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Improved Ozone Efficiency At Reduced Charges --An Electrochemical Model and New Experimental Approach

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ABSTRACT

The efficiency of the ozone bleaching of chemical pulps is dependent upon numerous factors. In this work, an electrochemical model was used to evaluate the impact of ozone charge, pH, consistency and kappa number on the efficiency of ozone bleaching. The model used in this analysis was created through a detailed investigation into the electrochemical reactions of the bleaching process and ozone itself. The model considers tow possible ozone reaction pathways and uses the electrochemical potential of lignin as the sole parameter. Application of this model indicates that operating at lower ozone charges, lower pH and higher consistency will greatly enhance the effectiveness of ozone bleaching. It was also found that this concept could be extended to non-bleaching processes.

EXECUTIVE SUMMARY

As environmental regulations mandate a change over to non-chlorine based bleaching techniques, ozone has become a popular alternative for both brightening and delignification. As ozone use becomes more wide spread, it becomes increasing important to have a through understanding of the underlying mechanisms that dictate its behavior while brightening and delignifying. This work adds to that knowledge by demonstrating the dramatic improvements that can be made on the both of those processes by manipulating several key process variables in the ozone bleaching process.

This research proposes a reaction scheme consisting of two where the higher oxidation potential path occurs with the exchange of six electrons and in the lower oxidation path only two electrons are exchanged. These paths were used to develop and electrochemical model that was subsequently used to examine the impact of pH, consistency, and ozone charge on the brightening and delignification efficiency. Specifically, it was found that the higher oxidation potential reaction, and therefore dramatically improved ozone efficiency, can be favored by optimizing the ozone charge, system pH, and

consistency when the electrochemical potential of the reaction of lignin and its oxidation product is known.

1. Introduction

Among the many challenges facing the pulp and paper industry today, searching for environmentally sound-bleaching technologies is an extremely important one. In chlorine-based bleaching, toxic substances such as 2,3,7,8-TCDD and 2,3,7,8 TCDF may be formed and released into the receiving water [1]. These chlorinated compounds in the effluents have been found to have a serious detrimental effect on the environment. Consequently, the industry has been in the transition from traditional to new bleaching technologies, such as the elemental-chlorine free (ECF) or the totally chlorine free (TCF) bleaching processes.

In addition to the reduction or elimination of chlorine and chlorine-based compounds, the new bleaching technology must be developed with an equal or better overall performance compared with the traditional ones, with regard to the production cost and product quality. ***Ozone bleaching*** (Z) has shown promise as an effective delignification stage and it has been investigated for many years. Liebergot, et al [3-5] and Byrd Jr. et al [6] have thoroughly reviewed the status of this technology. Recently, the process has been commercialized as an integral stage in TCF sequences in Europe, Scabdinavia and South American [7-12]. However, many questions remain to be addressed***, especially the bleaching efficiency*** and fiber protection.

In addition to the side reactions between ozone and non-lignin substances or decomposition, delignification efficiency can be lost to a great extent because of the change in reaction mechanism from ozone molecule accepting six(6) to two(2) electrons. There is a great need to understand how the change of oxidation power affects the processes and what should be done to optimize the delignification efficiency. And ozone is also known to attack cellulose if not used properly.

In this paper, we use an electrochemical approach to examine the variable crucial to the delignification efficiency by considering different ozone reactions. With the aid of experimental results, we also demonstrate improved performance of a Z stage at reduced ozone charge levels. Finally we give some guidelines for further improvement of ozone application.

2. Theory of Different Ozone Reactions: An Electrochemical Model

Loss of delignification efficiency is a concern to all bleaching operations. In general, this occurs when the bleaching chemical reacts with non-lignin substances, such as impurities in the system, or even worse, the cellulose fibers. Some chemicals also undergo decomposition, as is often seen in bleaching with hydrogen peroxide. While it is commonly agreed that the efficiency of ozone bleaching is affected by all these factors, less attention is paid to the fact that two ozone reactions take place, and each of them has very different impacts. Considering only semi-electrochemical reactions, these two reactions are:

$$O_3 + 6H^+ + 6e = 3H_2O \qquad 1.511\ (v) \qquad (1)$$

and $$O_3 + 2H^+ + 2e = H_2O + O_2 \qquad 2.075\ (v) \qquad (2)$$

Each reaction has a standard potential. Under the conditions of ozone bleaching, i.e. low temperature, low pH and short reaction time, oxygen is inert toward pulp. As these two equations indicate, the oxidation power of ozone varies dramatically if the reaction mechanism changes from one to another. In reaction (1) each ozone molecule accepts six electrons, and the reaction product is water. The potential oxidation power carried by ozone is fully utilized. In reaction (2), however, one ozone molecule only accepts two electrons, and the reaction products include oxygen with a molar ratio of unity. Compared to reaction (1), only one third of the oxidation power carried by ozone is used.

By introducing a relative standard for the oxidation power of the bleaching chemicals, the bleaching processes can be analyzed in a somewhat quantitative manner. The suggested standard, OXE, the oxidation equivalents for bleaching chemicals [14], is the gram molar equivalents of the chemicals in each kilogram. The OXE value for each chemical subsequently depends on the reaction pathway that determines how many electrons the chemical accepts in the oxidation process. When different chemicals are compared, the higher the OXE value the larger the oxidation ability in each kilogram of the chemical. For ozone, there are two possible OXE values. If the bleaching reaction proceeds as equation (1) its OXE is 125 eq/kg. This value becomes 41.7 eq/kg if it transpires through equation (2).

In an actual bleaching process, both reactions, more or less, play a role. The ratio of ozone utilized in different mechanisms depends upon bleaching conditions. However, the reaction schematics shown by (1) and (2) only constitute half of the overall bleaching reactions. In order to study bleaching, the semi-reaction of lignin needs to be considered:

$$p_L + 2e = L \qquad E_o \qquad (3)$$

where: L stands for lignin, P_L is its oxidation product and E_o is the standard potential of the reaction. The choice of two electrons in equation (3) is only for the simplicity of the model but it does not affect the primary parameter E_o. In fact, the Gibbs standard free energy change is [15]

$$\Delta G^o = -nFE_o = -RT\ Ln\ K \qquad (4)$$

where ΔG^o is the Gibbs standard free energy change of the reaction; n the number of electrons in the reaction formula; F the Faraday constant; K the reaction constant. Combining (3) with (1) and (2), we have two complete reactions, respectively, as:

High OXE reaction: $$O3 + 6H+ + 3L = 3H2O + 3p_L \qquad (5)$$

Low OXE reaction: $$O3 + 2H+ + L = O2 + H2O + p_L \qquad (6)$$

For each reaction, a minimum ozone pressure (or activity) is required to drive the bleaching process. An electrochemical model that defines the minimum ozone pressure can thus be established by considering the electrochemical potential in equation (3), Eo_3, as a variable. With thermodynamic data for the

species involved in (5) and (6) [14], and if equation (4) is applied at 298K, the minimum ozone pressures under standard conditions require by the reactions are:

For High OXE reaction **$\log Po_3 = (101.5Eo_3 - 153.2) + 6pH$** **(7)**

For Low OXE reaction **$\text{Log } Po_3 = (33.82Eo_3 - 70.17) + 2pH$** **(8)**

Where: Po_3 is the minimum ozone partial pressure required by the reaction. Equations (7) and (8) indicate that as pH decreases, the minimum ozone pressure decreases for both reactions. However, pH influence on the Low OXE reaction is less significant than on the High OXE reaction. This difference is illustrated graphically in **Figure 1**, which gives four preferential reaction regions described by this electrochemical model. Depending on system pH and ozone pressure, these four regions represent different reaction possibilities governed by thermodynamics. In Region A, ozone pressure is higher than that required by either High (5) and Low (6) OXE reactions for the given pH values. Both reactions, therefore, occur. and there is adequate thermodynamic driving force for both Low and High OXE reactions to occur. The amount of ozone consumed in each of these two reactions obviously will depend on kinetics of individual reactions, which is in turn determined by other bleaching parameters. In Region B, ozone pressure is higher than that required by the Low OXE reaction but lower than that by High OXE reaction. The bleaching efficiency will thus be very low because only the Low OXE reaction will proceed. On the other hand, in Region C only the High OXE reaction can take place thermodynamically, and this is where ozone pressure will be most effective. With a normal ozone charge commonly used in industry, unfortunately, the bleaching conditions fall in Region A. In Region D, however, ozone pressure is lower than that required by either of reactions so that no bleaching action takes place.

