# Chemical Releases from Canadian Pulp and Paper Mills

Prepared for

**Environment Canada**
Environmental Protection Service
New Substances Branch
Hull, Quebec, Canada

Prepared by

**Crechem Technologies Inc.**
Ottawa, Ontario, Canada

In association with

**JANCO**
Perth, Ontario, Canada

July 7, 2003

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# Executive Summary

This study presents an evaluation of chemical releases from the Canadian pulp and paper industry in support of the assessment of new substances carried out at Environment Canada. The method employed is based on release scenarios and chemical usage data obtained for the Canadian industry. It conforms to the framework established by the European Union and the U.S. The study is primarily focused on release estimates of specialty and bleaching chemicals used at kraft pulp mills, non-integrated paper mills and recovered paper mills.

Chemical usage data is essential to the release estimates derived. The data gathered from various sources includes use level, water content, and fraction retained by product for 39 classes of specialty chemicals and many bleaching chemicals. It provides a basis for estimating releases prior to wastewater treatment. When no specific data is available, estimates are derived for worst-case scenarios using most conservative assumptions. These most conservative assumptions include: 1) no chemicals are retained by products; and 2) all chemicals consumed are released to water.

Of the release scenarios evaluated for the Canadian industry, recovered paper mills were found to generate the largest aqueous release on a unit production basis. Their release rate was determined at 142-404 kg/tonne of pulp, while those for kraft pulp mills and non-integrated paper mills were at 163-343 kg/tonne and 60-184 kg/tonne, respectively. It should be noted that the release rates for recovered paper mills and kraft pulp mills include bleaching chemicals at 70-150 kg/tonne and 148-270 kg/tonne, respectively. Non-integrated paper mills, on the other hand, do not involve the use of bleaching chemicals.

The proportion of release with respect to consumption varied in a wide range, depending upon type of mills. Since the amounts of chemicals retained by the pulp were small, the release from kraft pulp mills could be as high as 96-99% of chemicals used. As indicated in the table below, the average consumption of specialty and bleaching chemicals was estimated at 325-547 kg/tonne for kraft pulp mills, non-integrated mills and recovered paper mills combined, while the release prior to wastewater treatment was in the range of 122-310 kg/tonne or 38-57% of chemicals used.

**Consolidated Consumption and Release Estimates for Pulp and Paper Mills**

| Mill Type | Consumption (kg/t) | Water Release (kg/t) | Water Release (%) |
|---|---|---|---|
| Kraft pulp mills | 164-357 | 163-343 | 96-99 |
| Non-integrated paper mills | 464-632 | 60-184 | 13-29 |
| Recovered paper mills | 346-652 | 142-404 | 41-62 |
| Average | 325-547 | 122-310 | 38-57 |

There were large variations in releases from different process areas. The highest release was found in the bleaching section of kraft pulp mills at 148-275 kg/tonne and accounted for 80-90% of the total mill release. The recovery and power boilers section of recovered paper mills or non-integrated paper mills had the lowest release at 0.01-0.1 kg/tonne and contributed less than 0.1% to the total release.

Releases of different classes of chemicals were also found to vary in a wide range. Bleaching chemicals used at kraft pulp mills were found to have the highest release at 148-270 kg/tonne. Of the specialty chemicals evaluated, the highest release was 5-30 kg/tonne for soap/fatty acids used at recovered paper mills, 0.1-13 kg/tonne for pitch control at kraft pulp mills, and 0.6-24 kg/tonne for sizes at non-integrated paper mills. Turpentine separation aids used at kraft pulp mills gave the lowest release at 0.008-0.004 kg/tonne.

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# 1 – Introduction

Industrial release data provides an important basis for the environmental assessment of new substances undertaken at the New Substances Branch of Environment Canada. The assessment is aimed at evaluating the hazard, fate and exposure of new substances prior to their introduction into Canada in order to protect the environment and the health of Canadians. The assessment is a dynamic process and is carried out on a continuous basis to reflect the environmental realty as industrial releases are improved constantly.

Development of release scenarios is one of many methods used to obtain industrial release data. A release scenario can be defined as a model of industrial facilities with similar operations and using similar chemical substances. The method provides release estimates based on standard operations and chemical usage. It is commonly used for screening purposes or cases in which actual release data is not available. Other methods for obtaining release data include direct measurement, mass balance, engineering estimation, emission factors, modeling, etc.

The present study focuses on the determination of chemical releases from the Canadian pulp and paper industry using the release scenario method. The study is consistent with the framework established by the European Union and the U.S. The development of release scenarios is based on both process data generic to the industry and chemical usage data gathered from Canadian sources. The results provide conservative release estimates for the Canadian industry.

# 2 – Overview of Pulp and Paper Industry

The pulp and paper industry produces commodity grades of wood pulp, primary paper products, and paper board products. Most pulp is produced for the purpose of subsequent manufacture of paper and board products (European Commission, 1999, p.10). Some is destined for other uses such as thick fiberboard or products manufactured from dissolved cellulose. Paper products are generally classified into: 1) printing and writing paper; 2) tissue paper; 3) newsprint; and 4) packaging paper.

In Canada, pulp, paper, and paperboard are the major products produced. As shown in Table 2.1, Quebec was ranked first in terms of the total production for the years of 1999 and 2000, and followed by British Columbia and then by Ontario (Quebec Forest Industries Association, http://www.aifq.qc.ca). The other provinces accounted for about 20% of the total. The production of newsprint is included in the total and also listed separately. The distribution of the production across Canada suggests that field data should be collected mainly within the provinces of Quebec, Ontario and British Columbia in order to establish representative release scenarios for the industry.

**Table 2.1 – Production of Pulp, Paper and Paperboard in Canada**
(Quebec Forest Industries Association: http://www.aifq.qc.ca)

| | **Pulp, Paper & Paperboard** (1000 tonne/year) | | **Newsprint** (1000 tonne/year) | |
|---|---|---|---|---|
| | 1999 | 2000 | 1999 | 2000 |
| Quebec | 10,084 | 10,206 | 4,007 | 3,848 |
| Ontario | 6,232 | 6,471 | 1,890 | 1,924 |
| British Columbia | 7,996 | 8,424 | 1,377 | 1,428 |
| Other Provinces | 6,865 | 7,098 | 1,930 | 2,022 |
| **Total** | **31,177** | **32,199** | **9,204** | **9,222** |

Pulp, an important intermediate product of the pulp and paper industry, can be categorized into various types depending upon pulping methods employed. In Quebec, important types are thermomechanical, kraft, and chemithermomechanical (Quebec Forest Industries Association, http://www.qifq.qc.ca). Their respective production figures for the years of 1999 and 2000 are compiled in Table 2.2, and their combined quantity accounted for about 85% of the total pulp produced. These pulp products are either used for paper making at integrated mills or sold as market pulp by non-integrated mills.

In the U.S., although various processes are used, the vast majority of pulp produced is manufactured by the kraft chemical pulping process (USEPA, 1995, p.5). Other methods include sulfite chemical pulping, mechanical pulping and semi-mechanical pulping. On a tonnage basis, the chemical pulping method produced approximately 85% of the pulp manufactured in 1991, the mechanical 10% and the semi-mechanical 5%. The kraft pulping process is the major source of water and air pollutants. It may also produce wastewater containing chlorinated compounds such as dioxins during bleaching.

**Table 2.2 – Breakdown of Pulp Production in Quebec**
(Quebec Forest Industries Association: http://www.aifq.qc.ca)

| | **Production** (1000 tonne/year) | |
|---|---|---|
| | 1999 | 2000 |
| Thermomechanical Pulp | 3,060 | 3,305 |
| Chemithermomechanical Pulp | 1,223 | 1,193 |
| Other Mechanical Pulp | 607 | 610 |
| Kraft Pulp | 2,227 | 2,261 |
| Other Pulp | 395 | 393 |
| Total | 7,512 | 7,762 |

Pulp and paper mills may be integrated or non-integrated. Integrated mills produce both pulp and primary paper products (USEPA, 1995, p.4). Non-integrated mills include pulp mills and paper mills. Pulp mills only produce pulp which is sold on the open market or shipped via pipe, conveyor, truck, train, or ship to other mills for the production of a final product. In contrast, paper mills only produce paper products from purchased pulp.

Cellulose-bearing materials are used as the raw feed to pulp and paper mills. Wood is the major raw material for virgin fiber and recovered paper is increasingly used as a source of secondary fiber (European Commission, 1999, p.10). Pulping renders individual fibers to

be freed from the matrix of wood or recovered paper and further processing produces a pulp suitable for paper making. Deinking is a special operation used in the production of pulp from recovered ink-containing paper.

Pulp and paper mills may be grouped into several categories to facilitate environmental release estimation. According to the European Commission (1999, p.13), mills can be classified as follows:

- kraft pulp and paper mills;
- sulfite pulp and paper mills;
- mechanical pulp and paper mills;
- recovered paper mills; and
- non-integrated paper mills.

Each group can be further divided into several types, as given in Table 2.3 (European Commission, 1999, p.13).

**Table 2.3 – Classification of Pulp and Paper Mills**
(European Commission, 1999, p.13)

| Category | Type |
|---|---|
| Kraft pulp & paper mills | Non-integrated bleached kraft pulp mills |
| | Integrated bleached kraft pulp & paper mills |
| | Integrated unbleached kraft pulp & paper mills |
| Sulfite pulp & paper mills | Integrated bleached sulfite pulp & paper mills |
| Mechanical pulp & paper mills | Non-integrated CTMP pulp mills |
| | Integrated newsprint mills |
| | Integrated LWC mills |
| | Integrated SC mills |
| Recovered fiber paper mills | Integrated recovered paper mills without deinking |
| | Integrated recovered paper mills with deinking |
| Non-integrated paper mills | Uncoated fine paper mills |
| | Coated fine paper mills |
| | Tissue mills based on chemical pulp |
| | Specialty paper mills based chemical pulp |

# 3 – Pulp and Paper Chemicals

## 3.1 – Classification

Numerous chemicals are used in the pulp and paper industry. These chemicals can be broadly divided between commodity and specialty chemicals. Since specialty chemicals are sources of new substances, they are dealt with in detail in this project. Specialty chemicals used in kraft pulp mills, non-integrated paper mills and recovered paper mills (deinking plants) can be classified into the following types.

1) Cooking aids/chip penetrants
2) Boilouts/cleaners
3) Scale control
4) Foam control
5) Washing/drainage aids
6) Pitch/stickies control
7) Clarification aids
8) Lime mud dewatering aids
9) Tall oil separation and acidulation aids
10) Turpentine separation aids
11) Microbiological control
12) Felt conditioners
13) Retention/drainage aids
14) Air pollution control
15) Condensate treatment
16) Boiler water treatment
17) Corrosion inhibitors
18) Settling aids
19) Nutrients
20) Sludge Conditioners
21) Odor control
22) Color control
23) Starch/sizes
24) Wet strength agents
25) Dry strength agents
26) Dyes/dye fixatives/fluorescent whites
27) Charge control
28) Fillers
29) Chelants/sequestrants
30) Emulsifiers
31) Antiskid agents
32) Saveall polymers
33) Formation aids
34) Latex
35) Surfactants/repulping aids
36) Dispersing agents

37) Deinking aids
38) Soap/fatty acids
39) Barrier chemistry

Summarized in Table 3.1 are chemical nature and applications of major specialty chemicals. The data compiled is based on information from suppliers obtained through their web sites, and while extensive, is not necessarily a complete listing. In addition to specialty chemicals, bleaching chemicals are also included. The web site addresses of major pulp and paper chemical suppliers are listed in Table 3.2.

## Table 3.1 – A Partial List of Specialty Chemicals Used at Pulp and Paper Mills

| Type | Chemical Nature | Applications | Supplier |
|---|---|---|---|
| Air pollution control | Wetting agents | Boiler, scrubber | Hercules, BASF |
| Bleaching chemicals | Oxidants | Bleaching | Akzo-Nobel, Iogen, Kemira, BASF, Clariant, Vinings |
| | Reductants | Bleaching | |
| | Alkalis | Bleaching | |
| Boilouts | Alkaline | Pulp machine, digester, paper machine, bleaching, deinking, coating kitchen | Hercules, Ondeo-Nalco |
| | Acid | | |
| | Alkaline-solvent | | |
| Cooking aids/chip penetrants | Surfactant-based | Digester | Hercules, Ondeo-Nalco, Westvaco |
| | Anthraquinone-based | | |
| | Anthraquinone-surfactant blend | | |
| Pitch/stickies control | Solvents & surfactants | Brown stock washing, bleach plant, paper making | Hercules, Ondeo-Nalco, Buckman, Ciba |
| Corrosion inhibitors | | Feed water and condensate systems, cooling water treatment, boiler | Hercules |
| Dyes/dye fixatives/fluorescent whites | Basic | Paper making | BASF, Clariant, Ciba |
| | Acid | | |
| | Direct | | |
| | UV-absorbing compounds (fluorescent whites) | Size press, calender stack | Clariant, Ciba, Netchem |
| Felt conditioners/cleaners | Alkaline | Pulp machine, digester, paper machine, bleaching, deinking, coating kitchen | Hercules, Ondeo-Nalco |
| | Acid | | |
| | Alkaline-solvent | | |
| | Polymer-surfactant | | |
| Fillers | PCC, GCC, $TiO_2$, clay, talc | Paper making | Hercules, ICI, Kemira, Raisio, Bayer, BASF, Clariant, Ciba, Angelhard, J.M. Huber, Thiele Kaolin, Omya, Dow, Union Carbide, GP, Westvaco, Cytec, Netchem, Nacan, Penford |
| Foam control | Water-based | Brown stock washing, effluent treatment, paper making, bleaching, deinking | Hercules, Ondeo-Nalco, BASF, Clariant, Vinings |
| | Oil-based | | |
| | Silicone-based | | |

| Type | Chemical Nature | Applications | Supplier |
|---|---|---|---|
| Microbiological control | | Paper machine, pulp machine, wastewater treatment, cooling water treatment | Hercules, Ondeo-Nalco, Kemira, BASF, Vinings |
| Retention/drainage aids | Inorganic salts | Paper making | Hercules, Kemira, Clariant, Ciba, Vinings |
| | Polyelectrolytes | | |
| Deinking aids | Soap-based | Deinking | Ondeo-Nalco, Raisio, Vinings |
| | Fatty acid-based | | |
| | Semi-synthetic | | |
| | Synthetic | | |
| Settling aids | Polyelectrolytes | Water and wastewater treatment, deinking, green liquor clarification | Hercules, Ondeo-Nalco, Kemira, Raisio, Ciba, Cytec |
| | Inorganic | | |
| Scale Control | Inorganic dispersants | Paper making, digester, bleach plant, evaporator, brown stock washing, chemical recovery, pulp drying, by-product separation, deinking, boiler, cooling water treatment | Hercules, Ondeo-Nalco, Vinings |
| | Organic salts of HCl | | |
| | Phosphate/polymer blend | | |
| Sizes | Acid-based | Paper making | Hercules, Akzo-Nobel, Dow, ICI, Kemira, Raisio, BASF, Ciba, Vinings, GP, Westvaco, Penford |
| | Rosin-based | | |
| | Wax-based | | |
| | Cellulose-reactive materials | | |
| | Synthetic | | |
| Wet strength agents | Water-soluble polymers | Paper making | Hercules, Akzo-Nobel, BASF, GP, Penford |
| | Water-dispersible latex | | |
| Dry strength agents | Natural polymer derivatives | Paper making | Hercules, Akzo-Nobel, BASF, Vinings, GP |
| | Synthetic polymers | | |
| Antiskid agents | Silica | Paper making | Buckman |
| Lime mud dewatering aids | Surfactant | Lime mud dewatering | Hercules, Ondeo-Nalco |
| Tall oil separation and acidulation aids | Surfactant | Tall oil separation and acidulation | Hercules, Ondeo-Nalco |
| Turpentine separation aids | Surfactant | Turpentine separation | Hercules, Ondeo-Nalco |

## Table 3.2 – Major Suppliers of Pulp and Paper Chemicals

| Supplier | Web Site |
|---|---|
| Akzo-Nobel | http://www.akzonobel.com |
| Angelhard | http://www.angelhard.com |
| BASF | http://www.basf.com |
| Buckman Laboratories International, Inc. | http://www.buckman.com |
| Ciba | http://www.cibasc.com |
| Clariant | http://www.clariant-northamerica.com |
| Cytec | http://www.cytec.com |
| Dow Chemicals | http://www.dow.com |
| Eka Chemicals | see Akzo-Nobel |
| Georgia-Pacific (GP) Corporation | http://www.gp.com |
| Hercules Inc. | http://www.herc.com |
| ICI | http://www.ici.com |
| Iogen | http://www.iogen.ca |
| J. M. Huber Engineered Materials | http://www.hubermd.com |
| Kemira | http://kc.kemira.com |
| Nacan Products | http://www.nationalstarch.com |
| Netchem | http://www.netcheminc.com |
| Omya | http://www.omya.com |
| Ondeo-Nalco | http://www.ondeo-nalco.com |
| Penford Products | http://www.penfordproducts.com |
| Raisio | http://www.raisiogroup.com/chemicals |
| Thiele Kaolin | http://www.thielekaolin.com |
| Union Carbide | see Dow Chemicals |
| Vinings | http://www.viningsind.com |
| Westvaco | http://www.westvaco.com |

## 3.2 – Specialty Chemicals

Described below are various specialty chemicals, including bleaching chemicals, used at pulp and paper mills. The description is based on both literature and available supplier information. The term "furnish" used in the description is defined as a fibrous raw material used in paper production (Hagemeyer et al., 1992, p.3).

### *3.2.1 – Bleaching Chemicals*

Bleaching chemicals are classified into three groups: 1) oxidants; 2) reductants; and 3) alkalis (Grace et al., 1989, p.406-409). Chlorine, oxygen, hypochlorite, chlorine dioxide, hydrogen peroxide and ozone are common oxidants. Hydrosulfite is the only reductant used for bleaching, while sodium hydroxide is the only alkali used. Because of their greater economy, chlorine and oxygen are used in the early stages (delignification) of bleaching for lignin removal. Chlorine dioxide, hypochlorite, and peroxide can be used in the later stages (brightening) because of their greater selectivity. Lately, peracetic acid has become commercially available as a bleaching chemical (European Commission, 1999, p.22). Other bleaching chemicals include sodium chlorite, potassium chlorate, and enzymes.

### *3.2.2 – Boilouts*

According to Hercules (http://www.herc.com), boilouts are divided into three groups: 1) alkaline; 2) acid; and 3) alkaline and solvent. Boilouts are chemically similar to felt conditioners and cleaners, but they are always applied in a slug mode. Starch enzyme boilout is especially useful in starch kitchens and coating areas (King and Stoner, 2000).

### *3.2.3 – Cooking Aids/Chip Penetrants*

There are three types of cooking aids/chip penetrants supplied by Ondeo-Nalco: 1) surfactant-based; 2) anthraquinone-based; and 3) anthraquinone-surfactant blend (http://www.ondeo-nalco).

### *3.2.4 – Pitch/Stickies Control*

Pitch/stickies control or contaminant control deals with pitches, stickies and any other hydrophobic matter. Pitch arises with varying frequency and in a variety of forms in every paper mill (Hagemeyer et al., 1992, p.16; Thorp et al., 1991, p.177). Pitch problems stem from pulp resins (resin acids, fatty acids, fatty alcohols) and, occasionally, sizing agents. Large pitch particles can plug screens and deposit on equipment surfaces. Pitch particles retained in paper may produce dark spots, and cause picking, sheet breaks, and wire and felt filling.

There are several approaches to pitch control (Hagemeyer et al., 1992, p.17). One approach involves using dispersants that stabilize colloidal pitch particles and prevent

their deposition. The dispersed pitch particles then leave the papermaking system at water loss points. Another approach involves adding a mineral (such as talc or bentonite clay) to induce colloidal pitch particles to precipitate and be carried out with the paper. A third approach is to precipitate pitch particles onto wood fibers with alum. In the U.S., talc is used for pitch control.

Stickies remain one of major obstacles in manufacture of quality tissue papers from recycled fiber (Hoekstra et al., 2001). Stickies can be generally described as tacky, hydrophobic, pliable organic materials found in recycled paper systems. These materials have a broad range of melting points and different degrees of tackiness dependent upon their chemical composition. Sources of stickies may include adhesives, hot melts, coating binders, ink residues, deinking chemicals, rosin, and wet strength resins. Actual tacky deposits found on paper machines may be a combination of several of these organic contaminants as well as inorganic particles such as talc, clay, or calcium carbonate. The presence of wood resins may be a factor as well.

Early treatment for stickies includes use of dispersants (organic solvents and surfactants) to break these materials into smaller particles and disperse them (Hoekstra et al., 2001). These dispersants are effective when used prudently. Recently it has been reported that certain enzymes are effective in reducing stickies problems. Polymers can be used to coagulate small stickies with fines, filler and other additives and remove them from the system.

Traditional approaches for chemically controlling stickies include fixation of stickies to fiber, dispersion of stickies using solvent and surfactant blends, polymeric stabilization and combinations of each of these programs. In addition, enzyme can be used for stickies control.

Pitch control agents supplied by Ondeo-Nalco and others are surfactant-based products (http://www.ondeo-nalco.com). They are used to emulsify and remove pitches from brown stock washers and the caustic extraction stage of a bleach plant.

### *3.2.5 – Corrosion Inhibitors*

Corrosion inhibitors are used in a number of process areas such as recovery and power boilers, water treatment systems, and paper machines. Those supplied by Hercules can be used in open and closed cooling water systems to minimize corrosion in condensate units (http://www.herc.com). As corrosion control, scavengers and passivators are used to protect boiler waterside against oxygen corrosion.

### *3.2.6 – Dyes/Dye Fixatives/Fluorescent Whites*

Colorants commonly used in the paper industry are basic dyes, acid dyes, direct dyes and colored pigments (Hagemeyer et al., 1992, p.100). Basic dyes are usually salts, such as chlorides, hydrochlorides, sulfates and oxalates of a color base. Acid dyes are generally

sodium, potassium or ammonium salts of corresponding color acids, such as sodium dye and sulfonic acid. Direct dyes are salts of dye acids, chemically similar to acid dyes, but are known as direct dyes because they have a direct, though varying, affinity for cellulose. The most important pigments used by the paper industry are white pigments such as clay, titanium dioxide, alumina hydrate, and calcium carbonate.

Fluorescent whites are frequently referred to as paper whites or optical brighteners and are used widely in the paper industry to brighten white papers (Hagemeyer et al., 1992, p.102). Fluorescent whites are chemical compounds which absorb light in the ultraviolet range of the spectrum and re-emit it in the visual range, giving a fluorescent effect. Fluorescent whites can be used for internal coloration by addition to the stock in batch coloration or metered continuously (Hagemeyer et al., 1992, p.102). They can also be applied at the size press or calender stack in surface application or into coatings.

### *3.2.7 – Felt Conditioners*

According to Hercules (http://www.herc.com), felt conditioners can be divided into three groups: 1) alkaline; 2) acid; and 3) alkaline and solvent. Felt conditioners are chemically similar to boilout chemicals, but they can be applied either continuously or in batches. The removal of dirt or deposits from solid surfaces involves a combination of mechanical action and surface chemistry. In the absence of a conditioner, water is often unable to remove deposits due to their high surface tension and poor wetting action (Thorp et al., 1991, p.175).

### *3.2.8 – Fillers*

Fillers are added to paper in various percentages to perform a number of different functions (Hagemeyer et al., 1992, p.20; Thorp et al., 1991, p.150). The choice of material and amount used is dependent upon specific properties desired. White mineral pigment fillers are used extensively by papermakers to improve a variety of paper properties including brightness, opacity, whiteness, gloss, smoothness and printability. Fillers can also be used as fiber substitutes in order to lower furnish costs. The principal fillers are kaolin clay, calcined clay, calcium carbonate, titanium dioxide, talc, plastic pigments, alumina trihydrate, calcium sulfoaluminates, amorphous silica and silicate. Also, a fair amount of zinc sulfide is used in Western Europe. In addition, small quantities of diatomaceous silica, barium sulfate and calcium sulfate are used in special applications.

Use of fillers in coating is often associated with use of a variety of additives. According to BASF (http://www.basf.com), additives used in coating include 1) coating modifiers; 2) rheology modifiers; 3) enzymes; 4) dispersants; 5) co-binders; 6) thickeners; 7) defoamers; 8) crosslinkers; 9) insolubilizers. According to Hercules (http://www.herc.com), coating modifiers are used in tissue production to modify the adhesive coating in order to control rewettability, coating development and uniformity. Rheology modifiers are used in paper coating for correct coating rheology. Many of

dispersants used in coating are based on polyacrylate chemistry (Dykstra, 1999). Some are homopolymers of acrylic acid and are usually available as water solutions of sodium or potassium salts of polyacrylic acid. Others are copolymers of acrylic acid with a variety of monomers for specialized uses. Again, most of these are available as water solutions of sodium or potassium salts. Polyphosphates are still used to some extent as dispersants for filler slurries, especially clays.

### *3.2.9 – Foam Control*

Foams are stabilized by two mechanisms: 1) adsorption of surface-active materials; and 2) concentration of finely divided solid particles around foam bubbles (Thorp et al., 1991, p.176). Surface active substances exist in abundance in most paper mill stock as salts of rosin acids and fatty acids. Foam-stabilizing, finely divided materials are also plentiful in the form of fillers, fines, alumina floc, etc.

Foam control agents, also known as defoamers or antifoams, can be divided into several classes (Dykstra, 1999):

- Silicones
- Silicone emulsions
- Polyglycols and formulated polyglycols
- Synthetic polyalcohols and formulated polyalcohols
- Amide-based defoamers
- Ester-based defoamers
- Specialized blends

Foam control products supplied by Hercules (http://www.herc.com) and Ondeo-Nalco (http://www.ondeo-nalco.com) include 1) water-based; 2) oil-based; 3) water extended oil-based; 4) silicone-based; 5) silicone concentrate; and 6) ester-based.

### *3.2.10 – Microbiological Control*

Microbiological control agents are used in many areas of a mill and include biocides and preservatives. Deposits are frequently started by an organic conditioning film which can attract either inorganics, other organics, such as pitch, or microorganisms (King and Stoner, 2000). The final deposit can be almost totally free of organisms, or can be almost exclusively microbiological. When deposits have a biological component, the most common method of control and abatement has been use of microbiocides.

Biocides are widely used to control microbial growth of bacterial and fungal origin in coating binders, filler slurries, and other specialty additives (Dykstra, 1999). Many coating fillers and additives require use of biocides to prevent degradation of filler or additive slurries by bacteria, fungi, and molds or spores. Many of the biocides used in coatings also serve as preservatives. This means that these particular biocides must not degrade quickly since they are often used to treat coating additives that are stored in a tank for a period of time. They must function over a long period of time and be able to

work in a tank or coating head over a range of temperature and pH.

Generic biocides used in coating include bromohydroxyacetophenone, bromonitropropanediol, dodecylguanidine hydrochloride, glutaraldehyde, isothiazolinones, and thione (Dykstra, 1999). The uncontrolled growth of microorganisms in paper mills results in the formation of deposits called slime (Oppong et al., 2000). Slimicides, together with dispersants, are commonly used for slime control (Hoekstra, 1990).

### *3.2.11 – Retention/Drainage Aids*

The term "retention" is defined as the relative ability to hold various components of a furnish in a paper sheet as it consolidates on the forming fabric of a paper machine (Hagemeyer et al., 1992, p.113). A retention aid can be any material that is added to a headbox system that will help to promote flocculation of solid fractions of a furnish and increase their retention (Hagemeyer et al., 1992, p.125; Thorp et al., 1991, p.150). In general, particulate and colloidal fractions are more difficult to retain than the fiber fraction.

Retention aids are divided into inorganic salts and organic polyelectrolytes (e.g., starch). Polyelectrolyte retention aids yield stronger flocs than alum and are commonly used to flocculate fine particles in paper making (Thorp et al., 1991, p.153). Alum ($Al_2(SO_4)_3$) is also an effective flocculating agent for fines and fillers under certain conditions.

A drainage aid is a polyelectrolyte that improves water removal (Hagemeyer et al., 1992, p.145). Common drainage aids include alum, cationic guar, cationic starch, and synthetic polyelectrolytes. Polyelectrolytes commonly used as dewatering aids are condensed polyamide/amines (PAA), polyacrylamide copolymers (PAM), and polyethyleneimines(PEI). Dewatering aids are used for sludge dewatering in effluent treatment (Hercules, http://www.herc.com).

### *3.2.12 – Formation Aids*

Formation can be defined as the visual appearance of a paper sheet when viewed in transmitted light (Hagemeyer et al., 1992, p.153). A sheet with good formation will look smooth and homogeneous and contain no apparent flocs or clumps of fibers. A number of additives have been used as formation aids in paper making and they are generally natural and synthetic water-soluble polymers. Common formation aids are mannogalactan gums (guar), deacetylated karaya gums, carboxymethyl cellulose, hibiscus root, okra pod, nonionic polymers, polyethylene oxide, polyvinyl alcohol and polyacrylamide, and polyacrylamide-acrylic acid copolymer. The deacetylated karaya gum, carboxymethyl cellulose and polyacrylamide-acrylic acid copolymers are anionic, all the others are nonionic.

### *3.2.13 – Deinking Aids*

Deinking aids are used in paper production from recovered paper (Buckman, http://www.buckman.com; Raisio, http://www.raisiogroup.com). Deinking aids supplied by Raisio are divided into four groups: 1) soap-based collectors; 2) fatty acid-based collectors; 3) semi-synthetic collectors; and 4) synthetic collectors.

### *3.2.14 – Settling Aids*

The purpose of settling aids is to facilitate precipitation of solid and colloidal particles in an aqueous system. They are used in water and wastewater treatment, deinking, green liquor clarification, etc. Examples of settling aids are coagulants and flocculants used in water and wastewater treatment. Those supplied by Raisio (http://www.raisiogroup.com) for water treatment have two types: 1) inorganic; and 2) organic. Organic coagulants/flocculants supplied by Ondeo-Nalco (http://www.ondeo-nalco.com) are further divided into cationic and anionic polymers and used for dissolved air flotation clarifiers and sludge dewatering operations at deinking plants.

### *3.2.15 – Scale Control*

Scale control deals with inorganic deposits, such as barium sulfate, calcium oxalate, and calcium carbonate scales, alumina scale, and filler deposits (Hagemeyer et al., 1992, p.16; Thorp et al., 1991, p.177). It should be noted that many inorganic deposits result from poor control over addition rates of chemical additives and low values of first-pass fines and filler retention. The formation of deposits as a result of overdosing has been a particular problem with alum, while alkaline papermaking in recent years has brought about deposition problems related to alkaline scale such as calcium carbonate.

Scale control agents can be used to remove inorganic deposits (calcium carbonate, calcium oxalate, and barium) from digesters, bleach plants, evaporators and recovery operations (http://www.ondeo-nalco.com).

### *3.2.16 – Sizes*

Sizes are used in paper production (newsprint, printing and writing, and packaging). The function of a size is to provide paper and paperboard with resistance to liquid wetting, penetration, and absorption (Hagemeyer et al., 1992, p.39). Since protection against aqueous liquids is a common concern, water repellency is generally achieved with the addition of a size.

Predominant types of sizes used are: 1) rosin-based; 2) wax-based; and 3) cellulose-reactive materials (Hagemeyer et al., 1992, p.43-45). Tall oil rosin, wood rosin, and gum rosin are the three main classes of rosin-based sizes. Commercial rosin sizes used consist of two distinctly different groups: highly neutralized rosin soaps and acidic rosin particle suspensions.

Sizes can be applied internally or on surface. Internal sizing is referred to as the addition of a size to an aqueous wood pulp suspension or slurry, while surface sizing as the addition to paper surface. Dow Chemicals (http://www.dow.com) supplies various surface sizes (polymers) which can improve ink-jet printability, toner adhesion and optical brightness. Alum is the primary retention aid added to all types of rosin sizes to form actual sizing agents (Hagemeyer et al., 1992, p.48).

### *3.2.17 – Wet-strength Agents*

Wet-strength agents are used in paper production (newsprint, printing and writing, and packaging) to prevent paper from disintegration after rewetting (Hagemeyer et al., 1992, p.65; Buckman, http://www.buckman.com). In some substrates, this wet strength property of paper need be only temporary, as in sanitary paper such as facial tissue, towelling, or napkin stock, while in other substrates such as food packaging, shipping cartons, map paper, wallpaper, and saturating paper, permanent wet strength is required.

Wet-strength agents include both water-soluble polymers and water-dispersible latexes (Hagemeyer et al., 1992, p.66). Water-soluble polymers are further divided between temporary and permanent. Water-soluble cationic resins for wet-end addition include urea-formaldehyde (U-F), melamine-formaldehyde (M-F), polyamide-epichlorohydrin (PAE), dialdehyde starch (DAS), polyamine-epichlorohydrin (polyamine), polyacrylamide-glyoxal (PAMG), and quaternary ammonium epoxide (base-reactivated amine polymer-epichlorohydrin). Commercial thermosetting wet-end additives include synthetic latexes, polyethyleneimine (PEI), chitosan, and carboxymethylcellulose (CMC).

### *3.2.18 – Dry-strength Agents*

The dry strength of paper generally refers to the performance of paper sheet when specific mechanical properties are tested, i.e., tensile, Mullen, tear, etc., under normal, dry conditions (Thorp et al., 1991, p.164). The main mechanism of attaining dry strength in paper is through development of hydrogen bonds between fibers in the sheet. The bonding between fibers can be enhanced by two means (Thorp et al., 1991, p.164). The first is by refining. Refining increases surface fibrillation and cell wall hydration which increases fiber flexibility, fiber conformability and surface contact between fibers. The second means is to add a dry strength agent that will enhance and increase the number of bonds between adjacent fiber surfaces.

Dry strength agents are used in paper production (newsprint, printing and writing, and packaging) and can be divided into two groups: 1) natural polymer-based derivatives; and 2) synthetic polymers (Hagemeyer et al., 1992, p.87; Buckman, www.buckman.com). Commercial materials that have been utilized as natural dry strength agents include natural gums and natural and derived starches (Thorp et al., 1991, p.164). These materials provide enhanced interfiber bonding and also increase the bonded area between fibers. Starch is the most common raw material for natural dry strength agents and cationic starch is the most widely employed starch derivative (Hagemeyer et al., 1992, p.87).

Synthetic polymers are usually co-polymers of acrylamide and cationic monomers such as diallyl dimethyl chloride, or co-polymers of acrylamide and an anionic monomer such as potassium acrylate (Hagemeyer et al., 1992, p.87). Other polymers in the form of plant extracts, derivatives of natural polymers and synthetic polymers have been and are still used as dry strength additives, but in some cases their use is declining and in others the use has never become widespread. Such materials include locust bean and guar gums which can reinforce fiber bonding, replacing the hemicellulose lost during the pulping operation. A cellulose derivative, sodium carboxymethyl cellulose, is used normally in conjunction with cationic wet strength resin and the use of a complex of polyvinyl alcohol has been proposed but its use is not believed to be widespread.

### *3.2.19 – Others*

In addition to chemicals described above, there are also many others used at pulp and paper mills. Due to lack of details, they are briefly compiled as follows.

Air pollution control agents are wetting chemicals used to suppress dust and remove particulates in a gas stream from a boiler or scrubber.

Washing aids are used in brown stock washing to reduce organic and inorganic carryover at pulp mills (Hercules, http://www.herc.com).

Antiskid agents are silica-based and used in paper production (newsprint, printing and writing paper, and packaging) (Buckman, http://www.buckman.com).

Lime mud dewatering aids, tall oil separation and acidulation aids, and turpentine separation aids are referred to as recovery additives. They are surfactant-based and used in chemical recovery operations at kraft pulp mills (Hercules, http://www.herc.com; Ondeo-Nalco, http://www.ondeo-nalco.com).

Nutrients include nitrogen, phosphorus, and bioaugmentation agents. They are used in wastewater treatment (Hercules, http://www.herc.com).

# 4 – Overview of Kraft Pulp Mills

The kraft process, also known as sulfate process, is commonly employed at non-integrated bleached kraft pulp mills. The process involves treatment of plant materials containing cellulose fibers with a solution of sodium hydroxide and sodium sulfide at temperatures above 170$^{o}$C (Grace et al., 1989, p.3). The main purpose of the treatment is to remove enough lignin so that fibers can be readily separated from one another, producing a pulp. Pulping conditions range from a pH of 13-14 at the start of a cook to 12-13 at the end. Plant materials treated include:

- softwoods, containing between 27 and 33% lignin;
- hardwoods, containing 16-24% lignin; and
- non-wood fibers such as straw, bagasse, bamboo, and esparto which contain 11-20% lignin.

## 4.1 – Process Description

Figure 4.1 shows a standard kraft process used at non-integrated bleached kraft pulp mills. The process consists of five sections: 1) wood handling; 2) pulping; 3) chemical recovery; 4) bleaching; and 5) water and wastewater treatment (USEPA, 1995, p.18-46; European Commission, 1999, p.18). A variety of chemicals are added to the process at various points and their numerical codes used in the process diagram are provided in Table 4.1. It should be noted that only specialty and bleaching chemicals are indicated in the process diagram. It should also be noted that chemicals listed in Table 4.1 are those used at three types of mills (kraft pulp mills, paper mills and recovered paper mills) and some may not be applicable to kraft pulp mills.

Wood handling is the first step of the process which prepares a homogenous furnish as a feedstock for pulping. Furnish is a fibrous material used for making pulp and wood is the most commonly used furnish (USEPA, 1995, p.19-21). In the case of roundwood furnish, wood logs are cut into manageable sizes and then debarked. The bark may then be burned for energy production in a boiler. If not burned for energy production, bark can be used for mulch, ground cover, or as an ingredient in charcoal. Debarked logs are cut into chips of equal size by chipping machines. They are then placed onto a set of vibrating screens to remove those that are too large or too small. Wood chips are commonly used in chemical pulping and uniform sized chips result in good pulp quality (European Commission, 1999, p.18).

Kraft or sulfate pulping proceeds as wood chips are received from the wood handling section. Wood chips are mixed in a reaction vessel (digester) with a sodium-based alkaline pulping solution, commonly known as white liquor (USEPA, 1995, p.22; European Commission, 1999, p.17-21). The cooking temperature is usually in the 170-173$^{o}$C range, with a cooking time of about 90 minutes (Grace et al., 1989, p.9). Normally, some 90 minutes are also needed to reach the cooking temperature. The white liquor is an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide ($Na_2S$). These salts are present in a weight ratio of approximately 5/2. Other sodium salts present in smaller

amounts include carbonate, sulfate, thiosulfate, polysulfide, sulfite, and silicate. Potassium is also present in most liquors, but at a much lower level than sodium. These latter inorganic salts have less effect on pulping reactions and are commonly referred to as dead load chemicals. Under the action of the white liquor, lignin is removed from wood matrix and wood fibers are liberated.

**Table 4.1 – Numerical Codes for Types of Chemicals Used at Pulp and Paper Mills**

| Numerical Code | Type of Chemicals |
|---|---|
| 1 | Cooking aids/chip penetrants |
| 2 | Boilouts/cleaners |
| 3 | Scale control |
| 4 | Foam control |
| 5 | Washing/drainage aids |
| 6 | Pitch/stickies control |
| 7 | Clarification aids |
| 8 | Lime mud dewatering aids |
| 9 | Tall oil separation and acidulation aids |
| 10 | Turpentine separation aids |
| 11 | Microbiological control |
| 12 | Felt conditioners |
| 13 | Retention/drainage aids |
| 14 | Air pollution control |
| 15 | Condensate treatment |
| 16 | Boiler water treatment |
| 17 | Corrosion inhibitors |
| 18 | Settling aids |
| 19 | Nutrients |
| 20 | Sludge Conditioners |
| 21 | Odor control |
| 22 | Color control |
| 23 | Starch/sizes |
| 24 | Wet strength agents |
| 25 | Dry strength agents |
| 26 | Dyes/dye fixatives/fluorescent whites |
| 27 | Charge control |
| 28 | Fillers |
| 29 | Chelants/sequestrants |
| 30 | Emulsifiers |
| 31 | Antiskid agents |
| 32 | Saveall polymers |
| 33 | Formation aids |
| 34 | Latex |
| 35 | Surfactants/repulping aids |
| 36 | Dispersing agents |
| 37 | Deinking aids |
| 38 | Soap/fatty acids |
| 39 | Barrier chemistry |
| 40 | Bleaching chemicals |

Certain volatile compounds are released during the digestion. These compounds include

turpentine, methanol, and reduced sulfur gases (Grace et al., 1989, p.473). Turpentine may be recovered as a by-product, while non-condensable gases are normally incinerated for odor control.

To achieve a degree of delignification sufficient to allow cooked chips to be fiberized without vigorous mechanical treatment, a certain minimum charge of alkali is necessary (Grace et al., 1989, p.98). The amount required depends on wood species and on other factors, such as chip dimensions, but is of the order of 12% (as $Na_2O$ on wood) for hardwood and 16% for softwood. The yield at which cooked chips become "easily" fiberized is about 50%.

The cooking process can be either batch or continuous (Grace et al., 1989, p.9). In the batch process, wood chips are cooked in an individual digester with loading, cooking, and dumping accomplished in sequence. In the continuous process, wood chips and white liquor are fed at a constant rate into the top of a digester and wood chips move downward in a continuous manner.

In both batch and continuous processes, cooked wood chips are discharged from the digester under pressure into a blow tank (Grace et al., 1989, p.9). As they are blown from the digester, cooked chips are broken up into individual fibers by the mechanical force of ejection, producing a wood pulp for further processing. When cooked chips are blown from the digester, considerable amounts of steam and other gases are generated. They are then condensed in heat exchangers, providing heat for general mill use.

Washing follows after cooked chips are discharged from the digester into the blow tank. The discharge consists of separated wood fibers (pulp) and a solution, known as black liquor, of reacted and unreacted pulping chemicals along with dissolved lignin solids (USEPA, 1995, p.22; European Commission, 1999, p.17-21; Grace et al., 1989, p.474). The black liquor is washed away from the pulp through a brownstock washing system. Modern washing systems employ vacuum drum washers, wash presses, diffusers or wire type washers. They normally recover at least 99% of chemicals charged into the digester. Knots and fiber bundles are removed from the pulp with pressure screens and centrifugal cleaners and then recycled to the digester. Rejects also result from the screening and removed as solid waste.

The black liquor contains lignin and other alkali-soluble constituents from the wood in addition to inorganic chemicals that entered with the white liquor (Grace et al., 1989, p.17, p.279). Compared to the white liquor, significant portions of sulfur compounds in the black liquor have been oxidized to sulfate and thiosulfate. There are also trace metals in the black liquor and calcium ion is of special concern, as it can lead to problems with scale in subsequent concentration of the black liquor. Silicate ion can give problems with scaling on heat transfer surfaces. The major difference between the white and black liquors is the presence of organic components as part of dissolved solids in the black liquor. These are present mainly as organic acids with a significant amount of dissolved alcohols such as methanol. Some organic components may be recovered in the chemical

recovery section as a mixture of resin and fatty acids known as tall oil or as turpentine recovered in a liquid separation sequence. However, most of organic components are carried through to a recovery furnace, where they are burned, generating heat, carbonate, and carbon dioxide.

The weak black liquor, or the diluted black liquor produced from the brown stock washing system, is recycled within the process via two routes. In the first route, the majority of the diluted black liquor is sent to a chemical recovery section to recover the pulping chemicals, while in the second route, a small fraction is recycled to the digester directly (USEPA, 1995, p.22; European Commission, 1999, p.17-21). The latter may, however, vary from 10% to 50% of the total in order to obtain desired liquor-to-wood ratio without additional water (Grace et al., 1989, p.9-11). The washed pulp is then sent to a bleaching plant if white pulp is desired or directly to a paper machine if unbleached grades of paper or board are to be produced.

There are various types of impurities present in the pulp, including shives, knots, debris, chops, etc. Kraft shives are bundles of two or more fibers which have not been separated by cooking or mechanical action (Grace et al., 1989, p.319). In printing papers, kraft shives can affect the strength and surface properties of the paper, in the same manner as mechanical pulp shives. For most grades, kraft shives are harmful mainly to the appearance of the sheet.

Knots are uncooked wood particles. They are removed from the brownstock washing system and recycled to the digester. For bleachable grade kraft pulps with yields below 47% (kappa number below 35-40) knots are removed by knotters, which are special coarse screens (Grace et al., 1989, p.318). Some medium-yield kraft mills employ both fiberizers and knotters. For high-yield kraft pulps knots are removed by pre-breaking in a fiberizer or an in-line refiner, or both. Knots are an order of magnitude larger than shives, and are much more rigid. These particles are too large and inflexible to be acceptable in any grade, and are detrimental to washing operations. They should be removed as early in the process as possible.

Debris in chemical pulp can be any material which adversely affects the appearance or use of a pulp sheet (Grace et al., 1989, p.319). Anything which shows up in a final bleached or unbleached sheet as a speck darker than the background of the sheet is undesirable. Some particles can create problems in calendering, coating, or printing. Debris originates from several different types of materials in the unscreened pulp. This includes non-cellulosic particles such as plastic.

Chops are cubical or irregularly shaped debris, and are normally more of a problem in hardwood than softwood (Grace et al., 1989, p.319). This is due to the presence of irregularly shaped vessels and cells not found in softwood. The particles are shorter than shives, and depending on the source, may be more rigid. It is harmful for the same reason as shives, and should be removed before bleaching. Improper brownstock washing can also lead to carryover of pitch and calcium carbonate complexes which will lead to

deposits in the system and spots in the final sheet.

Cooking chemicals used in the pulp digestion are recovered in the chemical recovery section. The majority of the weak black liquor collected from the brownstock washing system is concentrated by evaporation to yield a strong black liquor (USEPA, 1995, p.27; Grace et al., 1989, p.474). The evaporation can increase the solids content of the black liquor from 13-17% to 60-80%. Steam-heated, multiple-effect evaporators are commonly used for this purpose. Because some inorganic chemicals are absorbed on the pulp and lost through mechanical problems, makeup chemical, usually in the form of sodium sulfate ($Na_2SO_4$), is added to the liquor ahead of a recovery furnace (Grace et al., 1989, p.10-11). A typical quantity of makeup sulfate is 20-25 kg per ton of pulp. The makeup sulfate may also be replaced by caustic soda and soda ash ($Na_2CO_3$) in order to reduce the sulfur input into the process (Grace et al., 1989, p.139).

The strong black liquor is then sent to a recovery furnace where organic solids are burned for energy generation and the chemicals are recovered in a molten form, known as smelt (USEPA, 1995, p.27; Grace et al., 1989, p.11). The recovery furnace recovers both chemicals and energy from the concentrated black liquor. Organic components of the black liquor are combusted to generate heat and produce carbon dioxide which is subsequently absorbed by the alkaline residue to form sodium carbonate (Grace et al., p.11). During combustion, sulfur is converted to sulfate ($Na_2SO_4$) which then undergoes a series of reactions resulting in the reduction of sodium sulfate ($Na_2SO_4$) to sodium sulfide ($Na_2S$). Other inorganic sulfur compounds formed include sulfur dioxide ($SO_2$) and sodium sulfite ($Na_2SO_3$). Some sodium thiosulfate ($Na_2S_2O_3$) may be formed as a result of the oxidation of sulfide with oxygen from air. The overall combustion reactions can be represented by the following equation (Grace et al., 1989, p.474):

$$\text{Black Liquor} + O_2 = Na_2CO_3 + Na_2S + \text{Flue Gas}$$

It should be noted that the process aids added to the digester, the blow tank and the brownstock washing system will not likely contribute to aqueous releases. These process aids will end up in the weak black liquor which are combusted in the recovery furnace upon concentration through evaporators. As a result, they will be released through air emissions rather than effluent discharge (Whitford, 2002).

A green liquor is formed by dissolving the smelt into a weak liquor. The dissolution takes place in a dissolving tank and the main components in the green liquor are sodium carbonate ($Na_2CO_3$) and sodium sulfide ($Na_2S$) (Grace et al., 1989, p.11, p.475). The characteristic green color of the green liquor is caused by trace amounts of iron compounds. A clarifier is further used to remove contaminated solids, known as dregs, from the green liquor. The dregs are then washed prior to disposal and the resulting weak liquor is used for dissolving the smelt.

