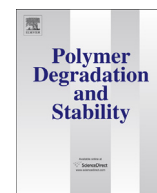




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Kinetics of accelerated degradation of historic iron gall ink-containing paper

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ABSTRACT

Although degradation of iron gall ink containing paper has been scientifically studied for almost 250 years, we still do not have a good understanding of the kinetics of the process. While many studies focussed on model samples to avoid the inhomogeneity of real historic samples or the need for sampling, this research was conducted on a selection of real documents. Accelerated degradation experiments were performed at six combinations of temperature and relative humidity (RH) in the intervals 50–80 °C/20–80% RH. The analytical methods were optimised such that sample consumption was minimised and errors and uncertainties were evaluated.

The results show that the rate of degradation, measured as change in the degree of polymerisation of cellulose in paper beneath ink, can be described in Arrhenius terms, and that the apparent activation energy for the process depends on the moisture content in the material. The variation is consistent with the process of hydrolysis becoming less prominent at lower moisture content values, although the results indicate that hydrolytic degradation predominates during natural ink-induced degradation. In the context of the historic samples used in the study, the presence of ink accelerated the degradation of paper by a constant factor of 1.59 in comparison to paper without ink, across the range of experimental *T* and RH. This indicates that a dose-response function could be developed for ink-induced degradation of paper.

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1. Introduction

Being the ink of choice from the early Middle Ages until the beginning of the 20th century, iron gall ink was the most important ink used in western history. Unfortunately, its chemical instability causes degradation of the support, which has been acknowledged as a major threat to library and archival heritage [1,2]. Ever since the first treatise on the stability of iron gall ink by the English chemist William Lewis in 1765 [3], extensive studies on the degradation of paper containing iron gall ink have been carried out. Conservators and material scientists are in agreement that acid-catalysed hydrolysis and metal-catalysed oxidation are the two major chemical processes that are responsible for the loss of mechanical strength of the paper support [4–6].

However, despite the large body of available research on the effect of different deterioration factors and the effectiveness of

conservation treatments [5–13], there is still no generally accepted kinetic model describing ink-induced natural ageing of paper. There are several limitations of the currently available data rendering it less useful for predictive modelling.

Firstly, the relative contribution of the two mechanisms to natural ageing is still not clear. The conservation significance of oxidative processes was assessed in several studies, either focusing on the beneficial effect of antioxidants or investigating oxidation products [14–16]. A potential dominant role of oxidation caused by iron was suggested by research on model samples where filter paper was immersed in model inks [7]. Such experiments shed light on the chemistry at the ink-paper interface in a highly acidic environment; however, they have less relevance to the degradation kinetics of historic paper with a surface ink application. It has been found that iron generally does not migrate substantially from the application [17–19], and that the oxidative effect of ferrous ions does not directly relate to loss of mechanical properties, especially in the absence of gallic acid [20]. Therefore, the effect of iron on the substrate underneath ink could be limited in a real ink-paper system.

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Secondly, the dependency of the degradation rate on temperature and RH needs to be quantified in the context of natural ageing. The many accelerated degradation conditions in use [21,22] make it difficult to extrapolate the results. Although the applicability of results obtained at 60–100 °C to room temperature has been theoretically and empirically demonstrated for paper degradation [23,24], it is unknown to what extent iron gall ink alters the major reaction pathways.

Water participates as both a reactant in hydrolysis and the reaction medium [22] and has been found to act as a controlling factor [24], determining the degradation pathways [21,25]. Cyclic RH conditions are often used in accelerated degradation experiments (e.g. 3-h cycles of 35%–80% RH) [6], as this causes faster degradation and is believed to better represent real ageing conditions [6,9,26,27]. However, such RH fluctuations are unusual in libraries and archives, where most fluctuations are within $\pm 10\%$. If stored in boxes, the extremes can easily be reduced to $\pm 5\%$ [28].

