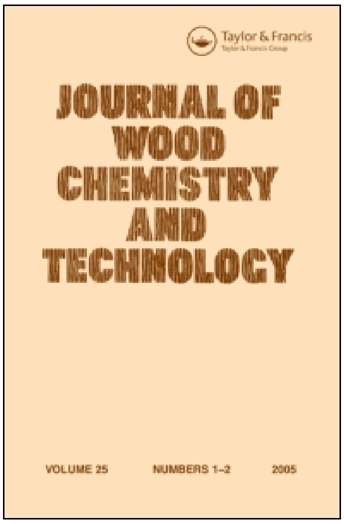

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D. G. Brown[a]; J. Abbot[a]
[a] Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia

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EFFECTS OF METAL IONS AND STABILISERS ON PEROXIDE DECOMPOSITION DURING BLEACHING

D.G. Brown and J. Abbot
Chemistry Department,
University of Tasmania,
Hobart, Tasmania, Australia,.

ABSTRACT

A mathematical model has been formulated to allow the total peroxide consumption during bleaching of a mechanical pulp to be represented by two separate components; peroxide consumed in reactions with the pulp and peroxide decomposed in metal catalysed reactions. Using this models it is possible to determine the extent of metal catalysed peroxide decomposition in the presence of pulp. This method enables the effects of transition metal ions and stabilisers during bleaching to be studied directly. The use of constant pH conditions facilitates the direct comparison of the results obtained during bleaching with those obtained for analogous systems in the absence of pulp. The presence of pulp can exert a significant influence on the behaviour of transition metal ions and stabilisers towards peroxide decomposition. It appears that both the lignin and cellulose components can be responsible for the modifications in the catalytic behaviour observed in the presence of pulp. The effects of stabilisers on the rates of metal catalysed peroxide decomposition during bleaching cannot be predicted by studies conducted in the absence of pulp.

INTRODUCTION

Hydrogen peroxide is widely used in the pulp and paper industry as a bleaching reagent, particularly for the brightening of mechanical pulps[1]. The presence of transition metal ions, particularly iron, copper and manganese, are generally considered undesirable during bleaching as they lead to a reduction in the effective charge of active bleaching agent through catalysed peroxide decomposition reactions[2,3]. Stabilising agents such as sodium silicate, magnesium salts and complexing agents such as DTPA and EDTA are commonly used to minimize these reactions[4,5,6]. The mechanism by which these additives operate has been subject to much discussion in the literature, with explanations including buffering action[7], interruption of free radical processes [8,9], and complex formation between the additive and the active metal ion[10].

Despite the large volume of work concentrating on the effects of transition metal ions and additives during peroxide decomposition in the absence of pulp, much less is known about the mechanistic effects for the corresponding systems in the presence of pulp. The inclusion of pulp produces a much more complex system, and it is conceivable that the mechanism by which the additives operate, as well as the response to stabilisation, could be significantly modified or indeed entirely different. It is therefore desirable to develop a greater understanding of the peroxide decomposition reactions which occur during bleaching, and the response in the presence of various stabilizers.

This study involves the computer modelling of peroxide consumption during bleaching reactions enabling the total consumption to be separated into two components; peroxide consumed by reactions with the pulp and peroxide consumed by metal catalysed decomposition reactions. The rate of peroxide decomposition in the presence of pulp can then be compared directly with that of the analogous reaction in the absence of pulp. These comparisons are facilitated by the use of constant pH conditions (pH 11.0) in both cases.

THEORY

Mathematical Models for Peroxide Consumption during Bleaching

Total peroxide consumption during pulp bleaching can be represented by the sum of two components:

$$\frac{-d[H_2O_2]}{dt} = \frac{-d[H_2O_2]p}{dt} \quad \frac{-d[H_2O_2]m}{dt} \qquad [1]$$

where $[H_2O_2]_p$ is the peroxide consumed by the pulp and $[H_2O_2]_m$ represents peroxide decomposed in side reactions due to the presence of metal ions. Numerous studies have shown that, in the presence of pulp[3] and in the absence of pulp[11,12,13], catalytic decomposition of peroxide can be represented by a first-order kinetic expression of the type:

$$\frac{-d[H_2O_2]m}{dt} = k_m[H_2O_2] \qquad [2]$$

This relationship can be used in equation 1 to represent a set of parallel first-order decomposition processes with overall rate constant k_m. Various approaches can be taken to formulate an expression to represent peroxide consumption due to bleaching processes:

MODEL A

A study of peroxide consumption during the bleaching of a groundwood pulp has been reported by Martin[3]. The rate of peroxide decomposition, measured by oxygen evolution, was found to be first-order[3]. Total peroxide consumption followed by titrimetric procedure was also shown to be first-order, implying that peroxide consumption through bleaching reactions also follows first-order kinetics:

$$\frac{-d[H_2O_2]p}{dt} = k_p[H_2O_2] \qquad [3]$$

MODEL B

An empirical kinetic expression of the form

$$\frac{-d[Chr]}{dt} = k[H_2O_2]^a[OH^-]^b[Chr]^c \qquad [8]$$

has been used by several workers to describe peroxide bleaching kinetics[14,15,16]. In all cases reported, the exponent c requires a high numerical value (usually in the range 4-5) to provide an adequate fit with experimental data. Assuming conditions of constant pH ($[OH^-]$ constant) a relationship describing peroxide consumption could be postulated according to the expression:

$$\frac{-d[H_2O_2]_p}{dt} = k_p[H_2O_2]^n \qquad [9]$$

where a high order in peroxide (n) would also be expected. It should be noted that model A is a special case of model B, with n=1.

EXPERIMENTAL

Pinus radiata thermo-mechanical pulp was provided by Australian Newsprint Mills, Boyer Mill. The pulp was stored at 8% consistency and 4°C until used. Hydrogen peroxide (30%) was obtained from Ajax Chemicals. Magnesium nitrate (99.999%), iron(III) nitrate (99.99+%), copper nitrate (99.999%), manganese nitrate (99.99%), vanillin, DTPA (97%), sodium silicate (30% SiO_2) and sodium hydroxide of semiconductor purity (99.99%) were supplied by Aldrich Chemicals. Chelated pulp was prepared by addition of DTPA (0.5% on pulp) to the TMP (2% consistency) at 20°C followed by stirring for ~30 minutes. The resulting pulp was filtered and washed thoroughly with Milli-Q deionised water. Bleached *Pinus radiata* kraft pulp was obtained from Tasman Pulp and Paper, New Zealand. The pulp was slurried and prebleached with hydrogen peroxide (initial conditions : 7.5% peroxide on pulp, pH 11, 50°C, 4% consistency) followed by filtration and thorough washing with Milli-Q deionised water prior to use.

