PRTR Estimation Manual

05. Hot-Dip Industry

January 2001
Revised: March 2002

Japan Galvanizers Association

1. How to Use This Manual

This is a manual to help facilities capture releases and transfers of Class I Designated Chemical Substances (referred to as “PRTR chemicals”) which started in April, 2001 and report on them which started in April 2002 both under the PRTR System.

1.1. PRTR Chemicals Related to the Industry

Government ordinance No.	CAS NO.	Name of substance	Example of chemical substance	Chemical formula	Process	Remarks
1	7646-85-7	Zinc (water- soluble) compound	Zinc chloride	$ZnCl_2$	Pickling Fluxing	Pickling Flux solution
	7733-02-0		Zinc sulfate (7-hydrate)	$ZnSO_4 \cdot 7H_2O$	Pickling	Flux solution
63	1330-20-7	Xylene	Xylene	$C_6H_4(CH_3)_2$	Finishing	Repairing paint
68	7440-47-3	Chromium and trivalent chromium compounds	Chromium	Cr	Pickling	Equipment (jigs)
	1308-38-9		Chromium (III) oxide	Cr_2O_3		
69	1333-82-0	Hexavalent chromium compounds	Chromium trioxide (chromic anhydride)	CrO_3	White rust prevention treatment	White rust prevention treatment agent
	10588-0-19		Sodium dichromate	$Na_2Cr_2O_7$		
	7789-12-0		Sodium dichromate (dihydrate)	$Na_2Cr_20_7 \cdot 2H_2O$		
230	—	Lead and its compounds	Lead	Pb	Hot dip galvanizing	Zinc and lead
283	7664-39-3	Hydrogen fluoride and its water-soluble salts	Aqueous solution of hydrogen fluoride (hydrogen fluoride)	HF	Pickling	Pickling of casting

1.2. Example of Hot-Dip Process

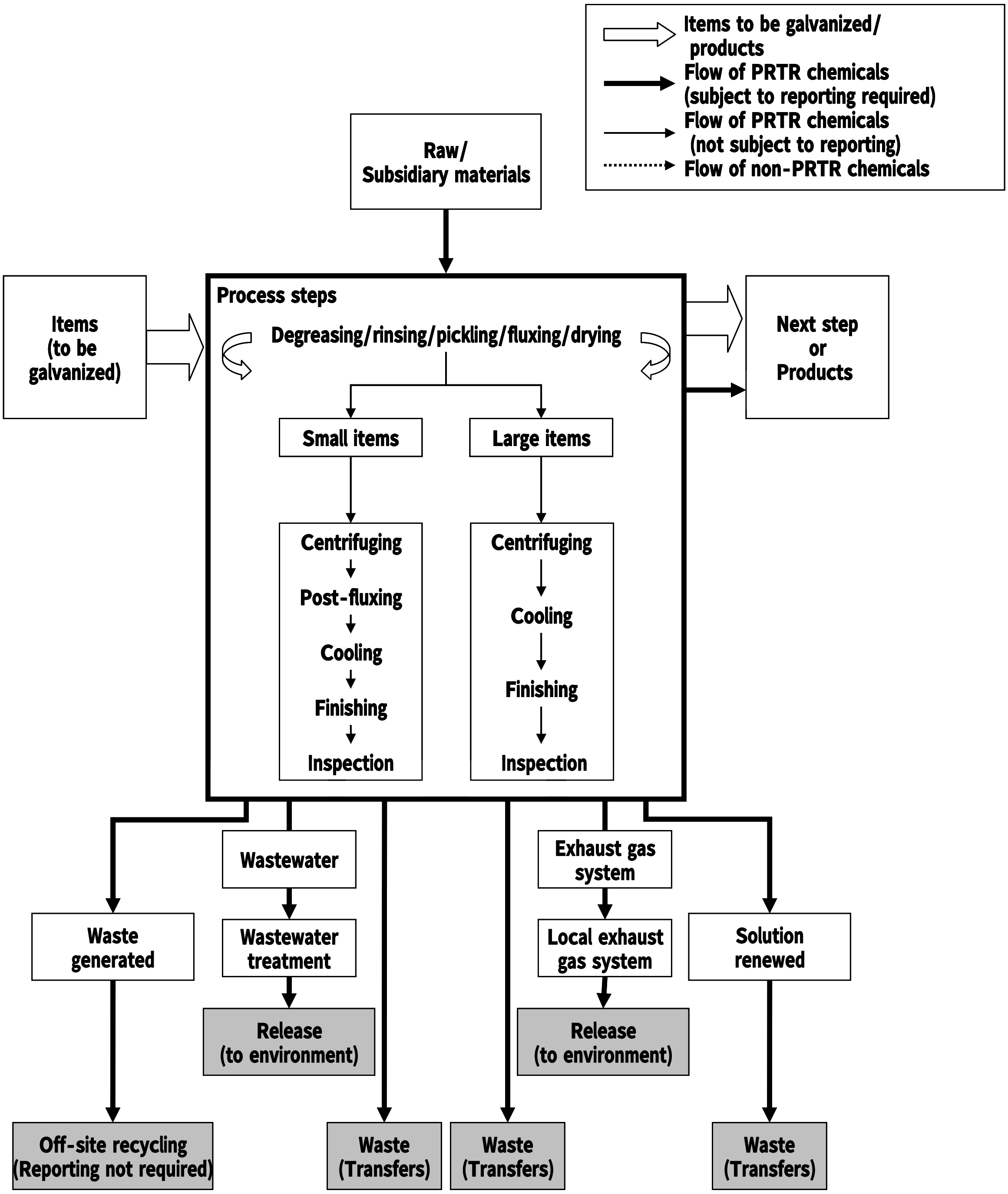
This table outlines operations of hot-dip process. Users may refer to this manual when calculating the quantities of PRTR chemicals released and transferred.

Process		Outline of processing	Outline of operating conditions
Large items to be galvanized	Small items to be galvanized		
1. Degreasing		Soaking items to be galvanized in a warmed alkaline water solution to completely remove oils on their surfaces.	Degreasing solution: 10-15 % solution of caustic soda Temperature: at 70-80 °C. Time: as appropriate
2. Water rinsing		Thoroughly rinsing the degreasing solution on the items to be galvanized.	Rinsing water: industrial water, clean water Temperature: room temperature Time: as appropriate
3. Pickling		Immersing items to be galvanized in an acidic water solution to completely remove rust and scale on their surface.	Pickling solution: 5-15% solution of hydrochloric acids or sulfuric acids Temperature: room temperature for solution of hydrochloric acids and 60-80 °C for solution of sulfuric acids Time: as appropriate
4. Water rinsing		Thoroughly rinsing acidic solution on the items to be galvanized.	Rinsing water: industrial water, clean water Temperature: room temperature Time: as appropriate
5. Fluxing		Soaking items to be galvanized in a warmed flux solution to create flux layers to protect the pickled items from corrosion and promote alloying reaction between the items and molten zinc.	Flux solution Galvanizing large items: solution of zinc chloride/ammonium chloride Galvanizing small items: solution of ammonium chloride Temperature: 70-90 °C Time: as appropriate
6. Drying		Drying items to prevent dispersing of zinc when they are soaked in a galvanizing tank.	Natural drying
7. Galvanizing		Soaking items to be galvanized in a molten zinc bath to form galvanized layers. Optimum galvanizing conditions may be chosen depending on the type of materials, shapes, and sizes of items to be galvanized.	Zinc bath: 97.5% or more of zinc purity Temperature: Large items: 430-460 °C Small items: 470-510 °Cfor Time: as appropriate
___	8. Centrifuging	Removing surplus zinc from galvanized products.	Used to centrifuge the dragout of zinc of small items galvanized
___	9. Ammonium chloride cleaning	Cleaning the galvanized surfaces.	Concentration: 10-15% Temperature: 90 °C or higher
10. Cooling		Cooling galvanized products in warm water. This cooling process retard growth of the alloy layers of iron and zinc of the galvanized layers.	Cooling water: industrial water or clean water Temperature: at 40-80 °C. Time: as appropriate
11. Inspection		Inspecting appearance, galvanized quantity, and adhesiveness of galvanized products.	In accordance with JISH8641 and JISH0401

1.3. Flow Chart of Hot-Dip Galvanizing Process and Releases and Transfers of PRTR Chemicals (Fig. 1)

The procedure for calculating quantities of PRTR chemicals released and transferred is shown in Fig. 1 to outline the entire flows of releases and transfers.

