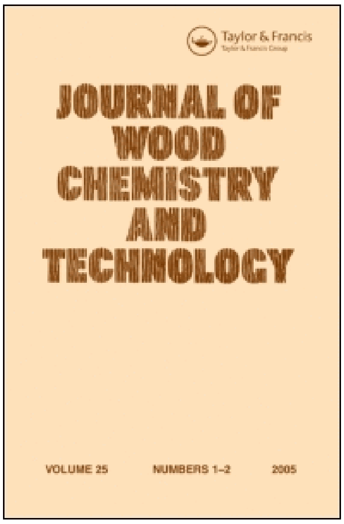

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

The Role of Transition Metal Species in Delignification with Distilled Peracetic Acid

X. -Z. Zhang[a]; R. C. Francis[b]; D. B. Dutton[c]; R. T. Hill[c]
[a] Empire State Paper Research Institute State University of New York, [b] College of Environmental Science and Forestry Syracuse, New York [c] Solvay Interox, Deer Park, Texas

To cite this Article Zhang, X. -Z. , Francis, R. C. , Dutton, D. B. and Hill, R. T.(1998) 'The Role of Transition Metal Species in Delignification with Distilled Peracetic Acid', Journal of Wood Chemistry and Technology, 18: 3, 253 — 266
To link to this Article: DOI: 10.1080/02773819809349580
URL: http://dx.doi.org/10.1080/02773819809349580

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 18(3), 253–266 (1998)

THE ROLE OF TRANSITION METAL SPECIES IN DELIGNIFICATION WITH DISTILLED PERACETIC ACID

X.-Z. Zhang and R.C. Francis
Empire State Paper Research Institute
State University of New York
College of Environmental Science and Forestry
Syracuse, New York 13210

D.B. Dutton and R.T. Hill
Solvay Interox
Deer Park, Texas 77536

ABSTRACT

An acid-washed, oxygen-delignified, softwood kraft pulp was delignified with peracetic acid (Pa) at initial pH 2.5, 4.8 and 7.0. The inclusion of 5 ppm on pulp of Mn^{2+}, Fe^{3+}, Cu^{2+}, V^{5+}, or Co^{2+} caused wasteful decomposition of Pa while Ni^{2+} had no effect. None of the cations caused a significant decrease in kappa number while Co^{2+} at all pHs and Fe^{3+} at pH 2.5 resulted in lower viscosities.

In pulp-free solutions, Co^{2+} and V^{5+} catalyzed Pa decomposition much more aggressively than the other cations. The kinetic data supported a previous free-radical mechanism for Co^{2+} and a similar type mechanism appears to be partially responsible for Pa decomposition by vanadium (V).

INTRODUCTION

The pulp and paper industry is under great pressure to bleach kraft pulps without chlorine-containing chemicals. The peracids, peroxymonosulfuric acid (H_2SO_5) and peracetic acid (CH_3CO_3H), are being investigated as replacement oxidants. European mills are now using the peracids during TCF (totally chlorine-free) production runs.[1,2]

www.dekker.com

In an earlier paper we reported on transition metal- and alkali-induced decomposition of peroxymonosulfate anion (HSO_5^-), the conjugate base of H_2SO_5.[3] Peroxymonosulfuric acid has a pKa <0 and is not present at a significant concentration under typical bleaching conditions.[3] We are now reporting on peracetic acid (Pa) decomposition catalyzed by the six transition metals used previously (Mn, Fe, Cu, Ni, V, Co). The same metals were chosen because, under acidic conditions, Co^{2+} is believed to be the most aggressive catalyst, and the mechanisms by which it decomposes both peracids are believed to be quite similar.[4] The initiation reactions are believed to be those in equations [1] and [2].[4] The mechanism of alkali-induced decomposition of Pa was not investigated because the postulated mechansim[5,6] appears to be conclusive. Again, the alkali-induced mechanism involving a reaction between the dissociated and undissociated Pa is similar to that proposed for peroxymonosulfate anion where there is reaction between HSO_5^- and $SO_5^=$.[3,7]

