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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 already 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. [6]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 $Ca(HCO_3)_2$-treat-

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

		Groundwood 1908	Groundwood 1923	chem. pulp	rag	Groundwood 1908	Groundwood 1923	chem. 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

ment, 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 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

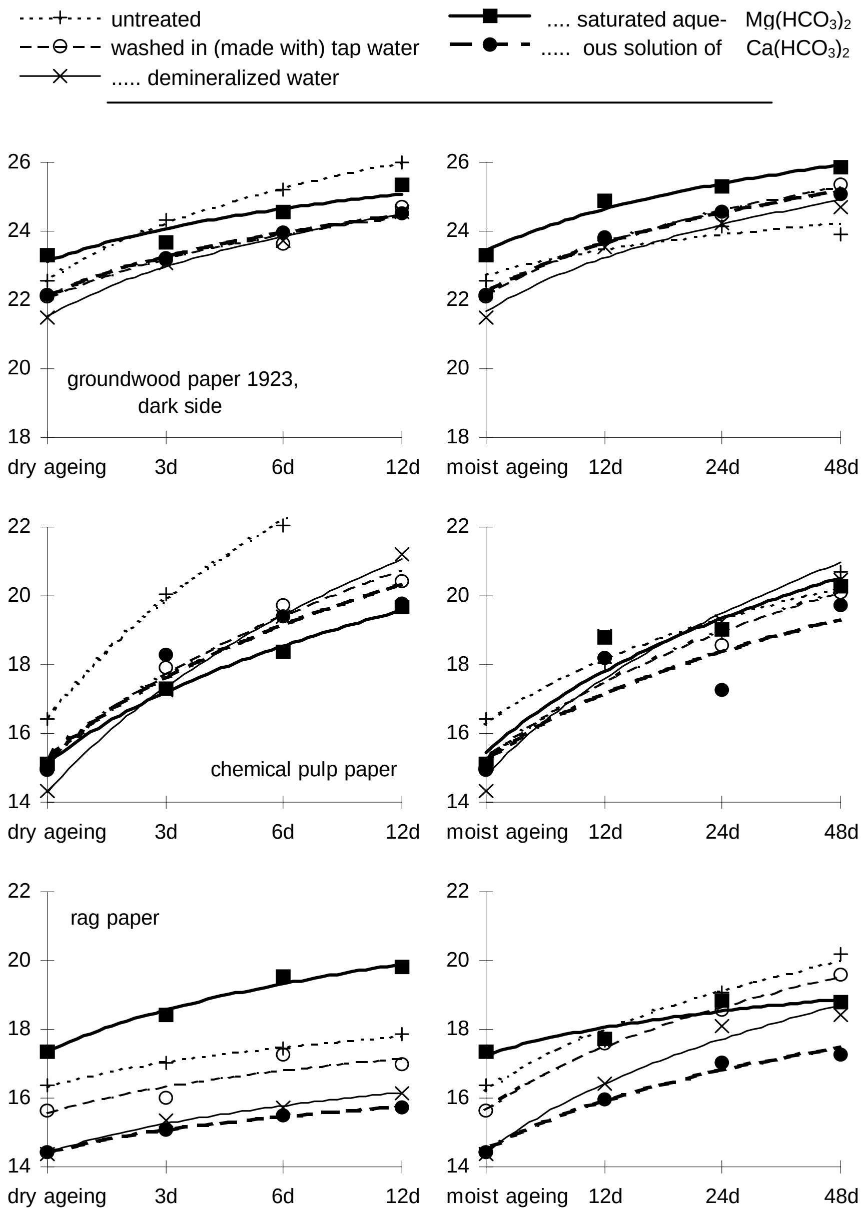
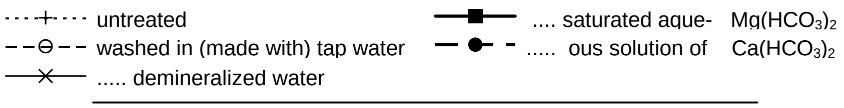


Fig. 1: Yellowing (CIE-b*) of old papers during accelerated ageing: those cases where Mg did not provoke the highest rate during both ageings.



