PRTR Estimation Manual

10. Die Casting Industry

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Japan Die Casting Association

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1. Basis of the Calculation of Releases and Transfers

If releases to the environment are identified, the amount of releases or transfers with their path should be evaluated.

Releases	Examples of releases
Amount leaked	Volatilization of the organic solvent etc.
Releases to air	Volatilization of the organic solvent etc.
Releases to water water bodies	Wastewater directly released to the river etc.
Releases to on-site land	Liquid penetrating into the ground etc.
Transfer as waste	Sludge coming out from wastewater treatment sent to industrial waste disposal business or to recycling business as non-valuable waste.
Transfers as recycled material	Aluminum slag sold to recycling business as valuable material is not required to report In case the materials carried out by recycling business as non-valuable material, those are treated transfers same as waste.
Transfers to POTWs	Wastewater discharged to POTWs
Releases toon-site land	Waste disposed by landfills on-site of facility
Amount of the products shipped and consumed	Products such as alloy or additives elements
Amount removed or recovered	Amount decomposed by wastewater treatment etc.

Table 1 Example of Possible Pathways for Releases and Transfers

POTWs: publicly owned treatment works

2. List of PRTR Chemicals in Die Casting Industry

		Melting ar furr	nd holding Iace		asting hine	Proces	sing after	casting
Cabinet Order No.	Name of substance	Base metal	Flux	Operatin g oil, lubricant oil	Mold Iubricant	Shot material	Cutting oil	Cleanin fluid
NO.		Releases to air Waste	Releases to air Waste (Slag)	Releases	Releases to water bodies or to air	Waste	Releases to water bodies Waste	
1	zinc compounds (water-soluble) *							
16	2-amino ethanol						0	
24	n-alkylbenzenesulfonic acid and its salts (alkyl C=10-14)			0	0			
42	ethylene oxide			0	0			
43	ethylene glycol			0	0			
56	1, 2-epoxy propane			0	0			
68	chromium and chromium(III) compounds *					0		
109	2-(Diethylamino)ethanol			0				
145	dichrolomethane							0
211	trichloroethylene							0
227	toluene			0				
230	lead and its compounds *							
231	nickel					0		
242	nonylphenol			0	0			
243	barium and its water-soluble compounds *		-					
283	hydrogen fluoride and its water-soluble salt *		0					
294	beryllium and its compounds *							
304	boron and its compounds *						0	
307	poly(oxyethylene)alkyl ether (alkyl C=2-15)				0			
308	poly(oxyethylene)octyl phenyl ether				0			
309	poly(oxyethylene)nonyl phenyl ether			0	0			
311	manganese and its compounds*			_				
346	molybdenum and its compounds			0				

Table 2 PRTR Chemicals used in Die Casting Plants

Remark symbol:

Specified Class I Designated Chemical Substances

(chemicals without • are designated as Class I Designated Chemical Substances: PRTR chemicals.)

A substance possibly entering into die casting process

A substance rarely contained in the materials used in die casting process

* A substance designated as a substance group, and conversion to the metal elements.

The Table 2 shows the PRTR chemicals used in die casting process and their releases and disposals. These substances listed are based on the list defined by Cabinet Order No. 138 "Cabinet Order for Law Concerning Reporting, etc. of Releases to the Environment of Specific Chemical Substances and Promoting Improvements in Their Management" (hereafter "Cabinet Order"). The list provides the substances which have been known as of July 2000, though this may be added to in the future.

Base metal could contain all the metal elements as impurities. Usually, about 0.1% is the upper limit of the impurity concentration. But the element added as an effective element is often contained more.

Chromium or Nickel of shot material are added as stainless steel.

The items marked with* in Table 2 are designated as substance groups in the Cabinet-Order list and thus the substance name cannot be easily identified. The names and conversion factors of substances currently used in the die-casting plants are shown in Table 3.

	Table 5 Designated Chemica				
Cabinet Order No.	Name of substance	Designated Chemica name and a chemic		Conversio n factor	Conversio n substance
1	zinc compounds (water-soluble) *	Zinc chloride	ZnCl ₂	0.48	Zn
68	chromium and chromium(III) compounds *	Chromium	Cr	1	Cr
230	Lead and its compounds	Lead	Pb	1	Pb
243	Barium and its water-soluble compounds	Barium chloride	BaCl ₂	0.659	Ba
		Barium chloride	BaCl ₂ H ₂ O	0.562	Ва
283	Hydrogen fluoride and its water-soluble salts	Sodium fluoride	NaF	0.452	F
294	Beryllium and its compounds	Beryllium	Be	1	Be
		Hoe potassium fluoride Hoe potassium fluoride	NaBF₄ KBF₄	0.098 0.086	B B
304	Boron and its compounds	Boron	B	0.066	B
304 1	·	Hoe acid	H_3BO_3	0.175	В
		Borax *1	Na ₂ B ₄ O ₇	0.113	В
		Anhydrous borax *2	Na ₂ B ₄ O ₇	0.215	В
311	Manganese and its compounds	Manganese chloride *3	MnCl ₂ 4H ₂ O	0.278	Mn
511	manyanese and its compounds	Manganese dioxide	MnO ₂	0.632	Mn

Table 3 Designated Chemical Substance Conversion Factors

Estimation method of conversion factors:

Example

The conversion factor for zinc chloride $ZnCl_2$ to zinc is calculated as follows: Given the atomic weight of zinc (Zn) of 65.37 and that of chlorine (Cl) of 35.45: Conversion factor = atomic weight of zinc / molecular weight of zinc chloride

= 65.37/ (65.37 + 35.45 x 2) = 0.480

- *1 Borax (Sodium tetraborate (decahydrate))
- *2 Anhydrous borax (tetraboric acid sodium)
- *3 Manganese chloride (II) (tetrahydrate)

3. Die Casting Process Flow





4. Example of Possible Release Path of PRTR Chemicals in Die Casting Process

5. Purchase and Storage of Raw Materials

5.1 Input Materials

All the raw materials (base metal etc.) purchased from outside are included, but the reusable materials from the process.