While the electrochemical model covers a full range of the electrochemical potential, $E_{o\_}$ of reaction (3), this constant is assumed to be +1.00 v in Figure 1. It should be noticed that there is not specific value available so far for this parameter even though some studies have dealt with electrochemical oxidation of model compounds [16-21]. The range of its value can be more reliably estimated by considering bleaching reactions with traditional chemicals. For example, in the chlorination processes aqueous chlorine solution is used and its semi-electrochemical reaction is[13]:

$Cl_{2\ (aq.)} + 2e = 2\ Cl^-$ **$E_o = +1.39$ v** **(9)**

where subscript aq. stands for aqueous solution. For lignin to be oxidized by aqueous chlorine, its electrochemical potential as shown in reaction (3) must be lower than +1.39 v under standard conditions. Because chlorine bleaching proceeds until eventually all active chlorine is consumed, when the actual electrochemical potential of reaction (10) will be 0.2-0.3 v lower than its value under standard conditions, we can see that Eo_3 should be lower than +1.10-1.20 v. This implies that the conditions used for the construction of Figure 1 are fairly close to practical.

This electrochemical model clearly indicates that lower pH is desired for higher bleaching efficiency. There is a critical pH where the two lines for corresponding reactions cross, indicating that the preference reaction condition for Low and High OXE reactions switches. Figure 1 shows that this

critical pH is 3.84 if the electrochemical potential of lignin is 1.00 volts. Evidently, critical pH is a function of Eo_3, which in turn depends on many factors such as the type of wood the extent of delignification and the history of delignification. And from equations (7) and (8), we have:

$$\textbf{Critical pH} = 20.76 - 16.93Eo_3 \qquad (10)$$

Similarly constructed under standard conditions, **Figure 2** illustrates the change in critical pH along with E_{o3}. The line in the Figure is the border of two preferential reaction regions. Bleaching below the critical pH will be more effective.

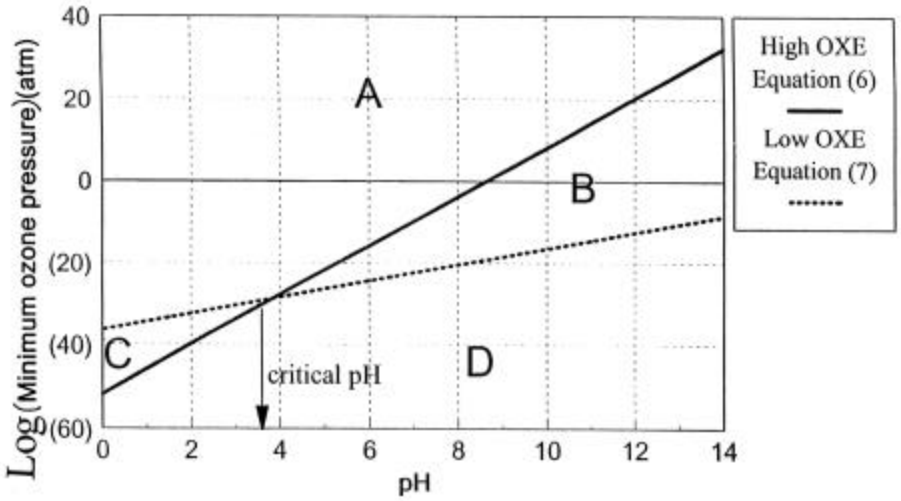

Figure 1. Preferential reaction regions (Under Standard Conditions, and E_o = +1.00 v).

