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PREDICTION OF EFFICACY OF DEACIDIFICATION PROCESS

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ABSTRACT

The aim of this work is to propose the first model hypothesis and function for predicting the efficacy of deacidification. We have used the d_{DEA} as the first basic factor influencing the efficacy. The resulting relationship is based on the best achieved reliable η data and related d_{DEA} data, from mass deacidification technologies used for the lifetime and usability increase of millions of books, historical documents worldwide. The resulting η predicting function is as follows $\eta = 0.732984+0.125612*d_{DEA}^{(-0.214237)}$. This first 1D function can serve as an impulse for continuing improvement of the prediction, and 2D, 3D and multidimensional models. It can be used for comparisons and connecting η with η-characteristic mechanical, physical, cellulose solution properties; the prediction can serve for continuing improvement of efficacy of the conservation technology in increasing the paper carriers of information, documents longevity and usability.

KEYWORDS: Longevity, heritage, acid paper, books, documents, deacidification, efficacy, prediction, folding endurance, hydrotalcites synthesis, in situ, organic-inorganic composite.

INTRODUCTION

To prevent the degradation, they should be monitored by right methods of quality control management systems (QMS) including the usability and functionality. New systems of forward control of quality, usability, lifespan and healthspan systems (FCS) should be continually developed and used in praxis (Katuščák et al. 2009, 2012a,b, Vizárová et al. 2016, Králik et al. 2021). One of the key problems of continuing improving and technology development is weeks or even months lasting artificial accelerated aging. An efficacy factor of deacidification (η) can be measured by cellulose mechanical, physical and solution properties; in such case it expresses by how many times the rate of strength loss or degree of polymerisation (DP) loss, during

accelerated aging, is decreased by a deacidification treatment in comparison to untreated acidic paper from the same source exposed to the same accelerated aging conditions (Anders et al. 2008, Hubbe et al. 2017, 2018). The necessary modelling and η, lifespan (LS), healthspan (HS) predicting multifactorial, multidimensional methods could help in pre-screening, selection of potential candidate substances, mixtures, methods, like in other technologies, but they are still missing. The dimension of some alkaline insoluble particles can be so large that they can neither penetrate the paper thickness or cross section, nor can diffuse to the critical glycosidic bonds of the cellulose endangered by acids and acid hydrolysis. They stay mostly on paper surfaces, at a distance in order 10^4 - 10^5 times larger than the size of the endangered glycosidic bonds of the cellulose macromolecule.

Comparison of the independent results of the studies (Katuščák et al. 2012a,b; Vizárová et al. 2016) can be seen on Fig. 1. The efficacy can be modified, improved during or after the mass deacidification in nonpolar solvents, carriers by secondary diffusion or migration (denoted as d*m), homogenization, redistribution of the water-soluble compounds, ions arising from the alkaline reserve. The homogenization secondary diffusion processes must be safe, subdeformation or subcritical in terms of paper and heritage safety; the processes must be safe for books, in terms of visible deformation of paper, bonds and all treated documents (Hubbe et al. 2017, Tiňo et al. 2016, Jablonský et al. 2012). These processes and apparatuses are specific for each deacidification technology and are out of the scope of this work.

