



## Effect of reaction medium on ozone mass transfer and applications to pulp bleaching

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### Abstract

Over the last few years, ozone has been considered as an effective reagent for the bleaching of chemical pulp and an alternative to conventional chlorinated compounds which induce environmental pollution. The purpose of this work was to investigate the optimal conditions of the ozonation process with the aim of avoiding the breakdown of carbohydrates present in the pulp. In order to limit the depolymerization of cellulose, which involves a decrease in the pulp strength, various organic compounds called “protectors” were added to the reaction medium. The results reported in this paper show the important role of most additives and their influence on the hydrodynamic phenomena taking place in the ozonation process. Indeed, these products improve the mass transfer and, more particularly, the diffusion of ozone in the pulp. Consequently, their presence enhances the performance of the ozonation stage. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Ozone; Pulp bleaching; Cellulose protector; Ozonation process

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### 1. Introduction

The recent legislation concerning environmental protection, which limits the discharge of bleaching effluents loaded with chlorinated organic compounds (adsorbable halogenated organic compounds: AOX), has promoted the development of chlorine-free processes. The limit of the AOX content of industrial effluents in Sweden is 0.5 kg of chlorine per ton of pulp.

Although ozone was previously used for the delignification of wood [1], this oxidizing compound did not gain recognition as a possible substitute for chlorine and chlorine dioxide because of its low selectivity and high production cost. However, as ozone can now be produced on an industrial scale at a reasonable cost, a new approach combining ozone with oxygen and hydrogen peroxide is considered as an attractive alternative for pulp bleaching. The number of installations using ozone has increased since 1992 (Table 1), but several improvements to the ozonation process are still necessary. Recent investigations show that the totally chlorine-free (TCF) process produces a pulp with 5–10% less strength than that produced by the

elemental chlorine-free (ECF) process. Many workers report that the decrease in pulp strength is due primarily to the strong oxidizing power of ozone which breaks down not only the lignin but also the carbohydrates [2–10]. Furthermore, the formation of intermediate products in the reaction medium reduces the degree of polymerization of cellulose.

Since the earliest report published by Brabender et al. [11], extensive research has been undertaken with the aim of optimizing the experimental conditions of ozonation, such as pH, temperature, ozone charge (quantity of ozone applied/amount of dried pulp), ozone concentration in oxygen and pulp consistency. Moreover, many investigations have been carried out in order to identify cellulose “protectors” which are generally organic compounds added to the reaction medium. Previous studies [12] have revealed two mechanisms which permit the role of these additives to be explained. First, the chemical function of these substances, which act by scavenging the radical species formed during the ozonation reaction and enhance the selectivity of the treatment. Indeed, contrary to the action of molecular ozone, the radical intermediates and, particularly, hydroxyl groups react very quickly with carbohydrates. Second, the presence of various additives tends to reduce the ability of ozone to reach the carbohydrates because cellulose in con-

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Table 1  
Ozone bleaching installations

| Company                   | Start-up | Capacity (kg O <sub>3</sub> h <sup>-1</sup> ) | Ozone product supplier |
|---------------------------|----------|---|------------------------|
| Lenzing (Austria)         | 1992     | 40  | Schmidding             |
| Union Camp (USA)          | 1992     | 280   | Ozonia                 |
| Sodra Cell (Sweden)       | 1992     | 210   | Trailigaz              |
| Stora Billerud (Sweden)   | 1992     | 42  | Ozonia                 |
| Wisaforest (Finland)      |          |   |                        |
| 1st cut                   | 1992     | 100   | Trailigaz              |
| 2nd cut                   | 1994     | 100   | Schmidding             |
| Modo (Sweden)             | 1993     | 200   | Ozonia                 |
| Metsa Botnia (Finland)    | 1993     | 300   | Ozonia                 |
| Petterson–Saffle (Sweden) | 1994     | 30  | Schmidding             |
| SCA (Sweden)              | 1995     | 180   | Ozonia                 |
| SAPPI (South Africa)      | 1995     | 240   | Ozonia                 |
| Ponderosa (USA)           | 1995     | 70  | Ozonia                 |

tact with the reaction medium swells less than when it is only impregnated with pure water. Furthermore, the results reported in this paper demonstrate a hydrodynamic role of additives in ozone transfer.