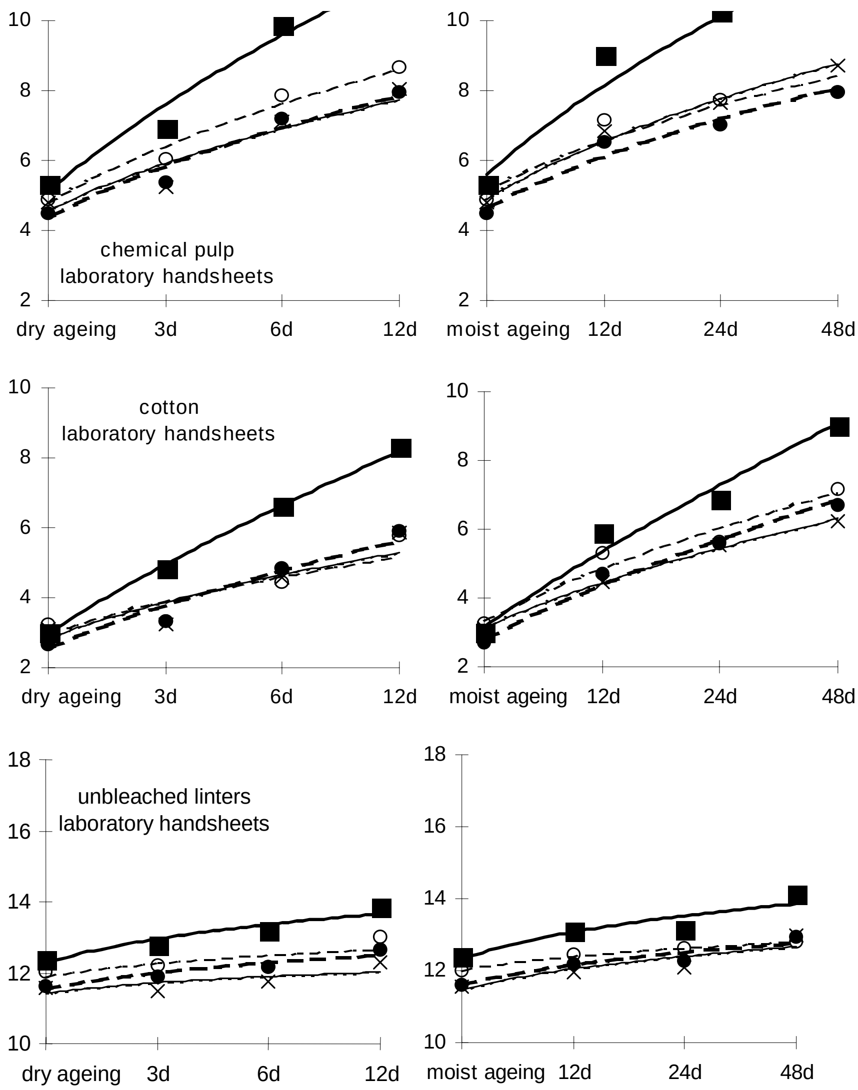


Fig. 2: Yellowing (CIE-b*) during accelerated ageing of laboratory handshets.

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 in-

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

fluencing 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 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

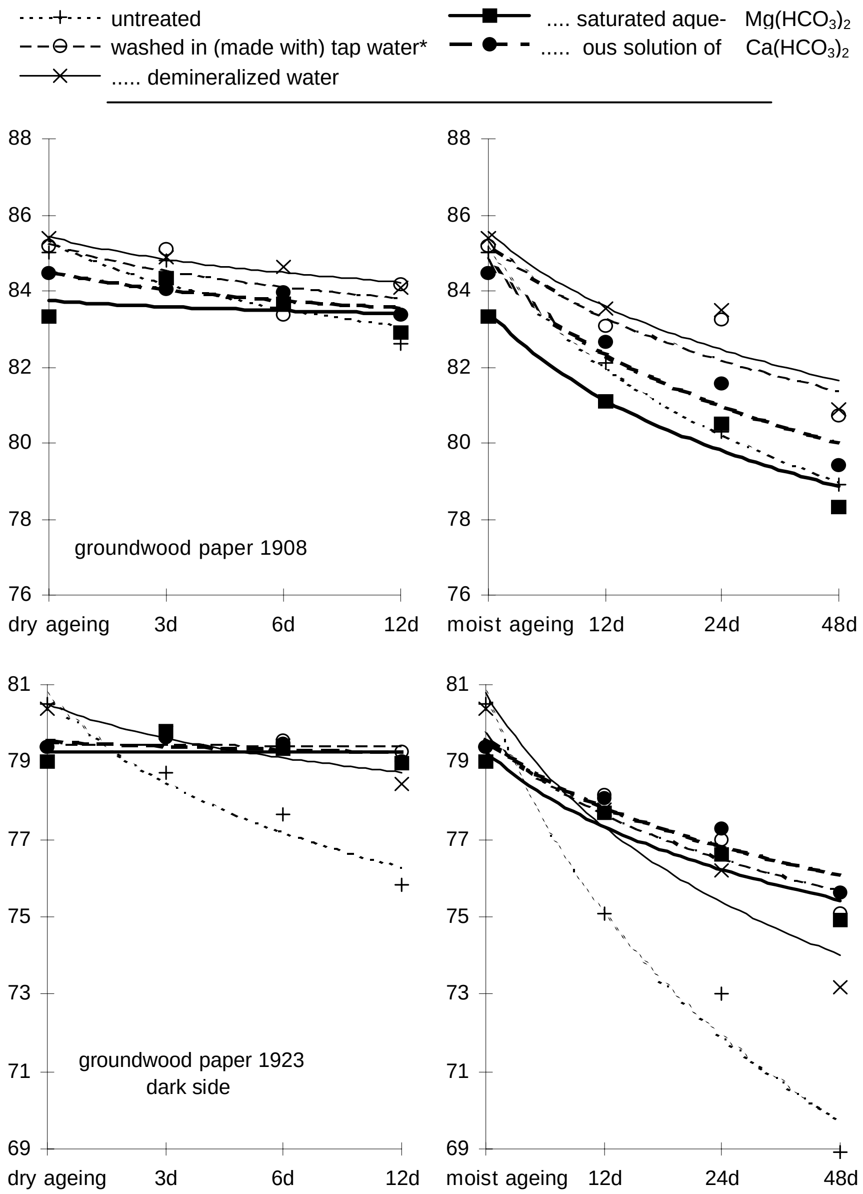


Fig. 3a: Change of brightness (CIE-L*) of groundwood papers during accelerated ageing.