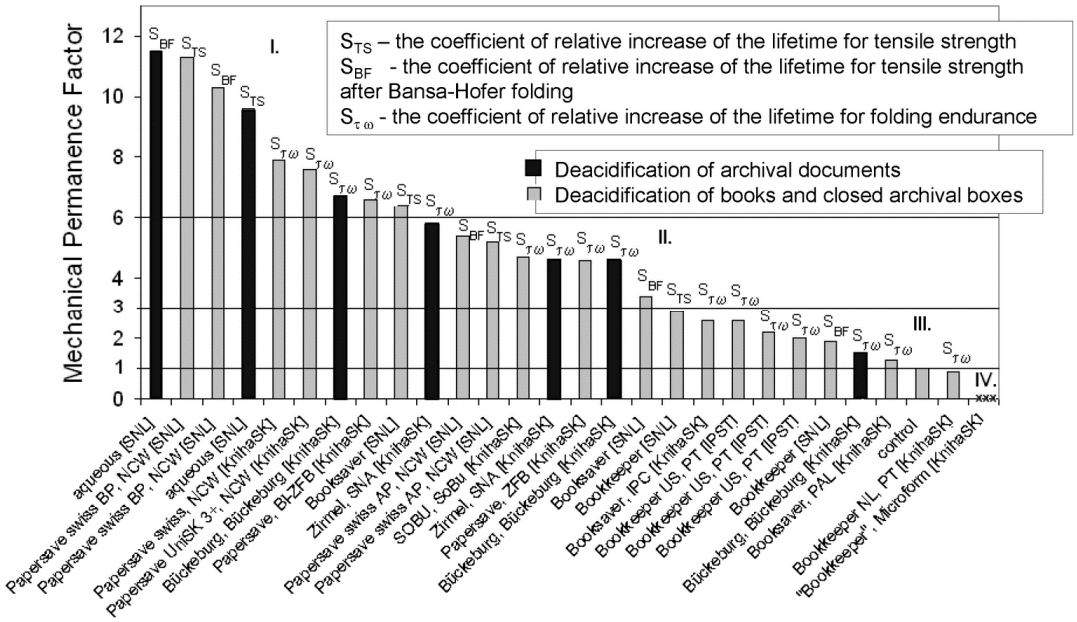


Fig. 1: Comparative evaluation of most important deacidification processes. Symbols and abbreviations: The efficacy of the mechanical permanence factors, as measured by the testing laboratories and projects in USA (Library of Congress -efficacy), SNL and the Consortium of national archives, libraries, universities, academy of sciences and accredited lab BN/EUROFINS SR– KnihaSK (St ω). The Testing laboratory on the x – axis, is shown in brackets: [SNL] – Swiss National Library; [KnihaSK] - Consortium of academic, memory and testing institutions SR; [IPST] – Institute of Paper Science and Technology, Atlanta.

The aim of this paper is to predict an effect of the first factor - the dimension of deacidification compound (d_{DEA}) after the 1st impregnation step, penetration, diffusion - on the efficacy; and then to discuss potential effect of polarity and solubility; the aim is also to predict effect of additional homogenization by air conditioning, water or increased humidity.

As an example of application of the model proposed in this paper, we propose prediction of maximum achievable efficacy after impregnation step by hydrotalcites (HT) or like compounds (HTlc). Hydrotalcites (HT) and like alkaline compounds (HTlc) are well known, elaborated and widely used as neutralizers, alkalisers, acid scavengers for stabilization, conservation and increasing lifetime of synthetic polymer materials (Thürmer 1998, Fink 2010). Contrary to these applications, information on application possibilities of hydrotalcites for modification of natural materials, such as cellulose, paper, wood and endangered materials and objects of cultural heritage does not exist, or are just starting to appear, but the information on the deacidification *efficacy* of cellulose materials and natural polymers is missing. Based on the testing achieved by known alkaline compounds, and proposed function $\eta = f(d_{DEA})$ this paper estimates and predicts the limits of possible efficacy achievable by basic types of HT, HTlc after the 1st conservation step - impregnation using most often in the apparatuses used for the mass deacidification.

MATERIAL AND METHODS

The specification of the hydrotalcites (HT) used in this paper: HT1: $d_{HT1} \approx 1.6$ μm; Mg:Al = 5:1; quick mixing of reactants with the addition of 10% wt. citric acid, centrifugation, gel dried at 60°C, 24 h, dusted in an agate bowl. HT2: $d_{HT2} \approx 0.65$ μm; Mg : Al = 3:1; used salts – $MgCl_2$, $AlCl_3$; $TiCl_3$ (10% wt. replacement of Al^{3+}); quick mixing of reactants, washing, centrifugation, gel dried at 60°C, 24 h, dusted in an agate bowl. $HT3_{is}$: d_{HT3} = 1 - 10 nm; prepared *in situ* after impregnation of paper with reactants aluminium tri-sec-butoxide ($(sec\text{-}BuO)_3Al$) and methyl methoxy magnesium carbonate. Alkaline hydrotalcite-like compounds are formed; after reaction *in situ* in paper microstructure with water, or paper humidity they ensure neutralization of the acid components, necessary pH and a sufficient alkaline reserve for the stabilization of the cellulosic materials in the future. Based on X-ray analysis, the size of the resulting $HT3_{is}$ particles in the paper is assumed to be in the range of 1-10 nm (Jablonský et al. 2022).

The life expectancy has been determined by linear regression of logarithm of the mechanical properties, folding endurance. The efficacy of a conservation or deacidification technology has been expressed as a factor of relative increase of life in terms of selected articular characteristic properties. The efficacy η it expresses factor of relative increase of the life expectancy in terms of the mechanical properties, folding endurance, and can be designed by symbols η_ω as follows (Fig. 6):

$$\eta_\omega = \frac{t_{log\omega=0,m}}{t_{log\omega=0,n}} \P \quad (1)$$

where: $t_{log\ \omega=0}$ is in days. The lifetime of the paper ends when the logarithm of the folding endurance reaches zero for modified ($t_{log\ \omega\ =\ 0,\ m}$) and non-treated (control) samples ($t_{log\omega\ =0,\ n}$) (Katuščák et. al 2012a).