## 2. Ozone bleaching procedure

The paper industry distinguishes three pulp concentration ranges designated by consistency, which represents the ratio of the quantity of pulp to water: 1%<low consistency<3%; 8%<medium consistency<15%; 20%<high consistency<50%.

Only low and high consistency pulps were studied at the laboratory scale, while medium consistency pulps require heavier equipment such as that used in pilot plants or industrial scale installations. Most laboratory studies, and notably those performed by Lindholm [13], indicate that the ozonation reactivity (percentage of ozone consumed/percentage of ozone applied) reaches its maximum level for consistency ranges 30–50%. For this pulp consistency range, the thickness of the water film surrounding the fibre is close to zero, and in such a case the ozone reaches the reaction site more quickly. However, in the process reactor, precise control of the stirring conditions is required, otherwise excess ozone consumption by fibres occurs on the periphery of the floc while those located within the floc do not react. Conversely, for low consistency pulps, the fibres surrounded by aqueous phase constitute a more homogeneous medium.

The ozonation efficiency was characterized by the delignification of the pulp and defined by the ratio of the Kappa number variation to the percentage of ozone consumed. The efficiency strongly depends on the presence of water which limits the ozone transfer reaction and increases the probability of chemical reactions between ozone and by-products or impurities present in the liquid phase. Consequently, when bleaching low consistency pulp, a higher ozone charge is needed to obtain good results.

Although low consistency pulps are not bleached on an industrial scale, it is attractive to use this consistency range to quantify the effect of organic additives on ozone transfer. Thus, in this work, experiments were carried out using a pulp consistency of 3%. The kraft pulp under consideration has an initial Kappa number of 37. The batch reactor (3 l) was equipped with baffles and a stirring device made up of impellers which allowed the homogeneous agitation of the pulp. The gaseous stream, supplied by a commercial ozonizer, enters at the bottom of the reactor through a diffuser which induces a good dispersion of the gas. A flow of water thermostatically controlled at 25°C circulates in the jacket of the reactor. The temperature and pH were continuously controlled during the experiments.

## 3. Ozone mass transfer equations

During the bleaching operation, cellulose fibres are in suspension in water. According to the Osawa and Schuerch model [14], the transfer of ozone occurs at the bulk of the liquid phase before reaching the reaction site. Thus, ozone diffuses into the reaction medium through layers of various thicknesses which change with pulp consistency (Fig. 1).

In order to quantify the effect of the organic additive on ozone mass transfer, a model based on the two-film theory of Lewis and Whitman [15] was developed and validated by experiments in the stirred batch reactor. The rate of transfer of ozone depends on its diffusion through the continuous gas and liquid phases. For the low consistency range, the equilibrium concentrations between the gas and liquid

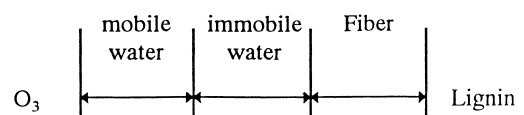


Fig. 1. Osawa and Schuerch model [14].

phases can be represented by the following relation:

$$C_G = mC_L^* \quad (1)$$

where  $m$  is the partition coefficient.

Furthermore, the relation between the global and individual mass transfer coefficients can be written as

$$\frac{1}{K_L} = \frac{1}{k_1} + \frac{1}{mk_g} \quad (2)$$

Owing to the fact that ozone is only slightly soluble in water, the gas phase resistance is neglected. Indeed, the partition coefficient of ozone between the gas and aqueous phases is about 400 (expressed as  $\text{mg l}^{-1}$  of ozone in the gas phase to  $\text{mg l}^{-1}$  of ozone in water). Thus, the value of the partition coefficient is such that  $1/k_1$  is very high in comparison with  $1/mk_g$ , showing a negligible difference between  $K_L$  and  $k_1$ . In other words, ozone encounters a principal resistance to transfer in the liquid film.

Consequently, the quantity of ozone transferred in the pulp can be expressed by the following relation:

$$\frac{dN}{dt} = k_1a(C_L^* - C_L)V \quad (3)$$

By writing,  $C_L = N/V$ , the previous relation becomes

$$\frac{dC_L}{dt} = k_1a(C_L^* - C_L) \quad (4)$$

Therefore, the parameters which determine ozone mass transfer to the liquid phase are the product of the mass transfer coefficient and the volumetric interfacial area ( $k_1a$ ) and the difference in exchange potential ( $C_L^* - C_L$ ). The determination of  $k_1a$  in an unsteady state was achieved through measurement of the variation of the ozone concentration in the aqueous phase as a function of time during the transfer of ozone from a gas phase of known composition to the aqueous medium.

Later, from the experimental results obtained in this work, we show that the presence of certain organic compounds in the liquid phase increases the value of the term  $k_1a$  and concentration  $C_L^*$  which consequently involves an improvement of the ozonation performance in pulp bleaching.

## 4. Results and discussion

The influence of organic additives, such as *tert*-butyl alcohol, on the mass transfer of ozone in the ozonation process for chemical pulp bleaching was examined.

### 4.1. Ozonation of low consistency pulp in the presence of *tert*-butyl alcohol

When the pulp is bleached by ozonation in the presence of even a small quantity of *tert*-butyl alcohol ( $0.027 \text{ mol l}^{-1}$ ), this additive induces a beneficial effect on the performance of the ozonation stage. Initially, the improvement in efficiency and selectivity of ozonation was explained by assigning a chemical role to *tert*-butyl alcohol. Indeed, according to Staehelin and Hoigne [16], *tert*-butyl alcohol inhibits the radical decomposition of ozone by scavenging hydroxyl radicals. In order to confirm this hypothesis, several experiments were performed using tertiary alcohols with a longer aliphatic chain [12]. The ability of additives to scavenge hydroxyl radicals and their inhibiting effect on the radical decomposition of ozone increase with the length of the alkyl chain. This observation tends to show that the improvement in ozonation performance with *tert*-butyl alcohol does not depend only on the ability of additives to scavenge hydroxyl radicals. On the other hand, the curve showing the evolution of the quantity of ozone consumed versus the quantity of ozone applied (Fig. 2), with or without the presence of

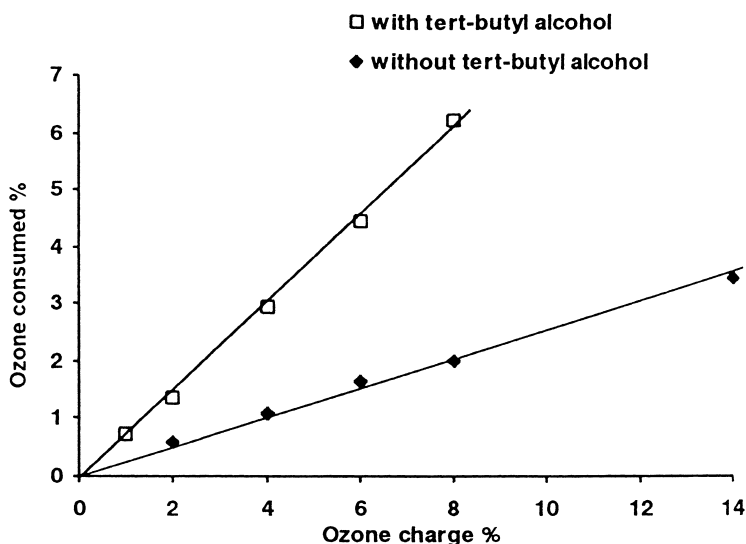


Fig. 2. Ozone reactivity with and without *tert*-butyl alcohol.

*tert*-butyl alcohol, demonstrates that the addition of *tert*-butyl alcohol involves a considerable increase in the ozone reactivity.

Moreover, the analysis of the reaction medium by gas phase chromatography shows that the *tert*-butyl alcohol is not consumed during the ozonation process. Thus, for a given ozone charge, the increase in ozone consumption is not due to a direct reaction between ozone and additive.

With regard to the ozonation reactivity, the *tert*-butyl alcohol appears to be chemically inert; however, its presence in the reaction medium enhances ozone transfer to the liquid phase. This can be explained by the action of *tert*-butyl alcohol which reduces the interfacial tension of the liquid phase and, consequently, the size of the gas bubbles. This latter phenomenon involves an increase in interfacial area and, consequently, of mass transfer. As it is difficult to measure the volumetric interfacial area between a liquid and a dispersed gaseous phase, the mass transfer is usually characterized by the product of the liquid film mass transfer coefficient and the volumetric interfacial area ( $k_1a$ ). Assuming that the gas film resistance to transfer is negligible, the quantity of ozone transferred can be determined from Eq. (4), where  $C_L^*$  is the saturation concentration in the liquid phase.

Owing to the rapid reaction of ozone with lignin, the value of the ozone concentration in the liquid phase is assumed to be close to zero; the quantity of transferred ozone is approximately equal to the product of the term  $k_1a$  and the saturation concentrations of ozone in the liquid phase  $C_L^*$ .

If a relation can be established between the reactivity of ozonation obtained from experiments and the theoretical reactivity calculated from the values of  $k_1a$  and concentration  $C_L^*$  measured under given conditions, the ozonation performance will be closely correlated with ozone mass transfer. Table 2 reports the values of  $k_1a$ , saturation concentration  $C_L^*$ , theoretical and experimental reactivities of ozonation obtained at a pH value of 3.2 and temperature of 25°C. The reactivity corresponds to the percentage of ozone consumed relative to the amount of gas admitted to the reactor. From fast reactions, such as the delignification with

ozone, where the reaction takes place in the liquid film region, the theoretical reactivity can be expressed by

$$\frac{\text{Reactivity}_{(\text{theoretical})}}{\text{Reactivity}_{(\text{no additive})}} = \frac{(k_1aC_L^*)}{(k_1aC_L^*)_{(\text{no additive})}}. \quad (5)$$

From the results given in Table 2, *tert*-butyl alcohol increases the values of the term  $k_1a$  as well as the saturation concentration of ozone  $C_L^*$ . Furthermore, the experimental ozonation reactivity obtained during pulp ozonation in the presence of *tert*-butyl alcohol is very close to the theoretical value. Therefore, *tert*-butyl alcohol plays a predominant role in ozone transfer.

The *tert*-butyl alcohol increases the ozone transfer coefficient in the liquid phase, but also influences the difference in exchange potential which increases with increasing saturation concentration of ozone. Thus, a more rapid diffusion of ozone reduces its decomposition but also limits its reactions with ozonation by-products. These advantages promote the delignification reaction, leading to better ozonation efficiencies, as shown in Table 2. The efficiency is defined as the degree of delignification relative to the quantity of ozone consumed. This parameter represents the effective capacity of reactant necessary for delignification of the pulp.

