METHODOLOGY OF KINETIC INVESTIGATION OF CELLULOSE DEGRADATION

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1. Introduction

Paper made since the middle of XIX century up to eighties of the current one is subject to autodestruction due to the presence of acid substances. The reasons for the acidity of paper are described by Carter [1]. Acids result in the hydrolysis of cellulose. Shortening of the cellulose chains implies its degradation, and, consequently, degradation of paper. This process depends on acidity of paper, temperature, water content in paper and on the presence of oxygen. Degradation of paper at room temperature is so slow, that its symptoms can be observed only after some years. It can be stopped by neutralization of acids and introduction of alkaline excess. A few technologies of deacidification of printed materials have been developed. They are described in the Porck's report [2].

2. Accelerated Ageing Tests – a Literature Review

Low rate of paper degradation results in a necessity of using artificial ageing tests. An ageing test consists in accelerating the observed changes of paper properties – usually by using high temperature. Ageing tests are used in the studies of degradation rate and mechanism, as well as for the assessment of long-lasting results of preservation procedures including deacidification of paper. The above-mentioned tests are widely used, nevertheless the reliability of their results is subject to various reservations.

The current state of knowledge in this field is summed-up in the next Porck's report [3], published in 1999. This report is a review based on about 150 papers and opinions of experts. In this review Porck presents the "state of the art" of knowledge about the ageing tests. Some of his most important opinions are given below.

The decision-making and reserving the necessary funds in the field of planning the conservation activity require a rational assessment of degradation rate of library collections and efficiency in their preservation. At the same time, experimental basic research on the credibility of artificial ageing methods is conducted only on a limited scale. There is no agreement on the most suitable conditions at which the accelerated ageing should be performed. Basing on some dozens of examples, Porck presents commonly applied ranges of temperature, relative humidity and ageing periods. In conclusion, he finds that a stalemate and uncertainty exists in which the views and opinions diverge. In this situation, an exchange of knowledge and experience between the researchers and decision-makers should be improved in the matters concerning the analysis based on the accelerated ageing of paper.

Porck's judgment is well demonstrated in an impressive example given in the book "Properties of Paper – the Introduction" [4]: "Some persons have taken 3 days at 100°C to be equivalent to about 25 years of natural age, while others have interpreted the same conditions to represent 300 years!".

Information sources are not evaluated in the Porck's report [3]. In our opinion the papers by Zou [5, 6] and Havermans [7] are worth a special attention. Earlier works of other authors

have been critically judged by Zou who expressed his reservations and concerns. This criticism is best presented when considering the mid-titles of his papers:

- The arbitrary definition of paper degradation rate
- The use of mechanical properties to obtain degradation rates
- No critical examination of the Arrhenius equation
- No quantitative kinetic description on the effect of acidity and moisture content
- No quantitative comparison of the results of accelerated and natural ageing.

The Zou's criticism is of constructive nature, as solutions to the discussed problems are given. The most important results are as follows:

- Elaboration of a kinetic model of paper degradation, allowing for calculation of the polymerization degree (DP) as a function of time (t), temperature (T), content of water in paper ([H₂O]), and pH of paper;
- Finding the dependence between the apparent activation energy of a network of parallel reactions and the activation energies of the individual reactions of the network. It seems that this result greatly surpasses the issue of paper degradation and is a significant advance in the general development of the chemical kinetics;
- Finding the qualitative agreement between predictions of the kinetic model and the results of natural ageing for a series of ca. 20 bleached sulphate cellulose pulps stored for 22 years.

These results are a real breakthrough in the research of the kinetics of paper degradation.

J. Havermans [7] summarized the results of the European Research Project on the influence of air pollutants upon the degradation of paper. Four laboratories used some dozens of research techniques in the period of this Project duration. Well-defined, standard sorts of paper, were especially developed for the Project. Some of them contain cellulose exclusively, do not contain any filling agents, and they were not sized. Significant quantities of these standard papers have been prepared, and they have been stored in standard conditions (23°C, 50% relative humidity (RH), no light). Havermans' own words are: "these materials could and should also be used in any future research program in order to compare and expand the results".