Bleaching experiments with both TMP and kraft pulps were carried out at 50°C and pH 11 in polyethylene reaction vessels using a pulp consistency of 4% and an initial peroxide charge of 3%. Metal ions and additives were added 5 minutes prior to the peroxide where appropriate. The pH was maintained at a constant level by addition of NaOH or sulphuric acid as required. In order to maintain a constant level of peroxide during constant conditions bleaching, a number of preliminary bleaching reactions were conducted to determine the initial rate of peroxide consumption. The desired amount of peroxide was then added to the bleaching mixture at regular time intervals (2.5-5 minutes) to maintain the initial peroxide charge over the course of the reaction. Pulp suspensions were stirred during the course of the bleaching reactions. Pulp samples were withdrawn at regular intervals and filtered, with the residual peroxide levels determined from the filtrate by iodometric titration with standard sodium thiosulfate, after acidification and addition of potassium iodide and a few drops of saturated ammonium molybdate solution[17]. Metal ion concentrations in the filtrates were measured using atomic absorption following a secondary filtration procedure using a 0.45 μm syringe filter system.

Peroxide decomposition experiments were carried out at 50°C and a constant pH of 11 in polyethylene bottles. The desired transition metal ions and additives were added 5 minutes prior to the peroxide. The initial peroxide concentration used (0.035M) corresponds to the initial charge used in the bleaching experiments. Solutions were stirred during the course of the reactions. Determinations of peroxide levels were carried out using the iodometric procedure described above. Metal ion analysis of the filtered, 0.45 μm, liquor was carried out by atomic absorption.

Transition metal ion contents of the TMP, chelated TMP, and kraft pulps were determined by atomic absorption after acid digestion and the measured levels of copper, iron, manganese and magnesium are shown in Table 1.

RESULTS AND DISCUSSION

Application of the proposed model for peroxide consumption assumes that the rates of peroxide consumption through the bleaching process and through catalytic decomposition induced by metal ions can be regarded as independent and additive. In order to examine the influence of metal ions on peroxide decomposition in the presence of pulp it is necessary to establish a baseline experimental condition where the effects of metal ions in the system are minimised. In this study this was taken as a bleaching system containing sodium silicate with a chelated pulp. Under these conditions maximum stabilisation of the

Table 1 : Transition metal ion content of pulps determined by atomic absorption following acid digestion..

Pulp Type	Mn (ppm)	Fe (ppm)	Cu (ppm)	Mg (ppm)
TMP	40-60	12-17	3-6	250-400
Chelated TMP	3-6	10-13	1-3	130-150
kraft	8	14	4	150

peroxide was obtained. Experiments under constant conditions of pH and peroxide concentration (Fig. 1a) show that introduction of silicate, or removal of metal ions from the pulp by chelation and washing has a negligible effect on brightness gain. This implies that the dominant influences of added silicate or transition metals is on peroxide decomposition, rather than through other processes directly involving chromophore removal or formation. This is also illustrated in Fig. 1b which shows that addition of copper, iron or manganese to a chelated pulp has little influence on brightness response with constant reagent concentrations. These results suggest that under alkaline conditions, bleaching pathways which might strongly depend on the concentration of peroxide decomposition products (eg radical species) do not exert a major influence on the rate of chromophore removal or formation [18].

Fig. 2 shows results for model fitting corresponding to peroxide consumption during bleaching of chelated TMP in the presence of sodium silicate. Only model B provides an adequate representation of the experimental behaviour, and consequently model A was not used in further fitting procedures. Using the calculated values of the parameters k_p and n for model B corresponding to maximum stabilisation, it is then possible to calculate values of the rate constant k_m to account for excess peroxide decomposition in subsequent bleaching experiments.

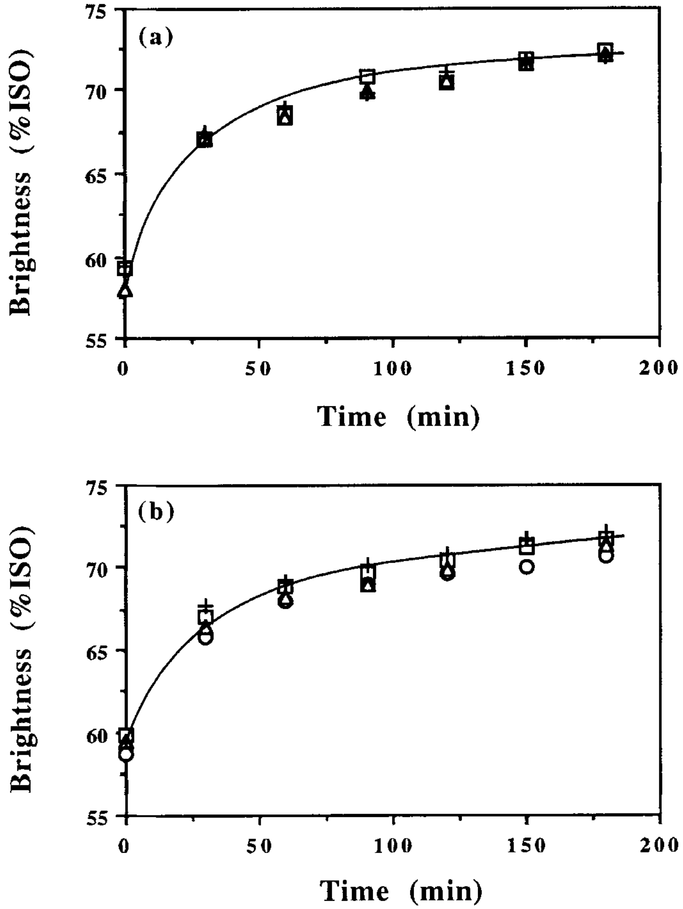

FIGURE 1. Bleaching of *P. radiata* TMP under constant reagent conditions : pH 11, 50°C, 4% consistency, 3% peroxide. (a) Effects of chelation or addition of 1.73x10^{-2} moles silicate (□ TMP ; Δ, TMP + silicate ; + chelated TMP), (b) Effects of added metal ions (4.46x10^{-6} moles Fe, 3.18x10^{-5} moles Cu, 1.83x10^{-5} moles Mn). (□ , no metals added ; O , Fe ; Δ , Cu ; + , Mn)

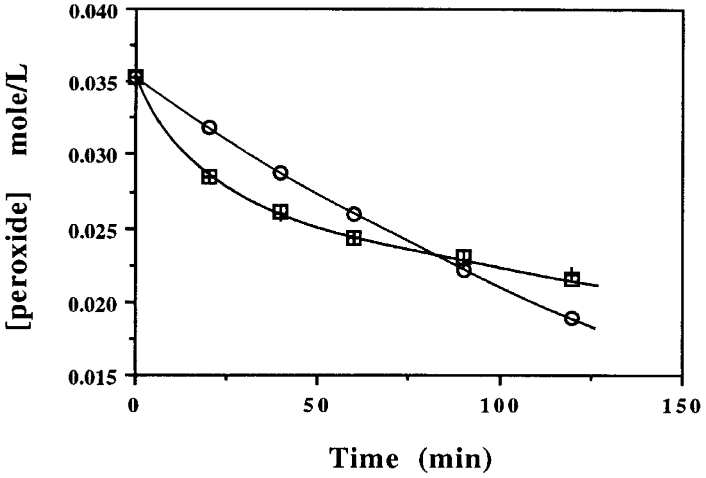

FIGURE 2. Computer model fittings for peroxide consumption during bleaching of chelated TMP in the presence of 1.73 x 10^{-2} moles sodium silicate. (□ , experimental ; O , model A ; X , model B)

Transition metal ions from the alkali or the water itself, as well as residual metals remaining in the pulp after chelation (Table 1) can induce catalytic decomposition of peroxide. The calculated rate constants for these processes are small in comparison to the effects of added transition metal ions at the levels used in the present studies. Fig. 3 shows that with added magnesium or silicate the contributions from these processes become almost negligible.

