

PRTR Estimation Manual

01. Paper Industry

January 2001
Revised: March 2002

Japan Paper Association

1. Outline and Features of Manufacturing Processes

(See Diagram 1: Typical process diagram for paper and pulp production)

Wood and recycled wastepaper are the main raw materials for paper pulp fiber, the former accounting for 43 percent and the latter accounting for the remaining 57 percent. Recently, the use of wastepaper accounts for more than half of the fiber raw materials from the viewpoint of energy and resource saving. The paper industry contributes to society as a recycling-oriented industry through the use of wastepaper and the promotion of afforestation projects.

Auxiliary materials and chemical agents such as loading materials and sizing agents are used to add required quality and functionality to paper.

Manufacturing methods for pulp made from wood are roughly classified into the mechanical pulp manufacturing methods in which physical force is applied to wood to mill it, and the chemical pulp manufacturing methods in which extract fibers with chemical agents. The former includes GP (groundwood pulp), RGP (refiner groundwood pulp), TMP (thermo-mechanical pulp) methods and others. The latter includes SP (sulfite pulp) and KP (kraft pulp) methods.

Use of wastepaper is roughly classified into gray stock to be used for baseboards for corrugated fiberboard and paperboard for paper boxes, and DIP (deinked pulp) from deinked and bleached wastepaper for use as printing paper and computer paper.

The process of preparation and papermaking by appropriately mixing such pulp is used to produce paper of various qualities and features.

Considerable energy (electricity and steam) is used in the manufacturing processes of both pulp and paper. Electric power is used to drive motors in machines and facilities, pumps to transport raw materials and wastewater and fan motors, and steam is used to heat and dry raw materials. Paper industry ranks fourth in energy consumption among manufacturing industries, following the iron and steel, chemical, and cement industries. Many paper mills therefore install boilers and turbines and try to improve energy efficiency by introducing cogeneration systems.

The following is an outline of principal manufacturing processes at a paper mill: pulp manufacturing processes (chemical pulp, mechanical pulp, and pulp derived from wastepaper); paper manufacturing processes (preparation and papermaking); and wastewater treatment process (including incineration).

2. Outline of Principal Manufacturing Processes

2.1. Chemical pulp manufacturing process (kraft pulp processing)

In Japan, most chemical pulp is produced using KP (kraft pulp processing) because this method produces strong pulp, is highly adaptable to any wood species, and pulping chemicals can be recovered and recycled. Another big advantage is that the method converts constituents other than wood fiber, such as lignin, into heat energy using boilers in the chemical recovery process and then makes use of such energy.

Seventy percent of wood material for paper is imported in the form of wood chips from advanced nations that manage forests sustainably, and many residual wood products resulting from lumbering and lumber from thinning are also used. Residual wood accounts for more than 50 percent of domestic lumber used.

As for environmental measures, a system combining biological treatment and coagulating sedimentation treatment is used for wastewater. To ensure the prevention against air pollution, desulfurizers, denitrification equipment and electrostatic precipitators have been installed. Deodorizing equipment is also indispensable for the KP method. Incineration processing is applied to high-density odorous gases. Beside these methods that process pollutants to be released outside, the industry has introduced many internal measures to prevent the release of pollutants by changing bleaching systems, combustion methods for boilers, etc., and by introducing low-odor recovery boilers that produce little odor. For the dioxins problem, which has been discussed a great deal recently, the whole industry has made a concerted effort to promote the installation of oxygen bleaching facilities, which has solved the problem completely. The industry is now advancing to the stage of adopting the Elemental Chlorine Free (ECF) method to further reduce environmental load.

(1) Cooking process

Woodchips and chemical (white liquor: $\text{NaOH} + \text{Na}_2\text{S}$) are placed in a digester, cooked at a high temperature and pressure (about 160 and 10 atmospheric pressures), and separated into cellulose fibers and lignin, etc.

The cellulose fibers are continuously washed in warm water and sent to the bleaching process after uncooked materials are removed with a screen. To be used as kraft paper for corrugated cardboard, they are sent directly to the papermaking process without bleaching.

(2) Bleaching process

The fibers are brownish after the cooking process, as they still contain some amount of lignin, etc. Higher brightness can be obtained by removing the remaining lignin with chlorinate bleach chemicals (chlorine, hypochlorite, and chlorine dioxide) and caustic soda in several phases.

At present, most mills adopt an oxygen bleaching process to remove lignin prior to the chlorine bleaching process to reduce the environmental load in the subsequent

process that uses chlorinated chemicals. This can reduce dioxins emission in bleaching wastewater almost to the limit of identification.

It is expected that an increasing number of mills will adopt the ECF method, which does not use chlorine to further reduce environmental load. Thus, the ECF method, which has neither chlorination nor hypochlorite processes that generate chloroform, can reduce the chloroform released to wastewater and air to an almost negligible level.

(3) Chemical recovery process

Lumber ingredients (lignin and hemicellulose excluding fibers), which are separated at the cooking process, and the remaining liquid chemicals are sent to the chemical recovery process. The chemical compound (black liquor) is burned in recovery boilers after being concentrated by vacuum evaporators and is effectively used as heat energy. Hydrazine hydrate, which is used as a deoxygenation agent in the boilers, is decomposed and consumed in the boilers and is not released outside.

Residual dross from black liquor after combustion is a compound of Na_2CO_3 and Na_2S . After Na_2CO_3 reacts with lime ($\text{Ca}(\text{OH})_2$) in the caustic process to be converted to NaOH and CaCO_3 , NaOH and Na_2S are used for cooking as white fluid. CaCO_3 is converted to CaO by using a kiln. CaO is slaked with lime and water to produce $\text{Ca}(\text{OH})_2$ which is then used to react with Na_2CO_3 .

2.2. Ground pulp manufacturing process

Because ground pulp is merely crushed wood, most lumber ingredients themselves become pulp. Therefore, the amount of pulp made from lumber is greater than chemical pulp. Its two disadvantages are that coniferous trees with comparatively longer fibers should be used because finely crushed fibers make the paper weaker, and milling requires a large amount of electric power. A large amount of lignin content prevents a high degree of whiteness in paper, although it is possible to produce thin paper with high opacity.

Mechanical pulp is classified into RGP (refiner groundwood pulp), GP (ground pulp), and TMP (thermo mechanical pulp) according to manufacturing methods. We explain a typical example of RGP below.

RGP was introduced as a mechanical pulp manufacturing method from the viewpoint of effectively utilizing resources. It uses refiners to process wood chips made from scrap timbers of sawmills that had been scrapped or burnt before.

(1) Process of delivery and washing of chips

An electromagnetic feeder adjusts the amount of chips that are supplied from a chip silo via a flow conveyor. Next, a measuring conveyor continuously measures their weight. The chips are then sent to the next process after foreign matter such as metallic materials, soil and sand is removed.

(2) Disaggregation process (refiner process)

A refiner is equipped with two rotating disks that face each other. Radial grooves are cut into the surfaces of the disks. Chips are passed between the disks and disaggregated (ground). The two types of refiners are; a single-disk refiner with one fixed disk and one rotating disk, and a double-disk refiner whose two disks rotate in opposite directions.

(3) Screening process

The two types of screening equipment are cleaners and screens. Screens are used to separate raw materials from foreign objects depending on the size and shape. Round holes or thin slits are made in a screen plate to allow the raw materials to pass through them and the foreign objects remain on the screen plate.

Cleaners, which are usually shaped as oblong cones, are used to separate raw materials from foreign objects by differences in specific gravity. Raw materials are placed in a large opening at the top of the equipment to flow and swirl down along the tangential line. During this time, centrifugal force ejects unwanted objects with large specific gravity, which then hit the surrounding walls, fall down and are drained out as dross.

The foreign objects removed by screens and cleaners are sent to the wastewater treatment process or burned after the dewatering process.

(4) Bleaching process

Parts of the screened raw materials are bleached and some are not. Targeted brightness can be obtained by changing the additive rate of bleaching chemicals (such as sodium hydrosulfite and hydrogen peroxide). Volatile materials (e.g., chloroform) may be released to air, depending on chemicals used.

(5) Drainage process

Because the concentration of pulp sent from the previous process is low, the pulp is drained with thickener to increase the concentration, and then continuously stored in the chest. The drained (white) liquor is sent to the wastewater treatment process.

2.3. Process of pulp derived from wastepaper

The Law on Promoting Green Purchasing will come into effect on April 1, 2001 to further improve the social foundation for the use of recycled paper. The paper industry, which had set a target to achieve a wastepaper utilization rate of 56 percent for 2000, achieved the target almost one year earlier. The industry has started a new scheme to achieve utilization rate of 60 percent by 2005 in order to further improve the wastepaper utilization rate.

The processes of pulp derived from wastepaper can be divided roughly into four parts: (1) defiberization, (2) dirt removal, (3) deinking, and (4) bleaching. While paperboard manufacturing only requires the processes of (1) and (2), paper manufacturing requires (1) through (4) to satisfy quality requirements.

(1) Defiberization process

Collected wastepaper and water are put in a pulper to make the treatment concentration about 3 to 5 percent. High-speed mechanical churning for 30 to 60 minutes reverts wastepaper back to the state of pulp. Heating or chemical substances are sometimes applied to facilitate defiberization. A new type of pulper that can continuously process wastewater with a high concentration (12 - 18 percent) has been introduced to replace conventional low-concentration batch type processing equipment.