3. Initial Assessment of the Literature Data – Goal of the Present Paper

Zou has found the kinetic model of degradation of lignin-less paper [6]. Parameters of this model are obviously specific to the degradation process. When one knows these parameters, it is possible to calculate the polymerization degree and the rate of its change for any combination of experimental data. Therefore we can, as Zou has done, to extrapolate the results to the room temperature in order to estimate the life expectancy of paper. Under these circumstances, discussion about the choice of the most suitable conditions of accelerated ageing of paper [3] becomes pointless. On the other hand, competence for re-creation of Zou's results, their reproducibility, and finding the limits of model application – become the most significant problems. In this context, terseness of description of the experiments in Zou's paper should be stressed.

Divergences in the previous research of paper degradation are due not only to different experimental conditions but also to different paper samples. As emphasized by Porck [3], paper is a multi-component system. But even the concept of a paper component can be doubtful. Maybe more relevant is the description: "paper is an ill-defined system" – but bickering over words is of no consequence here. Without any doubts, in the model experiments well-defined standard samples ought to be used. PAPER 1 and PAPER 2 from the

Havermans' paper [7] fulfill these criteria. The only component of both papers is cellulose of different origin but with a similar polymerization degree. Under these circumstances, application of Havermans' samples for testing the Zou's model seems to be the most suitable direction of studies. This is also a general, long-range aim of our studies.

4. Experimental Methods

Reams of PAPER 1 (P1 – bleached sulphite softwood cellulose paper) and PAPER 2 (P2 – cotton linters cellulose paper) have been obtained from TNO (Centre for Paper and Board Research, Delft, Netherlands). P1 contained exclusively cellulose from coniferous trees, whereas more then 95% of P2 mass is the cellulose originating from cotton linters. Paper [7] contains a general description of both paper sorts. Detailed information can be found in the report [8, p. 62–63].

Strips of the examined paper were inserted into closed vessels (with the capacity of 1 dcm³); more details of the vessel construction are given further in this paper. 100 cm³ of water was poured into a vessel in order to attain the 100% relative humidity (RH). <u>There</u> was no direct contact of paper strips with water. Not-completely-closed vessels were inserted into automated dryers (VENTICELL, BMT, Brno) and kept in darkness. Uninterrupted work of the dryers was monitored by a microcomputer. Each vessel was closed after the desired temperature and pressure had been stabilized. The temperature stability was $\pm 0.5^{\circ}$ C, and the time of ageing was measured with a precision of 30 minutes. After the assumed time of ageing had been attained, the vessels were cooled down and opened. Then the water volume was measured in order to determine the amount of water lost (due to a leakage) during the experiments lasting for many days, whereas the paper samples were conditioned. The conditioning was performed at constant partial pressure of water vapour over a saturated solution of magnesium nitrate (at RH \cong 50%) for at least 24 hrs at 23°C.

If the degradation of paper was done at another humidity value (RH = 75%), saturated solution of NaCl was placed on the vessel bottom. As the sodium chloride was deposited on the paper strips due to some process of mass transfer (remember that paper had no contact with the solution), it had to be removed form the paper strips – after the measurement had been finished – by double rinsing with water. Amount of the removed salt was determined from the difference of paper mass before and after rinsing. It has been found that NaCl was deposited on the individual strips in a very inhomogeneous way. The NaCl content changed in a wide range – from 0,02 % up to 10 %. Other details of the experimental procedure were the same for both humidity values – 100% and 75%.

