Process flow of waste paper recycle plant

JICA Training

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1. Raw materials of paper (1)

- Raw materials ---- Wood/plant fibers etc.
  (Waste paper)
  - Wood consist of cellulose, hemicellulose and lignin etc.
  - Cellulose becomes wood fibers, a polymer of glucose
    - Hemicelluloses (hemi=half); much less stable and degradable
  - Lignin is a very complex polymer, found between the cellulose fibers as binder
    - Lignin serves as the glue to bind cellulose fibers together
    - Under the bleaching process, the remaining lignin will be oxidized

2. Raw materials of paper (2)

- Net raw materials of paper are about 40-45% of wood chips (rest of 60-55% = waste?)
  - Ex. Dry wood: 45% cellulose, 25-35% hemicellulose, and 21-25 lignin, and rest 2-8%= resin acid, phenols, fatty acids, terpenes* etc. by weight

*Terpenes: a type of strong-smelling chemical substance found in some plants, especially trees that have cones.

  - The impurities including lignin may cause discoloration and the paper yellows upon aging.

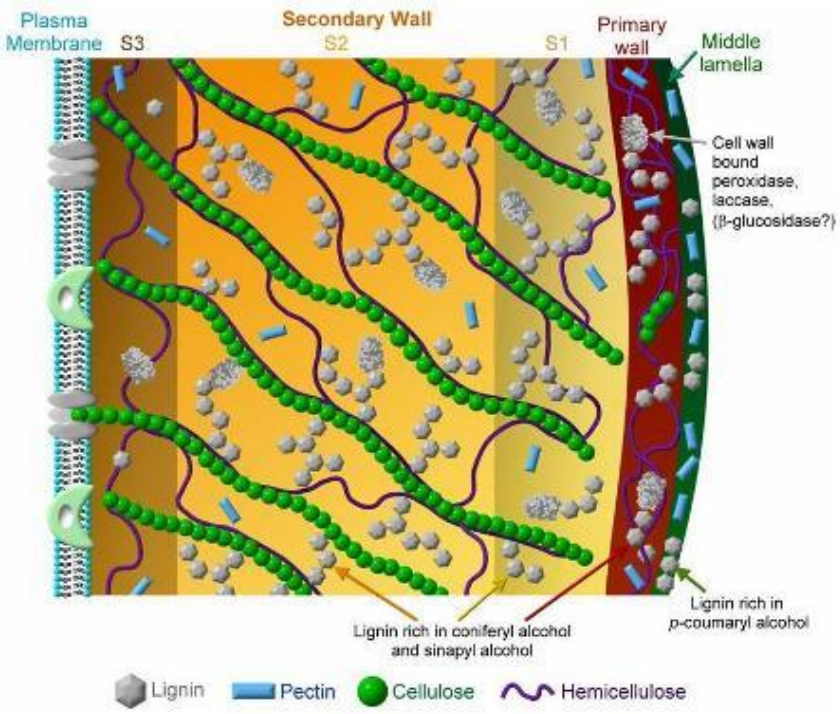


Figure: Molecules **2010**, *15*(12), 8641-8688

3. Pollutants - Biomass energy

http://www.hokuetsu-kishu.jp/environment/energy1.html

The black liquor is collected out of dissolved wood substance, processed wood chip and utilized as fuel in major paper mills.

Under 100℃ black liquor becomes solid and often causes clogging.

Then, 'Ion exchange resin method' is applied to separate chlorine and potassium (K) from black liquor. This is for the prevention of clogging in flue gas pipes of a black liquor collection boiler.

Hokuetsu co. saves heavy oil 5,022kL/year by utilizing black liquor, it also saves 14,976 tons of CO_2 according to their web site.

Source: HOKUETSU KISHU PAPER CO., LTD HP

4. Four basic steps for papermaking

Breaking down

- Breaking down the raw materials to fine particles

Dissolving chemically

- Dissolving the lignin and other non-cellulose compounds chemically

Paper sheet

- Forming a layer of pulp slurry, then dried on a paper machine, yielding a mat of cellulose fibers (a paper sheet)

Finish

- Addition of dyes, coating materials or preservatives etc.

4-1. Bleach

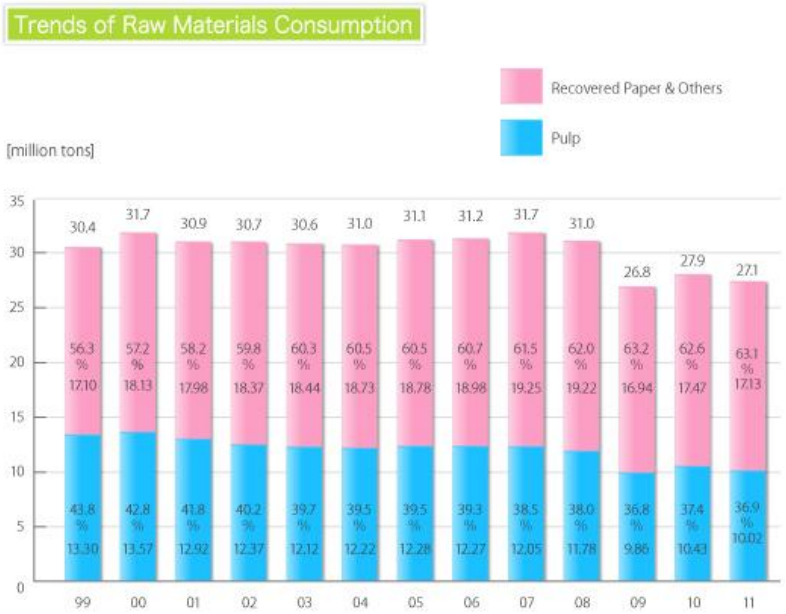
Bleaching of pulp

Chemical pulping, especially the Kraft process, produces dark colored pulp because of:

- remaining lignin, wood components which make paper turn yellow and brittle (not strong), and
- resinous bark as well as knot particles which leave tiny dark spots on the paper.

In order to obtain white and strong paper, these constituents should be removed further by bleaching operations. Bleaching is a successive process involving multiple steps consisting of several oxidation stages (one or two alkaline). It utilizes various chemical agents, such as chlorine, sodium hydroxide, and sodium hypochlorite

5. Japan Paper Association (1)



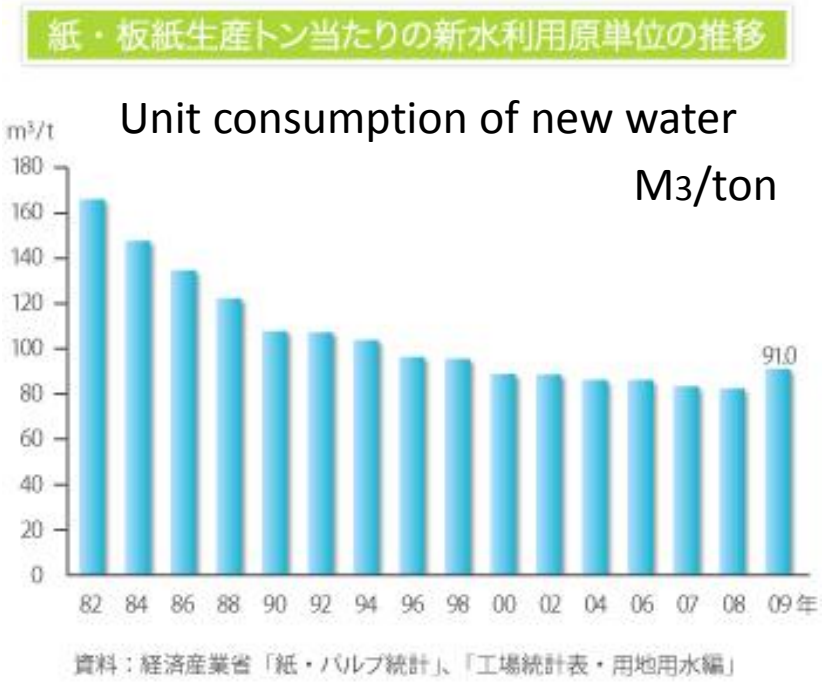
Japanese pulp and paper industry has been promoting the use of recovered paper as raw material.

- During the period from 1990 to 2007, recovered paper consumption increased by 4.8 million tons whereas wood pulp consumption declined.
- However, with the decreased demand for paper and paperboard due to the global recession triggered by the Lehman Shock in 2008, raw material consumption has been much below the 2008 levels since 2009.

- **In 2011, recovered paper utilization rate in 2011 is 63%,which is a top level in the world.**

http://www.jpa.gr.jp/en/industry/data04/

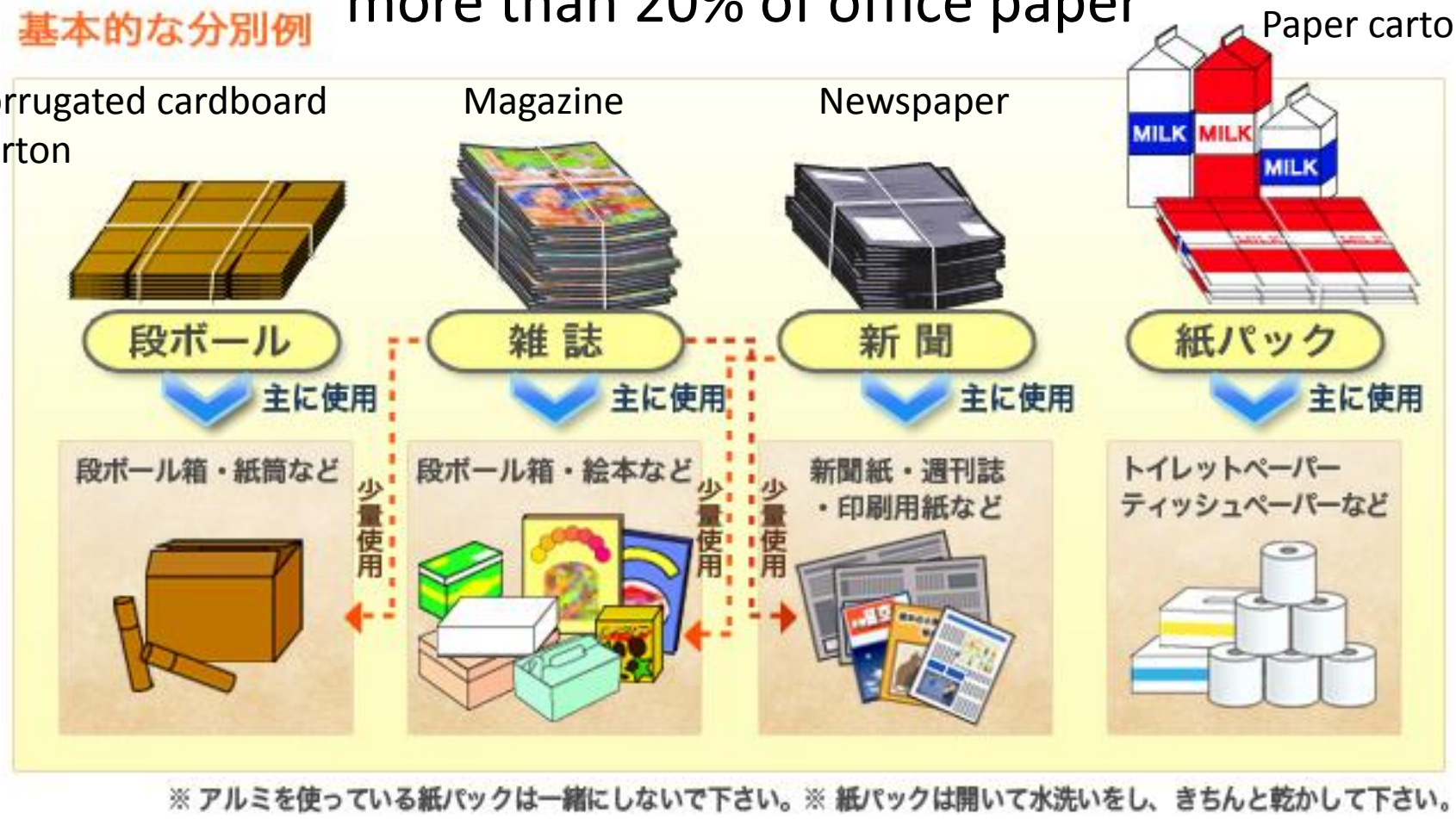
Japan Paper Association (2)