EFFECTS OF MANGANESE, COPPER AND IRON

Addition of manganese, copper or iron to the chelated TMP increases the rate of peroxide consumption as illustrated in Fig. 4. Using a computer fitting procedure, values of k_m can be calculated corresponding to each level of metal ion addition. Fig. 5a shows that, on a molar basis, iron is the most active towards peroxide decomposition in the presence of pulp, copper is the least, and manganese shows intermediate activity. This trend can be compared with the catalytic activities of these transition metals in the absence of the pulp. Fig. 5b shows that in the absence of pulp, manganese is most active, followed by copper,

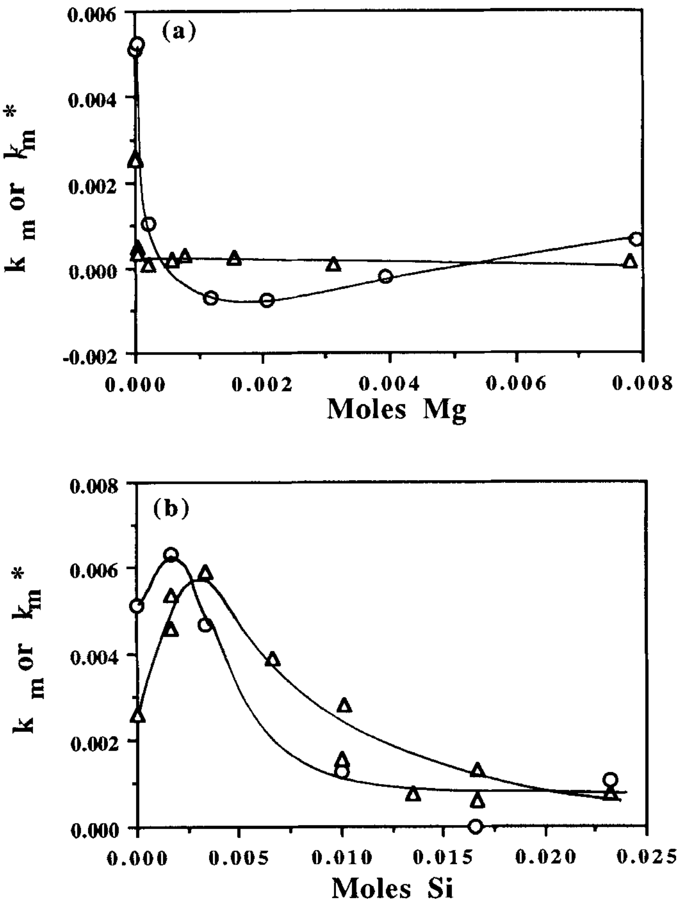

FIGURE 3. Effects of (a) magnesium or (b) sodium silicate addition on rates of metal catalysed peroxide decomposition in the presence and absence of chelated TMP. (O , model B ; Δ , absence of pulp)

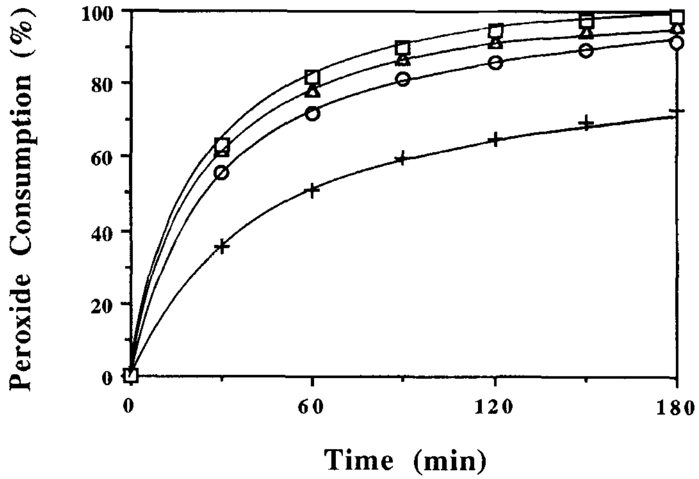

FIGURE 4. Effects of addition of transition metal ions on peroxide consumption during bleaching chelated TMP. (4.46 x 10^{-6} moles Fe, 3.18 x 10^{-5} moles Cu, 1.83 x 10^{-5} moles Mn). (+ , no metals added ; O , Fe ; Δ , Cu ; □ , Mn)

with iron showing much less activity. In each case, both in the presence and absence of pulp, the rate constant for peroxide decomposition is approximately proportional to the concentration of added metal.

Fig. 6 shows comparisons between rate constants for peroxide decomposition in the presence and absence of pulp for each metal additive. For manganese and copper it is apparent that the calculated rate constants are similar in the presence or absence of pulp. However, in the case of iron the presence of the pulp enhances the catalytic activity (Fig. 6), implying that the interaction between iron and pulp components has a much greater influence on the catalytic activity than in the case of either manganese or copper. It is well known that there is a significant affinity for iron to bind with cellulose[19,20]. However, as shown in Fig. 7a, the presence of bleached kraft pulp does not have a marked influence on peroxide decomposition in the presence of iron. Previous studies have shown that aged iron is relatively inactive toward peroxide decomposition in the presence of pulp[8]. Fig. 7b shows that the addition of aged iron to chelated pulp has little effect on