The efficacy η is measured by mechanical properties, in most cases (Fig. 1) by the folding endurance, kinetics of accelerated aging (ASTM D6819-02) at (98 ± 2)°C in closed glass tubes (of approximately 36,0 cm^3 internal volume per oven-dry gram of paper); the test samples were conditioned both before and after the aging and mechanical properties measurement, for 24 h, at (23 ± 1)°C, at the relative humidity of air (50 ± 2)% RH (ISO 187).

RESULTS AND DISCUSSION

The homogenization processes assure additional transformation of large particles by water, humidity and or CO_2 to low molecular products (Hubbe et al. 2017, 2018); the secondary diffusion and homogenisation processes, reactions are performed either in the mass deacidification apparatus of deacidification conservation industry, company, or they can be performed by a customer of mass deacidification conservation company as post-mass deacidification processes in a library, archive, other memory institution or owner of the cultural heritage objects.

The hypothetical $\eta = f(d_{DEA})$ functions on Fig. 2 represent the simplest linear relationships between the efficacy of deacidification and the dimensions of deacidifying alkaline substances. The set of hypothetical linear full lines at the Fig. 2 and the corresponding linear functions in Tab. 1 indicates alternative regions of dimensions on the d-axis in which the alkaline modification matters could possibly affect the efficacy; it can influence the paper lifetime or lifespan (LS), as well as usability, functionality or healthspan (HS).

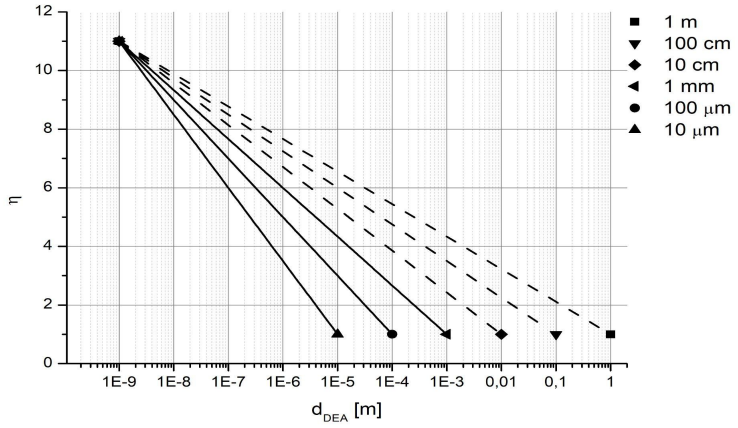


Fig. 2: Assumptions and estimate of a region of particle size d_{DEA} interval, in which the function $\eta = f(d_{DEA})$ will probably approach to the nominal value $\eta = 1$, and the η function should continue perpendicularly to the d-axis.

The probability of the positive effect on the LS and HS decreases with the increasing d_{DEA}. Too large particles, substances do not penetrate the paper structure, microstructure. These substances are represented on the Fig. 2 by the dashed lines connecting the point of highest possible efficacy achievable by the smallest molecules up till now and the lowest efficacy approaching $\eta = 1$ achievable by the very large substances, non-penetrating the paper

microstructure, neither the inner surfaces, interphases of paper micropores, although possibly contacting the paper geometrical outer surface.

The point on the left side, axis of the graph and of each line represents a maximum deacidification efficacy $\eta = 11$ achieved in the conservation industry and published up till now worldwide. As seen, it was achieved using compounds with dimensions below 1 nm, $d_{DEA} < 1$ nm. The $d_{DEA} < 10^{-9}$ m represents the order of smallest molecules with the highest maximum values of efficacy achieved in the range $\eta = f(d_{DEA})$ higher than 10.

The high efficacy can be achieved by deacidification of acid paper (with pH_0 between 4-5) if, simultaneously with the using small d_{DEA}, approaching the dimensions of critical cellulose endangered bonds, the other key conditions are fulfilled, namely *high polarity*, swelling the cell walls, fibrils, including elementary fibrils, and water *solubility* of effective substances, products, ions of deacidifying mixtures.

