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PRESERVATION AND RESTORATION OF FILMS AND PAPER DOCUMENTS AFTER THEIR EXPOSURE TO EXTREME ENVIRONMENTAL CONDITIONS (CASE STUDY OF THE HISTORICAL ARCHIVE OF THE COMMUNIST PARTY OF GREECE)

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ABSTRACT

The historical archive of the Greek Communist Party (paper, photographs etc) was badly affected in 1994 from a destructive flood. The aim of the paper is to report on the application of physicochemical methods to evaluate the damage and apply restoration techniques. The steps followed were: placing the 'muddy' material into fridges with low temperature to stop the development of the mould which was increasingly quick; cleansing and drying it, decontamination and sterilization in proper closets of 25 m^3; adapt the space within the proper conditions and to insert the dried material, perform specific chemical treatment (De-acidification– Neutralization), solidify and restore by using Japanese preservation papers, place the material into folders and boxes with antacid – antifungal protection, computerize and store it electronically (digitalization). The purpose is to slow-down its chemical downgrade. The primary action that is taken for the future physicochemical course of the material is to secure stable humidity and temperature conditions as defined by scientific literature. All the above, at different levels, have contributed to the non-decomposition of cellulose.

KEYWORDS: fungi, humidity, paper, maintenance, archival, chemical, cellulose, deacidification

1. INTRODUCTION

The protection and restoration of paper, cellulose materials, photographs, and films has been one of the major concerns of conservators. Chemistry and physical chemistry are at the heart of paper conservation, but as a science, paper conservation is a relatively new field. Salvage operations must be planned so that the environment of keeping the treated materials are appropriate to hold the preservation (Fischer 1977; Silverman et al., 2008; Williams 1994; McCabe 2005; IOS 2013).

It has been noticed that since the first publication in 1975 of Procedures for Salvage of Water-Damaged Materials there has been an increase in the frequency of accidents or unexpected disasters which have resulted in extensive water damage to library materials. There exist several indications that we have begun to learn the immense value of disaster preparedness planning. As Walters (1993) pinpointed: "Being familiar with the necessity of having to make a series of interrelated decisions promptly, understanding the effects of any particular course of action on subsequent ones--this is the best kind of preparation needed in the event of major water-damage problems. A well-organized plan can greatly reduce the costs of salvage and restoration as well as the proportion of outright losses. This preparedness can also go a long way to lessen the emotional and stressful impact upon human beings"[1].

In the present research work a case study is presented. The Historical Archive of the GCP (Greek Communist Party) is in the headquarters of the Central Committee of the Party in Perissos, Athens. It consists of more than 40.000.000 archival documents of all types, paper material (manuscripts and printed), objects, photographs, films, artworks, etc. This paper is part of a scientific work which takes place until today for its maintenance and restoration, after a big flood on 21st October 1994.

The fungi were growing in the paper that has got wet rapidly. Today in the archive all the archival material has been cleaned of its mud, it has been disinfected, the chemical treatment with Ca (OH) 2, 4% continues, the storage conditions of the archival material are those provided by the international literature (T = 18 ± 2 ° C and RH = 50 ± 5%) and the archival material is digitized to avoid additional damage. The aim is for all the archival material to be chemically processed and for there to be constant monitoring of the effectiveness of the methods over time. What is important is that it is possible to evaluate the effectiveness of the methods applied with samples that do not need to be artificially aged (Moropoulou et al., 2001; Zervos and Alexopoulou, 2015; Rushdya 2015). Similar studies in the past had used samples from the KKE archive and conclusions had been drawn about the methods of applying artificial aging. For the first time for the archive of GKP, the processed and non - archival material is controlled with Scanning Electron Microscopy (SEM) – micro-analysis Energy Dispersive Spectrometer, (EDS) and through X-Ray Diffraction (XRD). We consider that this will contribute to understand further what conduces to the decomposition of the cellulose chain, as well as to search better the various chemical actions' mechanism that causes the destruction of archives, libraries and museums. The aim is to formulate a methodology and criteria for assessing the suitability of paper maintenance operations following international practices (Mavrantonis et al., 2015; Peltikoglou,1995). At the same time, the electronic storage of the archives and the minimal – only when necessary - use of the original material can provide today the best conditions for its future physicochemical course (Photo 1).

