Prediction of paper permanence by accelerated aging II. Comparison of the predictions with natural aging results

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Accelerated aging tests are credible and useful to predict paper permanence only if such tests can be shown to correlate with natural aging. In the first part of this study, a kinetic model was developed based on the accelerated aging results. In this report, we have shown that this kinetic model can indeed predict the natural aging results of lignin-free sheets with a statistical confidence. This is the first *quantitative* comparison of accelerated aging with natural aging.

KEYWORDS: accelerated tests, aging tests, cellulose degradation, durability, kinetics

INTRODUCTION

Methods that significantly accelerate the aging process of paper are useful for predicting paper permanence only if such methods can be shown to correlate with natural aging. A kinetic analysis approach has previously been applied to determine the validity of the accelerated aging tests but without much success (Major, 1958; Millet *et al.*, 1967; Browning and Wink, 1969; Gray, 1969; Parks and Hebert, 1972; Roberson, 1976; Graminski *et al.*, 1979; Arney and Jacobs, 1979 and 1982; Luner, 1966 and 1982; Erhard *et al.*, 1988). This is due to the following fundamental problems:

(1) **The use of inappropriate parameters for kinetic analysis:** Almost all of the previous kinetic studies used physical properties to determine the degradation rate. This is an empirical application of kinetics because the loss of physical properties during aging is a consequence of but is not directly proportional to the chemical degradation of cellulose. As a result, the basic requirements of the kinetic analysis, such as the linear relationship between property degradation and time, are not necessarily met. Some chemical properties, such as alpha-cellulose content, have the same problem, because they do not necessarily describe a change in the essential chemical structure during aging. The use of degree of polymerization (*DP*) of cellulose is more relevant and appropriate to assess directly the progress of chemical degradation, as recently demonstrated (Zou *et al.*, 1996).

(2) **Lack of critical examination of the Arrhenius equation:** Since the aging of

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paper is a complicated process and may involve multiple reactions, the applicability of the Arrhenius equation has been questioned (Strofer-Hua, 1990; Priest, 1994; Shahani, 1994). This has been a major barrier to the acceptance of accelerated aging results as convincing predictions of the natural aging behaviour of paper. However, we have recently shown that the Arrhenius equation is still applicable even in the case of a multiple-reaction system if certain conditions are met (Zou et al., 1996).

(3) **No examination of the statistical errors of the predictions:** To predict the natural aging behaviour of paper, the results obtained from accelerated aging must be extrapolated to natural aging conditions. During this extrapolation (or prediction), the statistical errors associated with original data inevitably increase. Therefore, examination of the statistical error of prediction is important. In addition, since the natural aging of paper is a very slow process, small changes in properties during natural aging must be statistically examined to ensure reliable natural aging results.

(4) **No quantitative comparison of the results of accelerated and natural aging:** This is partly due to the difficulty of obtaining naturally aged samples with known initial properties. Even in cases where naturally aged samples were analysed (Lewis, 1932; Rasch and Scribner, 1933; Richter, 1934; Shaw and O'Leary, 1938; Hanson, 1939; Wilson et al., 1955; van Royen, 1957; Barrow, 1959–1967; Graminski, 1976; Wilson and Parks, 1980; Bansa, 1992), no *quantitative* comparison was made. However, to paper permanence researchers, it is essential to compare the predictions quantitatively with natural aging results in order to have full confidence in accelerated aging tests.

Therefore, there still remains a fundamental question about whether the accelerated aging test can predict the natural aging behaviour of paper (Strofer-Hua, 1990; Bansa, 1992; Priest, 1994; Shahani, 1994). In the previous report, we applied a kinetic approach to study cellulose degradation in paper aging and developed a kinetic model based on accelerated aging tests (Zou et al., 1996). In this report, we show that the kinetic model can indeed predict the degradation rates associated with natural aging with a statistical confidence. To our knowledge, this is the first quantitative comparison of accelerated and natural aging.

Kinetic model

According to the previously developed kinetic model, the degradation rate constant can be determined from the following simplified equation (Ekamstam, 1936; Zou et al., 1996).

$$\left(\frac{1}{DP} - \frac{1}{DP_0}\right) = k_1 t \tag{1}$$

where DP and DP_0 are the (viscosity) degree of polymerization at time t and zero (day), respectively, and k_1 is the degradation rate constant (day^{-1}). The dependence of the degradation rate constant on temperature can be described by the pseudo Arrhenius equation under certain conditions (Zou et al., 1996):

$$k_1 = A_a \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where A_a and E_a are the apparent frequency factor and activation energy, respectively.