5.2 Possible Releases of Chemicals

All the raw materials form the leakage in the storage to sludge accumulated in heavy oil tanks should be included.

Base metal	The metals contained as alloy elements may be included. However, these				
	metals are unlikely to be released into the environment as they usually				
	exist in the form of ingot.				
Oil	Machine operating oil, lubricating oil, cutting oil, grease, etc.				
	Possible PRTR chemicals contained in the aboves are:				
	Operating oil Ethyleneglycol, Diethylamino-ethanol				
	Lubricating oil, Grease Moibdenum compound				
	Cutting oil 2 aminoethanol, boron compounds				
	The above substances could be released to the environment.				
	Also, the volatile components might be included.				
Fuel	Electricity, gas, and heavy oil; out of which heavy oil is mostly used.				
	Heavy oil may be leaked from piping etc., whereas the bottom of a heavy				
	oil tank is often covered with sludge, which could be released into the				
	environment via waste (probably containing heavy metals).				
Mold lubricant	Polynonylphenylether etc.				
Organic solvent	Most organic solvents are used as cleaning fluids which could contain				
	dichrolomethane, trichloroethylene, etc. They are likely to volatilize during				
<u></u>	storage.				
Fluxes	Generally, chloride and fluoride, which are stable at room temperature, are				
	used as major component. Thus the leakage of those components unlikely				
Blast media	happens, unless package may be torn.				
Diast media	Metal grains are often used. Leakage is unlikely to happen, unless package				
Cutting / processing tools	may be torn.				
Cutting / processing tools	Metallic band saw, cutting tools or the nonmetallic whetstones are used.				
eaks Rec	overing Impossible to recover				
eaks Rec					
	to POTWs(wash out) Water bodies				
	Releases to ground On-site land				
	Recovered Inhouse recycle Purchase & storage				
ackings materials	→ Disposal → Transfers to off-site				

5.3 Examination of Purchase and Storage Process

5.3.1 Calculation of Releases and Transfers due to Leaks in Purchase and Storage

Fig. 5.3.1 Material Flow in Purchase and St	torage
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Amount of Designated Chemical Substances handled	=	(annual amount purchased stock amount at the end of term + stock amount at the beginning of term x content % x 0.01
Releases to air	=	amount leaked x content % x 0.01
Releases to water bodies	=	amount leaked x content % x 0.01
Releases to on-site land	=	amount leaked x content % x 0.01
Transfers as waste	=	disposal weight x content % x 0.01
Transfers as non-valuable recycled materia	=	disposal weight x content % x 0.01
Transfers to sewage	=	amount leaked x content % x 0.01
Amount of on-site land-fills	=	disposal weight x content % x 0.01
Amount of products shipped and consumed	=	0
Amount removed and recovered	=	0

6. Melting and Holding Furnace

Melting and holding furnace is the process in which base metal (solid metal) is molten in a reverbating furnace, crucible furnace, etc. The molten metal is purified and the elements are added to it during this process.

Input Materials Base metal and recycle	Solid metal containing various metal elements (e.g. Al, Zn, Mg
material	alloy, etc.) as impurities or added elements
	Al, Cu, Si, Mg, Zn, Fe, Mn, Ni, Ti, Pb
	Sn, Cr, V, Bi, Cd, Zr, Ga, Be, B, etc.
	Generally, the elements treated as impurities are 0.1% or less.
	Some alloys contain 10% or more as effective components.
Fuel	Usually heavy oil is used as fuel in the melting furnace process,
	whereas electricity or gas may be used in the holding furnace.
Fluxes	Generally, fluxes are used to remove oxides in the molten metal
	in the process.
	Fluxes may also be used for addition of Na, Ti, B in the form of:
	Chlorides (NaCl, KCl, MgCl ₂ , ZnCl ₂ , etc.),
	Fluorides (NaF, Na ₂ SiF ₆ , AIF ₃ , KBF ₄ , etc.),
	Others (Na ₂ CO ₃ , Na ₂ SO ₄ , etc.).
Exhaust gas	
Releases of Chemica	
Exhaust das	Gases from fuel combustion : (CO, CO2, SO2, NOx, etc.)
Exhaust gas	Gases from fuel combustion : (CO, CO2, SO2, NOx, etc.) Gases from flux processing : Chlorine gas from chloride
Exhaust gas	Gases from flux processing : Chlorine gas from chloride
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6.3 Possible Releases of PRTR Chemicals

Base metal and reusable material	230	Lead and its compound	Copper alloy component
	231	Nickel	Copper alloy component
	294	Beryllium and its compound	Zinc alloy component
	311	Manganese and its compound	Copper alloy component
Fluxes	1	A zincky water-soluble	Flux for zinc alloys
	243	Barium and its water-soluble compound	Flux for Magnesium alloys
	283	Hydrogen fluoride and its water-soluble salt	Flux for aluminum alloys
	311	Mn and its compound	Flux for copper alloys
Slag	Almos	st all the components contained	in a base metal, reusable
Exhaust gas	283	Hydrogen fluoride and its	
-		water-soluble salt	



6.4 Examination of Melting and Holding Furnace Process

6.4.1 Calculation of Releases and Transfers for Base Metal Component.

As for elements of base metal, some are added components and some are dissipated in the melting process. The dissipated elements are usually oxidized and transferred into a slag as oxides.

Slag from the melting process is sent to the industrial waste recycling business. The slag coming out from the melting process is containing normally about 5wt% of the molten base metal.

In general, since there is no significant difference in the metal contents between alloy base metals and the slag. The components of the base metal and the slag are considered equal to the calculation of the transfer amount. However, some elements might be decreased by vaporization, oxidization, or the like, because the liquid metal is exposed to a high temperature in the melting process. For the elements with considerable dissipation in the melting process, it is necessary to count those losses separately.

It is the same for additive elements, but the yields are significantly different by the elements, and therefore the yield of those elements should be counted in the calculation.



Fig.6.4.1 Material Flow in Melting and Holding Furnace Process

In most cases, the disposal of waste from melting process is handled by the one method out of wasting, non-valuable recycling and landfilling.

