

# **CarbOx, - Carbon dioxide boosted delignification and bleaching by hydrogen peroxide and/or ozone**

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## **Preface**

This is not a scientific paper in the usual sense, but an attempt to summarize years of scientific work aimed at developing eco-efficient delignifying and bleaching processes for the pulp and paper industry. This has resulted in the CarbOx-concept, where carbon dioxide is used to boost delignification and bleaching by hydrogen peroxide and/or ozone. Hopefully, these ideas can inspire both research and process development.

For questions and suggestions readers are wellcome to contact me by e-mail: [torbreit@gmail.com](mailto:torbreit@gmail.com) or [torbreit@kth.se](mailto:torbreit@kth.se)

## **Background**

The aim of chemical pulping of lignocelluloses, *e.g.*, wood, is to obtain a fibrous cellulose-rich pulp by removing the lignin part. Industrially, this is done in sequences usually starting with nucleophilic chemistries in alkaline cooking liquor. During cooking lignin is broken down into smaller soluble units but the produced pulp acquires a dark colour from modified lignin residues. Further removal of these lignin residues requires complementary electrophilic chemistries allowing both delignification and bleaching.

In delignification and bleaching, the challenge is to find the optimal balance between efficiency, *i.e.* lignin removal, and selectivity, *i.e.* cellulose conservation, using only environmentally acceptable processes. On account of the last criterion, use of chlorine gas for pulp delignification and bleaching is now abandoned in most industrial countries albeit that it is very efficient and selective. The reason for this is the formation of chlorinated organic compounds that severely harm the aquatic environment.

It is the common technique today to reduce the residual lignin content of the pulp obtained after a cooking stage by an oxygen treatment. This oxygen delignification further reduces the lignin content by oxidizing the lignin into smaller fragments that are removed from the fibers in one or several washing steps. The use of oxygen is very attractive from economic and environmental points of view but the chemistry involved results in formation of reduced

oxygen species, *e.g.* hydroxyl radicals, that through hydrogen atom abstraction can destroy cellulose molecules. This limited selectivity leads to impaired fiber strength properties.

If a white lignin free pulp is required, more selective chemistry must be adopted than that offered by oxygen delignification only. Since the oxidation potential of lignin is much lower than that of cellulose this can be achieved by appropriate one-electron oxidants<sup>1</sup>. In practice, chlorine dioxide (reduction potential  $E_0 = 0.94\text{V}$  vs. NHE) has proven to be very useful for this purpose and production of high quality pulp is today achieved by using oxygen and chlorine dioxide in different bleaching sequences, possibly also including a final treatment with hydrogen peroxide to eliminate remaining chromophores.

The present technology of delignification and pulp bleaching is efficient and fairly selective. From an environmental point of view, however, the process is not optimal since the use of chlorine dioxide still leads to some formation of chlorinated reaction products, *i.e.* the problems associated with chlorine bleaching are reduced but not eliminated. For this reason, there is still a need to find more environmentally friendly bleaching processes in accordance with a general quest for best technology. This can be achieved using oxidants, which, like  $\text{ClO}_2$ , react with aromatics through one-electron transfer reactions producing corresponding radical cations. Such transformations have previously been demonstrated using enzymes, transition metal complexes, polyoxymetalates, and photo-catalysts [Papers in "Oxidative Delignification Chemistry – Fundamentals and Catalysis", ACS Symposium Series 785, ISBN 0-8412-3738-7]. These "advanced oxidation technologies" are, however, generally difficult to implement on the industrial level.

The quest for an environmental benign reagent, that is compatible with existing technology, inspired us to investigate the delignifying properties of the carbonate radical,  $\text{CO}_3^{\cdot-}$  (reduction potential  $\text{CO}_3^{\cdot-} + e^- + \text{H}^+ \rightarrow \text{HCO}_3^-$ ,  $E_0 = 2.20\text{ V}$  vs. NHE). As a starting point, we performed pulse radiolysis

