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Mass Deacidification of Paper

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Abstract: Paper, the carrier of our written heritage, decays within a relatively short period of time mainly due to its acid content and the influence of air pollution. More than 50% of the records of our libraries and archives are already at risk. Mass deacidification allows this problem to be counteracted by significantly slowing down the deterioration of paper and thereby prolonging its life span. An overview of all relevant mass deacidification methods is given. As it was found that the 'papersave' method was the most suitable to meet Swiss requirements, a plant using an optimised version of this method was built and put into service in March 2000. Thanks to this optimisation, not only books and loose sheets but also documents in archival boxes could be mass-deacidified for the first time. Due to the necessity to analyse not only test papers but also original documents, new non-destructive testing methods had to be developed. Findings of basic investigations regarding treatment effects as well as results of routine quality control turned out to be very satisfactory.

Keywords: Conservation · Deacidification · Mass deacidification · Non-destructive testing · Paper

1. Introduction

Up until the beginning of the 19th century, paper was a hand-made quality product. At that time rag paper was manufactured from carefully prepared plant fibres and sized using animal glue to provide a surface suitable for inscription. As the demand for paper grew, the manufacturing process became more industrialised. In 1805 Moritz Illig introduced stock sizing with the rosin-alum sizing process, and in 1844 wood was first used as the new source of raw materials [1]. The poor ageing performance of papers manufactured with a pH value of 4.0–5.5 in the presence of aluminium sulphate and sulphuric acid, and with a high mechanical wood pulp content, has been well-known for some time (Fig. 1). Since around 1990 paper manufacturing has largely switched to neutral or alkaline production where alkyl ketene dimers are used as size and calcium carbonate as a filler. This has removed the main cause of acid decay. However, recycled paper presents a huge problem, especially for archives.

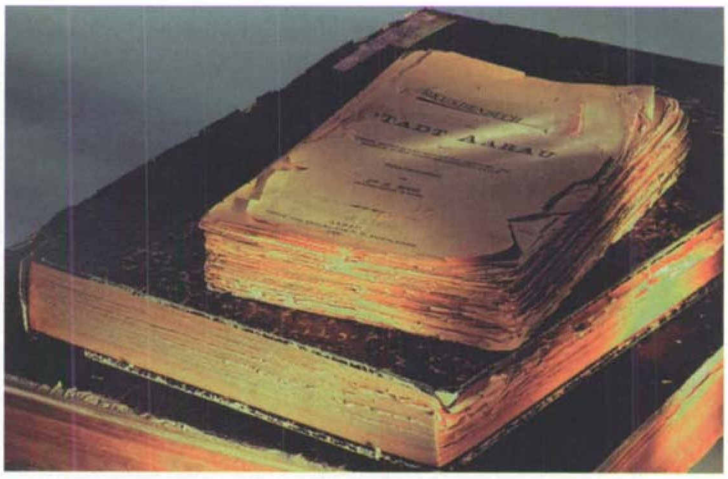

Fig. 1. Example of seriously deteriorated documents.

Acid decay describes the problem that affects all modern papers from the period 1850 to 1990 which were intended to last 'forever' in libraries and archives.

Paper is made from cellulose (40–100%), fillers and coatings (0–50%), sizing agents (0–4%) and additives (0–0.5%). Groundwood and unbleached papers also contain hemicelluloses and lignin (0–50%) [2]. Endogenous factors affecting the ageing performance of paper are the quality of the cellulose fibres, the lignin and hemicellulose contents, and the level of free sulphuric acid and presence of acid inscriptions. Exogenous factors are the climatic conditions of the storage facilities, light, the acid content of the air and wear and tear due to usage [3]. The ageing of paper is based on the complex interaction of decay and oxidation processes at the cellulose and hemicellulose molecules. The key reactions are [4]:

- The acid-catalysed cleavage of β-glucosidic bondings, detectable by the decrease in average degree of polymerisation (DP). The initial DP of cellulose is in the range 1000–36000, depending on its source, technological processes and other factors. From a DP of 400–500 the physical strength decreases rapidly [5][6].
- The oxidation of primary and secondary hydroxyl functions to carbonyl and carboxyl groups. The resulting acids boost the autocatalytic decay of the chains.

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Table 1. Mass deacidification methods in use