The dependence of the frequency factor A_a on the moisture content and hydrogen ion concentration of cellulose sheets was found to be described by the following equation (Zou et al., 1996):

$$A_a = A_{a0} + A_{a2}[H_2O] + A_{a5}[H^+][H_2O] \tag{3}$$

By substituting equation (3) into equation (2), we can predict the degradation rate constant of papers with various hydrogen ion concentrations, $[H^+]$ (M), and moisture contents, $[H_2O]$ (%),

$$k_1(\text{prediction}) = (A_{a0} + A_{a2}[H_2O] + A_{a5}[H^+][H_2O]) \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

The parameters in the above equation have been experimentally determined for bleached chemical pulps in the first part of this study (Zou et al., 1996):

$$A_{a0} = 4.54 \times 10^9 \text{day}^{-1}$$

$$A_{a2} = 2.83 \times 10^{12} \text{day}^{-1}$$

$$A_{a5} = 9.85 \times 10^{16} \text{ l mol}^{-1} \text{day}^{-1}$$

$$E_a = 109 \text{ kJ mol}^{-1}$$

Therefore, for naturally aged samples with known hydrogen ion concentrations and moisture contents, equation (4) can be used to predict the degradation rate constants. Statistical errors associated with this prediction can be estimated by using the procedures described in the Appendix.

MATERIALS AND METHODS

Bleached kraft pulps produced from various Canadian mills in the 1970s were carefully preserved at Paprican (kept in the dark during storage) and retested in 1993. Some of these (BKP-1 to 6) are the same samples used for developing the kinetic model (Zou et al., 1996). Cellulose DP and alpha-cellulose content were measured previously (de Grace and Page, 1976) and remeasured in 1993. In addition, the pH values of all the pulp samples were determined and the moisture content was also measured at 23 °C and 50% RH. The pH values and moisture content were assumed to be constant over storage period. Some of the pulps were in dry-lap form and stored under ambient conditions (T = 23 ± 3 °C and RH = 50 ± 20%, estimated); others were in the form of standard handsheets stored under a constant temperature and constant humidity (T = 23 ± 1 °C and RH = 50 ± 2%).

Cellulose DP was calculated from the intrinsic viscosity value as previously reported (Zou et al., 1993 and 1996). The standard deviation (σ) of the DP measurements was within 2% of the average value (based on eight repeated measurements). Alpha-cellulose content was measured according to CPPA standard method G.29. The cold

extract pH value of the samples was measured according to the CPPA standard testing procedures, but in 0.1 M NaCl solution instead of deionized water (Zou et al., 1993 and 1996).

RESULTS AND DISCUSSION

Natural aging results

Eighteen bleached softwood kraft pulps were retested after natural aging for 22 years under ambient conditions. The original DP values and alpha-cellulose content of these samples are listed in Table 1. As can be seen, the samples have very different pH values, depending on the different pulping and bleaching conditions that may have been used. Even though all of the samples are bleached softwood kraft pulps that have been stored under the same conditions, they have very different degradation rates, strongly dependent on their acidities. For instance, when a sample was very acidic (Sample BKP-15, pH = 3.20), its DP dropped from 760 and 250 in only 22 years ($k_1 = 32.1 \times 10^{-8}$ day^{-1}). On the other hand, when a sample had a higher pH value (Sample BKP-6, pH = 5.72), its DP did not change at all after 22 years of storage. This clearly demonstrates the profound effect of acidity on cellulose degradation during natural aging. In the literature, alpha-cellulose content has often been measured as an indicator of cellulose degradation (Wilson and Parks, 1980). However, as shown in Table 1, alpha-cellulose content did not change much for most of the samples, thus indicating that it is insensitive to aging (or to cellulose degradation).

Five *handsheet samples* naturally aged under controlled conditions (23 °C and 50% RH) were retested and the results are shown in Table 2. Once again, it is clear that degradation rate depends strongly on the acidity of the sheets.

Comparison of natural aging results with predictions

With the natural aging results, we can now test the previously developed kinetic model. The predicted degradation rate constants k_1 (prediction) using equation (4) are compared with natural aging results k_1 (natural aging) in Fig. 1. The error bars indicate twice the standard deviation (2σ) values of the predictors. The estimated values of the standard deviations were approximately 40% of the mean of k_1 (prediction). By considering the statistical error involved, the agreement between the predictions and natural aging results is found to be excellent for most of the data points.