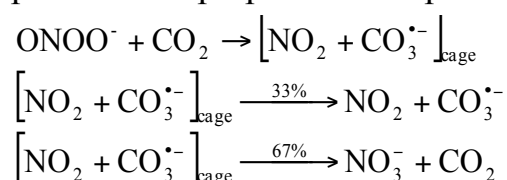
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<sup>1</sup> Reduction potentials for free radicals in aqueous solution is reported in P. Wardman "Reduction Potentials of One-Electron Couples Involving Free Radicals in Aqueous Solution", J. Phys. Chem. Ref. Data Vol. 18 No. 4, pp. 1639-1755J, 1989

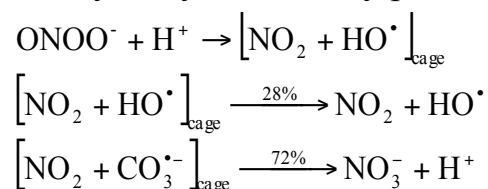
experiments to measure the reactivity of the carbonate radical towards various lignin and carbohydrate model compounds [D. Stenman *et al.* “Reactivity of the Carbonate Radical Anion Towards Carbohydrate and Lignin Model Compounds” *J. of Wood Chem. and Technol*, 2003, 23(1) pp. 47-69]. These studies showed that the carbonate radical anion rapidly oxidizes *both* phenolic and non-phenolic lignin structures by one-electron transfer forming corresponding radical cations. We also observed that the carbonate radical reacts with carbohydrates but at a much lower rate. The carbonate radical should thus be a suitable environmental benign reagent for selective and efficient delignification of pulp.

The kinetic studies also showed that carbohydrates are oxidation activated at high pH due to deprotonation. This was also the case for methyl- $\beta$ -D-glucopyranoside, for which a pKa-value of about 14.4 was estimated. Such activation of this cellulose model compound, representing *intra*-molecular cellulose units, implies that the cellulose itself will be oxidation activated at high pH. This could lead to lowered selectivity for those technical processes requiring high pH.

Inspired by the promising results obtained on model compounds, we completed a study on pulps and cotton linters. The carbonate radical was produced in pulp/linters suspensions from peroxyxynitrite and carbon dioxide.



and hydroxyl radicals by protonation of peroxyxynitrite.



These studies [David Stenman Doctoral Thesis “Advanced oxidation technologies for the pulp industry. – An investigation on the delignifying properties of the carbonate radical anion” KTH 2004, ISBN 91-7283-893-0] showed that:

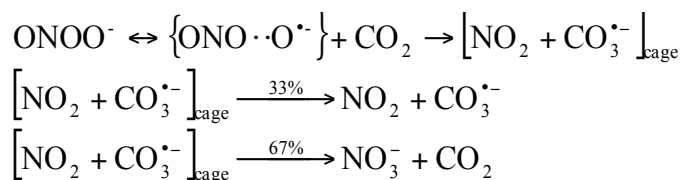
- Peroxynitrite can be used in connection with pulp as a controlled source of different radicals, *e.g.* hydroxyl and carbonate radicals.
- The selectivity of the carbonate radical was found to be much higher than that of the hydroxyl radical. Using a simple kinetic approach, we could relate the selectivity differences observed on pulp to the kinetic selectivity differences determined in model compound studies.
- Radical cation formation, given by the carbonate radical, results in a rapid direct delignification and high brightness increase. This reflects that aromatic radical cation formation in the lignin is an efficient way to induce lignin fragmentation *and* bleaching.
- Both radicals could degrade cotton linters as shown by viscosity and GP-SEC measurements. The degradation of cotton linters seems to be slightly more extensive in the presence of oxygen.
- For the carbonate radical, >90 % of the viscosity losses could be recovered with a NaBH<sub>4</sub> treatment before the viscosity measurements whereas the recovery of viscosity after hydroxyl radical degradation and a subsequent NaBH<sub>4</sub> treatment was only about 40 %.
- This indicates that carbonate radicals mainly abstracts H-atoms adjacent to hydroxyl groups, *i.e.* at C<sub>2</sub>, C<sub>3</sub> and C<sub>6</sub>. This *intramolecular selectivity* may reflect a polar effect, whereby hydrogen-atom abstractions from these positions are favoured by the less reactive carbonate radical. An abstraction at C<sub>6</sub> would also be sterically and statistically favoured. An oxidation at C<sub>6</sub> may even be beneficial in paper making. These ideas are further developed in “The inter- and intramolecular selectivity of the carbonate radical anion in its reactions with lignin and carbohydrates” [Magnus Carlsson Doctoral Thesis KTH 2005, ISBN 91-7178-098-X].
- Bleaching of various pulps were also performed, *e.g.*:  
Eucalyptus pulp with initial kappa number 20 was impregnated with peroxynitrite and treated with CO<sub>2</sub> in an autoclave for two minutes at room temperature. After treatment the pulp was fully bleached (final kappa number < 5) with insignificant viscosity loss.

