

Laboratory-scale medium-consistency ozone bleaching system

Chivukula Sreeram, V.S.M. Sundaram, Hasan Jameel, and Hou-min Chang

ABSTRACT: *A laboratory design for medium consistency ozone bleaching using high-shear mixer is outlined. Ozone is compressed to a high-pressure in order to reduce the phase ratio of gas to fiber suspension and inject a larger quantity of ozone. Using the designed system the bleachability of oxygen bleached kraft pulp was studied. Ozone bleaching at medium consistency followed by an alkaline extraction stage showed considerable improvement in delignification and brightness gain with high selectivity. Optimum operating conditions to perform ozone bleaching at medium consistency with the high-shear mixer were low temperatures and pH 2 to 3. Low temperatures and low pH reduced ozone decomposition and increased available ozone for bleaching. An increase in speed of mixing from 1200 rpm to 2400 rpm while bleaching 10% consistency pulp resulted in better delignification and increased viscosity loss together with an increase in freeness loss. Bleaching 5% consistency pulp at 2400 rpm mixing speed had higher selectivity and lower specific consumption with comparable delignification as 10% consistency pulp at the same mixing speed.*

KEYWORDS: *Chemical degradation, experimental design, medium consistency, mixers, ozone bleaching, velocity.*

Increased worldwide concern over the environmental impacts of chlorinated organic compounds from bleach plant effluents has stimulated great interest in the development of nonchlorine bleaching agents such

as oxygen, ozone, and hydrogen peroxide. The higher oxidation potential of ozone makes it a promising bleaching agent as compared to oxygen and hydrogen peroxide in replacing molecular chlorine and

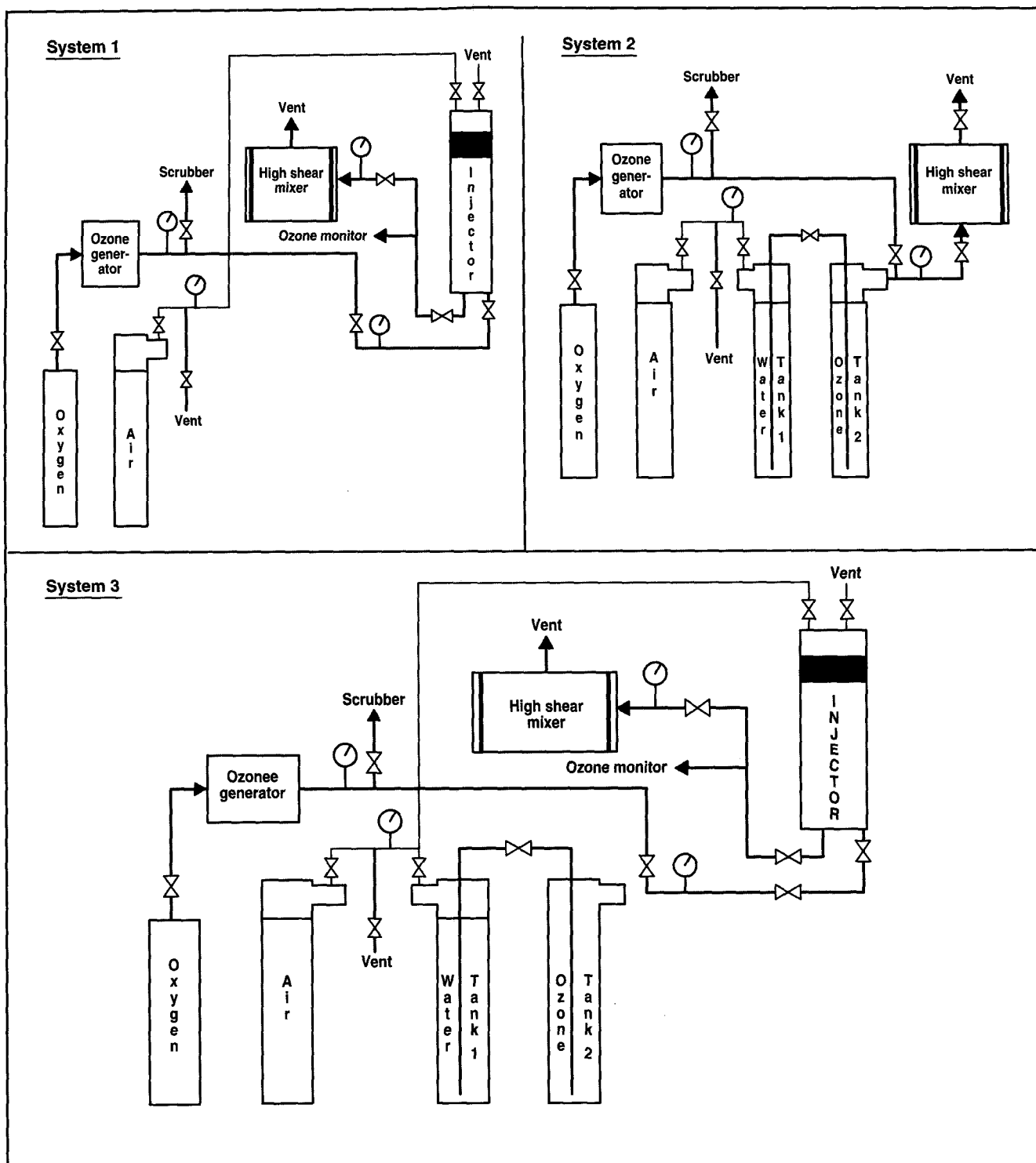
chlorine dioxide. However, the radicals generated due to ozone decomposition in water and during the reaction of ozone with lignin attack carbohydrates and reduce the pulp strength. The residual lignin in pulp seems to act both as a radical scavenger and a radical initiator (1). Until recently, because of problems with mixing ozone, ozone bleaching was conducted in the laboratory either at low consistency or at high consistency.