Fig. 1: Outline of hot-dip galvanizing process and releases and transfers of PRTR chemicals

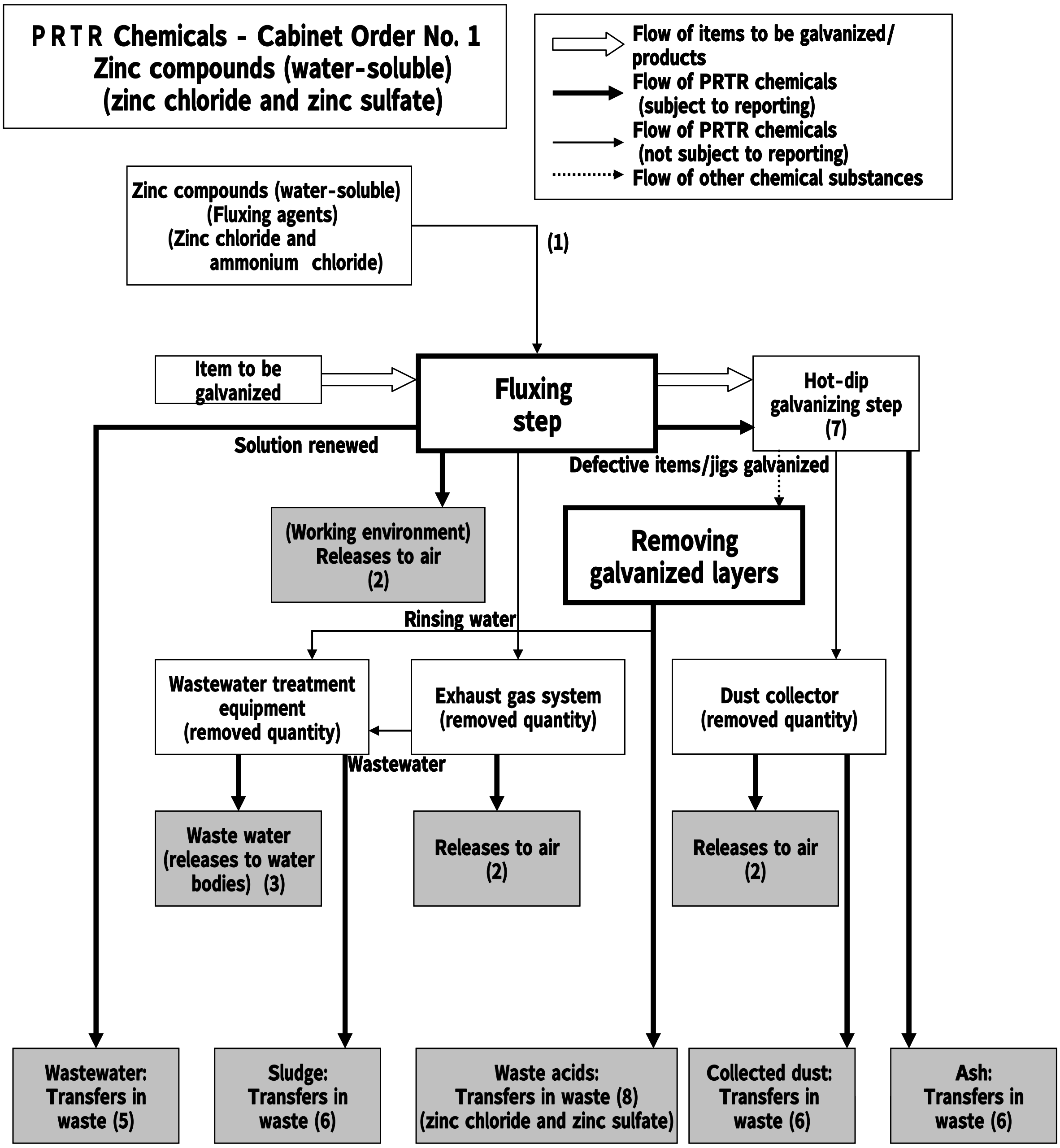


1.4. Notes

The procedures described in this manual are given as examples for reference. Therefore, facilities are not obliged to follow the procedures described in this manual. They may report on chemical releases and transfers calculated based on other methods which they believe can produce more accurate results in an efficient manner.

1.5. Procedures for Calculating Releases and Transfers of PRTR Chemicals and Calculation Examples

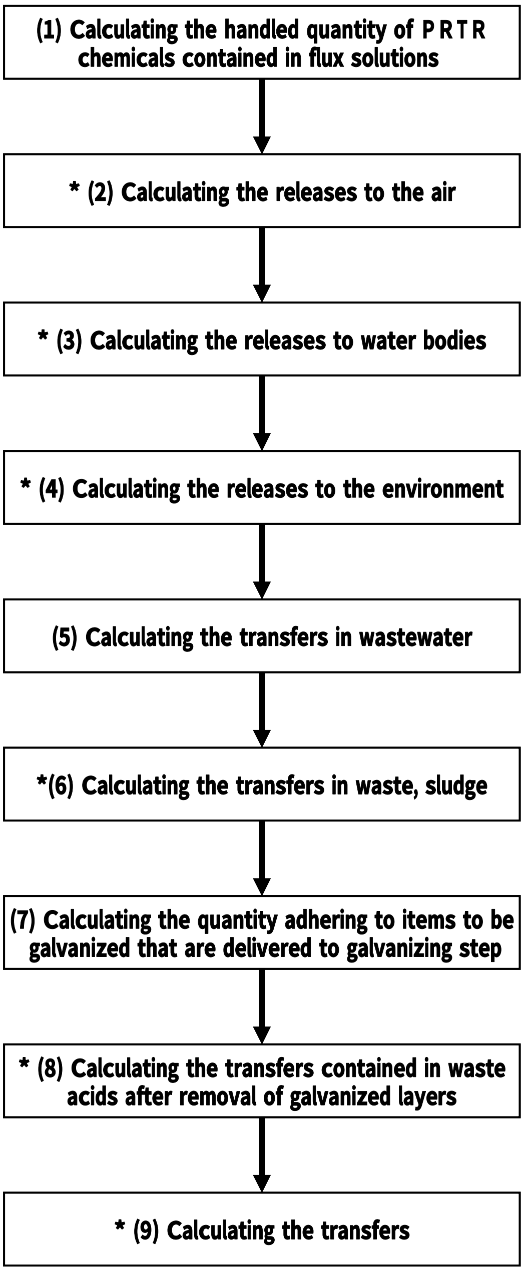
1.5.1. Zinc Compounds (water-soluble) (Fig. 2)



Note: Values in parentheses show the procedure for estimating releases/transfers

[Calculation Procedure]

Fluxing agents that contain zinc chloride are used mainly in plants which galvanize large items. However, plants for galvanizing small items involving a variety of manual operations, use only ammonium chloride and do not use zinc chloride for safety, because it is hygroscopic. Therefore plants which use only ammonium chloride for galvanizing small items may follow the steps marked with*.



Annual quantity of flux agents handled
x
Content of zinc chloride in fluxing agents
x
Conversion factor to metallic element (Zn)

Releases to air from local exhaust gas system and dust collectors

Releases from the solution surface to the air in the working environment

Releases from wastewater treatment equipment to water bodies

Releases to air
+
Releases to water bodies

Quantity of renewed flux solution
x
Content of zinc chloride
x
Conversion factor

Calculating the quantity of zinc (water-soluble) mixed in ash
Calculating the quantity of zinc (water-soluble) in dust collected
Calculating the quantity of zinc (water-soluble) in sludge

Quantity of zinc chloride handled
- **Releases from flux solution tanks to the air**
- **Releases to water bodies**
- **Transfers contained in waste solution**
- **Transfers contained in sludge**

Quantity of waste acids generated
x
Content of zinc (water-soluble) in waste acids

Transfers contained in waste/sludge
x
Transfers contained in waste acids

[Calculation Example]

For carrying out calculations, convert the quantity of zinc compounds (water-soluble) to that of elemental zinc by using a conversion factor.

(1)Annual quantity of zinc chloride handled

(Annual quantity handled)
= (Annual quantity of fluxing agents handled)
x (Content percent of zinc chloride / 100) x (Conversion factor)
= (58,000 kg/year) x (45.9%/100 (mole ratio: 1:3)) x (0.480)
= 12,779 kg

Flux No.	Molar ratio	Zinc chloride content
No. 1	1:1	71.8 %
No. 3	1:3	45.9 %

(2)Releases to the air

(2.1) Releases from local exhaust gas system to the air

For the concentration of zinc chloride in the exhaust gas emissions from local exhaust gas system for flux tanks, the threshold limit value of “1 mg/Nm^3” for zinc chloride recommended by the ACGIH is applied as a constant. In case where companies have their own measured values, they may be also used.

(Releases from local exhaust gas system)
= (Annual quantity of exhaust gas emissions)
x (Concentration of zinc chloride in exhaust gas emissions)
x (Conversion factor)
= (1,000 Nm^3 per minute x 60 minutes x 200 hours x 2 shifts x 12 months)
x (1 mg/Nm^3/1,000,000) x (0.480)
= 138 kg

(2.2) Releases from the surface of solutions to the air in working environment

Calculations are made on the assumption that the air within 2 m above the surface of flux solutions is ventilated 10 times per minute.

For the concentration of zinc chloride in the exhaust gas emissions from local exhaust gas system near the flux tanks in the working environment, the threshold limit value of “1 mg/Nm^3” for zinc chloride recommended by the ACGIH is applied as a constant. In case where companies have their own measured values, they may be also used.

(Releases from the surface of solutions)
= (Length (m) x Width (m) x Height (2 m) x 10 times/minute x 60 minutes x 24 hours x 365 days) x (Concentration of zinc chloride in working environment) x

(Conversion factor)
= (14 x 2.5 x 2 x 10 x 60 x 24 x 365) x (1 mg/Nm^3) x (0.480)/1,000,000
= 177 kg

(2.3) Releases from dust collectors to the air

The average collection efficiency of fume by dust collectors was assumed to be 90 percent. And the composition of chemical substances uncollected and released to the air was assumed to be equivalent to that of the collected ash.

For the quantity of zinc chloride contained in the dust collected, zinc compounds dissolved from the collected ash into solutions are regarded as zinc chloride, because zinc chloride is water-soluble.

Dissolved zinc is measured according to the “Dissolution test method for metals in waste (referred to as the analytical methods)” designated (in the Environment Agency Notice No. 14 dated February 17, 1973 – “Detection method of metals contained in waste to be used as landfill”, which is stipulated in Paragraph 1 of Article 5 of the Enforcement Ordinance for the Law Relating to the Prevention of Marine Pollution and Maritime Disaster) that is applied to mineral sludge to be used for marine reclamation. The arithmetic mean of the values measured by several member companies of this Association is applied as a constant. In case where facilities have their own measured values, they may be also used.