Process	Features	Agents	Operating Company	Location	Main users	Treated since start of operations
Viennese treatment [15][16]	Aqueous immersion with paper strengthening Freeze-drying	Effective agent: calcium hydroxide; since 1999: "borate buffer" (boric acid + sodium hydroxide) Re-sizing agent: methylcellulose (MC 400).	Österreichische Nationalbibliothek, Josefplatz 1, A-1015 Wien, Austria	Vienna, Austrian National Library	Österreichische National-bibliothek	5,300 volumes of newspaper since 1986 Capacity: 800 volumes or 2.4 t per year [16]
Paper-splitting machine [17]	Mechanical reinforcement by introduction of a core paper after splitting of the original paper Aqueous deacidification	Effective agent: calcium/magnesium carbonate Core paper: four different kinds of paper according to damage and format of objects Adhesive for the core: carboxymethylcellulose + methylcellulose (1:1) + calcium/magnesium carbonate	ZFB Zentrum für Bucherhaltung GmbH, Mommsenstrasse 7, D-04329 Leipzig, Germany	ZFB, Leipzig	Various libraries and archives	ca. 500,000 sheets since 1994 [18]
Bückeburger Konservierungs-verfahren für modernes Archivgut [19]	Aqueous immersion Fixation of water-soluble inks and dyes Paper strengthening Bückeburg: Two-stage-treatment Berlin: One-stage-treatment	Fixatives: Suspension Rewin EL® (cationic) and Mesitol NBS® (anionic) Effective agent: magnesium bicarbonate Re-sizing agent: methylhydroxyethylcellulose	Hans Neschen AG, Archivcenter, PO box 1340, D-31675 Bückeburg, Germany Hans Neschen AG, Aussenstelle: Lindenallee 53–57, D-15655 Dahlwitz-Hoppegarten, Germany	Neschen, Bückeburg Neschen, Berlin-Dahlwitz	State Archive of Lower Saxony, Saxonian State Archives Leipzig/Dresden Germany National Archive	2,8 mill. sheets since 7/1998 [20] Opening in June 2001. Annual capacity 13.5 mill. sheets (3 shifts). Planned for 2002: 9 mill. sheets [20]
Wei T'o [21][22]	Non aqueous liquid phase impregnation in vacuum Predrying	Effective agent: methoxy magnesium methyl carbonate Solvent: tetrafluoroethane (HFC-134a), methanol + ethanol	Operating institution: National Library of Canada, 395 Wellington Street, Ottawa, ON K1A ON4 Solution supplier: Wei T'o Associates, Inc., 21750 Main Street, Unit 27, Matteson, IL 60443-3702, Illinois, U.S.A.	National Library of Canada, Ottawa	National Library of Canada, National Archives of Canada	1,100,000 books since 1981 [22]
Sablé variant [23]	Non aqueous liquid phase impregnation in vacuum Predrying	Effective agent: methoxy magnesium methyl carbonate Solvent: hydrochloro-fluoro carbons, methanol		Sablé-sur-Sarthe, France	Bibliothèque nationale de France, Paris	Since 1987:
Battelle-Verfahren [24–27]						
'Das Verfahren der Deutschen Bibliothek'	Non-aqeous liquid phase impregnation in vacuum Thorough predrying	Effective agent: magnesium-titanim-alcoholate Solvent: hexamethyl disiloxane	ZFB Zentrum für Bucherhaltung GmbH, Mommsenstrasse 7, D-04329 Leipzig, Germany	Deutsche Bücherei, Leipzig	Various libraries and archives	Around 250 tons since 1994 [18]
papersave®			Battelle Ingenieurtechnik GmbH, Düsseldorfer Str. 9, D-65760 Eschborn, Germany	Battelle Technikum, Eschborn bei Frankfurt	Various libraries and archives	115 tons since 09/1996 [28]
papersave swiss [29]			Nitrochemie Wimmis AG, Niesenstrasse, CH-3752 Wimmis, Switzerland	Nitrochemie, Wimmis	Swiss national library, swiss national archives	90 tons since 3/2000 (145,000 books and 4,2 mill. sheets)
Bookkeeper [30]	Non-aqeous liquid phase impregnation No predrying	Effective agent: magnesium oxide, submicron powder Suspension liquid: perfluoro heptane with surfactant	Preservation Technologies, L.P., Thomson Park Drive, Cranberry Township, PA 16066 U.S.A. Middenweg 576B, 1704BR, Heerhugowaard, The Netherlans	Cranberry Tohnship Pennsylvania, U.S.A. Heerhugowaard, The Netherlands	Library of Congree Washington, Nat. Library of Quebec, Nat. Archives of Canada, 60 libraries and archives in U.S.A. Dutch Federal Archivies, Dutch Royal Library, Niedersächsisches Staatsarchiv, 30 libraries and archives in Europe	More than 700,000 books. More than 25 tonnes of archives [31] Since 1996 375'000 books for the LC [32]
Libertec [12][33]	Dry process Minimal predrying	Effective agent: 50% magnesium oxide – 50% calcium carbonate, submicron powder Transport: dry stream of air	Libertec Bibliothekendienst GmbH, Kilianstr. 86, D-90425 Nürnberg, Germany	Libertec, Nürnberg	Library of the Bavarian State, Library of the City of Munich, Library of the State of Berlin, Bundespresseamt	Around 100,000 volumes equivalent to around 90 tons since 1996 [33]

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- The new formation of hydrogen bondings and main valency bonds between the cellulose chains leading to compression and embrittlement of the paper structure.

Since the final goal of mass deacidification is to prolong the life span, it is necessary to investigate the behaviour of deacidified materials under artificial ageing. Artificial ageing, however, will never be able to perfectly simulate natural ageing. Hence the current differences of opinion regarding the best-suited ageing method. In recent years the standardised ISO 5630-3 method based on isothermal storage at 80 °C and 65% r.h. was most frequently used. Recent research, however, concludes that cycling of temperature and humidity allows better simulation of natural ageing [7]. An excellent review about the problems associated with artificial ageing of paper was published by Porck [8].