When a vaporization of elements occurs, the release to air should be calculated separately.

6.4.2 Examples of Calculation: Beryllium (Be) in a Zinc Alloy Melting Process

Beryllium (Be) is not considered to be dissipating in a simple melting process. However, it evaporates during flux processing by heat reaction or the like . A considerable amount of Be is transferred to the slag in the flux processing.

350kg of zinc alloys containing 0.015% Be is melted, and the emission of Be during flux processing is measured as follows.

Measured values Be concentration in the exhaust gas: 1.2 mg/m³, Flow rate of exhaust gas: 25m³/min., Flux processing time: 11minutes, Operation: 240 days/year, Melting amount: 350kg /day

In this case, releases and transfers of beryllium are calculated as follows:

The amount of the PRTR chemicals handled is considered to be equivalent to the annual melting amount

Amount of PRTR chemicals handled

	= melting amount x Be content % x number of operating days
	= 350kg/day x 0.015 x 0.01 x 240days = 13kg/year
Releases to air	= amount discharged from one processing
	x number of operating days
	= $1.2 \text{ mg/m}^3 \times 25 \text{m}^3/\text{min.} \times 11 \text{minutes} \times 240 \text{ days} = 0.08 \text{kg/year}$

Calculation method of the releases to air without actually measured values:				
Releases to air	= amount handled x Be emission factor			
	$= 13 \text{kg/year} \times 0.0063 = 0.08 \text{kg/year}$			
	(Emission factor = 0.0063 is estimated from measured values)			

The amount of slag from one processing is measured as 14.3kg with Be content of 967mg/kg. Slag is transferred to recycling business as non-valuable waste.

Recycle amount of non-valuable waste (amount of transfer)

= (amount of Be contained in slag coming out from one processing)

x (number of operating days)

= 967mg/kg x 14.3kg x 240Day = 3kg/year

Calculation metho	od of the t	ransfers of :	non-valu	able recy	ycled mate	rials without
measured values:						

Recycle amount of non-valuable waste (amount of transfer) = (annual amount of slag) x (Be content in molten base metal) x (Be slag factor) = 14.3kg x 240 Day x 0.015 x 0.01 x 6.5 = 3kg/year (Be slag factor = 6.5 is estimated from measured values)



6.4.3 Calculation of Zinc Chloride Fume (ZnCl₂) from Zinc Alloy Melting Process

350g of flux with 20% zinc is used in one batch with the operation of ten times per day for flux processing in a zinc alloy melting furnace process.

Zinc chloride fume is determined as follows for one batch:

Measured values Zinc chloride concentration in exhausted gas: 140 mg/m³, Flow rate of exhaust gas: 25m³/min., Processing time:11minutes, Number of operating

In this case, releases and transfers of zinc chloride fume are calculated as follows: The amount of PRTR chemicals handled is equivalent to the annual amount of flux used.

Amount of PRTR chemicals

	= (daily amount used) x (zinc chloride content%)
	x (zinc conversion factor) x (number of operating days)
	= 350g x 10 times x 20 x 0.01 x 0.480 x 240 days = 81kg/year
Zinc chlorides fu	me is released to air during flux processing
Releases to air	= (daily emission of zinc chloride) x (zinc conversion factor)
	x (number of operating days)
	$= 140 \text{ mg/m}^3 \times 25 \text{m}^3/\text{min.} \times 11 \times 10 \text{ times } \times 0.480 \times 240 \text{ days}$
	= 44kg/year
lculation method	of the releases of zinc chloride to air without measured values:
Pologo to air	= (amount handlad) x (zing ablaridg amission factor)

Calculation method of the releases of zinc chloride to air without measured values:				
Release to air	= (amount handled) x (zinc chloride emission factor)			
	$= 81 \text{kg/year} \times 0.55$			
	= 45 kg/year			
	(Emission factor = 0.55 is estimated from measured values)			

The zinc chlorideother than release to air are considered to be transferred to slag and thus treated as non-valuable recycled materials or waste.

Transfer of non-valuable recycled materials and waste = (amount handled) - (release to air) = 81kg/year - 44kg/year = 37kg/year



6.4.4 Calculation Method of Releases and Transfers of Fluoride from Flux in Aluminum Alloy Melting Process

HF is often released to air since fluoride is contained in a flux. The HF generation depends on kinds and usage of fluoride, it is desirable to adopt measured values.



In most cases, the disposal of waste from melting process is handled by one of the way out of waste, non-valuable recycle and landfills.

The removal amount for the case of exhaust gas treatment should be calculated separately.

6.4.5 Calculation of HF Gas from Aluminum Alloy Melting (reverberating furnace) Process

In a facility with 240 days/year operating days of the melting furnace, the flux processing is as follows: 10 kg of flux containing 20% of sodium fluoride for a batch, ten times a day for flux processing. HF emission per batch is measured as follows.

measured values HF concentration in exhaust gas: 11 mg/m^3 ,

Exhaust gas flow rate:	96 m ³ /minute,
Flux processing time:	15 min
In this case, releases and transfers of HF is calcu The handling amount of PRTR chemicals is Amount of PRTR chemicals handled = (daily amount used)	the annual amount of flux used.
x (sodium fluoride co	onversion factor)
x (number of operation	ng days)
= 10 kg x 10 times x 20 $= 2,170 kg/year$	0% x 0.01 x 0.452 x 240days
Releases to air = (amount per batch) x (n = $11 \text{mg/m}^3 \times 96 \text{m}^3/\text{min x}$ = 38kg/year	umber of batchper day) 15min x 10 times x 240days

Undecomposed fuluorides other than air release are transferred together with slag as recycled materials.