Thirdly, a quantitative relationship between degradation and material properties needs to be established and supported by sufficient data from historic samples. Due to the obvious constraints regarding sampling, model inks and papers are mostly used to understand the impact of ink components on degradation. Given the variability of historic iron gall inks and the possible effect of the accumulated degradation products over time [8,29,30], the representativeness of results obtained with model samples, where variability can be minimised, is limited. Recently, using historic samples, the extent of degradation (defined as colour change on the verso of the inked areas) was found to be correlated with the acidity of the inked areas, paper grammage, and the width of ink lines. Total iron content was also suggested to have a significant contribution, although beyond 100 $\mu\text{mol g}^{-1}$ its effect levelled-off [8]. These findings reveal that even samples vary considerably, it should be possible to develop a general dose-response function [31], linking the rate of ink-induced paper degradation with the most significant environmental parameters and material properties.

Fourthly, for a model to be useful, the degradation rate would need to be expressed as change in a property that is of actual conservation concern. Colour [5,11,13], mechanical strength [5,6,10,12], degree of polymerisation (DP) of cellulose [7,8] and cellulose crystallinity [9] have been used so far. To conservation practice, mechanical properties might be most meaningful in relation to fitness-for-use [32]. Bursting strength is considered to reflect the conditions of mechanical stress during use [6], however, the measurement uncertainty is high and large amounts of samples are required, which makes the technique unsuitable for historic samples. Viscometrically determined DP has been found to correlate with bursting strength of ink lines on paper [33] and the rate constant of paper degradation with and without ink may be expressed as loss of DP over time using the Ekenstam equation [24,34–36]. Furthermore, this DP has also been used to define the damage threshold of historic paper with iron gall ink, which would be of significance for decision making in practice [37].

To explore the above points, this research investigates the influence of iron gall ink on the mechanisms and rate of paper degradation. A series of accelerated degradation experiments were carried out using historic samples to explore whether a general dose-response model can be developed to quantify the synergistic effect of material properties and environmental impacts. This would support collection management in libraries and archives from a viewpoint of long term storage and preservation.

2. Methodology

2.1. Samples

Ten archival paper documents containing iron gall ink from 18th to 20th century of low historic value were purchased and used as sacrificial samples. In comparison with previous research, these cover a good variety of archival paper and ink properties (Table 1), although they do not seek to represent a statistically representative selection and the ink might not have been ‘pure’ iron gall. The extent of degradation of the samples varied and discolouration of paper was visible in some samples; however, none have reached an advanced stage of degradation yet. This was to ensure that degradation was still measurable as a consequence of accelerated degradation experiments. The presence of Fe^{2+} was confirmed using the bathophenanthroline test [38]. The method of paper production was estimated based on the presence of chain and laid lines. Paper thickness (resolution 0.001 mm) and width of ink lines (resolution 0.01 mm) were determined by averaging three measurements using a calliper.

2.2. pH

pH was determined for areas with and without ink in each document before degradation experiments, using the cold extraction method [39] which was modified to minimise the sample consumption [40]. Areas with ink were cut out with a scalpel. 1.0 ± 0.1 mg of a sample was extracted in 1 mL deionised MilliQ water (Millipore, Molsheim) and a Mettler Toledo SevenGo pro™ pH meter and an inLab® 413 SG (PN 51340288) electrode were used to take measurements. The typical uncertainty was 0.2 pH unit and the results in Table 1 represent averages of the determinations for three random samples from the same sheet.

2.3. Iron content

The total amount of iron was analysed for paper with ink (average sample amount used 0.8 mg) and without ink (2.4 mg in average) using inductively coupled plasma mass spectrometry (ICP-MS). Samples were placed in 100 μL of 65% HNO_3 for 24 h at room temperature and were diluted to 10 mL with MilliQ water before analysis. The multi-element standard solution IV (1113550) from Merck (Darmstadt, Germany) was used for calibration. The results are expressed in μmol of Fe per g of sample (Table 1). Triplicate measurements were taken of one sample (YL-IGI-8) which gave a standard deviation of iron content of 130% for paper and 13% for paper with ink.

