (see 4-5)

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## 4. Procedures for the investigation and the results of the measurements

### 4-1. Measurements of oxygen consumption rates

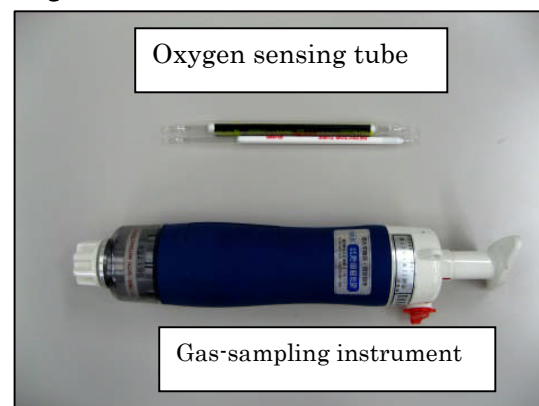
#### 4-1-1. Measured oxygen levels of Sample A with a void of 70%

Sample A was put into airtight Erlenmeyer flask (approximately 650ml) with a void of 70% (sample A: approximately 195ml) and the oxygen concentration were measured at each ambient temperature (40°C, 60°C, 80°C) \*<sup>1</sup> (see Figure 1). Oxygen concentration were measured by detaching the tetra pack, attaching the oxygen sensing tube and a gas-sampling instrument to the rubber tube (see Figure 2 and Figure 3).

**Figure 1**



**Figure 2**

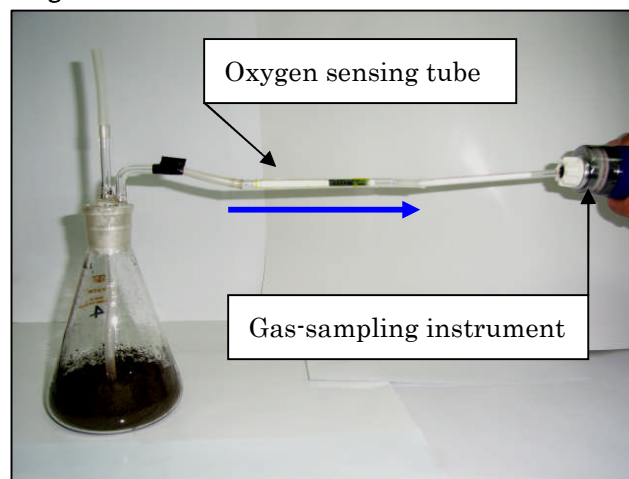


Oxygen sensing tube:

Kitagawa method oxygen sensing tube (SC model)

Gas sampler: Kitagawa method AP-20

**Figure 3**



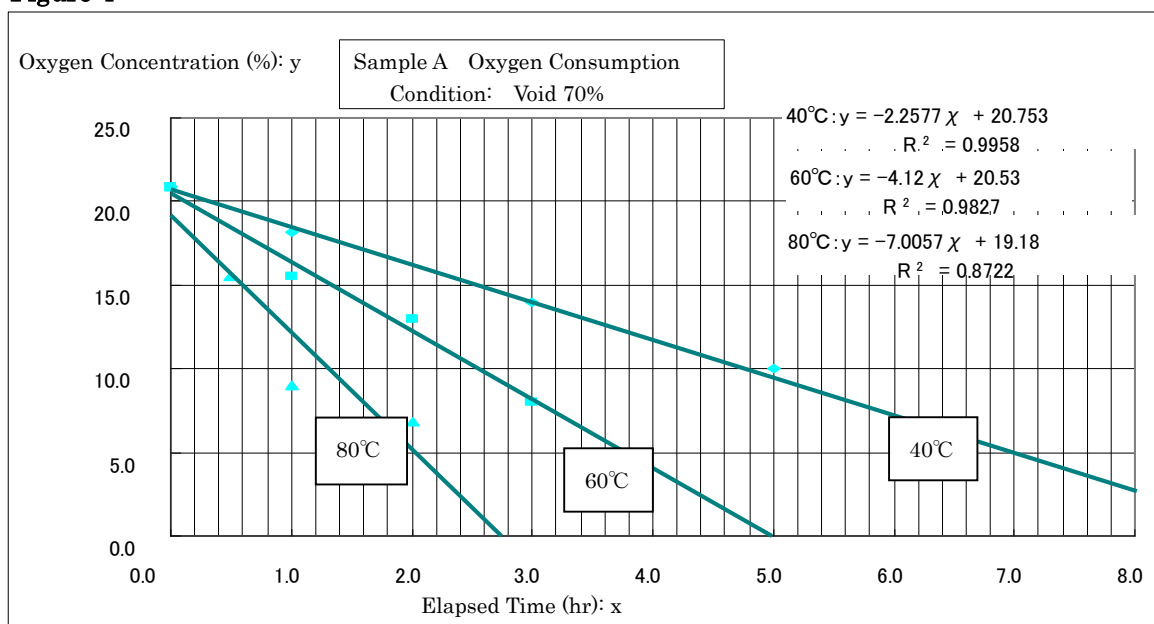
\*<sup>1</sup> The oxygen concentration = 20.9% at time 0.0hr.

Table 1 and Figure 4 show the measurement results

**Table 1** Oxygen (O<sub>2</sub>) concentration under a void of 70%

| Elapsed time (hr) | 40°C- O <sub>2</sub> concentration (%) | 60°C-O <sub>2</sub> concentration (%) | 80-O <sub>2</sub> concentration (%) |
|-------------------|--|---------------------------------------|-------------------------------------|
| 0.0               | 20.9                                   | 20.9                                  | 20.9                                |
| 0.5               |  |                                       | 15.5                                |
| 1.0               | 18.2                                   | 15.5                                  | 9.0                                 |
| 2.0               |  | 13.0                                  | 6.8                                 |
| 3.0               | 14.0                                   | 8.0                                   |                                     |
| 5.0               | 10.0                                   |                                       |                                     |
| 6.0               | 6.8                                    |                                       |                                     |

**Figure 4**



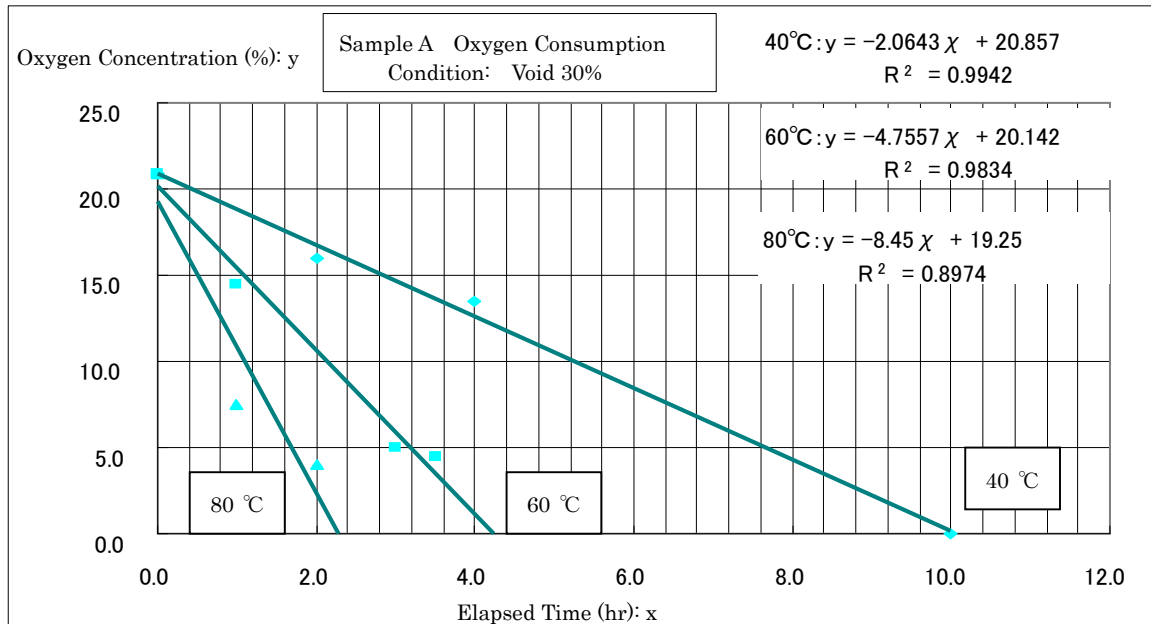
4-1-2. Measured oxygen concentration of Sample A with a void of 30%

Sample A was put into airtight Erlenmeyer flask (approximately 650ml) with a void of 30% (Sample A: approximately 455ml) and oxygen concentration were measured with the same measuring procedures as 4-1-1. Table 2 and figure 5 show the results.

**Table 2** Oxygen (O<sub>2</sub>) concentration under a void of 30%

| Elapsed time (hr) | 40°C-O <sub>2</sub> concentration (%) | 60°C- O <sub>2</sub> concentration (%) | 80°C-O <sub>2</sub> concentration (%) |
|-------------------|---------------------------------------|--|---------------------------------------|
| 0.0               | 20.9                                  | 20.9                                   | 20.9                                  |
| 1.0               |                                       | 14.5                                   | 7.5                                   |
| 2.0               | 16.0                                  |  | 4.0                                   |
| 3.0               |                                       | 5.0                                    |                                       |
| 3.5               |                                       | 4.5                                    |                                       |
| 4.0               | 13.5                                  |  |                                       |
| 10.0              | <3                                    |  |                                       |

**Figure 5**

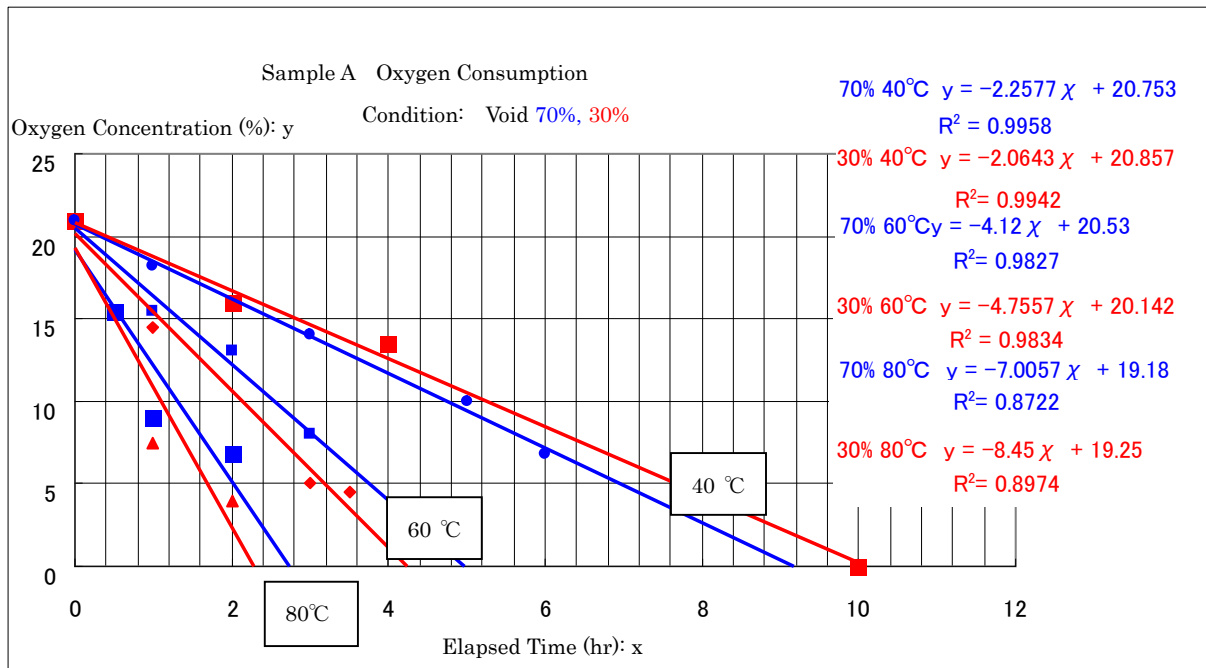


4-1-3. Sample A: comparison of the results of the measurements of oxygen concentration with a void of 30% and 70% (see Figure 3 and Table 6)