The limiting viscosity number $[\eta]$ of cellulose dissolved in the solution of cupri-ethylenediamine (CED) produced by Merck Co. was determined according to Polish Standard PN– 92/P–50101/01 [9]. Glass viscometers of Werner Glass&Instrument AB, Sweden, were applied. During the relative viscosity measurements in the range of 6–10 the mean shear velocity was 204±31 s⁻¹, whereas the standard PN–92/P–50101/01 requires this velocity to be in the range of 200±30 s⁻¹. Therefore one can say that <u>almost</u> all measurements were done strictly at the required shear velocity.

The mean polymerization degree DP was calculated from the Immergut equation [10]:

$$[\eta] = Q \cdot DP^a \tag{1}$$

where: Q = 1.33 ml/g, a = 0.905

Surface pH values of paper were measured with the pH-meter produced by Hanna Instruments, model HI 9318, with a contact electrode, according to the Polish Standard PN- 81/P–50149 [11]. Deionized water was used, with the conductance lower than 0.1 mS/m. Concentration of hydrogen ions in the solution was corrected to the initial volume of 100 ml.

5. Vessels for the Accelerated Ageing of Paper

Zou [5] used glass containers. On the bottom of each of them a glass vessel was placed with a solution used for supporting constant humidity. The most extreme conditions used in

these experiments were: $T = 100^{\circ}C$ and RH = 100%. However, corrosion of glass due to water, especially in liquid state, is a well-documented effect known in the technology of glass industry [12]. Therefore, for our experiments easy-to-make vessels have been prepared without application of any glass or easily corroding metals.

Polypropylene bottles with wide necks and screw-caps, of 1 liter capacity each (Merck catalog no. 1286 62) have been adopted for experiments. According to specification, these bottles are water-vapour resistive at the temperature of 121°C. The vessel scheme is presented in Fig. 1. A teflon moulder (produced by Z.A. Tarnów) with incisions at the bottom (used for



Fig. 1. A polypropylene vessel (with a screw-cap fitted with a teflon moulder) for the experiments of accelerated ageing of paper.

Table 1

the purpose of fastening the paper strips) was attached with a screw to the screw-cap. Paper was held with a Pt or Pt-Ir cotter. The screw, made of *Tarnamid* (polyacryl amide, produced by Z.A. Tarnów) was sealed with a teflon tape.

6. Degree of Polymerization of Non-aged Paper

Sheets of paper were selected at random from the reams of both papers (P1 and P2) – five from each ream. In each sheet a sample of paper was taken from a randomly selected

Dr values of non-aged paper							
Paper 1		Paper 2					
892		876					
928		807					
922	$\overline{DP} = 915,4 \pm 18,5$	855	$\overline{DP} = 838,4 \pm 32,3$				
935		802					
900		852*					
Corrected result from the Havermans paper**							
882		887					

DP values of non-aged paper

* Result obtained in PPRI.

** Havermans [13] assumed a = 1 in order to calculate *DP* according to eq. (1), whereas in this work the value of a = 0,905 is used.

place, and polymerization degree was determined according to the procedure described in section 4. For control, one of the *DP* determinations was done at the Pulp & Paper Research Institute, Łódź, Poland (PPRI). Additionally, corresponding *DP* values were read from Havermans' Thesis [13]. All *DP* values are collected in Table 1. It follows from this Table that the values of *DP* obtained by different methods are in agreement in the range within 10% (which seems to be a reasonable value for this type of experiments), and the supplied paper is sufficiently homogeneous and can be used for further experiments.

7. Accelerated Degradation of Standard Papers

Accelerated degradation of papers P1 and P2 was conducted:

- a) at the temperature of 100°C and RH = 100%, i.e. at the most extreme conditions of Zou's experiments;
- b) at the temperature of 90° C and RH = 75%, i.e. at the conditions allowing for direct comparison with Zou's results.

In both cases, dependence of polymerization degree of cellulose versus time was determined.

ad a) The results are presented in Fig.
2. The measurement of DP was repeated twice for each time value, so the error bars in Fig. 2 are equal to the values of interval. It follows from Fig. 2 that cellulose from coniferous trees is degraded faster, and depolymerization of both sorts of paper proceeds differently.

