PRTR Estimation Manual

03. Metal Heat Treatment Industry

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Heat Treatment Trade Association of Japan

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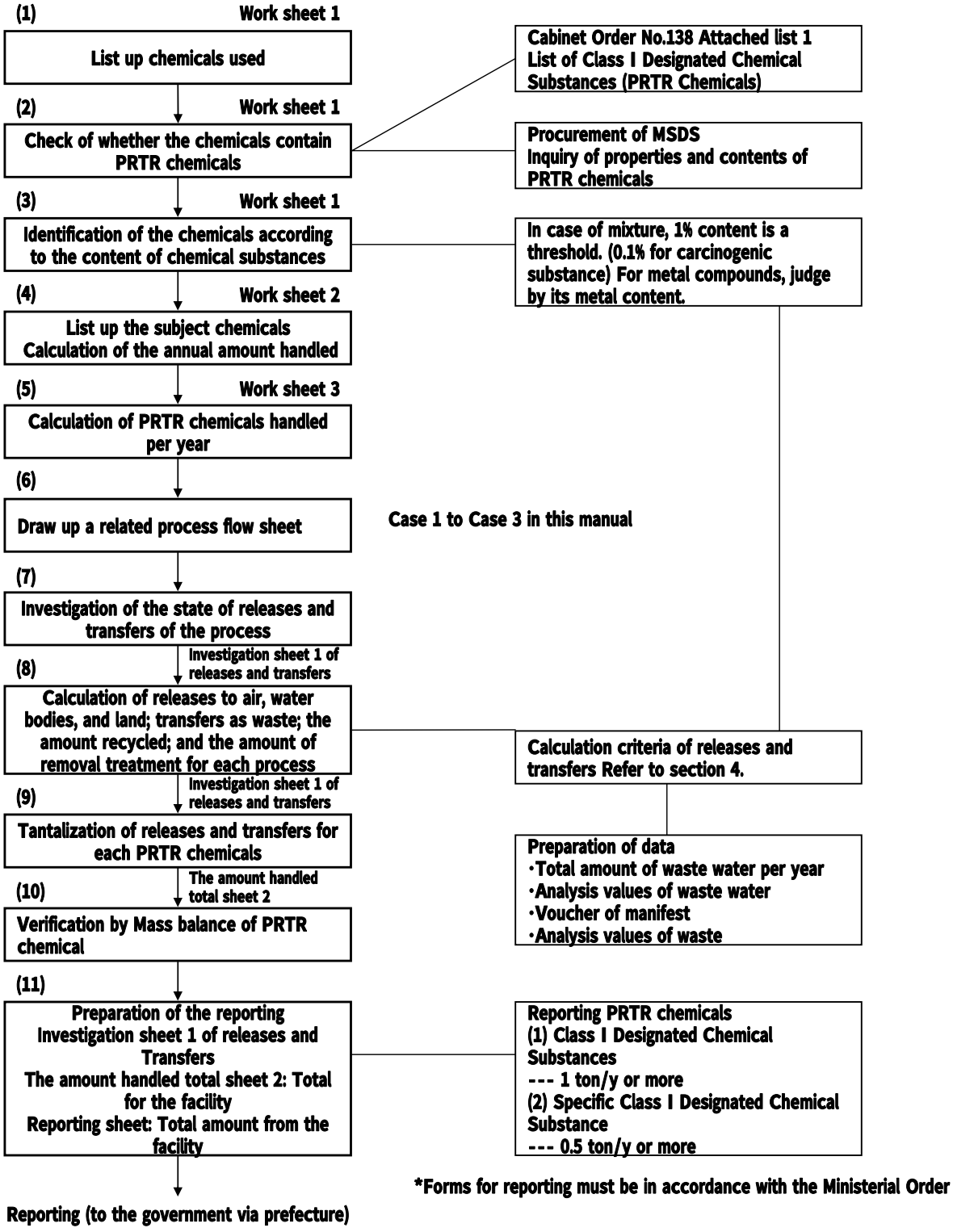
1 The flow of the estimation of releases and transfer



2 Calculation procedures of releases and transfers (Refer to 1. The flow of the estimation of releases and transfers)

(1)List up chemicals used. (Work sheet 1)

(2)Procure MSDS and check whether the product contains the Class I Designated Chemical Substance (PRTR chemicals) or not.

(Work sheet 1)

(Refer to the List of PRTR chemicals of Cabinet Order)

Investigate contents and properties (volatility, solubility, decomposability).

(Work sheet 1)

In case the content etc. are unknown, inquire the maker for its properties.

(3)In case of mixture, products shown in section 4. (3) are the subject.

If in MSDS the content of PRTR chemicals is expressed by a range, the maximum value should be used.

(4)Identify PRTR chemicals and list up these chemicals. (Work sheet 2)

Investigate and sum up the PRTR chemicals handled per year in the facility. The amount handled is calculated by the amount purchased and the variation of holdings. (Work sheet 2)

(5)Convert the annual amount handled for each PRTR chemical to its pure substance. (Work sheet 3)

(6)Draw up a flow sheet of the process in which PRTR chemicals are used.

(7)Investigate in what state PRTR chemicals are released and transferred in the process. Prepare the data required for the calculation of releases and transfers.

(8)Releases etc. for each PRTR chemicals are calculated by the measurement of concentrations.