Both high- and low-consistency ozone bleaching have disadvantages from an equipment point of view. High-consistency requires extra machinery for dewatering, feeding and fluffing, while low-consistency requires equipment for handling and dispersing large volumes of water. Medium-consistency treatment is more adaptable to mill practice, but because of low ozone concentration in oxygen (carrier gas), a large volume of gas must be mixed with the pulp suspension. This phase ratio of gas volume to pulp suspension volume is too high to be handled effectively by regular mixers. Medium-consistency ozone bleaching in combination with high-shear mixing has been a challenge in terms of efficient design and cost.

The main objective of this study is to design a laboratory system for compressing ozone and to carry out medium-consistency ozone bleaching using high-shear mixer. The effects of temperature, pH, consistency, mixing speed, and retention time on pulp during ozone treatment were

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1. System modifications



studied for a constant charge of ozone (0.7% on o.d. pulp) to evaluate the system efficiency.

Design of ozone compression system

Difficulty in generation of high ozone concentration and danger of an explosion for concentrations beyond

15% are the major constraints in designing a suitable ozone compression system (2). Pure or concentrated ozone is inclined to explosive decomposition due to its unstable character. The rate of ozone decomposition

depends on a number of factors, such as UV radiation, temperature, pressure, metal ions, moisture, dirt, and purity of the carrier gas. Rapid decomposition of ozone is caused by autodecomposition of molecular ozone or by reduction of ozone to highly reactive intermediate radicals. Explosion can take place by mechanical shock effects such as compression, friction, vibration, and impact at low temperatures. If the upper limits of ozone concentrations are kept at less than the threshold of explosion limit then relatively safe handling of ozone mixtures is possible. The limiting concentration for explosion decreases with rising pressures and increases with falling temperatures. In the gaseous state, the limiting concentration is between 9% and 16% at atmospheric pressure and room temperature (3). Several options are available to compress the ozone-oxygen gas mixtures. Waller (4) showed that ozone concentrations less than 10% can be compressed with a diaphragm pump to 70 bar pressure and stored at room temperature. Laxen (5) has used a high-pressure water pump to compress low-concentration ozone in the carrier gas to 7–9 bar pressure to reduce the phase ratio of gas volume to pulp suspension volume and charge higher dosages of ozone on pulp.

System 1

Minimizing ozone decomposition increases the ozone available for bleaching. The compression system configurations in Fig. 1 were altered as shown to increase ozone available for bleaching and allow control of ozone charge. In System 1, ozone is collected and compressed inside the injector with a floating piston. The injector has a free gas volume of 4.7 L (free gas volume = total volume - volume of piston). There are two possible options for injecting the ozone with this system: (a) collecting ozone in the injector and compressing it before injection, (b) collection of

ozone in the injector and then compressing it in the reactor.

Compressed ozone injected into the Quantum mixer (Mark II model—Quantum Technologies) reactor bowl reacts with a fixed quantity of pulp suspension. Each ozone charge on pulp by injection is called a “pulse.” The head space above the pulp suspension in the reactor limits the amount of ozone that can be charged in a single pulse.