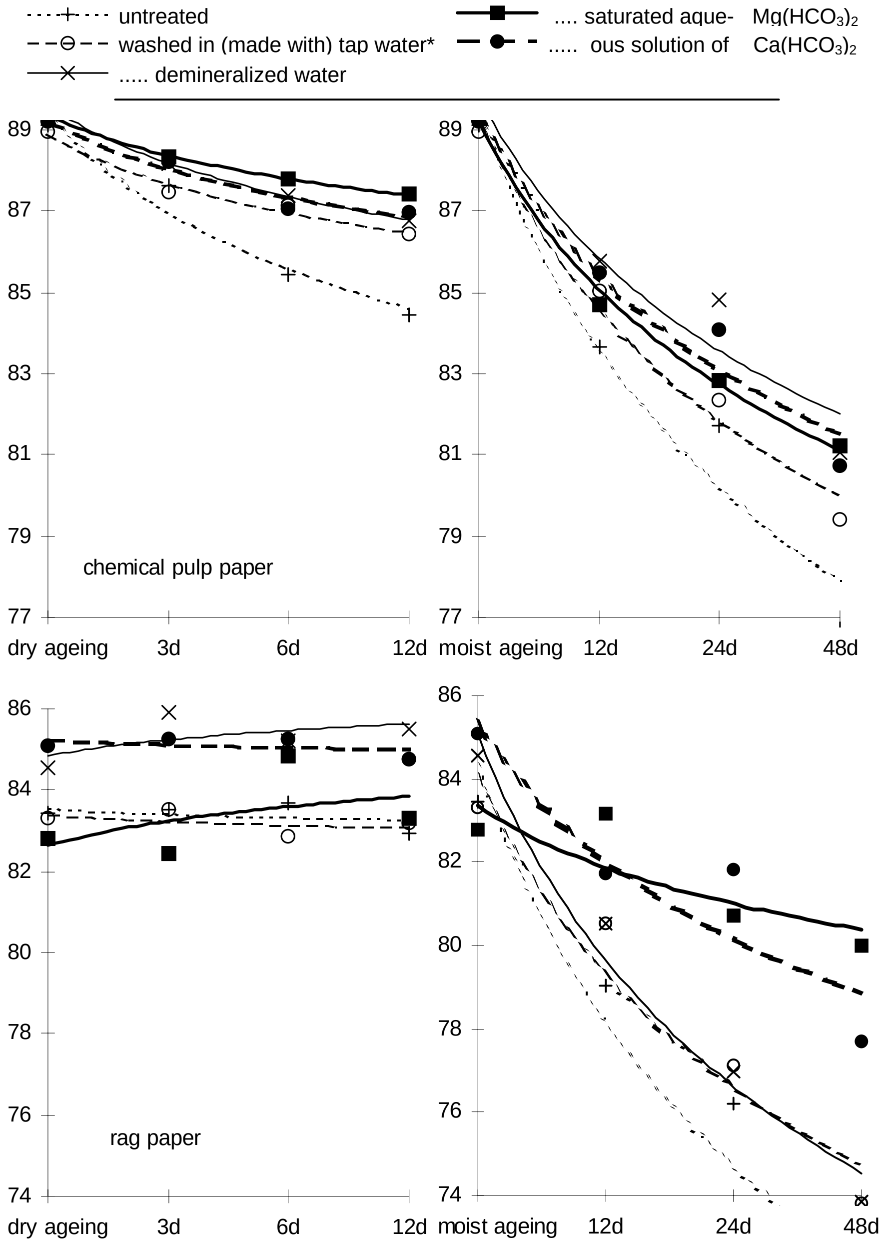


Fig.3b: Change of brightness (CIE-L*) of old papers during accelerated ageing

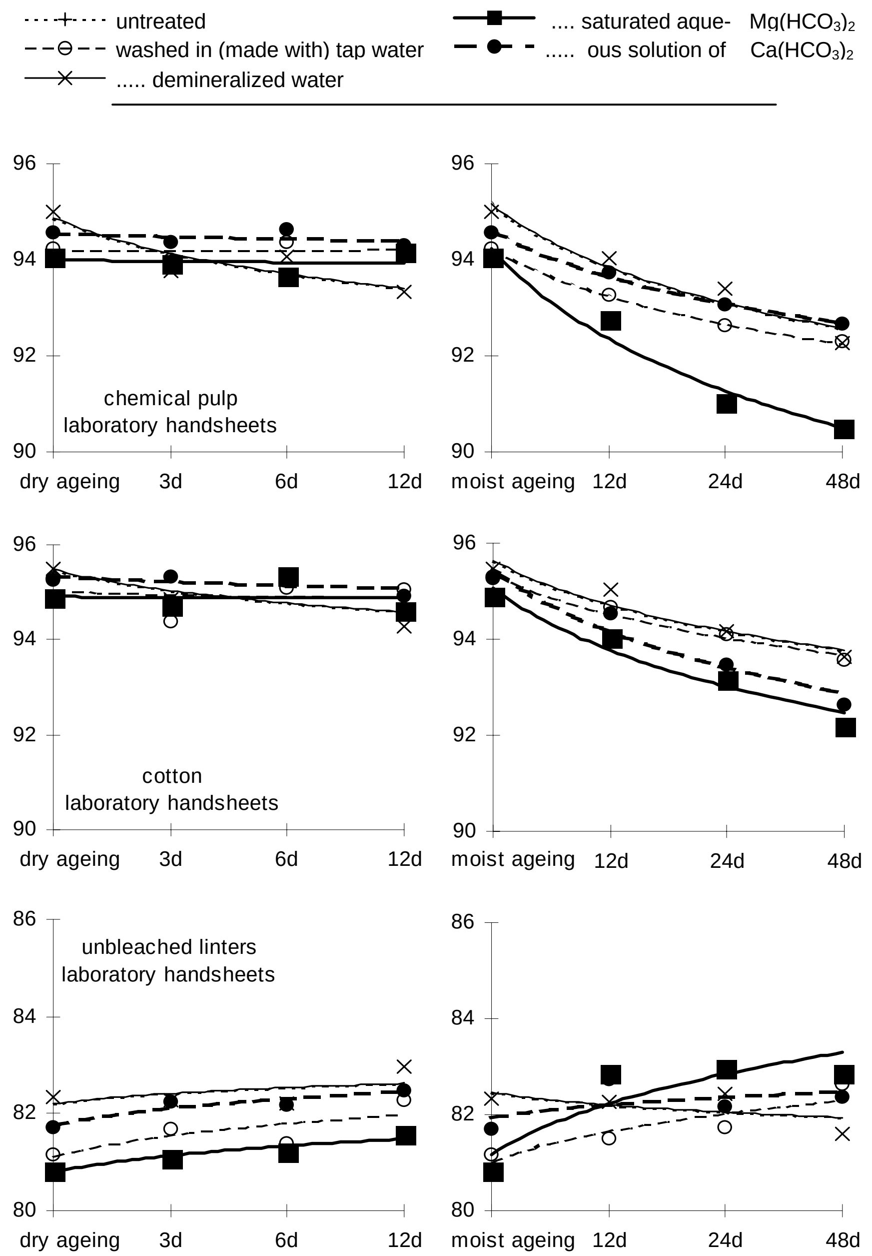


Fig.4: Change of brightness (CIE-L*) of laboratory handsheets during accelerated ageing.