- Waste water treatment
  - Biological treatment
  - Physical & Chemical treatment
  - Other methods
    - Activated carbon
    - Separation membrane
    - Dewatering
  - Sludge
    - Fuel
    - Concrete mixing
    - Heat insulating material for iron manufacturers

http://www.jpa.gr.jp/env/environment/equipment/index.html Japan Paper Association

5-1. Recycled paper: 90% of cardboard, 70% of newspaper, more than 20% of office paper



Major flow Only small quantity can be used

Limited usage of recycling paper because of the paper quality

Figure: Paper Recycling Promotion Center, http://www.prpc.or.jp/menu02/cont01.html

Newsprint	新聞用紙
Printing/writing	印刷用紙、筆記用紙
Woodfree	上質紙
Woodfree containing	中質紙（ＧＰ配合紙）
Casemaking materials	ケース材料
Kraftliner	クラフトライナー
Other wrapping papers	その他包装紙
Tissue	薄葉紙、家庭用薄葉紙
Other paper	その他の紙
Board (excl. Casing)	板紙（ケース用を除く）

古紙ハンドブック2010　　Paper Recycling Promotion Center

Note Woodfree: High quality white paper, not brown paper/cardboard

Need to separate or sort out used paper by class

Ex. Coniferous tree pulp is used for newspaper which includes lignin etc.

5-2. What is 'Woodfree‘ paper?

- The term 'woodfree' causes the most public confusion, as the paper is anything but 'wood-free'.

- The name indicates that when originally pulped the 'woody‘ lignins in the timber were destroyed in a chemical reaction to produce a higher quality paper.
- If not removed, the lignins - the inflammable part of the wood - cause paper to yellow and become brittle with age (as, for example, old newspapers do).
- You can see exactly the same process in the way pine furniture changes colour with age.

Source: http://rps.gn.apc.org/info3.htm

6. Foreign or alien substance

Impurities such as ink and plastics

Paints, ink & colors
Adhesive, glue

Waterproofing
Plastic/metal Coating

Various contamination
offensive odor etc.

- Chemical substance, heavy metals and other contaminants must be rejected for paper recycling
  - Adhesives, Hot-Melt, Manifold (carbon paper), Ultra-Violet [UV] Inks／Coatings, magnetic ink, tar (water-proof),

Photo: Paper Recycling Promotion Cantor, http://www.prpc.or.jp/menu02/cont01.html

7. Secondary Fiber Process Outline

- Sort and classify the waste paper (by class and grade)
  - Used corrugated boxes need to be cleaned
  - Remove hot melt coatings, plastic films, and latex etc.
- Process
  - To a continuous pulper w/impellor

impellor

    - Metal (ex. Staples) can be screened out or removed by a magnet.
  - Enhance the fiber separation (remove light debris)
  - De-ink by chemicals, heat, and mechanical energy
    - Dislodge the ink particles from the fibers and disperse them in an aqueous solution; detergents, forming agents, caustic soda, sodium silicate, and borax (surfactant effects)
    - *Surfactant: lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid*

Borax
硼砂

  - Undergoes washing and/or floatation to separate the ink
  - A final bleaching or a brightening process as needed

7-1. Pulper

- In paper-making, a pulper is a machine that **mechanically and chemically processes the fibers of wood chips** to reduce them to pulp.
- Pulpers are used widely in Paper and Pulp Industry for slushing all types of waste paper.

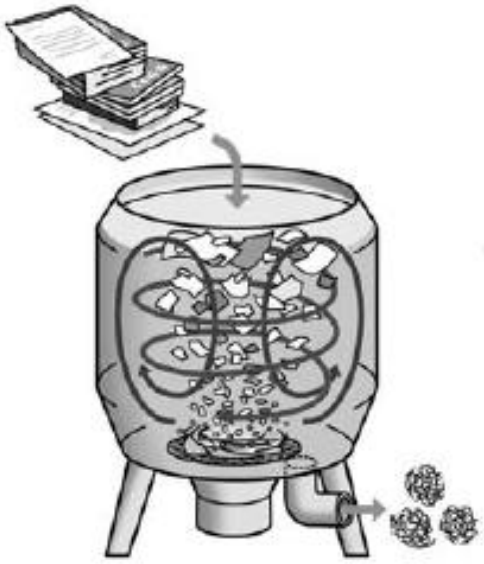


図1　パルパー

Waste Pulper (USA Navy/Marines: SER-014-99; Air Force)

Benefits:

Reduces volume of waste by up to 85 percent.

Reduces number of trash pickups.

Reduces labor hours needed to haul wastes to pick-up area.

Eliminates the need to sort paper from food waste.

Reduces rodent and insect problems.

Disadvantages:

High initial capital cost for waste pulper equipment.

Increased energy costs.

**The food wastes must be segregated from paper and cardboard packaging materials in advance.*

7-1-1. Secondary Pulper

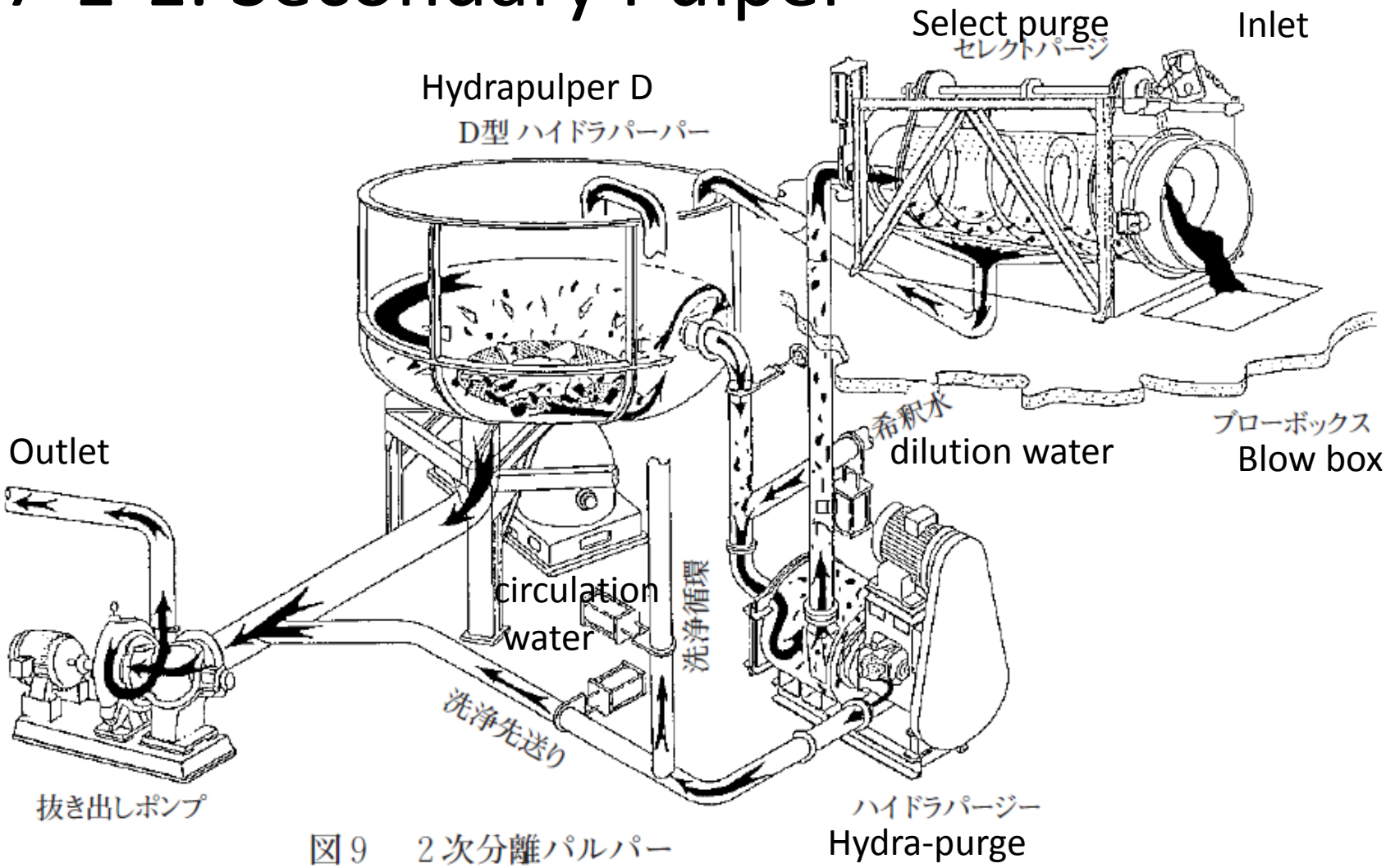


図９　２次分離パルパー

(1)Promotes pulping and (2) rejects foreign substance just before full pulverization/crushing