From these basic studies we conclude that the carbonate radical is a green oxidant that may substitute chlorine dioxide to achieve totally chlorine free

(TCF) delignification. This CarbOx concept has many potential advantages as a part of an advanced eco-efficient delignification process:

- Conditions are mild with pH in the range 4-10.
- Components of the system are inexpensive and environmentally friendly.
- A CarbOx stage can be easily integrated with existing oxygen and hydrogen peroxide stages
- No delignification and bleaching stages require sharp pH or temperature gradients.
- Reaction rates are high even at room temperature.
- A CarbOx stage between two oxygen stages can reactivate the lignin by hydroxylation-, dealkoxylation- and side-chain cleavage of non-phenolic lignin units.

Even if peroxyxynitrite may be used as a source of carbonate radicals in industrial applications implementation of CarbOx chemistry in pulp bleaching will probably require that carbonate radicals can be produced in a more simple and environmentally better way. On inspection,  $\text{CO}_3^{\cdot-}$  can be regarded as an adduct between carbon dioxide,  $\text{CO}_2$ , and an oxyl radical anion  $\text{O}^{\cdot-}$ . The oxyl radical anion is the base form of the hydroxyl radical,  $\text{HO}^{\cdot}$ ,  $\text{pK}_a = 11.8$ , *i.e.* in aqueous solution the oxyl radical anions are only present under strong alkaline conditions. However, carbon dioxide has acidic properties, so under alkaline conditions it reacts with  $\text{OH}^-$  by formation of (bi)carbonate. Consequently, the reaction  $\text{CO}_2 + \text{O}^{\cdot-} \rightarrow \text{CO}_3^{\cdot-}$  cannot be realized in a direct single step. This demonstrates that in order to allow an oxyl radical anion,  $\text{O}^{\cdot-}$ , reaction with carbon dioxide, it must proceed in an indirect way. In fact, this is what happens when peroxyxynitrite reacts with carbon dioxide (Note that  $\text{NO}_2$  is a stable radical):



Analogous transfer of oxyl radical anions may be achieved in carbon dioxide boosted delignification and bleaching by hydrogen peroxide or ozone. It is the purpose of this communication to indicate how this could be realized.

## Discussion

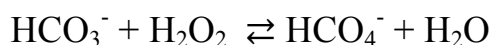
### *Hydrogen peroxide*

Hydrogen peroxide is widely used in mechanical pulp bleaching. It is usually applied under strong alkaline conditions to achieve nucleophilic lignin transformations and reduction of chromophores such as coniferaldehyde.

Hydrogen peroxide is also an oxidant with high active oxygen content, but it reacts rather slowly in the absence of activators. The activation is often accomplished by formation of peroxy acids, *e.g.* peracetic acid, by reacting the parent acid with high concentrations of hydrogen peroxide under strong acidic conditions.

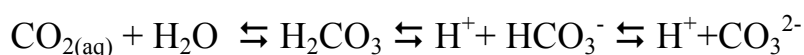
In the CarbOx concept similar activation is achieved by - *carbon dioxide/bicarbonate at near neutral pH*. The reactive species thus initially formed is peroxymonocarbonate ( $\text{HCO}_4^-$ ), which is a true peracid with the structure  $\text{HOOCO}_2^-$ .

In the presence of bicarbonate formation of peroxymonocarbonate ions is quite rapid ( $t_{1/2} \approx 300\text{s}$  at  $25^\circ\text{C}$ ):



For this equilibrium  $K = 0,32$  at  $25^\circ\text{C}$ .