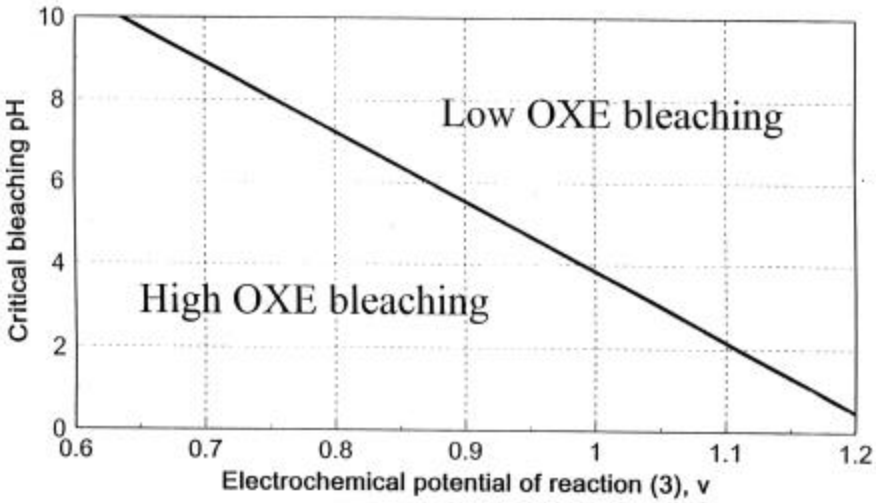

Figure 2. Critical pH vs. Electrochemical potential of lignin (Under Standard Conditions).

In addition to pH, the ozone charge also plays an important role. This model suggests that the bleaching performance will be improved with lower ozone charges. For example, at lower ozone pressure the driving force will be reduced for the Low OXE reaction more than the High OXE reaction if pH is low. Theoretically, the Low OXE reaction can be completely stopped if ozone pressure is accurately controlled and falls into Region C of Figure 1, where only the High OXE reaction is allowed to proceed. With a normal ozone charge commonly used in industry, unfortunately, the bleaching conditions fall in Region A and there is adequate thermodynamic driving force for both Low and High OXE reactions to occur. The amount of ozone consumed in each of these two reactions obviously will depend on kinetics of individual reactions, which is in turn determined by other bleaching parameters.

This model can be easily extended to non-standard conditions. By doing so, the reaction equations previously developed will all have additional terms concerned with the concentrations or activities of species involved in reactions. In fact, the effect of the product/lignin ratio on the bleaching efficiency can also be examined. Similar to the pH effect, there is also a critical ratio at which two-ozone reactions switch. For example, at room temperature, pH 3.0 and 1.0 atm oxygen pressure, the model shows the dependence of this critical ratio on the electrochemical potential of lignin:

$$\mathbf{Log\ (A_{PL}/A_L) = 35.51 - 33.84\ Eo_3} \qquad \mathbf{(11)}$$

Below this critical ratio ozone preferentially reacts through the High OXE reaction. Moreover, Equation (11) suggests again that ozone bleaching can be improved by lowering ozone charge. With a lower ozone charge, the oxidation product amount will be less, and so will be its activity in the system.

3. Experimental

The electrochemical model developed above only indicates the reaction possibilities governed by thermodynamics. If the ozone charge is high enough to drive both reactions, as under normal bleaching conditions, the kinetics determine how efficiently ozone is used. In order to understand how these two different ozone reactions proceed, we need to determine their contributions to the overall delignification. The efficiency of ozone delignification can be examined by the percent ozone consumed through the High OXE reaction. Assuming that there are no side reactions (including decomposition) and ozone is only consumed through the two reactions considered earlier, we have:

$$\mathbf{dK = \{12.5X_{125} + 4.17(1-X_{125})\}x\ \{O_3\%(wt)\}} \qquad \mathbf{(12)}$$

where dK is the kappa number reduction; X_{125} is the fraction of the total ozone consumed on pulp through the High OXE reaction with 125 eg/kg OXE; O_3 %(wt) is total ozone consumed on o.d. pulp. This equation indicates that the total kappa number reduction, dK, is the sum of that caused by High OXE reaction and that by Low OXE reaction. The parameters, 12.5 and 4.17, are theoretical reductions in kappa number caused by 1% ozone consumption through High and Low OXE reactions, respectively. They are calculated based on the OXE required by standard TAPPI method for the determination of pulp kappa number. With experimental data, such as initial and final kappa numbers of the pulp sample, the ozone charge, as well as its consumption percentage, the values of dK and O3

%(wt) are found. The values of X_{125} can then be evaluated with equation (12). The higher the X_{125} value, the more efficient the delignification.