Ozone decomposition at various compression pressures was studied by bleeding the gas continuously through an ozone monitor for sufficient periods of time. The results obtained are shown in Fig. 2. The figure shows increased rates of ozone decomposition with increasing compression pressure. The limitations with this ozone compression system are: (a) the time lag involved between ozone compression and reaction with pulp tends to offset the quantity of ozone consumed by pulp, (b) the small volume of the injector increases the number of ozone charges and overall pulp mixing time in the reactor.

System 2

Increasing the amount of ozone charged in each pulse reduces the overall mixing time. To charge larger quantities of ozone, using water to compress ozone eliminates floating piston and compression vessel (injector) size limitations. In System 2, a large quantity of ozone is collected in Tank II and is compressed by transferring water from Tank I. Dip legs facilitate this operation. Air cylinder from a commercial supplier is used to transfer water from Tank 1 at a desired compression pressure. The tanks have a capacity of 44 L each. The material of construction of the tanks is a stainless steel alloy of DOT-3AA 2265 specification. Compressed ozone at a pressure of 135 psig in Tank II was injected in pulses (constant volume) stored in the reactor bowl at fixed intervals of time. The quantity of ozone charged in each

pulse was measured by titrating the reacted KI solution with $\text{Na}_2\text{S}_2\text{O}_4$ solution. This testing was done to corroborate the ozone concentration values obtained from the ozone monitor. The decomposition of ozone observed over a period of time in Tank II is plotted in Fig. 3. The following observations were made:

- (a) The ozone concentration immediately after compression was approximately 30% lower than the initial filling concentration.
- (b) The same final compressed ozone concentration was difficult to obtain when repeatedly compressed to the same compression pressure.
- (c) A further reduction of 15% in ozone concentration was observed when stored for 30 min.

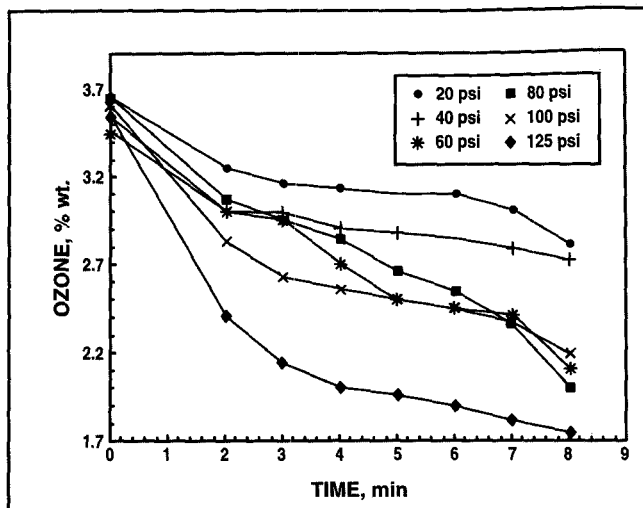
The increased loss in ozone concentration by compression with water can be due to increased solubility of compressed ozone in water (6). Ozone can also react with water to form reactive radicals. Once these radicals are generated they are known to initiate chain reactions to decompose ozone. Chelation of metal ions in water inside the tanks with EDTA and wrapping the injector with aluminum foil to reduce ozone decomposition did not prove beneficial. The other limitation with this system is that the time delays between consequent ozone pulses favors additional loss of ozone concentration.

System 3

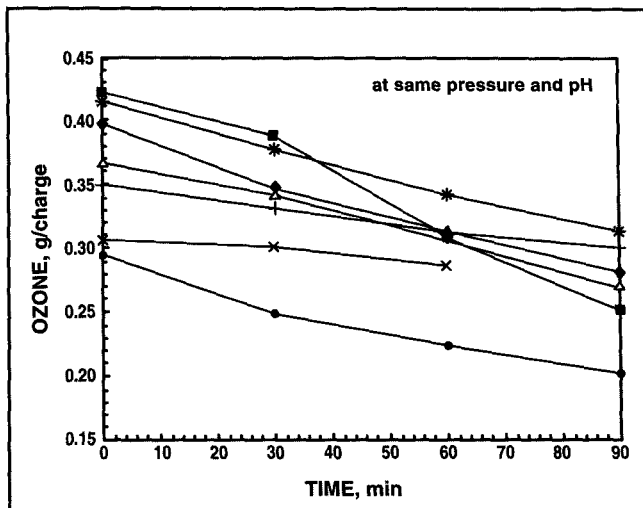
The failure of the above two systems to provide a constant ozone charge in each pulse necessitated further modification as shown in System 3. Addition of the injector with the floating piston to System 2 enabled phase separation of compressed ozone during storage. The phase separation was accomplished by transferring ozone in Tank II to the injector during compression. The injector prevents the water from being in contact with the compressed ozone during