(Releases from dust collectors)
= {(Quantity of collected dust/0.9) x 0.1} x (Zinc content in collected dust measured by means of released metal content test (%))
= {(14,550 kg/year/0.9) x 0.1} x (0.034%/100) = 1 kg

The zinc content in the collected dust measured by the dissolution test method (%)
= (Dissolved zinc mg/liter) x (1/quantity of collected dust x 1,000) x 100
= (dissolved zinc mg/liter) x (1/quantity of collected dust)/10
The quantity of collected dust is 30 g.

(2.4) Releases
(Releases to the air) = 138 kg + 177 kg + 1kg
= 316 kg

(3)Releases from wastewater treatment equipment to water bodies
(Releases to water bodies)
= (Quantity of wastewater used or quantity of wastewater released) x (Concentration of zinc in wastewater)

The arithmetic mean of measurements with the in-house wastewater treatment equipment at respective facilities in accordance with the “JIS K 0102 Wastewater Test Methods – 1998” is used as the concentration of zinc in wastewater.

As a result of measurement stipulated in “Paragraph 53 “Zinc” of JIS K 0102,” the “measurements” mean:

[1] “regulated values” in case where “< regulated values” are recorded;
[2] “measurement result” in case where “ ≦ measurement result” is recorded;
[3] “0.0 mg/liter” in case where “ND” is recorded.

= (97,000 m^3) x (2.5 mg/liter)/1,000
= 243 kg

(4)Releases to the environment
(Releases to the environment)
= (Releases to the air) + (releases to water bodies)
= 316 kg + 243 kg
= 559 kg

In case where wastewater is released to sewage, it is calculated as “transfers contained in waste,” not as “releases to the environment (releases to water bodies)” based on the following equation:
(Releases to the environment) = (Releases to the air)
= 316 kg

(5)Transfers contained in wastewater
(Quantity of zinc compounds (water-soluble) in wastewater)
= (Quantity of waste flux solutions)
x (Concentration of zinc chloride in wastewater)

(6)Transfers contained in waste/sludge
(6.1) Quantity of zinc mixed in ash

The quantity of zinc chloride in ash was measured in the same way with that of zinc chloride in the ash collected using the “Dissolutions Test Methods”.

Like the case for the collected dust, the arithmetic mean of measurements made by several member companies of this Association is applied as a constant. In case where facilities have their own measured values, they may be also used.

(Quantity of zinc in ash)
= (Quantity of ash) x (Zinc content in ash measured by the Dissolutions Test (%))
= (494,700kg/year) x (0.123%/100)

=608 kg

(6.2) Quantity of zinc in collected dust
(Quantity of zinc in collected dust)
= (Quantity of collected dust)
x (Content of zinc collected dust measured by the Dissolutions Test (%))
= (14,550 kg) x (0.034%/100)
= 5 kg

(6.3) Quantity of zinc in sludge
(Quantity of zinc in sludge)
= (Quantity of sludge)
x (Zinc content in sludge measured by the Dissolutions Test (%))
= (194,000 kg) x (0.004%/100)
= 8 kg

(6.4) Transfers
(Transfers contained in waste/sludge)
= (Quantity of zinc mixed in ash) + (Quantity of zinc in dust collected)
+ (Quantity of zinc in sludge) + (Transfers to sewage)
= 608 kg + 5 kg + 8 kg + 0 kg
= 621 kg

(7)Quantity of zinc chloride delivered to the galvanizing step by adhering to items to be galvanized

Fluxing is carried out in order to facilitate the contact between the surface of steel to be galvanized and molten zinc to produce nondefective galvanized layers.

Zinc chloride in flux agents reacts with basic ferric salts adhering to items to be galvanized in the molten zinc baths and zinc oxide on the surface of zinc baths to become black molten chloride and separates them from the surface of the galvanized items.

The black melt chloride is collected before products are pulled up from the zinc baths. Then, it is oxidized to become zinc oxide. However, the zinc oxide contains unoxidized zinc chloride.

The quantity of zinc chloride delivered to galvanizing step by adhering to items to be galvanized varies depending on conditions such as the surface area and surface roughness of items to be galvanized, concentration and temperature of fluxing solutions, and surface tension. For this reason, it is very difficult to measure it independently.

Therefore, as shown in the following equations, the quantity calculated by subtracting the releases to the environment, the transfers contained in wastewater, and the transfers contained in sludge from the quantity handled is regarded as the quantity delivered.

(Quantity delivered to galvanizing step)
= (Quantity of zinc chloride handled) – (Releases from fluxing tank to air)
– (Releases to water bodies) – (Transfers contained in wastewater)
– (Transfers contained in sludge)
= 12,779 kg – (177 + 138) kg – 243 kg – 0 kg – 8 kg
= 12,213 kg

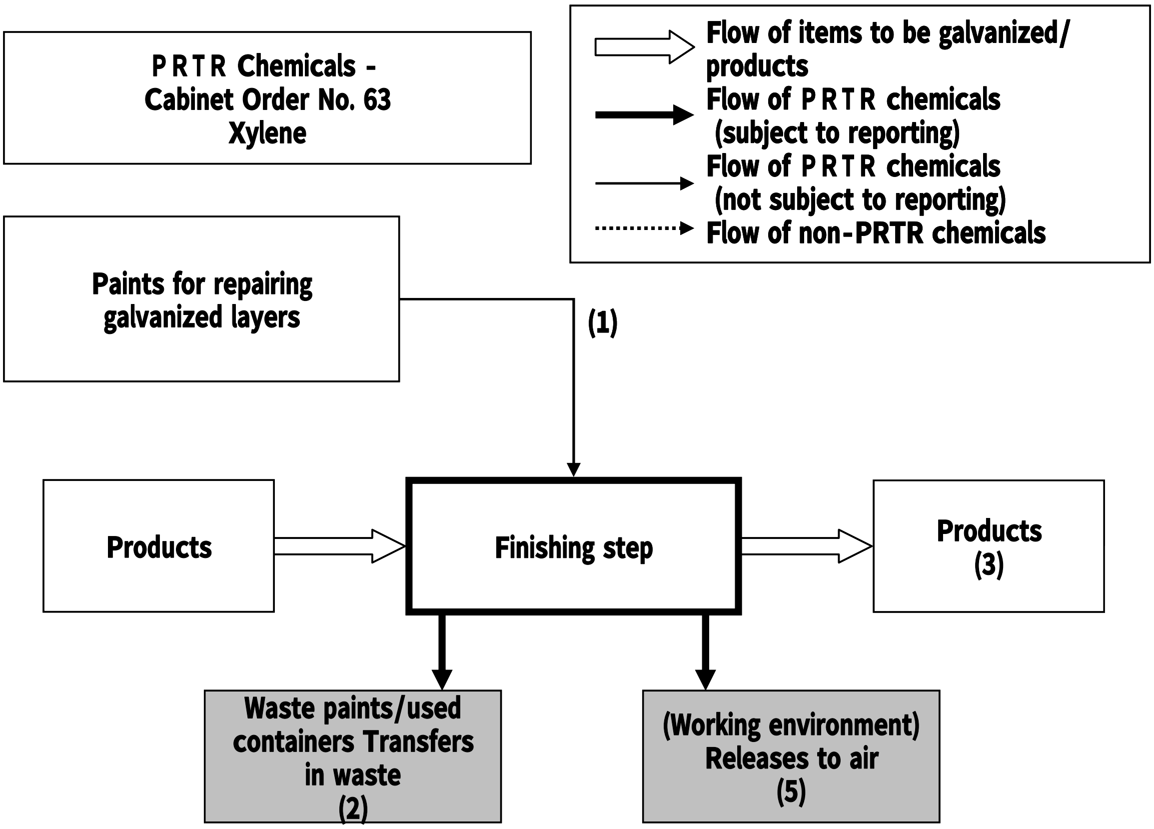
(8)Transfers of zinc contained in waste acids after removal of galvanized layers
(Transfers of zinc contained in waste acids after removal of galvanized layers)
= (Quantity of waste acids) x (Content of zinc in waste acids (%))
= (25,700 kg) x (11.7%/100)
= 3,007 kg

For the quantity of zinc contained in waste acids after removal of galvanized layers, values measured by respective facilities are used because their target zinc concentrations are considered to be different.

(9)Transfers
(Transfers)
= (Transfers of zinc contained in waste/sludge)
+ (Transfers of zinc contained in waste acids)
= 621 kg + 3,007 kg
= 3,628 kg

In case where wastewater is released to sewage, it is calculated as the “transfers contained in waste” using the following equation:
(Transfers to sewage)
= 243 kg + 621 kg + 3,007 kg
= 3,871 kg

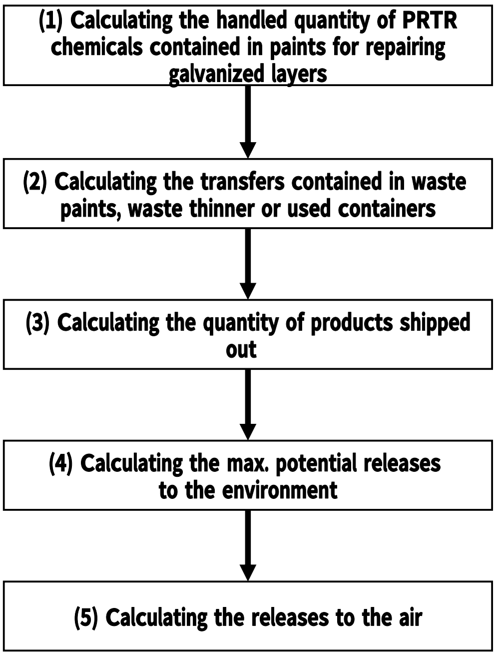
1.5.2. Xylene (Fig. 3)



Note: Values in parentheses show order of the procedure for calculating the releases/transfers.