The reaction proceeds by way of carbon dioxide, which is in equilibrium with bicarbonate.

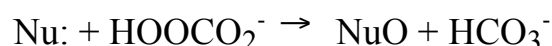


The hydration equilibrium is shifted far to the left, *i.e.* much in favour of  $\text{CO}_{2\text{aq}}$  over  $\text{H}_2\text{CO}_3$  [Latimer & Hildebrandt "Reference Book of Inorganic Chemistry 3<sup>rd</sup> Ed." Macmillan, p.285].



The rate of formation of peroxydicarbonate can thus be enhanced by adding carbon dioxide to (alkaline) hydrogen peroxide.

Peroxydicarbonate reacts *per se* as a non-radical two-electron oxidant (oxygen atom transfer agent). The reaction mechanism involves nucleophilic attack of a substrate on the electrophilic oxygen with displacement of bicarbonate:

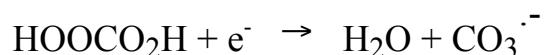


Note that this reaction is not equivalent to the nucleophilic reactions given by hydrogen peroxide at high pH where the hydrogen peroxide anion is the nucleophilic reagent.

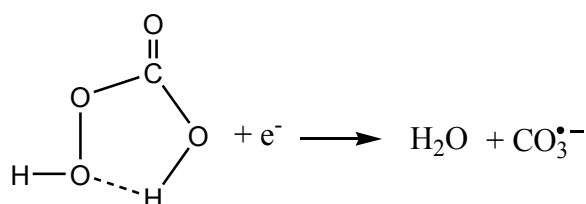
On the basis of the pK<sub>a</sub>-value of the conjugate acid associated with the leaving group it is expected that the reactivity of peroxydicarbonate will be intermediate between that of hydrogen peroxide (pK<sub>a</sub> = 11.9) and organic peroxyacids such as peracetic acid (pK<sub>a</sub> = 8.2). A higher reactivity may then be reached at pH ≈ 9 (estimated pK<sub>a</sub>-value for HOOCO<sub>2</sub>H) through the reaction:



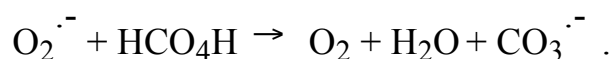
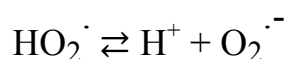
Alternatively, a one-electron reduction of peroxydicarbonate would generate strongly oxidizing carbonate radical anions:



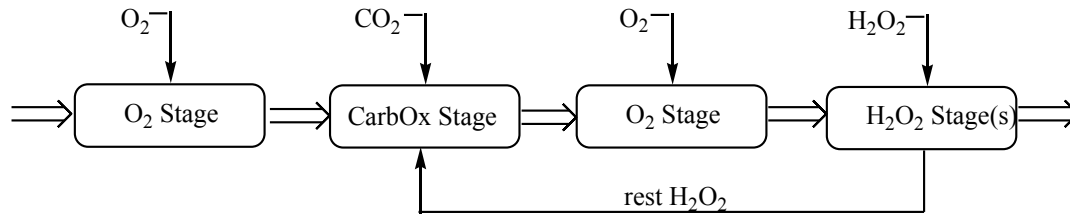
This electron transfer is facilitated by a five-membered ring transition state:



and may proceed autocatalytically at pH ≈ 9, perhaps enhanced by transition metal ion catalysis or enzymes, through following reaction steps:



The figure below is a principal suggestion of how the above described chemistry may be implemented to achieve a pulp of high brightness by totally chlorine free bleaching. (Washing stages not included)

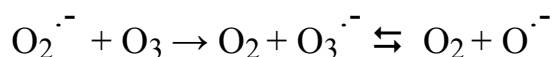


Modern H<sub>2</sub>O<sub>2</sub> bleaching under transition metal control results in high brightness increase and a high concentration of residual hydrogen peroxide. In the CarbOx concept this residual hydrogen peroxide is efficiently reused as source of carbonate radicals that reactivate the remaining lignin before a second oxygen stage.