7-1-2. High concentration Pulper & Drum Pulper

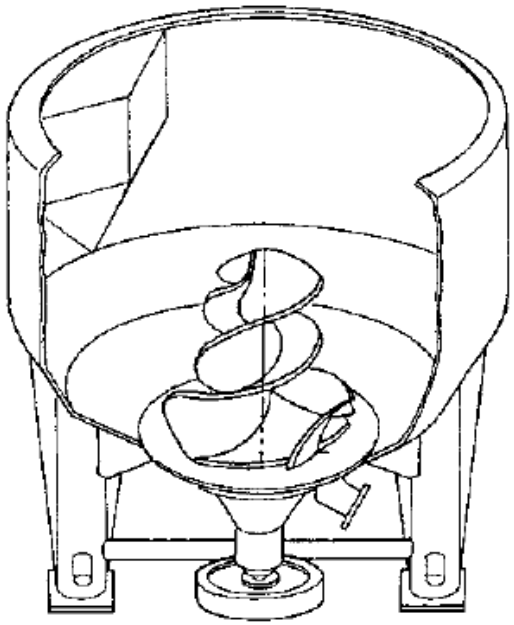


図 10　高濃度パルパー

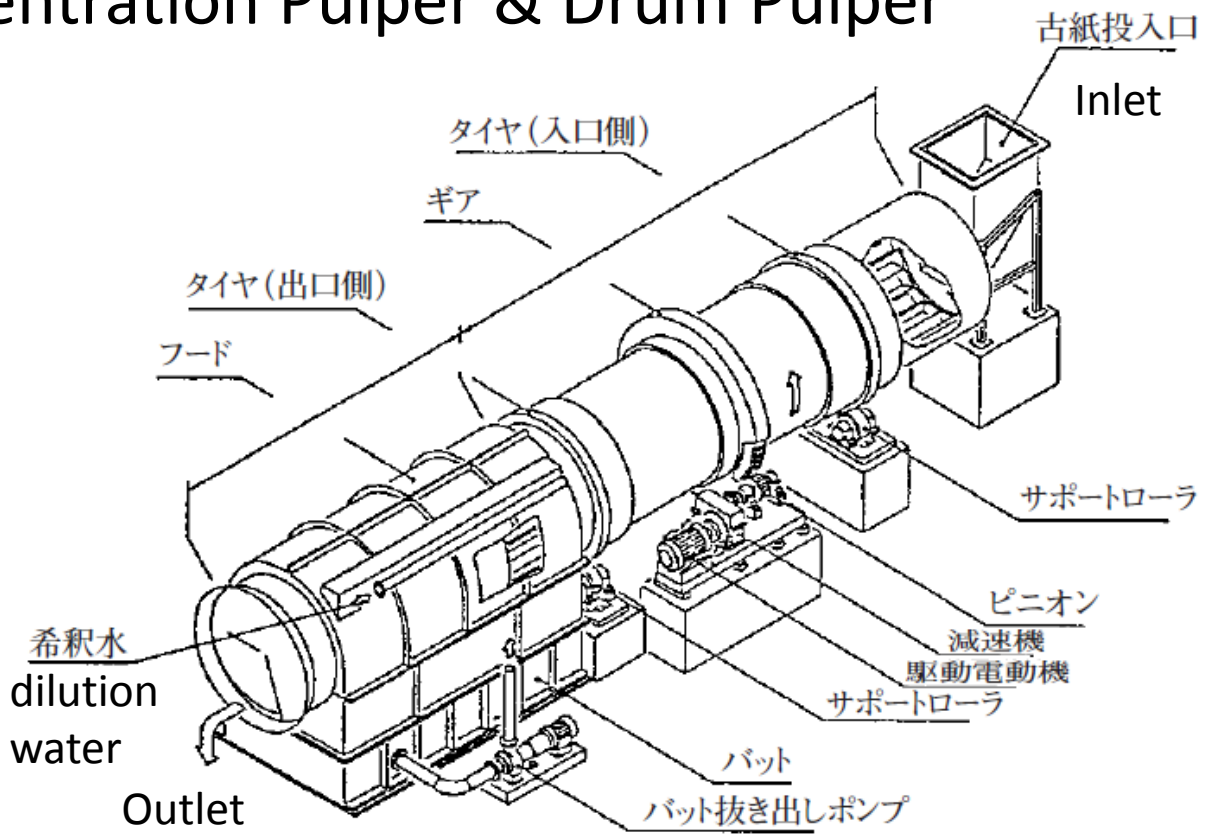


図 11　ドラムパルパー

Fig. 10 High concentration Pulper:　Utilizing friction among fibers in dense thickness as paper clay, pulping promotes with minimum crushing of foreign objects. Fig. 11 Rotating drum pulverizes waste paper but least damage to foreign objects

7-1-3. Mixer Pulper

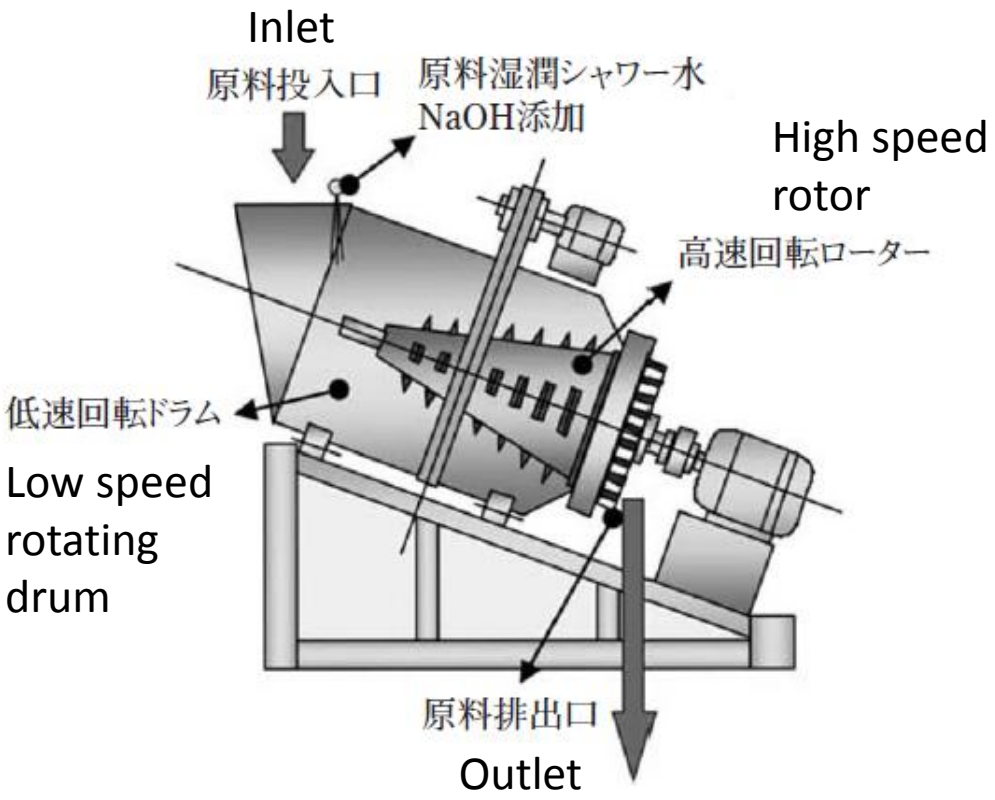


図12　ミキサーパルパー

Under very dry condition the rotor provides strong agitation power and shearing force, which rejects and separates films, hot-melt resin, strings and tapes.

Milk box paper and waxed paper cups can be processed.