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

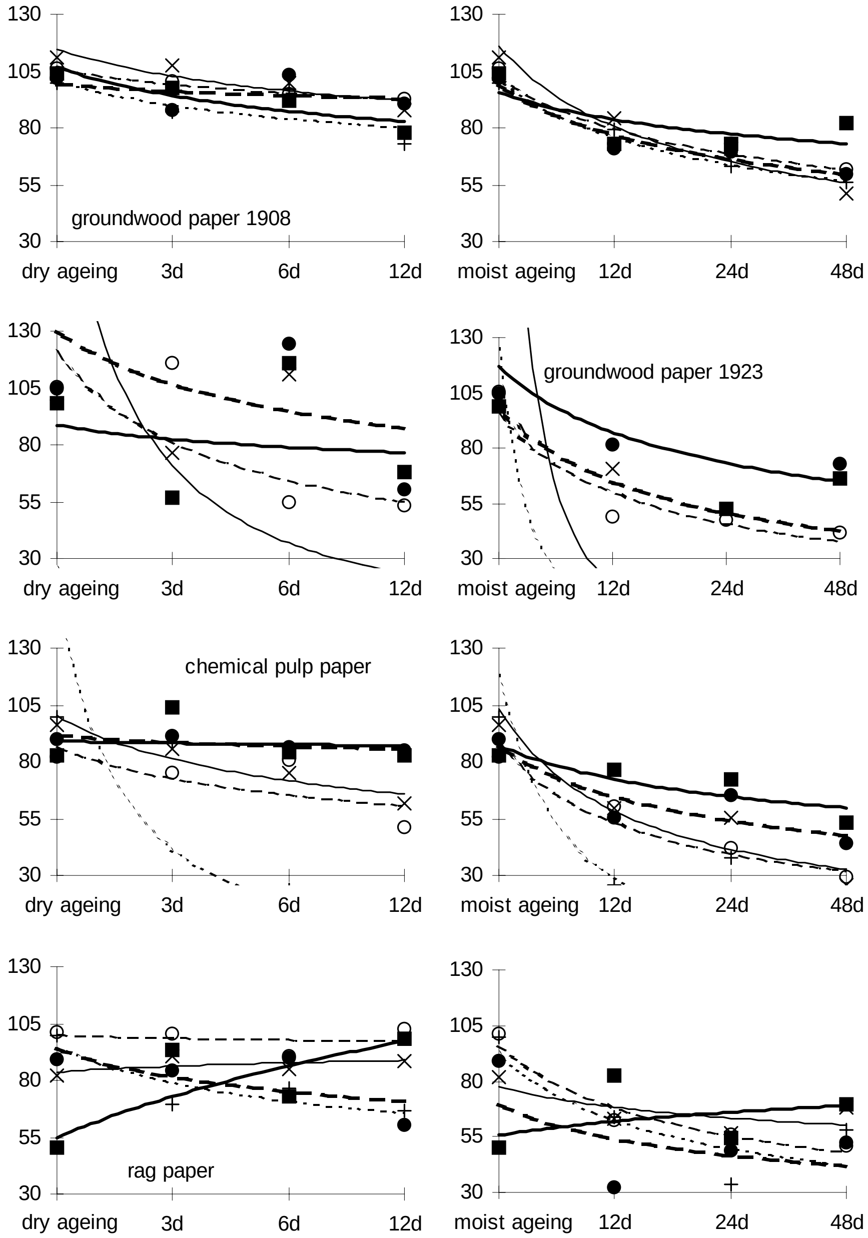


Fig. 5: Change of tensile strength (%) after one defined fold during accelerated ageing of old papers (100 = untreated, unanged).