Ozone Bleaching

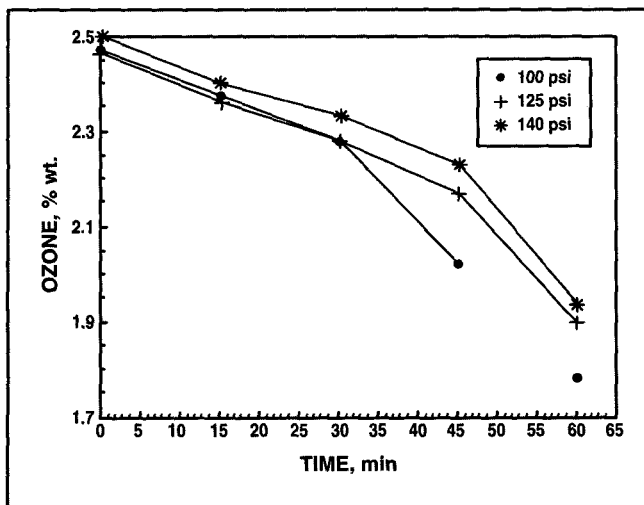
2. Decomposition of ozone in System 1



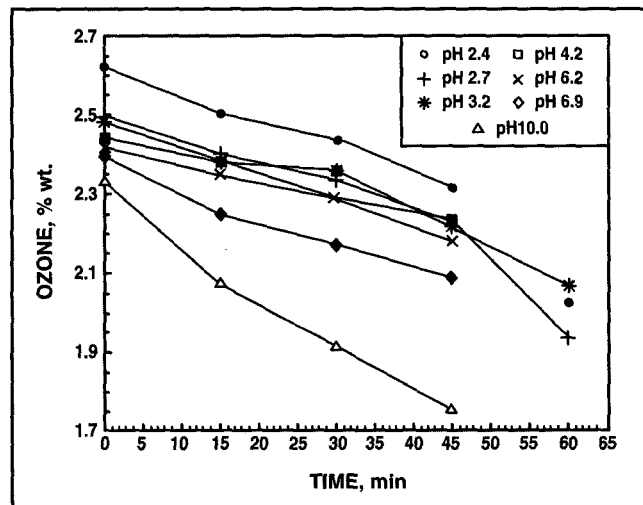
3. Decomposition of ozone in System 2



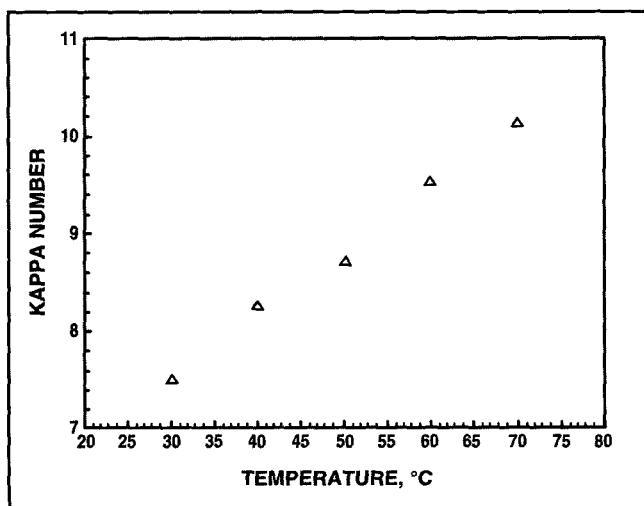
4. Decomposition of ozone in System 3



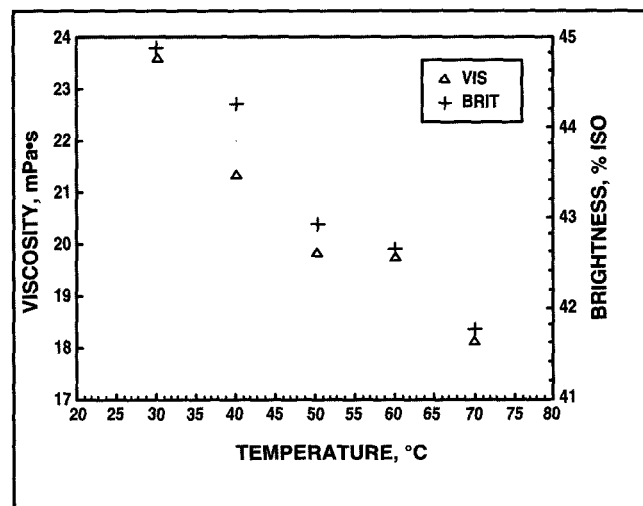
5. Decomposition of ozone at different water pH



6. Influence of temperature on kappa number



7. Influence of temperature on viscosity and brightness



storage. This inhibits the stored ozone from solubilizing at the gas/liquid interface to compensate probable decomposition of dissolved ozone. The concentrations of compressed ozone obtained at different compression pressures was the same and the rate of decomposition during storage was also the same, as shown in **Fig. 4**. This enabled the ozone charge on pulp in each pulse to be constant.

