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HARMFUL AQUATIC ORGANISMS IN BALLAST WATER

Application for Basic Approval of Active Substances used by Hitachi Ballast Water Purification System (ClearBallast)

Submitted by Japan

SUMMARY

Executive summary: This document contains an application for Basic Approval of Active Substances used by Hitachi Ballast Water Purification System (ClearBallast) in accordance with the Procedure for approval of ballast water management systems that make use of Active Substance (G9) adopted by resolution MEPC.126(53). Relevant documents and the complete dossier have been provided to Marine Environment Division of the Organization for review by the GESAMP-Ballast Water Working Group.

Action to be taken: Paragraph 5

Related documents: BWM/CON/36; MEPC 56/2/2; and BWM.2/Circ.10

Introduction

1 The Ballast Water Management Convention (BWM Convention), in its regulation D-3.2, provides that ballast water management systems which make use of Active Substances, to comply with the Convention, shall be approved by IMO based on a procedure developed by the Organization.

2 MEPC 53 adopted, by resolution MEPC.126(53), the 'Procedure for approval of ballast water management systems that make use of Active Substances (G9)'. Section 8 of the Procedure sets out the methodology to be followed for the approval of such systems and requests IMO to establish a Technical Group (the GESAMP-Ballast Water Working Group) to review the proposals submitted by Administrations and report to the Organization on its findings.

3 This document contains an application for Basic Approval of Active Substances used by Hitachi Ballast Water Purification System (ClearBallast) in accordance with the Procedure (G9) and its annex provides the non-confidential information on that system. Relevant documents and the complete dossier have been submitted to Marine Environment Division of the Organization for review by the GESAMP-Ballast Water Working Group.

For reasons of economy, this document is printed in a limited number. Delegates are kindly asked to bring their copies to meetings and not to request additional copies.

4 The Hitachi Ballast Water Purification System (ClearBallast) holds excellence in treatment capability and is safe not only to ships and crew but also to the environment.

Action requested of the Committee

5 The Committee is invited to consider the proposal for approval and decide as appropriate.

ANNEX

INFORMATION FOR BASIC APPROVAL OF ACTIVE SUBSTANCES USED BY HITACHI BALLAST WATER PURIFICATION SYSTEM (CLEARBALLAST)

This report is structured in accordance with the headlines in the “Procedure for approval of ballast water management systems that make use of Active Substances (G9)”.

1 INTRODUCTION

The purpose of this document is to clarify management responsibilities to the authorities concerned by providing data. Furthermore, the document describes Hitachi Ballast Water Purification System and its impact on the environment. This system uses coagulation magnetic separation as the major purification method in accordance with the Procedure (G9).

1.1 Glossary

Chemical Injector: A device to inject chemicals (triiron tetraoxide, PAC, or PASA), which is a part of the Hitachi Ballast Water Purification System.

Coagulator: A device to transform chemicals into flocs containing SS, plankton, bacteria, and so on, which is a part of the Hitachi Ballast Water Purification System.

Filter Separator: A device which removes flocs from the ballast water using a rotating filter drum, as a part of the Hitachi Ballast Water Purification System.

Floc: Gelatinous matter made up of fine particles such as a suspension colloid in water (suspended solids) formed by an inorganic coagulant or high-polymer coagulant.

Inorganic Coagulant: A chemical containing metallic ions of aluminium or iron that forms a larger floc of fine particles dispersed in water such as a suspension colloid by neutralizing the charge on their surfaces.

Magnetic Disk: A component of the magnetic separator of this system. A disk in which magnets (permanent magnets) are embedded.

Magnetic Disk Array: A component of the magnetic separator of this system. An assembly consisting of several magnetic disks arranged coaxially.

Magnetic Separator: A device which removes flocs from the ballast water using a magnetic disk array, as a part of the Hitachi Ballast Water Purification System.

PAC (Poly Aluminium Chloride): An inorganic coagulant consisting of poly aluminium chloride and referring to basic aluminium chloride.

PASA (Poly Acrylamide Sodium Acrylate): A crosslinking chemical consisting of high molecular weight polymer particles with a negatively charged surface, which forms a coagulation of fine particles suspended in water such as a suspension colloid. It is a kind of Anionic High-Polymer Coagulant.

Rotating Filter Drum: A component of the filter separator of this system. A drum with metallic or plastic filters attached on the cylindrical frame and that is continuously rotating.

Sludge Tank: Tank for storing the removed flocs containing chemicals, SS, plankton, bacteria, and so on, which is a part of the Hitachi Ballast Water Purification System.

SS (Suspended Solids): Particulate substances in water that are insoluble to water such as a suspension colloid. One of the indices that expresses the extent of suspension in water.

SS Concentration: Weight of suspended solids contained in 1 L of water in the unit of mg/L.

1.2 Features of Hitachi Ballast Water Purification System

The Hitachi Ballast Water Purification System purifies water by removing target organisms and other objects using flocculating agents. The system effectively promotes collision between these small target organisms and aggregates to form flocs, and separates the floc by magnetic separation technology to purify ballast water. The photograph shown in Figure 1-1 is of a pilot-scale test set-up of this system. Even when the seawater intake is turbid with SS, this system efficiently removes such suspension components as well as bacteria and plankton so that transparent, clear treated ballast water is obtained.



Figure 1-1: Example of Hitachi Ballast Water Purification System

2 OUTLINE OF HITACHI BALLAST WATER PURIFICATION SYSTEM

2.1 Principle of purification of the system

This system employs a coagulation magnetic separation method, in which organisms and other target objects are coagulated using coagulants and separated by magnetic separation technology. Specifically, coagulants and triiron tetraoxide are added to the seawater to form small agglomerates of about 1 mm in diameter called flocs, containing plankton, bacteria and sand (Figure 2-1).

Figure 2-2 shows the ballast water purification process in this system. First, triiron tetraoxide is added to seawater containing plankton, bacteria, and SS. Next, PAC and PASA are added to form flocs. These flocs are then separated from the seawater using permanent magnets. Finally, any flocs that were not removed by the magnetic separation are removed by filtering to produce purified water.

This coagulation magnetic separation method removes not only plankton and bacteria but also sand, mud, and SS contained in the ballast water, thereby reducing mud deposits (including muddy sediment such as dead organisms) and alleviating mud removal during ship inspections. With this system, the ballast water can be purified either during storage in the ballast tank, during intake, or during discharge. Purification during intake is the most effective way to ensure that a minimal amount of organisms and SS enter the ballast tanks and thus reduces sediment build-up in the tanks. Therefore, most of our attention is focused on the system components and operations for purification during intake.

PAC and PASA are widely used in drinking water purification plants so the safety of these chemicals has been confirmed. Triiron tetraoxide, whose composition is Fe_3O_4 , is a natural resource that exists broadly in nature, as is generally known. Table 2-1 shows the rated concentration of each chemical used in the coagulation magnetic separation method.

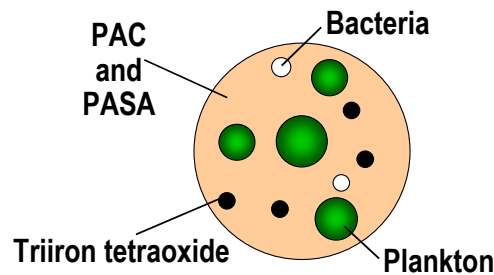


Figure 2-1: Schematic structure of a floc

Table 2-1: Rated concentration of each chemical

Additive agent	Additive concentration (mg/L)
Triiron tetraoxide	30
PAC	5 (as Al)
PASA	1

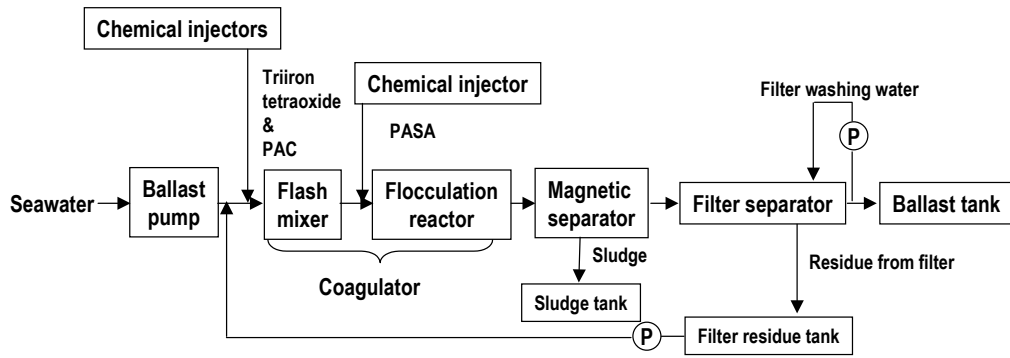


Figure 2-2: Outline of process of Hitachi Ballast Water Purification System

2.2 Specifications of the system

This section describes the specifications of the major components of the Hitachi Ballast Water Purification System described in the preceding section. Figure 2-3 is a schematic diagram of the structure of the Hitachi Ballast Water Purification System.

Since the Hitachi Ballast Water Purification System is automated, no manual operation by the crew is required and no dedicated operators for the purification system are necessary. Some manual operation is required for the pouring chemicals into the storage tank, preparing for unloading the sludge, and unloading the sludge onto land.

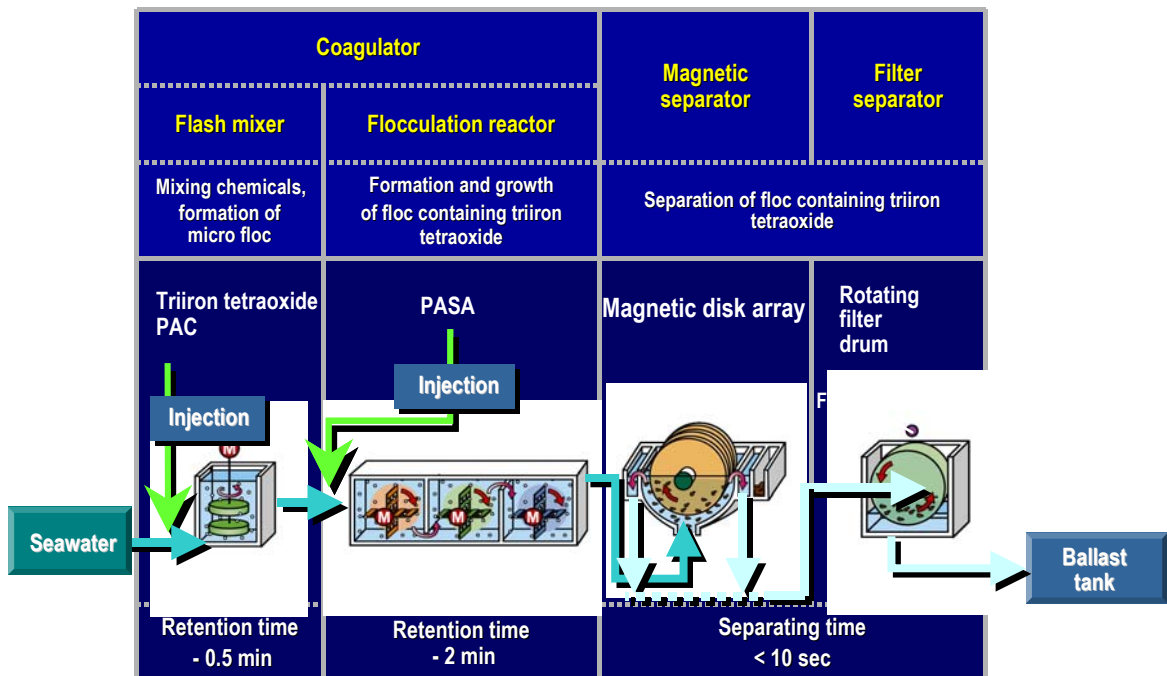


Figure 2-3: Schematic diagram of structure of Hitachi Ballast Water Purification System

2.2.1 Preparation for operation

Since some manual operation is required for the preparation of the purification operation, this section outlines the manual operation for the preparation.