7-1-4. Pulper Mature Tower

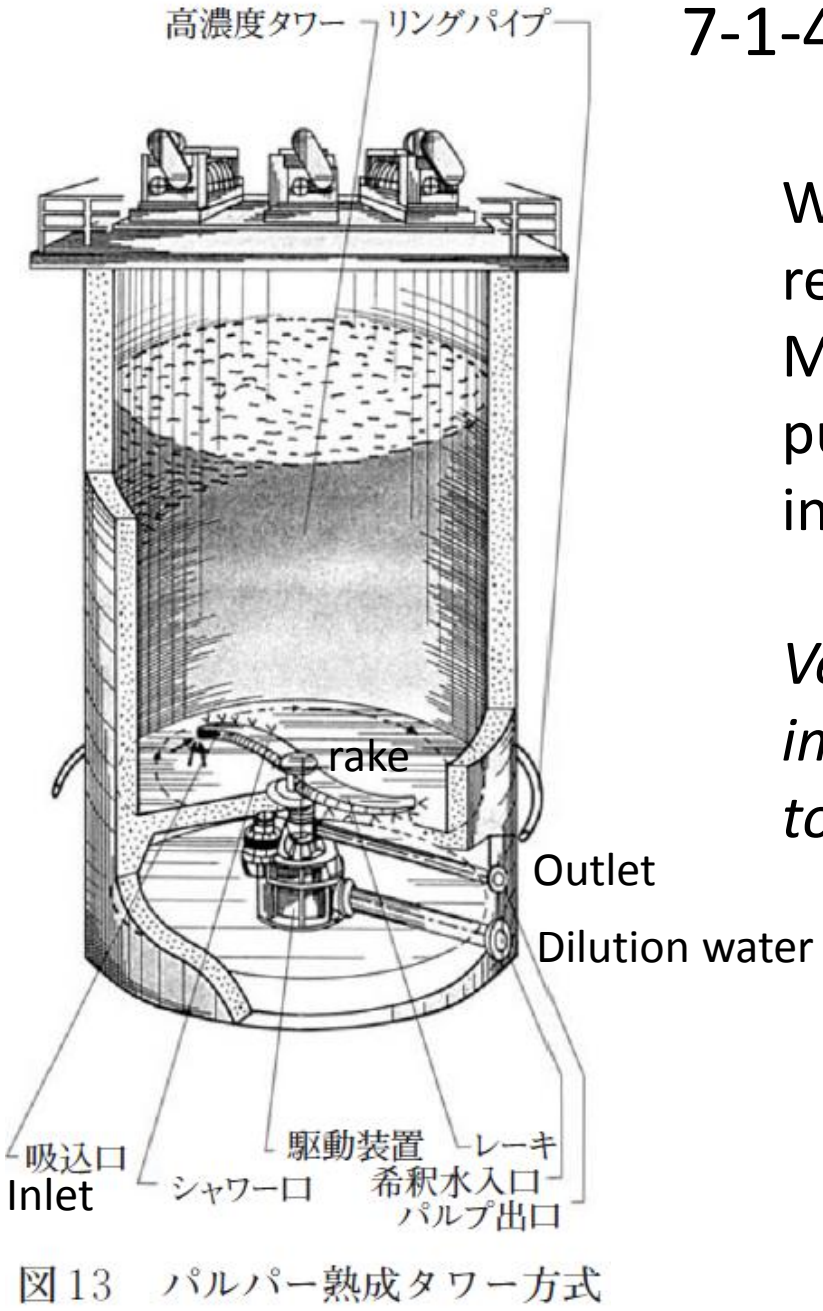


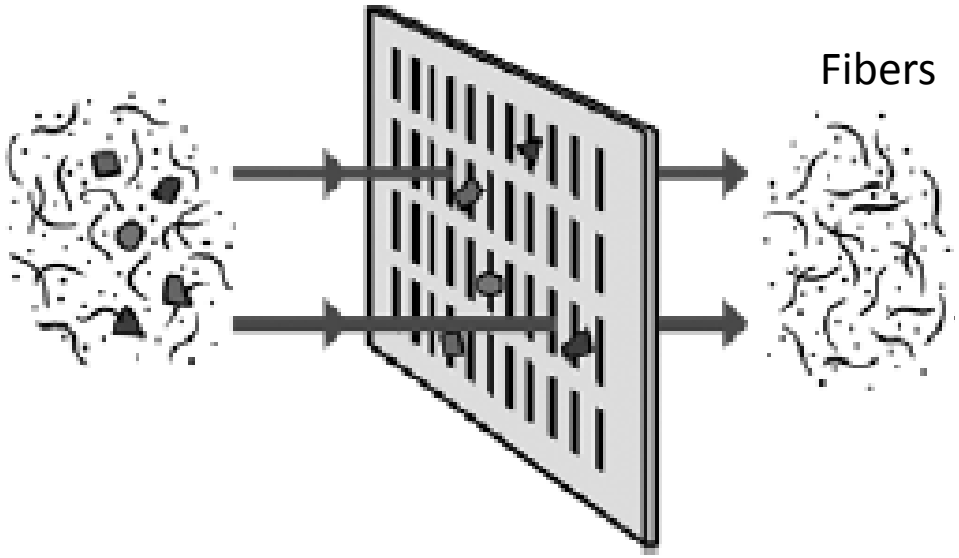
図13　パルパー熟成タワー方式

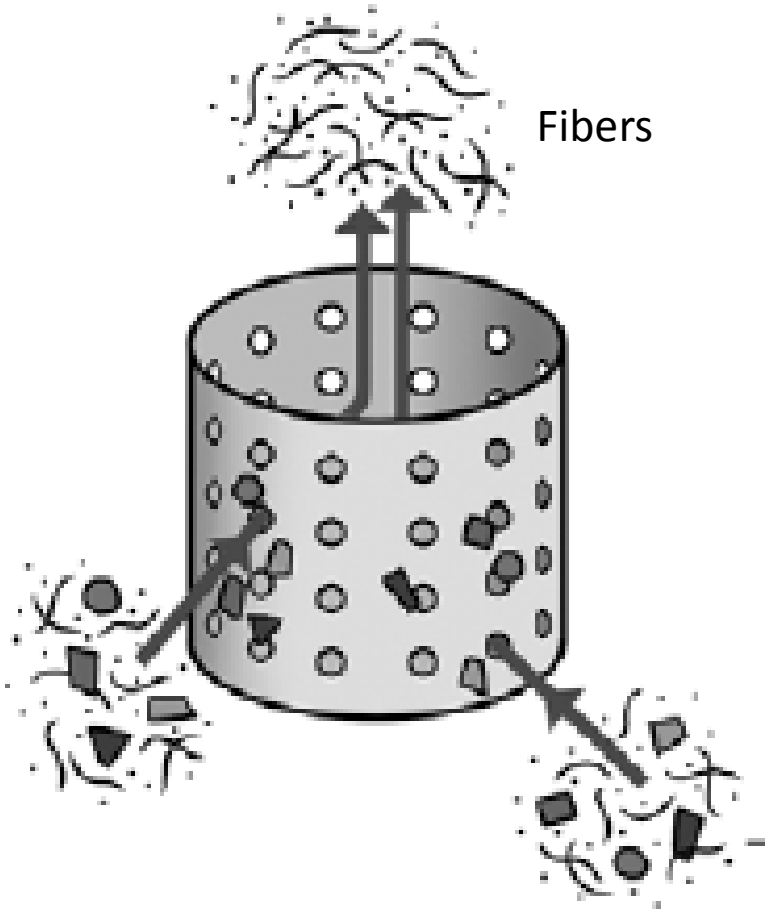
With limited pulper fluidity it requires long retention time. Maturing or digestion promotes pulping (fiber separation) and ink clean-up.

Very dirty laundry will be dipped in the liquid detergent one night to improve the clean-up effect.

7-2. Screening

Roughing and careful selection





Thin slit of 0.15mm segregates foreign objects helped by pressured water flow (pulping suspension).
This process is very important to purify the pulp suspension.

7-2-1. Screen Selection

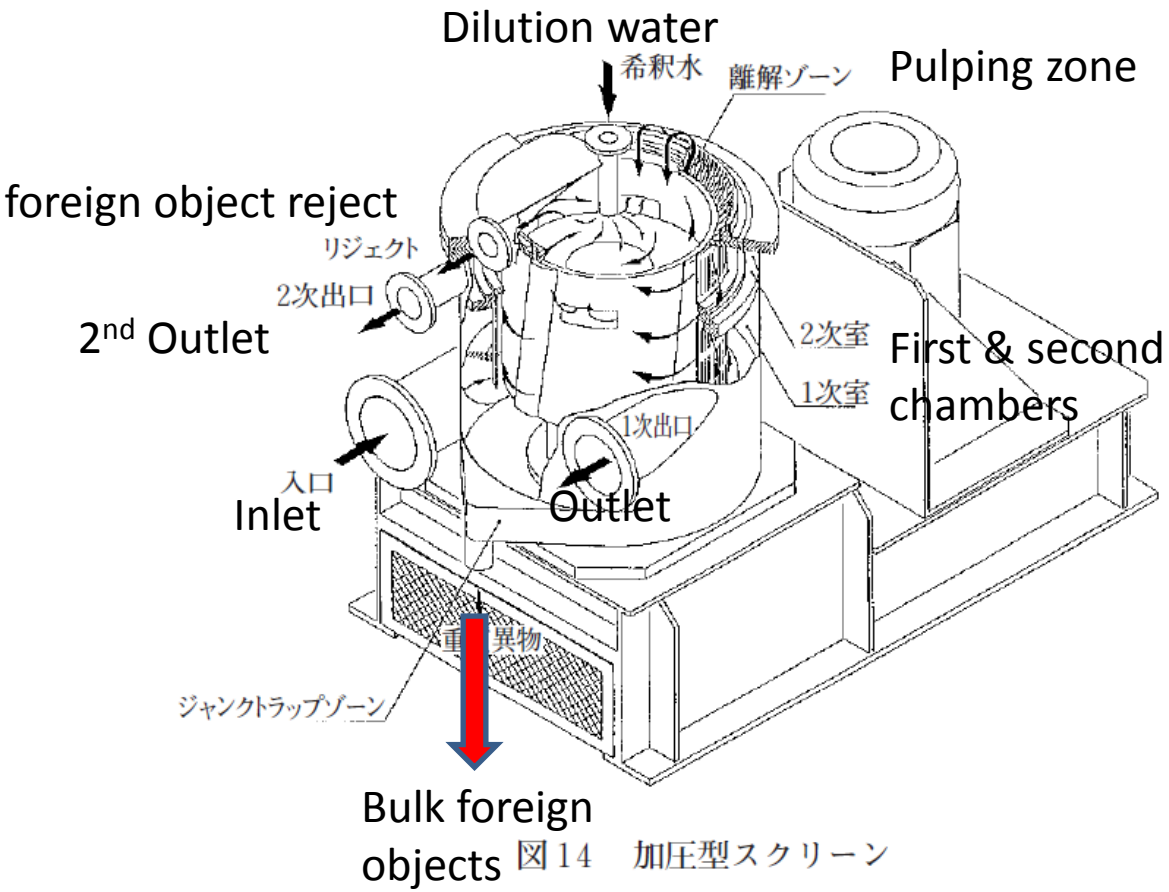


Fig. 14 Pressurization type screen

7-2-2. Cleaner (centrifugal separator)

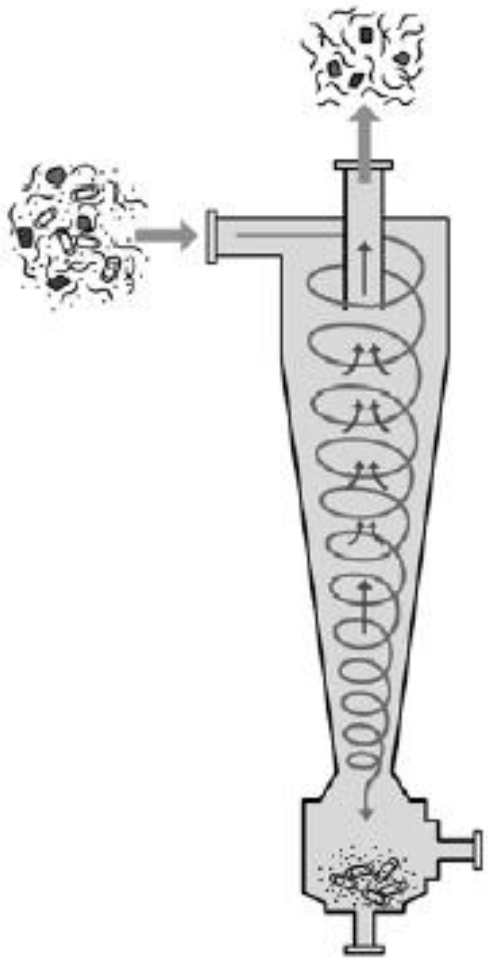
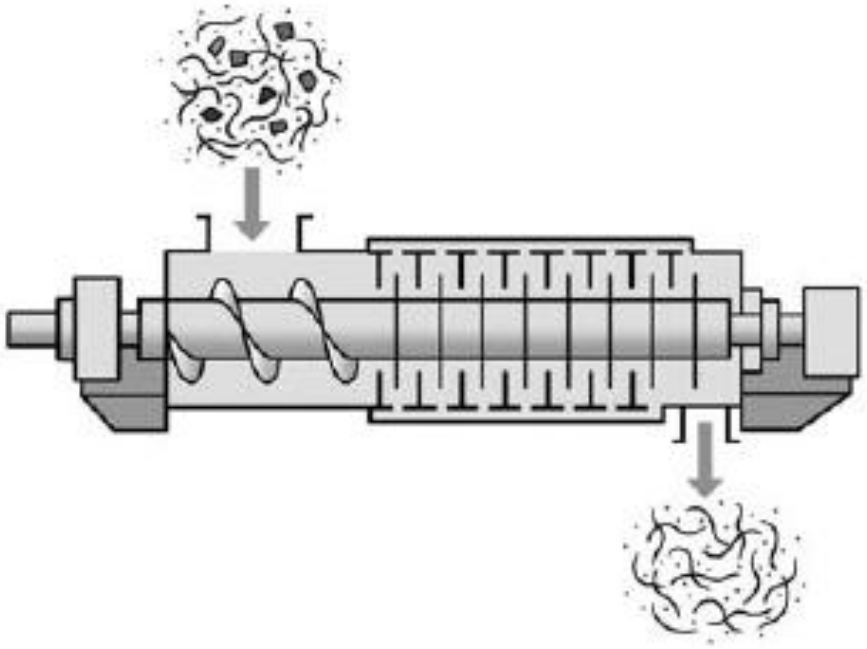