Dregs are insoluble impurities in the green liquor (Grace et al., 1989, p.563). They arise from unburned carbon, iron salts, and other miscellaneous substances in the smelt. Dregs

are light, fluffy black materials that are difficult to settle and dewater. Green liquor typically contains 800-1,200 ppm of dregs. Well-clarified green liquor will contain less than 100 ppm of dregs.

A white liquor is obtained through causticization. The clarified green liquor is first passed through a slaker where lime (CaO) is slaked into calcium hydroxide ($Ca(OH)_2$) (Grace et al., 1989, p.475). It is then causticized in a causticizer where sodium carbonate ($Na_2CO_3$) is converted into sodium hydroxide (NaOH), but sodium sulfide ($Na_2S$) passes through unchanged. The causticized green liquor is further clarified to remove precipitated lime mud ($CaCO_3$) and a white liquor is generated for use in the digestion. The overall chemical reaction occurring in the slaker and the causticizer can be described as

$$Na_2CO_3 + CaO + H_2O = 2NaOH + CaCO_3$$

Lime mud ($CaCO_3$) is converted into lime (CaO) through calcination (Grace et al., 1989, p.475). The lime mud filtered out from the white liquor clarifier is washed and the resulting weak liquor is used for dissolving the smelt. Upon water removal in a thickener, the lime mud is sent to a kiln where it is converted into lime (CaO) at high temperatures. In the meantime, the lime mud removed from the slaker is recycled to the lime kiln directly. The calcination reaction can be represented by

$$CaCO_3 = CaO + CO_2$$

Some other operations are frequently carried out in the chemical recovery section. These include soap skimming and tall oil recovery, black liquor oxidation, and waste gas incineration (Grace et al., 1989, p.475). Fatty and resin acids, known as tall oil, are a minor constituent in black liquor that precipitates as a soap when the liquor is concentrated. As the black liquor reaches about 25% solids it is sent to a skim tank where the soap is skimmed off and the skimmed liquor is returned to the evaporators. The soap can be acidulated with sulfuric acid to form crude tall oil which can be sold as a by-product. The spent acid from the soap acidulation is normally added back to the recovery system. For the majority of Canadian kraft pulp mills, turpentine and tall oil are used as fuels for energy generation rather than sold as by-products (Whitford, 2002). This is different from European and American mills which have been reported to produce turpentine and tall oil as by-products. As a matter of fact, the tall oil yield in northern woods is usually lower than that in the more temperate regions such as the southern US.

Black liquor oxidation is needed if the recovery furnace has a direct contact evaporator (Grace et al., 1989, p.475). Hydrogen sulfide ($H_2S$) is a very odorous gas produced from residual sodium sulfide ($Na_2S$) in the black liquor in the direct contact evaporator. To minimize odorous emissions, the black liquor can be reacted with air or oxygen to convert the hydrogen sulfide ($H_2S$) to sodium thiosulfate ($Na_2S_2O_3$). There are also other odorous sulfur gases released at many points of the process. For odor control purposes these gases are often collected and incinerated in the lime kiln.

Part of the white liquor generated from the chemical recovery section is used in oxygen delignification which is aimed at further removal of lignin from the pulp. The oxygen delignification operation is carried out after brownstock washing in the presence of oxygen under alkaline conditions and can be combined with conventional and extended digestion (European Commission, 1999, p.21). In order to maintain the sodium balance within the process, part of the white liquor is taken from the chemical recovery section and oxidized to convert sodium sulfide to thiosulfate, while sodium hydroxide present in the white liquor serves as the principal alkaline chemical. Magnesium salt ($MgSO_4$) is added in order to preserve the strength of the pulp. After oxygen delignification, the pulp is washed and the resulting spent water is recycled to the brownstock washing system.

Bleaching is carried out to improve the whiteness and brightness of the pulp. The whiteness and brightness are increased by decolorizing or dissolving colored components in the pulp, principally lignin. Many types of pulps are bleached, including 1) wood pulp from chemical and mechanical pulping processes; 2) pulp from recycled waste paper; and 3) pulp from agricultural wastes (Grace et al., 1989, p.391). It was estimated that 60% of chemical pulp and 10% of mechanical pulp, produced worldwide, were bleached.

Bleaching of chemical pulp is a multistage process. A typical bleaching plant consists of three to five stages with each stage containing pumps, mixers, a washer, and a retention tower (Grace et al., 1989, p.392-410; European Commission, 1999, p.22). These stages form a bleaching sequence which alternates between acid and alkaline conditions. A bleaching sequence can be further divided into two operations: delignification and brightening. In the delignification operation, lignin is removed, while in the brightening operation higher brightness is achieved. It should be noted that some brightening takes place in the delignification operation, and vice versa. Bleaching chemicals, wash water, and steam for heating are added to each stage which then generates an acidic or alkaline effluent. Chemical reactions with lignin during the acid stages increase the whiteness of the pulp, while the alkaline extraction stages dissolve the lignin/acid reaction products. Typically, 4-8% of the pulp is lost due to bleaching agent reactions with wood cellulose and hemicellulose (USEPA, 1995, p.30).

Bleaching chemicals are classified into three groups: 1) oxidants; 2) reductants; and 3) alkalis (Grace et al., 1989, p.406-409). Chlorine, oxygen, hypochlorite, chlorine dioxide, hydrogen peroxide and ozone are common oxidants. Hydrosulfite is the only reductant used for bleaching, while sodium hydroxide is the only alkali used for extraction. Because of their greater economy, chlorine and oxygen are used in the early stages (delignification) of bleaching for lignin removal, but cannot be used for more extensive treatment because their poor selectivity results in cellulose degradation. Chlorine dioxide, hypochlorite, and peroxide can be used in the later stages (brightening) of bleaching because of their greater selectivity. With the AOX and dioxin issues of the 70’s and 80’s most mills have replaced elemental chlorine with chlorine dioxide. Likewise, hypochlorite for kraft pulp bleaching is very limited. Lately, peracetic acid has become commercially available as a bleaching chemical (European Commission, 1999, p.22).

The bleached pulp is dried before leaving the process. The pulp is first dewatered with a drying machine and then dried with steam (European Commission, 1999, p.25). Two systems are employed in the production of dried pulp: conventional drying and flash drying (Grace et al., 1989, p.273). The conventional system is normally used for chemical pulps (bleached kraft and sulfite). The pulp is formed on a machine similar to a paper machine, with a fourdrinier, felted press section, and dryer. After drying, the continuous sheet is cut into smaller sheets which are stacked into bales. In the flash drying system, it is not necessary to form a sheet of pulp, and the final product is in the form of a bale of fiber rather than a stack of cut sheets.

There are two types of market pulps according to their moisture content: dry and wet pulps. Most of dry market pulps are dried and made into sheets which are then pressed into bales for shipment (Grace et al., 1989, p.273, p.393). They have a density of 600-800 $kg/m^3$ and contain approximately 10% water, the nominal water content of air-dry pulp. Wet market pulp is usually produced in the form of a 40-50% dry slab or a crumb or pellet of any consistency above 10%. The wet pulp is expensive to transport and subject to fungus growth if stored for long periods. It is, therefore, produced in small quantities for continuous delivery to an assured customer or market.

Kraft pulps are also classed as soft, medium, and hard pulps according to the degree of delignification (Grace et al., 1989, p.279). The kappa number of pulp is a means of establishing the amount of lignin left with the pulp at the end of a pulping cycle. Soft or bleachable hardwood pulp grades fall into a kappa number range of 12 to 18 while bleachable softwood pulps fall into a range between 23 and 35. The latter will contain 3.5-5.2% lignin. Medium softwood pulps, generally used for bag and saturating grades, fall into a kappa number range of 35 to 50 and thus contain 5.2 to 7.5% lignin. Hard softwood pulps, used primarily for linerboard, fall into two categories – top and bottom liner. Topliner generally has a kappa number range from 60 to 75 and bottom liner 80 to 110. The latter contains 12 to 16% lignin.

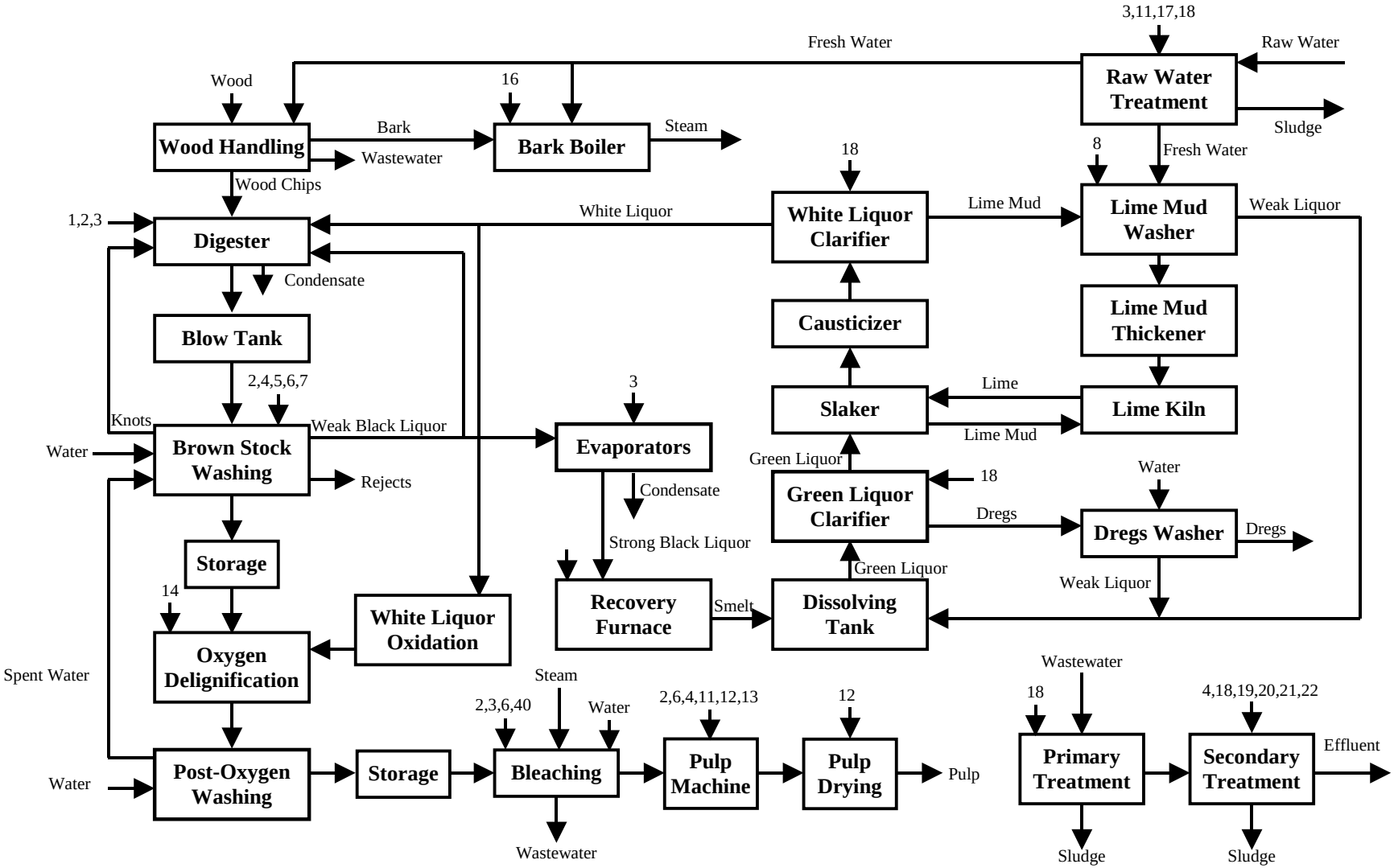


**Figure 4.1 – Standard Process for Non-integrated Bleached Kraft Pulp Mills**

## 4.2 – Operation Data

The production of kraft pulp consumes many different materials and generates various environmental releases. Summarized in Table 4.2 is typical operation data for kraft mills in the European Union (European Commission, 1999, p.31). Although the total wastewater volume is not available, individual quantities from wood handling, digestion and bleaching are obtained. In the U.S., the kraft process converts approximately 45-50% of input furnish into pulp (USEPA, 1995, p.22; Green and Hough, 1992, p.125). Generally speaking, the production of 1 tonne of kraft pulp requires 1.5-2 tonne of wood, 250 kg of new lime, 125 kg of soda ash, 6,500 kg of steam, 900 MJ of electricity, and 5.5 hours of direct labor (Austin, 1984, p.619).

**Table 4.2 – Operation Data of Non-integrated Bleached Kraft Pulp Mills**
(European Commission, 1999, p.30-51)

| | | |
|---|---|---|
| Wood | Total | 4-6.6 $m^3$ of wood per tonne of pulp |
| | Density | 0.4-0.6 $g/cm^3$ |
| | Bark content | 12-15 wt% |
| Product | Bleached kraft pulp | |
| Process chemicals | Total | 59-187 kg per tonne of pulp |
| Water | Total | 15-100 $m^3$ per tonne of pulp |
| Wastewater | Wood handling | 0.6-2$m^3$ per $m^3$ of wood (wet debarking) |
| | | 0.1-0.5 $m^3$ per $m^3$ of wood (dry debarking) |
| | Digester and evaporator | 8-10 $m^3$ per tonne of pulp |
| | Bleaching | 20-40 $m^3$ per tonne of pulp |
| | COD | 31-105 kg per tonne of pulp |
| | Nitrogen | 0.2-0.4 kg per tonne of pulp |
| | Phosphorus | 0.05-0.10 kg per tonne of pulp |
| Solid waste | Total | 43 kg (dry) per tonne of pulp |
| Air emissions | Sulfur-containing gases | 0.04-4 kg per tonne of pulp |
| | $NO_x$ | 0.85-2 kg per tonne of pulp |
| | Particulates | 0.25-3 kg per tonne of pulp |

Digestion conditions vary with wood species and type of pulp produced. A typical set of conditions for southern pine chips in the production of bleachable-grade pulp for fine papers are as follows: 18% active alkali on dry wood; 25% sulfidity; liquor-to-wood ratio at 4/1; 90 min to 170$^o$C; and 90 min at 170$^o$C (Green and Hough, 1992, p.125). Active alkali is defined as a sum of sodium hydroxide and sodium sulfide, while sulfidity is calculated as a percentage of sodium sulfide in active alkali. Hardwoods require less vigorous conditions primarily because of the lower initial lignin content.

An optimum dilution factor is normally used in brownstock washing. It is defined as an amount of water added in the washing operation to black liquor per unit mass of air-dried pulp (Green and Hough, 1992, p.26). The factor varies from 2.5 to 4.0 for a three-stage washing system.

The solids content of black liquor must be increased in order for it to burn in a recovery furnace without supplementary fuel. The current evaporation technology can increase the solids content from 13-17% to 60-80% (USEPA, 1995, p.27; Grace et al., 1989, p.474;

Green and Hough, 1992, p.28). As the solids content increases as a result of evaporation, the liquor becomes increasingly viscous (Minor, 1982). For this reason, the evaporation is conducted in two separate operations. Multiple-effect evaporation is used to bring the liquor to a concentration of about 45-50 wt% solids and forced-circulation evaporation or additional effects are used to bring it to about 65-70 wt% solids.

Black liquor recovered from brownstock washing contains both inorganic and organic solids. Inorganic solids account for about one third of total solids and originate from white liquor added to a digester, while organic solids account for about two-thirds and are extracted from wood (Green and Hough, 1992, p.2). Upon concentration from 13-17% to above 60% solids, black liquor can be burned without supplemental fuel. The combustion of black liquor in a modern recovery boiler generally produces between 3.5 and 4.0 lb of steam per lb of dry solids. The entire pulping process is self-sufficient in terms of thermal energy. H. A. Simons Ltd. (1995, p.4-67) reported that a 1,000 t/d mill could yield 1,670 lb of black liquor solids per day which was transformed into 1,070 GJ/h heat input with a gross steam generation rate at 265 t/h.

Wet scrubbers are commonly used to clean recovery boiler flue gas. H. A. Simons Ltd. (1995, p.4-67) reported that the flue gas generated from a 1,000 t/d kraft mill was 198 $m^3/s$ at 192$^oC$ and 710 mmHg and contained 22% moisture and 2.3% oxygen. The liquid-to-gas ratio is typically in the range of 0.54-2.0 $L/m^3$ (4-15 gal/1000 $ft^3$) for impingement scrubbers and 1.73-3.21 $L/m^3$ (12-24 gal/1000 $ft^3$) for venturi scrubbers.

The pulp suspension recovered from brownstock washing changes in consistency as it passes through delignification, bleaching and drying. Pulp consistency is defined as the percentage of pulp in total mass of suspension (Dence and Reeve, 1996, p.11). Since conventional centrifugal pumps can only handle pulp suspensions of up to 3 or 4% consistency, discharge of pulp from bleaching towers has traditionally required dilution to 3% consistency. This pulp suspension is further diluted to 1% to feed a rotary drum filter which, in turn, increases the consistency to 12-14%. Pressing is required for higher consistency at 30-45%.

The consistency of pulp suspension varies during bleaching. The variation is from a low of 2.5% to a high of 28%, depending upon bleaching agents, as summarized in Table 4.3 (Dence and Reeve, 1996, p.215-442).

**Table 4.3 – Variation of Pulp Consistency with Bleaching Agents**
(Dence and Reeve, 1996, p.215-442)

| **Bleaching Agent** | **Pulp Consistency (%)** |
|---|---|
| Oxygen delignification | medium (10-14%) and high (20-28%) |
| Chlorine | low (2.5-4%), medium (8-15%) |
| Chlorine dioxide | low (3-4%), medium (9-16%) |
| Alkaline extraction | medium (8-12%) |
| Hydrogen peroxide | medium (10%) |
| Hypochlorite | medium consistency (9-14%) |

By-products of kraft pulp mills include tall oil and turpentine. The quantity of tall oil recovered by a mill varies according to wood species, season of the year, and wood storage practices (Green and Hough, 1992, p.45). Summarized in Table 4.4 are quantities of tall oil available from several southeastern pine species (Green and Hough, 1992, p.45).

**Table 4.4 – Total Tall Oil Available by Pine Species**
(Green and Hough, 1992, p.45)

| **Pine Species** | **Tall Oil Available** (lb per oven dry ton) |
|---|---|
| Longleaf | 87 |
| Slash | 83 |
| Loblolly | 71 |
| Shortleaf | 69 |
| Spruce | 62 |

Tall oil recovered is usually somewhat lower than what is available in the wood, due to differences in storage methods and operating practices (Green and Hough, 1992, p.45). Table 4.5 provides yields of tall oil for mills from six North American and two Scandinavian wood procurement regions.

**Table 4.5 – Typical Tall Oil Yields**
(Green and Hough, 1992, p.45)

| **Region** | **Tall Oil Yield** (lb per oven dry ton) |
|---|---|
| Piedmont | 48 |
| Coastal | 52 |
| Canada | 23 |
| Southwestern U.S. | 63 |
| East of Cascades | 25 |
| West of Cascades | 15 |
| Finland | 39 |
| Sweden | 50 |

The yield of turpentine has been reported to be lower than that of tall oil. Champion International Corp. in the U.S. had five domestic mills that produced recoverable wood chemicals (Marlewski, 1984). Tall oil production was generally found in the range of 20-30 lb per ton of pine pulp, whereas turpentine was in the range of 0.2-0.3 gallon (12-19 lb) for the same ton of pulp. The density of turpentine at 24$^{o}$C is 62.2 lb/gal (Drew et al., 1971).

## 4.3 – Chemical Data

Chemicals used at non-integrated bleached kraft pulp mills can be divided between specialty and commodity chemicals. Types of specialty chemicals used are discussed in details in Section 7.3 – Estimates of Chemical Releases from Kraft Pulp Mills. Summarized in Table 4.6 are consumption rates of some major chemicals used for the

production of bleached kraft pulp in the European Union (European Commission, 1999, p.50). Most of these chemicals are used in bleaching. Magnesium sulfate ($MgSO_4$) is added to oxygen delignification in order to preserve pulp strength and calcium carbonate (CaO) is used in liquor causticization.

**Table 4.6 – Some Major Chemicals Used for Production of Bleached Kraft Pulp**
(European Commission, 1999, p.50)

| **Chemical** | **Consumption** (kg/tonne of pulp) |
|---|---|
| NaOH | 25-50 |
| $O_2$ | 5-25 |
| $NaClO_3$ | 20-50 |
| EDTA (chelant) | 0-4 |
| $SO_2$ | 2-10 |
| $H_2O_2$ | 2-30 |
| $O_3$ | 0-5 |
| $MgSO_4$ | 0-3 |
| CaO | 5-10 |

In addition, makeup chemicals for digestion are required. Since digestion chemicals are absorbed on pulp and lost through mechanical problems, a makeup chemical, usually in the form of sodium sulfate ($Na_2SO_4$), is added to black liquor ahead of a recovery furnace (Grace et al., 1989, p.10-11). A typical quantity of the makeup sulfate is 20-25 kg per ton of pulp. Part of sodium sulfate may be replaced with caustic soda (NaOH) and soda ash ($Na_2CO_3$) in order to reduce the sulfur input into the process (Grace et al., 1989, p.139).

Quantities of chemicals associated with digestion are dictated by several factors. These factors include type of pulp produced, type of wood used, and type of digester (Green and Hough, 1992, p.124). Summarized in Table 4.7 are typical values for active alkali charged, lime required, and lime mud produced for various grades of kraft pulp.

**Table 4.7 – Typical Values for Chemicals Associated with Digestion**
(Green and Hough, 1992, p.125)

| **Process Parameter** | **Units** | **Linerboard** | **Sack Paper** | **Bleachable Grades** |
|---|---|---|---|---|
| Pulp yield | % | 52-56 | 48-50 | 45 |
| White liquor required | $ft^3$/oven-dry short ton | 77-90 | 90-103 | 125 |
| | $m^3$/oven-dry metric ton | 2.4-2.8 | 2.8-3.2 | 3.9 |
| Lime required at 85% available | lb/oven-dry short ton | 400-460 | 460-520 | 640 |
| | kg/oven-dry metric ton | 200-230 | 230-260 | 320 |
| Lime mud produced | lb/oven-dry short ton | 660-790 | 790-870 | 1050 |
| | kg/oven-dry metric ton | 330-385 | 385-435 | 525 |
| Green liquor flow (to clarifier) | $ft^3$/oven-dry short ton | 96-112 | 112-128 | 154 |
| | $m^3$/oven-dry metric ton | 3.0-3.5 | 3.5-4.0 | 4.8 |

Bleaching chemicals commonly used include chlorine dioxide, oxygen, ozone and peroxide (European Commission, 1999, p.21-27). Chlorine dioxide must be generated on site because it is unstable as a gas and can only be stored as a solution of approximately

1% in water. Ozone ($O_3$) must also be generated on site because of its instability. The generation is carried out by applying high voltages (10-20 kV) to dry air or oxygen. Summarized in Table 4.8 are usage rates of bleaching chemicals in a common $C_DE_OHDED$ bleaching sequence (Grace et al., 1989, p.409).

**Table 4.8 – Typical Usage Rates of Bleaching Chemicals in a $C_DE_OHDED$ Sequence**
(Grace et al., 1989, p.409)

| Bleaching Chemical | Use Level (kg/ton of pulp) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_D$ | $E_O$ | H | $D_1$ | E | $D_2$ | Total |
| $Cl_2$ | 60 | | | | | | 60 |
| $Ca(OCl)_2$ or NaOCl | | | 10 | | | | 10 |
| $ClO_2$ | 2 | | | 8 | | 3 | 13 |
| NaOH | | 35 | | 4 | 5 | | 44 |
| $O_2$ | | 5 | | | | | 5 |

There are a number of possible reactions to produce chlorine dioxide (European Commission, 1999, p.21-27). Some techniques can produce up to 0.7 tonnes of chlorine by-product per tonne of chlorine dioxide whilst others produce very small amounts. In pulp and paper industry chlorine dioxide is produced by acidic reduction of sodium chlorate in the presence of reducing agents. These reducing agents include chlorine ion, hydrogen peroxide, sulfur dioxide and methanol. Ideally any sodium and sulfur by-product resulting from the preparation of chlorine dioxide can be recycled to the process as make-up chemicals. However, if sodium or sulfur by-products are produced in a quantity more than the make-up requirements, they have to be removed from the process.

## 4.4 – Wastewater

Wastewater generated from the kraft pulping process originates from various stages and accidental spills. Pulping and bleaching are the two major sources of water pollution (USEPA, 1995, p.38; European Commission, 1999, p.32). General water pollution concerns are BOD, COD, TSS, toxicity, and color. Toxicity concerns arise from the bleaching section which is the source of chlorinated organic compounds such as dioxins, furans, and others (collectively referred to as adsorbable organic halides, or AOX) present in wastewater. Color substances present in the effluent may also affect living species in receiving water bodies and nutrients (nitrogen and phosphorus) can cause eutrophication.

In the wood handling section, the major source of wastewater pollutants is debarking (European Commission, 1999, p.32). The debarking operation consumes water and generates a wastewater stream containing nutrients, fibers and oxygen-consuming organic compounds. Extractive compounds like resin acids can be leached out from bark, making the resulting effluent toxic to aquatic species. The water consumption for wet debarking is 0.6 to 2 $m^3$ per $m^3$ of wood. Dry debarking uses much less water, in the range of 0.1-0.5 $m^3$ per $m^3$ of wood, for log washing and some organic substances can be dissolved into the wastewater.

Condensates formed from condensation of vapors in digesters and multi-effect

evaporators are another source of wastewater (European Commission, 1999, p.33). Their combined volume ranged from 8 to 10 $m^3$ per tonne of pulp with a COD load of 20-30 kg per tonne of pulp and a BOD load of 7-10 kg per tonne of pulp. Methanol is the major source of the COD and other sources include ethanol, organic sulfur compounds, turpentine, and inorganic nitrous compounds. In addition, foul condensates contain ketones, terpenes, phenolics, resin acids, fatty acids, and various dissolved gases. Condensates further contain a large proportion of nitrogen nutrients discharged from kraft pulp mills.

Condensates from digesters and evaporators are normally treated in a steam stripping column (European Commission, 1999, p.33). The column has a removal efficiency of over 90% for most compounds and consumes 0.2 kg of steam per tonne of condensate. It usually removes malodorous gases and COD-contributing substances at the same time. The stripped condensates can have a reduced COD level at 1-1.5 kg per $m^3$ of condensate. The resulting overhead gases are either incinerated in a dedicated burner with subsequent $SO_2$ scrubbing or burned in a lime kiln.

Residual chemicals lost during the washing operation following the digestion eventually end up in wastewater. The objective of the pulp washing is to recover as much as possible of the pulping chemicals and the dissolved organic solids. The washing is, however, not 100% efficient and a residual amount of chemicals and pollutants is carried by the pulp into the bleaching section (European Commission, 1999, p.34). This amount, often referred to as “washing loss”, causes additional consumption of bleaching chemicals before discharged into wastewater. In the past, washing loss was measured in terms of kg sodium sulfate per tonne of pulp. Due to its environmental importance, washing loss is now measured in terms of COD. Typical washing loss is 5-10 kg of COD per tonne of pulp produced from softwood and 7-12 kg from hardwood.

Bleaching is the most important point of discharge of pollutants to water (European Commission, 1999, p.34-36). The bleaching section typically consumes 20 to 40 $m^3$ water per tonne of pulp produced. The pollutant loads contributed by the bleaching depend upon a number of factors such as degree of delignification, washing loss, bleaching sequence, bleaching chemicals, and type of wood. For example, the load of chlorinated organic substances (AOX) ranges from 0 to 2 kg per tonne of pulp produced from softwood and from 0 to 0.5 kg from hardwood.

Screening and cleaning operations during the pulp processing stage are usually sources of large volumes of wastewater (USEPA, 1995, p.39). This effluent stream, commonly referred to as white water, can contain significant BOD if washing efficiency is low and is always a source of suspended solids

Spills occur in various process stages. Fibers and black liquor can spill out in the digestion, screening, washing, and evaporation operations (European Commission, 1999, p.34). Spills of white liquor, weak liquor, and lime can be found during the causticization. Most spills can be collected and recycled if adequate buffer volumes are used and

appropriate procedures employed. Organic matters originating from spills normally contribute a COD load of 2 to 10 kg per tonne of pulp.

The volume of wastewater generated from a pulp and paper process is closely related to the water consumed. In the U.S., a typical pulp and paper mill consumed 16,000 to 17,000 gallons of water per ton of pulp produced (67-71 $m^3$/tonne of pulp) in 1988 (USEPA, 1995, p.38). In Canada, the water consumption for Quebec pulp and paper industry was 57 $m^3$ per ton of production in 1999 (Quebec Forest Industries Association, http://www.aifq.qc.ca). In the European Union, the water consumption varies considerably between different mills, ranging from 15 to 100 $m^3$ per tonne of pulp (European Commission, 1999, p.32). A consumption volume higher than 50 $m^3$ per tonne of pulp normally has included clean process cooling water. In addition, integrated and non-integrated mills differ in water management. In an integrated mill the pulp is transferred from the pulp making process to the paper making process and the wastewater discharged from both processes are usually treated in one single treatment plant. In contrast, the pulp manufactured at a non-integrated mill has to be dewatered and dried.

Wastewater pollutants can be effectively removed by treatment systems. In the U.S., virtually all mills have primary and secondary wastewater treatment systems (USEPA, 1995, p.38). These systems effectively remove BOD and TSS, as well as 30-70% of other pollutants such as COD and AOX. In the European Union, the removal efficiency of an activated sludge system is 85-98% for BOD, 40-70% for COD, 40-65% for AOX, 40-85% for total phosphorus and 20-50% for total nitrogen (European Commission, 1999, p.38). The pattern of a high removal rate for BOD and a moderate rate for COD is also observed in case of textile mill effluents. Operation data compiled from several U.S. textile mills indicated that activated sludge treatment could reduce BOD by 90% and COD by 70% (USEPA, 1979, p.218).

### 4.5 – Solid Waste

Solid waste is generated in various forms. They include inorganic sludge (dregs and lime mud) from the chemical recovery section, bark and wood residues and rejects (mainly sand) from the wood handling section, sludge from wastewater treatment, ashes from boilers and furnaces (European Commission, 1999, p.48). Organic waste such as bark and wood residues can be burned for energy recovery. Table 4.9 provides quantities of several types of solid waste generated from the kraft pulping process (European Commission, 1999, p.49).

Wastewater treatment sludge represents a large volume of solid waste. In the U.S., bleached kraft mills have been reported to generate wastewater treatment sludge in the range of 14 to 140 kg per ton of pulp produced (USEPA, 1995, p.41). Because of the tendency for chlorinated organic compounds (including dioxins) to partition from effluent to solids, wastewater treatment sludge has generated the most significant environmental concern for the pulp and paper industry.

**Table 4.9 – Solid Waste Generated from Non-integrated Bleached Pulp Mills**
(European Commission, 1999, p.49)

| **Type of Solid Waste** | **Generation** (kg/tonne of pulp, dry) |
|---|---|
| Wastewater treatment sludge | 10 |
| Ashes from combustion of wood waste | 9 |
| Other ashes from energy production | 14 |
| Fiber and coating waste | 5 |
| Wood waste | 6 |
| Hazardous waste | 0.2 |

In Canada, typical solid waste materials from pulp and paper mills include ash, lime mud, sludge from biological treatment systems, and unusable wood waste (Forest Products Association of Canada, 2001, p.19). There are also various methods used for treatment and disposal of solids waste such as incineration, landfilling, and composting. Summarized in Table 4.10 are quantities of solid waste treated by different methods for the Canadian pulp and paper industry as a whole in 1999.

**Table 4.10 – Pulp and Paper Solid Waste Treated by Different Methods**
(Forest Products Association of Canada, 2001, p.19, p.31)

| **Treatment or Disposal Method** | **Quantity of Solid Waste** (tonne/yr) |
|---|---|
| Energy generation | 2,477,117 |
| Incineration | 191,304 |
| Landfilling | 1,392,392 |
| Landspreading | 373,105 |
| Composting | 126,564 |
| Reuse or recycle | 30,447 |
| Off-site disposal | 12,257 |
| Landfill covering | 46,623 |

## 4.6 – Air Emissions

Air emissions originate from many process areas. These areas include chip storage, cooking digester, pulp washing, bleaching, chemical recovery, evaporation, bark furnace, recovery boiler, white liquor preparation, lime kiln, and pulp drying (European Commission, 1999, p.27-39). The major environmental concern is sulfur-containing gases including sulfur dioxide and malodorous reduced sulfur compounds such as hydrogen sulfide ($H_2S$), methyl mercaptan ($CH_3SH$), dimethyl sulfide ($CH_3SCH_3$) and dimethyl disulfide ($CH_3SSCH_3$). Strong malodorous gases are collected from the operations handling black liquor and generally burned in a separate burner or in a lime kiln. In most cases, the resulting flue gases are treated through a scrubber, and the scrubber water is sent back to the chemical recovery section. Sources for weak malodorous gases are chip pre-steaming, screening, pulp washing, smelt dissolving and tank ventilation. In addition, nitrogen oxides are emitted from furnaces along with small amounts of particulates. Chlorine compounds may also be released to the atmosphere from the preparation of bleaching chemicals.

Volatile organic hazardous air pollutants (HAPs) and volatile organic compounds (VOCs)

are also environmental concerns. These emissions were measured in a field test study of 13 kraft mills in the U.S. commissioned by the U.S. National Council of the Paper Industry for Air and Stream Improvement and are compiled in Table 4.11. The study showed that HAP emissions from brownstock washer systems with vacuum drum washers, pressure washers, diffusion washers, and horizontal belt washers were 0.96 lb, 0.083 lb, 0.075 lb, and 0.0011 lb per ton of oven-dried pulp, respectively (NCPI, 1994, No.678). VOC emissions from these sources were 1.0 lb, 0.18 lb, 0.24 lb, and 0.0004 lb per ton of oven-dried pulp, respectively. Methanol contributed over 90% of the HAPs emitted.

**Table 4.11 – Emissions of Volatile Organic Hazardous Air Pollutants (HAPs) and Volatile Organic Compounds (VOCs) from Various Process Areas of Kraft Mills**
(NCPI, 1994, No.675-679)

| **Process Area** | **Air Emissions (lb/ton of dry pulp)** | |
|---|---|---|
| | HAPs | VOCs |
| Brownstock screening and refining | 0.60 | 0.16 |
| Bleaching | 0.24 | 0.068 |
| Oxygen delignification | 1.1 | 0.66 |
| White liquor oxidation | 0.019 | 0.014 |
| Lime kiln | 0.036 | 0.017 |
| Smelt dissolving tank | 0.50 | 0.41 |
| Causticization | 0.12 | 0.064 |

At oxygen delignification systems and white liquor oxidation tanks, HAPs emitted consisted almost entirely of methanol (NCPI, 1994, No.675). The methanol content of the final post-oxygen washer water was found to be the most important factor affecting the total HAP emissions from oxygen delignification systems, whereas the total HAP emissions were not affected by wood species to be delignified (hardwood vs. softwood). In the bleaching section, methanol and chloroform were found to be the major components in the HAPs emitted (NCPI, 1994, No.679).

There are many sources of HAP and VOC emissions in the chemical recovery section.. The HAP and VOC emissions from recovery furnaces were 0.27 lb and 0.24 lb per ton of black liquor solids, respectively (NCPI, 1994, No.680). These emissions from black liquor oxidation systems were 0.32 lb and 0.20 lb per ton of black liquor solids. Methanol was found to contribute 74% and 84% of HAPs emitted from recovery furnaces and black liquor oxidation systems, respectively. Low levels of acetaldehyde, formaldehyde and acetone were also measured. Methanol was further found to dominate the HAPs emitted from lime kilns, smelt dissolving tanks, and all miscellaneous causticizing area vents (NCPI, 1994, No.676).

Methanol was found to be the major HAP in most of miscellaneous sources at kraft mills (NCPI, 1994, No.677). These sources include black liquor storage tanks, $ClO_2$ generators, batch digesters, pulp storage tanks, saltcake mix tanks, tall oil recovery plants, non-condensable gas thermal oxidizers, etc. Each of them exhibited a wide range of HAP emissions.

The Canadian pulp and paper industry has been tracking air emissions from mills since 1997 (Forest Products Association of Canada, 2001, p.14). Based on the data submitted by 25 mills, the primary source of $SO_2$ from pulp and paper came from combustion of sulphur-containing fuels such as oil, spent cooking liquor and non-combustible gases. Natural gas contains little sulphur and hence contributes an insignificant amount. Total reduced sulphur (TRS) is a group of sulphur compounds that originate from the kraft pulping and recovery process. These compounds give the process its characteristic, unpleasant odor and can be quite pronounced in the case of mills with older technology.

## 4.7 – Release Estimation Methods

Information on release estimation methods are available from some member countries of the Organization for Economic Cooperation and Development (OECD). These methods are a key aspect of Pollutant Release and Transfer Register established by OECD (OECD, 1999, p.1), which is an environmental database or inventory of potential harmful releases to air, water and soil as well as waste transported off-site for treatment and disposal. According to an OECD survey, Australia, Denmark, the Netherlands, Japan, the U.S., and Norway have relevant documents relating to release estimation methods for the pulp, paper and board industry and further information can be obtained from their respective web sites.

# 5 – Overview of Recovered Paper Mills

Recovered paper mills are referred to as deinking plants that produce a variety of grades from recycled paper. They may produce newsprint from recycled newspapers and magazines, packaging paper and board from recycled corrugated board, graphic paper from recycled household paper, and tissue paper from recycled office paper (European Commission, 1999, p.219-222). Generally speaking, deinked pulp can be divided into two categories: 1) pulp used for production of newsprint and board; and 2) pulp used for production of fine paper, tissue and toweling (Hamilton et al., 1987, p.235).

There are two methods employed for deinking of secondary fibers: washing and flotation (Hamilton et al., 1987, p.166-167). The degree of deinking by washing is proportional to the amount of water removed and depends to a great extent on size of ink particles detached. Flotation is not nearly so sensitive to particle size, and thus can be used to clean a variety of secondary fibers. Washing can remove up to 90% of ash and a major part of fines along with ink particles. Flotation, on the other hand, can only remove at best 50% of ash and subsequent washing is required for removal of the residual ash left by flotation.

Secondary fiber is referred to as paper or paperboard which is sent to a different paper mill for reuse (Hamilton et al., 1987, p.128). Broke, trim and rejects being put back into the manufacturing process at their original place of manufacture are not considered secondary fiber. All secondary fibers share a common distinction of carrying some content of foreign matter such as ink or coatings and contamination from all kinds of trash.

Recovered paper is the major source of secondary fiber for paper making. In the U.S., more than 200 mills relied exclusively on recovered paper for pulp furnish and the secondary fiber pulping accounted for approximately 30% of the U.S. pulp production in 1992 (USEPA, 1995, p.24). In the European Union, the average utilization of recycled paper was 43% (European Commission, 1999, p.215). To maintain the secondary fiber cycle primary fibers must be incorporated to ensure the strength and other properties of the paper to be produced.

Since 1989, the Canadian pulp and paper industry has invested over $1.7 billion in facilities to use various grades of recovered paper to manufacture recycled-content paper and packaging (Forest Products Association of Canada, 2001, p.18). In 1989, there was only one mill in Canada that could manufacture recycled-content newsprint. The number of recovered paper mills had increased to 22 by 2001. In 1999, Canadian pulp and paper producers recycled almost 5 million tonnes of paper into new products. On average, the paper produced in Canada was made up of 55% of chips and sawmill residues, 20% of recovered paper, and 25% of roundwood.

## 5.1 – Process Description

Figure 5.1 shows a standard deinking process for recovered paper mills. The makeup of recovered paper used in the process depends upon type of recovered paper and paper product intended (European Commission, 1999, p.215-220). For newsprint stock production, the raw material may consist of 50% newspapers and 50% magazines. Recovered paper is normally delivered to mills in bales or as loose materials. Codes for specialty chemicals used in the process diagram are provided in Table 4.1.

Cleaning may be required prior to pulping. Recovered paper is usually presorted before being delivered to a mill (USEPA, 1995, p.24). If not, it must be cleaned to remove contaminants. Common contaminants are adhesives, coatings, polystyrene foam, dense plastic chips, polyethylene films, wet strength resin, synthetic fibers. In some cases, contaminants of greater density than the desired secondary fiber are removed by centrifugal force, while lighter contaminants are removed by flotation.

Pulping is the first stage in paper making using recovered paper. A typical pulper is a large vessel filled with water which is sometimes heated (USEPA, 1995, p.24; European Commission, 1999, p.215). Pulping and deinking chemicals such as sodium hydroxide are added to dissolve the feed. Ink is released from fibers and dispersed in the solution in the presence of surfactants. The pulper may be equipped with a rotor for mixing. Debris and impurities are removed by a ragger and a junker. Flotation and bleaching chemicals may also be added to the pulp (Hamilton et al., 1987, p.167, p.209).

Deflaking is carried out at many secondary fiber pulping facilities (Hamilton et al., 1987, p.161). The special capability of a deflaker is to defiber tiny fiber bundles which cannot be broken up by pulping and even refining. This is achieved through high-speed turbulence of the deflaker.

Following the pulping and deflaking, cleaning and deinking are carried out. Contaminants removed from the pulp by cleaning and screening include stones, sand, metal, string, glass, textile, wood, plastic foils, paper clips, etc. (European Commission, 1999, p.217; European Commission, 1996, p.696). The cleaned pulp is then processed for ink removal by flotation or washing, or a combination of both. Air flotation is used to separate dispersed ink particles from the fiber slurry. Ink froth and rejects generated from the flotation are dewatered by a centrifuge or a wire press up to 50% dry solids and the resulting deinking sludge may be incinerated. The water collected may be clarified and reused in the process. Ink particles which pass through the flotation deinking step can be removed by wash deinking which is basically a multistage countercurrent washing operation. Besides ink particles, fillers and fines are also removed.

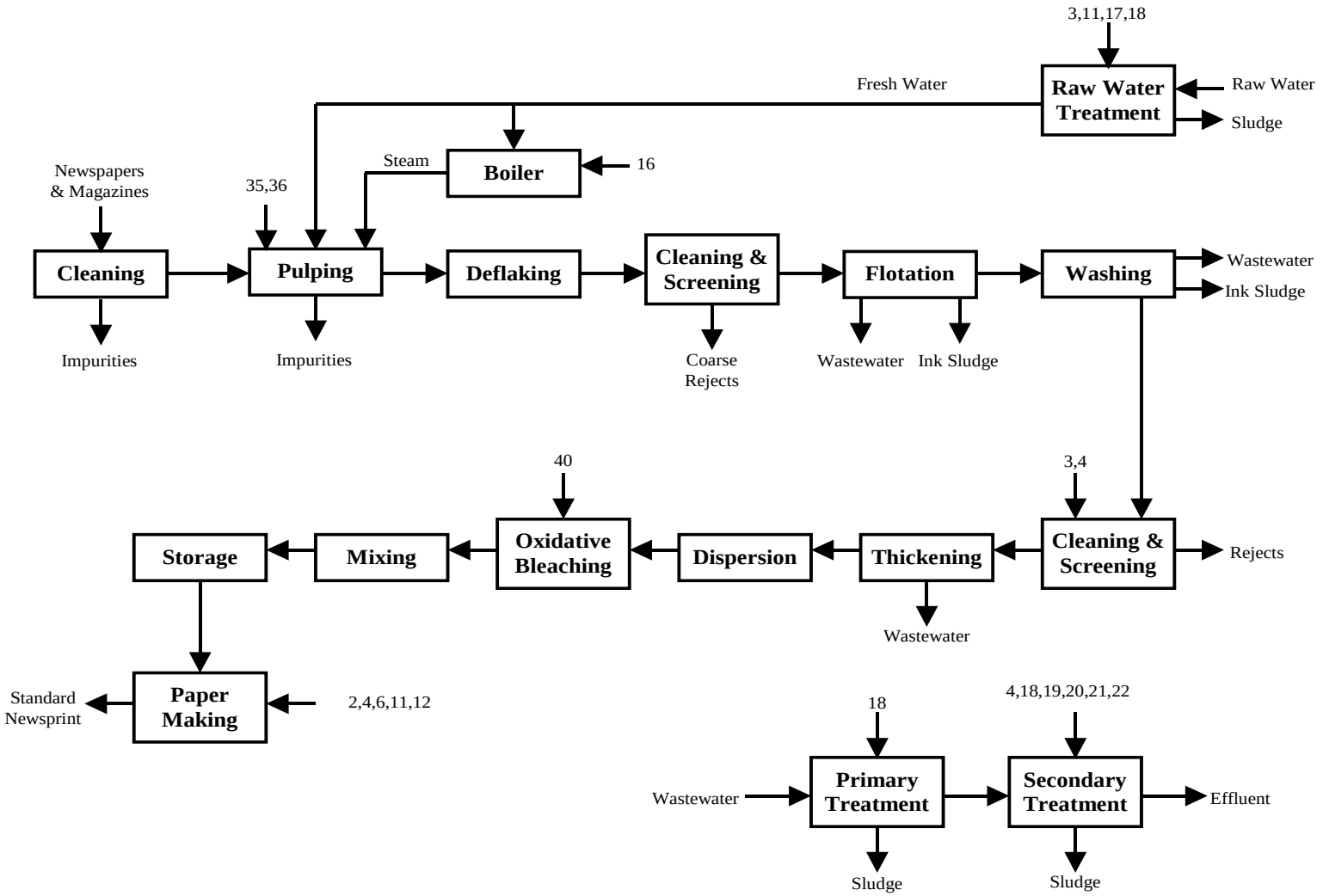


**Figure 5.1 – Standard Process for Recovered Paper Mills with Deinking**

The deinked pulp is then prepared for bleaching. Once again, cleaning and screening are carried out for further removal of contaminants (European Commission, 1999, p.218-219). These contaminants include high-density matter (e.g., sand), flat disturbing components, stickies, and fines. This step results in deflaking of the stock with good optical homogeneity. The pulp is then thickened using sieve belt press, disc thickeners, and screw press. After these cleaning steps, small amounts of impurities such as ink particles and wax may still be present in the pulp and can be dispersed with a disperser.

Oxidative bleaching is performed in a bleach tower to remove color matter from the pulp. Hydrogen peroxide is a common oxidative bleaching agent and used along with sodium hydroxide, sodium silicate and sometimes chelating agents (European Commission, 1999, p.218). Oxygen and ozone are unconventional bleaching agents and can be used for wood-free secondary fiber stock. After bleaching, the pulp is pumped to storage or mixing chests. In the mixing chests additives are added and correct fiber consistency is adjusted for proper sheet formation by a paper machine. Although the bleaching is usually carried out in a bleach tower, deinked secondary fibers may be bleached in the pulping stage by adding bleaching chemicals directly to the pulper (USEPA, 1995, p.34). For this type of operation, commonly used bleaching agents are hypochlorite (HClO, NaOCl, $Ca(OCl)_2$), hydrogen peroxide ($H_2O_2$) and sodium hydrosulfite ($Na_2S_2O_4$).

Additional steps are required for upgraded newsprint grades with a high degree of brightness. These additional steps are flotation, washing, thickening and reductive bleaching with hydrosulfite (European Commission, 1999, p.220). The upgraded newsprint can achieve about 63% ISO brightness and an ash content in the range of 10-12%. In comparison, the standard newsprint produced without the additional sequence of flotation-washing-thickening-bleaching has 59% ISO brightness and a higher ash content of 14-15%.

Primary and secondary systems are generally used for wastewater treatment. Wastewater generated from the process includes rejects from screening and centrifugal separation, filtrates from washers, thickeners and sludge dewatering, and excess water from the paper machine (European Commission, 1999, p.242).

## 5.2 – Operation Data

Presented in Table 5.1 is overall operation data of recovered paper mills for newsprint production in the European Union (European Commission, 1999, p.227-231). Major raw materials are recovered newspapers and magazines consumed at a combined quantity of 1,120 kg per tonne of newsprint produced. The total consumption of chemicals was 83 kg/t excluding those used in paper making. The water usage rate was 20 $m^3$/t, while the wastewater generation rate was between 8 and 16 $m^3$/t including the wastewater derived from paper making. The difference between the water used and the wastewater generated was due to the loss via water evaporation.