### Ozone

Ozone, O<sub>3</sub>, is in itself a powerful oxidant capable of reacting with most organic substances. This has inspired attempts to use ozone as a chlorine-free bleaching alternative that is superior from an environmental point of view. However, difficulties of mastering (hydroxyl) radical formation has prevented ozone bleaching from being widely adopted by the pulp industry.

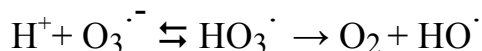
The formation of radicals when ozone reacts with phenolic and non-phenolic lignin model compounds in aqueous solutions at different pH was studied by Martin Ragnar, *et al.* 1999 [“Radical formation in ozone reactions with lignin and carbohydrate model compounds”, *Holzforschung* 53(4), pp 292-298 and “A new mechanism in the ozone reaction with lignin-like structures”, *Holzforschung* 53(4), pp 423-428, and his Doctoral Thesis “On the Importance of Radical Formation in Ozone Bleaching”, KTH 2000, ISSN 1104-7003]. Supported by quantum chemical calculations, it was concluded that, in those systems, superoxide is the initial radical formed. Extremely reactive hydroxyl radicals are then generated predominantly by the reaction of superoxide with ozone in the reaction sequence:







An earlier proposed mechanism [R.E.Bühler *et al.* “Ozone decomposition in water studied by pulse radiolysis. 1.  $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot -}$  and  $\text{HO}_3^{\cdot}/\text{O}_3^{\cdot -}$  as intermediates” J. Phys. Chem. 1984, 88(12), pp 2560-2564]:

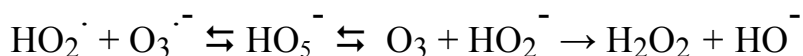


is not included here since the  $\text{pK}_a$ -value for  $\text{HO}_3^{\cdot}$  is estimated to be about -2. This value is derived from an empirical relation for hydrogen oxygen compounds for which:

$$\text{pK}_a \approx 19 - 7 \times \frac{\text{number of O-atoms}}{\text{number of H-atoms}}$$

[B.H.J. Bielski and H.S. Schwartz. “The Absorption Spectra and Kinetics of Hydrogen Sesquioxide and the Perhydroxyl Radical.” J. Phys. Chem. 1968, 72(11), 3836-3841].

Superoxide is the base form of the hydroperoxyl radical  $\text{HO}_2^{\cdot}$  ( $\text{pK}_a = 4.8$ ). In contrast to superoxide, the hydroperoxyl radical is a stronger one-electron oxidant than ozone,  $E = 1.49 - 0.059 \times \text{pH}$  V at 298K vs.  $E = 1.1$  V [footnote 1] so under sufficient acidic conditions generation of unselective hydroxyl radicals according to the above reaction scheme should be blocked. In fact, the hydroperoxyl radical reacts rapidly with the ozonide radical anion by formation of ozone and hydrogen peroxide [G. Merényi *et al.* “Reaction of Ozone with Hydrogen Peroxide (Peroxone Process): A Revision of Current Mechanistic Concepts Based on Thermokinetic and Quantum-Chemical Considerations”, Environ. Sci. Technol. 2010, 44, 3505-3507]:

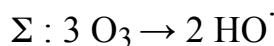
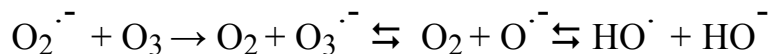
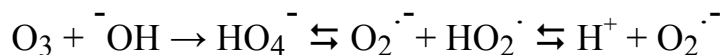


Industrially, it is also an established fact that ozone bleaching requires acidic conditions, typically about pH 3. However, accumulation of hydrogen peroxide may lead to formation of hydroxyl radicals in transition metal ion catalyzed reactions, which are difficult to prevent, *e.g.* by addition of chelators (*e.g.* DTPA), under acidic conditions.