(2) Removal of foreign objects

Wastepaper contains various objects, e.g., papermaking chemicals such as loading materials and paper durability promoter, printing ink, hot melt (resin starch), plastic, and staples. Wastepaper containing such foreign objects cannot be recycled, therefore they are carefully removed with cleaners and screens.

(3) Deinking process

Mere defiberization cannot make printed wastepaper a good raw material because the fibers contain a large amount of ink. Deinking is one way to remove the coloring matter or to clean stained raw materials. Ink is flaked off, dispersed, suspended, and separated from fibers in wastepaper by using mechanical power in addition to alkali and chemicals such as surface-active agents. In Japan, the paper industry mainly adopts flotators that deink wastepaper by separating the ink with bubbles floating in a liquor that uses little chemicals and water.

(4) Bleaching process

In order to further improve the quality of deinked wastepaper, a bleaching process is applied to increase brightness. Wastepaper pulp with the degree of brightness (55 - 75 percent) required for particular application such as (newspaper and fine paper) is achieved by using bleaching chemicals such as hydrogen peroxide, sodium hydrosulfite and sodium hypochlorite.

2.4. Preparation process

This is a process to finally prepare and send out raw materials for papermaking. Specifically, this process consists of defiberization of purchased pulp and broke, beating of raw materials, blending of raw materials, addition of fillers, sizers, and chemicals, dust removal, and de-aeration. Low consistency pulpers are used for defiberization of purchased pulp and broke, and cleaners and screens are used for dust removal. Pulpers use rotating blades in the tank to generate a vortex in the water to carry out defiberization. Low consistency pulpers carry out defiberization in concentrations of 3.5 - 5.5 percent. Cleaners and screens use the same principle and similar structures as those described in the “mechanical pulp manufacturing process” paragraph.

The following is a description of the beating of raw materials, blending of raw materials, and the addition of fillers, sizes, and chemicals.

(1) Beating of raw materials

Fundamental factors of beating are to swell fibers, increase the flexibility and surface area of fibers, fibrillate (making fibers fibril), and cut (trimming fibers) by beating fibers with a disk refiner, etc. The more fibers are beaten, the more their water retention is improved and sheet formation is facilitated.

(2) Blending of raw materials

Important factors of blending raw materials are to recycle broke generated during the papermaking, coating, and finishing processes and to blend raw materials and recovered white water released outside from preparation and papermaking processes. Keeping these procedures reduces raw materials loss as much as possible, improves retention, and reduces wastewater treatment load. White water refers to the water that contains flour (minute fibers), which is drained from the wire part of paper machines at the papermaking process, at a concentration of about 0.5 percent. Broke generated at the dryer part of paper machines, coating, and finishing processes is defibrated by pulpers.

Raw materials are beaten individually according to the tree species, mixed with other different types of pulp, such as wastepaper pulp or broke, and are added to recovered white water in the mixer. Specified quantities of different types of pulp are blended and stored in a mixing chest.

(3) Addition of fillers, sizing agents, and chemicals

The main purpose of fillers is to improve opacity, brightness, smoothness, and ink receptivity by filling the void between fibers to improve printability and appearance after printing. They are also effective at making paper thick, tight, and soft. Although kaolin and talc have been traditionally used as fillers, recently an increasing amount of calcium carbonate is used due to the increase of neutralized paper.

Sizing treatment is designed to prevent ink feathering on the paper for printing

or writing, or to add water resistance to wrapping paper and board liners for corrugated fiberboard due to their content and usage conditions. Although rosin (pine resin) and its fixing agent-aluminium sulfate-have been used as sizing agents (acidic sizing papermaking method), the neutral sizing papermaking method uses calcium carbonate as the filler and alkylketene dimers or alkenyl succinic anhydride as sizing agents. Sizing agents that give water-resistance to paper include melamine resin, urea formaldehyde resin and water-soluble thermosetting resins such as polyethylenimine.

Other chemicals, such as retention aids (that reduce retention loss with fixing flour), strengthening agents for paper (that improve sheet strength of paper by increasing the number of fiber bonding points), slime control agent (that keeps slime from developing by sterilizing microorganisms), antifoaming agent, and dyes, etc., are added as required.

2.5. Papermaking process

The papermaking process is to dilute and disperse the prepared materials, or paper stock, spray the paper stock on wire cloth to form a paper sheet, and drain water from the sheet and dry it. A paper machine consists of a paper machine mainframe and auxiliary equipment. The paper machine mainframe consists of a stock inlet, wire part, press part, dryer part, size press, calender, and reel along the flow of materials. The auxiliary equipment consists of a driving unit, approach pipes that supply raw materials and circulate white water, a vacuum system that drains water from the wire part and press part, a drainage system that supplies and recycles steam for the dryer bank, an air system that circulates and uses air for drying and recovers waste heat, etc. Papermaking machines are roughly classified into the Fourdrinier machine and the cylinder machine according to the type of wire part, and the multiple cylinder dryer and the Yankee dryer according to the type of dryer part.

(1) Dewatering process

Materials with which pulp, filler, and sizing agent, etc., are blended are put in a machine chest as mother stock, diluted with white water in the system, and jetted out on a wire net through the stock inlet.

The Fourdrinier machine uses a continuous wire net. The mother stock is sprayed or dropped onto the moving wire net. After the water is drained, a paper sheet is formed on the wire net. Table rolls and hydrofoils are arranged in the wire net part to optimize drainage kinetics for sheet formation. Paper stock is first dried on the wire net by suction generated by the rotation of table rolls or contact between the hydrofoil and wire net, and its concentration becomes about 20 percent where the sheet leaves at the end of the wire net part.

A cylinder mold rotates in the vat of the cylinder type paper machine, and mother stock forms a paper sheet on the net of the cylinder mold as it rotates.

The wet paper sheet (paper on the paper machine) contains too much water and its tensile strength is small when it is away from the wire net part. The press part compresses and drains it to form a stronger sheet. A wet paper sheet with high moisture content breaks under high pressure, therefore the concentration of the wet paper sheet is raised from 20 percent (moisture content: 80 percent) to 40 - 50 percent (moisture content: 60 - 50 percent) by gradually increasing pressure by several press rolls.

White water drained in the wire net part is circulated within the system, but white water drained at the press part is sent to a wastewater treatment process.

(2) Drying process

After the press part, the wet paper sheet is heated with the dryer to a moisture content level of 6 - 10 percent. Usually at the dryer part, there are several tens of cast-iron cylinders measuring 1.2 - 1.8 m in diameter and they hold the wet paper sheet with canvas and contact with the surface of the cylinders evaporates the paper

sheet's moisture. The Yankee dryer with one cylinder that measures 2.4 - 4.5 m in diameter is used to produce glazed paper.

If the used chemicals are volatile, they may be released to the air at the dryer part.

(3) Size press coating process

The size press machine applies starch to paper in the middle of the dryer process in order to give water resistance and surface strength to the paper. The size press was popularized with the progress of offset printing. Typical models of size press coater are the inclined type and the gate roll type. The inclined-type size press coater has a so-called dip coating structure with two inclined rolls that contact each other with pigment supplied between the rolls. Paper passes through the rolls. Although the structure is simple, concentration of the pigment is as low as 4 - 5 percent. The gate roll coater has a structure consisting of several rolls and applies pigment at a concentration of 10 - 20 percent with the same function of coating machines.

(4) Calendering and reel process

A calender consists of several steel rolls, or calenders, that rub the surface of the paper sent from the dryer part, to smooth and gloss it. Friction between calender rolls and paper generates heat, which may cause the diameter of rolls to slightly change in any direction. Therefore the calender has a device that blows out cool air to prevent thermal expansion of rolls and to finish a uniform thickness of paper.

The paper sent out of the calender is wound on a reel and shipped as a product after finishing.

2.6. Wastewater treatment process

Pulp and paper mills use a large amount of water as reaction media and washing water in the pulp and paper manufacturing processes. At the chemical pulp manufacturing process and the mechanical pulp manufacturing process, organic waste liquor containing lignin and other polysaccharides, which are principal constituents of wood, is generated. The process of pulp derived from wastepaper generates waste liquor containing fines, ink, and filler (powdery mineral matter blended to give opacity to paper). Pollutants contaminating the liquor are processed to satisfy laws and regulations and released to bodies of water.

The main wastewater treatment processes are pH adjustment using acid or alkali, removal of SS (suspended solids) using clarifiers, and decrease in BOD and COD by means of biological treatment and coagulative precipitation (flotation). The actual wastewater treatment is a combination of them. In this section, we explain wastewater treatment using the flow diagram, “Typical process diagram for pulp and paper production.”

The explanation includes the treatment of sludge generated from the wastewater treatment process.

(1) Neutralization process

The waste liquor ranges from a low pH area to a high pH area depending on the treatment conditions at the source of release. Such waste liquor is adjusted to a pH suitable for activated sludge treatment (biological treatment) by adding acid or alkali.

(2) Activated sludge treatment

After the adjustment, waste liquor to be treated is sent to an aeration tank and air (oxygen) is blown in with aerobic bacteria (return sludge) to decompose and remove organic substances (BOD ingredients). In this process, volatile substances (e.g. chloroform) in the liquor to be treated are released to the air because air is blown into the aeration tank or a cooling tower which is used when the temperature of liquor to be treated is high.