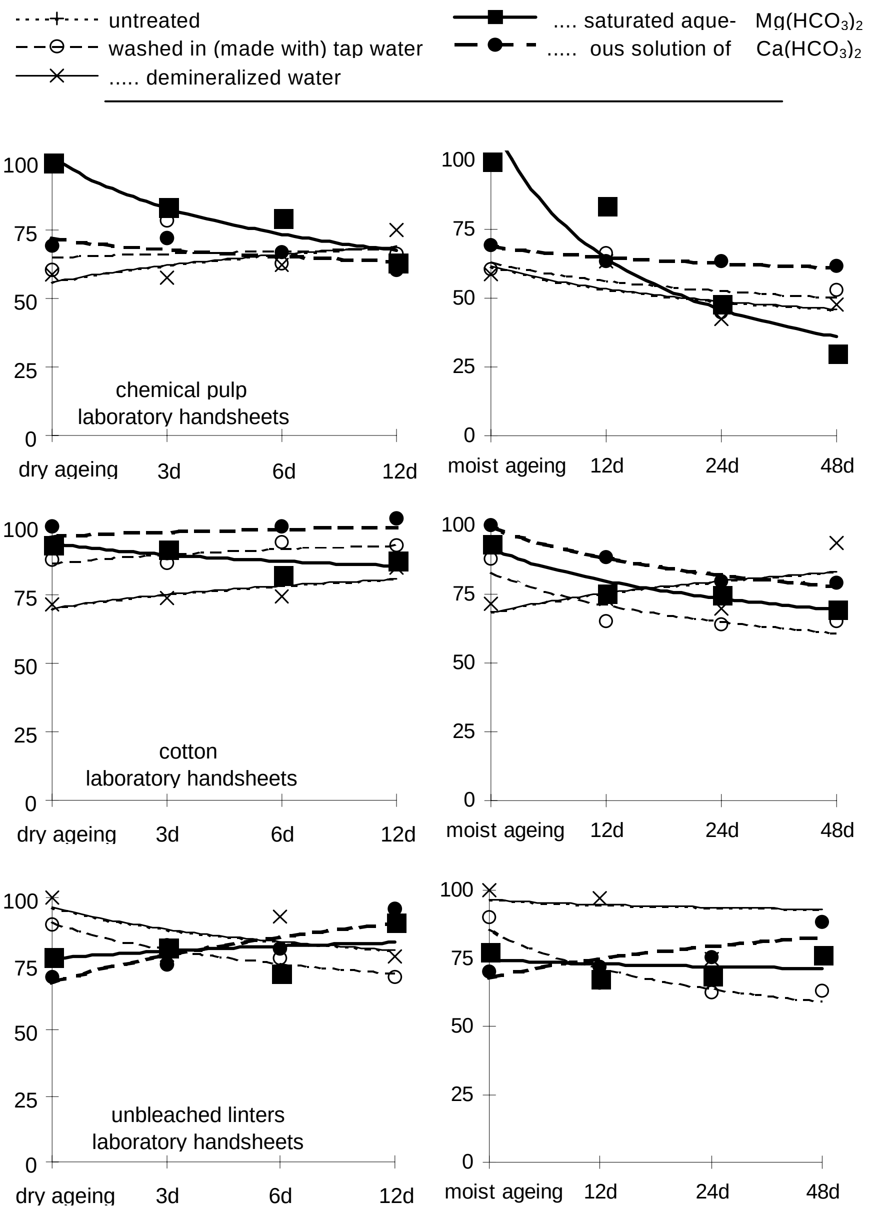


Fig. 6: Change of tensile strength (%) after one defined fold during accelerated ageing of laboratory handsheets (100 = best unaged. Chem. p.: Mg. Cotton: Ca. Linters: Aqu, demin.).

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*

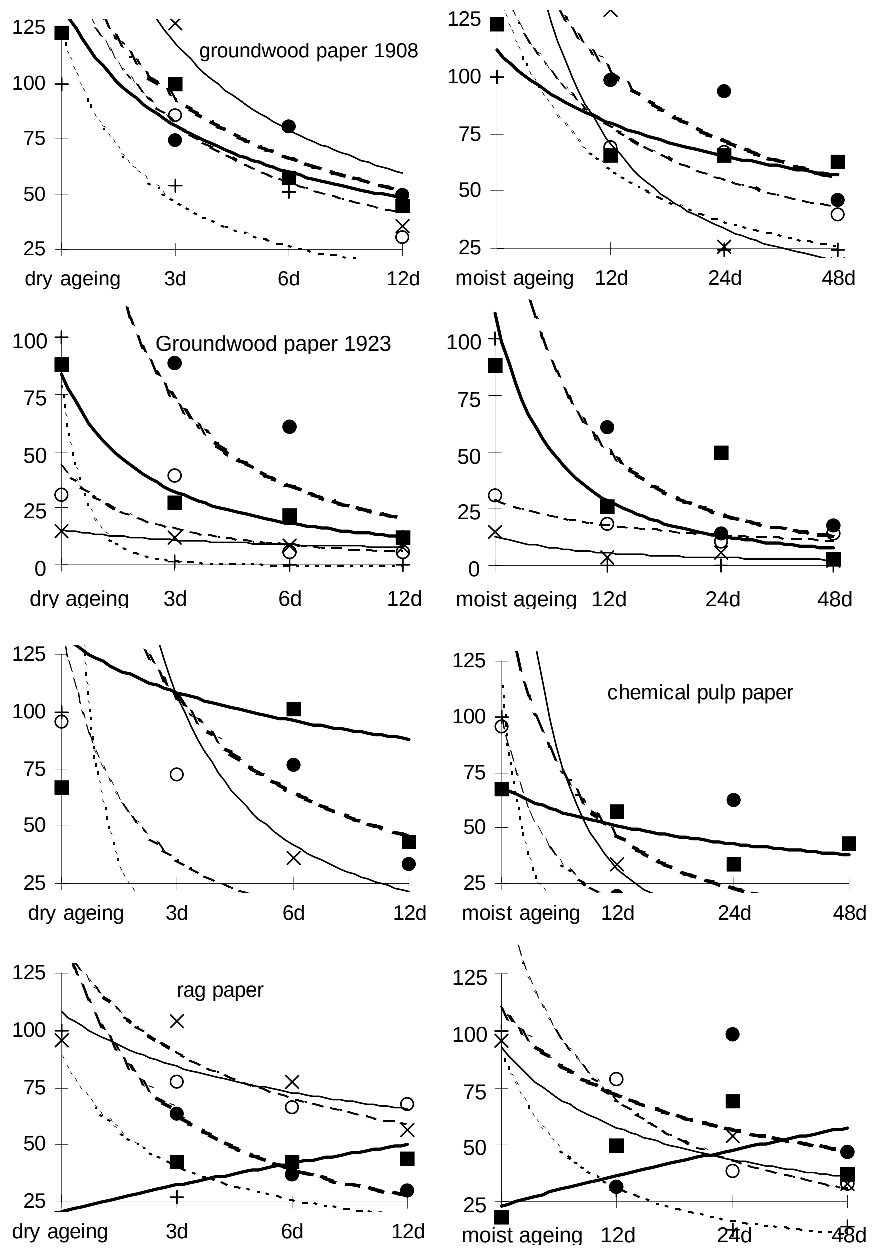


Fig. 7: Change of MIT fold number (%) of old papers during accelerated ageing (100 = untreated unaged).