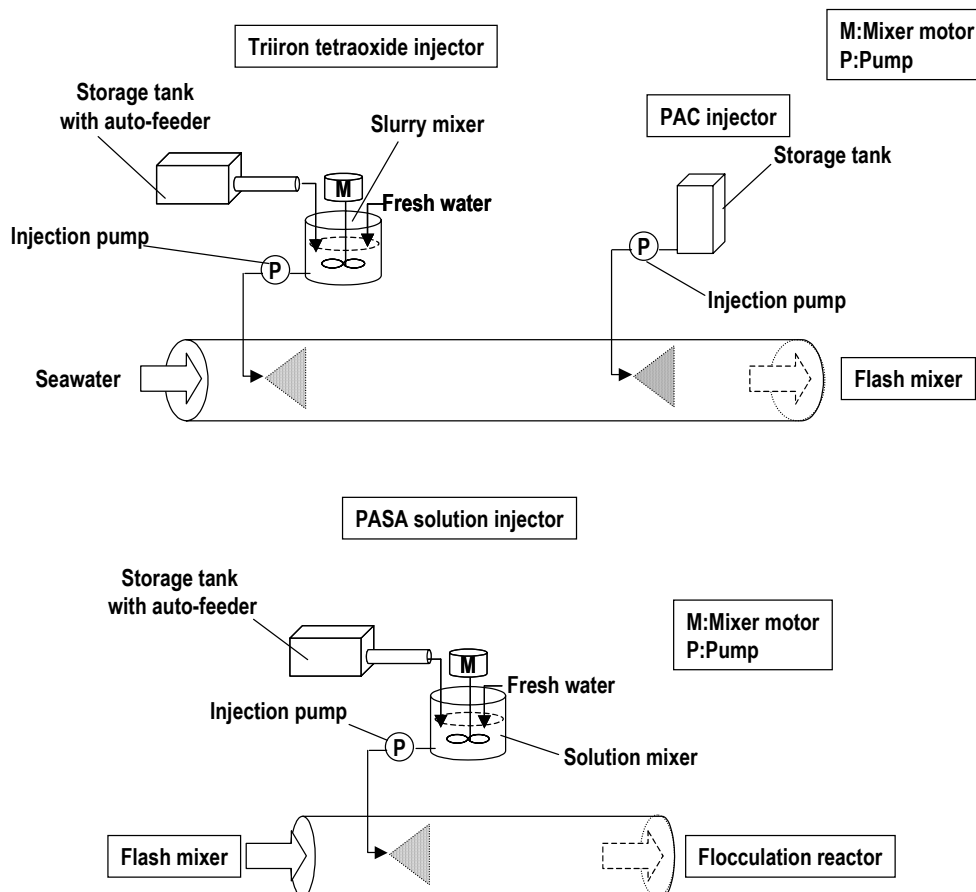


Figure 2-4: Schematic diagrams of chemical injectors

2.2.2 Chemical injector

Each chemical injector has a liquid or powder chemical storage tank, a slurry mixer or solution mixer, and a liquid chemical injection pump.

Triiron tetraoxide and PASA are available on the market in powder form while PAC is available in liquid form. The two powder chemicals are converted into slurry or solution before injection by mixing them with fresh water on the ship. The three chemicals in liquid form are injected into the ballast water feed pipes through the injection pumps (Figures 2-2 and 2-3).

2.2.3 Coagulator

The coagulator consists of two types of mechanical reactors: a flash mixer and a flocculation reactor (see Figure 2-3). The triiron tetraoxide and PAC injected from the chemical injectors are uniformly mixed in the flash mixer at high speed. In the process of sending the micro flocs from the flash mixer to the flocculation reactor, PASA is added. Agitation is milder in the flocculation reactor than in the flash mixer.

In this way, flocs containing triiron tetraoxide and aggregated particles (SS, bacteria, plankton, etc.) are formed in the untreated ballast water. Since the floc contains triiron tetraoxide, it is magnetically attractive at the next process, magnetic separator. Table 2-2 shows flocculation time.

Table 2-2: Required time for formation of flocs by coagulator

Item	Required time
Flash mixer	0.5 minutes (for micro floc formation)
Flocculation reactor	2 minutes (for floc formation)

(The required time shown in Table 2-2 corresponds to the amount of treatment at the rated operation of the ballast pump.)

2.2.4 Magnetic separator

The magnetic separator consists of a casing that receives the seawater containing flocs transferred from the coagulator and a magnetic disk array that removes the flocs magnetically. The magnetic disk array consists of multiple magnetic disks in which permanent magnets are embedded (see Figure 2-5). While the ballast water is transferred from the coagulator, it flows through the magnetic disks, and the flocs are attracted to the magnetic disks. The flocs attached to the disks are scraped off with scrapers in the open air and collected as sludge.

The coagulation magnetic separation method can remove flocs containing triiron tetraoxide within several seconds. Residual flocs are removed by filter separator described in the following section.

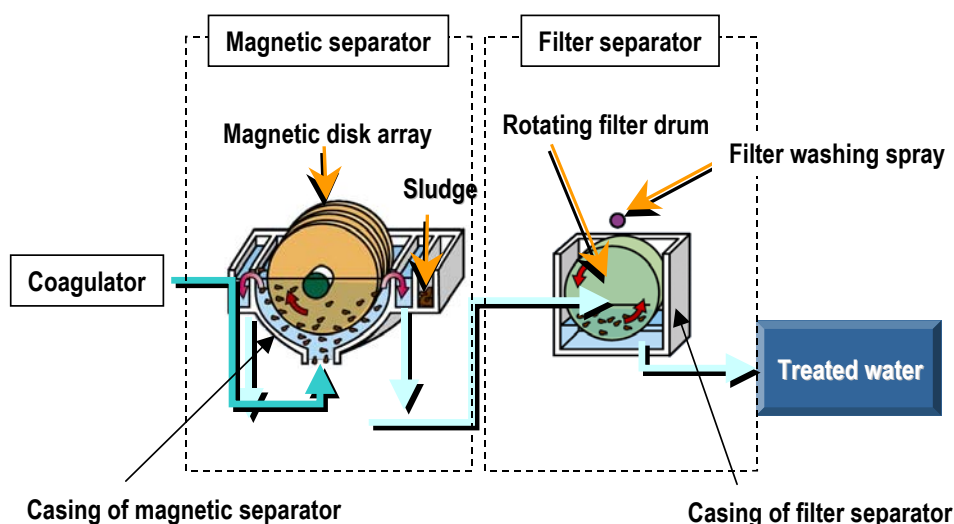


Figure 2-5: Schematic diagram of magnetic separator and filter separator

2.2.5 Filter separator

The filter separator consists of a continuously rotating filter drum, a casing, and filter washing sprays. The residue collected by filter washing is returned to the ballast water feed pipe before the first chemical injection points (see Figure 2-2) and is purified along with the untreated ballast water.

2.2.6 Sludge tank

The method being studied at present, after the temporary storage of flocs as sludge, is to handle the sludge on board and then unload it onto land. Since the situation differs from ship to ship, it may be necessary to take individual measures.

The flocs collected in the magnetic separator are automatically transferred to the sludge tank by conveyors without any manual handling. The stored sludge is taken out of the ship for unloading after sufficient preparation such as transferring to individual containers or removing water, etc. In the unloading process, some steps such as transport of the individual containers require manual handling. There is no human exposure in the rest of the steps since they are automated.

2.3 Purification performance of the system

2.3.1 Quality of water treated by this system

The quality of the water treated (at a flow rate of 50 m³/h) by the pilot-scale set-up on reclaimed land in Tokyo Bay was measured by the amount of zooplankton, phytoplankton, and *E. coli* it contained. The results meet the standards set in regulation D-2 for the discharge of ballast water (see Table 2-3).

Table 2-3: Results of organism removal performance

Item	Unit	Untreated seawater*	Treated seawater	Criteria
Plankton 50µm or larger	Viable organisms / m ³	67,600	0	<10
10 - 50µm	Viable organisms / ml	92.1	0	<10
<i>E. coli</i>	MPN/100 mL	1,100	2	<250

Average data in the period from October 2006 to February 2007.

* Seawater taken from Tokyo Bay.

The quality of the water treated by this system was also measured by its SS concentration, using the same set-up as the organism removal performance test mentioned above. The results show that the SS concentration in the treated water of the load test was the same as that of the control test (see Table 2-4).

Table 2-4: Results of SS removal performance

Sample	SS concentration (mg/L)	
	Untreated seawater	Treated seawater
Control ¹⁾	10	< 1
Load test ²⁾	50	< 1

Detection limit: 1mg/L

1) Actual seawater taken from Tokyo Bay on October 26, 2006.

2) Kaolin was added to the actual seawater before the treatment.

The following sections explain that the treated water by this system has no environmental and ecological risks.

2.3.2 pH of treated water

The treatment of seawater by the Hitachi Ballast Water Purification System slightly reduces the pH value of the treated water. This pH reduction is caused by reaction of PAC in water. PAC is a polybasic polyelectrolyte, and aluminium ions exist as an aqua-complex, $[\text{Al}(\text{OH}_2)_6]^{3+}$, in which six H_2O molecules are co-ordinated around the aluminium atom in octahedral configuration. The general formula of PAC is expressed by $[\text{Al}_2(\text{OH})_n\text{Cl}_{6-n}]_m$ (n: 1 to 5, m: 1 to 10). PAC reacts with calcium carbonate in the untreated water to lower the alkalinity. Therefore, the pH value of the water treated by the system will be reduced.

In this calculation, bicarbonic acid at 140 mg/L, determined from the standard seawater composition, is used as the alkalinity of seawater. A pH value of 8.3, which is the intermediate pH value of the untreated seawater sampled from the purification experiment carried out in Tokyo Bay, is used as the pH of the untreated seawater. In theory, the pH is the lowest when $m=1$ and $n=1$, and it does not become much lower than 7.0. The pH value is 7.2 (for $m = n = 1$) under the condition of 5mg/L used for rated operation. The same results are obtained for $m=2$ to 10. Therefore, it is theoretically impossible for the pH value to become much lower than 7.0.

2.4 Application capacity

The volume of the major components of this system, particularly the volume of the coagulator, increases in proportion to the flow rate. This is because the retention time of the ballast water in the equipment, which is the treating time, is constant regardless of the flow rate. The treatment time of the coagulator and the magnetic separator can be kept constant regardless of the flow rate, and the tank volume inside these two devices is proportional to the flow rate of ballast water. On the other hand, the process scale of the filter separator is related to filter flux (filtration speed) and the flux can be kept constant. The area is proportional to the flow rate of the ballast water.