These key conditions of high deacidification efficacy for deacidification of bound volumes by treatment with an low polarity alkoxide-type reagent dissolved in a non-polar low-energy liquid, non-swelling the cell walls to avoid the books, documents deformations, are visualised by Hubbe in the latest post impregnation step, or technology unite operation on Fig. 3 (Hubbe et al. 2017, 2018), with the effective factors assuring necessary homogenization and reactions are $H_2O + CO_2$ from the air, paper, and/or from the impregnation fluid.

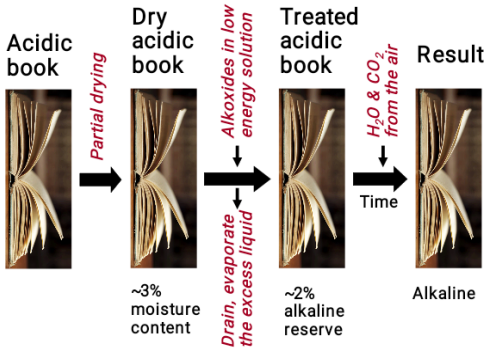


Fig. 3: Schematic procedure for deacidification of bound volumes by treatment with an alkoxide-type reagent dissolved in a nonpolar low-energy liquid (Hubbe et al. 2017).

Similar H_2O, or H_2O+CO_2 homogenization step is necessary for the fluids, and technologies using insoluble particles. Only in the presence of H_2O, or H_2O+CO_2 homogenization, reactions, and secondary diffusion step the deacidifying chemical technology could increase the paper lifetime or lifespan, usability and healthspan to high values, including those maximum values achieved up till now, achieving high values, even $\eta > 10$.

The maximum deacidification efficacy $\eta = 11.7$ shown on Fig. 1 was achieved, measured and published by the Swiss National Library (Ramin et al. 2009). Similar high efficacy had been achieved by the mass deacidification technology using the nonpolar organometal deacidification substances and solvents followed by the post-impregnation and the solvent evaporation processes of homogenization, humid air-conditioning, leading to water-soluble products arising with fluid water, humidity in air and paper have dimensions laying in the range of 0.5 to 0.05 nm, and their secondary diffusion to the paper cell walls microstructure (Ramin et al. 2009).

Aqueous systems, such as $Mg(HCO_3)_2$, or a mixture of Mg and Ca bicarbonates, can be effective in terms of increasing lifetime, as they assure homogeneity of pH and alkaline reserve in the paper microstructure. The disadvantages of the aqueous systems, such as the paper to become wavy, can cause the book to break, possible smearing or bleeding of water-susceptible print colorants, are well known. For all of these reasons, non-aqueous deacidification programs generally have been selected when bound volumes need to be acidified (Hubbe et al. 2017, 2018, Jablonský et al. 2014), followed by air conditioning by humid air (Fig. 3).

Important and effective conservation technologies, such as Papersave Swiss and SoBu, contain the second *homogenization* step in the deacidification in mass conservation apparatus and technology. The 2nd step - ensures homogenisation of pH and alkaline reserve (Ar) microdistribution in the cellulose material microstructure, accelerates *secondary diffusion* or *migration*, redistribution and homogenization of the alkaline substances and the alkaline reserve (Ar) from the outer geometrical surface into the cellulose materials microstructure. The time interval of the 2nd technology step, the pH and Ar homogenization step, is much longer than that of the first one, typically between days and weeks; it can also continue during next decades and centuries natural aging in deposits, but simultaneously with competing continuing acid formation and natural cellulose, paper documents degradation. For example, the 2nd step, the Ar homogenization, reactions producing low molecular alkali compounds and secondary diffusion, in the SoBu deacidification technology is 10 days; the 2nd step, in the *Papersave-Swiss* technology is 3 weeks (Andres et al. 2008, Fekete et al. 2008).

The second point of the linear functions on Fig. 2 indicates the dimensions of particles with dimension $d_{DEA} > 100$ nm; these particles have very low, questionable hydraulic flow and improbable diffusion into the paper microstructure. The region of full lines in Fig. 2 between 10 μm and 1 mm, or 10^{-5} m to 10^{-3} m, indicates the probable region where a predictive function should approach the constant $\eta = 1$ line; There is no evidence, neither rational reason for the functions to continue below $\eta = 1$, for alkaline deacidifying substances selected to be safe to the paper documents, causing no degradation, during the conservation, neither during the future natural aging in deposits, memory institutions. Therefore the linear functions are not suitable for the prediction or pre-screening; neither as a base for the continuing models improving, nor for the further developing 2D, 3D and multifactorial models in future.