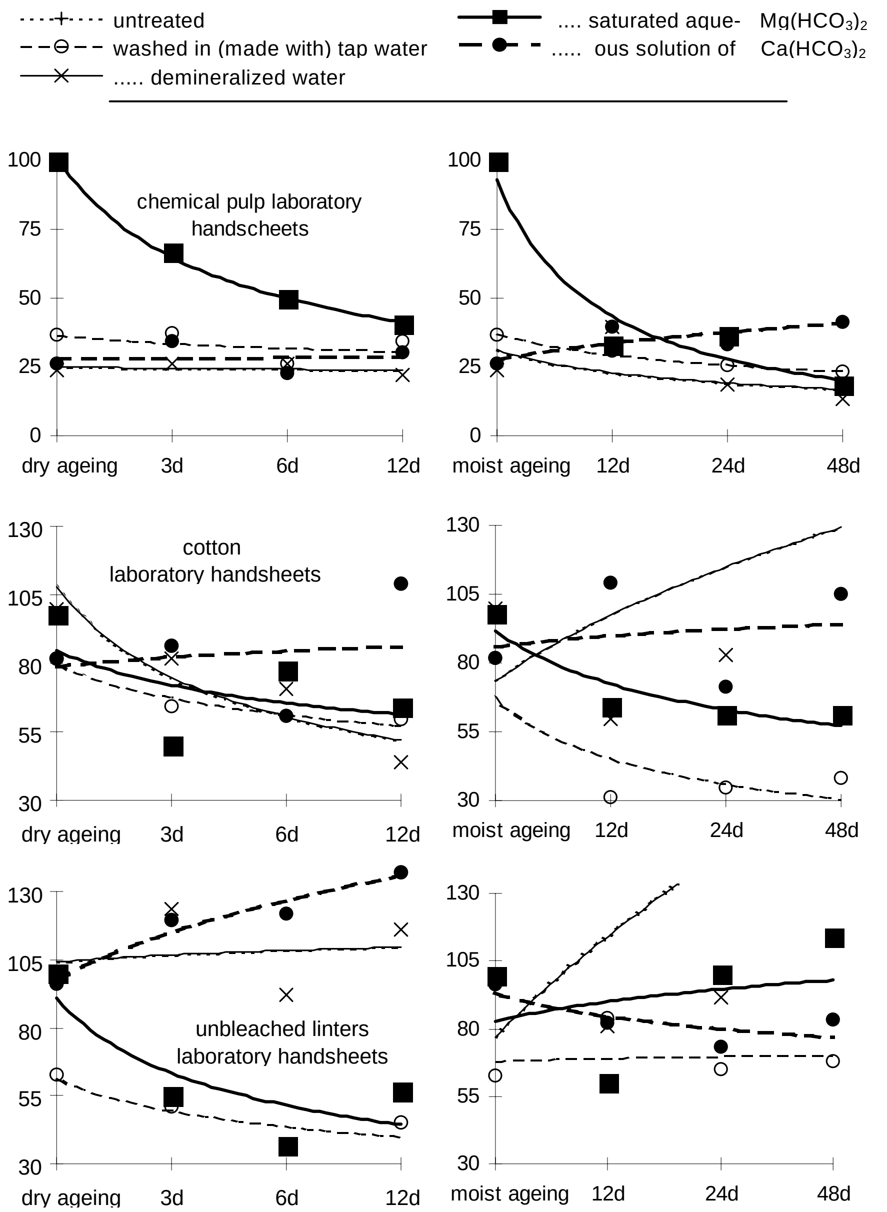


Fig. 8: Change of MIT fold number (%) during accelerated ageing of laboratory handsheets. Best unaged = 100. Chem. pulp: Mg. Cotton: Aqu. demin. Linters: aqu. demin and Mg.