It is agreed that the general requirements of a mass deacidification process are as follows [9]:

- Long-term stability of the treated material
- Results are archivally sound and do not produce any detrimental elements
- Neutralise acids and raise pH to a specified level
- Deposit alkaline buffer/reserve
- Will process books without damage to their bindings
- Will not cause inks and colours to 'bleed'
- Will not leave any residual smell or change the texture or feel of the paper
- Environmentally safe
- Safe to current and future users

Table 2. Mass deacidification methods under development

Process	Features	Agents	Developer	State of Development
CSC Book Saver® [34][9]	Non-aqueous liquid phase impregnation under pressure Slight predrying	Effective agent: carbonated magnesium di n-propylate Solvent: HFC 227 (1,1,1,2,3,3,3-heptafluoropropane)	CSC, S.L., Mallorca 269, E-08008 Barcelona, Spain	Pilot plant since 1999
Nanomer-Techno-logien [35]	Sol-gel-based reinforcing system	Effective agent: sol-gel silane-system modified with methacryloxy groupings, containing perfluorinated silanes; addition of MgO	Institute for New Materials (INM), Saarbrücken, Germany	Experimental stage

Table 3. Discontinued installations or developments

Process	Features	Agents	Developer/ Operating Company	State of Realisation
DEZ [36][37]	Gas-phase process Thorough pre-drying under exclusion of oxygen	Effective agent: diethylzinc	Library of Congress, Washington, DC/Texas Alkyls (Akzo) (U.S.A.)	Pilot plant in Houston, Texas from 1990–1994
FMC [38]	Liquid phase impregnation Predrying	Effective agent: carbonated magnesium dibutoxytriethylene glycolate (MG-3); since 1993: magnesium butyl glycolate (MBG) Solvent: Freon 113; since 1993: heptane	FMC, Lithium Corporation of America, LITHCO, U.S.A.	Pilot plant in Bessemer City, U.S.A., since 1990
Graft-copoly-meriza-tion [39]	Liquid phase impregnation Exposure to γ-rays Paper strength-ening and deacidification	Effective agents: solubilized acrylate monomers (e.g. ethyl acrylate + methyl methacrylate + alkaline monomers)	British Library, London	Laboratory chamber

2. Review of Mass Deacidification Methods

2.1. *History*

Paper deacidification dates back to the 1930s, when 'single sheet' neutralisation of paper in an aqueous solution of calcium bicarbonate was invented. Since then, washing and deacidifying of paper has been a topic of numerous investigations [10]. In the 1960s the first non-aqueous techniques were developed [11]. These were based on magnesium methoxide, solubilised in a mixture of methanol and freon compounds and applied to the paper by spraying. These activities formed the basis for the later development of mass deacidification processes. In 1981, the world's first mass deacidification plant opened in Toronto. During the 1980s and 1990s, a great deal of effort was invested in the improvement of existing deacidification processes and the development of new ones. More detailed reviews of the history of paper deacidification can be found in [12–14].

An overview of the most important methods in use, under development or discontinued is given in Tables 1–3. It must be added that numerous other deacidification systems were evaluated but failed for a variety of reasons. In particular, gas-phase treatments with ammonia or volatile amines were unable to cause a lasting deacidification effect and created serious health hazards.

2.2. *Classification and Comparison of Methods*

From Tables 1–3 it can be seen that magnesium-based deacidificants are generally favoured. The deacidificants can be applied either in dissolved form or as particles, using different solvent types or the gas phase as carrier. This leads to the following classification of deacidification methods:

A) Aqueous processes, usually with dissolved alkaline earth carbonates as a neutralisation agent (Bückeburg, Viennese process, paper splitting)
B) Non-aqueous processes using organometallic agents, usually magnesium alcoholates, with organic solvents such as alcohols, freons, perfluoro alkanes or siloxanes (Wei T'o, FMC, Sablé, Book Saver, Battelle).
C) Treatment with ultra-fine particles of agent, usually magnesium oxide, applied as a suspension in perfluoro alkanes (Bookkeeper).
D) Treatment with ultra-fine particles of agent, usually magnesium oxide, applied directly from a stream of air (Libertec).
E) Gas-phase processes with organo-metallic agents, namely diethyl zinc (DEZ).

All described methods, if correctly applied, allow not only complete neutralisation of acidic papers but also the incorporation of an alkaline reserve.

As a rule, the aqueous methods (A) are suitable for the treatment of single sheets and contain a paper-strengthening aspect. The paper splitting method is designed for the mechanical reinforcement of very fragile single sheets. The Bückeburger method is designed for archival material which has to be taken apart in single sheets as a first step. Since paper clips and plastic covers are removed in this process, the material is given comprehensive conservation treatment at the same time. The Vienna process is designed to deacidify and re-strengthen newspaper after removing the covers.