**Table 5.1 – Operation Data of Recovered Paper Mills for Newsprint Production**
(European Commission, 1999, p.227-231)

| | | | |
|---|---|---|---|
| Raw materials | Recovered newspapers | | 560 kg/t |
| | Recovered magazines | | 560 kg/t |
| | Wood chips | | 130 kg/t |
| | Round wood | | 50 kg/t |
| | Kraft pulp | | 10 kg/t |
| | Total | | 1,310 kg/t |
| Products | Newsprint | | 1,000 kg/t |
| | Market deinked pulp | | 5.9 kg/t |
| Process chemicals | Pulping | | 0.5-1.0% $H_2O_2$, 0.5-1.0% NaOH, 1-2% $Na_2SiO_3$ |
| | 1st stage flotation | | 0.3-0.6% soap |
| | 2nd stage flotation | | 0.2-0.4% soap (NaOH + fatty acids) |
| | Bleaching | | 1-2% $H_2O_2$, 0.5-1.2% NaOH, 1-1.8% $Na_2SiO_3$, 0.4-1% dithionite |
| | Flocculants | | 0.5-1 kg/t |
| | Total | | 83 kg/t (excluding chemicals for paper making) |
| Water | Total | | 20 $m^3$/t |
| Wastewater | Total | | 8-16 $m^3$/t |
| | Prior to biological treatment | COD | 17-27 kg/t or 1,700-2,700 mg/L |
| | | TSS | < 200 mg/L |
| | | AOX | < 10 g/t or 1 mg/L |
| | After biological treatment | BOD | 0.12 kg/t |
| | | COD | 3.3 kg/t |
| | | AOX | 2 g/t |
| | | Ammonia N | 20 g/t |
| | | P | 5 g/t |
| Solid waste | Bark | | 5.6 kg/t |
| | Paper residue rejects | | 100.2 kg/t |
| | Ash from waste incineration | | 90.8 kg/t |
| | Total | | 196.7 kg/t |

In paper making, pulp enters the headbox of a paper machine at 0.5-1.0% consistency and leaves the press section at about 40% consistency (Hagemeyer et al., 1992, p.174). Fresh water is added in the form of showers in the wire section. Shower water lubricates and cleans forming fabrics and wet press felts to maintain satisfactory dewatering performance (European Commission, 1999, p.326). It is generally consumed at 5-20 $m^3$ per tonne of pulp.

Steam is used in both paper drying and deinking operations. At a paper mill, about three-quarters of process steam is used in the dryer section of a paper machine (Kiiskinen and Edelmann, 2002). For 100% cylinder drying, the energy consumption is 3.6 GJ per tonne of paper. In comparison, the steam required for deinking is small at 1.00 MJ per tonne of pulp for production of newsprint (Huston, 1995, p.307).

Boilers are used for steam production. They can be package units and field erected units (H. A. Simons, 1995, p.8-5). Package boilers are generally limited to maximum pressures of 200-300 psig. Shipping size limitations impose a maximum of approximately 140 GJ/h in fuel heat input which represents about 36 t/h steam. Field erected boilers are designed

for larger steam generation rates. Their capacities range from 100 to about 950 GJ/h in fuel heat input and from 35 t/h up to about 300 t/h for steam generation.

## 5.3 – Chemical Data

Specialty chemicals used at recovered paper mills can be grouped into product and process aids. Product aids optimize specific product properties in accordance to customer requirements, while process aids facilitate mill operations. Product and process aids commonly used in the European Union are summarized in Table 5.2 (European Commission, 1999, p.236-237).

Chemicals used for flotation deinking are dependent upon type of secondary fibers. For groundwood-containing secondary fibers such as newspapers and magazines, typical chemicals used include sodium hydroxide, sodium silicate, hydrogen peroxide, soaps or fatty acids, dispersing agents, and chelants, and their use levels are given in Table 5.3 (Hamilton et al., 1987, p.208-216). Soaps or fatty acids are primary deinking agents and are added to a pulper where they saponify in an alkaline pulp suspension. Practice shows that soaps offer a higher operational dependability. In addition, surfactants, preferably nonionic types, can also be used to intensify the deinking process. For wood-free secondary fibers, hydroxide peroxide is not required because alkali does not cause the fibers to turn yellow. This further eliminates use of sodium silicate and chelants.

Provided in Table 5.3 are typical use levels of deinking chemicals found at mills (Hamilton et al., 1987, p.185). Caustic (sodium hydroxide) and soda ash (sodium carbonate) were frequently used either alone or in combination. Sodium silicate was employed in some cases. Sodium peroxide and hydrogen peroxide (with buffer alkali) were found to be particularly effective for deinking high-groundwood paper. Sodium hydrosulfite was found equally useful in the deinking of high-groundwood paper and as an aid to color removal in special cases.

Similar use levels of deinking chemicals have been reported from other sources. They are also listed in Table 5.3. It should be noted that the data reported by the European Commission includes those used in both deinking and bleaching for mills in the European Union. These chemicals are retained little by fibers and can be expected to release completely to wastewater (European Commission, 1999, p.238).

## 5.4 – Wastewater

Wastewater generated from recovered paper mills originates primarily from cleaning steps (European Commission, 1999, p.242). It includes three major sources:

- reject from screening and centrifugal separation;
- filtrates from washers, thickeners and sludge handling; and
- excess white water from paper making.

## Table 5.2 – Specialty Chemicals Commonly Used at Recovered Paper Mills

(European Commission, 1999, p.237)

| Category | Type | Examples | Functions |
|---|---|---|---|
| Product aids | Fillers | Kaolin or clay, talc, lime, gypsum, titanium dioxide | - Improve printability, opacity, brightness, smoothness and gloss<br>- Replace fibers |
| | Sizing agents | Modified starch, modified natural resins, wax emulsions, alkylketen dimers and maleic acid anhydride copolymers | - Improve surface quality<br>- Make paper hydrophobic |
| | Fixing agents | Alum ($Al_2(SO_4)_3$) | - Improve adsorption of additives to fibers |
| | Dry strength agents | Modified starch | - Improve strength under dry conditions |
| | Wet strength agents | Urea formaldehyde polymers, melamine-formaldehyde polymer, epichlorohydrin condensates | - Improve strength under wet conditions |
| | Dyes | Azo compounds, quarternary ammonium compounds | - Give paper a certain color and/or brightness |
| | Optical brighteners | Chemicals based on 4,4-diamino stilbene-2,2-disulfonic acid | - Give paper a white impression |
| | Coating chemicals | Pigments, binders, wet strength agents, dispersion and lubrication agents, defoaming agents, slimicides | - Give paper certain surface properties |
| Process aids | Retention aids | Alum, sodium aluminate, polyaluminum chloride, starch products, gums, anionic polyacrylamides, nonionic polyacrylamides, cationic polymers | - Retain fibers, fines and fillers<br>- Increase production by improving dewatering<br>- Reduce emissions of pollutants |
| | Deinking and bleaching chemicals | NaOH, fatty acids, $H_2O_2$, hydrosulfite, salts of fatty acids, complexing agents, sodium silicate, tensides (surfactants) | - Release ink from fibers<br>- Bleach<br>- Keep ink particles in dispersion |
| | Complexing (chelating) agents | DTPA or EDTA | - Remove metal ions by forming metallic complexes to prevent decomposition of bleaching chemicals |
| | Tensides (surfactants) | Acidic and alkaline surfactants | - Clean felts, wires and machinery<br>- Clean water circuit system<br>- Disperse substances |
| | Defoaming agents | Fatty acids, ethoxylates, poly-oxiethylene, fatty acid derivatives, alcohols, phosphoric acid esters, vegetable oil products | - Prevent and destroy foam |
| | Biocides (slimicides) | Organic bromine, sulfur or nitrogen compounds, quarternary ammonium compounds | - Prevent growth of microorganisms |

**Table 5.3 – Use Levels of Deinking Chemicals**

| Chemicals | Use Level (% on pulp) | | | |
|---|---|---|---|---|
| | Groundwood-Containing Secondary Fiber | Wood-Free Secondary Fiber | Deinking and Bleaching | Deinking Only |
| Sodium hydroxide | 1.0-2.0% | 2.0% | 1.0-2.0% | 0.6% |
| Sodium silicate | 3.0% | not used | 2.0-3.0% | 1.0% |
| Hydrogen peroxide | 0.8-1.2% | not used | 0.5-2.5% | 0.8% |
| Soap or fatty acid | 0.4-1.0% | 0.9-1.0% | 0.5-0.8% | no data |
| Dispersing agent | 0.1% | 0.1% | no data | no data |
| Chelant | 0.2% | not used | 0.2-0.3% | 0.2% |
| Sodium dithionite | not used | not used | 0.6-1.0% | no data |
| Talc | not used | not used | 1.0-1.5% | no data |
| Sulfuric acid | not used | not used | 0.8-1.0% | no data |
| Reference | Hamilton et al., 1987, p.216 | | European Commission, 1999, p.238 | Dingman & Perry, 1999 |

Compiled in Table 5.4 are typical pollutant loads and volume of wastewater discharged from recovered paper mills with and without deinking in the European Union. Conventional pollutants include BOD, COD, TSS, nitrogen, phosphorus, etc. In the European Union, mill effluents are discharged directly to the surface water after primary and biological treatment or to a municipal sewage treatment plant after primary clarification for solids removal (European Commission, 1999, p.243).

Data in Table 5.4 indicates that noticeable difference exists between mills with deinking and those without deinking. A higher COD content is observed after biological treatment for mills with deinking than those without deinking (European Commission, 1999, p.244). This may be due to the fact that much of COD is retained in paper products produced from mills without deinking. The BOD data, however, does not show significant difference. Low concentrations of nutrients (nitrogen and phosphorus) are found in wastewater and their presence is mainly caused by the addition of these nutrients for effective operation of biological treatment that needs a nutrient supply in the range of BOD:N:P = 100:5:1. Organic nitrogen compounds may also originate from some additives. During biological treatment part of the nitrogen may be hydrolyzed to ammonium and the rest is transformed to nitrate compounds.

The concentration of salts can be high in mill effluents. Salts, mainly sulfate and chloride, are introduced through recovered paper and certain additives as alum (European Commission, 1999, p.245). Sulfate concentrations up to 1,000 mg/L have been observed even when aluminum sulfate is not used.

In addition, heavy metals and halogenated compounds are present in mill effluents. Heavy metals are generally negligibly low (European Commission, 1999, p.244). Sources of organic halogenated compounds are certain additives (especially wet strength agents), recovered paper made from chlorine bleached pulp, and printing inks. Occasional measurements at recovered paper mills in Germany have shown that average AOX

concentrations were in the neighborhood of 200 μg/L. Chlorophenols up to 1 μg/L and polychlorinated biphenyls in trace amounts (values below the detection limit of 0.11 μg/L) have been observed.

**Table 5.4 – Typical Pollutant Loads of Wastewater Discharged from Recovered Paper Mills in European Union**

(European Commission, 1999, p.243)

| Discharge Point | Parameter | Units | Value | |
|---|---|---|---|---|
| | | | Without Deinking | With Deinking |
| After Primary Treatment | BOD | mg/L | 1900 | 550 |
| | | kg/t | 1.8 | 10 |
| | COD | mg/L | 3800 (570-9000) | 1100 (440-1900) |
| | | kg/t | 3.5 (3.2-3.8) | 20 (7-40) |
| | Organic & ammonia N | mg/L | 16 (10-40) | 20 (13-25) |
| | | kg/t | 0.05 (0.02-0.1) | 0.35 (0.19-0.62) |
| | Volume | $m^3/t$ | 3.6 (0.4-6.6) | 15 (9-39) |
| Before Biological Treatment | BOD | mg/L | 1800 | 770 |
| | | kg/t | 12.3 | 8.3 |
| | COD | mg/L | 3200 | 1900 |
| | | kg/t | 22 | 21 |
| After Biological Treatment | BOD | mg/L | 10 (3-28) | 9 |
| | | kg/t | 0.06 (0.01-0.13) | 0.09 |
| | COD | mg/L | 150 (60-270) | 290 |
| | | kg/t | 0.77 (0.29-1.12) | 3.1 |
| | Organic & ammonia N | mg/L | 5.6 (3-13) | 7.8 |
| | | kg/t | 0.03 (0.01-0.04) | 0.08 |
| | Total P | mg/L | 1.5 (0.5-1.8) | no data |
| | | kg/t | 0.01 | no data |
| | TSS | mg/L | 25 (17-40) | no data |
| | | kg/t | 0.13 (0.06-0.21) | no data |
| | Volume | $m^3/t$ | 5.7 (3.1-11) | 11 |

## 5.5 – Solid Waste

Recovered paper mills generate several types of solid waste. These include: 1) rejects; 2) sludge; and 3) incineration ash (European Commission, 1999, p.245-246). They are generated from stock preparation, process water clarification, and wastewater treatment. Rejects can be divided between heavy/coarse rejects and light/fine rejects. Sludge can be classified into deinking sludge, flotation sludge and wastewater sludge. The dry solid content obtained by dewatering and thickening is 60-80% for coarse rejects, 50-65% for fine rejects, and 60% for sludge. Although specific data for newsprint production is not available, data found for other product types, as compiled in Table 5.5, indicates that the total solid waste generated can be as low as 4-9% of the raw materials for paper board production and as high as 32-40% for market deinked pulp production.

Solid waste originating from recovered paper includes impurities and paper residue. Impurities present in recovered paper include lumps of fibers (shives), staples, ring binders, sand, glass and plastics. They account for 6.5% of recovered paper in total and

most of them end up as solid waste (European Commission, 1999, p.246-247). Paper residue is generated as sludge from process water clarification during fiber recovery in white water circuits and as sludge from wastewater treatment. It consists mainly of fibers and fillers. Paper residue is often recycled for the production of paper board and corrugated medium. However, for higher grade products, it does not meet the quality requirement for recycling and is therefore treated as waste.

**Table 5.5 – Solid Waste Generated from Recovered Paper Mills**
European Commission, 1999, p.246)

| **Product** | Graphic Paper | Tissue Paper | Market Deinked Pulp | Paper Board |
|---|---|---|---|---|
| **Raw Material** | Newspaper & Magazines | Recovered Office Paper | Recovered Office Paper | Shopping Centre Waste & Recovered Household Paper |
| **Heavy/coarse rejects** | 1-2% | 1-2% | <1% | 1-2% |
| **Light/fine rejects** | 3-5% | 3-5% | 4-5% | 3-6% |
| **Deinking sludge** | 7-16% | 8-13% | 12-15% | - |
| **Clarification sludge** | 1-5% | 15-25% | 15-25% | 0-1% |
| **Wastewater treatment sludge** | 1% | 1% | 1% | 1% |
| **Total** | 10-25% | 28-40% | 32-40% | 4-9% |

## 5.6 – Air Emissions

Air emissions for recovered paper mills are generated from four sources: 1) energy generation; 2) on-site incineration of sludge and/or rejects; 3) wastewater treatment (odor); and 4) raw material handling (dust) (European Commission, 1999, p.248-250). Energy generation (steam and electricity) is the major source of air emissions and leads to releases of $CO_2$, $NO_x$, $SO_2$, dust and low concentrations of heavy metals. Steam is normally generated on site by dedicated boilers, while electricity can be purchased from the grid.

Deinking operations are a source of emissions of volatile organic hazardous air pollutants (HAPs) and volatile organic compounds (VOCs). A study of four recovered paper mills in the U.S. found that HAP emissions from deinking operations ranged from 0.022 to 0.31 lb per ton of oven-dried pulp (NCPI, 1997, No.739). They consisted primarily of chloroform, methanol, biphenyl, toluene, and acetaldehyde. VOC emissions ranged from 0.032 to 0.87 lb per ton of oven-dried pulp. At mills which used hypochlorite for bleaching, chloroform was the most significant HAP and its emissions averaged 0.12 lb per ton of oven-dried pulp, compared to 0.006 lb per ton of oven-dried pulp for mills which did not use hypochlorite.

## 5.7 – Release Estimating Methods

Release estimation methods for environmental risk assessments of new and existing substances in the European Union are provided in the European Union Technical Guidance Document (TGD). The methods are used to estimate the release of a substance to the environment over the substance's lifecycle (Brooke et al., 2000, p.1). They consist

of three parts:

- Industry and use categories;
- A- and B-Tables; and
- Emission scenario documents (ESDs).

Industry and use categories are used to identify the industries in which a given substance is used (Industry Category or IC) and the function of the substance within the industries (Use Category or UC) (Brooke et al., 2000, p.1). This provides a relatively simple way of grouping substances with similar uses and allows release estimation to be carried out in a generic fashion by assuming that substances with similar uses and functions have similar releases to the environment. The TGD contains 16 industry categories and 55 use categories.

The A- and B-Tables are used to obtain the release estimates for a given industry category/use category combination (Brooke et al., 2000, p.1). The A-Tables contain generic emission factors, expressed as a fraction of the tonnage of a substance used. For each industry category, an A-Table contains emission factors to air, water and soil for five lifestages: production, formulation, processing, private use and recovery. Emission factors from the A-Tables are used to determine overall releases of a substance. The B-Tables are used to provide an estimate of the amount of a substance that might be used at a site and the number of days over which this use may occur.

The ESDs are provided for some industry categories (Brooke et al., 2000, p.1). In a risk assessment process, information provided in the ESDs is used in preference to that in the A- and B-Tables for estimating environmental releases. In some cases data in the A- and B-Tables are based on data reported in the ESDs, but this is not always the case.

The A-Tables generally relate emission factors to physico-chemical properties of a substance, most notably vapor pressure and water solubility (Brooke et al., 2000, p.5-6). For the pulp, paper and board industry (industry category: IC12), applicable A-Tables for each lifestage are listed in Table 5.6.

The ESDs for the pulp, paper and board industry (IC12) includes the releases from the manufacture of paper (e.g., biocides, dyes, papermaking additives), and recycling of paper (during pulping, washing deinking) (Brooke et al., 2000, p.23). The manufacture and application of paper are considered as a processing stage for a given substance, while the recycling is considered as a recovery stage. These releases pertain only to wastewater. Releases of a substance from production and formulation stages are not considered in the ESDs.

The approach taken in the ESDs is to categorize paper into four different types (printing and writing; tissue; newsprint; and board, carton, packaging, and wrapping) and to provide typical values for amounts produced at a site, water usage, recycling, etc. for each of the four types (Brooke et al., 2000, p.23). These, along with typical application rates and emission rates to water for various types of additives, allow concentrations of a given

substance to be determined.

**Table 5.6 – A-Tables in European Union Technical Guidance Document Applicable to Pulp, Paper and Board Industry**
(Brooke et al., 2000, p.6)

| Lifestage | Applicable A-Tables |
|---|---|
| Production | A1.1 for UC other than 10, A1.3 for UC = 10 |
| Formulation | A2.1 |
| Processing | A3.12 |
| Private Use | not applicable |
| Recovery | A5.2 |

Presented in Table 5.7 and Table 5.8 are chemical release rates to wastewater. The data in Table 5.7 is provided by TGD's ESDs, while that in Table 5.8 by TGD's A-Tables (Brooke et al., 2000, p.23). These release rates are believed to be those prior to wastewater treatment and are related to two separate processes: paper production and paper recycling. The paper production corresponds to the paper making carried out at non-integrated paper mills, while the paper recycling corresponds to the pulp making at recovered paper mills.

**Table 5.7 – Rate of Chemical Release to Wastewater Provided by European Union Technical Guidance Document's Emission Scenario Documents (TGD's ESDs)**
(Brooke et al., 2000, p.25)

| Process | Chemicals | Release Rate | |
|---|---|---|---|
| | | without water closure | with water closure |
| Paper Production | Anionic direct dye | 20% | 1-12% |
| | Anionic direct dye + fixing agent | 2% | 0.1-1.2% |
| | Cationic direct dye | 5% | 0.25-3% |
| | Basic dye for bleached pulp | 40% | 2-24% |
| | Basic dye for mechanical pulp | 30% | 1.5-18% |
| | Basic dye + anionic fixation for mechanical pulp | 5% | 0.25-3% |
| | Acid dye | 50% | 2.5-30% |
| | Acid dye + cationic fixation | 10-20% | 0.5-12% |
| | Antifoaming agents | 100% | 5-60% |
| | Charge control agents | 10-30% | 0.5-18% |
| | Retention aid and wet strength resin | 10-30% | 0.5-18% |
| | Softening agents | 25-40% | 1.25-24% |
| | Size, alum alone | 70-90% | 3.5-54% |
| | Size, alum + rosin | 30% | 1.5-18% |
| | AKD | 10-30% | 0.5-18% |
| Paper Recycling | Inks (default) | 100% | 100% |
| | Mineral oil-based inks | 14-28% or 60-80% | 14-28% or 60-80% |
| | Flexographic ink | 30-90% | 30-90% |
| | Non-impact toners | 6-28% | 6-28% |
| | Dyes (default) | 50% | 50% |
| | Temperature-sensitive coatings | 100% | 100% |
| | Color former from carbonless copy paper | 5-7% | 5-7% |

**Table 5.8 – Rate of Chemical Release to Wastewater Provided by European Union Technical Guidance Document's A-Tables (TGD's A-Tables)**
(Brooke et al., p.25)

| Process | Chemicals | | | Release Rate |
|---|---|---|---|---|
| Paper Production | Basic dye, anion | | | 2.3% |
| | Direct dye | | | 4% |
| | Direct dye, cation | | | 5.5% |
| | Direct dye, anion/cation | | | 2.8% |
| | Acid dye, cation/unknown | | | 7.9% |
| | Brightener | | | 6.4% |
| | Chemicals with | Water Solubility (mg/L) | Vapor Pressure (Pa) | |
| | | < 100 | < 100 | 85% |
| | | < 100 | 100-500 | 75% |
| | | < 100 | > 500 | 50% |
| | | 100-1,000 | < 100 | 87.5% |
| | | 100-1,000 | 100-500 | 85% |
| | | 100-1,000 | > 500 | 75% |
| | | 1,000-10,000 | < 100 | 90% |
| | | 1,000-10,000 | 100-500 | 87.5% |
| | | 1,000-10,000 | > 500 | 85% |
| | | > 10,000 | | 95% |
| | Fillers and impregnation agents | | | 5% |
| Paper Recycling | Colorants | | | 10% |
| | Reprographic agents for graphic paper | | | 20% |
| | Reprographic agents for cardboard | | | 1% |
| | Reprographic agents for newspaper | | | 15% |
| | Reprographic agents for sanitary paper | | | 1% |
| | Reprographic agents for packaging paper | | | 10% |
| | Reprographic agents for archive paper | | | 5% |
| | Reprographic agents (default) | | | 20% |

In Tables 5.7 and 5.8, chemical release rates are divided between dyes and non-dye substances. The release rates (without water closure) provided by TGD's ESDs are generally higher than those of TGD's A-Tables for the same dyes (Brooke et al., 2000, p.23). There are also differences in the classification of dyes from the two data sources. For non-dye substances, a range is provided by TGD's ESDs, whereas a specific rate is given in TGD's A-Tables on the basis of water solubility and vapor pressure.

In Table 5.7, release rates with water closure are derived from those without water closure. Although the degree of water closure is not explicitly defined, it appears to be equivalent to the percentage of fresh water saved by closing up water loops with respect to water consumption under the condition of no water reuse (Hagemeyer et al., 1992, p.177). The degree of water closure was reported in the range of 40-95% for paper production and the corresponding release was, therefore, 5-60% of the amount released under the condition without water closure (Brooke et al., 2000, p.25). It should be noted that the degree of water closure only applies to paper production and is considered zero for paper recycling. For the release data reported in Table 5.8, it is not clear whether or not water closure has been factored in.

Ink is removed by flotation and washing deinking operations. Flotation produces a sludge which is dewatered and disposed of as a solid waste, while washing results in aqueous releases of chemicals (European Commission, 1996, p.704). The total removal of ink by deinking depends upon the method for ink drying and varies between 30% to 100%, as given in Table 5.9. The distribution of ink removed between the flotation and washing operations varies with the type of ink and available data is compiled in Table 5.10. If no specific information is available, it should be assumed that 100% is released to water by the washing operation.

**Table 5.9 – Total Ink Removal during Deinking**
(European Commission, 1996, p.704)

| Method of Ink Drying | Ink Removal |
|---|---|
| Absorption, penetration or evaporation | 80-100% |
| Oxidation or IR radiation | 60-95% |
| Hot polymerization or UV fixation | 40-90% |
| Ink-jet, laser or xerographic copying | 30-60% |

**Table 5.10 – Ink Removal Distribution between Flotation and Washing**
(European Commission, 1996, p.704)

| Ink Type | Removal by Flotation | Removal by Washing |
|---|---|---|
| Mineral oil-based ink | 60-80% | 14-28% |
| Flexographic ink | very little | 30-90% |
| Non-impact toners | 60-80% | 6-28% |

Dyes are released by 70-90% to the sludge during the flotation operation and by 10-30% to the wastewater during the washing operation (European Commission, 1996, p.704). In the absence of specific data on dye removal, a removal rate of 50% should be assumed, which can be considered as a worst case scenario.

Temperature-sensitive coating substances, i.e., color former and co-reactant, in waste thermal paper remain unreacted except where printing has occurred (European Commission, 1996, p.704). They represent a very small proportion of waste generated and can be ignored. These substances are released by 100% to wastewater during alkaline pulping. For carbonless copy paper, most of the color former is hydrolyzed during alkaline pulping and released to wastewater. However, the shear force employed in the pulping machine can cause some color former to react with the montmorillonite clay. It can be assumed that 10% of the color former is bound to the clay and that 50-70% of this dye-clay complex is released to wastewater.

Removal of substances during wastewater treatment depend upon their solubilities. Readily soluble substances can be assumed to pass through primary treatment by 100%, while poorly soluble substances to be removed at 50% (European Commission, 1996, p.705). A primary sedimentation or clarification system may achieve a removal rate of 20% for dissolved substances and 90% for insoluble substances such as inks and toner constituents.

Upon primary treatment, the aqueous release of a chemical substance removed from deinking can be calculated by the equation (European Commission, 1996, p.705):

$$E_{aq} = \frac{W_{chem} F_{paper} R_{deink} (1 - R_{primary})}{N_{day} N_{site}}$$

where

| | |
|---|---|
| $E_{aq}$: | aqueous release of a chemical substance, kg/d |
| $F_{paper}$: | fraction of recovered paper used for raw materials, % |
| $N_{day}$: | number of working days per year, d/y |
| $N_{site}$: | number of sites |
| $R_{deink}$: | rate of ink removal by deinking, % |
| $R_{primary}$: | removal rate by primary wastewater treatment |
| $W_{chem}$: | total consumption of a substance on paper, kg/y |

# 6 – Overview of Non-integrated Paper Mills

## 6.1 – Process Description

Figure 6.1 shows a generic process for non-integrated paper mills. Raw materials can be either virgin fibers (chemical or mechanical pulp) or recovered fibers or their mixtures (European Commission, 1999, p.308; Hagemeyer et al., 1992, p.187). Dry fibers received are placed into a pulper to prepare a pumpable slurry. Undissolved impurities are removed from the slurry by screening and centrifugal cleaning. Refining is an optional step in order to improve the bonding ability of individual fibers. This step is accomplished in a vessel equipped with a rotating disc and conditions fibers to achieve required properties of the paper product. Chemicals added to various operations and their codes used in the flow diagram are given Table 4.1.

The sequence of pulping-screening-cleaning-refining is commonly referred to as stock preparation. Its purpose is to make fibers suitable for forming into a sheet of paper (Hagemeyer et al., 1992, p.187). Unrefined fibers produced by a pulp mill, or partially prepared from various materials, are not suitable as such for manufacture of paper. A sheet made from such fibers would have low strength, high bulk, irregular texture, and wild uneven formation.

There are two types of stock preparation systems: 1) common stock refining; and 2) separate stock refining (Hagemeyer et al., 1992, p.216-221). In a common stock refining system, refining is carried out in a simple line of chests and refiners. Different furnishes are blended in a blend chest or a furnish pulper and processed as a mixture through refiners. In a separate stock refining, each furnish is processed in a separate preparation line to obtain desired characteristics of that fiber and delivered to a separate storage chest. Different furnishes are then mixed in mixing chests in proportions appropriate for a particular grade of paper. As a result, a mill may have several preparation lines for one paper machine (European Commission, 1999, p.309).

The type of furnish to be refined is dependent upon the specific grade of paper to be manufactured. Newsprint, for example, might require mixing of groundwood, thermo-mechanical or chemi-mechanical pulp, and semi-bleached kraft pulp (Hagemeyer et al., 1992, p.216). Linerboard would require dealing with a mixture of virgin unbleached kraft and secondary fibers, while fine paper would involve blending of hardwood, softwood, and sometimes eucalyptus or sawdust sulfite, or some other fibers.

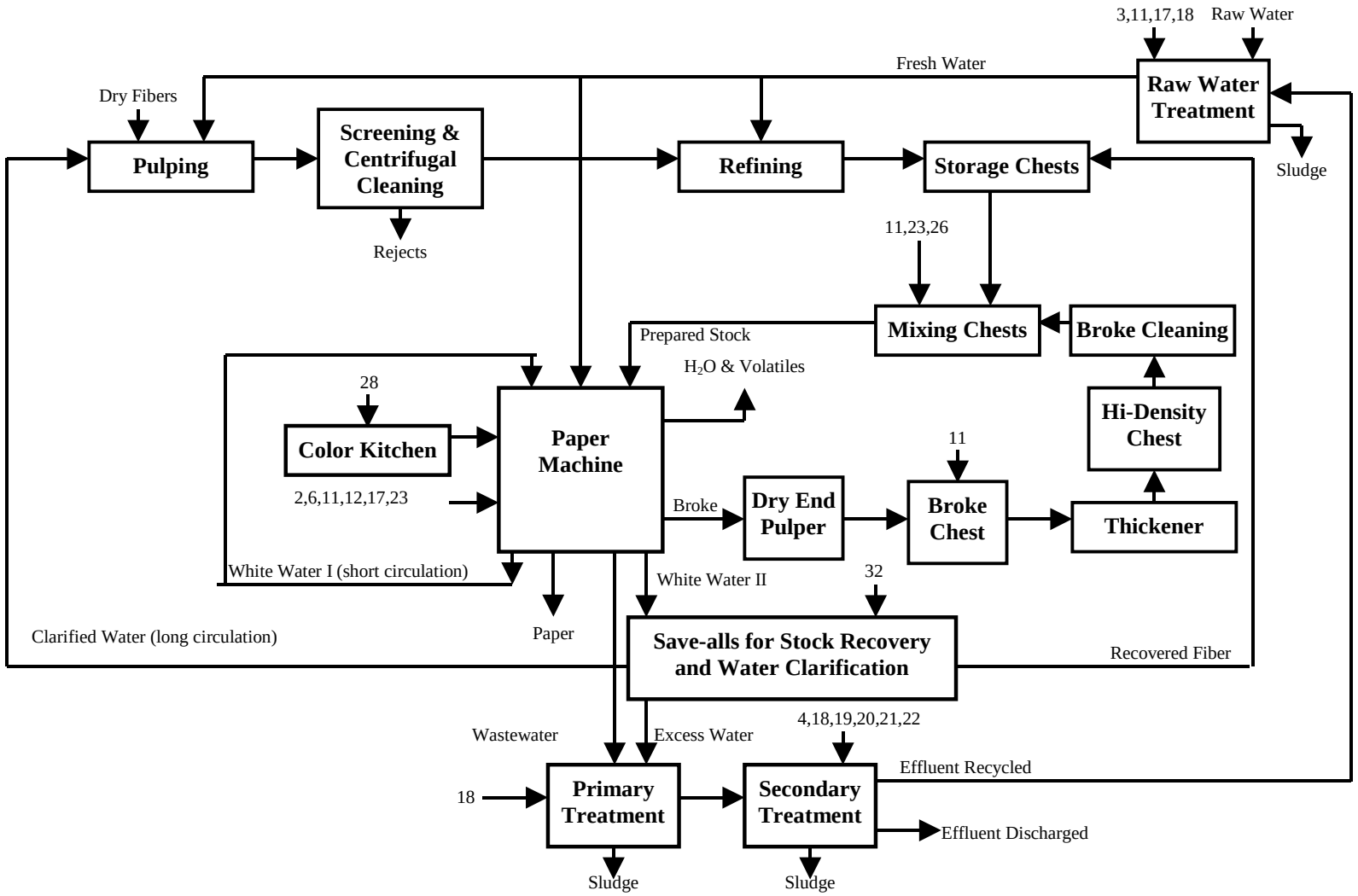


**Figure 6.1 – Standard Process for Non-integrated Paper Mills**

Refined furnish is converted into paper through a paper machine. The most common design of paper machines is the Fourdrinier type (USEPA, 1995, p.35). In a Fourdrinier system, a pulp slurry is deposited onto a moving wire belt and water is removed by gravity, vacuum chambers, and vacuum rolls. The water removed is normally recycled to the slurry deposition step because of its high fiber content. The continuous sheet is then pressed between a series of rollers to dry and compress fibers. In a simple paper machine, paper may be reeled only (European Commission, 1999, p.312). For a more complicated machine, a size press can be available for applying starch (a sizing agent) and other chemicals to paper surface by dipping or spraying.

A paper machine is actually a large dewatering device consisting of a head box, a wire section, a press section and a drying section (European Commission, 1999, p.309). A fiber suspension is introduced from the head box into a wire or a fabric on which a paper sheet is formed. In recent years, twin-wire formers have been used for web formation and become the state-of-the-art design. In a twin-wire former, a fiber suspension is led between two wires running at the same speed and drained through one or both sides. By the time the paper web has drained to around 10-20% solids on the wires, it can be supported by itself and is led away from the wires onto subsequent press and drying sections. The wire section can remove approximately 95% of the water entering the headbox along with certain proportions of fillers, fines and fibers (Hagemeyer et al., 1992, p.174).

The paper web is dried continuously through the press and drying sections. As it passes through the press section, the moisture content of the paper web can be reduced to 55-60% (European Commission, 1999, p.309-314). In some cases, it can be brought down to 50%. In the drying section, steam heated cylinders are used and the web can be dried to have a dry content of 90-95%. Water vapor in a volume of 1-1.5 $m^3$ is usually generated for every tonne of paper produced. The final paper product may contain a moisture content of 6-10%.

Paper waste generated from a paper machine is normally recycled within a mill. In most operations edges of the paper web are continually trimmed with cutting water jets and collected into a couch pit (European Commission, 1999, p.312). Whenever the web breaks which can happen a number of times a day, there is a considerable loss of paper. Similar losses occur during routine start-ups. All of this paper waste, known as broke, may be re-pulped immediately or stored and re-introduced to the process at a later date. Colored or coated broke is recycled if possible but sometimes needs to be bleached or chemically treated. The amount of broke produced during papermaking is normally 5-20% of the machine capacity and sometimes can be as high as 50%. A maximum broke reuse level is, however, recommended at 8% of the rate of a paper machine (Hagemeyer et al., 1992, p.169).

A typical broke cycle involves collection, pulping, cleaning, and mixing with stock pulp. Broke collected from a paper machine is first transported quickly to a dry end pulper and stored in a broke chest (Hagemeyer et al., 1992, p.162). It is then pulped and cleaned. For

machine production rates of 300 t/d or below, additional thickening and high-density storage are required. The cleaned broke is finally sent to mixing chests to blend with stock pulp prior to feeding to the paper machine (European Commission, 1999, p.312-314).

Various chemicals are used during both stock preparation and paper making. Chemicals added to the furnish ahead of a paper machine may include dyes, alum, size, strength building resins and texture adding filler materials, depending on the product to be manufactured (USEPA, 1995; Hagemeyer et al., 1992, p.221). Those added during the paper making include retention aids, sizes, coatings, dyes, etc. Retention aids are used to improve the fixation into the paper web of fibers, fines, fillers, etc. and therefore to minimize the loss into water (European Commission, 1999, p.312-316). Sizes such as starch are used to increase the strength of the base paper web and to modify the paper surface property.

Coatings are applied to one or both sides of the paper to improve gloss, color, printability, and brilliance (European Commission, 1999). They can be complex mixtures of ingredients and usually require preparation before use. The coating color preparation is often carried out in a coating kitchen where coating chemicals are mixed and adjusted. In general, lighter coatings are applied on-machine, while heavy coatings are performed off-machine (USEPA, 1995, p.36).

There are two methods for paper dyeing: stock dyeing and surface dyeing (European Commission, 1999, p.317). In stock dyeing, dyes, pigments, and optical brighteners are added to the pulper, or to the mixing chest or the stock flow. In surface dyeing, dyes are added to the size press liquor.

Water is recycled within the process through three circuits: 1) primary; 2) secondary; and 3) tertiary. In the primary circuit or short circulation, the water collected from the sheet-forming zone of a paper machine, commonly known as white water I, contains fibers, fines and fillers, and is recycled to the entrance of the paper machine for stock dilution (European Commission, 1999, p.312; Hagemeyer et al., 1992, p.174). The amount of suspended solids (fillers, fines and fibers) removed is dependent upon the grades of paper produced and the paper machine design. White water I originates from both pulp suspension and showers or sprays used by the paper machine to prevent solids buildup on fast moving wires, felts or rollers. Vacuum systems in the paper machine can also consume substantial amounts of water. The primary circuit is maintained as closed as possible.

In the secondary circuit (long circulation), excess water from the sheet-forming section of the paper machine, commonly known as white water II, is collected along with suction and press water and sent to a clarification system (European Commission, 1999, p.313). The clarification system, often called save-alls, may be a sedimentation or flotation plant or a drum or disc filter. The clarified water is recycled to the stock preparation section and the recovered fiber is returned to stock chests. The concentration of suspended solids

(fines and fillers) in the clear filtrate from a disc filter is usually 10-150 mg/L. A flotation plant can have an efficiency of close to 100% and reduce the suspended solids concentration to 10-50 mg/L. The advantage of the flotation is that small-size colloidal matter can be removed and especially useful for recovered paper mills. A sedimentation plant is suitable for the clarification of filler-loaded process water.

In the tertiary circuit, excess water from the clarification section and the wastewater from the paper machine are collected and treated in a wastewater treatment plant (European Commission, 1999, p.314). Upon primary and secondary (biological) treatment, part of the effluent can be sent to the raw water treatment section for reuse, while the rest is discharged.

## 6.2 – Operation Data

Overall operation data for non-integrated paper mills is presented in Table 6.1. The data is based on the largest non-integrated paper mill in the European Union which produced 1.02 million tonnes of fine paper in 1997 (European Commission, 1999, p.324). Consumption or generation rates of feed, chemicals, water, wastewater and solid waste are provided on a basis of unit production and wastewater pollutant loads refer to measurements made at a discharge point after biological treatment.

**Table 6.1 – Overall Operation Data for Non-integrated Paper Mills**
(European Commission, 1999, p.324)

| Classification | Material Type | Consumption or Generation |
|---|---|---|
| Feed | Chemical bleached pulp (5% moisture) | 610.0 kg/t |
| Chemicals | Fillers ($CaCO_3$) (73% dry solids) | 209.3 kg/t |
| | Coating pigments | 210.2 kg/t |
| | Starch | 40.3 kg/t |
| | Binders | 29.3 kg/t |
| | Sizing agents (20% dry solids) | 6.4 kg/t |
| | Other additives and dyes | 15.4 kg/t |
| Water | Raw water | 6 $m^3$/t |
| | Water vapor loss | 1.5 $m^3$/t |
| Wastewater | Discharge | 4.5 $m^3$/t |
| | BOD | 0.11 kg/t (24 mg/L) |
| | COD | 0.44 kg/t (97 mg/L) |
| | TSS | 0.14 kg/t (30 mg/L) |
| | AOX | 0.0007 kg/t (0.15 mg/L) |
| | Inorganic nitrogen | 0.041 kg/t (9.2 mg/L) |
| | Total phosphorus | 0.003 kg/t (0.8 mg/L) |
| Solid Waste | Sludge | 12.7 kg/t (100% dry solids) |
| | Others | 5.1 kg/t |

Steam is primarily used for paper drying. At a paper mill, about three-quarters of process steam is used in the dryer section of a paper machine (Kiiskinen and Edelmann, 2002). Other steam-consuming areas include the steam box on the press section, ventilation, and heating of the process water, web, and rolls in supercalenders. For 100% cylinder drying, the energy consumption is 3.6 GJ per tonne of paper.

Boilers are used for steam production. They can be package units and field erected units (H. A. Simons, 1995, p.8-5). Package boilers are generally limited to maximum pressures of 200-300 psig. Shipping size limitations impose a maximum of approximately 140 GJ/h in fuel heat input which represents about 36 t/h steam. Field erected boilers are designed for larger steam generation rates. Their capacities range from 100 to about 950 GJ/h in fuel heat input and from 35 t/h up to about 300 t/h for steam generation.

Paper mills consume between 10-25 $m^3$ of water per ton of paper, depending on the quality of paper produced and the degree of closure of the mill white water system (Hagemeyer et al., 1992, p.173). This constitutes about 20-30% of the total mill water consumption in an integrated pulp and paper mill. The white water system in a paper mill is an integral part of stock preparation.

## 6.3 – Chemical Data

Papermaking involves a range of chemistry phenomena that affect both paper quality and paper machine runnability (Thorp et al., 1991, p.141). Chemicals that are lost to effluent or retained inefficiently will result in increased operating costs. This is particularly true for more expensive materials like titanium dioxide. Common papermaking chemistry phenomena include

- Fines solids retention
- Paper machine drainage
- Fiber flocculation (sheet formation)
- Sizing agent retention and sizing development
- Wet strength agent retention
- Dry strength agent retention
- Dye retention
- Deposit formation and deposit control
- Foaming, foam prevention, and foam control
- Microbiological slime control

Types of chemicals used in papermaking are summarized in Table 6.2. Starch is the most commonly used sizing agent. When released to wastewater, it is a major source of BOD and COD (European Commission, 1999, p.312). The total spectrum of starch applications in the paper industry includes wet end addition for filler and fines retention, paper dry strength improvement, surface sizing, pigment coating, and converting adhesive functions (Hagemeyer et al., 1992, p.126). A typical coating formulation contains binders, starch for added stiffness, stearates (Ca and $NH_4$) to provide lubrication during the application, pigments, brighteners and other specialty chemicals. Major types of dyes are basic, direct, and acid. Carbon black is also used in paper dyeing. Pigments can be either inorganic or organic (e.g., azo and phthalocyanine types).

Use levels and loss rates of chemicals for papermaking are provided in Table 6.3 (European Commission, 1996, p.701). Although it is far from complete, the data gathered

indicates that the loss to wastewater varies with type of chemicals used, ranging from 10% for retention aids to 100% for anti-foaming agents. Use levels and loss rates are critical data for determining chemical releases from a mill.

**Table 6.2 – Chemicals Used in Papermaking**

(European Commission, 1999, p.324; Hagemeyer et al., 1992, p.43)

| Category | Type | Example |
|---|---|---|
| Sizes | Rosin-based sizes | tall oil rosin, wood rosin, gum rosin |
| | Wax-based sizes | |
| | Cellulose-reactive sizes | |
| Wet strength resins | Water-soluble polymers | urea-formaldehyde (U-F), melamine-formaldehyde (M-F), polyamide-epichlorohydrin (PAE), dialdehyde starch (DAS), polyamine-epichlorophydrin (polyamine), polyacrylamide-glyoxal (PAMG), quaternary ammonium epoxide (base-reactivated amine polymer-epichlorohydrin) |
| | Water-dispersible latexes | polyethylenimine (PEI), chitosan, carboxymethylcellulose (CMC) |
| Dry strength resins | Natural polymer-based derivatives | starch derivatives |
| | Synthetic polymers | co-polymers of acrylamide and cationic monomers such as diallyl dimethyl chloride, co-polymers of acrylamide and an anionic monomer such as potassium acrylate |
| Dyes | Basic dyes | chlorides, hydrochlorides, sulfates and oxalates of color bases |
| | Acid dyes | sodium, potassium or ammonium salts of color acids |
| | Direct dyes | salts of dye acids |
| | Colored pigments | clay, titanium dioxide, alumina hydrate, calcium carbonate |
| Fluorescent whites | Inorganic salts | alum |
| Retention aids (flocculation aids) | Inorganic salts | alum |
| | Organic polyelectrolytes | starch |
| Drainage aids | | alum, cationic guar, cationic starch |
| | Synthetic polyelectrolytes | polyamide/amines (PAA), polyacrylamide copolymers (PAM), polyethyleneimines (PEI) |
| Formation aids | Natural water-soluble polymers | mannogalactan gums (guar), deacetylated karaya gums, carboxymethyl cellulose, hibiscus root, okra pod |
| | Synthetic water-soluble polymers | polyethylene oxide, polyvinyl alcohol, polyacrylamide, polyacrylamide-acrylic acid copolymer |
| Fillers | | kaolin clay, calcined clay, calcium carbonate, titanium dioxide, talc, plastic pigments, alumina trihydrate, calcium sulfoaluminates, amorphous silica, silicate |
| Pitch control agents | | alum, talc |
| Others | | detergents, emulsifiers, defoamers, deposit control agents |

Predominant types of sizes used are: 1) rosin-based; 2) wax-based; and 3) cellulose-reactive materials (Hagemeyer et al., 1992, p.43). Tall oil rosin, wood rosin, and gum

rosin are the three main classes of rosin-based sizes. Commercial rosin sizes used consist of two distinctly different groups: highly neutralized rosin soaps and acidic rosin particle suspensions. For best sizing results, the pH of a treated pulp slurry must be reduced by alum to 4.0-4.5. The amount of fortified rosin soap sizes required is in the range of 5-15 lb/t, depending on the type of paper product and the degree of water repellency desired.

The amount of a wet-strength resin used is dependent upon on specifications of paper to be produced and the effectiveness of the resin (Hagemeyer et al., 1992, p.80). When a resin is used for wet strength per se (not as a size promoter, Yankee drier release agent, etc.), its use level is usually in the range of 0.1-1% based on dry pulp. A wet strength agent may be added at the headbox of a paper machine, but it is usually preferable to be added upstream. Added residence time allows the resin to be more completely retained on the pulp. Addition at the fan pump is frequently used because added residence time is combined with good mixing.

**Table 6.3 – Use Levels and Loss Rates of Chemicals for Papermaking**
(European Commission, 1996, p.701)

| **Chemicals** | **Use Level** | | | | **Loss to Wastewater** |
|---|---|---|---|---|---|
| | Newsprint | Board | Printing & Writing Paper | Tissue | |
| Anti-foaming | 0.2 mg/L | 0.03% | 0.003% | 0.003% | 100% |
| Charge control | 0.02-0.1% | no data | no data | no data | 10-30% |
| Retention aid | 0.1-0.5% | 0.1-0.5% | no data | no data | 10-30% |
| Retention aid and wet strength resin | no data | 2-3% | no data | 0.2-1.25% | 10-30% |
| Biocide | 5-40 mg/L | 5-40 mg/L | 5-40 mg/L | 5-40 mg/L | no data |
| Softening agents | no data | no data | no data | 0.2-0.3% | 25-40% |
| Size (e.g., alum/rosin) | 0.4-1.0% | 0.4-1.0% | no data | no data | 70-90% alum alone, 30% with rosin |
| AKD | no data | no data | 0.05-0.3% | no data | spillages & intermittent washout |
| Binding agents, e.g., starch, CMC | 0.5-1.5% | 0.5-1.5% | no data | no data | no data |
| Surface coating, e.g., wax | 0.1-0.8% | 8-15 g/side | no data | no data | spillages & intermittent washout |

Dry strength agents are divided into two groups: 1) natural polymer-based derivatives; and 2) synthetic polymers (Hagemeyer et al., 1992, p.87-94; Thorp et al., 1991, p.164; Buckman, www.buckman.com). Commercial materials that have been utilized as natural dry strength agents include natural gums and natural and derived starches. These materials provide enhanced interfiber bonding and also increase the bonded area between fibers. Starch is the most common raw material for natural dry strength agents and cationic starch is the most widely employed starch derivative. Typical addition rates for starch derivatives are 0.2-2.0% based on dry paper.