(3) Coagulative precipitation (clarifier)

Wastewater from the pulp manufacturing process contains colloidal particles such as lignin, which is difficult to remove by biological treatment means. Coagulating agents (inorganic or organic macromolecules) are used to remove the colloidal particles and large flocs are formed and precipitated. In this process, filler in wastewater from the papermaking process and wastepaper pulp process are also precipitated and removed.

(4) Dehydration process

Wastewater treatment sludge (paper sludge) that is naturally precipitated in the clarifier are pulled out as solid content at a concentration of about 3 percent, sent to a dehydrator, and dewatered to 40 - 60 percent in the solid content. Some of the dewatered products are effectively used as soil conditioner but most of them are

incinerated in sludge incinerators.

(5) Incineration process

Dehydrated sludge is incinerated in various types of incinerators, such as fluidized bed, fixed bed, and cyclonic incinerators. Organic substances in sludge become carbon dioxide and water, and inorganic substances become incinerated ash (including smoke dust). Most of the incinerated ash is effectively used as soil conditioner, steel-making heat insulant, and raw materials for cement. This incinerator is designated as a specified facility under Law Concerning Special Measures against Dioxins. Specifically speaking, regulatory standard figures are fixed with respect to exhaust gas, incinerated ash, smoke dust, and - if wet process treatment of exhaust gas is carried out - comprehensive wastewater, and measurement at least once a year is obligatory.

Inhomogeneous combustion in incinerators sometimes generates benzene as a byproduct and this is released to the air in the exhaust gas.

3. Typical Class I Designated Chemical Substances (Class I Substances) related to the industry

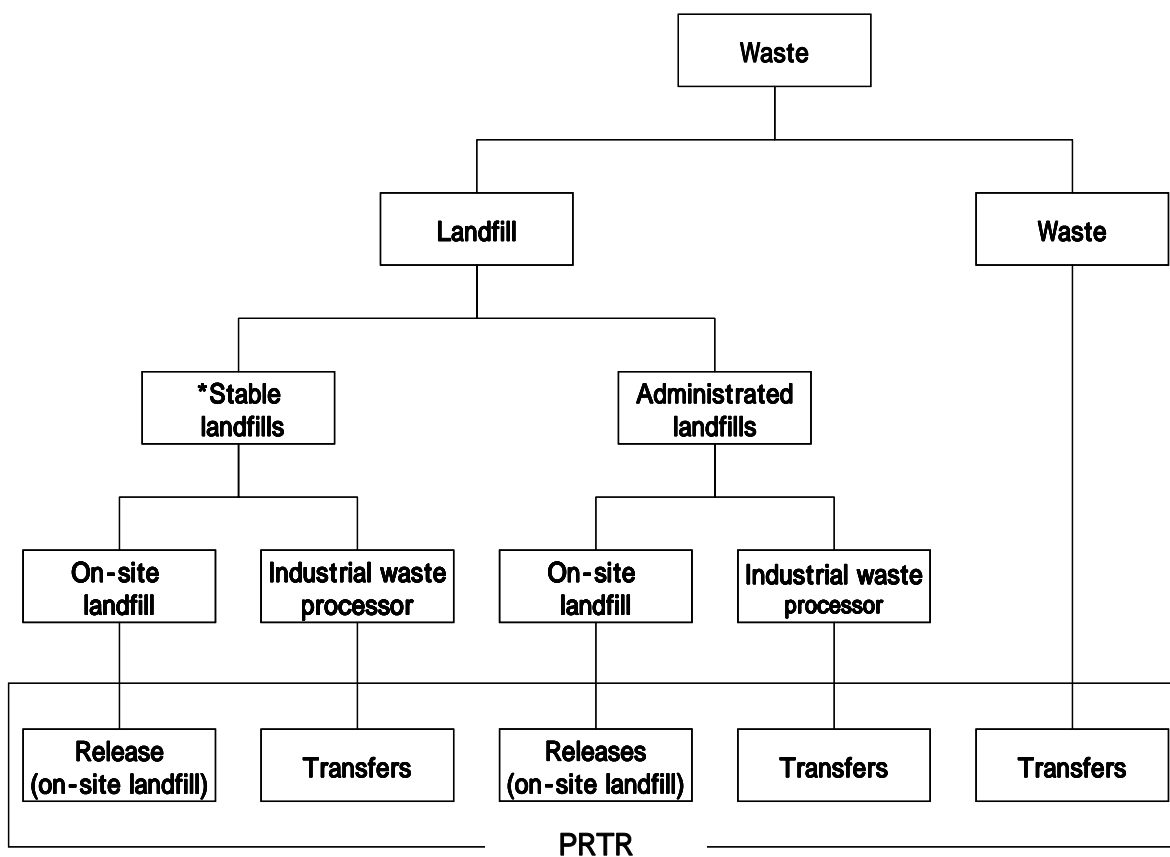
| Cabinet Order No. | CAS No. | Class I Substances | Process in which the substances are used | Remarks |
|-------------------|-----------|---|--|---|
| 1 | 7733-02-0 | Zinc sulfate [water-soluble compound of zinc] | Coated paper (cast-coat paper) | |
| 2 | 79-06-1 | Acrylamide (monomer) | Coagulating agent manufacturing | The whole amount is polymerized. |
| 16 | 141-43-5 | 2-aminoethanol | Specialty paper (rust-preventive agent) | |
| 65 | 107-22-2 | Glyoxal | Specialty paper (wet paper strength additives) | Coating after reaction to binder (PVA) |
| 95 | 67-66-3 | Chloroform | BKP bleaching process | Byproduct |
| 145 | 75-09-2 | Dichloromethane | Desensitization checker | Raw materials = products |
| | | | Cleaning agent | Used amount = released quantity to air |
| 172 | 68-12-2 | NN-dimethylformamide | Solvent for antiseptic agent, slime control agent | |
| 179 | - | Dioxins | BKP bleaching process, incinerator of waste | Byproduct |
| 227 | 108-88-3 | Toluene | Solvent | |
| 253 | 302-01-2 | Hydrazine | Deoxygenation agent scavenger for boiler | Hydrazine hydrate / Cas No. 7803-57-8 is also included. |
| 299 | 71-43-2 | Benzene | Waste gas from waste incinerators | Byproduct |
| 310 | 50-00-0 | Formaldehyde | Hydration resistance agents such as starch and PVA | |
| | | | Antiseptic agent | |
| | | | Encapsulant | No carbon required copying paper |
| | | | Flame retardant | Guanidine |
| | | | Wet paper strength enhancing additives | |

Note: Requiring notification

Annual quantity of benzene handled: 0.5 t/ year or more (Specific class 1 substance)

Annual quantity of class 1 substances handled: 1 t/ year or more

4. Waste management



* For landfill type, "stable" or "administrated" is designated by the Law.
 In case waste was sold for recycling, reporting is not required .

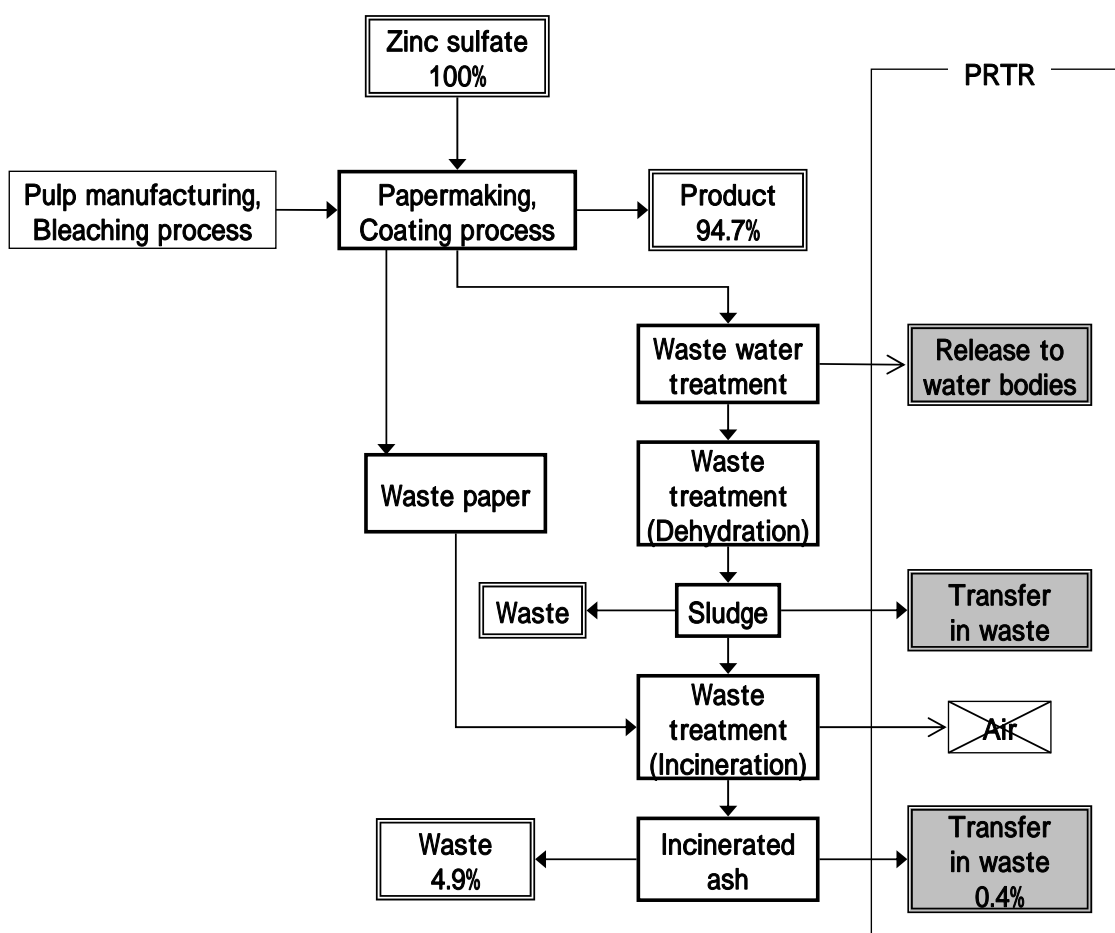
5. Procedures and Examples of Calculating Releases and Transfers in Typical Processes