2.4. Degree of polymerisation

A viscometric method based on BS ISO 5351 [41] was used to determine the intrinsic viscosity of samples before and after accelerated ageing experiments. Paper samples with and without ink were sampled from each document. Paper samples with ink were prepared by cutting out ink lines with a scalpel such that paper areas without ink were entirely avoided. Each sampling of such samples contained several lines of writing. Limited by sample availability, the sample weight was ~ 15 mg, dissolved in 5 mL deionised MilliQ water mixed with 5 mL cupri-ethylenediamine solution (1 mol L^{-1} , Merck). A modified apparatus was used to enable us to perform at least three repeated measurements. The DP was calculated using the Mark-Houwink-Sakurada equation: $\text{DP}^{0.85} = 1.1[\eta]$ [42] and DP before degradation experiments are presented in Table 1. Due to sample availability, a single

Table 1

List of the historic paper samples containing iron gall ink. Iron content represents the total amount of Fe²⁺ and Fe³⁺. The missing values of the iron content of YL-IGI-9 were due to lack of available sample for the experiment.

Sample No.	Year of writing	Method of paper production	Paper thickness (mm)	Typical width of ink lines (mm)	Paper without ink			Paper with ink		
					pH _p	DP _p	Iron content (μmol·g ⁻¹)	pH _i	DP _i	Iron content (μmol·g ⁻¹)
YL-IGI-1	1752	Handmade	0.175	0.84	4.4	723	0	4.5	464	56
YL-IGI-2	1760	Handmade	0.158	0.67	5.7	1318	2	5.8	744	31
YL-IGI-3	1771	Handmade	0.130	0.68	4.7	879	0	4.3	625	44
YL-IGI-4	1793	Handmade	0.118	0.72	4.5	983	4	5.2	698	75
YL-IGI-5	1877	Machine-made	0.101	1.05	5.2	922	0	5.3	614	106
YL-IGI-6	1885	Machine-made	0.125	0.66	5.7	940	4	5.8	915	31
YL-IGI-7	1914	Machine-made	0.126	0.69	4.8	654	0	4.8	598	22
YL-IGI-8	N/A	Machine-made	0.106	1.07	4.5	492	1	4.5	438	40
YL-IGI-9	N/A	Machine-made	0.109	0.60	5.2	536	NA	5.2	465	NA
YL-IGI-10	N/A	Handmade	0.099	0.74	4.3	678	0	4.3	714	11

determination of DP was made in most cases.

The reduced amount of sample and solvent still gave the same overall uncertainty as the standard, for Whatman (Maidstone, UK) filter paper No. 1 (<1%). The inhomogeneity of historic samples lead to higher uncertainties and triplicate determinations for areas with and without ink on YL-IGI-1, YL-IGI-5 and YL-IGI-10 were performed to assess this. Coefficients of variation of paper without ink (CV_p) and paper with ink (CV_i) are presented in Table 2. For handmade papers, the DP of paper with ink and without ink had a similar uncertainty of ~8%, demonstrating the inhomogeneity of the paper and of the ink applications. For the machine-made paper, the paper with ink showed a similar uncertainty of ~7% as handmade papers, whereas paper without ink showed a distinctly smaller uncertainty of ~2%, an indication of the higher homogeneity of such paper.

It has been reported that β-elimination reactions could lead to further chain scission of the cellulose samples in CED [43]. Since the relative amount of oxidised carbonyl groups compared to the reducing end groups does not seem to be increased by the presence of iron gall ink [16,35,44,45] and a reduction pre-treatment has not been found to be significantly beneficial (0.2–4.3%) [43] compared to the uncertainty of the historic samples (Table 2), no pre-treatment of the samples or correction of the measured data was carried out.

2.5. Accelerated degradation

Six combinations of *T* and RH were used in accelerated degradation experiments (Table 3) to explore the effects of environmental parameters. Each document was cut into several parts, each of them submitted to different degradation conditions. Samples at 50 °C and 40% RH were degraded in a VWR VENTI-Line® oven (Radnor, US) coupled with a V-Gen™ Dew Point/RH Generator (InstruQuest Inc., US), and the conditions were monitored using SL54TH temperature & humidity data loggers (Signatrol, Tewkesbury, UK). All other experiments were carried out using a Vötsch Climate chamber (Type VC 0018, Balingen-Frommern, Germany). Due to sample availability, only one data point was obtained after degradation times as specified in Table 3, determined such that

Table 2

Coefficients of variation for DP of three selected paper samples with iron gall ink (CV_i) and without ink (CV_p).