**Table 3** Comparison of the results of the measurements of oxygen(O<sub>2</sub>) concentration with a void of 30% and 70%

| Elapsed time | 30%40°C<br>O <sub>2</sub><br>Concentration<br>(%) | 70%40°C<br>O <sub>2</sub><br>Concentration<br>(%) | 30%60°C<br>O <sub>2</sub><br>Concentration<br>(%) | 70%60°C<br>O <sub>2</sub><br>Concentration<br>(%) | 30%80°C<br>O <sub>2</sub><br>Concentration<br>(%) | 70%80°C<br>O <sub>2</sub><br>Concentration<br>(%) |
|--------------|---|---|---|---|---|---|
| 0.0          | 20.9  | 20.9  | 20.9  | 20.9  | 20.9  | 20.9  |
| 0.5          |   |   |   |   |   | 15.5  |
| 1.0          |   | 18.2  | 14.5  | 15.5  | 7.5   | 9.0   |
| 2.0          | 16.0  |   |   | 13.0  | 4.0   | 6.8   |
| 3.0          |   | 14.0  | 5.0   | 8.0   |   |   |
| 3.5          |   |   | 4.5   |   |   |   |
| 4.0          | 13.5  |   |   |   |   |   |
| 5.0          |   | 10.0  |   |   |   |   |
| 6.0          |   | 6.8   |   |   |   |   |
| 10.0         | <3  |   |   |   |   |   |

**Figure 6**



4-1-4. Measured oxygen concentration of Sample A and a void of 70% (moisture added)

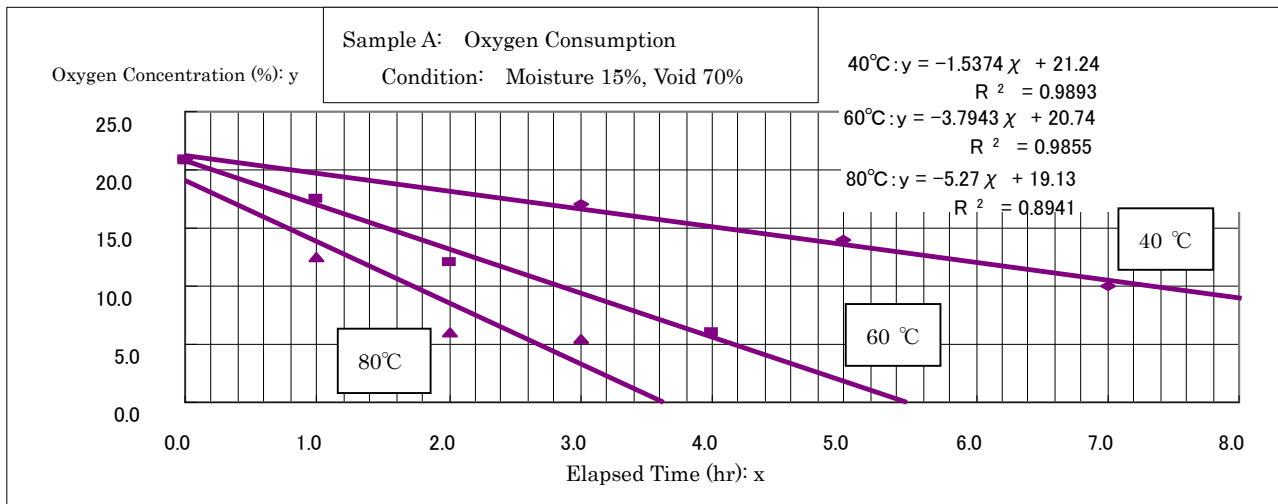
Moisture level of Sample A was increased to 15% and the measurement of the oxygen concentration was conducted with the same procedure as 4-1-2.

Results are shown in Table 4 and Figure 7.

**Table 4** Oxygen (O<sub>2</sub>) concentration with moisture level 15% and void 70%

| Elapsed time (hr) | 40°C-O <sub>2</sub> concentration (%) | 60°C- O <sub>2</sub> concentration (%) | 80°C-O <sub>2</sub> concentration (%) |
|-------------------|---------------------------------------|--|---------------------------------------|
| 0.0               | 20.9                                  | 20.9                                   | 20.9                                  |
| 1.0               |                                       | 17.5                                   | 12.5                                  |
| 2.0               |                                       | 12.0                                   | 6.0                                   |
| 3.0               | 17.0                                  |  | 5.5                                   |
| 4.0               |                                       | 6.0                                    |                                       |
| 5.0               | 14.0                                  |  |                                       |
| 7.0               | 10.0                                  |  |                                       |

**Figure 7**

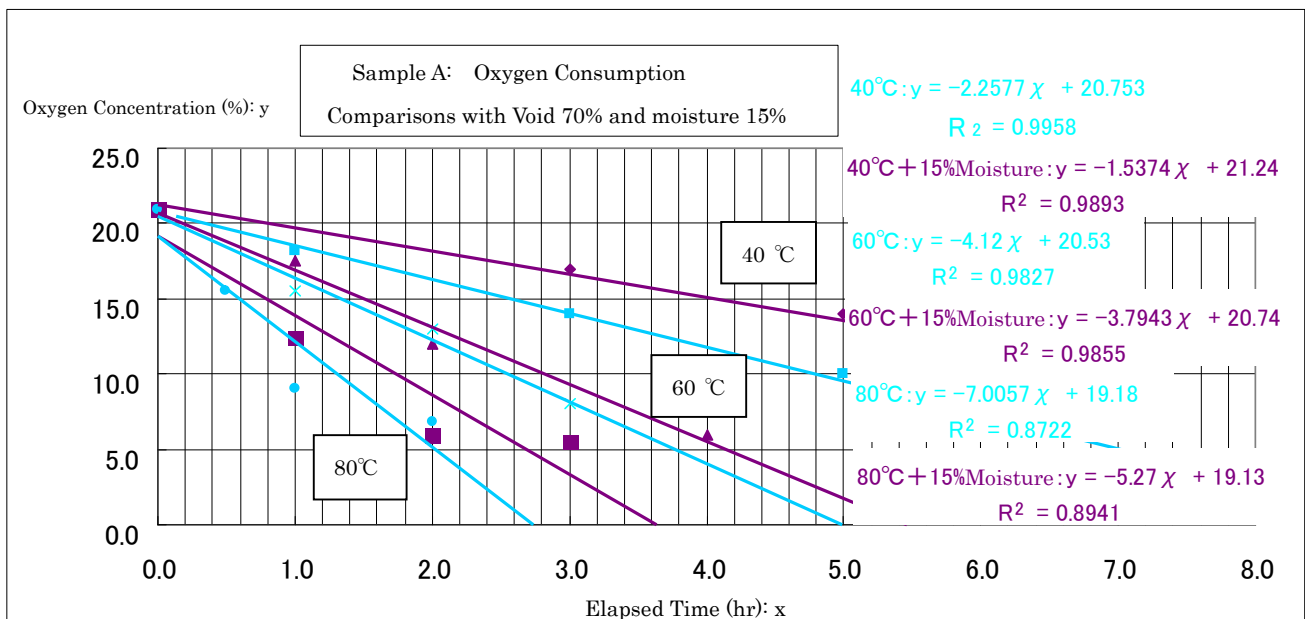


4-1-5. Sample A: Comparisons with a void of 70% with and without moisture (see Table 5 and Figure 8)

**Table 5** Comparison of sample A with and without moisture and a void of 70%

| Elapsed Time(hr) | Moisture 15%<br>40°C -<br>O <sub>2</sub> Concentration (%) | 40°C -<br>O <sub>2</sub> Concentration (%) | Moisture 15%<br>60°C -<br>O <sub>2</sub> Concentration (%) | 60°C -<br>O <sub>2</sub> Concentration (%) | Moisture 15%<br>80°C -<br>O <sub>2</sub> Concentration (%) | 80°C -<br>O <sub>2</sub> Concentration (%) |
|------------------|--|--|--|--|--|--|
| 0.0              | 20.9   | 20.9                                       | 20.9   | 20.9                                       | 20.9   | 20.9                                       |
| 0.5              |  |  |  |  |  | 15.5                                       |
| 1.0              |  | 18.2                                       | 17.5   | 15.5                                       | 12.5   | 9.0  |
| 2.0              |  |  | 12.0   | 13.0                                       | 6.0  | 6.8  |
| 3.0              | 17.0   | 14.0                                       |  | 8.0  | 5.5  |  |
| 4.0              |  |  | 6.0  |  |  |  |
| 5.0              | 14.0   | 10.0                                       |  |  |  |  |
| 6.0              |  | 6.8  |  |  |  |  |
| 7.0              | 10.0   |  |  |  |  |  |

**Figure 8**



(1) Regardless of the differences in temperature and volume of void, the oxygen concentration in the airtight containers decreased.

The relationship between elapsed time and oxygen concentration is considered to be almost proportional.

(2) Regarding the differences in the measured results for a void of 30% and 70%, the oxygen consumption rate for void 30% was shown to be somewhat higher than void 70% in atmospheric temperatures of 60°C and 80°C.

(3) Regarding the differences for void 30% and 70% with and without a moisture level of 15%, the oxygen consumption rates for void 30% and 70% with moisture was shown to be slower than without moisture in atmospheric temperatures of 60°C and 80°C.

4-1-6. Measured oxygen consumption rates under each ambient temperature (40°C, 60°C, 80°C) on different types of copper concentrate (Sample B and Sample C)

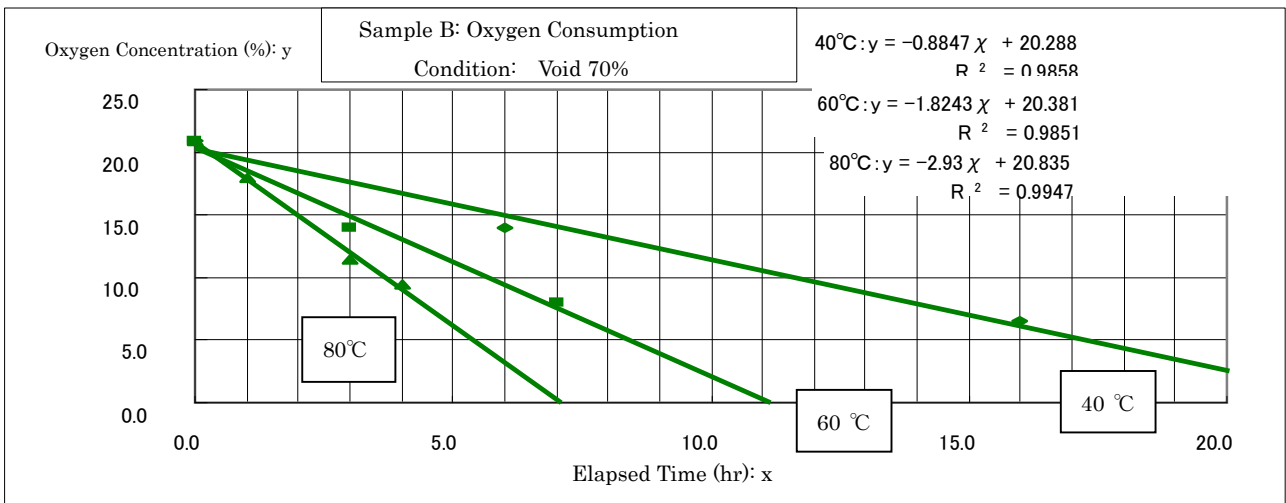
4-1-6-1. Measured oxygen concentration of copper concentrate (Sample B) under a void of 70% by the same measuring procedures of 4-1-11.

Results are shown in Table 6 and Figure 9.

**Table 6** Oxygen (O<sub>2</sub>) concentration for copper concentrate - Sample B

| Elapsed time (hr) | 40°C -<br>O <sub>2</sub> Concentration (%) | 60°C -<br>O <sub>2</sub> Concentration (%) | 80°C -<br>O <sub>2</sub> Concentration (%) |
|-------------------|--|--|--|
| 0.0               | 20.9                                       | 20.9                                       | 20.9                                       |
| 1.0               |  |  | 18.0                                       |
| 2.0               |  |  |  |
| 3.0               |  | 14.0                                       | 11.5                                       |
| 4.0               |  |  | 9.5  |
| 6.0               | 14.0                                       |  |  |
| 7.0               |  | 8.0  |  |
| 16.0              | 6.5  |  |  |

**Figure 9**





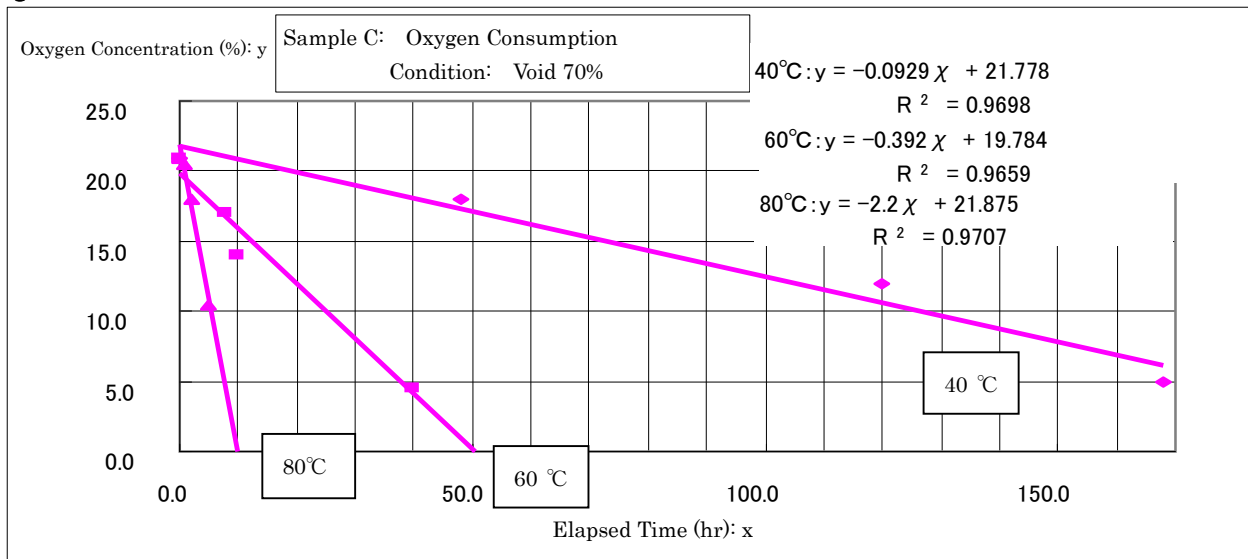
4-1-6-2. Measured oxygen concentration of copper concentrate (Sample C) under a void of 70% by the same measuring procedures of 4-1-1.