As the bleeding of inks and dyes constitutes the major problem associated with all aqueous methods, inks and dyes have to be either absent or chemically fixed before the treatment.

In the non-aqueous processes (B) impregnation with the treatment solution takes place in a vacuum chamber. Books as well as loose sheets and archival material in boxes can be treated. The more modern methods use non-polar solvents in order to minimise the 'bleeding' of alcohol-sensitive inks and dies. For ecological reasons, however, solvents such as freons or halogenated hydrocarbons are inappropriate in the long term. Siloxane solvents are an environmental friendly alternative, but since they are highly flammable they require extensive safety measures. One drawback of the solvent-based methods (B) is that due to the reactivity of the employed deacidificant with water, a certain amount of pre-drying is necessary. This entails physical stress for paper, leather and parchment and increases the costs of investment and treatment. Type B and E processes have the broadest range of application, and therefore come closest to a real 'mass' process.

In the methods with ultra-fine particles (C and D), bound documents – books or clipped-together sheets – are placed in a machine separately and fanned out. This ensures that the particles can reach the interior of the books. As no predrying is needed, moisture sensible materials like leather and parchment can be treated at lower risk. However, the ultra-fine particles are inherently unable to penetrate the paper as effectively as dissolved deacidificants. These can also form powdery deposits. Furthermore, the stream of air or solvent respectively used to introduce the particles causes physical stress on the pages and the book as a whole.

From the 'side-effect point of view', the solvent-free methods are clearly favoured. Unfortunately, they cause other problems. In the case of the only true gas-phase method (E), the handling of the deacidificant diethyl zinc, a highly explosive gas, is extremely dangerous – accidents have happened, and the pilot plant was put out of operation in 1994.

3. The Swiss Mass Deacidification Project

3.1. *Background and History*

Due to world-wide surveys one can assume that on average 80–90 % of the holdings in libraries and archives are threatened by acid decay. Of this, 10% is badly damaged or unusable, 30% affected and an additional 40% is at risk [41]. These figures apply equally to the Swiss National Library (SNL) and the Swiss Federal Archives (SFA) which are relatively young institutions. They each contain 3000 t of holdings at risk from acid decay, which would take 20 to 30 years to deacidify at the rate of 40 t per annum. The Swiss National Library has adopted a strategy for mass deacidification to prevent further decay of original stock which is at risk but still usable. Microfilming is used to preserve more badly damaged stock.

In 1990, both SNL and SFA started a joint venture aimed at establishing a Swiss deacidification plant. Between 1991 and 1994, the world's leading systems (Wei T'o, Battelle, FMC, DEZ and Bookkeeper) were evaluated. The Battelle process ('papersave') was concluded to be the most suitable because it is efficient, environmentally friendly and enables treatment not only of books but also of loose documents in boxes. In Summer 1998, the Swiss parliament decided to invest CHF 13 million in the construction and operation of the Swiss deacidification plant. This plant was built in Wimmis and became operational in March 2000.

The Swiss mass deacidification plant uses the third generation of the Battelle process – this improved procedure, called 'papersave swiss', is distinguished from its predecessors through greater variability and better control of process parameters as well as through an active reconditioning facility. The plant belongs to the Swiss Confederation and is privately run by NITROCHEMIE WIMMIS AG. With two treatment chambers allowing a capacity of 120 t per year, it is the largest and most modern of its kind. 40 tons of capacity each are utilised by the SNL and SFA, while a further 40 tons are available for other customers.

3.2. *The Process and the Chemistry*

Crates containing the books, documents and archival boxes to be treated (500–1200 kg) are placed in the treatment chamber (Fig. 2 and Fig. 3). Here the material is pre-dried, *i.e.* the normal moisture content of 5–8% is reduced to <1% by mild heating in a vacuum. Drying is followed by the actual deacidification. In this step, the chamber is completely flooded with deacidification solution which impregnates the material. After the solution is drained, the material is again vacuum-dried in order to remove the solvent. The evaporated solvent is condensed and recycled. These three steps of the process take three to four days. During the subsequent reconditioning period, air of a defined temperature, humidity and quantity is blown through the material for about three weeks. The paper regains the lost humidity and reactions take place between treatment agent and material, releasing alcohol. The deacidified material is then returned to the customers. Different treatment programs were developed for library material (mainly books) and archival material (documents with inscriptions, mainly in boxes). In particular, the concentration of deacidificant (METE) had to be reduced by one-third in the program for archival materials.

The main problem in developing a new mass deacidification method was to find an environmentally friendly, non-polar solvent able to dissolve magnesium alcoholates. The papersave method is based on Battelle's invention, according to which a complex of magnesium ethoxide and titanium ethoxide (METE) can be easily dissolved in hexamethyl disiloxane (HMDO), a highly inert, low-viscous and (with a boiling point around 100 °C) relatively volatile solvent [25].