Fluorescent whites are used in paper production for printing and writing grades as well as tissue paper (European Commission, 1996, p.699). Normal usage is 0.02-0.3%, although a maximum value of 1.2% has been reported.

Use of fixatives can increase the fixation rate of dyes greatly and, therefore reduce loss to wastewater. As shown in Table 6.4, the fixation rate of anionic direct dyes used for making printing and writing grades can be improved from a low of 79% to a high of up to 98% with fixatives (European commission, 1996, p.699). Similar improvement is also found for other types of dyes. Dye concentration applied to paper can range from 0.005% for very pale shades up to 10% for very dark shades and blacks. Typical concentration would, however, be in a range of 0.01 to 1.0%.

**Table 6.4 – Fixation Rates of Different Dyes**
(European Commission, 1996, p.700)

| Type of Dyes | Substrate | Fixation without Fixatives | Fixation with Fixatives |
|---|---|---|---|
| Anionic direct | Bleached & unbleached pulp | 79-90% | up to 98% |
| Cationic direct | All types | 90-99% | no data |
| Basic | Bleached pulp | 50-70% | no data |
| | Mechanical pulp | 60-80% | up to 95% |
| Acid | Sized packaging paper | 40-60% | 80-90% |

## 6.4 – Wastewater

The quantity of wastewater generated from non-integrated paper mills varies with the water usage of paper machines and the degree of water closure (European Commission, 1996, p.700). The degree of water closure is not defined in the reference, but according to the data provided by Hagemeyer et al. (1992, p.177) it is speculated to be the percentage of fresh water saved through water recycle with respect to water consumption under the condition of no water recycle. Although the degree of water closure does not affect the concentration of a substance in wastewater, it dictates the volume of wastewater discharged and therefore the total amount of a substance released. Estimates of water consumption for production of different paper grades are given in Table 6.5 and indicate that a higher degree of closure results in lower water consumption.

**Table 6.5 – Estimates of Water Consumption for Paper Production**
(European Commission, 1996, p.702)

| Type of Paper | Water Consumption ($m^3/t$) | Degree of Closure |
|---|---|---|
| Printing and writing | 40-75 | 40-70% |
| Tissue | 57 | 40-70% |
| Newsprint | 24-35 | 65-85% |
| Packaging and board | 2-20 | >95% |

Fresh water is required in many steps of the papermaking process and the consumption rate for each step is different. Provided below are occasions which require fresh water along with typical consumption data (European Commission, 1999, p.326).

- As cleaning water, commonly known as shower water, for paper machines. It

lubricates and cleans forming fabrics and wet press felts to maintain satisfactory dewatering performance. The consumption rate is 5-20 $m^3$ per tonne of pulp.

- As sealing water in stuffing boxes, suction boxes, vacuum systems and cleaners. The consumption rate is 1-6 $m^3$ per tonne of pulp.
- As a solvent and dispersant for fillers and additives. The consumption rate is 1.5-3 $m^3$ per tonne of pulp.
- As make-up water in stock preparation for certain paper grades.
- As cooling water for process equipment. It is often recirculated and not included in water consumption. The use level is 3-10 $m^3$ per tonne of pulp.
- As process water for power plants. It is normally not included in water consumption. The use level is 2-3 $m^3$ per tonne of pulp.

Demand for fresh water is very limited in stock preparation (European Commission, 1999, p.327). Fresh water is usually not required for dilution of incoming fiber raw materials. It is limited to dilution of chemicals and to sealing water for some process equipment. Most chemicals must be diluted with fresh water before being added to the process.

The amount of wastewater generated has been found to vary in a wide range from a survey of 24 paper mills in Finland (Braunschweiler, 2001; Sirkka, 2001). The average daily production of these mills was 1,144 tonnes of paper per mill or 413 tonnes per paper machine. The average rate of wastewater generation was 759 $m^3$/h or 15.9 $m^3$/t based on a 365 day/yr operation. The amount of wastewater generated, however, varied from 531 $m^3$/h for paper board production to 820 $m^3$/h for soft tissue and newsprint and further to 861 $m^3$/h for fine paper. In one scenario, a mill produced 540 tonnes of paper a day and generated 800 $m^3$/d of wastewater. In another scenario, a mill generated a much higher volume of wastewater at 8,470 $m^3$/d and the wastewater from the short circulation accounted for 60% of the total.

## 6.5 – Solid Waste

Sludge is the major type of solid waste for non-integrated paper mills. It is generated from wastewater treatment and water treatment (European Commission, 1999, p.340). Wastewater treatment includes primary clarification, chemical flocculation and biological degradation. Sludge from the primary clarification consists mainly of fibers, fines and inorganic materials like fillers. The chemical flocculation results in a considerable amount of sludge which varies from mill to mill, depending upon the dosage and type of flocculants used. The sludge generated from the biological treatment contains a high content of organic materials and the quantity from aerobic systems can be seven times of that from anaerobic systems. The sludge from the water treatment becomes significant when surface water used by mills requires special treatment such as chemical precipitation and flocculation.

## 6.6 – Air Emissions

Paper machines are a source of emissions of volatile organic hazardous air pollutants (HAPs) and volatile organic compounds (VOCs). A field test study of 13 full-scale paper machines located at 11 mills in the U.S. found HAP and VOC emissions at 0.15 lb and 0.44 per ton of air-dried pulp, respectively (NCPI, 1997, No.740). Methanol was the major component of the HAP emissions at 0.071 lb per ton of air-dried pulp, followed by acetaldehyde, biphenyl, phenol, and chloroform. Factors such as furnish and product type did not show significant influence on the HAP emissions.

## 6.7 – Release Estimation Methods

Release estimation methods for environmental risk assessments of new and existing substances in the European Union are provided in the European Union Technical Guidance Document (TGD). The methods estimate the release of a substance to the environment over the substance's lifecycle (Brooke et al., 2000, p.1). Details can be found in Section 5.7 – Release Estimation Methods for recovered paper mills.

Wastewater is the principal route for the release of chemicals to the environment. For example, more than 85% of reprographic agents is released to wastewater, whereas only 0.17% to soil and 0.05% to the atmosphere in the papermaking process (Brooke et al., 2000, p.44).

The aqueous release of a chemical substance from the papermaking process can be determined by the equation (European Commission, 1996, p.702):

$$E_{aq} = G_{chem} Q_{paper} (1 - F_{fix})(1 - C_{water})$$

where

| | |
|---|---|
| $C_{water}$: | degree of water system closure, % |
| $E_{aq}$: | aqueous release of a chemical substance, kg/d |
| $F_{fix}$: | degree of substance fixation, % |
| $G_{chem}$: | use of a substance in papermaking, kg/t of paper |
| $Q_{paper}$: | paper production, t/d |

# 7 – Chemical Releases

## 7.1 – Data Gathering Method

The data required for release estimation was gathered from various sources. It was first compiled according to our industrial experience and literature information and then confirmed or revised through a survey of pulp and paper mills and chemical suppliers. For this purpose, the data on chemical use level and fraction retained by products was compiled for three processes (kraft pulp mills, non-integrated paper mills, and recovered paper mills). It was then sent to 9 mills and 7 chemical suppliers for confirmation or revision. Although the response to the survey is low with only one facility returning the questionnaire, the data gathered is sufficiently adequate for preliminary release estimation. The data used as the basis for the estimation can be found in Appendix D and the questionnaire used in the survey in Appendix E.

Site visits were planned during the initial stage of this project. For this purpose, a more extensive questionnaire had been prepared, as compiled in Appendix F. This questionnaire was designed to gather mill-specific data through interviews with mill personnel and walk-through observations at mills. The data to be gathered includes production, process scheme, chemical usage, and chemical containers. Due to insufficient resources at mills, the data gathering effort through site visits was not pursued.

## 7.2 – Release Estimating Method

Chemical releases from pulp and paper mills are estimated on a per tonne of pulp basis. The equation used for the estimation is given as

$$R_{release} = L_{use}(1 - C_{water})F_{release} \times 1000\ kg / tonne$$

where

$R_{release}$: release rate for a type of chemicals, kg/tonne of pulp
$L_{use}$: use level, % on pulp
$C_{water}$: water content, %
$F_{release}$: release fraction, %

The above equation includes three parameters. The first one is use level which is obtained from various sources including mill survey, industry experts and literature. The second parameter is water content which is either based on survey data or assumed to be zero in case of no data. The third parameter is release fraction which is primarily based on fractions retained by products reported for the European Union (European Commissions, 1996 and 1999). When no data is available, the release fraction for a type of chemicals is assumed to be 100%.

Chemical releases are estimated for worst-case scenarios. For this purpose, chemicals are assumed not to change in chemistry when passing through various process areas and to be

all released to water. Considering the fact that use level, water content and release fraction are often provided with lower and higher bounds, release estimates are normally presented within a range.

Data on use level for a type of chemicals must be converted to mass percentage on pulp when it is provided on a different basis. The conversion is made through the equation

$$L_{use} = F_{conv} D_{use}$$

where

$L_{use}$: use level expressed in terms of % on pulp
$F_{conv}$: conversion factor from a different basis to % on pulp
$D_{use}$: use level based on a quantity different from % on pulp

Conversion factors for various units of use level are summarized in Tables 7.1, 7.2, and 7.3 for kraft pulp mills, non-integrated paper mills and recovered paper mills (deinking plants), respectively. They are derived based on normal process conditions, as compiled in Appendices G, H, and I. In estimating releases, data on use level obtained from various sources is first converted to mass percentage on pulp and then used in release estimation. It is obvious that the conversion factor becomes unity if use level is based on % on pulp.

## Table 7.1 – Conversion Factors for Chemical Use Level at Kraft Pulp Mills

| Process Area | Type of Chemicals | Units to be converted from ($D_{use}$) | Units to be converted to ($L_{use}$) | Conversion Factor ($F_{conv}$) |
|---|---|---|---|---|
| Digestion | boilouts | no data | % on pulp | no data |
| | scale control | ppm on liquor | % on pulp | $8.89\times10^{-4}$ |
| Brownstock Washing & Chemical Recovery | boilouts | % on volume treated | % on pulp | no data |
| | clarification aids | ppm on liquor | % on pulp | $8.7\times10^{-4}$ |
| | scale control | ppm on liquor | % on pulp | $4.18\times10^{-4}$ |
| | lime mud dewatering aids | lb/t on lime | % on pulp | 0.0162 |
| | tall oil separation & acidulation aids | ppm on volume | % on pulp | $2.56\times10^{-6}$ |
| | turpentine separation aids | ppm on volume | % on pulp | $7.78\times10^{-7}$ |
| Bleaching | bleaching enzymes | mL on pulp | % on pulp | $1.0\times10^{-4}$ |
| | boilouts | % on volume treated | % on pulp | no data |
| | scale control | ppm on volume | % on pulp | $1.0\times10^{-3}$ |
| Pulp Machine | microbiological control | ppm on chest volume | % on pulp | no data |
| | felt conditioning | ppm on shower water | % on pulp | $1.5\times10^{-3}$ |
| | boilouts | % on volume treated | % on pulp | no data |
| | retention aids | ppm on volume | % on pulp | 0.02 |
| Recovery & Power Boilers | air pollution control | ppm on scrubber liquid | % on pulp | $3.42\times10^{-3}$ |
| | condensate treatment | ppm on steam | % on pulp | $6.5\times10^{-4}$ |
| | boiler water treatment | | | |
| | scale control | | | |
| | corrosion inhibitors | | | |
| Water Treatment | corrosion inhibitors | ppm on water | % on pulp | $6.0\times10^{-3}$ |
| | microbiological control | | | |
| | scale control | | | |
| | settling aids | | | |
| Wastewater Treatment | settling aids | ppm on wastewater | % on pulp | $6.0\times10^{-3}$ |
| | foam control | | | |
| | nutrients | | | |
| | sludge conditioners | | | |
| | odor control | | | |
| | color control | | | |

## Table 7.2 – Conversion Factors for Chemical Use Level at Paper Mills

| Process Area | Type of Chemicals | Units to be converted from ($D_{use}$) | Units to be converted to ($L_{use}$) | Conversion Factor ($F_{conv}$) |
|---|---|---|---|---|
| Stock preparation (pulpers & broke system) | boilouts/cleaners | % on volume treated | % on pulp | no data |
| | retention/drainage aids | ppm on volume | % on pulp | 0.02 |
| | charge control | | | |
| | microbiological control | ppm on chest volume | % on pulp | no data |
| Paper machine | boilouts | % on volume treated | % on pulp | no data |
| | felt cleaning | ppm on shower water | % on pulp | no data |
| | antiskid agents | lb/t on paper | % on pulp | 0.05 |
| | microbiological control | ppm on chest volume | % on pulp | no data |
| | saveall polymers | ppm on volume | % on pulp | 0.0158 |
| Coating | microbiological control | ppm on chest volume | % on pulp | no data |
| | boilouts | % on volume treated | % on pulp | no data |
| Recovery & Power Boilers | air pollution control | ppm on scrubber liquid | % on pulp | $2.7\times10^{-5}$ |
| | condensate treatment | ppm on steam | % on pulp | $1.54\times10^{-4}$ |
| | boiler water treatment | | | |
| | scale control | | | |
| | corrosion inhibitors | | | |
| Water Treatment | corrosion inhibitors | ppm on water | % on pulp | $6.0\times10^{-3}$ |
| | microbiological control | | | |
| | scale control | | | |
| | settling aids | | | |
| Wastewater Treatment | settling aids | ppm on wastewater | % on pulp | $6.0\times10^{-3}$ |
| | foam control | | | |
| | nutrients | | | |
| | sludge conditioners | | | |
| | odor control | | | |
| | color control | | | |

## Table 7.3 – Conversion Factors for Chemical Use Level at Recovered Paper Mills

| Process Area | Type of Chemicals | Units to be converted from ($D_{use}$) | Units to be converted to ($L_{use}$) | Conversion Factor ($F_{conv}$) |
|---|---|---|---|---|
| Deinking | boilouts | % on volume treated | % on pulp | no data |
| | settling aids | ppm on volume | % on pulp | 0.02 |
| Paper Making | retention/drainage aids | ppm on volume | % on pulp | 0.0198 |
| | barrier chemistry | no data | % on pulp | no data |
| | charge neutralization | ppm on volume | % on pulp | 0.02 |
| | antiskid agents | lb/ton on paper | % on pulp | 0.05 |
| | felt cleaning chemicals | ppm on shower water | % on pulp | no data |
| | boilouts/cleaners | % on volume treated | % on pulp | no data |
| | microbiological control | ppm on chest volume | % on pulp | no data |
| | chelants | % on peroxide | % on pulp | 0.02 |
| Recovery & Power Boilers | air pollution control | ppm on scrubber liquid | % on pulp | $2.7\times10^{-5}$ |
| | condensate treatment | ppm on steam | % on pulp | $1.54\times10^{-4}$ |
| | boiler water treatment | | | |
| | scale control | | | |
| | corrosion inhibitors | | | |
| Water Treatment | corrosion inhibitors | ppm on water | % on pulp | $2.0\times10^{-3}$ |
| | microbiological control | | | |
| | scale control | | | |
| | settling aids | | | |
| Wastewater Treatment | settling aids | ppm on wastewater | % on pulp | $2.0\times10^{-3}$ |
| | foam control | | | |
| | nutrients | | | |
| | sludge conditioners | | | |
| | odor control | | | |
| | color control | | | |

## 7.3 – Estimates of Chemical Releases from Kraft Pulp Mills

Estimate results for chemical releases to water from kraft pulp mills are presented in Table 7.4 and Figures 7.1, 7.2 and 7.3. These releases are restricted to specialty and bleaching chemicals and were estimated to total 163-343 kg per tonne of pulp. Releases of specialty chemicals were estimated at 16-73 kg per tonne of pulp.

Chemicals used at kraft pulp mills are divided among seven process areas and classified into 3 to 11 types within each process area. The seven process areas are 1) digestion; 2) brownstock washing and chemical recovery; 3) bleaching; 4) pulp machine; 5) recovery and power boilers; 6) water treatment; and 7) wastewater treatment. Included in the estimation are 31 types of chemicals common to kraft pulp mills; one type of chemical is often found in more than one process area.

Presented in Figure 7.1 are chemical releases from the seven different process areas on a logarithmic scale. Bleaching is observed to have the highest release rate at 148-275 kg per tonne of pulp due to use of large quantities of bleaching chemicals. Chemicals released from recovery and power boilers are found to be the lowest in the range of 0.2-0.6 kg per tonne of pulp.

Chemical releases for various types of chemicals are presented in Figures 7.2 and 7.3. Figure 7.2 shows release rates over 1 kg per tonne of pulp on a logarithmic scale for 17 types of chemicals. Five bleaching chemicals (chlorine, oxygen, chlorine dioxide, peroxide and sodium hydroxide) are found among those with the highest release rates in the range of 10-80 kg per tonne of pulp. Pitch control, color control, felt conditioning, settling aids (coagulants) and hypochlorites are in the second highest release group with their highs at 10-13 kg per tonne of pulp. The rest, including odor control, retention aids (coagulants), peracetic acid, foam control, scale control, cooking aids/penetrants and washing/drainage aids, vary between 1 and 10 kg per tonne of pulp for their highs.

Figure 7.3 shows release rates under 1 kg per tonne of pulp on a logarithmic scale for 13 types of chemicals. Release rates of settling aids (flocculants), sludge conditioners, air pollution control, corrosion inhibitors, nutrients, retention aids (flocculants), lime mud dewatering aids and bleaching enzymes vary between 0.2 and 0.6 kg per tonne of pulp for their highs. With an order of magnitude less, boiler water treatment, clarification aids, condensate treatment and tall oil separation and acidulation aids are at their highs of 0.02-0.07 kg per tonne of pulp. The release rate for turpentine separation aids is the lowest at 0.001-0.004 kg per tonne of pulp because of small quantities of turpentine produced.

At time of this writing, two types of chemicals are not included in the estimation due to lack of data. These two types are 1) boilouts used in digestion, brownstock washing and chemical recovery, bleaching, and pulp machine; and 2) microbiological control used in pulp machine and water treatment.

## Table 7.4 – Estimates of Chemical Releases from Kraft Pulp Mills

| Process Area | Type of Chemicals | Water Release (kg/t) | | Use Level | | |
|---|---|---|---|---|---|---|
| | | low | high | low | high | units for use level |
| **Digestion** | cooking aids/chip penetrants | 0.25 | 1.25 | 0.025 | 0.125 | % on pulp |
| | digester boilouts | | | no data | no data | no data |
| | scale control | 0.01778 | 0.1778 | 2 | 20 | ppm on liquor |
| | ***subtotal*** | ***0.27*** | ***1.43*** | | | |
| **Brownstock Washing & Chemical Recovery** | foam control | 0.25 | 1.25 | 0.025 | 0.125 | % on pulp |
| | washing/drainage aids | 0.25 | 1.25 | 0.025 | 0.125 | % on pulp |
| | pitch control | 0.042 | 4.2 | 0.042 | 0.42 | % on pulp |
| | boilouts | | | 1 | 8 | % on volume treated |
| | clarification aids | 0.00087 | 0.0435 | 0.5 | 5 | ppm on liquor |
| | scale control | 0.00836 | 0.0836 | 2 | 20 | ppm on liquor |
| | lime mud dewatering aids | 0.081 | 0.243 | 0.5 | 1.5 | lb/ton on lime |
| | tall oil separation & acidulation aids | 0.01024 | 0.01536 | 400 | 600 | ppm on volume |
| | turpentine separation aids | 0.000778 | 0.00389 | 100 | 500 | ppm on volume |
| | ***subtotal*** | ***0.64*** | ***7.09*** | | | |
| **Bleaching** | chlorine (Cl2) | 60 | 80 | 6 | 8 | % on pulp |
| | hypochlorite (Ca(OCl)2 or NaOCl) | 10 | 10 | 1 | 1 | % on pulp |
| | chlorine dioxide (ClO2) | 20 | 40 | 2 | 4 | % on pulp |
| | sodium hydroxide (NaOH) | 10 | 40 | 1 | 4 | % on pulp |
| | oxygen (O2) | 22.5 | 55 | 2.25 | 5.5 | % on pulp |
| | hydrogen or sodium peroxide | 20 | 40 | 2 | 4 | % on pulp |
| | peracetic acid | 5 | 5 | 0.5 | 0.5 | % on pulp |
| | bleaching enzymes | 0.1 | 0.2 | 100 | 200 | mL/tonne on pulp |
| | boilouts | | | 1 | 8 | % on volume treated |
| | pitch control | 0.042 | 4.2 | 0.042 | 0.42 | % on pulp |
| | scale control | 0.02 | 0.2 | 2 | 20 | ppm on volume |
| | ***subtotal*** | ***147.66*** | ***274.60*** | | | |
| **Pulp Machine** | microbiological control | | | 1 | 50 | ppm on chest volume |
| | pitch control | 0.042 | 4.2 | 0.042 | 0.42 | % on pulp |
| | foam control | 0.025 | 2 | 0.025 | 0.2 | % on pulp |
| | felt conditioning | 0.75 | 12 | 200 | 800 | ppm on shower water |
| | boilouts | | | 1 | 8 | % on volume treated |
| | retention aids (coagulants) | 0.1 | 6 | 5 | 100 | ppm on volume |
| | retention aids (flocculants) | 0.0004 | 0.3 | 0.1 | 5 | ppm on volume |
| | ***subtotal*** | ***0.92*** | ***24.50*** | | | |
| **Recovery & Power Boilers** | air pollution control | 0.171 | 0.342 | 5 | 10 | ppm on scrubber liquid |
| | condensate treatment | 0.013 | 0.026 | 2 | 4 | ppm on steam |
| | boiler water treatment | 0.00325 | 0.065 | 0.5 | 10 | ppm on steam |
| | scale control | 0.013 | 0.13 | 2 | 20 | ppm on steam |
| | corrosion inhibitors | 0.0065 | 0.0325 | 1 | 5 | ppm on steam |
| | ***subtotal*** | ***0.21*** | ***0.60*** | | | |
| **Water Treatment** | corrosion inhibitors | 0.006 | 0.3 | 0.1 | 5 | ppm on water |
| | microbiological control | | | no data | no data | ppm on water |
| | scale control | 0.12 | 1.2 | 2 | 20 | ppm on water |
| | settling aids (coagulants, alum, PAC) | 0.3 | 6 | 5 | 100 | ppm on water |
| | settling aids (flocculants) | 0.0012 | 0.3 | 0.1 | 5 | ppm on water |
| | ***subtotal*** | ***0.43*** | ***7.80*** | | | |
| **Wastewater Treatment** | settling aids (coagulants) | 0.9 | 6 | 15 | 100 | ppm on wastewater |
| | settling aids (flocculants) | 0.0012 | 0.3 | 0.1 | 5 | ppm on wastewater |
| | foam control | 0.012 | 1.5 | 2 | 25 | ppm on wastewater |
| | nutrients | 0.12 | 0.3 | 2 | 5 | ppm on wastewater |
| | sludge conditioners (flocculants) | 0.006 | 0.6 | 0.1 | 10 | ppm on wastewater |
| | odour control | 0.3 | 6 | 5 | 100 | ppm on wastewater |
| | colour control (coagulants) | 12 | 12 | 200 | 200 | ppm on wastewater |
| | ***subtotal*** | ***13.34*** | ***26.70*** | | | |
| | **Total** | **163.46** | **342.71** | | | |

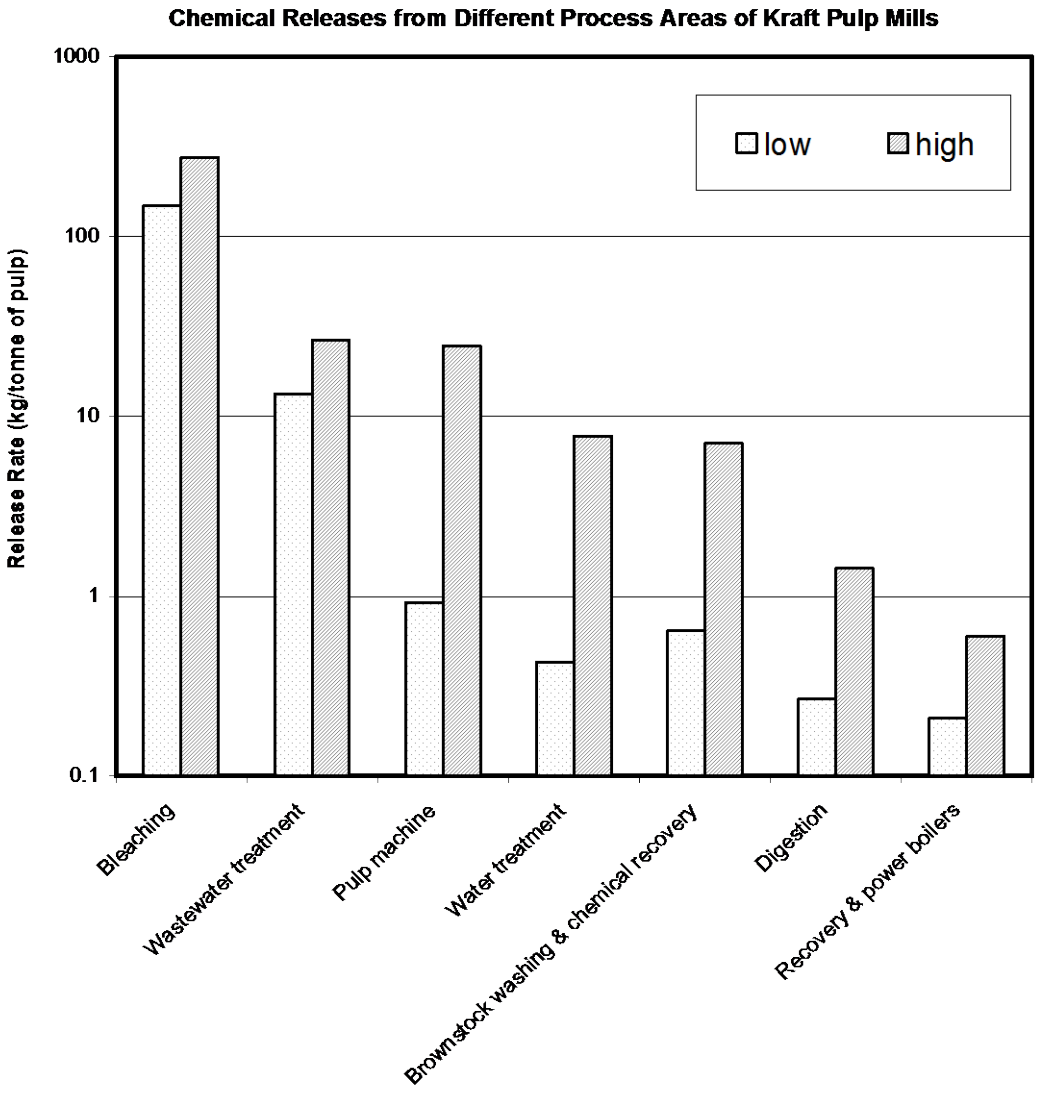


**Figure 7.1 – Chemical Releases from Different Process Areas of Kraft Pulp Mills**

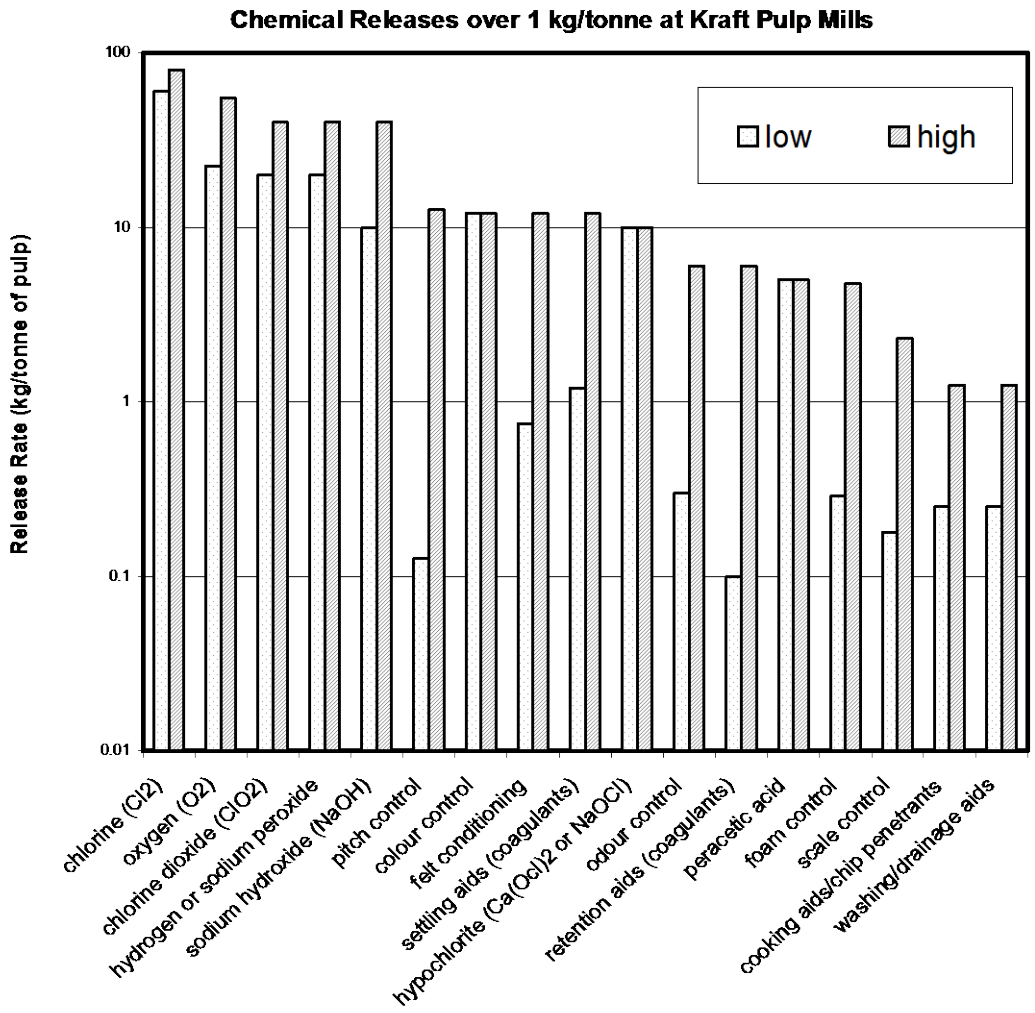


**Figure 7.2 – Major Chemical Releases at Kraft Pulp Mills**

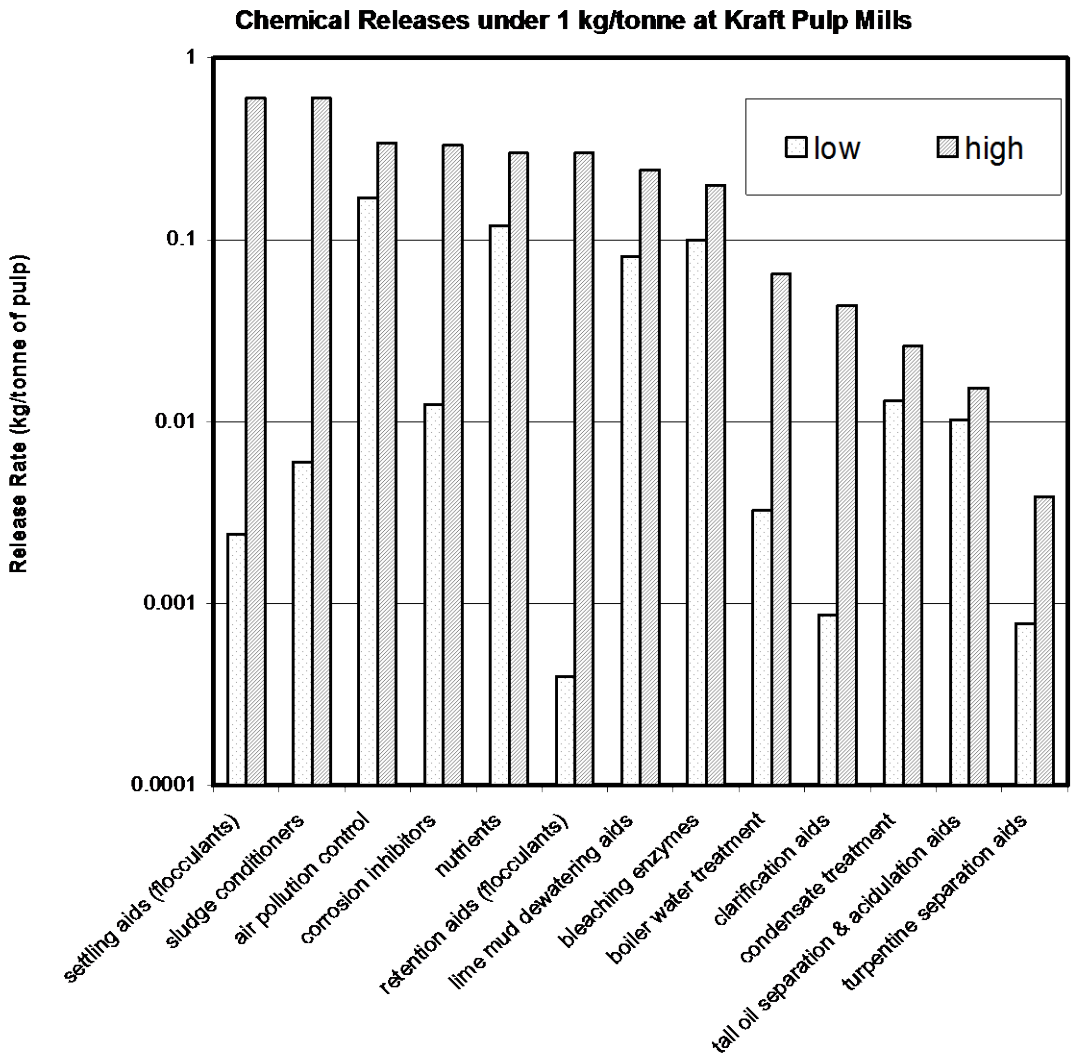


**Figure 7.3 – Minor Chemical Releases at Kraft Pulp Mills**

## 7.4 – Estimates of Chemical Releases from Non-integrated Paper Mills

Estimate results for chemical releases to water from non-integrated paper mills are presented in Table 7.5 and Figures 7.4, 7.5 and 7.6. These releases are restricted to specialty chemicals and were estimated to total between 60 to 184 kg per tonne of pulp.

Chemicals used at non-integrated paper mills are divided among six process areas and classified into 5 to 15 types within each process area. The six process areas are 1) stock preparation (pulpers and broke systems); 2) paper machine; 3) coating; 4) recovery and power boilers; 5) water treatment; and 6) wastewater treatment. Included in the estimation are 32 types of chemicals common to paper mills and one type of chemicals is often found in more than one process area.

Presented in Figure 7.5 are chemical releases from the six different process areas on a logarithmic scale. Stock preparation and paper machine are observed to have the highest release rate up to 50-58 kg per tonne of pulp. Releases from recovery and power boilers are found to be the lowest in the range of 0.01 to 0.1 kg per tonne of pulp.

Chemical releases for various types of chemicals are presented in Figures 7.5 and 7.6. Figure 7.5 shows release rates over 5 kg per tonne of pulp on a logarithmic scale for 14 types of chemicals. Release estimates for sizes, fillers, latex, pitch/stickies control, saveall polymers (coagulants), settling aids (coagulants), and color control (coagulants) vary between 12 and 24 kg per tonne of pulp for their highs, while those for odor control, dry strength agents, wet strength agents, retention/drainage aids (coagulants), charge control, dyes/dye fixatives/fluorescent white, and corrosion inhibitors are in the range of 5-9 kg per tonne of pulp.

Figure 7.6 shows release rates under 5 kg per tonne of pulp on a logarithmic scale for 12 types of chemicals. Release rates for the majority of these chemicals are in the range of 0.2-4 kg per tonne of pulp at highs, including foam control, scale control, formation aids, emulsifiers, saveall polymers (flocculants), antiskid agents, retention/drainage aids (flocculants), settling aids (flocculants), sludge conditioning, nutrients, and chelants. Boiler water treatment, condensate treatment, and air pollution control are found to have the lowest release rates at 0.001-0.02 kg per tonne of pulp.

At time of this writing, four types of chemicals are not included in the estimation due to lack of data. These four types are 1) boilouts used in stock preparation, paper machine and coating; 2) cleaners used in paper machine; 3) felt cleaning used in paper machine; 4) scale control used in stock preparation; and 5) microbiological control used in stock preparation, paper machine, coating and water treatment.

# Table 7.5 – Estimates of Chemical Releases from Paper Mills

| Process Area | Type of Chemicals | Water Release (kg/t) | | Use Level | | |
|---|---|---|---|---|---|---|
| | | low | high | low | high | units for use level |
| **Stock Preparation (pulpers & broke system)** | sizes | 0.0175 | 9 | 0.05 | 1 | % on pulp |
| | wet strength agents | 0.25 | 6 | 0.25 | 2 | % on pulp |
| | dry strength agents | 0.5 | 7.5 | 0.05 | 0.75 | % on pulp |
| | dyes/dye fixatives/fluorescent whites | 0.005 | 5.5 | 0.01 | 1 | % on pulp |
| | pitch/stickies control | 0.1 | 5 | 0.1 | 0.5 | % on pulp |
| | boilouts/cleaners | | | 1 | 8 | % on volume treated |
| | retention/drainage aids (coagulants) | 0.1 | 6 | 5 | 100 | ppm on volume |
| | retention/drainage aids (flocculants) | 0.0004 | 0.3 | 0.1 | 5 | ppm on pulp |
| | charge control | 0.1 | 6 | 5 | 100 | ppm on volume |
| | fillers (PCC, GCC, clay, TiO2, etc.) | 10.5 | 10.5 | 21 | 21 | % on pulp |
| | chelants | 0.08 | 0.16 | 0.4 | 0.8 | % on peroxide |
| | microbiological control | | | 1 | 50 | ppm on chest volume |
| | emulsifiers | 0.5 | 2 | 0.05 | 0.2 | % on pulp |
| | foam control | 0.0125 | 0.5 | 0.0125 | 0.05 | % on pulp |
| | scale control | | | no data | no data | no data |
| | ***subtotal*** | ***12.17*** | ***58.46*** | | | |
| **Paper Machine** | pitch/stickies control | 0.125 | 12.5 | 0.125 | 1.25 | % on pulp |
| | boilouts | | | 1 | 8 | % on volume treated |
| | corrosion inhibitors | 0.5 | 5 | 0.05 | 0.5 | % on pulp |
| | antiskid agents | 0.375 | 0.75 | 0.75 | 1.5 | lb/ton on paper |
| | cleaners | | | | | no data |
| | felt cleaning | | | 200 | 800 | ppm on shower water |
| | microbiological control | | | 1 | 50 | ppm on chest volume |
| | saveall polymers (coagulants) | 0.79 | 15.8 | 5 | 100 | ppm on volume |
| | saveall polymers (flocculants) | 0.00316 | 0.79 | 0.1 | 5 | ppm on volume |
| | foam control | 0.025 | 1.6 | 0.025 | 0.2 | % on pulp |
| | surface size | 0.5 | 10 | 0.05 | 1 | % on pulp |
| | retention aids | 0.005 | 0.3 | 0.025 | 0.1 | % on pulp |
| | formation aids | 2 | 3 | 0.2 | 0.3 | % on pulp |
| | ***subtotal*** | ***4.32*** | ***49.74*** | | | |
| **Coating** | latex | 20 | 20 | 2 | 2 | % on pulp |
| | fillers (PCC, GCC, TiO2, clay, talc) | 10.5 | 10.5 | 21 | 21 | % on pulp |
| | microbiological control | | | 1 | 50 | ppm on chest volume |
| | startch/size | 0.05 | 5 | 0.05 | 1 | % on pulp |
| | foam control | 0.0125 | 0.5 | 0.0125 | 0.05 | % on pulp |
| | boilouts | | | 1 | 8 | % on volume treated |
| | ***subtotal*** | ***30.56*** | ***36.00*** | | | |
| **Recovery and Power Boilers** | air pollution control | 0.00135 | 0.0027 | 5 | 10 | ppm on scrubber liquid |
| | condensate treatment | 0.00308 | 0.00616 | 2 | 4 | ppm on steam |
| | boiler water treatment | 0.00077 | 0.0154 | 0.5 | 10 | ppm on steam |
| | scale control | 0.0077 | 0.077 | 5 | 50 | ppm on steam |
| | corrosion inhibitors | 0.00154 | 0.0077 | 1 | 5 | ppm on steam |
| | ***subtotal*** | ***0.01*** | ***0.11*** | | | |
| **Water Treatment** | corrosion inhibitors | 0.006 | 0.3 | 0.1 | 5 | ppm on water |
| | microbiological control | | | no data | no data | ppm on water |
| | scale control | 0.3 | 3 | 5 | 50 | ppm on water |
| | settling aids (coagulants) | 0.3 | 6 | 5 | 100 | ppm on water |
| | settling aids (flocculants) | 0.0012 | 0.3 | 0.1 | 5 | ppm on water |
| | ***subtotal*** | ***0.61*** | ***9.60*** | | | |
| **Wastewater Treatment** | settling aids (coagulants) | 0.3 | 6 | 5 | 100 | ppm on wastewater |
| | settling aids (flocculants) | 0.0012 | 0.3 | 0.1 | 5 | ppm on wastewater |
| | foam control | 0.012 | 1.5 | 2 | 25 | ppm on wastewater |
| | nutrients | 0.06 | 0.3 | 1 | 5 | ppm on wastewater |
| | sludge conditioners (flocculants) | 0.006 | 0.6 | 0.1 | 10 | ppm on wastewater |
| | odour control | 0.3 | 9 | 5 | 150 | ppm on wastewater |
| | colour control (coagulants) | 12 | 12 | 200 | 200 | ppm on wastewater |
| | ***subtotal*** | ***12.68*** | ***29.70*** | | | |
| | **Total** | **60.35** | **183.61** | | | |

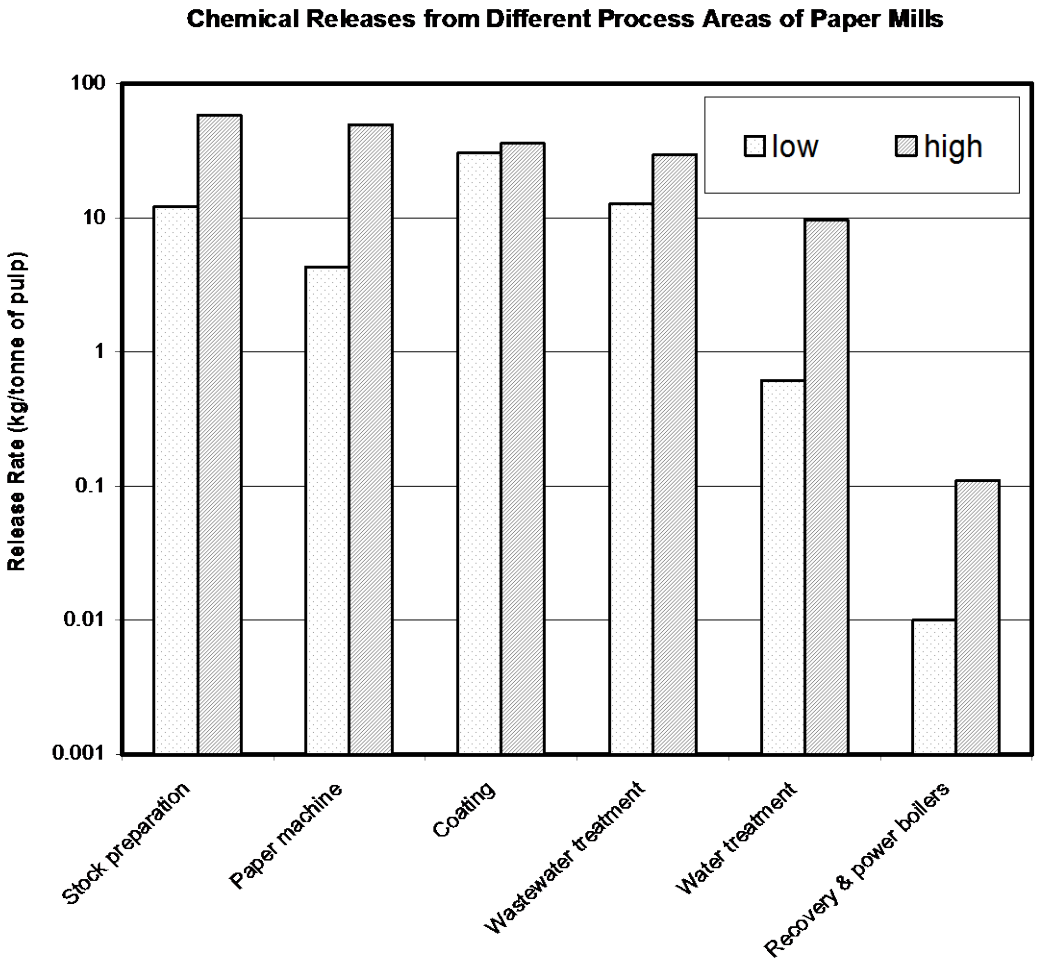


**Figure 7.4 – Chemical Releases from Different Process Areas of Paper Mills**

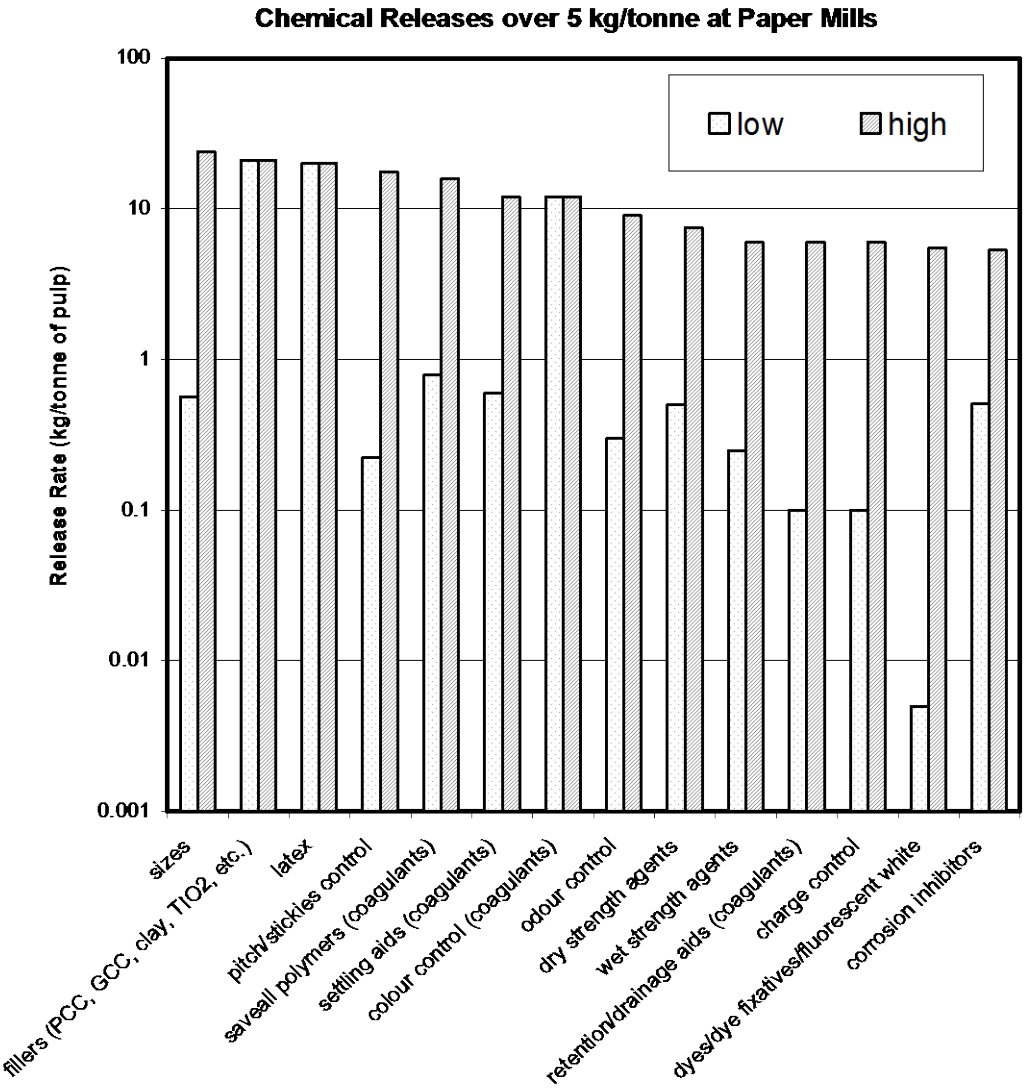


**Figure 7.5 – Major Chemical Releases at Paper Mills**

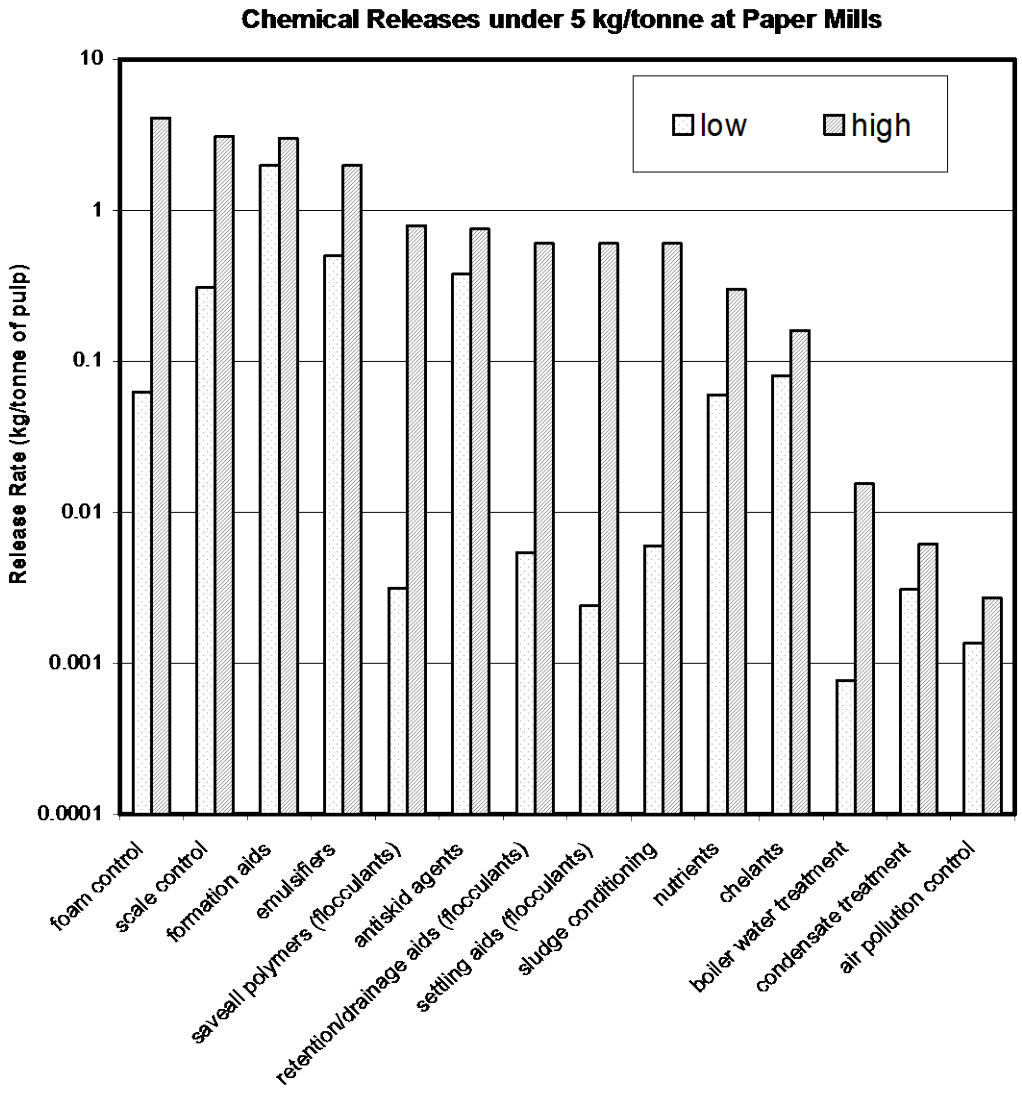


**Figure 7.6 – Minor Chemical Releases at Paper Mills**

## 7.5 – Estimates of Chemical Releases from Recovered Paper Mills

Estimate results for chemical releases to water from recovered paper mills (deinking plants) are presented in Table 7.6 and Figures 7.7, 7.8 and 7.9. These releases are restricted to specialty and bleaching chemicals and were estimated to total between 142 to 404 kg per tonne of pulp.