5.1. Zinc sulfate (Zinc compounds (water-soluble))

5.1.1. Process flow and releases and transfers

| | | | |
|------------------------|---------------------------|------------------------|-------------|
| Name of substance | Zinc sulfate heptahydrate | | |
| Cabinet order No. | 1 | CAS No. | 7733-02-0 |
| | | Requiring notification | 1.0t / year |
| Conversion coefficient | 0.227 | | |
| Use | Coated paper (Cast coat) | | |

Process flow example (release and transfer)



5.1.2. Calculation method

[Calculation procedure]

Quantities of pigment ingredients released and transferred throughout the coating and finishing processes are calculated according to the following procedure:

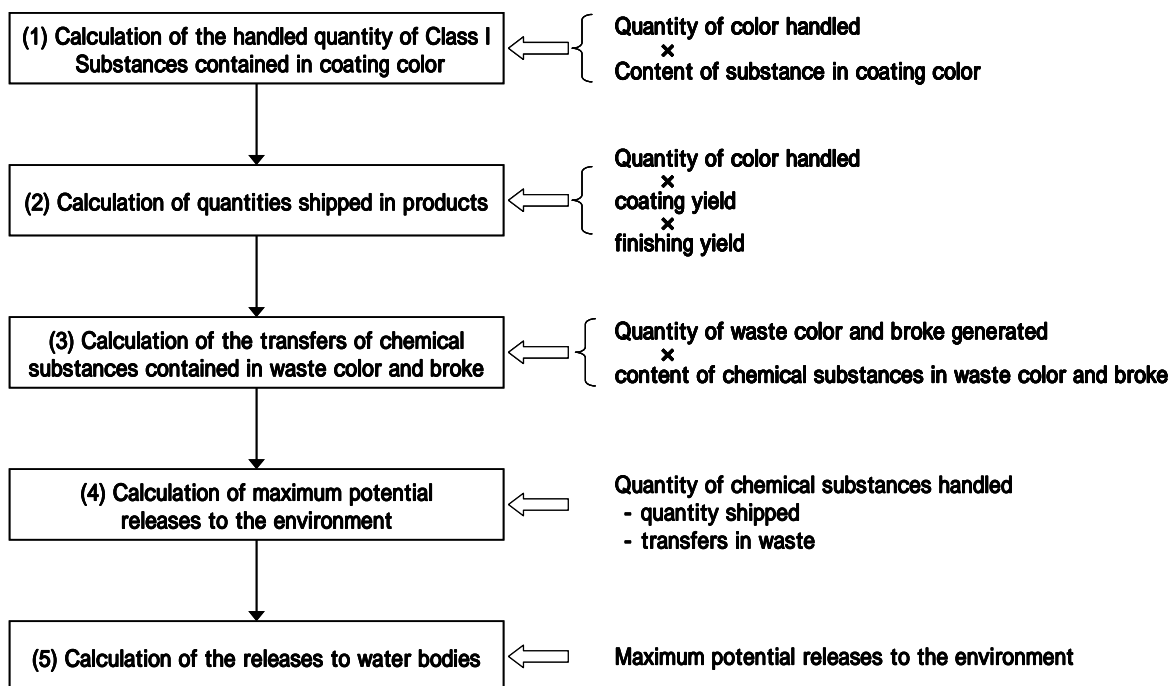


Figure: Procedures for calculating quantities of color ingredients released and transferred throughout the coating and finishing processes (Work sheet for coating/finishing processes)

5.1.3. Calculation examples

The following are examples of how to calculate the releases and transfers with facilities and under the conditions below:

(Overview of facilities)

Process: coating process of cast-coated paper

Equipment used: coating machine

Wastewater treatment equipment: activated sludge treatment (removal efficiency: 100%)

Coating color used: cast-coat color [zinc sulfate (7 hydrate) Content: 5 %]

Annual amount of coating color used: 500 tons / year (total amount is used)

(1) Calculation of annual quantity of zinc sulfate handled

Annual quantity of zinc compound handled is calculated by using the amount of coating color used, content of zinc sulfate (7 hydrate) contained in the coating color, and conversion factor from zinc sulfate (7 hydrate) to zinc.

(Annual quantity of zinc handled)

= (amount of coating color used) x (content (%) in the coating color)

x (conversion factor)

= 500 tons/year x 1,000 kg/ton x 5%/100 x 0.227

= 5,675 kg/year

(2) Calculation of the quantity shipped in products

The quantity shipped in products is calculated by using the annual quantity of zinc handled, coating yield, rate of broke in the coating process, and finishing yield.

(Quantity shipped in products)

= (annual quantity of zinc handled) x (coating yield)

x (1 - rate of broke in the coating process) x (finishing yield)

= 5,675 kg/year x 99.6%/100 x (1 - 3%/100) x 98%/100

= 5,373 kg/year

*(Coating yield)

= (quantity coated on paper)/(quantity in coating color used) x 100 (unit: %)

*(Rate of broke in the coating process)

= (quantity of broke in the coating process)

/ (total quantity of coated paper transferred from coating process)

x 100 (unit: %)

*(Finishing yield)

= (quantity shipped in products)

/ (total quantity transferred to finishing process) x 100 (unit: %)

(3) Estimation of quantity of chemical substances transferred in waste

For the transfers of chemical substances in waste, those in waste coating color and broke generated in the processes of coating and finishing are subject to estimations.

Waste color in the coating process is calculated by using the coating yield. Waste color is added as industrial waste to the transfers, through the waste treatment process. (dewatering and incineration treatment process; treatment efficiency: 100%).

$$\begin{aligned} & \text{(Transfers of chemical substances in waste color)} \\ &= (\text{annual amount of zinc handled}) \times [1 - (\text{coating yield})] \times (\text{treatment efficiency}) \\ &= 5,675 \text{ kg/year} \times (1 - 99.6\%/100) \times 100\%/100 \\ &= 22.7 \text{ kg/year} \end{aligned}$$

The quantity of waste generated through coating and finishing processes is calculated by using the rate of broke in coating process and finishing yield. Broke, which is usually off-site recycled, is added to transfer in waste, in case handed over to industrial waste collectors. When broke is sold for recycling, PRTR reporting is not required.

$$\begin{aligned} & \text{(Transfers of chemical substances in broke)} \\ &= (\text{annual amount of zinc handled}) \\ & \quad \times \{(\text{coating yield}) \times (\text{rate of broke in coating process}) + (\text{coating yield}) \\ & \quad \quad \times (1 - \text{rate of broke in coating process}) \times [1 - (\text{finishing yield})]\} \\ &= 5,675 \text{ kg/year} \times [99.6\%/100 \times 3\%/100 + 99.6\%/100 \\ & \quad \times (1 - 3\%/100) \times (1 - 98\%/100)] \\ &= 279 \text{ kg/year} \end{aligned}$$

(4) Calculation of maximum potential releases

The maximum potential quantity released is calculated by subtracting the quantity of zinc shipped in products and transfers in waste from annual quantity of zinc handled.

$$\begin{aligned} & \text{(Maximum potential releases)} \\ &= (\text{annual quantity of zinc handled}) - (\text{quantity of zinc shipped in products}) \\ & \quad - (\text{quantity of zinc transferred in waste}) \\ &= 5,675 \text{ kg/year} - 5,373 \text{ kg/year} - (22.7 \text{ kg/year} + 279 \text{ kg/year}) \\ &= 0.3 \text{ kg/year} \end{aligned}$$

(5) Calculation of releases to water bodies

The whole maximum potential quantity of zinc sulfate (7 hydrate) released, which is not volatile, is regarded as the quantity released to water bodies.

$$\begin{aligned} & \text{(Releases to water bodies)} \\ &= (\text{maximum potential releases}) \\ &= 0.3 \text{ kg/year} \end{aligned}$$

5.2.2. Calculation method

[Calculation procedure]

Quantities of coating color ingredients released and transferred throughout the coating and finishing processes are calculated according to the following procedure:

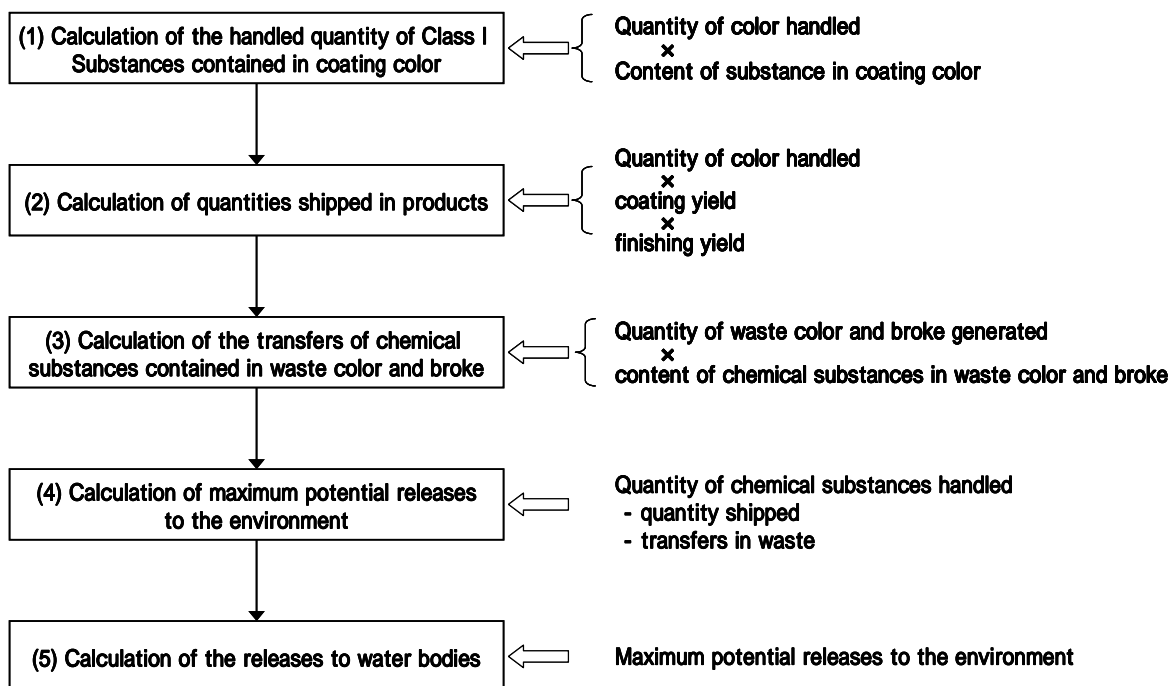


Figure: Procedures for calculating quantities of color ingredients released and transferred throughout the coating and finishing processes (Work sheet for coating/finishing processes)

5.2.3. Calculation examples

The following are examples of how to calculate the releases and transfers with facilities and under the conditions below:

(Overview of facilities)

Process: coating process of anti-corrosive paper

Equipment used: coating machine

Wastewater treatment equipment: activated sludge (removal efficiency: 90%)

Coating color used: coating color for anti-corrosive paper

[2-aminoethanol content: 2 %]

Annual amount of coating color used: 10 tons / year (total amount is used)

(1) Calculation of annual quantity of 2-aminoethanol handled

Annual quantity of 2-aminoethanol handled is calculated by using the amount of coating color used and content of 2-aminoethanol in the coating color.

(Annual quantity of 2-aminoethanol handled)

= (amount of coating color used) x (content (%) in the coating color)

= 10 tons/year x 1,000 kg/ton x 2 %/100

= 200 kg/year

(2) Calculation of the quantity shipped in products

The quantity shipped in products is calculated by using the annual quantity of zinc handled, coating yield, rate of broke in the coating process, and finishing yield. The quantity of 2-aminoethanol shipped in products is assumed to be calculated as (the annual quantity of 2-aminoethanol coated minus the annual quantity of 2-aminoethanol in the broke) times (finishing yield).

(Quantity shipped in products)

= (annual quantity of 2-aminoethanol handled) x (coating yield)

x (1 - rate of broke in the coating process) x (finishing yield)

= 200 kg/year x 95.5%/100 x (1 - 5%/100) x 97%/100

= 184.3 kg/year

*(Coating yield)

= (quantity coated on paper)/(quantity in coating color used) x 100 (unit: %)

*(Rate of broke in the coating process)

= (quantity of broke in the coating process)

/ (total quantity of coated paper transferred from coating process)

x 100 (unit: %)

*(Finishing yield)

= (quantity shipped in products)

/ (total quantity transferred to finishing process) x 100 (unit: %)

(3) Estimation of quantity transferred in waste

For the transfers of 2-aminoethanol in waste, those in waste coating color and broke generated in the processes of coating and finishing are subject to estimations.

Waste color in the coating process is calculated by using the coating yield. Waste color is added as industrial waste to the transfers, through the waste treatment process. (dewatering process; treatment efficiency: 90%).

(Transfers of 2-aminoethanol in waste color)

$$\begin{aligned} &= (\text{annual amount handled}) \times [1 - (\text{coating yield})] \times (\text{treatment efficiency}) \\ &= 200 \text{ kg/year} \times (1 - 95.5\%/100) \times 90\%/100 \\ &= 8.1 \text{ kg/year} \end{aligned}$$

The quantity of waste generated through coating and finishing processes is calculated by using the rate of broke in coating process and finishing yield. Broke, which is usually off-site recycled, is added to transfer in waste, in case handed over to industrial waste collectors. When broke is sold for recycling, PRTR reporting is not required.

(Transfers of 2-aminoethanol in broke)

$$\begin{aligned} &= (\text{annual amount of 2-aminoethanol handled}) \\ &\quad \times \{(\text{coating yield}) \times (\text{rate of broke in coating process}) + (\text{coating yield}) \\ &\quad \times (1 - \text{rate of broke in coating process}) \times [1 - (\text{finishing yield})]\} \\ &= 200 \text{ kg/year} \times [95.5\%/100 \times 0.5\%/100 + 95.5\%/100 \times (1 - 0.5\%/100) \\ &\quad \times (1 - 97\%/100)] \\ &= 6.7 \text{ kg/year} \end{aligned}$$

(4) Calculation of maximum potential releases

The maximum potential quantity released is calculated by subtracting the quantity of 2-aminoethanol shipped in products and transfers in waste from annual quantity of 2-aminoethanol handled.

(Maximum potential releases)

$$\begin{aligned} &= (\text{annual quantity of 2-aminoethanol handled}) \\ &\quad - (\text{quantity of 2-aminoethanol shipped in products}) \\ &\quad - (\text{quantity of 2-aminoethanol transferred in waste}) \\ &= 200 \text{ kg/year} - 184.3\text{kg/year} - (8.1\text{kg/year} + 6.7 \text{ kg/year}) \\ &= 0.9\text{kg/year} \end{aligned}$$

(5) Calculation of releases to water bodies

The whole maximum potential quantity of 2-aminoethanol released, which is easily soluble in water, is regarded as the quantity released to water bodies.

(Releases to water bodies)

$$\begin{aligned} &= (\text{maximum potential releases}) \\ &= 0.9 \text{ kg/year} \end{aligned}$$

5.3. Chloroform

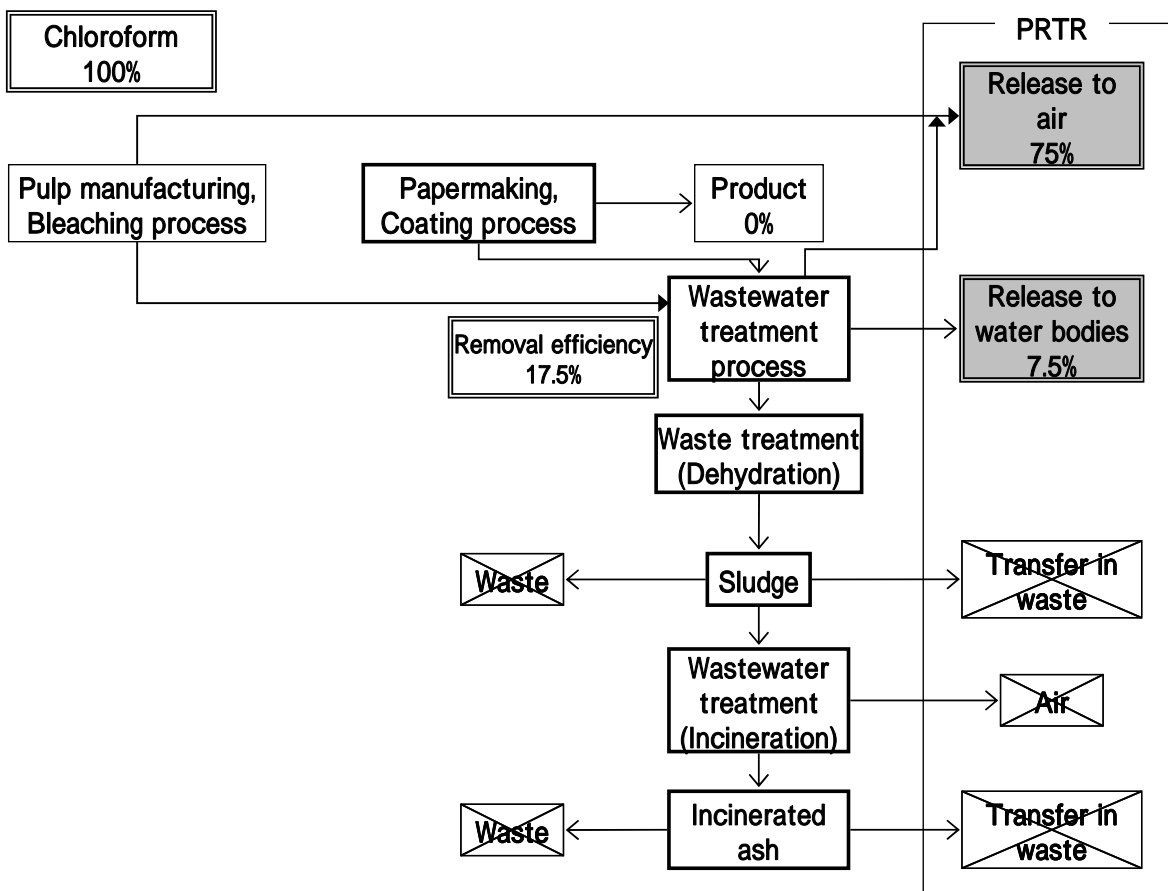
5.3.1. Process flow and releases and transfers

| | | | |
|-------------------|---|------------------------|-------------|
| Name of substance | Chloroform (trichloromethane) | | |
| Substance No. | 95 | CAS No | 67-66-3 |
| | | Requiring notification | 1.0t / year |
| Use | Byproduct from bleaching process of kraft pulp | | |
| Note | Self-management plan of toxic anpollutant (Japan paper Association) | | |

In case facility has the data, use that figures. When no data is available, calculation should be done as follows.

