Supplementary Information

Modelling the degradation of acidic and alkaline printing paper

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J. Tétreault[1], P. Bégin[1], D. Vedoy[1], S. Paris-Lacombe[2], A.-L. Dupont*[2]

[1] Canadian Heritage, Canadian Conservation Institute, 1030 Innes Road, Ottawa, ON K1B4S7, Canada

[2] Centre de Recherche sur la Conservation, CNRS, Muséum National d'Histoire Naturelle, 36 rue Geoffroy St Hilaire, 75005 Paris, France
***** corresponding author e-mail: anne-laurence.dupont@mnhn.fr

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1. Experimental

1.1 Hygrothermal ageing

Paper samples were hygrothermally aged in Lab-Line hybridization tubes (35 mm internal diameter (ID), 144 ml) hermetically closed, according to TAPPI Test Method T573 pm-09 at various temperatures and time intervals as shown in Table S1. During the ageing, the humidity in the tube is supplied and buffered by the paper and stabilizes between 50 and 60% RH (Sawoszczuk et al. 2008) and between 49 % and 52 % when the tubes are tightly closed (Vibert et al. 2023).

1.2 Degree of polymerization of cellulose (DP)

The preferred method used for the determination of the average degree of polymerization of cellulose was size-exclusion chromatography with multiangle light scattering and differential refractive index detection (SEC-MALS-DRI) (DP_n, DP_w, DP_z). Paper samples were dissolved in *N*,*N*-dimethylacetamide (DMAc) with 8% lithium chloride according to a procedure detailed in a previous publication (Dupont 2003). A 515 isocratic HPLC pump (Waters), ACC-3000T autosampler (Dionex), Dawn EOS MALS detector (Wyatt Technologies), and 2414 (Waters) differential refractive index (DRI) detector were part of the chromatographic set-up. The separation was carried out on a set of three PLgel MiniMIX B polystyrene divinyl benzene (PSDVB) columns (10-µm particle diameter mixed bed pores, 250 × 4.6 mm columns, Agilent) preceded by a MiniMIX B guard column (10-µm particle diameter, Agilent). The columns show a linear separation in the range of 500 g mol^{-1}–10,000 kg mol^{-1}. The columns compartment and the MALS detector were thermostated at 60 °C, the DRI was set to 55 °C. The mobile phase was DMAc with 0.5% lithium chloride (wt/vol). The system was operated at a flow rate of 0.4 mL min^{-1} with an injection volume of 100 µL. Run time was 31 min. The data acquisition was carried out in 0.5 s intervals with the ASTRA software version 4.73.04 (Wyatt Technologies Corp.). The data was computed using the Wyatt Technologies software Astra (v 5.3.414). The *dn/dc* for cellulose in LiCl/DMAc was previously determined as 0.140 mL g^{-1} (Souguir et al. 2008). The repeatability of the method was determined to be RSD% = 2.5 on DP_w for 3 separate cellulose samples analyzed two to three times non-consecutively. The molar mass distribution profiles of the chemical pulp samples being bimodal due to the presence of hemicelluloses, it was decided to treat the data by deconvoluting the peaks according to the method developed in Dupont et al. (2108), and consider the peak of cellulose only as DP.

Because of their poor solubility in the chromatographic solvent (LiCl/DMAc), the papers that contain large proportions of lignin in the form of mechanical pulp (TMP4.7 and BSGWP5.1) were dissolved in CED (cupriethylenedamine) and analyzed by viscometry. This may lead to slightly overestimated DP, the most recalcitrant low-DP cellulose, which is the portion complexed with lignin, being the most recalcitrant to dissolution. However, no currently available dissolution methodology can ensure full dissolution without degrading cellulose to some extent. A viscometer Routine 100 (Cannon-Fenske™) was used to measure the specific viscosity (based on the efflux times), according to the standard method ASTM D1795-13. From the calculated intrinsic viscosity ([η]), the DP_v of cellulose followed, based on Mark–Houwink–Sakurada equation: $[\eta] = K' DP_v^a$, where K' = 0.91 and a = 0.85 (Evans and Wallis 1987). It must be noted that only a proportion of the samples dissolved in CED: about 70 to 75% for BSGWP5.1 and 50 to 62% for TMP4.7.