図４　クリーナー

Selection by centrifugal force

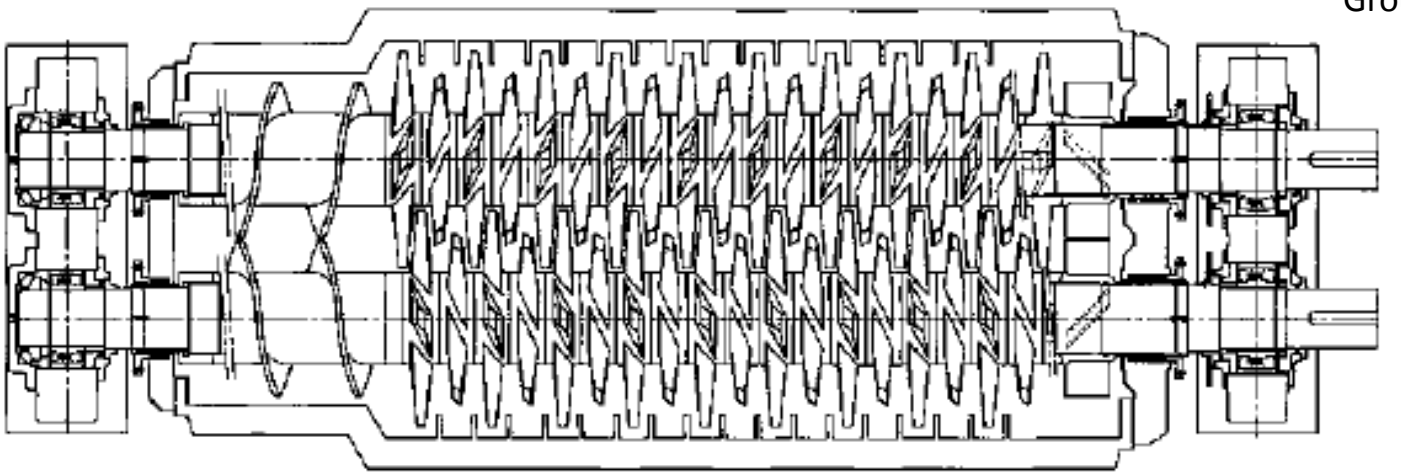
Pulp suspension containing heavy objects such as sand, stone and metal parts will be pumped up to the cleaner. Only heavy objects or particles will be rejected and collected on the bottom.

7-3. Deinking and Cleaning



So-called ‘kneader’ strongly washes printed waste paper with chemicals and separates ink

Ground /floor plan
（平面）



Side view
（側面）

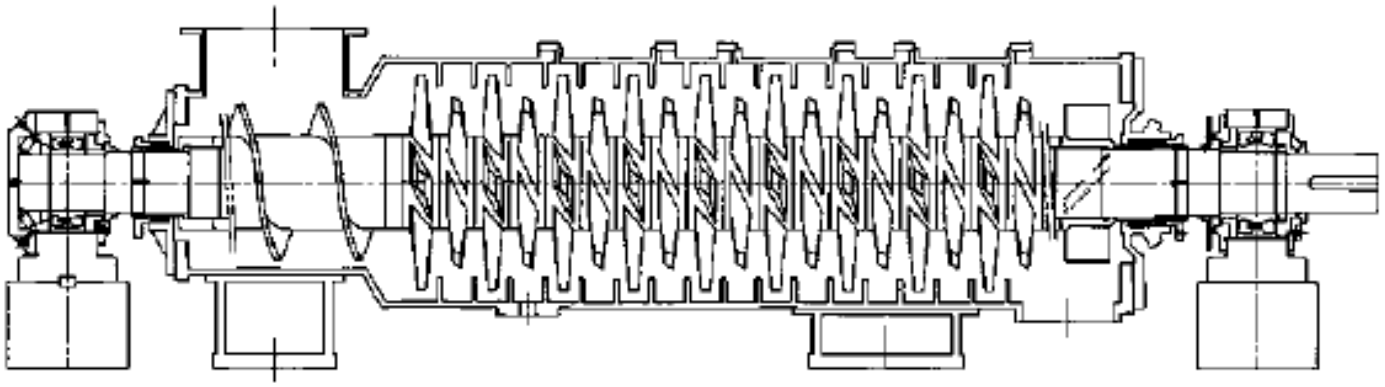


図 20　ニーディング設備

Fig. 20 Kneading equipment

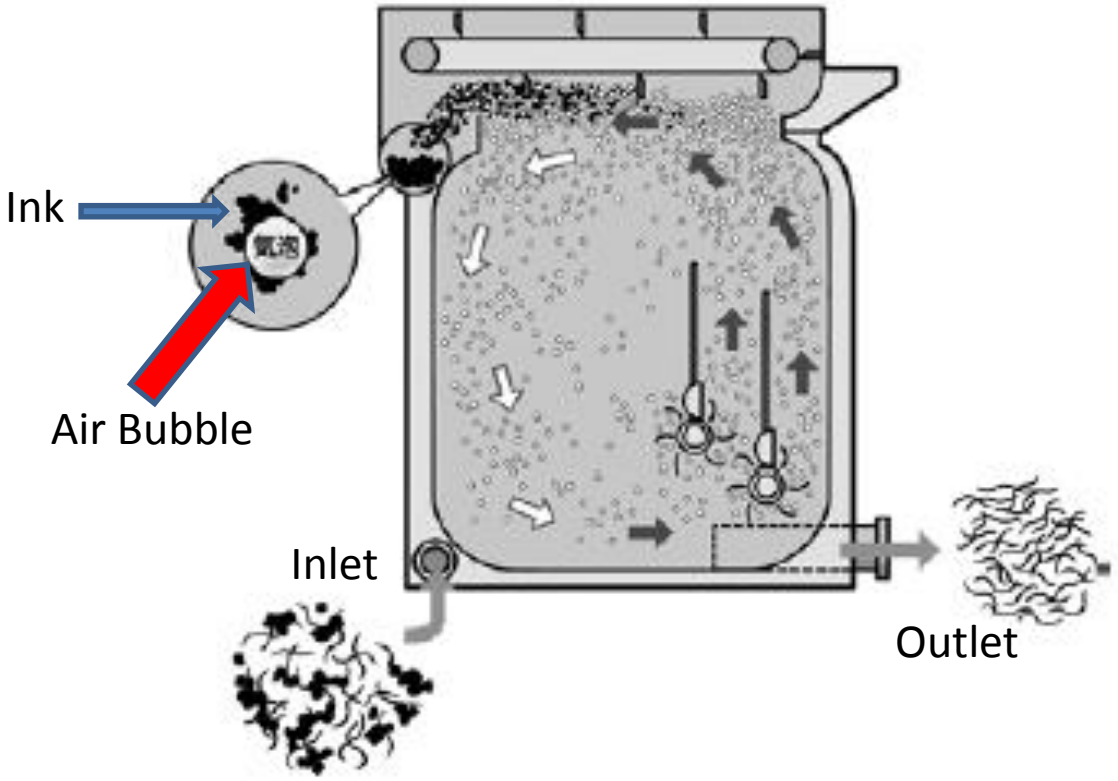


Fig. 6 Floatater

図 6　フローテーター

Flotation process is very important for waste paper treatment. Lots of fine air bubbles inject into (blow into) the suspension and capture the ink particles, floating up to the surface.