Another comparison of the predictions with natural aging results is shown in Fig. 2 for sheets naturally aged under controlled conditions. In this case, a better agreement is obtained because of the well-controlled storage conditions for these samples.

It should be noted that the predicted degradation rates are consistently lower than the measured ones at relatively high hydrogen ion concentration (in both Figs 1 and 2 when pH < 4.0). This is due to the fact that in a general (multiple) reaction system, the activation energy and frequency factor are not completely independent of each other, as seen in the previous analysis (Zou et al., 1996); the activation energy determined for more acidic sheets tends to be slightly higher than the one for less acidic sheets. In the first part of this kinetic analysis, the activation energy was obtained from the average of the samples with pH between 4.0 and 5.7. Therefore, the prediction gives lower degradation rate when paper is extremely acidic (pH < 4).

TABLE I. Natural aging results from 18 bleached kraft dry-lap pulps

Sample no.	Moisture content (%) (1993)	pH (1993)	Alpha-cellulose (%)		Alpha-cellulose change (%)	DP ($\times 10^{-3}$)		k_f (natural) ($\times 10^8$, day^{-1})	k_f (predicted) ($\times 10^8$, day^{-1})
			1971	1993		1971	1993		
BKP-1	6.49	4.18	85.9	85.7	−0.2	1.35	1.08	2.21 ± 0.30	3.55
BKP-2	5.94	3.94	88.3	87.3	−1.0	0.95	0.67	5.24 ± 0.46	4.91
BKP-3	6.69	3.75	86.0	84.1	−1.9	0.98	0.63	6.75 ± 0.48	7.94
BKP-4	5.75	3.82	84.9	83.7	−1.2	1.03	0.69	5.70 ± 0.44	5.95
BKP-5	5.77	5.17	88.2	87.6	−0.6	0.99	0.93	0.78 ± 0.36	1.20
BKP-6	5.42	5.72	87.4	88.0	0.6	1.00	1.00	0.00 ± 0.36	0.98
BKP-7	6.21	4.70	87.3	87.0	−0.3	1.31	1.30	0.07 ± 0.28	1.76
BKP-8	6.08	4.17	89.3	88.1	−1.2	0.97	0.73	4.04 ± 0.42	3.38
BKP-9	5.62	5.05	88.7	89.0	0.3	1.14	1.12	0.19 ± 0.32	1.24
BKP-10	5.80	3.72	86.7	85.9	−0.8	1.02	0.55	9.98 ± 0.52	7.31
BKP-11	6.33	5.08	86.7	86.5	−0.2	1.35	1.16	1.45 ± 0.28	1.37
BKP-12	6.56	4.90	86.4	86.6	0.2	1.43	1.21	1.51 ± 0.26	1.58
BKP-13	6.21	5.05	89.2	89.0	−0.2	1.06	1.06	0.00 ± 0.34	1.36
BKP-14	6.09	4.77	84.8	85.0	0.2	1.17	1.10	0.65 ± 0.32	1.62
BKP-15	5.61	3.20	84.9	78.6	−6.3	0.76	0.25	32.1 ± 1.06	25.00
BKP-16	5.55	4.00	85.9	85.3	−0.6	1.13	0.76	5.13 ± 0.40	4.11
BKP-17	5.99	4.60	86.4	85.0	−1.4	1.04	0.80	3.44 ± 0.40	1.88
BKP-18	5.72	3.92	85.7	84.7	−1.0	1.09	0.71	5.85 ± 0.42	4.90