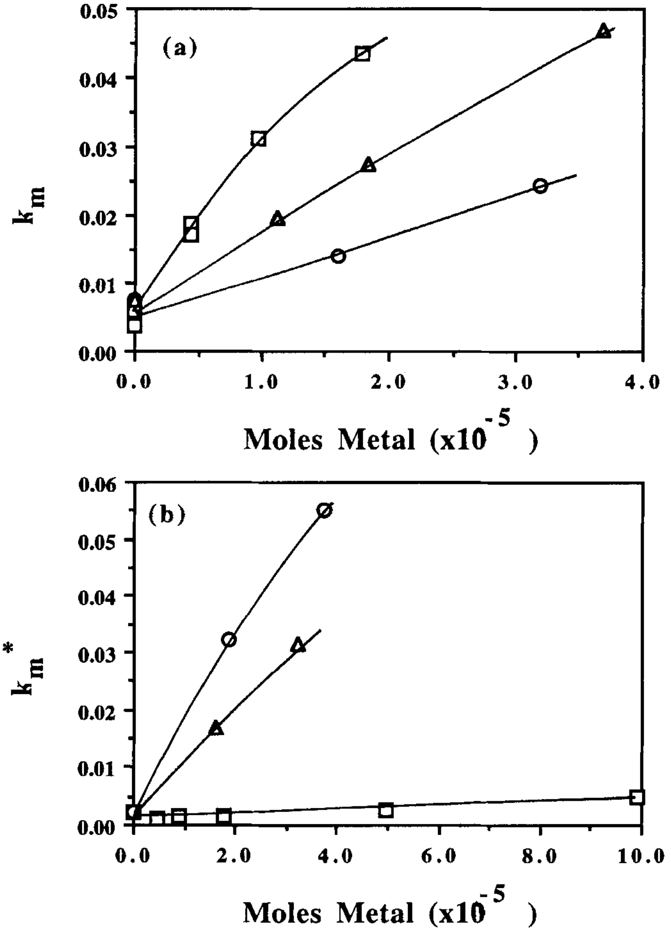

FIGURE 5. (a) Calculated rate constants (k_m) for metal catalysed peroxide decomposition during bleaching of chelated TMP. (∏ , Fe ; Δ, Cu ; O , Mn) with model B. (b) Measured rate constants (k_m*)for metal catalysed peroxide decomposition in the absence of pulp. (G , Fe ; Δ , Cu ; O , Mn).

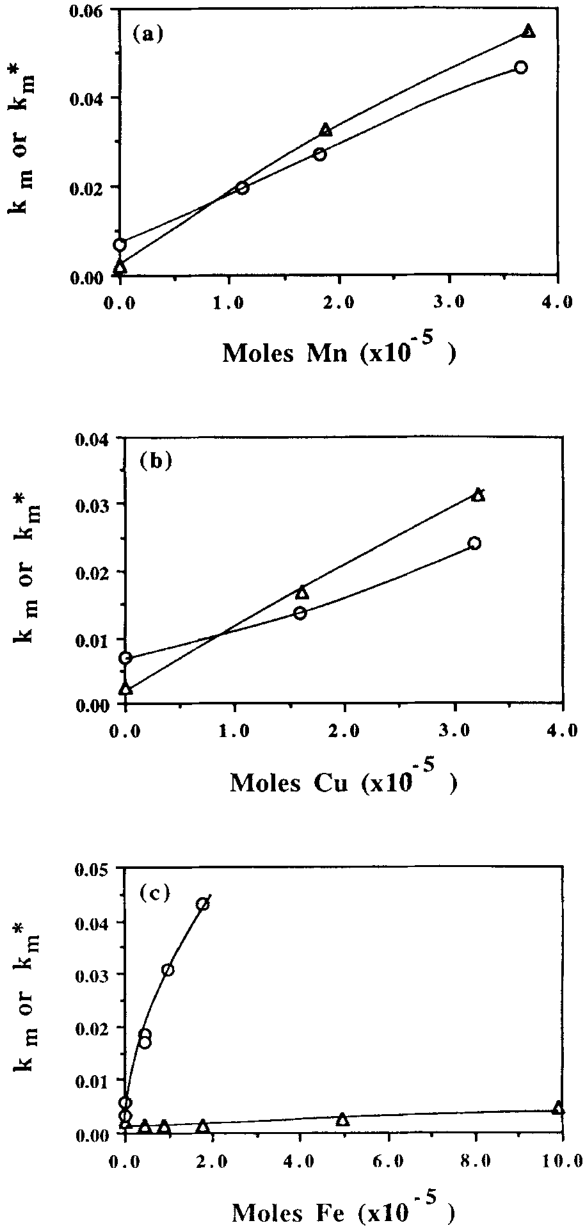

FIGURE 6. Comparison of rates of metal catalysed peroxide decomposition in the presence and absence of pulp; (a) Mn, (b) Cu, (c) Fe. (O , model B ; Δ , absence of pulp)

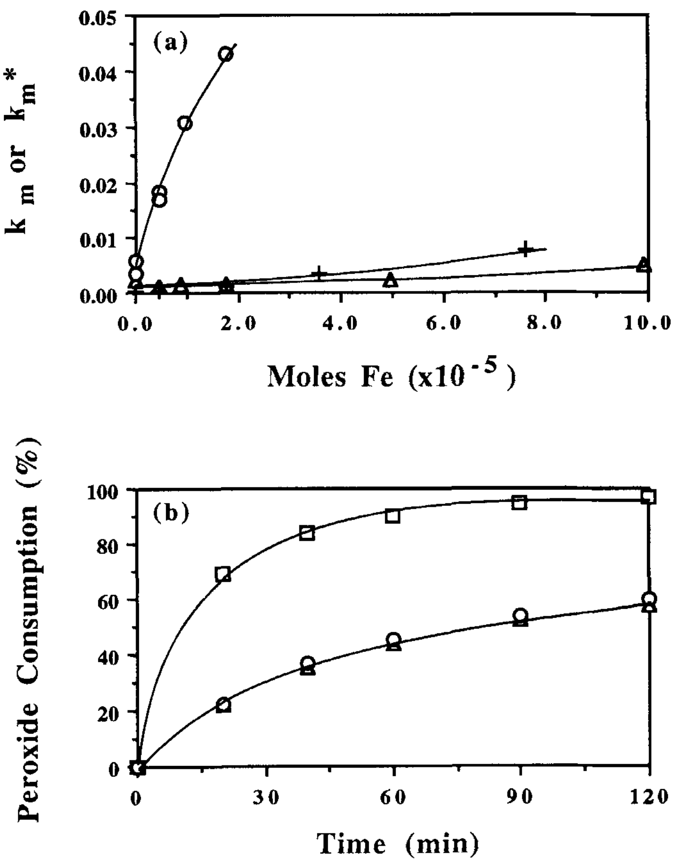

FIGURE 7. (a) Comparison of rates of iron catalysed peroxide decomposition in the presence of chelated TMP (O , model B ;), bleached kraft pulp (+), and in the absence of pulp (Δ). (b) Effects of addition of aged and fresh iron on peroxide consumption during bleaching of chelated TMP (1.79 x 10^{-5} moles Fe). (Δ , no added Fe ; □ , fresh Fe ; O , aged Fe).

peroxide consumption compared to the addition of fresh iron. It can be concluded then that an interaction between the fresh iron and the lignin component of the pulp is responsible for the enhanced catalytic activity observed.