During treatment the magnesium ethoxide immediately neutralises free acids present in the paper as follows:

$$Mg(OC_2H_5)_2 + H_2SO_4 \rightarrow MgSO_4 + 2C_2H_5OH \quad (1)$$

During reconditioning, the excess of magnesium ethoxide reacts with humidity and carbon dioxide, thus forming the desired alkaline buffer consisting of magnesium carbonate which will protect the paper from future acid attacks:

$$Mg(OC_2H_5)_2 + 2H_2O \rightarrow Mg(OH)_2 + 2C_2H_5OH \quad (2)$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \quad (3)$$

Note: It has not yet been determined whether the alkaline buffer consists of $MgCO_3$, $4Mg(CO_3){\cdot}Mg(OH)_2$ or even $Mg(OH)_2$.

The titanium ethoxide also present in the paper reacts with humidity to titanium hydroxide, which will decay into inert titanium dioxide and water. Therefore, titanium ethoxide does not contribute to the deacidification effect but has to be incorporated in the solution since magnesium ethoxide alone is not soluble in HMDO.

Fig. 3. Treatment chamber; charging with frame containing crates with books is in progress.

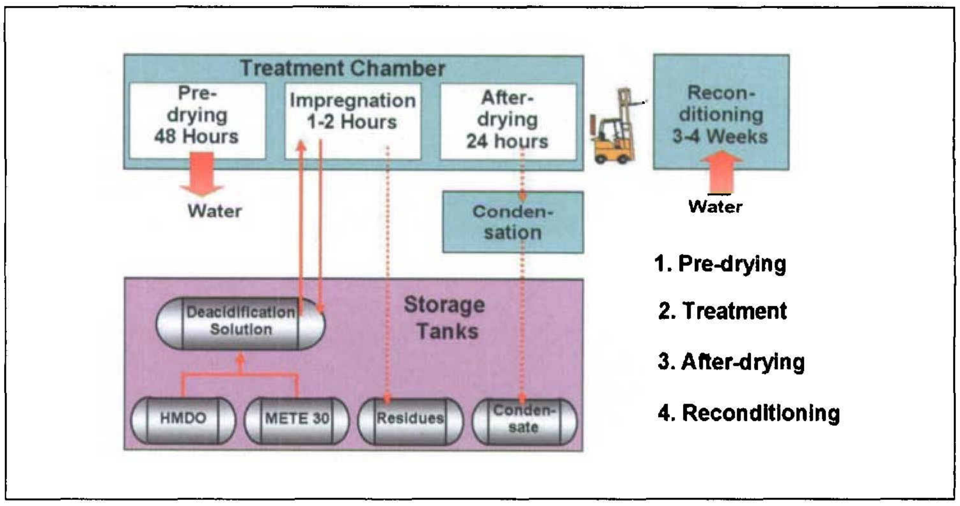

Fig. 2. Flow diagram of the 'papersave swiss' mass deacidification process.

4. Quality Control

4.1. *Quality Requirements*

The basic contract between the private operator and its main customer, the Swiss Confederation, contains numerous provisions governing the quality of the treatment as well as the safety, infrastructure and logistics of the process [29][42]. According to these quality standards, the general suitability of the 'papersave swiss' process must be established. Furthermore, compliance with the requirements must be verified for each single batch.

4.2. *Non-destructive Analysis*

As destructive testing of original material is not possible, suitable non-destructive analytical techniques had to be found. Most side effects can be determined qualitatively by visual and physical assessment. A spectrometric method was implemented for the quantitative determination of colour changes. The analysis of treatment intensity, however, turned out to be more difficult. Surface-pH measurements only indicate whether the document is acidic or alkaline but give no quantitative information about the amount of incorporated $MgCO_3$. Therefore, a quantitative technique based on X-ray fluorescence (XRF) was developed. A commercial XRF spectrometer was fitted to a huge, specially constructed vacuum chamber. The system was equipped with an xy-table which allows each position of a book or document to be located above the XRF detector (Fig. 4). At each position, an area of about 1.5 cm^2 of the paper page is measured. Since it was established that Mg and Ti are deposited on the paper in stoichiometric ratios, the treatment intensity – usually expressed as $\%MgCO_3$-uptake – can be determined by the increase in both Mg or Ti. This is very important since, due to the physics of XRF, Mg is detected only on the paper surface (Mg X-rays penetrate only about 5% of paper sheet thickness), whereas for the Ti-measurement a few sheets are penetrated. The new technique was validated according to SN EN 45001 and allows now the intensity and homogeneity of mass deacidified original documents to be analysed for the first time on a routine basis.

4.3. *Results of Basic Investigation*

Several investigations were performed in order to establish basic findings on the effectiveness of the 'papersave swiss' process. First it was demonstrated that the treatment intensity (uptake of magnesium) is highly constant both with-

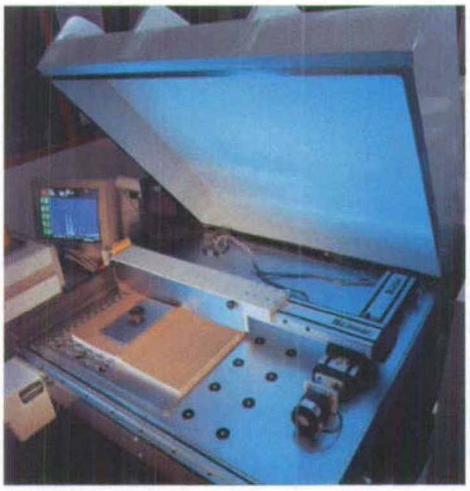

Fig. 4. Sample chamber of XRF spectrometer for non-destructive analysis of Mg and Ti-uptake; test book is located on xy-table.