[Calculation Procedure]

1. Solvents



Annual quantity of handled paint for repairing galvanized layers
x
Xylene content in paints

Quantity of waste paints and waste thinner generated

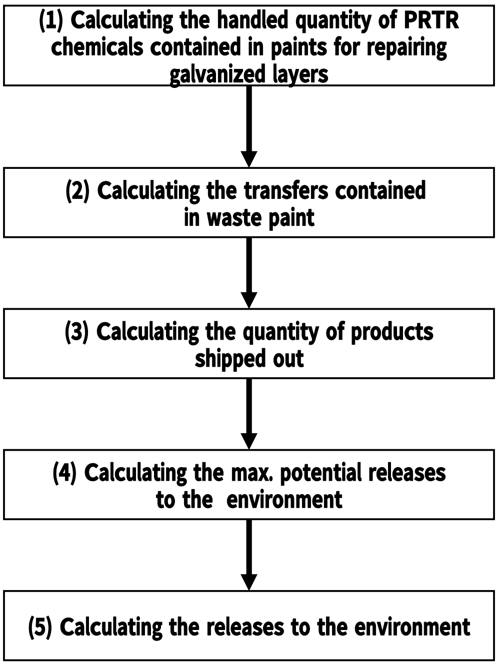
Amount of residues in containers

Since solvents (PRTR chemicals) are not contained in the repairing galvanized layers, calculations are omitted.

Quantity handled - Transfers

Max. potential releases to the environment

2. Pigments



Annual quantity of the handled paints for repairing galvanized layers
x
Content in paints

Quantity of waste paints generated
x
Content in paint or waste paints

Since PRTR chemicals are not contained in the pigments, calculations are omitted.

Quantity handled - Transfers of waste paints

Quantity handled - Transfers of waste paints

[Calculation Example]

Two kinds of paints; spray type and brush type, are used for repairing galvanized layers in galvanizing plants. Calculation procedures for these two types are shown below:

A. Spray type of paint for repairing

1. Solvents ingredients

(1)Annual quantity of xylene handled

(Annual amount handled)
= (Annul amount of spray type paints handled) x (Xylene content %)
= (5,285 pcs. x 300 ml x Density1.2 g/cm^3) x (5.1%/100)/1,000
= 97 kg

(2)Transfers contained in waste containers

Waste containers of spray type of paints are drilled, when disposing, to prevent them from exploding. As a result, residues in the waste containers are entirely released to the air. Therefore residues in waste containers are assumed to be zero when carrying out calculations.

(Transfers) = (Annual quantity of xylene handled) x (Residue in waste containers)
= (97 kg) x (0.0%/100)
= 0 kg
= 0 kg

(3)Maximum potential releases to the environment

(Maximum potential releases to the environment)
= (Annual quantity handled) - (Transfers)
= 97 kg - 0 kg
= 97 kg

(4)Releases to the air

(Releases to air) = (Maximum potential releases to the environment)
= 97 kg

2. Pigments ingredients

PRTR chemicals are not contained in the pigments.

B. Brush type paints for repairing galvanized layers

1. Solvents ingredients

(1)Annual quantity of xylene handled

(Annual quantity handled)
= (Annul quantity of brush type paints handled) x (Xylene content %)

+ (Annual quantity of thinners for brush type of paints) x (Xylene content (%))
= (650 kg) x (19.6%/100) + (870 kg) x (90.1% /100)
= 911 kg

(2)Transfers contained in waste paints

The amount of waste paint generated is assumed to be 5% of the quantity of paints used. And the solvents in waste paints were considered to remain in the same content. The thinner is considered not to be contained in the waste paints but entirely consumed.

(Transfers)
= (Annual quantity of waste paints generated) x (Xylene content (%) in paints)
= (650 kg x 5%/100) x (19.6%/100)
= 6 kg

When a large amount of paints are disposed of, calculations shall be made separately following the above example.

(3)Maximum potential releases to the environment

(Maximum potential releases to the environment)
= (Annual quantity handled) - (Transfers)
= 911 kg - 6 kg
= 905 kg

(4)Releases to the air

(Releases to air)
= (Maximum potential releases to environment)
= 905 kg

2. Pigments ingredients

PRTR chemicals are not contained in the pigments.

C. Releases to the air and transfers in waste

1. Releases to the air
= 905 kg + 97 kg
= 1,002 kg

2. Transfers contained in waste
= 6 kg

[Reference]:

Example of MSDS for paints (spray type)

Chemical substance	CAS No.	
Xylene	1330-20-7	5.1%
Cyclohexanone	108-94-1	25 - 30 %
Tetrahydrofuran	109-99-9	05 - 10 %
Dimethyl ether	115-10-6	35 - 40 %
Zinc powder		10 - 15 %

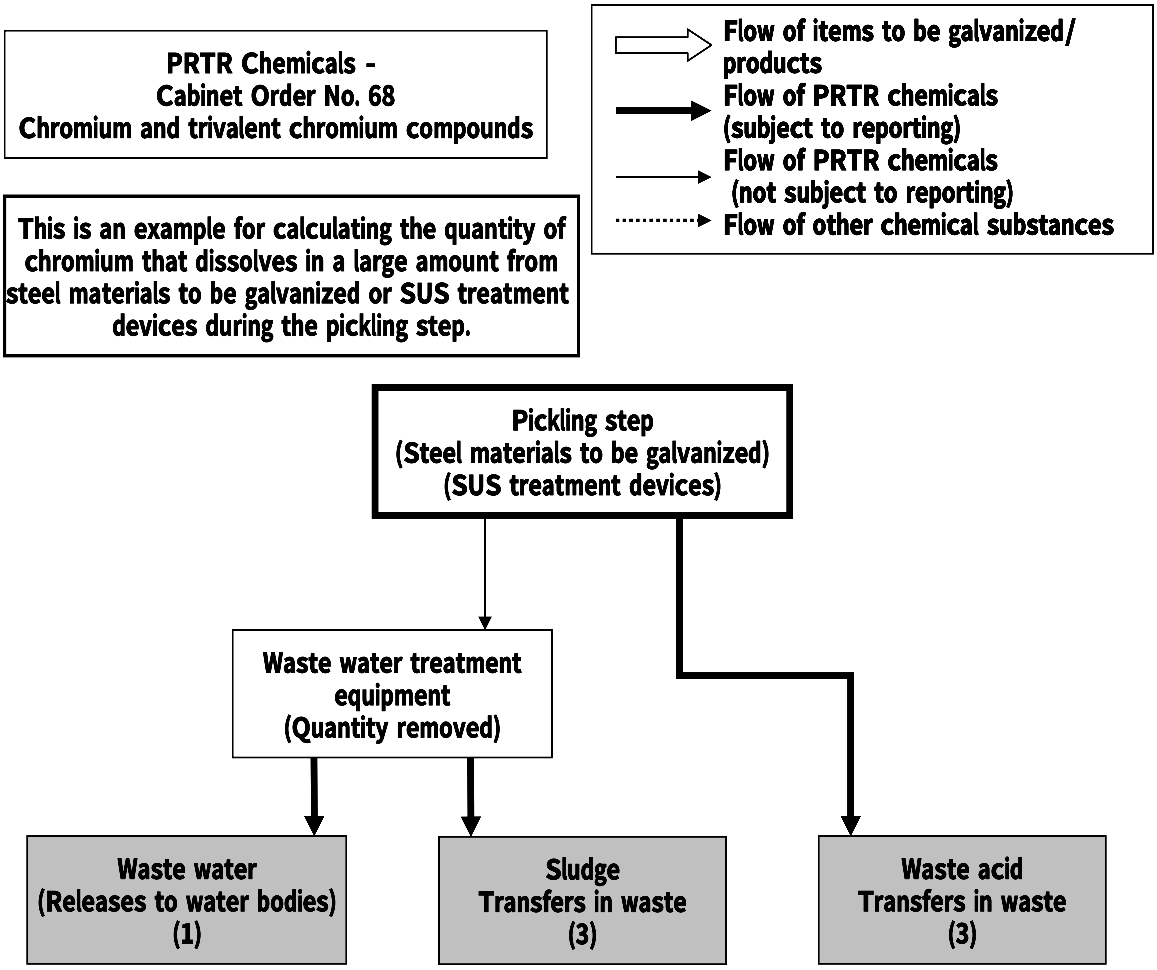
Example of MSDS for paints (brush type)

Chemical substance	CAS No.	
Xylene	1330-20-7	19.6%
Zinc powder		60 - 70 %

Example of MSDS for Thinner

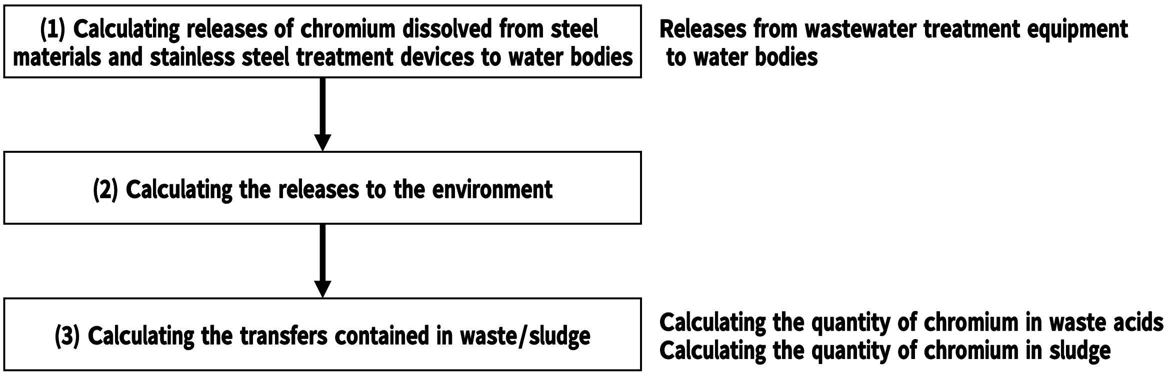
Chemical substance	CAS No.	
Xylene	1330-20-7	90.1%

1.5.3. Chromium and Trivalent Chromium Compounds (Fig. 4)



Note: Values in parentheses show order of the procedure for calculating the releases/transfers.