THE INFLUENCE OF SILICATE AND MAGNESIUM

Magnesium

Fig. 8a shows the influence of magnesium addition on k_m during the bleaching of unchelated TMP. It is apparent that there is an optimum level of magnesium addition, corresponding to the minimum value of k_m. Fig. 8b shows a similar trend in k_m with magnesium addition to a chelated pulp with manganese added. Comparison with Fig. 8a shows that the minimum in k_m corresponds closely to that observed for the unchelated pulp, and occurs at a similar level of magnesium addition. This observation can be explained by the fact that manganese is the dominant transition metal ion in the pulp responsible for excess peroxide decomposition. Figs. 8c and 8d show the dependence of k_m on magnesium addition for the bleaching of chelated TMP in the presence of added copper or iron. The rate of excess peroxide decomposition is reduced to a low level at concentrations of magnesium corresponding to the minima observed in Figs. 8a and 8b.

Fig. 8 also shows that for magnesium addition in the presence of copper or iron, values of rate constants k_m^* for peroxide decomposition in the absence of pulp are similar to values of k_m found with chelated pulp present. Addition of magnesium to solutions containing copper or iron retards peroxide decomposition in the absence of pulp[10,12]. In contrast, for addition of magnesium to solutions containing manganese in the absence of pulp peroxide decomposition is accelerated (Fig. 8b). The promoting effects of magnesium on manganese catalysed peroxide decomposition are well known[8,9,11]. The decrease in rate constant as the magnesium level is increased above ~ 2×10^{-3} moles can be attributed to an effective decrease in the surface concentration of manganese due to coprecipitation of $Mn(OH)_2$ with $Mg(OH)_2$[21]. In the case of manganese, the isolated system does not provide a reasonable model for the stabilising action of magnesium during pulp bleaching.

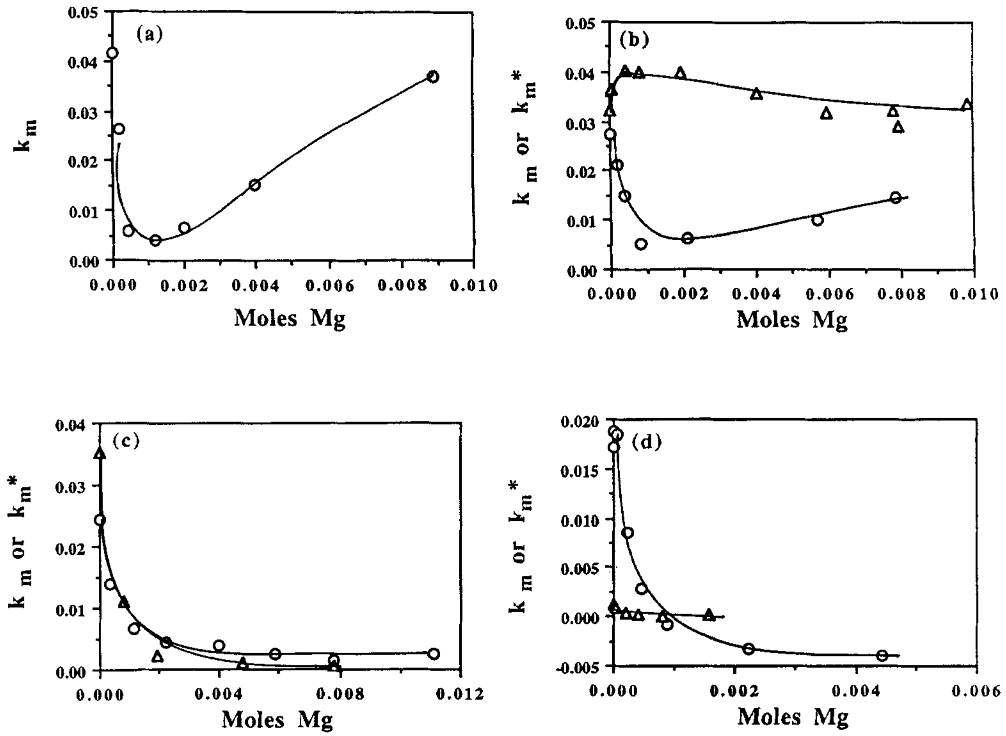

FIGURE 8. Influence of magnesium on the calculated rates of metal catalysed peroxide decomposition during the bleaching of (a) unchelated TMP; chelated TMP with added transition metals ; (b) 1.83×10^{-5} moles Mn, (c) 3.18×10^{-5} moles Cu, and (d) 4.45×10^{-6} moles Fe. (O, model B ; Δ , absence of pulp)

Previous studies have shown that under neutral pH conditions dissolved manganese salts interact much more strongly with lignin components of TMP than with carbohydrate components[22]. Fig. 9a shows that addition of a bleached kraft pulp to the Mn/Mg system enhances peroxide decomposition. It would appear unlikely therefore that the stabilising effect of magnesium during peroxide bleaching of TMP in the presence of manganese is attributable to an interaction involving a carbohydrate component. In contrast, it has been shown that there is a strong interaction between manganese ions and the TMP[22], suggesting that the presence of lignin may explain the stabilising effect of magnesium in the presence of manganese.

A study of the solubility of manganese was subsequently undertaken to gain a further insight into the behaviour of these systems. Although in the absence of peroxide manganese has been found to be insoluble under alkaline conditions[8,9], peroxide addition has been reported to lead to the solubilisation of various manganese species, including solid manganese dioxide and freshly precipitated manganese hydroxide[21,23]. Fig. 10a shows that manganese is predominantly soluble during decomposition experiments in the absence of magnesium, provided that not all of the peroxide is consumed. In contrast, Fig. 10a also shows that in the presence of magnesium, manganese exists solely in an insoluble form. Fig. 10b shows that magnesium is also insoluble under these conditions. This result is consistent with the findings of Razouk and co-workers who reported that a coprecipitate forms between manganese and magnesium under alkaline conditions[21]. Fig. 11a shows the solubility of naturally occuring manganese during the bleaching of unchelated TMP, both with and without added magnesium. As observed in the absence of pulp, the solubility of manganese was found to be dependent on the presence of peroxide, when no magnesium was added. This is clearly demonstrated in Fig. 11a, where an additional charge of peroxide added to the bleach after 155 minutes increased the solubility of Mn. However, in contrast to the system in the absence of pulp, the level of soluble manganese observed in the presence of magnesium during bleaching was quite significant, (Fig. 11a). Similarly, the level of magnesium in a soluble form is also significant during bleaching, (Fig. 11b). Clearly the presence of TMP can result in considerable differences in the nature of the catalytic species present, reflected by the changes in the solubility of the metal ions present.