The equipment can be scaled up or multiple sets of equipment can be installed in accordance with the amount of ballast water to be treated. As a result, the commercial process scale would be designed at the ranges from 50 to 10,000 m^3/h .

2.5 Specifications for chemicals

The following chemicals are used in the Hitachi Ballast Water Purification System.

2.5.1 Triiron tetraoxide

.1 Identification of the chemical

Name of substance (IUPAC): triiron tetraoxide
Molecular formula or structural formula: Fe_3O_4

.2 Quality standard for safety of human health

High purity grade is used.

2.5.2 PAC

.1 Identification of the chemical

Name of substance (IUPAC): Basic aluminium chloride

Molecular formula or structural formula: $[Al_2(OH)_nCl_{6-n}]_m$ (n: 1 to 5, m: 1 to 10)

.2 Quality standard for safety of human health

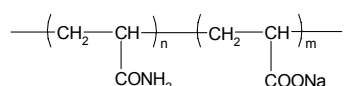
The following requirements relating to impurities specified by ANSI/AWWA B408-03 Liquid Polyaluminium Chloride (AWWA, 2004) of the American Water Works Association (AWWA) Standard shall be satisfied. The specifications of “Japan Industrial Standard JIS K 1475 for poly aluminium chloride” (JIS, 1996) and “European Standard EN 883:2004 Chemicals used for treatment of water intended for human consumption-Polyaluminium chloride hydroxide and polyaluminium chloride hydroxide sulfate” (CEN, 2004) are stricter than that of ANSI/AWWA B408-03 Liquid Polyaluminium Chloride. Poly aluminium chloride conforming to JIS or EN may be used.

2.5.3 PASA

.1 Identification of the chemical

Name of substance (IUPAC): Acrylamide sodium acrylate copolymer

Molecular formula or structural formula:



.2 Quality standard for safety of human health

The following requirements relating to impurities specified by ANSI/AWWA B453-06 Polyacrylamide (AWWA, 2006) of the (AWWA, American Water Works Association) Standard shall be satisfied. “Japan Water Works Association (JWWA, 1980) standard K 126-1980 for polyacrylamide used for water works” and “The European Standard EN 1407:1998 Chemicals used for treatment of water intended for human consumption-Anionic and non-ionic polyacrylamides” (CEN, 1998) are similar quality standards. PASA conforming to JWWA or EN standard may be used.

3 HANDLING CHEMICALS ON BOARD SHIP

This section explains the procedure of loading chemicals onto ship, using chemicals for ballast water treatment and unloading sludge from ship to land.

3.1 Carrying-in procedure and mechanism to prevent leakage of chemicals from piping

3.1.1 Triiron tetraoxide and PASA

Triiron tetraoxide and PASA powder are loaded onto the designated position on board packed in a flexible container. The outlet of the container is connected to the inlet in the carry-in room and the triiron tetraoxide and PASA are poured to the onboard each dedicated tank respectively. To prevent scattering of the powder, the storage tank and piping equipped with safety valves are tightly sealed. An exhaust duct positioned close to the storage tank provides forced ventilation, preventing any spilled dust from scattering.

3.1.2 PAC

PAC liquid is loaded onto a designated position on board packed in an acid-resistant plastic container. The container outlet is connected to the inlet in the carry-in room using an acid-resistant hose, and the safety valve is opened to pour the PAC to the on-board PAC storage tank. The storage tank is made of plastics or is lined with plastics on the inner surface to prevent corrosion of the tank due to contact with the acidic chemical. The feeding pipes connecting the PAC storage tank to the ballast water feed pipe are also made of acid-resistant materials, such as plastic. If PAC leakage occurs, coamings with a height of about 10 cm around the PAC storage tank prevent the spread of the chemicals over the floor, enabling the crew to safely and smoothly stop the leakage. In case the system is designed to use PAC in powder form, the storage tank and hose connecting the PAC container to the inlet are made of plastics. To prevent the scattering of powder, the storage tank and piping equipped with safety valves are tightly sealed. An exhaust duct providing forced ventilation is provided close to the storage tank to prevent any dust from scattering if the powder spills.

3.2 Use of chemicals on ship and operation protocol

The chemicals used in the system are continuously injected from the piping of ballast water treatment equipment using three dedicated pumps. They are automatically controlled as part of the automated operation of ballast water treatment. Since these chemicals are manually poured into the storage tanks by operators or crew, the operators wear goggles, masks, rubber gloves, and work clothes in anticipation of accidental chemical dispersion to prevent inhalation and adhesion of the dust to the skin. A notice regarding the use of appropriate protective gear is to be placed on the injector.

The flocs collected in the magnetic separator are automatically transferred to the sludge tank by the conveyor without any manual handlings. The part related to the sludge is basically covered so that the sludge does not scatter. The stored sludge is unloaded from the ship after sufficient preparations such as subdividing into individual containers or removing water with drum dryers, etc. In the unloading process, some steps partially require manual handling. Since the sludge contains chemicals, the operators should wear goggles, rubber gloves, mask, and protective clothes. Warnings should be displayed on the devices to emphasize the need to use such safety gear.

4 ANALYSIS OF TREATED WATER

The treated water was tested to determine whether substances derived from the chemicals (triiron tetraoxide, PAC, and PASA) used in the purification system were present and also to determine if harmful heavy metal were present (CERI, 2007a). All tests were carried out using a pilot-scale ballast water purification system (with a flow rate of 50 m³/h) on reclaimed land in Tokyo Bay. Actual seawater from Tokyo Bay was treated, and samples of untreated water and treated water were analysed.

4.1 Identification and determination of substances contained in raw and treated water

4.1.1 Test method

(1) Samples

The seawater was treated (marked “(1)” in this section) at the pilot-scale system mentioned above (flow rate of 50 m³/h) that is installed on reclaimed land in Tokyo Bay. The pilot-scale system simulates the ballast water purification system. Untreated seawater (marked “(2)” in this section) was pumped in at the location where the test equipment was installed.

(2) Amounts of additive chemicals

In this test, the chemicals were added at the rated concentrations (see Table 4-1).

Table 4-1: Amounts of additive chemicals (rated concentration)

Additive chemical	Addition concentration (mg/L)
Triiron tetraoxide	30
PAC	5 (as Al)
PASA	1

(3) Water sampling

Samples of untreated water and treated water were taken from the respective sampling positions (see Figure 4-1).

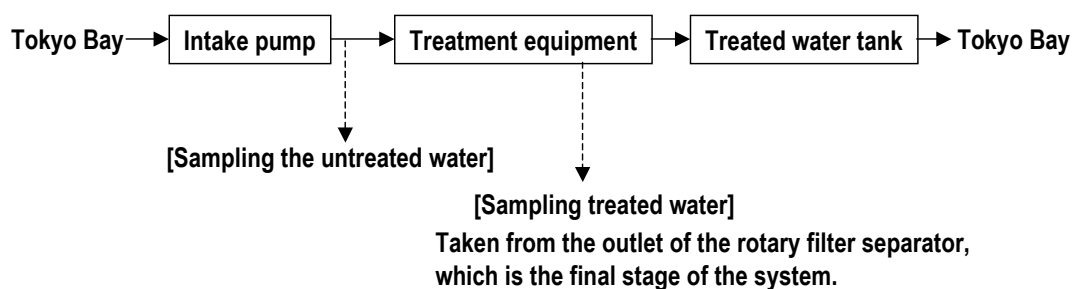


Figure 4-1: Schematic diagram of water sampling positions

(4) Test item and method

Elemental analysis was done using inductively coupled plasma atomic emission spectrometry (ICP-AES)*.

Volatile organic compounds: Purge and trap gas chromatograph-mass spectrometry

pH: JIS K 0102 12.1 Glass-electrode method
 Arsenic: JIS K 0102 61.2 Atomic absorption spectrometry by hydride
 Aluminum: JIS K 0102 58.4 Inductively coupled plasma atomic emission spectrometry
 Manganese: JIS K 0102 56.4 Inductively coupled plasma atomic emission spectrometry
 Acrylamide: Gas chromatograph spectrometry
 Acrylic acid: Gas chromatograph mass spectrometry after solid-phase extraction and derivatization
 Total organic carbon: JIS K 0102 22.2 Combustion oxidation-infrared type TOC automatic analysis method

* The ICP methods used in JIS K 0102 correspond approximately to ISO 11885:2007; Water quality -- Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES).

Only the aluminium was measured for the samples taken both before and after the filtering with a glass and a membrane filter (see Table 4-2 and 4-3). All the other items were analysed for the samples taken before the filtering.

4.1.2 Test results

(1) Quantitative analysis of harmful heavy metals and water treatment agents (acrylamide, acrylic acid, aluminum)

**Table 4-2: Results of quantitative analysis of harmful metals and water treatment agents
Unit: mg/L**

Test item \ Sample	(1) Treated water	(2) Untreated water	detection limit
PH	7.7(23.5°C)	7.9(23.5°C)	-
Arsenic (As)	Not detected.	0.001	0.001
Aluminium (Al)	0.08	Not detected.	0.02
Manganese (Mn)	0.01	Not detected.	0.01
Acrylamide monomer	Not detected.	Not detected.	0.0001
Acrylic acid monomer	Not detected.	Not detected.	0.0001
Organic carbon (TOC)	1.3	1.3	0.5

* Cadmium(Cd), Lead(Pb), Mercury(Hg), Chromium(VI), and Selenium(Se) were not detected in both of treated water and untreated water.

Table 4-3: Comparison of aluminium content before and after filtration
Unit: mg/L

Filter treatment	Sample	(1) Treated water	(2) Untreated water	Detection limit
Not filtered*		0.02	ND	0.02
Glass filter (1 µm)**		ND	ND	0.02
Membrane filter (0.45µm)**		ND	ND	0.02

* In order to detect total aluminium in the sample (suspended aluminium in solid form and dissolved aluminium in ion form)

** In order to detect aluminium ions in the sample

(2) Qualitative and quantitative analyses of volatile organic compounds (VOCs)

Quantitative and qualitative analysis was conducted for the VOC compounds. Although scanning analysis was also conducted, no differences were detected between treated water and untreated water.

(3) Qualitative analysis of semivolatile organic compounds

Each sample was extracted with dichloromethane and analysed by scanning measurement on a gas chromatograph-mass spectrometer. No substance was detected (detection limit: 0.002 mg/L as hexane equivalent).

(4) Elemental analysis by ICP-AES

A qualitative analysis was conducted on the treated water to find out whether the elements shown in Table 4-4. Since there was hardly any difference between the results of the treated water and the untreated water, the treated water does not seem to contain any new elements due to the processing of the Hitachi Ballast Water Purification System.

Table 4-4: Results of elemental analysis by ICP-AES
Unit: mg/L

No.	Measured element		(1) Treated water	(2) Untreated water	Detection limit
1	Sodium	(Na)	1,600	2,000	10
2	Magnesium	(Mg)	760	750	0.01
3	Silicone	(Si)	2	2	1
4	Sulphur	(S)	1,300	1,300	10
5	Potassium	(K)	330	330	5
6	Calcium	(Ca)	78	79	0.1
7	Manganese	(Mn)	0.1	Not detected.	0.1
8	Iron	(Fe)	Not detected.	Not detected.	1
9	Strontium	(Sr)	22	22	0.1

Remarks: Values are semiquantative (reference values).