1.3 Equilibrium moisture content (EMC)

The water sorption isotherms were measured using a TGA Q5000 SA sorption analyzer (TA Instruments). For each paper, 4.5 to 5.0 mg of samples aged in the different conditions cut in small fragments were placed in the instrument and conditioned at 21 °C and 0% RH under nitrogen for 60 minutes. This was followed

by two adsorption (90 minutes dwell time)/desorption (90 minutes dwell time) cycles from 0 to 96% RH at 21 °C. A final adsorption/desorption cycle was performed where the RH was increased or decreased in increments of 5% in the ranges of 0 to 10% and 90 to 95%, increments of 10% in the 10 to 90% range, and by 1% in the 95 to 96% range. The RH was increased or decreased after a weight change of less than 0.015% for 5 minutes consecutively or a maximum dwell time of 180 minutes. In the final step the sample was dried at 60 °C and 0% RH under nitrogen for 120 minutes and its dry weight determined. The EMC obtained by the instrument is measured in g/g dry, which is transformed into g H2O/g conditioned sample weight in the model. The isotherm served also to determine EMC for the viscosity and zero-span tensile measurements.

The Guggenheim-Anderson-de Boer (GAB) sorption equation, which represents the isotherm relation at equilibrium between the paper and vapor phases of water was used (Parker et al. 2006; Timmermann 2003). GAB parameters were obtained automatically by the TGA Q5000 SA sorption analyzer with a r^2 equal or above 0.998. The GAB equation was used for different degradation stages of the papers at 10, 21 and 30 °C. The unit of EMC from GAB equation is g /g dry.

1.4 Zero-span breaking length and grammage

The zero-span tensile strength of paper samples was measured in the machine direction of the paper according to TAPPI Test Method T231 cm-96 using a Troubleshooter Pulmac Instrument with a clamping pressure of 551 kPa. Twenty repeat measurements were carried out per sample type. The repeatability of the measurement was 5%. Zero-span Breaking Length (BL) was calculated using the moisture-free grammage of the paper samples as follows:

$BL = 102000\ (T/R)$

where BL = breaking length (m), T = tensile strength (kN m^{-1}) (1kgf/15 mm = 0.654 kN m^{-1}) and R = grammage (dry) (g m^{-2}).

1.5 Cold extract pH

The cold extract pH was measured according to TAPPI Test Method T 509 om-02 using an EA 940 Orion Ion Analyzer equipped with an 8155 Orion Ross combination electrode (all samples except TMP4.7 and BSGWP5.1), and a Mettler Toledo FiveEasy pH-meter equipped with a LE438 combined pH electrode (TMP4.7 and BSGWP5.1). The sample mass was 1.0 g for the acidic papers and 0.5 g for the alkaline and near-neutral papers. All determinations were carried out in triplicate. The repeatability indicated in the standard method is ± 0.1 pH units.

1.6 Alkaline Reserve

After completing the cold extract pH measurements, 20 to 30 ml of 0.1 N HCl was added to the sample and the mixture was incubated for 16 hours to ensure complete neutralization of the buffer. The excess acid was then titrated with 0.1 N NaOH. A potentiometer end-point (to pH 7) was used instead of the methyl red indicator end-point as described in the ASTM D 4988-89 Standard (1990). During titration, nitrogen gas was vigorously bubbled through the mixture and the gas flow was stopped near the pH 7 endpoint. The alkaline reserve of the paper is expressed as a percentage of calcium carbonate. All determinations were carried out in triplicate.