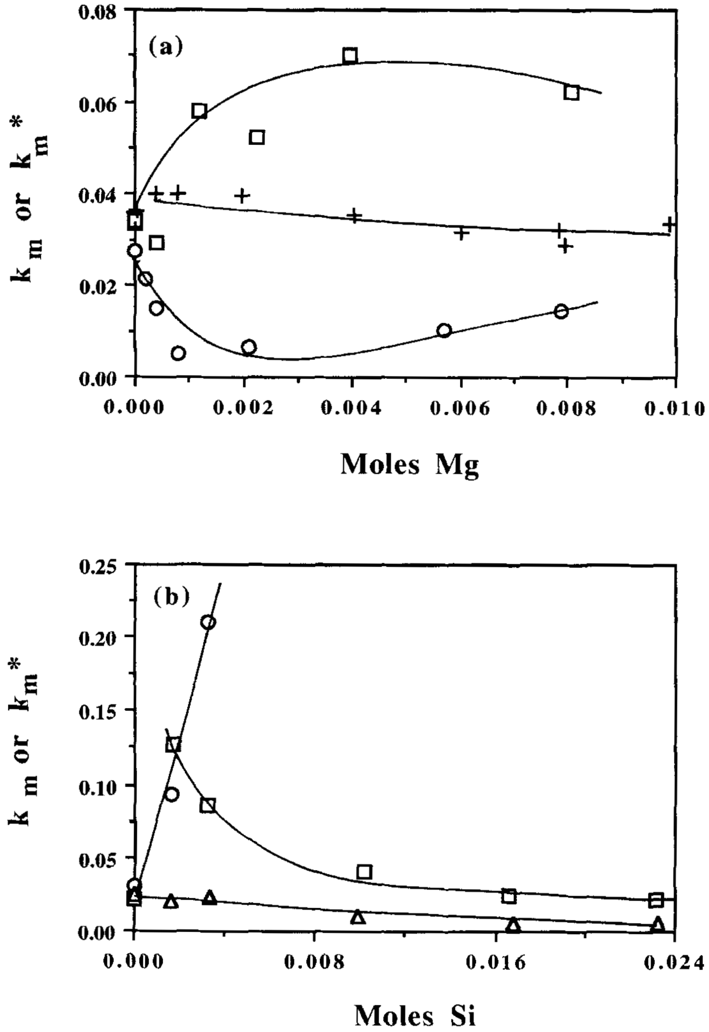

FIGURE 9. Effects of bleached kraft pulp on the rate of metal catalysed peroxide decomposition in the presence of: (a) added manganese (1.86×10^{-5} moles Mn) and magnesium: O, model B; ☐ , kraft pulp ; + , no pulp)

(b) added copper and sodium silicate (3.18×10^{-5} moles Cu). O , model B ; ☐ , kraft pulp ; Δ , no pulp.

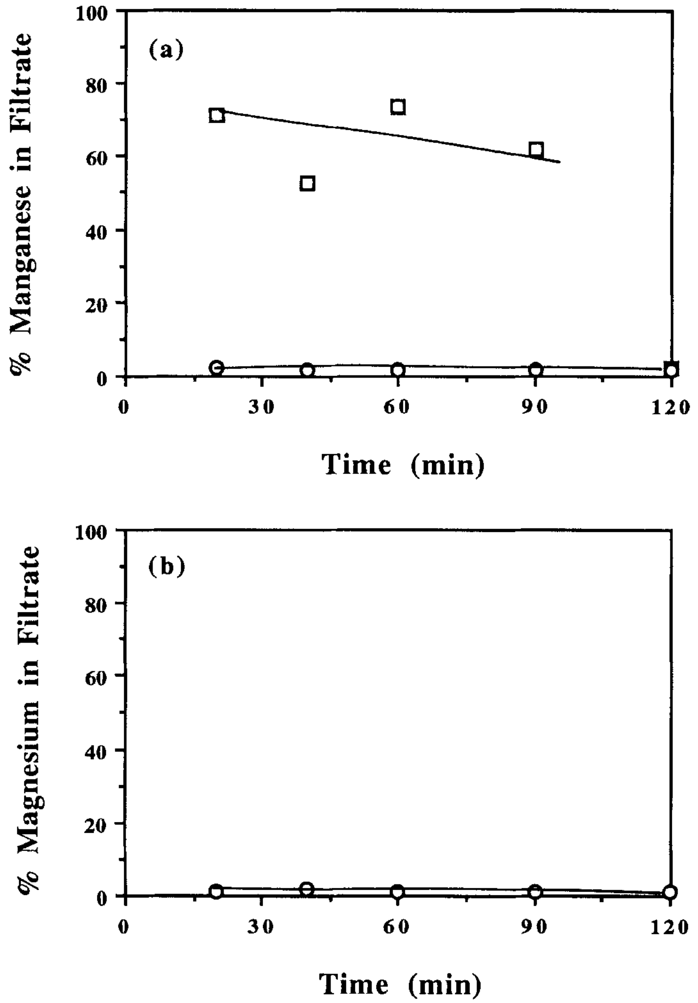

FIGURE 10. Solubility of (a) manganese and (b) magnesium during peroxide decomposition experiments in the absence of pulp (1.86 x 10^{-5} moles Mn, 1.95 x 10^{-3} moles Mg). □, Mn alone ; O , Mn + Mg.

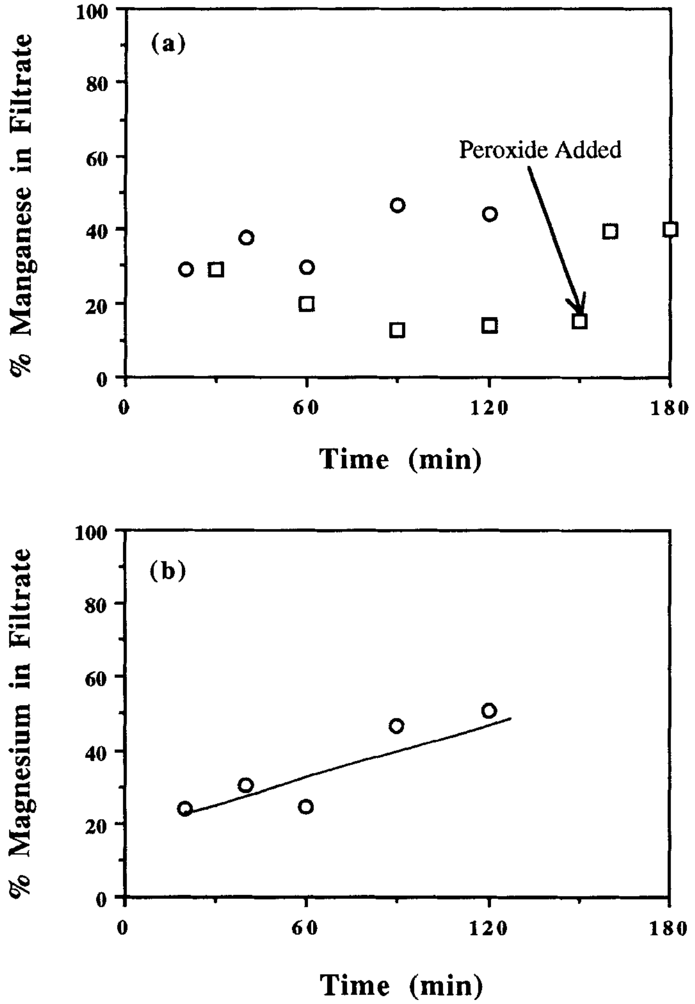

FIGURE 11. Solubility of (a) manganese and (b) magnesium during bleaching of unchelated TMP (1.95 x 10^{-3} moles Mg). □ , TMP ; O , TMP + Mg. moles.