[1] https://cool.culturalheritage.org/bytopic/disasters/primer/waters.html

(A)

(B)

Photo 1. Flood caused severe devastation to books and documents. Water-damaged books were prioritized to develop a salvage plan. A) The material comes out of the mud to be cleaned, b) Cleaning and drying of the material and participation of students as a socio-educational learning.

2. MATERIALS AND SAMPLING

2.1. Materials

2.1.1. The disinfection of the archived material of the GCP was done by using ethylene oxide, C_2H_4O, in proportion 90/10% CO_2 (T-gas), to reduce its detonation, in special premises and by specialized personnel. T-gas is widely accepted for the disinfection of libraries and archives, highly effective against insects and microorganisms - fungi, with few negative consequences on the collections in archives and museums (Ballard et al., 1986; Hengemihle et al., 1995; Craig,1986).

2.1.2. For the case of the Historical Archive of the GCP it was decided to process chemically the entire archive material by following the BARROW WILLIAM liquid method with $Ca(OH)_2$ of high purity (Barrow, 1974; Lineardy, 1990; Roberts,1996; Bansa,1998).

2.1.3 Scanning electron microscopy (SEM) - microanalysis (EDTS) as well as X-ray diffraction (XRD) will be used to characterize the paper material before and after chemical treatment with 4% $Ca(OH)_2$ solution (Fetisov V., 2020; Glezos, 2012).

2.2. Sampling

2.2.1. The results of maintenance of the KKE's historical archive based on ph measurements in standard samples within 27 years

In the beginning of the maintenance and restoration process of the historical archive the following have been created:

A) Six processed stable samples (from three samples each) to monitor the evolution of pH stored in the room where the archival storage conditions (T = 18 ± 2°C and RH = 50 ± 5) are stable (Table 2).

B) Two sets of samples from three documents in each row (Table 3), not chemically treated. These are kept under maintenance conditions and their pH is being monitored to reach more overall conclusions regarding the Archive space and archival material (humidity and temperature conditions, ventilation mode, etc.) since all the archive material is kept there, ie chemically treated and not.

C) Sample 6 (shown in Table 3, chemically treated and unprocessed chemicals) is that are exposed to extreme moisture and temperature conditions, unstable and out of maintenance (all-weather conditions).

D) An attempt was made to collect representative samples of the entire archival material while selecting them, which was very complex because of the great volume and the different kinds of paper.

The samples are:

Sample 1: Document state quite acidic, **Sample 2:** Document state very acidic, **Sample 3:** Document state very acidic, **Sample 4:** Document state acidic, **Sample 5:** Document state acidic, **Sample 6:** Document state moderately acidic.

2.2.2. Chemical processing - deacidification of the paper

In this processing two samples were used: Sample code Doc. 1 and Doc. 2.

2.2.3. Characterization of paper with electronic sensor microscope (SEM) - micro-analysis (EDS) and x-ray (XRD) pattern characterization.

Five paper samples (A, B, C, E, D) were selected from specific time periods (in terms of construction, quality and use). The same paper samples (A1, B1, C1, D1, E1) have undergone treatment with a 4% $Ca(OH)_2$ solution, that is they have an alkaline $CaCO_3$ stock (Moropoulou et al., 2001).

3. TECHNIQUES – INSTRUMENTATION

3.1. *Techniques*

3.1.1. Disinfection

The disinfection closets were of 25 m^3, with a vacuum pump of 40 Torr so that the permeability of the gas in the material is increased to maximum and its detonation is reduced further, as well as with a blind system of gas injection of 200 ml/m^3, in the closet. After the material is placed in the closet, a test vacuum takes place, to examine if there is a leak in the pipelines. In case of a leak, an abrupt increase of the pressure in the closet is observed, because of the almost absolute vacuum that is created. The T-gas is injected in the closet, with a vacuum of almost 40 Torr, in a slow pace. The injection lasts for more than 15 minutes and the system is allowed to stand for 6 hours. Then, air washes take are conducted (circular injection of air in the closet) and measurements of the gas rests up to 2 ppm. Natural ventilation for around 24 hours in the location of the disinfection follows and after that, natural ventilation in a specially adapted location in the archive, for about 60 days. The air washes are the most important part of the disinfection. The measurements take place with the closet door closed, through a special receptor in the door.

It has been demostrated elsewhere the T-gas desorption from paper (and other materials e.g. wood, newsprint, book paper, leather) is reduced through the air washes performed. It has been shown that paper expels the gas easier than other materials (Hengemihle, 1995; Wilson et al.,1988; Craig, 1986).

