

AOX CONTENT OF PAPER MANUFACTURED WITH “CHLORINE FREE” PULPS

RICHARD T. CLAPP, CRAIG A. TRUEMPER, SALMAN AZIZ, AND TERRI RESCHKE

ENVIRONMENTAL pressures have generated interest in bleaching processes that minimize the use of chlorine chemicals. Methods such as AOX developed over the past few years can measure environmental impacts of bleaching with chlorine chemicals and can also provide environmental labeling.

Measuring the AOX in effluents is an accepted technique. It finds increasing use as a “standard” for environmental issues.

In this paper, we present data on the AOX content of some common materials used in the manufacture of pulp and paper products. Additionally we present data on AOX content of pulp and paper products manufactured with and without the use of chlorine chemicals to bleach the pulp (virgin and deinked pulps).

OVERVIEW

There is growing interest and debate concerning the use of chlorine chemicals to bleach pulp. These have led to products offered as totally chlorine free (TCF) or elemental chlorine free (ECF). These labels attempt to portray information about the product in terms of environmental issues.

Labeling issues are among the more complex environmental issues facing the forest products industry (1). Customers, marketers, governments, and environmental groups all have an interest in environmental labeling. European criteria for environmental labeling may even become barriers to North American exports (1). Green

USING COMMON AOX ANALYSIS TECHNIQUES CAN DISTINGUISH BETWEEN BLEACHED VIRGIN CHEMICAL PULPS PRODUCED WITH OR WITHOUT THE USE OF CHLORINE CONTAINING BLEACH CHEMICALS. THE AOX CONTENTS OF RAW MATERIALS CONTRIBUTE TO THE AOX CONTENT OF THE FINAL PRODUCT. AOX MEASUREMENTS ON COMMERCIAL PAPER SAMPLES PRODUCED WITH TCF AND NON-TCF PULPS SHOW SIGNIFICANT DIFFERENCES.

Seal has recently issued an Environmental Standard for certification of “no chlorine bleach” (2). This standard uses an audit of the manufacturing process.

The concepts in this paper may form the basis to confirm some environmental labeling claims. Today one can find claims for “chlorine free” chemical market pulps, deinked market pulps, and printing paper. We have measured

the chlorine content in terms of AOX for some commercial printing papers, market pulps, and some common raw materials used to manufacture printing paper. Not surprisingly, there is a measurable AOX content in nearly all these materials. While this makes the phrase “chlorine free” somewhat ambiguous, the data suggest that there are measurable differences between pulp and paper samples manufactured with or without the use of chlorine containing bleach chemicals.

AOX MEASUREMENTS

The AOX analyses used the method of Stevens *et al.* (3). An air-dried sample of 10–20 mg was weighed and compressed in the 4.5-mm diameter stem of a funnel between two plugs of ceramic wool. About 5 mL of 0.08 M KNO₃ solution was pulled through the plug (ceramic wool and sample) by low vacuum. The plug was placed in a quartz boat and analyzed by a Mitsubishi TOX-10 AOX analyzer. This unit performed a pyrolysis at 950°C in an oxygen atmosphere followed by a coulometric titration for chloride. Samples were run in duplicate with a series of blanks and trichlorophenol standard.

Pulp sample	TCF	Avg. AOX, mg/kg	Paper sample	TCF	Avg. AOX, mg/kg
No Amer SWKr 1	Y	6.0	Europe 1	Y	2.0
No Amer SWKr 2	Y	8.4	Europe 2	Y	21.8
No Amer SWSu 3	Y	2.6	Europe 3	Y	45.2
No Amer HWSu 4	Y	16.4	Europe 4	Y	85.9
No Amer SWKr 5	N	124.6	Europe 5	Y	107.7
No Amer SWKr 6	N	132.8	Europe 6	Y	154.2
No Amer SWKr 7	N	225.0	Europe 7	Y	175.7
No Amer SWKr 8	N	229.6	Europe 8	Y	255.8
No Amer HWSu 9	N	391.6	Europe 9	Y	321.8
No Amer Deink 10 (A)	Y	271.2	Europe 10	Y	333.8
No Amer Deink 10 (A')	Y	418.2	Europe 11	Y	360.2
No Amer Deink 11	Y	287.0	Europe 12	Y	362.8
No Amer Deink 12	Y	244.0	Europe 13	N	757.5
No Amer Deink 12 (B)	N	272.4	Europe 14	N	1265.8
No Amer Deink 12 (B')	N	302.7	No Amer 15	Y	47.4
			No Amer 16	Y	64.8
			No Amer 17	Y	99.2
			No Amer 18	Y	274.8
			No Amer 19	Y	398.6
			No Amer 20	N	534.8
			No Amer 21	N	570.9

I. AOX content of pulp samples

AOX CONTENT OF PULP SAMPLES

We obtained a variety of bleached chemical pulps and bleached deinked pulps and tested them for AOX content. All the pulps are commercially available market pulps except in-house hardwood sulfite and deinked pulp. All samples came from purchased pulp lots.