Amount of non-valuable recycle = (amount handled) - (releases to air) = 2,170 kg - 38 kg = 2,132 kg/year

Calculation of releases to air without measured values:			
Releases: = (amount handled) x (HF emission factor)			
	$= 2,170 \text{kg/year} \times 0.02 = 43 \text{kg/year}$		
(Emission factor = 0.02 is estimated from measured values)			
Non-valuable recycle	= (Amount handled) - (releases) = $2,170$ kg - 43 kg = $2,127$ kg/year		

Fig. 6.4.5 HF Balance in Aluminum Alloy Melting Process



 $\begin{array}{ll} \mbox{Calculation of fluoride other than PRTR chemicals (AlF_3, Na_3AlF_6, Na_2SiF_6 etc.):} \\ \mbox{Amount handled} = 0, releases to air is estimated as amount released (estimation is according to the method described above) \\ \mbox{Amount of non-valuable recycled material} = (amount handled) - (releases to air) \\ \mbox{AlF_3:} & F conversion factor = 0.679 \\ \mbox{Na_3AlF_6:} & F conversion factor = 0.543 \end{array}$

Na₂SiF₆: F conversion factor = 0.606

6.4.6 Calculation of HF Gas from Aluminum Alloy Holding Furnace (Crucible Furnace) Process

In the facility with 240days/year of melting furnace operation, the flux processing is as

follows: 3kg of flux with 20% sodium processing in the holding furr measured values HF concern Exhaust gas f Flux processi	ace. HF emission is meas tration in exhaust gas: low rate:	
In this case, releases and transfers The handling amount of PRT amount of flux used.	R chemicals is assumed to	
Amount of PRTR chemicals I		v 0.01
	ount used) x (content %) : n fluoride conversion facto	
	er of operating days)	01)
	times x 20% x 0.01 x 0.45	52 x 240 days
= 1,106 kg/y		
x (numb	of HF per batch) x (numbe per of operating days)	
= 0.98 mg/r = 0.528kg/y	$m^3 \times 11m^3$ /min. x 12min x	x 17times x 240days
Undecomposed fluorides other than non-valuable recycled materials.		red together with slag as
Amount of non-valuable recycled = (amount l	material nandled) - (releases to air)	= 1,106kg - 0.528kg

= 1,105kg/year

Calculation of the air emission without measured value:			
Release to air	= (amount handled) x (HF emission factor)		
	= 1,106kg/year x $0.0015 = 1.659$ kg/year		
	(Emission factor = 0.0015 is estimated from measured values)		
Amount of non-valua	ble recycled material = amount handled - release to air = 1,106kg - 1.659kg = 1,104kg/year		

 $\begin{array}{ll} \mbox{Calculation of fluorides other than PRTR chemicals (AlF_3, Na_3AlF_6, Na_2SiF_6 etc.):} \\ \mbox{Amount handled} = 0, releases to air is estimated as amount released.} \\ (Estimation is according to the method -described above) \\ \mbox{Amount of non-valuable recycled material} = amount handled - releases to air \\ \mbox{AlF_3:} & F conversion factor = 0.679 \\ \mbox{Na_3AlF_6:} & F conversion factor = 0.543 \\ \mbox{Na_2SiF_6:} & F conversion factor = 0.606 \\ \end{array}$



7. Casting and Die Casting Machine

The process in which the molten metal is injected into the die, cooled and removed as a casting product.

7.1 Input Materials

Operating oil	Applied for a mold clamp of a die-casting machine. Fire-resistant and nonflammable oil, water solution of ethylene glycol, etc. are
Lubricating oil	Used abundantly for wear prevention of various equipment, including a die-casting machine. The various oils are used from liquid oil to half-solid grease depending on the use.
Die lubricant	Used to facilitate the removal of the product from mold. Generally applied by spraying onto the surface of mold. Water is also used for cooling the surface of mold.

7.2 Releases of Chemicals

Water, oil, and mold lubricant mist	Water, oil or mold lubricant sprayed onto the metallic mold surface might be partly released to air as mist, which are not generally be recovered.
Leakage of water, oil, and mold lubricant	Since water, oil and mold lubricant are usually stored in tanks and supplied through pipeline, leakage from those pipes may Lubricant oil, grease or other materials often ooze out and drip. Though could be recoverable by collecting in a pit, but .in many cases left as it is.
Water, oil, and mold lubricant taken out in the machine maintenance etc.	When carrying out maintenance of the equipment, the considerable amount of agent is often taken out, which is collected in a drum etc. and reused.

7.3 Possible Release of PRTR Chemicals

7.5 Possid	le Release of PRTR Chemicals	
24	Alkyl benzenesulfonic acid and its salts	Mold lubricant and lubricating oil
42	Ethylene oxide	Mold lubricant and lubricating oil
43	Ethylene glycol	Operating oil and mold lubricant
56	1,2-epoxypropane	Mold lubricant and lubricating oil
227	Toluene	Lubricating oil
242	Nonylphenol	Mold lubricant and lubricating oil
307	Poly (oxyethylene) alkyl ether	Mold lubricant
	Poly (oxyethylene) octylphenyl ether	Mold lubricant
309	Poly (oxyethylene) nonylphenyl ether	Mold lubricant
346	Molybdenum and its compounds	Lubricant oil
5. Water, oil, mist of molubricant 12. Spent cutting oil 14. Mist of water or organic solvents 6. Leakage of water, oil, mold lubricant	and Flow into pit and recovering	Direct releases to air Air Emission to POTWs(wash out) Water bodies Releases to ground On-site land Vaporization, etc. Air Emission to POTWs(wash out) Water bodies
	Recovered Materials	Waste
	Wastewater treatment	Recovered Materials Transfers to off-site

Effluent to POTWs Water bodies

7.4 Calculations for Metal Casting and Die Casting Machine Process7.4.1 Calculation Method of Releases and Transfers of Mold Lubricant

Since a mold lubricant is sprayed on a surface of die, a part of it is released to air as mist, and an excess amount of the sprayed agent could be released to water bodies. An extremely small amount could adhere to the die casting products and carried to the next process, but the total amount might be released to water bodies.



Since the mold lubricant is usually diluted with water, the amount of stock solution used is considered equal to the amount handled of mold lubricant. Actually, the annual consumption of stock solution would be equivalent to the annual amount purchased.

Mold lubricant adhered to the products could be carried over to the next process, but the amount might be extremely small and negligible. In case wastewater is treated, the waste sludge comes out from the treatment, of which amount should be calculated as transfers.

