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Aqueous Deacidification – with Calcium or with Magnesium?

by HELMUT BANSA

1. INTRODUCTION

Aqueous deacidification is the most widespread chemical treatment in paper conservation[1], and starting with the law of nature that the most common way of decomposition of natural polymers is hydrolysis catalyzed by acid, it can be stated as having generally a stabilizing effect anyhow. The only drawback against this treatment of aqueous deacidification lies in the actual condition of the object whose either ink, colour or anything else could be alkaline sensitive.

Conservation chemists will contradict to this simplified way of thinking, and they will point out that the relation between acidity, alkalinity and degradation of paper is much more complex. Of course they are right, but again of course their relevant discussions are of little use for the conservator in the workshop, as al-

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ready stated in the most recent one of them[2]. The practical working conservator – not necessarily a non-technician[3], but in any way not a specialist for the details of cellulose chemistry – is in need for a method to treat old papers: a practical applicable method, as simple as possible and as complicated as inevitable. He (most always she) has learned and understood the statement on acid hydrolysis given above. She has also learned and understood that in the course of long-term storage paper will pick up acids from the pollutants in the air and, moreover, that cellulose itself turns to become partly an acid by oxidation that is inevitable in the course of time: generally that the way of paper in the stacks of an archive and a library and in the showcases or the drawers of a graphic collection is from neutral or alkaline to acidic and that it would be beneficial to provide an alkaline buffer against that process: most obviously calcium carbonate, as this substance is found in nearly any old paper, at least in the well preserved ones. Calcium carbonate, however, is hardly soluble in water, and enriching the water with carbon dioxide will increase the amount to be dissolved only slightly. The solubility of calcium oxide, that will quickly turn to become carbonate, at least when the paper is drying and partly already during the soaking, is somewhat better, but still less than would be desirable, and moreover such a solution has a quite high pH (up to 12)[4] that can provoke harm during the treatment: old paper can become quite flabby when treated with calcium oxide (or hydroxide) solution, not to speak of iron gallotannate inks fading out. The phenomenon of paper becoming flabby reminds the restorer on the quick lime used in old paper making in order to prepare the rags for beating and on the warning that this can result in the pulp being "eaten away"[5]. Moreover it reminds him on the short-chained celluloses (hemicellulose, partly degraded cellulose) being soluble in alkali, while the notion of "alkaline deterioration" sometimes to be found in reports written by scientists for conservators is less in accordance with what he has learned on cellulose degradation. The obvious alternative to calcium is magnesium (bi)carbonate: better soluble in water up to ten times.

2. State of the Art

In workshop practice, four methods of aqueous, i.e. single-sheet or sheet-staple (the Vienna method) deacidification based on these ideas of chemical common sense are used: A saturated solution of calcium hydroxide, prepared by simply dissolving the solid in water[6]; a saturated solution of calcium bicarbonate prepared by floating carbonic acid, i.e. water enriched with carbon dioxide, through a flow bed filled with marble granules[7], a saturated or even over-saturated (as prepared under pressure of carbon dioxide[8]) solution of magnesium bicarbonate

or a combination of both, prepared by using dolomite granules instead of marble in the mentioned flow bed[9] [10]. If for the third method (over-saturated solution of $Mg(HCO_3)_2$) tap water of good quality and high temporary hardness is used, it can also be understood as a method combining calcium and magnesium. The same is true for using mineral water as deacidification and buffering agent for paper, as suggested recently[11], even if this would be a quite expensive method.

As already indicated, there are intensive discussions on the chemical details of the reactions that may happen if cellulose and cellulose accompanying compounds such as lignin, in different states of decay are brought in contact with earth alkaline ions, alone or together with other ions that may be present in the paper or in the treatment medium, i.e. in the water: discussions not directly affecting the practical working restorer's daily work, but providing details and statements that provoke his attention. Those details are a warning against magnesium, as provoking yellowing, at least in newsprint[12] and even as having, compared to calcium, a negative or, more correct, a less positive influence on the ageing behaviour[13], at least during dry accelerated ageing[14]. A most recent research[15] is giving a reasonable understanding of one of these phenomena, i.e. of the yellowing, in so far as it explains that in the alkaline medium oxidation of cellulose is accelerated. Paper treated with a saturated solution of magnesium (bi)carbonate provides a higher pH than if treated with lime water. The calcium compound of lime water quickly turns to $CaCO_3$, which is less alkaline than what remains and stays for some time in the state of precipitation when water (or carbonic acid) containing a maximum of $Mg(HCO_3)_2$ evaporates. Another statement given recently by scientists from a related field of research, i.e. from research in mass deacidification, provokes the practical working restorer's attention: the statement that "magnesium buffers are ... chemically active"[16]. The context is: more chemically active than zinc oxide. This has no impact in the context of aqueous deacidification, but it refers to general chemical activity.

3. Why another Research Project

These observations presented recently by scientists in the course of their ongoing work to understand the way of cellulose degradation in full detail provokes the practical working restorer's attention and the question arises: what is the impact of these details on practical work? These observations do not lead to avoiding magnesium immediately in any treatment, and this for several reasons, e.g.:

- The obvervations regarding the possibly negative effect of magnesium were made on pulp or laboratory handsheets resp. The restorer, however, has to work with real old papers.

- Moreover, the celluloses were submitted to certain chemical treatments (reduction with sodium borohydride, washing with acetic acid, washing with distilled water), nececessary in order to get reproducible data of certain chemical measurements, but the test results can be far different from actual real old paper as it is practically treated in the restoration workshop.
- There is a difference in the behaviour of the samples during dry and moist accelerated ageing, what is to be regarded as a reason against the reliability of accelerated ageing, not against a conservation method.
- The specific ageing behaviour of magnesium containing paper is influenced by the amount of other ions present in the paper, sodium, e.g.: "low" concentration is beneficial, "high" is harmful. Just sodium, however, is sometimes present in old papers, in different amounts.

4. THE EXPERIMENT

To find out in what amount the findings reported above are of impact on practical deacidification, in other words whether it is better to use calcium or magnesium for aqueous deacidification, the following project was performed:

Four different old papers, one rag, two groundwood and one chemical pulp (Table 1), were soaked for 30 min in

- demineralized water
- tap water (cf. Table 2)
- water containing a maximum of magnesium (bi)carbonate
- water containing a maximum of calcium (bi)carbonate

Table 1: The papers

Paper	Origin	Fibre	g/m²	Ø (mm)
rag paper	Arenberg, C.: Flores seraphici. 1640	100 % rag	70	0,12
groundwood paper 1908	Der Kunstwart 22. 1908	50% groundwood 50 % chem. pulp	88	0,14
groundwood paper 1923	Grimsehl, Lehrbuch der Physik große Ausgabe 1. "1923	50% groundwood 50 % chem. pulp	65	0,07
chemical pulp paper	Ostasiatische Zeitschrift 10. 1935	100 % chem. pulp	128	0,15

Table 2: Mineral content (mg/l) of the tap water used for the experiment*

Ca	Mg	Na	K	SO_4	Cl	pH
82,5	19,9	3,6	1,0	25,8	5,8	7,66

* The date have been provided by Stadtwerke München, Labor der Wasserversorgung. All ions present in an amount > 1 are given

The deacidification solutions, i.e. the water containing a maximum of earth alkaline carbonate, were prepared in a closed container filled with tap water (Table 2) and with magnesium or calcium carbonate resp.: up to the double amount of the white powder that, according to practical experience, could be dissolved. Carbon dioxide was bubbled through the milky dispersion while the container was open until all air above its surface was displaced by CO_2. Then the container was closed and, under permanent stirring, the bubbling-through of CO_2 was continued until a pressure of 1 bar was achieved. The flow of the gas was controlled in a way as to reach this desired pressure after ca. 1 h. The undissolved carbonate was allowed to deposit over night. The clear solution was then removed while the container was still under pressure. This is the usual way to prepare aqueous deacidification solution (magnesium until now) in the Institute where the experiment was performed.

Moreover, in order to get a closer relation to the reported research done mostly on laboratory handsheets, these handsheets were also included into the experiment, namely the three types of fibre used in this Institute for leafcasting:

- chemical pulp (mixed pine and birch; provided by Nordland Papier AG, Dörpen, Germany)
- bleached cotton (provided by Papierfabrik Louisenthal, Gmund, Germany)
- unbleached cotton linters (provided by Peter Temming AG, Glückstadt, Germany)

There was no further specification of the fibre (degree of beating, fibre length, impurities etc.). They were the same, of course, for the whole experiment.

Out of each of these fibres laboratory handsheets were made using the same kinds of water (or deacidification solution resp.) as has been used for treating the papers. Altogether, there were 32 kinds of samples:

- 4 papers x 5 (untreated + 4) treatments: 20
- 3 handsheets x 4 ways of preparing: 12.

Each kind was submitted to the 7 stages of accelerated ageing

- unaged
- dry ageing (105°C) 3 days
- dry ageing 6 days
- dry ageing 12 days
- moist ageing (80% 65%) 12 days
- moist ageing 24 days
- moist ageing 48 days.

The duration of ageing was chosen arbitrarily, based on the following: 1) three days in an oven at 100/105°C equal to 25 years of natural ageing; 2) a temperature change of ±10°C means doubling or bisecting the ageing rate; 3) reducing 100/105°C two times by 10°C is compensated by two times doubling the duration. 4) 3/12 days then equal to 25 years, 12/48 to 100. Even if these conditions are not absolutes, they are based on common opinion. Others have chosen the duration ratio 10 : 1 for parallel ageing at 80°C 65% and at 105°C dry[17].

Each of the 32 x 7 = 224 samples different in treatment and in ageing were submitted to some measurements that seemed to be reasonable for the aspired result, i.e. to find out whether it is better to use the magnesium or the calcium containing deacidification solution. Physical strength in terms of "usability" was estimated as most important, because it is the real aim of a conservation treatment. Colour change is meaningful, too, as it is of impact on the aesthetic quality. As one of the groundwood papers was, as it sometimes happens, distinctly two-sided regarding the colour, both sides were measured. For further comparisons some chemical numbers were also measured: DP, mineral content and, as it is most widely used, pH. The results are given in Tables 4–9 and, to emphasise and make perceptible the relative changes, the diagrams are presented in same comparable scale, Fig. 1–12.

5. Results and Discussion

5.1 Mineral Pick.-up

Looking at the data of mineral pick up what will be noticed most is that very little amounts of the compounds generally accepted as favouring the ageing stability are brought into the papers during wet deacidification treatments. In terms of mg it would be between 2,51 and 5,28 Ca in 1 g paper with the $Ca(HCO_3)_2$-treatment, between 1,8 and 4.28 Mg with $Mg(HCO_3)_2$. As mmol (Table 3a) the numbers are nearer to each other: 0,06–0,13 for Ca, 0,07–0,18 for Mg, and it becomes evident that for the chemical pulp and for the rag paper the magnesium containing solution is a little bit superior. The same fact, for all papers, is to be seen with the alkaline reserve. Some substances are washed out during wet treatment, even calcium; it must be present in the old papers as sulphate or as chloride. Of course water soluble alkaline compounds are washed out, too. For the opposite, i.e. that the chemical pulp paper picks up potassium, more during Mg-, but some also during Ca-treatment, no explanation can be suggested. From the loss in potassium,

Table 3a: Mineral pick-up and wash-out (mmol / 1 g paper) by deacidification treatment of old papers

		Groundwood		chem.		Groundwood		chem.	
		1908	1923	pulp	rag	1908	1923	pulp	rag
		Ash (mg/g)				**Aluminium**			
untreated		215	215	159	20	2,08	2,04	0,71	0,03
change caused by	$Mg(HCO_3)_2$	0	25	41	6	-0,06	0,19	1,24	0,04
treatment with	$Ca(HCO_3)_2$	10	12	20	5	-0,12	0,09	0,50	0,01
		Calcium				**Silicium**			
untreated		0,08	0,03	0,17	0,09	2,58	2,43	0,68	0,08
change caused by	$Mg(HCO_3)_2$	-0,02	0,01	-0,13	-0,01	0,12	0,33	1,80	0,07
treatment with	$Ca(HCO_3)_2$	0,12	0,13	0,06	0,13	-0,07	0,11	0,50	0,02
		Magnesium				**Sulphur**			
untreated		0,00	0,00	0,00	0,00	0,06	0,10	0,58	0,03
change caused by	$Mg(HCO_3)_2$	0,12	0,13	0,07	0,18	-0,06	0,00	-0,53	-0,02
treatment with	$Ca(HCO_3)_2$	0,00	0,00	0,00	0,05	-0,06	0,00	-0,15	-0,03
		Barium				**Chlorine**			
untreated		0,00	0,08	0,46	0,00	0,00	0,00	0,00	0,03
change caused by	$Mg(HCO3)_2$	0,00	0,00	-0,40	0,00	0,00	0,00	0,01	-0,03
treatment with	$Ca(HCO3)_2$	0,00	0,01	-0,16	0,00	0,00	0,00	0,00	-0,03
		Sodium				**Iron**			
untreated		0,00	0,00	0,00	0,03	0,08	0,08	0,03	0,02
change caused by	$Mg(HCO_3)_2$	0,00	0,00	0,00	-003	0,04	0,00	0,03	0,01
treatment with	$Ca(HCO_3)_2$	0.00	0.00	0.00	-0,03	0,01	0,00	0,02	0,00
		Potassium				**Alkaline reserve**			
untreated		0,18	0,15	0,03	0,06	0,01	0,00	0,00	0,20
change caused by	$Mg(HCO_3)_2$	-0,01	-0,01	0,14	-0,04	0,12	0,20	0,16	0,16
treatment with	$Ca(HCO_3)_2$	-0,03	-0,05	0,06	-0,05	0,08	0,09	0,06	0,12

Table 3b: Mineral content (/ 1 g paper) of laboratory handsheets

		Chemical pulp		cotton		Chemical pulp		cotton	
		mg	mmol	mg	mmol	mg	mmol	mg	mmol
		Ash				**Sulphur**			
in	aqu. demin.	3		3		0,39	0,012	0,04	0,001
handsheets	tap water	3		4		0,05	0,002	0,04	0,001
made	$Mg(HCO_3)_2$	4		6		0,12	0,004	0,27	0,008
with	$Ca(HCO_3)_2$	6		18		0,04	0,001	0,26	0,008
		Calcium				**Chlorine**			
in	aqu. demin.	0,93	0,023	1,43	0,036	0,00	0,000	0,00	0,000
handsheets	tap water	1,18	0,029	1,84	0,046	0,03	0,001	0,02	0,000
made	$Mg(HCO_3)_2$	0,62	0,015	1,47	0,037	0,03	0,001	0,02	0,001
with	$Ca(HCO_3)_2$	3,94	0,098	11,32	0,282	0,03	0,001	0,00	0,000
		Magnesium				**Iron**			
in	aqu. demin.	0,33	0,013	0,19	0,008	0,00	0,000	0,10	0,002
handsheets	tap water	0,40	0,016	0,31	0,013	0,02	0,000	0,03	0,001
made	$Mg(HCO_3)_2$	1,49	0,061	1,65	0,068	0,03	0,001	0,12	0,002
with	$Ca(HCO_3)_2$	0,45	0,018	0,34	0,014	0,12	0,002	0,14	0,003
		Potassium				**Copper**			
in	aqu. demin.	0,04	0,001	0,03	0,001	0,13	0,002	0,00	0,000
handsheets	tap water	0,03	0,001	0,04	0,001	0,08	0,001	0,09	0,001
made	$Mg(HCO_3)_2$	0,02	0,000	0,03	0,001	0,11	0,002	0,00	0,000
with	$Ca(HCO_3)_2$	0,00	0,000	0,06	0,002	0,00	0,000	0,00	0,000
		Aluminium				**Titanium**			
in	aqu. demin.	0,02	0,001	0,02	0,001	0,00	0,000	0,11	0,001
handsheets	tap water	0,02	0,001	0,02	0,001	0,00	0,000	0,14	0,001
made	$Mg(HCO_3)_2$	0,00	0,000	0,04	0,001	0,00	0,000	0,21	0,001
with	$Ca(HCO_3)_2$	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000
		Silicium				**Phosphor**			
in	aqu. demin.	0,07	0,002	0,10	0,003	0,00	0,000	0,08	0,002
handsheets	tap water	0,13	0,005	0,10	0,003	0,00	0,000	0,24	0,008
made	$Mg(HCO_3)_2$	0,12	0,004	0,12	0,004	0,00	0,000	0,14	0,004
with	$Ca(HCO_3)_2$	0,08	0,003	0,09	0,003	0,00	0,000	0,18	0,006

aluminium and sulphur with the older groundwood and the rag paper it may be concluded that some alum ($KAl(SO_4)_2$) was present in these papers: if this is true, the comparatively good ageing stability of the groundwood paper's mechanical strength (defined as tensile strength after one defined fold; cf. Fig. 5) is contradictory to common opinion, but not necessarily to the experience of practical working people, who have in their hands a lot of paper in a better condition than

it should be if the prognosis that some 90% of the early industrial production paper will become brittle within half a century were true. Again based on common opinion among paper conservation researchers, concern may be drawn from the fact that a paper can pick up iron during an aqueous deacidification treatment; it is soothed by the fact that this seems to have no negative influence on the ageing behaviour.

With the laboratory handsheets it is enough to establish again the very low amount of earth alkali to be found even in a paper made with water extremely enriched with such a compound. If we assume all Ca and Mg in that very laboratory handsheet which is richest in these compounds (cotton made with $Ca(HCO_3)_2$-water) to be present as carbonate, i.e. able to react as buffer, and if we compute from that amount on the buffer capacity present in the paper, we find a far less value than that required, e.g., in ISO 9706 as necessary for permanent durable paper. Nevertheless all laboratory handsheets behave very good during accelerated ageing. This meets with an observation recently done in the context of research for mass deacidification, i.e. that the amount of buffer substance is not so important as its presence[16]. For a conclusion from results found with laboratory handsheets on the behaviour of real old paper the observation may be interesting that the ratio between Ca- and Mg-pickup, expressed as mmol per unit (=1 g paper), is in favour of calcium (1:0,24) for the cotton laboratory handsheet, but in favour of magnesium (1:1,38) with the rag paper The ratio for chemical pulp laboratory handsheets (1:0,62) is nearer to that for chemical pulp paper (1:0,86). With both groundwood papers the ratio is 1:1.