The dashed linear lines represent functions with low probability; they represent the alkaline matter too large to penetrate to the paper, such as above 100 μm. It can be assumed that very large particles, such as with dimensions above 1 mm, will have minimum, negligible or zero penetration and diffusion into the disintegrated surface layers, and into mass of the cellulose macromolecules, corresponding in the graph $d_{DEA} = 10^9$ nm and higher.

Nonpolar impregnation systems, such as a system based on a mixture of magnesium methyl carbonate and magnesium methoxide in a fluorocarbon solvent (Smith 1970, 1977, 1988, Scott 1987, Morrow 1988) and a related system developed by Battelle Laboratories (Wittekind 1994), or the papersave use alkoxides. Reaction of the alkoxide with water in the paper converts the organomagnesium to $Mg(OH)_2$, which then is able to react with CO_2 from the air, forming $MgCO_3$ (Polovka et al. 2006); the main steps in the type of treatments just described indicates Fig. 3 (Hubbe et al. 2017).

Tab. 1: $\eta = f(d_{DEA})$ functions used for the order estimate of a region of particle size d_{DEA} in which the function $\eta = f(d_{DEA})$ stop declining, approaching the nominal value $\eta = 1$, and the function should continue as perpendicularly to the d-axis.

No.	Equation/function $\eta = f(d_{DEA})$	Note
1	$\eta = -0.25-0.54287*\ln(d_{DEA})$	100 cm
2	$\eta = -1.85714-0.62042*\ln(d_{DEA})$	10 cm
3	$\eta= -4 - 0.72382*\ln(d_{DEA})$	1 mm
4	$\eta = -7 - 0.86859*\ln(d_{DEA})$	100 μm
5	$\eta = -11.49999 - 1.08574*\ln(d_{DEA})$	10 μm
6	$\eta = 1.36757 + 0.0000219637 * d_{DEA}\text{^}(-0.633084)$	Model relationship $\eta = f(d_{DEA})$; $R^2 = 92.0462\%$; SEE: 1.2653
7	$\eta = 1.21104 + 0.00117995 * d_{DEA}\text{^}(-0.440373)$	Model relationship $\eta = f(d_{DEA})$; $R^2 = 96.0295\%$; SEE: 0.893987; the improved estimation of equation in the line 6, using 130 iterations
8	$\eta = 0.714116+ 0.664093 * d_{DEA}\text{^}(-0.247361)$	Model relationship $\eta = f(d_{DEA})$; $R^2 =98.7462\%$; SEE: 0.502366
9	$\eta = 0.702406+ 0.103295 * d_{DEA}\text{^}(-0.224017)$	Model relationship $\eta = f(d_{DEA})$; $R^2 =99.3372\%$; SEE: 0.387592; Without considering the $d_{DEA} = 1*10^{-5}$ m.
10	$\eta = 0.732984+ 0.125612 * d_{DEA}\text{^} (-0.214237)$	Model relationship $\eta = f(d_{DEA})$; $R^2 =99.5573\%$; SEE: 0.339089; assumed $\eta_{max} = 11$; $d_{DEA} = 10^{-9}$ m; Without considering the $d_{DEA} = 1*10^{-4}$ m and $d_{DEA} = 1*10^{-5}$ m.
11	$\eta = 0.94871+0.0246913*d_{DEA}\text{^}(-0.213215)$	Model relationship $\eta = f(d_{DEA})$; $R^2 =99.8429\%$; SEE: 0.0417834; assumed $\eta_{max} =3$; $d_{DEA} = 10^{-9}$ m;

Note: SEE – Standard error estimation.

As it can be seen, the Eq. 6 in Tab. 1 has been made in a Statgraphic program, and a good fit has been achieved with the R-squared value $R^2 = 92.0462\%$ (the closer to 100% value the better), and the Standard error of estimation SEE = 1.2653 (the smaller the error the better the relationship). The Eq. 7 (Tab. 1) has been estimated after 130 iterations, while the R-squared value increased to the $R^2 = 96.0295\%$ and the other quality parameter decreased from the standard error of estimation SEE = 1.2653 in the Eq. 6 to 0.893987.

The first evidence-based model can be seen on Fig. 4. This model function accept the maximum relative lifetime increase of paper by deacidification in comparison with the non-deacidified controle paper achieved up till present time; the efficacy factor $\eta = 11.7$ has been achieved by deacidification using of $Mg(HCO_3)_2$ or a mixture of Mg and Ca bicarbonates in water, $d_{DEA} \approx 10^0$ nm, as well as by Papersave Swiss technology using magnesium and titanium ethoxide (METE) in hexamethyldisiloxane (HMDSO) using the estimation of increasing the test paper and test books lifetime as measured by mechanical properties for tensile strength after Bansa-Hofer folding (Ramin et al. 2009, Katuščák et al. 2012a,b).