[Calculation Procedure]



[Calculation Example]

There are cases where chromium is detected and removed from the wastewater treatment equipment, although chromating solutions are not released through the chromating equipment. These are chromium and trivalent chromium compounds which dissolve from stainless steel to be galvanized or jigs used in the preparation. The amount of these substances cannot be managed at hot-dip galvanizing plants.

For the case where chromium and trivalent chromium compounds are removed in a large amount and facilities are required to report them as transfers, calculations shall be made based on the calculation examples shown in this manual.

If the amount of chromium handled is needed for reporting, the “amount of removed” shall be used as the “amount handled” because it is not actually available.

(1)Releases of chromium from wastewater treatment equipment to water bodies

(Releases to water bodies)
= (Quantity of wastewater used or quantity of wastewater)
x (Chromium concentration in wastewater)

For the chromium concentration in wastewater, the arithmetic mean of measurements of wastewater with in-house wastewater treatment equipment at respective facilities may be used. The “measurements” here refer to the following:

As a result of measurement stipulated in “JIS K 0102 Paragraph 65.1 Chromium,” the “measurements” mean:

[1] “regulated values” in case where “< regulated values” are recorded;
[2] “measurement result” in case where “≦ measurement result” is recorded.
[3] “0.0 mg/liter” in case where “ND” is recorded.

= (97,000 m^3) x (0.2 mg/liter)/1,000
= 19 kg

(2)Releases to the environment

(Releases to environment)
= (Releases to water bodies)
= 19 kg

(3)Transfers contained in waste acids/sludge

For the chromium concentration in waste acids/sludge, the arithmetic mean of measurements made by respective facilities may be used.

(Transfers contained in waste acids)
= (Quantity of waste acids generated) x (Content (%) of chromium in waste acids)
= (436,000 kg/year) x (0.005%/100)
= 22 kg

(Quantity of chromium in sludge)
= (Quantity of sludge generated) x (Content of chromium (%) in sludge)
= (194,000 kg) x (0.003%/100)
= 6 kg

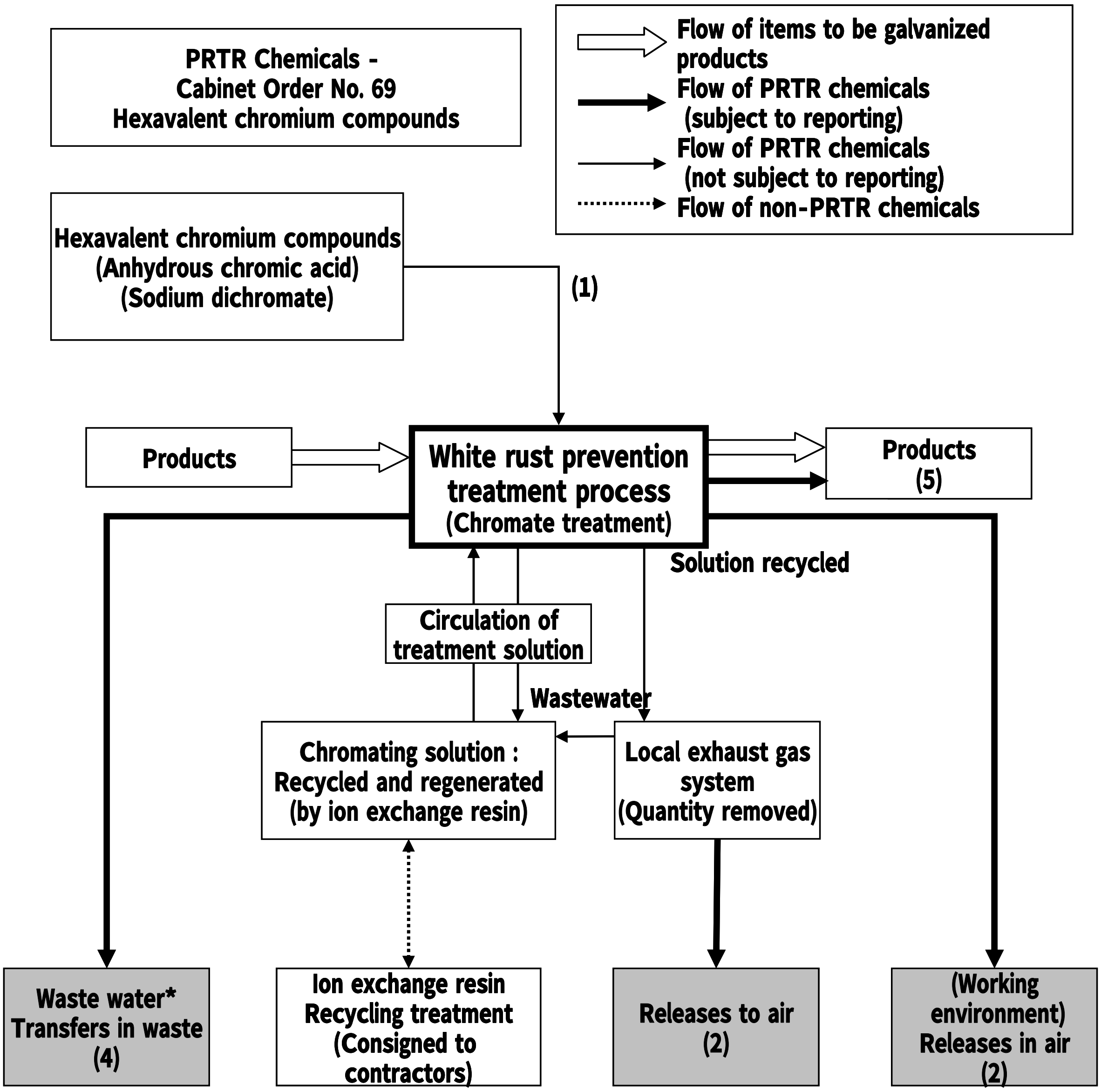
(4)Calculating transfers

(Calculating transfers of chromium)
= (Transfers contained in waste acids/sludge)
= 22 kg + 6 kg
= 28 kg

In case where wastewater is released to sewage, it is calculated as "transfers contained in waste," not as "release to the environment (release to water bodies)" using the following equation:

= 28 kg + 19 kg
= 47 kg

1.5.4. Hexavalent Chromium Compounds (Fig. 5)

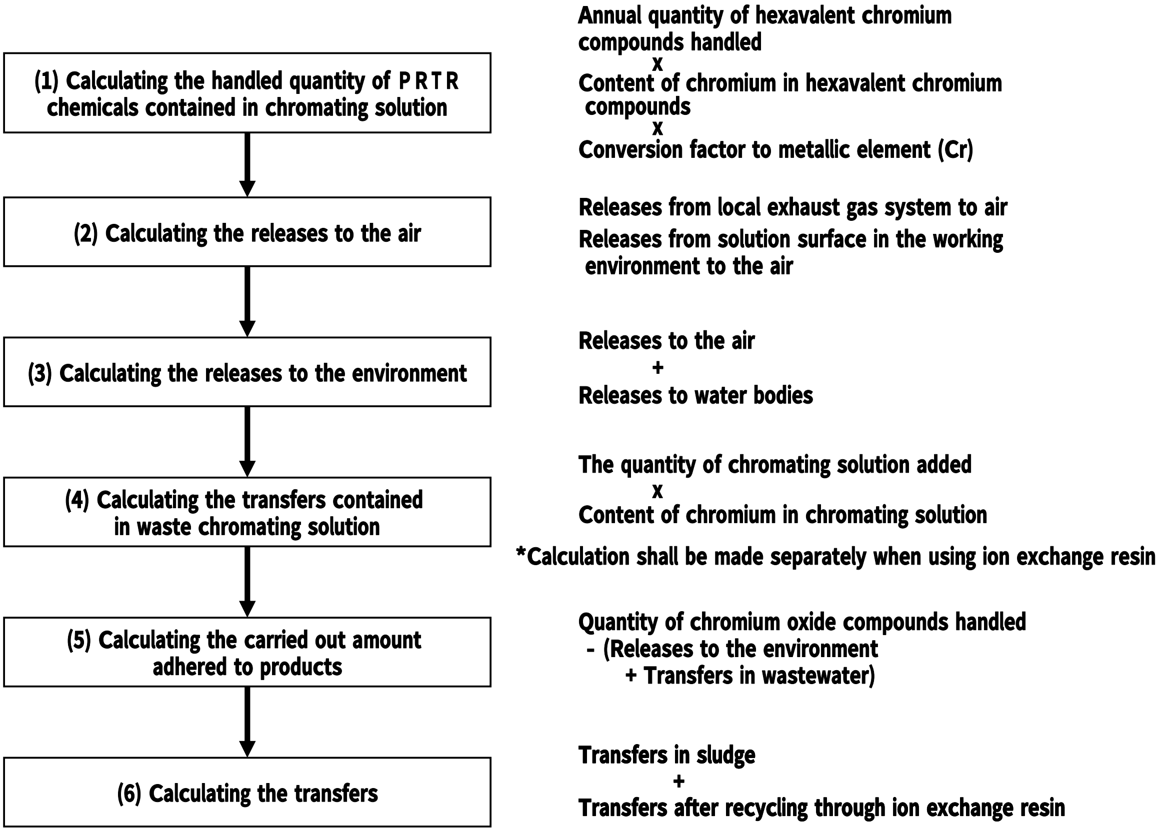


* The [estimation example] is shown separately in case where wastewater is processed by means of ion exchange resin.