$$Co^{2+} + ROOH \longrightarrow Co^{3+} + RO\bullet + OH^- \qquad [1]$$

$$Co^{3+} + ROOH \longrightarrow Co^{2+} + ROO\bullet + H^+ \qquad [2]$$

RESULTS AND DISCUSSION

Effect of Transition Metal Species on Pa Delignification

Starting with an acid-washed pulp, the approach was to add 5 ppm on pulp of each metal cation separately and investigate its effect on Pa delignification at pH 2.5, 4.8 and 7.0. A salt containing the transition metal was added to the pulp slurry at pH ~6 before it was preheated for 1 hour. Peracetic acid was then mixed into the pulp followed by acid or base for pH adjustment. Any metal that had a significant effect would then be studied more intensively in pulp-free solutions.

TABLE 1

Concentrations of Metals in Oxygen Delignified Pulp (mg/kg) Before and After Acid Washing

	Ca	Mg	Al	Mn	Fe	Cu	Ni	Cr	V	Co
Before Acid-Wash	1484	440	38	95	14	0.2	ND[1]	0.3	-	ND
After Acid-Wash	83	16	4.7	1.2	4.3	<0.1	ND	ND	ND	ND

[1] Non-detect at ~0.1 mg/kg

An oxygen delignified, softwood kraft pulp with kappa number 12.8 and 24.0 cP viscosity was used. The O_2-pulp was obtained from a mill in the American Northwest and its kappa number and viscosity were not affected by the acid-pretreatment which was conducted at room temperature (Experimental). The concentrations of metals in the unwashed and acid-washed samples are documented in Table 1.

The acid-washed pulp in Table 1 was the control sample for Pa delignification. It was treated along with other samples each containing 5 ppm on pulp of a selected cation. The results for the three pHs are documented in Tables 2-4. The results will be discussed in the order of increasing pH.

A constant Pa dose of 1.5% on pulp (0.67% equiv. H_2O_2) was used and the consumption of oxidant was lowest at pH 2.5 for the control and all the metal-enriched pulps. Amongst the control pulps, viscosity was also the lowest at pH 2.5. This follows a trend observed with HSO_5^- where for most of the cations the decomposition rate decreased with decreasing pH but the reaction mechanism became more dominated by free radical reactions.[3,8] As expected, Co^{++} was the most aggressive catalyst, and the chemical intermediates generated during Pa decomposition reacted with both lignin and carbohydrates, resulting in a

TABLE 2

Effect of Transition Metal Species on Pa Delignification at Initial pH 2.5[1]

	Control	Mn(II)	Fe(III)	Cu(II)	Ni(II)	V(V)	Co(II)
Kappa no.	8.6	8.7	8.3	8.7	8.7	8.2	7.9
Viscosity, cP	19.8	18.7	15.7	19.0	19.5	18.1	16.0
Brightness, %[2]	40.7	40.2	40.0	39.9	40.1	40.5	39.8
Residual Pa (% of applied)	63	60	48	61	62	33	11

[1]Oxygen delignified pulp with kappa 12.8 and 24.0 cP viscosity
[2]Brightness after PaE, % GE

marginally lower kappa number and a significantly lower viscosity (Table 2). The likely reactive intermediate is the acetoxy radical (AcO°).[4,9] However, we will check for °OH in later experiments. Hydrogen-abstracting free radicals are normally quite efficient at degrading carbohydrates.

The only other metals that had a significant effect were Fe, and V. Ferric ions caused some decomposition of Pa and lowered kappa number and viscosity. Vanadium (V) caused significant decomposition and lowered kappa number. When 33 mmol/L Pa solutions free of pulp and transition metal species are stored at pH 2.5 and 60°C, approximately 14% hydrolyzes to H_2O_2 (equation [3]) after 2h. Ferric ions are known to generate °OH from H_2O_2 at pH<3.0.[10] Vanadium species are known to slowly decompose HSO_5^- ,[11,12] and VO_3^- was found to be a highly catalytic anion for the decomposition of Pa.[13] While mechanisms were postulated for HSO_5^- decomposition catalyzed by V species,[11,12] a mechanism was not postulated for Pa decomposition.[13]