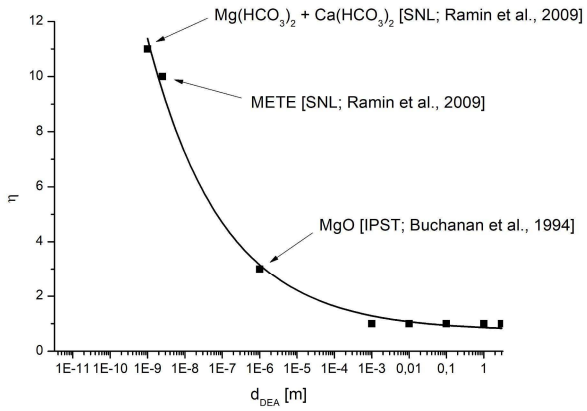
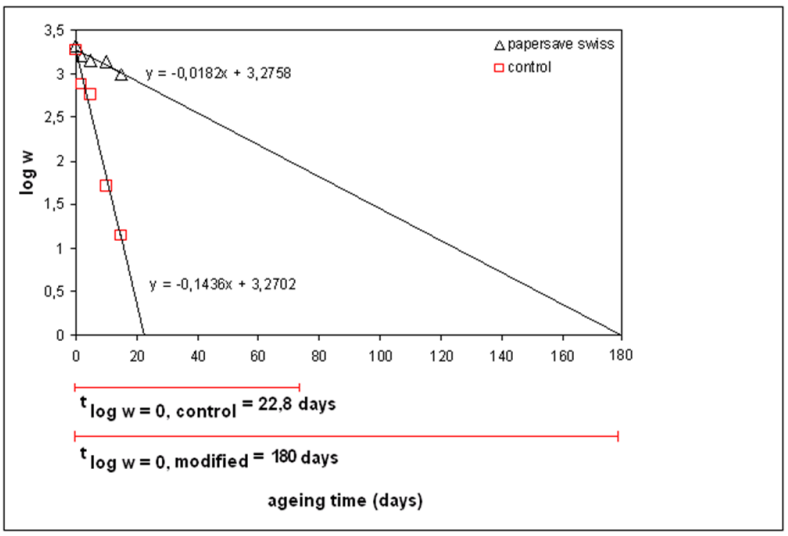


Fig. 4: The model relationship for predicting efficacy using one dimension - the size of the particles and compounds used for the deacidification η = 0.732984+ 0.125612 d_{DEA}^(-0.214237); R^2 =99.5573%.*

The method used for efficacy estimation, using samples of the test paper with initial pH before deacidification approximately $pH_0 = 5$, can be seen on Fig. 5. Using logarithmic kinetic functions for these type of mechanical properties is reasonable; The behaviour of the *folding endurance* during the aging time and the related kinetic function is similar to the kinetics of the correlating decrease of the paper cellulose molecular weight M_w and of the degree of polymerization of cellulose.



$$\eta_\omega = \frac{t_{log\omega=0,m}}{t_{log\omega=0,n}} = \frac{180}{22,8} = 7,9$$

Fig. 5: The efficacy η, if measured by folding endurance designed as factor of relative increase of the life expectancy for acid paper deacidified by Papersave Swiss method.

The other data important for estimation of dimensions of effective substances used are as follows: The d_{DEA} of magnesium ethanolate, with the topological polar surface area (TPSA) 46.1 □², considering the circle-like surface, the TPSA corresponds to the diameter like

dimension d_{DEA} = 3.83 □ = 0.39 nm (Magnesium ethanolate 2022). Titanium tetraethoxide (titanium(4+) ethanolate) with the TPSA = 92.2 □², corresponding to the diameter like dimension = 5.42 □ = ca 0.54 nm (Titanium tetraethoxide 2022). Magnesium ethanolate reacts with moisture to form $Mg(OH)_2$:

$$(C_2H_5O)_2Mg + 2H_2O \rightarrow Mg(OH)_2 + 2C_2H_5OH \quad (2)$$

Magnesium ethanolate reacts with sulfuric acid, neutralizing it:

$$(C_2H_5O)_2Mg + H_2SO_4 \rightarrow MgSO_4 + 2C_2H_5OH \quad (3)$$

Magnesium hydroxide further reacts with carbon dioxide and forms magnesium carbonate, which remains in the paper as an alkaline reserve:

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \quad (4)$$

Titanium tetraethoxide reacts with atmospheric moisture to form hydroxide, which is converted to titanium dioxide. TiO_2 does not damage paper, it is used as a white pigment in paper production:

$$(C_2H_5O)_4Ti + 4\ H_2O \rightarrow Ti(OH)_4 + 4C_2H_5OH \quad (5)$$

$$(C_2H_5O)_4Ti + 2\ H_2O \rightarrow TiO_2 + 4C_2H_5OH \quad (6)$$

This article deals with the *dimensions of deacidifying substances* (d_{DEA}), as well as the *dimensions of target cellulose bonds* (dT,cell) in the range of 10 orders, while we consider $d_{T,cell}$ target bonds to be those bonds that are, and can be in the future, during natural aging, continuously attacked by acids, and which should therefore be protected, stabilised and preserved. Taking in mind the deacidifying substances of the most important deacidification processes used for mass deacidification of millions of books worldwide, mainly those with evidence based highest efficacy achieved up till present time η = 10, using an alkoxide-type reagent dissolved in a low-energy liquid such as Papersave process mentioned above, we consider for the max efficacy prediction in this paper the value $d_{DEA} \leq 0.5$ nm, in the rage of 10^{-9} to 10^{-10} m.

Similar high efficacy η in the range of 7 to 10 was measured in other testing labs (Fig. 1), such as the example illustrated on Fig. 5 with the η = 7.9 for the samples deacidified by *Papersave Swiss* method estimated in our testing laboratory of the Cellulose department STU. Variability and differences between efficacy values measured and published by various labs are caused by the other important factors influencing the increasing the lifetime and usability of the saved, conserved, deacidified documents; From the other factors listed in the Introduction - namely kind of paper, acidity or initial pH of the acid paper before the deacidification (pH_0), degree of paper degradation before deacidification, air-conditioning - the H_2O, or $H_2O + CO_2$ driven pH and Ar homogenization unit operation time, and more, we consider the most important key η-affecting factor is the *humidity, temperature, and the time, or time cycles* allowed for water to perform *homogenization* of alkaline reserve and the resulting pH inside of the microstructure of paper.

The predicting functions (Tab. 1) can be applied for continuing development and increasing efficacy of heritage paper, documents stabilisation and protection using new deacidification compounds. An example of such compounds are hydrotalcites. The effects of other factors can be solved in multi-factorial, multidimensional models, during continuing improvement, research and development of the η-predicting models in future. Important factors to be considered in the future predicting models are presence of humidity (water concentration)

and temperature differences or cycles driven secondary diffusion. The first application of the model function $\eta = 0.732984+0.125612*d_{DEA}^{(-0.214237)}$ is shown on Fig. 6 for hydrotalcites. Here the deacidification efficacy prediction is based on the first considered efficacy factor d_{DEA}.

The hydrotalcites (HT) and like alkaline compounds (HTlc) are well known, elaborated and widely used as neutralizers, alkalisers, acid scavengers for synthetic polymer materials, but contrary to the applications for synthetic polymers (Thürmer 1998, Fink 2010), information on application possibilities of hydrotalcites for modification of natural materials, cellulose, paper, wood and endangered materials and objects of cultural heritage does not exist, or are just starting to appear. This paper predicts the limits of possible efficacy achievable by basic types of HT, HTlc after the 1st conservation step - impregnation using most often in the apparatuses used for the mass deacidification.