5.2. Yellowing

The most obvious and clearest result of the experiment is: magnesium provokes more yellowing than calcium! This is in accordance with previous findings[12 18]. It seems to be true for any kind of paper. As much more interesting are the exceptions (Fig. 1): Chemical pulp paper, already naturally aged and slightly yellowed (Table 4a), if soaked in tap water (cf. Table 2) , demineralized water and calcium containing deacidification solution, is yellowing more during further accelerated ageing – only dry – than if soaked in magnesium containing deacidification solution. This doubtless fact, supported by three stages of ageing, must, however, not be overestimated: During moist accelerated ageing the yellowing of that paper is closely resembling that of the other samples. Looking at single states of accelerated ageing, it is to be noted that with the old papers it can even be magnesium that provokes the least yellowing (chemical pulp paper, dry ageing 6 and 12 days; cf. Table 4a), and with groundwood paper after longer moist ageing the untreated

Table 4a: Yellowing (CIE b*) of old papers

	dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d	12d	24d	48d
Groundwood paper 1908							
untreated	20,95	21,64	22,08	23,15	22,46	23,32	23,64
aqu. demin.	20,30	20,73	21,18	22,26	21,36	21,94	23,00
tap water	19,90	20,33	21,66	21,75	22,00	21,61	22,95
Mg	21,73	21,40	22,80	23,78	24,02	25,32	24,81
Ca	20,30	20,85	21,29	22,20	22,20	22,79	23,77
Groundwood paper 1923, light side							
untreated	18,97	20,52	21,05	22,13	19,61	20,45	20,83
aqu. demin.	18,06	19,44	19,94	20,90	19,75	20,51	21,13
tap water	18,57	19,34	19,93	20,97	20,01	20,53	21,20
Mg	19,66	19,85	20,76	21,32	20,99	21,40	21,97
Ca	18,74	19,72	20,44	20,86	20,20	20,71	21,19
Groundwood paper 1923, dark side							
untreated	22,54	24,32	25,22	26,00	23,82	24,12	23,92
aqu. demin.	21,50	23,06	23,74	24,57	23,55	24,25	24,70
tap water	22,11	23,15	23,65	24,68	23,78	24,48	25,37
Mg	23,32	23,69	24,57	25,37	24,89	25,31	25,87
Ca	22,14	23,21	23,94	24,51	23,83	24,57	25,06
Chemical pulp paper							
untreated	16,42	20,03	22,03	24,13	18,05	18,94	20,68
aqu. demin	14,32	17,27	19,38	21,19	18,83	19,25	20,48
tap water	14,99	17,92	19,72	20,42	18,17	18,56	20,10
Mg	15,10	17,31	18,36	19,66	18,77	19,02	20,27
Ca	14,95	18,26	19,39	19,77	18,20	17,24	19,72
Rag paper							
untreated	16,37	17,02	17,46	17,86	17,69	19,09	20,19
aqu. demin.	14,36	15,36	15,73	16,15	16,41	18,08	18,42
tap water	15,64	16,02	17,25	17,00	17,59	18,57	19,58
Mg	17,36	18,44	19,52	19,81	17,73	18,85	18,80
Ca	14,42	15,09	15,48	15,73	15,98	17,02	17,27

sample is the least yellowed. With the rag paper, however, the least yellowed samples are the calcium treated ones, closely followed by demineralized water. These two treatments seem to have nearly a "bleaching" effect. To some extent also tap water can be seen in this way. The effect proves to be relatively stable during any accelerated ageing.

Regarding the laboratory handsheets there is a clear distinction: if made with $Mg(HCO_3)_2$-solution they tend towards yellowing during accelerated ageing, while there is little difference between the other production methods. Sometimes $Ca(HCO_3)_2$-solution provokes the least yellowing, sometimes tap water and most often demineralized water.

It is said that yellowing is to be understood as a sign for carbonyl groups formed by oxidation during accelerated ageing. As there is no general, i.e. valid for all samples, correlation between yellowing and mechanical strength, this chemical process seems to be of no impact, neither on the "usability" of the paper – yellowing can be understood as patina – nor on the further ageing behaviour. The phenomenon of increased yellowing must therefore not necessarily be taken as a valid argument against deacidification with magnesium.

As hypothesis to explain the reported phenomena it may be presumed that during washing, as it is part of any aqueous deacidification and any paper (laboratory handsheet) making, substances that are prone to be oxidized are washed out. If the paper is alkalized by magnesium, then this effect interferes with further oxidation promoted by alkalinity. This oxidation takes place exclusively in the form of dehydrogenization along the chain at C^2 and C^3 changing them from H–C–OH to H–C=O.

Table 4b: Yellowing (CIE b*) of laboratory handsheets

	dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d	12d	24d	48d
Chemical. Pulp laboratory handsheets							
aqu. demin.	4,81	5,24	7,10	8,05	6,83	7,64	8,69
tap water	4,90	6,06	7,86	8,67	7,18	7,73	7,97
Mg	5,31	6,94	9,85	11,59	9,03	10,25	11,12
Ca	4,49	5,36	7,18	7,96	6,52	7,01	7,96
Cotton laboratory handsheets							
aqu. demin.	3,11	3,26	4,56	5,87	4,47	5,52	6,22
tap water	3,24	3,32	4,45	5,77	5,29	5,63	7,16
Mg	3,04	4,84	6,61	8,32	5,92	6,90	9,02
Ca	2,68	3,32	4,86	5,90	4,70	5,59	6,68
Unbleached linters laboratory handsheets							
aqu. demin.	11,57	11,48	11,73	12,27	11,96	12,09	12,96
tap water	12,01	12,18	12,16	13,00	12,43	12,63	12,80
Mg	12,38	12,80	13,20	13,87	13,11	13,15	14,14
Ca	11,62	11,87	12,14	12,66	12,18	12,25	12,95

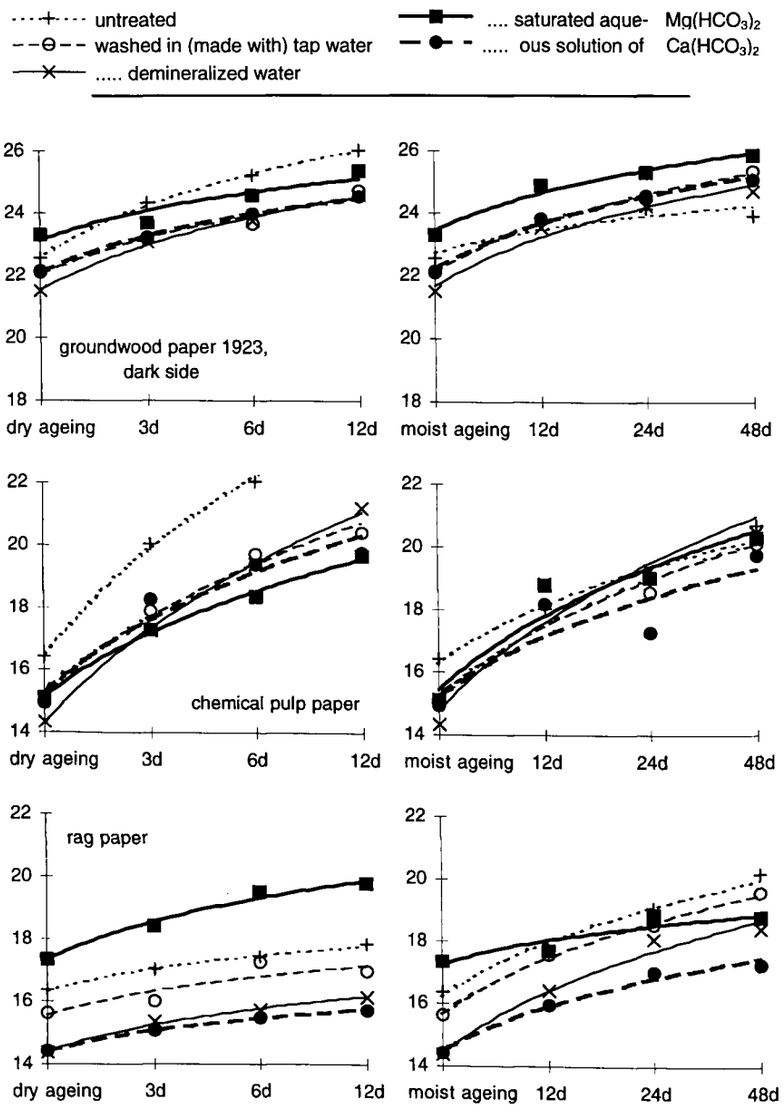

Fig. 1: Yellowing (CIE-b*) of old papers during accelerated ageing: those cases where Mg did not provoke the highest rate during both ageings.

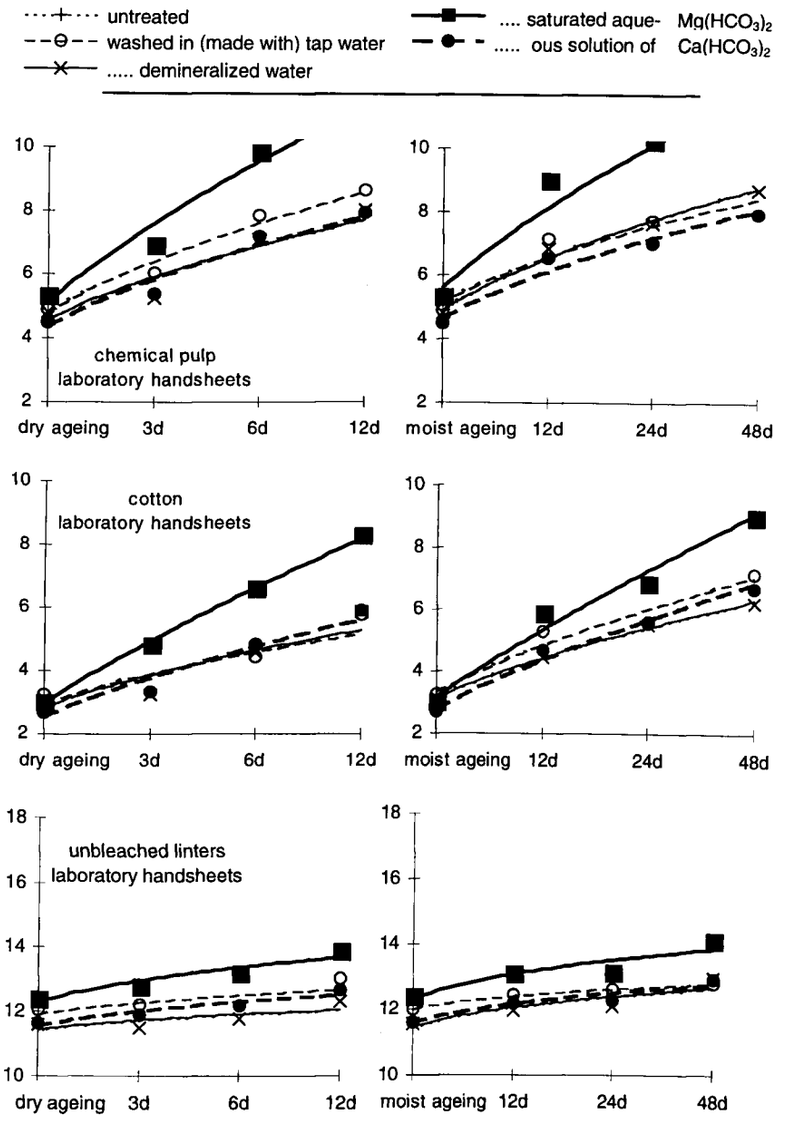

Fig. 2: Yellowing (CIE-b*) during accelerated ageing of laboratory handshets.

5.3 Brightness

Regarding brightness the most striking fact is the pronounced difference between dry and moist ageing. It can already be observed with the laboratory handsheets Fig. 4), and it is very clear with the old papers (Fig. 3b). As already stated, such a difference is an argument against relying too much on the results of accelerated ageing. Obviously, the different processes that all together and in their mutual influencing and overlapping are what we call "ageing" of a material take place at high temperature differently in dry and in moist atmosphere. In moist a process seems to prevail which, in lack of a chemical explanation, may be called "carbonization". It has been reported[19] that at a higher temperature (95°C) in moist atmosphere (85%) any paper becomes deeply blackish-brown in colour and totally unusable in mechanical strength. During the milder ageing conditions of the experiment reported here this final stage was not reached, but the chemical processes provoking it have slightly been initiated. The unchanged or even increasing brightness of the linters laboratory handsheets is not an argument against this hypothesis. Here the result of the process discernible in brightness decrease interferes with decay processes affecting the brownish natural colour of the unbleached fibre.

Regarding the main question of this study brightness gives little answer. Most often the results of Mg- and Ca-deacidification are closely together. As quite often the best results are obtained with demineralized water – 16 times it gives the highest number in the six right columns of Tab. 5 a/b representing the six ageing stages, followed by Mg (11 times highest) and calcium (10 times highest) – it seems that the alkaline ion is of no influence on that very ageing processes which becomes discernible in loss of brightness.

Table 5a: Brightness (CIE L*) of old papers

	dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d	12d	24d	48d
Groundwood paper 1908							
untreated	85,01	84,78	83,81	82,60	82,12	80,28	78,89
aqu. demin.	85,38	84,86	84,64	84,08	83,53	83,49	80,86
tap water	85,18	85,08	83,35	84,19	83,08	83,24	80,71
Mg	83,34	84,35	83,66	82,90	81,09	80,50	78,33
Ca	84,46	84,04	83,96	83,37	82,65	81,54	79,40
Groundwood paper 1923, light side							
untreated	82,35	80,52	79,93	78,32	78,03	75,91	73,03
aqu. demin.	82,26	81,42	80,99	80,39	80,07	78,60	76,21
tap water	81,43	81,53	81,36	81,01	80,40	79,39	78,09
Mg	81,04	81,52	81,25	80,76	79,93	78,93	77,38
Ca	81,38	81,60	80,96	81,00	80,34	79,49	78,02
Groundwood paper 1923, dark side							
untreated	80,52	78,74	77,64	75,83	75,09	73,00	68,90
aqu. demin.	80,38	79,76	79,43	78,43	77,76	76,20	73,19
tap water	79,38	79,65	79,54	79,25	78,13	76,99	75,09
Mg	79,01	79,80	79,35	78,96	77,71	76,63	74,94
Ca	79,38	79,65	79,48	79,00	78,07	77,29	75,60
Chemical pulp paper							
untreated	89,13	87,64	85,42	84,45	83,67	81,72	76,69
aqu. demin	89,61	88,18	87,37	86,78	85,75	84,81	81,07
tap water	88,98	87,49	87,14	86,45	85,02	82,32	79,42
Mg	89,39	88,33	87,79	87,42	84,71	82,82	81,21
Ca	89,22	88,20	87,07	86,98	85,49	84,06	80,74
Rag paper							
untreated	83,43	83,52	83,68	82,95	79,06	76,22	70,77
aqu. demin.	84,55	85,93	85,22	85,49	80,52	76,98	73,86
tap water	83,32	83,52	82,86	83,17	80,54	77,11	73,81
Mg	82,79	82,42	84,82	83,29	83,15	80,72	79,98
Ca	85,11	85,24	85,27	84,77	81,75	81,84	77,71

Table 5b: Brightness (CIE L*) of laboratory handsheets

	dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d	12d	24d	48d
Chemical. pulp laboratory handsheets							
aqu. demin.	95,01	93,76	94,06	93,33	94,04	93,39	92,26
tap water	94,25	93,99	94,38	94,19	93,27	92,63	92,29
Mg	94,08	93,94	93,68	94,17	92,78	91,04	90,49
Ca	94,57	94,37	94,62	94,30	93,74	93,08	92,65
Cotton laboratory handsheets							
aqu. demin.	95,48	94,84	95,29	94,28	95,05	94,16	93,62
tap water	95,29	94,39	95,08	95,04	94,66	94,11	93,57
Mg	94,90	94,71	95,36	94,60	94,03	93,18	92,21
Ca	95,26	95,33	95,28	94,91	94,53	93,47	92,63
Unbleached linters laboratory handsheets							
aqu. demin.	82,35	82,28	82,21	82,96	82,28	82,44	81,61
tap water	81,15	81,68	81,38	82,26	81,51	81,72	82,62
Mg	80,84	81,10	81,22	81,60	82,88	82,97	82,88
Ca	81,71	82,25	82,17	82,48	82,73	82,18	82,35

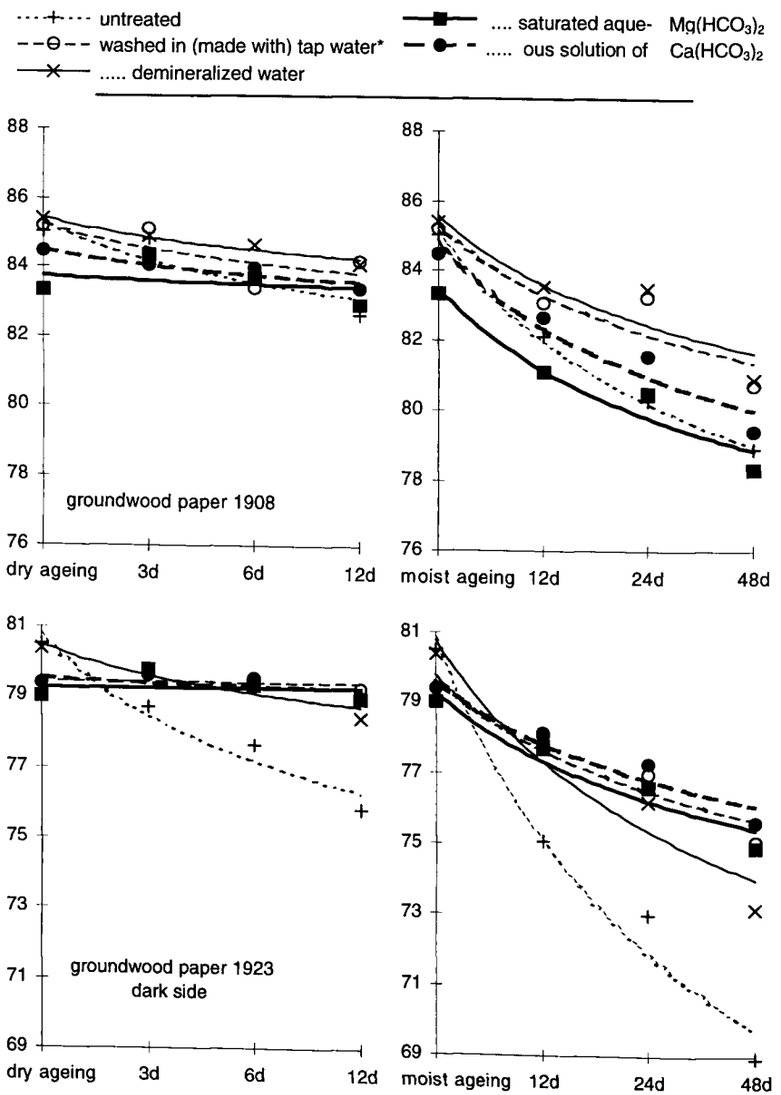

Fig. 3a: Change of brightness (CIE-L*) of groundwood papers during accelerated ageing.

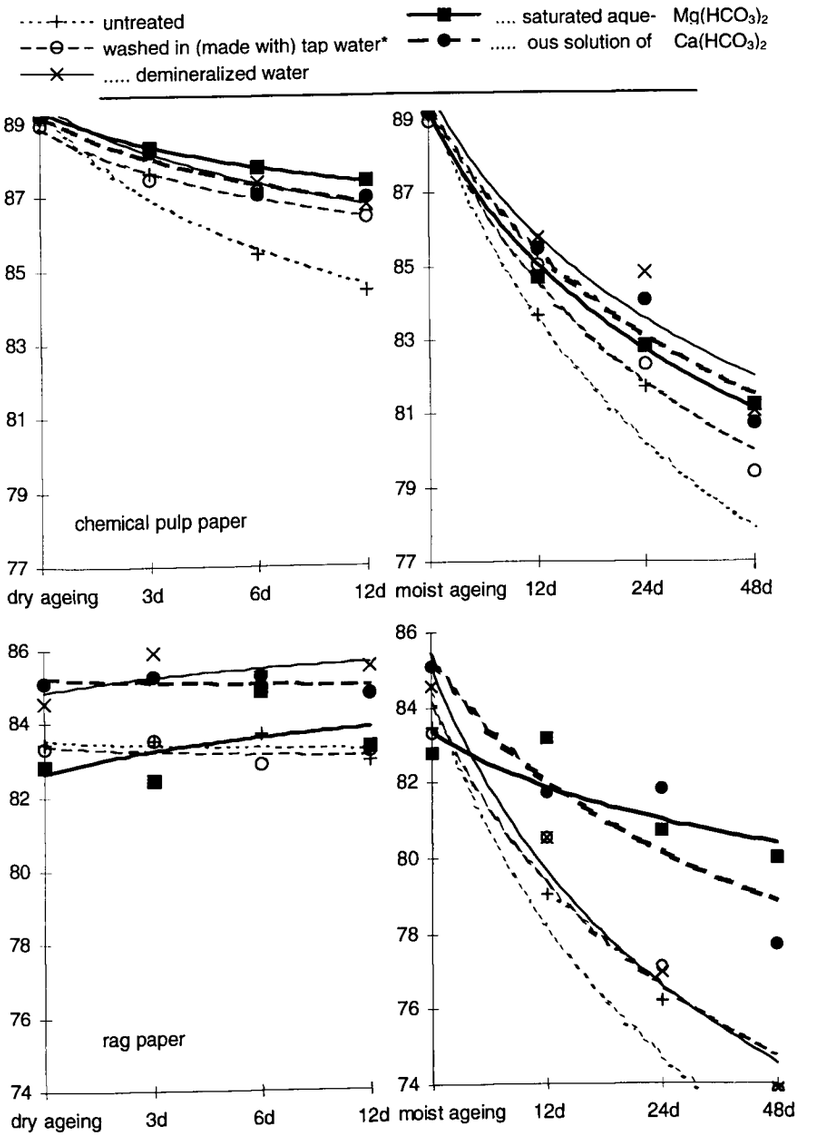

Fig.3b: Change of brightness (CIE-L*) of old papers during accelerated ageing

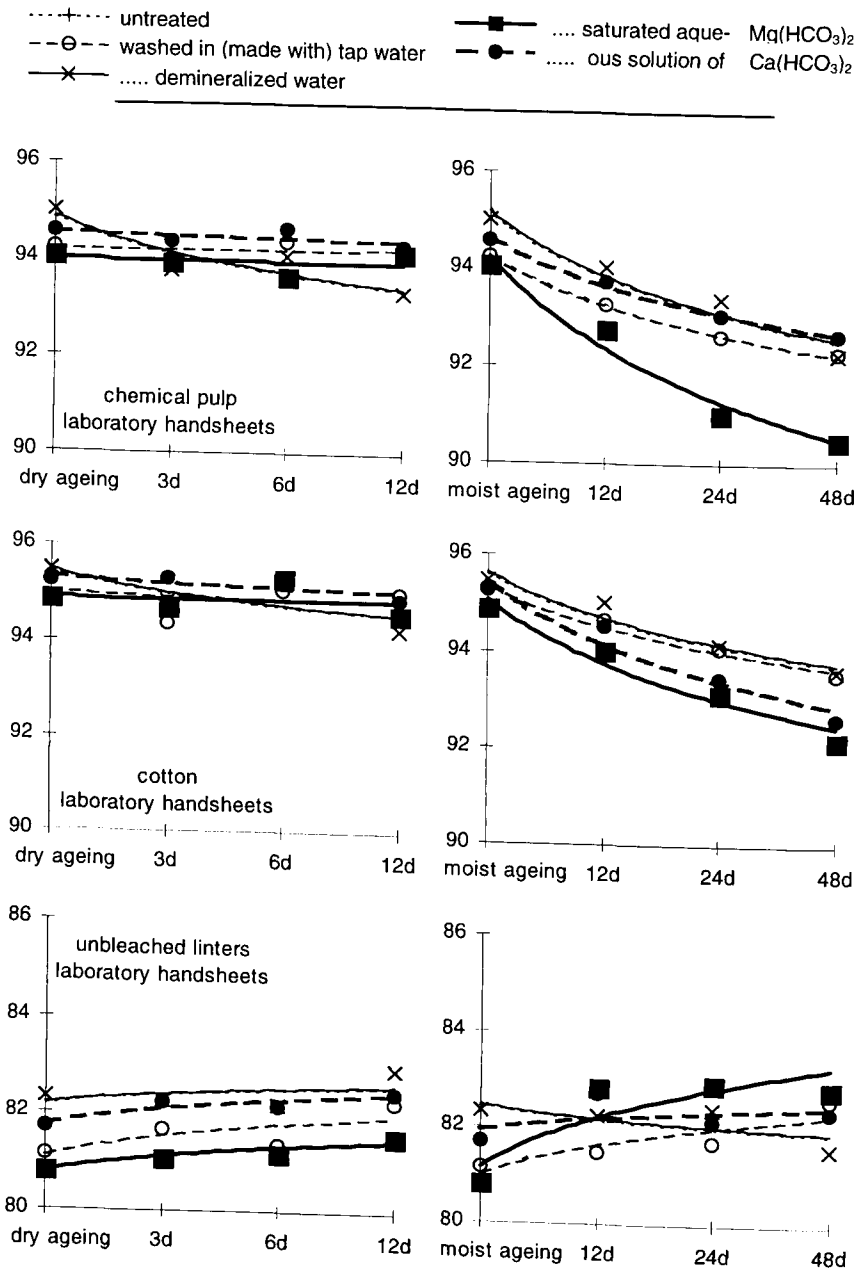

Fig.4: Change of brightness (CIE-L*) of laboratory handsheets during accelerated ageing.

5.4. Mechanical Strength

5.4.1 Tensile post Fold

Fig. 6 demonstrates in charts that laboratory handsheets made with Ca-containing water keep their initial mechanical strength, described as tensile strength after one defined fold[20], generally better than the others: In three (that for chem.p. moist, cotton dry and linters dry) or even the fourth (cotton moist) of the six charts, the relevant trendline shows the highest value, the slightest decreased and even an increase in tensile strength. The magnesium curve is sometimes quite near, but it is never better. For the old papers (Fig. 5) the contrast is true. Only in the case of groundwood 1908 dry ageing the calcium trendline can be understood as having the better shape than magnesium, and this only slightly. To compare the Ca trendline of groundwood 1923 and the more even Mg trendline, both approaching nearly the same final value, the question which one represents a better ageing behaviour is difficult to answer. The same is true with both ageings of rag paper. Here the tensile strength post fold of the unaged magnesium sample is very low, possibly by case: working with old paper includes the difficulty that those papers are quite often very uneven. The relative weakness of the magnesium treated unaged sample may not be a result of the treatment, but originated in the sample as provided before. Nearly all numbers for tensile post fold of magnesium treated rag paper samples after ageing of any kind and duration are higher than the relevant number for calcium (cf. Table 6; exception: 6 days dry).

If the relative weakness of the magnesium treated unaged rag paper samples is not a chance result, then a significant increase in mechanical strength during accelerated ageing must be stated: quite unlikely, at least in this amount, but not without parallel. For new papers and laboratory handsheets it is a well known phenomenon, most probably the result of slight crosslinking that takes place during accelerated (and also natural ?) ageing. In the case of magnesium treated old papers as the rag paper of this experiment and also with the chemical pulp paper (only dry ageing) a crosslinking via magnesium may be discussed, as already hypothesized: R(Cell)–COO–Mg–OOC–R(Cell)[21].

Altogether, and coming back to the main interest of this report, the following may be stated: From tests with laboratory handsheets the influence on the mechanical strength caused by magnesium can be stated as to be less positive than that caused by calcium. From the second and the third chart row of Fig. 5 another, and more important, fact becomes evident: for acidic paper any washing in water is of positive influence on the ageing stability of the mechanical strength, even that in demineralized water, this last true only for chemical pulp paper. If earth alkaline ions are present in the wash water, then the positive effect is greater. And

Table 6: Tensile post fold (N); sqrt (MD*CD)

	dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d	12d	24d	48d
Groundwood paper 1908							
untreated	19,41	16,83	18,84	14,23	15,43	12,23	10,92
aqu. demin.	21,60	20,87	19,31	17,00	16,37	13,76	9,90
tap water	20,56	19,48	18,43	18,01	14,22	14,14	12,01
Mg	20,15	18,99	17,83	15,14	14,12	14,14	15,93
Ca	19,80	16,96	20,02	17,57	13,74	13,50	11,58
Groundwood paper 1923							
untreated	3,12	0,00	0,00	0,00	0,35	0,04	0,01
aqu. demin.	5,15	2,38	3,47	0,29	2,19	0,16	0,01
tap water	3,28	3,60	1,70	1,65	1,53	1,47	1,29
Mg	3,07	1,77	3,60	2,12	4,36	1,64	2,07
Ca	3,27	4,57	3,87	1,87	2,53	0,69	2,27
Chemical pulp paper							
untreated	38,38	33,99	9,21	2,47	9,88	14,43	1,23
aqu. demin	37,03	32,92	28,71	23,69	22,78	21,33	9,88
tap water	31,50	28,75	30,94	19,58	23,26	16,02	11,15
Mg	31,81	39,83	32,24	31,86	29,37	27,67	20,42
Ca	34,57	35,04	33,12	32,46	21,31	24,91	17,02
Rag paper							
untreated	19,06	13,25	14,58	12,66	12,15	6,41	11,04
aqu. demin.	15,64	17,30	16,25	16,88	12,09	10,80	13,03
tap water	19,24	19,20	17,26	19,58	11,87	10,62	9,64
Mg	9,55	17,77	13,96	18,69	15,69	10,42	13,25
Ca	16,95	16,03	17,08	11,51	6,17	9,31	9,92
Chemical. pulp laboratory handsheets							
aqu. demin.	15,37	15,16	16,38	19,65	16,57	11,09	12,48
tap water	15,94	20,68	16,47	17,41	17,33	11,78	13,95
Mg	26,26	21,92	20,90	16,59	22,03	12,74	7,92
Ca	18,24	18,86	17,60	15,82	16,58	16,57	16,13
Cotton laboratory handsheets							
aqu. demin.	31,75	32,91	33,10	37,77	32,59	31,07	41,78
tap water	39,03	38,45	42,06	41,48	28,87	28,42	29,02
Mg	41,70	40,83	36,87	39,20	33,72	33,52	31,08
Ca	44,53	40,11	44,55	45,82	39,25	35,57	35,28
Unbleached linters laboratory handsheets							
aqu. demin.	24,35	19,13	22,58	18,95	23,56	18,25	26,73
tap water	21,88	19,91	18,71	16,99	16,01	15,16	15,34
Mg	18,97	19,87	17,47	22,11	16,50	16,81	18,58
Ca	17,00	18,21	19,66	23,37	17,45	18,31	21,47

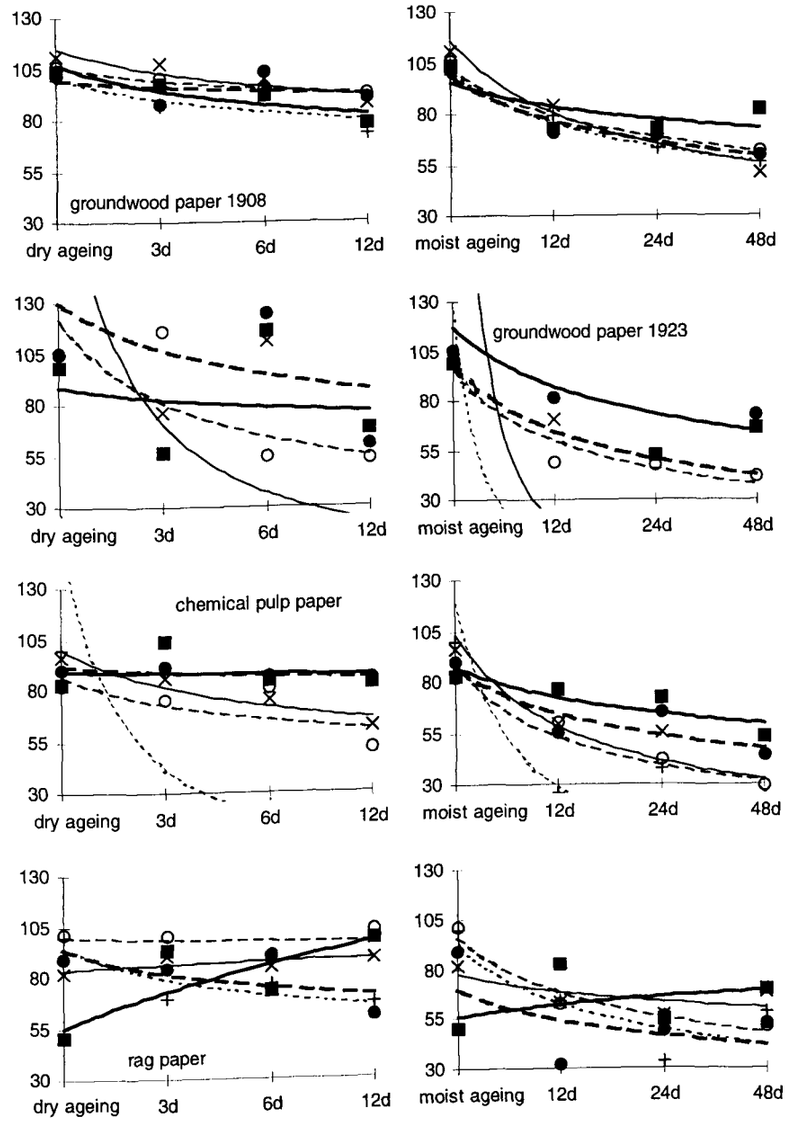

Fig. 5: Change of tensile strength (%) after one defined fold during accelerated ageing of old papers (100 = untreated, unanged).

