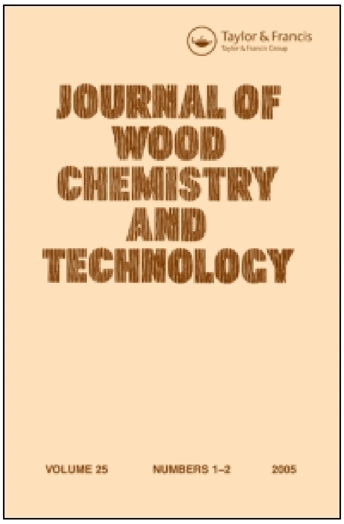

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THE EFFECT OF ELECTROLYTES ON THE LEACHING OF LIGNIN FROM UNBLEACHED KRAFT PULP FIBERS

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ABSTRACT

When an unbleached kraft pulp is suspended in aqueous solutions of electrolytes, the rate of leaching of lignin from the fiber wall is found to decrease with an increase in the ionic strength of the electrolyte. The effect was found to be greater with divalent ions (Mg^{++}, Ca^{++}, Zn^{++}) than with a monovalent ion, Na^{+}.

INTRODUCTION

When unbleached kraft pulp fibers are suspended in water, lignin macromolecules are leached slowly out of the fiber walls. In an earlier paper we showed that the release of lignin was diffusion controlled and that the diffusion coefficient was several orders of magnitude lower than expected for soluble macromolecules[1].

In the present paper, we report the results of a study of the effect of dissolved electrolytes on the leaching process. The influence of a monovalent cation (Na^{+}) and three divalent cations (Mg^{++}, Ca^{++},

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Zn^{++}) was investigated over a range of electrolyte concentrations. An attempt is made to interpret the behavior observed in terms of the known effects of electrolytes on the swelling of gels.

EXPERIMENTAL

The fiber stock used in the present experiments was an unbleached kraft pulp of 52% yield prepared from black spruce chips. The procedure and apparatus used in the leaching experiments have been described previously[1]. A 9.5 g (dry weight) sample of fiber was stirred gently in 1 L of the appropriate electrolyte solution at 20°C. The concentration of lignin leached out of the fiber was measured at suitable time intervals. The electrolytes used were all chlorides. The effect of NaCl was studied at 5 concentrations (1×10^{-3} M, 1×10^{-2} M, 3×10^{-2} M, 1×10^{-1} M, and 3×10^{-1} M), $MgCl_2$ at 3 concentrations (3×10^{-4} M, 1×10^{-3} M, and 1×10^{-2} M) and $CaCl_2$ and $ZnCl_2$ at 1×10^{-3} M. The pH of the solutions, measured at the beginning and at the end of the leaching experiments, was found to be close to neutrality (pH 6-8).

RESULTS

In Table 1, the concentration of lignin in the wash liquid, $C_f(t)$, is given for various times of leaching, t. The data for NaCl are plotted in Fig. 1 as $C_f(t)$ versus t. A similar dependence of leaching on electrolyte concentration is shown in Fig. 2 for $MgCl_2$. Note that the curve for 1×10^{-3} M $CaCl_2$ is coincident with the curve for 1×10^{-3} M $ZnCl_2$ and lies near to the curve for $MgCl_2$ at the same electrolyte concentration. The curves shown in Figs. 1 and 2 are the best polynomial fits. The standard error is 9%. In both Figs. 1 and 2, the previous results in pure water[1] are included.