If the measurement is impossible, estimate these by taking the mass balance using the amount purchased, the amount used and the amount handled, etc.

If necessary in summing up, following the previous paragraph (7), calculate the releases to air, water bodies, and land and transfers as waste to a industrial waste processor for each process. (Investigation sheet of releases and transfers 1)

(9)Total the releases and transfers for each PRTR chemical. (Investigation sheet of releases and transfers 1)

(10) Verification

Verify the result of calculation of the previous paragraph (9) by the equation below. (The amount handled total sheet 2)

The amount handled

= the amount released + the amount transferred

+ the amount converted + others

(11) Reporting criteria of releases and transfers are given in section 4. (4).
Class Ⅰ Designated Chemical Substances --- 1 ton/y or more
(5 ton/y or more for the first two years)
Specific Class Ⅰ Designated Chemical Substance --- 0.5 ton/y or more
Prepare reporting sheet (by designated form).

Note: 1. Examples of filling out of work sheets are shown in the next page.
2. Work sheets shown are only as an example, preparing appropriate sheets for each facility is recommended.

[Examples of filling out the sheets]

List of chemicals

Work sheet 1 **Facility name (Tokyo Factory)**

Process	chemical used	Yes or No
Degreasing/Washing	Trichloroethylene	Yes
Salt bath for soft nitriding	SNC-1 (tentative name)	Yes
Salt bath for tempering	SBB-1 (tentative name)	Yes

Total annual amount handled of the subject chemicals

Work sheet 2

No	Name of subject chemicals	Calculation of the total amount handled per year			
		(a) Amount purchased (kg/y)	(b)Amount of stock at the start of fiscal year (kg/y)	(c)Amount of stock at the end of fiscal year (kg/y)	Amount handled (kg/y) (a)+(b)-(c)
1	Trichloroethylene	5,000	1,000	3,000	3,000
2	SNC-1	120,000	10,000	30,000	100,000
3	SBB-1	6,000	1,000	2,000	5,000

Total amount handled per year of PRTR chemicals

Work sheet 3

No	Name of Chemical products	Calculation of the total amount of PRTR chemicals handled per year					Applicable Yes or No
		Annual amount handled of Subject chemicals (kg/y)	Name of PRTR chemicals	Content (%)	Conversion Factor to pure substance	Annual amount handled of PRTR chemicals (kg/y)	
1	Trichloroethylene	3,000	Trichloroethylene	100	1.000	3,000	Yes
2	SNC-1	100,000	NaCN	22	0.531	11,682	Yes
			KCN	15	0.400	6,000	Yes
3	SBB-1	5,000	$BaCl_2$	50	0.659	1,647.5	Yes

Investigation sheet of releases and transfers 1

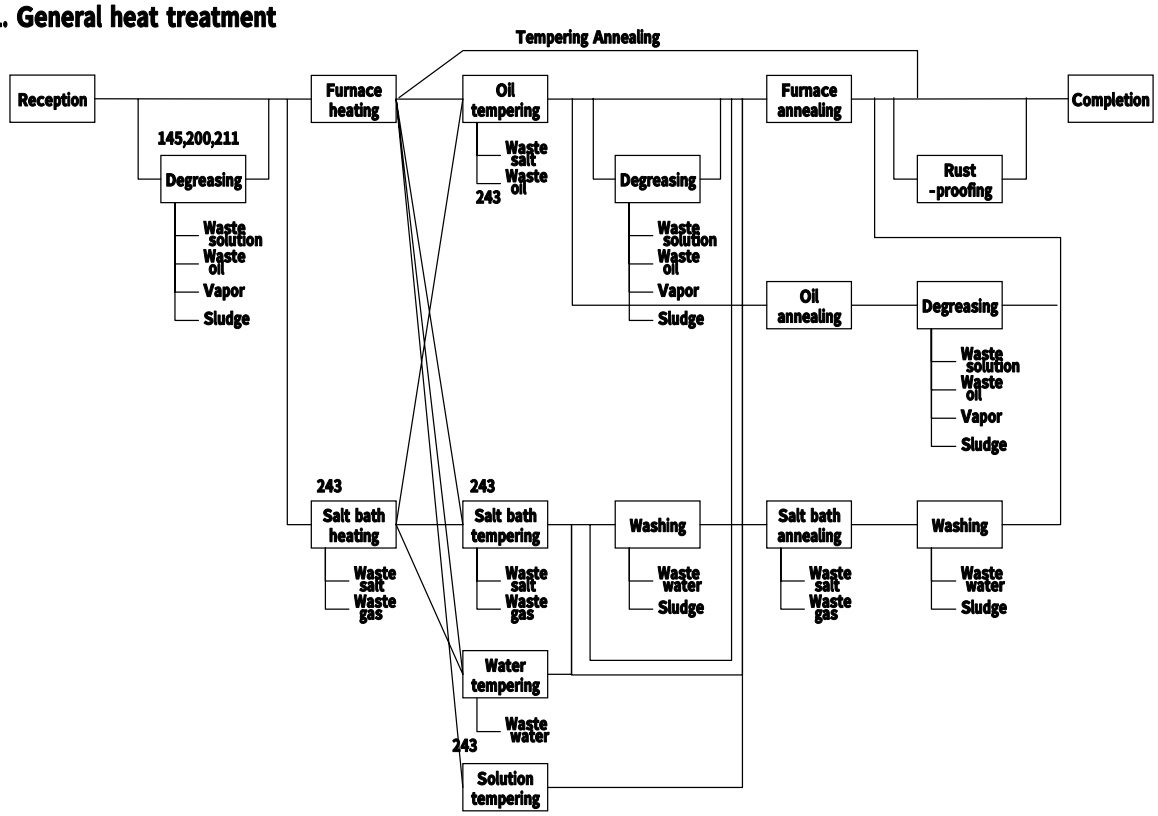
Class	Item		Name of PRTR chemicals		
			Trichloroethylene	Cyanide	Barium
	Amount handled	(kg/y)	3,000	17,682	1,647.50
Transfer	Amount of waste	Transfer(kg/y)	1,275	900	190
	Amount of recycle	Transfer(kg/y)	0	0	0
Total	Amount of transfer (kg/y)		1,275	10,899.90	950
	Amount of release (kg/y)		1,725	0.1	40
	Amount of Conversion deterioration (kg/y)		0	6,782	657.5
Grand total	Transfer + Release + Conversion (kg/y)		3,000	17,682	1,647.50