Polymerization degree is a linear function of time for the cellulose originating from cotton. The correlation coefficient is R = -0.99. The value of DP(0) was not taken into account in calculations, as the samples were selected for measurements in a different way. The results of experiments for paper P1 are presented in Fig. 3 in the coordinate system (1/DP - 1/DP(0)) vs. time. The evident linear correlation (R = 0.99) means, according to Zou's formalism [5], that deg-



Fig. 2. Depolymerization of papers P1 and P2 at 100°C and at RH = 100%. The mean values of interval: for P1 $\Delta DP = 8,7$; for P2 $\Delta DP = 15,6$



Fig. 3. Plot of 1/DP(t)-1/DP(0) vs. time for paper P1 aged at temp. 100°C and at RH = 100%.

radation of cellulose originating from coniferous trees follows a first-order reaction. Fig. 3 was a basis for rate constant determination, which allowed for plotting the solid line in Fig. 2.

In order to determine quantitative differences in degradation rates for both functions DP = f(t), the initial rates (-dDP/dt) have been calculated. These rates are equal to 4,84 h⁻¹ and 0,89 h⁻¹ for papers P1 and P2, respectively.

ad b) The data obtained at 90°C and 100°C are similar. For P2 paper, zero order plot has been found again. In Fig. 4 our results are compared with the results of Zou, as taken from Fig. 2 in his paper [5]. A fair similarity can be observed for paper P1.



Fig. 4. Plot of 1/DP(t)-1/DP(0) vs. time for papers P1 and P2 aged at 90°C and at RH = 75%. The data of Zou [5] for the measurement done at the same conditions are also plotted in this figure.

8. pH Changes During the Degradation of Paper

The Zou's model is a generalization of empirical correlations. One of them is a relation between the initial pH-value of paper (i.e. pH of non-aged paper) and the rate constant of the degradation reaction. In our work we decided to monitor the pH changes during the degradation process presented in Fig. 2. As the *in-situ* measurements were not possible, determina-

tion of pH was done with a contact electrode at room temperature – after opening the degradation vessel. Dependence of pH on time for papers P1 and P2 is shown in Fig. 5. The acidity of paper P1 grows beyond any doubts. Existence of this effect for P2 can be a subject of dispute.

Fig. 6 presents the time dependence of pH of water placed at the bottom of a vessel. The concentration of hydrogen ions grows linearly for both cases of paper degradation. It is worth noticing, however, that acidification of water is smaller for paper P2.



Fig. 5. pH changes of papers P1 and P2 aged at 100° C and at RH = 100%.

A control experiment was done in parallel with paper degradation and pH measurements. The vessel was filled with water but no paper was placed inside. Simultaneously with every take-out of paper from the measuring vessel, pH in the control vessel was measured. Fig. 6 shows that the hydrogen ion concentration can be regarded as approximately invariable. A small drop in the water acidity can be explained by lowering the CO_2 content in consecutive cycles: heating the vessel at 100°C and its opening. The control experiment is a distinct evidence that growth of the water acidity is a result of paper degradation.



Fig. 6. Concentrations of hydrogen ions of papers P1 and P2 aged at 100° C and at RH = 100%. The results of a control experiment have been also shown in this plot.

9. Discussion

Essential differences in the kinetics of degradation of papers P1 and P2 can be observed in Fig. 2. Paper P1 contains cellulose originating from coniferous trees. Paper and pulp of the same origin was an object of research of Zou [5]. Degradation of paper P1 follows the equation numbered as (10) in Zou's paper:

$$\frac{1}{DP(t)} - \frac{1}{DP(0)} = kt \tag{2}$$

In Zou's formalism this equation can be obtained after assuming that the relative velocity of breaking glycoside bonds does not change with time. In traditional kinetic considerations, eq. (2) is a consequence of an assumption of random scission of bonds in cellulose chains.