Delignification at pH 4.8 resulted in slightly lower kappa numbers and higher viscosities. The only cation that gave a low viscosity was Co^{2+} (Table 3). A free radical mechanism is believed to be the primary one for Co^{2+} catalysis at

TABLE 3

Effect of Transition Metal Species on Pa Delignification at Initial pH 4.8

	Control	Mn(II)	Fe(III)	Cu(II)	Ni(II)	V(V)	Co(II)
Kappa no.	8.1	7.9	7.7	8.0	8.0	8.1	8.0
Viscosity, cP	23.0	22.5	21.4	19.5	23.4	20.6	15.1
Brightness, %[1]	41.1	43.0	43.0	42.2	42.2	41.4	38.4
Residual Pa (% of applied)	41	31	32	34	41	25	1.0

[1] Brightness after PaE, % GE

pH 5.4 [9]. Only 37% of the Pa was utilized by the control pulp at pH 2.5, and that was enough to lower the kappa number from 12.8 to 8.6. A Pa utilization of 59% at pH 4.8 lowered the kappa number to only 8.1. There was more decomposition at pH 4.8 for the control and most of the metal-enriched samples. Kappa numbers of the delignified samples are plotted against Pa utilization in Figure 1. The highest efficiency was obtained at pH 2.5. The Pa utilization in Figure 1 does not include the fraction that hydrolyzed to H_2O_2 at pH 2.5 (equation [3]). Hydrolysis of Pa was insignificant at pH 4.8 and 7.0.

$$AcOOH + H_2O \overset{H^+}{\rightleftharpoons} H_2O_2 + AcOH \qquad [3]$$

The highest residual at pH 7 was for the control pulp, and it was only 3% of that applied. Alkali-induced decomposition would be very significant at pH 7.[5,6] The only sample with a low viscosity was the one enriched with Co^{2+} (Table 4). The free radical mechanism is apparently still operative at pH 7. However, the high kappa number and low brightness for the Co-enriched sample would suggest that there was wasteful decomposition of Pa. The decomposition of HSO_5^- is known to be much more rapid at pH 8 than at pH 2 but the mechanism is less dominated by free radical reactions.[3] The addition of the radical scavenger,

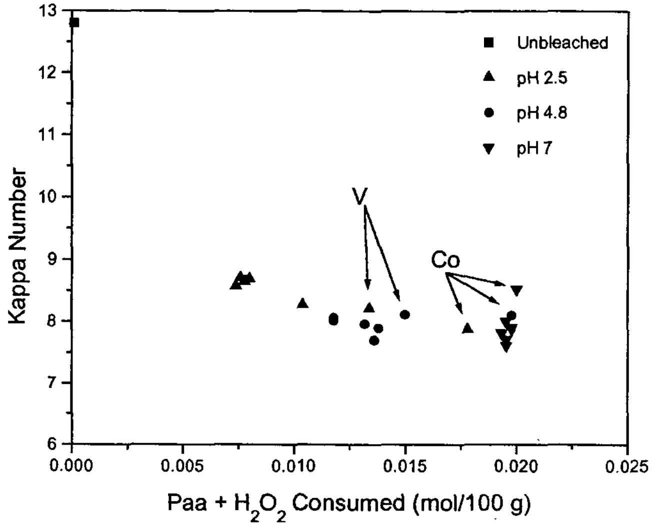

Figure 1. Effect of initial pH on peracetic acid delignification of an oxygen pre-bleached pulp.

N,N'-(5-nitro-1,3-phenylene) bisglutaramide (GAMID), retarded HSO_5^- decomposition by 90% at pH 2, but only by 13% at pH 8.[3] The highest brightnesses were obtained at pH 7 due to the presence of the peracetate anion (pKa of Pa = 8.2), a nucleophile capable of degrading carbonyl structures. However, pulp brightness is relatively insignificant at such high kappa numbers.

Delignification experiments were repeated for selected metals at all three levels of pH. Kappa number was reproduced to ±0.1, viscosity to ±0.3 cP and brightness to ±0.5% ISO.