Influence of vanillin on the manganese/magnesium combination

Further studies were undertaken to examine the influence of the lignin model compound vanillin on peroxide decomposition in the manganese-magnesium system. Solutions with the desired levels of manganese and vanillin were prepared and allowed to age overnight. Magnesium nitrate, sodium hydroxide, and hydrogen peroxide were then added sequentially and peroxide consumption was measured with time. The addition of vanillin to the system containing manganese had no apparent effect on the rate of peroxide consumption as shown in Fig. 12a. However, with the introduction of magnesium a significant increase in peroxide stabilisation was found in the presence of vanillin. Fig. 12b shows the peroxide consumption for solutions containing manganese and magnesium for various levels of vanillin addition. Low levels of vanillin addition appear to significantly decrease peroxide consumption while higher levels have an accelerating effect. The optimum level of vanillin for producing stabilisation was found to be $\sim 3.3\mathrm{x}10^{-4}$ moles. Excess vanillin appears to be decomposed by the peroxide resulting in increased consumption. Fig. 12c shows the effects of magnesium dose on peroxide consumption for a system containing manganese and the optimum level of vanillin. Using this vanillin concentration the optimum level of magnesium addition was found to be $\sim 2\mathrm{x}10^{-3}$ moles, as shown in Fig. 13. This figure also shows that in the presence of chelated TMP with added manganese, the optimum addition of magnesium corresponds to $\sim 1.2\mathrm{x}10^{-3}$ moles Mg. Although these magnesium levels are not identical, the similar order of magnitude observed is an indication that the model system using vanillin in combination with magnesium probably has the same mechanistic characteristics as found during the bleaching of pulp.

The stabilising effects observed on the inclusion of vanillin can be attributed to an interaction involving the vanillin, or decomposition products from the vanillin, and the manganese and magnesium ions. The initial rate of peroxide consumption appears to be dependent on the amount of vanillin added, Fig. 12b, with high levels of vanillin addition giving rapid rates of consumption. This is consistent with the decomposition of vanillin by peroxide. Following the initial rapid reaction, the rate of consumption is significantly reduced and appears to be essentially independent of the level of vanillin initially added. The stabilisation

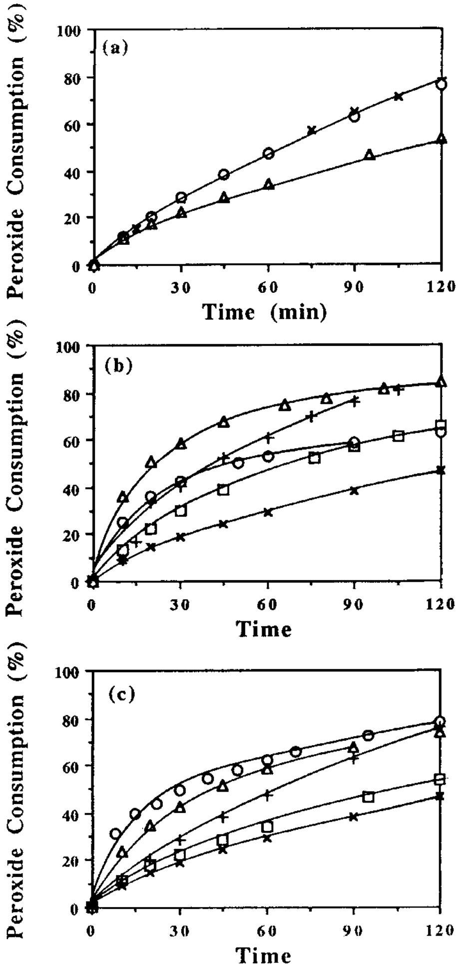

FIGURE 12.(a) Effect of vanillin and magnesium on peroxide decomposition in the presence of manganese. ($1.1\text{x}10^{-5}$ moles Mn, $3.3\text{x}10^{-4}$ moles vanillin, $3.9\text{x}10^{-3}$ moles Mg). X , Mn alone ; O , Mn+vanillin ; Δ Mn+vanillin+Mg. (b) Effects of vanillin addition on manganese catalysed peroxide decomposition in the presence of magnesium ($1.1\text{x}10^{-5}$ moles Mn, $2.0\text{x}10^{-3}$ moles Mg). Vanillin added :

+ , 0.0 moles ; □ , $6.6\text{x}10^{-5}$ moles ; X , $3.3\text{x}10^{-4}$ moles ; O , $1.6\text{x}10^{-3}$ moles ; Δ , $3.3\text{x}10^{-3}$ moles. (c) Effects of addition of magnesium on peroxide decomposition in the presence of manganese and vanillin. ($1.1\text{x}10^{-5}$ moles Mn, $3.3\text{x}10^{-4}$ moles vanillin). Magnesium added : + , 0.0 moles ; O , $3.9\text{x}10^{-4}$ moles ; □ , $2.0\text{x}10^{-3}$ moles ; X , $3.9\text{x}10^{-3}$ moles ; Δ , $2.0\text{x}10^{-2}$ moles.

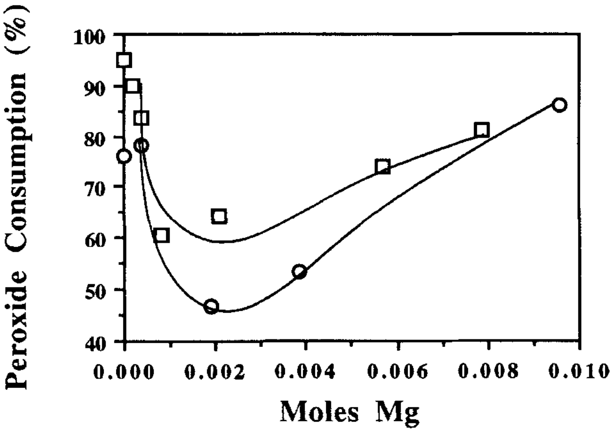

FIGURE 13. Effects of magnesium addition on the level of peroxide consumed after 120 minutes in the presence of added manganese ($1.1\text{x}10^{-5}$ moles Mn) □, chelated TMP, and O , vanillin ($3.3 \text{ x } 10^{-4}$ moles).

observed in the presence of vanillin is therefore likely to be due to interactions between manganese, magnesium and a decomposition product of vanillin. Two major decomposition reaction types are generally believed to occur[24,25]. With highly stabilised peroxide solutions a Dakin type reaction yielding methoxyhydroquinone reportedly occurs, with the perhydroxyl anion being the active species. The second general reaction is the oxidative degradation of the aromatic structure leading to the formation of a dicarboxylic acid by either perhydroxyl anions or radical species formed upon the catalysed decomposition of hydrogen peroxide.

