Journal of Korea TAPPI
Vol. 32. No. 1, 2000
Printed in Korea

Deinking of White Ledger with Ozone

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ABSTRACT

The objective of this study is to assess the possibility of ozone as an environmentally friendly new deinking alternative for conventional deinking method. It is well known that the white ledger is very difficult to deink because the toner ink has the peculiar shape and size. Ozonization could remove the ink particles above 300 microns and thus improved the ink removal efficiency. Ozonization also improved the WRV of recycled fiber and apparent density, scott bond strength, breaking length, double fold and tear index. Thus, we believe that ozonization could be used as a deinking means of white ledger instead of the conventional deinking method.

1. Introduction

The significant increases in fossil fuel use have led to increasing concentrations of greenhouse gases in the atmosphere. Accumulation of greenhouse gases contributes to global warming, dramatic climate change and negative environmental consequences. Greenhouse gas emissions are often measured in carbon units, because carbon dioxide accounts for the majority of the greenhouse gases. Carbon dioxide cycle consists of the natural process of photosynthesis, plant respiration and decomposition. Thus, the concentration of greenhouse gases can be reduced through the delay of carbon dioxide cycle with the increase of wood and paper recycling. It was confirmed by the recent research conducted by the Forest Products Laboratory that 10 to 20 percent of the U.S. carbon reduction goal could be met through a range of scenarios for paper and wood recycling.[1] What is more, wastepaper recycling can also contribute to the reduction of solid wastes (Ca. 45-50%).[2]

However, there are two important problems to increase the recycling of wastepaper. One is the significant change in the pulp and papermaking properties during recycling of wastepaper. Most important changes, especially in chemical pulp, is the irreversible fiber bonding within the fiber wall that resists reswelling and which is called the hornification.[3-21] The paper made of stiffer hornified fiber have lower strength than those of virgin fiber.[22-25] Second problem is the fact that the conventional deinking processes are not the environmentally friendly processes. When conventional technologies are used to recycle paper, large quantities of sludge and effluent which is high in oxygen demanding materials are generated. Considerable electrical energy is also required to upgrade wastepaper. If

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xerographic and/or laser printed papers are included in wastepaper, it is difficult to obtain a satisfied ink removal efficiency.[26]

In order to minimize these problems, a number of research works including enzymatic deinking, neutral pH deinking, short sequence recycling, reductive deinking, selective agglomeration, ultrasonic deinking, steam explosion process with magnetic deinking, etc. are carried out to develop the new alternative technologies which are beneficial to preserve the environment. Although some processes are already tried for commercial applications, there are still a number of problems to be solved. Ozone is a powerful oxidizing agent that reacts readily with most organic materials. Its oxdizing potential is +2.07 eV. Ozone is a nonlinear allotropic form of oxygen in which three atoms form one molecule. The ozone molecule may exist in different mesomeric structure shown in Fig. 1. The dipole character of these mesomers means that the ozone can behave as an electrophile and/or nucleophile. However, the strongly electrophilic character of ozone promotes its reaction with functional groups in the lignin.

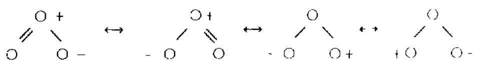

Fig. 1. Resonance hybrid of four mesomeric form.

Ozone is very unstable in water solution, the decomposition of ozone is increased with the increase of pH. The decomposition of ozone is generally the free radical process which form oxygen, hydroxyl and perhydroxyl(or superoxide anion) radical, and hydrogen peroxide as follows.

$$O_3 + HO^- \rightarrow O_2 + HOO\cdot \quad (1)$$
$$O_3 + O_2 \rightarrow 2O_2\ (^1O_2,\ \text{singlet oxygen}) + HO\cdot \quad (2)$$
$$O_3 + HO \rightarrow HO_4\cdot \quad (3)$$
$$HO_4\cdot \rightarrow HOO\cdot\ (O_2) + O_2 \quad (4)$$
$$HO_4\cdot + HO_4\cdot \rightarrow H_2O_2 + 2O_3 \quad (5)$$

The initial process(1) was proceeded slowly, but their propagation and termination step were proceeded rapidly compared to the former. Hydroxyl radical and perhydroxyl radical also have a potential to contribute to the lignin degradation reaction. Although hydroxyl radical was detected at the reaction of lignin model compounds and ozone, it was confirmed that its contribution to the lignin degradation seems to be negligible.