Overall, lignin oxidation efficiency was highest at pH 2.5, but the risk of severe cellulose depolymerization was also the greatest. The best compromise between the oxidation of lignin and carbohydrates was obtained at pH 4.8. Lignin

TABLE 4

Effect of transition metal species on Pa delignification at initial pH 7.0

	Control	Mn(II)	Fe(III)	Cu(II)	Ni(II)	V(V)	Co(II)
Kappa no.	7.8	8.0	7.7	7.9	7.6	7.9	8.5
Viscosity, cP	23.8	24.3	22.3	20.7	23.8	23.9	15.0
Brightness, %[1]	48.8	49.3	49.4	49.5	49.4	48.8	43.6
Residual Pa (% of applied)	3.4	2.3	2.3	1.1	2.3	1.0	0

[1] Brightness after Pa, % GE

degradation was rather inefficient at pH 7.0 and no further studies were conducted at that pH.

Metal-induced decomposition of Pa in the absence of pulp

We selected pH 4.8 for our initial experiments because all the metals, except Ni, catalyzed Pa decomposition when delignification was performed at this pH. The effect of each metal on Pa decomposition is shown in Figure 2. The catalyst concentrations were 0.2 ppm Co^{2+} in solution and 1 ppm of the other cations. The rate equation was first order in Pa concentration on all occasions and the rate constants are summarized in Table 5.

Peracetic acid is produced commercially by the reaction of acetic acid and H_2O_2 (equation [3]). There is always a high concentration of unreacted H_2O_2 if the equilibrium product mixture is not distilled. Cellulose depolymerization is normally more severe when there is a high concentration of H_2O_2 [14,15]. In the present experiments the initial H_2O_2 concentration was only 3% as high as the Pa concentration. However, while only V^{4+}, V^{5+} and Co^{2+} caused significant decomposition of Pa (Figure 2), all the metals except Cu^{2+} rapidly decomposed the low concentration of H_2O_2 (Figure 3). Free radicals are likely to be generated by metal catalyzed decomposition of H_2O_2 at pH 4.8.

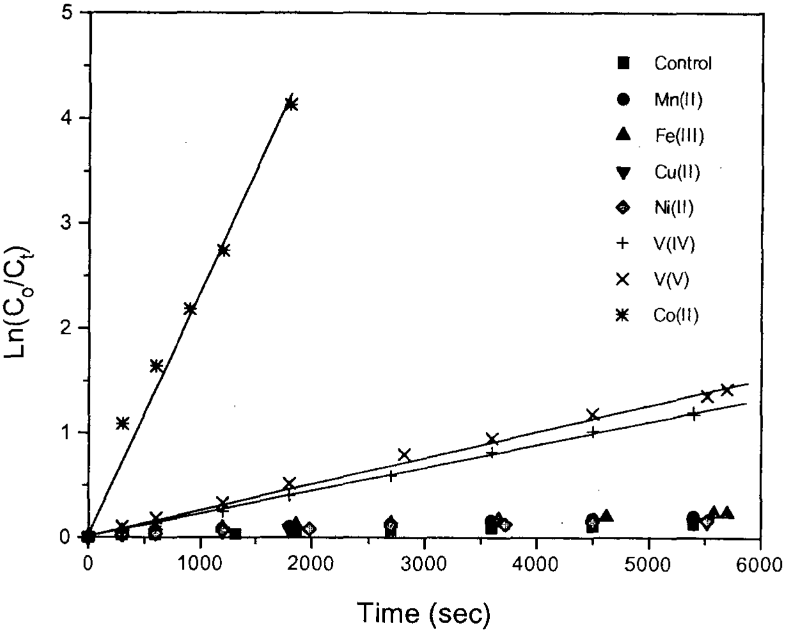

Figure 2. Peracetic acid decomposition catalyzed by transition metal species at pH 4.8 and 60°C. [Co^{2+}]=0.2 ppm, 1 ppm for other cations.