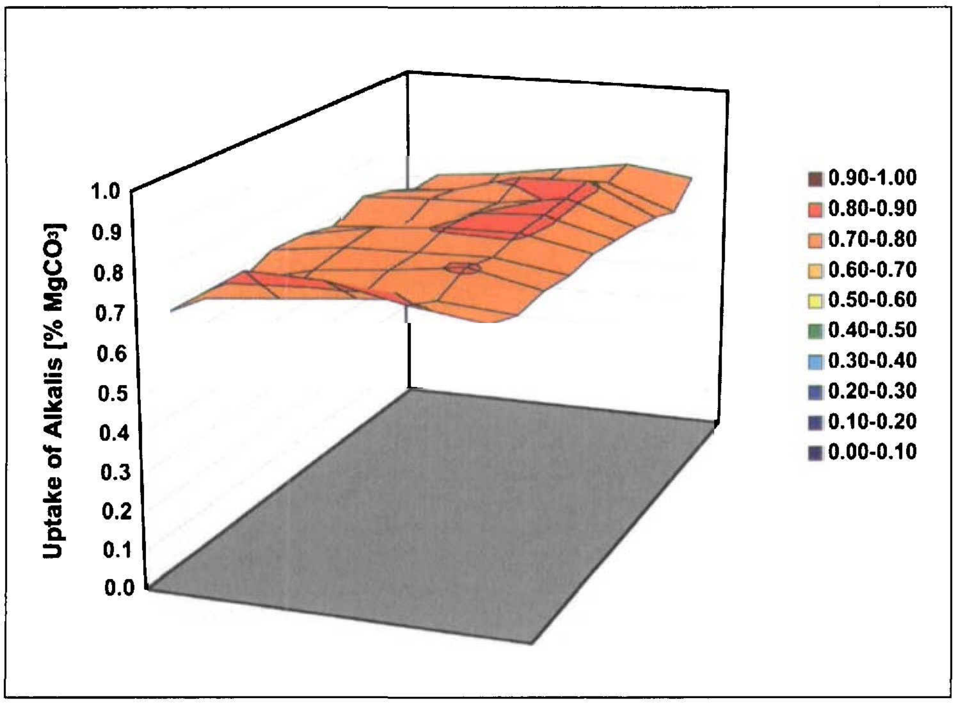

Fig. 5. Homogeneity of treatment of an archive document. The alkali uptake ranges between 0.7% and 0.85% $MgCO_3$ over the whole paper sheet, proving complete and homogeneous deacidification.

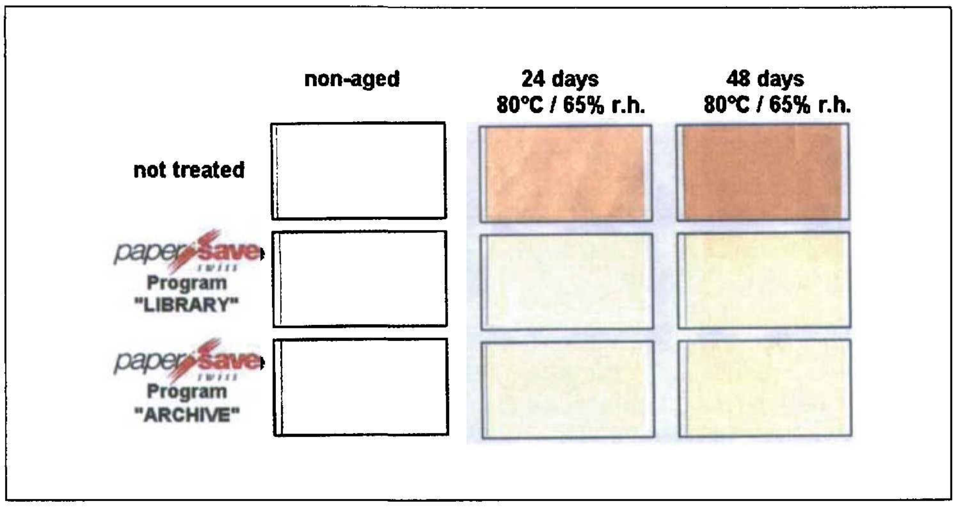

Fig. 6. Influence of treatment and/or ageing on paper made from sulphate cellulose. The 'papersave swiss' treatment causes only small colour changes. During ageing, strong discoloration occurs however at a much lower rate for the two deacidified papers than for the untreated one.

in and between the batches and does not depend on the location of the document within the treatment chamber.