Chemicals used at recovered paper mills are divided among seven process areas and classified into 3 to 21 types within each process area. The seven process areas are 1) pulping; 2) deinking; 3) bleaching; 4) paper making; 5) recovery and power boilers; 6) water treatment; and 7) wastewater treatment. Included in the estimation are 40 types of chemicals common to recovered paper mills and one type of chemicals is often found in more than one process area.

Presented in Figure 7.7 are chemical releases from the seven different process areas on a logarithmic scale. Bleaching and paper making are observed to have the highest release rate up to 95-170 kg per tonne of pulp. Recovery and power boilers are at the lowest in the range of 0.01 to 0.1 kg per tonne of pulp.

Releases for various types of chemicals are presented in Figures 7.8 and 7.9. Figure 7.8 shows release rates over 10 kg per tonne of pulp on a logarithmic scale for 13 types of chemicals. Sodium silicate and sodium hydroxide are found to have the highest release rates at 50-80 kg per tonne of pulp for their highs. Soap/fatty acids, chlorine, settling aids (coagulants), chelating agents/sequestrants, surfactants/repulping aids, peroxide, and latex form the next highest group at 20-30 kg per tonne of pulp. Release rates for the rest are in the range of 10-13 kg per tonne of pulp, including pitch/stickies control, fillers, deinking aids, and hydrosulfites.

Figure 7.9 shows release rates under 10 kg per tonne of pulp on a logarithmic scale for 23 types of chemicals. Release rates for the majority of these chemicals vary between 1 and 10 kg per tonne of pulp at highs, including sizes, dry strength agents, wet strength agents, dyes/dye fixatives/fluorescent whites, charge neutralization, retention/drainage aids (coagulants), corrosion inhibitors, dispersing agents, color control, formation aids, odor control, emulsifiers, settling aids (flocculants), scale contro, and foam control. Estimates for antiskid agents, sludge conditioners, retention/drainage aids (flocculants), and nutrients are 0.1-0.8 kg per tonne of pulp at their highs. Boiler water treatment, condensate treatment and air pollution control are found to be at the lowest rates in the range of 0.0008 and 0.015 kg per tonne of pulp.

At time of this writing, four types of chemicals are not included in the estimation due to lack of data. These four types are 1) boilouts used in deinking and paper making; 2) felt cleaning chemicals used in paper making; 3) barrier chemistry used in paper making; and 4) microbiological control used in paper making and water treatment.

# Table 7.6 – Estimates of Chemical Releases from Recovered Paper Mills

| Process Area | Type of Chemicals | Water Release (kg/t) | | Use Level | | |
|---|---|---|---|---|---|---|
| | | low | high | low | high | units for use level |
| **Pulping** | surfactants/repulping aids | 2 | 20 | 0.2 | 2 | % on pulp |
| | sodium silicate | 20 | 40 | 2 | 4 | % on pulp |
| | dispersing agents | 1 | 5 | 0.1 | 0.5 | % on pulp |
| | ***subtotal*** | ***23.00*** | ***65.00*** | | | |
| **Deinking** | deinking aids | 1 | 10 | 0.1 | 1 | % on pulp |
| | soap/fatty acids | 5 | 30 | 0.5 | 3 | % on pulp |
| | boilouts | | | 1 | 8 | % on volume treated |
| | settling aids (coagulants) | 1 | 20 | 5 | 100 | ppm on volume |
| | settling aids (flocculants) | 0.02 | 1 | 0.1 | 5 | ppm on volume |
| | ***subtotal*** | ***7.02*** | ***61.00*** | | | |
| **Bleaching** | peroxide (H2O2 or Na2O2) | 10 | 20 | 1 | 2 | % on pulp |
| | sodium hydroxide | 30 | 50 | 3 | 5 | % on pulp |
| | sodium silicate | 20 | 40 | 2 | 4 | % on pulp |
| | chelating agents/sequestrants | 1 | 20 | 0.1 | 2 | % on pulp |
| | hydrosulfites | 5 | 10 | 0.5 | 1 | % on pulp |
| | chlorine | 5 | 30 | 0.5 | 3 | % on pulp |
| | ***subtotal*** | ***71.00*** | ***170.00*** | | | |
| **Paper Making** | sizes | 0.35 | 9 | 0.05 | 1 | % on pulp |
| | wet strength agents | 0.25 | 6 | 0.25 | 2 | % on pulp |
| | dry strength agents | 0.05 | 7.5 | 0.005 | 0.75 | % on pulp |
| | dyes/dye fixatives/fluorescent whites | 0.005 | 6 | 0.01 | 1 | % on pulp |
| | corrosion inhibitors | 0.5 | 5 | 0.05 | 0.5 | % on pulp |
| | retention/drainage aids (coagulants) | 0.099 | 5.94 | 5 | 100 | ppm on volume |
| | retention/drainage aids (flocculants) | 0.00198 | 0.297 | 0.1 | 5 | ppm on volume |
| | retention/drainage aids (micro-particles) | 0.0099 | 0.1188 | 0.5 | 2 | ppm on volume |
| | barrier chemistry | | | no data | no data | ppm on volume |
| | formation aids | 2 | 3 | 0.2 | 0.3 | % on pulp |
| | charge neutralization | 0.1 | 6 | 5 | 100 | ppm on volume |
| | chelants | 0.08 | 0.16 | 0.4 | 0.8 | % on peroxide |
| | antiskid agents | 0.375 | 0.75 | 0.75 | 1.5 | lb/ton on paper |
| | emulsifiers | 0.5 | 2 | 0.05 | 0.2 | % on pulp |
| | foam control | 0.125 | 0.5 | 0.0125 | 0.05 | % on pulp |
| | pitch/stickies control | 1.25 | 12.5 | 0.125 | 1.25 | % on pulp |
| | felt cleaning chemicals | | | 200 | 800 | ppm on shower water |
| | boilouts/cleaners | | | 1 | 8 | % on volume treated |
| | microbiological control | | | 1 | 50 | ppm on chest volume |
| | latex | 20 | 20 | 2 | 2 | % on pulp |
| | fillers (PCC, GCC, TiO2) | 10.5 | 10.5 | 21 | 21 | % on pulp |
| | ***subtotal*** | ***36.20*** | ***95.27*** | | | |
| **Recovery and Power Boilers** | air pollution control | 0.00135 | 0.0027 | 5 | 10 | ppm on scrubber liquid |
| | condensate treatment | 0.00308 | 0.00616 | 2 | 4 | ppm on steam |
| | boiler water treatment | 0.00077 | 0.0154 | 0.5 | 10 | ppm on steam |
| | scale control | 0.0077 | 0.077 | 5 | 50 | ppm on steam |
| | corrosion inhibitors | 0.00154 | 0.0077 | 1 | 5 | ppm on steam |
| | ***subtotal*** | ***0.01*** | ***0.11*** | | | |
| **Water Treatment** | corrosion inhibitors | 0.002 | 0.1 | 0.1 | 5 | ppm on water |
| | microbiological control | | | no data | no data | ppm on water |
| | scale control | 0.1 | 1 | 5 | 50 | ppm on water |
| | settling aids (coagulants) | 0.1 | 2 | 5 | 100 | ppm on water |
| | settling aids (flocculants) | 0.002 | 0.1 | 0.1 | 5 | ppm on water |
| | ***subtotal*** | ***0.20*** | ***3.20*** | | | |
| **Wastewater Treatment** | settling aids (coagulants) | 0.1 | 2 | 5 | 100 | ppm on wastewater |
| | settling aids (flocculants) | 0.002 | 0.1 | 0.1 | 5 | ppm on wastewater |
| | foam control | 0.04 | 0.5 | 2 | 25 | ppm on wastewater |
| | nutrients | 0.04 | 0.1 | 2 | 5 | ppm on wastewater |
| | sludge conditioners (flocculants) | 0.002 | 0.2 | 0.1 | 10 | ppm on wastewater |
| | odour control | 0.1 | 3 | 5 | 150 | ppm on wastewater |
| | colour control (coagulants) | 4 | 4 | 200 | 200 | ppm on wastewater |
| | ***subtotal*** | ***4.28*** | ***9.90*** | | | |
| | **Total** | **141.72** | **404.47** | | | |

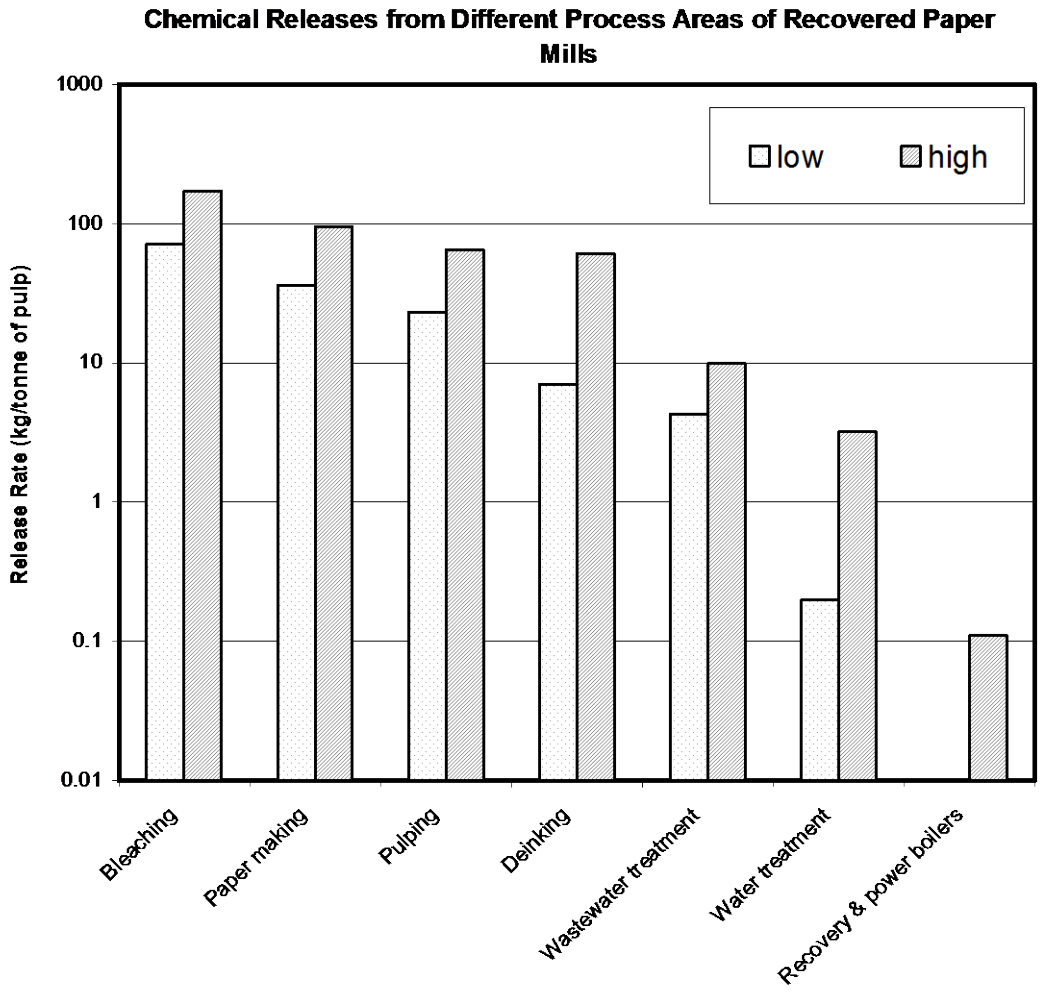


**Figure 7.7 – Chemical Releases from Different Process Areas of Recovered Paper Mills**

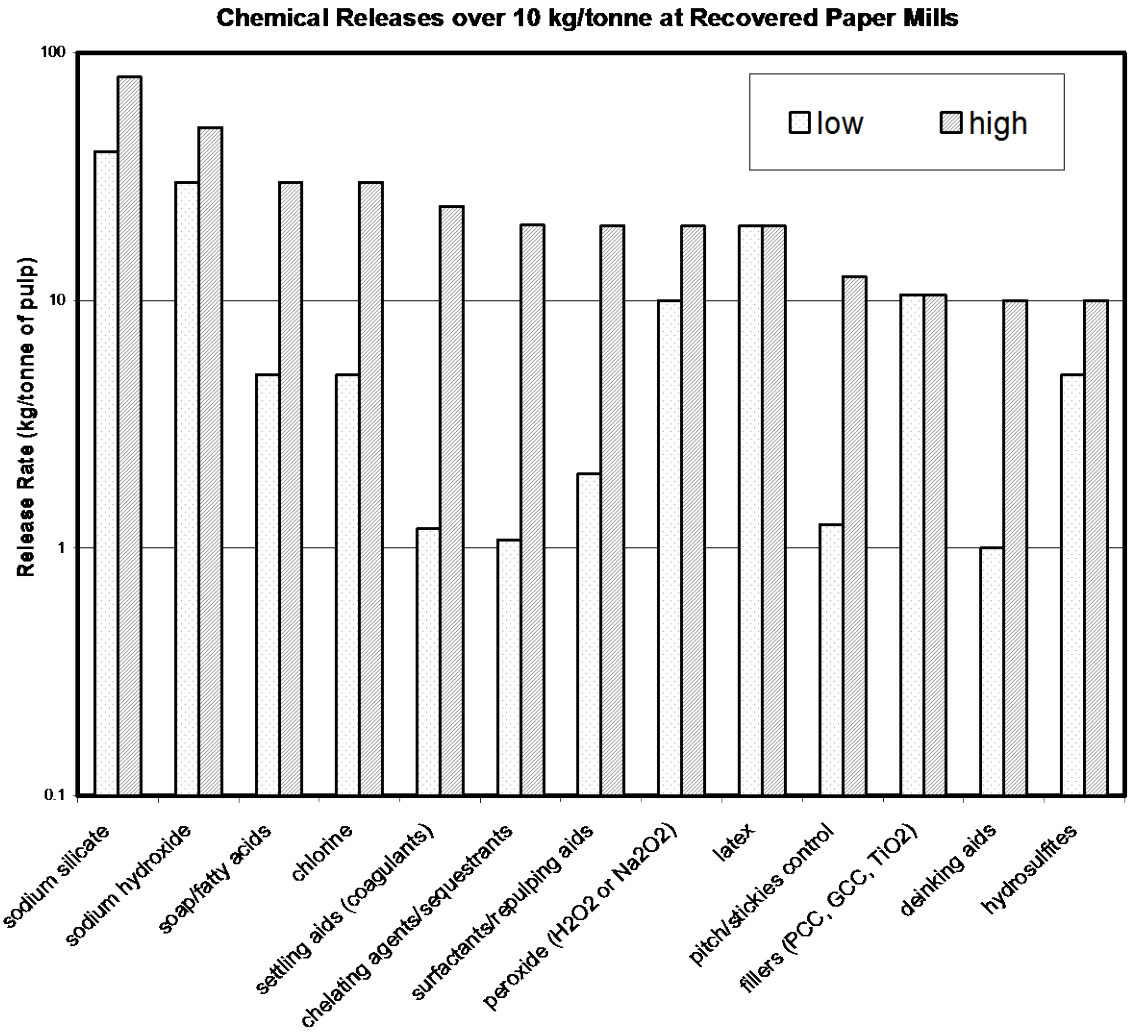


**Figure 7.8 – Major Chemical Releases at Recovered Paper Mills**

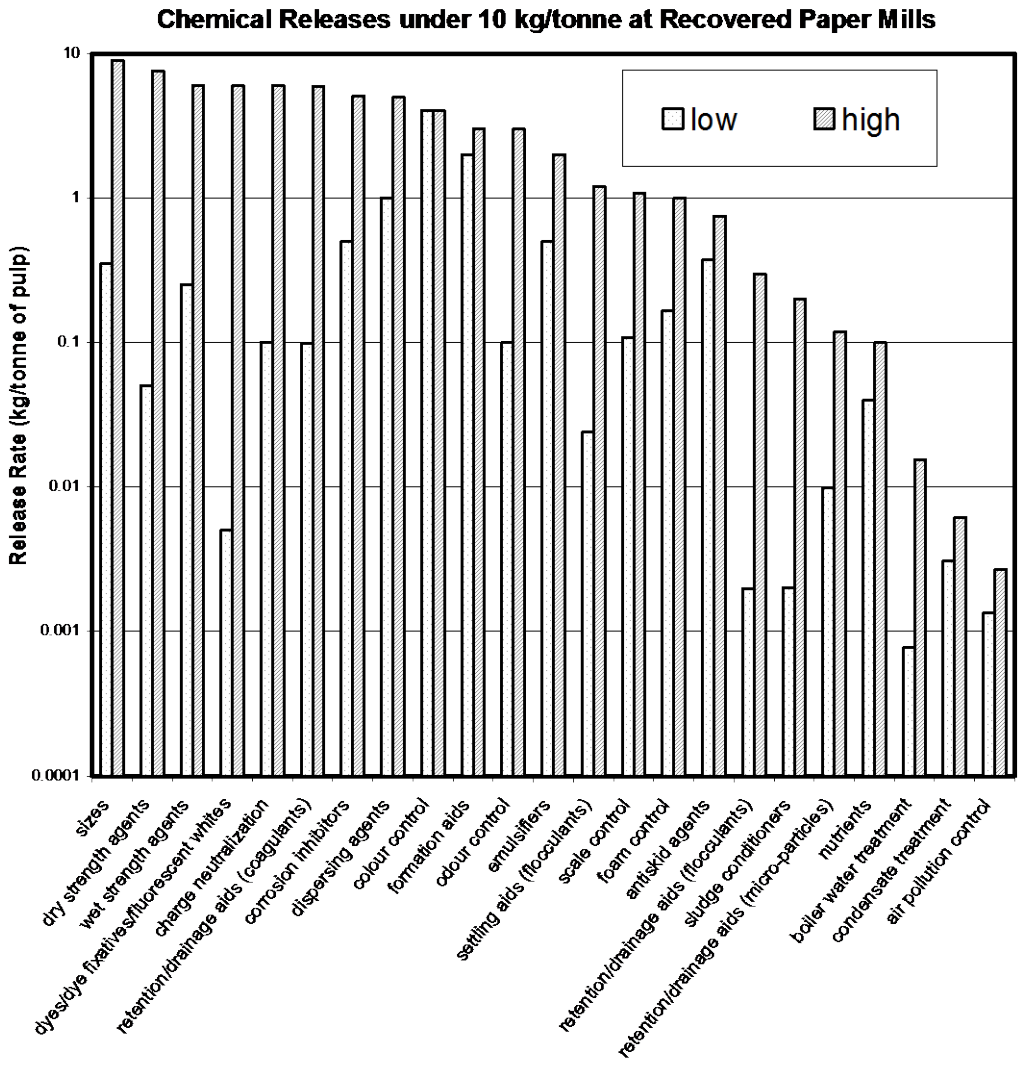


**Figure 7.9 – Minor Chemical Releases at Recovered Paper Mills**

## 7.6 – Consolidated Consumption and Release Estimates

Presented in Tables 7.7, 7.8 and 7.9 are consumption and release estimates for kraft pulp mills, non-integrated paper mills, and recovered paper mills, respectively. These estimates provide water-free quantities of bleaching and specialty chemicals consumed during the pulp or paper production and subsequent amounts released to wastewater. The estimation is based on use level, water content, and fraction retained by product. When no specific data is available, the water content and the fraction retained by product are each assumed to be zero and the results represent the most conservative estimates.

The consumption and release estimates are consolidated in Table 7.10. Recovered paper mills are found to have the highest release rate at 142-404 kg per tonne of pulp, while non-integrated paper mills have the lowest at 60-184 kg/tonne. Since the amounts of chemicals retained by the pulp are low, the release from kraft pulp mills can be as high as 96-99% of chemicals used. On average, the three types of mills consume 325-547 kg of chemicals per tonne of pulp and release 122-310 kg/tonne or 38-57% of chemicals used to wastewater.

## Table 7.7 – Consumption and Release Estimates for Kraft Pulp Mills

| Chemical Class | Consumption (kg/t) | | Water Release (kg/t) | | Water Release (%) | |
|---|---|---|---|---|---|---|
| | low | high | low | high | low | high |
| chlorine (Cl2) | 60 | 80 | 60 | 80 | 100.00 | 100.00 |
| oxygen (O2) | 22.5 | 55 | 22.5 | 55 | 100.00 | 100.00 |
| chlorine dioxide (ClO2) | 20 | 40 | 20 | 40 | 100.00 | 100.00 |
| hydrogen or sodium peroxide | 20 | 40 | 20 | 40 | 100.00 | 100.00 |
| sodium hydroxide (NaOH) | 10 | 40 | 10 | 40 | 100.00 | 100.00 |
| pitch control | 0.126 | 12.6 | 0.126 | 12.6 | 100.00 | 100.00 |
| color control (coagulants) | 12 | 12 | 12 | 12 | 100.00 | 100.00 |
| felt conditioners | 0.75 | 12 | 0.75 | 12 | 100.00 | 100.00 |
| settling aids (coagulants) | 1.2 | 12 | 1.2 | 12 | 100.00 | 100.00 |
| hypochlorite (Ca(OCl)2 or NaOCl) | 10 | 10 | 10 | 10 | 100.00 | 100.00 |
| retention aids (coagulants) | 1 | 20 | 0.1 | 6 | 10.00 | 30.00 |
| odor control | 0.3 | 6 | 0.3 | 6 | 100.00 | 100.00 |
| peracetic acid | 5 | 5 | 5 | 5 | 100.00 | 100.00 |
| foam control | 0.287 | 4.75 | 0.287 | 4.75 | 100.00 | 100.00 |
| scale control | 0.17914 | 1.7914 | 0.17914 | 1.7914 | 100.00 | 100.00 |
| cooking aids/chip penetrants | 0.25 | 1.25 | 0.25 | 1.25 | 100.00 | 100.00 |
| washing/drainage aids | 0.25 | 1.25 | 0.25 | 1.25 | 100.00 | 100.00 |
| settling aids (flocculants) | 0.0024 | 0.6 | 0.0024 | 0.6 | 100.00 | 100.00 |
| sludge conditioners (flocculants) | 0.006 | 0.6 | 0.006 | 0.6 | 100.00 | 100.00 |
| air pollution control | 0.171 | 0.342 | 0.171 | 0.342 | 100.00 | 100.00 |
| corrosion inhibitors | 0.0125 | 0.3325 | 0.0125 | 0.3325 | 100.00 | 100.00 |
| retention aids (flocculants) | 0.004 | 1 | 0.0004 | 0.3 | 10.00 | 30.00 |
| nutrients | 0.12 | 0.3 | 0.12 | 0.3 | 100.00 | 100.00 |
| lime mud dewatering aids | 0.081 | 0.243 | 0.081 | 0.243 | 100.00 | 100.00 |
| bleaching enzymes | 0.1 | 0.2 | 0.1 | 0.2 | 100.00 | 100.00 |
| boiler water treatment | 0.00325 | 0.065 | 0.00325 | 0.065 | 100.00 | 100.00 |
| clarification aids | 0.00087 | 0.0435 | 0.00087 | 0.0435 | 100.00 | 100.00 |
| condensate treatment | 0.013 | 0.026 | 0.013 | 0.026 | 100.00 | 100.00 |
| tall oil separation & acidulation aids | 0.01024 | 0.01536 | 0.01024 | 0.01536 | 100.00 | 100.00 |
| turpentine separation aids | 0.000778 | 0.00389 | 0.000778 | 0.00389 | 100.00 | 100.00 |
| boilouts | 0 | 0 | 0 | 0 | | |
| microbiological control | 0 | 0 | 0 | 0 | | |
| **Total** | **164.37** | **357.41** | **163.46** | **342.71** | **95.89** | **99.45** |

## Table 7.8 – Consumption and Release Estimates for Non-integrated Paper Mills

| **Chemical Class** | **Consumption (kg/t)** | | **Water Release (kg/t)** | | **Water Release (%)** | |
|---|---|---|---|---|---|---|
| | low | high | low | high | low | high |
| sizes | 0.575 | 25 | 0.5675 | 24 | 96.00 | 98.70 |
| fillers (PCC, GCC, clay, TiO2, etc.) | 420 | 420 | 21 | 21 | 5.00 | 5.00 |
| latex | 20 | 20 | 20 | 20 | 100.00 | 100.00 |
| pitch/stickies control | 0.225 | 17.5 | 0.225 | 17.5 | 100.00 | 100.00 |
| saveall polymers (coagulants) | 0.79 | 15.8 | 0.79 | 15.8 | 100.00 | 100.00 |
| color control (coagulants) | 12 | 12 | 12 | 12 | 100.00 | 100.00 |
| settling aids (coagulants) | 0.6 | 12 | 0.6 | 12 | 100.00 | 100.00 |
| odor control | 0.3 | 9 | 0.3 | 9 | 100.00 | 100.00 |
| dry strength agents | 0.5 | 7.5 | 0.5 | 7.5 | 100.00 | 100.00 |
| retention/drainage aids (coagulants) | 1.05 | 21 | 0.105 | 6.3 | 10.00 | 30.00 |
| charge control | 1 | 20 | 0.1 | 6 | 10.00 | 30.00 |
| wet strength agents | 2.5 | 20 | 0.25 | 6 | 10.00 | 30.00 |
| dyes/dye fixatives/fluorescent whites | 0.1 | 10 | 0.005 | 5.5 | 5.00 | 55.00 |
| corrosion inhibitors | 0.50754 | 5.3077 | 0.50754 | 5.3077 | 100.00 | 100.00 |
| foam control | 0.062 | 4.1 | 0.062 | 4.1 | 100.00 | 100.00 |
| scale control | 0.3077 | 3.077 | 0.3077 | 3.077 | 100.00 | 100.00 |
| formation aids | 2 | 3 | 2 | 3 | 100.00 | 100.00 |
| emulsifiers | 0.5 | 2 | 0.5 | 2 | 100.00 | 100.00 |
| saveall polymers (flocculants) | 0.00316 | 0.79 | 0.00316 | 0.79 | 100.00 | 100.00 |
| antiskid agents | 0.375 | 0.75 | 0.375 | 0.75 | 100.00 | 100.00 |
| settling aids (flocculants) | 0.0024 | 0.6 | 0.0024 | 0.6 | 100.00 | 100.00 |
| sludge conditioners (flocculants) | 0.006 | 0.6 | 0.006 | 0.6 | 100.00 | 100.00 |
| retention/drainage aids (flocculants) | 0.004 | 1 | 0.0004 | 0.3 | 10.00 | 30.00 |
| nutrients | 0.06 | 0.3 | 0.06 | 0.3 | 100.00 | 100.00 |
| chelants | 0.08 | 0.16 | 0.08 | 0.16 | 100.00 | 100.00 |
| boiler water treatment | 0.00077 | 0.0154 | 0.00077 | 0.0154 | 100.00 | 100.00 |
| condensate treatment | 0.00308 | 0.00616 | 0.00308 | 0.00616 | 100.00 | 100.00 |
| air pollution control | 0.00135 | 0.0027 | 0.00135 | 0.0027 | 100.00 | 100.00 |
| felt cleaning chemicals | 0 | 0 | 0 | 0 | | |
| boilouts | 0 | 0 | 0 | 0 | | |
| cleaners | 0 | 0 | 0 | 0 | | |
| microbiological control | 0 | 0 | 0 | 0 | | |
| **Total** | **463.55** | **631.51** | **60.35** | **183.61** | **13.02** | **29.07** |

## Table 7.9 – Consumption and Release Estimates for Recovered Paper Mills

| Chemical Class | Consumption (kg/t) | | Water Release (kg/t) | | Water Release (%) | |
|---|---|---|---|---|---|---|
| | low | high | low | high | low | high |
| sodium silicate | 40 | 80 | 40 | 80 | 100.00 | 100.00 |
| sodium hydroxide | 30 | 50 | 30 | 50 | 100.00 | 100.00 |
| chlorine | 5 | 30 | 5 | 30 | 100.00 | 100.00 |
| soap/fatty acids | 5 | 30 | 5 | 30 | 100.00 | 100.00 |
| chelants | 1.08 | 20.16 | 1.08 | 20.16 | 100.00 | 100.00 |
| settling aids (coagulants) | 1.2 | 24 | 1.2 | 24 | 100.00 | 100.00 |
| hydrogen or sodium peroxide | 10 | 20 | 10 | 20 | 100.00 | 100.00 |
| latex | 20 | 20 | 20 | 20 | 100.00 | 100.00 |
| surfactants/repulping aids | 2 | 20 | 2 | 20 | 100.00 | 100.00 |
| pitch/stickies control | 1.25 | 12.5 | 1.25 | 12.5 | 100.00 | 100.00 |
| fillers (PCC, GCC, TiO2) | 210 | 210 | 10.5 | 10.5 | 5.00 | 5.00 |
| deinking aids | 1 | 10 | 1 | 10 | 100.00 | 100.00 |
| hydrosulfites | 5 | 10 | 5 | 10 | 100.00 | 100.00 |
| sizes | 0.5 | 10 | 0.35 | 9 | 70.00 | 90.00 |
| dry strength agents | 0.05 | 7.5 | 0.05 | 7.5 | 100.00 | 100.00 |
| charge neutralization | 1 | 20 | 0.1 | 6 | 10.00 | 30.00 |
| wet strength agents | 2.5 | 20 | 0.25 | 6 | 10.00 | 30.00 |
| dyes/dye fixatives/fluorescent whites | 0.1 | 10 | 0.005 | 6 | 5.00 | 60.00 |
| retention/drainage aids (coagulants) | 0.99 | 19.8 | 0.099 | 5.94 | 10.00 | 30.00 |
| corrosion inhibitors | 0.50354 | 5.1077 | 0.50354 | 5.1077 | 100.00 | 100.00 |
| dispersing agents | 1 | 5 | 1 | 5 | 100.00 | 100.00 |
| color control (coagulants) | 4 | 4 | 4 | 4 | 100.00 | 100.00 |
| formation aids | 2 | 3 | 2 | 3 | 100.00 | 100.00 |
| odor control | 0.1 | 3 | 0.1 | 3 | 100.00 | 100.00 |
| emulsifiers | 0.5 | 2 | 0.5 | 2 | 100.00 | 100.00 |
| settling aids (flocculants) | 0.024 | 1.2 | 0.024 | 1.2 | 100.00 | 100.00 |
| scale control | 0.1077 | 1.077 | 0.1077 | 1.077 | 100.00 | 100.00 |
| foam control | 0.165 | 1 | 0.165 | 1 | 100.00 | 100.00 |
| antiskid agents | 0.375 | 0.75 | 0.375 | 0.75 | 100.00 | 100.00 |
| retention/drainage aids (flocculants) | 0.0198 | 0.99 | 0.00198 | 0.297 | 10.00 | 30.00 |
| sludge conditioners (flocculants) | 0.002 | 0.2 | 0.002 | 0.2 | 100.00 | 100.00 |
| retention/drainage aids (micro-particles) | 0.099 | 0.396 | 0.0099 | 0.1188 | 10.00 | 30.00 |
| nutrients | 0.04 | 0.1 | 0.04 | 0.1 | 100.00 | 100.00 |
| boiler water treatment | 0.00077 | 0.0154 | 0.00077 | 0.0154 | 100.00 | 100.00 |
| condensate treatment | 0.00308 | 0.00616 | 0.00308 | 0.00616 | 100.00 | 100.00 |
| air pollution control | 0.00135 | 0.0027 | 0.00135 | 0.0027 | 100.00 | 100.00 |
| felt cleaning chemicals | 0 | 0 | 0 | 0 | | |
| barrier chemistry | 0 | 0 | 0 | 0 | | |
| boilouts/cleaners | 0 | 0 | 0 | 0 | | |
| microbiological control | 0 | 0 | 0 | 0 | | |
| **Total** | **345.61** | **651.80** | **141.72** | **404.47** | **41.01** | **62.05** |

## Table 7.10 – Consolidated Consumption and Release Estimates for Pulp and Paper Mills

| Mill Type | Consumption (kg/t) | Water Release (kg/t) | Water Release (%) |
|---|---|---|---|
| Kraft pulp mills | 164-357 | 163-343 | 96.1-99.4 |
| Non-integrated paper mills | 464-632 | 60-184 | 12.9-29.1 |
| Recovered paper mills | 346-652 | 142-404 | 41.0-62.0 |
| Average | 325-547 | 122-310 | 37.5-56.7 |

## 7.7 – Missing Data

Releases for several chemicals cannot be determined due to lack of data. Data gaps include both use level and process-specific parameters, as summarized in Table 7.11.

**Table 7.11 – Data Gaps Concerning Chemical Releases from Pulp and Paper Mills**

| Mill Type | Type of Chemicals | Process Area | Data Gap |
|---|---|---|---|
| Kraft Pulp Mills | boilouts | digestion | use level, volume treated, application, frequency, production rate |
| | | brownstock washing & chemical recovery | volume treated, application frequency, production rate |
| | | bleaching | volume treated, application frequency, production rate |
| | | pulp machine | volume treated, application frequency, production rate |
| | microbiological control | pulp machine | chest volume, application frequency, production rate |
| | | water treatment | use level |
| Paper Mills | boilouts | stock preparation | volume treated, application frequency, production rate |
| | | paper machine | volume treated, application frequency, production rate |
| | | coating | volume treated, application frequency, production rate |
| | cleaners | paper machine | use level |
| | felt cleaning | paper machine | use rate of shower water |
| | microbiological control | stock preparation | chest volume, application frequency, production rate |
| | | paper machine | chest volume, application frequency, production rate |
| | | coating | chest volume, application frequency, production rate |
| | | water treatment | use level |
| | scale control | stock preparation | use level |
| Recovered Paper Mills | boilouts | deinking | volume treated, application frequency, production rate |
| | | paper making | volume treated, application frequency, production rate |
| | felt cleaning chemicals | paper making | use rate of shower water |
| | microbiological control | paper machine | chest volume, application frequency, production rate |
| | | water treatment | use level |
| | barrier chemistry | paper chemistry | use level |

# 8 – Conclusions

Chemical releases from the Canadian pulp and paper industry were evaluated in support of the environmental assessment of new substances undertaken at Environment Canada. The method employed was based on release scenarios and conformed to the framework established by the European Union and the U.S. Typical release scenarios were developed for use in the evaluation of releases associated with kraft pulp mills, recovered paper mills (deinking plants), and non-integrated paper mills. While generic aspects of these scenarios were based on standard industrial operations, chemical usage data was specific to the Canadian industry and was used to provide conservative release estimates.

Chemical usage data is essential to the release estimates derived. Specialty chemicals are the primary focus because they are the most likely carriers for new substances. Chemical usage data includes three attributes: 1) use level; 2) water content; and 3) fraction retained by products. Based on the data gathered for the Canadian industry, a total of 39 classes of specialty chemicals were identified and the ranges of their releases to water were evaluated. In addition, bleaching chemicals were also included in the evaluation and reported along with the specialty chemicals.

Of the release scenarios evaluated for the Canadian industry, recovered paper mills were found to cause the largest aqueous release on a basis of unit production. The release rate for recovered paper mills was determined at 142-404 kg/tonne of pulp, while those for kraft pulp mills and non-integrated paper mills were at 163-343 kg/tonne and 60-184 kg/tonne, respectively. It should be noted that the release rates for recovered paper mills and kraft pulp mills included bleaching chemicals at 70-150 kg/tonne and 148-270 kg/tonne, respectively. Non-integrated paper mills, on the other hand, do not involve the use of bleaching chemicals.

The proportion of release with respect to consumption varied in a wide range, depending upon type of mills. Since the amounts of chemicals retained by the pulp were small, the release from kraft pulp mills could be as high as 96-99% of chemicals used. On average, the consumption of bleaching and specialty chemicals was estimated at 325-547 kg/tonne for kraft pulp mills, non-integrated mills and recovered paper mills combined, while the release prior to wastewater treatment at 122-310 kg/tonne or 38-57% of chemicals used.

Releases from different process areas were found to vary in a wide range. The highest release was found at 148-275 kg/tonne in the bleaching section of kraft pulp mills and accounted for 80-90% of the total mill release. The recovery and power boilers section of recovered paper mills or non-integrated paper mills had the lowest release at 0.01-0.1 kg/tonne and contributed less than 0.1% to the total release.

Releases of different classes of chemicals were also found to vary in a wide range. Bleaching chemicals used at kraft pulp mills were found to have the highest release at 148-270 kg/tonne. Of the specialty chemicals evaluated, the highest release was 5-30 kg/tonne for soap/fatty acids used at recovered paper mills, 0.1-13 kg/tonne for pitch

control at kraft pulp mills, and 0.6-24 kg/tonne for sizes at non-integrated paper mills. Turpentine separation aids used at kraft pulp mills gave the lowest release at 0.008-0.004 kg/tonne.

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meeting, Ottawa, February 6, 2002.

# Appendix A – Mills Selected as Candidates for Site Visit

Smurfit-Stone, medium kraft mill, hardwood, Portage-Du-Fort (near Shawville), Quebec

Donohue (St-Felicien) Inc.
PO Box 6000, 4000 Chemin St-Eusebe, St-Felicien, Quebec G8K 2R6
Product: bleached kraft pulp (320 metric tonnes per year)
Number of employees: 315
Source: Madison's Canadian Lumber Directory, 44th ed

Papiers Fraser, medium kraft mill, Thurso, Quebec

Smurfit-Stone (formerly St. Laurent Paperboard, La Tuque Division)
1000 Chemin de L'Usine, La Tuque, Quebec G9X 3P8
Product: white top linerboard, bleached kraft pulp

Domtar, integrated kraft pulp & paper mill, hardwood, Cornwall, Ontario
Domtar, integrated kraft pulp & paper mill, softwood, Windsor, Quebec
Papier Mason Ltee, large integrated thermo-mechanical pulp & newsprint mill, hardwood, Masson-Angers, Quebec
Bowater, newsprint from recovered paper with deinking and TMP, Gatineau, Quebec
Domtar-EB Eddy, fine paper mill, Ottawa & Hull
Tembec, sulphite and BTCMP, paper & board mill, Temiscaming, Quebec
Weyerhaeuser, softwood, Grande Prairie, Alberta
Alpac (Alberta-Pacific Forest Industries), hardwood, Boyle, Alberta
Daishowa-Marubeni, hardwood, Peace River, Alberta

Whitford (2002) confirmed that the above candidate mills selected for site visits are equipped with modern technology and represent the industry well.

# Appendix B – Meeting Minutes

**Minutes of January 3rd Meeting on Pulp & Paper Mill Release Scenarios**
Prepared by Jesse Shen, January 3, 2002

Meeting Agenda: - Selection of candidate pulp & paper mills for site visits
- Review of questionnaire
- Communication plan

Date: January 3, 2002
Place: Environment Canada, Place Vincent Massey, 351 St. Joseph Blvd., Hull, Quebec K1A 0H3

Attendees: Jonathan Tigner, Jean-Francois Levasseur, Robert Larocque, Andy Atkinson and David Niemi (all from Environment Canada).
Jesse Shen (consultant, Ottawa), and Joel Jossinet (consultant, Mississauga) via teleconference.

This is a kick-off meeting for a contract study of standard release scenarios for the Canadian pulp and paper industry. The study will be carried out by two consultants, Jesse Shen and Joel Jossinet, under the direction of Jonathan Tigner of Environment Canada. The goal of the study is to obtain conservative estimates of new and existing chemicals released to the environment from the pulp and paper industry. Discussed at the meeting are the following:

**Other related projects**

- 2000 inventory of 6000 Canadian companies including pulp & paper processes (David Niemi), available end of March;
- Industrial Multi-pollutant Emissions Reduction Strategy (MERS), a joint project with the CCME, focusing on air emissions, including those from pulp and paper mills (Jean-Francois Levasseur), end of March;
- NPEs survey of 160 pulp and paper mills (Robert Larocque); and
- FPAC's annual survey (if accessible), very detailed survey (20 pages in excel)

These studies will not affect the study in terms of burden on industry, and will greatly help in the provision of needed data.

**Candidate mills for site visits**

- Pates Thurso, Kraft mill, hardwood;
- Domtar Cornwall, large integrated Kraft pulp & paper mill, hardwood;
- Domtar Windsor, integrated Kraft pulp & paper mill, softwood;
- Papier Mason, large integrated thermo-mechanical pulp & paper mill, hardwood;
- Bowater Gatineau, newsprint from recovered paper with deinking, also including a sulfite process; and
- Domtar-EB Eddy Ottawa & Hull, fine paper mill.

- Tembec, Temiscaming, hardwood, paper & board mill
- Smurfit-Stone Shawville, medium Kraft mill, hardwood;
- La Tuque, softwood Kraft mill
- St.-Felicien, softwood Kraft mill.
- Alberta mills, large softwood Kraft mills

The first six may be the only ones we get into for this project, although, for completeness, we may need to gather information for some of the softwood mills and Alberta mills reflect modern large mills. Smurfit-Stone we may get into for other reasons, so it is placed 7th. The Alberta mills, indeed the total number visited, will depend upon available resources.

**Recommended additions or changes to questionnaire**

- as much data as possible to be used to complete the questionnaire before it is presented and a new version should be used for each facility.
- separate the company information page so that a company can elect to not complete it, if confidentiality is an issue.
- production data section: break wood between hardwood and softwood, use 350 days/y and 24 hrs/d for normal operations, add number of shutdown days;
- process data section: prepare a generic process diagram for each mill visited and as the mill to verify what's presented and identify major differences between mill's process and the generic one;
- mass balance data: break raw material into hardwood (debarked), softwood (debarked), pulp, and recovered paper, add water loss via evaporation (about 20-30% of water consumption in summer);
- retention, highly variable, 1-5 % make-up to some processes, high recycle, all factors
- chemical usage data section: add specialty chemicals to each process area, add type of containers used for each category of chemicals, residual loss, and cleaning method, add shipping method for bulk chemicals (train, truck, etc.), residual loss and cleaning method. Starting point will be the presentation "Pulp & Paper Chemical Applications" (not to be cited), to identify perhaps 20 chemical categories (Jonathan, Joel and Jesse to work through), and ascertain if continuous or batch (including semi-continuous, like frequent batches or periodic, like boil-outs;
- effluent discharge data section: add discharge of cooling water, add effluent pH and temperature (Quebec web site may have useful information; also may find it useful to consider pH as a classification criteria); and
- chemical handling data section: combine it into chemical usage data section.

**Communications**

- A one-page briefing note will be prepared to inform both the Forest Products Association of Canada (FPAC) and individual mills of the intention of the present study. It will be designed to clearly indicate the reason to collect data and why that will benefit the industry and its suppliers. The information will also be presented to Quebec and Ontario provincial and regional offices to gain cooperation, avoid confusion/duplication and to see if we can identify sources of data useful for the

completion of the questionnaire. FPAC will host meeting the end of January that could serve as a forum to announce our intentions and interests. That affects our schedule such that contacting plants will be delayed until February.

- A briefing note will be prepared describing the project for EC, which will be circulated up our respective organizational lines.