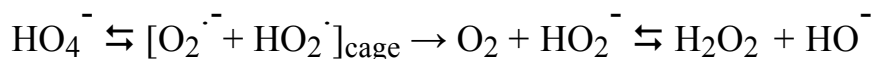
Under alkaline conditions ozone decomposes fairly rapidly by formation of hydroxyl radicals and some hydrogen peroxide [G. Merényi *et al.* “The reaction of ozone with the hydroxide ion. Mechanistic considerations based on

thermokinetic and quantum-chemical calculations. The role of  $\text{HO}_4^-$  in superoxide dismutation.” Chem. – Eur. J. 2009, 16, 1372-1377]:

Dominant reaction (free radical mechanism):

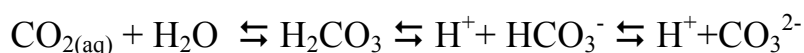


Minor reaction (charge exchange mechanism) :



Ozone bleaching under alkaline conditions has thus been regarded impracticable. Surprisingly, Nemes *et al.* 2000 found that ozone is fairly stable in alkaline bicarbonate solutions [“Kinetics and Mechanism of the Carbonate ion Inhibited Aqueous Ozone Decomposition” J.Phys. Chem. A , 104(34), 7995-8000]. One possible explanation for the unexpected stability of  $\text{O}_3$  in bicarbonate solutions could be that carbonate radicals are formed, terminating the radical chain reactions normally leading to rapid ozone degradation by removal of the dominant chain carrier radicals  $\text{HO}^{\cdot}$ ,  $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$  and  $\text{HO}_3^{\cdot}/\text{O}_3^{\cdot-}$  :

- Equilibrium reactions:



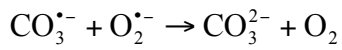
The hydration equilibrium is shifted far to the left, *i.e.* much in favour of dissolved  $\text{CO}_2$ , *i.e.*  $\text{CO}_{2(\text{aq})}$ , over  $\text{H}_2\text{CO}_3$  [Latimer & Hildebrandt “Reference Book of Inorganic Chemistry 3<sup>rd</sup> Ed.” Macmillan, p.285].

- Accepted radical reactions<sup>2</sup>:

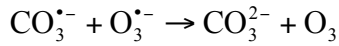



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<sup>2</sup> Radical reaction rates can be obtained from : J.Phys.Chem Ref. Data, Vol 17, No 2-3, 1988



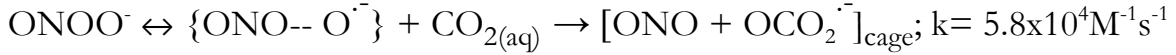
$$k = 10^8 \text{ M}^{-1}\text{s}^{-1}$$



$$k = 5.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$

- Suggested radical reactions:

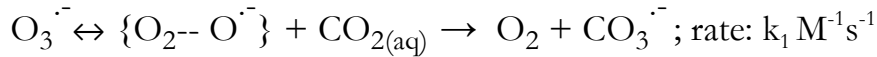
The reaction between peroxyxynitrite and carbon dioxide is fairly fast:



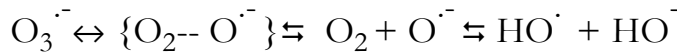
Another nucleophilic reaction of the same type is:



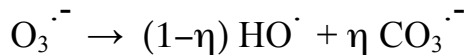
Analogous to these examples, a direct nucleophilic oxyl radical anion transfer from the ozonide radical anion to carbon dioxide is suggested:



This reaction may afford an upstream solution to the problem of hydroxyl radical formation when ozone is applied in pulp bleaching. It is not previously described but thermodynamically feasible and should be fast enough to compete with the reaction leading to formation of unselective hydroxyl radicals:



Formally we may then summarize the initial radical yield as:

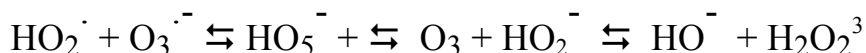


The intrinsic life time of  $\text{O}_3^{\cdot-}$ ,  $\tau$ , is expected to be unaffected by pH since direct protonation of  $\text{O}_3^{\cdot-}$  does not take place as  $\text{pKa}(\text{HO}_3) \approx -2$ . Competition kinetics gives:

$$\eta = \frac{k_1 \tau [\text{CO}_2]_{\text{aq}}}{k_1 \tau [\text{CO}_2]_{\text{aq}} + 1} = \frac{1}{1 + \frac{1}{k_1 \tau [\text{CO}_2]_{\text{aq}}}}$$