Figure 5 shows that the pH of water used influenced the concentration of ozone obtained after compression and the compressed ozone decomposition rate. Low pH water produced higher ozone concentration and slower decomposition rate after compression. Ozone charges in pulses at 0.5% and 0.6% on o.d. pulp were repeated several times and the system showed good reproducibility.

Experimental methods

The oxygen treated pulp used in this study was obtained from a nearby mill. The kappa number of the pulp was 19.6 with a viscosity of 33.6 mPa.s. The ozone was produced in Polymetrics Laboratory Ozonator that can generate up to 4% ozone concentration. The ozone concentration was measured using PCI Ozone & Control Systems Inc. monitor. Ozone was injected in pulses to a constant volume of pulp slurry at various consistencies. The injected ozone was left to react with the pulp for 1 min; this is called "reaction time." After reaction the charged ozone was vented into potassium iodide solution, acidified and titrated with sodium thiosulfate solution to measure the unreacted residual ozone. Ozone bleaching was followed by an alkaline extraction stage. The pulp after the extraction stage was analyzed for kappa number, viscosity, and brightness according to TAPPI test methods. The ozone compression system used is System 3. The experimental design followed is

shown in **Table I**, and conditions for alkaline extraction are shown in **Table II**.

Effect of reaction variables

The effect of reaction variables on pulp properties is critical to understand the commercial viability of a new process and to establish the process conditions. The reaction variables studied are: temperature, pH, consistency, mixing speed, and reaction time.

Effect of temperature

Commercialization of ozone bleaching involves the complete recirculation of process water. This leads to an increased system temperature. To understand the effect of temperature on ozone bleaching the experiment was done at 30°C, 40°C, 50°C, 60°C, and 70°C. The kappa number of pulp after ozone treatment at 0.7% ozone charge was found to be 7.5 at 30°C and 10.1 at 70°C as shown in **Fig. 6**. Lower temperatures tended to favor better delignification. Liebergott *et al.* (7) also reported similar findings for oxygen treated kraft softwood pulp that indicated decrease of kappa number by 2 units while reducing the temperature from 80°C to 20°C. The viscosity and brightness were lower at higher temperatures as shown in **Fig. 7**. Allison (8) reported that high temperatures tend to promote ozone decomposition and reduce the effectiveness of available ozone.

Effect of pH

Operating at high water pH promotes ozone decomposition presumably through ozone interaction with hydroxide anions to form hydroxyl radicals (9). The kappa number, viscosity, and brightness dependence of pulp on pH of ozonation were studied as shown in **Figs. 8 and 9**. Kappa number obtained decreased by about 3 units as the pulp pH was lowered from 8 to 2. However, reducing the

pH down to 1 reduced the delignification, and the kappa number was higher than that at pH 2 by about 2 units. The sulfuric acid demand increased exponentially for decreasing the pH lower than 2. The pulp viscosity was high at low pH and was found to decrease with increasing pH.

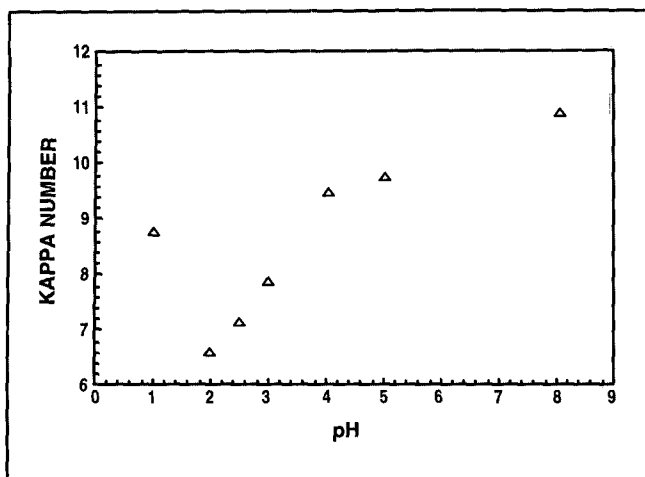
Effect of consistency

Bleaching low-consistency pulps with the technological advancements in mixing improved the contact between ozone and pulp. The kappa number, viscosity, and brightness dependence of pulp on the consistency of ozonation was studied from 1% to 10% consistency. The increase in pulp consistency from 1% to 10% resulted in the decrease of kappa number obtained as shown in **Fig. 10**. Varying the pulp consistency decreased the viscosity and increased the brightness as shown in **Fig. 11**.