**Actions to be taken:**

- Jonathan Tigner: prepare the briefing notes and circulate for comments. Once ready, Bob will contact FPAC to let them know what's coming, followed by a call and then the note from Jonathan. The EC briefing note will be circulated as soon as ready.
- Contact mills around February 11, 2002, in order to pursue site visit by March.
- Jesse Shen: revise the questionnaire using input from Jonathan and Joel, and complete it as much as possible using existing data.
- Joel, Jean-Francois, Bob and David: review the revised questionnaire and data entered, and make suggestions for changes.
- Site visits…

**Minutes of February 6th Meeting on Pulp & Paper Mill Emission Scenarios**

Prepared by Jesse Shen, February 7, 2002

Agenda: - Review of project scope
- Identification of existing data and data to be collected from mills
- Further action

Date: February 6, 2002

Place: Environment Canada, Place Vincent Massey, 351 St. Joseph Blvd., Hull, Quebec K1A 0H3

Attendees: Environment Canada (EC) – Jonathan Tigner, Andy Atkinson, Jean-Francois Levasseur, Robert Larocque, and Marie-Louise Geadah
Consultants to EC – Jesse Shen, and Joel Jossinet (via conference call)
Forest Products Association Canada (FPAC) – Lucie Veilleux, and Tim Whitford (via conference call)

This is a 2nd meeting for a study of standard release scenarios for the Canadian pulp and paper industry. Jonathan coordinated the meeting and gave a brief review of the project scope. The objective of the study is to evaluate releases of substances used by the industry and the outcome of the study will be a release scenario document similar to those published by European Union and USEPA. In a broad sense, release scenario studies are important to exposure assessment and can help EC better understand and serve the industry.

Lucie expressed a concern over the timeline initially scheduled for the study, and the group acknowledged that additional time will be needed, especially for industry input. The industry is currently preoccupied with work on DSL categorization and NPRI

reporting, and so the availability of staff within the next two months for the release scenario study will be limited. Tim suggested that an industry group could provide valuable feedback and data for the scenario, and it was agreed that input should be solicited once a draft document is ready perhaps late in the spring.

Upon review of a questionnaire for kraft pulp mills, data available from FPAC and data which likely needs to be collected from mills were identified and are itemized below:

Data available from FPAC:

- number of operation days per year: 350-355 d/y for kraft mills (paper mills may have more shutdown days);
- pulp production (quantity, density, and moisture);
- total effluent discharge and BOD, TSS, and AOX;
- total solid waste (including water content) and proportions treated by various methods;
- total air emissions, total reduced sulphur, sulphur dioxide, and particulate matter; and
- bleaching chemicals (chlorine, hypochlorite, chlorine dioxide, sodium hydroxide, hydrogen peroxide, sodium chlorate, and peracetic acid).

Data which needs to be collected from mills:

- total wood consumption, total chemical consumption, and total water consumption;
- chemicals other than those for bleaching;
- primary and secondary treatment efficiencies for TSS; and
- handling and shipping containers.

Tim provided several valuable inputs. He pointed out that turpentine and tall oil produced by the majority of Canadian kraft mills are commonly used as fuels rather than sold as by-products. This is different from European and American mills which have been reported to produce turpentine and tall oil as by-products. Tim indicated that any process aid directed to the recovery furnace will not be present in wastewater and therefore does not contribute to aqueous releases. He also suggested, based on a quick review of the candidate mills selected for site visits listed below, that they generally represent the industry well:

- Smurfit-Stone, medium kraft mill, hardwood, Portage-Du-Fort (near Shawville), Quebec
- Donohue (St-Felicien) Inc., bleached kraft pulp, St-Felicien, Quebec
- Papiers Fraser, medium kraft mill, Thurso, Quebec
- Smurfit-Stone (formerly St. Laurent Paperboard, La Tuque Division), white top linerboard, bleached kraft pulp, L'Usine, La Tuque, Quebec
- Domtar, integrated kraft pulp & paper mill, hardwood, Cornwall, Ontario
- Domtar, integrated kraft pulp & paper mill, softwood, Windsor, Quebec
- Papier Mason Ltee, large integrated thermo-mechanical pulp & newsprint mill, hardwood, Masson-Angers, Quebec
- Bowater, newsprint from recovered paper with deinking and TMP, Gatineau,

Quebec
- Domtar-EB Eddy, fine paper mill, Ottawa & Hull
- Tembec, sulphite and BTCMP, paper & board mill, Temiscaming, Quebec
- Weyerhaeuser, softwood, Grande Prairie, Alberta
- Alpac (Alberta-Pacific Forest Industries), hardwood, Boyle, Alberta
- Daishowa-Marubeni, hardwood, Peace River, Alberta

A number of actions were agreed to move the project forward:

1. Tim will examine the list of mills suggested for site visits (above) to see if they reasonably represent the industry;
2. FPAC will examine its database to determine if there is a sufficient number of mills in each of the following three release scenarios:
   - kraft pulp mills, non-integrated, from wood to market pulp;
   - recovered paper mills, from recovered paper to newsprint; and
   - paper mills, non-integrated, from pulp to paper.
3. Lucie will discuss with their data management consultant on extracting mill data, as itemized previously, in an aggregated form (range and average) from their FPAC database;
4. Lucie will look into the availability of Paprican reports relevant to chemical use and wastewater treatment of the pulp and paper industry;
5. With assistance of FPAC, EC will contact candidate mills to find volunteer facilities that are willing to cooperate on data gathering via site visits;
6. Jesse will continue to refine the questionnaires and populate them with available data; and
7. Once draft an emission scenario document is available, industry will be asked to provided additional information and comments.

**Minutes of February 13th Meeting on Pulp & Paper Mill Emission Scenarios**

Prepared by Jesse Shen, February 14, 2002

Agenda: Identification of chemical classes used by pulp and paper mills

Date: February 13, 2002
Place: Environment Canada, Place Vincent Massey, 351 St. Joseph Blvd., Hull, Quebec K1A 0H3

Attendees: Environment Canada (EC) – Jonathan Tigner and Robert Larocque
Consultants to EC – Jesse Shen and Joel Jossinet

Bob informed the group that FPAC would likely only be able to provide a limited response by March 31 as the consultant working with their data is buried. Plus, the industry may be mandated to produce P2 plans for some 178 compounds, considering all containers on-site.

A total of 31 chemical classes were identified and are listed below:

1) Air pollution control (wetting agents used in boiler and scrubber)
2) Bleaching chemicals
3) Boiler and cooling water treatment
4) Boilout chemicals (same chemistry as belt conditioners/cleaners, but used as slug)
5) Chip penetrants (cooking additives)
6) Contaminant control (stickies, pitches, adhesives, and any other foreign matter)
7) Corrosion control (filming agents and phosphates)
8) Water treatment (chlorine, pH control, etc.)
9) Dyes and fixatives
10) Felt conditioners/cleaners (used in both continuous and slug modes)
11) Fillers/additives (including coating agents, and pigments)
12) Foam control (water and oil-based)
13) Microbiological control (biocides)
14) Oxygen delignification (O2, NaOH, MgSO4)
15) Retention/drainage aids
16) Clarification aids
17) Deinking agents (dispersants and soaps)
18) Settling aids (wastewater, deinking, and green liquor)
19) Scale control
20) Sizing agents (internal and external, i.e., starch)
21) Wet strength agents
22) Dry strength agents
23) Washing aids (brownstock washer)
24) Flotation aids
25) Antiskid agents
26) Lime mud dewatering aids
27) Nutrients (bioaugmentation)
28) Odor control
29) Release aids
30) creping aids
31) Others (tracer chemicals, barrier chemistry, saltcake)

- In order to be able to identify areas where different compounds are used, Joel will use a coding system to identify where those chemicals are used on each of the process diagrams used for the questionnaires and emission scenario document.
- To better complete the questionnaires before going to mills, Robert, JF and Joel will, based on their knowledge and experience, provide typical usage data for each class, as a range and, if they are comfortable, as a mean. This is felt to be more useful and easier for plant personnel to address than having a blank questionnaire.
- Jonathan will scan the water balance figure mentioned by Bob.
- Bob will follow up with Lucie to see what FPAC is able to provide, and then to make some initial contacts with the mills identified during the meeting. and
- Jonathan will then contact each mill to see if they are willing to participate in the

survey or even allow a site visit.

# Appendix C – Short List of Pulp and Paper Mills Selected for Site Visit

Updated September 3, 2002

Kraft Mills:

1) Papiers Fraser, Thurso, Quebec (medium kraft mill)
   Renée Riffon, Environnement, 819-985-2233
   Thomas McNeil, Service Techniques
2) Smurfit-Stone, L'Usine, La Tuque, Quebec (bleached kraft pulp)
   Christine Dufresne, Environnement, 819-676-8100, ext.2684
   Other contacts: Yves Gilbert, Gilles Labonne
3) Domtar, Windsor, Quebec (integrated kraft pulp and paper mill from softwood)
   Robert Dufresne, Directeur Technique/Environnement, 819-845-8431
   Hélène Bergeron, Directrice Technique, 819-845-8508
   Patsy Inglis, Directrice Environnement, 819-845-8445
   Yves Boyer, Environnement/Air, 819-845-8365
4) Domtar, Cornwall, Ontario (integrated kraft pulp and paper mill from hardwood)
   Amy Low, Technical Director
   Sobino Rossi, Superintendent
   Brian Hall, Superintendent (p.m.)

Paper Mills:

Included at Domtar mills in Windsor, Quebec and Cornwall, Ontario.

Recovered Paper Mills:

5) Bowater, Gatineau, Quebec (newsprint from recovered paper with deinking and TMP)
   Mario Courtemanche, Environnement, 819-643-7200 ext.7469
   Bernard Begin, Sur. Technique, ext.7510
   Roger Brouillette, Service Technique, ext.7507
6) Papier Masson Ltee, Masson-Angers, Quebec (large integrated mill, thermo-mechanical pulp from hardwood and newsprint)
   Michel Soucy, Environnement
   Luc Massi, Process Engineer
   Michel Blouin, Superintendent (p.m.)

## Appendix D – Chemical Use Level, Water Content and Fraction Retained by Products

Compiled in Tables D.1, D.2, and D.3 are use level, water content and fraction retained by products for chemicals used at kraft pulp mills, non-integrated paper mills, and recovered paper mills, respectively. Sources of data are listed below.

1. Joel Jossinet, pulp and paper consultant, 2002.
2. Ash, M.; and I. Ash, Handbook of Paper and Pulp Chemicals, Synapse Information Resources, Endicott, NY, USA, 2001.
3. Grace, T. M.; E. W. Malcolm; and M. J. Kocurek (eds.), Pulp and Paper Manufacture Volume 5: Alkaline Pulping, Joint Textbook Committee of the Paper Industry, Canada, 1989.
4. European Commission, "Integrated pollution prevention and control (IPPC) – draft reference document on best available techniques in the pulp and paper industry," August 1999.
5. European Commission, "Technical guidance document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No. 1488/94 on risk assessment for existing substances," Part IV, Office for Official Publications of the European Communities, Luxembourg, 1996.
6. Brooke, D; M. Crookes; and P. Quarterman, "Review of industry and use categories and emission estimation methods in the EU technical guidance document," prepared for CEFIC-Long Range Research Initiative, 2000.
7. Dence, C. W.; and D. W. Reeve (eds.), Pulp Bleaching: Principles and Practice, TAPPI Press, Atlanta, GA, USA, 1996.
8. Braunschweiler, H., "A reasonable worst-case slimicide PEC-model for paper industry using wastewater treatment in Finland," FEI/Chemicals Division, Tel: +358-9-40300535, Fax: +358-9-40300591, Web: http://www.vyh.fi/eng/fei/fei.html.
9. David Hall, Vinings Industries, Inc., private communications, December 2002.
10. Survey of pulp and paper mills and chemical suppliers.

## Table D.1 – Data for Kraft Pulp Mills

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Wood handling | cleaner | dropped from survey | not used regularly (ref.1) | | | |
| | pitch control | dropped from survey | not used regularly (ref.1) | | | |
| Digestion | cooking aids/chip penetrants | | 0.025-0.125% (ref.1) | | c | |
| | digester boilouts | | ? | | s | |
| | scale control | | 2-50 ppm on liquor flow (ref.1) | | c | |
| Brown Stock Washing & Chemical Recovery | foam control | | 0.025-0.125% (refs.1, 10) | 0 (ref.1) | c | 0% (refs.5, 10) |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | wash aids/drainage aids | | 0.025-0.125% (ref.1) | | c | |
| | pitch control | both used | 0.042-0.42% (refs. 1, 10) | | c | |
| | | liquids | 0.008-0.083% (ref.1) | 20-90 (ref.1) | c | |
| | | talc | 0.67-6.7 lb/ton (ref.1) | 0 (ref.1) | c | |
| | boilouts | | 1-8% on volume treated (ref.1) | 75-80 (enzyme) (ref.1) | s | |
| | | acid boilout | 3-6% on volume treated (ref.1) | 55-75 (ref.1) | | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | 50-70 (ref.1) | s | |
| | clarification aids (white & green liquor) | | 0.5-5.0 ppm on liquor flow (refs.1, 10) | 0-80 (ref.1) | c | |
| | scale control | | 2-50 ppm on liquor flow (ref.1) | | c | |
| | lime mud dewatering aids | | 0.5-1.5 lb/ton on reburned lime (ref.1) | | c | |
| | cleaner | dropped from survey | not used regularly (ref.1) | | s | |
| | tall oil separation & acidulation aids | | 400-600 ppm on volume (ref.1) | | c | |
| | turpentine separation aids | | 100-500 ppm on volume (ref.1) | | c | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| | screen room pH control ($H_2SO_4$ or $CO_2$) | dropped from survey | commodity chemicals | | c | |
| Bleaching | chlorine ($Cl_2$) | | 6-8% (refs.1, 10) | | c | |
| | hypochlorite ($Ca(OCl)_2$ or NaOCl) | | 10 kg/t (ref.3, p.409) | | c | |
| | | | 1% (ref.7, p.401; ref.10) | | c | |
| | chlorine dioxide ($ClO_2$) | | 2-4% (refs.1, 10) | | c | |
| | sodium hydroxide (NaOH) | | 1-4% (refs.1, 10) | | c | |
| | oxygen ($O_2$) | both used | 2.25-5.5% (ref.1) | | c | |
| | | for bleaching | 0.5-1.0% (ref.1) | | c | |
| | | for delignification | 1.75-4.5% (ref.1) | | c | |
| | hydrogen or sodium peroxide | | 2-30 kg/tonne (ref.4, p.50)<br>2-4% (ref.7, p.418) | | c | |
| | peracetic (peroxy) acid | | 0.5% (ref.7, p.437) | | c | |
| | bleaching enzymes | | 100-200 mL/tonne (refs.1, 10) | | c | |
| | boilouts | | 1-8% on volume treated (ref.1) | | s | |
| | | acid boilout | 3-6% on volume treated (ref.1) | | s | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | | s | |
| | pitch control | both used | 0.042-0.42% (ref.1) | | c | |
| | | liquids | 0.008-0.083% (ref.1) | 20-90 (ref.1) | c | |
| | | talc | 0.67-6.7 lb/ton (ref.1) | 0 (ref.1) | c | |
| | scale control | | 2-50 ppm on flow (ref.1) | | c | |
| Pulp Machine | microbiological control | | 1-50 ppm on chest volume (ref.1) | 60-90 (ref.1) | s or c | 0% (ref.5) |
| | pitch control | both used | 0.042-0.42% (ref.1) | | c | |
| | | liquids | 0.008-0.083% (ref.1) | 20-90 (ref.1) | c | |
| | | talc | 0.67-6.7 lb/ton (ref.1) | 0 (ref.1) | c | |
| | foam control | both used | 0.025-0.2 (ref.1) | 0-90 (ref.1) | c | |
| | | oil-based | 0.0125-0.1% (ref.1) | 0 (ref.1) | c | 0% (ref.5) |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Pulp Machine | foam control | water-based | 0.0125-0.1% (ref.1) | 80-90 (ref.1) | c | |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | felt conditioning | | 200-800 ppm on shower water (ref.1)<br>0.009% per tonne of pulp (ref.10) | | c | |
| | | | 2.5-7.5% (ref.1) | | s | |
| | boilouts | | 1-8% on volume treated (ref.1) | 75-80 (enzyme) (ref.1) | s | |
| | | acid boilout | 3-6% on volume treated (ref.1) | 55-75 (ref.1) | s | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | 50-70 (ref.1) | s | |
| | retention aids | coagulants | 5-100 ppm (ref.1) | | c | 70-90% (ref.5) |
| | | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| Recovery and Power Boilers | air pollution control | polymer dispersant | 5-10 ppm on scrubber flow (ref.1) | | c | |
| | condensate treatment | amines | 2-4 ppm on steam (refs.1, 10) | | c | |
| | boiler water treatment | both used | 0.5-10 ppm on steam (ref.1) | | c | |
| | | phosphate | 0.5-2 ppm on steam (ref.1) | | c | |
| | | polymer dispersant | 1-8 ppm on steam (ref.1) | | c | |
| | cleaner | dropped from survey | not used regularly (ref.1) | | s | |
| | scale control | | 2-50 ppm (refs.1, 10) | | c | |
| | | Unihib 905 (Lonza) | 50-75 ppm (ref.2) | | c | |
| | corrosion inhibitors | sulphites | 1-7 ppm on steam (refs.1, 10) | | c | |
| Water Treatment | corrosion inhibitors | | 0.1-5 ppm on water (ref.1) | | c | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Water Treatment | oxygen scavengers | dropped from survey | used as needed (ref.1) | | c | |
| | passivators/filming agents | dropped from survey | used as needed (ref.1) | | c | |
| | microbiological control | chlorine or hypochlorite | to positive residue at 0.2 ppm (refs.1, 10) | 60-90 (ref.1) | s or c | |
| | scale control | | 2-50 ppm (ref.1) | | c | |
| | settling aids | coagulants (alum, PAC) | 5-100 ppm (refs.1, 10) | | c | |
| | | flocculants | 0.1-5 ppm (refs.1, 10) | 0-80 (ref.1) | c | |
| | | alum, polyaluminum chloride (dropped from survey) | 5-10 ppm (ref.1) | | c | |
| | chelating agents (metal removal) | dropped from survey | not used regularly (ref.1) | | c | |
| | | Lastabil 928 OE (BK Giulini Chemie) | 0.4-0.8% (ref.2) | | c | |
| | pH control | dropped from survey | commodity chemicals | | c | |
| Wastewater Treatment | settling aids | coagulants | 15-100 ppm (ref.1) | | c | |
| | | flocculants | 0.1-5 ppm (ref.1) | 0-80 (ref.1) | c | |
| | foam control | both used | 2-25 ppm (ref.1); 0.1 ppm (ref.10) | 0-90 (ref.1) | c | |
| | | oil-based | 2-10 ppm on flow (ref.1) | 0 | c | |
| | | water-based | 5-25 ppm on flow (ref.1) | 80-90 (ref.1) | c | |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | nutrients | all | 2.0-5.0 ppm (ref.1), 75 ppm continuous basis (ref.10) | | s | |
| | | $NH_3$ | 1-3 ppm on flow (ref.1) | | s | |
| | | P | 1-2 ppm on flow (ref.1) | | s | |
| | | bioaugmentation | 0.1 kg/1000 $m^3$ on flow (ref.1) | | s | |
| | sludge conditioners | flocculants | 0.1-10 ppm (refs.1, 10) | | c | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Wastewater Treatment | odor control | average | 5-100 ppm (refs.1, 10) | | c | |
| | | initial dose | 50-100 ppm (ref.1) | | c | |
| | | maintenance | 5-15 ppm (ref.1) | | c | |
| | color control | high dose coagulant (ref.1) | 200 ppm (ref.1) | | c | |

## Table D.2 – Data for Non-integrated Paper Mills

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Stock Preparation (pulpers and broke system) | sizes | | 0.05-1.0% (ref.1) | 0-95(ref.1) | c | 10-30% (ref.6, p.25) |
| | wet strength agents | | 0.25-2.0% (ref.1) | | c | 70-90% (ref.6, p.25) |
| | dry strength agents | | 0.05-0.75% (ref.1) | | c | |
| | dyes/dye fixatives/fluorescent whites | | 0.01-1.0% (ref.5) | | c | |
| | | dyes | 15.4 kg/tonne (ref.4, p.324) | | c | 50-98% (ref.6, p.25) |
| | | Cartafix F Liq (dye fixative) (Clariant UK) | 0.05-0.5% (ref.2) | | c | |
| | pitch control/stickies control | Bilt-Plates 156 (R. T. Vanderbilt) (ref.2) | 2-10 lb/ton of paper or 0.1-0.5% (ref.1) | 20-90 (liquid), 0 (solids) (ref.1) | c | |
| | boilouts/cleaners | all | 1-8% on volume treated (ref.1) | 75-80 (enzyme) (ref.1) | s | |
| | | acid boilout | 3-6% on volume treated (ref.1) | 55-75 (ref.1) | s | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | 50-70 (ref.1) | s | |
| | retention & drainage aids | coagulants | 5-100 ppm (ref.1) | | c | 70-90% (ref.6, p.25) |
| | | flocculants | 0.1-5 ppm (ref.1) | 0-80 (ref.1) | c | |
| | charge control | coagulants | 5-100 ppm (ref.1) | | c | 70-90% (ref.6, p.25) |
| | | Praestafix (Stockhausen) | 0.1-0.4% (ref.2) | | c | |
| | fillers (PCC, GCC, clay, $TiO_2$, etc) | all | 209 kg/tonne (ref.4, p.324) | | c | 95% (ref.6, p.25) |
| | | Lastabil 928 OE (BK Giulini Chemie) | 0.4-0.8% (ref.2) | | c | |
| | microbiological control | | 1-50 ppm on chest volume (ref.1) | 60-90 (ref.1) | s or c | 0% (ref.5) |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Stock Preparation (pulpers and broke system) | emulsifiers | Lumisorb PSMO-20, Lambent Tech | 0.05-0.2% (ref.2) | | c | |
| | foam control | | 0.0125-0.05% (ref.1) | 0-90 (ref.1) | c | 0% (ref.5, p.701) |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | scale control | | ? | | c | |
| Paper Machine | pitch/stickies control | both used | 0.125-1.25% (ref.1) | | c | |
| | | liquids | 0.025-0.25% (ref.1) | 20-90 (ref.1) | c | |
| | | talc | 2-20 lb/ton (ref.1) | 0 (ref.1) | c | |
| | boilouts | | 1-8% on volume treated (ref.1) | 75-80 (enzyme) (ref.1) | s | |
| | | acid boilout | 3-6% on volume treated (ref.1) | 55-75 (ref.1) | s | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | 50-70 (ref.1) | s | |
| | corrosion inhibitors | Elfugin AKT Liq (Clariant UK) | 0.05-0.5% on dry paper (ref.2) | | c | |
| | antiskid agents | aluminum silicate spray | 0.75-1.50 lb/ton paper (ref.9) | | c | |
| | cleaners | Eldorado ALK-6000 | 3-5% batch cleaning, 5-20% general purpose cleaner (ref.2) | | s | |
| | felt cleaning | | 200-800 ppm on shower water (ref.1) | 25-75 (surfactant based), 0 (solvent based) (ref.1) | c | |
| | | | 2.5-7.5% (ref.1) | | s | |
| | | | 0.5-1.0 lb/ton paper (ref.9) | | c | |
| | | Qemifeltwash 8020A (Qemi Int'l) | 3-7 lb/ton paper (ref.2) | | c | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Paper Machine | microbiological control | | 1-50 ppm on chest volume (ref.1) | 60-90 (ref.1) | s or c | 0% (ref.5) |
| | | slimicide | 0.02-0.2% (ref.8) | | ? | |
| | saveall polymers | coagulants | 5-100 ppm (ref.1) | | c | |
| | | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| | foam control | both used | 0.025-0.2% (ref.1) | 20-90 (ref.1) | c | |
| | | oil-based | 0.0125-0.1% (ref.1) | | c | 0% (ref.5, p.705) |
| | | water-based | 0.0125-0.1% (ref.1) | | c | |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | surface size | | 0.05-1.0% (ref.1) | 50-90 | c | |
| | scale control | dropped from survey | not used regularly (ref.1) | | c | |
| | retention aids | flocculants | 0.025-0.1% (ref.1) | | c | 70-90% (ref.6, p.25) |
| | | Cartafen ZFN Liq. (Clariant UK) | 0.03-0.08% (ref.2) | | c | |
| | formation aids | Lycoid 260 (Vinings) | 4-6 lb/ton (ref.2) | | c | |
| Coating | latex | Acumer 9400 (Rohm & Hass) | < 2% (ref.2) | | c | |
| | fillers (PCC, GCC, $TiO_2$, clay, talc) | all | 209 kg/tonne or 21% (ref.4, p.324) | | c | 95% (ref.6, p.25) |
| | microbiological control | | 1-50 ppm on chest volume (ref.1) | 60-90 (ref.1) | s or c | 0% (ref.5) |
| | starch/size | | 0.05-1.0% (ref.1) | | c | |
| | foam control | | 0.0125-0.05% (ref.1) | 0-90 (ref.1) | c | 0% (ref.5, p.705) |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | boilouts | all | 1-8% on volume treated (ref.1) | 75-80 (enzyme) (ref.1) | s | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Coating | | acid boilout | 3-6% on volume treated (ref.1) | 55-75 (ref.1) | s | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | 50-70 (ref.1) | s | |
| Recovery and Power Boilers | air pollution control | polymer dispersant | 5-10 ppm on scrubber flow (ref.1) | | c | |
| | condensate treatment | amines | 2-4 ppm on steam (ref.1) | | c | |
| | boiler water treatment | both used | 0.5-10 ppm on steam (ref.1) | | c | |
| | | phosphate | 0.5-2 ppm on steam (ref.1) | | c | |
| | | polymer dispersant | 1-8 ppm on steam (ref.1) | | c | |
| | cleaners | dropped from survey | not used regularly (ref.1) | | s | |
| | scale control | | 5-50 ppm on steam (ref.1) | | c | |
| | | Unihib 905 (Lonza) | 50-75 ppm (ref.2) | | c | |
| | corrosion inhibitors | sulphites | 1-5 ppm on steam (ref.1) | | c | |
| Water Treatment | corrosion inhibitors | | 0.1-5.0 ppm on water (ref.1) | | c | |
| | oxygen scavengers | dropped from survey | use as needed (ref.1) | | c | |
| | passivators/filming agents | dropped from survey | used as needed (ref.1) | | c | |
| | microbiological control | chlorine or hypochlorite | to positive residue at 0.2 ppm (ref.1) | 60-90 (ref.1) | s or c | |
| | scale control | | 5-50 ppm (ref.1) | | | |
| | settling aids | coagulants | 5-100 ppm (ref.1) | | c | |
| | | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| | chelating agents (metal removal) | dropped from survey | not used regularly (ref.1) | | c | |
| | chelating agents (metal removal) | Lastabil 928 OE (BK Giulini Chemie) | 0.4-0.8% (ref.2) | | c | |
| | pH control | dropped from survey | commodity chemicals | | c | |
| Wastewater Treatment | settling aids | coagulants | 5-100 ppm (ref.1) | | c | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Wastewater Treatment | | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| | foam control | | 2-25 ppm (ref.1) | 0-90 (ref.1) | c | |
| | | oil-based | 2-10 ppm on flow (ref.1) | 0 (ref.1) | c | |
| | | water-based | 5-25 ppm on flow (ref.1) | 80-90 (ref.1) | c | |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | nutrients | all | 1.0-5.0 ppm (ref.1) | | c | |
| | | $NH_3$ | 1-3 ppm on flow (ref.1) | | s | |
| | | P | 1-2 ppm on flow (ref.1) | | s | |
| | | bioaugmentation | 0.1 kg/1000 $m^3$ on flow (ref.1) | | s | |
| | sludge conditioners | flocculants | 0.1-10 ppm (ref.1) | | c | |
| | odor control | average | 5-100 ppm (ref.1) | | c | |
| | | initial dose | 50-150 ppm (ref.1) | | c | |
| | | maintenance | 5-15 ppm (ref.1) | | c | |
| | color control | high dose coagulants (ref.1) | 200 ppm (ref.1) | | c | |

## Table D.3 – Data for Recovered Paper Mills

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Pulping | surfactants/repulping aids | | 0.2-2.0% (ref.1) | | c | |
| | sodium silicate | | 2.0-4.0% (ref.1) | | c | |
| | dispersing agents | | 0.1-0.5% (ref.1) | | c | |
| Deinking | deinking aids | | 0.1-1.0% (ref.1) | | c | |
| | | Eldorado DIC-100 | 0.5-1 gal/ton dry furnish (ref.2) | | c | |
| | | Hartaflot SE (Huntsman) | 0.1-0.6% (ref.2) | | c | |
| | soap/fatty acids | | 0.5-3.0% (ref.1) | | c | |
| | boilouts | | 1-8% on volume treated (ref.1) | 75-80 (enzyme) (ref.1) | s | |
| | | acid boilout | 3-6% on volume treated (ref.1) | 55-75 (ref.1) | s | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | 50-70 (ref.1) | s | |
| | settling aids | coagulants | 5-100 ppm (ref.1) | | c | |
| | | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| Bleaching | hydrogen or sodium peroxide | $H_2O_2$ or $Na_2O_2$ | 1.0-2.0% (ref.1) | | c | |
| | sodium hydroxide | NaOH | 3.0-5.0% (ref.1) | | c | |
| | sodium silicate | | 2.0-4.0% (ref.1) | | c | |
| | chelating agents/sequestrants | | 0.1-2.0% (ref.1) | | c | |
| | hydrosulfites | | 0.5-1.0% (ref.1) | | c | |
| | chlorine | | 0.5-3.0% (ref.1) | | c | |
| | sodium hypochlorite | | 1-4% on pulp (ref.7, p.401) | | c | |
| Paper Making | sizes | | 0.05-1.0% (ref.1) | 50-90 (ref.1) | c | 10-30% (ref.6, p.25) |
| | wet strength agents | | 0.25-2.0% (ref.1) | | c | 70-90% (ref.6, p.25) |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Paper Making | dry strength agents | | 0.05-0.75% (ref.1) | | c | |
| | dyes/dye fixatives/fluorescent whites | | 0.01-1.0% (ref.5) | | c | |
| | | dyes | 15.4 kg/tonne (ref.4, p.324) | | c | 50-98% (ref.6, p.25) |
| | corrosion inhibitors | Arquad 12-50 (Akzo Nobel) (ref.2) | Joel will ask sale rep at Akzo Nobel | | c | |
| | corrosion inhibitors | Elfugin AKT Liq (Clariant UK) | 0.05-0.5% on dry paper (ref.2) | | c | |
| | retention/drainage aids (saveall polymers) | coagulants | 5-100 ppm (ref.1) | | c | 70-90% (ref.6, p.25) |
| | | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| | | micro-particle system (bentonite, alum, silica, cationic starch) | 0.5-2% (ref.1) | | c | |
| | | bentonite | 0.1-0.5% (ref.1) | | c | |
| | | alum | 0.1-0.25% (ref.1) | | c | |
| | | silica | 0.1-0.2% (ref.1) | | c | |
| | | cationic starch | 0.5-1.0% (ref.1) | | c | |
| | barrier chemistry | | ? | | c | |
| | formation aids | | 4-6 lb/ton or 0.2-0.3% (ref.2) | | c | |
| | | Lycoid 260 (Vinings) | 4-6 lb/ton (ref.2) | | c | |
| | | Jaguar CB-11 (Vinings) | 2-25 lb/ton (ref.2) | | c | |
| | charge neutralization | coagulants | 5-100 ppm (ref.1) | | c | 70-90% (ref.6, p.25) |
| | | Praestafix (Stockhausen) | 0.1-0.4% (ref.2) | | c | |
| | chelants | Lastabil 928 OE (BK Giulini Chemie) | 0.4-0.8% on peroxide (ref.2) | | | |
| | antiskid agents | | 0.75-1.50 lb/ton paper (ref.9) | | c | |
| | emulsifiers | | 0.05-5% (ref.2) | | | |
| | | Volpo S10 (Croda) | 0.5-5% (ref.2) | | c | |
| | | Lumisorb PSMO-20 (Lambent Tech) | 0.05-0.2% (ref.2) | | c | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Paper Making | foam control | | 0.0125-0.05% (ref.1) | 20-90 (ref.1) | c | 0% (ref.5, p.705) |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | scale control | dropped from survey | not used regularly (ref.1) | | c | |
| | pitch/stickies control | both used | 0.125-1.25% (ref.1) | | c | |
| | | liquids | 0.025-0.25% (ref.1) | 20-90 (ref.1) | c | |
| | | talc | 2-20 lb/ton (ref.1) | 0 (ref.1) | c | |
| | felt cleaning chemicals | | 200-800 ppm on shower water (ref.1) | 25-75% (surfactant based), 0 (solvent based) (ref.1) | c | |
| | | | 2.5-7.5% (ref.1) | | s | |
| | | Qemifeltwash 8020A (Qemi Int'l) | 3-7 lb/ton paper (ref.2) | | c | |
| | boilouts/cleaners | | 1-8% on volume treated (ref.1) | 75-80 (enzyme) (ref.1) | s | |
| | | acid boilout | 3-6% on volume treated (ref.1) | 55-75 (ref.1) | s | |
| | | chelant boilout | 1-2% on volume treated (ref.1) | | s | |
| | | caustic boilout | 4-8% on volume treated (ref.1) | 50-70 (ref.1) | s | |
| | microbiological control | | 1-50 ppm on chest volume (ref.1) | 60-90 (ref.1) | s or c | 0% (ref.5) |
| | latex | Acumer 9400 (Rohm & Hass) | < 2% (ref.2) | | c | |
| | fillers (PCC, GCC, $TIO_2$) | Camel-CAL (MERYS) | 209 kg/tonne or 21% (ref.4, p.324) | | c | 95% (ref.6, p.25) |
| Recovery and Power Boilers | air pollution control | polymer dispersant | 5-10 ppm on scrubber flow (ref.1) | | c | |
| | condensate treatment | amines | 2-4 ppm on steam (ref.1) | | c | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Recovery and Power Boilers | boiler water treatment | both used | 0.5-10 ppm on steam (ref.1) | | c | |
| | | phosphates | 0.5-2 ppm on steam (ref.1) | | c | |
| | | polymer dispersant | 1-8 ppm on steam (ref.1) | | c | |
| | cleaners | dropped from survey | not used regularly (ref.1) | | s | |
| | scale control | | 5-50 ppm on steam (ref.1) | | c | |
| | | Unihib 905 (Lonza) | 50-75 ppm (ref.2) | | c | |
| | corrosion inhibitors | sulphites | 1-5 ppm on steam (ref.1) | | c | |
| Water Treatment | corrosion inhibitors | | 0.1-5 ppm on water (ref.1) | | c | |
| | oxygen scavengers | dropped from survey | use as needed (ref.1) | | c | |
| | passivators/filming agents | dropped from survey | use as needed (ref.1) | | c | |
| | microbiological control | chlorine or hypochlorite | to positive residue at 0.2 ppm (ref.1) | 60-90 (ref.1) | s or c | |
| | scale control | | 5-50 ppm (ref.1) | | c | |
| | settling aids | coagulants | 5-100 ppm (ref.1) | | c | |
| | settling aids | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| | chelating agents (metal removal) | dropped from survey | not used regularly (ref.1) | | c | |
| | | Lastabil 928 OE (BK Giulini Chemie) | 0.4-0.8% (ref.2) | | c | |
| | pH control | dropped from survey | commodity chemicals | | c | |
| Wastewater Treatment | settling aids | coagulants | 5-100 ppm (ref.1) | | c | |
| | | flocculants | 0.1-5.0 ppm (ref.1) | 0-80 (ref.1) | c | |
| | foam control | | 2-25 ppm (ref.1) | 0-90 (ref.1) | | |
| | | oil-based | 2-10 ppm on flow (ref.1) | 0 (ref.1) | c | |
| | | water-based | 5-25 ppm on flow (ref.1) | 80-90 (ref.1) | c | |
| | | Adekanate B-187 (Asahi Denka Kogyo) | 50-100 ppm (ref.2) | | c | |
| | nutrients | | 2.0-5.0 ppm (ref.1) | | c | |
| | | $NH_3$ | 1-3 ppm (ref.1) | | s | |

| Process Area | Type of Chemicals | Note | Use Level (% on pulp unless otherwise noted) | Water Content (%) | Use Mode s-slug c-continuous | Fraction Retained by Product (%) |
|---|---|---|---|---|---|---|
| Wastewater Treatment | nutrients | P | 1-2 ppm (ref.1) | | s | |
| | | bioaugmentation | 0.1 kg/1000 $m^3$ on flow (ref.1) | | s | |
| | sludge conditioners | flocculants | 0.1-10 ppm (ref.1) | | c | |
| | odor control | average | 5-150 ppm (ref.1) | | c | |
| | | initial dose | 50-150 ppm (ref.1) | | c | |
| | | maintenance | 5-15 ppm (ref.1) | | c | |
| | color control | high dose coagulant | 200 ppm (ref.1) | | c | |

# Appendix E – Questionnaire Used in Survey of Pulp and Paper Mills

**Chemical Usage Survey – Kraft Pulp Mills**
(updated December 20, 2002)

**Company Information**

| | | | | |
|---|---|---|---|---|
| Company | | | | |
| Address | | | | |
| Contact Person | | Tel: | Fax: | Email: |

**Chemical Usage Data**

| Operation | Chemical | Use √-yes ×-no | Use Level (% on pulp unless otherwise noted) | | Water Content (%) (supplier only) | | Use Mode S – slug C – continuous | | Fraction Retained by Product (%) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | verify | | verify | | verify | | verify |
| Digestion | cooking aids/chip penetrants | | 0.025-0.125% | | | | C | | | |
| | digester boilouts | | no data | | | | S | | | |
| | scale control | | 10-100 ppm on liquor | | | | C | | | |
| Brown Stock Washing and Chemical Recovery | foam control | | 0.025-0.125% | | | 0 | C | | 0% | |
| | wash aids/drainage aids | | 0.025-0.125% | | | | C | | | |
| | pitch control | | 0.125-1.25% | | | 0-90 | C | | | |
| | boilouts | | 1-8% | | | 50-80 | S | | | |
| | clarification aids | | 0.5-5.0 ppm on liquor | | | 0-80 | C | | | |
| | scale control | | 10-100 ppm on liquor | | | | C | | | |
| | lime mud dewatering aids | | 0.5-1.5 lb/t on lime | | | | C | | | |
| | tall oil separation & acidulation aids | | 400-600 ppm on volume | | | | C | | | |
| | turpentine separation aids | | 100-500 ppm on volume | | | | C | | | |
| Bleaching | chlorine ($Cl_2$) | | 6-8% | | | | C | | | |
| | hypochlorite ($Ca(OCl)_2$ or NaOCl) | | 1% | | | | C | | | |
| | chlorine dioxide ($ClO_2$) | | 2-4% | | | | C | | | |
| | sodium hydroxide (NaOH) | | 1-4% | | | | C | | | |
| | oxygen ($O_2$) | | 2.25-5.5% | | | | C | | | |
| | hydrogen or sodium peroxide | | 2-4% | | | | C | | | |
| | peracetic acid | | 0.5% | | | | C | | | |
| | bleaching enzymes | | 100-200 mL/t on pulp | | | | C | | | |
| | boilouts | | 1-8% | | | | S | | | |
| | pitch control | | 0.125-1.25% | | | 0-90 | C | | | |
| | scale control | | 10-100 ppm on volume | | | | C | | | |

| Operation | Chemical | | Use √-yes ×-no | Use Level (% on pulp unless otherwise noted) | | Water Content (%) (supplier only) | | Use Mode S – slug C – continuous | | Fraction Retained by Product (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | verify | | verify | | verify | | verify |
| Pulp Machine | microbiological control | | | 1-50 ppm on chest volume | | | 60-90 | S or C | | 0% | |
| | pitch control | | | 0.125-1.25% | | | 0-90 | C | | | |
| | foam control | | | 0.025-0.2% | | | 0-90 | C | | 0% | |
| | felt conditioning | | | 200-800 ppm on shower water | | | 0-75 | C | | | |
| | boilouts | | | 1-8% | | | 50-80 | S | | | |
| | retention aids | coagulants | | 5-100 ppm on volume | | | | C | | 70-90% | |
| | | flocculants | | 0.1-5.0 ppm on volume | | | 0-80 | C | | 70-90% | |
| Recovery and Power Boilers | air pollution control (polymer dispersant) | | | 5-10 ppm on scrubber liquid | | | | C | | 0% | |
| | condensate treatment (amines) | | | 2-4 ppm on steam | | | | C | | 0% | |
| | boiler water treatment | | | 0.5-10 ppm on steam | | | | C | | 0% | |
| | scale control | | | 10-100 ppm on steam | | | | C | | 0% | |
| | corrosion inhibitors (sulphites) | | | 1-5 ppm on steam | | | | C | | 0% | |
| Water Treatment | corrosion inhibitors | | | 0.1-5 ppm on water | | | | C | | | |
| | microbiological control (chlorine or hypochlorite) | | | to positive residue at 0.2 ppm | | | 60-90 | C or S | | | |
| | scale control | | | 10-100 ppm on water | | | | C | | | |
| | settling aids | coagulants, alum, PAC | | 5-100 ppm on water | | | | C | | | |
| | | flocculants | | 0.1-5 ppm on water | | | 0-80 | C | | | |
| Wastewater Treatment | settling aids | coagulants | | 15-100 ppm on water | | | | C | | 0% | |
| | | flocculants | | 0.1-5 ppm on wastewater | | | 0-80 | C | | 0% | |
| | foam control | | | 2-25 ppm on wastewater | | | 0-90 | C | | 0% | |
| | nutrients | | | 2-5 ppm on wastewater | | | | S | | 0% | |
| | sludge conditioners (flocculants) | | | 0.1-10 ppm on wastewater | | | | C | | 0% | |
| | odor control | | | 5-100 ppm on wastewater | | | | C | | 0% | |
| | color control (coagulants) | | | 200 ppm on wastewater | | | | C | | 0% | |

## Chemical Usage Survey – Paper Mills

(updated December 20, 2002)

**Contact Information**

| | | | | |
|---|---|---|---|---|
| Company | | | | |
| Address | | | | |
| Contact Person | Name: | Tel: | Fax: | Email: |

**Chemical Usage Data**

| Operation | Chemicals | | Use √-yes ×-no | Use Level (% on pulp unless otherwise noted) | | Water Content (%) (supplier only) | | Use Mode S – slug C – continuous | | Fraction Retained by Product (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | verify | | verify | | verify | | verify |
| Stock Preparation (pulpers and broke system) | sizes | | | 0.05-1.0% | | | 0-95 | C | | 10-30% | |
| | wet strength agents | | | 0.25-2.0% | | | | C | | 70-90% | |
| | dry strength agents | | | 0.05-0.75% | | | | C | | | |
| | dyes/dye fixatives/fluorescent whites | | | 0.01-1.0% | | | | C | | 40-95% | |
| | pitch/stickies control | | | 0.1-0.5% | | | 0-90 | C | | | |
| | boilouts/cleaners | | | 1-8% on volume | | | 50-80 | S | | | |
| | retention/drainage aids | coagulants | | 5-100 ppm on volume | | | | C | | 70-90% | |
| | | flocculants | | 0.1-5 ppm on volume | | | 0-80 | C | | 70-90% | |
| | charge control (coagulants) | | | 5-100 ppm on volume | | | | C | | 70-90% | |
| | fillers (PCC, GCC, clay, $TiO_2$, etc) | | | 21% | | | | C | | | |
| | chelants | | | 0.4-0.8% | | | | C | | | |
| | microbiological control | | | 1-50 ppm on chest volume | | | 60-90 | S or C | | 0% | |
| | emulsifiers | | | 0.05-0.2% | | | | C | | | |
| | foam control | | | 0.0125-0.05% | | | 0-90 | C | | 0% | |
| | scale control | | | no data | | | | C | | | |
| Paper Machine | pitch/stickies control | | | 0.125-1.25% | | | 0-90 | C | | | |
| | boilouts | | | 1-8% | | | 50-80 | S | | | |
| | corrosion inhibitors | | | 0.05-0.5% | | | | C | | | |
| | antiskid agents (aluminum silicate) | | | no data | | | | C | | | |
| | cleaners | | | no data | | | | S | | | |
| | felt cleaning | | | 200-800 ppm on shower water | | | 0-75 | C | | | |
| | microbiological control | | | 1-50 ppm on chest volume | | | 60-90 | S | | 0% | |
| | saveall polymers | coagulants | | 5-100 ppm on volume | | | | C | | | |
| | | flocculants | | 0.1-5.0 ppm on volume | | | 0-80 | C | | | |
| | foam control | | | 0.025-0.2% | | | 20-90 | C | | 0% | |
| | surface size | | | 0.05-1.0% | | | | C | | | |

| Operation | Chemicals | | Use √-yes ×-no | Use Level (% on pulp unless otherwise noted) | | Water Content (%) (supplier only) | | Use Mode S – slug C – continuous | | Fraction Retained by Product (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | verify | | verify | | verify | | verify |
| | retention aids (flocculants) | | | 0.025-0.1% | | | 0-80 | C | | 70-90% | |
| | formation aids | | | 0.2-0.3% | | | | C | | | |
| Coating | latex | | | 2% | | | | C | | | |
| | fillers (PCC, GCC, $TiO_2$, clay, talc) | | | 21% | | | | C | | | |
| | microbiological control | | | 1-50 ppm on chest volume | | | 60-90 | S or C | | 0% | |
| | starch/size | | | 0.05-1.0% | | | 50-90 | C | | | |
| | foam control | | | 0.0125-0.05% | | | 0-90 | C | | 0% | |
| | boilouts | | | 1-8% | | | 50-80 | S | | | |
| Recovery and Power Boilers | air pollution control (polymer dispersant) | | | 5-10 ppm on scrubber liquid | | | | C | | 0% | |
| | condensate treatment (amines) | | | 2-4 ppm on steam | | | | C | | 0% | |
| | boiler water treatment | | | 0.5-10 ppm on steam | | | | C | | 0% | |
| | scale control | | | 10-100 ppm on steam | | | | C | | 0% | |
| | corrosion inhibitors (sulphites) | | | 1-5 ppm on steam | | | | C | | 0% | |
| Water Treatment | corrosion inhibitors | | | 0.1-5.0 ppm on water | | | | C | | | |
| | microbiological control (chlorine or hypochlorite) | | | to positive residue at 0.2 ppm | | | 60-90 | S or C | | | |
| | scale control | | | 10-100 ppm on water | | | | C | | | |
| | settling aids | coagulants | | 5-100 ppm on water | | | | C | | | |
| | | flocculants | | 0.1-5.0 ppm on water | | | 0-80 | C | | | |
| Wastewater Treatment | settling aids | coagulants | | 5-100 ppm on volume | | | | C | | 0% | |
| | | flocculants | | 0.1-5.0 ppm on volume | | | 0-80 | C | | 0% | |
| | foam control | | | 2-25 ppm on volume | | | 0-90 | C | | 0% | |
| | nutrients | | | 1-5 ppm on volume | | | | S | | 0% | |
| | sludge conditioners (flocculants) | | | 0.1-10 ppm on volume | | | | C | | 0% | |
| | odor control | | | 5-150 ppm on volume | | | | C | | 0% | |
| | color control (coagulant) | | | 200 ppm on volume | | | | C | | 0% | |

## Chemical Usage Survey – Recovered Paper Mills (Deinking Plants)

(updated December 20, 2002)

**Company Information**

| | | | | |
|---|---|---|---|---|
| Company | | | | |
| Address | | | | |
| Contact Person | Name: | Tel: | Fax: | Email: |

**Chemical Usage Data**

| Operation | Chemical | | Use √-yes ×-no | Usage Rate (% on pulp unless otherwise noted) | verify | Water Content (%) (supplier only) | verify | Use Mode S – slug C – continuous | verify | Fraction Retained by Product (%) (if available) | verify |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pulping | surfactants/repulping aids | | | 0.2-2.0% | | | | C | | | |
| | sodium silicate | | | 2.0-4.0% | | | | C | | | |
| | dispersing agents | | | 0.1-0.5% | | | | C | | | |
| Deinking | deinking aids | | | 0.1-1.0% | | | | C | | | |
| | soap/fatty acids | | | 0.5-3.0% | | | | C | | | |
| | boilouts | | | 1-8% | | | 50-80 | S | | | |
| | settling aids | coagulants | | 5-100 ppm on volume | | | | C | | | |
| | | flocculants | | 0.1-5.0 ppm on volume | | | 0-80 | C | | | |
| Bleaching | hydrogen peroxide ($H_2O_2$ or $Na_2O_2$) | | | 1.0-2.0% | | | | C | | | |
| | sodium hydroxide (NaOH) | | | 3.0-5.0% | | | | C | | | |
| | sodium silicate | | | 2.0-4.0% | | | | C | | | |
| | chelating agents/sequestrants | | | 0.1-2.0% | | | | C | | | |
| | hydrosulfites | | | 0.5-1.0% | | | | C | | | |
| | chlorine | | | 0.5-3.0% | | | | C | | | |
| Paper Making | sizes | | | 0.05-1.0% | | | 50-90 | C | | 10-30% | |
| | wet strength agents | | | 0.25-2.0% | | | | C | | 70-90% | |
| | dry strength agents | | | 0.05-0.75% | | | | C | | | |
| | dyes/dye fixatives/fluorescent whites | | | 0.01-1.0% | | | | C | | 40-95% | |
| | corrosion inhibitors | | | 0.05-0.5% | | | | C | | | |
| | retention/drainage aids (saveall polymers) | coagulants | | 5-100 ppm on volume | | | | C | | 70-90% | |
| | | flocculants | | 0.1-5.0 ppm on volume | | | 0-80 | C | | 70-90% | |
| | | micro-particle system | | 0.5-2.0% on volume | | | | C | | 70-90% | |
| | barrier chemistry | | | no data | | | | C | | | |
| | formation aids | | | 0.2-0.3% | | | | C | | | |
| | charge neutralization (coagulants) | | | 5-100 ppm | | | | C | | 70-90% | |
| | chelants | | | 0.4-0.8% | | | | C | | | |

| Operation | Chemical | | Use √-yes ×-no | Usage Rate (% on pulp unless otherwise noted) | | Water Content (%) (supplier only) | | Use Mode S – slug C – continuous | | Fraction Retained by Product (%) (if available) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | verify | | verify | | verify | | verify |
| | antiskid agents | | | no data | | | | C | | | |
| | emulsifiers | | | 0.05-5% | | | | C | | | |
| | foam control | | | 0.0125-0.05% | | | 20-90 | C | | 0% | |
| | pitch/stickies control | | | 0.125-1.25% | | | 0-90 | C | | | |
| | felt cleaning chemicals | | | 200-800 ppm on shower water | | | 0-75 | C | | | |
| | boilouts/cleaners | | | 1-8% | | | 50-80 | S | | | |
| | microbiological control | | | 1-50 ppm on chest volume | | | 60-90 | S or C | | 0% | |
| | latex | | | 2% | | | | C | | | |
| | fillers (PCC, GCC, $TIO_2$) | | | 21% | | | | C | | | |
| Recovery and Power Boilers | air pollution control (polymer dispersant) | | | 5-10 ppm on scrubber liquid | | | | C | | 0% | |
| | condensate treatment (amines) | | | 2-4 ppm on steam | | | | C | | 0% | |
| | boiler water treatment | | | 0.5-10 ppm on steam | | | | C | | 0% | |
| | scale control | | | 10-100 ppm on steam | | | | C | | 0% | |
| | corrosion inhibitors (sulphites) | | | 1-5 ppm on steam | | | | C | | 0% | |
| Water Treatment | corrosion inhibitors | | | 0.1-5 ppm on water | | | | C | | | |
| | microbiological control (chlorine or hypochlorite) | | | to positive residue at 0.2 ppm | | | 60-90 | S or C | | | |
| | scale control | | | 10-100 ppm on water | | | | C | | | |
| | settling aids | coagulants | | 5-100 ppm on water | | | | C | | | |
| | | flocculants | | 0.1-5.0 ppm on water | | | 0-80 | C | | | |
| Wastewater Treatment | settling aids | coagulants | | 5-100 ppm on water | | | | C | | 0% | |
| | | flocculants | | 0.1-5.0 ppm on water | | | 0-80 | C | | 0% | |
| | foam control | | | 2-25 ppm on volume | | | 0-90 | C | | 0% | |
| | nutrients | | | 2-5 ppm on volume | | | | S | | 0% | |
| | sludge conditioners (flocculants) | | | 0.1-10 ppm on volume | | | | C | | 0% | |
| | odor control | | | 5-150 ppm on volume | | | | C | | 0% | |
| | color control (coagulants) | | | 200 ppm on volume | | | | C | | 0% | |

# Appendix F – Questionnaire Designed for Site Visit of Pulp and Paper Mills

Updated October 21, 2002

**Company Information**

| | | | | |
|---|---|---|---|---|
| Company | | | | |
| Address | | | | |
| Contact | | Tel: | Fax: | Email: |

**Container Data for Pulp and Paper Mills**

| Container Type | Container Size | Residue | On-site Cleaning (yes or no) | Fate of Container |
|---|---|---|---|---|
| Paper bag | | | | |
| Super sac | | | | |
| Pail | 5 gal (i.d. = 12") | | | |
| Drum | 45 gal (i.d. = 24") | | | |
| Tote | 1000-1600 litres (42"×42" cross section) | | | |
| Tanktruck | 4000 imperial gal | | | |
| Rail car | | | | |
| Others (specify) | | | | |

**Data about solid waste and air emissions**

Are relevant reports available?