4.1.3 Amounts of substances derived from additive chemicals in treated water

Since the Hitachi Ballast Water Purification system uses triiron tetraoxide, PAC, and PASA as the chemicals, any iron, aluminium, or acrylamide detected in the treated water could possibly be derived from the additive chemicals.

As shown in Tables 4-2 and 4-3, iron and acrylamide were not detected in either the treated water or the untreated water. Aluminium was not detected in the untreated water but 0.08 mg/L was detected in the treated water (see Table 4-2). Since 5 mg/L (as Al) of PAC is added, the maximum ratio (%) of PAC contained in the treated water can be approximately to be 1.6% of the PAC added.

4.2 Measurement of pH

4.2.1 Test method

(1) Samples

The samples for this test were prepared by purifying seawater using the same equipment as used for the identification and determination tests (see Section 4.1.1 (1)).

(2) Amounts of additive chemicals

The amounts of chemicals used in this test were double those used under rated operating conditions (see Table 4-5).

Table 4-5: Amounts of additive chemicals

Additive chemical	Additive concentration (mg/L)
Triiron tetraoxide	60
PAC	10 (as Al)
PASA	2

(3) Method

The pH measurement was started after the system was launched to make sure all the devices were filled with water. Sampling of the treated water and untreated water was conducted 16 to 32 minutes after the start-up of treatment in the same way as described in Section 4.1.1 (3).

4.2.2 Results

The measurement was carried out within 10 minutes of sampling. As described in Section 2.3, the pH of the treated water was between 6.9 and 7.4 while the pH of the untreated water was between 8.0 and 8.6. Since the equilibrium is assumed to continue after treatment, the pH of the treated ballast water should not decrease until it is released (in about two weeks).

5 DATA SET

In this section, the identification of substances used in the Hitachi Ballast Water Purification System and the data-set required for section 4.2 of Procedure (G9) are reported.

As for the data of each substance, international peer reviewed documents, databases, original study reports, etc. were searched comprehensively and broadly, and all the available data were checked to evaluate their reliability. Only the data judged to be reliable have been adopted for this application.

5.1 Identification of substances or preparation (G9: 4.1)

5.1.1 Preparation (G9: 4.2.2)

No substance corresponding to the preparation defined by paragraph 2.1.3 of Procedure (G9) is included in this system.

5.1.2 Active Substances

Triiron tetraoxide, PAC, and PASA correspond to Active Substances (see Table 5-1). In this purification system, since almost all the additive agents collected in the flocs are removed (see 2.3.1), the amount of Active Substances released into the environment together with the treated ballast water is negligible.

Table 5-1: Active Substances

	Active Substance 1	Active Substance 2	Active Substance 3
Name of substance (IUPAC)	Triiron tetraoxide	Basic aluminum chloride	Acrylamide sodium acrylate copolymer
Synonym (used in this document)	Triiron tetraoxide	PAC	PASA
CAS number	1317-61-9	1327-41-9	25085-02-3
UN number	None	None	None
Shipping name	None	None	None
Molar weight	231.53	Not applicable	More than several million
Empirical formula or structural formula	Fe ₃ O ₄	Al _n (OH) _m Cl _(3n-m) 0<m<3n	$\text{---} \left(\text{CH}_2 \text{---} \underset{\text{CONH}_2}{\text{CH}} \right)_n \left(\text{CH}_2 \text{---} \underset{\text{COONa}}{\text{CH}} \right)_m \text{---}$
Purity	100%	Percent of content: 10-11% of water solution (aluminium oxide equivalent)	90% or more
Impurity	None	None	Acrylamide monomer: 0.05% or less (CAS No. 79-06-1)
Stabilizers or additives	None	None	None

5.1.3 Relevant Chemicals (G9: 2.1.4)

Since triiron tetraoxide, PAC, and PASA do not have active functional groups, no by-products are generated as a result of a reaction with seawater. Consequently, no substance corresponding to a Relevant Chemical exists in this system.

5.1.4 Other substances

A substance that corresponds to other substances is acrylamide monomers that remain in PASA as an impurity. Although its mass concentration is only 0.05% or less of PASA, a data survey was performed.

5.1.5 Configuration of PAC in water

Since PAC, which is the Active Substance in this system, can be transformed into water, its details are explained below.

PAC, which is used as an inorganic flocculating agent, is a polybasic polyelectrolyte. In water the aluminium ions take the form of the aqua-complex, $[Al(H_2O)_6]^{3+}$, in which six H_2O molecules are co-ordinated around the aluminium atom in octahedral formation. The general formula of PAC is expressed as $[Al_2(OH)_nCl_{6-n}]_m$ (n : 1 to 5, m : 1 to 10). The more detail is described in 2.3.2. The composition of this hydroxide is not well-defined, being a gel-like precipitate formed by the linkage of Al^{3+} with OH^- and being co-ordinated with many water molecules.

5.2 Data on effects on aquatic plants, invertebrates and fish, and other biota, including sensitive representative organisms (G9: 4.2.1.1)

Since PAC is dissociated into chloride ions and aluminium ions in an aqueous solution, and the aluminium ions exist as an aqua complex, as described before (5.1.5), its form in the water depends on pH values. Furthermore, since chloride ions exist in seawater in large amounts, the assessment of the ecotoxicity of PAC can be conducted based on the toxicity of aluminium.

In addition, collecting the data on the toxicity of aluminium ions is limited to the pH range of 6.5 to 7.5, which is actually applied in the coagulation sedimentation process of the Hitachi Ballast Water Purification System (see 2.3.2).

5.2.1 Acute aquatic toxicity

Triiron tetraoxide

For triiron tetra oxide, there is a report on the use of fresh water fish, Japanese dace (*Leuciscus idus*), and the value of 48-h LC_0 is $> 1,000$ mg/L (EU, 2000a). There are no corresponding data available for algae and invertebrates. Considering that naturally-occurring triiron tetraoxide is abundant in the environment and is not absorbed or accumulated in the body due to consisting of water insoluble particles, the toxicity of triiron tetraoxide for algae and invertebrates is considered to be very low.

PAC

- (1) Toxicity data on PAC is obtained from reports on algae, shellfish and fish. There is a report on the acute toxicity of PAC in algae using seaweed, and the 48-h LC₅₀ values are 1,500 mg/L and > 10,000 mg/L (growth inhibition as the index), when the pH is not adjusted and adjusted to neutral, respectively (Asada Chemical Industry, 2003).

Regarding the acute toxicity of PAC in shellfish, there is a report on the study of Manila clams in which the 48-h LC₅₀ values are 6,800 mg/L and > 10,000 mg/L, when the pH is not adjusted and adjusted to neutral, respectively (Asada Chemical Industry, 2003). As for the acute toxicity of PAC in fish, there is a report on the study of *Oryzias latipes* in which the 48-h LC₅₀ values are 840 mg/L and > 10,000 mg/L, when the pH is not adjusted and adjusted to neutral, respectively (Asada Chemical Industry, 2003).

- (2) Looking at the acute toxicity of PAC, data on water soluble aluminium salts such as aluminium chloride can be examined to evaluate the toxicity of PAC in aquatic organisms because the salts are dissociated in water and form the same aqua complex as PAC. For aluminium ions, toxicity data are reported in invertebrates and fish.

For the acute toxicity of aluminium ions in invertebrates, the minimum 96-h LC₅₀ value is 0.097 mg Al/L for *Ctenodrilus serratus*, a sand worm marine species (IPCS, 1997; Petrich & Reish, 1979). Regarding the acute toxicity of aluminium ions in fish, the minimum value of 96-h LC₅₀ in the pH range from 6.5 to 7.5, which is actually applied in the ballast water treatment, is 4.25 mg Al/L (pH: 7.4) for *Pimephales promelas* (IPCS, 1997).

PASA

Acute toxicity data on PASA are reported on invertebrates and fish. There is a report on the acute toxicity of PASA in invertebrates in which the fresh water species, *Ceriodaphnia dubia* is used, and the 48-h LC₅₀ value is 218 mg/L (De Rosemond & Liber, 2004).

Looking at the acute toxicity of PASA, there is a report on the study of the marine species *Girella punctata*, and the 48-h LC₅₀ value is 840 mg/L (Tabata and Ishibashi, 1984). For fresh water species, there is a report on the study of *Oryzias latipes*, *Carassius auratus*, *Cyprinus carpio*, and *Salvelinus namaycush*, in which the LC₅₀ values are between 180 and >600 mg/L (Dia-Nitrix, 2004; Liver et al., 2005; Tabata and Ishibashi, 1984). Since the data provided by Tabata and Ishibashi in 1984 are reliable because the testing methods and conditions are described in detail, the original report in Japanese has been translated into English and is listed in the References.

No data on the toxicity in algae are reported. As PASA consists of particles containing high molecular weight polymers (several millions or more), it is not absorbed and accumulated in the body. The toxicity of PASA in algae is considered to be low, not including any physical harmful effect.

Acrylamide monomers

Regarding the acute toxicity of acrylamide monomers in algae, there is a report on the fresh water green alga *Pseudokirchneriella subcapitata*, in which the 72-h EC₅₀ (growth inhibition as the index) is 33.8 mg/L (EU, 2002).

There is a report on the acute toxicity of acrylamide monomers in invertebrates in which the marine crustacean, *Mysidopsis bahia*, is used, and the 96-h LC₅₀ is 78 mg/L (EU, 2002). For fresh water fish, there is a report on *Daphnia magna* and *chironomid species*, and the 48-h EC₅₀ (swimming inhibition) is 98 mg/L for the former (EU, 2002).

As for the acute toxicity of acrylamide monomers in fish, the minimum value of 96-LC₅₀ is 59 mg/L for *Danio rerio* (Kovriznych & Urbancikova, 2001).

5.2.2 Chronic aquatic toxicity

There are no chronic toxicity data available for triiron tetraoxide and PAC in aquatic organisms. Naturally occurring triiron tetraoxide is abundant in the environment. Although it is highly possible that wild organisms are exposed to this substance, no adverse effects have been identified. Therefore, it may be concluded that chronic toxicity of triiron tetraoxide is not significant. For PAC, data on water soluble aluminium salts such as aluminium chloride are available for the evaluation of the toxicity of PAC in aquatic organisms because the salt dissociate in water and form the same aqua- complexes as those formed by PAC.

PAC

To evaluate the toxicity of PAC in aquatic organisms, data on water soluble aluminium salts such as aluminium chloride can be examined because the salts are dissociated in water and form the same aqua complex as PAC. For aluminium ions, chronic toxicity data are reported in invertebrates and fish. As for the chronic toxicity of aluminium ions in invertebrates, there is a report on *Ctenodrilus serratus*, a kind of sandworm, in which the 28-day NOEC for reproduction is 0.02 mg Al/L (pH: 7.6 - 8.0) (Petrich & Reish, 1979).

Looking at the chronic toxicity of aluminium ions in fish, there is a report on the fresh water species, *Salvelinus fontinalis*, in which the 60-day NOEC for growth is 0.088 mg Al/L (pH: 6.5 - 6.6) (IPCS, 1997).

PASA

Data on the chronic toxicity of PASA are reported on fish.

