Chapter 2
Industrial Processes and Contaminants at Pulp and Paper Mill Sites

Introduction

The pulp and paper industry in the United States is one of the largest fully integrated industries in the world. Each year, mills in every part of the country produce millions of tons of paper and paper products for domestic and foreign use. The Environmental Protection Agency estimates the total value of shipments from the pulp and paper industry as close to $135 billion, as much as the petroleum refining industry. Yet despite this success, as with most other modern industries, the pulp and paper industry has seen an unprecedented wave of mergers in recent years, concentrating the production of the country's paper into a few mega-corporations. As a result, many small pulp and paper mills close each year. When they do, communities have the opportunity to redevelop these industrial "brownfields" and incorporate them into the community at large.

This section provides a brief overview of the different types of pulp and paper mills; summarizes the activities and land uses at a typical pulp and paper mill; describes the contaminants likely present on the sites of former pulp and paper mills; and outlines remediation strategies typically used in the redevelopment of pulp and paper mill brownfields.

Pulp and Paper Mills in America

The first paper mill in the United States was located in Philadelphia and opened around 1690. The first continuous papermaking machine (the first modern mill) was patented in 1798. Improved designs were patented in the early 1800s and were being used in the United States before 1830 (Smook, 1992).

The 1995 EPA Sector Notebook on the Pulp and Paper Industry estimated that there are approximately 555 manufacturing pulp and paper mills in the U.S. Of these 555 mills, an estimated 55 are market pulp facilities, 300 are non-integrated facilities, and 200 are integrated facilities. The Sector Notebook did not provide an estimate on the number of converting facilities and de-inked pulp mills in the U.S.

These mills are for the most part evenly spread throughout the US, though they are concentrated in rural regions in close proximity to large standing crops of timber, such as Northern New England and the Upper Midwest.

Pulp and paper mills are typically classified into the following categories:

- *Market Pulp Mills* These mills produce pulp which is shipped to other facilities for the production of paper and paper products.
- *Non-integrated-Mills* These mills manufacture paper from pulp, but do not produce either the pulp or the final paper goods.
- *Integrated Mills* These mills produce pulp for use in producing paper at the same facility (pulp and paper mills).
- *Converting Facilities* These facilities use paper and paperboard stock to manufacture products such as envelopes and stationery, corrugated and paperboard boxes, bags, fiber cans and drums, napkins, tissues, and paper towels.
- *De-inked Pulp Mills* These facilities remove ink from recycled paper and produce pulp that is blended with virgin pulp to form paper.

Pulp and Paper Mill Pollution

Pulp and paper manufacturing involves a series of steps, each producing one or more characteristic wastes. These wastes can contain contaminants that can remain on site for years, and mangers and developers interested in pursuing a brownfields project need to know what those contaminants could possibly be. This section will briefly describe the major steps of the pulp and paper process and outline the potential contaminants produced during each one. All information was taken from "Handbook for Pulp & Paper Technologists" (Smook, 1992).

Pulping

Pulp making involves the steps from preparation of the paper fiber source (typically wood) through final pulp stock preparation before pulp is sent to the papermaking process.

Pulp is prepared by primarily physical processes. Typically, an integrated pulp and paper mill will have an on site wood/log pile that the raw materials are taken from. These logs are debarked and chipped, with the waste bark being burned for energy.

The actual process of pulping (whereby the woodchips are transformed into pulp) can be accomplished in a few different ways, the primary two being mechanical or chemical pulping. Mechanical pulping involves using huge kettles to cook the chips under high pressure, but since chemical pulping is more likely to produce contaminants, we will focus on that type of pulping.

The first type of chemical pulping is called the kraft/soda process. This process uses a sodium-based alkaline solution (white liquor), consisting of sodium hydroxide and sodium sulfide, to digest the wood chips and produce pulp.

The second type of chemical pulping is sulfite process. In this process, an acidic solution of sulfurous acid and bisulfate ion is used to degrade the lignin. Sulfite processing only accounted for 4 percent of total pulp production in 1993 (Smook, 1992).

After producing the raw pulp, it must be processed to remove impurities, and this step also introduces a distinct set of contaminants to the process. The pulp is first screened and defibered to create a more homogeneous mixture. It is then chemically treated to recover residual white liquor for reuse. Typically, heavy metals are also removed here though chemical treatment. Waste products such as excess sodium hydroxide and sodium sulfite are also removed.