7-3-1. Deinking and Flotation

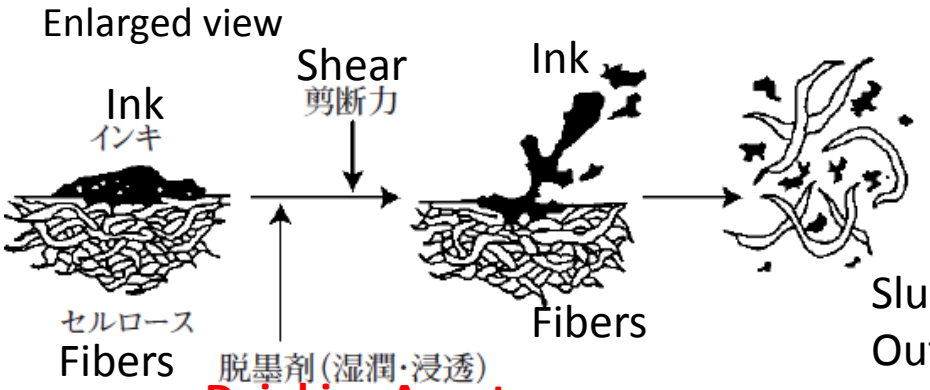


図 15　古紙融解，熟成工程

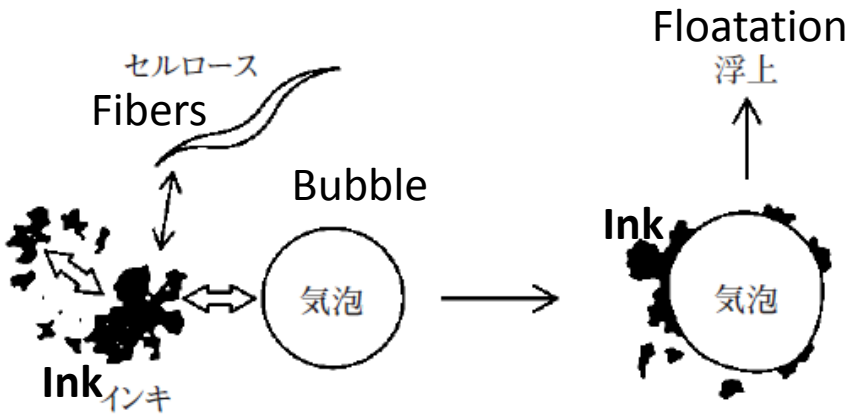


図 16　フロテーション工程

Flotation

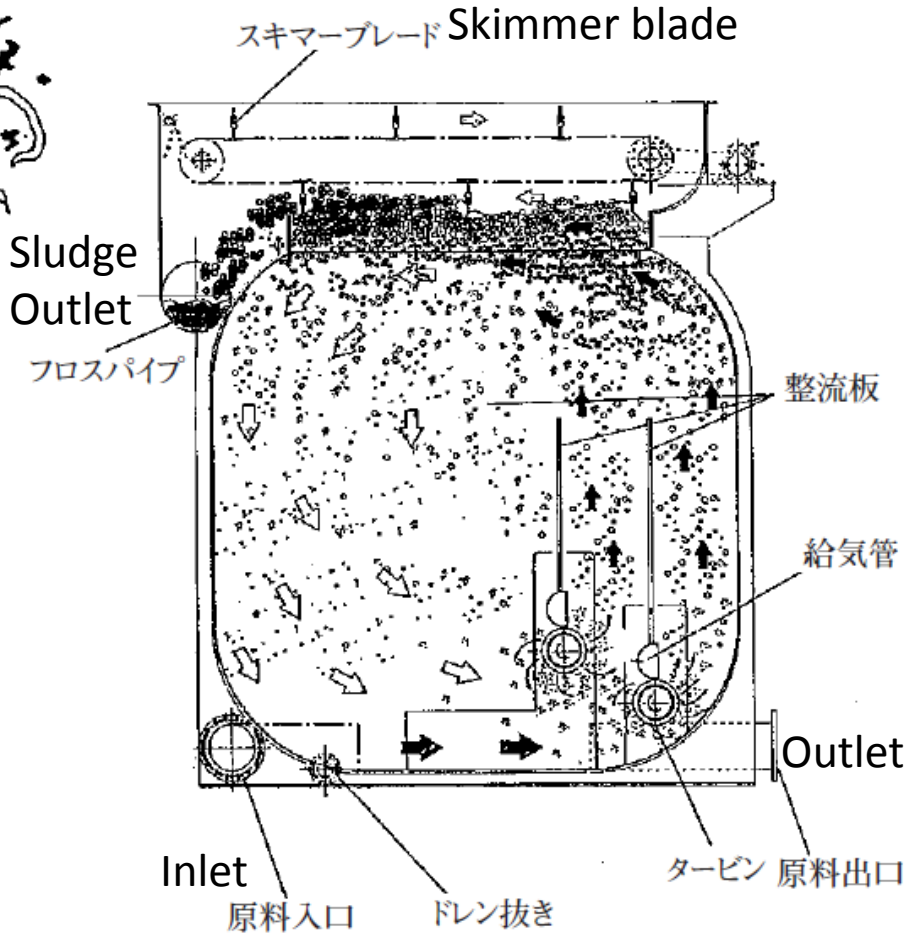


図 17　フローテーター断面図

Fig. 17 **Floatater** cross section

7-3-2. Deinking agent

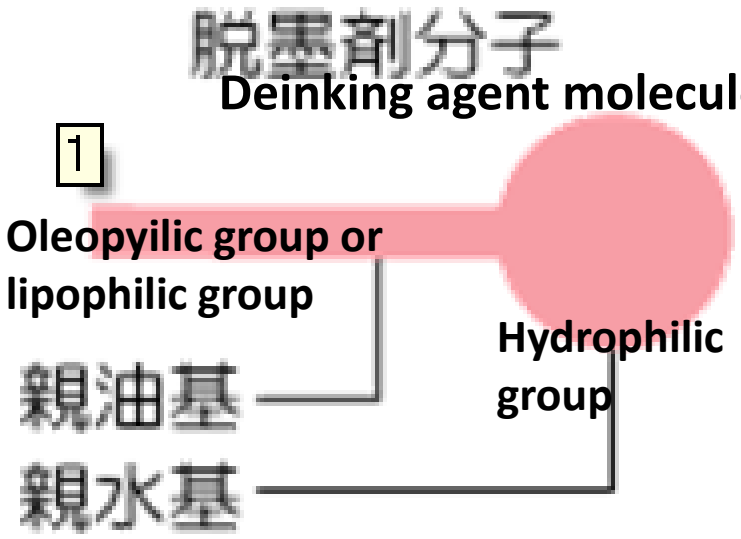
- Deinking Agents or deinking solutions help to enhance the removal of ink/paint from recovered paper
- Some modifies cellulosic fibers to aid in the separation of ink and other debris from recycled paper

- Ex. High-quality alcohol derivative , fatty acid, derivatives of oil/fat etc. such as soap

Source: Nissin-kk.co

7-3-2-1 Deinking agent

1. Penetration behavior (osmosis)
   - Promote osmotic/penetrating action of water or alkali fluid
   - Waste paper pulping (break)
   - Penetrate both ‘lipophilic & hydrophilic group’ part

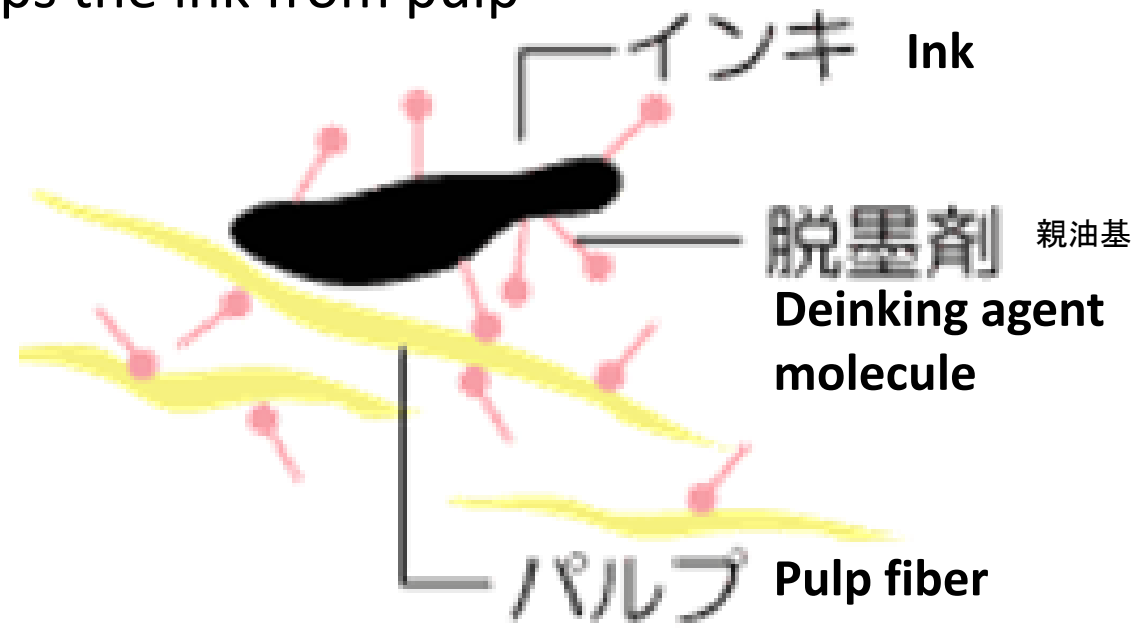


Source: Nissin-kk.co

7-3-2-2 Deinking agent

2. Exfoliation (stripping action)

- Approach the ink surface by ‘lipophilic group’ of the agent
- Dispersion force strips the ink from pulp



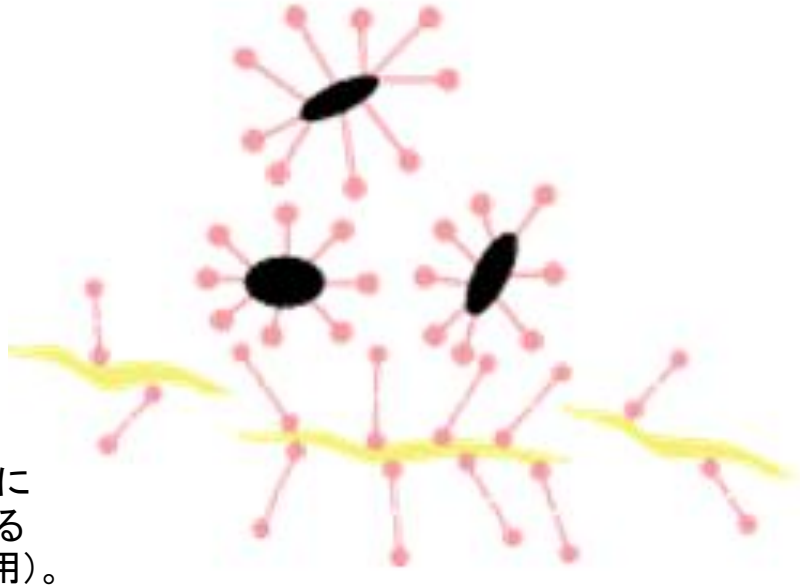
‘lipophilic group’ is a friend of oily ink

Source: Nissin-kk.co

7-3-2-3 Deinking agent

3. Dispersion of ink

- Covered by ‘lipophilic group’ of the agent
- Dispersion promotes and they prevent re-attaching to the fibers when dewatering sludge ink separates from the sludge