Ozone itself is approximately 106 times more reactive toward lignin than toward carbohydrates,[27] but the byproducts from these reactions react more readily with carbohydrates.[28-30] Two such intermediates are hydroxyl(HO_{*}) and perhydroxyl (HOO_{*}) radicals formed by direct decomposition of ozone in water or indirectly by the reaction of ozone with an organic substrate.[31-34] The strongly electrophilic hydroxyl radical, in particular, has been shown in model compound studies to attack lignin structures only 5-6 times faster than carbohydrate structure.[30] The susceptibility of carbohydrates to react with ozone reaction byproducts restricts the delignification capabilities of ozone in pulp bleaching process.

The application of ozone to deinking process of wastepaper was carried out by Yamaguchi etc.[35] They have chosen the ozone treatment as a pretreatment means for the conventional deinking. They insisted that pulp brightness should be increased 1.5-2 points and residual ink area should be decreased 30-60% compared to control.

The objective of this study is to evaluate the potential of ozone treatment as a new deinking means. The change of the ink size distribution and ink removal efficiency were investigated for this purpose. The physical properties of ozone deinked pulp were also measured.

2. Experimentals

White ledger was torn in small pieces by hand and diluted with warm water (50°C) to 10% consistency and pulped by the laboratory pulper for 30 min without any external heating. No chemicals were added to pulper except for surfactant. The pulp slurry was added to the reactor (2L) designed specially for this study and treated with ozone at several conditions (different pH, treatment time, amount of surfactant). The amount of ozone injected into the reactor was 6 g/hr. The consistency of wastepaper slurry was adjusted to 10% for ozone treatment. Conventional deinking was also carried out to compare with the result of ozone deinking. For this purpose, 2% Sodium hydroxide, 2% sodium silicate, 1% sodium dodecylsulfate, 1% hydrogen peroxide and 0.2% DTPA were added and treated for 20 min at 50°C. After pulping, the slurry was diluted to 0.5% consistency and the ink was removed by the flotation.

The distribution of ink particle size and ink removal efficiency were measured by the image analyzer. WRV of deinked pulp, brightness, apparent density, scott bond strength, breaking length, tear index and folding endurance of paper made from deinked pulp were also measured to evaluate the performance of ozone deinking.

3. Results and Discussion

3.1 Distribution of Ink Particle Size

Ink particle size distribution of W/L slurry was measured in order to asses the possibility of the introduction of ozone treatment into deinking process for white ledger which is difficult to deink with conventional deinking method. The ozone treatment reduced significantly the ink particle size, and removed the ink particle above 300 microns in diameter as shown in Fig. 2. The result means that the ozone treatment can be used as a means to replace the conventional deinking method. There were no significant differences and the obvious trend in the reduction of particle size distribution between treatment times although the ink particles above 300 microns were removed at all conditions tested (Fig. 3).

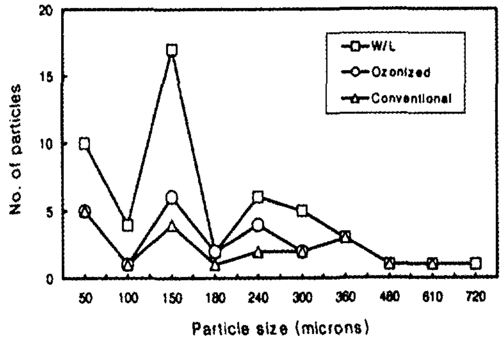

Fig. 2. Ink particle size distribution of W/L pulped with conventional method and ozonization.

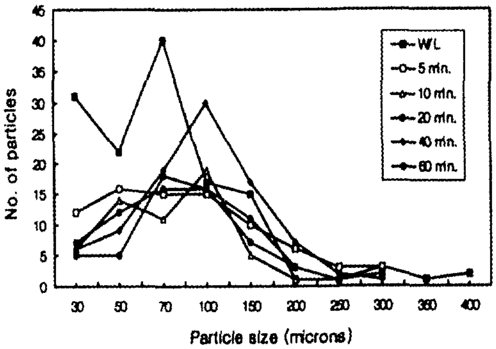

Fig. 3. Effect of ozonization time on the particle size distribution (1% surfactant).