Results are shown in Table 7 and Figure 10.

**Table 7** Oxygen (O<sub>2</sub>) concentration for copper concentrate - Sample C

| Elapsed time (hr) | 40°C -<br>O <sub>2</sub> Concentration (%) | 60°C -<br>O <sub>2</sub> Concentration (%) | 80°C -<br>O <sub>2</sub> Concentration (%) |
|-------------------|--|--|--|
| 0.0               | 20.9                                       | 20.9                                       | 20.9                                       |
| 1.0               |  |  | 20.5                                       |
| 2.0               |  |  | 18.0                                       |
| 5.0               |  |  | 10.5                                       |
| 8.0               |  | 17.0                                       |  |
| 10.0              |  | 14.0                                       |  |
| 40.0              |  | 4.5  |  |
| 48.0              | 18.0                                       |  |  |
| 120.0             | 12.0                                       |  |  |
| 168.0             | 5.0  |  |  |

**Figure 10**



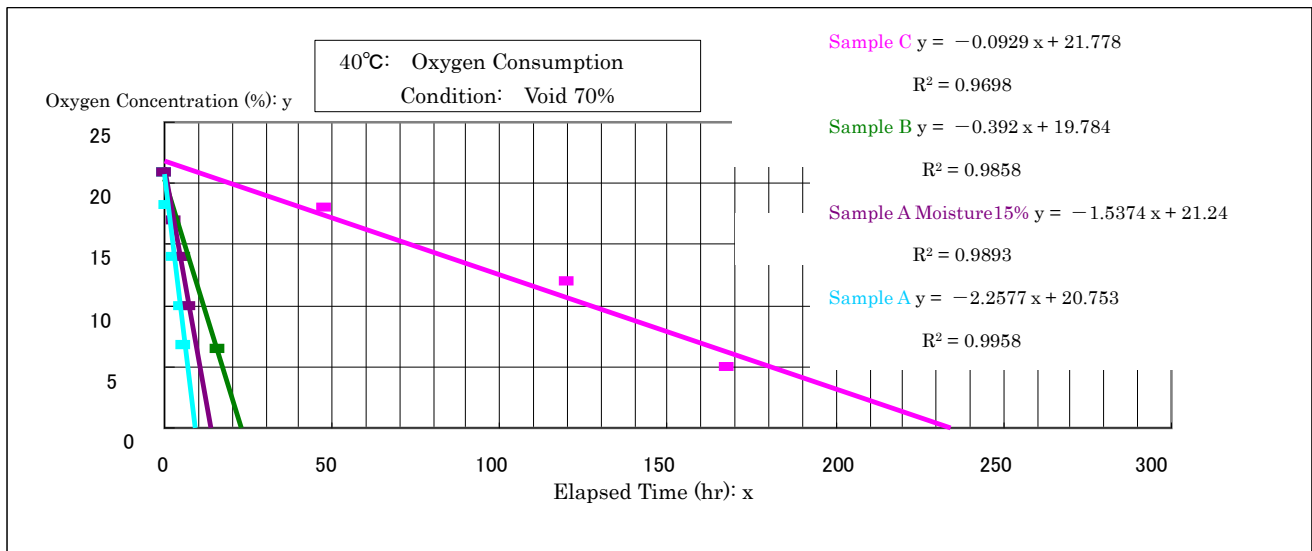
4-1-6-3. Comparison of oxygen consumption rates of different types of copper concentrate  
(Sample A, Sample B and Sample C)

4-1-6-3-1. Comparison of oxygen consumption rates of different types of copper concentrate  
(Sample A, Sample B and Sample C) with an ambient temperature of 40°C  
(see Table 8 and Figure 11)

**Table 8** Oxygen (O<sub>2</sub>) consumption rates of the different types of copper concentrate at 40°C

| Elapsed time (hr) | Sample C O <sub>2</sub> Concentration (%) | Sample B O <sub>2</sub> Concentration (%) | Sample A O <sub>2</sub> Concentration (%) | Sample A Moisture 15% O <sub>2</sub> Concentration (%) |
|-------------------|---|---|---|--|
| 0.0               | 20.9                                      | 20.9                                      | 20.9                                      | 20.9   |
| 1.0               |   |   | 18.2                                      |  |
| 3.0               |   |   | 14.0                                      | 17.0   |
| 5.0               |   |   | 10.0                                      | 14.0   |
| 6.0               |   | 14.0                                      | 6.8                                       |  |
| 7.0               |   |   |   | 10.0   |
| 16.0              |   | 6.5                                       |   |  |
| 48.0              | 18.0                                      |   |   |  |
| 120.0             | 12.0                                      |   |   |  |
| 168.0             | 5.0                                       |   |   |  |

**Figure 11**

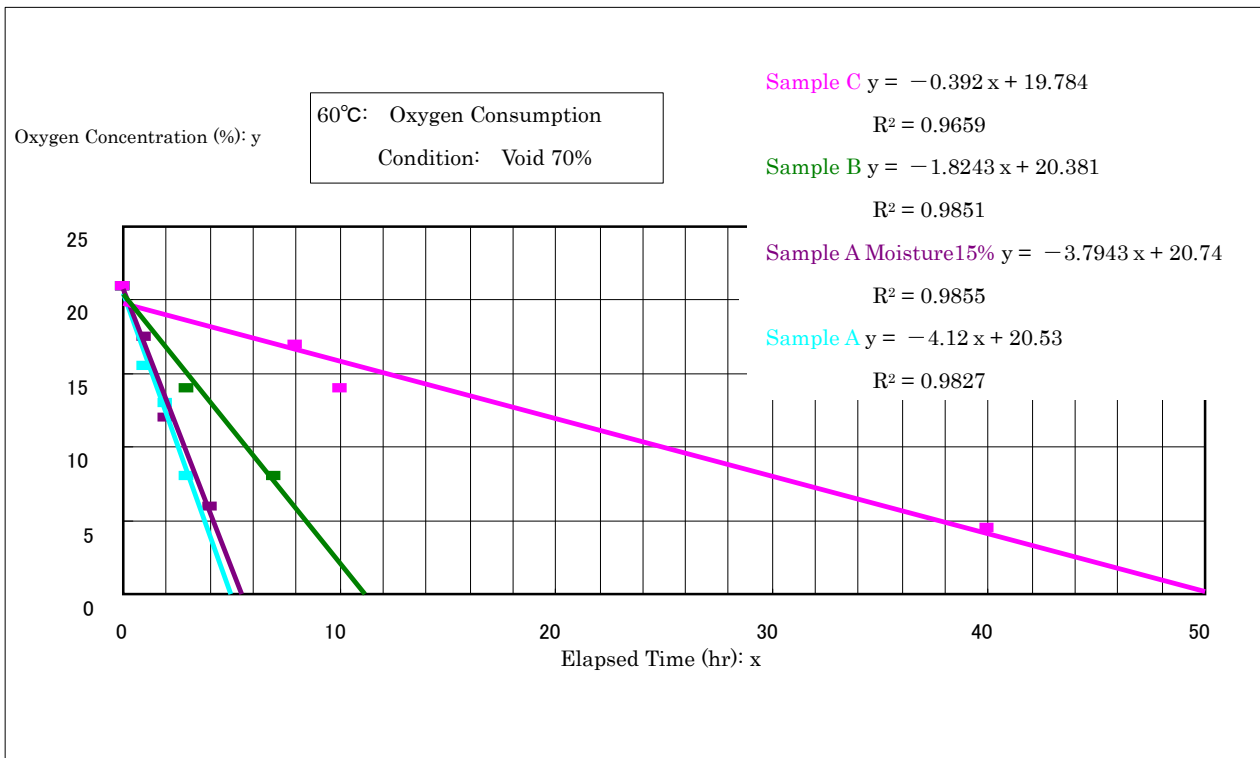


4-1-6-3-2. Comparison of oxygen consumption rates of different types of copper concentrate (Sample A, Sample B and Sample C) with an ambient temperature of 60°C (see Table 9 and Figure 12)

**Table 9** Oxygen (O<sub>2</sub>) consumption rates of the different types of copper concentrate at 60°C

| Elapsed time (hr) | Sample C O <sub>2</sub> Concentration (%) | Sample B O <sub>2</sub> Concentration (%) | Sample A O <sub>2</sub> Concentration (%) | Sample A Moisture 15% O <sub>2</sub> Concentration (%) |
|-------------------|---|---|---|--|
| 0.0               | 20.9                                      | 20.9                                      | 20.9                                      | 20.9   |
| 1.0               |   |   | 15.5                                      | 17.5   |
| 2.0               |   |   | 13.0                                      | 12.0   |
| 3.0               |   | 14.0                                      | 8.0                                       |  |
| 4.0               |   |   |   | 6.0  |
| 7.0               |   | 8.0                                       |   |  |
| 8.0               | 17.0                                      |   |   |  |
| 10.0              | 14.0                                      |   |   |  |
| 40.0              | 4.5                                       |   |   |  |

**Figure 12**

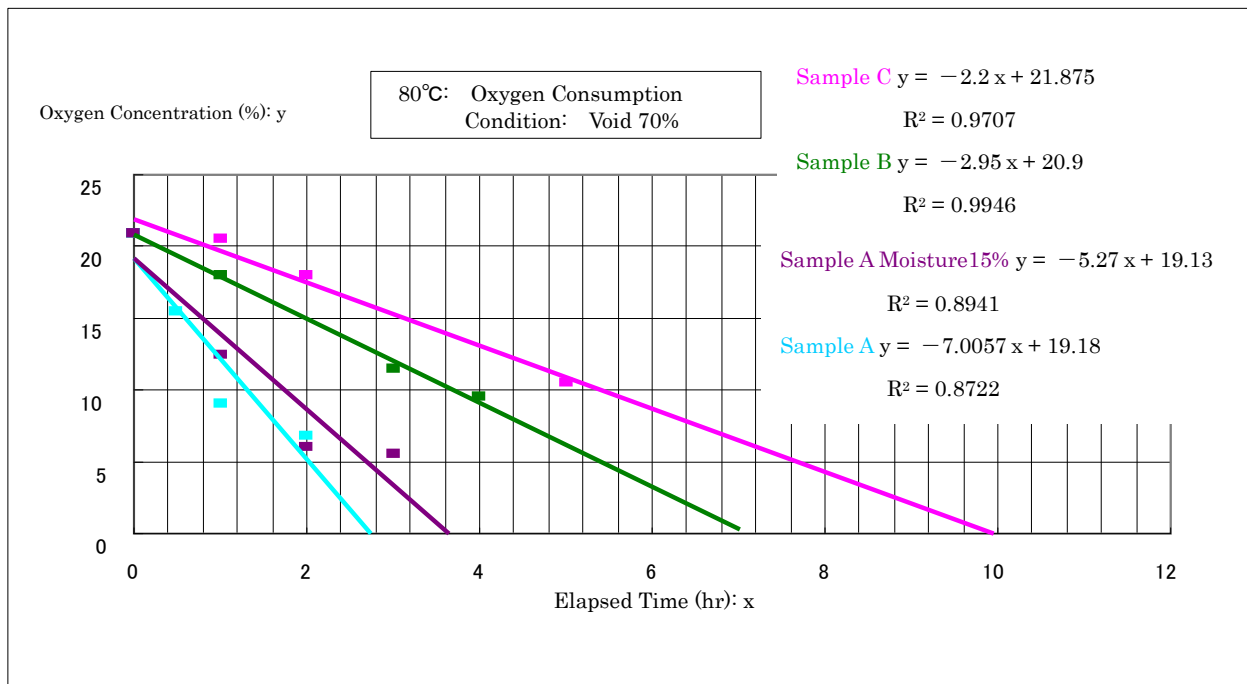


4-1-6-3-3. Comparison of oxygen consumption rates of different types of copper concentrate (Sample A, Sample B and Sample C) with an ambient temperature of 80°C (see Table 10 and Figure 13)