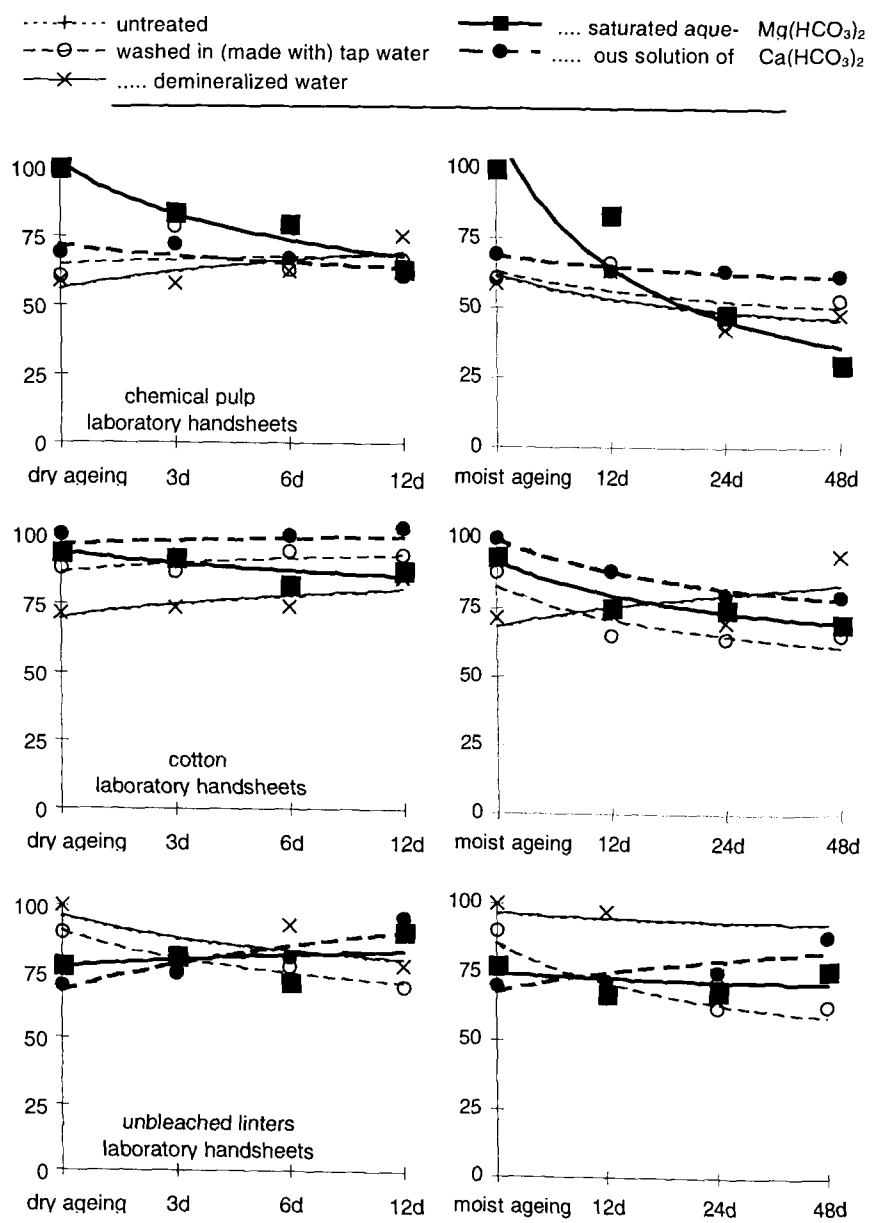

Fig. 6: Change of tensile strength (%) after one defined fold during accelerated ageing of laboratory handsheets (100 = best unaged. Chem. p.: Mg. Cotton: Ca. Linters: Aqu, demin.).

Table 7a: MIT Fold Number (MD only) of old papers

		dry ageing: 105°C				moist ageing: 80°C 65%		
		0d	3d	6d	12d	12d	24d	48d
Groundwood paper 1908	**tension: 300 g**							
untreated		78	42	40	8	106	19	19
	Standard deviation	*36,78*	*23,14*	*27,35*	*6,15*	*50,64*	*5,30*	*8,41*
aqu. demin.		156	99	112	28	101	20	14
	Standard deviation	*52,72*	*51,73*	*39,49*	*7,55*	*48,1*	*7,28*	*5,49*
tap water		114	67	63	24	54	52	31
	Standard deviation	*42,65*	*29,17*	*40,16*	*8,03*	*26,94*	*25,45*	*11,86*
Mg		96	78	45	35	51	51	49
	Standard deviation	*45,76*	*37,62*	*22,17*	*15,53*	*18,00*	*22,92*	*17,17*
Ca		142	58	63	39	77	73	36
	Standard deviation	*51,79*	*16,31*	*20,21*	*13,21*	*15,25*	*35,12*	*15,02*
Groundwood paper 1923	**tension: 300 g**							
untreated		30	1	0	0	0	0	0
	Standard deviation	*37,19*	*0,53*			*0,42*	*0,32*	
aqu. demin.		4	4	3	2	1	2	1
	Standard deviation	*1,17*	*3,63*	*2,27*	*0,68*	*0*	*0,68*	*0,52*
tap water		9	12	2	2	5	3	4
	Standard deviation	*5,85*	*8,10*	*1,16*	*1,42*	*4,74*	*3,29*	*2,28*
Mg		26	8	7	4	8	15	1
	Standard deviation	*32,76*	*6,80*	*5,44*	*1,72*	*1,81*	*14,88*	*0,42*
Ca		61	27	18	4	18	4	5
	Standard deviation	*47,12*	*34,38*	*26,05*	*1,26*	*15,03*	*4,15*	*1,99*
Chemical pulp paper	**tension: 400 g**							
untreated		21	32	1	1	1	0	0
	Standard deviation	*12,43*	*13,91*	*0*	*0*	*0,32*		
aqu. demin.		207	73	8	3	7	2	0
	Standard deviation	*80,17*	*62,01*	*2,60*	*1,69*	*5,16*	*0,67*	*0*
tap water		20	15	3	1	4	1	1
	Standard deviation	*9,40*	*10,33*	*1,13*	*0,70*	*1,40*	*0,42*	*0,63*
Mg		14	87	21	9	12	7	9
	Standard deviation	*4,72*	*36,23*	*11,99*	*10,83*	*9,19*	*5,40*	*9,31*
Ca		75	31	16	7	4	13	2
	Standard deviation	*38,19*	*19,13*	*9,91*	*1,91*	*1,29*	*10,70*	*1,35*
Rag paper	**tension: 400 g**							
untreated		71	19	29	12	21	9	10
	Standard deviation	*20,30*	*4,27*	*10,31*	*6,85*	*7,87*	*2,91*	*5,23*
aqu. demin.		68	74	55	40	35	38	23
	Standard deviation	*23,58*	*29,22*	*12,53*	*8,29*	*13,5*	*13,43*	*12,1*
tap water		108	55	47	48	56	27	23
	Standard deviation	*41,95*	*13,96*	*21,53*	*9,28*	*34,8*	*8,51*	*13,3*
Mg		13	30	30	31	35	49	26
	Standard deviation	*3,97*	*5,72*	*12,78*	*9,06*	*12,5*	*41,01*	*4,99*
Ca		105	45	26	21	22	70	33
	Standard deviation	*42,07*	*10,52*	*7,8*	*12,61*	*12,8*	*27,94*	*11,8*

from the first chart row (groundwood paper 1908) it becomes evident that acidic pH (cf. Table 8) does not necessarily mean loss of mechanical strength, at least during accelerated ageing.

5.4.2. MIT Fold Number

If we compare the charts of Fig. 5 and 6 with those of Fig. 7 and 8 most often a striking parallelism is to be noted: obviously, as the parameters checked here and there represent the same quality, i.e. mechanical strength. The MIT fold numbers

Table 7b: MIT Fold Number of laboratory handsheets

		dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d		12d	24d	48d
Chemical pulp	tension: 500 g							
aqu. demin.	23	25	25	21		38	18	13
Standard deviation	*5,22*	*7,78*	*3,30*	*3,15*		*5,97*	*3,64*	*1,60*
tap water	35	36	25	33		30	24	22
Standard deviation	*4,73*	*8,97*	*6,28*	*3,62*		*6,66*	*3,49*	*5,23*
Mg	96	64	48	39		32	35	18
Standard deviation	*15,60*	*5,93*	*5,76*	*6,80*		*4,59*	*8,36*	*4,40*
Ca	25	33	22	29		38	32	40
Standard deviation	*3,26*	*13,78*	*5,38*	*6,79*		*10,97*	*8,58*	*10,39*
Cotton	tension: 1000 g							
aqu. demin.	89	73	63	39		53	74	190
Standard deviation	*15,43*	*12,06*	*3,83*	*9,56*		*9,29*	*6,92*	*30,17*
tap water	73	57	54	53		28	31	34
Standard deviation	*9,79*	*9,81*	*10,34*	*9,82*		*2,25*	*4,47*	*4,44*
Mg	87	45	69	57		57	55	55
Standard deviation	*9,24*	*6,58*	*12,28*	*11,92*		*10,50*	*9,52*	*8,26*
Ca	73	77	54	97		97	63	93
Standard deviation	*8,52*	*6,40*	*8,42*	*6,08*		*16,80*	*10,53*	*15,17*
Unbleached linters	tension: 700 g							
aqu. demin.	51	63	47	59		41	47	148
Standard deviation	*10,14*	*8,08*	*8,36*	*9,53*		*7,36*	*8,63*	*26,40*
tap water	32	26	19	23		43	33	35
Standard deviation	*7,40*	*11,49*	*2,45*	*2,43*		*6,57*	*8,76*	*7,23*
Mg	51	28	19	29		31	51	58
Standard deviation	*7,32*	*2,82*	*1,98*	*3,09*		*5,58*	*4,97*	*20,60*
Ca	49	61	62	70		42	37	42
Standard deviation	*5,93*	*10,10*	*7,25*	*8,33*		*6,46*	*4,10*	*7,01*

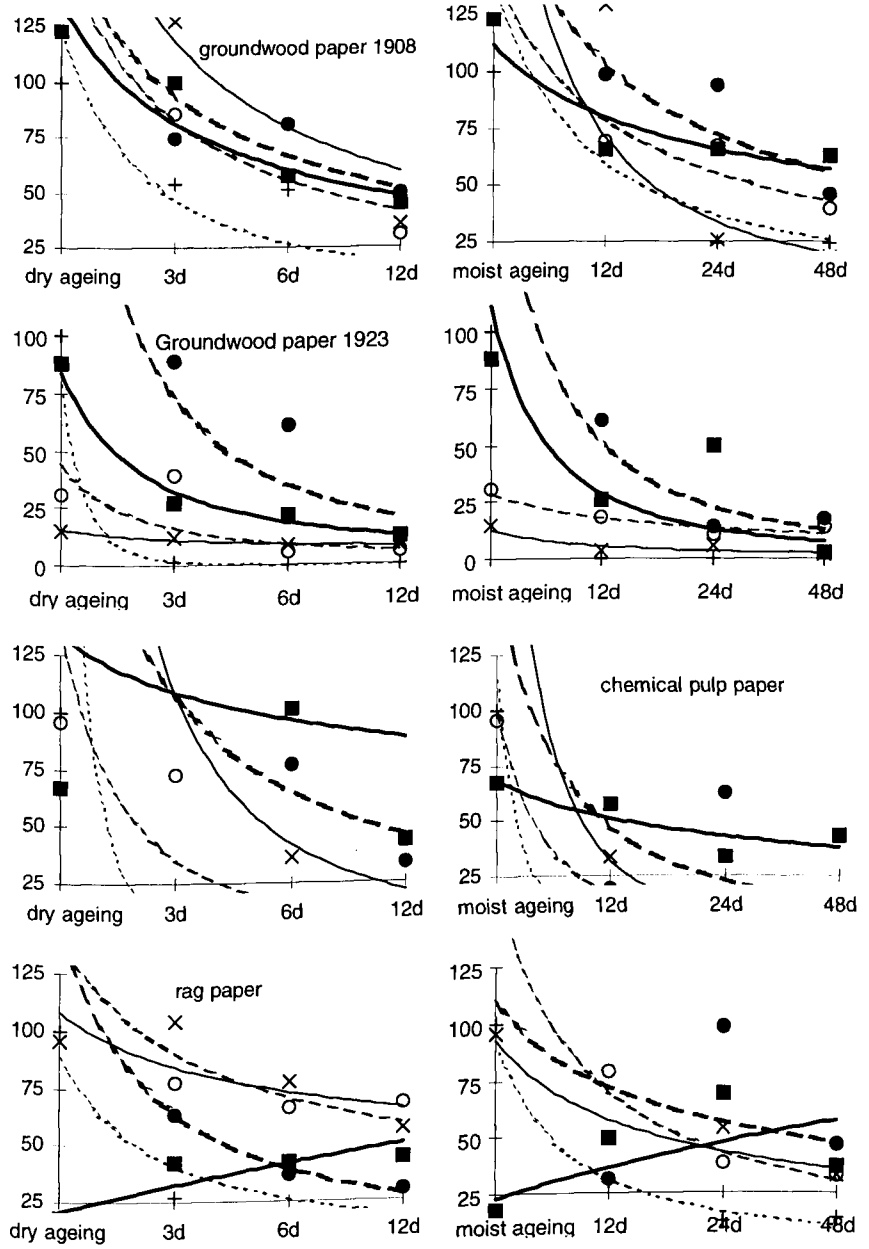

Fig. 7: Change of MIT fold number (%) of old papers during accelerated ageing (100 = untreated unaged).

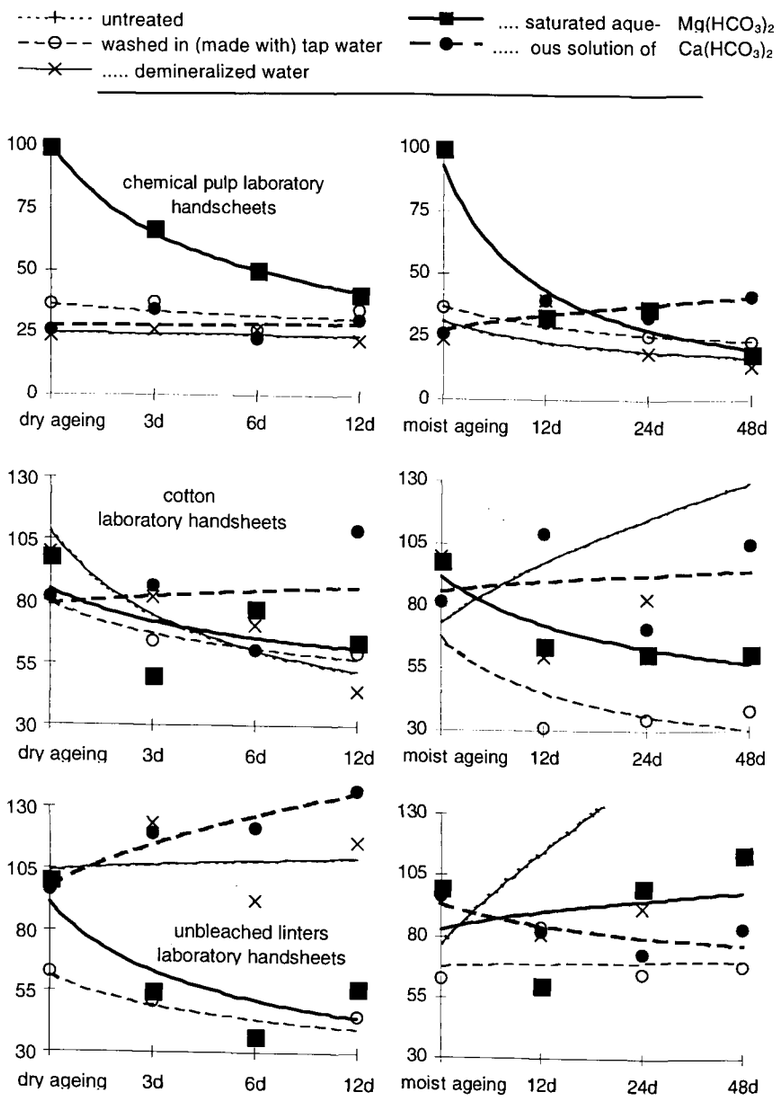

Fig. 8: Change of MIT fold number (%) during accelerated ageing of laboratory handsheets. Best unaged = 100. Chem. pulp: Mg. Cotton: Aqu. demin. Linters: aqu. demin and Mg.

therefore support the conclusions drawn in the previous chapter, especially in the cases with strange results. Sometimes there are also unequal or even contradictory results of the two mechanical strength measurements, just with regard to the main question of this experiment, i.e. whether calcium or magnesium gives better results: groundwood 1923 moist, linters moist. As an explanation we must rely on unevenness of the samples and inaccuracy of the measuring.

The immense scattering, mainly for old papers (cf. Table 7a), does not speak high of the reliability of MIT fold number measuring. The standard deviation is sometimes half the amount of the average. Another reason against this parameter is the long time needed to measure that number: a two-figured multiple of the seconds necessary to check tensile post fold.

In the interest of the research reported here, it could honestly be reported that the trendlines on the MIT fold number charts are quite confusing for sound general conclusions. The findings based on the tensile post fold numbers generally concur with MIT fold numbers and this information can be usable for evaluating paper mechanical strength.

5.5 Chemical Characteristics

5.5.1 pH

Regarding the pH, the most often checked number in paper conservation research, the obvious fact is to state that all washing or deacidification procedures used for this experiment bring the pH up for the old papers, the most with Mg, followed by Ca and tap water, the least with demineralized water. Laboratory handsheets made with $Mg(HCO_3)_2$ containing water have a pH about 10 that in the case of high quality fibre (cotton and linters) maintains this pH level during accelerated ageing (cf. Fig. 10) while with chemical pulp it goes down, at least with moist ageing. A pH about 10 is also found with the rag paper (initial pH 5 6) immersed in $Mg(HCO_3)_2$ containing water, and in the same way as with the laboratory handsheets it remains high during dry ageing. A constant high pH during dry ageing was also found with the chemical pulp paper (Fig. 9), while with the groundwood papers the initial pH went down not only during moist ageing (as with the others), but also during dry.

The pH found immediately after treatment is > 8 with all Mg-treated papers: not stable with groundwood, as just mentioned, but nevertheless regarded as too high by some restorers and researchers. As there is little or no correlation with mechanical strength nor with DP, this seems to be over-cautious – if we ignore yellowing. With $Ca(HCO_3)_2$ containing water it can happen (groundwood paper

Table 8: pH (surface)

	dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d	12d	24d	48d
Groundwood paper 1908							
untreated	4,13	4,35	4,76	4,52	4,70	4,40	4,43
aqu. demin.	5,33	5,12	5,00	4,92	4,55	4,42	4,34
tap water	6,42	5,66	5,55	5,34	5,27	4,83	4,58
Mg	8,93	7,31	6,75	7,49	7,00	6,63	6,14
Ca	7,64	6,97	6,17	6,69	6,75	6,68	6,52
Groundwood paper 1923							
untreated	3,32	3,49	3,49	3,35	3,36	3,21	3,26
aqu. demin.	4,30	4,50	4,16	3,81	3,74	3,58	3,60
tap water	6,26	5,65	5,51	5,00	5,23	4,81	4,66
Mg	8,24	7,22	7,04	6,55	6,30	6,08	6,16
Ca	6,72	6,07	5,77	5,46	5,48	5,49	4,98
Chemical pulp paper							
untreated	4,82	4,92	4,31	3,90	4,26	3,89	4,12
aqu. demin	5,04	5,06	4,83	4,86	4,40	4,50	4,24
tap water	5,79	6,38	5,80	5,70	5,01	4,90	5,06
Mg	7,87	7,38	7,43	7,83	6,84	6,63	6,29
Ca	6,94	6,69	7,12	6,82	6,28	6,70	7,04
Rag paper							
untreated	5,45	5,50	5,84	5,60	5,37	5,39	5,41
aqu. demin.	6,21	5,59	5,79	5,61	5,00	4,88	4,98
tap water	7,12	6,64	6,52	6,28	6,00	5,67	5,17
Mg	10,10	9,68	9,77	9,71	9,10	8,32	7,49
Ca	7,82	7,36	7,35	7,14	7,21	6,02	6,61
Chemical. pulp laboratory handsheets							
aqu. demin.	6,72	7,23	6,24	5,02	5,96	5,40	5,44
tap water	8,12	6,78	6,70	6,13	6,76	6,29	6,12
Mg	10,01	9,92	10,50	10,40	9,98	8,66	7,72
Ca	8,92	7,52	7,56	7,58	8,42	8,06	8,05
Cotton laboratory handsheets							
aqu. demin.	6,80	6,86	6,61	6,26	6,36	5,99	6,02
tap water	8,21	8,25	7,30	7,28	7,90	7,28	7,00
Mg	10,00	9,84	9,85	10,37	10,39	10,71	10,41
Ca	8,75	8,31	8,63	8,78	8,74	8,50	8,21
Unbleached linters laboratory handsheets							
aqu. demin.	6,61	6,73	6,89	6,37	6,43	6,45	5,74
tap water	8,96	7,78	7,33	7,86	7,03	7,12	7,00
Mg	9,91	9,82	9,97	9,57	10,48	10,47	9,53
Ca	8,64	7,87	8,46	8,27	8,90	8,08	8,64

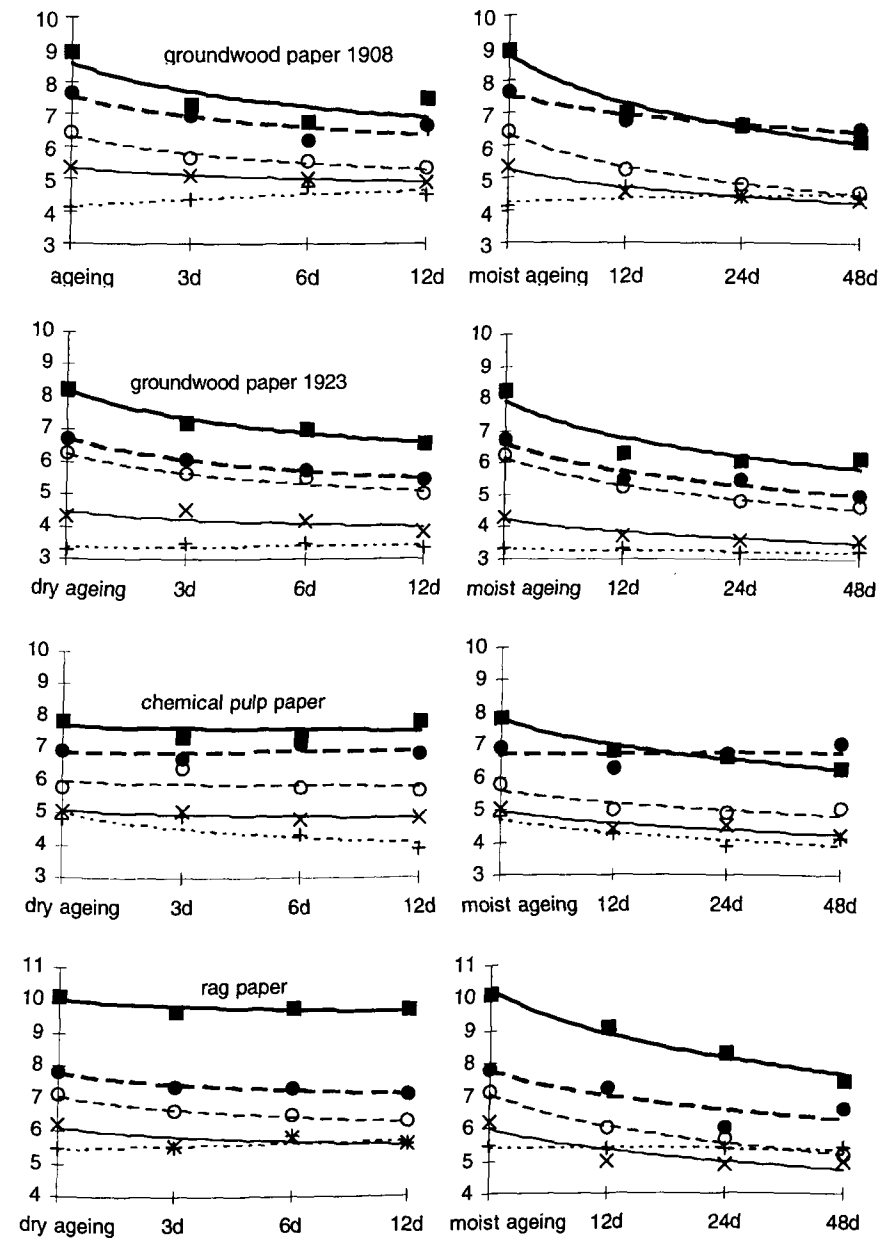

Fig. 9: Change of pH during accelerated ageing of old papers.

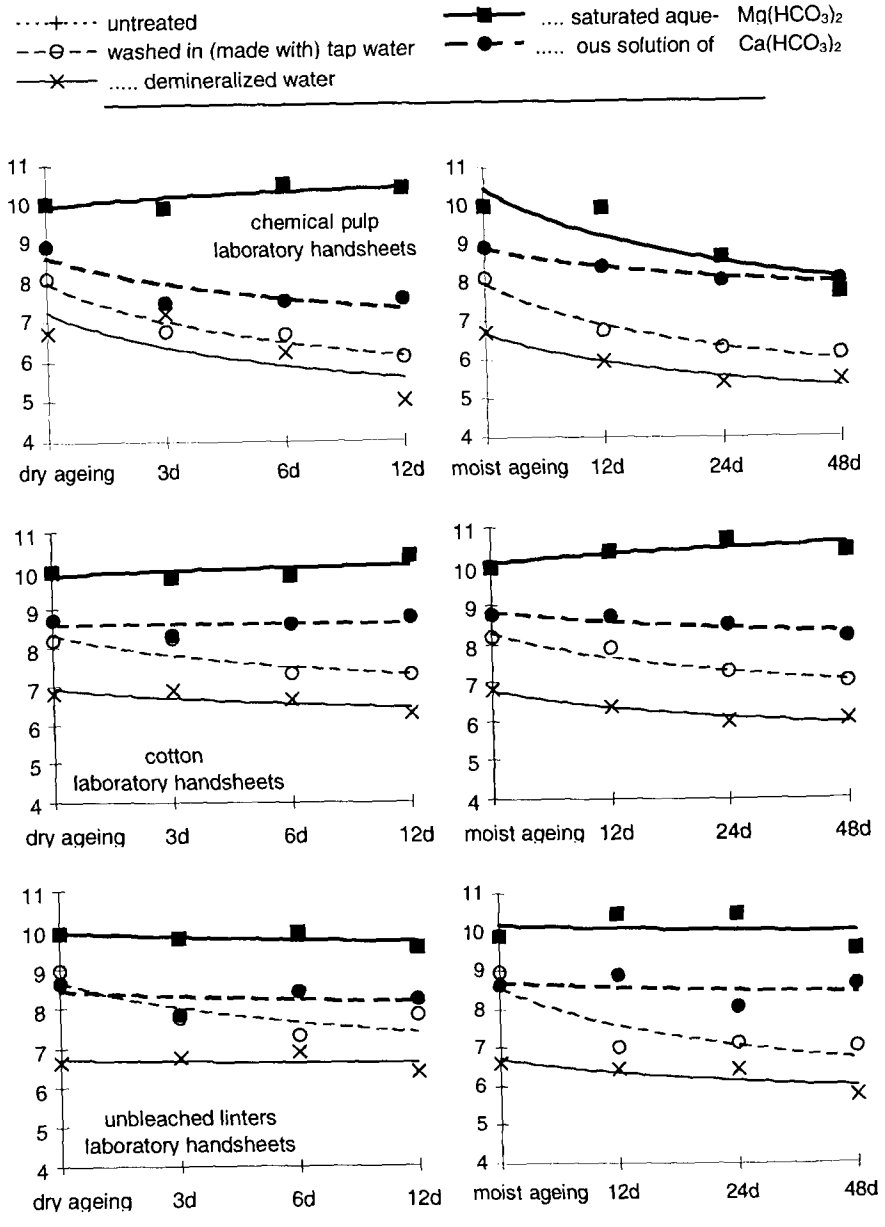

Fig. 10: Change of pH during accelerated ageing of laboratory handsheets.

1923) that the pH after treatment is hardly neutral and goes down during accelerated ageing, mainly moist, to an area usually estimated as detrimental.

The most striking observation looking at Fig. 9 and, to some extent, also at Fig. 10, is, as with brightness, the significant difference between dry and moist ageing. This will be discussed later.

5.5.2 *Degree of Polymerisation*

Looking at Fig. 12 what hit the eye most is the little distance between the trendlines. This indicates that the DP of laboratory handsheets decreases, regardless of the manner of production, at least during dry accelerated ageing. There is nearly

Table 9: Average degree of polymerization

	dry ageing: 105°C				moist ageing: 80°C 65%		
	0d	3d	6d	12d	12d	24d	48d
Chemical pulp paper							
untreated	320	360	230	200	240	250	190
aqu. demin	320	320	320	290	290	290	230
tap water	330	350	300	260	280	240	220
Mg	320	380	330	330	320	280	260
Ca	390	340	350	320	300	300	240
Rag paper							
untreated	350	400	430	350	400	360	280
aqu. demin.	460	410	420	400	330	320	270
tap water	510	450	420	380	390	310	280
Mg	520	440	430	360	460	470	440
Ca	530	500	470	420	370	430	320
Chemical. pulp laboratory handsheets							
aqu. demin.	838	730	670	670	770	640	600
tap water	850	750	680	660	780	750	710
Mg	840	720	650	590	700	680	600
Ca	929	730	700	640	770	740	660
Cotton laboratory handsheets							
aqu. demin.	1750	1270	1040	920	1610	1340	1240
tap water	1750	1280	1260	1050	1540	1480	1310
Mg	1750	1300	1180	990	1480	1480	1270
Ca	1735	1320	1200	990	1450	1270	1200
Unbleached linters laboratory handsheets							
aqu. demin.	1740	1380	1260	1070	1520	1510	765
tap water	1720	1410	1270	1100	1590	1510	1350
Mg	1690	1390	1280	1110	1580	1540	1250
Ca	1700	1360	1170	1050	1510	1370	1210

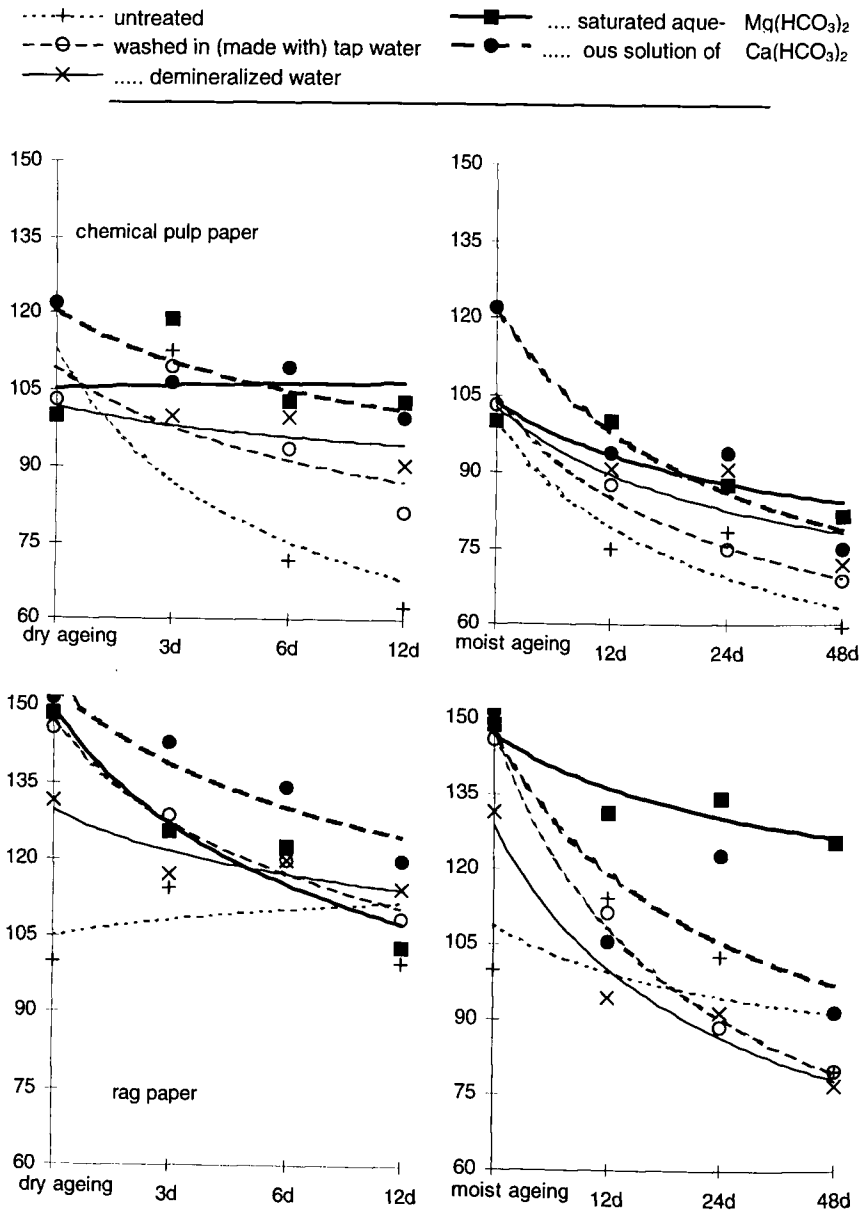

Fig. 11: Change of DP (%) during accelerated ageing of old papers (100 = untreated unaged).

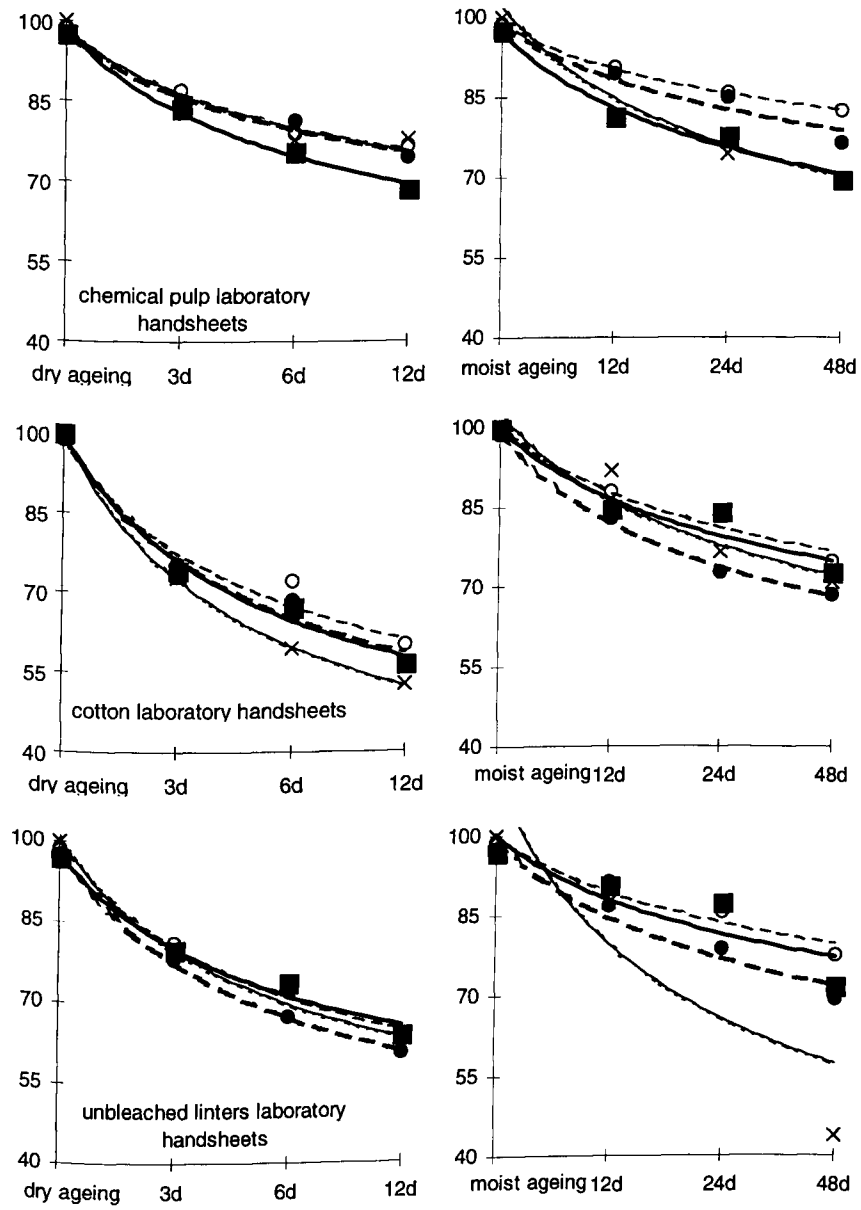

Fig. 12: Change of DP (%) during accelerated ageing of laboratory handsheets. Best unaged = 100. Chem. pulp and linters: aqu. demin. Cotton: aqu. demin., tap water and Mg.

no difference between Ca and Mg with cotton, both, and even more tap water, being slightly superior to demineralized water; there is a slight superiority of Ca with chemical pulp and a slight superiority of Mg with unbleached linters, these two giving the best results in the named cases. The differences, however are so little that it is dubious whether they are more representing uncertainties of the measuring method than the differences caused by treatment. With moist ageing the picture is only slightly better. The very low DP number of moist aged unbleached linters made with demineralized water is ignored, even if a repeated check gave the same result. If a specific problem stems from this deviated result, then it is outside the perspective of this experiment. If we want to conclude any one superior production method based on the DP number results, we take tap water followed by demineralized water (not considering the deviated result).

The most conspicuous fact to be observed in Fig. 11 is the change in DP caused by wet treatment of the two old papers: by any in a quite high amount with rag, by Ca only with chemical pulp. Again the hypothesis of crosslinking via earth alkaline ion is to be mentioned [21]. If this phenomenon is true, then in the case of the chemical pulp paper used for this experiment it took place only with calcium – for what reason? If for any, then it seems to be rooted in the state of decay of this specific paper, hardly identifiable, and it is hardly to be taken as an argument for calcium as the better deacidification agent. The effect is not stable with accelerated ageing: after the dry method, the DP of the two samples (Ca and Mg) is nearly the same; after the moist we see a superiority of Mg, but this conclusion could be doubted because of inaccuracy of the measurement method. With the rag paper we note again the queer fact of contradiction between dry and moist ageing: Ca treatment is superior in dry, Mg treatment is superior in moist ageing.

5.6 Correlations

It is not possible to see a clear correlation, valid for all papers and all samples, between the different parameters measured in the course of this experiment. We may assume that any of the measured parameters is linked primarily to one specific chemical quality of the paper and the pulp that were chosen for the experiment and in the second, third rate etc. to others. In the same way we may assume that these chemical qualities are changed in the course of accelerated ageing. Then we must state that the mutual interference of these changes in these chemical qualities is too big as to make tangible the change in one of them, i.e. that primarily represented by one of the measured parameters. To give an example: if the length of the cellulose molecular chain, presumably being the main reason for

mechanical strength, is reduced in the course of accelerated ageing, then this may interfere with consequently formed decomposition products that, under certain and unknown circumstances and in a certain and unknown state of decomposition, may act as cement between the shortened chains thus enhancing mechanical strength.

If a correlation can be seen, then with moist ageing of chemical pulp laboratory handsheets: in all measured parameters we have the extreme result – highest rate of yellowing, most reduced brightness, most reduced mechanical strength, pH and DP – with the Mg-treated samples, most favourable results – except DP, were tap water is better – with Ca. Looking at the dry aged samples this correlation can be seen only between yellowing and DP. A correlation can also be seen with the chemical pulp paper, here with dry ageing and with contrary result regarding Mg and Ca: the last never giving the better numbers. The untreated samples of this paper giving the worst numbers of any measured parameter is a very clear observation, and the correlation is self explanatory.

6. CONCLUSION

6.1 How to Deacidify

From this last finding it can clearly be concluded that with chemical pulp paper any wet treatment improves the ageing behaviour, and that if the water used for that treatment is containing earth alkaline carbonate, the positive effect is enhanced. Possibly this well known platitude is the only valid statement regarding wet treatment and deacidification that can be given without restriction and further reasoning. If we disregard colour change, it can be extended to groundwood paper, while rag paper, slightly acidic, but strong, even if some hundred years old, does not necessarily and under all circumstances benefit from earth alkaline wet treatment: a bath in $Mg(HCO_3)_2$ containing water is reducing its mechanical strength, while $Ca(HCO_3)_2$ seems to result in slightly reduced ageing stability of this parameter. From the mechanical strength numbers achieved with laboratory handsheets a generally slight superiority of Ca can be concluded; it does not prove true with the real old papers. Yellowing and also brightness numbers are giving a clear superiority of Ca, which is reduced, but not contradicted by the real old papers.

Altogether, these results were the reason for a change in the Institute where the experiment was done. In this Institute, the deacidification solution is prepared by further enriching the very good and hard tap water with earth alkaline carbonate under pressure of carbon dioxide[8], and this solution is widely used,

routinely, e.g., in the leafcasting machine. Following the results of the experiment the enriching procedure was changed from Mg to Ca. If it is true that the amount of buffer substance brought into the paper by deacidification is of less importance[16], then this is a good decision. After a year or two it will be re-evaluated on the basis of experience in daily conservation practice.

6.2. Further Research

6.2.1. Cellulose Chemistry and Paper Decay

As it is always the case with a research project on a complicated matter, more questions arose from this experiment than could be answered. These unanswered questions do not pertain to practical conservation, but to paper decay and its detailed chemistry. Nearly any article dedicated to this topic is ending with the demand for further research; so does this one. But it is adding the question whether the results of such further research will be of impact on practical paper conservation. It may sound as an appeal to paper chemists working in the field of conservation not to lose sight of their findings being applied in practice, and this means: not to restrict their research on laboratory handsheets and base their statements and suggestions for practice on findings that are discernible only with well defined cellulose. To give an example: it would be of immense difficulty, enormously slowing down practical work and reducing the output of a workshop if, as paper decay and influencing it by deacidification is as extremely complicated in its chemical details as this experiment has once more demonstrated, these chemical details must be checked prior to any treatment: degree of polymerization, carbonyl, carboxyl content along the chain or at the chain end, relevant state of cellulose decay and accompanying compounds, etc. The paper chemists active in conservation research must pose strong arguments if they think it necessary to introduce such analytical work into daily routine of a conservation workshop – not to speak of the difficulty to execute it with real old paper instead with laboratory handsheets.

6.2.2 Accelerated Ageing

The primary aim of conservation research is to find out whether a certain treatment, done now in favour of an object, will keep this positive effect in the future or will, on the long term, prove to be useless or even detrimental. For this kind of research accelerated ageing is indispensable. On the other hand it is well known

that, from the viewpoint of true science, such a look into the future is impossible[19 22] and that relevant conclusions must be drawn with reserve, restricted to mere comparison of one single quality – that representing the conservation treatment, while all other qualities are the same – and its direction: better or worse. To give, again for better understanding, an example: if a certain paper having submitted to a certain conservation treatment such as deacidification with Mg, behaves better during accelerated ageing than the same paper without treatment, then it may be concluded that the same behaviour will take place during storage in the future. If, however, as has been demonstrated in the course of this experiment – not for the first time[14] – different methods of accelerated ageing have contrary results even in this restricted interpretation, then this technique to foresee the future becomes totally useless. An urgent need of further conservation research is therefore to clear up more in detail which of the chemical reactions that, in their summation of overlapping and mutually influencing form what we call "ageing" prevail in dry, in moist and possibly in a third and a fourth method (light, radiation, pollution) of accelerated ageing, and to develop a combined method that imitate these processes and their relation to each other as near as possible to real ageing. There is already a promising beginning of such research[23].

ACKNOWLEDGEMENTS

An extensive experiment as that reported above cannot be done by a single person and, as it is encompassing several fields of specialization – practical paper conservation and paper science –, even not by one specialized institute.

Thanks are to be said to the students of the course 1994/97 of the *Staatliche Fachakademie zur Ausbildung von Restauratoren für Bibliotheks- und Archivgut* in Munich, who, as part of their being educated how to do and how to understand scientific research, performed a great lot of the immense amount of strength and colour checks necessary for the experiment.

Particular thanks are to be said to Ritsuko Ishii and other staff members of the *Institut für Buch- und Handschriftenrestaurierung* in Munich, who supervised the work of the students and completed it.

As neither the Institute nor the Fachakademie are equipped for chemical analysis on a level higher than that usual and, according to the state of art in practical conservation, necessary for this field of activity, the DP measuremts were done by the *Institute of Macromolecular Chemistry, Dept. of Renewable Materials, University of Technology in Darmstadt* and the measurements of mineral content by the *Papiertechnische Stiftung* in Munich. For both we say our thanks.

APPENDIX

Remarks on the analytical methods, taken from the reports of the Institutions that did the analytical work for the project:

- The average degree of polymerization (DP) was found by measuring the intrinsic viscosity number according to Zellcheming Merkblatt IV/50/69 (EWNN).
- For measuring the mineral content the paper samples were ashed (3 h 550° C). Then x-ray micro analysis (RMA) was made.
- The numbers for ash were given as % related to oven dry paper (105°C). The different elements were given as % related to ash.
- Conversion to the numbers given in Table 3 was done by the author according to the formula : element as percent * ash as percent / 10 = element as mg; element as percent * ash as percent / 10 / molecular weight = element as mmol.

SUMMARIES

Aqueous Deacidification – with Calcium or with Magnesium?

In order to check the validity of the arguments recently presented against aqueous deacidification using $Mg(HCO_3)_2$ four old papers representing the types "brittle groundwood", "quality groundwood", "chemical pulp" and "rag", and three types of laboratory handsheets (chemical pulp, cotton and unbleached linters, as used in the reporting institute for leafcasting together with deacidification) have been submitted to different aqueous treatments or production methods resp.: $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ solution, demineralized and tap water. Because in the previous reports contrary behaviour of relevant samples during dry and during moist accelerated ageing has been emphasized, the samples have been submitted to both methods of accelerated ageing and then checked for mechanical strength, colour change, pH, DP and mineral content. The evaluation of the widely diverse results is bringing about four main conclusions:

- there is no clear superiority of one aqueous deacidification method using earth alkaline carbonate
- conservation research should take into account the situation of practical conservation work and avoid overinterpreting chemical details
- an urgent need of conservation research would be a method of accelerated ageing imitating natural changes more closely than the methods usual at this time.

Désacidification aqueuse au calcium ou au magnésium

Afin de vérifier la validité des arguments formulés récemment contre la désacidification aqueuse utilisant une solution de bicarbonate de magnésium on a soumis quatre sortes de vieux papiers, pâte mécanique de qualité et pâte mécanique fragile, papier de cellulose et papier chiffon, et trois types de feuilles de laboratoire (pâte chimique, coton et linters non blanchis, telles qu'on les utilise dans le laboratoire en question pour le laminage du papier en combinaison avec la désacidification), à différents traitements aqueux ou méthodes de production respectivement: à des solutions de bicarbonate de calcium et de magnésium, à de l'eau déminéralisée et à l'eau du robinet. Etant donné que des recherches antérieures avaient donné des résultats contraires lors du vieillissement accéléré du papier en fonction de l'humidité ou de la sécheresse de l'atmosphère, on a soumis les échantillons aux deux méthodes de vieillissement et on a ensuite testé leur résistance mécanique, leur changement de couleur, leur pH, leur degré de polymérisation et leur contenu minéral. L'évaluation des résultats mesurés fort divergents mène aux conclusions principales suivantes:

- aucune des méthodes de désacidification aqueuse à base de carbonate alcalino-terreux ne s'est avéré être nettement supérieure à une autre,
- la recherche dans le domaine de la restauration devrait davantage prendre en compte le côté pratique du travail de restauration et éviter de surinterpréter les détails chimiques,
- ce dont la recherche a un besoin urgent dans le domaine de la restauration serait de trouver une méthode de vieillissement accéléré qui imiterait mieux que les méthodes actuelles les processus naturels de changement.

Wäßriges Entsäuern – mit Calcium oder mit Magnesium?

Um die kürzlich gegen das wäßrige Neutralisieren von Papier mit Magnesiumbicarbonat-Lösung vorgebrachten Argumente zu prüfen, wurden vier alte Papiere, welche die Typen „Holzschliff fest", „Holzschliff brüchig", „Zellstoff" und „Hadern" repräsentieren, und drei Arten Laborblätter (Zellstoff, Baumwolle und ungebleichte Linters, wie im berichterstattenden Institut für das Papieranfasern kombiniert mit Neutralisieren verwendet) verschiedenen wäßrigen Behandlungen unterworfen bzw. mit dem entsprechenden Wasser hergestellt: $Ca(HCO_3)_2$- und $Mg(HCO_3)_2$-Lösungen, demineralisiertem und Leitungswasser. Da frühere Forschungen ein gegenteiliges Verhalten bei der beschleunigten Alterung in trockener und in feuchter Atmo-sphäre ergeben hatten, wurden die Proben beiden Alterungsmethoden unterworfen und dann auf mechanische Festigkeit, Farbveränderung, pH, Polymerisationsgrad und Mineralgehalt hin untersucht. Die Auswertung der sehr divergenten Meßergebnisse führt zu folgenden hauptsächlichen Schlüssen:

- keine der wäßrigen Neutralisierungsmethoden mit Erdalkalicarbonat ist der anderen klar und in jeder Hinsicht überlegen
- konservierungskundliche Forschung sollte die Situation der praktischen Konservierung stärker in Betracht ziehen und es vermeiden, einzelne chemische Beobachtungen überzuinterpretieren
- ein dringendes Bedürfnis der konservierungskundlichen Forschung wäre eine Methode der beschleunigten Alterung, die besser als die derzeit üblichen die Vorgänge des wirklichen Alterns imitiert.

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Effect of Gamma Rays on Pure Cellulose Paper

as a Model for the Study of a Treatment of "Biological Recovery" of Biodeteriorated Books

by A. M. ADAMO, M. GIOVANNOTTI, G. MAGAUDDA, M. PLOSSI ZAPPALÀ, F. ROCCHETTI, G. ROSSI

INTRODUCTION

As is known, the physical properties of electromagnetic waves (for example ionising gamma radiation from a Co-60 source) allow them to penetrate material without leaving any residue and, if suitably dosed, without noticeably altering the substratum in chemical-physical terms.

However, on living organisms, the effect is extremely harmful, but this property has become an interesting tool for those who have preservation problems caused by biological agents. There are now about 800 plants of an industrial type in the world (about 15 of which are in Italy) which use electron accelerators and another 200 (4 in Italy) with radioisotope sources which are used mostly in the sterilization of medical products and for industrial applications. About 50 of these are used on more than 40 types of foodstuffs, their "hygienization" from micro-organisms and animal parasites which would endanger a longer and more hygienic preservation.

Irradiation technologies and relative plant guarantee versatility in terms of the material to be treated, so much so that those materials which are subjected to irradiation have increased over the years, and have also come to include paints, inks, wood, plastic, sludges and wastewater, cosmetics, etc. At the same time, the number of related international and national regulation has also grown; they now establish exact limits in terms of what doses to use for which purposes.

For some time now analysis has been going on – and from a large number of research groups[1–5] – into the possibility of using gamma radiation on books and archive documents attacked by arthropods and micro-organisms. This research activity has developed in two ways: the analysis of the reaction of biological populations to radiation treatment[6–8] and that on the eventual negative effects on the paper substratum[5, 9–11].

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G.O. Phillips[12] has analyzed the effects of gamma radiation and beams of accelerated electrons on cellulosic systems. It has been shown that irradiauion at high energy levels produces free radicals which induce chemical and physical modifications in the cellulose. Combining ESR (Electron Spin Resonance) and ENDOR (Electron Nuclear Double Resonance) it has been possible to clarify the reaction processes and single out such free radicals which, however, are probably to be found in both the irradiated cellulose and in the cellulosic systems photosensitised in natural conditions.

Certain experimental evidence in the seventies demonstrated the negative effect on the polymeric molecule of cellulose subjected to relatively high gamma doses. Therefore in Italy the research has been put on one side. Some comfort derives from the fact that as far as treatment of endangered books is concerned, use – and it is still possible in Italy – could be made of treatment with gaseous fumigation such as Ethylene Oxide.

We should stress in this introduction that the research activity carried out up to now has always had as an objective to develop a method, like fumigation, which could lead to the complete sterilization of the book. Such a drastic objective implies the complete elimination, not only of infesting animals, but also all microbial *flora*, including spores and radio-resistant micro-organisms. For the moment, and as long as no clarification of all the parameters for the creation of a complete radiation process is made, we have not thought it useful to begin tests of biological resistance of the radiated material to microbial attack.

We should remember that the composition of printing paper, in terms of the quantity and quality of the cellulose and of other components, is most variable. Moreover, the reaction of amorphous components to radiation differs from the crystalline component of cellulose. As far as the crystalline part – the most resistant – is concerned, it has been known for some time[13–18] that only extremely high gamma doses are able to impair it and therefore facilitate the action of cellulolytic micro-organisms. The same is true of past experiences concerning radioresistance and radiosensitivity of numerous fungine strains[14 16 17 19] and insects[15]; for the moment it has been decided to forego *ad hoc* experiences. The intention is to return to this subject matter in a further work of a speculative nature. However, here we wish to talk about the alterations which high gamma doses cause in cellulose, evaluating the importance of these alterations over a long, successive preservation of the book. We chose a wide range of doses to include also those that were certainly excessive for an hypothetical practical application, but which allowed us to highlight the negative effects on the *substratum*. The choice of Whatman n° 1 paper (Carlo Erba) has allowed us to work on a material which, although it is far from being real printing paper, consists exclusively of cellulose (98% cotton).

For a more complete understanding of the phenomena, a comparison has been made between the effect of treatment with ionized gamma radiation and that of fumigation treatment with Ethylene Oxide gas.

Finally, we tested combined treatments of radiation, humidity (in saturation conditions) and low temperatures, which allowed us to simulate the drastic environmental conditions to which the material under examination is subjected during particular natural calamities (floods).