3.2 Ink Removal Efficiency

The ozone bleaching of pulp is usually carried out at about pH 2 because the selective delignification can be obtained at this condition. However, our intention is to find the optimum pH for deinking. There were no significant difference between pH except that the lowest ink removal efficiency was obtained at pH 1.7 (Fig. 4).

As we described already, it is well known that ozone is a powerful oxidizing agent, especially the reaction with lignin higher than with carbohydrates. The reaction with lignin at the acidic condition is also better than at the alkaline condition. In the deinking process of white ledger, the reaction of carbohydrates and the byproducts of ozone (Hydroxyl and perhydroxyl radical) seems to be more beneficial for the deinking effect. As pH is shifted to neutral and/or alkaline side, the decomposition of ozone is increased, and then the degradation of fiber surface by the hydroxyl and perhydroxyl radicals should help the removal of ink. Thus, ozone treatment without pH control will give better ink removal efficiency. It is also expected that the exclusion of deinking chemical except for surfactant will improve the effluent quality and decrease the production costs.

The effect of the surfactant addition was shown in Fig. 5. The increase of surfactant addition improved the ink removal efficiency. The ink removal efficiency above 90%

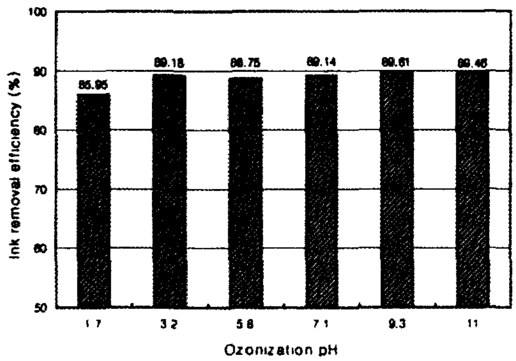

Fig. 4. Effect of ozonization PH on the ink removal efficiency (surfactant 1%, ozonization time 10 min).

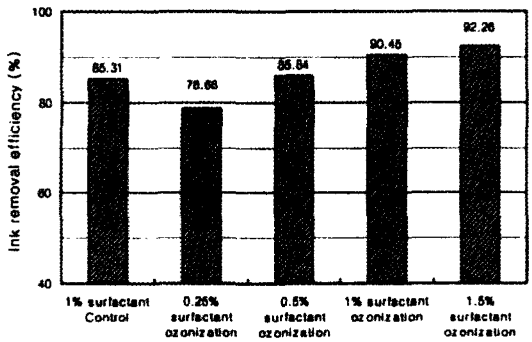

Fig. 5. Effect of surfactant addition on the ink removal efficiency (ozonization time 10 min).

can be obtained with the addition of 1% surfactant. It is well known that it is better to use the lower surfactant as possible in the view of papermaking process. Although the increase of ozone treatment improved the ink removal efficiency, there was no significant difference above 10 min as shown in Fig. 6. Thus it is considered that ozone treatment above 10 min is not desirable in the view of pulp quality vs. economy.

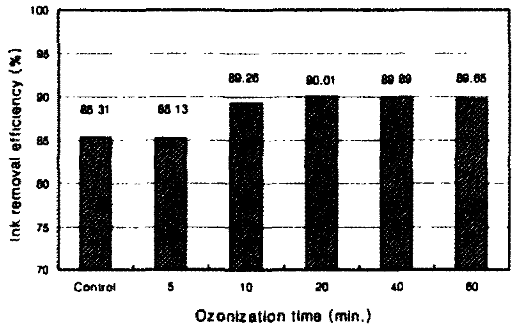

Fig. 6. Effect of ozonization time on the ink removal efficiency (1% surfactant).

3.3 Properties of Deinked Pulp

The main disadvantage of recycled fiber is the reduction of fiber bonding potential. Thus when one plan to develop the environmentally friendly new deinking process, it is important to consider the possibility that can improve the fiber bonding potential, ink removal efficiency and the quality of effluents.

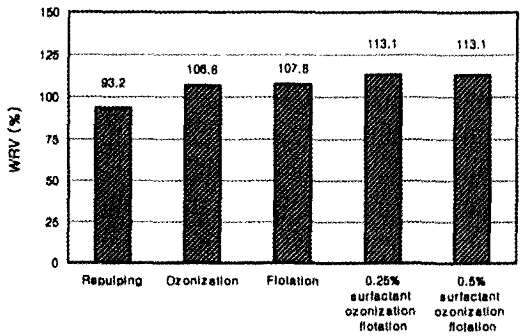

Fig. 7. Effect of ozonization on the WRV of white ledger.