The amount handled total sheet 2 **(for Facility)**

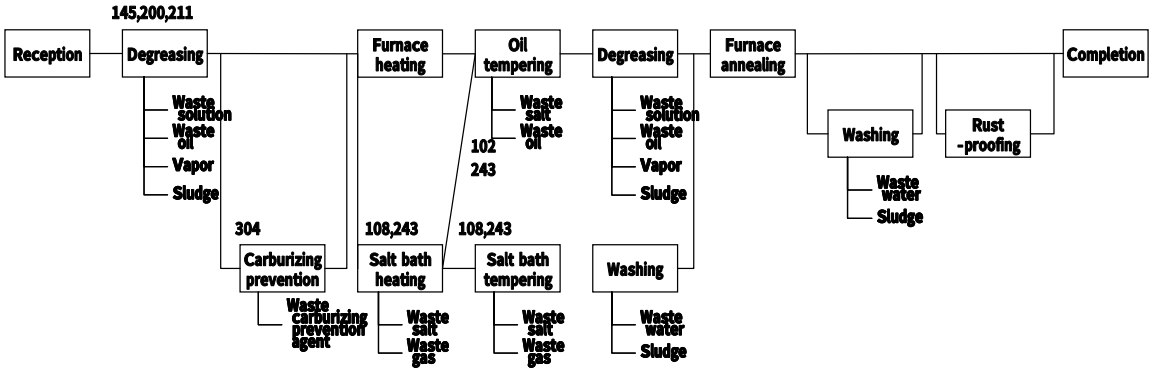
Cabinet Order No	PRTR chemicals	(a)Total amount handled after conversion (kg/y)	(b)Total of release, transfer and conversion (kg/y)	Check (Material balance) (a) - (b) = 0
211	Trichloroethylene	3,000	3,000	0
108	Cyanide	17,682	17,682	0
243	Barium	1,647.50	1,647.50	0