3.1.2. Chemical processing - deacidification of the paper

The procedure that was followed is this:

- The material was extracted gradually from the

special site where it was installed, under conditions of controlled humidity and temperature.

- The materials were wrapped in special membranes (HOLITEX) substrates. Many membranes are placed on top of each other and along with the paper documents, the "packets" for the process of deacidification were created. The material was immersed in water at 40°C for about 30 minutes, until the water-soluble acidity is eliminated. In practice, this resulted in the elimination of yellowing.
- The package was immersed in a $Ca(OH)_2$ bath 4% by weight.
- The pH of the bath at the beginning was pH=12 - and at the end of the procedure pH=9.

(The clear solution was used and not the suspension).

- The material was spread on special tumblers so that $CaCO_3$ calcium carbonate is formed in the cellulose macromolecule, a material that will also protect the paper, in the future, from endogenous and exogenous destructive agents.

3.2. Instrumentation

3.2.1. Characterization of paper with electron microscope (SEM-EDS)

Currently, information about the paper structure can be obtained by using even higher resolution through scanning electron microscopy (SEM) (Kyriakidis et al., 2014; Glezos, 2012). In the scanning electron microscope, the solid sample surface is swept back by a high energy electron beam. The procedure of scanning, using an electron microscopy was followed for all test materials shown in Table 5. The samples' microstructure was analyzed in various magnifications ranging from 50x (for some samples from 25x) to 3000x, while for some of them an energy distribution analysis (EDS) was performed, for a qualitative and percentage elemental analysis of the X-ray sample data after it was bombarded by the active electrons of the beam. For each characterization a high vacuum at 15 kV, 25 kV and 30 kV voltages was applied, depending on the sample characterized. In the Tables which present the results of the SEM - EDS Elementary Analysis, the trend applied to each set of measurements is mentioned.

Table 1: Characterization of paper samples with Electron Scanning Microscope (SED-EDS) model QUANTA 200 - FEI

Sample code	Electronic Scanning Microscopy (SEM / EDS)	Measurement conditions Voltage (kV)
A	+	25 (30 one measurement)
A1	+	25
B	+	15
B1	+	15
C	+	15
C1	+	15
D	-	-
D1	+	15
E	-	-
E1	-	-

3.2.2. X-ray (XRD) pattern characterization - principle of the method - experimental process

For crystalline materials, radiation diffraction is one of the most efficient methods for characterizing the materials' crystalline structure and can reveal the size of crystals, microscopic strains, as well as the quantitative phase analysis. It is based on monochromatic X-ray diffraction, known wavelength λ, on the levels of the crystalline lattice of the examined compounds and then its determination by the corresponding angle θ of the internal spaces d of the levels by applying the Bragg law (Moropoulou, 2003; Koui, 2005; Day, 2004).

Table 2: Characterization of paper samples from a GCP file by X-ray diffraction (XRD)

Sample code	X-ray diffraction (XRD)	Bruker D8 Advance Twin X-ray diffractometer with a Cu Ka radiation source (wavelength 1.5418 Å)	D 5000 SIEMENS / software DIFFRAC PLUS Search Programm (SIEMENS)	2θ (°)	Step (°)
A	+	-	+	5 - 60	0,02
A1	+	-	+	5 - 60	0,02
B	+	+	-	8 – 60	0,02

B1	+	+	-	8 – 60	0,02
C	+	+	-	8 – 60	0,02
C1	+	+	-	8 – 60	0,02
D	-	-	-	-	-
D1	-	-	-	-	-
E	+	+	-	8 – 60	0,02
E1	+	+	-	8 – 60	0,02

4. RESULTS

4.1. On the procedure of disinfection

The fungi (mould), are low plant organizations (without chlorophyll), having the ability to develop rapidly, they are fed with polysaccharides (paper cellulose) and their macromolecules are disintegrated by excretion of special substances (enzymes), that paint and leave stains on the paper. They develop, when the conditions allow them to, in RH 65-80%, in acidic environment, in temperatures between 20-30^{o}C. The whole archived material was disinfected, following the above-mentioned procedure. It was a difficult and time-consuming procedure, whose primary aim was to neutralize and stop the mould development, ensuring the further safe use of the archived material. The gas desorption from the paper was faster than other materials. In fact, it was proved that it was not possible that air washes achieve measurements under 2 ppm.