安定分散され、パルプへの再付着を防止。安定に分散されたインキは脱水時に搾り水へと移動することによりインキとパルプが分離される（洗浄作用）。

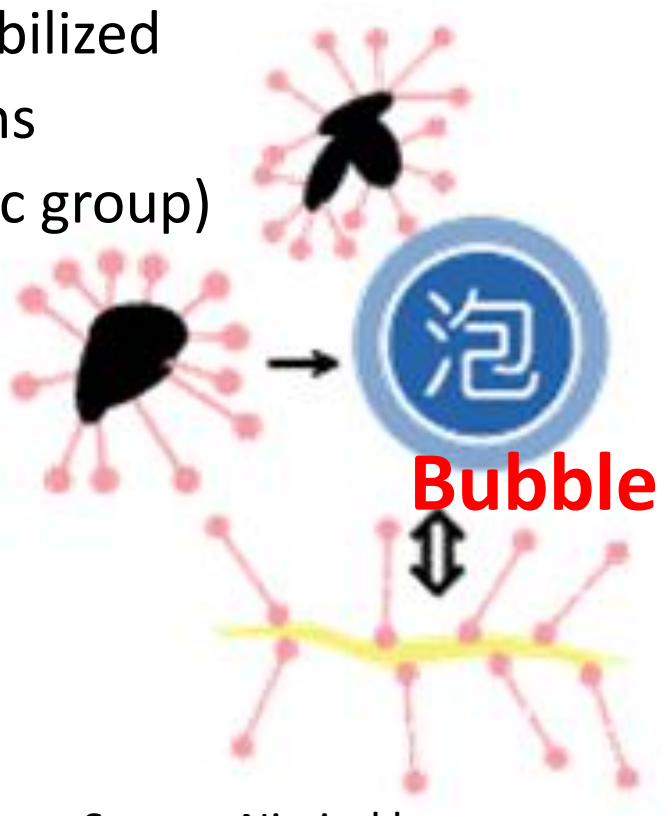
Source: Nissin-kk.co

7-3-2-4 Deinking agent

4. Foaming

- Array of the agents in/on interface of water and air
- The foaming, the bubble film, stabilized
- The agent controls foam conditions

  (the balance lipophilic & hydrophilic group)

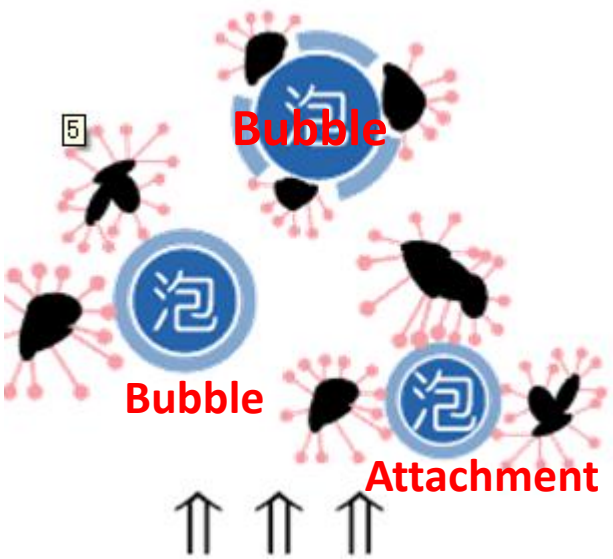


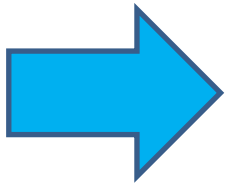
Source: Nissin-kk.co

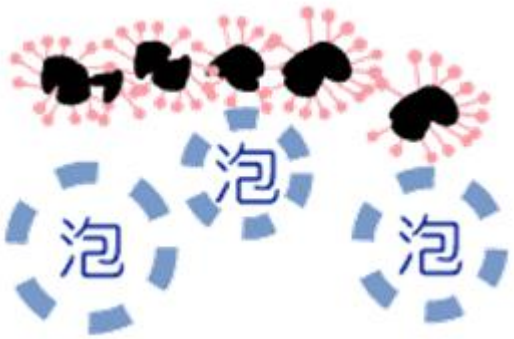
7-3-2-5 Deinking agent

5. Coagulation

- The agents on the inks stick together, making larger particles
- Hydrophilic part of the agent array attracts the bubble surface
- The ink attached bubble goes up (float) to the water surface
- Ink concentrated layer and the bubble layer







The separated foam will be broken soon as designed

Source: Nissin-kk.co

7-3-2-6 Deinking agent comparison

Deinking agent	Strip	Foam	Skim	Usability
Neutral detergent	△	✸	X	☺
Fatty acid	X	X	✸	X
Fatty acid derivatives	△	☺	☺	☺
Fat and oil derivatives	☺	☺	△	☺
High-quality alcohol derivative	✸	△	△	☺

http://www.nissin-kk.co.jp/product/datsuboku/datsuboku.html

✸ Best ☺ Good

	剥離性	発泡性	捕集性	作業性
●汎用中性洗剤	△	◎	×	○
●脂肪酸	×	×	◎	×
●脂肪酸誘導体	△	○	○	○
●油脂誘導体	○	○	△	○
●高級アルコール誘導体	◎	△	△	○

Source: Nissin-kk.co

Selecting the deink agent (1)

- Popular agent is alkylene-oxide added high-quality alcohol derivatives (Non-ionic surfactant)
- They are sensitive to water temperature etc.
  - For example, 40 degree and 55 degree indicate the significant difference in dynamic surface tension
  - Forming effect will be influenced as well
  - Mutual relationship between air bubbles and ink particles
  - Waste paper contents, added substances and various processes/condition etc. affect the performance
- Complicated parameters must be considered

Selecting the deink agent (2)

- Focus on ‘Flotation process and floating sludge’
  - Forming (air bubbles)will be influenced by various factors such as used pulp conditions, process equipment, circulating white water, pH, ORP etc.
- Bigger or smaller G/L（Gas/Liquid) ratio = often excessive floating sludge

Source: http://www.lion.co.jp/ja/chem/gijutsu/fiber/fiber01/

7-3-3. Washer

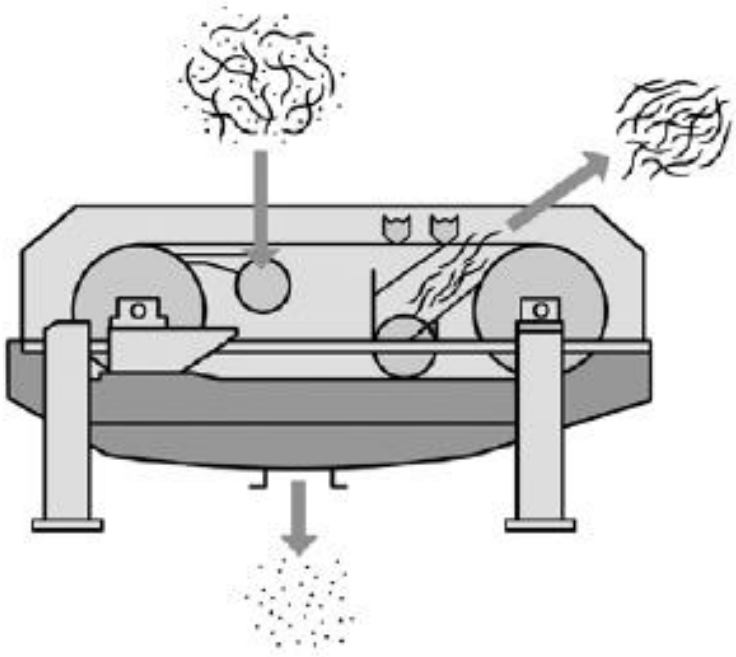


図7　ウォシャー

- Repeated washing, rinsing, and drying
- Recycling water

Cleanup by the ‘Washer’ separates small particles other than paper fibers. Then, de-watering processes

7-4. Bleaching

In case of high quality paper they apply ‘bleaching’ utilizing chemicals such as;

Hydrogen peroxide solution

Sodium hypochlorite

Thiourea dioxide, thioureadioxide etc.

In addition, Bactericidal action or germicidal action and Decomposition of impurities

The process temperature; often 40℃~60℃

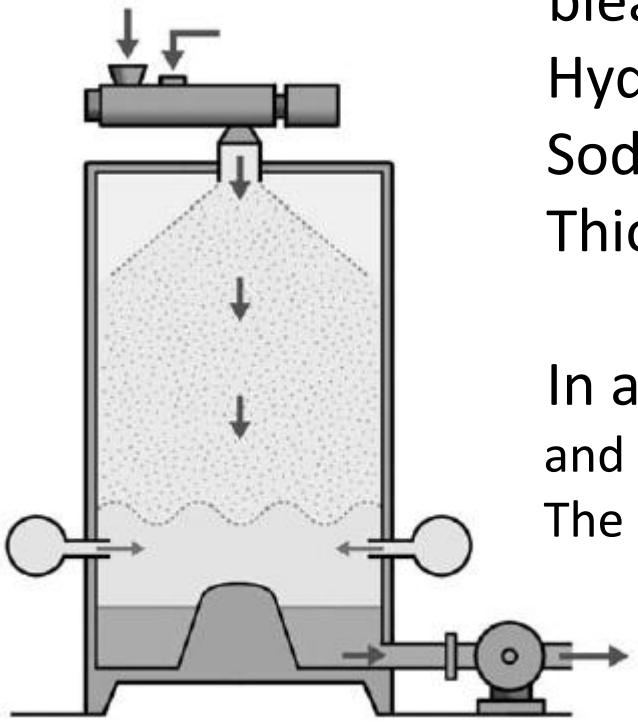


図８　漂白タワー

漂白薬品:過酸化水素水、次亜塩素酸ナトリウム、二酸化チオ尿素、60℃から40℃に加温して漂白されることが多く、所定の白さを確保すると同時に殺菌作用や一部の不純物の分解が進みパルプの純度が上がる