Sample	Paper production method	CV _p	CV _i
YL-IGI-1	Handmade	8.2%	8.3%
YL-IGI-5	Machine-made	1.9%	7.3%
YL-IGI-10	Handmade	9.3%	8.5%

substantial degradation was measurable (DP loss >10%). The samples were conditioned at room conditions (22 ± 1 °C, 50% ± 10% RH) for at least 24 h before analyses and no further pre-treatment was carried out.

2.6. Model inks

Four model inks were synthesized based on historically representative recipes to estimate their density and the concentration of solids [29]. Each of the inks contained tannin, ferrous sulfate (FeSO₄·7H₂O, Sigma-Aldrich), gum Arabic (Kremer Pigmente), and water. The source of tannin and the molar ratio of FeSO₄·7H₂O to gallic acid varied, depending on the recipe (Table 4).

For Ink 1, 5.00 g of coarsely crushed Aleppo gall nuts were boiled in 60 mL MilliQ water for 30 min, stirred at regular intervals. FeSO₄·7H₂O and gum Arabic were dissolved in 20 mL of MilliQ water each and added to the Aleppo gall nuts suspension. Inks 2–4 were prepared by dispersing the chemicals separately and mixing the dispersions in a similar manner. After production, the dispersions were left in capped glass bottles for eight months to complete the precipitation, following which the content of ink solids was estimated by measuring the density of the colloidal suspensions. In average, the inks contained 0.04 g mL⁻¹ of solids.

3. Results and discussion

3.1. Evaluation of errors and uncertainties

According to the viscometry standard [41], the efflux times of sample solutions should be similar in order to minimise biases due to turbulent flow and uncertainty in extrapolation of intrinsic viscosity. However, because of the extremely limited sample availability (only one measurement per sample possible) and sample variability, the efflux times ranged from 39 s to 64 s, the majority being around 45 s. In order to evaluate the influence of efflux time on DP determinations, DP of Whatman No. 1 filter paper samples of 3 mg–30 mg was determined using the standard viscometric method, as shown in Fig. 1. It is evident that the difference in DP

Table 3

Environmental conditions and degradation times used for accelerated degradation experiments.

	20% RH	40% RH	80% RH
50 °C		90 d	
60 °C	28 d		
70 °C	10 d		7 d
80 °C	8 d		6 d

Table 4
Recipes used for the synthesis of model iron gall inks.

Tannin source	Ink 1	Ink 2	Ink 3	Ink 4
	Aleppo gall nuts (Kremer Pigmente)	Tannic acid extracted from Chinese gall nuts (Sigma-Aldrich)	Gallic acid (Sigma)	Gallic acid (Sigma)
Molar ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to gallic acid	18:13	18:13	18:13	3:1
Tannin or gallic acid (g)	5.00	2.50	2.21	0.10
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (g)	5.00	5.00	5.00	5.00
gum Arabic (g)	2.50	2.50	2.50	2.50
H_2O (mL)	100	100	100	100
pH	2.8	2.8	3.1	2.6

determinations resulting from the differences in efflux times as measured in this research, is smaller than the typical uncertainty of DP determination of 8% for paper with ink and handmade paper, and 2% for machine-made paper. Therefore, differences in efflux times were not considered to be statistically significant in comparison with the overall uncertainties of DP determination of the samples used in this research.