Silicate

Fig. 14a shows the effects of silicate addition on the bleaching of TMP. Increasing the silicate addition results in a decrease in the rate constant k_m, with the optimum level of silicate found to be ~0.015 moles, which corresponds to ~5% silicate (as SiO_2) on pulp. Fig. 14b shows the influence of silicate addition on peroxide decomposition for a chelated pulp with manganese added. The

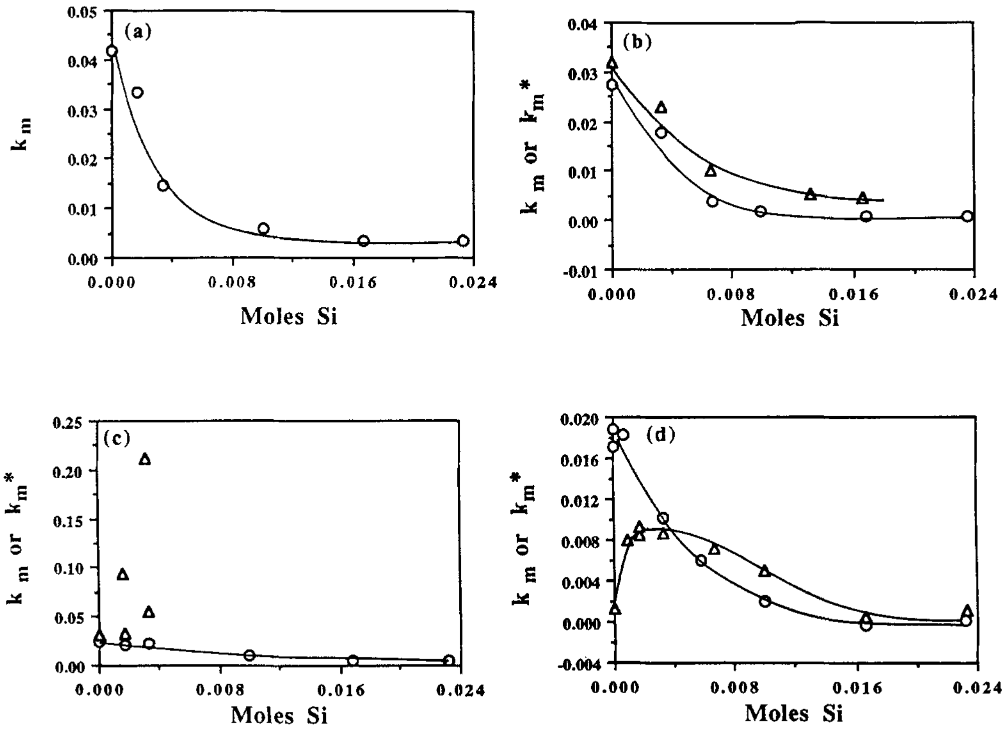

FIGURE 14. Influence of sodium silicate on the calculated rates of metal catalysed peroxide decomposition during the bleaching of (a) unchelated TMP, and chelated TMP with added transition metals ; (b) 1.83 x 10^{-5} moles Mn, (c) 3.18 x 10^{-5} moles Cu, and (d) 4.45 x 10^{-6} moles Fe. (O, model B ; Δ , absence of pulp)

calculated values of rate constants (k_m) for peroxide decomposition using model B correspond well to the experimental values of rate constants (k_m^*) in the absence of pulp. Reasonable correlations between observed and calculated rate constants for peroxide decomposition are also found for the iron-silicate system, as illustrated in Fig. 14c. However, inspection of Fig. 14d reveals that the effects of silicate on copper catalysed decomposition are greatly affected by the presence of pulp. While the calculated rate constants for copper in the presence of various silicate doses are similar to those of iron and manganese during bleaching, the addition of silicate to peroxide solutions containing copper in the absence of pulp results in greatly accelerated rates of decomposition. Indeed, the rate of decomposition observed at high silicate levels is such that no peroxide remains after ~5 minutes of reaction. Clearly the behaviour of the copper/silicate system in the absence of pulp does not reflect the behaviour of the analogous system during bleaching. An investigation of the effects of silicate on copper catalysed decomposition in the presence of bleached kraft pulp was subsequently carried out, as copper is reported to interact with cellulose fibres [25]. Fig. 9b shows that the peroxide decomposition behaviour observed in the presence of kraft pulp closely resembles that observed in the presence of TMP, particularly at the higher levels of silicate addition. However, at lower levels of silicate addition the behaviour in the presence of kraft pulp is intermediate between that observed in the presence of TMP and in the absence of pulp. It appears that while the presence of cellulose fibres can account to a large extent for the behaviour of the copper/silicate system in the presence of TMP, other components of the pulp may also exert a significant influence.

CONCLUSIONS

The rates of transition metal catalysed peroxide decomposition during the bleaching of *P. radiata* TMP, together with the effects of the additives magnesium nitrate and sodium silicate, have been evaluated with the aid of mathematical models. The use of constant pH conditions allows direct comparisons of the calculated rates with those measured for the analogous systems in the absence of pulp. The results demonstrate that the behaviour of peroxide decomposition catalysts and stabilizers during bleaching cannot be predicted by their behaviour exhibited in the absence of pulp. The major findings of this study can be summarised as follows;

1) Manganese is the primary peroxide decomposition catalyst present in the *P. radiata* TMP used in this study.

2) The catalytic activities of manganese and copper are similar in the presence and absence of pulp, whereas the presence of pulp greatly enhances the catalytic activity of fresh iron.

3) The order of catalytic activity for transition metal ions in the presence of pulp was found to be Fe > Mn > Cu, while the order in the absence of pulp was Mn > Cu > Fe.

4) Addition of magnesium to systems containing copper or iron resulted in stabilization both in the presence and absence of pulp.

5) Addition of magnesium to manganese in the presence of pulp results in stabilization, whereas in the absence of pulp the rate of decomposition is increased.

6) The addition of the lignin model compound vanillin to the system containing manganese and magnesium in the absence of pulp simulates the behaviour observed during bleaching.

7) Addition of sodium silicate to systems containing manganese or iron produced stabilization in the presence and absence of pulp.

8) The copper catalysed decomposition of peroxide is retarded by sodium silicate during bleaching, but is accelerated in the absence of pulp.

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