TABLE 5

Summary of First Order Rate Constants (s^{-1}) for Transition Metal-Induced Decomposition of Peracetic Acid at 60°C

	pH 2.4	pH 4.8
No catalyst	8.2×10^{-6}	2.4×10^{-5}
1 ppm Mn(II)	2.5×10^{-5}	4.3×10^{-5}
1 ppm Fe(III)	2.5×10^{-5}	4.5×10^{-5}
1 ppm Cu(II)	1.5×10^{-5}	3.0×10^{-5}
1 ppm Ni(II)	1.9×10^{-5}	3.4×10^{-5}
1 ppm V(IV)	2.0×10^{-4}	2.2×10^{-4}
1 ppm V(V)	2.1×10^{-4}	2.5×10^{-4}
0.2 ppm Co(II)	5.4×10^{-5}	2.4×10^{-3}

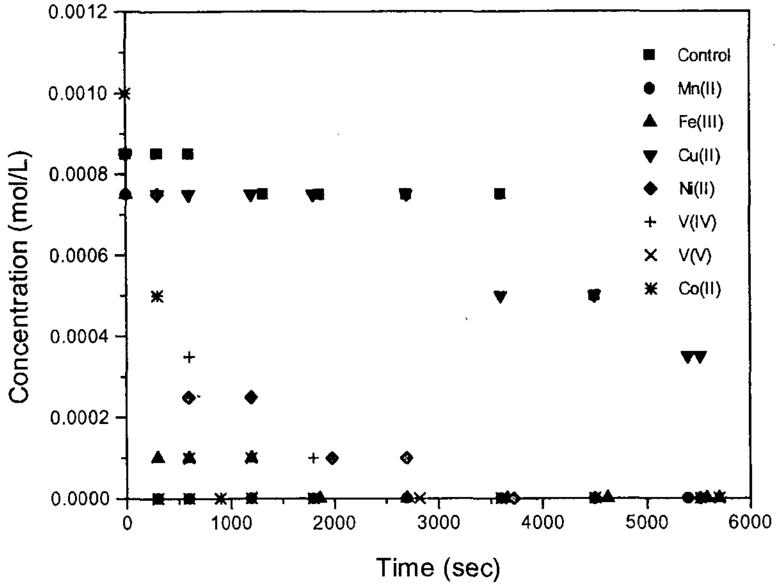

Figure 3. Metal-catalyzed decomposition of H_2O_2 present in distilled peracetic acid solutions. Similar conditions as Figure 2.

All the decomposition experiments in Figures 2 were repeated, but GAMID was included at a concentration of 10 mmol/L to trap °OH. The hydroxylation reaction and UV/Vis analysis of the resulting phenolates were previously described.[3,16] Only Cu^{++} caused a minor amount of hydroxylation. Approximately 1 mmol/L of hydroxylated GAMID was detected for every 20 mmol/L of Pa decomposed. The ratio was 1:4 for HSO_5^- decomposition catalyzed by Cu^{2+}.[17]

The Pa decomposition results for pH 2.4 are shown in Figure 4. The first order rate constants are compared to those from pH 4.8 in Table 5. It can be seen that the rate increased for V^{4+}or V^{5+} and decreased for Co^{2+} as the pH was lowered from 4.8 to 2.4. The rate of vanadium-induced decomposition was

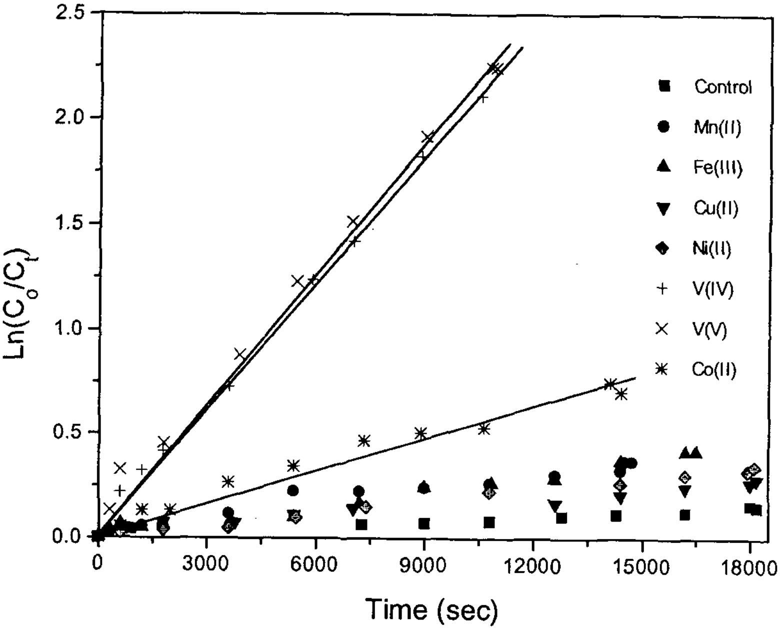

Figure 4. Peracetic acid decomposition catalyzed by transition metal species at pH 2.4 and 60°C.