**Classification of Chemicals Used at Pulp and Paper Mills**

| Code | Class | Chemistry | Application |
|---|---|---|---|
| 1 | Air pollution control | wetting agents used in boiler & scrubber | |
| 2 | Bleaching chemicals | | bleaching |
| 3 | Boiler & cooling water treatment | | bark boiler |
| 4 | Boilout chemicals | same chemistry as belt conditioners/cleaners, but used as slug | pulp machine |
| 5 | Chip penetrants | | digester |
| 6 | Contaminant control | control for stickies, pitches, adhesives, etc. | brown stock washing, bleaching, pulp machine |
| 7 | Corrosion control | filming agents & phosphates | pulp machine |
| 8 | Water treatment | chlorine, etc. | raw water treatment |
| 9 | Dyes & fixatives | | |
| 10 | Felt conditioners/cleaners | used in both continuous & slug modes | pulp machine, pulp drying |
| 11 | Fillers/additives | including coating agents & pigments | |
| 12 | Foam control | water & oil-based | brown stock washing, pulp machine |
| 13 | Microbiological control | biocides | pulp machine |
| 14 | Oxygen delignification | $O_2$, NaOH, $MgSO_4$ | oxygen delignification |
| 15 | pH control | | raw water treatment |
| 16 | Retention/drainage aids | | |
| 17 | Deinking agents | dispersants & soaps | |
| 18 | Settling aids | used for wastewater, deinking, & green liquor | green liquor clarifier, white liquor clarifier, raw water treatment, primary & secondary wastewater treatment |
| 19 | Scale control | | digester, evaporator, bleaching |
| 20 | Sizing agents | internal & external such as starch | |
| 21 | Wet strength agents | | |
| 22 | Dry strength agents | | |
| 23 | Washing aids | | brown stock washing |
| 24 | Flotation aids | | |
| 25 | Antiskid agents | | |
| 26 | Lime mud dewatering aids | recovery additives | lime mud washer |
| 27 | Nutrients | bioaugmentation | |
| 28 | Odor control | | |
| 29 | Release aids | | |
| 30 | Creping aids | | |
| 31 | Others (specify) | | |

## Kraft Pulp Mills

**Facility Data**

| | | | | |
|---|---|---|---|---|
| Product (check one or more) | ❑ market pulp | ❑ turpentine | ❑ tall oil | ❑ others (specify): |
| Production (tonne/yr) | | | | |
| Raw material (check one or more) | ❑ roundwood (hardwood) | ❑ roundwood (softwood) | | ❑ others (specify): |
| | ❑ wood chips (hardwood) | ❑ wood chips (softwood) | | |
| Total effluent discharge | | | | |
| Number of operation days per year | | | | |

**Process Scheme**

Identify major deviations from a standard scheme provided next page.

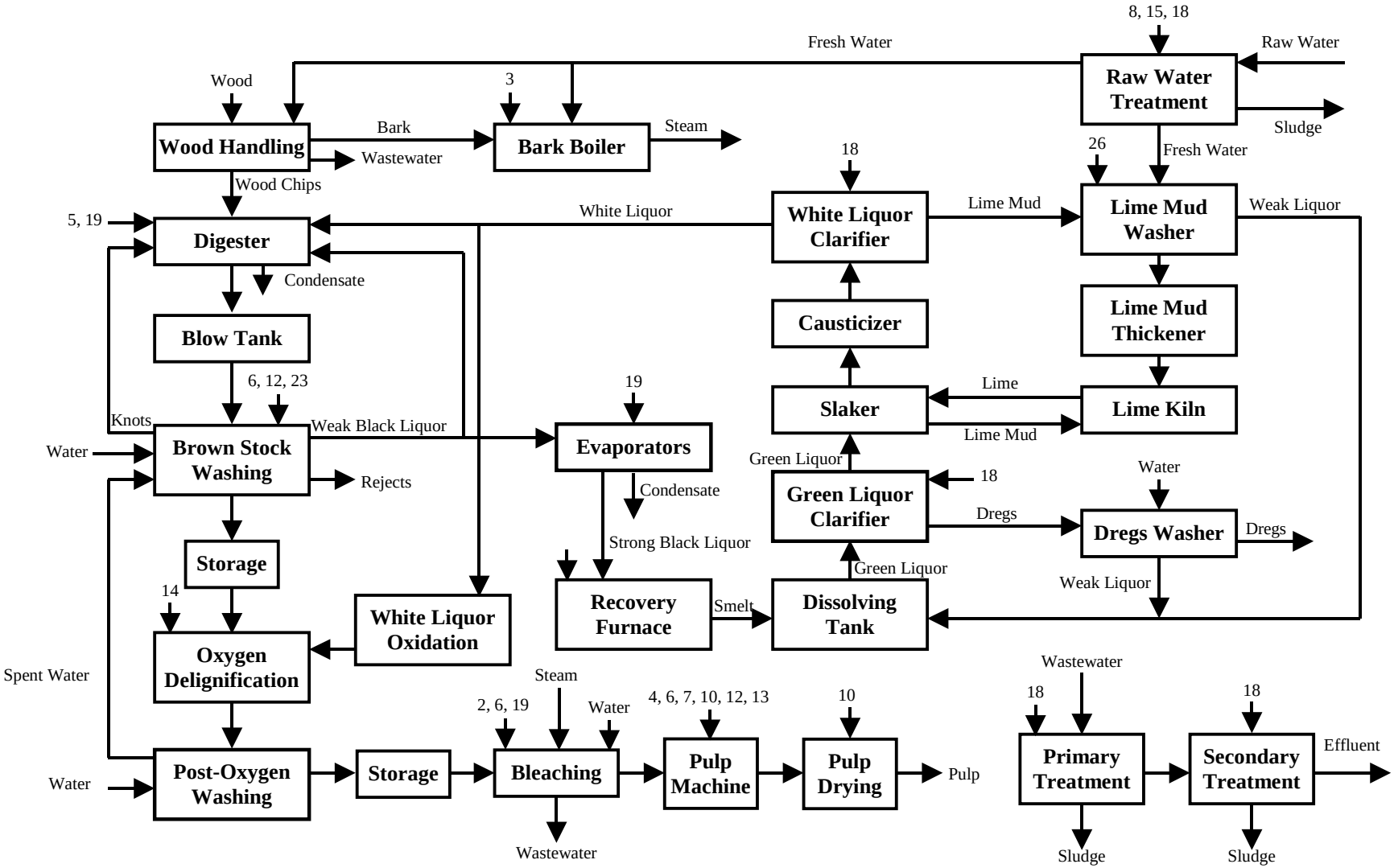


**Figure F.1 – Standard Process for Non-integrated Bleached Kraft Pulp Mills**

**Chemical Usage Data for Kraft Pulp Mills**

| Operation | Chemical | Consumption (kg/t of pulp) | Water Content (%) | Application Mode (slug or continuous) | Amount Retained by Product (%) | Container Type* | Note |
|---|---|---|---|---|---|---|---|
| Wood handling | | | | | | | |
| Digestion | cooking aids | | | | | | |
| | digester boilouts | | | | | | |
| | scale control | | | | | | |
| Brown Stock Washing | foam control | | | | | | |
| | wash aids | | | | | | |
| | drainage aids | | | | | | |
| | pitch control | | | | | | |
| Chemical Recovery | makeup sodium sulphate ($Na_2SO_4$) | | | | | | |
| | makeup caustic soda (NaOH) | | | | | | |
| | makeup soda ash ($Na_2CO_3$) | | | | | | |
| | lime (CaO) | | | | | | |
| | boilouts | | | | | | |
| | clarification aids | | | | | | |
| | scale control | | | | | | |
| | lime mud dewatering aids | | | | | | |
| | cleaners | | | | | | |
| | tall oil separation & acidulation aids | | | | | | |
| | turpentine separation aids | | | | | | |
| Delignification | oxygen | | | | | | |
| | magnesium sulphate ($MgSO_4$) | | | | | | |
| Bleaching | chlorine ($Cl_2$) | | | | | | |
| | hypochlorite ($Ca(OCl)_2$ or NaOCl) | | | | | | |
| | chlorine oxide ($ClO_2$) | | | | | | |
| | sodium hydroxide (NaOH) | | | | | | |
| | oxygen ($O_2$) | | | | | | |
| | hydrogen peroxide | | | | | | |
| | sodium chlorate | | | | | | |
| | peracetic acid | | | | | | |
| | potassium chlorate | | | | | | |
| Bleaching | bleaching enzymes | | | | | | |
| | boilouts | | | | | | |
| | catalase control | | | | | | |
| | pitch control | | | | | | |

| Operation | Chemical | Consumption (kg/t of pulp) | Water Content (%) | Application Mode (slug or continuous) | Amount Retained by Product (%) | Container Type* | Note |
|---|---|---|---|---|---|---|---|
| Bleaching | deposit (scale) control | | | | | | |
| Pulp Machine | microbiological control | | | | | | |
| | pitch control | | | | | | |
| | foam control | | | | | | |
| | felt conditioning | | | | | | |
| | boilouts | | | | | | |
| | retention aids | | | | | | |
| Water Treatment | corrosion inhibitors | | | | | | |
| | scavengers | | | | | | |
| | passivators | | | | | | |
| | microbiological control | | | | | | |
| | deposit (scale) control | | | | | | |
| | coagulants & flocculants | | | | | | |
| | metal removal | | | | | | |
| | cleaners | | | | | | |
| Wastewater Treatment | coagulants & flocculants | | | | | | |
| | metal removal | | | | | | |
| | foam control | | | | | | |
| | nutrients | | | | | | |
| | boilouts | | | | | | |
| | sludge conditioners | | | | | | |
| | biocides | | | | | | |
| | odor control | | | | | | |
| | color control | | | | | | |

*Container type: paper bag, super sac, pail, drum, tote, tanktruck, rail car, etc.

## Paper Mills

**Facility Data**

| | | |
|---|---|---|
| Product (check one or more) | ❑ paper | ❑ others (specify): |
| Production (tonne/yr) | | |
| Raw material (check one or more) | ❑ pulp | ❑ others (specify): |
| Total effluent discharge | | |
| Number of operation days per year | | |

**Process Scheme**

Identify major deviations from a standard scheme provided next page.

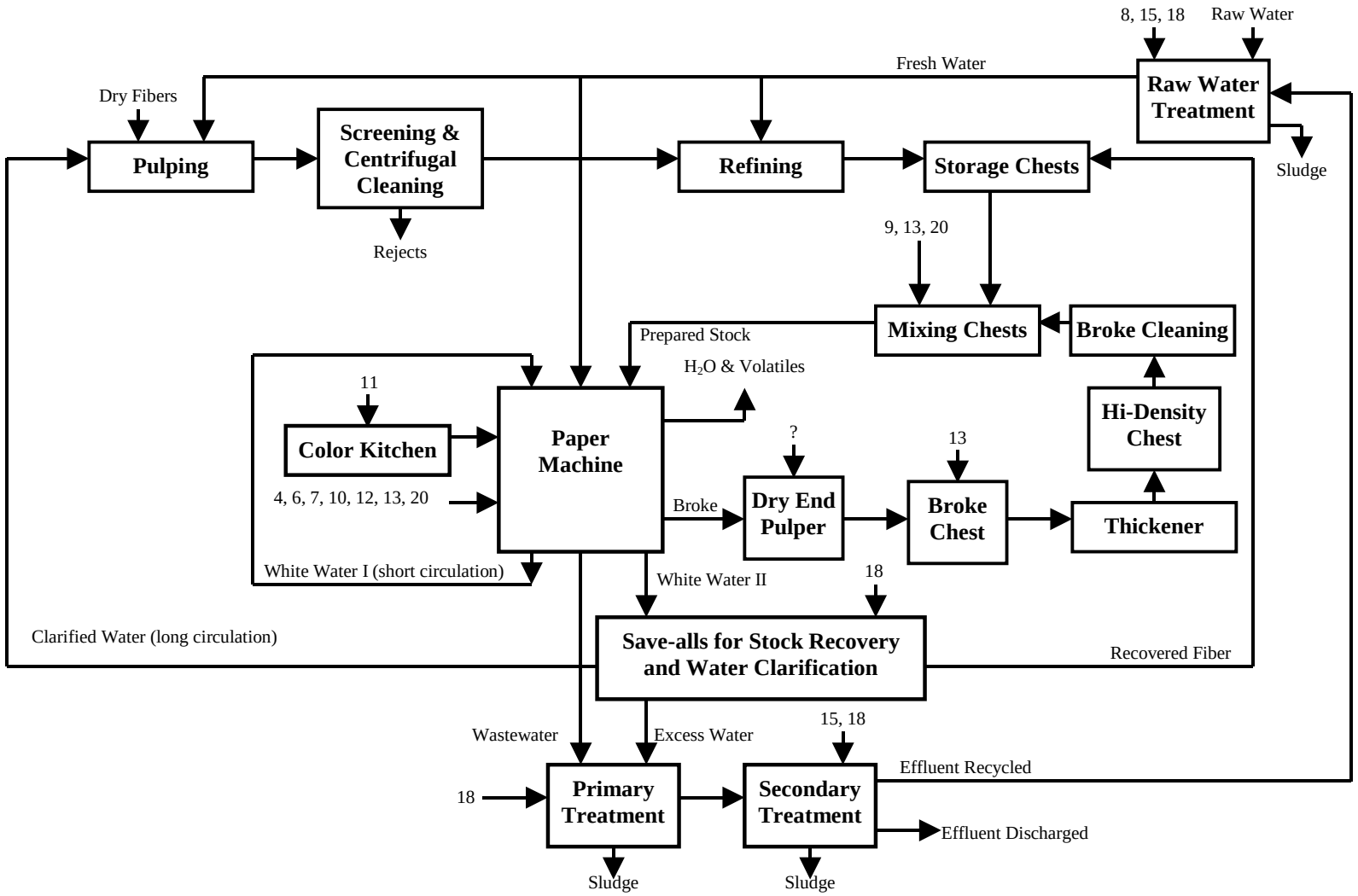


**Figure F.2 – Standard Process for Non-integrated Paper Mills**

**Chemical Usage Data for Paper Mills**

| Operation | Chemical | Consumption (kg/t of pulp) | Water Content (%) | Application Mode (slug or continuous) | Amount Retained by Product (%) | Container Type* | Note |
|---|---|---|---|---|---|---|---|
| Paper Making | sizes | | | | | | |
| | wet strength agents | | | | | | |
| | dry strength agents | | | | | | |
| | dyes | | | | | | |
| | dye fixatives | | | | | | |
| | fluorescent whites | | | | | | |
| | retention aids (flocculating aids) | | | | | | |
| | drainage aids | | | | | | |
| | formation aids | | | | | | |
| | charge neutralization | | | | | | |
| | fillers | | | | | | |
| | chelants | | | | | | |
| | antiskid agents | | | | | | |
| | emulsifiers | | | | | | |
| | defoamers | | | | | | |
| | deposit (scale) control | | | | | | |
| Paper Machine | pitch control | | | | | | |
| | boilouts | | | | | | |
| | cleaners | | | | | | |
| | biocides | | | | | | |
| | microbiological control | | | | | | |
| | boilouts | | | | | | |
| | catalase control | | | | | | |
| | pitch control | | | | | | |
| | deposit (scale) control | | | | | | |
| Water Treatment | corrosion inhibitors | | | | | | |
| | scavengers | | | | | | |
| | passivators | | | | | | |
| | microbiological control | | | | | | |
| | deposit (scale) control | | | | | | |
| | coagulants & flocculants | | | | | | |
| | metal removal | | | | | | |
| | cleaners | | | | | | |

| Operation | Chemical | Consumption (kg/t of pulp) | Water Content (%) | Application Mode (slug or continuous) | Amount Retained by Product (%) | Container Type* | Note |
|---|---|---|---|---|---|---|---|
| Wastewater Treatment | coagulants & flocculants | | | | | | |
| | metal removal | | | | | | |
| | foam control | | | | | | |
| | nutrients | | | | | | |
| | boilouts | | | | | | |
| | sludge conditioners | | | | | | |
| | biocides | | | | | | |
| | odor control | | | | | | |
| | color control | | | | | | |

*Container type: paper bag, super sac, pail, drum, tote, tanktruck, rail car, etc.

## Recovered Paper Mills

**Facility Data**

| | | |
|---|---|---|
| Product (check one or more) | ❑ newsprint | ❑ others (specify): |
| Production (tonne/yr) | | |
| Raw material (check one or more) | ❑ recovered paper | ❑ others (specify): |
| Total effluent discharge | | |
| Number of operation days per year | | |

**Process Scheme**

Identify major deviations from a standard scheme provided next page.

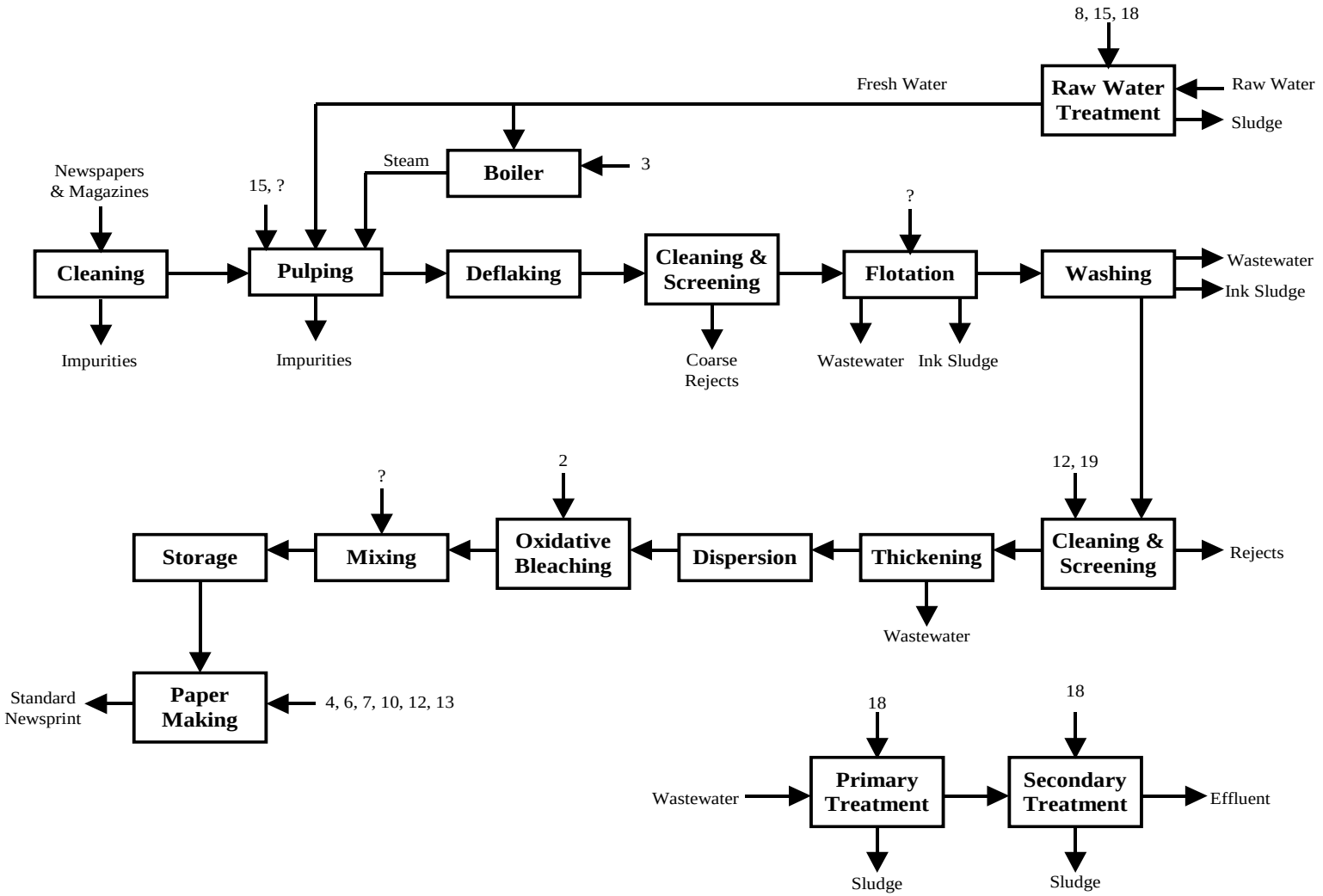


**Figure F.3 – Standard Process for Recovered Paper Mills with Deinking**

**Chemical Usage Data for Recovered Paper Mills**

| Operation | Chemical | Consumption (kg/t of pulp) | Water Content (%) | Application Mode (slug or continuous) | Amount Retained by Product (%) | Container Type* | Note |
|---|---|---|---|---|---|---|---|
| Pulping | sodium hydroxide (NaOH) | | | | | | |
| | surfactants | | | | | | |
| | repulping aids | | | | | | |
| | hydrogen peroxide | | | | | | |
| | sodium silicate | | | | | | |
| | soap/fatty acids | | | | | | |
| | dispersing agents | | | | | | |
| | chelating agents | | | | | | |
| Deinking | lime (CaO) | | | | | | |
| | deinking aids | | | | | | |
| | boilouts | | | | | | |
| | coagulants & flocculants | | | | | | |
| Bleaching | hydrogen peroxide ($H_2O_2$) | | | | | | |
| | sodium hydroxide (NaOH) | | | | | | |
| | sodium silicate | | | | | | |
| | chelating agents (EDTA) | | | | | | |
| | oxygen ($O_2$) | | | | | | |
| | ozone ($O_3$) | | | | | | |
| Paper Making | sizes | | | | | | |
| | wet strength agents | | | | | | |
| | dry strength agents | | | | | | |
| | dyes | | | | | | |
| | dye fixatives | | | | | | |
| | fluorescent whites | | | | | | |
| | retention aids (flocculating aids) | | | | | | |
| | drainage aids | | | | | | |
| | formation aids | | | | | | |
| | charge neutralization | | | | | | |
| | fillers | | | | | | |
| | chelants | | | | | | |
| | antiskid agents | | | | | | |
| | emulsifiers | | | | | | |
| | defoamers | | | | | | |
| | deposit (scale) control | | | | | | |

| Operation | Chemical | Consumption (kg/t of pulp) | Water Content (%) | Application Mode (slug or continuous) | Amount Retained by Product (%) | Container Type* | Note |
|---|---|---|---|---|---|---|---|
| Paper Making | pitch control | | | | | | |
| | boilouts | | | | | | |
| | cleaners | | | | | | |
| | biocides | | | | | | |
| | microbiological control | | | | | | |
| Water Treatment | corrosion inhibitors | | | | | | |
| | scavengers | | | | | | |
| | passivators | | | | | | |
| | microbiological control | | | | | | |
| | deposit (scale) control | | | | | | |
| | coagulants & flocculants | | | | | | |
| | metal removal | | | | | | |
| | cleaners | | | | | | |
| Wastewater Treatment | coagulants & flocculants | | | | | | |
| | metal removal | | | | | | |
| | foam control | | | | | | |
| | nutrients | | | | | | |
| | boilouts | | | | | | |
| | sludge conditioners | | | | | | |
| | biocides | | | | | | |
| | odor control | | | | | | |
| | color control | | | | | | |

*Container type: paper bag, super sac, pail, drum, tote, tanktruck, rail car, etc.

# Appendix G – Derivation of Conversion Factors for Chemical Use Level at Kraft Pulp Mills

In estimating chemical releases from kraft pulp mills, data on chemical use level must be converted to mass percentage on pulp produced if it is provided on a different basis. The conversion is made through the equation

$$L_{use} = F_{conv} D_{use}$$

where

- $L_{use}$: use level for a type of chemicals expressed in % on pulp
- $F_{conv}$: conversion factor from a different basis to % on pulp
- $D_{use}$: data on use level for a type of chemicals based on a quantity different from % on pulp

Provided below are conversion factors determined for chemical use level commonly expressed on a basis other than mass percentage on pulp produced.

## G.1 – Conversion Factor for Boilouts in Digestion

At time of this writing, no data is available for use level of boilouts in digestion.

## G.2 – Conversion Factor for Scale Control in Digestion

Scale control used in digestion is expressed in terms of ppm on digester liquor and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on digester liquor, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ digester\ liquor}$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ digester\ liquor} \times liquor\ to\ wood\ \ ratio \times \frac{1}{pulp\ \ yield}$$

In digestion, the liquor-to-wood ratio is normally 4:1 (Minor, 1992) and the pulp yield for bleachable grades is 45% (Green and Hough, 1992, p.125). Based on these values, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ digester\ liquor} \times liquor\ to\ wood\ \ ratio \times \frac{1}{pulp\ \ yield}$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ digester\ liquor} \times \frac{4\ tonne\ of\ \ digester\ liquor}{tonne\ of\ \ wood} \times \frac{tonne\ of\ \ wood}{0.45\ tonne\ of\ \ pulp}$$

$$= \frac{8.89\ g\ of\ \ scale\ control}{tonne\ of\ \ pulp}$$

$$= \frac{8.89\ g\ of\ \ scale\ control}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 8.89 \times 10^{-4}\%$$

The conversion factor for scale control used in digestion is, therefore, determined to be

$$F_{conv} = 8.89 \times 10^{-4}\ (\%\ per\ \ ppm)$$

## G.3 – Conversion Factor for Boilouts in Brownstock Washing and Chemical Recovery

Boilouts used in brownstock washing and chemical recovery are expressed in terms of % on volume treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ \ boilouts}{m^3\ \ of\ \ volume\ treated}$$

$$= \frac{10\ kg\ of\ \ boilouts}{m^3\ \ of\ \ volume\ treated} \times \frac{volume\ treated \times application\ \ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of pulp produced per day) must be known. At time of this writing, the three values are not available.

## G.4 – Conversion Factor for Clarification Aids in Chemical Recovery

Clarification aids used in chemical recovery are expressed in terms of ppm on a sum of white and green liquor and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on white and green liquor, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ white\ and\ \ green\ liquor}$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ white\ and\ \ green\ liquor} \times generation\ of\ \ white\ and\ \ green\ liquor$$

White and green liquor are generated at 3.9 and 4.8 $m^3$ per tonne of pulp, respectively (Green and Hough, 1992, p.124). When the combined total of 8.7 $m^3$ per tonne of pulp is used, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ scale\ control}{tonne\ of\ white\ and\ green\ liquor} \times generation\ of\ white\ and\ green\ liquor$$

$$= \frac{1\ g\ of\ scale\ control}{tonne\ of\ white\ and\ green\ liquor} \times \frac{8.7\ m^3\ of\ white\ and\ green\ liquor}{tonne\ of\ pulp} \times density$$

$$= \frac{1\ g\ of\ scale\ control}{tonne\ of\ white\ and\ green\ liquor} \times \frac{8.7\ m^3\ of\ white\ and\ green\ liquor}{tonne\ of\ pulp} \times \frac{1\ tonne}{m^3}$$

$$= \frac{8.7\ g\ of\ scale\ control}{tonne\ of\ pulp}$$

$$= \frac{8.7\ g\ of\ scale\ control}{tonne\ of\ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 8.7 \times 10^{-4}\%$$

In the above conversion, the density of white and green liquor is assumed to be 1 tonne/$m^3$. The conversion factor for clarification aids used in chemical recovery is, therefore, determined to be

$$F_{conv} = 8.7 \times 10^{-4}\ (\%\ per\ ppm)$$

## G.5 – Conversion Factor for Scale Control in Brownstock Washing and Chemical Recovery

Scale control used in brownstock washing and chemical recovery is expressed in terms of ppm on black liquor and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on black liquor, i.e.,

$$1\ ppm = \frac{1\ g\ of\ scale\ control}{tonne\ of\ black\ liquor}$$

$$= \frac{1\ g\ of\ scale\ control}{tonne\ of\ black\ liquor} \times black\ liquor\ generation$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ black\ liquor} \times \frac{solids\ \ generation}{average\ solids\ content\ of\ \ black\ liquor}$$

As an approximation, black liquor is assumed to contain 40% solids on average as it is concentrated from 14-17% to 60-80% solids through an evaporation process (Green and Hough, 1992, p.2; USEPA, 1995, p.27; Grace et al., 1989, p.474). The solids generation rate is assumed to be 1.67 tonne of black liquor solids per tonne of pulp produced according to H. A. Simons (H.A. Simons Ltd., 1995, p.4-67). Based on these assumptions, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ black\ liquor} \times \frac{solids\ \ generation}{average\ solids\ content\ of\ \ black\ liquor}$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ black\ liquor} \times \frac{1.67\ tonne\ of\ \ solids\ \ per\ tonne\ of\ \ pulp}{40\%}$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ black\ liquor} \times \frac{tonne\ of\ \ black\ liquor}{0.40\ tonne\ of\ \ solids} \times \frac{1.67\ tonne\ of\ \ solids}{tonne\ of\ \ pulp}$$

$$= \frac{4.175\ g\ of\ \ scale\ control}{tonne\ of\ \ pulp}$$

$$= \frac{4.175\ g\ of\ \ scale\ control}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 4.18 \times 10^{-4}\%$$

The conversion factor for scale control used in brownstock washing and chemical recovery is, therefore, determined to be

$$F_{conv} = 4.18 \times 10^{-4}\ (\%\ per\ \ ppm)$$

## G.6 – Conversion Factor for Lime Mud Dewatering Aids in Chemical Recovery

Lime mud dewatering aids used in chemical recovery are expressed in terms of lb/t on lime and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 lb/t on lime, i.e.,

$$1\ lb/t = \frac{1\ lb\ of\ \ lime\ mud\ \ dewatering\ \ aids}{ton\ of\ \ lime}$$

$$= \frac{1\ lb\ of\ \ lime\ mud\ \ dewatering\ \ aids}{ton\ of\ \ lime} \times \frac{ton}{2000\ lb} \times \frac{lb/kg}{lb/kg}$$

$$= \frac{1\ kg\ of\ \ lime\ mud\ \ dewatering\ \ aids}{2000\ kg\ of\ \ lime}$$

The quantity of lime required for bleachable grades is 324 kg per tonne of pulp produced (Green and Hough, 1992, p.125). When this value is used for the conversion, the 1 lb/t use level becomes

$$1\ lb/t = \frac{1\ kg\ of\ \ lime\ mud\ \ dewatering\ \ aids}{2000\ kg\ of\ \ lime} \times lime\ requirement$$

$$= \frac{1\ kg\ of\ \ lime\ mud\ \ dewatering\ \ aids}{2000\ kg\ of\ \ lime} \times \frac{324\ kg\ of\ \ lime}{tonne\ of\ \ pulp}$$

$$= \frac{0.162\ kg\ of\ \ lime\ mud\ \ dewatering\ \ aids}{tonne\ of\ \ pulp} \times \frac{tonne}{1000\ kg} \times 100\%$$

$$= 0.0162\%$$

The conversion factor for lime mud dewatering aids used in chemical recovery is, therefore, determined to be

$$F_{conv} = 0.0162\ (\%\ \ per\ lb/t)$$

## G.7 – Conversion Factor for Tall Oil Separation and Acidulation Aids in Chemical Recovery

Tall oil separation and acidulation aids used in chemical recovery are expressed in terms of ppm on quantity of tall oil and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on tall oil, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ tall\ oil\ \ separation\ and\ \ acidulation\ aids}{tonne\ of\ \ tall\ oil}$$

$$= \frac{1\ g\ of\ \ tall\ oil\ \ separation\ and\ \ acidulation\ aids}{tonne\ of\ \ tall\ oil} \times tall\ \ oil\ \ yield \times \frac{1}{pulp\ \ yield}$$

The tall oil yield for Canadian mills was found at 23 lb per ton of wood (Green and Hough, 1992, p.45) and the pulp yield at 45% (Green and Hough, 1992, p.125). Based on these values, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ tall\ oil} \times tall\ oil\ yield \times \frac{1}{pulp\ yield}$$

$$= \frac{1\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ tall\ oil} \times \frac{23\ lb\ of\ tall\ oil}{ton\ of\ wood} \times \frac{ton\ of\ wood}{0.45\ ton\ of\ pulp}$$

$$= \frac{1\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ tall\ oil} \times \frac{51.11\ lb\ of\ tall\ oil}{ton\ of\ pulp}$$

$$= \frac{1\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ tall\ oil} \times \frac{51.11\ lb\ of\ tall\ oil}{ton\ of\ pulp} \times \frac{ton}{2000\ lb}$$

$$= \frac{1\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ tall\ oil} \times \frac{0.0256\ lb\ of\ tall\ oil}{lb\ of\ pulp}$$

$$= \frac{1\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ tall\ oil} \times \frac{0.0256\ lb\ of\ tall\ oil}{lb\ of\ pulp} \times \frac{lb/tonne}{lb/tonne}$$

$$= \frac{1\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ tall\ oil} \times \frac{0.0256\ tonne\ of\ tall\ oil}{tonne\ of\ pulp}$$

$$= \frac{0.0256\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ pulp}$$

$$= \frac{0.0256\ g\ of\ tall\ oil\ separation\ and\ acidulation\ aids}{tonne\ of\ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 2.56 \times 10^{-6}\%$$

The conversion factor for tall oil separation and acidulation aids used in chemical recovery is, therefore, determined to be

$$F_{conv} = 2.56 \times 10^{-6}\ (\%\ per\ ppm)$$

## G.8 – Conversion Factor for Turpentine Separation Aids in Chemical Recovery

Turpentine separation aids used in chemical recovery are expressed in terms of ppm on quantity of turpentine and the conversion factor can be determined by deriving the use

level expressed in terms of % on pulp from 1 ppm on turpentine, i.e.,

$$1\ ppm = \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine}$$

$$= \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times turpentine\ production \times turpentine\ density$$

Turpentine was produced at 0.2-0.3 gallons per ton of pulp from five U. S. mills (Marlewski, 1984) and turpentine density is 62.2 lb/gal (Drew et al., 1971). Assuming an average turpentine production rate of 0.25 gallons per ton of pulp, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times turpentine\ production \times turpentine\ density$$

$$= \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times \frac{0.25\ gal\ of\ turpentine}{ton\ of\ pulp} \times \frac{62.2\ lb}{gal}$$

$$= \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times \frac{15.55\ lb\ of\ turpentine}{ton\ of\ pulp}$$

$$= \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times \frac{15.55\ lb\ of\ turpentine}{ton\ of\ pulp} \times \frac{ton}{2000\ lb}$$

$$= \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times \frac{0.007775\ lb\ of\ turpentine}{lb\ of\ pulp}$$

$$= \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times \frac{0.007775\ lb\ of\ turpentine}{lb\ of\ pulp} \times \frac{lb/tonne}{lb/tonne}$$

$$= \frac{1\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ turpentine} \times \frac{0.007775\ tonne\ of\ turpentine}{tonne\ of\ pulp}$$

$$= \frac{0.007775\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ pulp}$$

$$= \frac{0.007775\ g\ of\ turpentine\ separation\ aids}{tonne\ of\ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 7.78 \times 10^{-7}\%$$

The conversion factor for turpentine separation aids used in chemical recovery is, therefore, determined to be

$$F_{conv} = 7.78 \times 10^{-7} \ (\%\ per\ \ ppm)$$

## G.9 – Conversion Factor for Enzymes in Bleaching

Enzymes used in bleaching is expressed in terms of mL/tonne of pulp and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 mL/tonne of pulp, i.e.,

$$1\ mL/tonne\ of\ \ pulp = \frac{1\ mL\ of\ \ enzymes}{tonne\ of\ \ pulp}$$

$$= \frac{1\ mL\ of\ \ enzymes}{tonne\ of\ \ pulp} \times \frac{m^3}{1 \times 10^6\ mL} \times enzyme\ density$$

Assuming the enzyme density is 1 tonne/$m^3$, the use level at 1 mL/tonne of pulp becomes

$$1\ mL/tonne\ of\ \ pulp = \frac{1\ mL\ of\ \ enzymes}{tonne\ of\ \ pulp} \times \frac{m^3}{1 \times 10^6\ mL} \times enzyme\ density$$

$$= \frac{1\ mL\ of\ \ enzymes}{tonne\ of\ \ pulp} \times \frac{m^3}{1 \times 10^6\ mL} \times \frac{1\ tonne}{m^3}$$

$$= \frac{1 \times 10^{-6}\ \ tonne\ of\ \ enzymes}{tonne\ of\ \ pulp}$$

$$= \frac{1 \times 10^{-6}\ \ tonne\ of\ \ enzymes}{tonne\ of\ \ pulp} \times 100\%$$

$$= 1 \times 10^{-4}\%$$

The conversion factor for enzymes used in bleaching is, therefore, determined to be

$$F_{conv} = 1.0 \times 10^{-4} \ (\%\ per\ mL/tonne\ of\ \ pulp)$$

## G.10 – Conversion Factor for Boilouts in Bleaching

Boilouts used in bleaching are expressed in terms of % on volume treated and the

conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated}$$

$$= \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated} \times \frac{volume\ treated \times application\ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of pulp produced per day) must be known. At time of this writing, the three values are not available.

## G.11 – Conversion Factor for Scale Control in Bleaching

Scale control used in bleaching is expressed in terms of ppm and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm, i.e.,

$$1\ ppm = \frac{1\ g\ of\ scale\ control}{tonne\ of\ pulp\ suspension}$$

$$= \frac{1\ g\ of\ scale\ control}{tonne\ of\ pulp\ suspension} \times \frac{1}{solids\ content}$$

Pulp consistency (solids content) at a bleaching stage varies, depending upon bleaching agents used. As shown in Table G.1, pulp consistency ranges from 2.5 to 28% as different bleaching agents are used (Dence and Reeve, 1996, p.215-442). In other words, each tonne of pulp suspension consists of 25-280 kg of pulp and 720-975 kg of water.

**Table G.1 – Pulp Consistency for Various Bleaching Agents**
(Dence and Reeve, 1996, p.215-442)

| **Bleaching** | **Pulp Consistency (%)** |
|---|---|
| Oxygen delignification | medium (10-14%) and high (20-28%) |
| Chlorine | low (2.5-4%), medium (8-15%) |
| Chlorine dioxide | low (3-4%), medium (9-16%) |
| Alkaline extraction | medium (8-12%) |
| Hydrogen peroxide | medium (10%) |
| Hypochlorite | medium consistency (9-14%) |

As an approximation, a medium consistency value at 10% is assumed for pulp suspension being bleached. The use level at 1 ppm becomes

$$1\ ppm = \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content}$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ pulp\ suspension} \times \frac{1}{10\%}$$

$$= \frac{1\ g\ of\ \ scale\ control}{tonne\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{0.10\ tonne\ of\ \ pulp}$$

$$= \frac{1\ g\ of\ \ scale\ control}{0.10\ tonne\ of\ \ pulp}$$

$$= \frac{1\ g\ of\ \ scale\ control}{0.10\ tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 1.0 \times 10^{-3}\%$$

The conversion factor for scale control used in bleaching is, therefore, determined to be

$$F_{conv} = 1.0 \times 10^{-3}\ (\%\ \ per\ \ ppm)$$

## G.12 – Conversion Factor for Microbiological Control at Pulp Machine

Microbiological control used at pulp machine is expressed in terms of % on chest volume and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on chest volume, i.e.,

$$1\%\ on\ chest\ volume = \frac{10\ kg\ of\ \ microbiological\ control}{m^3\ \ of\ \ chest\ volume}$$

$$= \frac{10\ kg\ of\ \ microbiological\ control}{m^3\ \ of\ \ chest\ volume} \times \frac{chest\ volume \times application\ \ frequency}{production\ rate}$$

In order to proceed with the above conversion, the chest volume ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of pulp produced per day) must be known. At time of this writing, the three values are not available.

## G.13 – Conversion Factor for Felt Conditioning at Pulp Machine

Felt conditioning used at pulp machine is expressed in terms of ppm on volume of shower water and the conversion factor can be determined by deriving the use level expressed in

terms of % on pulp from 1 ppm on shower water, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ felt\ conditioning}{m^3\ of\ \ shower\ water}$$

$$= \frac{1\ g\ of\ \ felt\ conditioning}{m^3\ of\ \ shower\ water} \times shower\ water\ requirement$$

As an approximation, the volume of shower water required for pulp machine is assumed to equal that required for paper machine. In the European Union, paper machines were reported to consume 5-20 $m^3$ of shower water per tonne of pulp for lubricating and cleaning fabrics and wet press felts (European Commission, 1999, p.326-327). Assuming an average rate at 15 $m^3$ of shower water per tonne of pulp for pulp machines, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ felt\ conditioning}{m^3\ of\ \ shower\ water} \times shower\ water\ requirement$$

$$= \frac{1\ g\ of\ \ felt\ conditioning}{m^3\ of\ \ shower\ water} \times \frac{15\ m^3\ of\ \ shower\ water}{tonne\ of\ \ pulp}$$

$$= \frac{15\ g\ of\ \ felt\ conditioning}{tonne\ of\ \ pulp}$$

$$= \frac{15\ g\ of\ \ felt\ conditioning}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 1.5 \times 10^{-3}\%$$

The conversion factor for felt conditioning used at pulp machines is, therefore, determined to be

$$F_{conv} = 1.5 \times 10^{-3}\ (\%\ per\ ppm)$$

## G.14 – Conversion Factor for Boilouts at Pulp Machine

Boilouts used at pulp machine are expressed in terms of % on volume treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ \ boilouts}{m^3\ of\ \ volume\ treated}$$

$$= \frac{10\ kg\ of\ \ boilouts}{m^3\ of\ \ volume\ treated} \times \frac{volume\ treated \times application\ \ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of pulp produced per day) must be known. At time of this writing, the three values are not available.