#### 4.2. Modification of surface tension in the presence of *tert*-butyl alcohol

To understand the phenomena involved at the gas–liquid interface and to explain the effect of *tert*-butyl alcohol on the mass transfer term  $k_1a$ , we measured the surface tension, which represents the work needed to increase the gas–liquid interfacial area. For a constant amount of energy supplied to the system, a reduction in the surface tension is accompanied by an increase in the interfacial area. Fig. 3 represents the variation in surface tension at the interface between air and an aqueous solution of *tert*-butyl alcohol for a range of concentrations from 0 to 40 g l<sup>-1</sup>. Fig. 3 shows that *tert*-butyl alcohol reduces the surface tension at the gas–liquid interface and therefore underlines the surfactant

Table 2  
Ozonation performance with various organic additives

| Additive                   | $k_1a$ (s <sup>-1</sup> ) | $C_L^*$ (mg l <sup>-1</sup> ) | $\sigma$ (N m <sup>-1</sup> ) | Experimental reactivity | Theoretical reactivity | Efficiency |
|----------------------------|---------------------------|-------------------------------|-------------------------------|-------------------------|------------------------|------------|
| No additive                | 0.019                     | 9.8                           | 0.0723                        | 22.7                    | 22.7                   | 6.6        |
| <i>tert</i> -Butyl alcohol | 0.032                     | 12.0                          | 0.0649                        | 44.5                    | 46.8                   | 8.3        |
| 1-Butyl alcohol            | 0.031                     | 11.5                          | 0.0670                        | 41.6                    | 43.5                   | 8.5        |
| Dimethylformamide          | 0.019                     | 9.8                           | 0.0737                        | 26.1                    | 22.7                   | 7.0        |
| Tetrahydrofuran            | 0.019                     | 10.1                          | 0.0695                        | 24.5                    | 23.4                   | 7.3        |
| 1,4-Dioxane                | 0.018                     | 10.3                          | 0.0623                        | 25.1                    | 22.6                   | 7.2        |
| Dimethylsulphoxide         | 0.017                     | 9.9                           | 0.0719                        | 24.7                    | 20.5                   | 7.1        |
| Ethyl acetate              | 0.028                     | 10.9                          | 0.0697                        | 37.5                    | 37.2                   | 7.9        |
| Diethyl ether              | 0.028                     | 10.7                          | 0.0697                        | 37.0                    | 33.9                   | 7.7        |
| Acetic acid                | 0.025                     | 10.7                          | 0.0718                        | 26.5                    | 32.6                   | 7.1        |
| Oxalic acid                | 0.017                     | 9.8                           | 0.0729                        | 21.5                    | 20.3                   | 6.5        |
| Malic acid                 | 0.018                     | 9.8                           | 0.0624                        | 22.0                    | 21.5                   | 7.0        |

Experimental conditions: pH=3.2;  $G=55 \times 10^{-3}$  m<sup>3</sup> h<sup>-1</sup>;  $[O_3]=30$  g m<sup>-3</sup>; charge O<sub>3</sub>=2%; [additive]=0.027 mol l<sup>-1</sup>; stirring speed: 25 rpm; T=25°C.

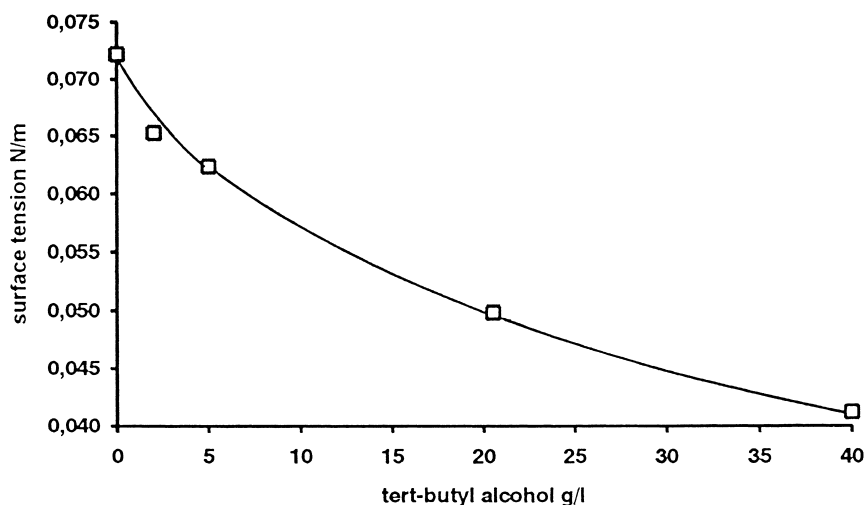


Fig. 3. Surface tension of *tert*-butyl alcohol aqueous solution.