Note: Values in parentheses show order of the procedure for calculating the releases/transfers.

[Calculation Procedure]

(1) Calculating the quantity of handled PRTR chemicals contained in chromating solutions



[Calculation Example]

When making calculations, convert the quantity of hexavalent chromium compounds to that of a metallic element (Cr.).

(1)Annual quantity of hexavalent chromium compounds handled

(Annual quantity handled)
= (Annual quantity of sodium dichromate handled) x (100%/100)
x (Conversion factor)
= (1,100 kg/year) x (0.397)
= 437 kg

Conversion factors:

Sodium dichromate	**0.397**	**(when purchased as aqueous solution)**
Sodium dichromate (dihydrate)	**0.349**	
Chromium trioxde (anhydrous chromic acid)	**0.52**	

When the content (%) of these chemical compounds are 95% or more, it should be regarded as 100 mass % for calculations.

In the chromate treatment carried out for corrosion prevention by member companies of this Association, the chromium concentrations of 0.01 – 0.1% have been used.

The OEL for hexavalent chromium in the work environment has been set at 0.1 mg/Nm^3. However measurements in the work environment near the chromate treatment tanks have not found chromium.

Recycling and regeneration (from trivalent chromium into hexavalent chromium) are carried out in the closed systems which use ion exchange resin.

As a result, there is no chromating solutions directly contained in wastewater treatment equipment.

(2)Releases to the air

Since measurements did not show chromium in the work environment, releases to the air are assumed as zero. Therefore releases from local exhaust gas systems and the surface of solutions are as follows:

(Releases to the air)
= 0 kg

(3)Releases to the environment

(Releases to the environment) = (Releases to the air)

Since the substance is not released through wastewater treatment equipment, there is no release of this substance to water bodies.

= 0 kg

(4)Transfers contained in waste chromating solutions

Trivalent chromium other than hexavalent chromium is also contained in waste solutions. However, it should be calculated as hexavalent chromium for the purpose of facilitating calculations.

(Quantity of hexavalent chromium in waste solutions)
= (Quantity of waste chromating solutions)
x (Concentration of chromium in waste solutions)

In case where chromate treatments waste solutions are processed by the ion exchange resin and in wastewater treatment equipment, releases to water bodies are calculated by the following equations:

(Transfers adhered to iron exchange resin)
= (Quantity of waste chromating solutions)
x {(Chromium concentration in waste solutions)
– (Chromium concentration after the ion exchange processing)}

(5)Calculating the carried out quantity adhered to products

(Carried out quantity of hexavalent chromium adhered to products)
= (Quantity of hexavalent chromium compounds handled)
- (Releases of hexavalent chromium compounds to the environment)
- (Transfers in waste chromating solutions)
= (437 kg) – (0 kg) – (0 kg)
= 437 kg

Quantity (%) of hexavalent chromium per ton of products
= {(Carried out quantity of the substance adhered to products)/Quantity of products to be chromated)} x 100
= {(437 kg/1,000/(48,500 tons x 60%/100)} x 100
= 0.002%

In case where the content is 1 percent or more, it is necessary to issue an MSDS. Therefore, an MSDS is not required for the above case.

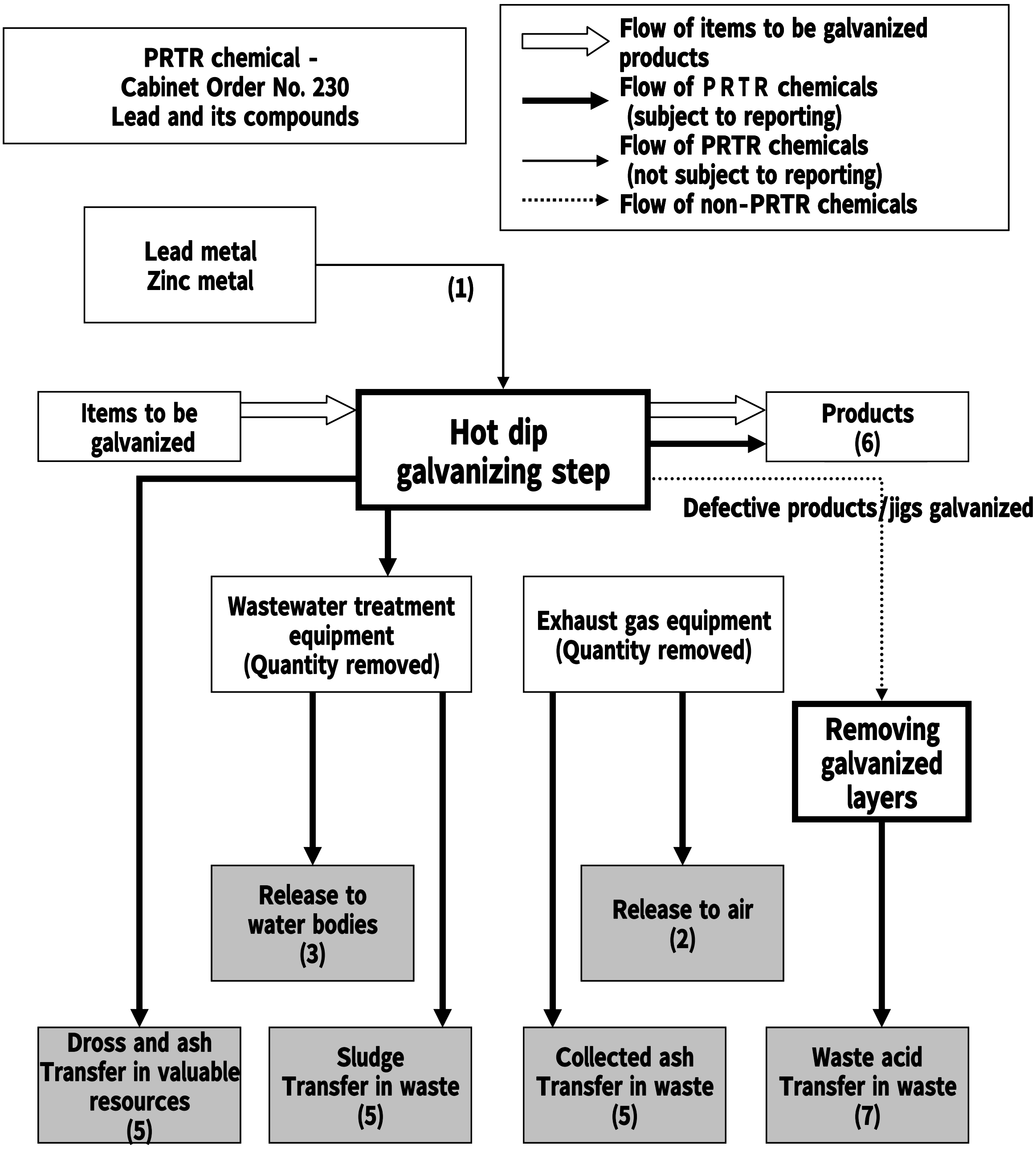
(6)Calculating transfers

(Calculating the transfers of hexavalent chromium)
= (Transfers contained in waste solutions)
= (0 kg)
= 0 kg

In case where wastewater is released to sewage, it is calculated as “transfers contained in waste” using the following equation.