## G.15 – Conversion Factor for Retention Aids at Pulp Machine

Retention aids used at pulp machine are expressed in terms of ppm on volume of pulp suspension and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on pulp suspension, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ retention\ aids}{m^3\ of\ \ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ retention\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

The pulp consistency (solids content) at the feeding point of pulp machine is 0.5%, i.e., 0.005 tonne of pulp per tonne of pulp suspension (J. Jossinet, December 2002). Based on this data, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ retention\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ retention\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{0.5\%}$$

$$= \frac{1\ g\ of\ \ retention\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{0.005\ tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ retention\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times suspension\ density$$

$$= \frac{200\ g\ of\ \ retention\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times \frac{1\ tonne}{m^3}$$

$$= \frac{200\ g\ of\ \ retention\ aids}{tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ retention\ aids}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 0.02\%$$

In the above conversion, the density of pulp suspension is assumed to be 1 tonne/$m^3$. The conversion factor for retention aids used at pulp machine is, therefore, determined to be

$$F_{conv} = 0.02\ (\%\ \ per\ \ ppm)$$

## G.17 – Conversion Factor for Air Pollution Control in Recovery and Power Boilers

Air pollution control used in recovery and power boilers is expressed in terms of ppm on volume of scrubber liquid and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on scrubber liquid, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times liquid\ \ to\ gas\ ratio \times\ flue\ gas\ generation$$

Literature data is used to provide estimates for the liquid-to-gas ratio and the flue gas generation rate. H. A. Simons (1995, p.4-67) reported an actual flue gas flow of 198 $m^3$/s at 192$^o$C and 710 mmHg for a mill producing 1,000 tonne of pulp per day and liquid-to-gas ratio in a range of 0.54 to 3.21 L/$m^3$ for wet scrubbers. The actual flue gas flow is determined to be 17,107 $m^3$ per tonne of pulp and the liquid-to-gas ratio is assumed to have an average value of 2.0 L/$m^3$. Based on these estimates, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times liquid\ \ to\ gas\ ratio \times\ flue\ gas\ generation$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{2.0\ L\ of\ \ scrubber\ liquid}{m^3\ of\ \ flue\ gas} \times \frac{17107\ m^3\ of\ \ flue\ gas}{tonne\ of\ \ pulp}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{34214\ L\ of\ \ scrubber\ liquid}{tonne\ of\ \ pulp}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{34214\ L\ of\ \ scrubber\ liquid}{tonne\ of\ \ pulp} \times \frac{m^3}{1000\ L}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{34.214\ m^3\ of\ \ scrubber\ liquid}{tonne\ of\ \ pulp}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{34.214\ m^3\ of\ \ scrubber\ liquid}{tonne\ of\ \ pulp} \times liquid\ \ density$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{34.214\ m^3\ of\ \ scrubber\ liquid}{tonne\ of\ \ pulp} \times \frac{1\ tonne}{m^3}$$

$$= \frac{34.214\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ pulp}$$

$$= \frac{34.214\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 3.42 \times 10^{-3}\%$$

The conversion factor for air pollution control used in recovery and power boilers is, therefore, determined to be

$$F_{conv} = 3.42 \times 10^{-3}\ (\%\ \ per\ \ ppm)$$

## G.18 – Conversion Factor for Chemicals Based on Steam in Recovery and Power Boilers

Condensate treatment, boiler water treatment, scale control, and corrosion inhibitors used in recovery and power boilers are expressed in terms of ppm on quantity of steam and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on steam, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ based\ \ on\ steam}{tonne\ of\ \ steam}$$

$$= \frac{1\ g\ of\ \ chemicals\ based\ \ on\ steam}{tonne\ of\ \ steam} \times steam\ requirement$$

The quantity of steam required at kraft pulp mills was reported to be 6.5 tonne per tonne of pulp (Austin, 1984, p.619). Based on this data, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times steam\ requirement$$

$$= \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times \frac{6.5\ tonne\ of\ \ steam}{tonne\ of\ \ pulp}$$

$$= \frac{6.5\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ pulp}$$

$$= \frac{6.5\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 6.5 \times 10^{-4}\%$$

The conversion factor for chemicals based on steam and used in recovery and power boilers is, therefore, determined to be

$$F_{conv} = 6.5 \times 10^{-4}\ (\%\ per\ \ ppm)$$

## G.19 – Conversion Factor for Chemicals in Water Treatment

Chemicals used in water treatment include corrosion inhibitors, microbiological control, scale control, and settling aids. They are expressed in terms of ppm on volume of water treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on water, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water}$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times water\ consumption$$

In the European Union, the water consumption for non-integrated bleached kraft pulp mills was reported in the range of 15 to 100 $m^3$ per tonne of pulp (European Commission, 1999, p.32). Assuming an average water consumption rate of 60 $m^3$ per tonne of pulp, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times water\ consumption$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times \frac{60\ m^3\ \ of\ \ water}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 6.0 \times 10^{-3}\%$$

The conversion factor for chemicals used in water treatment is, therefore, determined to be

$$F_{conv} = 6.0 \times 10^{-3}\ (\%\ per\ \ ppm)$$

## G.20 – Conversion Factor for Chemicals in Wastewater Treatment

Chemicals used in wastewater treatment include settling aids, foam control, nutrients, sludge conditioners, odor control, and color control. They are expressed in terms of ppm on volume of wastewater treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on wastewater, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater}$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times wastewater\ \ generation$$

In the European Union, the water consumption for non-integrated bleached kraft pulp mills was reported in the range of 15 to 100 $m^3$ per tonne of pulp (European Commission, 1999, p.32). Assuming the wastewater generation equals the water consumption which averages at 60 $m^3$ per tonne of pulp, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times wastewater\ \ generation$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times \frac{60\ m^3\ \ of\ \ wastewater}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 6.0 \times 10^{-3}\%$$

The conversion factor for chemicals used in wastewater treatment is, therefore, determined to be

$$F_{conv} = 6.0 \times 10^{-3}\ (\%\ \ per\ \ ppm)$$

# Appendix H – Derivation of Conversion Factors for Chemical Use Level at Paper Mills

In estimating chemical releases from paper mills, data on chemical use level must be converted to mass percentage on pulp if it is provided on a different basis. The conversion is made through the equation

$$L_{use} = F_{conv} D_{use}$$

where

$L_{use}$: use level for a type of chemicals expressed in % on pulp
$F_{conv}$: conversion factor from a different basis to % on pulp
$D_{use}$: data on use level for a type of chemicals based on a quantity different from % on pulp

Provided below are conversion factors determined for chemical use level commonly expressed on a basis other than mass percentage on pulp.

## H.1 – Conversion Factor for Boilouts in Stock Preparation

Boilouts used in stock preparation are expressed in terms of % on volume treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated}$$

$$= \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated} \times \frac{volume\ treated \times application\ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

## H.2 – Conversion Factor for Chemicals Based on Volume in Stock Preparation

Chemicals used in stock preparation with use level expressed in terms of ppm on volume of pulp suspension include: 1) retention/drainage aids; and 2) charge control. The conversion factor for these chemicals can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on pulp suspension, i.e.,

$$1\ ppm = \frac{1\ g\ of\ chemicals}{m^3\ of\ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ chemicals}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

The pulp consistency (solids content) in stock preparation is 0.5 to 1.0%, i.e., 0.005 to 0.01 tonne of pulp per tonne of pulp suspension (J. Jossinet, December 2002). As a conservative approximation, the lower pulp consistency value at 0.5% is assumed and the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ chemicals}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{0.5\%}$$

$$= \frac{1\ g\ of\ \ chemicals}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{0.005\ tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ chemicals}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times suspension\ density$$

$$= \frac{200\ g\ of\ \ chemicals}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times \frac{1\ tonne}{m^3}$$

$$= \frac{200\ g\ of\ \ chemicals}{tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ chemicals}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 0.02\%$$

In the above conversion, the density of pulp suspension is assumed to be 1 tonne/$m^3$. The conversion factor for chemicals based on volume of pulp suspension and used in stock preparation is, therefore, determined to be

$$F_{conv} = 0.02\ (\%\ per\ \ ppm)$$

### H.3 – Conversion Factor for Microbiological Control in Stock Preparation

Microbiological control used in stock preparation is expressed in terms of % on chest volume and the conversion factor can be determined by deriving the use level expressed

in terms of % on pulp from 1% on chest volume, i.e.,

$$1\%\ on\ chest\ volume = \frac{10\ kg\ of\ \ microbiological\ control}{m^3\ of\ \ chest\ volume}$$

$$= \frac{10\ kg\ of\ \ microbiological\ control}{m^3\ of\ \ chest\ volume} \times \frac{chest\ volume \times application\ \ frequency}{production\ rate}$$

In order to proceed with the above conversion, the chest volume ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

### H.4 – Conversion Factor for Boilouts at Paper Machine

Boilouts used at paper machine are expressed in terms of % on volume treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ \ boilouts}{m^3\ of\ \ volume\ treated}$$

$$= \frac{10\ kg\ of\ \ boilouts}{m^3\ of\ \ volume\ treated} \times \frac{volume\ treated \times application\ \ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

### H.5 – Conversion Factor for Felt Cleaning at Paper Machine

Felt cleaning used at paper machines is expressed in terms of ppm on volume of shower water and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on shower water, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ felt\ cleaning}{m^3\ of\ \ shower\ water}$$

$$= \frac{1\ g\ of\ \ felt\ cleaning}{m^3\ of\ \ shower\ water} \times shower\ water\ requirement$$

In the European Union, paper machines were reported to consume 5-20 $m^3$ of shower

water per tonne of pulp for lubricating and cleaning fabrics and wet press felts (European Commission, 1999, p.326-327). Assuming an average rate at 15 $m^3$ of shower water per tonne of pulp for paper machines, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ felt\ cleaning}{m^3\ of\ \ shower\ water} \times shower\ water\ requirement$$

$$= \frac{1\ g\ of\ \ felt\ cleaning}{m^3\ of\ \ shower\ water} \times \frac{15\ m^3\ of\ \ shower\ water}{tonne\ of\ \ pulp}$$

$$= \frac{15\ g\ of\ \ felt\ cleaning}{tonne\ of\ \ pulp}$$

$$= \frac{15\ g\ of\ \ felt\ cleaning}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 1.5 \times 10^{-3}\%$$

The conversion factor for felt cleaning used at paper machine is, therefore, determined to be

$$F_{conv} = 1.5 \times 10^{-3}\ (\%\ per\ \ ppm)$$

## H.6 – Conversion Factor for Antiskid Agents at Paper Machine

Antiskid agents used at paper machine are expressed in terms of lb/t on paper and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 lb/t on paper, i.e.,

$$1\ lb/t = \frac{1\ lb\ of\ \ antiskid\ \ agents}{ton\ of\ \ paper}$$

$$= \frac{1\ lb\ of\ \ antiskid\ \ agents}{ton\ of\ \ paper} \times \frac{ton}{2000\ lb} \times \frac{lb/kg}{lb/kg}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ paper}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ paper} \times \frac{1\ kg\ of\ \ paper}{kg\ of\ \ pulp}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ pulp}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ pulp} \times 100\%$$

$$= 0.05\%$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The conversion factor for antiskid agents used at paper machine is, therefore, determined to be

$$F_{conv} = 0.05\ (\%\ \ per\ lb/t)$$

## H.7 – Conversion Factor for Microbiological Control at Paper Machine

Microbiological control used at paper machine is expressed in terms of % on chest volume and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on chest volume, i.e.,

$$1\%\ on\ chest\ volume = \frac{10\ kg\ of\ \ microbiological\ control}{m^3\ \ of\ \ chest\ volume}$$

$$= \frac{10\ kg\ of\ \ microbiological\ control}{m^3\ \ of\ \ chest\ volume} \times \frac{chest\ volume \times application\ \ frequency}{production\ rate}$$

In order to proceed with the above conversion, the chest volume ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

## H.8 – Conversion Factor for Saveall Polymers at Paper Machine

Saveall polymers used at paper machine are expressed in terms of ppm on volume of total flow to a saveall and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on total flow volume, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ saveall\ \ polymers}{m^3\ \ of\ \ total\ \ flow\ volume}$$

$$= \frac{1\ g\ of\ \ saveall\ \ polymers}{m^3\ \ of\ \ total\ \ flow\ volume} \times \frac{total\ \ flow\ volume}{tonne\ of\ \ pulp}$$

According to the principle of mass balance, the volume of total flow to a saveall per tonne of pulp converted can be estimated from the equation

$$V_{total} = V_{machine} + V_{shower} - V_{wastewater}$$

where

| | |
|---|---|
| $V_{total}$: | volume of total flow to a saveall, $m^3$/tonne of pulp |
| $V_{machine}$: | volume of water removed between headbox and press section of a paper machine, $m^3$/tonne of pulp |
| $V_{shower}$: | volume of shower water, $m^3$/tonne of pulp |
| $V_{wastewater}$: | volume of wastewater generated from a paper machine, $m^3$/tonne of pulp. |

The volume of water removed between the headbox and press section of a paper machine can be estimated from the change in pulp consistency. Pulp enters the headbox at 0.5-1.0% consistency and leaves the press section at about 40% consistency (Hagemeyer et al., 1992, p.174). Based on this data (0.5% consistency at entry to the headbox), the volume of water removed is

$$V_{machine} = \frac{1 - consistency\ at\ start\ of\ headbox}{consistency\ at\ start\ of\ headbox} - \frac{1 - consistency\ at\ end\ of\ press}{consistency\ at\ end\ of\ press}$$

$$= \frac{1 - 0.5\%}{0.5\%} - \frac{1 - 40\%}{40\%}$$

$$= \frac{(100 - 0.5)\ tonne\ of\ water}{0.5\ tonne\ of\ pulp} - \frac{(100 - 40)\ tonne\ of\ water}{40\ tonne\ of\ pulp}$$

$$= \frac{199\ tonne\ of\ water}{tonne\ of\ pulp} - \frac{1.5\ tonne\ of\ water}{tonne\ of\ pulp}$$

$$= \frac{197.5\ tonne\ of\ water}{tonne\ of\ pulp}$$

$$= \frac{197.5\ tonne\ of\ water}{tonne\ of\ pulp} \times \frac{1}{water\ density}$$

$$= \frac{197.5\ tonne\ of\ water}{tonne\ of\ pulp} \times \frac{1}{1\ tonne / m^3}$$

$$= \frac{197.5\ m^3\ of\ water}{tonne\ of\ pulp}$$

In the above calculation, the water density is taken at 1 tonne/$m^3$.

The volume of shower water ($V_{shower}$) is assumed to be 20 $m^3$/tonne of pulp based on a reported range of 5-20 $m^3$/tonne of pulp (European Commission, 1999, p.326-327), while the volume of wastewater generated ($V_{wastewater}$) is assumed to be 60 $m^3$/tonne of pulp considering it varies between 40 and 75 $m^3$/tonne of paper (European Commission, 1996, p.702). In converting units, the quantity of pulp converted is assumed to equal that of paper produced.

With values for water removed between the headbox and press section of a paper machine, shower water and wastewater, the volume of total flow to a saveall is determined

$$V_{total} = V_{machine} + V_{shower} - V_{wastewater}$$

$$= 197.5\ m^3 / tonne\ of\ \ pulp + 20\ m^3 / tonne\ of\ \ pulp - 60\ m^3 / tonne\ of\ \ pulp$$

$$= 157.5\ m^3 / tonne\ of\ \ pulp$$

The 1 ppm use level for saveall polymers becomes

$$1\ ppm = \frac{1\ g\ of\ \ saveall\ \ polymers}{m^3\ \ of\ \ total\ \ flow\ volume} \times \frac{total\ \ flow\ volume}{tonne\ of\ \ pulp}$$

$$= \frac{1\ g\ of\ \ saveall\ \ polymers}{m^3\ \ of\ \ total\ \ flow\ volume} \times \frac{157.5\ m^3\ \ of\ \ total\ \ flow\ volume}{tonne\ of\ \ pulp}$$

$$= \frac{157.5\ g\ of\ \ saveall\ \ polymers}{tonne\ of\ \ pulp}$$

$$= \frac{157.5\ g\ of\ \ saveall\ \ polymers}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 0.0158\%$$

The conversion factor for saveall polymers used at paper machine is, therefore, determined to be

$$F_{conv} = 0.0158\ (\%\ \ per\ \ ppm)$$

## H.9 – Conversion Factor for Microbiological Control in Coating

Microbiological control used in coating is expressed in terms of % on chest volume and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on chest volume, i.e.,

$$1\%\ on\ chest\ volume = \frac{10\ kg\ of\ microbiological\ control}{m^3\ of\ chest\ volume}$$

$$= \frac{10\ kg\ of\ microbiological\ control}{m^3\ of\ chest\ volume} \times \frac{chest\ volume \times application\ frequency}{production\ rate}$$

In order to proceed with the above conversion, the chest volume ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

## H.10 – Conversion Factor for Boilouts in Coating

Boilouts used in coating are expressed in terms of % on volume treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated}$$

$$= \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated} \times \frac{volume\ treated \times application\ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

## H.11 – Conversion Factor for Air Pollution Control in Recovery and Power Boilers

Air pollution control used in recovery and power boilers is expressed in terms of ppm on volume of scrubber liquid and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on scrubber liquid, i.e.,

$$1\ ppm = \frac{1\ g\ of\ air\ pollution\ control}{tonne\ of\ scrubber\ liquid}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times\ flue\ gas\ generation\ rate \times liquid\ to\ gas\ ratio$$

Literature data is used to provide estimates for the flue gas generation rate and the liquid-to-gas ratio. The mass rate of flue gas generated from recovery and power boilers is estimated by

$$F_{gas} = \frac{G_{pollu\tan t}}{Q_{boilers} C_{pollu\tan t}}$$

where

| | |
|---|---|
| $F_{gas}$: | mass rate of flue gas generated from recovery and power boilers, kg/tonne of pulp |
| $G_{pollutant}$: | mass of a pollutant generated from recovery and power boilers per unit fuel heat input to boilers, kg/GJ |
| $C_{pollutant}$: | concentration of a pollutant in flue gas, % |
| $Q_{boilers}$: | rate of fuel heat input to recovery and power boilers, GJ/tonne of pulp |

The values of $G_{pollutant}$, $C_{pollutant}$ and $Q_{boilers}$ are derived from literature data. A study conducted by the National Council of Air and Stream Improvement indicates that carbon monoxide (CO) was generated at 43-65 g/GJ from three different mill boilers and had concentration of 97-146 ppm in the flue gas (H. A. Simons, 1995, p.8-19). Using average values from this study, the mass of carbon monoxide generated ($G_{pollutant}$) is assumed to be 54 g/GJ and its concentration in flue gas ($C_{pollutant}$) is assumed to be 122 ppm. The rate of fuel heat input to recovery and power boilers ($Q_{boilers}$) at a paper mill is estimated to be 4.8 GJ/tonne of paper according to the data provided by Kiiskinen and Edelmann (2002) who reported that the energy consumption for paper machine cylinder drying was 3.6 GJ/tonne of paper and represented about three-quarters of the process steam required by the mill. Based on the above values, the mass rate of flue gas generated from recovery and power boilers at a paper mill is

$$F_{gas} = \frac{G_{pollu\tan t}}{Q_{boilers} C_{pollu\tan t}}$$

$$= \frac{54\ g\ of\ \ CO/GJ}{4.8\ GJ/tonne\ of\ \ paper \times 122\ \ ppm}$$

$$= \frac{54\ g\ of\ \ CO/GJ}{4.8\ GJ/tonne\ of\ \ paper \times 122\ \ ppm} \times \frac{kg}{1000\ g} \times \frac{10^6\ \ ppm}{100\%}$$

$$= \frac{0.054\ kg\ of\ \ CO / GJ}{4.8\ GJ / tonne\ of\ \ paper \times 0.0122\%}$$

$$= \frac{0.054\ kg\ of\ \ CO / GJ}{4.8\ GJ / tonne\ of\ \ paper \times \frac{0.0122\ kg\ of\ \ CO}{100\ kg\ of\ \ flue\ gas}}$$

$$= \frac{92.2\ kg\ of\ \ flue\ gas}{tonne\ of\ \ paper}$$

$$= \frac{92.2\ kg\ of\ \ flue\ gas}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= 92.2\ kg\ of\ \ flue\ gas / tonne\ of\ \ pulp$$

In the above calculation, the mass concentration of carbon monoxide is assumed to be equal to the volume concentration and the paper produced is equal to the pulp prepared.

The volume rate of flue gas generated from recovery and power boilers at a paper mill is estimated by assuming the flue gas obeys the ideal gas law and enters a wet scrubber at conditions reported by H. A. Simons (1995, p.4-67), i.e., 192$^{o}$C and 710 mmHg.

$$V_{gas} = \frac{F_{gas} RT}{MP}$$

where

- $V_{gas}$: volume rate of flue gas generated from recovery and power boilers, m$^3$/tonne of pulp
- $F_{gas}$: mass rate of flue gas generated from recovery and power boilers, $F_{gas}$ = 92.2 kg/tonne of pulp
- R: gas constant, R = 0.082 m$^3$-atm/kgmol-K
- T: flue gas temperature, T = 192$^{o}$C = 465 K
- P: flue gas pressure, P = 710 mmHg = 0.93 atm
- M: average molecular weight of flue gas, M = 28 kg/kgmol (assumed)

Using the values given above, the volume rate of flue gas is

$$V_{gas} = \frac{F_{gas} RT}{MP}$$

$$= \frac{\frac{92.2\ kg}{tonne\ of\ \ pulp} \times \frac{0.082\ m^3\ \ atm}{kgmol\ K} \times 465\ K}{\frac{28\ kg}{kgmol} \times 0.93\ atm}$$

$$= 135.0\ m^3 / tonne\ of\ \ pulp$$

Assuming the liquid-to-gas ratio at 2 L/m$^3$ for wet scrubbers based on a range of 0.54-3.21 L/m$^3$ reported by H. A. Simons (1995, p.4-67), the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times\ flue\ gas\ generation\ rate \times liquid\ to\ gas\ ratio$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ L}{m^3}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ L}{m^3} \times liquid\ \ density$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ L}{m^3} \times \frac{1\ kg}{L}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ kg}{m^3} \times \frac{1\ tonne}{1000\ kg}$$

$$= \frac{0.27\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ pulp}$$

$$= \frac{0.27\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 2.7 \times 10^{-5}\%$$

In the above calculation, the liquid density is assumed to be 1 kg/L (water). The conversion factor for air pollution control used in recovery and power boilers is, therefore, determined to be

$$F_{conv} = 2.7 \times 10^{-5}\ (\%\ per\ \ ppm)$$

## H.12 – Conversion Factor for Chemicals Based on Steam in Recovery and Power Boilers

Condensate treatment, boiler water treatment, scale control, and corrosion inhibitors used in recovery and power boilers are expressed in terms of ppm on quantity of steam and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on steam, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam}$$

$$= \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times steam\ requirement$$

The steam requirement at a paper mill is estimated by

$$F_{steam} = Q_{boilers} R_{steam}$$

where

$F_{steam}$: steam requirement at a paper mill, tonne/tonne of pulp
$Q_{boilers}$: rate of fuel heat input to recovery and power boilers, GJ/tonne of pulp
$R_{steam}$: steam conversion rate from fuel heat input to recovery and power boilers, tonne/GJ

The values of $Q_{boilers}$ and $R_{steam}$ are derived from literature data. The rate of fuel heat input to recovery and power boilers ($Q_{boilers}$) at a paper mill is estimated to be 4.8 GJ/tonne of paper according to the data provided by Kiiskinen and Edelmann (2002) who reported that the energy consumption for paper machine cylinder drying was 3.6 GJ/tonne of paper and represented about three-quarters of the process steam required by the mill. The steam conversion rate ($R_{steam}$) is estimated to be 0.32 tonne/GJ according to average values for field erected boilers which can convert 100-950 GJ/h of fuel heat input (average = 525 GJ/h) to 35-300 tonne/h of steam (average = 168 tonne/h) (H. A. Simons, 1995, p.8-5).

With the values of $Q_{boilers}$ and $R_{steam}$, the steam requirement is determined to be

$$F_{steam} = Q_{boilers} R_{steam}$$

$$= \frac{4.8\ GJ}{tonne\ of\ \ paper} \times \frac{0.32\ tonne\ of\ \ steam}{GJ}$$

$$= \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ paper}$$

$$= \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ pulp}$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times steam\ requirement$$

$$= \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ pulp}$$

$$= \frac{1.54\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ pulp}$$

$$= \frac{1.54\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 1.54 \times 10^{-4}\%$$

The conversion factor for chemicals based on steam and used in recovery and power boilers is, therefore, determined to be

$$F_{conv} = 1.54 \times 10^{-4}\ (\%\ per\ \ ppm)$$

### H.13 – Conversion Factor for Chemicals in Water Treatment

Chemicals used in water treatment include corrosion inhibitors, microbiological control, scale control, and settling aids. They are expressed in terms of ppm on volume of water treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on water, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water}$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times water\ consumption$$

In the European Union, the water consumption at non-integrated paper mills was 40-75 $m^3$/tonne of paper for printing and writing grades (European Commission, 1996, p.702). Assuming an average water consumption rate at 60 $m^3$/tonne of paper, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times water\ consumption$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times \frac{60\ m^3\ \ of\ \ water}{tonne\ of\ \ paper}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ paper}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 6.0 \times 10^{-3}\%$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The conversion factor for chemicals used in water treatment is, therefore, determined to be

$$F_{conv} = 6.0 \times 10^{-3}\ (\%\ per\ \ ppm)$$

## H.14 – Conversion Factor for Chemicals in Wastewater Treatment

Chemicals used in wastewater treatment include settling aids, foam control, nutrients, sludge conditioners, odor control, and color control. They are expressed in terms of ppm on volume of wastewater treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on wastewater, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater}$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times wastewater\ \ generation$$

In the European Union, the water consumption at non-integrated paper mills was 40-75 $m^3$/tonne of paper for printing and writing grades (European Commission, 1996, p.702). Assuming the wastewater generation equals the water consumption which averages at 60 $m^3$/tonne of paper, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times wastewater\ \ generation$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times \frac{60\ m^3\ \ of\ \ wastewater}{tonne\ of\ \ paper}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ paper}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ pulp}$$

$$= \frac{60\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 6.0 \times 10^{-3}\%$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The conversion factor for chemicals used in wastewater treatment is, therefore, determined to be

$$F_{conv} = 6.0 \times 10^{-3}\ (\%\ \ per\ \ ppm)$$

# Appendix I – Derivation of Conversion Factors for Chemical Use Level at Recovered Paper Mills

In estimating chemical releases from recovered paper mills (deinking plants), data on chemical use level must be converted to mass percentage on pulp if it is provided on a different basis. The conversion is made through the equation

$$L_{use} = F_{conv} D_{use}$$

where

- $L_{use}$: use level for a type of chemicals expressed in % on pulp
- $F_{conv}$: conversion factor from a different basis to % on pulp
- $D_{use}$: data on use level for a type of chemicals based on a quantity different from % on pulp

Provided below are conversion factors determined for chemical use level commonly expressed on a basis other than mass percentage on pulp.

## I.1 – Conversion Factor for Boilouts in Deinking

Boilouts used in deinking are expressed in terms of % on volume treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated}$$

$$= \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated} \times \frac{volume\ treated \times application\ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

## I.2 – Conversion Factor for Settling Aids in Deinking

Settling aids used in deinking are expressed in terms of ppm on volume of pulp suspension and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on volume, i.e.,

$$1\ ppm = \frac{1\ g\ of\ settling\ aids}{m^3\ of\ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ settling\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

The pulp consistency (solids content) in deinking is 0.5 to 1.0%, i.e., 0.005 to 0.01 tonne of pulp per tonne of pulp suspension (J. Jossinet, December 2002). As a conservative approximation, the lower pulp consistency value at 0.5% is assumed and the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ settling\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ settling\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{0.5\%}$$

$$= \frac{1\ g\ of\ \ settling\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{0.005\ tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ settling\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times suspension\ density$$

$$= \frac{200\ g\ of\ \ settling\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times \frac{1\ tonne}{m^3}$$

$$= \frac{200\ g\ of\ \ settling\ aids}{tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ settling\ aids}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 0.02\%$$

In the above conversion, the density of pulp suspension is assumed to be 1 tonne/$m^3$. The conversion factor for settling aids used in deinking is, therefore, determined to be

$$F_{conv} = 0.02\ (\%\ \ per\ \ ppm)$$

## I.3 – Conversion Factor for Retention/Drainage Aids in Paper Making

Retention/drainage aids used in paper making are polymers used in a saveall and are expressed in terms of ppm on volume of total flow to the saveall. The conversion factor for retention/drainage aids can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on total flow volume, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ retention/drainage\ aids}{m^3\ of\ \ total\ \ flow\ volume}$$

$$= \frac{1\ g\ of\ \ retention/drainage\ aids}{m^3\ of\ \ total\ \ flow\ volume} \times \frac{total\ \ flow\ volume}{tonne\ of\ \ pulp}$$

According to the principle of mass balance, the volume of total flow to a saveall per tonne of pulp can be estimated from the equation

$$V_{total} = V_{removal} + V_{shower} - V_{wastewater}$$

where

$V_{total}$: volume of total flow to a saveall, $m^3$/tonne of pulp
$V_{removal}$: volume of water removed between headbox and press section of a paper machine, $m^3$/tonne of pulp
$V_{shower}$: volume of shower water, $m^3$/tonne of pulp
$V_{wastewater}$: volume of wastewater generated from a paper machine, $m^3$/tonne of pulp.

The volume of water removed between the headbox and press section of a paper machine can be estimated from the change in pulp consistency. Pulp enters the headbox at 0.5-1.0% consistency and leaves the press section at about 40% consistency (Hagemeyer et al., 1992, p.174). Based on this data (0.5% consistency at entry to the headbox), the volume of water removed is

$$V_{removal} = \frac{1 - consistency\ at\ start\ of\ \ headbox}{consistency\ at\ start\ of\ \ headbox} - \frac{1 - consistency\ at\ end\ of\ \ press}{consistency\ at\ end\ of\ \ press}$$

$$= \frac{1 - 0.5\%}{0.5\%} - \frac{1 - 40\%}{40\%}$$

$$= \frac{(100 - 0.5)\ tonne\ of\ \ water}{0.5\ tonne\ of\ \ pulp} - \frac{(100 - 40)\ tonne\ of\ \ water}{40\ tonne\ of\ \ pulp}$$

$$= \frac{199\ tonne\ of\ \ water}{tonne\ of\ \ pulp} - \frac{1.5\ tonne\ of\ \ water}{tonne\ of\ \ pulp}$$

$$= \frac{197.5\ tonne\ of\ \ water}{tonne\ of\ \ pulp}$$

$$= \frac{197.5\ tonne\ of\ \ water}{tonne\ of\ \ pulp} \times \frac{1}{water\ \ density}$$

$$= \frac{197.5\ tonne\ of\ \ water}{tonne\ of\ \ pulp} \times \frac{1}{1\ tonne/m^3}$$

$$= \frac{197.5\ m^3\ \ of\ \ water}{tonne\ of\ \ pulp}$$

In the above calculation, the water density is taken at 1 tonne/$m^3$.

The volume of shower water ($V_{shower}$) is assumed to be 20 $m^3$/tonne of pulp based on a reported range of 5-20 $m^3$/tonne of pulp (European Commission, 1999, p.326-327), while the volume of wastewater generated ($V_{wastewater}$) is assumed to equal the volume of water used which was reported to be 20 $m^3$/tonne for recovered paper mills (European Commission, 1999, p.227-231).

With values for water removed between the headbox and press section of a paper machine, shower water and wastewater, the volume of total flow to a saveall is determined

$$V_{total} = V_{removal} + V_{shower} - V_{wastewater}$$

$$= 197.5\ m^3/tonne\ of\ \ pulp + 20\ m^3/tonne\ of\ \ pulp - 20\ m^3/tonne\ of\ \ pulp$$

$$= 197.5\ m^3/tonne\ of\ \ pulp$$

The 1 ppm use level for retention/drainage aids becomes

$$1\ ppm = \frac{1\ g\ of\ \ retention/drainage\ aids}{m^3\ \ of\ \ total\ \ flow\ volume} \times \frac{total\ \ flow\ volume}{tonne\ of\ \ pulp}$$

$$= \frac{1\ g\ of\ \ retention/drainage\ aids}{m^3\ \ of\ \ total\ \ flow\ volume} \times \frac{197.5\ m^3\ \ of\ \ total\ \ flow\ volume}{tonne\ of\ \ pulp}$$

$$= \frac{197.5\ g\ of\ \ retention/drainage\ aids}{tonne\ of\ \ pulp}$$

$$= \frac{197.5\ g\ of\ \ retention/drainage\ aids}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$= 0.0198\%$

The conversion factor for retention/drainage aids used at paper making is, therefore, determined to be

$$F_{conv} = 0.0198\ (\%\ per\ ppm)$$

## I.4 – Conversion Factor for Barrier Chemistry in Paper Making

The conversion factor for barrier chemistry used in paper making cannot be determined at this moment because the basis for its use level is not known yet.

## I.5 – Conversion Factor for Charge Neutralization in Paper Making

Charge neutralization used in paper making is expressed in terms of ppm on volume of pulp suspension at entry to a paper machine. The conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on volume, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ charge\ neutralization}{m^3\ of\ \ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ charge\ neutralization}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

The pulp consistency (solids content) at entry to a paper machine is 0.5 to 1.0%, i.e., 0.005 to 0.01 tonne of pulp per tonne of pulp suspension (J. Jossinet, December 2002). As a conservative approximation, the lower pulp consistency value at 0.5% is assumed and the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ charge\ neutralization}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{solids\ content\ of\ \ pulp\ suspension}$$

$$= \frac{1\ g\ of\ \ charge\ neutralization}{m^3\ of\ \ pulp\ suspension} \times \frac{1}{0.5\%}$$

$$= \frac{1\ g\ of\ \ charge\ neutralization}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{0.005\ tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ settling\ aids}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times suspension\ density$$

$$= \frac{200\ g\ of\ \ charge\ neutralization}{m^3\ of\ \ pulp\ suspension} \times \frac{tonne\ of\ \ pulp\ suspension}{tonne\ of\ \ pulp} \times \frac{1\ tonne}{m^3}$$

$$= \frac{200\ g\ of\ \ charge\ neutralization}{tonne\ of\ \ pulp}$$

$$= \frac{200\ g\ of\ \ charge\ neutralization}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 0.02\%$$

In the above conversion, the density of pulp suspension is assumed to be 1 tonne/$m^3$. The conversion factor for charge neutralization used in paper making is, therefore, determined to be

$$F_{conv} = 0.02\ (\%\ per\ \ ppm)$$

## I.6 – Conversion Factor for Antiskid Agents in Paper Making

Antiskid agents used in paper making are expressed in terms of lb/t on paper and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 lb/t on paper, i.e.,

$$1\ lb/t = \frac{1\ lb\ of\ \ antiskid\ \ agents}{ton\ of\ \ paper}$$

$$= \frac{1\ lb\ of\ \ antiskid\ \ agents}{ton\ of\ \ paper} \times \frac{ton}{2000\ lb} \times \frac{lb/kg}{lb/kg}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ paper}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ paper} \times \frac{1\ kg\ of\ \ paper}{kg\ of\ \ pulp}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ pulp}$$

$$= \frac{1\ kg\ of\ \ antiskid\ \ agents}{2000\ kg\ of\ \ pulp} \times 100\%$$

$$= 0.05\%$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The conversion factor for antiskid agents used in paper making is, therefore, determined to be

$$F_{conv} = 0.05\ (\%\ per\ lb/t)$$

## I.7 – Conversion Factor for Felt Cleaning Chemicals in Paper Making

Felt cleaning chemicals used in paper making are expressed in terms of ppm on volume of shower water and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on shower water, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ felt\ cleaning\ chemicals}{m^3\ of\ \ shower\ water}$$

$$= \frac{1\ g\ of\ \ felt\ cleaning\ chemicals}{m^3\ of\ \ shower\ water} \times shower\ water\ requirement$$

In the European Union, paper machines were reported to consume 5-20 $m^3$ of shower water per tonne of pulp for lubricating and cleaning fabrics and wet press felts (European Commission, 1999, p.326-327). Assuming an average rate at 15 $m^3$ of shower water per tonne of pulp for paper machines, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ felt\ cleaning\ chemicals}{m^3\ of\ \ shower\ water} \times shower\ water\ requirement$$

$$= \frac{1\ g\ of\ \ felt\ cleaning\ chemicals}{m^3\ of\ \ shower\ water} \times \frac{15\ m^3\ of\ \ shower\ water}{tonne\ of\ \ pulp}$$

$$= \frac{15\ g\ of\ \ felt\ cleaning\ chemicals}{tonne\ of\ \ pulp}$$

$$= \frac{15\ g\ of\ \ felt\ cleaning\ chemicals}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ g} \times 100\%$$

$$= 1.5 \times 10^{-3}\%$$

The conversion factor for felt cleaning chemicals used in paper making is, therefore, determined to be

$$F_{conv} = 1.5 \times 10^{-3} \ (\%\ per\ ppm)$$

## I.8 – Conversion Factor for Boilouts in Paper Making

Boilouts used in paper making are expressed in terms of % on volume treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on volume treated, i.e.,

$$1\%\ on\ volume\ treated = \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated}$$

$$= \frac{10\ kg\ of\ boilouts}{m^3\ of\ volume\ treated} \times \frac{volume\ treated \times application\ frequency}{production\ rate}$$

In order to proceed with the above conversion, the volume treated ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

## I.9 – Conversion Factor for Microbiological Control in Paper Making

Microbiological control used in paper making is expressed in terms of % on chest volume and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1% on chest volume, i.e.,

$$1\%\ on\ chest\ volume = \frac{10\ kg\ of\ microbiological\ control}{m^3\ of\ chest\ volume}$$

$$= \frac{10\ kg\ of\ microbiological\ control}{m^3\ of\ chest\ volume} \times \frac{chest\ volume \times application\ frequency}{production\ rate}$$

In order to proceed with the above conversion, the chest volume ($m^3$), the application frequency (number of times of treatment per day) and the production rate (tonne of paper produced per day) must be known. At time of this writing, the three values are not available.

## I.10 – Conversion Factor for Air Pollution Control in Recovery and Power Boilers

Air pollution control used in recovery and power boilers is expressed in terms of ppm on volume of scrubber liquid and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on scrubber liquid, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times\ flue\ gas\ generation\ rate \times liquid\ to\ gas\ ratio$$

Literature data is used to provide estimates for the flue gas generation rate and the liquid-to-gas ratio. The mass rate of flue gas generated from recovery and power boilers is estimated by

$$F_{gas} = \frac{G_{pollu\tan t}}{Q_{boilers} C_{pollu\tan t}}$$

where

| | |
|---|---|
| $F_{gas}$: | mass rate of flue gas generated from recovery and power boilers, kg/tonne of pulp |
| $G_{pollutant}$: | mass of a pollutant generated from recovery and power boilers per unit fuel heat input to boilers, kg/GJ |
| $C_{pollutant}$: | concentration of a pollutant in flue gas, % |
| $Q_{boilers}$: | rate of fuel heat input to recovery and power boilers, GJ/tonne of pulp |

The values of $G_{pollutant}$, $C_{pollutant}$ and $Q_{boilers}$ are derived from literature data. A study conducted by the National Council of Air and Stream Improvement indicates that carbon monoxide (CO) was generated at 43-65 g/GJ from three different mill boilers and had concentration of 97-146 ppm in the flue gas (H. A. Simons, 1995, p.8-19). Using average values from this study, the mass of carbon monoxide generated ($G_{pollutant}$) is assumed to be 54 g/GJ and its concentration in flue gas ($C_{pollutant}$) is assumed to be 122 ppm. The rate of fuel heat input to recovery and power boilers ($Q_{boilers}$) at a recovered paper mill is assumed to be equal to 4.8 GJ/tonne of paper estimated for a paper mill (see Conversion Factor for Air Pollution Control in Recovery and Power Boilers in Appendix X). Based on the above values, the mass rate of flue gas generated from recovery and power boilers is

$$F_{gas} = \frac{G_{pollu\tan t}}{Q_{boilers} C_{pollu\tan t}}$$

$$= \frac{54\ g\ of\ \ CO/GJ}{4.8\ GJ/tonne\ of\ \ paper \times 122\ \ ppm}$$

$$= \frac{54\ g\ of\ \ CO/GJ}{4.8\ GJ/tonne\ of\ \ paper \times 122\ \ ppm} \times \frac{kg}{1000\ g} \times \frac{10^6\ \ ppm}{100\%}$$

$$= \frac{0.054\ kg\ of\ \ CO / GJ}{4.8\ GJ / tonne\ of\ \ paper \times 0.0122\%}$$

$$= \frac{0.054\ kg\ of\ \ CO / GJ}{4.8\ GJ / tonne\ of\ \ paper \times \frac{0.0122\ kg\ of\ \ CO}{100\ kg\ of\ \ flue\ gas}}$$

$$= \frac{92.2\ kg\ of\ \ flue\ gas}{tonne\ of\ \ paper}$$

$$= \frac{92.2\ kg\ of\ \ flue\ gas}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= 92.2\ kg\ of\ \ flue\ gas / tonne\ of\ \ pulp$$

In the above calculation, the mass concentration of carbon monoxide is assumed to be equal to the volume concentration and the paper produced is equal to the pulp prepared.

The volume rate of flue gas generated from recovery and power boilers at a recovered paper mill is estimated by assuming the flue gas obeys the ideal gas law and enters a wet scrubber at conditions reported by H. A. Simons (1995, p.4-67), i.e., 192$^{o}$C and 710 mmHg.

$$V_{gas} = \frac{F_{gas} RT}{MP}$$

where

- $V_{gas}$: volume rate of flue gas generated from recovery and power boilers, m$^3$/tonne of pulp
- $F_{gas}$: mass rate of flue gas generated from recovery and power boilers, $F_{gas}$ = 92.2 kg/tonne of pulp
- R: gas constant, R = 0.082 m$^3$-atm/kgmol-K
- T: flue gas temperature, T = 192$^{o}$C = 465 K
- P: flue gas pressure, P = 710 mmHg = 0.93 atm
- M: average molecular weight of flue gas, M = 28 kg/kgmol (assumed)

Using the values given above, the volume rate of flue gas is

$$V_{gas} = \frac{F_{gas} RT}{MP}$$

$$= \frac{\frac{92.2\ kg}{tonne\ of\ \ pulp} \times \frac{0.082\ m^3\ \ atm}{kgmol\ K} \times 465\ K}{\frac{28\ kg}{kgmol} \times 0.93\ atm}$$

$$= 135.0\ m^3 / tonne\ of\ \ pulp$$

Assuming the liquid-to-gas ratio at 2 L/m$^3$ for wet scrubbers based on a range of 0.54-3.21 L/m$^3$ reported by H. A. Simons (1995, p.4-67), the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times\ flue\ gas\ generation\ rate \times liquid\ to\ gas\ ratio$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ L}{m^3}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ L}{m^3} \times liquid\ \ density$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ L}{m^3} \times \frac{1\ kg}{L}$$

$$= \frac{1\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ scrubber\ liquid} \times \frac{135.0\ m^3}{tonne\ of\ \ pulp} \times \frac{2\ kg}{m^3} \times \frac{1\ tonne}{1000\ kg}$$

$$= \frac{0.27\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ pulp}$$

$$= \frac{0.27\ g\ of\ \ air\ \ pollution\ control}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 2.7 \times 10^{-5}\%$$

In the above calculation, the liquid density is assumed to be 1 kg/L (water). The conversion factor for air pollution control used in recovery and power boilers is, therefore, determined to be

$$F_{conv} = 2.7 \times 10^{-5}\ (\%\ per\ \ ppm)$$

## I.11 – Conversion Factor for Chemicals Based on Steam in Recovery and Power Boilers

Condensate treatment, boiler water treatment, scale control, and corrosion inhibitors used in recovery and power boilers are expressed in terms of ppm on quantity of steam and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on steam, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam}$$

$$= \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times steam\ requirement$$

The steam requirement at a recovered paper mill is estimated by

$$F_{steam} = Q_{boilers} R_{steam}$$

where

$F_{steam}$: steam requirement at a recovered paper mill, tonne/tonne of pulp
$Q_{boilers}$: rate of fuel heat input to recovery and power boilers, GJ/tonne of pulp
$R_{steam}$: steam conversion rate from fuel heat input to recovery and power boilers, tonne/GJ

The values of $Q_{boilers}$ and $R_{steam}$ are derived from literature data. The rate of fuel heat input to recovery and power boilers ($Q_{boilers}$) at a recovered paper mill is estimated to be 4.8 GJ/tonne of paper according to the data provided by Kiiskinen and Edelmann (2002) who reported that the energy consumption for paper machine cylinder drying was 3.6 GJ/tonne of paper and represented about three-quarters of the process steam required by the mill. The steam conversion rate ($R_{steam}$) is estimated to be 0.32 tonne/GJ according to average values for field erected boilers which can convert 100-950 GJ/h of fuel heat input (average = 525 GJ/h) to 35-300 tonne/h of steam (average = 168 tonne/h) (H. A. Simons, 1995, p.8-5).

With the values of $Q_{boilers}$ and $R_{steam}$, the steam requirement is determined to be

$$F_{steam} = Q_{boilers} R_{steam}$$

$$= \frac{4.8\ GJ}{tonne\ of\ \ paper} \times \frac{0.32\ tonne\ of\ \ steam}{GJ}$$

$$= \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ paper}$$

$$= \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ pulp}$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times steam\ requirement$$

$$= \frac{1\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ steam} \times \frac{1.54\ tonne\ of\ \ steam}{tonne\ of\ \ pulp}$$

$$= \frac{1.54\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ pulp}$$

$$= \frac{1.54\ g\ of\ \ chemicals\ based\ on\ steam}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 1.54 \times 10^{-4}\%$$

The conversion factor for chemicals based on steam and used in recovery and power boilers is, therefore, determined to be

$$F_{conv} = 1.54 \times 10^{-4}\ (\%\ per\ \ ppm)$$

## I.12 – Conversion Factor for Chemicals in Water Treatment

Chemicals used in water treatment include corrosion inhibitors, microbiological control, scale control, and settling aids. They are expressed in terms of ppm on volume of water treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on water, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water}$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times water\ \ consumption$$

In the European Union, the water consumption at recovered paper mills was 20 $m^3$/tonne of paper (European Commission, 1999, p.227-231). Using this data, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times water\ \ consumption$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{m^3\ \ of\ \ water} \times \frac{20\ m^3\ \ of\ \ water}{tonne\ of\ \ paper}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ paper}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ pulp}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ water\ treatment}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 2.0 \times 10^{-3}\%$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The conversion factor for chemicals used in water treatment is, therefore, determined to be

$$F_{conv} = 2.0 \times 10^{-3}\ (\%\ \ per\ \ ppm)$$

### I.13 – Conversion Factor for Chemicals in Wastewater Treatment

Chemicals used in wastewater treatment include settling aids, foam control, nutrients, sludge conditioners, odor control, and color control. They are expressed in terms of ppm on volume of wastewater treated and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from 1 ppm on wastewater, i.e.,

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater}$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times wastewater\ \ generation$$

In the European Union, the water consumption at recovered paper mills was 20 $m^3$/tonne of paper (European Commission, 1999, p.227-231). Assuming the wastewater generation equals the water consumption, the 1 ppm use level becomes

$$1\ ppm = \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times wastewater\ \ generation$$

$$= \frac{1\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{m^3\ \ of\ \ wastewater} \times \frac{20\ m^3\ \ of\ \ wastewater}{tonne\ of\ \ paper}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ paper}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ paper} \times \frac{1\ tonne\ of\ \ paper}{tonne\ of\ \ pulp}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ pulp}$$

$$= \frac{20\ g\ of\ \ chemicals\ used\ in\ wastewater\ treatment}{tonne\ of\ \ pulp} \times \frac{tonne}{10^6\ \ g} \times 100\%$$

$$= 2.0 \times 10^{-3}\%$$

In the above calculation, the paper produced is assumed to be equal to the pulp prepared. The conversion factor for chemicals used in wastewater treatment is, therefore, determined to be

$$F_{conv} = 2.0 \times 10^{-3}\ (\%\ \ per\ \ ppm)$$

## I.14 – Conversion Factor for Chelants in Paper Making

Chelants used in paper making are expressed in terms of % on peroxide and the conversion factor can be determined by deriving the use level expressed in terms of % on pulp from % on peroxide, i.e.,

$$1\,\%\ on\ peroxide = \frac{1\ g\ of\ chelants\ used\ in\ paper\ making}{100\ g\ of\ peroxide}$$

$$= \frac{1\ g\ of\ chelants\ used\ in\ paper\ making}{100\ g\ of\ peroxide} \times peroxide\ use\ level$$

Assuming the peroxide use level is 2% on pulp (see Table D.3 – Data for Recovered Paper Mills in Appendix D – Chemical Use Level, Water Content and Fraction Retained by Products), the 1% use level on peroxide becomes

$$1\,\%\ on\ peroxide = \frac{1\ g\ of\ chelants\ used\ in\ paper\ making}{100\ g\ of\ peroxide} \times peroxide\ use\ level$$

$$= \frac{1\ g\ of\ chelants\ used\ in\ paper\ making}{100\ g\ of\ peroxide} \times 2\%\ on\ pulp$$

$$= \frac{1\ g\ of\ chelants\ used\ in\ paper\ making}{100\ g\ of\ peroxide} \times \frac{2\ g\ of\ peroxide}{100\ g\ of\ pulp} \times 100\%$$

$$= 0.02\%\ on\ pulp$$

The conversion factor for chelants used in paper making is, therefore, determined to be

$$F_{conv} = 0.02\ (\%\ on\ pulp\ per\ \%\ on\ peroxide)$$