3 The flow diagram of the chemical substances use for metal heat treatment process

1. General heat treatment

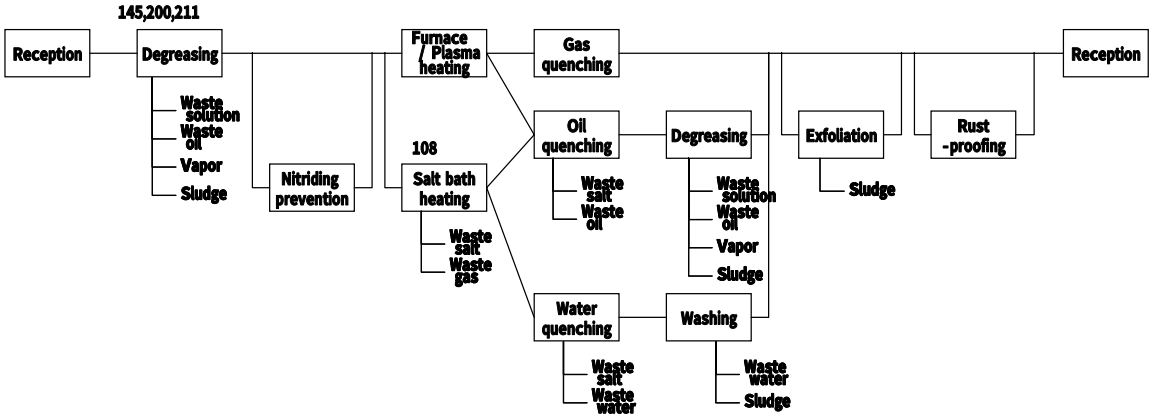


2. Carburizing tempering / annealing

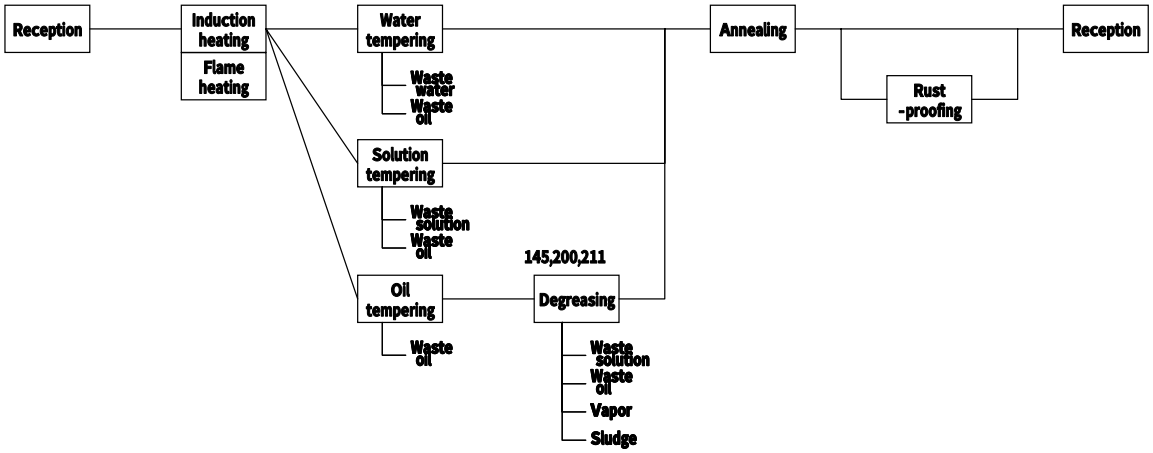


Cabinet Order	Name of specified substance	Purpose
108	inorganic cyanide compounds	Salt bath
145	dichloromethane(methylene dichloride)	Degreasing
200	tetrachloroethylene	Degreasing
211	trichloroethylene	Degreasing
243	barium and its water-soluble compounds	Salt bath
304	boron and its compounds	Carburizing prevention

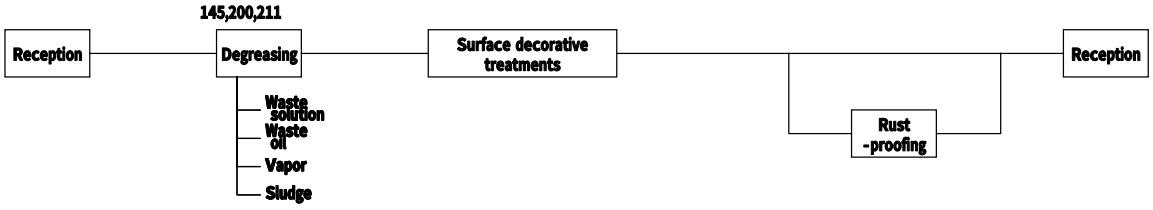
3. Nitriding / Softnitriding



4. Induction tempering / annealing
Flame tempering / annealing



5. Vacuum metallization / Others

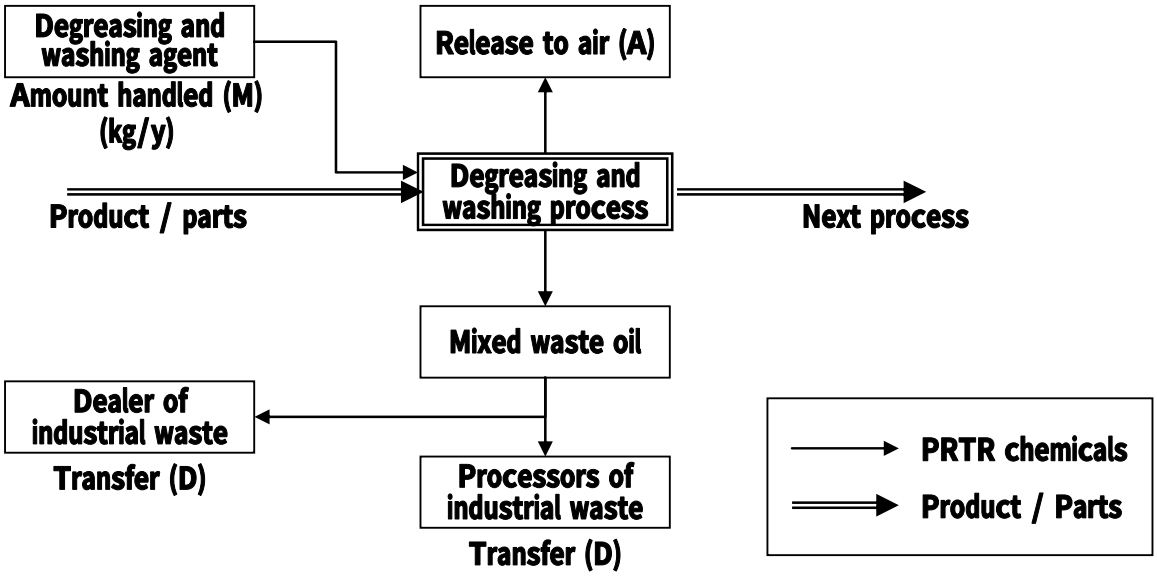


4 Calculation procedures of releases and transfers for PRTR reporting

Case-1

Calculation procedure of releases and transfers of solvents at the degreasing and the steam washing processes using chlorinated organic solvents

Cabinet Order No.	Name of Chemical substance	CAS No.	Composition formula	Molecular weight	Boiling Point (°C)	Vapor pressure (mmHg)
145	Dichloromethane (Methylene chloride)	75-09-2	CH_2Cl_2	84.9	39.75	400 at 24°C
200	Tetrachloroethylene	127-18-4	C_2Cl_4	165.8	121	18.47 at 20°C
211	Trichloroethylene	79-01-6	C_2HCl_3	131.4	87	57.8 at 20°C