Regarding the chronic toxicity of PASA in fish, there is a report in which the fresh water species, *Salvelinus namaycush* is used, and the 30-day NOEC for activity is 75 mg/L and that for survival and growth is 300 mg/L (Liver et al., 2005).

Acrylamide monomers

Data on the chronic toxicity of acrylamide monomers were gathered because traces of unpolymerized acrylamide monomers remain in PASA as an impurity. For acrylamide monomers, toxicity data are reported in algae and invertebrates. The chronic toxicity of acrylamide monomers in algae is 16 mg/L for a 72-hour NOEC in a growth inhibition test using the fresh water green alga, *Pseudokirchneriella subcapitata* (EU, 2002). There is a report on the chronic toxicity of acrylamide monomers in the invertebrate marine species, *Mysidopsis bahia*, in which the 28-day NOEC for death is 2.04 mg/L (Springborn Bionomics, 1985).

5.2.3 Endocrine disruption

There are no reports of triiron tetraoxide, PAC, PASA, and acrylamide monomers having an effect on endocrine disruption in aquatic organisms. None of these substances are listed as suspected endocrine disruptors (MOE, 2005).

5.2.4 Sediment toxicity

There are no reports of triiron tetraoxide, PAC, or PASA having sediment toxicity. Triiron tetraoxide and PAC are inorganic compounds. They are accumulated and presented as triiron tetraoxide or aqua-complex ions of aluminium in the sediment. As all these substances are naturally occurring elements, the probability of their having an adverse effect on the sediment organisms is considered to be low.

Although PASA is accumulated in the sediment, it is not absorbed or accumulated in the sediment organisms because it consists of particles of high molecular weight polymers (several million or more). Therefore, the possibility of PASA having an adverse effect on sediment organisms is considered to be low.

Data on the sediment toxicity of acrylamide monomers were gathered because traces of unpolymerized acrylamide monomers remain in PASA as an impurity. Since acrylamide is biodegraded and mineralized easily, the possibility of acrylamide monomers being accumulated in the sediment is low. In addition, although acrylamide monomers are water soluble (204 g/100 mL) (IPCS, 2000), both log K_{OW} and soil adsorption coefficient, K_{OC} , are low with values of -1.65 to -0.67 and 0.195 l/kg, respectively (EU, 2002). Therefore, it is not absorbed or accumulated in the sediment and the possibility of adverse effects on sediment organisms is very low.

5.2.5 Bioconcentration

For PAC, data on water-soluble aluminium salts such as aluminium chloride may be examined to evaluate the bioconcentration of PAC in aquatic organisms because the salts dissociate in water and form the same aqua-complexes as those formed by PAC. In a test using *Salvelinus fontinalis*, the value of BCF was 36 at pH 7.2 (Cleveland et al., 1991). Although the concentration (0.2 mg/L) in this study was higher than the 60-day NOEC (0.088 mg Al/L) with growth as the index (pH 6.5 - 6.6) in the test in which *Salvelinus fontinalis* was used (see 5.2.2), it is reasonable to consider the result of that study, because it indicated no effects at a pH of 7.2. In a test that used the marine species, *Salmo salar*, the BCF values at pH 5.5 were in the range of 76 to 190 (Buckler et al., 1995). Therefore, the bioconcentration of aluminium ions was low.

As PASA consists of high molecular weight polymers particles (several millions or more), it exhibits no biomembrane permeation and the possibility of its accumulation is low. The BCF values in a test using *Cyprinus carpio* are between 0.23 and 0.41, indicating that the bioconcentration of PASA is low (OEC, 2003).

For acrylamide monomers, when *Cyprinus carpio* and *Oryzias latipes* are exposed to water at concentrations of 1 mg/L and 10 mg/L for 20 days, the BCF values are 0.26 and 0.77 for *Cyprinus carpio* and 0.31 and 2.53 for *Oryzias latipes* (EU, 2002). In an exposure test of *Oncorhynchus mykiss* in water with a concentration of 0.710 mg/L, concentration and excretion reached a balance after 72 hours, and the BCF values are 1.44 and 1.65 for the whole body and internal organs, respectively (EU, 2002). These results indicate that the bioconcentration of acrylamide monomers is low.

No reports on the bioconcentration of triiron tetraoxide were found. However, because it consists of water insoluble particles, triiron tetraoxide is not absorbed or accumulated in living organisms and has no bioaccumulation.

5.2.6 Food web/population effects

As the bioaccumulation of the chemicals used in this system is low, the possibility of secondary poisoning is low and no adverse effects on algae, invertebrates or fish are observed. Therefore, it is assumed that none of these substances affect food webs or populations.

5.3 Data on mammalian toxicity (G9: 4.2.1.2)

5.3.1 Acute toxicity

Table 5-2: 50% lethal dose of triiron tetraoxide, PAC, PASA, and acrylamide monomers

Exposure path	Animal species	End point	Value	Reference
Triiron tetraoxide				
Oral administration	Rats	LD ₅₀	>10,000 mg/kg bodyweight	EU, 2000a
PAC				
Oral administration	Mice	LD ₅₀	Ca. 7,000 mg/kg	EU, 2000b
	Rats	LD ₅₀	>2,000 mg/kg bodyweight	EU, 2000b
PASA				
Oral administration	Rats	LD ₅₀	>4,000 mg/kg bodyweight	Cosmetic Ingredient Review, 2005
Acrylamide monomers				
Oral administration	Mice, rats, rabbits, and guinea pigs	LD ₅₀	150 - 180 mg/kg bodyweight	ACGIH, 2001a
	Mice and rats	LD ₅₀	107 - 203 mg/kg bodyweight	EU, 2002
Percutaneous administration	Rabbits	LD ₅₀	About 1,150 mg/kg bodyweight	EU, 2002

* Although no data are available for the dermal route for triiron tetraoxide, PAC, or PASA, irritation is not caused by these substances or the extent of irritation is very low (see Section 5.3.2). Therefore, acute dermal toxicity is considered to be weak, and only the data on oral acute toxicity are described below.

5.3.2 Effects on skin and eyes

Table 5-3: Skin irritation

Substance	Species	Method Guidelines	Result	Reference/ Comments
Triiron tetraoxide	Rabbits	OECDTG404	No	EU, 2000a
PAC	Rabbits	OECDTG404	No	EU, 2000b
	Rabbits, mice, and pigs	Not specified	No	EU, 2000b
	Humans	Not specified	Yes	EU, 2000b
PASA	Rabbits	Not specified	No	Cosmetic Ingredient Review, 2005
Acrylamide monomers	Rabbits	Not specified	No: for uninjured skin Very mild erythema and edema: for injured skin	ACGIH, 2001a
	Rabbits	Not specified	No or quite mild	EU, 2002
	Humans	Occupational exposure	Dermal irritation, skin separation	EU, 2002

Table 5-4: Eye irritation

Substance	Species	Method Guidelines	Result	Reference/ Comments
Triiron tetraoxide	No data	No data	No data	It is expected that triiron tetraoxide causes no chemical irritation because of its insolubility.
PAC	Rabbits	OECDTG404	Mild	EU, 2000b
	Humans	Not specified	Yes	EU, 2000b
PASA	Rabbits	Not specified	Solid: Mild 5% water solution: No	Cosmetic Ingredient Review, 2005
Acrylamide monomers	Rabbits	Not specified	10% water solution: Mild 40% water solution: Yes	ACGIH, 2001a
	Rabbits	Not specified	Yes	EU, 2002

5.3.3 Sensitization

Table 5-5: Skin sensitization

Substance	Species	Method Guidelines	Sensitizer (yes/no)	Reference/ Comments
Triiron tetraoxide	Guinea pigs	Not specified	No	EU, 2000a
PAC	Rabbits	Not specified	No	EU, 2000b
PASA	No data	No data	No	It is not expected to exhibit any sensitization because it is not absorbed in the body due to its high molecular weight.
Acrylamide monomers	Guinea pigs	Not specified	Yes	EU, 2002

Repeated dose toxicity (subacute/subchronic toxicity).

5.3.4 Triiron tetraoxide

There is a report on intracavernous administration in rats over three weeks and intracavernous administration in dogs over three weeks which shows that pigment deposition increases in cells of the reticuloendothelial system but no injury in tissues occurs (EU, 2000a). Triiron tetraoxide is expected to have no adverse effects with repeated dose toxicity (subacute/subchronic toxicity) because it consists of insoluble inorganic microparticles which are not absorbed in the body.

PAC

In an inhalation exposure test of 22 days in which PAC solutions of 0.34µg/L and 2.5µg/L were given to rats 4 hours a day at a frequency of 5 days a week, no toxicity or accumulation in tissues were observed (EU, 2000b).

PASA

No chronic toxicity was observed in a test in which feedstuffs containing 500 to 50,000 ppm of polyacrylamide were given to rats and dogs (Cosmetic Ingredient Review, 2005). PASA is expected to have no adverse effects with repeated dose toxicity (subacute/subchronic toxicity) because it consists of high molecular weight polymer particles (several million or more) which are not absorbed in the body.

Acrylamide monomers

According to several tests by peroral administration to laboratory animals, the major toxic effects are on the nervous system and male generative organs. In a test in which feedstuffs containing 3 to 400 ppm of acrylamide monomers were given to rats for 90 days, neurotoxicity appeared at 300 ppm or more, seminiferous epithelium degeneration appeared at 400 ppm, and the NOAEL was 110 ppm (corresponding to 5.5 mg/kg bodyweight/ day). In a test in which 0.05 to 20 mg/kg bodyweight/day of acrylamide monomers contained in drinking water was given to rats for 90 days, neurotoxicity symptoms appeared at 1 mg/kg bodyweight/day or more, severe degeneration of peripheral nerves appeared at 20 mg/kg bodyweight/day, and the

NOAEL was 0.2 mg/kg bodyweight/day. The value in a peroral administration test for 90 days using rats with the minimal change of peripheral nerves as the index was 0.2 mg/kg/day (ACGIH, 2001a).

There is a report of repeated exposure of acrylamide monomers to humans causing adverse effects on the central nerve system, such as loss of muscle strength, disturbance of muscle co-ordination, gait abnormality, tremor, and hallucination (ACGIH, 2001a).

5.3.5 Chronic toxicity

Triiron tetraoxide

No data on chronic toxicity for laboratory animals are available. Chronic toxicity is not caused in humans because humans are only exposed to triiron tetraoxide if an accident occurs when the chemical is being brought in, and the duration of exposure is limited to a short period.

PAC

In several reports on inhalation exposure using laboratory animals, the accumulation of aluminium in the lungs, lymph nodes around the lung alveoli, and adrenal glands, and lung disorders are reported. In tests in which rats and guinea pigs were exposed to three levels of PAC content, 0.25, 2.5, and 25 mg/m³ for 6 hours a day at a frequency of five days a week for six months, the value of the NOAEL could not be obtained, the LOAEL was 0.25 mg/m³ (EU, 2000b), lung injury occurred at a PAC concentration of 0.25 mg/m³ or more, and an increase in weight was suppressed at a concentration of 25 mg/m³.

PAC is widely used in the municipal purification of water, and no adverse effects to human health have been identified. Therefore, the possibility of influence in humans is low.