Degradation of paper P2 is a zero-order reaction and is slower than degradation of paper P1. Under these circumstances, information found in the Havermans paper becomes significant. According to the report [8, p. 179–180]: (i) crystallinity index of paper P2 is higher than that of paper P1, (ii) crystallites of cellulose have a high area-to-volume ratio because they are "thin". Additionally, it is known from [13, p. 12] that microfibrilles of cellulose can be grouped into platelets. A zero-order kinetic equation results directly from the following assumptions:

- Crystallites are flat cuboids with dimensions satisfying the inequalities a > b and a >> c. The relation a:b:c = 100:10:1 is a good example.
- Reaction occurs on the *ac* walls.

It is worth mentioning that other assumptions also give a possibility of explaining the zeroorder reaction. The reader interested in geometric aspects of kinetic modeling may find more information in the monograph by Bamford [14].

The assumptions suggested in the present paper, though speculative in nature, are in agreement with one of possible mechanisms of cellulose degradation proposed by Havermans [13, Fig. 1.7, mechanism 3]. This degradation mechanism is valid during the action of water vapour. As found previously by the same author [8, p. 8] [15], during accelerated

erated ageing at the temperature of 90°C and RH = 50%, pH of paper P1 was lowered by 0,5 and that of paper P2 by 0,9. The action of water vapour lasted for 12 days. Results of this work are in agreement with the Havermans communication, but they are concerning not one but eight time values – in the range from 2 to 21 days (Fig. 5).

More thorough comparison of the results obtained in the present paper with the Havermans' results obtained by complementary methods leads to the expected conclusion about higher reactivity of paper P1 when compared to paper P2. In our work a higher reactivity of P1 is documented by: a higher initial degradation rate, higher value of *DP* lowering, higher acidification of paper due to the degradation, and lower pH as well as higher conductivity of water solution. In the Havermans' paper higher values of copper number, the alkalineextracted fraction and total number of organic carbon compounds extracted with water – all of these suggest a higher reactivity of paper P1.

The experiments on accelerated ageing allowed for preliminary comparison of our results with the Zou's paper [5]. Let us consider the results obtained in both works at temperature 90°C and relative humidity 75%. Let's choose the rate constant defined by eq. (2) as a criterion of conformity. The results of calculations concerning Fig. 4 are shown in Table 2.

The rate constants calculated by linear regression make it possible to compare results of experiments directly. For paper P1 and Zou's data the agreement of results is good. Both cases are dealing with the degradation of cellulose originating from coniferous trees. The rate constant for paper P2 cannot be calculated because these data do not obey the Zou's model. In this case, cellulose originating from cotton is degraded.

			Table 2	,
Volues of k constant	dafinad	by aqua	tion(2)	

values of κ constant defined by equation (2)						
Way of <i>k</i>	$k \cdot 10^5 [\text{day}^{-1}]$					
calculation	Zou's data	P1	P2			
Regression	$8,1 \pm 0,1$	$7,1 \pm 0,1$	*			
Zou model**	8,5	6,4	*			

* The kinetic curve doesn't obey the eq. (2)

** Calculations performed under assumption that the water content in paper amounts to 9.5%

In order to estimate applicability of the Zou's model, one has to calculate the rate constant based on the model parameters [6] and on the experimental values of: (i) temperature, (ii) pH of non-aged paper, and (iii) water content in paper at the experiment temperature. The last quantity can be estimated – for the temperature 90° C – from Figs. 5 and 6 of the Zou's paper [5] for any value of relative humidity.