Figure 3 shows the results obtained with an oxygen-delignified southern pine pulp, with a kappa number of 14.6 and a viscosity of 11.6. The experimental details were given in a earlier publication [22]. The figure shows the dependence of X_{125} on the total ozone consumption at two levels of bleaching pH and also compare the bleaching in sulfuric acid to acetic acid at pH 2.0. The type of acid did not affect delignification under the experimental conditions used in this study. Ozone bleaching in either sulfuric or acetic acid environment shows no difference in the ozone consumed through the High OXE reaction. However, the effect of pH was obvious. By reducing pH from 4.0 to 2.0 in sulfuric acid systems, about 20-40% more ozone was consumed through the High OXE reaction. More importantly, Figure 3 clearly demonstrated the benefits with low ozone charges. In all cases, the lower the ozone charge, the higher percent ozone reacted through the High OXE reaction.

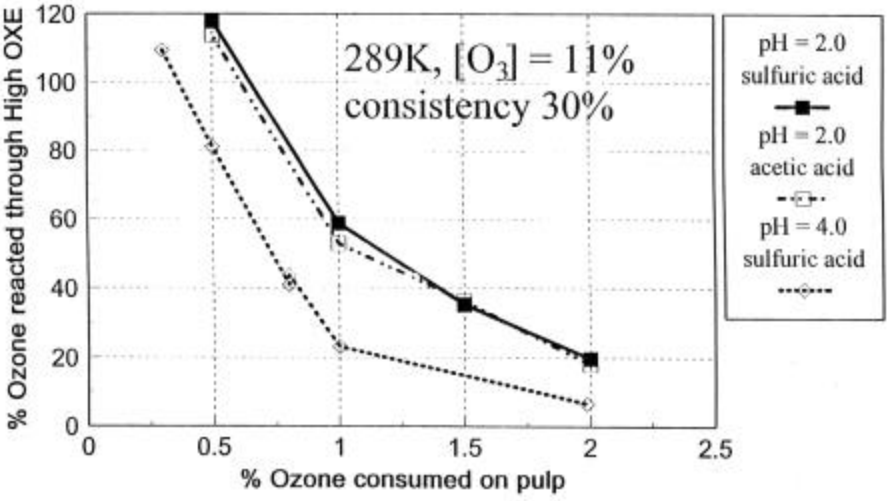

Figure 3. Effect of ozone charge on bleaching efficiency.

It is very interesting to note that as ozone charge is further decreased the calculated percent ozone consumed through the High OXE reaction is actually higher than 100%. Recalling equation (12) and its coefficients, 12.5 and 4.17, respectively, we can see that it is assumed in equation (12) that kappa number reduction during bleaching results only from complete oxidation of lignin, as in the determination of kappa number by permanganate. Therefore, X_{125} higher than 100% means that lignin can actually be removed from the fiber by partial oxidation. Overall it appears that ozone delignified at an oxidation power higher than 125 eq/kg. This speculation was verified in our laboratory. The bleaching filtrates were sometimes tested by normal kappa number method. It has been found that some water-soluble substances in bleaching liquors could be oxidized by permanganate. Specifically for the trial at 30% consistency and 0.5% ozone consumption, the content of such substances in the effluent would contribute 0.7-0.8 units to the overall kappa number reduction for the fiber. The OXE value then became 124-126 eq/kg if the calculation of experimental OXE is modified by effluent's behavior. The apparent OXE values higher than 125 eq/kg for ozone have also been found in industry. For instance,

under conditions very similar to the one discussed above, it has been reported that the high consistency ozone bleaching operation [23] has achieved an average of 1.3 kappa reduction for 1 kg ozone consumed per one ton pulp. This is equivalent to an OXE value of 130 eq/kg.

A more interesting question will then be whether ozone's OXE value can be further increased. While there is no specific data to illustrate it at this time, the trend in Figure 3 suggests that it is very possible. An estimate based on our results is that ozone's maximum apparent OXE value is close to 150 eq/kg. The apparent OXE value can also decrease, as we will discuss shortly. If ozone only reacts through the Low OXE reaction and some undergoes side reactions, the calculated percent ozone consumed through the High OXE reaction could be lower than zero.