7.4.2 Calculation Example for Mold Lubricant

In the facility with the operating days of 240/year, the stock solution of mold lubricant containing poly(oxyethylene)alkylether by 5% is used by diluting with water.

Even it is diluted, the calculation is made based on the amount of stock solution used.

Usually, it is considered that "annual amount of stock solution used = annual amount of the stock solution purchased".

With the 400 kg/day consumption of stock solution, releases and transfers of poly(oxyethylene)alkylether are estimated as follows:

Amount of PRTR chemicals handled

Amount handled	= daily amount used x content% x 0.01
	x number of operating days
	= 400 kg/day x 5 x 0.01 x 240 days = 4,800 kg/yr
Or, amount handled	= annual amount of stock solution purchased x content%
	x 0.01
	= annual amount of stock solution purchased $x 5\%$
	x 0.01

The mold lubricant could not be released to air or on-site land, and then whole amount is released to water bodies or transferred to POTWs.

Releases to water bodies = 4,800 kg/yr Or Transfers to POTWs = amount handled = 4,800 kg/yr

In the case of wastewater treatment, it is necessary to estimate the amount removed by the treatment.

Releases to water bodies or transfers to POTWs

= (amount handled) - (amount removed)

Amount removed: (measured values or the following factors as a soluble organic compound)

Plain sedimentation apparatus factor = 0Coagulating sedimentation apparatus factor = 0Microbial degradation apparatus factor = 0.6(The factors are based on the Pilot Project Manual)

Case of wastewater treatment by a coagulating sedimentation apparatus

Amount removed = $4,800 \text{ kg/yr} \times 0 = 0 \text{ kg/yr}$

Released to water bodies or transfers to POTWs

= Amount handled - amount removed

$$= 4,800 - 0 = 4,800 \text{ kg/yr}$$

Sludge coming out from wastewater treatment is sent to industrial waste business.

Amount of waste = Amount removed = 0 kg/yr



7.4.3 Calculation Method of Releases and Transfers of Operating Oil and Lubricant

Operating oil:

Since the operating oil in a die casting machine is usually in a sealed container, it is not necessary to count releases unless leakage occurs or maintenance is carried out. The leak of operating oil is released to water bodies, of which amount would be equivalent to the make up amount.

Lubricant:

Lubricant is used abundantly for the machinery including a die casting machine. Its release is considered to be equivalent to the amount make up.



The transfers of those oils such as operating or lubricant oil for disposing as waste or as non-valuable recycled material are occurred only when such oils are taken out from the machine for maintenance etc.

In case of carrying out of wastewater treatment, releases to water bodies and transfers to POTWs should be calculated by using the amount removed and recovered.

Oily substances (operating oil, grease, etc.)	
Amount removed = make up amount x content % x 0.01 x removal factor	Removal Factor: actually measured figures or following figures for suspended organic
	Plain sedimentation apparatus factor $= 0.2$ Coagulating sedimentation apparatus factor $= 0.7$ Microbial degradation apparatus factor $= 0.6$ (The factors are quoted from the Pilot Project
Water-soluble substances (Ethylene glycol, etc.)	
Amount removed = make up amount x content % x 0.01 x removal factor	Removal Factor: actually measured figures or following figures for suspended organic
	Plain sedimentation apparatus factor = 0 Coagulating sedimentation apparatus factor = 0 Microbial degradation apparatus factor = 0.6 (The factors are quoted from the Pilot Project

Releases to water bodies and transfer to POTWs = make up amount x content % x 0.01 - amount removed

As the removed substance goes into sludge for disposal as waste, it should be added to the waste.

8. Removing Sprue Gate

This process is for the removal of a sprue gate, burr or alike attaching to the casting product.

8.1 Input Materials

Cutting tool Generally, cutting by a press, a band saw machine, etc.

8.2 Releases of Chemicals

Reusable materials Swarf, etc.

Large pieces are kept in stock to be melted and reused with base Fine metal powder by-produced from cutting process of base metal or cutting tool. They are not generally reused inhouse but sent to recycling business.

8.3 Possible Releases of PRTR Chemicals

All metal elements contained in base metal and in a cutting tool



8.4 Examination of Sprue Gate Removal Process

8.4.1 Calculation of Releases and Transfers of Metal Scrap from Sprue Gate Removal

All cut out sprue gates are basically returned to the melting process as reusable materials. A small amount of metal scrap becomes waste.

Fig. 8.4.1 Material Flow of Sprue Gate Removal Process



9. Abrasive Finishing

Abrasive finishing (shotblast) is the process in which metal balls etc. are blasted onto the casting product surface for cleaning, of which the sprue gate was removed in the previous process. The application of this process depends on the type of casting products.

9.1 Input Materials

Metal balls are often used as shot material. The material utilized is straight metal or alloy, such as Zn, Fe, and stainless steel (containing nickel, Cr)

9.2 Releases of Chemicals

The dust are generated of the components of the casting product and shot material.



(contained in stainless steel)

9.3 Possible Releases of PRTR Chemicals

All metallic elements contained in shot material and a casting product

- 68 Chromium
- 231 Nickel (contained in stainless steel)

9.4 Examination of Abrasive Finishing Process

9.4.1 Calculation of Releases and Transfers of Shot Material Components

Since the shot material loses weight by abrasion loss during its use, it is repeated the make up and dispose of shot material. For this reason, the handling amount of PRTR chemicals is considered to be equivalent to the annual amount purchased (the amount of make up).