**Table 10** Oxygen (O<sub>2</sub>) consumption rates of the different types of copper concentrate at 80°C

| Elapsed time (hr) | Sample C O <sub>2</sub> Concentration (%) | Sample B O <sub>2</sub> Concentration (%) | Sample A O <sub>2</sub> Concentration (%) | Sample A Moisture 15% O <sub>2</sub> Concentration (%) |
|-------------------|---|---|---|--|
| 0.0               | 20.9                                      | 20.9                                      | 20.9                                      | 20.9   |
| 0.5               |   |   | 15.5                                      |  |
| 1.0               | 20.5                                      | 18.0                                      | 9.0                                       | 12.5   |
| 2.0               | 18.0                                      |   | 6.8                                       | 6.0  |
| 3.0               |   | 11.5                                      |   | 5.5  |
| 4.0               |   | 9.5                                       |   |  |
| 5.0               | 10.5                                      |   |   |  |

**Figure 13**



- (1) Of the three(3) samples, at every temperature (40°C, 60°C and 80°C) the oxygen consumption rate of Sample A was high and the oxygen concentration in the void decreased from 20.9% to under 10% 6 hours after being sealed.
- (2) Regarding Sample C, it was ascertained that the oxygen consumption rate was especially low at 40°C.  
Looking at the measurements for the oxygen consumption rate at 60°C, the same difference was found.
- (3) Regarding Sample B, the rate was found to be between that of Sample A and Sample C.

#### 4-2. An investigation of the effects from various floatation reagents

##### 4-2-1. Measured oxygen concentration after adding various floatation reagents

Sample A was dried at 105°C. The four types of floatation reagents were added separately to the dried version of Sample A in quantities equivalent to 15% of Sample A.

Making four distinct mixtures which were then sealed into cylindrical glass containers (approximately 880ml) making a void of 70% (material volume was approximately 264ml) (see Figure 14).

After they were left to stand for 24 hours at 40°C, oxygen concentration were measured.

Measuring points: upper layer and lower layer.

The oxygen concentration were measured 2 points(upper layer and lower layer )at the same time.

The following equipment was used (see Figure 15):

Gas-sampler: Kitagawa method AP- 20

Oxygen sensing tube: Kitagawa method oxygen sensing tube (SC model)

Floatation reagents

- [1] Reagent W Used for Sample A
- [2] Reagent X Used for Sample A
- [3] Reagent Y
- [4] Reagent Z

Figure 14

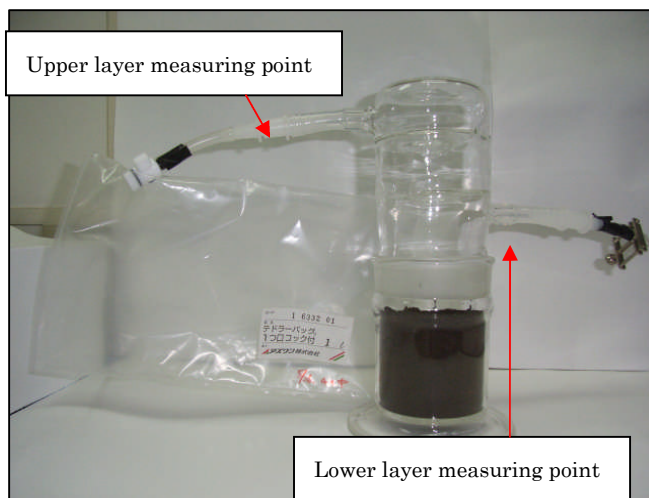


Figure 15



Table 11 shows the measured results.

**Table 11** Oxygen (O<sub>2</sub>) concentration after adding different types floatation reagents

| Measuring points                         | Floatation Reagents |           |           |           |
|--|---------------------|-----------|-----------|-----------|
|  | Reagent W           | Reagent X | Reagent Y | Reagent Z |
| Upper layer O <sub>2</sub> concentration | 13.5%               | 10.1%     | 17.0%     | 13.5%     |
| Lower layer O <sub>2</sub> concentration | 11.8%               | 6.3%      | 15.1%     | 12.0%     |

4-2-2. Measured oxygen concentration without the addition of floatation reagents in Sample A

The same method was applied to dried and un-dried Sample A - without the addition of floatation reagents.

Results shown in Table 12.

**Table 12** Oxygen (O<sub>2</sub>) concentration without the addition of floatation reagents

| Measuring points                         | Sample A before drying at 105°C | Sample A after drying at 105°C |
|--|---------------------------------|--------------------------------|
| Upper layer O <sub>2</sub> concentration | 5.4%                            | 16.3%                          |
| Lower layer O <sub>2</sub> concentration | 3% and below                    | 16.0%                          |

4-2-3. Measured oxygen concentration of each floatation reagent

Each floatation reagent was individually put into airtight Erlenmeyer flask (approximately 650ml) with the void of 30% (material volume was approximately 445ml) and left to stand for 24 hours at 40°C.

After 24hrs, the oxygen concentration were measure.

At the time of the measurement, the tetrapack was detached and a indicator tube was attached to the rubber tube (see Figure 16). The results for the oxygen concentration in the space above each floatation reagent is shown in Table 13.

**Figure 16**



**Table 13** Oxygen concentration for each floatation reagent

|                      | Floatation reagent |           |           |           |
|----------------------|--------------------|-----------|-----------|-----------|
|                      | Reagent W          | Reagent X | Reagent Y | Reagent Z |
| Oxygen concentration | 14.7%              | 18.7%     | 20.8%     | 3.0%      |

4-2-4. Measured oxygen concentration of Sample A (cleaned), with each floatation reagent

4-2-4-1. Cleaning procedures for Sample A

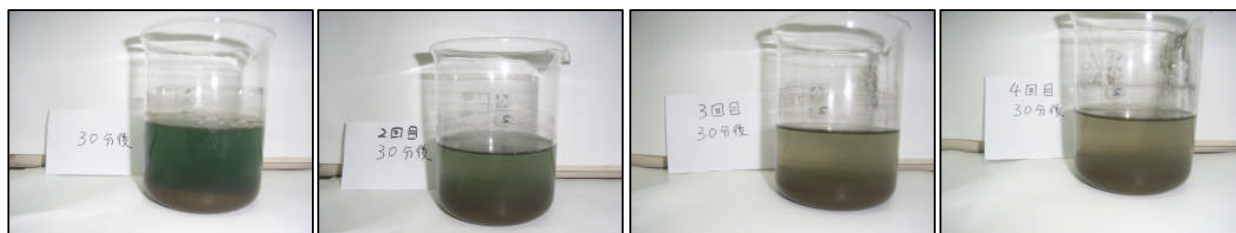
100g of sample A was put into a beaker and approximately 300ml of purified water was added.

After being stirred by a rotor, it was left to stand for 30 minutes.

After that, the supernatant liquid was filtered through filter paper.

Again, 300ml of purified water was added to the residual liquid, and the same procedure was repeated four (4) times.

The photos below show the solution before filtering.



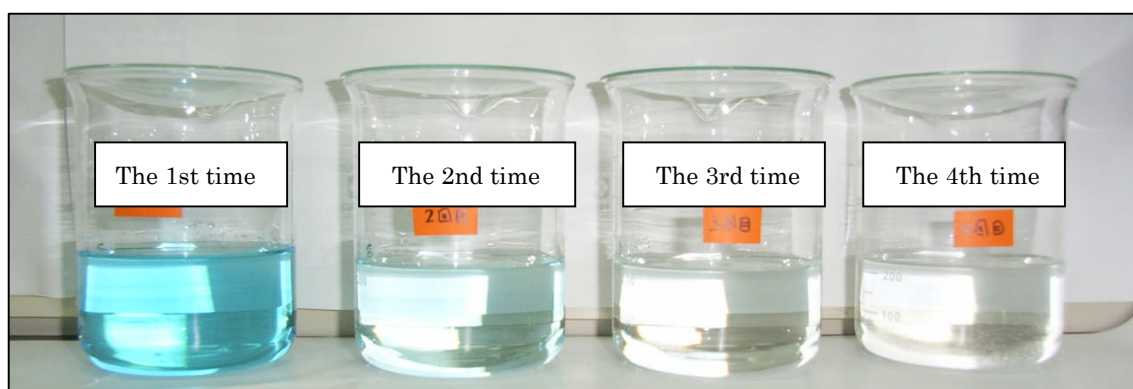
The 1st time

The 2nd time

The 3rd time

The 4th time

The photos below show the solution after filtering.



ICP qualitative results and pH of filtrate are shown in Table 14.4

**Table 14** Qualitative analysis of filtrate and pH Unit: %(excluding pH)

| Number of times of cleaned | Ca   | Cu   | Fe    | Mg    | Mn    | SO <sub>4</sub> | Zn    | pH  |
|----------------------------|------|------|-------|-------|-------|-----------------|-------|-----|
| 1                          | 0.06 | 0.42 | <0.01 | 0.01  | <0.01 | 0.77            | 0.07  | 3.6 |
| 2                          | 0.05 | 0.08 | <0.01 | <0.01 | <0.01 | 0.31            | 0.01  | 3.8 |
| 3                          | 0.05 | 0.02 | <0.01 | <0.01 | <0.01 | 0.18            | <0.01 | 4.0 |
| 3                          | 0.03 | 0.01 | <0.01 | <0.01 | <0.01 | 0.09            | <0.01 | 4.2 |

⇒ As the elution of Cu from Sample A is decreased by repeated cleaning with purified water, the effect of cleaning is inferred to make a difference of pH.

4-2-4-2. Measured oxygen concentration after adding each floatation reagent

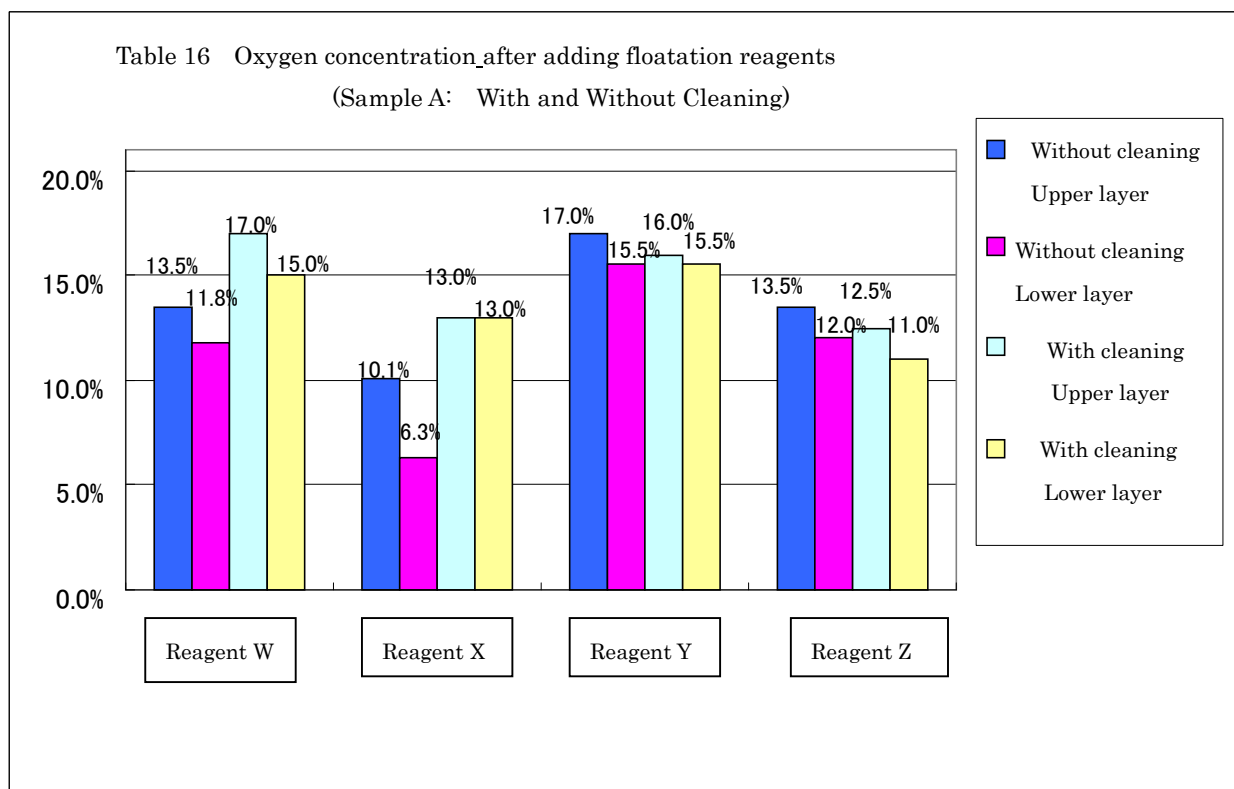
The measurement was done for the upper and lower layers with the same procedures as 4.2.1.1. Results with and without cleaning are shown in Table 15.