Agreement of Zou's data with the Zou's model is self-explanatory. A small divergence of about 5% is mainly due to the procedure of taking the values used for calculations directly from the figures. In this context, the agreement of rate constant for paper P1 with the Zou's model (about 10%) can be regarded as a very good one. This is, however, only a partial agreement, as it concerns only one combination of temperature, pH and humidity. Full estimation of applicability of Zou's model requires the parameters of this model for paper P1 to be found, based on experiments conducted in very differentiated conditions. This task implies a necessity of standarization of both: pH measurements and determination of isotherms of water adsorption. The consequences of growth of paper acidity with the degradation advance require a thorough analysis. Kinetic curves do not indicate autocatalysis phenomenon. The degradation rate drops with time or it is constant (Fig. 2). In this context, it is necessary to estimate quantitatively the influence of ratio of paper mass to the vessel volume on paper degradation. The role played by liquid phase is also important. This phase,

according to the Shahani's [17] fears, may absorb not only protons but also products of degradation. Their identification requires spectroscopic methods to be applied. Therefore, a discussion of mechanism of degradation should be added to the phenomenological description.

10. Conclusions

A success of Zou's model implies questions about the objectives of further research. The answer to this question requires a definition of the research object. We want to refer to the Porck's statement [3] which is an estimation of the "state of art" of an interdisciplinary research bordering with chemistry, technology, library science, and the art of conservation – encompassing also the present paper:

" unequivocal assertion about the natural ageing process, which **a paper sheet** undergoes seems to be impossible. The situation is even more complicated in the case of **paper stack** such as **book**, ... not even mentioning a whole **archive** or **library collection**."

In the words quoted here Porck refers to the research subjects such as a paper sheet, a book or a collection of books. In the present paper we are interested in paper as an information carrier, so a book or, typical of archives, a stack of touching each other paper sheets – become a focus of our attention.

A specific feature of the natural ageing of paper occurring as book sheets consists in their contact with the degradation products accumulating in the intra-sheet spaces. Implications of this effect have been described by Shahani [17]. The concept of preserving the acid products of degradation was the main reason for application of closed containers in the experiments on accelerated ageing done by Zou. The Porck's report [3] stresses that the *"stack versus single sheet phenomenon*" is essential for ageing of paper of books, and it will be further explored thoroughly.

However, a question can be asked: "Can closed containers adequately simulate the situation in the intra-sheet spaces?". There is a difference between a closed container and an intra-sheet space, open to surroundings: the degradation products may migrate outside of books – due to diffusion.

It should be clearly said that this rethoric question is knowingly asked in a bad way. This is a direct implication of our previous reasoning referring directly to the Porck's report of 1999. This reasoning must be now changed, and natural ageing of books should be described in the terms of chemical kinetics.

Degradation of book sheets is a process of mixed-control mechanism. In the simplest version of description two partial processes should be taken into account:

- 1) chemical reactions occurring inside a solid (paper is a solid),
- 2) diffusion of degradation products out of pores (the intra-sheet spaces can be considered as pores).

If the kinetic equations of partial processes are known, then application of steady-state approximation makes it possible to derive the kinetic equation of the overall process. In a general case none of the partial processes is the determining step. In the limiting cases each of the partial processes may be the determining one (e.g. [18, 19]).

The strategy of research in the case of mixed-mechanism reactions may take two scenarios into account:

- a) The experiments are planned separately for each of the partial processes in such a way that this process is the determining step. The kinetic equation of the partial process is established. By means of model calculations a synthesis of obtained information is done for all partial processes. The overall kinetic equation contains all the parameters describing the partial processes.
- b) A correctly planned experiment gives a possibility of conducting the reaction in the region of mixed mechanism. Mixed-mechanism equations are fitted to the experimental

results. Thus, the parameters characteristic of all partial processes are determined simultaneously.

If information about the studied system is poor, the (a) strategy should be applied. The (b) strategy may be applied for studies of better-known systems. In the case of cellulose degradation mechanism, the research efforts is directed towards establishing the reaction network. According to the Boudart [20] definition this is an early stage of studying of system, and this means that the (a) strategy is preferred. This statement implies a necessity of examination of diffusion phenomena occurring inside the books. Some methodological problems may arise here, heralded by the question: "How to define the distance between consecutive sheets of a closed book?".

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