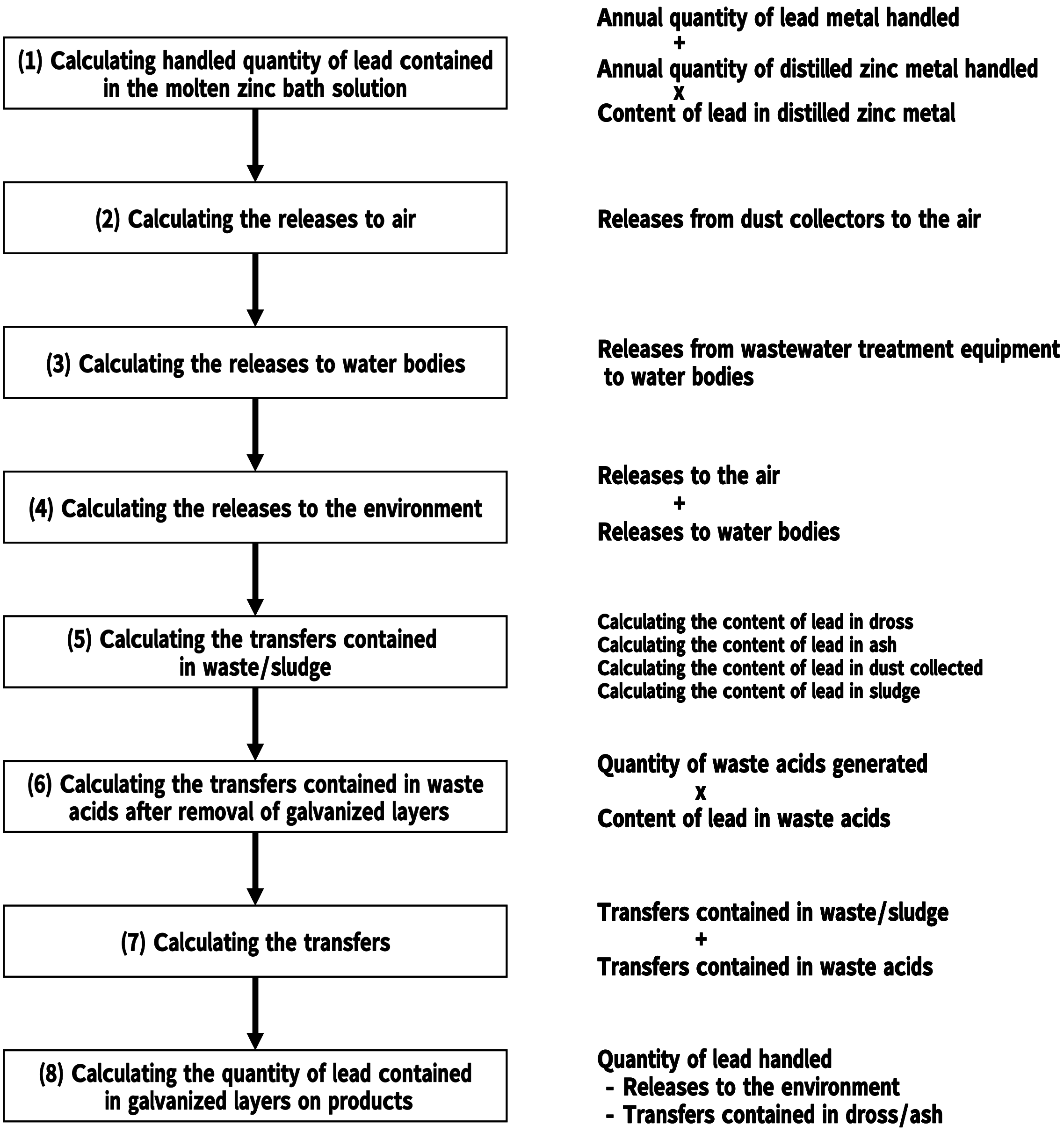
= (0) kg + (0) kg
= 0 kg

1.5.5. Lead and Its Compounds (Fig. 6)



Note: Values in parentheses show the procedure for calculating the releases/transfers.

[Calculation Procedure]



[Calculation Example]

(1)Annual quantity of lead handled

(Annual quantity of lead handled)
= (Annual quantity of lead metal handled)
+ (Annual quantity of distilled zinc metal handled) x (Lead content (%))
= (0 kg/year) + (2,429,850 kg/year) x (1.12%/100)
= 27,214 kg

The constant of 1.12% is used as the lead content in the distilled zinc metal.

Zinc is distilled at two refineries in Japan. Therefore we use the average lead content in the distilled zinc based on the data which have been provided by the two refineries for one year.

(2)Releases from dust collectors to the air

The average collection efficiency of fume with dust collectors is assumed to be of 90 percent. And the composition of substances that are released to the air without being collected is considered equivalent to that of the dust collected.

For the quantity of lead contained in the dust collected, the arithmetic mean of measurements obtained by several member companies of this Association is applied as a constant.

Facilities that have their own measured values, they may be also used.

(Releases from dust collectors)
= {(Quantity of dust collected/0.9) x 0.1} x (Lead content in dust collected (%))
= {(14,550 kg/0.9) x 0.1} x (2.46%/100)
= 40kg

(3)Releases from wastewater treatment equipment to water bodies

For the lead content in wastewater, the arithmetic mean of measurements with in-house wastewater treatment equipment at respective facilities is used.

As a result of measurement stipulated in “JIS K 0102 Paragraph 54 Lead,” the “measurements” mean:

[1] “regulated values” in case where “< regulated values” are recorded;
[2] “measurement result” in case where “ ≦ measurement result” is recorded.
[3] “0.0 mg/liter” in case where “ND” is recorded.

(Releases to water bodies)
= (Quantity of wastewater used or quantity of wastewater released)
x (Lead content in wastewater)
= (97,000 m^3) x (0.1 mg/liter)/1,000
= 10 kg

(4)Releases to the environment

(Releases to the environment)
= (Releases to the air) + (Releases to water bodies)
= 40 kg + 10 kg
= 50 kg

In case where wastewater is released to sewage, it is calculated as “transfers contained in waste,” not as “release to the environment (release to water bodies)” based on the following equation:

(Releases to the environment) = (Releases to the air)
= 40 kg

(5)Transfers contained in waste/sludge

When the dross and ash are carried out as valuables, the amount is not included in the transfers because they are not listed as the target PRTR chemicals under the PRTR system.

However in case where they are carried out as waste, they should be calculated according to the following procedure.

The lead contents (%) in dross/ash (valuables) and in the dust collected/sludge vary depending on the operating temperatures of the hot-dip galvanizing baths, because the content of lead which dissolves in zinc is different.

Therefore the lead content (%) was set depending on the differences in the operating temperature.

The arithmetic mean of lead contents (%) applied here has been obtained from measurements at some plants which galvanize small items and large items respectively selected among the member companies of this Association.

Facilities that have their own measured values, those may be also used.

(5.1) Transfers of lead contained in dross

(Lead content in dross)
= (Annual quantity of dross generated) x (Lead content in dross (%))
= (218,250 kg) x (0.98 %/100)
= 2,139 kg

Lead content in dross (%)	**In plants galvanizing large items: 0.98%**	**In plants galvanizing small items: 1.00%**

(5.2) Transfers of lead contained in ash

(Lead content in ash)
= (Annual quantity of ash generated) x (Lead content in ash (%))
= (494,700 kg) x (4.51%/100)
= 22,311 kg

Lead content in ash (%)	**In plants galvanizing large items: 4.51%**	**In plants galvanizing small items: 5.55%**

(5.3) Transfers of lead contained in the dust collected

(Lead content in dust collected)
= (Annual quantity of dust collected) x (Lead content in dust collected (%))
= (14,550 kg) x (2.46%/100)
= 358 kg

Lead content in dust collected (%)	**In plants galvanizing large items: 2.46%**	**In plants galvanizing small items: 3.33%**

(5.4) Transfers of lead contained in sludge

(Lead content in sludge)
= (Annual quantity of sludge generated) x (Lead content in sludge (%))
= (194,000 kg) x (0.14%/100)
= 272 kg

Lead content in sludge (%)	**In plants galvanizing large items: 0.14%**	**In plants galvanizing small items: 0.22%**

(5.5) Transfers contained in waste/sludge

(Transfers contained in waste/sludge)
= (Lead content in dross) + (Lead content in ash) + (Lead content in dust collected) + (Lead content in sludge)
= 2,139 kg + 22,311 kg + 358 kg + 272 kg
= 25,080 kg

In case where wastewater is released to sewage:

(Transfers contained in waste/sludge)
= (Lead content in dross) + (Lead content in ash) + (Lead content in dust collected)
+ (Lead content in sludge) + (Transfers of lead contained in wastewater)
= 2, 139 kg + 22,311 kg + 358 kg + 272 kg + 10 kg
= 25,090 kg

(6)Transfers contained in waste acids after removal of galvanized layers

(Transfers contained in waste acids)
= (Quantity of waste acids generated after removal of galvanized layers)
x (Lead content in waste acids (%))
= (25,700 kg) x (0.054%/100)
= 14 kg

Since the target quantities of dissolved zinc are considered to be different depending on the facilities, the lead content in waste acids (%) which was obtained from measurements by respective facilities is used instead of a constant.

(7)Transfers

(Calculation of transfers)
= (transfers contained in waste/sludge) + (Transfers contained in waste acids)
= 25,080 kg + 14 kg
= 25,094 kg

In case where wastewater is released to sewage, the transfers are calculated as "transfers in waste" using the following equation:
= 25,090 kg + 14 kg
= 25,194 kg