**Table 15** Oxygen(O<sub>2</sub>) concentration after adding the different types of floatation reagents into the samples with/without cleaning

| Measuring point                             | Floatation reagents |               |                  |               |                  |               |                  |               |
|---|---------------------|---------------|------------------|---------------|------------------|---------------|------------------|---------------|
|   | Reagent W           |               | Reagent X        |               | Reagent Y        |               | Reagent Z        |               |
|   | Without cleaning    | With cleaning | Without cleaning | With cleaning | Without cleaning | With cleaning | Without cleaning | With cleaning |
| O <sub>2</sub> concentration of Upper layer | 13.5%               | 17.0%         | 10.1%            | 13.0%         | 17.0%            | 16.0%         | 13.5%            | 12.5%         |
| O <sub>2</sub> concentration of Lower layer | 11.8%               | 15.0%         | 6.3%             | 13.0%         | 15.5%            | 15.5%         | 12.0%            | 11.0%         |

Figure 16 shows the comparison of oxygen concentration (Sample A: with/without cleaning by purified water) for each floatation reagent.

**Figure 16**



- (1) Reagent W and Reagent X: non-cleaned sample tended to have a lower oxygen concentration .
- (2) Reagent Y: high oxygen concentration compared to other floatation reagents.
- (3) The oxygen concentration were shown to be lower in the lower level of the flask.
- (4) It was shown that the oxygen concentration differed by the type of floatation reagent.



#### 4-2-5. Measurements of generated odorous gases

##### 4-2-5-1 Measurements of odorous gases after combining sample A with each type of floatation reagents

Each of the four floatation reagents were mixed with Sample A (dried at 105°C) - with the reagent volume being 5% of the volume of sample A. The mixtures were put into cylindrical glass containers (approximately 880ml) in order to have a void of 70% (mixture volume being approximately 195ml).

The gases were measured after being left to stand for 24hrs.

The generated odorous gases were measure at the lower layer (see Figure 17).

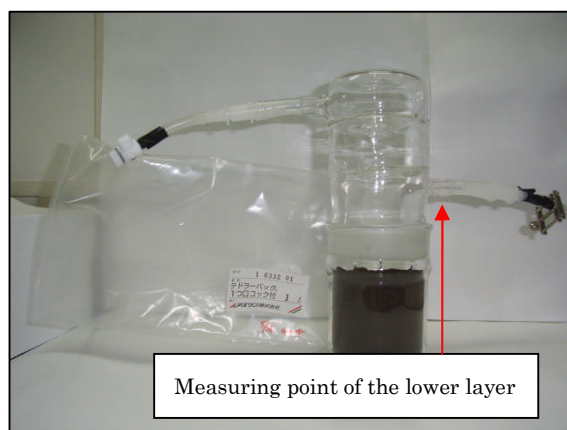
Fixed microextraction<sup>\*2</sup> -gas chromatograph mass spectrometric analysis was used for the measurement of the gas composition.

Non-polar solid-phase adsorption fiber was used for the solid phaseextraction.

Detected components were identified based on GC-MS Library Database (Wiley), not checked by standard substances.

Detected components shown in Table 17.

**Figure 17**



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<sup>\*2</sup> Volatile components in the sample container were collected by solid-phase microextraction (40°C, 20 minutes)

**Table 17** Detected components of odorous gases after floatation reagents added

|                    | Floatation Reagents                |                        |                       |                       |
|--------------------|------------------------------------|------------------------|-----------------------|-----------------------|
|                    | Reagent W                          | Reagent X              | Reagent Y             | Reagent Z             |
| Odorous components | * 2-methyl-2-pentanal              | *Toluene               | *Propylene glycol     | * $\alpha$ -pinene    |
|                    | * 2-ethyl-2-hexanal                | *Ethyl benzene         | monomethyl ether      | *Camphor              |
|                    | *2-propyl-2-hexanal                | *Xylene                | *Dipropylene glycol   | *Cineole              |
|                    | *Butyl butyrate                    | *Xylen(an isomer)      | monomethyl ether      | * $\alpha$ -terpinene |
|                    | *Amyl butyrate                     | *Isobutanol            | *Tripropylene glycol  | *Cymene               |
|                    | *butyl                             | *1-butanol             | methyl ether          | *dl-limonene          |
|                    | acid-2-ethylhexyl                  | *Butyl ether           | *Tetra propylene      | *Terpinene            |
|                    | *1-butanol                         | *Diiso butyl disulfide | glycol monomethyl     | *1-terpineol          |
|                    | *2-ethylhexanol                    | *No quantitative;      | ether                 | * $\beta$ -terpineol  |
|                    | *2-methyl pentyl butyrate          | Approximately 70%      | *Methoxy acetone      | *(-)-borneol          |
|                    | *No qualitative; approximately 30% |                        | *4-oxa-6-heptene-2-ol | *4-terpineol          |
|                    |                                    |                        |                       | * $\alpha$ -terpineol |
|                    |                                    |                        | * $\gamma$ -terpineol |                       |
|                    |                                    |                        | *Isolongifolene       |                       |
|                    |                                    |                        | *4-isopropenyltoluene |                       |
|                    |                                    |                        | *Phenethyl alcohol    |                       |

■ Aldehydes    ■ Carvones    ■ Alcohols    ■ Ester    ■ Aromatics  
■ Ethers    ■ Glycol ethers    ■ Ketones    ■ Terpenoid    ■ Others

4-2-5-2. Measurements of odorous gases of each floatation reagent individually

Only floatation reagents were put into cylindrical glass containers using the same procedure as 4.2.5.1 and left to stand for 24 hours.

Afterward, the odorous gases were measured.

Detected components shown in Figure 18 .

**Figure 18**



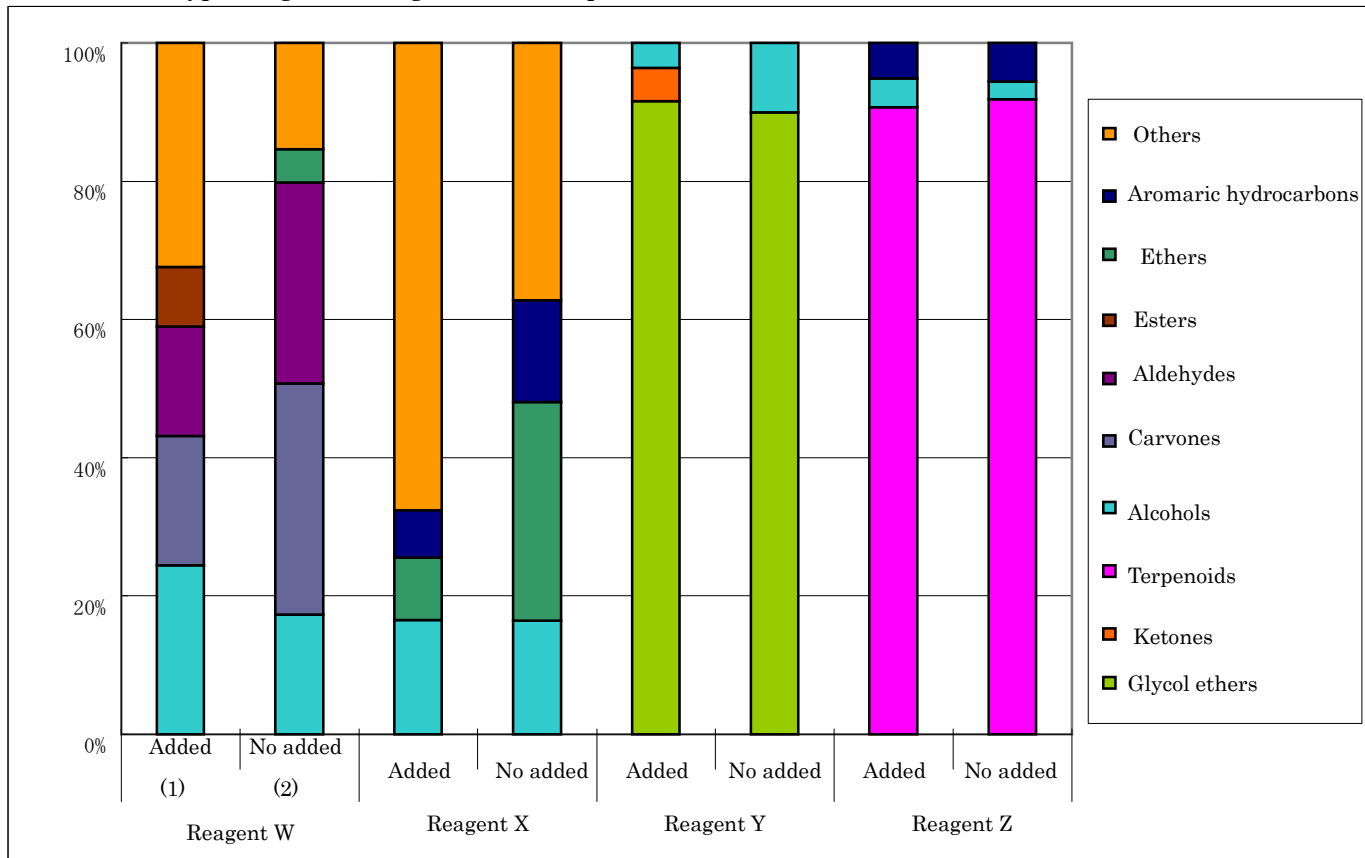
**Table 18** Detected components of odorous gases for each individual floatation reagents

|                    | Floatation Reagents  |   |  |   |
|--------------------|--|---|--|---|
|                    | Reagent W  | Reagent X   | Reagent Y  | Reagent Z   |
| Odorous components | *Butyraldehyde<br>dibuthyl acetal<br>* 2-ethyl2-hexanal<br>*2-propyl-2-hexanal<br>*Butyl butyrate<br>*Amyl butyrate<br>*butyl<br>acid-2-ethylhexyl<br>*1-butanol<br>*2-ethylhexanol<br>*cs-1-Butane<br>*No qualitative;<br>approximagely 30% | *Toluene<br>*Xylene<br>*Isobutanol<br>*Butyl ether<br>*Isobutyl ether<br>*No quanlitative;<br>Approximately 40% | *Propylene glycol<br>monomethyl ether<br>*Dipropylene glycol<br>monomethyl ether<br>*Tripropylene glycol<br>methyl ether<br>*1-allyloxy-2-propanol | * $\alpha$ -pinene<br>*Camhen<br>*Myrcene<br>*Cineole<br>* $\alpha$ -terpinene<br>*Cymene<br>*dl-limonen<br>*Terpinene<br>*Terpineol<br>* $\beta$ -terpineol<br>*(-)-borneol<br>*4-terpineol<br>* $\alpha$ -terpineol<br>* $\gamma$ -terpineol<br>*longifolene<br>*4-isopropenyltolune<br>*Phenthyl alcohol |

■ Aldehydes    ■ Carvones    ■ Alcohols    ■ Ester    ■ Aromatics  
■ Ethers    ■ Glycol ethers    ■ Ketones    ■ Terpenoid    ■ Others

For the comparison of gas components generated from copper concentrate with or without floatation reagents, see Figures 19 and 20.

