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.

### Table 1 Example of Possible Pathways for Releases and Transfers

<table>
<thead>
<tr>
<th>Pathway Description</th>
<th>Pathway Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>POTWs: publicly owned treatment works</td>
<td>POTWs: publicly owned treatment works</td>
</tr>
</tbody>
</table>

POTWs: publicly owned treatment works
2. List of PRTR Chemicals in Die Casting Industry

Table 2 PRTR Chemicals used in Die Casting Plants

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Releases to Environment</th>
<th>Disposals</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Base metal</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

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 3 Designated Chemical Substance Conversion Factors**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Conversion Factor</th>
<th>Estimation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc chloride ZnCl₂ to zinc</td>
<td>0.480</td>
<td>Example: The conversion factor for zinc chloride ZnCl₂ 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)² = 0.480</td>
</tr>
<tr>
<td>*1 Borax (Sodium tetraborate (decahydrate))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*2 Anhydrous borax (tetraboric acid sodium)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*3 Manganese chloride (II) (tetrahydrate)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.

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

6.1 Input Materials

<table>
<thead>
<tr>
<th>Input Materials</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.2 Releases of Chemicals

<table>
<thead>
<tr>
<th>Releases of Chemicals</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.3 Possible Releases of PRTR Chemicals

<table>
<thead>
<tr>
<th>Possible Releases of PRTR Chemicals</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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](image-url)
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.

<table>
<thead>
<tr>
<th>Beryllium (Be) content in slag</th>
<th>Amount of Beryllium emitted to air</th>
</tr>
</thead>
<tbody>
<tr>
<td>967mg/kg</td>
<td>14.3kg</td>
</tr>
</tbody>
</table>

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

- **Amount of PRTR chemicals handled**
  \[
  \text{Amount of PRTR chemicals handled} = \text{melting amount} \times \text{Be content} \times \text{number of operating days} = 350\text{kg/day} \times 0.015 \times 0.01 \times 240\text{days} = 13\text{kg/year}
  \]

- **Releases to air**
  \[
  \text{Releases to air} = \text{amount discharged from one processing} \times \text{number of operating days} = 1.2 \text{mg/m}^3 \times 25\text{m}^3/\text{min.} \times 11\text{minutes} \times 240\text{days} = 0.08\text{kg/year}
  \]

**Calculation method of the releases to air without actually measured values:**

\[
\text{Releases to air} = \text{amount handled} \times \text{Be emission factor} = 13\text{kg/year} \times 0.0063 = 0.08\text{kg/year}
\]

(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)**
  \[
  \text{Recycle amount of non-valuable waste} = (\text{amount of Be contained in slag coming out from one processing}) \times \text{(number of operating days)} = 967\text{mg/kg} \times 14.3\text{kg} \times 240\text{Day} = 3\text{kg/year}
  \]

**Calculation method of the transfers of non-valuable recycled materials without measured values:**

\[
\text{Recycle amount of non-valuable waste (amount of transfer)} = \text{(annual amount of slag)} \times \text{(Be content in molten base metal)} \times \text{(Be slag factor)} = 14.3\text{kg} \times 240\text{Day} \times 0.015 \times 0.01 \times 6.5 = 3\text{kg/year}
\]

(Be slag factor = 6.5 is estimated from measured values)
6.4.3 Calculation of Zinc Chloride Fume (ZnCl$_2$) 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:

\[
\text{Amount of PRTR chemicals} = \text{daily amount used} \times \text{zinc chloride content%} \times \text{zinc conversion factor} \times \text{number of operating days}
\]

\[
= 350\, \text{g} \times 10 \times 0.01 \times 0.480 \times 240 = 81\, \text{kg/year}
\]

Zinc chlorides fume is released to air during flux processing.

\[
\text{Releases to air} = \text{daily emission of zinc chloride} \times \text{zinc conversion factor} \times \text{number of operating days}
\]

\[
= 140\, \text{mg/m}^3 \times 25\, \text{m}^3/\text{min.} \times 10 \times 0.480 \times 240 = 44\, \text{kg/year}
\]

The zinc chloride other 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

\[
= \text{amount handled} - \text{release to air}
\]

\[
= 81\, \text{kg/year} - 44\, \text{kg/year} = 37\, \text{kg/year}
\]
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.

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/m³,
Exhaust gas flow rate: 96 m³/minute,
Flux processing time: 15 min

In this case, releases and transfers of HF is calculated as follows:
The handling amount of PRTR chemicals is the annual amount of flux used.