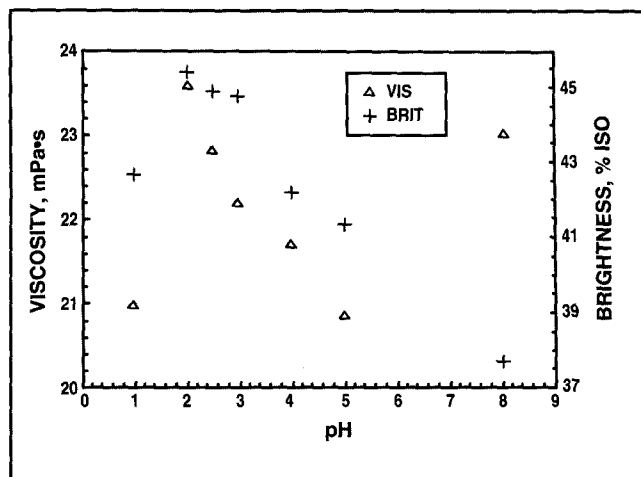
Effect of mixing speed

Improved mixing promotes uniform distribution of chemical and increases the overall rate of reaction so that the chemical is consumed more rapidly and efficiently (10). The kappa number, viscosity, and brightness dependence of 5% and 10% consistency pulps at various mixing speeds is shown in **Figs. 12–14**. At a given consistency, an increase in mixing speed resulted in lower kappa number with higher brightness and lower viscosity. As the mixing speed was increased from 600 rpm to 2400 rpm the variation in kappa number between the two consistencies reduced to about 1 kappa unit. The influence of higher mixing speeds was greater at 5% consistency and it had about 5 additional units of kappa number reduction. The viscosity at both consistencies showed a linear decrease with increase in mixing speed. The viscosity at 5% consistency was about 6 units higher than that at 10% consistency at 2400 rpm mixing speed. The effect of mixing speed on selectivity ($\Delta K/\Delta V$) and spe-

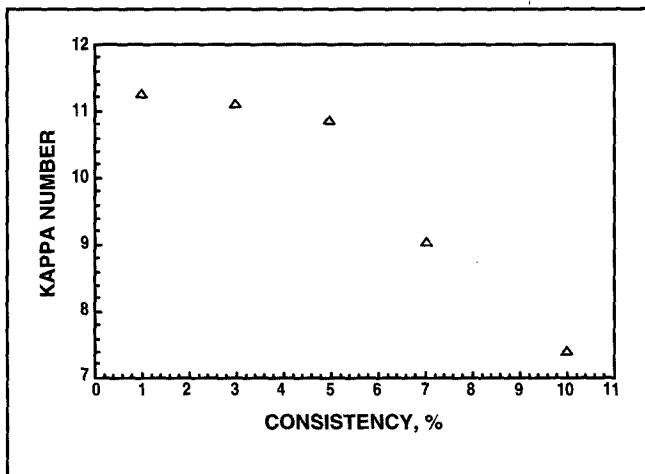
8. Influence of pH on kappa number



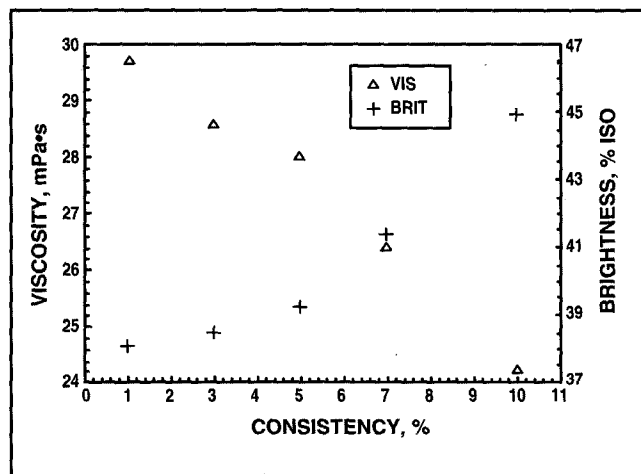
9. Influence of pH on viscosity and brightness



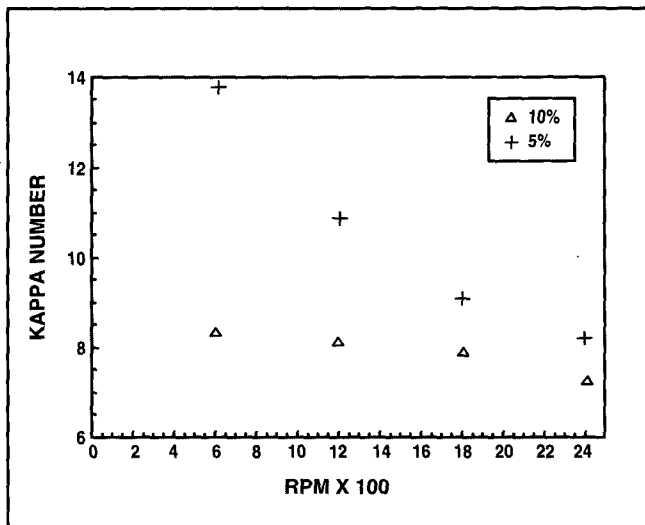
10. Influence of consistency on kappa number



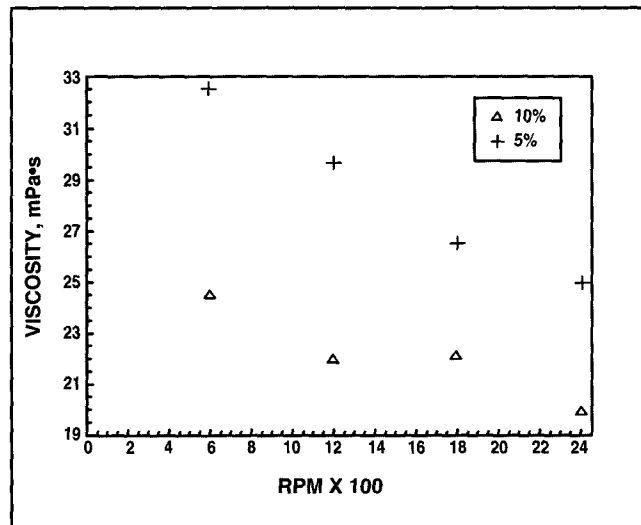
11. Influence of consistency on viscosity and brightness



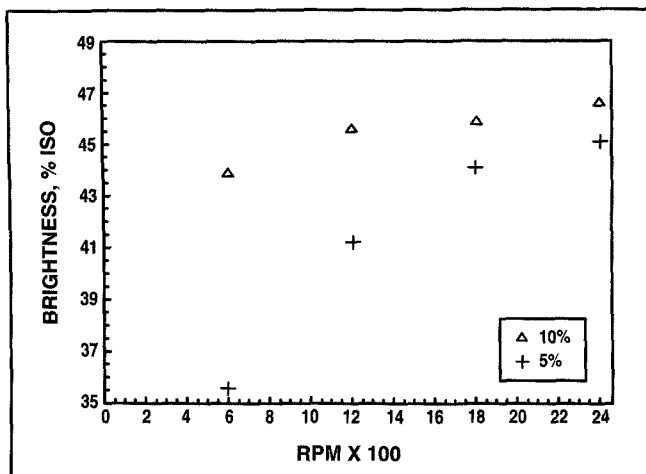
12. Influence of mixing speed on kappa number



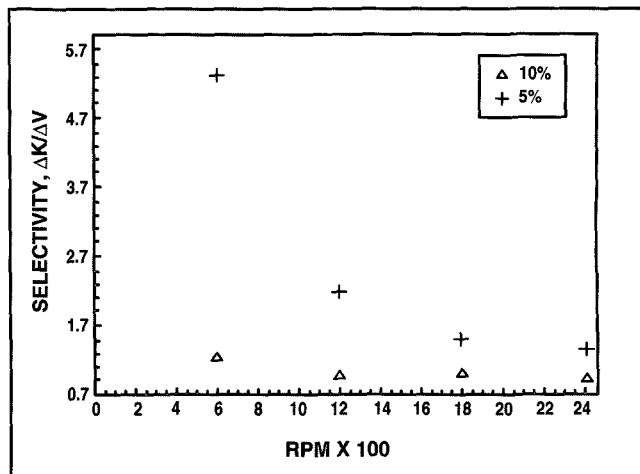
13. Influence of mixing speed on viscosity