PASA

Several tests have been conducted in which feedstuffs containing 500 to 100,000 ppm of polyacrylamide were given to rats for two years. No toxic effects or pathological changes related to the administration were observed in any of the tests (Cosmetic Ingredient Review, 2005). Regarding chronic toxicity in humans, no adverse effects have been observed on workers exposed to dust containing polyacrylamide (1 mg/m³) over five years or more in polyacrylamide manufacturing plants (Cosmetic Ingredient Review, 2005).

Acrylamide monomers

There are several reports of tests on laboratory animals by peroral administration, and the major toxic effect is on the neural system. ACGIH has set the time-weighted average threshold limit value (TLV - TWA) of acrylamide monomers to 0.03 mg/m³ (ACGIH, 2001a).

5.3.6 Reproductive/developmental toxicity

Triiron tetraoxide

There are no data available on the reproductive and developmental toxicity of triiron tetraoxide. Triiron tetraoxide is not expected to have any adverse effects on reproduction and development because it consists of insoluble inorganic microparticles which are not absorbed in the body.

PAC

There is a report of a decrease in the number of implantations and fetal deaths observed in a test in which PAC was given by peroral administration to rats during day 7 to day 19 of pregnancy, in which the TDLo was 13,000 mg/kg/day, but further details are unknown (EU, 2000b; U.S. NIOSH, 2007).

PASA

No effects on reproduction were observed in a three-generation test in which feedstuffs containing two levels of polyacrylamide, 500 and 2,000 ppm, were given to rats (Cosmetic Ingredient Review, 2005).

Acrylamide monomers

There are several reports of reproductive toxicity in peroral administration to laboratory animals, and it has been shown that male genital toxicity and male sterility are caused. The value of the NOAEL with the effect on fertility potential was 5 mg/kg/day as for rats, and was 9 mg/kg/day as for mice (EU, 2002).

For developmental toxicity, there is a report of acrylamide monomers being given to pregnant female animals by peroral administration. Neither fetal toxicity nor teratogenicity is observed with a dose that does not cause mother animal toxicity (EU, 2002).

5.3.7 Mutagenicity/genotoxicity

Triiron tetraoxide

In an *in vitro* reverse mutation test using *Salmonella typhimurium* (Ames test), the results were negative regardless of the existence of metabolic activation (EU, 2000a).

There are no *in vivo* reports available. Triiron tetraoxide is not expected to exhibit mutagenicity (genotoxicity) because it consists of insoluble inorganic microparticles which are not absorbed in the body.

PAC

Although no reports on mutagenicity and genotoxicity are available, it can be assessed based on test data on aluminium chloride and so on, which exhibit behaviour identical to that of PAC in living organisms (formation of aqua-complexes). Negative results have been obtained in an *in vitro* reverse mutation test (Ames test) using *Salmonella typhimurium* with aluminium sulfate as the test substance and a gene mutation test using L5178Y cells of the lymphoma of a mouse, but positive results have been obtained in a chromosomal aberration test using human leukocytes with aluminium sulfate as the test substance (IPCS, 1997).

In two *in vivo* tests, one in which aluminium chloride was given to mice by intraperitoneal administration and the other in which aluminium sulfate was given to rats, the induction of chromosomal aberrations in marrow cells was observed (IPCS, 1997).

PASA

Although no reports on the mutagenicity/genotoxicity of polyacrylamide are available, since polyacrylamide is not absorbed by the body, it is not expected to exhibit mutagenicity/genotoxicity.

Acrylamide monomers

Among the *in vitro* tests, the results of mutation tests using bacteria were negative but the results of tests using animal cells were clearly positive in a micronucleus test, unscheduled DNA synthesis (UDS) test, and sister chromatid exchange (SCE) test. Acrylamide monomers are mutagenic substances that act directly on the target, and there are many pieces of evidence of genotoxicity in body cells and generative cells in *in vivo* tests. In particular, it has been proved that transgenerational mutagenicity is induced in generative cells (ACGIH, 2001a; EU, 2002).

5.3.8 Carcinogenicity

Triiron tetraoxide

Several reports on the carcinogenicity of triiron tetraoxide are available, all of which are insufficient to assess its carcinogenicity.

PAC

Although there are no reports available on the carcinogenicity of PAC, aluminium ions are an important factor as to the effects of PAC on living organisms, and the assessment of PAC can be implemented on the basis of the carcinogenicity of aluminium compounds that exhibit behaviour similar to that of PAC in living organisms. Among such aluminium compounds, several tests have been conducted relating to aluminium potassium sulfate. For the two tests in which the increase in tumours was observed, since the tests were conducted using a single dose, the dose dependency is not clear and nothing is described about the type of tumours or the organs with tumours. Therefore, the results of these tests do not support the carcinogenicity.

PASA

Several tests have been conducted, in which feedstuffs containing 500 to 100,000 ppm of polyacrylamide were given to rats for two years, and feedstuffs containing 500 to 50,000 ppm of polyacrylamide were given to dogs also for two years. In both of these tests, no lesions related to the administration were observed (Cosmetic Ingredient Review, 2005).

Acrylamide monomers

There has been a test on the carcinogenicity of acrylamide, in which acrylamide monomers were given to F344 rats by drinking water administration for two years, and an increase in the incidence ratio of tumours in tissues of various organs, such as thyroid gland, adrenal glands, and testis was observed. Judging from the types of tumours developed, a relationship with endocrine disruption is suggested. Furthermore, a relationship with the development of brain tumours and spinal cord tumours is suggested although the evidence is not sufficient. IARC has classified acrylamide monomers as Group 2A (probably carcinogenic to humans) (IARC, 1994).

5.3.9 Kinetics and metabolism

Triiron tetraoxide

There is a report that the clearance half-life period of a rat that has inhaled triiron tetraoxide for two hours is 47 days (EU, 2000a).

PAC

In an inhalation exposure test in which rats were exposed to PAC for 24 months and guinea pigs for 21 months, aluminium was mainly accumulated in the lungs in both rats and guinea pigs, secondary to the adrenal glands in the rats and to the lymph nodes around the lung alveoli in the guinea pigs (EU, 2000b).

PASA

In a test in which polyacrylamide was given to rats by peroral administration, most of the acrylamide was recovered in feces and bowel contents and was not detected in the tissues, which shows that polyacrylamide is not absorbed in the body (Cosmetic Ingredient Review, 2005).

Acrylamide monomers

Acrylamide monomers are rapidly absorbed orally and percutaneously by many animals so that unchanged substances and metabolites are widely distributed in living organisms. In particular, they are distributed to the male reproductive organs and to unborn babies through the placenta. In rats and mice, acrylamide monomers are mainly excreted in urine after undertaking glutathione conjugation. Absorbed acrylamide monomers are also excreted in exhaled breath as carbon dioxide, while only small portion is excreted in feces (EU, 2002). In a test that used rats, the selective accumulation in nerve cells was not observed (ACGIH, 2001a). There are only limited data on the *in vivo* fate of acrylamide monomers in humans, and it has been indicated that acrylamide is absorbed orally or percutaneously because acrylamide monomer adducts are detected in hemoglobin (EU, 2002).

5.4 Data on environmental fate and effect under aerobic and anaerobic conditions (G9: 4.2.1.3)

5.4.1 Degradation

5.4.1.1 Hydrolysis

Hydrolysis properties do not apply to triiron tetraoxide and PAC because they are inorganic compounds. Since the half-life period of acrylamide monomers for hydrolysis is more than one year under the conditions of pH 5 to 9 and 55°C, acrylamide monomers are considered not to be easily hydrolyzed in environmental water (EU, 2002). Therefore, it is assumed that PASA is resistant to hydrolysis, as in the case of acrylamide in environmental water.

5.4.1.2 Biodegradability

Biodegradability does not apply to triiron tetraoxide or PAC because they are inorganic compounds. Regarding the biodegradability of PASA, there is a report on the degradation rate of activated sludge taken from an urban sewage treatment plant using the coulometer method, in which PASA was assessed to be non-biodegradable because it was hardly degraded after 300 hours (OEC, 2003).

The biodegradability of acrylamide monomers has been tested based on OECD TG301D. Since the biochemical oxygen demand (BOD) values for 28 days under the two levels of the concentration of testing substance, 2 mg/L and 5 mg/L, were 100 and 53.3%, respectively, it has been determined that acrylamide monomers are easily degraded at lower concentrations (<2 mg/L) (EU, 2002).

5.4.2 Partition coefficient

A partition coefficient is not applied to triiron tetraoxide or PAC because they are inorganic compounds. Further, a partition coefficient is not applied to PASA because it is a high molecular weight polymer compound. The octanol/water partition coefficient ($\log P_{OW}$) for acrylamide monomer is -0.67 to -1.65, and soil adsorption coefficient, K_{OC} , is 0.195 l/Kg (EU, 2002).

5.4.3 Persistence and identification of main metabolites in relevant media (ballast water, marine, and fresh water)

No generation occurs of degradation products from any of triiron tetraoxide, PAC, and PASA. Since acrylamide monomers are resistant to hydrolysis and easily biodegraded and mineralized under aerobic conditions, degradation products are not generated.

5.4.4 Reaction with organic matter

Triiron tetraoxide, PAC, PASA, and acrylamide monomers all do not generate free radicals, and do not react with organic compounds.

5.4.5 Potential physical effects on wildlife and benthic habitats

Triiron tetraoxide, PAC, PASA, acrylamide monomers, and flocs would have no physical effect on the habitat of fish species, avian species, marine mammals or benthic organisms.

5.4.6 Potential residues in seafood

The substances used in this system do not exhibit bioconcentration and so exhibit no potential persistence in seafood.

5.5 Physical and chemical properties for the Active Substances and preparations and treated ballast water (G9: 4.2.1.4)

Table 5-6 shows the physicochemical properties of triiron tetraoxide, PAC, PASA, acrylamide monomers, and treated ballast water.