Amount of PRTR chemicals handled
= (daily amount used) □ (content%) □ 0.01
□ (sodium fluoride conversion factor)
□ (number of operating days)
= 10kg □ 10 times □ 20% □ 0.01 □ 0.452 □ 240 days
= 2,170kg/year

Releases to air = (amount per batch) □ (number of batch per day)
= 11mg/m³ □ 96m³/min □ 15min □ 10 times □ 240 days
= 38kg/year

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 - 38kg = 2,132 kg/year

Calculation of releases to air without measured values:
Releases:
= (amount handled) □ (HF emission factor)
= 2,170kg/year □ 0.02 = 43kg/year
(Emission factor = 0.02 is estimated from measured values)

Non-valuable recycle = (Amount handled) - (releases)
= 2,170kg - 43 kg
= 2,127kg/year

Calculation of fluoride other than PRTR chemicals (AlF₃, Na₃AlF₆, Na₂SiF₆ etc.):
Amount handled = 0, releases to air is estimated as amount released (estimation is according to the method described above)
Amount of non-valuable recycled material = (amount handled) - (releases to air)
AlF₃: F conversion factor = 0.679
Na₃AlF₆: F conversion factor = 0.543
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 240 days/year of melting furnace operation, the flux processing is as
follows:

3kg of flux with 20% sodium fluoride per batch, 17 times per day of flux processing in the holding furnace. HF emission is measured as follows:

- measured values HF concentration in exhaust gas: 0.98 mg/m³,
- Exhaust gas flow rate: 96 m³/minute,
- Flux processing time: 12 min

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

The handling amount of PRTR chemicals is assumed to be equivalent to the annual amount of flux used.

Amount of PRTR chemicals handled

\[
\text{Amount of PRTR chemicals handled} = (\text{daily amount used}) \times (\text{content \%}) \times 0.01 \times (\text{sodium fluoride conversion factor}) \times (\text{number of operating days})
\]

\[
= 3\text{kg} \times 17\text{times} \times 20\% \times 0.01 \times 0.452 \times 240\text{days}
\]

\[
= 1,106\text{kg/year}
\]

Release to air = (amount of HF per batch) \times (number of batch per day) \times (number of operating days)

\[
= 0.98 \text{mg/m}^3 \times 11\text{m}^3/\text{min} \times 12\text{min} \times 17\text{times} \times 240\text{days}
\]

\[
= 0.528\text{kg/year}
\]

Undecomposed fluorides other than air releases are transferred together with slag as non-valuable recycled materials.

Amount of non-valuable recycled material

\[
= (\text{amount handled}) - (\text{releases to air}) = 1,106\text{kg} - 0.528\text{kg}
\]

\[
= 1,105\text{kg/year}
\]

Calculation of the air emission without measured value:

Release to air = (amount handled) \times (HF emission factor)

\[
= 1,106\text{kg/year} \times 0.0015 = 1.659\text{kg/year}
\]

(Emission factor = 0.0015 is estimated from measured values)

Amount of non-valuable recycled material

\[
= \text{amount handled} - \text{release to air} = 1,106\text{kg} - 1.659\text{kg}
\]

\[
= 1,104\text{kg/year}
\]

Calculation of fluorides other than PRTR chemicals (AlF₃, Na₃AlF₆, Na₂SiF₆ etc.):

Amount handled = 0, releases to air is estimated as amount released.

(Estimation is according to the method -described above)

Amount of non-valuable recycled material = amount handled - releases to air

- AlF₃: F conversion factor = 0.679
- Na₃AlF₆: F conversion factor = 0.543
- Na₂SiF₆: F conversion factor = 0.606
Fig. 6.4.6 HF Balance for Aluminum Alloy Casting
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

7.2 Releases of Chemicals

7.3 Possible Release of PRTR Chemicals

7.4 Calculations for Metal Casting and Die Casting Machine Process
7.4.1 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

\[
\text{Amount handled} = \text{daily amount used} \times \text{content\%} \times 0.01 \\
= 400 \, \text{kg/day} \times 0.01 \times 240 \, \text{days} = 4,800 \, \text{kg/yr}
\]

Or, amount handled = annual amount of stock solution purchased \times 5\%

\[
= \text{annual amount of stock solution purchased} \times 0.01
\]
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 = 0
  Coagulating sedimentation apparatus factor = 0
  Microbial 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 kg/yr  \[0 = 0 \text{ kg/yr}\]
Released to water bodies or transfers to POTWs
= Amount handled - amount removed
= 4,800 - 0 = 4,800 kg/yr
Sludge coming out from wastewater treatment is sent to industrial waste business.
Amount of waste = Amount removed = 0 kg/yr

Fig. 7.4.2 Balance of Mold Lubricant

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.