More detailed XRF analysis proved that all paper sheets were fully deacidified over the entire area. In addition, good to excellent homogeneities of Mg/Ti-deposition were established (Fig. 5). It was then demonstrated that the 'papersave swiss' deacidification acts in a three-dimensional way: the paper sheets are neutralised not only on the surface but throughout the paper matrix. This was demonstrated by (i) direct REM-EDXRF measurements which found Mg and Ti throughout the diameter of a treated paper sheet, (ii) XRF measurement of Mg in split paper which determined even slightly higher Mg-contents on the interior of the sheet than at the surface, and (iii) the fact that sheets treated in fully sealed paper envelopes receive the same $MgCO_3$ uptake as open-treated sheets.

Mechanical testing on artificially aged papers established that the 'papersave swiss' treatment slows down paper ageing at least by a factor of 2–7 (depending on the test) and therefore significantly prolongs the document's life span. For this purpose two different paper types were deacidified with the two different deacidificant concentrations and aged for 24 and 48 days at 80°C at 65% r. h. (ISO 5630-3). All non-aged and aged samples were tested with respect to tensile strength (EN-ISO 1924/2), tensile strength after Bansa-Hofer folding, tearing resistance (Elmendorf; EN 21974), and folding index (Schopper; ISO 5626). Data analysis showed that the treatment itself does not significantly alter the mechanical properties of the two papers (neither strengthening nor weakening). During ageing, however, the deacidified samples show a much slower deterioration rate of mechanical properties than the untreated ones.

All papers undergo a small but measurable colour change during treatment (slight yellowing and darkening). This treatment-induced change, however, is negligible compared to the discoloration during ageing. In case of the investigated papers, deacidification also showed a positive effect regarding ageing-induced discoloration – the rate of discoloration was significantly reduced (Fig. 6).

4.4. *Results of Routine Analysis*

Since the start of the operation more than 12000 analytical results have been collected. In the first four months of operation ten test and ten original documents per batch were analysed. In the

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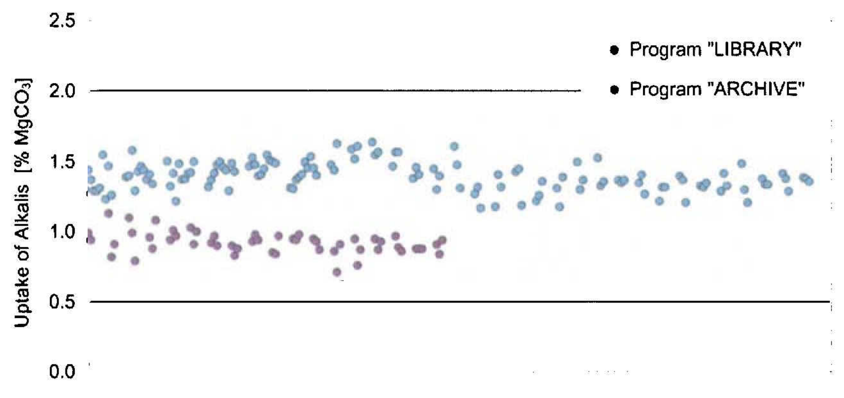

Fig. 7. Process chart showing $MgCO_3$ uptake of 34 batches library books and of 27 batches archival material, from XRF analysis of three to ten test books per batch. The good stability of process as well as the difference between the two programmes are clearly visible.

current routine operation three test books and five original books per batch of 1850 library documents are analysed and the results returned to the customers together with the treated material. Analysis of this huge amount of data provides an excellent overview of the main features of the 'papersave swiss' process:

From XRF analysis of testbooks it can be concluded that the process is highly stable and robust: the quality requirements (95% of test papers between 0.5% and 2.0% $MgCO_3$) can easily be fulfilled. For the library programme the $MgCO_3$ uptake is around 1.35%, while for the archive program it amounts to around 0.90% (Fig. 7). The difference in $MgCO_3$ uptake between the two programs perfectly represents the difference in deacidificant concentration in the treatment solution (factor 0.67).

More than 99.5% of analysed original and test papers resulted in pH values >7.0 following treatment. Hence the quality requirements (98% of documents fully deacidified) are fulfilled. pH values of untreated original documents ranged between 2.3 and 9.0. After treatment, pH-values between 7.0 and 10.0 were obtained.

Routine measurements using the colour spectrometer showed that colour change is highly reproducible for a given paper type. Again, the impact of the type of paper was found to vary: wood-pulp-free, high-quality papers undergo much smaller colour changes than wood-containing papers (primarily due to lignin, which inherently changes its colour between the acidic and alkaline regions). A surprising finding was that several papers, all of them carefully manufactured in the 18th century from textile fibres, even exhibited much lower colour changes than modern, wood-free high-quality papers.