Table 5-6: Physicochemical properties

	Triiron tetraoxide	PAC	PASA	Acrylamide monomers	Treated ballast water
CAS No.	1317-61-9	1327-41-9	25085-02-3	79-06-1	None
Melting point (°C)	1,538 ¹⁾	About -12 ²⁾	Not Applicable	84.5 ¹⁾	NR ⁹⁾
Boiling point (°C)	Not Applicable	About 103 ²⁾	Not Applicable	125 at 3 kPa ¹⁾	NR
Flammability (Flash point for liquids ; °C)	Not Applicable	Noncombustible ⁵⁾	None ^{#1, 4)}	138 (closed method) ³⁾	NR
Density (20 °C; kg/m ³)	5,200 (5.2 g/cm ³) ¹⁾	1,340 (1.34 g/cm ³) ²⁾	Bulk specific gravity; 0.55-0.65 ⁴⁾	1,130(1.13 g/cm ³) ³⁾	NR
Vapour pressure (20 °C; Pa)	Not Applicable	Non-evaporable ⁵⁾	Non-evaporable ^{#2}	1 ³⁾	NR
Vapour density (air = 1)	Not Applicable	Not Applicable	Not Applicable	2.46 (calculated value)	NR
Water solubility	Insoluble ⁶⁾	Soluble ¹⁾	Mixing with water forms highly viscous gel-like material ⁴⁾	2,040,000 (25°C) (204 g/100 ml) ³⁾	NR
pH in solution	NR	NR 4.3 (15%) ¹⁾	NR	NR	7 - 7.3 (see 4.2)
Dissociation constant (pKa)	Not Applicable	No dissociable group	No dissociable group	No dissociable group	NR
Oxidation-reduction potential	Not Applicable	None ⁵⁾	None ⁴⁾	None ⁷⁾	None
Corrosivity to material or equipment	None	Corrosive to metals	None	None	None

	Triiron tetraoxide	PAC	PASA	Acrylamide monomers	Treated ballast water
Reactivity to container material	None	None	None	None	NR
Autoignition temperature (°C)	Not Applicable	Noncombustible ⁵⁾	None ⁴⁾	424 ³⁾	NR
Explosive properties	Not Applicable	None	None	None ⁷⁾	NR
Oxidizing properties	Not Applicable	None ⁵⁾	None ⁴⁾	None ⁷⁾	NR
Surface tension	None	Equal to water because of aqueous solution	None	None	NR
Viscosity	None	28 mPa.s (25°C) ²⁾	Mixing with water forms highly viscous gel-like material ⁴⁾	2.71 mPa.s (25°C) (50% aqueous solution) ⁸⁾	1.55cP (16°C)
Thermal stability	Transformed into iron oxide (Fe ₂ O ₃) by heating in air ¹⁾	Nonflammable	Combustible by heating at high temperature	Violently polymerizes when heated to over 85°C or when exposed to of light or oxidizing agents. When heated to decomposition, fumes and nitrogen oxide are generated. ^{3), 8)}	NR
Other physico-chemical properties	None	None	None	Because acrylamide readily polymerizes, common products contain polymerization inhibitors ¹⁾	None

- 1) Merck, 2006, 2) EU, 2000b, 3) IPCS, 2000, 4) Dia-Nitrix, 2004, 5) Asada Chemical Industry, 2003, 6) Dean, 1999, 7) EU, 2002, 8) HSDB, 2007, 9) NR: not required for G9
#1 Noncombustible under conditions of normal use (normal pressure, 0-50°C).
#2 Non-evaporable under normal pressure and normal temperature because of high molecular weight polymers (several million or more).

5.6 Analytical method at environmentally relevant concentration (G9: 4.2.1.5)

Triiron tetraoxide

The sample water is analysed by ICP emission spectroscopic analysis (ICP-AES) and detected as iron ions.

PAC

The sample water is analysed by ICP emission spectroscopic analysis (ICP-AES) and detected as aluminum ions.

PASA

The sample water is filtered with a membrane filter, and the infrared spectra of the substances on the filter paper is analysed by infrared spectrometry (IR). Its spectra are compared with that of the standard substance to know whether PASA is present or not. The substances gathered on the membrane filter are weighed on a scale to obtain the rough amount of PASA.

Acrylamide monomers

Acrylamide monomers in the sample water are brominated using potassium bromide solution and potassium bromate solution under acidic conditions to obtain dibromo-derivatives. Excess bromine is reduced and eliminated with sodium thiosulfate, and the dibromo-derivatives are then extracted with ethyl acetate. Triethylamine is added to the solution to remove hydrogen bromide, and the obtained monobromo-derivatives are analysed by gas chromatography (GC).

6 ECOTOXICITY STUDIES

In this section, the results of ecotoxicity studies of saltwater representatives for three trophic levels (algae, invertebrates and fish) are presented and the hazards of the ballast water treated by the Hitachi Ballast Water Purification System to the aquatic organisms are evaluated. (Refer to IDEA Consultants, Inc., 2007a; 2007b; 2007c for more details.)

6.1 Methods of water treatment and water sampling

6.1.1 Set-up for Hitachi Ballast Water Purification System

The system used for the test was identical to the one used in section 4 Analysis of treated water (see 4.1.1 (1)).

6.1.2 Amounts of chemicals added to set-up

In order to evaluate the hazards of Active Substances to aquatic organisms, the substances were injected into the raw seawater to produce final concentrations two times higher than those of the standardized processing conditions for the Hitachi Ballast Water Purification System (Table 6-1).

Table 6-1: Final concentrations of chemicals after injection

Active Substance	Concentration in untreated seawater (mg/L)
Triiron tetraoxide	60
PAC	10 (as Al)
PASA	2

6.1.3 Method of water sampling and water treatment procedure

Processing of seawater by the set-up was carried out and supplied to the test facility daily from the day before the beginning of the toxicity tests to the last day of the tests. Approximately 20 L of the treated-seawater was sampled from the effluent in the outfall of the filter-separation unit when the processing had been carried out for 16 to 32 minutes (see 4.1.1 (3)).

6.2 Ecotoxicity testing

6.2.1 Testing on algae

(1) Test guidelines applied to the study

The toxicity study in algae was conducted according to the International standard ISO 10253 “Water quality – Marine algae growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricorutum*, Second edition” (2006) and the US EPA guidelines “Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, Third Edition” (2002). (Refer to IDEA Consultants, Inc., 2007a for more details.)

(2) Test method and conditions

The marine diatom *Skeletonema costatum* was selected as the test species for this study, and the exposure experiment was conducted under the conditions shown below:

Type of exposure:	Static, continuous shaking at 100 rpm
Exposure duration:	72 hours
Number of treatments:	5 treatment groups (1/1-, 1/2-, 1/4-, 1/8-, and 1/16-groups) and a control group
Number of replicates:	3 replicates per treatment and 6 replicates for control
Volume of test solution per vessel:	30 mL
Initial cell density:	0.5×10^4 cells/mL
Temperature:	20 ± 2 °C
Illumination:	Cool-white type fluorescent bulbs, continuous at 7,000 Lux \pm 20%

(3) Results and conclusion

It is concluded that the ballast water treated by the Hitachi Ballast Water Purification System has no toxicity impact on the marine Diatom *S. costatum* without any dilutions.

6.2.2 Testing on invertebrates

(1) Test guidelines applied to the study

The toxicity study on invertebrates was conducted according to the modified method reported by Anasco *et al.*¹⁾ and the US-EPA guidelines “Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, Third Edition” (2002). (Refer to IDEA Consultants, Inc., 2007b for more details.)

(2) Test method and conditions

The marine gammarid *Hyale barbicornis* was used as the test species in this study, and the exposure experiment was conducted under the conditions shown below.

Type of exposure:	Semi-static, whole renewal every 24 hours
Exposure duration:	21 days
Number of treatments:	5 treatment groups (1/1-, 1/2-, 1/4-, 1/8- and 1/16-groups) and a control group
Number of replicates:	20 replicates per group
Volume of test solution per vessel:	10 mL
Test animal: Age;	Neonates within 24 hours post-hatch
Number exposed;	20 animals per group (one animal per vessel)
Temperature:	24 ± 1°C
Illumination:	Cool-white type fluorescent bulbs, 14-hours light/10-hours dark
Feeding:	Artificial flake food Tetra Marine® (< 0.5 mm crushed pieces), once a day

(3) Results and conclusion

It is concluded that the ballast water treated by the Hitachi Ballast Water Purification System has no toxicity impact on the marine Gammarid *H. barbicornis* without any dilutions.

6.2.3 Testing on fish

(1) Test guidelines applied to the study

The toxicity study in fish was conducted in accordance with the OECD guidelines No.210 “Fish, Early-life Stage Toxicity Test” (1992) and the US-EPA guidelines “Shortterm Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, Third Edition” (2002). (Refer to IDEA Consultants, Inc., 2007c for more details)

¹⁾ Anasco N., Takenouchi A., Koyama J., Noro T., Imai S, Uno S. Toxicity of chemicals used to treat ballast waters (hydrogen peroxide and sodium hypochlorite) to four marine organisms., terminal report: Toxicity of Hydrogen peroxide and sodium hypochlorite to marine organisms, *in preparation*.

(2) Test method and conditions

The saltwater fish Java medaka, *Oryzias javanicus*, was selected as the test species for this study, and the exposure experiment was conducted under the conditions shown below

Type of exposure:	Semi-static, whole renewal every 24 hours
Exposure duration:	From 1 day post-fertilization embryo to 28 days post-hatch
Number of treatments:	5 treatment groups (1/1-, 1/2-, 1/4-, 1/8-, and 1/16-group), and a control group
Number of replicates:	3 replicates per group
Volume of test solution per vessel:	100 mL (embryonic phase), 500 mL (post-hatch phase, until 14 days post-hatch), and 1,000 mL (post-hatch phase, after 14 days post-hatch)
Test animal:	Age; Fertilized eggs 1 day post-fertilization
Number exposed:	60 eggs per group (20 eggs per vessel)
Temperature: 26 ± 1 °C	
Illumination:	Cool-white type fluorescent bulbs, 14-hours light/10-hours dark
Feeding:	Brine shrimp nauplii, once a day

(3) Results and conclusion

It is concluded that the ballast water treated by the Hitachi Ballast Water Purification System has no toxicity impact on the saltwater fish *O. javanicus* without any dilutions.

7 MATERIAL SAFETY DATA SHEET (MSDS) (G9: 4.2.7)

Samples of MSDS for triiron tetraoxide, PAC, and PASA are attached to the original assessment report.

8 RISK CHARACTERIZATION

8.1 Screening for persistence, bioaccumulation and toxicity (G9: 5.1)

Table 8-1 shows the results of an assessment of PBT. None of the triiron tetraoxide, PAC, PASA, and acrylamide monomers are classified as PBT substances.

Table 8-1: Assessment of PBT

	Low degradability (P)	Bioaccumulation (B)	Toxicity (T)
	Half-life: >60 days in marine water, or >40 days in freshwater, or >180 days in marine sediment, or >120 days in freshwater sediment	BCF > 2,000 or Log P _{ow} ≥ 3	Chronic NOEC < 0.01 mg/L
Triiron tetraoxide	Not applicable*	No	No
PAC	Not applicable*	No	No
PASA	Yes	No	No
Acrylamide monomers	No	No	No

* As described in 5.4.1, biodegradability and hydrolysis do not apply to triiron tetraoxide and PAC because they are inorganic compounds.

8.2 Evaluation of treated ballast water (G9: 5.2)

To investigate the toxicity of the seawater treated by the Hitachi Ballast Water Purification System, ecotoxicity tests were carried out on three types of marine. The seawater was treated (at a flow rate of 50 m³/h) by the land-based pilot set-up on reclaimed land in Tokyo Bay which simulates the Hitachi Ballast Water Purification System, and was tested by adding twice as much of the three chemicals (triiron tetraoxide, PAC, and PASA) compared with rated operation. All the ecotoxicity studies with the treated ballast water as a test substance were conducted under the conditions specified by the OECD principles of Good Laboratory Practice and were performed according to international standards such as OECD test guidelines or US EPA guidelines. (For details, see section 6.)

The above test results show that seawater treated with the addition of chemicals in rated operation does not have any adverse effect on marine organisms even if released without dilution, because seawater treated with twice as much chemical as in the rated operation does not influence marine organisms at all even if released without dilution (100%).

8.3 Risk characterization and analysis

8.3.1 Reaction with organic matter (G9: 4.2.1.3; this report 5.4.4)

Since triiron tetraoxide, PAC, and PASA all do not generate free radicals, they are not reactive with organic matter.

8.3.2 Characterization of degradation route and rate (G9: 5.3.5)

Since triiron tetraoxide and PAC are inorganic substances, hydrolysis and biodegradability are not applicable. Acrylamide monomers are resistant to hydrolysis but biodegraded in a relatively short period. PASA is considered to be resistant to hydrolysis. In addition, PASA is scarcely biodegraded in activated sludge after 300 hours and is therefore not biodegradable.