The amount handled: M = the amount of chlorinated organic solvents

(1)Release to air

A = M—D—E (others)

(2)Release to water bodies or transfer to sewerage

B = 0

(3)Release to land

C = 0

(4)Transfer as waste

D = the amount of waste consigned to processor of industrial waste x content of chlorinated organic solvent in the waste

(5)Transfer as valueless recycle material (Note 1)

D = the amount of recycled material consigned to processor of industrial waste x content of chlorinated organic solvent in the recycled material

(6)Landfill (controlled type in its own facility)

F = 0

(7)The amount eliminated by treatment

R = 0 (for the case without activated carbon treatment)

Measurement of the content of chlorinated organic solvents in the waste each time is advisable, however, following coefficient may be used on the assumption that the waste is steadily discharged. In case of disposal : 0.40 (with solvent distillation recovery) : 0.75 (without recovery) An approximate content can also be estimated from the density and the boiling point of the wastes.

Note 1.) In case when the waste materials are consigned to a dealer of industrial waste as a valueless material, these are not “materials recycled” but “wastes” so that they are classified as “transfer”.

[Calculation example 1]

The following is a calculation example of the releases and transfers in the process using degreasing/washing equipment.

(Overview of equipments)

- Process:
  degreasing and washing of metal parts
- Equipments used:
  steam-washing type cleaning device (without solvent distillation recovery device and waste water system)
- Waste gas treatment equipment:
  Not provided
- Degreasing/washing agent used:
  washing solvent A (Content of trichloroethylene is 100 %)
- Annual amount of degreasing/washing agent handled:
  3 tons/year
- Contaminated degreasing and washing agent (waste solution) of 1.7 tons/year is delivered to processors of industrial waste (the content is unknown).

1. Calculation of the annual amount of trichloroethylene handled

The annual amount of trichloroethylene handled is calculated by using the amount of degreasing and washing agent used and the content of

trichloroethylene contained in the agent.

(Annual amount of trichloroethylene handled) = (amount of degreasing and washing agent used) x (content in degreasing and washing agent)

= 3 tons x 10^3 x 1.0

= 3,000 kg/y

2. Estimation of the transfers contained in industrial waste

The amount of trichloroethylene transferred is calculated by multiplying the amount of contaminated degreasing and washing agent (waste solution) delivered to processors of industrial waste by the content of trichloroethylene.

Coefficient of 0.75 is used because the content is unknown here.

(Amount of trichloroethylene transferred) = (amount delivered to processors of industrial waste) x (content in waste solution) = 1.7 tons x 10^3 x 0.75

= 1,275 kg/y

3. Estimation of the maximum potential releases

The maximum potential amount released is calculated by subtracting the transfers contained in industrial waste from the annual amount of trichloroethylene handled.

(Maximum potential releases) = (annual amount of trichloroethylene handled) – (transfers contained in industrial waste)

= 3,000 kg/y – 1,275 kg/y

= 1,725 kg/y

4. Estimation of the releases to water bodies

The amount released to water bodies is zero because there is no waste water.

(Amount released to water bodies) = 0 kg/y

5. Estimation of the releases to air

The amount released to air is calculated by subtracting the releases to water bodies from the maximum potential releases.

(Releases to air) = (maximum potential releases)

– (releases to water bodies)