Two further potential errors in relation to sample preparation were evaluated: sample cutting and estimation of cellulose content. Sampling of paper with ink was performed using a scalpel along the ink lines, which resulted in a collection of thin cuttings. This could result in a lower viscosity as a result of mechanical degradation. The effect of cutting a sample into thin strips (~1 mm) was assessed using Whatman No. 1 filter paper. With the efflux time ~60 s, cutting of a sample resulted in $\text{DP } 2393 \pm 90$ ($n = 4$), compared to the standard ($\text{DP } 2510 \pm 56$, $n = 5$). The systematic error is 4.7%, which is lower than the uncertainty of DP determination of historic handmade paper. However, all DP values for paper with ink were corrected by a factor of 1.05.

The content of sizing and other additives (except fillers) in historic paper is often considered to be negligible, and even if not, there is rarely enough sample available to perform a rigorous

determination of water and ash content. Therefore, calculations of DP in this research were based on the assumption that at room conditions, paper contains ~95% of cellulose and 5% water. However, for samples with ink, an estimation of the proportion of the latter is needed. In order to evaluate whether the %m/m of ink could lead to significant underestimation of DP, ink content was estimated by calculating the average concentration of solids in iron gall inks (0.04 g mL^{-1}), estimated thickness of a dry ink application (0.1 mm) and grammage of historic papers (0.0037 g cm^{-2} to 0.0105 g cm^{-2}) as acquired from 97 historic samples from 14th to 20th century [8]. Based on these estimations, the ink content is typically 4%–10% w/w.

To validate this assumption, the ink content of a rag paper sample (reference historic material collection at UCL Institute for Sustainable Heritage) with an intensive ink application was analysed by sampling adjacent areas of paper with and without ink. After weighing, the calculations indicated an 11% ink content, suggesting that the above estimation of the average intensity of iron gall ink application is reasonable.

If the above estimations are applied to the samples used in this research, the average ink in %w/w is ~5%, which results in ~6% underestimation of DP. We therefore applied an additional correction factor of 1.06 for DP determinations of paper containing ink, to account for this systematic error.

3.2. Effect of iron gall ink on degradation mechanisms

Assuming that the presence of historic ink does not lead to significant deviations to the moisture content (MC) of the paper underneath, moisture content of the samples during accelerated degradation experiments was calculated using the equation given by Paltakari and Karlsson for 'fine paper' [46], which correlates well with moisture content as determined using an infrared sensor [24]. The results for different combinations of T and RH are presented in Table 5.

For the acidic inks, it would be reasonable to assume that hydrolysis is more prominent at higher moisture content. To verify this hypothesis and explore whether the degradation mechanism depends on moisture content, we grouped the samples into two groups with $1.8\% \pm 0.4\%$ MC (all at 20% RH) and $5.1\% \pm 0.9\%$ MC (all other accelerated degradation conditions). The Arrhenius relationship was analysed and the Arrhenius equation parameters (pre-exponential factor, apparent activation energy) were calculated (Table 6).

In Fig. 2, we examine how the apparent activation energies for samples with ink (E_{a_i}) and samples without ink (E_{a_p}) at the lower and higher moisture contents correlate. In addition, t -test confirms that at 95% confidence level, differences in apparent activation energies between paper with ink and paper without ink degraded at the same moisture content are not statistically significant. It is clear that there is a correspondence of mechanisms at play in paper