Releases to water bodies and transfer to POTWs = make up amount \( \times \) content \( \times \) 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

8.2 Releases of Chemicals

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.

9.3 Possible Releases of PRTR Chemicals
All metallic elements contained in shot material and a casting product

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

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)**

<table>
<thead>
<tr>
<th>Material</th>
<th>Handling amount</th>
<th>Annual amount purchased</th>
<th>Annual amount of non-valuable recycled material</th>
<th>Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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
= 6,000kg/yr - 5,500kg/yr = 500kg/yr

Waste = amount of waste □content % □0.01 □Cr conversion factor
= 500kg/yr □8 □0.01 □1.000 = 40kg/yr

**Nickel (Ni)**

<table>
<thead>
<tr>
<th>Material</th>
<th>Handling amount</th>
<th>Annual amount purchased</th>
<th>Annual amount of non-valuable recycled material</th>
<th>Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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
= 6,000kg/yr - 5,500kg/yr = 500kg/yr

Waste = amount of waste □content % □0.01 □Ni conversion factor
= 500kg/yr □18% □0.01 □1.000 = 90kg/yr

Fig. 9.4.2 Ni and Cr Balance
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 °C and the aluminum die casting product at 200 - 250 °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.
In case of wastewater treatment and incineration, the amount of releases 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
\[ = \text{annual amount used} \times \text{content} \%
\]  
\[ = 25,000\text{kg/yr} \times 0.20 \times 0.215 = 1,075\text{kg/yr} \]

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

Transfer of non-valuable recycled material
\[ = \text{annual amount of non-valuable recycled material} \times \text{content} \%
\]  
\[ = 24,000\text{kg/yr} \times 0.01 \times 0.215 = 1,032\text{kg/yr} \]
Amount of disposal
\[ = \text{amount of annual waste metals} \times \text{cutting oil deposit efficiency} \times \text{sodium borate conversion factor} \]
\[ = 20,000\text{kg/yr} \times 5 \times 0.01 \times 0.215 = 215\text{kg/yr} \]

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
\[ = \text{amount handled - amount recycled} = 1,075 - 1,032 \]
\[ = 43\text{kg/yr} \]

**Case: In house wastewater treatment (the amount removed by treatment is calculated)**
The amount removed is based on measured values or the following factors as a soluble Inorganic Compounds.
- Plain sedimentation apparatus factor = 0
- Coagulating sedimentation apparatus factor = 0
- Microbial degradation apparatus factor = 0.6
(The factors are based on the pilot project manual)

Wastewater treatment by coagulating sedimentation method: Amount removed = 0\text{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\text{kg/yr}
Release to water bodies or transfer to POTWs
\[ = \text{amount handled - amount recycled - amount of waste - amount removed} \]
\[ = 1,075 - 1,032 - 0 = 43\text{kg/yr} \]

**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 \times \text{content \%} \times 0.01 \times \text{sodium borate conversion factor}
\[ = 24,000\text{kg/yr} \times 20 \times 0.01 \times 0.215 = 1,032\text{kg/yr} \]
Amount released to air = amount incinerated - amount removed
Amount removed (based on measured values or the following factors)
- Cyclone = 0.6,
- Bag filter = 0.9
- Electric dust collector = 0.9
- Combustion equipment = 0
- Scrubber = 0.8
(The factors are based on the Pilot Project Manual)
Amount removed = amount incinerated \( \div 0.6 \)
= 1,032kg/yr \( \div 0.6 \) = 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:

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.

Fig. 12.4.1 Material Flow of Cleaning Process
12.4.2 Calculation Example of Cleaning Agents

9,000 kg/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. 1,000 kg/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/yr
Transfer as waste with 50% trichloroethylene in spent trichloroethylene liquor

Amount of waste = 1,000 kg/yr
\[ \frac{50}{100} \times 1,000 = 500 \text{ kg/yr} \]

1,000 kg/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
\[ \frac{100}{100} \times 1,000 = 1,000 \text{ kg/yr} \]

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 should 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 equipment (as trichloroethylene is a gaseous organic compound).