= 1,725 kg/y – 0 kg/y

= 1,725 kg/y

6. Verification of estimation

Amount handled = releases to air + releases to water bodies

+ transfers contained in industrial waste

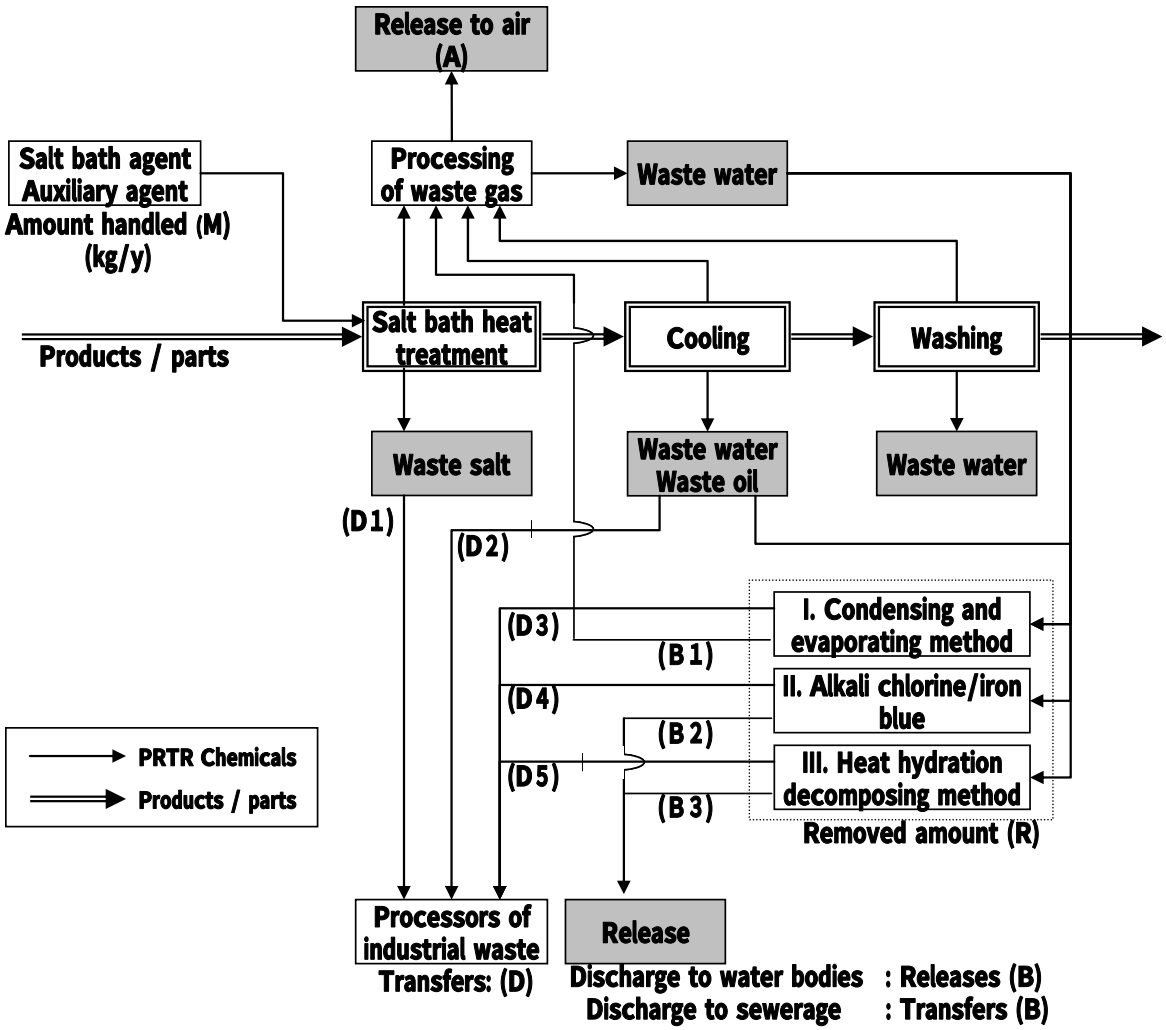
3,000 kg/y = 1,725 kg/y + 0 kg/y + 1,275 kg/y

Material balance calculation provides the same answer.

Case-2

Calculation procedure of releases and transfers of cyanide compounds at the salt bath nitrocarburizing and carbonitriding processes

Cabinet Order No.	Name of Chemical substance	CAS No.	Composition formula	Molecular weight	Conversion factor
108	Sodium cyanide	143-33-9	NaCN	49	0.531
108	Potassium cyanide	151-50-8	KCN	65.1	0.4



The amount handled: M = the amount handled of cyanide containing chemicals

(1)Release to air A = 0

(2)Release to water bodies or transfer to sewerage

B = CN concentration in discharged water after treatment

x amount of discharged water

B1 = waste water treatment method I
= discharged water 0
B2 = waste water treatment method II
= CN concentration x amount of discharged water
B3 = waste water treatment method III
= CN concentration x amount of discharged water

(3)Release to land

C = 0

(4)Transfer as waste

D = the amount of waste consigned to processor of industrial waste
(D1, D2, D3, D4, D5)
x CN contents in the waste

(5)Landfill (controlled type in its own facility)

F = 0

(6)The amount eliminated by treatment

R = the amount of CN eliminated by waste water treatment
waste water treatment method I = 0
waste water treatment method II =
(amount of waste water x CN concentration)
— (amount of discharged water x CN concentration)
waste water treatment method III =
(amount of waste water x CN concentration)
— (amount of discharged water x CN concentration)

(7)The amount of heat decomposition (at salt bath heat treatment process)

H = amount handled (M) x decomposition ratio

(8)The amount of hydrolysis and conversion

Cq = the amount of CN converted to CNO or NH_3 by hydrolysis at water cooling or washing process

(9)The amount of conversion by converting to complex salt

Co = the amount of CN^- reacted with Fe^{++} to convert to ferrocyanide complex salt

[Calculation example 2]

The following is an example of how to estimate the amounts of cyanides released and transferred through the salt bath nitrocarburizing and salt bath carbonitriding processes by using the equipments and under the conditions below.

(Overview of facilities)

- Process: salt bath nitrocarburizing and carbonitriding processes for steel and metal products
- Waste water treatment equipment: alkali chlorine method

+ Prussian blue method

- Salt bath agent used: sodium cyanide (Content: 22%), potassium cyanides (Content: 15%)
- Annual amount of salt bath agent used: 100 tons/year
- Amount of discharged water: 5.0 m^3/day, operation days: 200 days/year (release to water bodies)
- Concentration of cyanides in discharged water: 0.1 ppm (The upper limit value is adopted.)
- Transfers of waste water: 0 m^3/year
- Concentration of cyanides in waste water: 1 %
- Amount of waste salt generated: D1 = 6,000 kg/y, D4 = 54,000 kg/y
- Concentration of cyanides in waste salt: D1 = 15%, D4 = 0%

1. Calculation of the annual amount of cyanides handled

(Annual amount of cyanides handled)

= (annual amount of salt bath nitrocarburizing agent and salt bath carbonitriding agent used) x {(content of sodium cyanide) x (conversion factor) + (content of potassium cyanide) x (conversion factor)}

= 100 tons x (0.22 x 0.531 + 0.15 x 0.400) x 10^3

= 17,682 kg/y

2. Estimation of the releases and transfers of cyanides

(1) Estimation of the releases to air

Wet waste gas processing equipment catches dust and fume of cyanide and catching fluid goes through waste water treatment. Therefore the amount of cyanides released to air is zero.