Amount of chloroform generated (g / 1ton of pulp produced) = {87.8 x (amount of chlorine added(%) - 92.7) + {401 x amount of sodium hypochlorite added (%) - 15}

And usually; amount of chloroform generated = release to air (75%) + release to water bodies (7.5%) + amount removed at wastewater treatment equipment (17.5%), as shown in the following fig..(Example of the process where cooling tower is equipped before wastewater treatment facility)



5.3.2. Calculation example (Chloroform; Cabinet Order No. 95)

The following are examples of how to calculate releases and transfers with facilities where no data is available.

(Overview of facilities)

Process: bleaching process with chlorinate bleach chemicals manufacturing bleached kraft pulp (BKP)

Wastewater treatment equipment: activated sludge treatment (removal efficiency: 17.5 %) with cooling tower

Chlorinate bleach chemicals used: chlorine, sodium hypochlorite

Operating conditions; amount of BKP produced: 1,000 t / day

Working days: 340 days / year

Amount of chlorine added: 1.5 %

Amount of sodium hypochlorite added: 0.5 %

(1) Calculation of annual quantity of chloroform generated (handled)

Annual quantity of chloroform generated is the total of the amount of chloroform generated at chlorine bleaching process and the amount of that at hypochlorite bleaching process.

Annual quantity of chloroform generated(handled) from chlorine bleaching process

$$= (87.8 \times \text{amount of chlorine added (\%)} - 92.7) (\text{g / t})$$

$$\times \text{amount of BKP produced(t / day)} \times \text{working days(days / year)} \div 1,000,000(\text{g / t})$$

$$= (87.8 \times 1.5 - 92.7) (\text{g / t}) \times 1,000 (\text{t / day}) \times 340 (\text{days / year}) \div 1,000,000 (\text{g / t})$$

$$= 13.3 (\text{t / year})$$

Annual quantity of chloroform generated(handled) from hypochlorite bleaching process

$$= \{401 \times \text{amount of sodium hypochlorite added (\%)} - 15\}$$

$$\times \text{amount of BKP produced(t / day)} \times \text{working days(days / year)} \div 1,000,000(\text{g / t})$$

$$= (401 \times 0.5 - 15) (\text{g / t}) \times 1,000 (\text{t / day}) \times 340 (\text{days / year}) \div 1,000,000 (\text{g / t})$$

$$= 63.1(\text{t / year})$$

Annual quantity of chloroform generated(handled) from bleaching process

+

$$= 13.3 (\text{t / year}) + 63.1(\text{t / year})$$

$$= 76.4 (\text{t / year})$$

(2) Calculation of annual quantity released to air

By model example aforementioned (fig.), annual quantity released to air is calculated as $\times 75\%$

$$= 76.4 (\text{t / year}) \times 75 \div 100$$

$$= 57.3 (\text{t / year})$$

(3) Calculation of annual quantity released to water bodies

By model example aforementioned (fig.), annual quantity released to water bodies is calculated as $\quad \times 7.5\%$

$$= 76.4 \text{ (t /year)} \times 7.5 \div 100 = 5.7 \text{ (t /year)}$$

(4) Calculation of annual quantity removed at wastewater treatment equipment

By model example aforementioned (fig.), annual quantity removed at wastewater treatment equipment is calculated as $\quad \times 17.5\%$

$$= 76.4 \text{ (t /year)} \times 17.5 \div 100 = 13.4 \text{ (t /year)}$$

5.4.2. Calculation procedure

The releases of N,N-dimethylformamide used as solvent for antiseptic agent and slime control agent are estimated according to the following procedure:

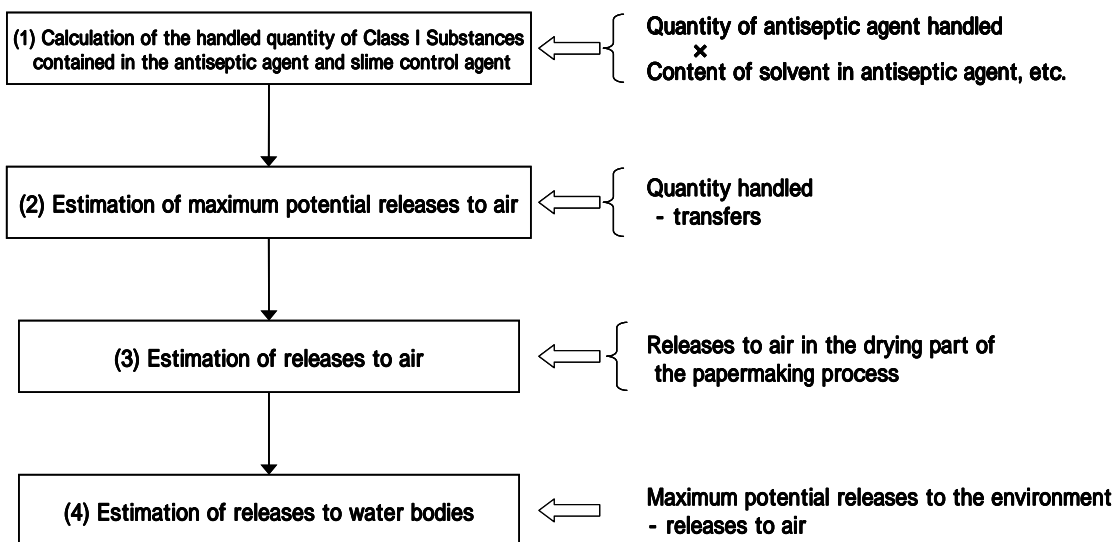


Figure: Estimation procedure for the releases and transfers of solvent ingredients of antiseptic agent/slime control agent

5.4.3. Calculation example

The following are examples of how to estimate quantities released and transferred in the process below:

(Overview of facilities)

Process: sterilization of surroundings of paper machines and inside of tanks and pipes

Wastewater treatment facilities: activated sludge treatment (Efficiency of removal is 4.4 %; quoted from “Safety data of existing chemical substances under the Law Concerning the Examination and Regulation of Manufacture, etc. of Chemical Substances” issued by Japan Chemical Industry Ecology-Toxicology & Information Center on October 1992)

Agents used: antiseptic agent and slime control agent (Content of N,N-dimethylformamide: 5%)

Annual quantity of antiseptic agent and slime control agent used: 20 tons/year

(1) Calculation of annual quantity of N,N-dimethylformamide handled

Annual quantity of N,N-dimethylformamide handled is calculated by using the quantity of antiseptic agent and slime control agent used and the content of N,N-dimethylformamide in them.

(Annual quantity of N,N-dimethylformamide handled)

= (quantity of antiseptic agent and slime control agent used)

x (content of solvent %)

= 20 tons/year x 1,000 kg/ton x 5%/100 = 1,000 kg/year

*The quantity shipped is zero because antiseptic agent and slime control agent are not contained in products. The quantity shipped is therefore omitted from the work procedure.

*The antiseptic agent and slime control agent are used up and no waste is generated through the process. Therefore the quantity of transferred N,N-dimethylformamide in waste is zero and is omitted from the work procedure.

(2) Estimation of maximum potential releases

In this process, the annual quantity of N,N-dimethylformamide handled itself is equal to the maximum potential quantity released.

(Maximum potential releases)

= (annual quantity of N,N-dimethylformamide handled) = 1,000 kg/year

(3) Estimation of releases to air

Although antiseptic agent and slime control agent are used in the open air, estimation should be made to assume that 0.5 percent of N,N-dimethylformamide is released to air, only in the drying part of the papermaking process, because it is highly water soluble.

(Releases to air)

$$\begin{aligned} &= (\text{maximum potential releases}) \times (\text{ratio of releases to air}) \\ &= 1,000 \text{ kg/year} \times 0.5\%/100 \\ &= 5 \text{ kg/year} \end{aligned}$$

(4) Estimation of releases to water bodies

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

(Potential releases to water bodies)

$$\begin{aligned} &= (\text{maximum potential releases}) - (\text{releases to air}) \\ &= 1,000 \text{ kg/year} - 5 \text{ kg/year} \\ &= 995 \text{ kg/year} \end{aligned}$$

Then, the quantity released after treatment is calculated using the efficiency of removal in the activated sludge treatment process. It is assumed that the quantity transferred in the sludge generated through the activated sludge process is zero because N,N-dimethylformamide is highly water soluble.