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

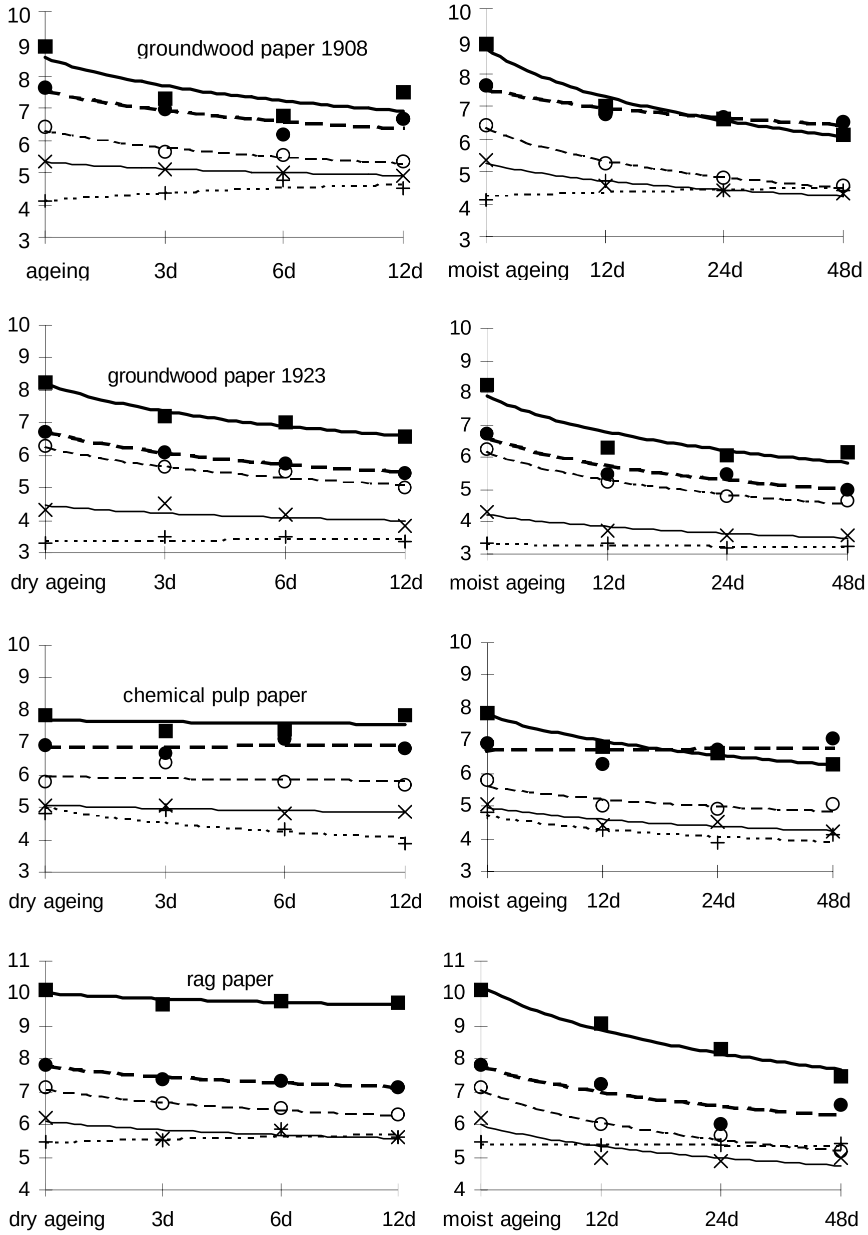


Fig. 9: Change of pH during accelerated ageing of old papers.

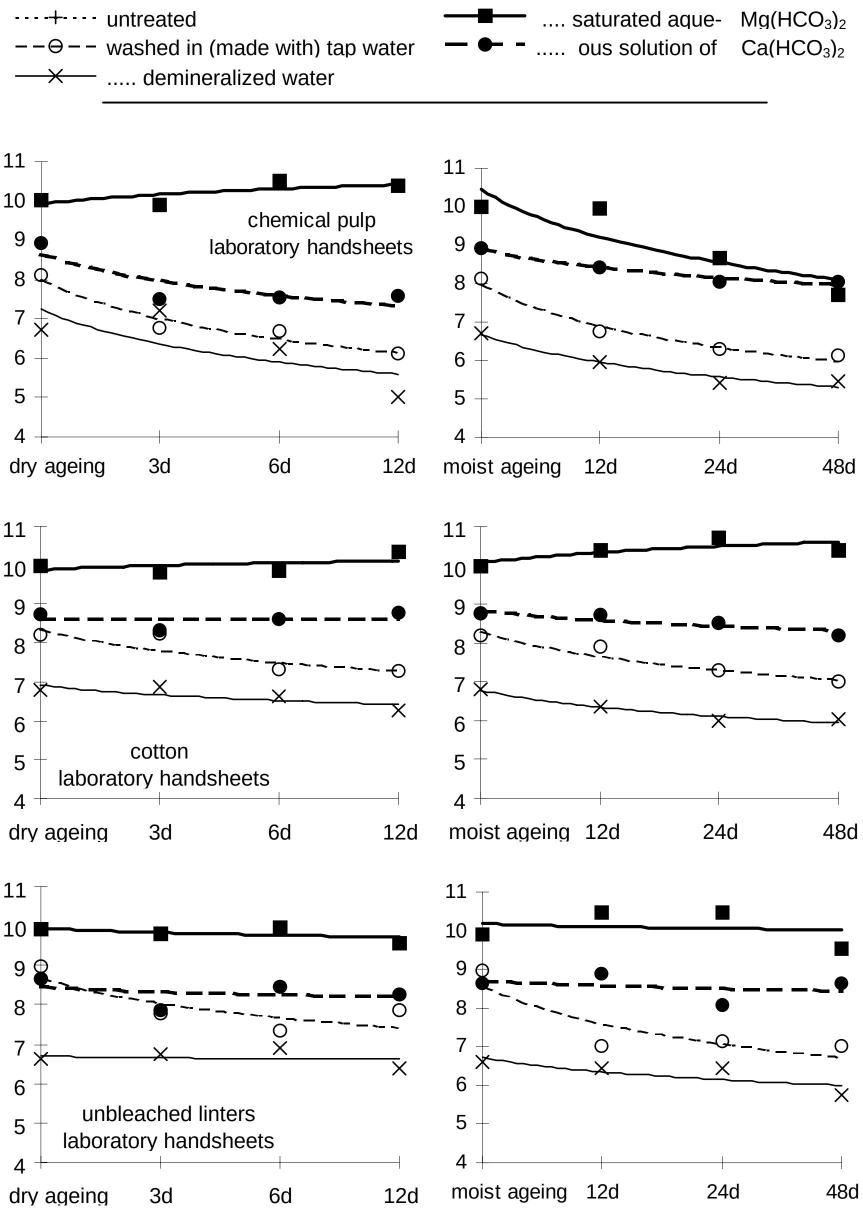


Fig. 10: Change of pH during accelerated ageing of laboratory handsheets.