Fig. 9.4.1 Material Flow of Abrasive Finishing Process

Shot Materials	Abrasive Finishing
	Waste
Amount of PRTR chwmicals handled	 (annual amount purchased stock amount at the end of term stock amount at the beginning of term) x content % x 0.01
Releases to air	= 0
Releases to water bodies	= 0
Releases to on-site land	= 0
Transfers as waste	= disposal weight x content % x 0.01
(Usually amount supplied = disposal weight.)	
Transfers as non-valuable recycled material	= disposal weight x content % x 0.01
Transfers to POTWs	= 0
Amount of on-site land-fills	= 0
Amount of products shipped and consumed	= 0
Amount removed and recovered	= 0

9.4.2 Calculation Example of Abrasive Finishing Process

6,000kg/yr of stainless steel balls (containing 8% Cr, 18% Ni) are purchased and used in the abrasive finishing process. 5,500kg/yr of used stainless steel balls are sent to recycling business as non-valuable recycled material. Also 1,000kg/yr of metal dust coming out from the process is handed over to the waste disposal business as waste. In this case, the releases and transfers are calculated as follows: Since it is repeated the make up and dispose of shot material in the process, the handling amount = the annual amount purchased

Chromium (Cr)

Handling Amount of PRTR Chemicals	= annual amount purchased x content % x 0.01 x chromium conversion factor
	= 6,000kg/yr x8%x0.01x1.000=480kg/yr
Transfers of non-valuable recycled material	 annual amount of non-valuable recycled material x content % x 0.01 x chromium conversion factor 5,500kg/yr x 8 x 0.01 x 1.000 = 440kg/yr

The metallic dust from this process is collected by the dust collector; and all dust is usually recovered. Of 1,000kg/year of metallic dust from this process, stainless steel dust is estimated to be 500kg. Remaining 500kg/yr are from the abrasion of casting product.

Amount of waste	= annual amount purchased - annual amount of non-valuable recycled material
	= 6,000 kg/yr - 5,500 kg/yr = 500 kg/yr
Waste	= amount of waste x content $\%$ x 0.01
	x Cr conversion factor
	= 500kg/yr x 8 x 0.01 x 1.000 = 40kg/yr

Nickel (Ni)

Handling Amount of PRTR Chemicals	 annual amount purchased x content % x 0.01 x Ni conversion factor
	$= 6.000 \text{kg/yr} \times 18 \% \times 0.01 \times 1.000 = 1.080 \text{kg/yr}$
Transfers of non-valuable recycled material	 Annual amount of non-valuable recycled material
	x content % x 0.01x chromium conversion factor
	= 5,500kg/yr x 18% x 0.01 x 1.000 = 990kg/yr

The metallic dust from this process is collected by the dust collector and all dust is usually recovered. Of 1,000kg/year of metallic dust from this process, stainless steel dust is estimated to be 500kg. Remaining 500kg/yr are from the abrasion of casting product.

Amount of waste	= annual amount purchased
	- annual amount of non-valuable recycled material
	= 6,000 kg/yr - 5,500 kg/yr = 500 kg/yr
Waste	= amount of waste x content % x 0.01
	x Ni conversion factor
	= 500kg/yr x 18%x 0.01 x 1.000 = 90kg/yr



10. Heat Treatment

This process is for the improvement of mechanical properties of the die-casting products by heating up or cool down its temperature.

10.1 Input Materials

In most cases, electricity is used for heating.

10.2 Released Materials

The zinc die casting product is heated at 100 $^{\circ}$ C and the aluminum die casting product at 200 - 250 $^{\circ}$ C. There are no releases from this process, because heat treatment is applied before the machining process and objects are not contaminated by oils or others.



11. Machining

Machining is the process for casting products to be faced or drilled with a drill or turning tool etc.

11.1 Input Materials

A drill or turning tool is commonly used as a machining tool. Cutting oil is often applied.

11.2 Releases of Chemicals

The mixtures of swarf or cutting scrap and cutting oil come out of the process. Spent cutting oil is released from the cutting process.

11.3 Possible Releases of PRTR Chemicals

All the elements contained in casting metals and cutting oil components



11.4 Examination of Machining Process

11.4.1 Calculation Method of the Releases and Transfers of Cutting Oil

The cutting oil used in the machining process is generally reused, but some of it becomes waste and is disposed of together with waste metal. Moreover, the water-soluble cutting agent is treated by wastewater treatment and released to water bodies.



Fig. 11.4.1 Material Flow of Cutting Oil and Cutting Agent

In case of wastewater treatment and incineration, the amount ofreleases to air and the amount removed should be calculated.

11.4.2 Calculation Example of Cutting Oil and Cutting Agent Component

25,000kg/yr of cutting oil with 20% sodium borate is used in the machining process, whereas 24,000kg/yr of waste cutting oil is sent to recycling business as non-valuable material. 20,000kg/yr of metal scrap attaching cutting oil (5% of cutting oil deposit efficiency) is sent to waste disposal as waste. And the casting product after machining is washed with water.

In this case, the releases and the transfers of sodium borate are calculated as follows:

The annual amount of cutting oil used is supposed to be equivalent to annual amount purchased.

Amount of PRTR chemicals handled

= annual amount used x content %

x 0.01 x sodium borate conversion factor

= 25,000kg/yr x 20 x 0.01 x 0.215 = 1,075kg/yr

Assuming that the sodium borate concentration of waste cutting oil does not change: Transfer of non-valuable recycled material

= annual amount of non-valuable recycled material

x content % x 0.01 x sodium borate conversion factor

= 24,000kg/yr x 20 x 0.01 x 0.215 = 1,032kg/yr

Assuming that the sodium borate concentration of the cutting oil on the waste metal does not change:

Amount of disposal

= amount of annual waste metals x cutting oil deposit efficiency x sodium borate conversion factor

 $= 20,000 \text{kg/yr} \times 5 \times 0.01 \times 0.215 = 215 \text{kg/yr}$

Sodium borate is released with washing water to remove the remaining oil on casting products.

Case: Sodium borate is released to POTWs or to water bodies

Release to water, or transfer to POTWs = amount handled - amount recycled = 1,075 - 1,032 = 43kg/yr

<u>Case: In house wastewater treatment (the amount removed by treatment is</u> <u>calculated)</u>

The amount removed is based on measured values or the following factors as a soluble Inorganic Compounds.

Plain sedimentation apparatus factor= 0Coagulating sedimentation apparatus factor= 0Microbial degradation apparatus factor= 0.6(The factors are based on the pilot project manual)

Wastewater treatment by coagulating sedimentation method: Amount removed = 0 kg/yr

All the sludge from the wastewater treatment is sent to the industrial waste disposal business as waste.