TABLE 2. Natural aging results for handsheets aged under controlled conditions

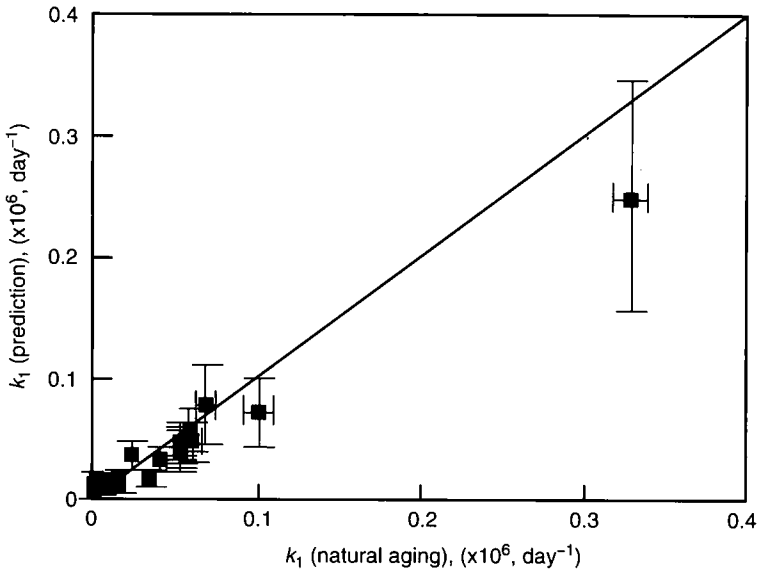| Handsheet sample	H-1 (BKP)	H-2 (BKP)	H-3 (BKP)	H-4 (Sisal)	H-5 (BKP)
Moisture content (%) (1993)	6.52	6.76	6.25	6.87	5.97
pH (1993)	5.08	3.86	4.84	3.91	4.11
Aging time (years)	22	22	22	20	17
DP ($\times 10^{-3}$, before natural aging)	1.35	1.06	1.43	1.69	1.10
DP ($\times 10^{-3}$, after natural aging)	1.18	0.57	1.22	0.96	0.84
k_1 (natural aging), ($\times 10^8$, day^{-1})	1.40 $\pm$ 0.28	9.99 $\pm$ 0.50	1.50 $\pm$ 0.26	6.11 $\pm$ 0.30	4.59 $\pm$ 0.38
k_1 (prediction), ($\times 10^8$, day^{-1})	1.41	6.23	1.63	5.67	3.98

FIGURE 1. Comparison of the predictions with natural aging results (18 bleached kraft pulp samples naturally aged under ambient conditions).
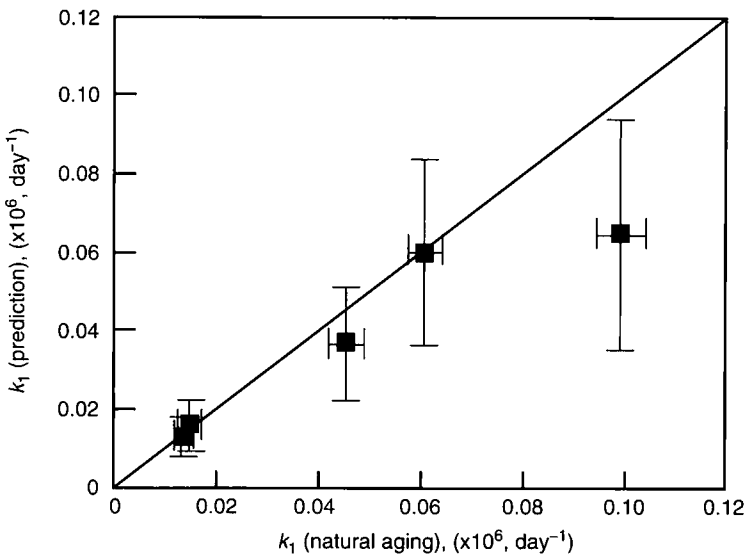

FIGURE 2. Comparison of the predictions with natural aging results (five handsheet samples naturally aged at 23 °C and 50% RH).

Relationship between degradation rate constant and hydrogen ion concentration

The effect of hydrogen ion concentration on the degradation rate constants under *natural aging conditions* is shown in Fig. 3. Since these samples have different moisture contents, for comparison purposes, the rate constants in the figure were corrected using a constant
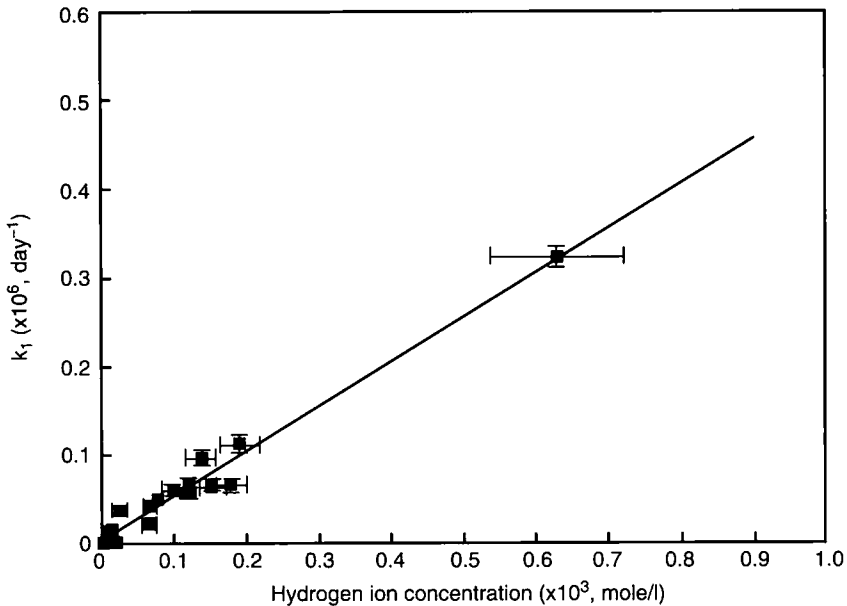
FIGURE 3. Relationship between degradation rate constant and hydrogen ion concentration (natural aging).