**Table 19** Types of generated gases and composition ratio



**Table 20** Comparison on gases generated from floatation reagents (%)

| Types                 | Reagent W           |                        | Reagent X |          | Reagent Y |          | Reagent Z |          |
|-----------------------|---------------------|------------------------|-----------|----------|-----------|----------|-----------|----------|
|                       | Added* <sup>3</sup> | No Added* <sup>4</sup> | Added     | No Added | Added     | No Added | Added     | No Added |
| Glycol ethers         | 0.0                 | 0.0                    | 0.0       | 0.0      | 91.5      | 89.9     | 0.0       | 0.0      |
| Ketones               | 0.0                 | 0.0                    | 0.0       | 0.0      | 4.8       | 0.0      | 0.0       | 0.0      |
| Terpenoids            | 0.0                 | 0.0                    | 0.0       | 0.0      | 0.0       | 0.0      | 90.7      | 91.8     |
| Alcohols              | 2.4                 | 17.3                   | 16.5      | 16.4     | 3.6       | 10.1     | 4.1       | 2.6      |
| Carbones              | 18.8                | 33.4                   | 0.0       | 0.0      | 0.0       | 0.0      | 0.0       | 0.0      |
| Aldehydes             | 15.8                | 29.0                   | 0.0       | 0.0      | 0.0       | 0.0      | 0.0       | 0.0      |
| Esters                | 8.6                 | 0.0                    | 0.0       | 0.0      | 0.0       | 0.0      | 0.0       | 0.0      |
| Ethers                | 0.0                 | 4.8                    | 9.0       | 31.7     | 0.0       | 0.0      | 0.0       | 0.0      |
| Aromatic hydrocarbons | 0.0                 | 0.0                    | 6.9       | 14.7     | 0.0       | 0.0      | 5.2       | 5.6      |
| Others                | 32.4                | 15.4                   | 67.6      | 37.2     | 0.0       | 0.0      | 0.0       | 0.0      |

- (1) Gases generated from reagent W: Ethers were detected without being added to Sample A. However, in the case of being added into Sample A, Esters were detected. This change can be considered to be a result of reagent W reacting to Sample A.
- (2) Gases generated from reagent X: the types were the same with or without Sample A. However, the composition ratio was different.
- (3) Gases generated from reagent Y: the types were different if mixed with Sample A. However, the ratio of Glycol ethers, which was the principal component, was the same.
- (4) Gases generated from reagent Z: the composition ratio and the types were almost the same.

#### 4-3. Sample from the cargo ship and results of qualitative analysis

##### 4-3-1. Qualitative analysis of the components of odorous gas

Odorous gas and water condensation adhering to a hatch cover were taken from the cargo hold of one of the cargo ships which had been in the Port of Saganoseki. Both samples were taken almost the same time as the hatch cover was opened.

Next day, Sample A was taken from No. 1 cargo hold just after the cargo was discharged

The cargo temperature was 42.6°C.

At that time, the outer air temperature of Oita city was between 10.7°C and 13.3°C.

The gas in a cargo hold loading copper concentrate was taken in a tetrapack, and qualitative analysis was done by Fixed Microextraction-Gas Chromatograph mass spectrometric analysis.

Nonpolar solid-phase adsorption fiber was used for solid phase extraction. (see Table 21)

\*<sup>3</sup> Gas components generated when 5% of floatation reagent was added into copper concentrate.

\*<sup>4</sup> Gas components generated only from floatation reagents.

**Table 21** Qualitative analysis on the components of odorous gas

| Name of sample  | Components detected | Remarks               |
|---|---------------------|-----------------------|
| The components of odorous gas in the cargo hold in which copper concentrate were loaded | Toluene             | Aromatic hydrocarbons |
|   | Xylene              |                       |
|   | Dimethyleacetamide  | Ester compound        |
|   | Phenol              | Phenols               |

## 4-3-2. Analysis of condensation water

The pH value of the condensation water was measured by a pH meter.

Qualitative analysis of cation and anion was done with an ICP-Atomic Emission Spectrometry Analyzer and an ION Chromatograph Unit.

## 4-3-2-1. Results of pH measurements of condensation water

**Table 22** pH measurements of condensation water

| Name of sample     | pH  |
|--------------------|-----|
| Water Condensation | 7.7 |

## 4-3-2-2. Results of ICP-Atomic Emission Spectrometry Analyzer and ION Chromatograph measurements of condensation water

**Table 23** Qualitative analysis of condensation water

| Range of Concentration | Elements detected   |
|------------------------|---|
| 100mg/L and over       | Ca: 130mg/L   |
| 10~100 mg/L            | -   |
| 1~10 mg/L              | Cl: 6mg/L Na: 4mg/L, SO <sub>4</sub> <sup>2-</sup> : 2mg/L<br>Mg: 1mg/L, Ba: 1 mg/L |
| 1 mg/L and under       | K   |

4-4. Results of X-ray diffraction measurements of copper concentrate by type

4-4-1. Results of X-ray diffraction measurement on Sample A, Sample B and Sample C  
Result of X-ray diffraction measurements by type shown in Figures 19, 20 and 21

Figure 19 Sample A

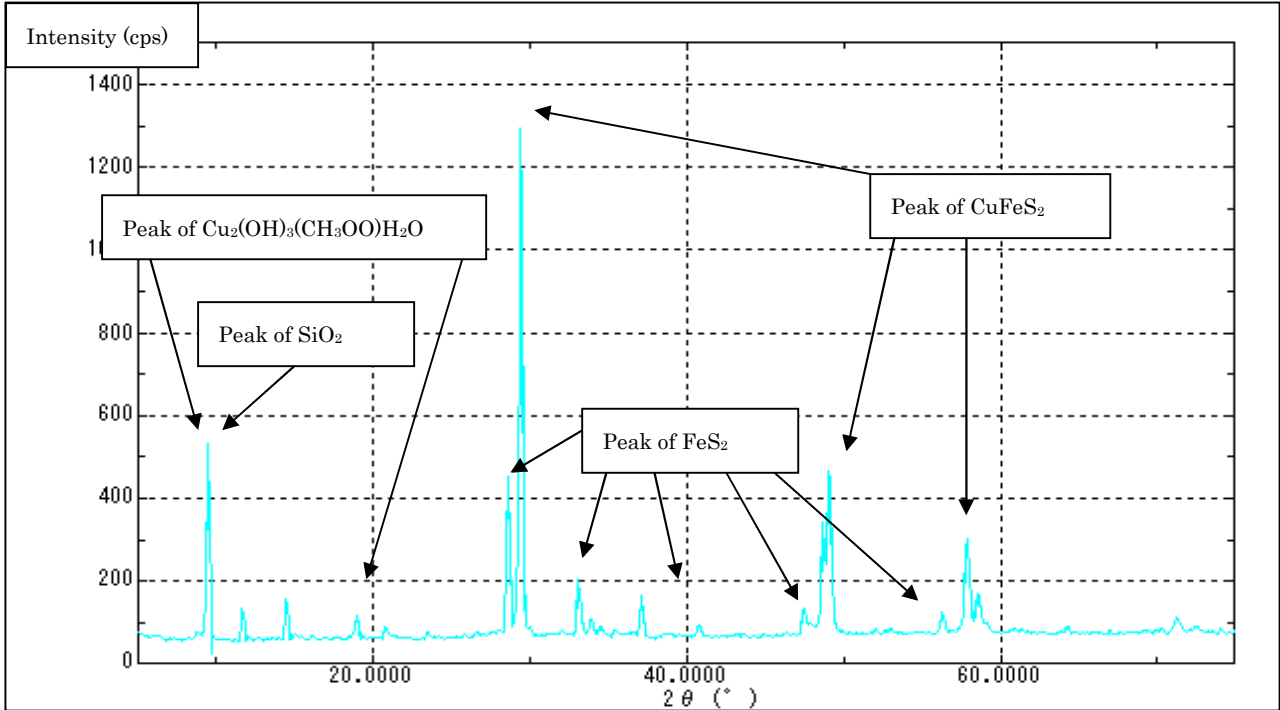


Figure 20 Sample B

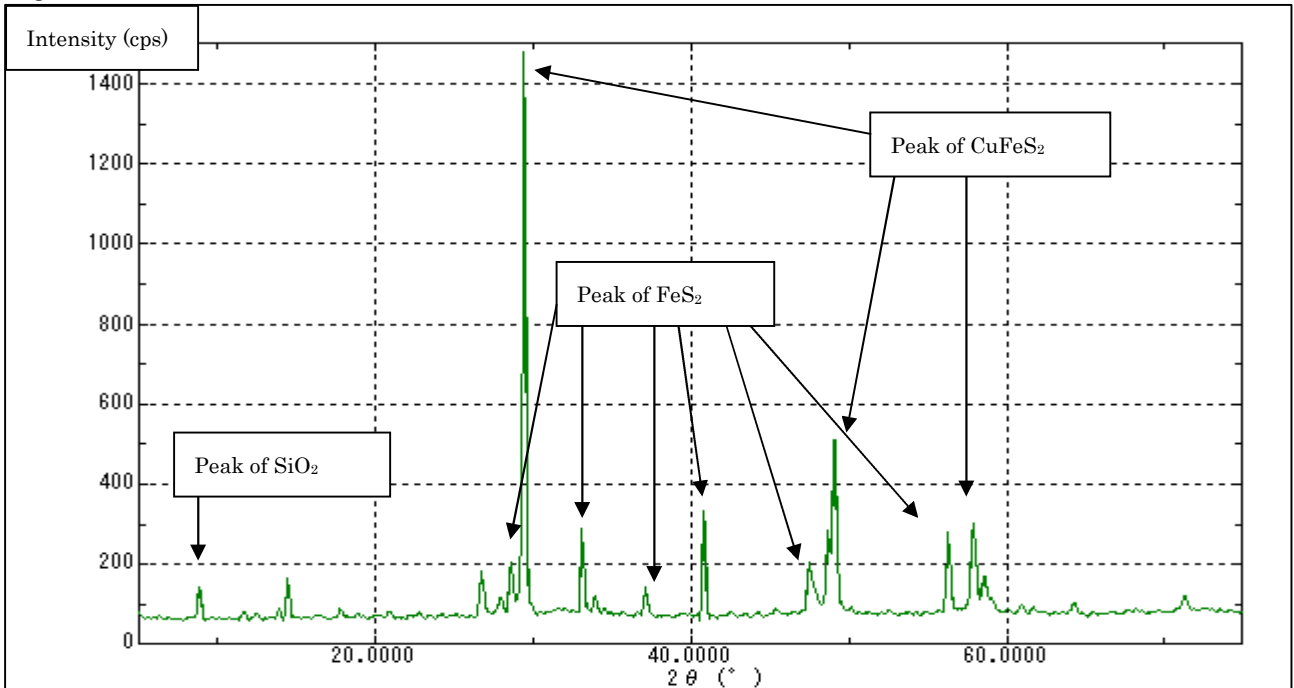
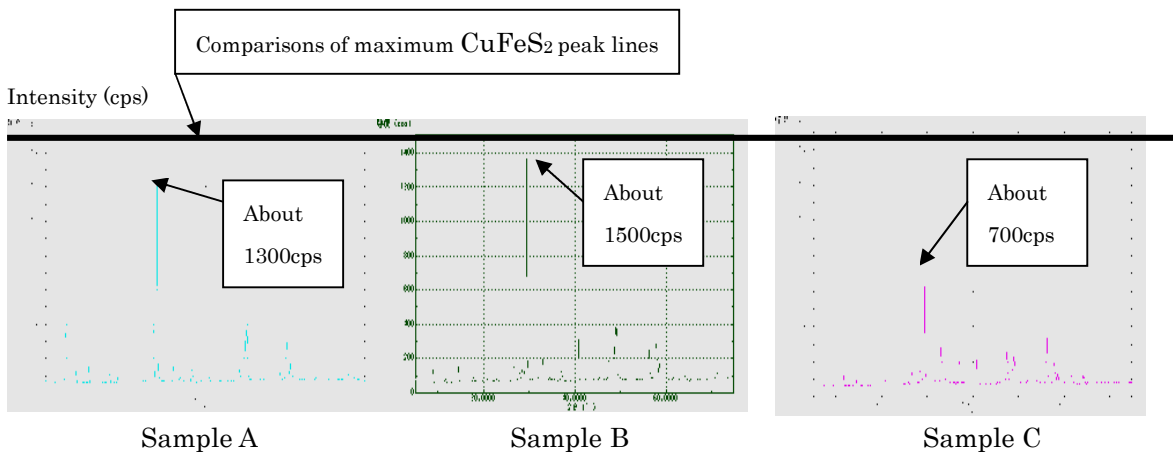
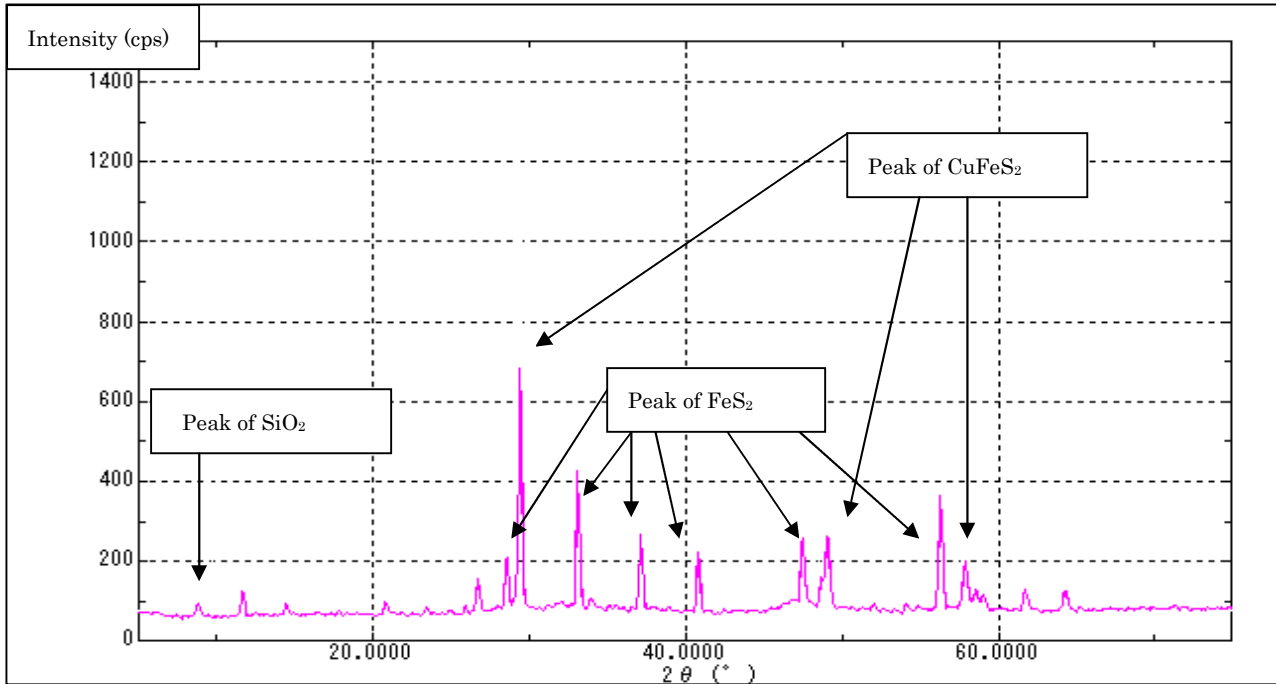