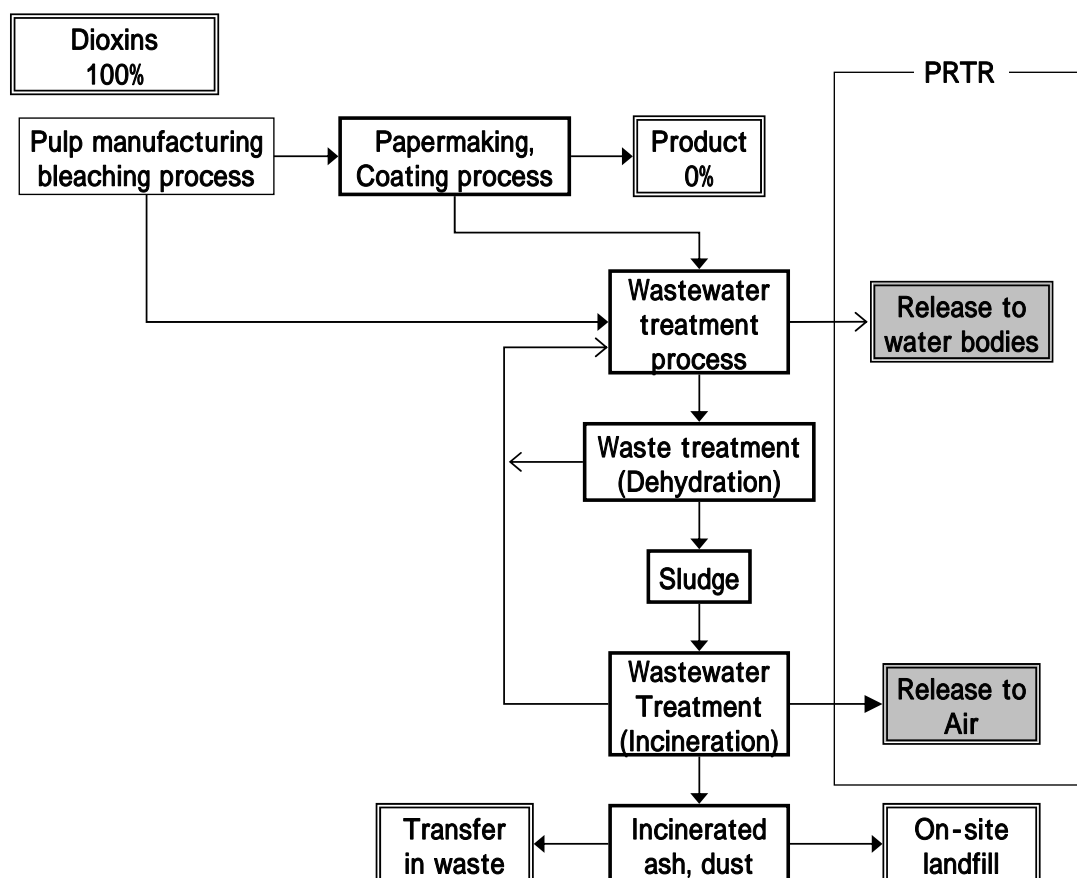
(Releases to water bodies after treatment)

$$\begin{aligned} &= (\text{potential releases to water bodies}) \times [1 - (\text{efficiency of removal})] \\ &= 995 \text{ kg/year} \times (1 - 4.4\%/100) \\ &= 951 \text{ kg/year} \end{aligned}$$

5.5. Dioxins

5.5.1. Process flow and releases and transfers

| | | | |
|-------------------|--|------------------------|-----|
| Name of substance | Dioxins | | |
| Cabinet order No. | 179 | CAS No | - |
| | | Requiring notification | All |
| Use, etc. | Wastewater...Byproduct from bleaching process of kraft pulp, incinerator of waste(in case of water treatment of vent gas) Release to air...Incinerator of waste Transfer in waste...Incinerated ash, dust from incinerator | | |



Requiring notification for dioxins (examples)

- Specified facilities by “ Law Concerning Special Measures against Dioxins “should report releases and transfers based on the measured figures.
- Facilities which have chlorinate bleaching process of kraft pulp and/or incinerator of waste with water treatment of vent gas should measure content of dioxins in wastewater at least once a year by the Law. So, release to water bodies is calculated by annual amount of wastewater times content of dioxins.
- Content of dioxins in exhaust gas, incinerated ash and dust from incinerator should also be measured at least once a year by the Law. Release to air and so on should also be calculated in the same way.

5.5.2. Calculation example (Dioxins)

[Example - 1]

The following are examples of how to calculate quantities released and transferred in the process below:

(Overview of facilities)

Process: Incinerator of waste (no water treatment of vent gas)

(Release and transfer)

Release to air: Exhaust gas from incinerator

Transfer in waste: Ash and dust from incinerator

(Operating condition for calculation)

The amount of exhaust gas from incinerator and content of dioxins in exhaust gas (measured) are $9,900 \text{ Nm}^3/\text{hour}$ (working hours: 8,000 hours / year) and $0.09 \text{ ng-TEQ} / \text{Nm}^3$, respectively. The annual amount of incinerated ash transferred for mixing in raw materials for Portland cement, is 5,100 tons and content of dioxins in incinerated ash is $0.0019 \text{ ng-TEQ} / \text{g}$.

Calculation of release to air: Exhaust gas from incinerator

$$0.09 \text{ ng-TEQ} / \text{Nm}^3 \times 9,900 \text{ Nm}^3 / \text{hour} \times 8,000 \text{ hours} / \text{year} \div 1,000,000 \text{ ng} / \text{mg} \\ = 7.13 \text{ mg-TEQ} / \text{year}$$

Calculation of transfer in waste: In incinerated ash

$$0.0019 \text{ ng-TEQ} / \text{g} \times 5,100 \text{ tons} / \text{year} \times 10^6 \text{ g} / \text{ton} \div 1,000,000 \text{ ng} / \text{mg} \\ = 9.7 \text{ mg-TEQ} / \text{year}$$

There is no release to water bodies in this case,

[Example - 2]

The following are examples of how to calculate quantities released and transferred in the process below:

(Overview of facilities)

Process: Incinerator of waste (water treatment of exhaust gas)

(Release and transfer)

Release to air: Exhaust gas from incinerator

Release to water bodies: Wastewater used for exhaust gas treatment from incinerator

Transfer in waste: Ash and dust from incinerator

(Operating condition for calculation)

The amount of exhaust gas from incinerator and content of dioxins in exhaust gas (measured) are $6,670 \text{ Nm}^3/\text{hour}$ (working hours: 8,000 hours / year) and $0.042 \text{ ng-TEQ} / \text{Nm}^3$, respectively. The annual amount of dust from incinerator and incinerated ash, transferred for mixing in raw materials for Portland cement, etc. are 800 tons and 7,300 tons respectively. Content of dioxins in them are 0.00012 ng-TEQ

/ g and 0.00011 ng-TEQ / g respectively.

Wastewater used for exhaust gas treatment from incinerator is released to water bodies, through wastewater treatment facility. The amount of wastewater from wastewater treatment facility and content of dioxins in wastewater (measured) are 4,000 m³ /hour (working hours: 8,280 hours / year) and 1.2 pg-TEQ /liter., respectively.

Calculation of release to air: Exhaust gas from incinerator

$$0.042 \text{ ng-TEQ / Nm}^3 \times 6,670 \text{ Nm}^3 \text{ /hour} \times 8,000 \text{ hours / year} \div 1,000,000 \text{ ng / mg} \\ = 2.24 \text{ mg-TEQ / year}$$

Calculation of release to water bodies

$$1.2 \text{ pg-TEQ /liter} \times 4,000 \text{ m}^3 \text{ /hour} \times 8,280 \text{ hours / year} \times 1,000 \text{ liter / m}^3 \\ = 39.7 \times 10^9 \text{ pg-TEQ/ year} = 39.7 \text{ mg-TEQ / year}$$

Calculation of transfer in waste

Dust from incinerator *(transferred)

$$0.00012 \text{ ng-TEQ / g} \times 800 \text{ tons / year} \times 10^6 \text{ g / ton} \div 1,000,000 \text{ ng / mg} \\ = 0.096 \text{ mg-TEQ / year}$$

Incinerated ash *(transferred)

$$0.00011 \text{ ng-TEQ / g} \times 7,300 \text{ tons / year} \times 10^6 \text{ g / ton} \div 1,000,000 \text{ ng / mg} \\ = 0.80 \text{ mg-TEQ / year}$$

* When sold for recycling and so on, reporting is not required.

[Example - 3]

The following are examples of how to calculate quantities released and transferred in the process below:

(Overview of facilities)

Process: Kraft pulp processing (bleaching, non-bleaching), waste incinerator

(Release and transfer)

Release to air: Exhaust gas from incinerator

Release to water bodies: Wastewater from bleached kraft pulp manufacturing process

Transfer in waste: Ash and dust from incinerator

(Operating condition for calculation)

The amount of exhaust gas from incinerator and content of dioxins in exhaust gas (measured) are 15,000 Nm³ /hour (working hours: 8,000 hours / year) and 0.095 ng-TEQ / Nm³, respectively. The annual amount of dust and ash from incinerator, transferred for mixing in raw materials for Portland cement, etc. are 10,400 tons and content of dioxins in them is 0.0052 ng-TEQ / g .