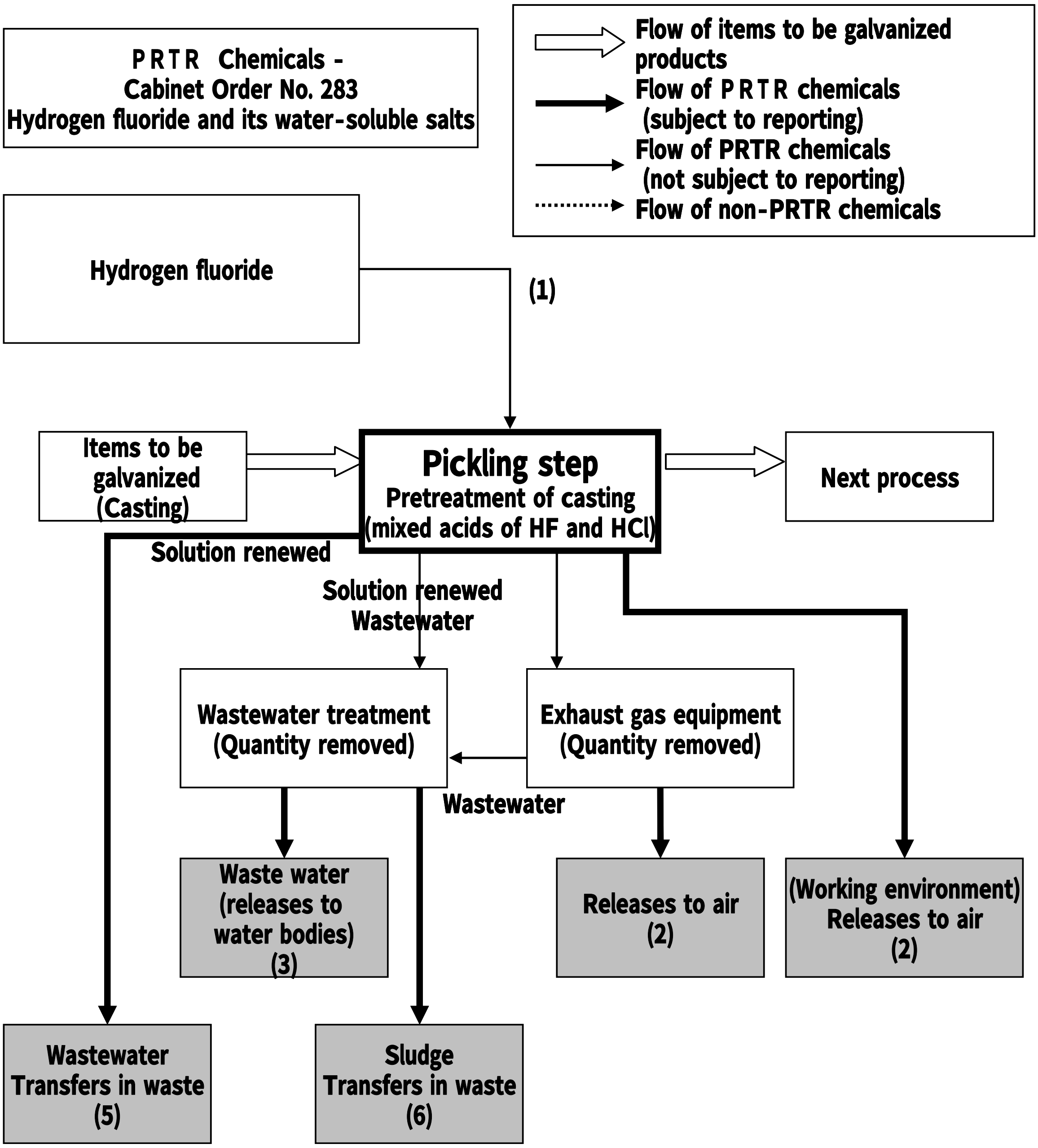
(8)Quantity of lead contained in galvanized layers on products

(Quantity of lead contained in galvanized layers
= (Annual quantity of lead handled) – (Releases to the environment)
– (Transfers contained in waste/sludge/waste acids)
= 27,214 kg – 50 kg – 25,094 kg
= 2,070 kg

(Percentage of lead contained in galvanized layers on products)
= {(2,070 kg/1,000)/48,500 tons (production)} x 100
= 0.004%

In case where the content is 1 percent or more, it is necessary to issue an MSDS. Therefore an MSDS is not required for the above case.

1.5.6. Hydrogen Fluoride and Its Water-Soluble Salts (Fig. 7)



Note: Values in parentheses show order of the procedure for calculating the releases/transfers.

[Calculation Procedure]

(1) Calculating the handled quantity of PRTR chemicals contained in hydrogen fluoride	**Annual quantity of hydrogen fluoride handled** **x** **Content of hydrogen fluoride in aqueous solution of hydrogen fluoride**
(2) Calculating the releases to air	**Releases to the air from local exhaust gas system** **Releases from the solution surface to the air in the working environment**
(3) Calculating the releases to water bodies	**Releases from wastewater treatment equipment to water bodies**
(4) Calculating the releases to the environment	**Releases to the air** **+** **Releases to water bodies**
(5) Calculating the transfers in sludge	**Calculating the quantity of hydrogen fluoride in sludge**
(6) Calculating the transfers in wastewater	**Quantity of the renewed aqueous solution of hydrogen fluoride** **x** **Content of hydrogen fluoride**
(7) Calculating the transfers	**Transfers contained in wastewater** **+** **Transfers in sludge**

[Calculation Example]

The concentrations of “hydrogen fluoride” in the working environment and of “fluoride” in wastewater are regulated under the related laws.

Under the PRTR system, these chemicals need to be calculated as “fluorine”. Therefore the calculated values as “hydrogen fluoride” are converted to values using conversion factor of 0.950.

(1)Annual quantity of hydrogen fluoride handled

(Annual quantity fluoride handled)
= (Annual quantity of aqueous solutions of hydrogen fluoride)
x (Hydrogen fluoride content (%)/100)
= (11,380 kg/year) x (55%/100) = 6,259 kg

Fluorine
= (6,259 kg) x (0.950)
= 5,946 kg

(2)Releases to the air

(2.1) Releases from local exhaust gas systems to the air

For the concentration of fluorine compounds released to air from local exhaust gas systems placed near the pickling tanks of aqueous solution of hydrogen fluoride, 0.8 mg (F^-)/Nm^3 has been obtained by members companies from measurements using the analytical methods based on the JIS L 0105 “Methods for determination of fluorine compounds in flue gas (Spectrophotometric Method of Fluoride with Lanthanum/Alizarin Complexone)”.

Therefore this value is used as a constant for the calculations.

Facilities that have their own measured values, those may be also used.

(Releases from local exhaust gas systems)
= (Annul amount of exhaust gas generated)
x (Fluorine concentration in exhaust gas emissions)
= (19,900Nm^3/hour x 167 hours x 1shift x 12 months) x (0.8 mg/Nm^3/1,000,000)
= 32 kg (F^-)

(2.2) Releases from solutions surface to the air in the working environment

It was assumed that the air 2 m above the surface of the aqueous solutions of hydrogen fluoride in the pickling tanks is ventilated 10 times per minute.

Facilities that have their own measured values, they may be also used.

For the concentrations of hydrogen fluoride near the pickling tanks of aqueous solution of hydrogen fluoride in the work environment, 0.3 cm^3/Nm^3 has been obtained by members companies from measurements using the analytical method (Spectrophotometric Method of Fluoride with Lanthanum/Alizarin Complexone)”.

Therefore this value is used as a constant for the calculations.

Facilities that have their own measured values, those may be also used.

(Releases from solutions surface to the air)
= (Length x Width x Height x 10 times/minute x 60 minutes
x 24 hours x 365 days) x (Number of tanks)
x (Hydrogen fluoride concentration in the working environment)

Since no cover is put on the tanks, hydrogen fluoride is assumed to constantly diffuse to the air.

= (2.6 m x 1.9 m x 2 m x 10 x 60 x 24 x 365) x (3) x (0.3 cm^3/Nm^3/1,000,000)
= 46.74 Nm^3 (HF)

Converting the weight of hydrogen fluoride gas to that of fluorine.

(Fluorine weight)
= (Annual releases)/(Volume at 1 kmol HF 25℃, atmospheric pressure)
x (HF 1kmol) x (Conversion factor)
= 46.7Nm^3/22.4 Nm^3 x (273 + 25) ℃/273 ℃)x 20 kg x (0.950)
= 36 kg

(2.3) Releases to the air

(Releases to the air) = 32 kg + 36 kg
= 68 kg

(3)Releases from wastewater treatment equipment to water bodies

For the fluorine concentration in wastewater, the arithmetic mean of “measurements” with in-house wastewater treatment equipment at respective facilities using the analytical methods based on the “JIS K 0102 Testing methods for industrial wastewater” is used.

(Releases to water bodies)
= (Quantity of wastewater used or wastewater)
x (Fluorine concentration in wastewater)
= (52,063m^3) x (2mg/litre)/1,000
= 104 kg

(4)Releases to the environment

(Releases to environment)
= (Releases to air) + (Releases to water bodies)
= 68 kg + 104 kg
= 172 kg

In case where wastewater is released to sewage, the releases to the environment

= 68 kg

(5)Transfers contained in sludge

For the content of fluorine in sludge, the arithmetic mean of measurements obtained by respective facilities is used.

(Quantity of fluorine in sludge)
= (Quantity of sludge generated) x (Content of fluorine in 1 kg of sludge)
= (195,840 kg) x {(100,000 mg)/kg dry sludge
x (100% - Water content 77.7%)/100}/1,000,000
= 4,367 kg

(6)Transfers contained in wastewater

The typical measurements for fluorine contained in wastewater and in sediments in wastewater tanks are 14,000 mg/kg (in wastewater) and 44,000 mg/kg (in sediments), respectively.

However, the sediments in the tanks are not always separated from wastewater before being sent to contractors for treatment. For this reason, these values may not reflect the actual state if used for the calculations in this manual.

Therefore when releases to environment and transfers contained in sludge are identified, the transfers in wastewater are calculated using the following equations:

(Transfers contained in wastewater)
= (Annul quantity handled) – (Releases to environment)
– (Transfers contained in sludge)
= 5,946 kg – 172 kg – 4,367 kg
= 1,407 kg

(7)Calculating transfers

(Transfers)
= (Transfers in sludge) + (Transfers in wastewater)
= 4,367 kg + 1,407 kg
= 5,774 kg

In case where wastewater is released to sewage, they are calculated as transfers in waste using the following equation:

= 4,367 kg + 1,407 kg + 104 kg
= 5,878 kg