higher during the first 20 minutes (Figure 4) and this is likely due to free radicals from the rapid decomposition of H_2O_2 by V^{4+} or V^{5+}. These radicals would react fairly rapidly with Pa.

Koubeck and Edwards[9] studied Pa decomposition catalyzed by low concentrations of Co^{2+} at pH 5.4. They observed that the rate equation was first order in both Pa and Co^{2+} concentrations and postulated a free radical mechanism involving the acetoxy (AcO°) and peracetoxy (AcOO°) radicals.[9] We observed that the rate equation was also first order in both Pa and Co^{2+} at pH 4.8. Furthermore, GAMID addition decreased the decomposition rate by about 70% and there was no significant hydroxylation, indicating that °OH was not involved.

The possibility that there was hydroxylation but that the resulting phenols were oxidized by Pa was examined. Peracetic acid was added to the HSO_5^-/Cu^{2+} system and the result was an increase in hydroxylated products. We accepted the mechanism of Koubek and Edwards.[9]

No postulated mechanism for Pa decomposition catalyzed by V^{4+} or V^{5+} could be found. To date we have only used GAMID to see if the mechanism is dominated by free radical reactions. The decomposition rate was decreased by ~50% at pH 3.3 and ~10% at pH 4.8. Vanadium (V) accelerated cellulose depolymerization less significantly than Co^{2+} and correspondingly, it appears to generate less free radicals. Further investigations will be conducted because V might be the most deleterious transition metal in a pulp bleaching system. While Co is a more aggressive catalyst, we have never detected it at a concentration as high as 0.5 mg/kg pulp but we have detected V at > 2 mg/kg on several occasions.

CONCLUSIONS

An oxygen-delignified, softwood kraft pulp with kappa number 12.8 and 24.0 cp viscosity was acid washed and delignified at initial pH 2.5, 4.8 and 7.0 with peracetic acid. The inclusion of 5 ppm on pulp of Mn^{2+}, Fe^{3+}, Cu^{2+}, V^{5+} or Co^{2+} caused wasteful decomposition of Pa while Ni^{2+} had no effect. None of the cations caused a significant decrease in kappa number, while Co^{2+} at all pHs and Fe^{3+} at pH 2.5 resulted in lower viscosities. Lignin degradation efficiency was highest at pH 2.5 and lowest at pH 7.0. However, pulp viscosity was lowest at pH 2.5. Initial pH 4.8 was the best compromise for selective delignification.

In pulp-free solutions, Co^{2+} and V^{5+} catalyzed Pa decomposition much more aggressively than the other cations. The kinetic data supported a previous free-radical mechanism for Co^{2+} and a similar type mechanism appears to be partially responsible for vanadium (V) catalysis. N,N'-(5-nitro-1,3-phenylene) bisglutaramide (GAMID) was an effective radical scavenger and catalysis by Co^{2+} was more dominated by free radical reactions than was vanadium (V) catalysis.

EXPERIMENTAL

Reagents

The water used was purified by a MILLI-Q Water System. Frequent analysis of Cu, Fe, Zn, Al, Mn and Co concentrations are conducted. The concentration of each metal is always < 10 ppb. The following reagent grade chemicals were obtained for various suppliers: $MnSO_4{^\circ}H_2O$, $FeCl_3{^\circ}6H_2O$, $CuSO_4{^\circ}5H_2O$, $NiSO_4{^\circ}6H_2O$, $VOSO_4{^\circ}3H_2O$, V_2O_5 (dissolved in H_2SO_4 to give VO_2^+) and $CoSO_4{^\circ}$ x H_2O. Ultrapure NaOH was obtained from Alfa Chemicals. N,N^1-(5-nitro-1,3-phenylene)-bisglutaramide was synthesized by the method of Singh and Hider.[16] Distilled peracetic acid was obtained by reacting H_2O_2 and acetic acid (both at ~20 wt.%) in dilute H_2SO_4 solution at ~40°C and ~60 torr. Peracetic acid and water are the most volatile products and are distilled off in a apparatus specially designed to avoid peracetic acid concentrations >40 wt. %.