Figure 21 Sample C



(1) For Sample C it was found that the intensity of the peak<sup>\*5</sup> of CuFeS<sub>2</sub> was the lowest of the three samples.

Thus it is considered that the ratio of CuFeS<sub>2</sub> was the lowest.

(2) For Sample C it was found that the intensity of the peak of FeS<sub>2</sub> was high.

(3) From the results of the X-ray diffraction of the copper concentrates (by type), Sample C which had the slowest oxygen consumption rate of the three samples was also found to have the lowest peak CuFeS<sub>2</sub> level.

It is not analyzed whether this directly relates to oxygen consumption rate at this stage.

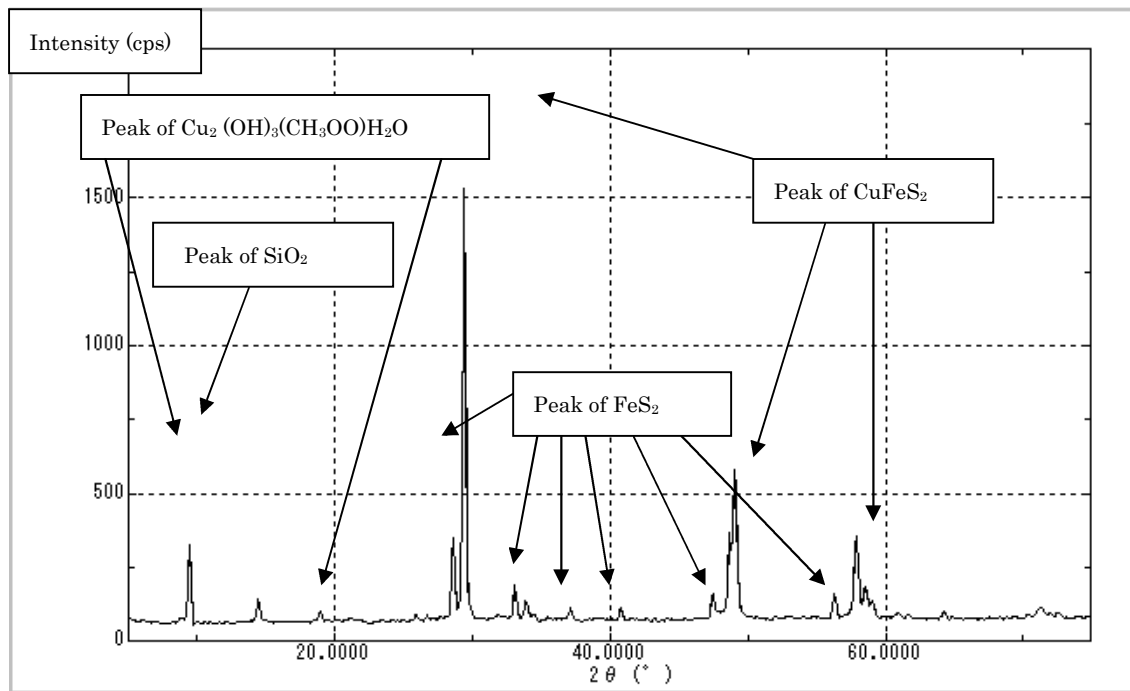
The low peak of CuFeS<sub>2</sub> in the sample is considered to be because the structural compound morphology of Sample C differed from the other samples.

<sup>\*5</sup> The high intensity of the peak (when simply being analyzed under the same conditions) indicates that the compound ratio is high in the sample.

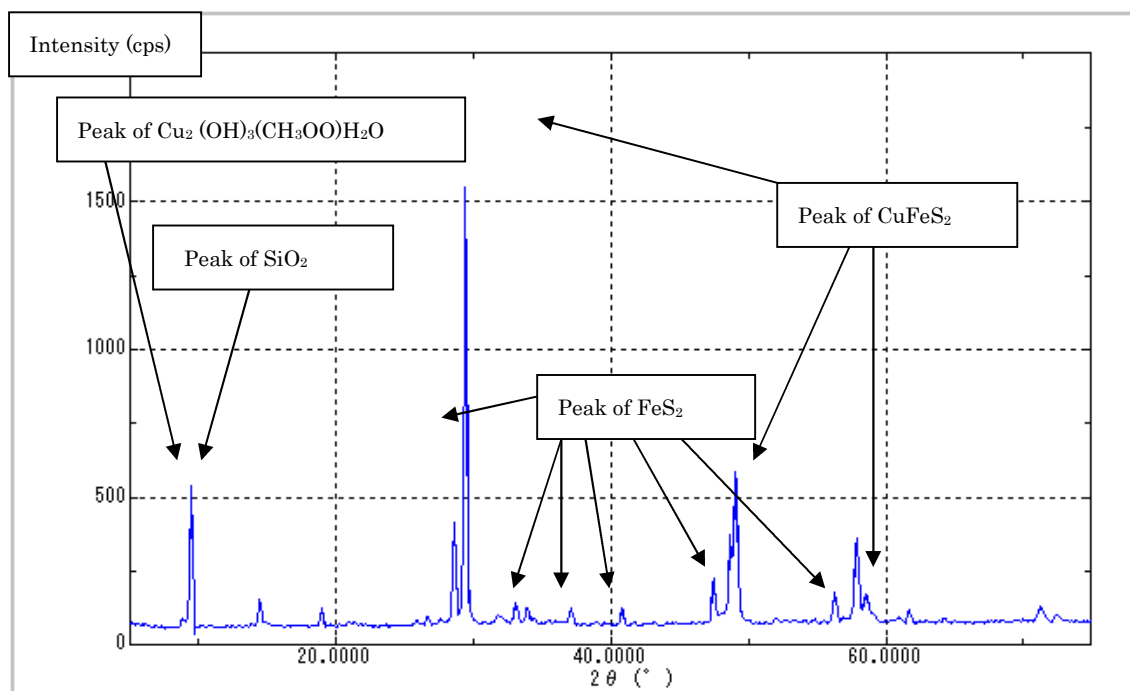
4-4-2. Results of X-ray diffraction measurement on Sample A, Sample B and sample C after heating

Heating tests at 100°C, 200°C and 300°C were conducted on Sample A. The changes from heating were checked by X-ray diffraction equipment. Figure 22 ~ Figure 24 shows X-ray diffraction peaks after heating.

**Figure 22** X-ray diffraction peak after heating at 100°C

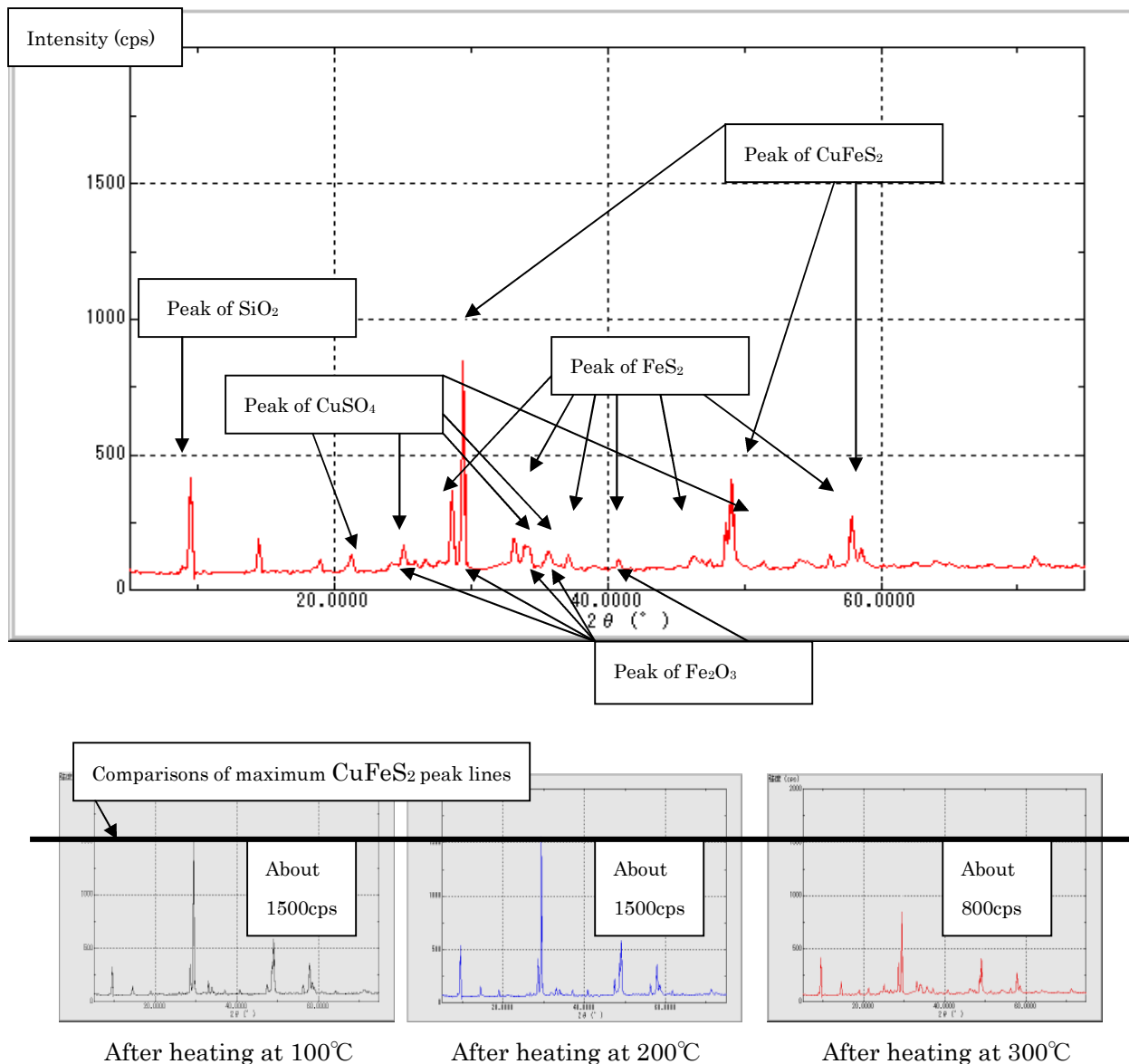


**Figure 23** X-ray diffraction peak after heating at 200°C





**Figure 24** X-ray diffraction peak after heating at 300°C



- (1) The peak after heating at 100°C and 200°C showed almost no change.
- (2) After heating at 300°C, the peak of  $\text{CuFeS}_2$  decreased, and the peak of  $\text{Fe}_2\text{O}_3$  and  $\text{CuSO}_4$  was ascertained.
- (3) From the results of (1) and (2), it is considered that the compound morphology of  $\text{CuFeS}_2$  was changed by heating.