The effect of bleaching consistency at different ozone charges is shown in **Figure 4**. While the benefit of bleaching with low ozone charge is again obvious at all three consistency levels studied, the results indicate that under the same mixing condition, high consistency bleaching was more efficient than low consistency. For example, when consistency increased from 20% to 30%, 20% more ozone would react through the High OXE reaction. The effective mixing achieved at high consistency should enhance the transfer of ozone from the pulp surface to the lignin sites, leaving less ozone to undergo decomposition or reaction with other materials. In addition, the removal of bleaching products from the reaction site should also be more effective, resulting in a lower activity ratio, A_{PL}/A_L. As discussed earlier, more ozone would preferentially react through the High OXE reaction. At 10% consistency, through, the results indicate a negative value. As expected, poorer mixing may have allowed enough time for ozone decomposition before it ever had a chance to reach reaction sites.

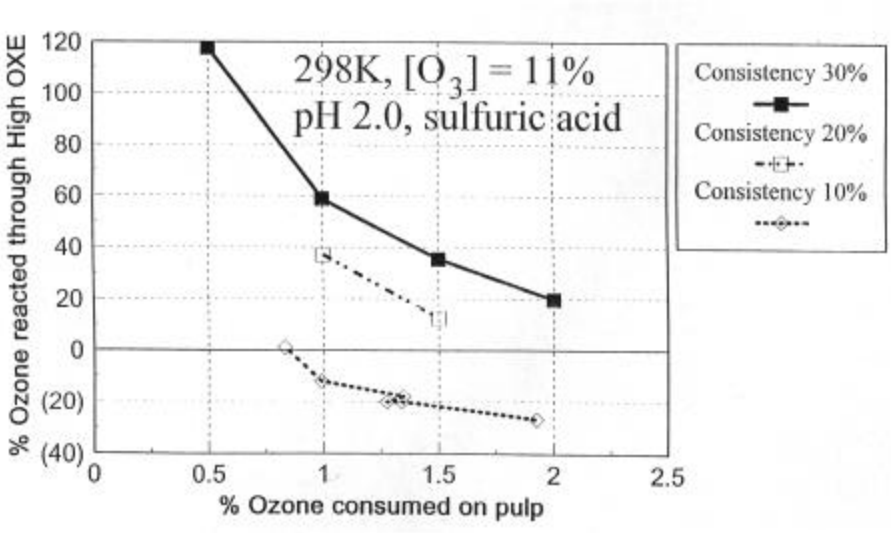

Figure 4. Effect of pulp consistency on ozone efficiency.

In the delignification of different types of pulp, examining the ozone distribution in two reactions allows a clear comparison of the bleach efficiency. **Figure 5** shows the change in pulp kappa number during ozone bleaching for three pulps: one Kraft southern pine pulp and two oxygen-delignified pulps. Both oxygen-delignified pulps were prepared from the same Kraft pulp by controlling the extent of delignification[24]. Applying equation (12), we transformed the results into **Figure 6**, which shows the

ozone fraction consumed through the High OXE reaction as a function of applied ozone. Even though initial kappa number was much lower in oxygen-delignified pulps than in the original Kraft pulp, it can be seen that at the same ozone charge level the fraction of ozone reacted through the High OXE reaction is consistently higher. In other words, ozone is more efficient for delignification if applied after an oxygen stage.

As shown before, low ozone charge is once again preferred, and it always results in higher bleaching efficiency. Since bleaching selectivity is also better with lower ozone charge, the results here suggest that splitting the required total ozone charge into different stags will be beneficial. It is also expected that a plug flow bleach reactor with multiple ozone injections will have the best performance. If adequate mixing is allowed between injections, the overall bleaching efficiency as well as selectivity can be greatly improved.