PULPING CONTAMINANTS:

Sodium Hydroxide Residues
Sulfuric/Sulfurous Acid
Hydrochloric Acid
Hydrogen Sulfide
Ammonia
Lead
Cyanide
Zinc
Chromium
Resin
Unnatural Fatty Acids and Chlorinated Analogs

Bleaching

It is in the bleaching process that the most problematic contaminant for pulp and paper mills is produced: dioxins. Dioxins (and also furans) are a class of chemicals of the highest toxicity to all life. They are extremely persistent and cannot be broken down by bacteria. Dioxins bioaccumulate, that is to say its concentration in the tissues of animals increases as you move higher up the food chain. Dioxins are a byproduct of the use of elemental chlorine and, to a lesser extent, other chlorinated substances.

In bleaching, the processed and refined pulp is chemically altered to increase brightness. Besides chlorine, hydrogen peroxide and sodium hydrosulfate can also be used in the bleaching process. Waste is produced when water is used to flush the chlorine and other substances from the paper. It is estimated that over 28,000 gallons of water are used (mostly in bleaching) to produce one ton of paper. When this water is released, it can only be treated so well, and many contaminants are released into the environment.

BLEACHING CONTAMINANTS

Hydrogen Peroxide
Elemental Chlorine
Chlorinated Compounds
Sodium Hydrosulfite
Polychlorinated Biphenyls (PCBs)
Dioxins and Furans

Paper Manufacture

The actual papermaking process consists of two primary processes: dry end operations and wet end operations. In wet end operations, the cleaned and bleached pulp is formed into wet paper sheets. In the dry end operations, those wet sheets are dried and various surface treatments are applied to the paper. Each operations regime has its own characteristic waste stream.

➢ **Wet End Operations**

This step begins with the spreading of the wet pulp onto a moving screen. That screen is sent through a series of vacuums to remove water from it. It is then passed through high speed rollers to press it into firmer sheets and remove more water. This product is then sent to dry end operations.

The only true waste stream produced in the wet end operations is the wastewater that is collected from the pulp. This wastewater has the same contaminants, in much smaller concentrations, that the pulping process produces.

➢ **Dry End Operations**

In dry end operations, the paper is driven through steam heated rollers to further compress the sheets and to bind the paper fibers together. The sheet is then sent through machines which apply coatings to the paper, depending on its ultimate use. These coatings can be released into the environment when the coating machines are cleaned.

In addition, after the dry end operations are completed, the process water that remains is filtered to remove particulate matter and then recycled back into the process. The filtered solids have high concentrations of dioxins and chlorinated substances and this "sludge" poses a large compliance burden. Many older plants disposed of this hazardous waste on site in landfills, and brownfield development at these mills should investigate to determine if there was a solid waste landfill on the site.

PAPERMAKING CONTAMINANTS

Waste sludge
Bleaching and pulping contaminants
SVOCs (in coatings)
VOCs (in coatings)
Slimicides
Chlorinated phenols
Some aminos, and quaternary ammonium compounds
Some organosulfur compounds
Some silver compounds
Titanium residues
Oil and grease discharges collected in sediments
Polychlorinated biphenyls (from carbonless paper)
pesticides, dyes , asbestos fibers from agricultural residues

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All three major steps in the pulp and paper process produce contaminants of some kind. Managers should remember that each pulp and paper operation is unique in scale and character. Integrated mills, for example, participate in all three of these steps in one location, while market pulp mills only participate in the first. Also, mills differ in what final product they produce. Some papers produce less hazardous waste per ton than others. Developers wishing to pursue brownfields projects should investigate the mill that operated on site to determine what contaminants they will have to deal with, and on what scale these contaminants may be present.

Typical Remediation Strategies for Pulp and Paper Mill Sites

There are two separate but related media that any remediation of a pulp and paper mill brownfield must treat: the soil and the water. Each media can be contaminated by the same chemicals, but the ways that developers and managers reduce or eliminate contamination in these media can vary.