In the Hitachi Ballast Water Purification System, since almost the entire additive chemicals are collected in the flocs, the amount of Active Substances released into the environment together with the treated ballast water is negligible. Therefore, the characteristics described here do not have a serious environmental effect.

8.3.3 Prediction of discharge and environmental concentrations

Table 8-2: Summary of predicted discharged concentration PEC

	Predicted concentration at discharge (mg/L)	PEC (mg/L)
Triiron tetraoxide	0.69	<0.69
PAC	0.15	<0.15
PAC (aluminium ions)	0.01	<0.00358*
PASA	0.016	<0.016
Acrylamide monomers	0.00005	<0.00005

* Estimation of environmental concentration based on the MAM-PEC Model.

The environmental concentration when the treated ballast water is discharged in Rotterdam Port was estimated using the MAM-PEC Model (version 1.6). It is assumed that all ships entering Rotterdam Port are provided with the Hitachi Ballast Water Purification System.

The concentration of original aluminium ions in the seawater of Rotterdam Port, which is the background concentration, is assumed to be 0.035 mg/L based on the value shown in the reference (Kobayashi et al., 2006). Table 8-3 shows the results of the estimation. The average concentration in the water is calculated to be 0.00350 mg/L, which is the same as the background concentration. Therefore, it is concluded that aluminium ions in the ballast water discharged from the Hitachi Ballast Water Purification System do not have an influence on the environmental concentration. (CERI, 2007b).

Table 8-3: Estimated concentrations in water using MAM-PEC Model

Item	Concentration of Aluminium ions (µg/L)
Maximum concentration	3.58 (0.00358 mg/L)
Average concentration	3.50 (0.00350 mg/L)

8.3.4 Assessment of potential for bioaccumulation (G9: 5.3.7)

As described in section 5.2.5, the substances are not bioaccumulative.

8.3.5 Effects assessment (G9: 5.3.9)

Triiron tetraoxide

The data on ecotoxicity of triiron tetraoxide do not correspond to the GHS acute toxicity hazard category.

PAC

The data on ecotoxicity of PAC do not correspond to the GHS acute toxicity hazard category.

PASA

The data on ecotoxicity of PASA do not correspond to the GHS acute toxicity hazard category.

Acrylamide monomers

The data on ecotoxicity of acrylamide monomers correspond to the GHS acute toxicity hazard category III (harmful). But, acrylamide monomers contained as an impurity in PASA account for 0.05% or less of PASA by weight as given in 2.5. As a result, the acrylamide monomer concentration in ballast water is 0.0005 or less mg/L (before magnetic separation). Because the acrylamide monomer concentration in the treated water is 0.0001 or less mg/L as given in 4.1.2, the risk to aquatic organisms is negligible (see 9.3 for details).

8.3.6 Derivation of Predicted No-Effect Concentration (PNEC)

Table 8-4: PNECs

	Toxicity (mg/L)		Assessment factor	PNEC (mg/L)	
Triiron tetraoxide	48-h LC ₀ (acute)	> 1,000	1000	> 1	PNECshort
PAC	48-h LC ₅₀ (acute)	840	1000	0.84	PNECshort
PAC (aluminium ions)	96-h LC ₅₀ (acute)	0.097	1000	0.003597 ^{a)}	PNECshort
	28-day NOEC (chronic)	0.02	1000	0.00352 ^{a)}	PNEClong
PASA	48-h LC ₅₀ (acute)	180	1000	0.18	PNECshort
	30-day NOEC (chronic)	75	100	0.75	PNEClong
Acrylamide monomers	96-h LC ₅₀ (acute)	59	1000	0.059	PNECshort
	28-day NOEC (chronic)	2.04	100	0.02	PNEClong

a) The natural background concentration is added.

Since the PNEClong is smaller than the PNECshort for PAC (aluminium ions), PASA, and acrylamide monomers, PNEClong is applied in the PEC/PNEC ratio described in section 9.3.1.

9 RISK ASSESSMENT

9.1 Risk to ship safety

9.1.1 Risk during the storage of chemicals and operation of equipment

The IBC code is not applied to triiron tetraoxide, PAC, or PASA.

As seen from the physical properties described in 5.5, triiron tetraoxide, PAC, PASA, and acrylamide monomers are not corrosive, do not react with the storage tank, do not ignite spontaneously, do not vaporize, and do not have oxidizing properties under the assumed on-board circumstances. Therefore, there is no concern that this substance may cause an accident such as corrosion, spontaneous ignition, or explosion of the vessel's body and on-board structures during the storage or operation of the equipment.

9.1.2 Risk from the treated ballast water

The treated ballast water is not corrosive, and the concentrations of volatile and semivolatile substances are comparable to those in the seawater of the reference site as described in 4.1.2 (2) and 4.1.2 (3). Therefore, there is no concern about accidents occurring in the ballast tank.

9.2 Risk to human health (sailors)

9.2.1 Exposure to humans

Since the operation of the Hitachi Ballast Water Purification System is automated from the chemical injection into the ballast water through to the sludge transfer into the sludge tank, no manual operation by the crew is required and no dedicated operators are necessary.

External to the purifying operation, there are small potential risks of short-time exposure to humans because some manual operation is required for pouring the chemicals into the storage tank, preparing for unloading the sludge, and actually unloading the sludge onto land.

When the chemicals are poured into the storage tanks, the transfer is from one closed container to another closed container, so the risk of exposure is minimal. The operator must wear safety gear such as goggles, rubber gloves, and a mask in anticipation of accidents such as powder being scattered. Warnings should be displayed on the equipment of this system to emphasize the need to use such safety gear.

9.2.2 Risk to human health

As described in 5.3, triiron tetraoxide is not a toxic substance. Furthermore, the only operations that may cause exposure to humans are the pouring of chemicals into the storage tank, preparing for unloading the sludge, and unloading the sludge onto land. In these operations, the potential exposure periods are limited and the workers wear protective gear, so there is virtually no risk to human health.

PAC is not toxic, as described in 5.3, but it is an irritant and has been shown to have adverse effects in reproductive/developmental toxicity tests on animals. Therefore, the Hitachi Ballast Water Purification System minimizes the risk to human health by using PAC conforming to the standards for water purification chemicals established by the American Water Works Association (AWWA) and by automating the purification operation. The only operations that may cause exposure to humans are the pouring of chemicals into the storage tank, preparing for unloading the sludge, and unloading the sludge onto land. In these operations, the potential exposure periods are limited and exposure is prevented by protective gear. Furthermore, the frequency of these operations is limited so there is virtually no risk to human health.

As described in Section 5.3, PASA is not a toxic substance. The Hitachi Ballast Water Purification System minimizes the risk to human health by using PAC conforming to the standard for water purification chemicals established by the American Water Works Association and by automating the purification operation. The only operations that may cause exposure to humans are the pouring of the chemicals into the storage tank, preparing for unloading the sludge, and unloading the sludge onto land. In these operations, the exposure periods are limited and exposure is prevented by protective gear. Furthermore, the frequency of these operations is limited so there is virtually no risk to human health.

The risk of acrylamide monomers to human health was investigated because traces of unpolymerized acrylamide monomers remain in PASA as an impurity. However, the PASA used in the system conforms to the standard for water purification chemicals established by the American Water Works Association. The level of contamination is 0.05% or less, which has been proven safe. It poses virtually no risk to human health.

9.3 Risk to aquatic environment

9.3.1 Assessment by PEC/PNEC ratio

An assessment by PEC/PNEC ratio was carried out on triiron tetraoxide, PAC, PASA, and acrylamide monomers. The assessment for PAC was conducted by using the acute toxicity data for PAC and aluminium ions and the chronic toxicity data for aluminium ions.

As derived in 8.3.6, the PNEC values are > 1 mg/L for triiron tetraoxide, 0.84 mg/L for PAC, 0.003597 mg /L for PAC (aluminium ions), 0.18 mg/L for PASA, and 0.02 mg/L for acrylamide monomers (see Table 8-4).

As derived in 8.3.3, the PEC values are 0.69 mg/L for triiron tetraoxide, 0.3 mg/L for PAC, 0.00358 mg /L for PAC (aluminium ions), 0.016 mg/L for PASA, and 0.00005 mg/L for acrylamide monomers (see Table 8-2).

From the above data, the PEC/PNEC ratio values are derived. The PEC/PNEC ratios are <1 for triiron tetraoxide, PAC, PASA and acrylamide monomers, which shows that there is virtually no risk to aquatic organisms.

At this moment, the PEC/PNEC ratio for PAC (aluminium ions) is not low enough to be assessed as having no effect on the aquatic environment. However, the analysis of treated water described in section 4.1 was carried out before the flocculation technique was fully developed. It has been confirmed that the amount of flocs remaining in the water treated by the current improved structure is drastically less than the amount remaining in the water treated by the previous structures. Since detailed improvements on the equipment are ongoing, new data on water quality will be collected and shown in the application for final approval.

Table 9-1: PEC/PNEC ratio

	PEC (mg/L)	PNEC (mg/L)	PEC/PNEC ratio
Triiron tetraoxide	0.69	> 1	< 0.69
PAC	0.15	0.84	0.18
PAC (aluminium ions)	0.00358	0.00352	1.02
PASA	0.016	0.18	0.09
Acrylamide monomer	0.00005	0.02	0.0025

9.3.2 Assessment of treated ballast water by ecotoxicity test (G9: 5.3.14)

A chronic ecotoxicity test was conducted based on GLP principles and in accordance with test guidelines established by OECD, ISO, and USEPA to assess the effects of ballast water treated by the Hitachi Ballast Purification System on aquatic organisms (for details, see section 6).

As described in 6.1.2, since the concentration of chemicals added was twice that of rated concentration, the volume of substances contained in the treated water supplied for the testing was twice of the predicted concentration described in 8.3.3. Consequently, the concentrations of each substances are expected 1.38 mg/L for triiron tetraoxide, 0.3 mg/L for PAC, 0.02 mg /L for aluminium ions, 0.032 mg/L for PASA, and 0.001 mg/L for acrylamide monomers.

Table 9-2 shows the NOEC values derived from the results of the chronic ecotoxicity test. The 100% concentration treated ballast water affected none of the organisms examined. Given that the quantities of chemicals added in the rated operation of the Hitachi Ballast Purification System are half of those added in the test, it is concluded that the treated water under the rated conditions has virtually no effect on aquatic organisms.

Table 9-2: NOEC of treated ballast water

Test substance	Classification of organism	Organism species	End point	Toxicity (Maximum no observed effect concentration)
Treated ballast water (containing triiron tetraoxide; 1.38 mg/L, PAC; 0.3 mg/L, aluminium ions; 0.02 mg/L, PASA; 0.032 mg/L, acrylamide monomers; 0.0001 mg/L)	Algae	<i>Skeletonema costatum</i>	NOEC for 72 hrs	100% treated ballast water*
	Invertebrates	<i>Hyale barbicornis</i>	NOEC for 21 days	100% treated ballast water*
	Fish	<i>Oryzias javanicus</i>	NOEC for 40 days	100% treated ballast water*

* These findings conclusively demonstrated that ballast water treated by the Hitachi Ballast Water Purification System has virtually no impact on aquatic organisms.

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