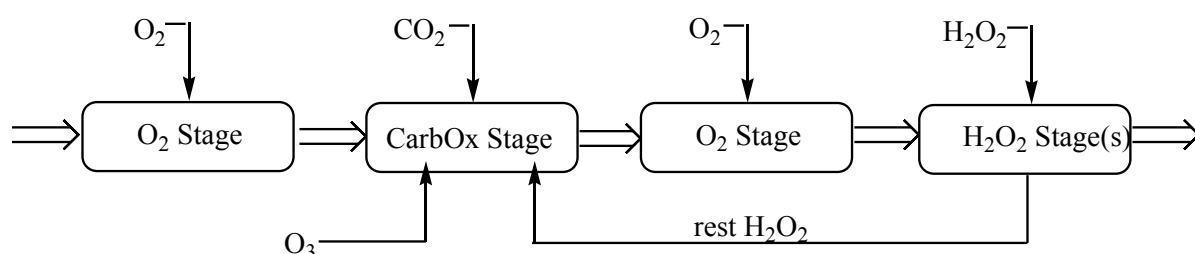
In order to block formation of  $\text{HO}^{\cdot}$   $\eta$  must be  $\approx 1$ . Consequently,  $k_1 \tau [\text{CO}_2]_{\text{aq}} \gg 1$  or  $[\text{CO}_2]_{\text{aq}} \gg (k_1 \tau)^{-1}$ . If we assume that  $k_1 \approx 10^4 \text{ M}^{-1}\text{s}^{-1}$ , as suggested by above mentioned reactions, and  $\tau \approx 10^{-3} \text{ s}$ , as a reasonable life-time for  $\text{O}_3^{\cdot-}$ , the concentration of  $[\text{CO}_2]_{\text{aq}}$  must be  $\gg 0.1 \text{ M}$ . This concentration would probably require addition of  $\text{CO}_{2(\text{g})}$  at over pressure. Under these conditions,

pH will be about 3.5, *i.e.* close to common conditions for ozone bleaching. However, a lower pH will not increase the hydroxyl radical yield because the ozonide radical anion is not protonated, *i.e.*  $\tau$  is pH invariant. Moreover, as discussed above, the hydroperoxyl radical ( $\text{HO}_2^\cdot$ ,  $\text{pK}_a = 4.8$ ) reacts rapidly with the ozonide radical anion by formation of ozone and hydrogen peroxide:



Consequently, reaction conditions may be realized were addition of carbon dioxide can be used to control the radical chemistry of ozone bleaching.

The CarbOx stage presented above can now be expanded by addition of ozone as suggested in the figure below:



A conceptual description of the CarOx stage and its integration in a delignifying and bleaching process can be presented in following steps:

1. After the initial oxygen stage and subsequent washing, pulp is transferred to the CarbOx stage where carbon dioxide is applied at some overpressure. This brings down pH to about 3.5.
2. Ozone is introduced in short sequences and under mixing to establish a uniform treatment.
3. Residual alkaline hydrogen peroxide from the final stage is brought back to the CarbOx stage under carbon dioxide and mixing, pH is then established at about 9. Temperature is raised to about 60<sup>0</sup>C to allow a faster treatment.
4. After the CarbOx stage pulp is washed and conditioned for a second oxygen stage.

<sup>3</sup> The back-reaction is realized under peroxone conditions, *i.e.* by mixing ozone and hydrogen peroxide

Realization and optimization of this process will of course require more detailed analysis of process parameters. As described here, ozone and hydrogen peroxide are added in sequences. If they are added together, *i.e.* under so-called peroxone conditions, reaction rates are expected to increase considerably, but probably at expense of selectivity due to less controllable chemistries<sup>4</sup>. Other embodiments of the basic CarbOx concept can also be considered; most obvious is to exclude the ozone addition.

### **Comment**

Many recent studies have demonstrated that bicarbonate-carbon dioxide stimulates oxidation and peroxidation of several biological targets. It is recognized that carbonate radical and peroxymonocarbonate mediate these processes. Peroxymonocarbonate is reported to react with superoxide dismutase, SOD, by formation of carbonate radical. This reaction may also be included in a CarbOx-stage.

### **Acknowledgement**

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<sup>4</sup> Small amounts of ozone may be added as radical initiator, e.g:

