Effect of carry-over on the kinetics of chlorine dioxide delignification of an unbleached hardwood kraft pulp

MARIA J. M. C. BARROCA*, ROGÉRIO M. S. SIMÕES† AND JOSÉ ALMIRO A. M. CASTRO*

This work is concerned with the kinetics of the prebleaching stage of a kraft pulp of *Eucalyptus globulus* with chlorine dioxide. Its main purpose is to discuss the influence of the degree of washing, expressed as the COD of the pulp, on the kinetics and stoichiometry of chlorine dioxide delignification. The effect of the carry-over on the rate of delignification of a D_0 stage was studied over time for pulps with different initial organic charges (COD). A set of experiments was specially designed to discriminate the individual role of lignin and of COD upon the initial consumption of chlorine dioxide. A modified mathematical model, taking into account the reactions of chlorine dioxide with both lignin and the carry-over, has been developed. In this model, the initial chlorine dioxide consumption (in the fast phase of reaction) is dependent on two factors: the carry-over of the pulp and the temperature of operation. However, the carry-over does not affect the corresponding initial depletion factor for the Kappa number. The role of the dissolved organic material, carried with the pulp, upon the rate of reaction in the slow period is better described in the stoichiometry. The fit of the experimental results obtained for pulps with different COD reveals good prediction capabilities for both Kappa number and chlorine dioxide concentration in a conventional D_0 stage.

Keywords
Kraft pulp, bleaching, kinetics, mathematical model, carry-over, hardwood pulp, *Eucalyptus globulus*

The main purpose of pulp washing before any delignification or bleaching stage is to remove the inorganic chemicals and the dissolved organic material in the liquid phase around and inside the fibres. Due to recent improvements of the washing process in modern kraft mills, the sodium washing losses have diminished but the importance of organic carry-over remains. Dissolved organic matter greatly affects the consumption of chemicals during bleaching and, thus, the overall operating costs of the bleach plant. Moreover, its removal during washing is the key to decreasing the formation of pollutant charge in the bleaching effluents, especially of organochlorides. During the prebleaching stage with chlorine dioxide, many complex and simultaneous reactions occur with the pulp and with the organic materials carried with it. These reactions are usually described in the literature by kinetic models obtained from extensive kinetic and stoichiometric studies that are based on the measurement of the Kappa number after a standard alkaline extraction stage, E_1 (*2,3,4*). In a recent study, Barroca et al. (*1*) proposed a kinetic model for the D_0 prebleaching stage, in a five-stage sequence $D_0E_1D_1E_2D_2$, where the total chlorine dioxide consumption was correlated with the total Kappa number drop after D_0 by a nonlinear function. This integrated form of stoichiometry was better described by a polynomial with respect to Kappa number drop and is independent of temperature. In all of these kinetic models it is assumed that the only source of consumption of chlorine dioxide is its reaction with the lignin in the pulp.

In industry, despite the large investments in washing of the unbleached pulp to improve the removal of most of the inorganic and organic matter, the pulp suspension still contains some organic material that is carried over to the bleaching plant. This leads to an increase in the consumption of chlorine dioxide, and more importantly to a competition for this chemical between the lignin in the pulp fibres and the dissolved material in the liquid phase. Parming et al. (*8*) developed a mathematical model for the reactions between the organic material in an E_1 spent liquor and chlorine dioxide in the absence of pulp; in their study this corresponded to a blank D_1 stage. The consumption of chlorine dioxide and of reactive lignin was measured by the change in light absorption at 357 nm and 278 nm, respectively. Combining this model with that proposed by Teder and Tormund (*9*) for pulp bleaching in a D_1 stage, the above researchers simulated the effect of the carry-over from the preceding E_1 liquid effluent on the brightness development at the end of the D_1 stage. Their conclusion was that for the few situations that were evaluated, this combined model is unable to predict the experimental data in a satisfactory manner. Since all previous kinetic studies on D_0 bleaching have ignored this issue, it is extremely important to determine the extra consumption of chlorine dioxide arising from such dissolved matter, in order to reliably describe the whole of the bleaching operation.

The purpose of this work was to investigate the effect of the degree of washing, and in particular of the Chemical Oxygen Demand (COD) of the pulp, upon the kinetics of the delignification reaction in the D_0 stage. The model described by Barroca et al. (*1*) was extended to incorporate the influence of the organic material upon some of the kinetic parameters and its prediction capabilities were assessed.

MATERIALS AND METHODS

Three pulps produced in the laboratory, by kraft cooking of *E. globulus* chips, with Kappa numbers of 12.7, 13 and 14.2 after full washing of the pulp samples (see Appendix 1) were used in this study. Each of the above pulps was submitted to laboratory washings of varying extents with distilled water in order to produce samples with different organic charges (COD) prior to delignification in a standard D_0 stage.

All D_0 bleaching experiments were carried out in a 3-litre thermostatic glass reactor at low pulp stock concentration (0.7%), chlorine dioxide charge (3% on o.d. pulp) and a stirring rate of 600 rpm.

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* Department of Chemical Engineering, The University of Coimbra, Polo II - Pinhal de Marrocos, 3030 Coimbra, Portugal.
† Department of Paper Science and Technology, University of Beira Interior, Rua Marquês d'Avila e Bolama, 6200 Covilhã Portugal.

The pulp suspension was continuously stirred and sulfuric acid added just before chlorine dioxide, in order to impose a pH around the desired value at the beginning of the reaction (pH = 4). This was kept constant during the run by successive additions of sodium hydroxide. Temperature was maintained constant using a special cooling/heating bath. In each experiment, a liquid sample was quickly taken with a syringe equipped with a special glass filter, cooled and immediately analysed after thermal conditioning. Rapid washing of the pulp with cold water stopped the bleaching reaction and the sample was then further washed with an excess of warm water prior to Kappa number determination. Each run comprised a set of experiments that were interrupted at different sampling times so that chlorine dioxide concentration and Kappa number could be monitored throughout the reaction time.

The organic material carried over with the pulp was monitored by measuring its chemical oxygen demand. This variable is widely used in industry to express the amount of dissolved organic material entering the bleaching plant with the pulp suspension and plays an important role in the consumption of chorine dioxide in the prebleaching stage. It is possible to measure the COD of a pulp sample by means of a variety of procedures that are all strongly dependent on the sample stock concentration (s.c.), e.g. by squeezing the free liquor out of the pulp suspension or by diluting and thickening the pulp sample (SCAN CM 45:91). The COD in the filtrate that results from any of those procedures is later analysed. When squeezing a high s.c. sample, the dissolved organic matter remains mainly located inside the fibres while in the medium/low s.c. case most of the carry-over is in the free liquor. Thus, in the present work a sample of pulp was diluted to a given ultra-low stock concentration and stirred mechanically for a specified period of time and temperature. After this, the free liquor was withdrawn by filtration for COD analysis and the corresponding result expressed either in mg/l or in kg/t o.d. pulp (see Appendix 2). This liquid was also later employed for kinetic experiments between chlorine dioxide and the organic matter in order to discriminate the individual role of lignin in the fibres and the organic matter in the liquid phase in the global consumption of chlorine dioxide. These experiments were conducted in a series of dark glass flasks of 125 mL capacity containing a given volume of the liquid that had been previously conditioned in a temperature-controlled bath before chlorine dioxide addition. The initial operating conditions imposed in all these cases were very similar to those used in the kinetic experiments with pulp.

RESULTS AND DISCUSSION

Several bleaching experiments with chlorine dioxide were carried out using a kraft pulp with different values of COD, at constant temperature (T=55°C) and pH (pH=4). The profiles of chlorine dioxide concentration and Kappa number along the reaction are shown in Figures 1 and 2, respectively. The different values of COD of the starting samples of pulp are expressed in kg/t o.d. pulp.

As expected, an increase in COD sharply increases the total consumption of chlorine dioxide, although without any noticeable decrease in the delignification rate (see Fig. 2).

The particular cases of pulps with a COD of 7 and 55 kg/t o.d. pulp, and initial Kappa numbers of 12.7 and 13, respectively, highlight this observation. In fact, the consumption rate of chlorine dioxide is so high for the latter that its concentration is practically zero after five minutes. This explains the slight decrease in the global rate of delignification of the pulp with the higher COD. These results are indeed an indication that chlorine dioxide also reacts extensively with the carry-over in the liquid phase in addition to the lignin in the fibres. To further clarify this, the free liquor resulting from the washing of each original pulp for COD analysis (expressed in mg/l) was submitted to chlorine dioxide at the same operating conditions as for the experiments carried out with pulp.

The profiles illustrated in Figure 3 confirm the above observations, i.e. that the reactions between chlorine dioxide and the organic matter in the liquid phase are responsible for a large consumption of chlorine dioxide. It is worth mentioning that the values of COD in the pulp, shown in Figures 1 and 2 (with CODs of 7, 21, and 55 kg/t o.d. pulp) correspond to the values of COD (50, 150 and 390 mg/l) in the liquid shown in Figure 3. The pattern of the chlorine dioxide concentration profiles is similar in shape to that exhibited by the profiles in Figure 1, i.e. there is an initial phase with an instantaneous and extensive consumption of chlorine dioxide, followed by a slow phase, with a lower rate of reaction. This behaviour for the reaction in the liquid phase demonstrates that the responsibility for such a pattern in the case of pulp bleaching can not be exclusively explained by inter and/or intra mass transfer limitations.

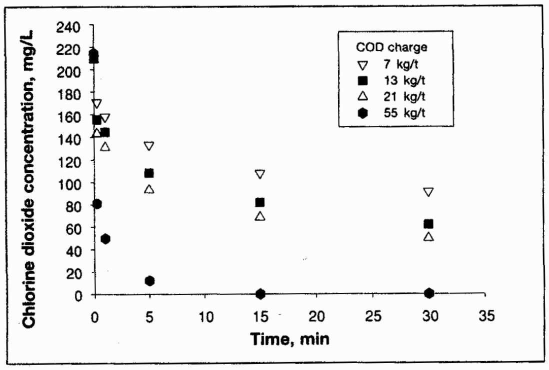

Fig. 1 **Profiles of chlorine dioxide concentration for pulps with different values of COD.**

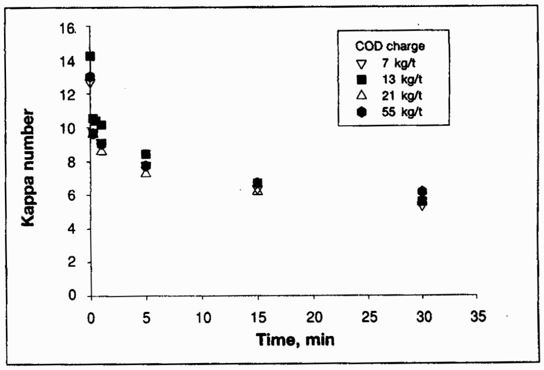

Fig. 2 **Profiles of Kappa number for pulps with different values of COD.**

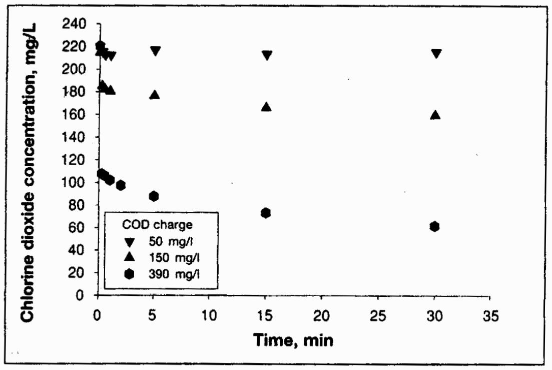

Fig. 3 **Chlorine dioxide concentration profiles for the reaction with dissolved organic material (in the absence of pulp).**

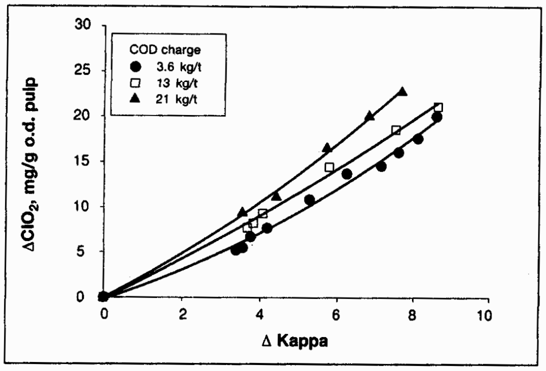

Fig. 4 **Total chlorine dioxide consumption versus total Kappa number drop at different COD levels.**

This undesired chlorine dioxide consumption occurs mainly during the first seconds of reaction, i.e. in the fast phase and is strongly affected by the concentration of the carry-over in the pulp. As expected, the higher the COD in the unbleached pulp the higher the initial consumption of chlorine dioxide. The COD of the pulp is so important that up to 75% of the initial charge can be wasted in secondary reactions with the carry-over.

Mathematical model for the chlorine dioxide reactions with lignin and carry-over

As shown by Barroca et al. (*1*) the kinetic model for the delignification stage, D_0, can be expressed by two depletion factors, K_θ and $[ClO_2]_\theta$ for the very short initial stage ($\theta \approx 15$ seconds) and by equations 1 and 2 for the slow phase: (see equation 1 & 2) where $[ClO_2]$ and K represent the chlorine dioxide concentration and the Kappa number, respectively, K_∞ is the floor Kappa number (which has been identified as a strong linear function of temperature), Ea = activation energy (33.7 kJ/mol), T = temperature (°C), m_{pulp} = mass of oven dry pulp (g), V = volume of the liquid in the suspension (dm^3), t = reaction time and α = stoichiometry factor (mg of chlorine dioxide/(g o.d. pulp×units Kappa).

In recent studies, some authors (*6,7*) claim that the hexenuronic acids content in hardwoods is higher than in softwoods and that this strongly contributes to the Kappa number determination. This issue was not taken into account here because it was assumed that the effect of hexenuronic acids does not vary significantly during the first chlorine dioxide stage, and because a reliable and reproducible quantitative method for the determination of their content is not fully established.

The initial depletion factor for Kappa number, expressed as an extent of delignification, is not affected by the carry-over as long as there is chlorine dioxide in solution. However, as shown above, the observed initial chlorine dioxide consumption is strongly dependent on both lignin and carry-over. Thus, the contribution of COD to the initial depletion factor for chlorine dioxide, $[ClO_2]_\theta$, per initial chlorine dioxide concentration and Kappa number, can be represented by one single parameter in the corresponding equation proposed by Barroca et al. (*1*). The new correlation for the modified normalised depletion factor is expressed by equation 3, where COD is the chemical oxygen demand of the pulp expressed as kg/t o.d. pulp and T is the temperature, °C. Subscripts 0 = initial condition and θ = time of transition.

Since the rate of delignification in the slow stage is also not affected by the COD in the pulp (see Fig. 2) as long as there is some residual chlorine dioxide in solution, the enhanced consumption of this chemical by the dissolved organic material can be incorporated in the above kinetic model (equation 1 and 2) by means of the stoichiometry of the reaction, α. In the literature, this parameter is often referred to as the consumption of chlorine dioxide per Kappa number drop in the pulp, and in all previous studies it has been associated only with the reaction between chlorine dioxide and lignin in the fibres. However, if carry-over is present, the total consumption of chlorine dioxide is the sum of two contributions: reaction with the lignin in the fibre wall and reaction with the organic matter in the liquid phase.

In accordance with the conclusions of Germgard and Karlsson (*5*) for a CE stage, Barroca et al. (*1*) showed that for kraft pulps from *E. globulus* the stoichiometry is not constant in a D_0 prebleaching stage. They also found that in its integrated form, stoichiometry can be described by a second-degree polynomial of the Kappa number drop (equation 4). Adopting a similar strategy, the chlorine dioxide consumption of three pulps with COD values between 3.6 and 21 kg/t o.d. pulp (a range covering most industrial situations) was used here as a source of data.

[1] $$\frac{dK}{dt} = -k_0 e^{-\frac{Ea}{R(T+273)}} [ClO_2]^{1.6} [K - K_\infty]^{2.6}$$

[3] $$\frac{[ClO2]_0 - [ClO2]_\theta}{[ClO2]_0 \times K_0} = (0.661 + 0.069 \times COD) + 0.017 \times e^{0.052 \times}$$

[2] $$\frac{d[ClO_2]}{dt} = -\alpha \frac{m_{pulp}}{V} k_0 e^{-\frac{Ea}{R(T+273)}} [ClO_2]^{1.6} [K - K_\infty]^{2.6}$$

[4] $$\Delta[ClO_2] = \gamma_1 \Delta K^2 + \gamma_2 \Delta K + \gamma_3$$

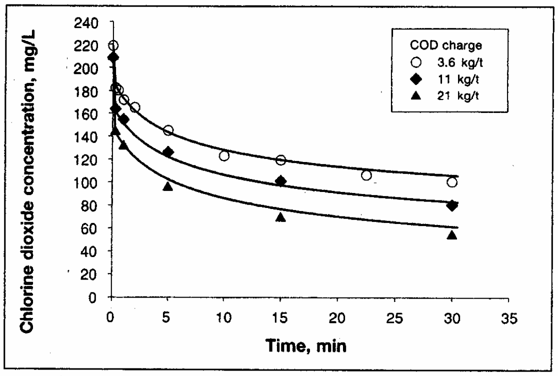

Fig. 5 Experimental and model predicted profiles of chlorine dioxide concentration.

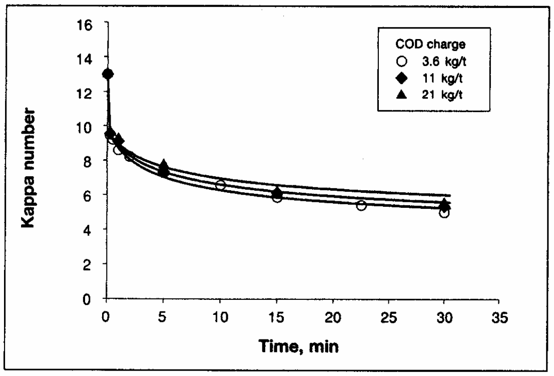

Fig. 6 Experimental and model predicted profiles of Kappa number.

This data is later employed to fit the above equation in order to identify which of the parameters is correlated with COD.

After processing the available data (see Fig. 4), i.e. after fitting the best second-degree polynomial to the three data sets, the only parameter that exhibits a strong correlation with the dissolved organic matter (COD) is the parameter γ_2. Based on this, and for values of temperature and COD often practised in industry, the parameter γ_1 assumes the value of 0.148, which is the same as that proposed by Barroca et al. (*1*) for well washed pulps. Thus, the dependence of stoichiometry on the carry-over, can be represented, in its differential form, by the following equation:

$$\alpha = 0.296 \times \Delta K + 0.866 \times e^{(0.035 \times COD)} \quad [5]$$

With the help of the above equations, pulp delignification and total chlorine dioxide consumption in the presence of carry-over can be predicted. In this situation, the consumption of chlorine dioxide during the entire D_0 bleaching stage can be expressed by the:

1) depletion factor $[ClO_2]_\theta$ (equation 3) in the initial fast phase of reaction,
2) stoichiometry factor, α, (equation 5) in the slow phase.

Figures 5 and 6 illustrate the fit of the modified kinetic model to data from experiments carried out with three pulps having CODs of 3.6, 11 and 21 kg/t o.d. pulp. These experiments were performed at a temperature of 55°C, which is very close to the value often practised in an industrial D_0 stage.

The fit of the experimental data reveals the good ability of the model to predict chlorine dioxide concentration and Kappa number profiles for three different levels of COD in the pulp. Figure 6 shows that the organic matter has a marginal effect on the global delignification rate, but leads to an extensive additional consumption of chlorine dioxide (especially during the very short reaction period). In fact, in the pulp with a COD of 3.6 kg/t o.d. pulp, the content of dissolved organic material in the fibre suspension is very low, and therefore most of the chlorine dioxide consumption is due to the reaction with lignin in the fibre wall. However, the pulp with high carry-over exhibits an extremely large consumption of chlorine dioxide, probably due to the residual black liquor still entrapped in the fibres. For the purpose of better understanding this, the total consumption of chlorine dioxide in the first 15 seconds of reaction (the initial fast phase) is plotted in Figure 7 as a function of the COD of the pulp (filled squares).

This reveals a clear linear dependence (full line) which, when extrapolated to zero (i.e. COD = 0 kg/t o.d. pulp), enables prediction of an estimate for the individual contribution of lignin with respect to the consumption of chlorine dioxide. From this linear equation, it can be seen that 3.8 kg ClO_2/t o.d. pulp is consumed by lignin in the fibres while 0.27 kg ClO_2/t o.d. pulp is consumed per kg of COD in the pulp. Assuming that the initial consumption of chlorine dioxide with lignin alone is the same for all pulps, then the amount of chlorine dioxide that reacted with the organic matter can be determined.

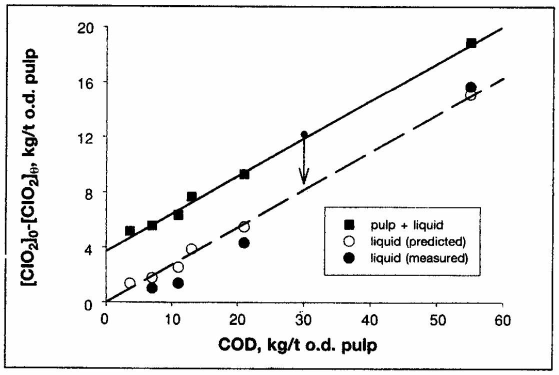

Fig. 7 Initial consumption of chlorine dioxide as a function of the COD of the pulp.

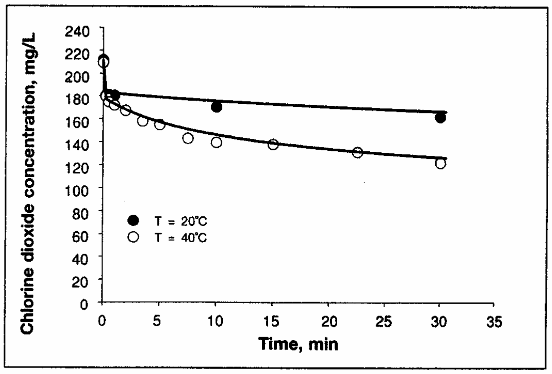

Fig. 8 Experimental and model predicted chlorine dioxide concentration profiles for a pulp with an initial Kappa number of 12.7 and COD of 7 kg/t o.d. pulp, at different temperatures.