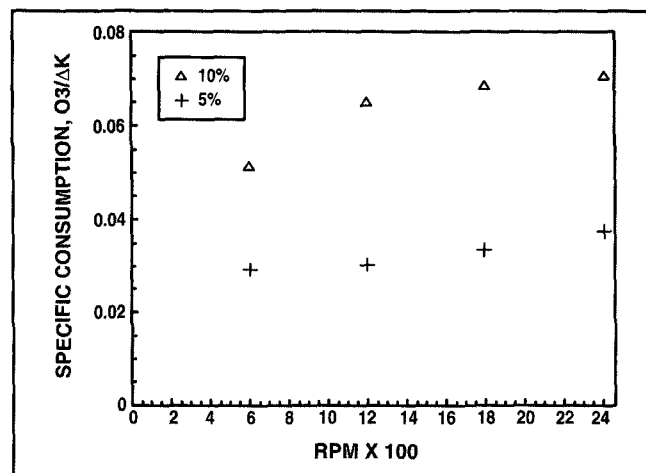
14. Influence of mixing speed on brightness



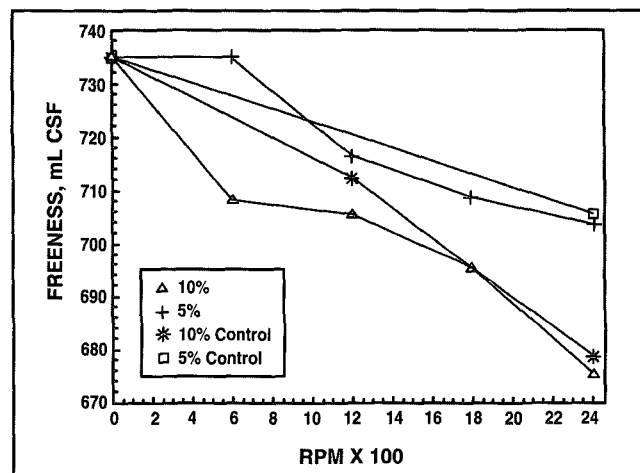
15. Influence of mixing speed on selectivity



16. Influence of mixing speed on specific consumption



17. Influence of mixing speed on freeness



cific consumption ($O_3/\Delta K$) at various mixing speeds is shown in **Figs. 15 and 16**. Bleaching 5% consistency pulp at 2400 rpm mixing speed improved selectivity and reduced specific consumption due to increased delignification and reduced viscosity loss. The freeness at 2400 rpm for 5% consistency was higher than 10% consistency as shown in **Fig. 17**. The control values of freeness for both consistencies indicate that the reduction in freeness is due to high-shear mixing.

Effect of reaction time

The effect of increasing reaction time after each pulse from 1 min to 5 min showed no significant difference in

kappa number reduction, indicating that no further reaction occurred after the initial instantaneous reaction. The viscosity, brightness, and specific consumption obtained also had negligible differences.

Conclusion

This study indicates that System 3, using compressed air and distilled water for compressing ozone, is ideal for performing medium-consistency ozone bleaching in the laboratory without the use of high-pressure water pumps. Ozone compressed with this system has the same ozone charge in each pulse. Ozone bleaching at pH 2 to 3 with low tempera-

tures has better delignification with high kappa number reduction and high selectivity. Bleaching at higher consistencies improves the efficiency of delignification. An increase in speed of mixing from 1200 rpm to 2400 rpm while bleaching 10% consistency pulp resulted in better delignification and increased viscosity loss together with an increase in freeness loss. Bleaching 5% consistency pulp at 2400 rpm mixing speed had delignification comparable to that at 10% consistency and higher viscosity. The selectivity was high with reduced viscosity loss and greater kappa number reduction. Bleaching at 5% consistency also avoids unnecessary additional capi-

Ozone Bleaching

I. Experimental design for ozone stage

Temperature, °C	pH	Consistency, %	Mixing speed, rpm	Time, min
30,40,50,60,70	2.5	10	1200	1
30	2,2.5,3,4,5	10	1200	1
30	2.5	1,3,5,7,10	1200	1
30	2.5	3,5,7,10	2400	1
30	2.5	5,10	600,1200, 1800, 2400	1
30	2.5	10	1200	1, 5

Retention time after each pulse, 1 min
Mixing time for each pulse, 15 s

II. Bleaching conditions for extraction stage

Item	Conditions
Consistency, %	10
Temperature, °C	70
Time, min	60
Caustic charge, %	1.5
End pH	12

tal expenditure on medium-consistency pumps for pulp suspension transport. Increase in reaction time does not contribute to increase in delignification. **□**

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