DISCUSSION

As can be seen from Fig. 1, leaching from the fiber wall can be markedly reduced by increasing the sodium ion concentration. When the external liquid was 1×10^{-3} M NaCl, the rate of leaching was the same as with pure water. Increasing the concentration of NaCl resulted in

TABLE 1

The Dependence of Lignin Leaching from the Fiber Wall on Differing Electrolytes and Electrolyte Concentrations

Ion Species	Electrolyte Conc. (M)	$C_f(t) \times 10^3$ (gL^{-1})										
		15 min	30 min	45 min	60 min	90 min	120 min	150 min	180 min	210 min	240 min	270 min
Na	1×10^{-3}	3.16	5.58	6.27	7.65	9.49	11.2	11.6	12.7	14.2	15.1	15.7
Na	1×10^{-2}	3.40	5.24	5.24	8.26	7.22	8.48	8.80	8.24	9.07	10.6	9.98
Na	3×10^{-2}	-	2.46	3.64	3.32	5.24	7.81	4.81	7.65	6.52	6.84	-
Na	1×10^{-1}	-	1.44	2.41	3.10	2.51	2.94	4.81	4.22	3.05	5.51	-
Na	3×10^{-1}	-	-0.80	-	-	0.60	2.80	-	-	-0.80	2.40	-
Mg	3×10^{-4}	3.16	5.13	6.85	7.86	9.14	-	10.5	10.9	12.3	12.8	13.1
Mg	1×10^{-3}	0.70	3.16	-	6.47	5.29	5.40	6.36	6.68	-	7.43	7.22
Mg	1×10^{-2}	-	-0.50	0.05	-0.30	0.70	0.80	0.50	-0.80	-0.05	0.70	-0.20
Ca	1×10^{-3}	2.00	3.16	3.69	4.12	5.11	5.21	5.21	6.39	6.60	5.80	7.35
Zn	1×10^{-3}	1.68	2.75	2.81	-	5.78	5.16	4.89	7.70	6.79	6.34	6.71

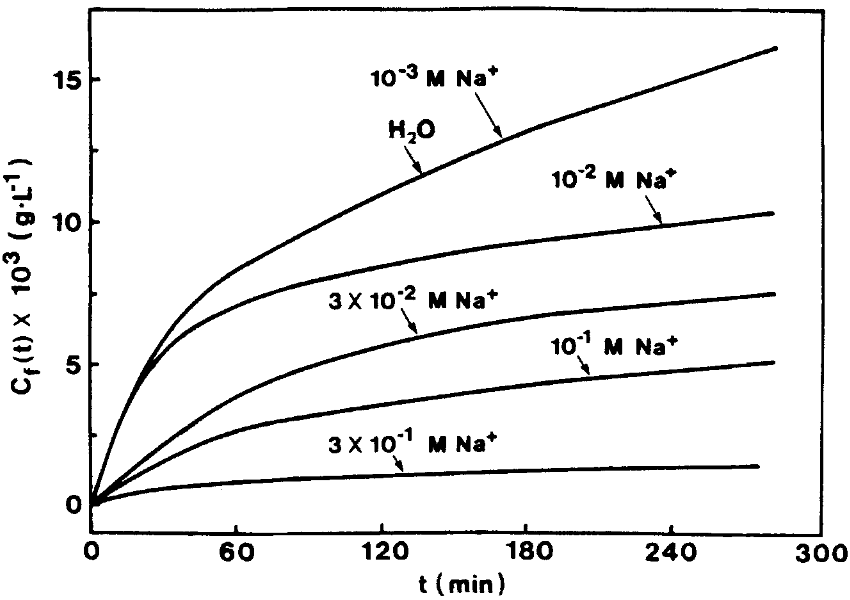

FIGURE 1. The effect of various concentrations of NaCl in the wash liquid on the leaching of lignin. The pure water curve obtained previously[1] is included for comparison.