Wastewater from bleaching process is transferred to wastewater treatment facility and then is released to water bodies. The amount of wastewater from

wastewater treatment facility and content of dioxins in wastewater (measured) are 6,700 m³ /hour (working hours: 8,280 hours / year) and 0.39 pg-TEQ /liter., respectively.

Calculation of release to air: Exhaust gas from incinerator

$$0.095 \text{ ng-TEQ / Nm}^3 \times 15,000 \text{ Nm}^3 \text{ /hour} \times 8,000 \text{ hours / year} \div 1,000,000 \text{ ng / mg} \\ = 11.4 \text{ mg-TEQ / year}$$

Calculation of release to water bodies

$$0.39 \text{ pg-TEQ /liter} \times 6,700 \text{ m}^3 \text{ /hour} \times 8,280 \text{ hours / year} \times 1,000 \text{ liter / m}^3 \\ = 21.6 \times 10^9 \text{ pg-TEQ/ year} = 21.6 \text{ mg-TEQ / year}$$

Calculation of transfer in waste: Incinerated ash

$$0.0052 \text{ ng-TEQ / g} \times 10,400 \text{ tons / year} \times 10^6 \text{ g / ton} \div 1,000,000 \text{ ng / mg} \\ = 54.1 \text{ mg-TEQ / year}$$

Diagram 1: Typical pulp and paper manufacturing processes

(1) Pulp manufacturing process

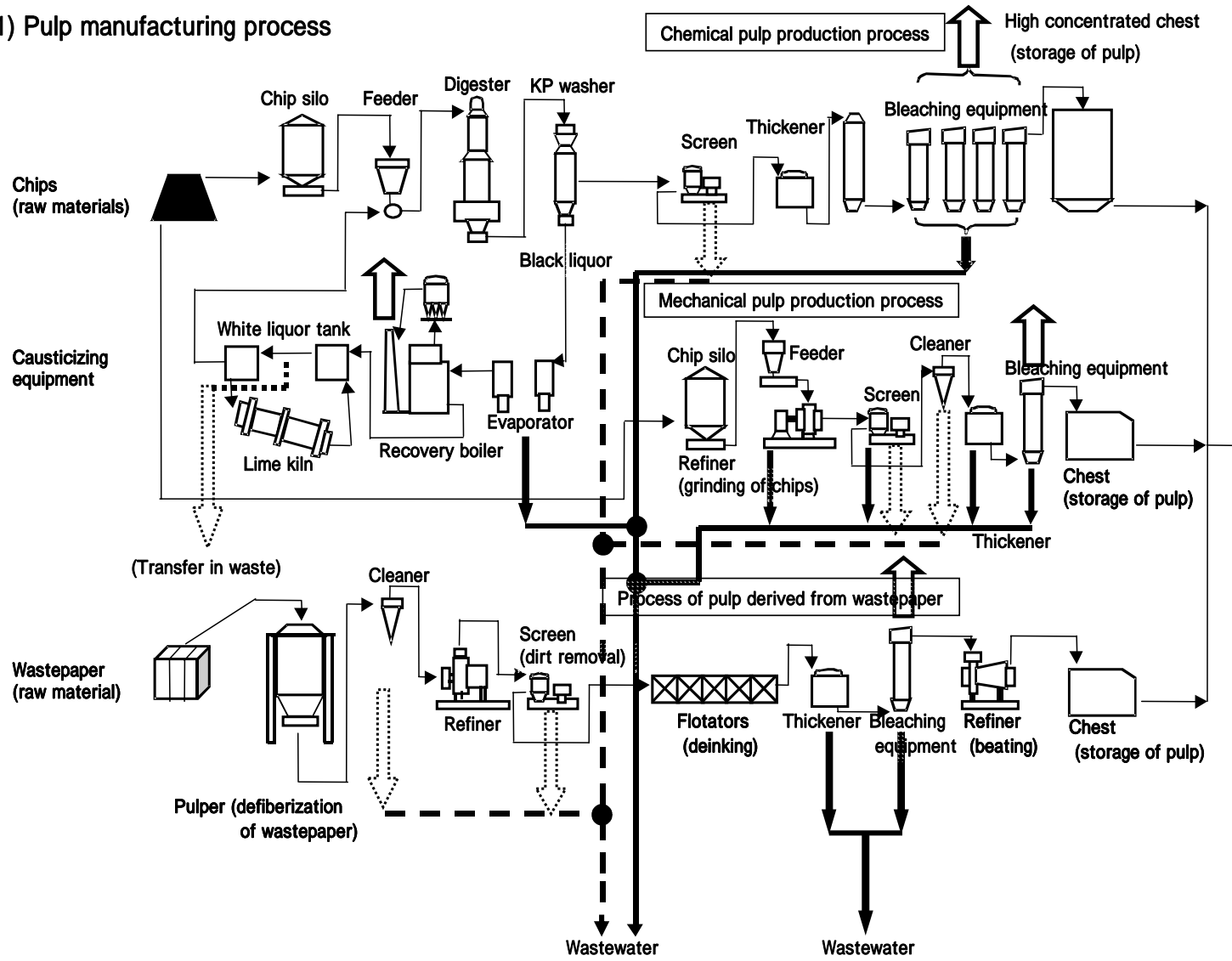


Diagram 1: Typical pulp and paper manufacturing processes

(2) Paper making process

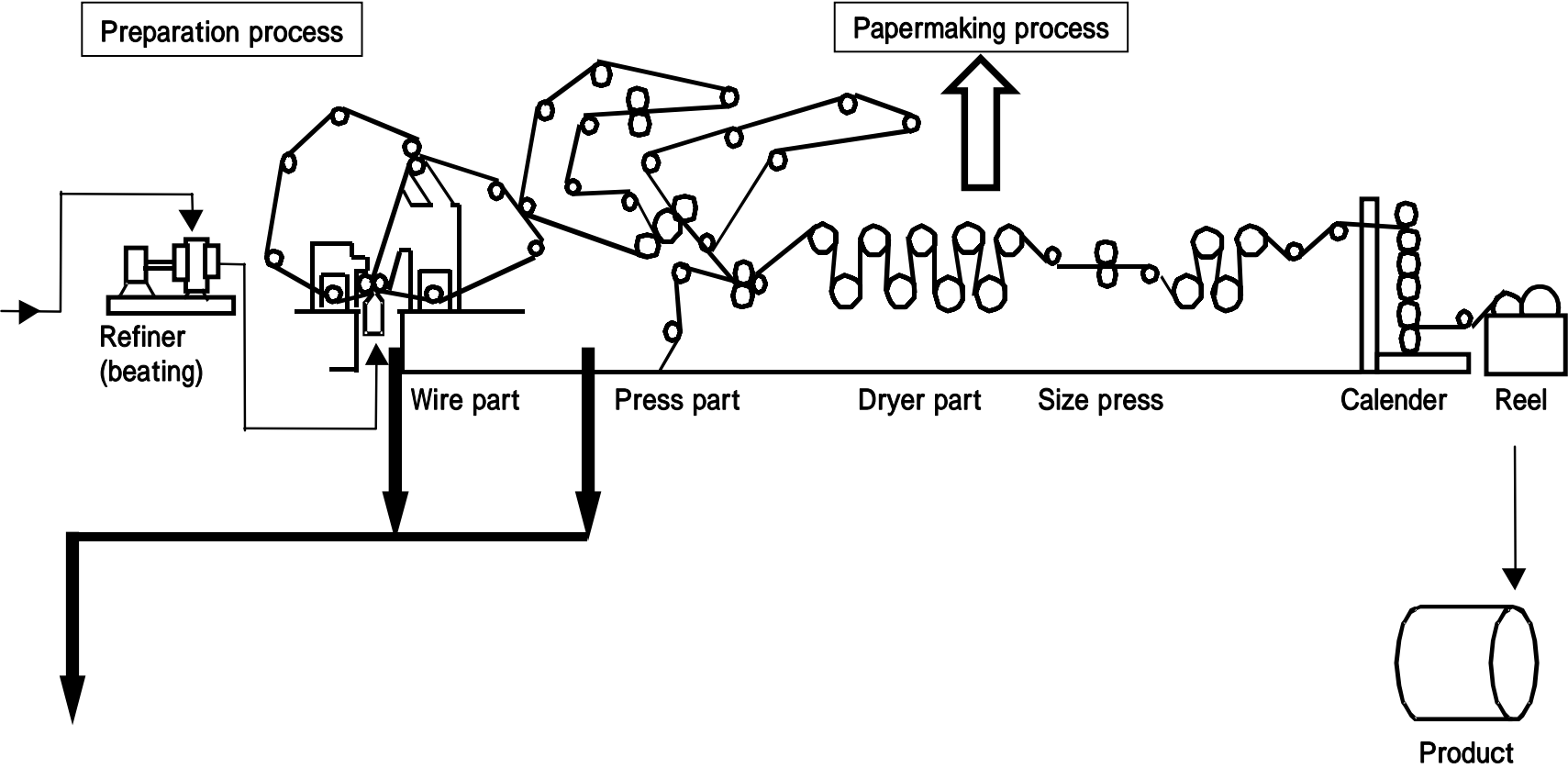


Diagram 1: Typical pulp and paper manufacturing processes

(3) Waste treatment process