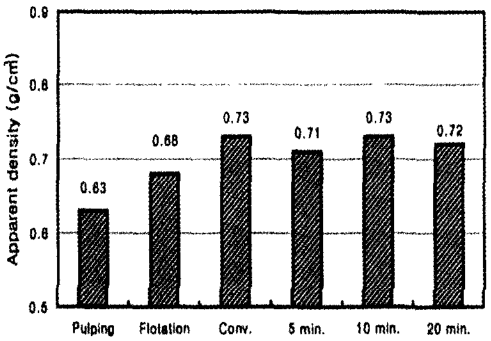

Fig. 8. Effect of ozonization on the apparent density (1% surfactant).

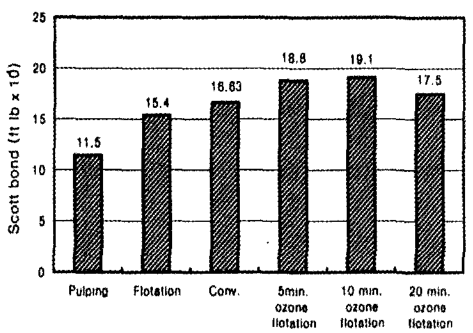

Fig. 9. Effect of ozonization on the scott bond (1% surfactant).

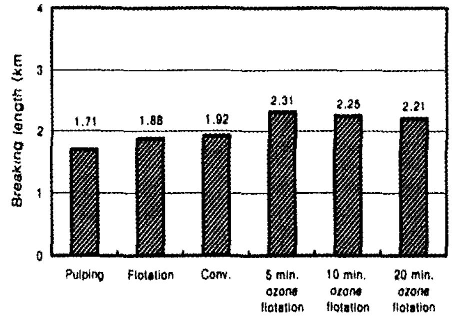

Fig. 10. Effect of ozonization on the breaking length (1% surfactant).

The change of the WRV of white ledger with ozone treatment was shown in Fig. 7. Although ozone treatment can increase the carboxyl group content[36] and WRV, the ozone treatment without ink removal did not increase WRV significantly. The ink removal without ozone treatment increased WRV significantly and further increased by the ozonization.

Fig. 11. Effect of ozonization on the double fold (1% surfactant).

The apparent density, Scott bond, breaking length and double fold also increased by the ozonization and flotation and were similar to the result from conventional deinking method (Figs. 8-11). It is considered that the improvements of those properties were resulted from the removal hydrophobic ink and the increase of WRV.

The interesting result was the increase of tear index by the ozonization (Fig. 12). If any chemical additives are not applied to papermaking, the tear index is usually decreased with the increase of other paper properties including apparent density, breaking length, burst index etc. However, ozone deinking resulted in all paper properties including tear index.

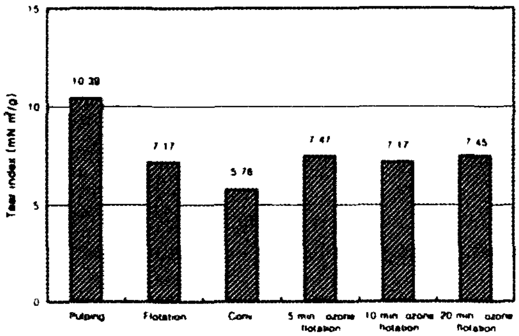

Fig. 12. Effect of ozonization on the tear index (1% surfactant).

4. Conclusions

Ozone is a powerful oxidizing agent and approximately 10^6 times more reactive toward lignin than toward carbohydrate. However, the byproducts (hydroxyl and perhydroxyl radicals) of ozone decomposition react more readily with carbohydrates. We directed our attention to the reaction of carbohydrates and byproducts of ozone reaction. We expected that these reaction of carbohydrates with byproducts of ozone reaction will help the removal of ink from white ledger.

Ozonization removed the ink particles above 300 microns, thus improved the ink removal efficiency significantly. Ozonization also improved WRV of recycled pulp and apparent density, scott bond strength, breaking length, double fold and tear index. However, these improvements could be obtained on condition that ink is removed from pulp slurry. Ozonization is considered as an environmentally friendly good alternative for conventional deinking from our results obtained in this study.

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