Amount removed = (amount handled - amount of waste - transfer of effluent) \times 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
\[ 9,000 - 500 - 1 - 6,799 = 1,700 \text{ kg/yr} \]
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,

\[ \text{Amount of waste} = 500 + 6,799 = 7,299 \text{kg/yr}. \]

**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.

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

<table>
<thead>
<tr>
<th>Chemical Type</th>
<th>Removal Factor 1</th>
<th>Removal Factor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TVTQFOEFE</td>
<td>TVTQFOEFE</td>
<td>TVTQFOEFE</td>
</tr>
<tr>
<td>IFLOPJEF</td>
<td>IFLOPJEF</td>
<td>IFLOPJEF</td>
</tr>
<tr>
<td>5IFLJOEPGQSPDFT</td>
<td>5IFLJOEPGQSPDFT</td>
<td>5IFLJOEPGQSPDFT</td>
</tr>
<tr>
<td>OJU*OPSHBOJD</td>
<td>OJU*OPSHBOJD</td>
<td>OJU*OPSHBOJD</td>
</tr>
<tr>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
</tr>
<tr>
<td>0SHBOJD</td>
<td>0SHBOJD</td>
<td>0SHBOJD</td>
</tr>
<tr>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
</tr>
<tr>
<td>1MBJOTFE</td>
<td>1MBJOTFE</td>
<td>1MBJOTFE</td>
</tr>
<tr>
<td>HSBEBUJPOF</td>
<td>HSBEBUJPOF</td>
<td>HSBEBUJPOF</td>
</tr>
<tr>
<td>RVJQNU</td>
<td>RVJQNU</td>
<td>RVJQNU</td>
</tr>
<tr>
<td>$PBHVMBUJPOT</td>
<td>$PBHVMBUJPOT</td>
<td>$PBHVMBUJPOT</td>
</tr>
<tr>
<td>JPEF</td>
<td>JPEF</td>
<td>JPEF</td>
</tr>
<tr>
<td>6TVBMMZ</td>
<td>6TVBMMZ</td>
<td>6TVBMMZ</td>
</tr>
<tr>
<td>BOBDUJWBUFET</td>
<td>BOBDUJWBUFET</td>
<td>BOBDUJWBUFET</td>
</tr>
<tr>
<td>MVEHFNFUIPEFP</td>
<td>MVEHFNFUIPEFP</td>
<td>MVEHFNFUIPEFP</td>
</tr>
<tr>
<td>.FNCSBOFGJMUFS</td>
<td>.FNCSBOFGJMUFS</td>
<td>.FNCSBOFGJMUFS</td>
</tr>
<tr>
<td>*CTPSQUJPO5PXFS</td>
<td>*CTPSQUJPO5PXFS</td>
<td>*CTPSQUJPO5PXFS</td>
</tr>
<tr>
<td>4DSVCCFS</td>
<td>4DSVCCFS</td>
<td>4DSVCCFS</td>
</tr>
<tr>
<td>DUJWBUFEDBSCPOBETPS</td>
<td>DUJWBUFEDBSCPOBETPS</td>
<td>DUJWBUFEDBSCPOBETPS</td>
</tr>
<tr>
<td>4VCTUBODFT</td>
<td>4VCTUBODFT</td>
<td>4VCTUBODFT</td>
</tr>
</tbody>
</table>

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: Mold lubricant, lubricating oil, etc.
- Soluble Inorganic compound: Boron in a cutting agent
- Soluble organic compound: Ethylene glycol, mold lubricant