The maximum efficacy predicted for processes using hydrotalcites and like compounds can be achieved with substances able to penetrate the cell wall. The predicted efficiency for the $HT3_{is}$ with dimensions d_{DEA} in the range of 1 -10 nm is in the range $\eta_{HT3is} \approx 7.2 - 11.4$ (Fig. 6). The 2 basic conditions for penetrating cell walls are as follows: the dimensions lower than the equivalent of the polyethylene glycol macromolecule with DP 300 in water ($d \approx 1$ nm), and polarity on the level of water or higher. The closest corresponding dimension $d_{DEA} < 1$ nm has the $HT3_{is}$; Such hydrotalcites like compounds and reactants have been prepared from low molecular reactants by synthesis *in situ* $HT3_{is}$ in cellulose microstructure of acid paper. The $HT3_{is}$ is mixture of reactants of aluminium tri-sec-butoxide ($(sec\text{-}BuO)_3Al$) and methyl methoxy magnesium carbonate, their reaction products with water or paper humidity, such as $Mg(OH)_2$, with dimensions < 0.5 nm; the reactants are able to penetrate the cell walls, swell them and reach the elementary fibrils and cellulose molecules. Important deacidification compounds arising by reactions of the HT reactants with water and CO_2 are created during the processes namely $CaCO_3$, $MgCO_3$, $Ca(HCO_3)_2$ ($d_{DEA} \approx 1$ nm, $\eta = 11$), MgO ($d_{DEA} \leq 50$ nm) can ensure neutralization of the acid components, necessary pH and a sufficient alkaline reserve. It is supposed that simultaneously with low molecular compounds also larger hydrotalcite like products can be created *in situ* in cellulose micro and nano structure, with the size of the resulting HT particles in the paper cell walls assumed to be in the range of 1-10 nm, as measured by X-ray analysis (Jablonský et al. 2022). The modification of paper using *in situ* reactions of the inorganic reactants leads to creation of cellulose - inorganic composite polymer material, transforming chemical and mechanical properties as well as stability of paper endangered by acid hydrolytical and oxidation degradation. All the mentioned reactants, low molecular products with $d_{HT3is} < 0.5$ nm, and arising hydrotalcites with $d_{HT3is} \approx 1$ - 10 nm or larger can ensure neutralization of the acid components, necessary pH, create sufficient alkaline reserve important for stabilisation of the cellulosic materials in the future, increasing lifetime, usability, functionality or healthspan.

Predicted maximum efficacy for the larger hydrotalcite HT2 on Fig. 6 with the size $d_{HT2} \approx 0.65$ μm would be $\eta = 1.8$. The predicted efficacy achievable with the largest particles of hydrotalcite HT1 with the $d_{HT1} \approx 1.6$ μm is lower, about $\eta = 1.6$. The efficacy data predicted using these models are in agreement with the efficacy estimated by cellulose measurement of solution properties and chain scission (Kačík et al. 2009, 2016).

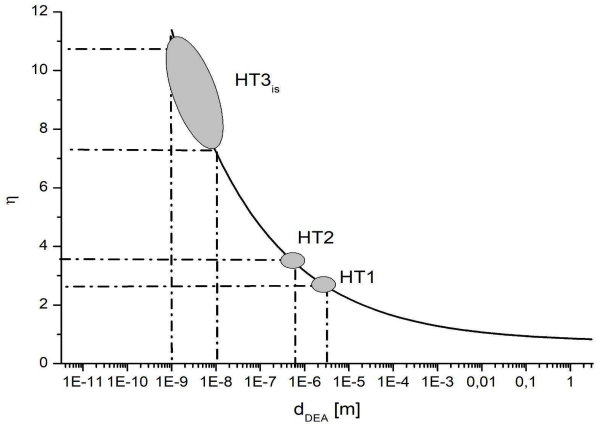


*Fig. 6: Prediction of deacidification efficacy for 3 hydrotalcite like compounds HT1, HT2 and $HT3_{is}$ after the first deacidification step - impregnation, using the function η =0.732984+ 0.125612 * d_{DEA}^(-0.214237); R^2 =99.5573%*

The predicting functions can be applied for continuing development and increasing efficacy of heritage paper, documents stabilisation and protection. They can be applied also for continuing improvements and optimising of post mass deacidification processes and factors, H_2O containing air conditioning, homogenization of alkaline reserve (Ar) in the paper microstructure, for increasing the efficacy of deacidification of both acid paper and incompletely deacidified documents.

CONCLUSIONS

A fundamental factor influencing the relative increase of lifetime and usability of acid paper in comparison with non-deacidified paper, or the η, is dimension of deacidification substance (d_{DEA}), together with polarity and reactivity of deacidification substances, water in air and paper during deacidification and post-deacidification processes.

The highest efficacy of the deacidification up till now achieved by the testing labs (η = 10 to 12) by alkaline compounds with d_{DEA} = 0.5 Å to 1 nm, approaching the dimension of critical glycosidic cellulose bond endangered by degradation with dimension d = 0.5 Å = 0.05 nm, and the efficacy of deacidification decreases with increasing dimensions of the deacidifying compound or particles, approaching the efficacy of non-effective process value η = 1.

The function proposed and used for the first η predictions is as follows: η =0.732984+ 0.125612*d_{DEA}^(-0.214237). This model function was applied for predicting efficacy for three types of hydrotalcites (HT) and like compounds (HTlc) while the highest efficacy was predicted for hydrotalcites prepared *in sit*u in deacidified paper microstructure.

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