Amount of disposal = amount removed = 0 kg/yr

Release to water bodies or transfer to POTWs

= amount handled - amount recycled - amount of waste - amount removed

= 1,075 - 1,032 - 0 = 43 kg/yr

Case: waste oil is incinerated in the plant (boron is released to air)

In case the waste oil is not recycled in the above example, but the full amount is incinerated with installing the cyclone as waste gas treatment equipment:

Amount incinerated= annual amount of waste oil x content % x 0.01
x sodium borate conversion factor
= 24,000kg/yr x 20 x 0.01 x 0.215 = 1,032kg/yrAmount released to air= amount incinerated - amount removedAmount removed (based on measured values or the following factors)
Cyclone= 0.6,
Bag filterBag filter= 0.9
Electric dust collector = 0.9
Combustion equipment = 0
ScrubberScrubber= 0.8
(The factors are based on the Pilot Project Manual)

Amount removed = amount incinerated x 0.6 = 1,032kg/yr x 0.6 = 619kg/yr Amount released to air = 1,032kg/yr - 619kg/yr = 413kg/yr

The dust collected by the cyclone is sent to the industrial waste disposal business. Amount of waste = amount removed = 619kg/yr



Fig. 11.4.2 Balance of Waste Oil Treatment

12. Cleaning

This process is for removing the adhered metal swarfs or oils on the products after machining.

12.1 Input Materials

Liquids such as water and organic solvents might be used.

12.2 Releases of Chemicals

Mists of water or organic solvents are released from the process. Wastewater and/or waste organic solvent containing metal swarfs could be discharged.

12.3 Possible Releases of PRTR Chemicals

All the components contained in a casting product and the organic-solvents:

145 Dichrolomethane Cleaning liquor component 211 Trichloroethylene Cleaning liquor component 14. Mist of water or organic solvents
Cleaning liquor component
Cleaning liquo



12.4 Examination of Cleaning Process

12.4.1 Calculation Method of Releases and Transfers of Cleaning Agents

The volatile organic solvents are used and those could be released to air.





Amount of PRTR chemicals handled	 (annual amount purchased stock amount at the end of term stock amount at the beginning of term) x content % x 0.01
Releases to air Transfers as waste liquor Releases to on-site land Transfers as waste Transfers as non-valuable recycled material Transfers to sewage Amount of land-filled on-site Amount of products shipped and consumed Amount removed /recovered	 exhaust gas x concentration effluent x concentration 0 disposal weight x content % x 0.01 disposal weight x content % x 0.01 0 0 0 0 (calculate the amount in case with exhaust gas treatment.)

12.4.2 Calculation Example of Cleaning Agents

9,000kg /yr of trichloroethylene (100%) is used for cleaning of a product in a cleaning tub installed with a mist separator and activated carbon adsorption equipment in a plant. 1,000kg/yr of spent trichloroethylene solvent containing trichloroethylene by 50% is sent to the industrial waste business as waste (non-recycled material).

In this case, the releases and transfers of trichloroethylene are calculated as follows:

Amount of PRTR chemicals handled = 9,000 kg/yrTransfer as waste with 50% trichloroethylene in spent trichloroethylene liquor $= 1,000 \text{kg/yr} \times 50 \times 0.01 = 500 \text{kg/yr}$ Amount of waste

1,000kg/yr of wastewater containing a small amount of trichloroethylene is coming out from the mist separator of cleaning equipment. The concentration of trichloroethylene is far exceeding the water quality standards. Trichloroethylene is then transfers as waste. Transfer of liquor

= 1.000 kg/yr

x trichloroethylene concentration in the spent liquor In case no measured value is available, it could be used the solubility in water of 0.11%.

 $= 1,000 \times 0.11 \times 0.01 = 1 \text{kg/yr}$

Since the release to on-site land would not be realistic and therefore it is supposed to be zero. Then the releases to air should be taken into account. As exhaust gas is treated, the amount removed should be calculated:

Amount releases to air	= amount handled - amount of waste - transfers of waste liquor - amount removed			
The amount removed sho	buld preferably be the measured value. In case no			
observed value is available, it could be used the removal rate of 0.8 for activated				
carbon adsorption equipr	nent (as trichloroethylene is a gaseous organic			
compound).				
Amount removed	= (amount handled - amount of waste			
	- transfer of effluent) x 0.8			
	$= (9,000 - 500 - 1) \times 0.8 = 6,799 \text{kg/yr}$			
In this case				
Amount released to air	= amount handled - amount of waste			
	- transfer of effluent - amount removed			
	= 9,000 - 500 - 1 - 6,799 = 1,700kg/yr			

As the spent activated carbon contains trichloroethylene, then the amount of transfers as waste should include the amount of trichloroethylene contained in both waste liquor and spent activated carbon.

Finally,

Amount of waste = 500 + 6,799 = 7,299 kg/yr.

Fig. 12.4.2 Material Balance of Trichloroethylene



13. Finished Products

Products which can be shipped as final products or assembled as finished parts.

13.1 Input Materials

Products are protected by packing materials (plastic, paper, wood, etc.).

13.2 Releases of Chemicals

The excess unused packing material is usually handed over to the waste treatment business without further processing.

14. Shipment

Delivering finished products to users etc.

15. References

The amount of the PRTR chemicals removed by wastewater or exhaust gas treatment can be estimated by referring to the following table in case that no measured values are available. The removed chemicals contained in sludge or collected dust, etc. are equivalent to the transfer as waste.

	Substances		Substances	
	suspended	suspended	Soluble	Soluble
The kind of processing unit	Inorganic	Organic	Inorganic	Organic
	Compounds	compound	Compounds	compound
Plain sedimentation equipment	0.4(0)	0.2(0)	0(0)	0(0)
Coagulation sedimentation equipment	0.8(0)	0.7(0)	0(0)	0(0)
Biodegradation equipment (Usually, an activated sludge method)	0.7(0)	0.7(0.3)	0(0)	0.6(0.4)
Membrane filter	1.0(0)	1.0(0)	0(0)	0(0)
Activated-carbon adsorption equipment	0.1(0)	0.1(0)	0.2(0)	0.8(0)

Table 4 Removal Factors of Wastewater Treatment
(based on PRTR Pilot Project Manual in 2000FY)

Figures in brackets shows "Harmless Rate"

In the die casting plants, the substances in wastewater are often treated by using the coagulation sedimentation method.