(2) Estimation of the transfers of cyanides contained in waste

Slagged-off sludge (waste salt) containing cyanide generated in association with the maintaining of nitrocarburizing salt bath and carbonitriding salt bath, and dewatered cake generated from waste water treatment are transferred as waste.

(Annual amount of cyanides transferred)

= (amount of waste salt generated(D1) x concentration of free cyanide) + (amount of waste salt generated(D4) x concentration of free cyanide)

= 6,000 x 0.15 + 54,000 x 0

= 900 kg/y

(3) Estimation of the releases to water bodies

Cyanides are removed by means of waste water treatment to the level below the regulatory standard. Cyanides contained in such discharged water are released to water bodies.

Concentration of the whole cyanides in discharged water can be calculated by using measured value below the regulatory standard.

In case of alkali chlorine method + Prussian blue method.:

($0.1\ mg/L = 0.1 \times 10^{-3}\ kg/m^3$) can be used

(Releases to water bodies)

= concentration in discharged water x amount of discharged water

$= 0.1 \times 10^{-3}\ kg/m^3 \times 5.0\ m^3/day \times 200\ days/year$

$= 0.1\ kg/y$

(4) Estimation of the amount removed

The amount of cyanides removed by means of waste water treatment can be calculated in accordance with the following formula.

(Amount removed)

= (amount of waste water treatment (m^3) x concentration of cyanides in waste water) — (amount of discharged water (m^3) x concentration of cyanides in discharged water)

$= (5.0 \times 200 \times 0.01) \times 10^3 – (5.0 \times 200 \times 0.1 \times 10^{-3})$

$= 9{,}999.9\ kg/y$

(5) The difference between the amount handled and the totaled amount of transfers, releases and removal is regarded as the amount that is converted to other substances through the processes of heat decomposition, hydrolysis and conversion, and complex salt making.

(Amount converted through these processes)

= (amount handled) – (transfers + releases + amount removed)

$= 17{,}682 – (900 + 0.1 + 9{,}999.9)$

$= 6{,}782\ kg/y$

3. Verification of calculation

Amount handled

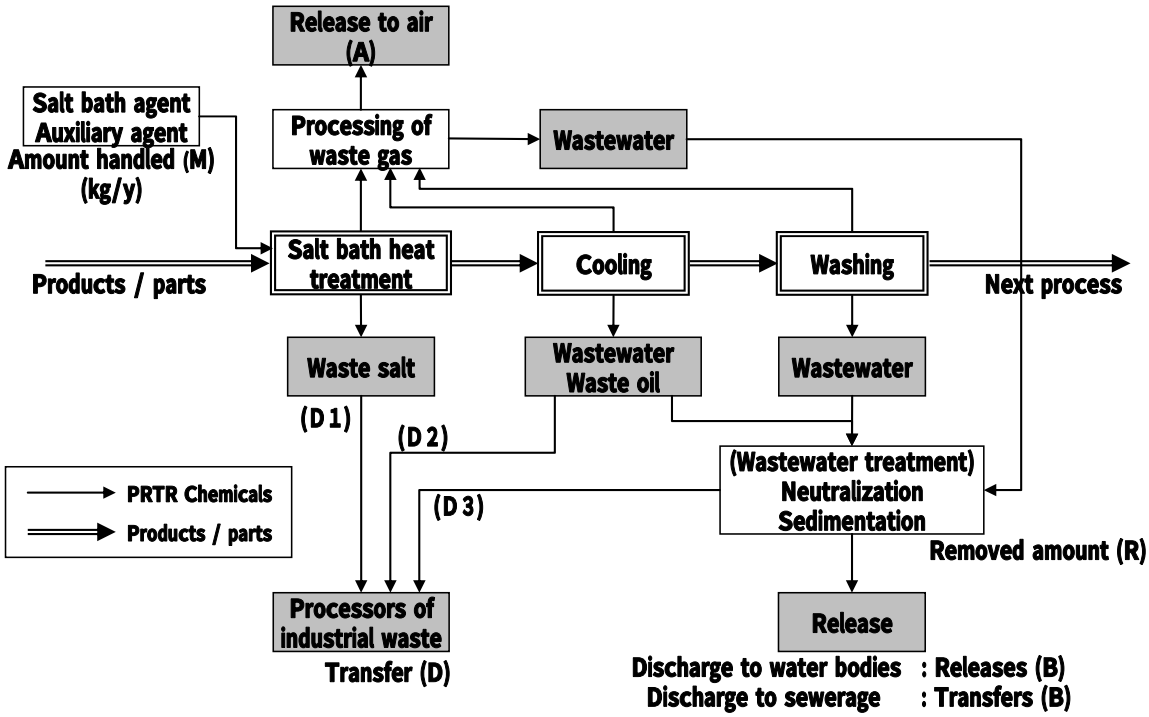
= transfers + releases + amount removed + amount converted