7-5. Hot Disposer

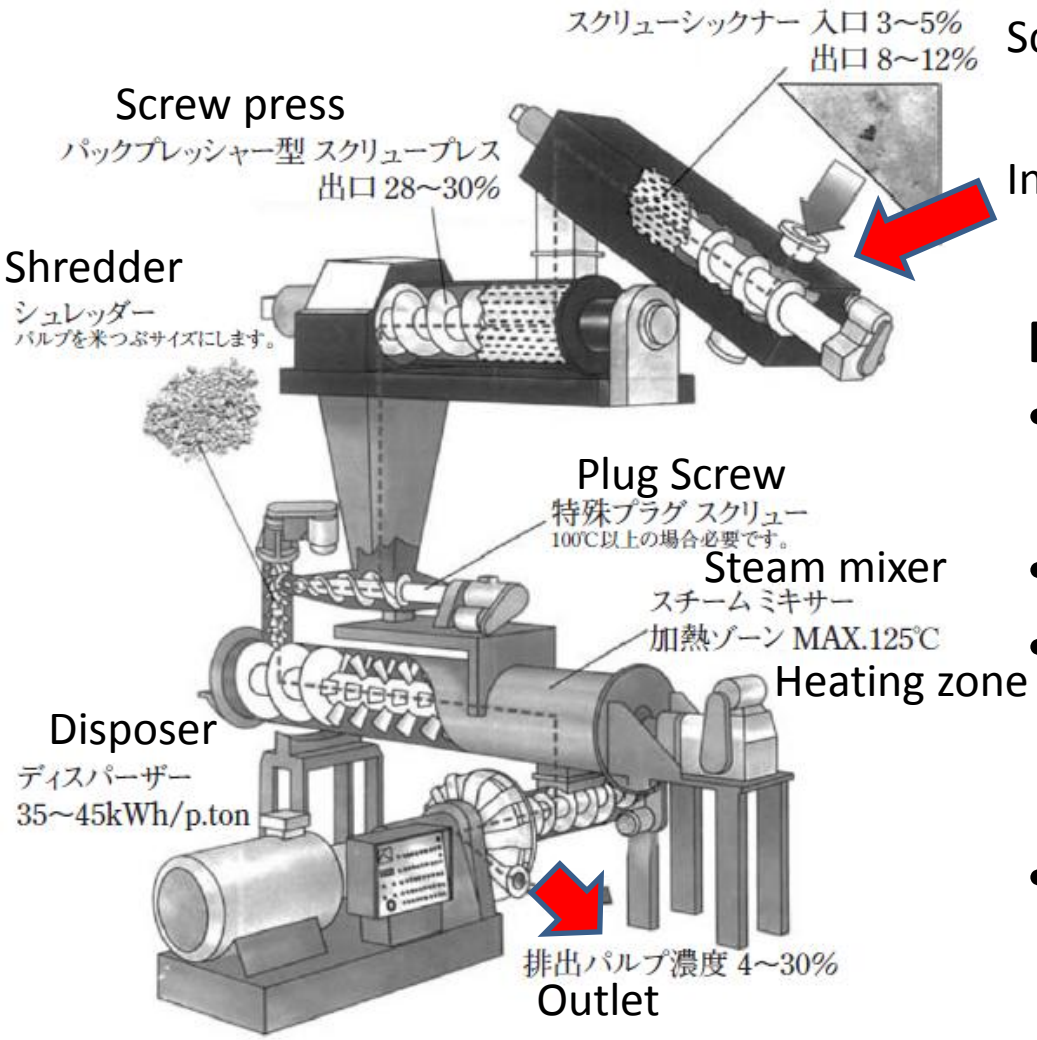


図 21　ホットディスパーザー設備

For high quality paper

- Rubbing and kneading very strongly with heat
- Thermal decomposition
- Residual impurities such as ink particles will be broken-up
- Additional washing and rinsing effects

Figures on slides 1~21: Paper Recycling Promotion Center 2010

8. Recycled paper manufacturing (actual examples)

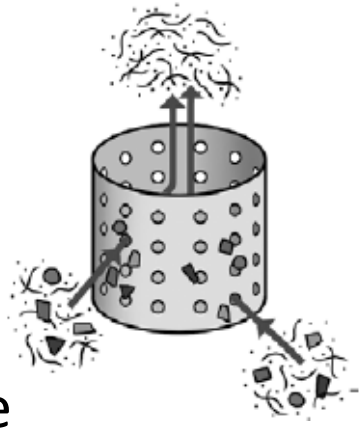
http://www.np-g.com/npi_koshi/a_4.html.

Inside of the pulper Dissolution/melting

1. Mixed with hot water and chemical in the pulper and paper will be broken into small pieces
2. High-concentration pulper: Caustic soda (sodium hydroxide) and deinking agent in hot water will be mixed with the paper (Break up paper/deinking process)

3. ***'Pair pulper'*** (debris and grit removing screen)
- First stage: Round holes of 7mm in diameter
- Second stage: Round holes of 3.5 mm in diameter

Large solid and foreign objects will be rejected by the two kinds of screens



Source: Nippon Paper Industries Co. Ltd

8-1.Two stages, screening and floatation

- Small slit of 0.2mm in width
  - To reject foreign substances
- Smaller slit of 0.15mm in width
  - Reject small foreign substance/dust

- Floatater
  - Bubble of the detergent remove ink and paints from crushed paper
  - Injected fine air bubbles capture small ink or paint particles and loading material that come up to the surface except fiber

http://www.np-g.com/npi_koshi/a_4.html

Source: Nippon Paper Industries Co. Ltd

8-2. Bleaching tower

- De-coloration or bleach of fiber
  - At the bleaching tower **hydrogen peroxide** solution ($2H_2O_2$) is mixed to decolorize fiber $2H_2O_2 \longrightarrow 2H_2O + O_2$
- Wash the fiber with clean water and dewater process follows and then, recycled pulp occurs

Pulp after dewatering

Stock tower of recycled pulp

http://www.np-g.com/npi_koshi/a_4.html

Source: Nippon Paper Industries Co. Ltd

9. Pulping pollution problems (1)

- The main wastewater problems
  - BOD, COD
  - SS
  - Odor and unpleasant color etc.
  - Adsorbable organic halogen , AOX

    (AOX is a measure of halogenated organic compounds)
    - Chlorinated phenols, chlorinated XXX -----
  - Dioxins and furans
  - Acetone, methyl ethyl ketone, chloroform, and chlorinated phenolic compounds

Source: WEF USA etc.

Pulping pollution problems (2)

Causes of pollution (Examples)

The some causes of pollution from paper industries:

- Price fluctuations
  - Raw material in use
  - Type of fuel and chemicals in use
- Obsolete old technology and machinery in use
- Lower production capacities
- PCM (insufficiency)
- No strict environmental regulations
- Thinking that it is an extra expenditure without any return

10. Detailed Treatment Flow examples

- Treatment flow
  - Equalization
  - Neutralization
  - Precooling
  - Primary sedimentation
  - Nutrient addition, aerobic biological treatment
  - Addition of floccurants to secondary clarifiers to improve settling
  - Multimedia filtration is recommended for the mechanical pulp subcategory.
    - To dissolve as much of the lignin that holds the cellulose fibers together, either extended cooking or oxygen delignification may also be used if necessary.

10-1. De-ink (1)

- When waste newsprint paper is stored for a short period, the ink carrier on the wastepaper is not sufficiently dried.
- However, it is absorbed by the fiber only.
  - Under the action of chemical reagents and under conditions of suitable temperature and consistency, the carrier is saponified.
- The ink is dispersed (scattered) easily and the pigment is also released easily.
- The **pigment**, which consists of **carbon black**, usually forms good particles under the treatment of pulp shredder.

TECHNOLOGY, ENERGY EFFICIENCY AND ENVIRONMENTAL EXTERNALITIES IN THE PULP AND PAPER INDUSTRY 1997

De-ink (2)

- If waste paper has been stored for a long time, the ink carriers are solidified due to drying and aging. In this case, an increased quantity and density of de-inking chemical (such as NaOH) must be added and reaction temperature and reaction time should be increased so that the ink can be saponified.
- Shredding of the wastepaper and putting it in the de-inking chemical are done in high density pulp shredder, in which the waste newsprint paper is soaked, osmosed, absorbed and expanded by the solution of de-inking chemicals.
- The main chemicals used in de-inking process are NaOH and formic acid (HCOOH).

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**Saponify oils and fats: become converted into soap by being hydrolized into an acid and alcohol as a result of being treated with an alkali*

*HCOOH: a colorless pungent fuming vesicatory liquid acid HCOOH found naturally in **ants** and many plants or made catalytically from carbon monoxide and steam*

- **The re-pulping breaks the fibers into shorter lengths**
  - contains significant amounts of previously recycled pulp (paper)
- **Removing ink by 'floatation' or by dispersing it throughout the pulp**
  Dispersing makes the paper less white
- **Recycled paper is not always good**
  - LCA, energy consumed, quality, and life span
  - Short-term uses - for ex. newspapers and telephone directories

11. Some Key words

Aluminium hydroxide (aluminum)

- Contained in toothpaste
- White powder, reportedly safe to human health
- In order to prevent occurrence of dioxins and furans they are considering to add aluminium hydroxide in the paper with over 70% recycling pulp.
- It also absorbs toxic gasses including dioxins.

SS and Calcium carbonate

- Potential colloids or SS particles
- SS occurs in over flowed pulp fibers and out of the pulverized paper coating and additives etc.
- Calcium carbonate in paper coating and Silicon-based polymer etc.

Dioxins

- During wood chip cooking and pulp bleaching it occurs if chlorine is utilized.
- Dioxins=More than 96% reduction in Japan
  - Strict effluent controlling
  - Non-chlorine chemicals
  - Oxygen bleaching
  - Advanced waste water treatment
  - 1990= 2.23 ng-TEQ, 1996= 0.085, 2000=0.083

Ink in or on paper

Ink: a liquid or paste that contains pigments or dyes

- a complex medium, composed of solvents, pigments, dyes, resins, lubricants, solubilizers, surfactants, particulate matter, fluorescers/*keiko*, and other materials
  - **Pigment molecules** typically link together in crystalline structures that are 0.1–2 µm in size and comprise 5–30 percent of the ink volume
  - **Dyes** are dissolved in the liquid phase, they have a tendency to soak into paper, dye-based inks are made with solvents that dry rapidly
  - Ink is often toxic if swallowed. If ingested, ink can be hazardous to one's health because of VOCs, heavy metals etc.

Rice straw and silica

- Rice straw contains 8-14 % of silica (SiO_2). For chemical pulp produced from rice straw, about half of this silica gets dissolved in the black liquor.
  - This causes problems in all stages of the chemical recovery process.
- For a pulp mill that depends on non-wood fiber, silica must be eliminated from black liquor to produce pulp economically and to meet environmental restrictions.

Key words

Totally-Chlorine-Free

- Chlorine bleach was used in conventional wood-pulp papermaking to create woodfree paper, and it has been recognized for some years that this can be a serious pollutant from paper mills.
- In recent years newer methods have been developed, principally using **hydrogen peroxide**, which breaks down harmlessly to oxygen and water.

  Elemental-Chlorine-Free (ECF) or Totally-Chlorine-Free (TCF)
- White recycled papers are now mostly created by sophisticated de-inking processes, which separate the ink from the fibre, so that it can be removed completely. Where it is necessary to further whiten the pulp, either peroxide bleaching is used, or 'brighteners' are added (as used in washing powders), which are inert.

Source: http://rps.gn.apc.org/faq.htm

Hydrogen peroxide: a chemical used in bleaches, dyes, cleansers, antiseptics, and disinfectants. in a concentrated form, it is toxic and irritating to tissues.