effect of this additive. On Griffin's scale [17], *tert*-butyl alcohol is classified as a non-ionic agent which presents a slightly hydrophilic active surface. Owing to the low polarity of this additive and its short carbon chain, *tert*-butyl alcohol, like other alcohols, is generally considered to have a destructuring effect on water.

#### 4.3. Ozonation of low consistency pulp in the presence of other additives

Following the study of the effect of *tert*-butyl alcohol, ozonation tests were performed using other additives recognized as cellulose "protectors". The objective was to determine whether ozonation performance could be correlated with parameters characterizing the mass transfer mechanism. For each additive, we determined the term  $k_1a$ , the ozone saturation concentration in the liquid phase  $C_L^*$  and the surface tension between air and "water+additive" phase. The results obtained are reported in Table 2. From these results, the theoretical reactivities were compared with the experimental data. For most additives, the experimental reactivity values are close to the theoretical ones. Like *tert*-butyl alcohol, these additives improved the ozonation performance, in particular 1-butyl alcohol, diethyl ether and ethyl acetate. Most of the additives tend to reduce the surface tension and increase the value of the term  $k_1a$ .

## 5. Conclusions

The reactivity, efficiency and selectivity of ozonation essentially depend on the transfer and diffusion of ozone within the reaction medium for low consistency pulp. A few additives reported in the literature as cellulose "protector" in the chemical sense actually play the role of transfer promoters, by modifying parameters such as the term  $k_1a$  and the saturation concentration  $C_L^*$ . They improve the

ozonation performance. Although the use of these additives on an industrial scale is still limited because of their high cost and their real impact on bleaching effluents, this study has permitted the determination of the limiting stage in the ozone reaction in low consistency pulp. Furthermore, the experimental results obtained were used to explain the increase in efficiency and selectivity of ozonation of medium and high consistency pulps in the presence of organic additives. The phenomena involved during the treatment of medium and high consistency pulps are different. As the additives do not specifically play, in the case of low consistency pulps, the role of scavenging radical species, the improvement in the efficiency and selectivity of the process results from the increase in ozone solubility in the aqueous phase which induces good penetration of gas in the pulp fibres.

## 6. Nomenclature

|              |  |
|--------------|--|
| $N$          | mass of ozone transferred (kg)   |
| $K_L$        | overall mass transfer coefficient for liquid film ( $\text{m s}^{-1}$ )                  |
| $k_1$        | individual mass transfer coefficient for liquid film ( $\text{m s}^{-1}$ )               |
| $k_g$        | individual mass transfer coefficient for gas film ( $\text{m s}^{-1}$ )                  |
| $a$          | interfacial area per unit of volume ( $\text{m}^2 \text{m}^{-3}$ )                       |
| $C_G$        | ozone concentration in gas phase ( $\text{kg m}^{-3}$ )                                  |
| $C_L$        | ozone concentration in liquid phase ( $\text{kg m}^{-3}$ )                               |
| $C_L^*$      | ozone concentration in liquid phase in equilibrium with gas phase ( $\text{kg m}^{-3}$ ) |
| $m$          | partition coefficient  |
| $G$          | gas flow rate ( $\text{m}^3 \text{h}^{-1}$ at normal conditions)                         |
| Kappa number | percentage of lignin in pulp divided by 0.15   |
| $\sigma$     | surface tension ( $\text{N m}^{-1}$ )  |

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