Soil Remediation

By far the largest remediation burden for contaminated soils is the removal of dioxins. These toxins have especially high residence times in the soil, and many times cannot be broken down by conventional biological or physical treatment techniques. In fact, many times, dioxin contaminated soils must be excavated and shipped off site for disposal in a hazardous waste landfill. Other contaminants that are typically found in the soil, such as VOCs and SVOCs and chlorinated compounds, can be treated effectively with more conventional soil treatment techniques.
Some of these techniques include:

- **Bioremediation (ex situ)**

  This technology offers permanent destruction of chlorinated and other organic compounds through use of the white rot fungus. This technique requires sufficient resources to excavate and transport the affected soil, as well as an EPA registered landfill or hazardous waste dump to carry out the treatment at. (IRM, 2000)

- **Surfactant Flushing**

  This process is very popular with pulp and paper mill remediations. It is based on the principles of hydrodynamics, physics, and chemical and biological principles. It allows for the efficient and homogeneous treatment of a wide variety of contaminants (very valuable with pulp and paper mills because of the diversity of contaminants). The process involves the use of a surfactant (a component of detergent) to “wash” soil of its contaminants. These contaminants can then be collected and moved or further treated off site. This technology is especially useful treating heavy metals and halogenated volatiles. (IRM, 2000)

- **Oxidation/Reduction**

  This treatment process uses chemical reagents to destroy contaminants in the soil matrix. Theoretically, contaminants should be broken down into carbon dioxide and water. Practically, managers can use oxidation and reduction to at the very least break down contaminants into less harmful, biologically available compounds. This treatment process can sometimes be used to treat dioxins and furans, with the added component of UV light to help in the breakdown of the chemicals. (IRM, 2000)

- **In situ vitrification (ISV)**

  ISV is a commercially available mobile, thermal treatment process that involves the electric melting of contaminated soils, sludges, or other earthen materials, for the purposes of permanently destroying, removing, and/or immobilising hazardous substances. It is used primarily for the degradation and collection of organics (both volatile and non-volatile) but it can also be used for chlorinated compounds. A typical site set-up diagram is shown below. (IRM, 2000)

Contaminated Water

Both surface and groundwater can be contaminated with pulp and paper mill wastes. In general, surface water contamination tends to be short term, especially if the contaminated body of water is a river. Only in rare instances will significant treatment programs be necessary to deal with surface water contamination, and for that reason, this document will not address such programs. On the other hand, groundwater contamination is a very long term problem, where contamination can persist in aquifers for years without treatment. In addition, groundwater is the source of significant amounts of our drinking water, especially in rural areas where it is widely used in homes with wells.

➢ **Treatment Walls**

This treatment technique is a very affordable way to treat contaminated groundwater. After determining the direction of groundwater flow and ascertaining the source of the contamination, a trench is dug perpendicular to the direction of water flow, and a wall is constructed in the trench. The wall can be made from a variety of different materials, depending on the contaminants that are present. The walls are constructed such that water can flow through, while contaminants bond with chemicals in the wall. Activated carbon is typically used to remove contaminants.

➢ **Groundwater Extraction/Injection**

This groundwater treatment technique requires the drilling of treatment wells into the contaminated aquifer. These wells are then used either as injection or extraction wells. With an injection well, uncontaminated water (either surface water or water from an uncontaminated region of the aquifer) is injected into the contaminated region of the aquifer, with the purpose being to 'dilute' the pollution to the point that it is not hazardous. The alternative is to use the well as an extraction well, where contaminated water is drawn from the aquifer and treated on the surface. In most remediation situations, both of these techniques are used in tandem. Contaminated groundwater is removed from the aquifer, treated, and then returned via an injection well. These treatment techniques are typically very expensive and can take years to effectively treat contamination, as withdrawal and injection rates must be low to avoid surface subsidence.

Conclusion

Contamination from pulp and paper mills can pose a very real danger to human and environmental health. The contaminants released span the full spectrum of toxicity, from suspended solids to carcinogens like dioxins. Remediation of sites contaminated by these chemicals can be costly and time consuming, but it can be done. The contaminants and remediation techniques listed in this chapter are ones typically used at pulp and paper mill brownfields, yet every site is unique, and developers will need to develop a remediation plan based upon the contamination actually present on-site.

On site Vitrification Process