Table I shows that the pulps labeled as chlorine free actually contained 6.0–16.4 ppm of AOX. The pulps labeled as either ECF or not labeled contained 124.6–391.6 ppm of AOX.

The two hardwood sulfite samples represent samples collected from a bleach washer using O_pH and O_pP bleaching sequences. These samples—Samples 4 and 9 in Table I—were manufactured at Cross Pointe's Flambeau Mill.

Using this data, measurable differences in AOX content obviously exist between "TCF" and "non-TCF" pulps. In addition, the term "TCF" is clearly a misnomer. Although the pulps were bleached without the use of chlorine containing bleach chemicals, Table I shows that a significant but small amount of AOX is present.

Measurement of AOX content on deinked pulp samples showed higher AOX values and gave no correlation to the bleach process used. Three samples of deinked pulp bleached without the use of chlorine chemicals

II. AOX content of paper samples

showed 287–418 ppm of AOX. Samples bleached with sodium hypochlorite showed 272–303 ppm of AOX.

AOX CONTENT OF PAPER SAMPLES

We next obtained a variety of commercial printing papers marketed as "chlorine free." This means manufacture with TCF pulps. These were tested for AOX content. For comparison, we also tested papers manufactured with chlorine based bleaching sequences.

Table II shows the results of these tests. A variety of European papers marketed as "chlorine free" showed AOX contents of 2.0–362.8 ppm of AOX. Samples not marketed as "chlorine free" showed much higher AOX levels. Test results on North American samples showed similar trends with "chlorine free" papers containing 47–275 ppm of AOX and "nonchlorine free" papers containing higher amounts of AOX.

AOX CONTENT OF RAW MATERIALS

Table III shows results for some raw materials used in pulping and papermaking. Wood chips from several geographical locations in North America contained 2.5–8.8 ppm of AOX. Calcium carbonate from an on-site plant was free of AOX. Wet-end and surface starches contained 25.4–32.1 ppm of AOX.

Sample	Avg. AOX, mg/kg
--------	-----------------

Wood chips, No SW	2.5
Wood chips, So SW	5.7
Wood chips, So HW	6.8
Wood chips, No SW	8.8
Wood chips, No HW	8.8

Prec. calcium carbonate	0.0
Cationic wet end starch	25.4
Ethylated S press starch	32.1

III. AOX content of raw materials

pulp, the results are less clear. It appears that the AOX content of deinked pulp has a high degree of variability. This relates to the final paper product. Paper containing deinked pulp bleached without the use of chlorine chemicals shows AOX contents between those of the "chlorine free" papers and "nonchlorine free" papers. Samples we have measured do show less AOX content than paper manufactured with pulps bleached with chlorine chemicals.

A key observation is that TCF deinked pulps have the same AOX content as chlorine-based deinked pulps. Table I shows the level in the pulps studied thus far was greater than 240 ppm of AOX.

TRACING AOX THROUGH MANUFACTURING PROCESSES

We have manufactured commercial printing paper containing only virgin pulps bleached with only oxygen and peroxide. Table II indicates that testing on this paper showed 47–65 ppm of AOX. Table I shows this paper used pulps having AOX contents of 8–16 ppm of AOX. Manufacturing the same paper with the addition of 20% deinked pulp (from 100% post consumer waste and bleached with peroxide and hydrosulfite) gave a paper with AOX content 275–400 ppm as Table II shows.

Table III shows that wood chips have a measurable AOX content. The amount contained in wood chips is comparable to the amount of AOX in pulp samples not bleached with chlorine compounds. This accounts for the AOX content of pulps bleached without chlorine compounds.

The addition of starches to the fiber in the paper manufacturing process accounts for additional AOX in the final paper product as Table III shows. We have not tested other additives used in manufacturing fine papers, but we would expect measurable AOX in many additives used.

When looking at paper made with virgin pulps not bleached with chlorine chemicals, the AOX content of the paper can relate to the AOX content of the pulps and additives. When looking at paper containing deinked

CONCLUSIONS

Our data shows measurable differences in AOX content for pulp bleached with and without chemicals containing chlorine. Fine printing papers manufactured from these pulps show measurable differences in AOX content. Papers produced using TCF bleaching have significantly lower AOX content. Deinked pulp bleached with and without chemicals containing chlorine shows little difference in AOX content—AOX is greater than 240 ppm. The AOX content of paper relates to the major components of the paper—pulp and starch. TJ

Clapp and Truemper are technical director and product development manager, respectively, for Cross Pointe Paper Corp., P.O. Box 340, Park Falls, WI 54552. Aziz and Reschke are vice president-technology and chemist, respectively, for Integrated Paper Services, Inc., P.O. Box 446, Appleton, WI 54915.

LITERATURE CITED

1. Lucier, A., Pinkerton, J., and Miner, R., *Technical Studies of Environmental Issues Affecting Forest-Based Manufacturing Industries*, NCASI, New York, 1994.
2. Anon., *Green Seal Standard GS-7*, 3rd edn., Green Seal, Washington, 1994.
3. Stevens, B. J., Sell, L. O., and Easty, D. B., *Tappi J.* 72(7): 181(1989).