The working group has been able to take advantage of the interest of those Italian Institutions with expertise in this field:

- Istituto Centrale per la Patologia del Libro (I.C.P.L.) del Ministero per i beni culturali e ambientali
- Ente per le Nuove Tecnologie , L'Energia e l'Ambiente (ENEA)
- Istituto Poligrafico e Zecca dello Stato.

EXPERIMENTAL PART

Irradiation Technologies

Irradiation of paper, at room temperature and humidity was carried out at the "Calliope" plant of ENEA in its Research Centre in the Casaccia. The Calliope plant is a pool-type irradiation facility equipped with a Co-60 source – at the moment of a cylindrical geometry with maximum nominal activity of 3.7×10^{15} Bq (100,000 Ci).

To determine the levels of pre-set doses to use in the experimental programme, the Fricke dosimetry was used following the ASTM Standard D 1671-72. Doses of 0, 1, 2, 5, 10 kGy were administered using a dose/rate of 2,843 Gy/h, where the Gray (Gy) corresponds to an absorption of ionizing energy equal to I Joule per kg of material treated.

Fumigation

On the paper being examined at 26–27° C and at about 55% Relative Humidity (R.H)., fumigation treatment was carried out with Ethylene Oxide by the Industrial Services of Monterotondo (Rome) in a $13m^3$ autoclave (with pre-vacuum) letting in 30 kg of mixture at 12% of an Ethylene Oxide/Carbon Dioxide, equal to about 280 g/m^3 of Ethylene Oxide. The treatment lasted 44 hours.

Combined Treatments

We also subjected to irradiation Whatman paper soaked with water (treatment A), and paper, first soaked in water and then frozen at -25 °C for 12 h (treatment B). For the latter type of treatment, this temperature was maintained for the whole irradiation time. The paper subjected to both treatments, after irradiation and before measurement was left to dry for 24h in a ventilated oven at 35° C. At the same time a number of samples, irradiated in the freezing state, were dried under vacuum at room temperature for 24 h (treatment C). These treatments require imbibition of the paper with water and successive variants, as regards the temperatures reached (water in the liquid state or ice), and the times and ways of drying.

Accelerated Ageing

To verify a radiation effect over time, two treatments of accelerated ageing were carried out on those samples not subject to combined treatments. The irradiated samples and the relative controls were maintained in a climatic oven at 65% R.H. and at a temperature of 80° C, respectively for 12 days and for 24 days (UNI Standard 10256).

Mechanical Resistance Test

Mechanical Resistance tests were carried out on all the samples:

- the Tensile Strength (breaking load) with Lever Dynamometer by Enrico Toniolo, Milan, Italy, following the UNI Standard 6438
- the Tearing Resistance with Elmendorf by Enrico Toniolo, Milan, Italy, following the UNI Standard 6444.

The samples were previously conditioned for 24 hours at 23°C at 50% of R.H.. according to the UNI Standard 7727. The measures were carried out on paper samples taken from the sheet in question, cutting in both machine direction and cross direction. The results in the tables are obtained from an average of 10 measures per experimental point. Mechanical resistance was also tested through the measurement of folding endurance (number of double folds) and bursting strength (g/cm^2). However, given the initial insufficient mechanical resistance of the Whatman n° 1 paper, the measures carried out on this type of paper with these two last analyses are not to be considered as significative and therefore are not mentioned.

*Chromaticity Measurements (CIE L*a*b* Colour System)*

We measured the Lightness Factor and the Chromaticity co-ordinates to prove the eventual variations of colour in the paper treated and non-treated, according to the CIE L*a*b* System: L* is the Lightness Factor and a* b* are chromaticity co-ordinates (a* for red-green and b* for yellow-blue). Co-ordinate b* is particularly important in that an increase towards more positive levels indicates the loss of blue, and the consequent increase in yellow, and therefore indicates a yellowing of the sample. For these measurements we made use of a Minolta Chrameter CR-221 using the CIE Illuminant C.

Chemical Analyses

On all the samples irradiated and the non-irradiated controls the following was determined:

- the average viscosimetric degree of polymerization of the cellulose, according with AFNOR Standard T 12-005, which provides the solubilization of cellulose in a Cupriethylenediamine solution;
- the cold extraction pH in distilled and de-ionized water according to TAPPI Standard T-435m.

RESULTS

Mechanical Tests

In Tables 1 and 2 we find the measures, respectively of the breaking load and tearing resistance, concerning the samples of irradiated paper in room conditions (Whatman "as such"); irradiated in conditions of maximum humidity (treat-

Table 1. Effect of gamma irradiation and different combined treatments on the breaking load g(g/15 mm).

Irradiation doses	"As such"			Treatment A			Treatment B			Treatment C		
0 kGy	*100*	**2672**	100	*100.0*	**2278**	85.2	*100.0*	**1968**	73.6	*100*	**1131**	42.3
1 kGy	*103.2*	**2760**	100	*104.8*	**2387**	86.5	*117.5*	**2312**	83.8	*114.7*	**1297**	47
2 kGy	*102.7*	**2743**	100	*107.9*	**2459**	89.6	*122.9*	**2418**	88.1	*117.4*	**1328**	48.4
5 kGy	*106.9*	**2856**	100	*102.8*	**2343**	82.0	*119*	**2343**	82	*103*	**1165**	40.8
10 kGy	*104.3*	**2787**	100	*110*	**2506**	89.9	*120*	**2362**	84.7	*121.1*	**1370**	49.1

ment A); irradiated at a temperature of -25° C (treatment B) and finally (treatment C) equally irradiated at -25° C, but later subjected to drying treatment under vacuum and at room temperature, rather than in a ventilated oven at 35° C as in the case of treatments A and B.

In the tables we find:

- the absolute value of the measurement to which the single table refers (bold face);
- the percentage compared with the non-irradiated sample (in italics to the left), which well illustrates the influence of the gamma dose absorbed;
- the percentage of the absolute value in comparison with the sample, subjected to irradiation in room conditions of temperature and humidity ["As such"] (in the right of each absolute value).

This last type of comparison allows us to evaluate not only the effect of the combined treatment but also the role of this treatment in relation to an eventual dose-effect of the gamma ionizing radiations.

From an examination of these two tables we realize that the gamma ionizing radiations, also the maximum doses used in this series of experiments (10 kGy), do not have any immediate negative effect on the mechanical properties of the Whatman paper. Indeed a small, but not very significant effect is to be only found in the tearing resistance levels of the irradiated paper in water in a liquid state (Treatment A, Table 2). Likewise the percentage fluctuations of the values, almost exclusively positive, do not require particular interpretative efforts.

Moreover, an analysis of the results found in Tables 1 and 2 shows a marked effect on the mechanical properties of the paper ascribable only to the treatment A, B or C, with no apparent link with the irradiation treatment, because manifested also in the non-radiated controls samples, in the non-combined treatments

Table 2. Effect of gamma irradiation and different combined treatments on the tearing resistance (g)

Irradiation doses	"As such"			Treatment A			Treatment B			Treatment C		
0 kGy	*100*	**74**	100	*100*	**78**	105.4	*100*	**66**	89.2	*100*	**53**	71.6
1 kGy	*102.7*	**76**	100	*89.7*	**70**	92.1	*124.2*	**82**	107.9	*105.7*	**56**	73.7
2 kGy	*105.4*	**78**	100	*92.3*	**72**	92.3	*118.2*	**78**	100	*103.8*	**55**	70.5
5 kGy	*116.2*	**86**	100	*89.7*	**70**	81.4	*103*	**68**	79.1	*128.3*	**68**	79.1
10 kGy	*105.4*	**78**	100	*97.4*	**76**	97.4	*106.1*	**70**	89.7	*94.3*	**50**	64.1

Table 3. Mechanical resistance tests (breaking load expressed in g/15 mm) related to irradiation and accelerated ageing

Irradiation doses		Unaged			12 ageing days			24 ageing days		
0 kGy	MD	*100*	**3675**	100	*100*	**3625**	98 6	*100*	**3750**	102.0
	CD	*100*	**2475**	100	*100*	**2405**	97.2	*100*	**2500**	101
1 kGy	MD	*97.3*	**3575**	100	*102.1*	**3700**	103.5	*96*	**3600**	100.7
	CD	*93.9*	**2325**	100	*102.9*	**2475**	106.4	*96*	**2400**	103.2
2 kGy	MD	*97.3*	**3575**	100	*94.5*	**3425**	95.8	*99.3*	**3725**	104.2
	CD	*101*	**2500**	100	*101.9*	**2450**	98	*98*	**2450**	98
5 kGy	MD	*99.3*	**3650**	100	*100*	**3625**	99.3	*94.7*	**3550**	97.3
	CD	*101*	**2500**	100	*105*	**2525**	101	*96*	**2400**	96
10 kGy	MD	*100*	**3675**	100	*100.7*	**3650**	99	*94*	**3525**	95.9
	CD	*101*	**2500**	100	*102.9*	**2475**	99.3	*95*	**2375**	95

and with a constant relation and independent of the dose. In other words, the treatments A and B cause a reduction in the breaking load of the paper of about 15% compared to a non wet paper (Table 1). The reduction is minor if measured as tearing resistance (Table 2). The treatment C caused much more serious mechanical damage, measurable as reduction of the breaking load of about 50% and about 30% of the tearing resistance.

In order to prove the possible differences between the measurements – attributable to the orientation of the cellulose fibres in the paper – in Tables 3 and 4 we see, separately, the analytical data concerning the paper samples obtained with machine and cross direction (MD, CD) of the paper sheets. However, the values do not show significant variations.

In Tables 3 and 4 we find the values of mechanical properties of the irradiated papers, before and after two different degrees of accelerated ageing, respectively of 12 and 24 days. The results in these tables refer respectively to the measurements of breaking loads (tensile strength) and tearing resistance .

The values shown refer to:

- the average of measurements carried out per experimental point (values in bold face);
- the percentage of such value in relation to the non-irradiated control (left-hand column in italics) which well express the effect of the ionizing treatment;
- the percentage value of every experimental point (after ageing) in relation to the non-aged equivalent (level shown in the column to the right of the measured value).

The trend of the mechanical properties values of non-aged paper confirms that of the Tables 1 and 2 (first line "as such"). Also with these measurements we have

Table 4. Mechanical resistance tests (tearing expressed in g) related to irradiation and accelerated ageing

Irradiation doses		Unaged			12 ageing days			24 ageing days		
0 kGy	MD	*100*	**80**	100	*100*	**58**	72.5	*100*	**68**	85
	CD	*100*	**84**	100	*100*	**68**	80.9	*100*	**68**	80.9
1 kGy	MD	*100*	**80**	100	*100*	**58**	72.5	*85.3*	**58**	72.5
	CD	*95.2*	**80**	100	*100*	**68**	85.0	*94.1*	**64**	*80*
2 kGy	MD	*100*	**80**	100	*100*	**58**	72.5	*94.1*	**64**	80
	CD	*100*	**84**	100	*100*	**68**	80.9	*94.1*	**64**	76.2
5 kGy	MD	*95*	**76**	100	*120.7*	**70**	92.1	*82.3*	**56**	73.7
	CD	*104.8*	**88**	100	*117.6*	**80**	90.9	*94.1*	**64**	72.6
10 kGy	MD	*90*	**72**	100	*89.6*	**52**	72.2	*79.4*	**54**	75
	CD	*109.5*	**92**	100	*85.3*	**58**	63.0	*88.2*	**60**	65.2

not registered variation of mechanical properties of the paper subjected to irradiation with a range of doses from 0 to 10 kGy. As far as the breaking load is concerned, analysing the absolute values and the relative percentages in relation to the non-irradiated control (left-hand column), there seems to be no radiation effect on the mechanical properties of the paper, even after an accelerated ageing of 12 days. Such an effect, even though only in vague terms, began to be seen after an ageing of 24 days. For a better understanding of the phenomenon we should also refer to the values of the right-hand column which, as already recalled, were obtained by comparing the absolute values of the measurements with those of the non-aged samples; this comparison allows us to grasp the synergic effect of the gamma radiation treatment and an accelerated ageing more or less prolonged over time. We should point out that certain anomalous data in Table 4 (5 kGy) do not affect the understanding of the general trend of the phenomenon and can probably be justified by the inhomogeneity of the samples of the particular material used. On the other hand, resistance to tearing is more sensitive to the radiation effect and the differences between irradiated and non-irradiated samples become clear already 12 days after the accelerated ageing.

Interestingly, the two ageing treatments cause appreciable mechanical damage only if measured as tearing resistance and not as breaking load, but such damage is of the same extent (about 20% compared to non-aged) for the two ageing treatments. In other words, already with the first ageing of 12 days the resistance of the Whatman paper, measured as tearing is heavily impaired and a following treatment of a further 12 days does not increase this damage.

What is also very interesting is that from this type of comparison, differences begin to emerge which seem to indicate a link between dose and effect of the radiation only on the samples aged for 24 days.

Chemical analyses

Table 5 refers to the measurements of the degree of polymerization of cellulose fibres as a result of a growing series of gamma doses absorbed by the paper. In the same table the results of the three treatments A, B and C are shown already illustrated in relation to Tables 1 and 2. It is equally necessary to refer to these two tables to be able to understand the type of data presented.

The values shown in Table 5 indicate clearly the negative influence of radiation on the degree of polymerization of the cellulose. It is equally obvious (left-hand column) that this phenomenon is closely related to the dose absorbed and that at higher doses the values are reduced to 45–50% of the non-radiated control, while at lower doses (2 kGy) the reduction is 15–25%. As opposed to what was found with mechanical measurements, the degree of polymerization of cellulose does not undergo significant variations following combined treatments of temperature and humidity and the different conditions of drying (right-hand column).

In Table 6 we find the levels of the degree of polymerization of paper subjected to increasing doses of gamma radiations compared to analogous levels measured after 12 and 24 days of accelerated ageing. In this table too, for each experimental point, the central levels (in bold face) represent the average data of the measurements carried out; the left-hand column, (italics) the percentage level compared

Table 5. Degree of polymerization as an index of irradiation effects and combined treatments

Irradiation doses	"As such"			Treatment A			Treatment B			Treatment C		
0 kGy	*100*	**1110**	100	*100*	**1121**	101	*100*	**1084**	98	*100*	**1081**	97
1 kGy	*85*	**945**	100	*85*	**956**	101.1	*90*	**971**	102.7	*93*	**1010**	106.9
2 kGy	*75*	**830**	100	*76*	**854**	102.9	*84*	**915**	110.2	*80*	**864**	104.1
5 kGy	*57*	**636**	100	*58*	**650**	102.2	*70*	**759**	119.3	*69*	**748**	117.6
10 kGy	*45*	**498**	100	*46*	**512**	102.8	*51*	**557**	111.8	*47*	**515**	103.4

Table 6. Effect of accelerated ageing on polymerization degree of irradiated and non-irradiated samples

Irradiation doses	Unaged			12 ageing days			24 ageing days		
0 kGy	*100*	**1058**	**100**	*100*	**983**	92.9	*100*	**779**	73.6
1 kGy	*92.2*	**978**	**100**	*86.1*	**846**	86.5	*84.3*	**657**	67.2
2 kGy	*84.3*	**892**	**100**	*76.3*	**750**	84.1	*77.9*	**607**	68
5 kGy	*62.4*	**660**	**100**	*51.2*	**503**	76.2	*58.9*	**459**	69.5
10 kGy	*50.1*	**538**	**100**	*40.5*	**398**	74	*46.6*	**363**	67.5

to the non-irradiated control; the right-hand column the percentage level calculated in relation to the analogous level of the non-aged paper sample.

The values of the degree of polymerization relating to the irradiated and non-aged paper reproduce the course of the values of the previous Table 5 (treatment "as such"); on the whole they confirm the cause/effect relation already described and the relation with the dose absorbed. As regards the accelerated ageing effect, we should point out (values of left-hand column in italics) that these do not modify the course we have just recalled of the reaction with growing doses of gamma radiation and that significant differences between the two ageings are not to be found.

The right-hand values which, we recall, represent the comparison with the cellulose of non-aged paper, indicate the differences between aged and non-aged paper. After the first ageing (12 days) we see a reduction in the degree of polymerization of about 20% (average value of all the doses), which reach 30% on average after the second ageing (24 days). The values measured after the first ageing indicate significant differences of depolymerization according to the gamma dose absorbed, but with a synergic effect, also in relation to ageing. It is clear that, after a further period of ageing the synergic effect is more difficult to show, on the irradiated samples compared to those non-irradiated in consideration of the low degree of initial polymerization.

In Table 7 we see the degree values of polymerization of samples treated with Ethylene Oxide according to days of ageing. The results show that the treatment with Ethylene Oxide does not modify appreciably the degree of polymerization of the cellulose, and not even after accelerated ageing.

Table 7. Effect of accelerated ageing on degree of polymerization (± 100) of non treated and treated with Ethylene Oxide samples

Treatment with Ethylene Oxide	Unaged	12 ageing days	24 ageing days
Untreated	1114	648	495
Treated	1095	720	526

Table 8. Variation of cold extraction pH (± 0.1) in relation to gamma irradiation treatment before and after accelerated ageing

Irradiation doses	Unaged	12 ageing days	24 ageing days
0 kGy	6.25	6.20	6.16
2 kGy	6.25	6.10	5.95
10 kGy	6.10	6.00	5.95

(pH of distilled and demineralized water = 6.20)

Table 9. Variation of cold extraction pH (± 0.1) in relation to Ethylene Oxide treatment before and after accelerated ageing

Treatment with Ethylene Oxide	Unaged	12 ageing days	24 ageing days
Untreated	6.25	6.20	6.16
Treated	6.25	6.10	5.95

(pH distilled and demineralized water = 6.20)

Table 10. Variation of cold extraction pH (± 0.1) in relation to gamma irradiation treatment and to different combined treatments

Irradiation doses	Untreated	Treatment A	Treatment B	Treatment C
0 kGy	6.00	5.95	5.95	6.10
2 kGy	6.10	5.90	5.95	5.95
10 kGy	6.00	6.00	5.90	5.95

(pH distilled and demineralized water = 6.20)

In Table 8 we see the pH values measured on paper samples irradiated with 2 and 10 kGy and the relative non-irradiated control according to ageing times. An analysis of the data seems to indicate a very slight increase in acidity according to the gamma doses absorbed, to be highlighted after ageing. However, such differences are within the limits of experimental error and are therefore not significative.