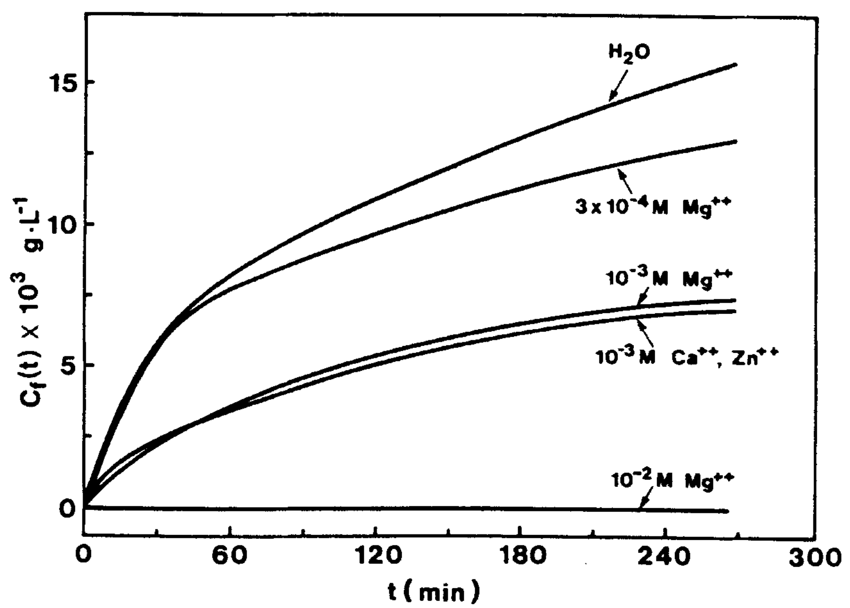

FIGURE 2. The effect of various concentrations of $MgCl_2$ in the wash liquid on the leaching of lignin. The leaching curves for 1 x 10^{-3} M $CaCl_2$ and $ZnCl_2$ are also shown. The pure water curve is included for comparison.

a gradual decline in leaching until, as can be seen from Fig. 1, a concentration of 0.3 M NaCl in the wash liquid reduced the leaching of lignin from the fiber wall to a small effect. Similar trends were found with solutions of magnesium chloride, as shown in Fig. 2. Here, however, the electrolyte concentration required to cause an effect was considerably lower than in the case of sodium chloride. Leaching was completely eliminated when the concentration of $MgCl_2$ in the wash liquid was 1×10^{-2} M.

It was not possible to calculate a diffusion coefficient for each ionic strength because the precision of the data and the duration of the experiment did not permit extrapolations to infinite time. Instead, the value of $C_f(t)$ at 240 minutes was taken as a rough measure of the rate of diffusion. In Fig. 3, $C_f(240)$ is plotted against the cationic strength, I_E, defined as

$$I_E = c\,Z^2 \qquad (1)$$

where $I_E \equiv$ the cationic strength

$c \equiv$ molarity of cation

$Z \equiv$ charge on the cation

It can be seen from Fig. 3 that leaching depends on the cationic strength of the electrolyte solution as well as on the charge of the cation.

Previous results[1,2,3] have suggested that the diffusion of lignin through the fiber wall is governed by an interaction of the lignin macromolecule with the porous structure of the fiber. It is evident therefore, that in order to slow down the leaching, the electrolytes must be affecting this interaction.

It is well known that the swelling behavior of cellulose fibers is affected by the presence of electrolytes[4,5,6]. Procter[7] proposed that swelling was related to a difference in the concentration of mobile ions in the gel as compared to the external solution. This concentration difference is caused by the presence of a certain number of cations associated with bound ionic groups in the gel itself. Procter considered the movement of water into the gel as being directly proportional to the excess concentration of mobile ions in the gel or, in other words, the osmotic pressure differential.