2. Results

Table S1 Experimental data for each paper

TMP4.7, grammage: 47 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_v	EMC (%) @21 °C & 50% RH	pH	BL (km)
21	0	1458	6.83	4.65	15.10
60	77	738	6.81	4.04	12.98
60	181	553	6.67	3.78	11.03
60	230	470	6.69	3.83	10.09
60	362	414	6.69	3.92	8.39
70	28	753	6.77	3.96	11.62
70	62	567	6.69	3.95	10.71
70	120	428	6.45	3.80	7.96
70	196	378	6.27	3.65	6.23
80	14	641	6.66	3.99	11.64
80	30	445	6.54	3.92	9.20
80	57	347	6.29	3.82	6.39
80	100	281	6.05	3.76	4.76
90	6	565	6.59	4.00	11.38
90	12	425	6.44	3.90	8.98
90	20	384	6.28	3.82	6.80
90	35	289	6.03	3.82	5.17
100	2	680	6.59	4.05	11.73
100	4	473	6.52	3.99	9.71
100	7	434	6.30	3.79	7.49
100	11	313	5.99	3.86	5.49

BKP4.9, grammage: 118 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	pH	BL (km)
21	0	1301	5.10	4.93	10.07
50	90	1149	5.01	4.96	9.37
50	200	1009	4.94	4.91	8.35
50	340	840	4.86	4.71	7.66
50	580	707	4.82	4.57	6.18
60	40	1045	5.03	4.94	9.04
60	90	911	4.82	4.82	8.18
60	160	661	4.75	4.57	6.21
60	260	567	4.66	4.48	4.60
90	2	792	4.70	4.83	7.03
90	4	599	4.56	4.69	5.24
90	8	488	4.28	4.48	3.41
90	12	434	4.22	4.42	2.64
100	1	711	4.52	4.59	6.19
100	2	539	4.29	4.54	4.49
100	3	518	4.15	4.44	3.31
100	4	440	4.08	4.43	2.82

BSGWP5.1, grammage: 80 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_v	EMC (%) @21 °C & 50% RH	pH	BL (km)
21	0	2177	5.42	5.12	9.36
70	71	1025	5.32	4.52	7.35
70	151	649	5.23	4.33	5.97
70	230	504	5.22	4.22	4.60
70	363	379	5.18	4.22	3.38
80	35	855	5.21	4.42	6.71
80	75	507	5.08	4.25	4.60
80	140	353	4.94	4.02	2.98
80	197	332	4.81	3.92	2.54
90	15	767	5.14	4.45	6.56
90	29	530	5.02	4.26	4.62
90	50	370	4.88	4.09	3.21
90	70	337	4.80	4.04	2.63
100	5	857	5.12	4.50	6.71
100	10	522	4.95	4.26	4.34
100	16	430	4.87	4.11	3.55
100	23	358	4.77	4.02	2.88

BKP5.1, grammage: 76 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	pH	BL (km)
21	0	1188	5.30	5.09	13.19
50	90	1143	5.13	5.07	12.84
50	200	1114	5.11	4.96	12.46
50	340	1042	5.10	4.89	12.05
50	580	917	5.06	4.70	10.73
60	40	1105	5.18	4.95	12.54
60	90	1076	5.10	4.88	11.93
60	157	865	5.01	4.86	10.66
60	257	786	4.93	4.75	9.62
70	14	1024	5.15	4.94	12.54
70	30	914	5.08	4.79	11.70
70	60	834	5.00	4.73	10.44
70	112	594	4.86	4.54	8.13
80	7	923	5.08	4.85	11.74
80	15	790	4.99	4.72	10.51
80	28	727	4.83	4.59	8.53
80	50	500	4.74	4.50	6.62
90	3	823	5.00	4.77	11.58
90	6	727	4.87	4.66	10.20
90	10	605	4.78	4.56	8.04
90	14	530	4.68	4.51	6.77
100	1	928	4.95	4.78	11.72
100	2	742	4.86	4.68	10.19
100	3	678	4.72	4.54	9.13
100	5	535	4.55	4.48	6.89

C5.9, grammage: 96 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	pH	BL (km)
90	0	665	5.08	5.91	10.6
90	2	520	4.88	5.76	9.97
90	5	306	4.67	5.61	8.52
90	10	218	4.42	5.4	5.94
90	14	157	4.15	5.34	3.99
90	21	104	3.88	5.23	1.56
90	30	92	3.41	5.25	1.24

BSP6.2, grammage: 76 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	pH	BL (km)
21	0	540	5.723	6.21	10.77
70	71		5.564		10.11
70	150	363	5.563		9.42
70	301	281	5.442		7.65
70	560		5.359		6.18
80	35	481	5.520		9.82
80	74	361	5.484		8.84
80	140	267	5.377		6.86
80	253	263	5.330		5.52
90	15	432	5.446		9.72
90	30	334	5.352		8.15
90	50	303	5.259		6.62
90	70	250	5.179		5.52
100	5	372	5.359	5.62	9.73
100	10	334	5.290	5.37	8.53
100	16	257	5.178	5.22	6.80
100	23	220	5.117	5.14	5.84

C6.5 grammage: 88 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	pH[a]	BL (km)
21	0	2366	5.34	6.49	12.21
60	77	1923	5.25	6.40	11.98
60	180	1462	5.28	6.27	11.70
60	320	756	5.27	5.95	10.76
60	500	425	5.28	5.65	8.69
70	28	2029	5.36	6.42	12.17
70	60	1687	5.16	6.34	12.09
70	120	979	5.12	6.08	11.06
70	213	412	5.00	5.63	9.03
80	14	1853	5.22	6.38	12.32
80	30	1316	4.99	6.22	11.74
80	57	617	4.92	5.85	10.42
80	100	276	4.51	5.38	6.93
90	6	1794	5.06	6.37	12.20
90	12	1287	5.00	6.21	11.74
90	20	777	5.03	5.97	10.93
90	35	428	4.73	5.65	7.83
100	2	1847	4.90	6.38	12.11
100	4	1481	5.07	6.28	12.06
100	7	876	4.87	6.03	11.39
100	11	506	4.69	5.75	9.74

[a] pH from Equation 14 in Tétreault et al. (2019).

C8.5, grammage: 80 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	$CaCO_3$ content (%)	pH	BL (km)
21	0	1378	4.757	4.31	8.49	15.15
70	71	1108	4.655			14.94
70	150	789	4.625			14.11
70	301	501	4.529			13.58
70	560	289	4.461			10.99
80	35	795	4.599			14.25
80	74	551	4.539			13.53
80	140	345	4.494			12.14
80	253	240	4.340			9.77
90	15	690	4.525			14.20
90	30	461	4.391			13.18
90	50	260	4.356			11.16
90	70	218	4.285			9.79
100	5	707	4.456	4.24	8.43	14.14
100	10	430	4.351	4.14	8.34	13.03
100	16	295	4.293	4.04	8.22	11.31
100	23	224	4.216	4.08	8.22	9.92

C9.1, grammage: 69 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	$CaCO_3$ content (%)	pH	BL (km)
21	0	1338	4.631	7.34	9.09	15.56
70	71	1103	4.655			15.17
70	150	909	4.625			14.77
70	301	624	4.529			14.03
70	560	356	4.461			12.25
80	35	1062	4.599			14.93
80	74	730	4.539			14.45
80	140	442	4.494			12.35
80	253	377	4.340			12.27
90	15	849	4.525			14.32
90	30	532	4.391			13.06
90	50	344	4.356			12.42
90	70	327	4.285			11.75
100	5	814	4.456	7.22	8.91	14.43
100	10	491	4.351	7.19	8.78	13.20
100	16	335	4.293	6.92	8.63	12.01
100	23	300	4.216	6.78	8.58	11.55

BKP9.6, grammage: 77 g/m²

Ageing temperature (°C)	Ageing duration (day)	DP_n	EMC (%) @21 °C & 50% RH	$CaCO_3$ content (%)	pH	BL (km)
21	0	2419	5.251	10.46	9.64	14.33
70	71	2286	5.122			13.77
70	150	1985	5.077			13.69
70	301	1594	5.077			13.58
70	560	1248	5.051			12.33
80	35	2005	5.099			14.16
80	74	1692	5.088			13.21
80	140	1288	5.035			12.25
80	253	1098	5.024			11.51
90	15	1864	4.982			13.70
90	30	1479	4.981			12.64
90	50	1186	4.932			11.97
90	70	1049	4.959			11.30
100	5	1760	4.898	10.42	9.40	13.53
100	10	1406	4.853	10.30	9.26	12.99
100	16	1089	4.825	10.03	9.10	12.00
100	23	947	4.815	9.91	8.97	11.56
100	33	884	4.910	9.66	8.69	10.91
100	44	788	4.881	9.32	8.58	10.13
100	57	689	4.851	9.21	8.47	9.27
100	72	627	4.863	8.75	8.41	8.44

Table S2 GAB parameters and EMC calculated from the experimental data for three different temperatures at 50% RH used for Eq. 7 in the article.

Temperature (°C)	Cg	Km	Wm	EMC (g /g dry)
TMP4.7				
10	10.92	0.7682	0.06030	0.0854
21	8.705	0.7801	0.05571	0.0774
30	6.530	0.7488	0.05503	0.0700
BKP4.9				
10	12.07	0.8072	0.03984	0.0595
21	9.557	0.7998	0.03856	0.0555
30	7.818	0.7884	0.03729	0.0514
BSGWP5.1				
10	11.79	0.7685	0.04618	0.0660
21	9.132	0.7733	0.04361	0.0606
30	7.021	0.7349	0.04381	0.0556
BKP5.1				
10	12.72	0.7867	0.04144	0.0609
21	9.682	0.7837	0.04004	0.0567
30	7.848	0.7693	0.03921	0.0529
C5.9				
10	11.19	0.7808	0.04762	0.0686
21	9.103	0.78	0.04554	0.0637
30	7.405	0.7658	0.04429	0.0589
BSP6.2				
10	11.19	0.7808	0.04762	0.0686
21	9.103	0.78	0.04554	0.0637
30	7.405	0.7658	0.04429	0.0589
C6.5				
10	11.19	0.7808	0.04762	0.0686
21	9.103	0.78	0.04554	0.0637
30	7.405	0.7658	0.04429	0.0589
C8.5				
10	11.82	0.8053	0.03902	0.0580
21	9.074	0.8056	0.03733	0.0537
30	7.672	0.7951	0.03595	0.0498
C9.1				
10	12.81	0.8215	0.03616	0.0552
21	10.06	0.8206	0.0348	0.0516
30	7.732	0.8075	0.0339	0.0477
BKP9.6				
10	13.19	0.8059	0.04237	0.0638
21	10.39	0.8042	0.04036	0.0591
30	8.539	0.7923	0.03913	0.0550

Table S3 EMC at 21 °C and 50% RH calculated using the GAB equation (Eq. 7 in the article) for different degradation stages of paper[a]

Samples	DP[b]	EMC (g/g dry)	Samples	DP[b]	EMC (g/g dry)
TMP4.7	1458	0.0774	C6.5	2366	0.0534
	565	0.0710		2029	0.0536
	425	0.0692		1923	0.0525
	384	0.0678		1853	0.0522
	289	0.0665		1794	0.0506
				1687	0.0516
BKP4.9	1301	0.0555		1462	0.0528
70C	902	0.0535		1316	0.0499
	792	0.0520		1287	0.0500
80C	481	0.0500		979	0.0512
	434	0.0462		876	0.0487
				777	0.0503
BSGWP5.1	2177	0.0606		617	0.0492
	767	0.0557		506	0.0469
	530	0.0537		428	0.0473
	370	0.0528		276	0.0451
	337	0.0518			
			C8.5	1378	0.0537
BKP5.1	1188	0.0568		707	0.0518
	1024	0.0561		430	0.0501
	928	0.0553		295	0.0493
	786	0.0541		224	0.0480
	500	0.0515			
			C9.1	1338	0.0516
BSP6.2	540	0.0637		814	0.0495
	373	0.0618		491	0.0479
	334	0.0596		335	0.0470
	257	0.059		300	0.0469
	219	0.0576			
			BKP9.6	2419	0.0591
				1760	0.0577
				1460	0.0566
				1089	0.0568
				947	0.0563

[a] EMC measurements were done with each paper sample and were used for determining *Ma* in Table 2 of the article. EMC data for C5.9 are included with data of C6.5.

[b] DP values are DP_n for all paper samples except for TMP4.7 and BSGWP5.1 which are DP_v.

Table S4 Parameters of the equation BL as a function of *n* (Equation 13 in the article)

Samples	Slope *d*	BL_0[a]
TMP4.7	2.566	14.81
BKP4.9	3.745	9.80
BSGWP5.1	1.148	8.60
BKP5.1	4.849	12.84
C5.9	1.556	10.60
BSP6.2	3.526	10.90
C6.5	0.656	12.54
C8.5	1.026	15.14
C9.1	1.097	15.23
BKP9.6	1.986	14.22

[a] BL_0 is obtained from a curve fit program (TableCurve 2D v5.01) and may be different than BL in Table S1.

Error propagation on the decay simulation

Two key parameters are required to model paper decay accurately, E_a and pH_0, as shown in the article. Unfortunately, determining the value of E_a is time-consuming and obtaining the most accurate value can be challenging. The average standard deviation of E_a for the papers tested was approximately 3 kJ mol^{-1}, as reported in Table 1 in the article. This uncertainty on E_a has a significant impact on the simulated decay, as demonstrated in Fig. S1. The simulation for TMP4.7 is displayed with different standard deviation values (up to ±10%), and shows that, at high uncertainty on E_a, the prediction becomes meaningless. The deviation value of ±10% was used based on Coppola et al. (2018) who reported an E_a with a standard deviation of 10 kJ mol^{-1} corresponding to 10%. Even though our model bears considerably less uncertainty, the associated activation energy still varies slightly. Despite this inconvenience, simulations still provide valuable insight for relative comparisons in different climate conditions. The uncertainty on the temperature has a smaller effect on the decay rate: a difference of 3, 9, and above 25 °C is needed to match the deviations of 1, 3 and, 10 kJ mol^{-1} on E_a, respectively.

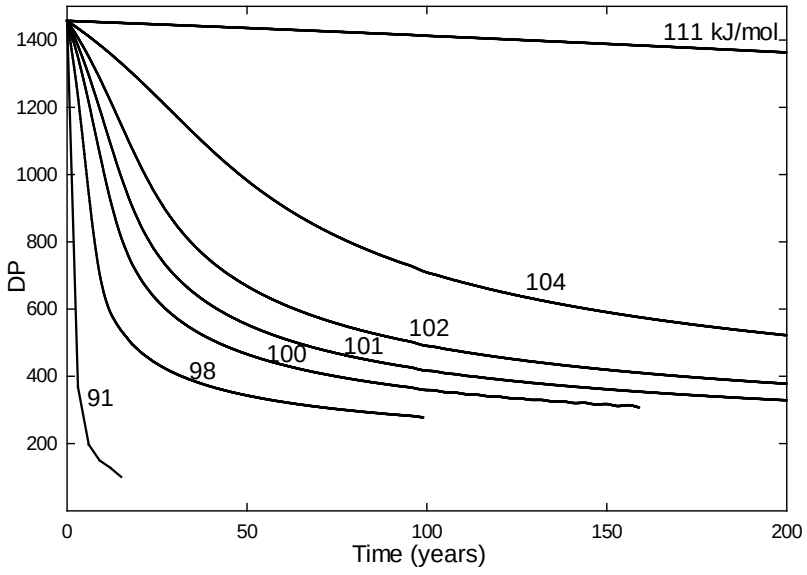

Fig. S1 Degradation simulation of TMP4.7 with an E_a of 102 kJ mol^{-1} at 21 °C and 50% RH with a standard deviation of ±1%, ±3% and, ±10%

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In this article, EMC_{GAB} was defined as ‘equilibrium moisture content (weight fraction: 100 × g H_20/g dry sample weight).’ It should be read without ‘100 ×’