Example of substances used in die casting plants

Suspended organic compound
Soluble Inorganic compound
Soluble organic compound

Mold lubricant, lubricating oil, etc. Boron in a cutting agent Ethylene glycol, mold lubricant

Table 5 Removal Factors of Exhaust Gas Treatment(based on PRTR Pilot Project Manual in 2000FY)

		Substances	
The kind of processing unit	metallic dust	Gaseous	Gaseous
		organic	inorganic
		compound	compound
Cyclone	0.6(0)	0(0)	0(0)
Bug filter	0.9(0)	0(0)	0(0)
Electric dust collector	0.9(0)	0(0)	0(0)
Incinerator	0(0)	0.995(0.995)	0(0)
Absorption Tower (Scrubber)	0.8(0)	0(0)	0.8(0.8)
Activated carbon adsorption equipment	0.1(0)	0.8(0)	0.5(0)

Figures in brackets shows "Harmless Rate"

Example of substances used in die-casting plants

Metallic dust	Metal powder dust, such as from a sprue gate
	removal process and an abrasive finishing process
Gaseous organic compound	Cleaning agents (organic solvent)
Gaseous inorganic compound	HF gas from melting furnace

Calculation of the removal factors for the case that exhaust gas is treated by two kinds of treatment equipment connected in series

Supposing R_1 is the removal factor of the first device and R_2 is for the second one, the

overall removal factor R is calculated by the following equation.

 $R = R_1 + (1 - R_1) \times R_2$

<Example> In case that suspended organic compounds (lubricant oil etc.) are treated by the activated sludge method for the first step and the coagulation sedimentation method for the second step:

$$R = 0.7 + (1 - 0.7) \times 0.7$$

= 0.7 + 0.21
= 0.91

The amount of the organic solvent released to air in a cleaning process can be estimated by referring to the factors in the following table in case with no available measured values.

Table 6 Emission Factors for Cleaning Process (based on PRTR Pilot Project
Manual in 2000FY)

	/
Organic solvent	Air emission factor
Trichloroethylene	0.838
Tetrachloroethylene	0.79
Dichrolomethane	0.891

A small amount of organic solvents in a cleaning process contacting with water could transfer to water. The transfer is estimated by referring to the solubility in the following table in case the measured value is not available.

Table 7 Solubility in Water of Organic Solvent

Tuble 7 Solubility in Water of Organie Solvent		
Solubility in water		
0.11%		
0.02%		
2.00%		

Emission factors used for calculation for the case with no available measured value:

Substances Released	Process and Release		Emission factor	
Beryllium Beryllium Zinc chloride Hydrogen fluoride Hydrogen fluoride	Zinc melting Zinc melting products Zinc melting Aluminum melting, Melting furnace (reverberating furnace) Aluminum melting, Holding furnace (crucible furnace)	Air Waste and recycling Air Air Air	0.0063 6.5 0.55 0.02 0.0005	

Table 8 List of Emission Factors

No.	Process	Process Flow	Input Chemicals	PRTR Chemicals
1	Purchase of Raw Materials: An alloy ingot for casting is a major material	OIL Chemicals Ingot LPG	Main material: alloy Sub-materials: oil, gas, cutting agent, etc.	None except for leakage by accident
2	Melting Process Fresh alloy and recycled metals in a factory are molten in reverberating furnace or crucible furnace etc.	Exhaust Gas	[1] Al alloy, Zn alloy, Mg alloy etc.[2] heavy oil, gas	Exhaust Gas Emission (CO, CO ₂ , SO ₂ , Nox, etc.)
3	Flux Treatment In order to remove oxides and gas in the molten metal, a flux treatment is applied to molten metal for deoxidization or degassing treatment, if needed.	[3] Flux Emission Dross/Slag Furnace	[3] Flux Flux Composition : NaCl, KCl, MgCl ₂ , ZnCl ₂ , BaCl ₂ , BeCl, MnCl ₂ ,MnO ₂ ,KBF ₄ , NaBF ₄ , NaF, AlF ₃ , Na ₂ SiF ₆ , Borax, Boric acid	Exhaust Gas Emission from Furnace(Chloride gas, fluorine gas) Dross, slug (components contained in base metal, reusable material, and flux) Ni, Be, Mn, F

Table 9. Process Flow of Die Casting Process



No.	Process	Process Flow	Input Chemicals	PRTR Chemicals
5	Sprue Gate Removal: Removing sprue gate, burr etc. other than the product by pressing mold etc	Product CUT Return to process [2]		Cut off materials such as sprue gate etc. are recycled for reuse.
6	Abrasion Finishing: For the removal of small burrs and improvement in adhesion of painting, metal balls (abrasion material) are shot on the surface of products.	Abrasion machine	[7] Abrasion material (zinc ball, material made by cutting aluminum or stainless wire)	Dust in [7] and [1] is collected by dust collector Powdery pieces of worn [7] and [1]
7	Heat Treatment: For improving the dimensional stability or removal of internal stress, heat treatment at 100-250°C for 2-4Hr is applied to the products.	Heat treatment electric furnace	[8] (electricity)	Nothing in particular (treatment temperature of not higher than 250°C)

No.	Process	Process Flow	Input Chemicals	PRTR Chemicals
8	Machining: Machining of products such as facing, drilling, tapping etc.	Machining tool	[9] Cutting agent (oil, water soluble) (boron and its compound, 2-amino ethanol)	Wastewater, waste oil Waste oil attached to alloy turnings and degraded
9	Cleaning: Products are cleaned to remove contamination or cutting oil on their surface.	Cleaning [10] Apparatus	[10] Organic solvent (trichloroethylene, dichloromethane)	Organic solvent mist (the same as the left)

: Release to air : Release to water compartment : Transfer (non-valuable recycled material) or waste generated