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

<table>
<thead>
<tr>
<th>Chemical Type</th>
<th>Removal Factor 1</th>
<th>Removal Factor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TVTQFOEFE</td>
<td>TVTQFOEFE</td>
<td>TVTQFOEFE</td>
</tr>
<tr>
<td>IFLOPJEF</td>
<td>IFLOPJEF</td>
<td>IFLOPJEF</td>
</tr>
<tr>
<td>5IFLJOEPGQSPDFT</td>
<td>5IFLJOEPGQSPDFT</td>
<td>5IFLJOEPGQSPDFT</td>
</tr>
<tr>
<td>OJU*OPSHBOJD</td>
<td>OJU*OPSHBOJD</td>
<td>OJU*OPSHBOJD</td>
</tr>
<tr>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
</tr>
<tr>
<td>0SHBOJD</td>
<td>0SHBOJD</td>
<td>0SHBOJD</td>
</tr>
<tr>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
<td>DPNQPVOE</td>
</tr>
<tr>
<td>1MBJOTFE</td>
<td>1MBJOTFE</td>
<td>1MBJOTFE</td>
</tr>
<tr>
<td>HSBEBUJPOF</td>
<td>HSBEBUJPOF</td>
<td>HSBEBUJPOF</td>
</tr>
<tr>
<td>RVJQNU</td>
<td>RVJQNU</td>
<td>RVJQNU</td>
</tr>
<tr>
<td>$PBHVMBUJPOT</td>
<td>$PBHVMBUJPOT</td>
<td>$PBHVMBUJPOT</td>
</tr>
<tr>
<td>JPEF</td>
<td>JPEF</td>
<td>JPEF</td>
</tr>
<tr>
<td>6TVBMMZ</td>
<td>6TVBMMZ</td>
<td>6TVBMMZ</td>
</tr>
<tr>
<td>BOBDUJWBUFET</td>
<td>BOBDUJWBUFET</td>
<td>BOBDUJWBUFET</td>
</tr>
<tr>
<td>MVEHFNFUIPEFP</td>
<td>MVEHFNFUIPEFP</td>
<td>MVEHFNFUIPEFP</td>
</tr>
<tr>
<td>.FNCSBOFGJMUFS</td>
<td>.FNCSBOFGJMUFS</td>
<td>.FNCSBOFGJMUFS</td>
</tr>
<tr>
<td>*CTPSQUJPO5PXFS</td>
<td>*CTPSQUJPO5PXFS</td>
<td>*CTPSQUJPO5PXFS</td>
</tr>
<tr>
<td>4DSVCCFS</td>
<td>4DSVCCFS</td>
<td>4DSVCCFS</td>
</tr>
<tr>
<td>DUJWBUFEDBSCPOBETPS</td>
<td>DUJWBUFEDBSCPOBETPS</td>
<td>DUJWBUFEDBSCPOBETPS</td>
</tr>
<tr>
<td>4VCTUBODFT</td>
<td>4VCTUBODFT</td>
<td>4VCTUBODFT</td>
</tr>
</tbody>
</table>

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.

\[
R = R_1 + (1 - R_1) R_2
\]

<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:

\[
R = 0.7 + (1 - 0.7) R_2
\]

\[
= 0.7 + 0.21
\]

\[
= 0.91
\]

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)**

<table>
<thead>
<tr>
<th>Emission Factors</th>
<th>List of Emission Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**

<table>
<thead>
<tr>
<th>Solubility in Water</th>
<th>List of Solubility in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

**Table 8 List of Emission Factors**

<table>
<thead>
<tr>
<th>List of Emission Factors</th>
<th>List of Emission Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

32
Table 9. Process Flow of Die Casting Process

<table>
<thead>
<tr>
<th>No.</th>
<th>Process</th>
<th>Process Flow</th>
<th>Input Chemicals</th>
<th>PRTR Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>Purchase of Raw Materials:</strong></td>
<td></td>
<td>Main material: alloy</td>
<td>None except for leakage by accident</td>
</tr>
<tr>
<td></td>
<td>An alloy ingot for casting is a</td>
<td>OIL</td>
<td>Sub-materials: oil, gas, cutting</td>
<td></td>
</tr>
<tr>
<td></td>
<td>major material</td>
<td>Chemicals</td>
<td>agent, etc.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ingot</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>LPG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><strong>Melting Process</strong></td>
<td></td>
<td>[1] Al alloy, Zn alloy, Mg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fresh alloy and recycled</td>
<td>Exhaust Gas</td>
<td>alloy etc.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>metals in a factory are</td>
<td>[1] Alloy</td>
<td>[2] heavy oil, gas</td>
<td></td>
</tr>
<tr>
<td></td>
<td>molten in reverberating</td>
<td>Furnace</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>furnace or crucible furnace etc.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td><strong>Flux Treatment</strong></td>
<td></td>
<td>[3] Flux</td>
<td>Exhaust Gas Emission from</td>
</tr>
<tr>
<td></td>
<td>In order to remove oxides</td>
<td>[1] Flux</td>
<td>Flux Composition: NaCl, KCl,</td>
<td>Furnace (Chloride gas, fluorine gas)</td>
</tr>
<tr>
<td></td>
<td>and gas in the molten metal, a</td>
<td>Emission</td>
<td>MgCl₂, ZnCl₂, BaCl₂, BeCl,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>flux treatment is applied to</td>
<td>Dross/Slag</td>
<td>MnCl₂, MnO₂, KBF₄, NaBF₄,</td>
<td>Dross, slag (components contained</td>
</tr>
<tr>
<td></td>
<td>molten metal for</td>
<td>Furnace</td>
<td>NaF, AlF₃, Na₂SiF₆, Borax,</td>
<td>in base metal, reusable</td>
</tr>
<tr>
<td></td>
<td>deoxidization or degassing</td>
<td></td>
<td>Boric acid</td>
<td>material, and flux)</td>
</tr>
<tr>
<td></td>
<td>treatment, if needed.</td>
<td></td>
<td></td>
<td>Ni, Be, Mn, F</td>
</tr>
</tbody>
</table>
4 Casting Process