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

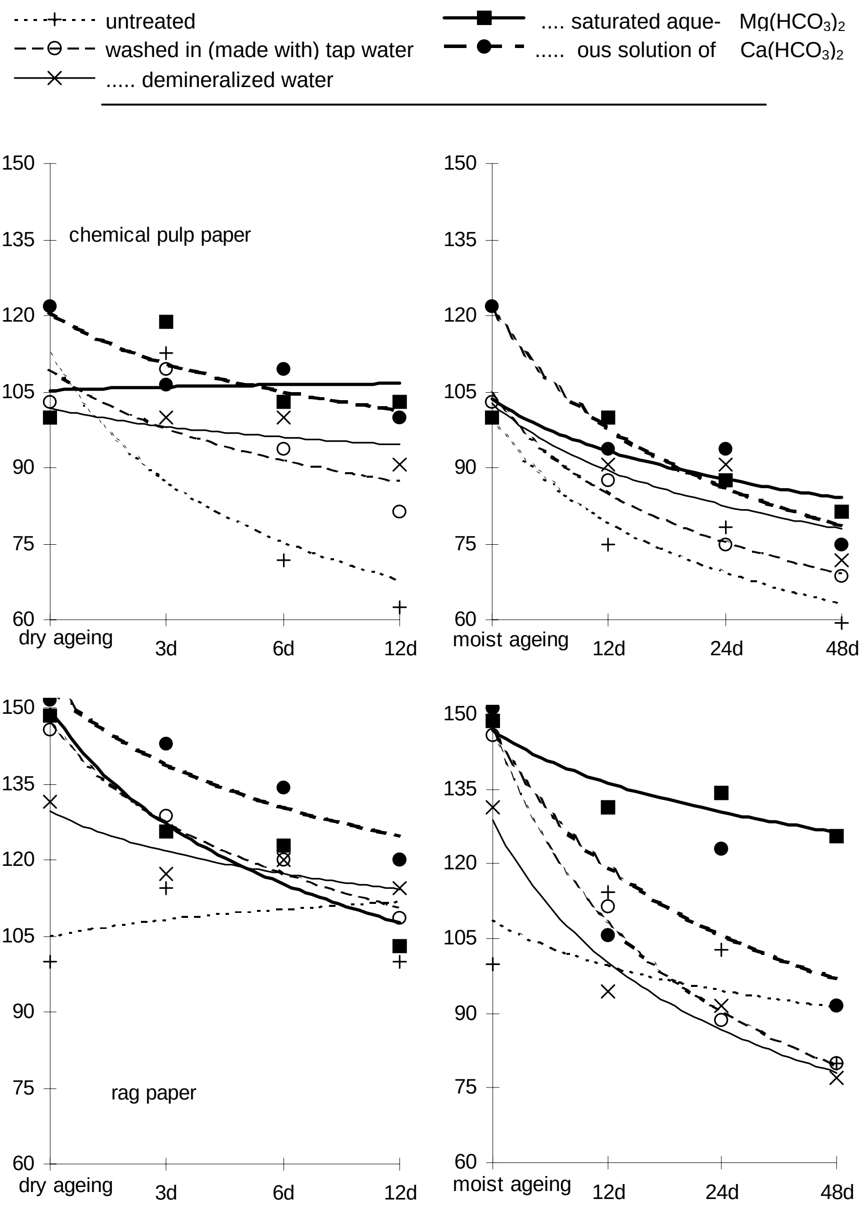


Fig. 11: Change of DP (%) during accelerated ageing of old papers (100 = untreated un-aged).

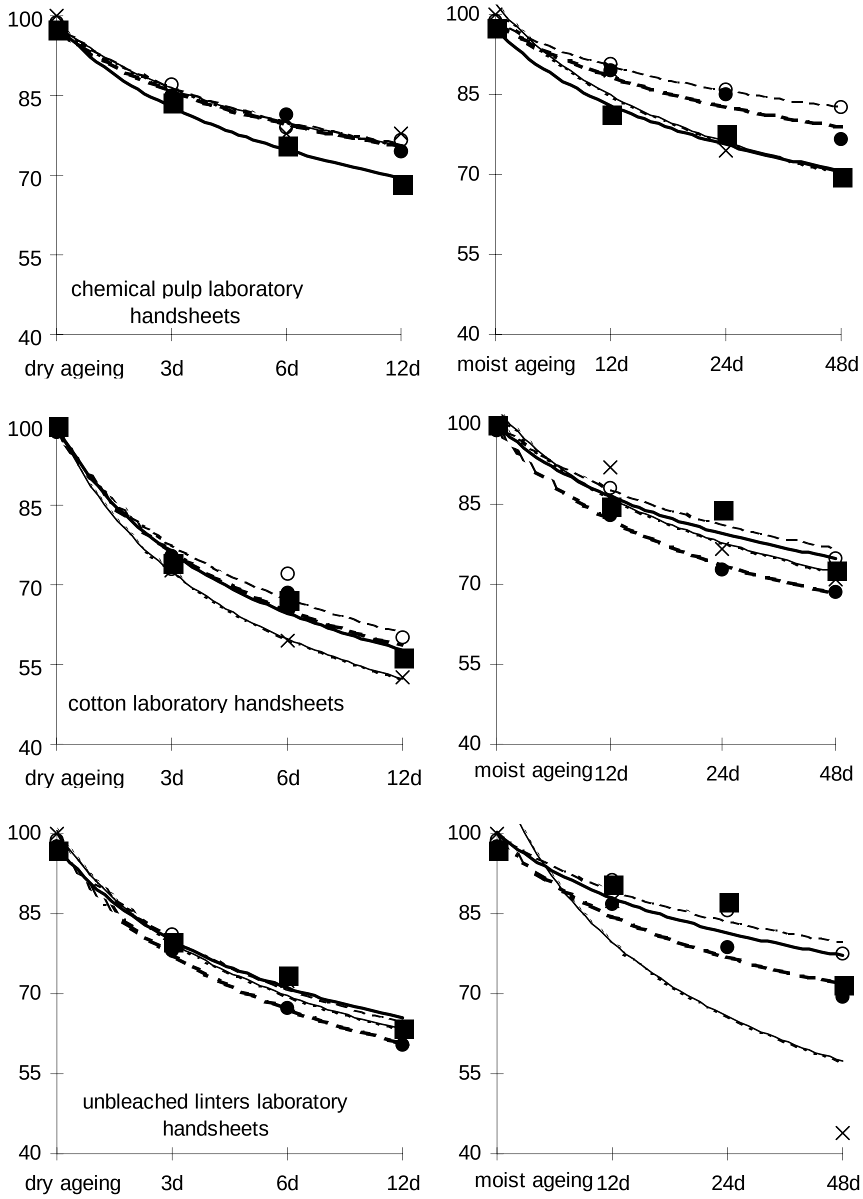


Fig. 12: Change of DP (%) during accelerated ageing of laboratory handsheets. Best unaged = 100. Chem. pulp and linters: aqu. demin. Cotton: aqu. demin., tap water and Mg.

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 désacidifi-

cation), 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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Helmut Bansa
Institut für Buch- und Handschriftenrestaurierung der Bayerischen Staatsbibliothek
Ludwigstraße 16
D-80328 München P.O.B. 340150