moisture content of 6.2% (an average from the samples used in the study) for all the samples. As shown in Fig. 3, a good linear relationship is obtained between k_1 (natural aging) and hydrogen ion concentration. This shows that a linear relationship previously found in the *accelerated aging* is equally valid for natural aging.

CONCLUSIONS

The accelerated aging test can predict very well the natural aging behaviour of lignin-free sheets. This is the first time that a *quantitative* comparison of the accelerated aging with natural aging was made. These results should give papermakers and end-users more confidence in using accelerated aging tests to predict paper permanence.

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APPENDIX

Estimation of statistical errors

For a quantity X which is a function of at least two variables u and v (i.e., $X = f(u, v, \ldots)$), the propagation of errors (variance) during the calculations of X can be estimated:

$$\sigma_x^2 \simeq \sigma_u^2 \left(\frac{\partial X}{\partial u}\right)^2 + \sigma_v^2 \left(\frac{\partial X}{\partial v}\right)^2 + 2\sigma_{uv}^2 \cdot \left(\frac{\partial X}{\partial u}\right)\left(\frac{\partial X}{\partial v}\right) + \cdots \tag{A1}$$

where σ^2 is the variance (or covariance) of the corresponding quantity (X, u, or v) and only the first-order terms of σ^2 are shown. Based on this equation, the following procedures were used to estimate the error in the measured and predicted values of k_1:

(1) k_1 **measurement errors (in natural aging):** Since DP_0 and DP measurements are not correlated, the measurement error of k_1 can be estimated from the following equation:

$$\sigma^2(k_1) = \frac{1}{t^2}\left[\frac{\sigma^2(DP_0)}{DP_0^4} + \frac{\sigma^2(DP)}{DP^4}\right] \tag{A2}$$

As can be seen, they are determined by the measurement errors of DP.

(2) k_1 **prediction errors from the kinetic model:** Equation (4) can be written in an alternative form:

$$k_1(\text{prediction}) = (k_{a0} + k_{a2}[H_2O] + k_{a5}[H^+][H_2O])$$

$$\times \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_a}\right)\right] \tag{A3}$$

where T_a is the temperature used for the accelerated aging test, $k_{a0} = A_{a0} \exp(-E_a/RT_a)$, $k_{a2} = A_{a2} \exp(-E_a/RT_a)$, and $k_{a5} = A_{a5} \exp(-E_a/RT_a)$. In the actual prediction, equation (A3) was used instead of (4): E_a was determined by a series of accelerated aging tests at different temperatures at constant hydrogen ion concentrations and moisture contents. The constants k_{a0}, k_{a2} and k_{a5} were directly determined by the accelerated aging test at a temperature of 90 °C. Therefore, E_a and the k_as are not correlated statistically and the error in the prediction of k_1 can be estimated from the following equation by taking into account of the second-order term of σ^2 in equation (A1):

$$\frac{\sigma^2(k_1)}{k_1^2} = \frac{\sigma^2(k_a)}{k_a^2} + \frac{\sigma^2(E_a)}{R^2} \left(\frac{1}{T} - \frac{1}{T_a}\right)^2 - 4\frac{\sigma^4(E_a)}{R^4} \left(\frac{1}{T} - \frac{1}{T_a}\right)^4 \tag{A4}$$

where

$$\sigma^2(k_a) = \sigma^2(k_{a0}) + \sigma^2(k_{a2})[H_2O]^2 + \sigma^2(k_{a5})[H_2O]^2[H^+]^2 \tag{A5}$$

As can be seen, the error in the predicted value of k_1 depends on the natural aging temperature (T) and also the temperature (T_a) used for obtaining the kinetic parameters. The variances in equations (A4) and (A5) were estimated from the regression analysis used in the first part of this study. It should be noted that the term $\sigma^2(E_a)/R^2(1/T - 1/T_a)^2$ is significantly larger than the term $\sigma^2(k_a)/k_a^2$.