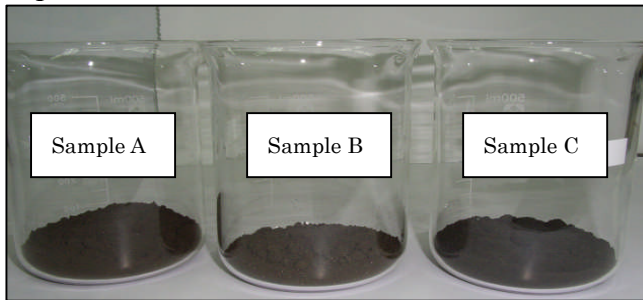
4-5. Supplementary tests

Cleansing of each copper concentrate with purified water

Tests involving cleansing of each type of copper concentrate with purified water were conducted using the same procedures as 4-2-4-1.

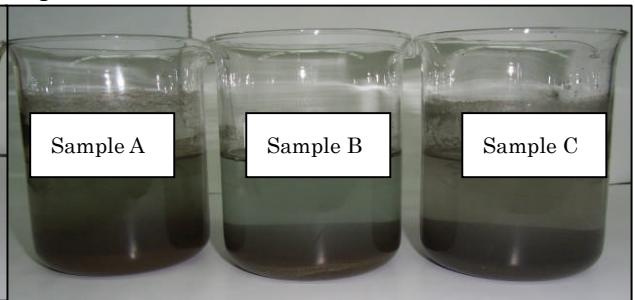
Figure 25 - Samples before filtration; Figure 26 – 30 minutes after the first cleaning; Figure 27 – The first filtrate; Figure 28 –The second filtrate

**Figure 25**



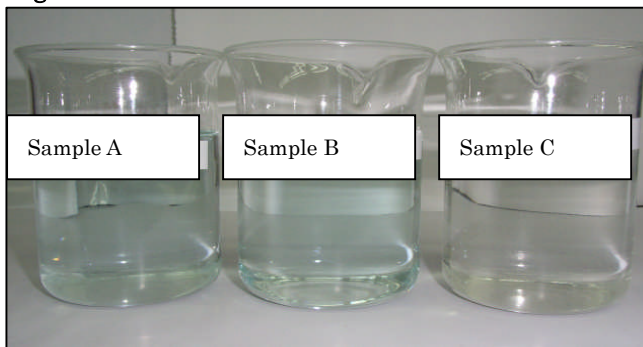
Samples before filtration

**Figure 26**



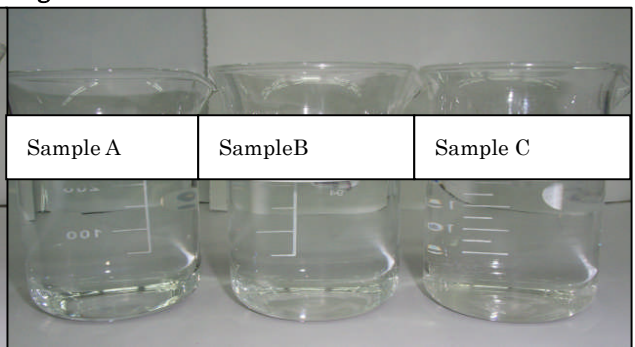
1<sup>st</sup> time: 30 minutes later after leaving to stand

**Figure 27**



1<sup>st</sup> time: Filtrate

**Figure 28**



2<sup>nd</sup> time: Filtrate

Table 24 and Table 25 show the result of qualitative analysis by pH measurement and ICP of the filtrate.

**Table 24** Results of pH measurement

| Ranges of concentration      | Sample A |     | Sample B |     | Sample C |     |
|------------------------------|----------|-----|----------|-----|----------|-----|
|                              | 1st      | 2nd | 1st      | 2nd | 1st      | 2nd |
| The result of pH measurement | 4.1      | 4.5 | 4.7      | 4.9 | 7.9      | 7.7 |

**Table 25** Qualitative analysis of copper concentrate (by types)

Unit: %

| Ranges of concentration | Sample A  |   | Sample B  |                                     | Sample C  |   |
|-------------------------|---|---|---|-------------------------------------|---|---|
|                         | 1st   | 2nd   | 1st   | 2nd                                 | 1st   | 2nd   |
| 0.1% and above          | SO <sub>4</sub> <sup>2-</sup> :0.78<br>Cu :0.12<br>Ca :0.16 | SO <sub>4</sub> <sup>2-</sup> :0.43<br>Ca :0.16 | SO <sub>4</sub> <sup>2-</sup> :0.95<br>Cu :0.14<br>Zn :0.30 | SO <sub>4</sub> <sup>2-</sup> :0.13 | SO <sub>4</sub> <sup>2-</sup> :0.52<br>Ca :0.18 | SO <sub>4</sub> <sup>2-</sup> :0.38<br>Ca :0.15 |
| 0.1% ~ 0.01%            | Mg :0.04<br>Mn :0.03<br>Zn :0.05                            | Cu :0.02  | Ca :0.07<br>Mg :0.04  | Cu :0.03<br>Ca :0.01<br>Zn :0.04    | -   | -   |
| Under 0.01%             | Fe  | Fe, Mg<br>Mn, Zn                                | Fe, Mn  | Fe, Mg, Mn                          | Cu, Fe, Mg<br>Mn, Zn                            | Cu, Fe, Mg<br>Mn, Zn                            |

SO<sub>4</sub><sup>2-</sup> was detected at 0.1% and above in all filtrates.

Cu was detected at 0.1% and above in Sample A and Sample B, however, that of Sample C was under 0.01%.

Further, the filtrates of Sample A and Sample B were acidic, and that of Sample C was weak alkaline.

Thus, it is considered that the reactivity to oxygen in air of Sample A and Sample B is high are thus easily oxidized, and water soluble Cu SO<sub>4</sub><sup>2-</sup> is produced

## 5. Review

- (1) Regarding the oxygen consumption rate of copper concentrate in airtight containers, a big difference was not shown between the ratios of void 70% and 30% because the capacity of the containers was small.

Oxygen consumption rates were found to be higher under very high temperatures.

Regarding the addition of moisture, the moisture level contained in the copper concentrates was usually about 5% ~ 8%.

Therefore, the measurements were made after raising the moisture level by approximately 10%.

The results in the case of moisture being 15% was that oxygen consumption rates became lower compared with those without moisture added.

Regarding the measurements of oxygen consumption rates of copper concentrate by type, the oxygen consumption rate of Sample C was shown to be slow compared with that of the other samples.

Moreover, the oxygen consumption rate of Sample C at 40°C was shown to be considerably slower compared with those of Sample A and Sample B.

- (2) Toxic substances such as toluene, xylene and phenol were detected in the odorous gas in the cargo hold, which was loaded with copper concentrate.

- (3) Condensation water adhering to the hatch cover of the hold in which Sample A was loaded was analyzed.

It is considered probable that sulfide gas was generated and was absorbed into condensation water. However,  $\text{SO}_4^{2-}$  was low.

Thus, it is believed that a high level of sulfide gas was generated during transportation.

- (4) Regarding the effects of the floatation reagents\*<sup>6</sup>, the measurement for oxygen concentration on each reagent was conducted under a void of 30%.

From the results, it was verified that oxygen concentration differed by floatation reagent.

Floatation reagents themselves were found to become oxidized.

Furthermore, odorous gas components such as toluene and xylene were detected in Sample X.

- (5) Regarding the X-ray diffraction of each copper concentrate, Sample C, which had the slowest oxygen consumption rate of the three samples, was found to have a lower peak of  $\text{CuFeS}_2$  compared with the other types.

It is not still determined whether this phenomenon directly relates to oxygen consumption rates at this stage.

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\*<sup>6</sup> Generally speaking, the surface of rocks is of a hydrophilic nature, and that of metals are of a hydrophobic nature. Useful minerals are separated out from mined ores by using this characteristic trait. Mined rocks are crushed to pieces by large mills until becoming a slime state. After that, foaming agents (floatation reagents) are added and agitated. Ores including metals are gathered together on the surface of the foam and become easy to collect. In most cases, floatation reagents such as surfactant and oil are chosen for use on ores and in effluent treatments.

However, the low peak of  $\text{CuFeS}_2$  shows that Sample C has a different compound morphology from the others.

As for the result of heating Sample A, it remained almost unchanged until  $200^\circ\text{C}$ .

However, the  $\text{CuFeS}_2$  peak lowered when the sample was heated above  $300^\circ\text{C}$ , and the peaks of  $\text{Fe}_2\text{O}_3$  and  $\text{CuSO}_4$  were verified.

Therefore, it is considered that the compound morphology of  $\text{CuFeS}_2$  was changed by heating.

(6) Whiteness 1

In the test for oxygen consumption at  $80^\circ\text{C}$ , whiteness separated (Figure 29).

The whiteness was measured by EDX.

Oxygen (54%), sulfur (17%) and calcium (26%) and copper (2%) were detected.

The elements extracted in the supplementary cleaning tests (4-5.) were detected.

It is considered that the elements were separated out by moisture evaporation after the water soluble components in Sample A dissipated.

Figure 29



(7) Whiteness 2

Whiteness was found when Sample A was dried at  $105^\circ\text{C}$  (Figure 30).

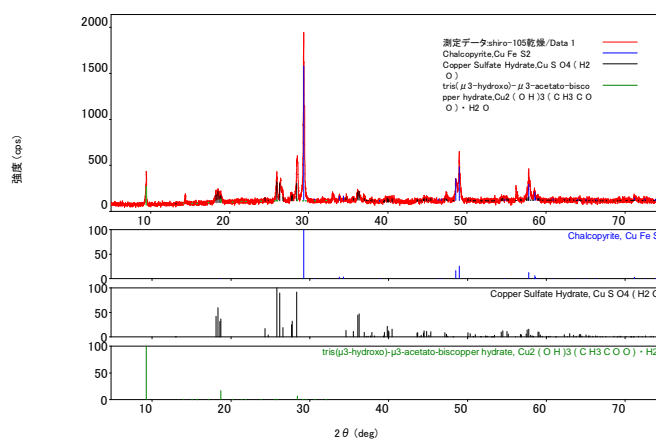
Only the whiteness was taken and measured by X-ray diffraction equipment.

As the result,  $\text{CuFeS}_2$  and  $\text{CuSO}_4(\text{H}_2\text{O})$  were detected (see Figure 31).

Figure 30



Figure 31



(8) Remarks

Oxygen consumption of copper concentrate increases in a liner manner as time passes.

It was verified that the reaction rates of oxygen consumption, which corresponded to the slopes of straight lines, differed by the type of copper concentrate.

And also it was verified that the reaction rates differed by the origin of the copper concentrate (compound molecular form · floatation reagents).

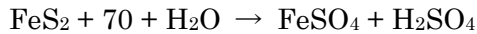
From the above mentioned:

⇒ Flootation reagent X used in Sample A is a strong alkali, however, the filtrate indicated acidity when the cleaning test was conducted.

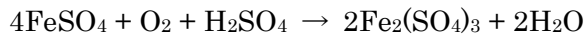
Therefore, it is considered that Sample A is a concentrate prone to oxidation reactions, or possibly the reactions occurred under certain conditions.

Generally, the oxidation of  $\text{CuFeS}_2$  (copper pyrites) is described by the following reaction formula\*<sup>7</sup>

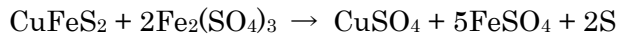
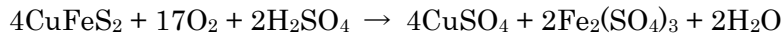
[1] Sulfuric acid and ferrous sulfate is generated by the oxidation of  $\text{CuFeS}_2$ .



[2] Oxidation from ferrous sulfate to ferric sulfate occurs



[3] It leads to oxygenate  $\text{CuFeS}_2$  (copper pyrites) and generate copper sulfate



⇒ Seeing the result of X-ray diffraction measurement on Sample C, the peak of  $\text{CuFeS}_2$  is low (the ratio of the compounds of  $\text{CuFeS}_2$  in the sample is low), and Cu leaching rate was shown to be low when the cleaning test was conducted. Thus, it is considered that the oxidation nature of Sample C is lower than the other copper concentrate and is stable.

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\*<sup>7</sup> Reference: "Koushou Chishitsugaku, Takeo Kato, 1937", "Konishi, Saitoh, Nomura (Osaka Prefecture Univ.) PYRITE BY THE THERMOPHILIC ARCHAE ACIDINUS BRIERLEYI 120 IN BATCH AND CONTINUOUS-FLOW STIEERED TANK REACTORS, Cu2007, The John E. Dutrizac international Symposium on Copper Hydrometallurgy, 2007", [http://www.jogmec.go.jp/mric\\_web/current/08\\_56.html](http://www.jogmec.go.jp/mric_web/current/08_56.html) and JOGMEC News & Report No. 56, 2008