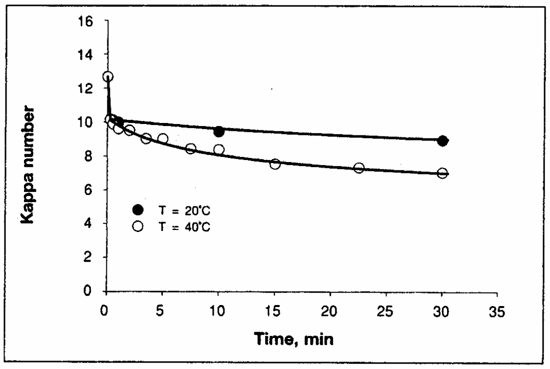

Fig. 9 Experimental and model predicted Kappa number profiles for a pulp with an initial Kappa number of 12.7 and COD of 7 kg/t o.d. pulp, at different temperatures.

This is shown in Figure 7 (dashed line) where it can be seen that while for the pulp with a COD of 3.6 kg/t the consumption of chloride dioxide by the dissolved organic matter was 21% of the total initial consumption, this relative value rises to 60% for the case of a pulp with a COD of 21 kg/t. One way to assess the reliability of this calculation is to evaluate the initial consumption of chlorine dioxide by the organic matter from an independent source of data. This can be obtained from the experiments carried out in the absence of pulp, and in particular from the initial data points ($\theta = 15$ seconds) of the curves shown in Figure 3. This is highlighted in Figure 7 by the filled circles, which confirm the quality of the predictive correlation discussed above for the initial consumption of chlorine dioxide due to the organic matter dissolved in the liquid phase in the fibre suspension.

To evaluate the model's ability to predict the process with different operating conditions, namely for other values of temperature and COD, a set of experiments was conducted using a new pulp sample with a Kappa number of 12.7 and a COD of 7 kg/t o.d. pulp, at different temperatures (20°C and 40°C).

As highlighted in Figures 8 and 9, the modified model proposed here is capable of predicting the experimental profiles of both chlorine dioxide concentration and Kappa number after D_0. Thus, the model can be used for simulation and optimisation studies concerning an industrial D_0 stage, as it incorporates the effect of most of the more important industrial process variables: unbleached pulp Kappa number, reaction temperature and COD of the pulp.

CONCLUSIONS

The influence of the degree of pulp washing, expressed as the COD of the pulp, on the kinetics of chlorine dioxide delignification was investigated. The results show that an increase in the carry-over of pulp increases the total consumption of chlorine dioxide without decreasing the global delignification rate significantly. A set of experiments, specially designed to determine the individual role of lignin and COD on the initial consumption of chlorine dioxide, enabled a better characterisation of the initial fast reaction phase. A modified mathematical model has been developed to take into account the reactions of chlorine dioxide with both lignin and carry-over. This has a strong effect on the initial depletion factor for chlorine dioxide, but shows no influence on the initial depletion factor for the Kappa number. In the slow phase of the reaction, the role of the dissolved organic material is better described by the stoichiometry. The fit of the experimental results for different temperatures and pulps with different values of COD, reveals good prediction capabilities for both Kappa number and chlorine dioxide concentration in a D_0 stage.

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APPENDIX 1

Washing of unbleached pulp samples for Kappa number determination

Kappa number measurement is carried out only after full washing of the pulp; this is achieved by a set of consecutive washing cycles in each of which a sample of pulp at 1% stock concentration is continuously stirred in warm water (30°C) for thirty minutes, with a mechanical stirring device. At the end of each cycle, the pulp is filtered and a sample taken for Kappa determination. This cyclic procedure is repeated until an asymptotic value of the Kappa number is obtained and this is considered the final value of the Kappa number of the original pulp.

APPENDIX 2

COD analysis

The amount of dissolved material was determined according to the following procedure: a sample of 21g oven dry pulp was washed at very low stock concentration (0.7%) at a temperature of 60°C and mechanically stirred for 30 minutes. The pulp suspension was later filtered and the free liquor collected for COD analysis using a photometer. The resulting amount of COD in the filtrate, in mg/l can then be expressed in kg/t o.d. pulp.