

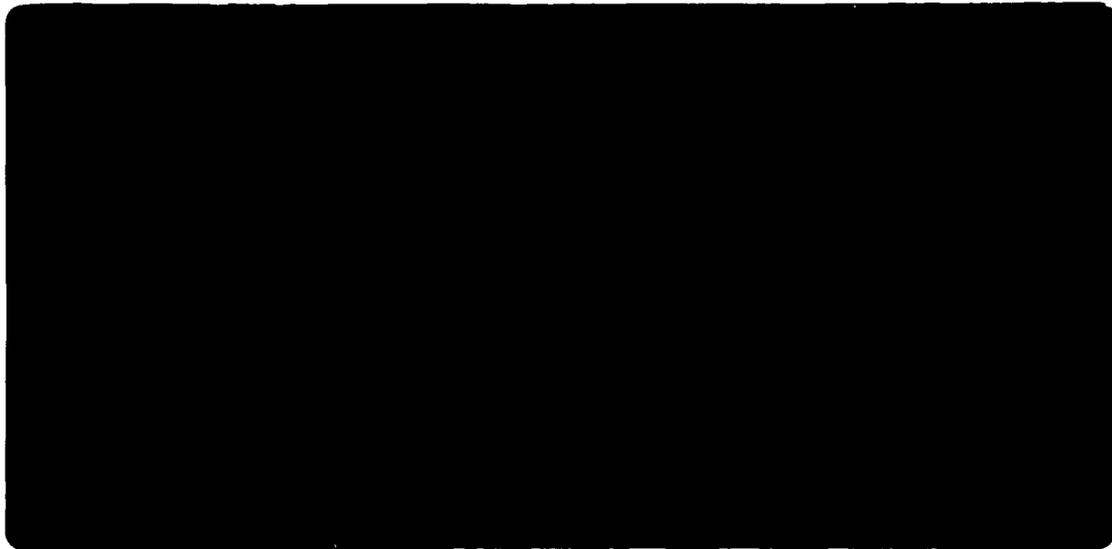


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**PERMEABILITY-STRENGTH RELATIONSHIPS  
IN OZONATED RECYCLED NEWSPRINT**

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# Permeability-Strength Relationships in Ozonated Recycled Newsprint

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## Permeability-Strength Relationships in Ozonated Recycled Newsprint

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### ABSTRACT

There are economic incentives to improve the strength in many grades of paper having significant secondary fiber content. We hypothesized that mild pretreatment of secondary fibers with ozone might attack the surface of the fibers and increase bonding potential without significant losses in the permeability to water of the wet web. Previous IPST research suggested this possibility for unbleached kraft fibers (OCC). Our fiber source for this study was old newsprint produced with a 40% recycled paper content.

We found that ozone pretreatment of the high-consistency pulp or of moist handsheets could significantly increase the strength of paper made from the old newsprint. Best results required elevation of the pH immediately after ozonation. While a significant drop in freeness was not detected with ozonation, the measured Darcian permeability did decrease. Kozeny-Carman analysis suggests that the decreased permeability was due to an increase in the specific surface area of the pulp rather than an increase in fiber swelling. A surface "etching" effect from the ozone may contribute to fiber roughness or fibrillation or fines generation which increases the specific surface area. Reactions with lignin may be most important in enhancing bonding. Much remains unknown about the effect of ozone pretreatment on surface chemistry and on fiber-water interactions for recycled paper manufacture, and further work is needed in this area.

### KEYWORDS

Ozonation, recycled paper, newsprint, strength, permeability, porosity.

## INTRODUCTION

Unlike chemically pulped fibers, mechanical fibers do not experience hornification as they are dried (1). Hornification causes a loss in swelling and strength in chemical pulps. There need not be a loss in strength for recycled mechanical pulps if the paper has not been aged for more than a few weeks and if the pulping and stock preparation procedures are gentle. In some cases, at least in the lab, increases in strength occur due to increased flexibility of the fiber after successive mechanical treatments such as pressing and pulping (1). However, contaminants and high fines content in recycled newsprint may compound runnability problems, and increased web strength would be desirable. As recycled content increases in North American paper, the average fiber age will increase and average secondary fiber properties will decrease, leading to increased runnability problems and perhaps the need to size newsprint. Economic incentives to reduce kraft content (especially virgin kraft) and to reduce basis weight in newsprint also make increased web strength a useful goal.

Using conventional refining strategies, deinked newsprint has shown little gain in strength. However, Canon and DeFoe (2) and DeFoe and Demler (3) report that low-intensity refining can be used to obtain strength improvements. In one experiment with 100% ONP, low-intensity refining yielded an 18% increase in tensile index, with a 34% decrease in freeness.

Ozone, a strong oxidant, can affect both internal and external fiber structures. Ozone's reactions with hemicellulose and lignin compounds of cellulose fibers may have the potential to increase interfiber bonding for mechanical fibers (4). Conflicting results have been published for chemical pulps, but proper application of ozone may also increase bonding in unbleached kraft fibers. For example, previous work with ozonated OCC at IPST indicated the potential for strength gains without a significant loss in freeness (5). In bleached kraft pulp, however, ozone generally decreases strength.

While some work has examined freeness changes with ozonation, we know of no previous work that has explored the relation between ozonation and wet sheet permeability (a measure of the flow resistance to water flow in a wet, compressed sheet), which is more directly tied to sheet performance in pressing and drying than is freeness. Indeed, previous work studies of permeability at IPST have demonstrated that two similar pulps with identical freenesses can have significantly different wet permeabilities if the

pulps are treated differently (e.g., different methods of refining) (6). As a result, the lack of change in freeness reported for ozonated OCC need not indicate that drainage properties (especially in the press section) were preserved, though it is likely they were. It would be highly desirable if ozone could be applied to improve strength without the loss in water removal ability that comes from refining. We hypothesized that ozonation could be used to increase strength in mechanical fibers without a significant loss in permeability, and began this study to explore that possibility. Improved runnability with recycled newsprint at high levels of production is the ultimate goal.

### DARCIAN PERMEABILITY

Paper permeability is commonly expressed in terms of gas flow rates through a sheet. This practice is useful for comparing similar sheets, but does not truly characterize the interaction of flowing fluid with the porous structure and provides no direct information about flow in a wet sheet. The standard engineering definition of permeability provides a more useful parameter, though one less easily measured. The standard definition is based on Darcy's law (7), which, for one-dimensional flow, states that the velocity of fluid flow through a saturated porous medium is directly proportional to the pressure gradient:

$$v = \frac{K \Delta P}{\mu L} \quad (1)$$

where  $v$  is the superficial velocity (flow rate divided by area),  $K$  is the permeability,  $\mu$  is the fluid viscosity, and  $\Delta P$  is the pressure drop in the flow direction across a distance  $L$ . The units of  $K$  are  $m^2$ . In Equation (1), the permeability is an empirical parameter linking fluid velocity to pressure drop and viscosity. For a homogeneous medium,  $K$  is not a function of  $\Delta P$ , sample length, or viscosity, but is an intrinsic parameter describing the flow resistance of the medium. In a compressible medium, permeability will be a strong function of the degree of compression.

Darcian permeability is commonly a fundamental parameter for processes involving fluid flow in fibrous webs (8-11). Permeability can control the amount of water removal possible in a press nip. Permeability is also of direct importance in drying operations, where it affects vapor flow and liquid flow driven by bulk pressure gradients (12).

We define porosity,  $\epsilon$ , as the fraction of the sample volume not occupied by solid. It is determined from the sheet thickness (under compression during a permeability measurement) and oven-dry weight:

$$\epsilon = 1 - \frac{m}{(\rho_c A L)} \quad (2)$$

where  $m$  is the sheet mass,  $L$  is the compressed thickness of the sheet,  $A$  is the sheet area, and  $\rho_c$  is the density of the solid itself, taken as the density of pure cellulose,  $1.55 \text{ g/cm}^3$ .

The permeability of a deformable porous medium changes as porosity is reduced through sheet compression. Formulas relating permeability and porosity can be derived by making simplifying assumptions about the structure of the medium. For example, by assuming that the pore network consists of many distinct, continuous, and regular channels passing from one end of the porous medium to another, the well-known Kozeny-Carman equation can be obtained:

$$K = \frac{1}{\kappa S_o^2} \frac{\epsilon_o^3}{(1-\epsilon_o)^2} \quad (3)$$

where  $S_o$  is the surface area per unit volume of solid material, and  $\kappa$  is a shape factor (the Kozeny constant) that accounts for effects of channel shape and orientation. Here,  $\epsilon_o$  is the extrafiber pore space, which excludes the pore space trapped in the cell wall or lumen of the fiber. The water trapped in the cell wall presumably does not contribute to flow and in effect increases the apparent volume of the solid (immobile) phase.

The Kozeny constant,  $\kappa$ , can be derived for ideal, simple pore structures, but becomes an empirical factor for real porous media. In many cases, it is not constant but a function of porosity. For fibrous media, 5.55 is a widely used value which works well in many cases (13), although values typically may lie in the range of 3-7 for porosities less than 0.8 (14).

The effective volume of the swollen fibers is defined as  $\alpha$ , with units of  $\text{cm}^3/\text{g}$ . At a concentration of  $c \text{ g/cm}^3$ , the extrafiber porosity is

$$\epsilon_o = 1 - \alpha c \quad (4)$$

which can be used instead of  $\epsilon$  in Equation 3, with the assumption that  $\kappa = 5.55$ , to yield

$$K = \frac{1}{5.55 S_o^2} \frac{(1-\alpha c)^3}{\alpha^2 c^2} \quad (5)$$

Now, we note that  $\alpha S_o = S$ , where  $S$  is the flow-exposed surface area of the fibers per unit mass, commonly called the specific surface area. Incorporating this definition into Equation 5 and rearranging, we obtain

$$(Kc^2)^{1/3} = \left( \frac{1}{5.55 S^2} \right)^{1/3} (1-\alpha c) \quad (6)$$

which is a classic equation that has been applied frequently to pulp mats (15). By plotting permeability data from a single sample at various compressive plots as  $(Kc^2)^{1/3}$  versus  $c$ , the specific volume,  $\alpha$ , can be obtained from the slope and the specific surface,  $S$ , can be obtained from the intercept.

## OZONE TREATMENT OF PAPER

A general review of ozone reactions with lignocellulosic materials can be found in (16). Here we will briefly review its effects with mechanical fibers and recycled materials. Bleaching effects will not be discussed.

### Ozone Treatment of Virgin Mechanical Pulp

Mechanical pulps are weaker than chemical pulps due to lignin. Ozone reacts with available lignin more aggressively than with holocellulose. Ozone will primarily attack the phenolic groups of lignin which results in increased carbonyl groups at the cost of reduced aromaticity (17).

In a study by Lindholm and Gummerus (18), groundwood (GW), pressurized groundwood (PGW) and thermomechanical pulp (TMP) were treated by alkaline sulfite and ozone to determine delignification. The results were expressed as absolute reduction in void volume per weight of pulp. Ozone treatment did not reduce the void volume as much as sulfite did. SEM micrographs show that sulfite-treated fibers developed more fibril-like threads that seemed more loosely bonded than ozone-treated fibers did. The ozone-treated fibers were bonded by filmy formations.

Lindholm's study of Scott Bond and other strength parameters (19) give further indication of the bonding properties, showing that ozone was superior to sulfite in improving the strength properties in all tested pulping types. Ozone reacts very slowly with pulp in the consistency range of 1-20%. In low consistencies 1-3% it was necessary to apply intensive stirring, the negative effects of which can be prevented by choice of a proper ozonation reactor. Less acidic groups were formed in low consistency ozonation than in high consistency gas ozonation. Also, in low consistency, the major proportion of ozone reacted with fines compared to high consistency ozonation where reaction was far less selective allowing all fiber sizes to be ozonated.

Another study about Tamarack TMP ozonation contends that the increase of acidic COOH groups

was more rapid when low ozone charge was used compared to high charges (20). This is based on the lesser availability of attack sites on the fiber surface. The higher content of COOH groups will increase the number of hydrogen bonds and result in better interfiber bonding. An increase in density was also observed as ozone charge was raised. This would result from growing hydrophilicity due to COOH groups. This swelling would cancel the effect of void formation. In conclusion, ozonation may not have any significant net effect on mechanical pulp sheet density.

Lindholm has also compared the effects of various delignification methods on the coarse section of groundwood pulp (21). He found that ozone treatment, especially at low consistency, improved tear and tensile without changing the density as drastically as chlorine dioxide did. Based on his study, it can be concluded that ozone did not affect the proportion of excess fines that result from other treatments. This is important for drainage as well as for optical and printing properties. In a related study (22), Lindholm concluded that use of low consistency ozone-treated coarse groundwood pulp could allow considerable reduction in the proportion of kraft pulp in newsprint furnish without impairing tear properties. Groundwood containing 30% of ozone-treated coarse components reduced the need for adding kraft pulp from 18% to 10%.

### Ozone and Recycled Fibers

Above, we have mentioned a previous IPST study on the ozonation of OCC (23). The recycled corrugated containers were made from softwood unbleached kraft and hardwood NSSC pulps. Fluffed pulp of 40-50% consistency was ozonated in a gaseous oxygen stream containing 2% ozone at room temperature. Ozone consumption ranged from 0.8 to 12% of o.d. fiber weight. At the optimum level of 2.3% ozone consumption, burst improved by 35%, breaking length increased by 26% and density grew by 10%. Simultaneously, tear and standard freeness were reduced by only 3%. These changes were attributed to increased interfiber contact and conformability contributed by microfibrillation.

The British PIRA (24) studied secondary fiber ozonation including unprinted newspaper, sized and unsized semibleached kraft, computer paper, sulfite pulp, and unbleached kraft. In the PIRA experiments the stock consistency ranged from 30-56%, ozone concentration in oxygen stream was 2.7%, flow rate was 2.1 l/min and pH was adjusted to 4.5. The ozone consumed ranged from 0.5-10% of o.d. fiber weight. Relatively more

ozone was used for mechanical and unbleached pulps. The burst and breaking length of selected pulps changed as follows:

Material	Oz. use, % o.d. wt.	Burst, % change	Tensile, % change
newspaper	3.1	+25	+24
sized semi-bleached kraft	0.6	+14	+7
unsized semi-bleached kraft	0.4	+10	+13
sulfite pulp	2.2	+15	+23
unbleached kraft	2.0	+19	+15

Table 1. Physical property changes with ozonation from the PIRA study.

The PIRA study points out that ozone demand varies from pulp to pulp. The results also show that burst and tensile of unprinted newsprint increased. This is likely due to improved inter-fiber bonding. At the same time, bulk, tear and drainage time decreased. Also in this study, ozonation was conducted at various pH levels. The alkaline range (except very high pH values) appeared more favorable compared to acid or neutral ranges.

Soteland and others at the Norwegian PFI (25-30) have examined ozonation in recycled and virgin pulps. In Soteland's recycling study, he ozonated two types of recycled pulps. The first contained corrugated containers and old bags. The second contained non-deinked printing papers. Both pulps were of undetermined composition. The fluffed pulp was ozonated in the consistency of 35% at room temperature and pressure using 2% ozone in an oxygen stream. After ozonation the pulp was diluted with water and the pH was adjusted to 8.5. Mechanical refining was applied afterwards.

For the first pulp, the maximum increase in burst and least loss in tear were obtained by using 1% ozone based on o.d. pulp weight. Higher ozone dosages gave less favorable results. For the second pulp, two different refining techniques were used after ozonation. Test results did not show any clear effect of ozone on strength properties. It was speculated that the ozonation conditions were not optimized and the dilution after ozonation was detrimental. This is a hint that post-ozonation treatment may be important in determining the net effect of ozonation on mechanical properties.

## EXPERIMENTAL WORK

### Raw Materials and Preparation

Old newspapers having roughly 40% recycled paper content were repulped for raw material. Old local newspapers were pulped and refined using a lab pulper. 1kg of dry paper was added to 20 l of water resulting in about 5% consistency. The repulping required 6 min and the total power consumed was 74 Wh. The freeness obtained was 180 CSF. The 5% pulp slurry was further disintegrated without deinking in a laboratory disintegrator using 40,000 rotations to a freeness of 103 CSF.

Ozonation at high consistency required vacuum draining of disintegrated pulp slurry in a buechner funnel. Drained slurry formed a solid cake, which was "fluffed" into smaller fiber bundles for ozone exposure. A high-speed laboratory mixer with a propeller that beat the pulp to desired texture was used.

High solids content during bulk ozonation was targeted. Optimum tensile strength according to preliminary experiments seemed to be achieved around 35-40% solids. If the moisture content was too high, the pulp tended to stick to the walls of the reactor regardless of the rotation and mixing.

Preliminary testing showed that ozonation required substantial moisture content in the sheet. Two different solids levels, 15% and 43%, were chosen.

Handsheets were tested for strength properties, optical properties, air flow and Darcian permeability.

### Ozonation Generator

A corona discharge ozone generator, PCI model GL-1, was used to generate 3% ozone by weight in an oxygen stream at 15 psig pressure at standard ambient laboratory temperature and RH. Operating dew point is required to be -60F or lower. The power to generate ozone featured 8kV and 1.5 kVA. The attached monitor, Model HC Nema 12, displayed the ozone stream reading "on line" at  $\pm 3\%$  accuracy using absorption of ozone by UV light. The charge was adjusted to 0.025 g ozone/min using a flowmeter and output dial. For practical purposes, it was decided to use constant ozone charge per time unit and vary the processing time. For hand sheet ozonation, the same flows were used as for fiber treatment, and the time was kept constant.

## Application of Ozone

**Bulk Ozonation.** For fiber bulk treatment, ozone gas in an oxygen stream was led directly to a reactor through tubing. The reactor was a round glass flask attached to a variable speed rotovapor turner to rotate the flask as ozone passed over the fibers. The rotation speed sometimes had to be varied, and occasionally, the reactor bottle had to be tapped to loosen the fibers that were driven to the walls by centrifugal force. Excess gases were led from the flask to several KI quenching solution traps. Fluffed fibers and glass beads for better mixing were placed in the flask. Optimal solids content of the fluffed fibers for ozonation was 35-40% based on preliminary testing. Constant charge of 0.025 g ozone/min was used and the time was varied.

In determining the applied ozone charge, it is assumed that all of the generated ozone reacted with the pulp. Some ozone probably did leave the reaction vessel in our tests, but this was not measured. As a result, our reported ozone charges are likely to be slightly higher than the true ozone consumed by the fibers.

After ozonation, deionized water was poured into the flask to remove all the fibers. The pH of the fiber slurry was then adjusted to 8.5 using NaOH. After gentle disintegration, using 5000 rotations, 45 g/m<sup>2</sup> handsheets were formed in the British handsheet mold using the TAPPI method. Control sheets were made of untreated fibers and fibers treated with NaOH only.

**Sheet Ozonation.** For sheet ozonation, handsheets were supported on a buchner funnel in a sealed chamber with controlled inlet and outlet flows. Ozone gas was pushed through the sheet by above-ambient pressure; the exiting gas was then quenched in aqueous KI solution.

Handsheets of the disintegrated old newsprint slurry were made to 45 g/m<sup>2</sup> basis weight in the British handsheet mold using the TAPPI method, except that they were pressed to two different solids contents: 15% and 43%. The handsheet was placed to cover the bottom funnel's perforated surface.

Various procedures were applied. First, a set of sheets including high and low solids contents was ozonated for 1 minute per sheet. After ozonation, half of the sheets were treated with NaOH spray. A second set of sheets were sprayed with NaOH before ozonation for 1 min/sheet. After ozonation, half of the sheets were further treated with NaOH spray.

The above procedures for the first set of sheets were conducted again, but with an ozonation time of 0.5 min/sheet.

## Testing

**Physical Properties.** Tensile, tear, basis weight, and Bentsen air flow were tested in the IPST paper analysis laboratory using TAPPI and IPST standard methods.

Freeness as CSF was measured from untreated pulps disintegrated using the "standard" 40,000 revolutions as well as 50,000 revolutions and from ozonated pulps that had been ozonated to various degrees. The test results did not show any significant differences between any of the samples.

Optical properties, TAPPI brightness (s-4), and TAPPI opacity were initially measured from ozonated and control samples in the IPST optical properties laboratory. The test results did not indicate significant differences. Optical measurements were not conducted further.

**Permeability.** The equipment used to measure transverse permeability is shown in Figure 2. Not shown is a pneumatically-driven Carver press which controls the applied load and motion of the upper permeability head. The basic features of the equipment and its applications have been previously reported (31,32).

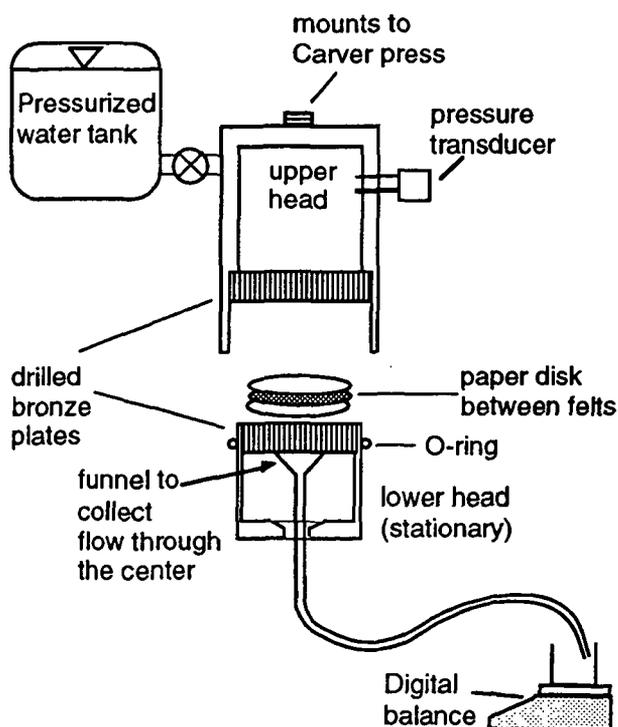


Figure 1. Schematic of the water flow system for transverse permeability measurements.

In making transverse permeability measurements, a saturated paper disk is compressed between two wet felts. The felts are in contact with finely drilled bronze plates that transmit mechanical pressure while allowing water to flow through. By measuring the flow rate through the sheet for a given pressure drop, information about the sheet permeability can be obtained. The permeability is given by:

$$K_z = \frac{L}{\frac{A_{\text{flow}} \Delta P}{Q \mu} - R_f}, \quad (7)$$

where  $A_{\text{flow}}$  is the cross-sectional area of the flow collection region (23% of the sheet area),  $L$  is the sheet thickness,  $Q$  is the volumetric flow rate,  $\mu$  is the viscosity of the water, and  $R_f$  is the inherent resistance of the felts and flow system.

Sheet thickness was obtained using a Kaman eddy-current transducer (ECT). By measuring the position of the upper head while compressing two felts alone and then while compressing the two felts plus paper, the thickness of the sheet could be obtained from the difference. Cubic regression of the thickness-versus-load data was done for the felts before and after each run. For the thin samples (often near 70  $\mu\text{m}$  when compressed) used in this study, we departed from our normal procedures because uncertainties in felt thicknesses were sometimes leading to large errors for the sheet thickness. Using results from several reproducible runs, we established compression curves for the recycled fibers, giving thickness as a function of mechanical load and sheet basis weight. We then relied on load and basis weight measurements to obtain sheet thickness for the samples in permeability measurements. This approximation increases the uncertainty in porosity and permeability measurements compared to our normal procedures with much thicker sheets. While absolute values for permeability may be in error by 30% and porosity values in error by 10%, these errors are unlikely to affect observed trends significantly.

## RESULTS AND ANALYSIS

We present sheet property results separately for bulk ozonation runs (ozonated pulp subsequently made into handsheets) and for sheet ozonation runs (handsheets to which ozone was applied).

### Bulk Ozonation

For each ozonation and pH condition run, four to five handsheets were made and tested for physical properties. Results for tensile strength index as a function of ozone charge are shown in Figure 2. Each symbol on this plot is the average tensile value for the four or five handsheet set. The typical range for the entire set of handsheets for each test condition is  $\pm 2$  Nm/g (i.e., range bars on Figure 2 would typically extend over a range of  $\pm 2$  Nm/g around each plotted symbol). Three sets of data are shown. The data labeled "pH Elevated" had the pH following ozonation raised to 8.5 or higher by addition of a fixed quantity of caustic. The low pH data stayed acidic following ozonation.

Two runs labeled "Delayed pH Elevation" refer to tests in which pH elevation was delayed by roughly an hour following ozonation, instead of the normal, nearly immediate addition of caustic to the pulp after ozone treatment. At 2% ozone charge, high tensile strength improvement is seen for the normal procedure, but if there is a substantial delay before pH elevation, the strength gain is much less. The reasons for the apparent effect of timing in the addition of caustic are not known. The important result is that it appears possible to obtain over 25% increased tensile strength with 2% ozone, and that pH elevation after ozonation is required for strength increase. This strength gain cannot be explained by caustic addition alone, for at zero ozone charge, the low pH batch had a slightly higher tensile strength than the batch at elevated pH (10.9). There seems to be synergism between ozonation and a subsequent elevation of pH. For example, acid groups may be added to the lignin during ozonation, which are then modified by caustic to enhance surface-water interactions and hydrogen bonding. Or, perhaps, more cellulose is exposed by ozonation, which can then swell in the presence of caustic to enhance fiber flexibility and bonding. If the time between ozonation and pH elevation is indeed important, additional mechanisms must be invoked. Further work will be required to confirm and elucidate this effect.

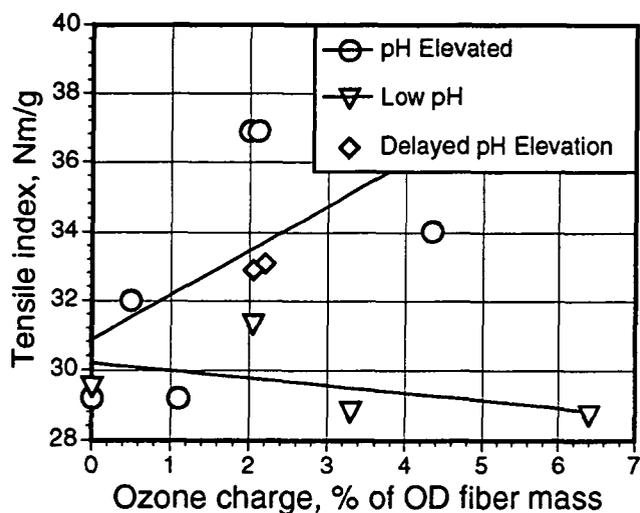


Figure 2. Tensile versus ozone charge for three different pH treatments.

While freeness measurements did not show a noticeable difference in ozonated and unozonated pulps, the low freeness range of newsprint may make changes in true water removal capacity difficult to detect using freeness alone. And, as we have mentioned above, water removal behavior for a given pulp can be changed substantially without always causing a change in freeness. We therefore must examine permeability data, which are a clearer indicator of water removal behavior on the paper machine.

Permeability measurements were conducted in many of the pulps, but not all. Kozeny-Carman analysis of the results showed no clear trend in fiber specific volume of the fibers. A relationship between specific surface and ozone charge was detected, as shown in Figure 3. In general, ozone is decreasing sheet permeability by increasing the apparent surface area per unit mass of the fibers through which the fluid must flow in the mat.

The available tensile and specific surface data are plotted against each other in Figure 4. Now we see no obvious trend, even though we know that on the average, a higher ozone charge will increase specific surface. The implication is that optimum conditions may exist for strength improvement without serious drainage reduction.

Analysis of tear data showed no detectable change from 0% to 2% ozone charge, with tear index ranging between 6.7 and 7.4  $\text{Nm}^2/\text{g}$ . Above 2% ozone, tear values decreased (e.g., 6.3  $\text{Nm}^2/\text{g}$  at 6% ozone).

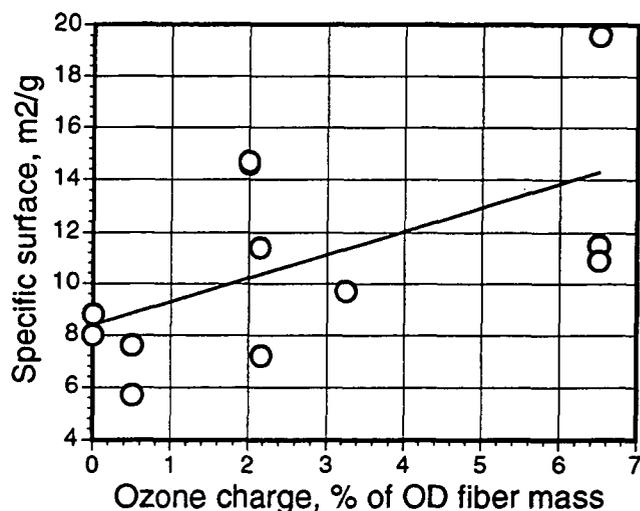


Figure 3. Relationship between ozone charge and sheet specific surface for bulk ozonated pulp.

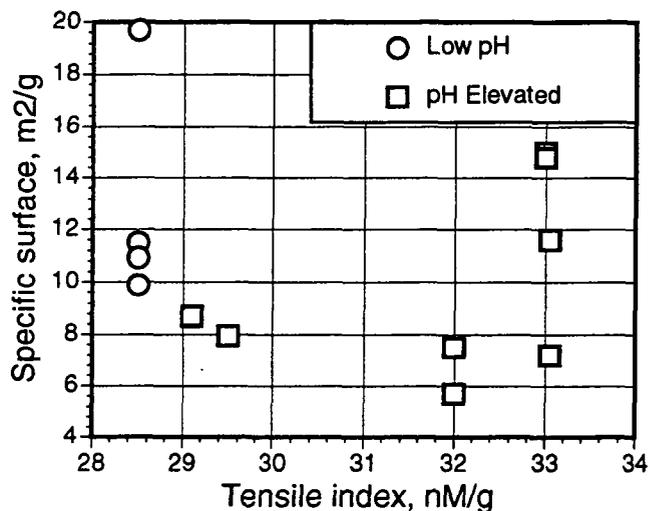


Figure 4. Specific surface versus tensile index for bulk ozonated pulp.

### Sheet Ozonated Runs

Relative tensile and relative tear results are shown in Figures 5 and 6, respectively. Ozonation sequences include ozone treatment alone ( $\text{O}_3$ ), ozonation followed by caustic spray ( $\text{O}_3$  NaOH), caustic spray followed by ozonation (NaOH  $\text{O}_3$ ), and caustic spray, ozonation, then caustic spray (NaOH  $\text{O}_3$  NaOH). Sheets were pressed to solids levels of 15% or 43% prior to treatment. Ozone gas was applied for 1 minute or 30 seconds. All data are relative to the nonozonated case.

The tensile data show the importance of ozonation sequence. Best results were obtained using

NaOH treatment after ozonation at high solids content, where tensile was increased by about 10%. This result is consistent with previous bulk ozonation results, but the smaller strength increase may result from uneven coverage by NaOH and ozone, or from not ozonating at the optimum level.

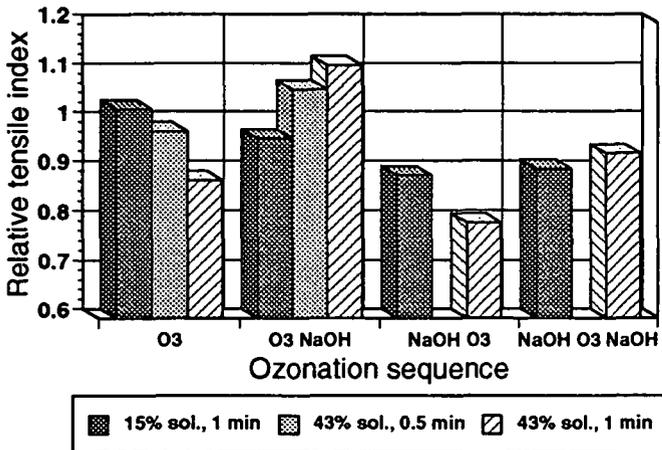


Figure 5. Effect of ozonation sequence on ozonated sheet tensile index.

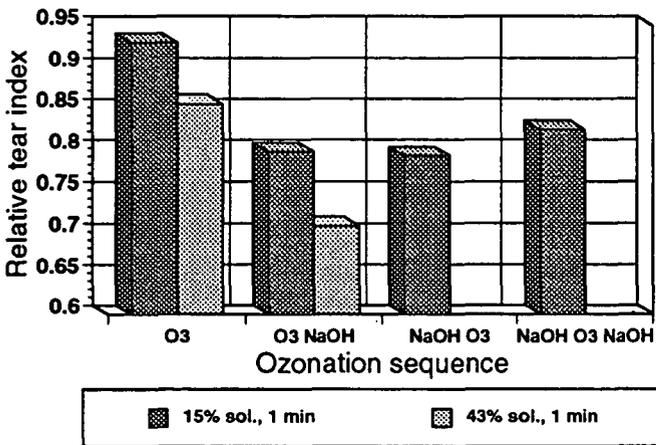


Figure 6. Effect of ozonation sequence on ozonated sheet tear index.

Tear decreases most in the cases where tensile is increased the most. Tear deteriorated in all cases of sheet ozonation. Ozonation alone at low solids had the least impact on both tensile and tear, indicating perhaps a condition where ozone attack was inhibited due to low solids.

Permeability data for sheet ozonation are not available.

## CONCLUSIONS

Ozone has the potential to increase the strength of recycled newsprint. For the furnish we studied, pH elevation following ozone treatment was required for good strength development. The best strength gain, over a 25% increase in tensile index, was obtained with 2% ozone charge applied to high consistency pulp. Under these conditions, however, a delay in pH elevation would not result in as great a strength gain. Further work is required to confirm the possible relationship between ozonation and subsequent pH adjustments.

Ozone attack favors lignin over cellulose, exposing more cellulose. It is possible that NaOH was able to enter the exposed fiber structure helping to increase fiber swelling and flexibility, improving bonding capacity of the fibers. There is also the possibility of chemical modification to the fiber surface that enhanced hydrogen bond formation under alkaline conditions.

Caustic addition alone does not account for the observed strength gains in recycled newsprint. Caustic addition before ozonation was more detrimental than useful. Usually tear is reduced when tensile is increased. However, in the best tensile range (ozone charge of 2%), tear was not significantly reduced.

While freeness was not clearly changed, permeability did tend to decrease with ozonation, but the correlation was weak; it may be possible to increase strength with ozone pretreatment without sacrificing drainage of the pulp. Kozeny-Carman analysis of the pulp indicates that the permeability decrease was due primarily to an increase in specific surface of the fibers rather than an increase in specific volume. This could mean that fiber swelling is not occurring under ozonation. However, the permeability measurements are done in neutral water. Temporary fiber swelling in the presence of caustic may have enhanced sheet strength. Our preliminary results warrant further investigation of permeability-ozonation effects.

It appears that the strength of recycled newsprint can be improved considerably by ozonation followed by caustic treatment and wet pressing. In the pulping of old newsprint, both neutral and alkaline conditions are used for pulping. However, on the papermachine, wood-containing papers are traditionally manufactured under acidic conditions. We do not yet know if the pH-elevated, ozonated stock will lose its strength if returned to acidic conditions. On the other hand, some mills have experimented with alkaline

papermaking for mechanical pulps also. Further work is clearly needed to identify the potential of ozone pretreatment followed by pH elevation for enhanced newsprint runnability, although ozonation currently must be regarded as an expensive operation.

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