Standard Conditions for Treatment of Pulp

Acid-pretreatment: Pulp at 3% consistency was adjusted to pH 1.5 by H_2SO_4 and retained at room temperature for 30 min.

Pa Stage: In plastic bags at 10% consistency, 60°C, 2h with H_2SO_4 for pH adjustment at 2.5, NaOH at pH 4.8 and 8.13% $NaHCO_3$ on pulp for pH 7.0.

Extraction Stage: In plastic bags at 12% consistency, 80°C, 2% NaOH on pulp, 2h.

Peracetic Acid Decomposition

The cations were pre-heated in acid-washed polyethylene bottles. An aliquot of concentrated Pa was added and a zero-time sample taken after pH adjustment. When GAMID was used, crystals were added to give an initial concentration of 10 mmol/L just prior to Pa addition. Residual Pa was determined by iodometric titration while ceric sulfate titration was used for H_2O_2. Solutions containing hydroxylated GAMID were made alkaline and diluted by a factor of ten. Their UV/Vis spectra were obtained against a solution containing 1 mmol/L GAMID and 30 mmol/L Pa.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the National Science Foundation through Grant CHE 9412985. In addition to their financial support we are also grateful to Solvay Interox for allowing us to use their peracetic acid generation unit.

REFERENCES

1. R. Seccombe, R.T. Hill, H. Martens, and A. Haakana, Proceedings of 1994 International Non-Chlorine Bleaching Conference, Miller Freeman, San Francisco.
2. B. Strandell and L.-E. Myhrman, Svensk Papperstid. 93(3), 36 (1996).
3. R.C. Francis, X.Z. Zhang, P.M. Froass, and O. Tamer, Tappi J. 77(6), 133 (1994).
4. C. Marsh and J.O. Edwards, Prog. React. Kinet. 15, 35 (1989).
5. Z. Yuan, Y. Ni, and A.R.P. van Heiningen, Can J. Chem. Eng. 75, 37 (1997).
6. E. Koubek, M.L. Haggett, C.J. Battaglia, K.M. Ibne-Rasa, H.Y. Pyun, and J.O. Edwards, J. Amer. Chem. Soc. 85, 2263 (1963).
7. D.L. Ball and J.O. Edwards, J. Amer. Chem. Soc. 78, 1125 (1956).
8. R.C. Francis, N.A. Troughton, X.Z. Zhang, and R.T. Hill, Tappi J. 77(7), 135 (1994).
9. E. Koubek and J.O. Edwards, J.Inorg. Nucl. Chem. 25, 1401 (1963).

10. W.H. Koppenol and J. Butler, Adv. Free Radical Bio. Med. 1, 91 (1985).

11. R.C. Thompson, Inorg. Chem. 20, 3745 (1981).

12. Z.Zhang, Ph.D. Thesis, Brown University, Providence, RI, 1990.

13. Ya.M. Vasyutyn, V.O. Garenko, I.A. Garbuzyuk, O.P. Ivanchishin, and R.G. Makitra, Soviet Prog. Chem. 55(6), 25 (1989). Trans. From Ukr. Khim. Zh. 55(6), 584(1989).

14. R.T. Hill, P.B. Walsh, and J.A. Hollie, Proceedings of 1992 Tappi Pulping Conf., Tappi Press, Atlanta, p. 341.

15. Walsh, P.B., "Process for the Delignification of a Chemical Pulp with Organic Peroxy Acid", U.S. Patent 5,431, 781 (1995).

16. S. Singh and R.C. Hider, Anal. Biochem. 171, 47 (1988).

17. A.R. Negri, G. Gimenez, R.T. Hill, and R.C. Francis, Tappi J. 81 (5): (1998).