In Table 9 we see the pH values measured on samples of paper subjected to a fumigation treatment with Ethylene Oxide and successively aged artificially.

In Table 10 we see the pH values concerning samples of paper irradiated and/or subjected to combined treatments previously described. The results of the two last tables confirm the slight influence of the radiation treatment and the combined treatments on the pH values.

*Chromaticity Measurements (CIE L*a*b* Colour System)*

Lightness L* – feature which is in relation to the white of the paper and inversely proportional to its darkening – is slightly influenced by ionizing radiations on the non-aged samples.

Indeed, the results seen in Table 11 give practically no indication of factor L* variations, compared to the control, in the paper sheets which have absorbed dif-

Table 11. Lightness Factor L* of the paper (CIE L*a*b* Colour System) measured after irradiation and in relation to different combined treatments

Irradiation doses	Untreated	Treatment A	Treatment B	Treatment C
0 kGy	96.68±0.06	96.59±0.08	96.46±0.05	96.80±0.11
1 kGy	96.57±0.08	96.29±0.01	96.50±0.10	96.92±0.03
2 kGy	96.60±0.10	96.39±0.08	96.26±0.15	96.36±0.22
5 kGy	96.42±0.09	96.35±0.11	96.35±0.07	96.81±0.03
10 kGy	96.09±0.07	96.08±0.15	96.28±0.14	96.67±0.14

Table 12. Lightness L* factor in relation to the gamma dose absorbed and the accelerated ageing

Irradiation doses	Unaged	12 ageing days	24 ageing days
0 kGy	96.32±0.16	96.85±0.16	95.54±0.10
1 kGy	96.43±0.09	96.65±0.18	94.75±0.48
2 kGy	96.44±0.19	95.42±0.20	94.56±0.20
5 kGy	96.41±0.21	94.18±0.17	92.90±0.18
10 kGy	96.18±0.19	92.93±0.09	91.14±0.16

Table 13. Lightness L* factor in relation to accelerated ageing and treatment with ethylene oxide

Treatment with Ethylene Oxide	Unaged	12 ageing days	24 ageing days
Untreated	96.12±0.39	95.20±0.23	93.87±0.03
Treated	96.51±0.07	95.17±0.18	93.33±0.69

ferent doses of radiation. And neither does any significant variation of such a factor reveal itself as consequent to treatments characterised by maximum values of humidity and low temperatures (treatments A, B and C) or consequent to the combination of these treatments with even high doses of radiation (5–10 kGy).

However, the effect of the radiation on the reduction of the L* index is noticeable after the accelerated ageing and in connection with the ageing times (Table 12). In this table it is also interesting to see that the duration of the ageing of the paper determines a reduction of factor L* in proportion to the dose of radiations absorbed. The synergy is particularly clear for high doses.

In Table 13 we see the measurements of the L* factor for paper subjected to ageing treatments after having being treated with ethylene oxide. The treatment with ethylene oxide does not seem to have influenced lightness. Indeed, the treated and non-treated samples undergo practically the same reduction of L* after the accelerated ageing.

Table 14. Chromaticity measurements (CIE L*a*b* Colour System) in relation to the gamma dose and different combined treatments. Chromacity co-ordinates: a* (red-green), b* (yellow-blue)

Irradiation doses		"As such"	Treatment A	Treatment B	Treatment C
0 kGy	a*	-0.17±0.01	-0.30±0.02	-0.31±0.01	-0.32±0.02
	b*	+0.72±0.02	+1.22±0.10	+1.05±0.08	+0.91±0.04
1 kGy	a*	-0.19±0.04	-0.28±0.04	-0.37±0.04	-0.29±0.02
	b*	+0.91±0.18	+1.61±0.13	+1.30±0.09	+0.80±0.08
2 kGy	a*	-0.18±0.01	-0.28±0.03	-0.33±0.02	-0.31±0.04
	b*	+0.98±0.06	+1.55±0.13	+1.38±0.08	+1.05±0.12
5 kGy	a*	-0.23±0.04	-0.40±0.04	-0.33±0.03	-0.30±0.01
	b*	+1.34±0.12	+1.83±0.25	+1.37±0.05	+1.01±0.05
10 kGy	a*	-0.26±0.04	-0.38±0.04	-0.38±0.03	-0.40±0.03
	b*	+1.72±0.18	+2.08±0.28	+1.78±0.11	+1.60±0.21

Table 15. Chromaticity measurements (CIE L*a*b* Colour System) in relation to the gamma dose absorbed, before and after accelerated ageing

Irradiation doses		Unaged	12 ageing days	24 ageing days
0 kGy	a*	+0.01±0.04	-0.04±0.02	+0.04±0.02
	b*	+1.46±0.07	+2.33±0.08	+2.89±0.10
1 kGy	a*	-0.02±0.03	0.00±0.02	+0.21±0.09
	b*	+1.42±0.09	+2.72±0.03	+3.60±0.18
2 kGy	a*	-0.06±0.03	-0.01±0.06	+0.11±0.05
	b*	+1.49±0.04	+3.04±0.11	+4.04±0.10
5 kGy	a*	-0.04±0.01	+0.21±0.03	+0.42±0.11
	b*	+1.60±0.07	+5.04±0.13	+6.22±0.18
10 kGy	a*	-0.06±0.03	+0.54±0.06	+0.92±0.05
	b*	+1.76±0.07	+6.49±0.12	+8.28±0.12

In Table 14 we see the values of the co-ordinates a* and b* of a series of irradiated sheets and/or subjected to combined treatments. We should recall that the b* co-ordinate allows also us to evaluate and measure variations of yellowing which are invisible to the naked eye.

An examination of the table indicates for the a* co-ordinate, minimum variations towards negative values in relation both to the doses absorbed and the combined treatment; for the b* co-ordinate, variations of small import attributable to combined treatments, but a significant increase in relation to the dose absorbed independently of the treatment: an almost doubled value to the higher dose of 10 kGy.

Table 16. Chromaticity measurements (CIE L*a*b* Colour System) in relation to treatment with Ethylene Oxide, before and after accelerated ageing

Treatment with Ethylene Oxide		Unaged	12 ageing days	24 ageing days
Untreated	a*	0.08±0.10	-0.06±0.02	+0.17±0.04
	b*	+1.12±0. 10	+3.26±0.16	+5.04±0.06
Treated	a*	-0.21±0.03	-0.11±0.03	+0.21±0.10
	b*	+1.01±0.04	+3.50±0.20	+5.23±0.27

Table 15 illustrates the colour measurement of another series of irradiated and artificially aged sheets. The co-ordinate a* values do not seem to vary either in relation to radiation or ageing. The value of co-ordinate b*, on the other hand, increased significantly as a result of the gamma dose absorbed and more clearly after accelerated ageing. This synergic action leads to a more than doubled b* value.

In Table 16 we see the measurement values of sheet colour treated with Ethylene Oxide and aged: the a* and b* values do not seem to be affected by fumigation treatment.

CONCLUSIONS

In commenting the results, we can state that the viscosity measurements of cellulose seem very interesting since they confirm that radiation causes a depolymerization of its molecule and there is a clear cause/effect relation (Table 5). The viscosity variation, a result of the radiation, is not influenced by combined treatments with water and low temperature and this confirms that it is a typical effect of radiochemistry which does not seem to have repercussions on mechanical characteristics (Table 1–4). What is also noteworthy is that the reduction of the degree of polymerization, attributable to the doses of gamma absorbed, remains constant in percent, also after accelerated ageing (Table 6). The ageing itself causes a drastic fall in the degree of polymerization and – together with radiation – has a synergic effect too (values of the right-hand column of the same Table 6).

The mechanical tests of paper subjected to irradiation and without ageing do not show any effect of this treatment (Tab 1–4). Moreover, it is well known that variations in mechanical characteristics can be seen only after significant reductions in the degree of polymerization. Ageing has caused damage to the mechanical properties of the paper which, in our experimental conditions, we have been

able to detect only in the tearing measurement (Table 4). The different behaviour of the irradiated samples as regards tearing resistance compared to tensile strength, expressed as breaking load, is linked to the fact that, while the former depends mainly and significantly on the length of the fibres (which, in turn depend on the length of the cellulosic chain expressed by the degree of polymerization), the tensile strength is linked mainly to the number of inter-fibre links. It is unlikely that these links vary, or that they re-arrange themselves, after gamma radiation.

However, particularly heavy damage is caused by defreezing from ice treatment under vacuum: treatment C (Table 1 and 2). The slow passage of water from the solid phase to vapour phase must have negatively influenced the reticular structure of the paper, causing a decline in mechanical resistance. A similar interpretation is confirmed by the fact that minimal or irrelevant damage has been registered in the experimental samples relating to treatment B (very similar to C) – but defrozen in a ventilated oven at 35° – and in those concerning treatment A.

Accelerated ageing, especially if prolonged over time, is able to show those effects which are only slight or unimportant in an examination carried out immediately after the irradiation (Tables 4, 8, 9, 10, 12 and 15).

The results of pH measurements tell us nothing important about radio-induced acidification (Table 8–10), while the colour measurements show yellowing of the irradiated paper, mostly to be seen after accelerated ageing. Depolymerization, the result of hydrolysis of the β-glucosidic linkage, does not lead necessarily, and always, to a reduction of the pH which is verified only if carboxyl groups are formed. On the other hand, the formation of double conjugated chromophore links leads to a yellowing of the paper.

The analysis of the obtained results allows us to conclude that the irradiation effects on cellulose Whatman paper can only be evaluated following certain premises. Above all, we have to distinguish between the effects caused by low gamma doses, which can be used in a real hygienization treatment (around 3 kGy), and that of the doses two or three times greater (5–10 kGy) wherein we chose to intensify eventual negative effects. It is also important to establish what parameter to choose to measure the eventual modifications, since the alterations caused by the radiation are very similar to those caused by an accelerated ageing. For example, if we analysed Table 1 and 5 at the same time, we would think the effect of treatment C (about 55% of reduction of breaking load; cf. Table 1) comparable to the effect of 10 kGy (about 55% of depolymerization of the cellulose; cf. Table 5). We have to measure with different analytical instruments (mechanical and chemical characteristics) the effects of physical phenomena which are significantly different from each other (for example, swelling due to the formation of ice crystals and breaking of glucosidic linkage) and which influence different structures

of the paper (reticule formed of cellulose fibre and polymeric structure of the singular cellulose molecules). Undoubtedly, the viscosity measurement is a very sensitive and practical instrument because it allows us to evaluate the depolymerization immediately after the treatment (Table 5 and 6).

It is clear that this work, also for these reasons, cannot be considered exhaustive as far as the problem posed at the beginning is concerned but, as often happens, it is a stimulus to shed light on those aspects which have remained obscure. Of these, we should study further the effect of the treatment of irradiation in ice which, moreover, seems to mitigate – if only slightly – the depolymerizing effect of the radiations on cellulose. Taking into account the fact that a reduction of the degree of polymerization leads to an increased susceptibility of the cellulose to new attacks of cellulolyitic micro-organisms and referring also to what was said in the introduction of this study, we also need to evaluate carefully the different reaction to irradiation of the amorphous fraction of the cellulose compared to the crystalline.

However, the question remains: can a slight depolymerization of cellulose, caused by low doses of radiation (2 kGy) be accepted in a disinfection/disinfestation treatment of a biodeteriorated paper material taking into account that we would be interfering with a material which, left to itself, would be destroyed. Finally we must ask if a complete sterilization of the material is necessary or if it is better to irradiate with low doses – which guarantee. in any case, a good disinfestation and reduction of the microbial load – without neglecting the importance of a good thermohygrometric control of the preservation environment.

SUMMARIES

Effect of Gamma Rays on Pure Cellulose Paper as a Model for the Study of a Treatment of "Biological Recovery" of Biodeteriorated Books

The effects of increased doses of gamma rays on cellulose paper (Whatman n° 1) were tested under different experimental conditions, before and after accelerated ageing. The polymerization degree, tensile strength, internal tearing resistance and pH were measured following the standard procedures: the L* lightness factor and the a* and b* chromaticity co-ordinates were also determined. The results showed the irradiation treatment to have a negative effect both on the polymerization degree and on yellowing. The effect, comparable to accelerated ageing of paper, depends on the dose absorbed. Before accelerated ageing the tensile strength and degree of acidity do not seem to be affected even by high doses of radiation.

The effect of the gamma rays was also compared with some measurements on another Disinfection/Disinfestation system: fumigation with Ethylene Oxide. Treatment with commonly used concentration of Ethylene Oxide has no negative effects on the parameters we measured, but this

treatment will probably soon be banned in Italy, as has already occurred in other countries. Thus we need to assess the feasibility for the future of treatment with low doses of ionizing rays in the biological recovery of biodeteriorated books. This assessment has to take into account the effective weight of certain parameters analysed in relation to subsequent conservation of material and, on the other hand, the need to intervene urgently on those books at particular risk of biological attack.

Effet des Rayons Gamma sur le papier en cellulose pure comme modèle pour une étude sur le „rétablissement biologique" de livres biodétériorés

Les effets de doses croissantes de rayons gamma sur le papier en cellulose (Whatman n°1) ont été testés dans différentes conditions expérimentales, avant et après le vieillissement artificiel. Le degré de polymérisation, la résistance à la traction, la résistance interne au déchirement et le pH ont été mesurés selon les procédures standard : le L* facteur de luminosité et les valeurs chromatiques a* et b* ont été également déterminés. Les résultats ont démontré que le traitement par irradiation avait un effet négatif tant sur le degré de polymérisation que sur le jaunissement. L'effet, comparable à celui du vieillissement artificiel, dépend de la dose absorbée. Avant le vieillissement artificiel la résistance à la traction et le degré d'acidité ne semblent pas être affectés par une radiation, même à forte dose.

On a également comparé l'effet des rayons gamma en ce qui concerne certains paramètres avec celui d'un autre système de désinfection/désinfestation: la fumigation avec de l'oxyde d'éthylène. Le traitement à l'oxyde d'éthylène dans la concentration couramment utilisée ne présente aucun effet négatif sur les paramètres que nous avons mesurés mais ce traitement sera probablement bientôt interdit en Italie, comme c'est déjà le cas dans d'autres pays. Ceci nous contraint à l'avenir à nous pencher sur les possibilités de traitement avec des rayons ionisants à faible dose pour le rétablissement biologique des livres biodétériorés. Il s'agit d'apprécier correctement l'influence effective de certains paramètres analysés sur la conservation subséquente du matériel et, d'autre part de saisir la nécessité d'intervenir immédiatement en cas d'urgence lorsque ces livres sont menacés de détérioration biologique.

Die Wirkung von Gammastrahlen auf Papier aus reinem Zellstoff als Modell für eine Studie über die „biologische Wiederherstellung" von Büchern mit biogenem Schaden

Es wurde die Wirkung von Gammastrahlen in steigender Stärke und unter verschiedenen experimentellen Bedingungen auf Zellstoffpapier vor und nach beschleunigter Alterung untersucht. Polymerisationsgrad, Zugfestigkeit, Durchreißwiderstand und pH wurden nach den entsprechenden Standardprozeduren gemessen. Auch die Helligkeit (L*) sowie die Farbwerte a* und b* wurden bestimmt. Die Ergebnisse zeigen, daß die Bestrahlung einen negativen Einfluß auf Polymerisationsgrad und Vergilbung hat, vergleichbar dem einer beschleunigten Alterung, im Ausmaß abhängig von der Strahlendosis. Vor einer weiteren beschleunigten Alterung (Ofenalterung) läßt sich an Zugfestigkeit und Säuregrad keine Schädigung durch eine Bestrahlung feststellen, auch bei hoher Dosis nicht.

Die Wirkung von Gammastrahlen wurde bezüglich einiger Meßparameter auch mit der anderer Desinfektionsmethoden verglichen. Die Vergasung mit Äthylenoxid beeinflußt beim Arbei-

ten in der üblichen Konzentration die gemessenen Parameter nicht negativ, wird aber in Italien wahrscheinlich demnächst verboten, wie das in anderen Ländern bereits geschehen ist. Das zwingt zur Auseinandersetzung mit der Anwendung ionisierender Strahlen in niedriger Dosierung zum Wiederherstellen eines biologisch intakten Zustands von entsprechend geschädigten Büchern. Es gilt, die Wirkung der Behandlung auf bestimmte Parameter richtig zu gewichten, die die konservatorische Qualität beschreiben, und die Notwendigkeit herauszustellen, im Falle drohenden biologischen Befalls unverzüglich eine Behandlung einzuleiten.

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CORRECTION

Unfortunately in no. 3, vol. 17 (1996) of this journal a mistake has occurred concerning the article *Degradation of Cellulose at the Wet/Dry Interface II. An Approach to the Identification of the Oxidation Compounds* by A.-L. Dupont. On p. 153 in Table 4 it is not indicated that spot b of the TLC plates of brown line extracts means that cellobiose is likely to be present. This correction is important to make since spot b was revealed in all brown line extracts analysed. The presence of cellobiose in the paper at the wet/dry interface is worth noting. The following is correct:

Table 4. Compounds present in brown line extracts as compared with reference compounds

	Compounds detected	Combination of development and visualization used
Sugars	D-glucose	1 }
	D-arabinose	1 } (spot c)[a]
	D-galactose	1 }
	cellobiose	1 (spot b)
Uronic arcids and lactones	D-glururonic acid	1 (spots b or c) and 2 (spot a')
	D-gluconic acid	1 (spot c)
	D-gluconic acid δ-lactone	1 (minor component)

a. Spot c seems to represent a mixture of compounds of similar hRf and coloration with naphthoresorcinol.

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