$=17{,}682\ kg/y = 900\ kg/y + 0.1\ kg/y + 9{,}999.9\ kg/y + 6{,}782\ kg/y$

Case-3

Calculation procedure of releases and transfers of barium compounds at the neutral salt bath heat tempering process

Cabinet Order No.	Name of Chemical substance	CAS No.	Composition formula	Molecular weight	Conversion factor
243	Barium chloride	10361-37-2	$BaCl_2$	208.1	0.659



The amount handled: M = the amount handled of barium compounds containing chemicals

(1)Release to air A = 0

(2)Release to water bodies or transfer to sewerage

B = Ba concentration in waste water after treatment x amount of discharged water

(3)Release to land C = 0

(4)Transfer as waste

D = the amount of waste consigned to processor of industrial waste (D1, D2, D3) x water soluble Ba content in the waste

(5)Landfill (controlled type in its own facility)

F = 0

(6)The amount eliminated by treatment

R = the amount of Ba eliminated by waste water treatment

(7)The amount of conversion by chemical reaction

Cq = the amount of Ba converted to water insoluble Ba salt in water quenching and washing processes in the salt bath plant.

[Calculation example 3]

The following is an example of how to estimate the amounts of Barium released and transferred through the neutral salt bath heat tempering process by using the equipments and under the conditions below.

(Overview of facilities)

・Process: neutral salt bath heat tempering processes for steel and metal products

- Waste water treatment equipment: neutralization sedimentation separation
- Salt bath agent: neutral heat treatment salt bath agent:

  Barium chloride (content = 50%)
- Annual amount used of salt bath agent: 5 t/y
- Discharged water: 0.2 m^3/d, operation days: 200 d/y (discharged to water bodies)
- Transfer of waste water: 5 m^3/y
- Barium concentration in waste water: 2%
- Barium concentration in discharged water: 0.1%
- Amount of waste salt: 300 kg/y
- Content of water soluble barium in waste salt: 30%

1. Calculation of the annual amount handled of barium

   Amount handled of barium

   = amount used of neutral heat treatment salt bath agent x content of barium compound x conversion factor

   = 5 x 0.5 x 0.659 x 10^3

   = 1,647.5 kg/y

2. Calculation of releases and transfers of barium

   (1) Estimation of the releases to air

   Wet waste gas processing equipment catches dust and fume of barium compounds and catching fluid goes through waste water treatment. Therefore the amount of barium released to air is zero.

   (2) Estimation of the transfers of barium contained in waste

   Slagged-off sludge (waste salt) containing barium compound that is generated in association with the maintaining of the neutral salt bath heating atomosphere, and waste water are transferred as waste.

   Calculation of transfers of barium per year

   Transfers of barium per year

   = (amount of waste salt x soluble barium concentration)

+ (amount of transfer of waste water x barium concentration)

= (300 x 0.3) + (5 x 10^3 x 0.02) = 90 + 100

= 190 kg/y

(3) Estimation of the releases to water bodies

The amount of barium discharged to water bodies after a neutralization treatment are calculated using a measured value of soluble barium in the discharged water.

Releases to water bodies of soluble barium

= amount of discharged water x concentration of soluble barium

= 0.2 x 200 x 0.001 x 10^3

= 40 kg/y

(4) Estimation of the amount removed

The amount of barium removed by means of waste water treatment can be calculated in accordance with the following formula.

Amount removed

= [amount of waste water treatment (m^3)

x soluble barium concentration in waste water]

—[amount of discharged water (m^3)

x soluble barium concentration in discharged water]

= 0.2 (m^3/d) x 200 (d) x (0.02 — 0.001) x 10^3

= 760 kg/y

(5) The difference between the amount handled and the totaled amount of transfers, releases and removal is regarded as the amount that is converted to insoluble barium salts (barium carbonate, etc).

(Amount converted)

= (amount handled) – (transfers + releases + amount removed)

= 1,647.5 —(190 + 40 + 760) = 657.5 kg/y

3. Verification of calculation

Amount handled

= transfers + releases + amount removed + amount converted

= 190 kg/y + 40 kg/y + 760 kg/y + 657.5 kg/y

= 1,647.5 kg/y

Reference 1

Properties of main PRTR chemicals

Cabinet Order No.	Name of substance	CAS No.	Example of chemicals	Composition formula	Molecular weight	Target elements (M)	Conversion factor
108	Inorganic cyanide (excluding complex salt and cyanate)	151-50-8	Sodium cyanide	KCN	65.1	26.0	0.400
		143-33-9	Potassium cyanide	NaCN	49.0	26.0	0.531
145	Dichloromethane (Methylene chloride)	75-09-2	-	CH_2Cl_2	84.9	84.9	1.000
200	Tetrachloroethylene	127-18-4	-	C_2Cl_4	165.8	165.8	1.000
211	Trichloroethylene	79-01-6	-	C_2HCl_3	131.4	131.4	1.000
243	Barium and its water-soluble compound	10361-37-2	Barium chloride (anhydride)	$BaCl_2$	208.2	137.3	0.659
304	Boron and its compound	1303-86-2	Boric oxide	B_2O_3	69.6	21.6	0.311
		10043-35-3	Boric acid	H_3BO_3	61.8	10.8	0.175