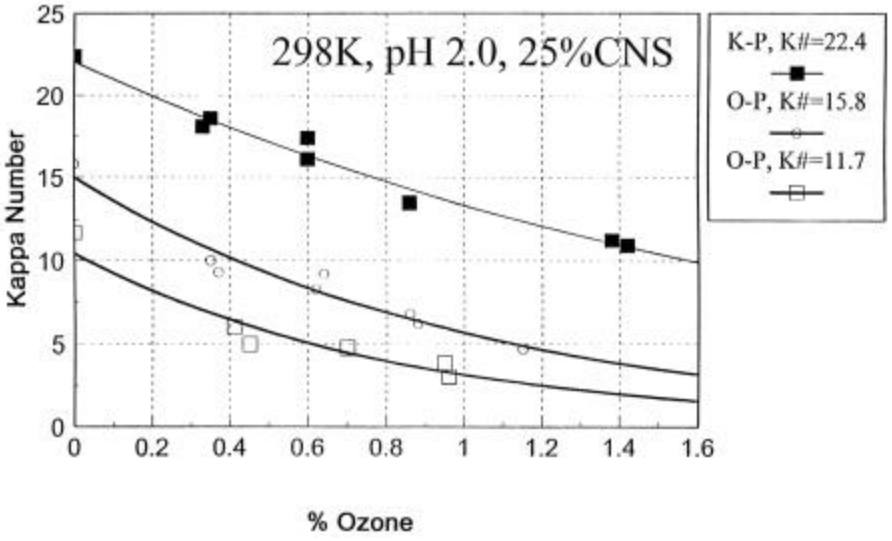

Figure 5. Pulp Kappa number of three pulps at different ozone charges.

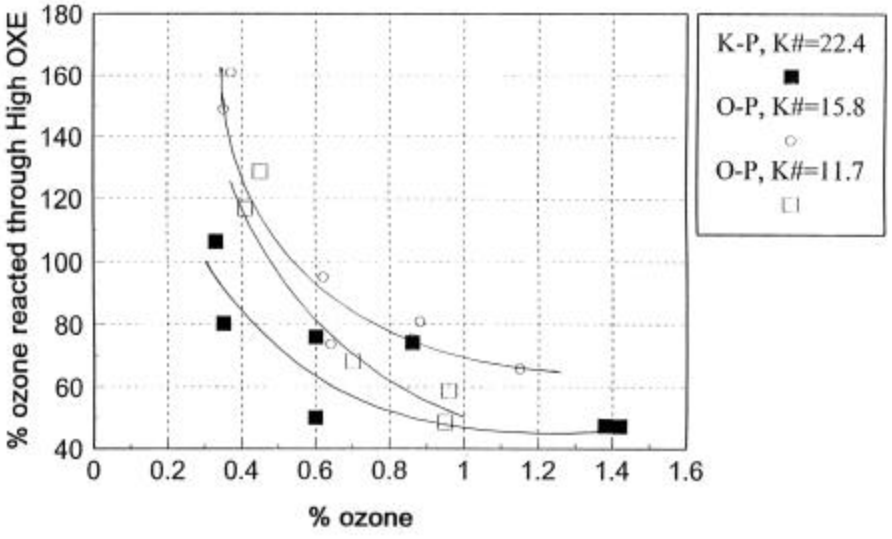

Figure 6. Beneficial ozone bleaching after an oxygen stage.

4. Conclusions

An electrochemical model has been established to examine the effects of process variables on the effectiveness of ozone bleaching. The model deals with two possible oxidation reactions by ozone. Its basic parameter is the electrochemical potential of lignin. It shows that the loss of bleaching efficiency in an ozone stage can be explained by the change in reaction mechanism. In addition to pH, ozone charge level is shown to be crucial. At lower ozone charges the process efficiency is much improved. Experimental data are used to evaluate the fraction of total ozone consumed through the higher efficiency reaction, and it is an indicator of the bleaching efficiency. Regardless of pH, consistency, or the type of acid used, results show that bleaching at reduced ozone charge is always more beneficial. Sometimes low ozone charge even results in delignification levels higher than theoretically predicted. Splitting ozone usage into multiple stages or modifying reactor design to allow multiple ozone injection is suggested.

Since the electrochemical model mainly deals with the semi-reaction of ozone itself, this low-charge for effectiveness concept can also be applied in non-bleaching area such as wastewater treatment and sterilization.