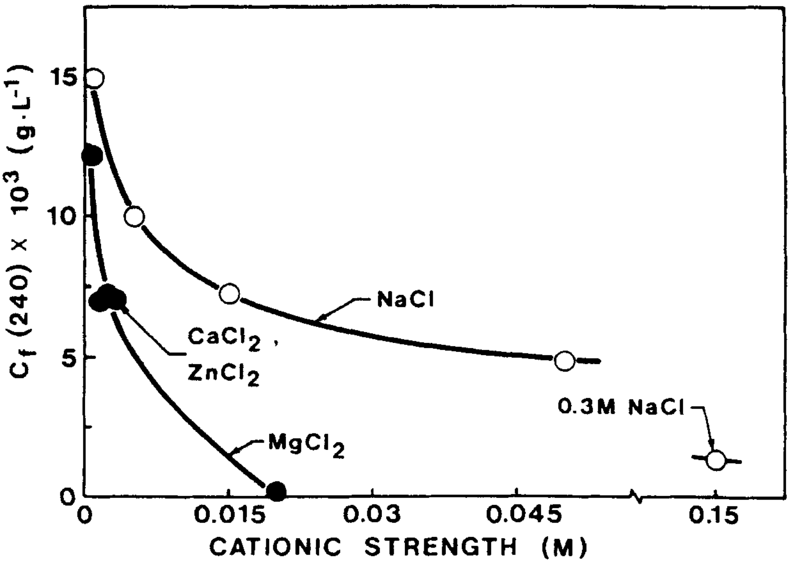

FIGURE 3. The concentration of lignin in the wash liquid at 240 minutes, $C_f(240)$, versus the cationic strength of the wash liquid.

If the gel is placed in an external liquid which is rich in electrolytes a partition of ions takes place according to Donnan equilibrium[8] and the excess concentration of mobile ions in the fiber decreases, resulting in reduced swelling.

The present results may be explained by the concepts described above. Reduced swelling, due to significant electrolyte concentrations in the external liquid, causes a shrinkage of the pores. Less lignin can then escape from the fiber. The increased effect of Ca, Zn, and Mg ions, as compared with Na ion at the same concentration, would also be expected based on the greater ionic strength of bivalent ions.

It should be noted that kraft lignin probably has some polyelectrolyte properties and therefore would also tend to shrink at higher concentrations of electrolytes. The fact, however, that leaching decreases with increasing electrolyte concentration indicates that the fiber wall probably shrinks more than the lignin macromolecule.

CONCLUDING REMARKS

It is evident from this study that the presence of electrolytes in the wash liquid can significantly reduce leaching from the fiber wall, with bivalent cations causing an even greater reduction than monovalent cations. This decrease in leaching can be related to a de-swelling of the fiber wall caused by the presence of electrolytes in the wash liquid. It is important to note, however, that electrolytes may offset the intra-fiber diffusion of lignin in ways other than swelling. For example, electrokinetic effects would be expected to decrease with increase in ionic strength. A further factor, not yet studied, is the effect of pH which under some circumstances could be more pronounced than the elctrolyte effect.

What are the technological implications of the present work? Electrolyte levels in pulping are high, typically in the order of about 1 M Na^+. High concentrations of electrolytes can also be found in the brown stock wash, especially as more mills are moving towards a closed mill system where process waters are recycled from the bleach plant. It is obvious therefore, that if, in the future, control of lignin leaching is to be undertaken, the effect of electrolytes will be critical in the washing and low consistency storage of chemical pulps.

REFERENCES

1. B.D. Favis, P.M.K. Choi, P.M. Adler, and D.A.I. Coring, Trans. Tech. Sect. CPPA, 7, TR35 (1981).

2. B.D. Favis, J.M. Willis, and D.A.I. Goring, J. Wood Chem. Technol. 3, 1 (1983).

3. B.D. Favis, Ph.D. Thesis, McGill University, Montreal (1981).

4. T. Lindstrom and G. Carlsson, Proc. EUCEPA Conf., Warsaw, p. 32 (1978).

5. A.M. Scallan and J. Grignon, Svensk Papperstidn., 82, 40 (1979).

6. J. Grignon and A.M. Scallan, J. Appl. Polym. Sci., 25, 2829 (1980).

7. H.R. Procter, J. Chem. Soc., 105, 313 (1914).

8. G.M. Barrow, Physical Chemistry, McGraw-Hill, New York, 3rd ed., p. 759 (1973).