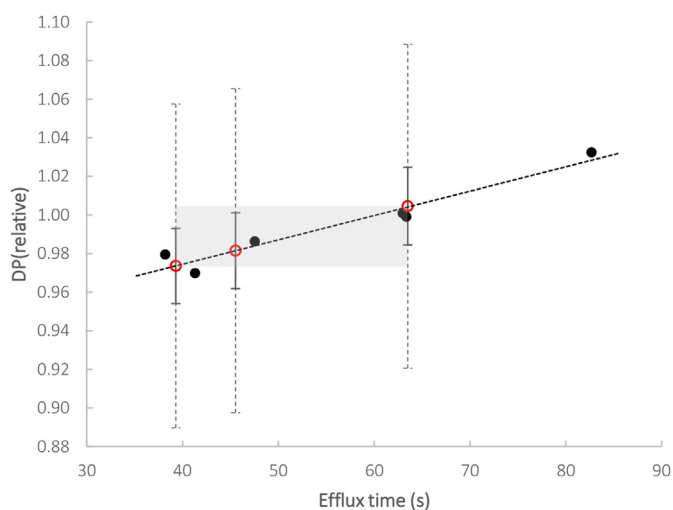


Fig. 1. DP determination against efflux time, as obtained for Whatman No. 1 filter paper samples of different weights (solid circles), expressed as relative to the average DP of the same sample obtained at 0.021 g (~63 s efflux time). The shaded rectangle reflects the range of efflux times that was measured for historic samples (39–64 s) and the associated potential systematic error (<3%). The empty circles represent the minimum, mode and maximum values for the same. Error bars denote the typical uncertainties of DP determination for historic paper with ink and handmade historic paper (8%, dotted line bars) and machine-made historic paper (2%, full line bars). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Effect of iron gall ink on degradation rate

Since the linearity of change $1/DP$ over time has been established for both un-sized model papers and sized original papers with and without ink [35,36], two measurements of DP, i.e. before and after accelerated degradation experiments, were considered sufficient to estimate the rate constant (k , year⁻¹) of degradation using the Ekenstam equation [34]. The rate constant (k) of iron gall ink induced degradation of paper was studied comparatively to the degradation rate constant of paper without ink for the six accelerated degradation experiments. To account for the range of values of k , we compare the values for pairs of data obtained for the same historic document sample in a log-log plot (Fig. 3). Evidently, there is a high correlation between the values of paper with ink (k_i) and paper without ink (k_p) which demonstrates that the presence of ink induces a constant promotion of degradation across the range of samples and accelerated degradation conditions. This acceleration factor derived from the regression analysis is 1.59 ($k_i = 1.59 \cdot k_p$) with intervals of 1.22–2.06 estimated from the standard errors.

This acceleration factor is in agreement with the results obtained by Henniges et al. [15] and Potthast et al. [16] that the number of reducing end groups in inked areas of historic paper is about 1.2–2.5 times as much as that in areas without ink. The correlation of the rate constants reveals that iron gall ink promotes the degradation of paper substrate equally throughout the range of T and RH as used in the experiments. This indicates that the promotion effect of ink on degradation rates is independent of degradation conditions, and the associated shifts in reaction pathways.

According to Kolar et al. [8], iron accelerates degradation to a constant factor when its concentration surpasses $100 \mu\text{mol g}^{-1}$ as measured by proton-induced X-ray spectrometry (PIXE). Given that the iron content we measured represents the bulk value rather than a surface value measured by PIXE, we applied a factor calculated as $\text{thickness}_{\text{paper}}/\text{thickness}_{\text{ink deposit}}$ to the iron content values for paper with ink in Table 1, under the assumption that the deposit thickness of ink is $\sim 0.035 \text{ mm}$ [18,53]. The adjusted iron content of our samples gives an average of $165 \pm 95 \mu\text{mol g}^{-1}$, almost all beyond the levelling-off value of $100 \mu\text{mol g}^{-1}$. Therefore, iron

could have contributed to the faster degradation induced by ink with a constant acceleration factor, which could potentially explain the correlation of rate constants observed in Fig. 3.

According to Zou et al. [24], for hydrolysis-dominated cellulose degradation, the pre-exponential factor A_a in the Arrhenius equation can be expressed as $A_a = A_{a0} + A_{a2}[\text{H}_2\text{O}] + A_{a5}[\text{H}_2\text{O}][\text{H}^+]$, which expresses the dependence of the degradation rate on moisture content, $[\text{H}_2\text{O}]$, and on the acidity of paper, $[\text{H}^+]$. The pre-exponential factors were calculated from the intercepts of Arrhenius plots for paper samples with ink (A_i) and paper samples without ink (A_p) (Table 6). As is evident, it is generally the case that $A_i > A_p$ at both moisture contents. Assuming that the difference in moisture content between paper with and without ink in adjacent areas is minimal, this suggests a larger amount of hydrogen ions may be present in the paper underneath ink lines than paper without ink, which may exert a promoting effect on degradation.

3.4. Considerations about the measured acidity of iron gall ink

The effect of acidity of iron gall ink on paper degradation has long been acknowledged. The acidity of ink depends on the content of gallic acid, ferrous sulfate, and acidic additives such as vinegar, wine or even sulfuric acid [8,29]. It has been frequently assumed that iron gall ink adds acidity to the paper substrate, yet not much literature data is available for quantitative analysis. While all the samples in our study are acidic (Table 1), pH of paper without ink (pH_i) does not differ much from pH of paper without ink (pH_p). The slight difference in pairwise pH values is within the uncertainty of the analytical method, which is ~ 0.2 pH unit [40], suggesting that iron gall ink does not seem to induce a lower pH of the paper substrate as measured in aqueous extracts.

In order to estimate the amount of acidity that can be introduced by iron gall ink into paper, we considered the four model inks (average $\text{pH } 2.8 \pm 0.2$, Table 4). The pH of these inks is in a good agreement with the values obtained for different ink recipes reported in the literature: 2–3.5 [30,54]. The pH of paper underneath ink, as well as the pH of aqueous extracts of paper with ink, can be calculated by taking into account the argument in Section 3.1, where we estimated that the %w/w of ink on the paper samples used in this study is $\sim 5\%$ in average, from which the volume of applied fresh ink and conversely, the amount of added acidity, can be calculated.

In Table 7, we show the pH values as calculated for the volume of water contained in paper with 5% moisture content, and in the volume of water as used for pH determination. In these calculations, we look at various values of paper pH before ink application and we assume that acidity is homogeneously distributed throughout the thickness of paper.

These calculations indicate that the amount of acidity is so small that after extraction, the pH of the resulting extract is high due to dilution, while the pH of the condensed water phase in paper at 5% MC could be considerably lower. These estimations clearly demonstrate that while there may not be a detectable difference in pH between paper with and without ink, as measured using the cold extraction method, the acidity in the paper substrate beneath ink could still be considerable. It is worth pointing out that in reality, acidity may not be homogeneously distributed in paper beneath ink and is affected by the alkaline reserve of the paper before having been written on. It seems that methods are needed to be able to assess the pH of paper beneath ink locally and more reliably.

A linear correlation between acidity and degradation rate of paper has been suggested by several studies. According to the study of bleached bisulfite pulp and bleached kraft pulp at about 6% MC by Zou et al. [24], a 59% increase in the rate constant would require

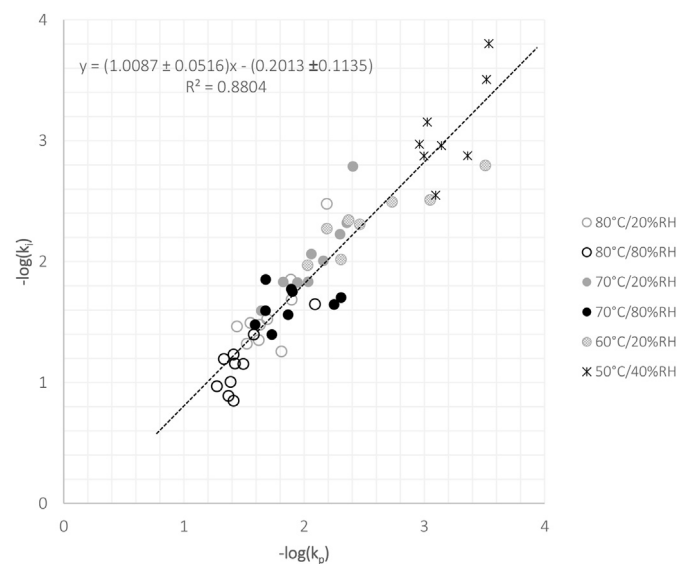


Fig. 3. Comparison of rate constants (year⁻¹) of paper samples containing iron gall ink (k_i) and without ink (k_p) at six different combinations of T and RH during the accelerated degradation experiments, with the associated linear fit across all data points.

Table 7

Estimations of hydrogen ion concentrations $[H^+]$ and pH in water contained in paper underneath iron gall ink (5% MC) and in the volume of aqueous extract as used for pH determination. We assume the pH of inks to be 2.8 and various starting pH values of paper prior to ink application.

pH _i	pH _p	$[H^+]$ (mol·L ⁻¹) in paper underneath ink	$[H^+]$ (mol·L ⁻¹) in 1 mL water extract	pH of paper underneath ink	pH of 1 mL water extract
2.8	3.5	5.82×10^{-2}	3.19×10^{-4}	2.7	3.5
2.8	4.5	5.80×10^{-2}	3.45×10^{-5}	2.8	4.5
2.8	5.5	5.79×10^{-2}	6.06×10^{-6}	2.8	5.2
2.8	6.5	5.79×10^{-2}	3.21×10^{-6}	2.8	5.5
2.8	7.5	5.79×10^{-2}	2.93×10^{-6}	2.8	5.5

a decreased pH of paper of ~0.3 unit. The dose-response function for historic paper suggests a larger pH decrease of ~1 unit [23]. Based on the above estimations, it is likely that a sufficient amount of hydrogen ions can be donated by the ink to the paper underneath, to enable a 59% faster degradation than the surrounding paper without ink.

This study demonstrates that in the context of samples as used here, the 59% acceleration factor could be applied to the dose-response function for historic paper [23], and this would constitute the dose-response function for iron gall ink-containing paper as used in our research. However, the samples in this study were rather similar, with similar pH, paper thickness and amount of ink application. It is known from previous research [8] that these parameters would need to be taken into account so that not only the variability of ink composition but also that of the support and of the application itself, could feature in such a function. Naturally aged historic samples covering a wide range of material compositions and degradation states could be used to support the modelling and validation processes, and non-destructive analytical methods [37,55,56] could be used to obtain the required amount of data. This is currently the focus of our work.

4. Conclusions

A series of accelerated degradation experiments using historic samples was carried out to investigate the iron gall ink induced degradation of paper. The rate of degradation was estimated in terms of decrease of the degree of polymerisation of cellulose in paper measured using viscometric method. Uncertainties and systematic errors were evaluated. The following conclusions can be reached:

- Arrhenius relationship was demonstrated to be applicable to paper degradation in the presence of iron gall ink over temperatures 50–80 °C.
- Activation energies were found to be different for samples degraded at different moisture contents, which suggests a difference in reaction pathways. This finding also suggests that the degradation mechanism of naturally aged papers with ink is likely going to be the same as for the samples artificially degraded at 5% moisture content, and an extrapolation of the results obtained from these accelerated degradation experiments to natural ageing processes is likely going to be valid.
- The activation energies obtained from paper samples with ink at 5% moisture content were similar to those values that have been reported for hydrolytic chain scission of cellulose, suggesting that hydrolysis is likely to be the dominant mechanism for ink induced degradation of paper during natural ageing.
- As expected, the presence of iron gall ink promoted the rate of degradation of the paper support. In the context of the sample set used in this research, ink accelerated the degradation by 59% throughout the range of environmental conditions investigated (50–80 °C and 20%–80% RH).

- Acidity introduced by iron gall ink is likely to be the main factor promoting the faster degradation, which confirms earlier observations. However, there is evidence that oxidation gains in importance as moisture content of the support decreases.
- The pH of inked areas as measured using the currently available methods, i.e. the cold extraction method and the correlated methods such as the surface method, needs to be interpreted with caution. Neither of these may give accurate results for the hydrogen ion concentration within cellulose beneath an ink application.

Having thoroughly evaluated the limitations, as well as the uncertainties and the systematic errors of the techniques and methods used in this study, it still became evident that a general dose-response equation quantitatively describing the dependency of the degradation rate constant on environmental factors and material properties is likely going to be possible. However, for this to be achieved, we would need analyses of a wide variety of naturally aged samples, covering a large variety of material compositions and degradation states. Having such a function would significantly improve collection care and preventive conservation in heritage institutions with invaluable collections of iron gall ink documents, scores and drawings.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymdegradstab.2017.07.010>.

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