Inject molten metal (molten chief material [1]) into an injection sleeve and press it into a die with an injection piston to form a metal shape instantaneously. After removal of the product, mold lubricant is coated on the mold surface and the lubricant oil is applied to the inside of the injection sleeve.

- **No.**
- **Process Flow**
- **Input Chemicals**
- **PRTR Chemicals**

<table>
<thead>
<tr>
<th>No.</th>
<th>Process</th>
<th>Process Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Casting Process</td>
<td><img src="image" alt="Diagram" /></td>
</tr>
</tbody>
</table>

- **4** Mold lubricant components (oil, polymer compound, silicon, black lead, surface active agent, poly nonyl phenyl ether)
- **5** Machine operating oil (mineral oil, ethylene glycol, diethyl ethanol amine)
- **6** Lubricant oil for machine and die (mineral oil, graphite, Mo)

- **PRTR Chemicals**

- Mold lubricant mist (drops at the height lower than 10m on the ground, but not released to air)
- Drop mold lubricant (poly nonyl phenyl ether, ethylene oxide, nonyl phenol, polyoxyethylene alkyl ether etc.)
- Oil (ethylene glycol, molybdenum etc.)
- Wastewater treatment sludge (the same as the above description)
<table>
<thead>
<tr>
<th>No.</th>
<th>Process</th>
<th>Process Flow</th>
<th>Input Chemicals</th>
<th>PRTR Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Sprue Gate Removal:</td>
<td></td>
<td></td>
<td>Cut off materials such as sprue gate etc. are recycled for reuse.</td>
</tr>
<tr>
<td></td>
<td>Removing sprue gate, burr etc. other than the product by pressing mold etc..</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Product</td>
<td>Sprue gate</td>
<td>Return to process [2]</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Abrasion Finishing:</td>
<td>Abrasion machine</td>
<td>[7] Abrasion material (zinc ball, material made by cutting aluminum or stainless wire)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>For the removal of small burrs and improvement in adhesion of painting, metal balls (abrasion material) are shot on the surface of products.</td>
<td>[7] Abrasion materials</td>
<td>Dust in [7] and [1] is collected by dust collector</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Powdery pieces of worn [7] and [1]</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Heat Treatment:</td>
<td>Heat treatment electric furnace</td>
<td>[8] (electricity)</td>
<td>Nothing in particular (treatment temperature of not higher than 250°C)</td>
</tr>
<tr>
<td></td>
<td>For improving the dimensional stability or removal of internal stress, heat treatment at 100-250°C for 2-4Hr is applied to the products.</td>
<td>[8]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Process</td>
<td>Process Flow</td>
<td>Input Chemicals</td>
<td>PRTR Chemicals</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------</td>
<td>--------------</td>
<td>---------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>8</td>
<td>Machining:</td>
<td></td>
<td>[9] Cutting agent (oil, water soluble) (boron and its compound, 2-amino ethanol)</td>
<td>Wastewater, waste oil</td>
</tr>
<tr>
<td></td>
<td>Machining of products such as facing, drilling, tapping etc.</td>
<td></td>
<td></td>
<td>Waste oil attached to alloy turnings and degraded</td>
</tr>
<tr>
<td>9</td>
<td>Cleaning:</td>
<td></td>
<td>[10] Organic solvent (trichloroethylene, dichloromethane)</td>
<td>Organic solvent mist (the same as the left)</td>
</tr>
<tr>
<td></td>
<td>Products are cleaned to remove contamination or cutting oil on their surface.</td>
<td></td>
<td></td>
<td>Wastewater release</td>
</tr>
<tr>
<td></td>
<td>Cleaning [10]</td>
<td></td>
<td></td>
<td>Degraded solvent</td>
</tr>
</tbody>
</table>

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