4.5. *Results of Visual and Physical Assessment*

While the deacidification treatment described above is applied only to paper, the process involves the library and archival materials as a whole. In an ideal situation a mass treatment process must not affect

- cover and binding including synthetic and natural glues
- covers such as leather, parchment, textiles, plastics, metals
- printing inks, modern printing materials and stamping inks, ferro-gallic ink, historic inks and pigments, colour and gilt edge, marbled paper *etc.*
- photographs, prints, graphics, plastic sleeves, overhead slides *etc.*

Since it is impossible to check each document (1850 library documents or 64000 sheets of archives per batch), spot checks are carried out (between 1% and 25% depending on the material being processed). From 20 library documents per batch a full protocol is drawn up.

The condition of the papers and documents before and after deacidification is documented according to quality standards governing paper structure, function and appearance of the cover, print and inscriptions, smell and dimensional stability.

Between the start of the project in March 2000 and June 2001 145,000 documents (43 t) belonging to the SNL and 4.2 million documents (48 t) belonging to the SFA have been deacidified. More than 98% (SFA) rsp. 96% (SNL) survived the treatment without a change, and the required quality standards were exceeded. A slight change was visible on an average of 1 to 2% of the documents, although both legibility and usability remained unimpaired. The main things to be affected were several unstable red inks in covers, printing inks and in coloured pens. Iridescent reflections which are reported to appear sometimes in liquid processes [14][23], were not observed. Impairments were detected on fewer than 0.1% (SFA) rsp. 2% (SNL) of the documents, but never complete loss. Ongoing investigations are conducted to identify reasons for side effects and ways of avoiding them or at least further reducing their intensity.

Despite the excellent results achieved by the 'papersave swiss' process it is still not possible to dispense with the preparation and selection of the holdings in the SNL. For example, the following library stock is not treated: parchment bindings, leather bindings, certain synthetic folders and some red-covered books. Out of the 145000 documents treated, 964 (0.65%) were excluded from the deacidification treatment for conservation reasons. In addition, some tightly-packed documents are opened and sometimes foil covers and plastic covers removed. The SFA stock is deacidified in the archive boxes without any kind of selection [43].

5. Conclusions and Outlook

After decades of world-wide research and development on the subject of mass deacidification, four different principles of process have become well established on the market, serving a wide range of libraries and archives. Although the original goals have almost been met it is still clear that there is not, and never will be, a single universal process. The range of materials is too wide, and the requirements of different libraries and archives too varied. As a rule, mass deacidification generally constitutes part of the overall conservation concept. In some institutes it is integrated logistically into a stock maintenance or inventory process. The choice of the most suitable process is dictated by the stock, the financial resources, and of course the local availability of a provider of deacidification services.

Preparation and selection of the stock is generally unavoidable. The effort involved depends largely on the deacidification process selected. In this respect the principle of the Battelle process has the widest field of application, which is why it was regarded as the most suitable process for the Swiss National Library and the Swiss Federal Archives. It was further developed into the 'papersave swiss' process in order to make it more suitable for processing archive materials.

Under the present circumstances, the Swiss mass deacidification project must be regarded as a complete success. The quality of the treatment exceeded our expectations. The plant, including logistics and analytics, was successfully put into operation. Within one year of operation, experience and findings on mass deacidification in general and the 'papersave swiss' process in particular was broadly expanded. Nevertheless, several questions are still unresolved.

One question concerns the effect of deacidification on leather covers. At a pH value of over 6, leather is no longer stable and the drying process after wet processing causes the leather to embrittle beyond the point where it can be fully restored. Although up to now no damage to the leather could be ascertained [26], research including conservation aspects is still necessary in this field. A project was therefore launched to investigate this issue in depth.

Another question concerns the optimum amount of alkaline buffer to be incorporated in the paper. Since DIN 6738 recommends a minimum content of 2% $CaCO_3$ (equivalent to 1.68% $MgCO_3$) in newly produced papers in the highest life-span class, many conservators believe that this concentration should also be the target value in deacidification. With most mass deacidification processes, however, the deposition of such high amounts of alkaline buffer is either difficult to obtain, increases the severity of side effects, or causes excessive costs. As described above, we (and others) also obtained good results with much lower buffer concentrations. Recent research even indicates that excess alkaline buffer might increase the degradation of treated papers [44]. Further research is required in order to assess the optimum amount of buffer content, and a project aimed at this is currently under way in our laboratories.

Whereas mass deacidification allows further deterioration to be stopped or slowed down, it does not restore the original strength of the paper. Books and documents which are already been badly damaged before treatment will remain unusable. Until now, re-strengthening of paper was limited to 'single sheet' treatment. For several years efforts have been under way to develop 'mass re-strengthening' techniques, preferably in combination with mass deacidification [45]. The problem, however, is not straightforward – all approaches have so far been unsuccessful [39][40] or are still at the basic stage of research (*e.g.* the use of a sol-gel based reinforcing system [35]). The reinforcing of paper is a field of research in which considerable progress is still anticipated.

Additional research projects carried out elsewhere concern the best methods of selecting stock prior to processing [46], including the development of new, non-destructive analysis methods for micro-analytic evaluation of the condition of the paper [47].

Despite all these promising research projects, it must be noted that the deterioration of paper is advancing rapidly, and waiting for the perfect system presents a much greater risk to our written heritage than using a less perfect method.

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