5. Literature

1. Shrinath, S. A. and Bowen, I. J., ***1993 TAPPI Pulping Conference Proceedings***, TAPPI Press, Atlanta, p. 1. **1993**.
2. "***Federal Register; Part II - Environmental Protection Agency***", 40 CFR Parts 63 and 430, Vol. 58, No. 241, pages 66120, 66196 and 66213. December, **1993**.
3. Liebergott, N.; van Lierop, B. and Skothos, A ***TAPPI Journal***, 75(1):45. **1992**.
4. Liebergott, N.; van Lierop, B. and Skothos, A ***TAPPI Journal***, 75(2):117. **1992**.
5. Liebergott, N.; van Lierop, B. and Skothos, A. ***1992 Environmental Conference Proceedings,*** TAPPI press, Atlanta, p. 1105. **1992**.
6. Byrd Jr., M. V.; Gratzl J. S. and Singh, R. P. ***TAPPI Journal***, 75(3):207. **1992**.
7. Gottlieb, P. M.; Nutt, W. E.; Miller, S. R. and Macas, T. S ***1993 TAPPI Pulping Conference Proceedings***, TAPPI press, Atlanta, p. 1183. **1993**.
8. Gottlieb, P. M.; Nutt, W. E.; Miller, S. R. and Macas, T. S. ***TAPPI Journal***, 77(6):117. **1994**.
9. Helander, R. and Nelson, B ***1994 International Bleaching Conference Proceedings***, Vancouver, Canada. June 13-16, p. 289. **1994**.
10. Kappel, J.; Brauer, P. and Kittel, F. ***1993 TAPPI Pulping Conference Proceedings***, TAPPI press, Atlanta, p. 1173. **1993**.
11. Kappel, J.; Brauer, P. and Kittel, F. ***TAPPI Journal***, 77(6):109. **1994**.
12. Nutt, W. E.; Eachus, S. W.; Griggs, B. F. and Pikulin, M. A. ***1992 TAPPI Pulping Conference Proceedings***, TAPPI press, Atlanta, p. 1109. **1992**.
13. Bard, A. J; Parsons, R. and Jordan, J. ***Standard Potentials in Aqueous Soulion".*** Marcel Dekker, Inc., New York and Basel., 1985.
14. Grundelius, R., ***Nordisk Cellulosa,*** 7(4):71. **1990.**
15. Peters, E., ***Proceedings of The Second International Hydrometallurgy Symposium,*** TMS, Port City Press, Baltimore, MD., Pages 205-228, **1972.**
16. Vasil'eva, L. V., Shukin, I. V., Antakova, M. Yu., and Babkin, V. A., ***Issledovaniya v oblasti khimii drevesiny (Institut khimii drevesiny)***:20 (**1991)**.

17. Shchukin, I. V., and Babkin, V. A., *CTAPI 7th International Symposium Wood Pulping Chemical Process.* Vol. 1 (Bejing): p127-131. (**1993**).
18. Borovkova, G. G., and Borovkov, F. F., *Izv. VUZ Khim. i Khim. Tekhnol.* 32, no. 7:58-62 (**1989**).
19. Cauquis, G., Limosin, D., Pieree, G., *Colloque Sci. Ind. Bois* (Grenoble) 3 (Transform. Biol. Chim.): p161-183 (**1982**).
20. Anisimova, M. I., Babkin, V. A., Kozhevnikova, L. G., Zaitseva, L. A., Vasyanovich, G. P., and Isakova, N. V., *Khim. Drev.* (Riga)no.2: 72-77 (**1980**).
21. Evstigneev, E. I., Bronov, L. V., and Nikitin, V. M., *Khim. Drev*. (Riga) no.6:71-81 (**1979**)
22. Meng, M. X., and Hsieh, J. S., *Symposium of Forest Products Group, **AIChE 1994 National Meeting***. San Francisco, CA., November 13-18, **1994.**
23. Steffes, F., and Reeves, R., ***1994 International Non-Chlorine Bleaching Conference Proceedings***, March 6-10, The Ritz-Carlton, Amelia Island, FL., paper 4-3. **1994.**
24. Sonneberg, L. B., and Poll, K. M., ***1994 International Bleaching Conference Proceedings***, Vancouver, Canada. June 13-16, p101-107. **1994.**

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