An important role in the gas desorption was played by the porosity of the paper material and by the natural ventilation. The final measurements for gas rests in the historical archive of the GCP, before placing it in the main archive location are null (Wilson, 1988; Hengemile, 1995; Yasin et al., 2017).

4.2. Maintenance of the archive material based on ph measurements in samples within 28 years.

Overall, the chemical process of abrasion is:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The acids are neutralized by the resulting calcium carbonate as shown by the reaction:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

By forming neutral salts of calcium and releasing carbon dioxide.

In the following table the description of the documents and their respective pH measurements are demonstrated before and after being treated chemically.

Table 3: Documents in which pH was measured before and after chemical treatment (deacedification).

The pH course in samples during the 21 years of the laboratory is shown in Table 3 ,4,5,6.

	Sample 1	**Sample2**	**Sample3**	**Sample4**	**Sample5**	**Sample6**
Initial measurement pH	Average **5.1**	Average **5.4**	Average **5.0**	Average **5.5**	Average **5.3**	Average **6.0**
2015	Average **8.2**	Average **8.7**	Average **8.2**	Average **8.8**	Average **8.7**	Average **8.8**

Table 4: Progress of pH on processed samples of the historical Archive [6].

	Sample 1	Sample **2**	Sample **3**	Sample **4**	Sample **5**	Sample **6**
Initial measurement pH	Average **5.1**	Average **5.4**	Average**5.0**	Average**5.5**	Average**5.3**	Average**6.0**
2020	Average **4.8**		Average**4.7**			

Table 5: Evolution of pH of unprocessed chemical documents under maintenance conditions [6].

	Sample 6 unprocessed chemical	**Sample 6** processed chemical
Initial measurement pH	Average **6.0**	Average **6.0**
2015	Average **3.6**	Average **6.7**

Note: pH measurements are carried out with a WTW pH 320 pH meter equipped with a surface electrode.

Table 6: Rate of pH value for treated and untreated chemical sample (Sample 6), which is in weather conditions.

Sample Code	Description / Comments	pH Sample		pH Bath	
		Before chemical treatment	After chemical treatment	Before chemical treatment	After chemical treatment
Doc. 1	Rape paper 1950-1960	**Average: 6.0**	**Average : 8.9**	**12.0**	**9.0**
Doc. 2	Journal of Rizospastis period 1940-1950	**Average : 5.9**	**Average: 8.7**		

Based on the measurements of Table 4, how chemical treatment has contributed to the cellulosic chain disintegration can be clearly seen. The deacidification produces calcium carbonate, a strong alkaline stock which essentially protects the carbon chain from the constant acidic action of the endogenous and exogenous factors that eventually lead to the breakdown of the cellulosic chain bonds according to the below reaction:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Which forms neutral calcium salts and releases carbon dioxide (Barrow,1974; Hey, 1974). As it can be seen, samples 1 and 3 that were more acidic than samples 2, 4, 5 and 6 did not have a great increase in pH. The course of acidity of all samples over time is quite good, and that confirms bibliographic estimates on how effective calcium carbonate is as an alkaline stock on paper. This, of course, is related with the conditions of constant humidity and temperature that have been secured in the entire location of the archive. The pH recorded in Table 5 (unprocessed chemical documents, under maintenance conditions) leads us to the following conclusions. The two most acidic specimens under maintenance conditions behave well regarding their acidity course and do not have an alkaline stock since there was no chemical treatment. This is not independent of the maintenance conditions in which they are stored which minimizes the action of external factors. At the same time, the fact that the conditions are stable does not favor the cellulose molecules' expansion and contraction, which minimizes intermolecular stresses, a cellulose breakdown agent. All the above can be also confirmed by the pH test results (shown in Table 5) for sample 6 (chemically treated and unprocessed chemicals) that are exposed to extreme moisture and temperature conditions, unstable and out of maintenance (all-weather conditions). The course of the pH value for these samples is quite different from the one of all the previous samples. The decrease in the pH value over time is clearly greater. That is, especially in the untreated samples the paper (the cellulose) is led to complete decomposition while again it is confirmed that the calcium carbonate is durable as an alkaline stock on the paper (Dupont, 1996b, 2000; Moropoulou et al., 2000, 2001).

4.3. The SEM images and the elemental analysis of both spot and surface

Selected figures of the paper samples, as well as the elemental analysis obtained with the scanning electron microscope (SEM / EDS), are presented below (Figs 1, 2). In Fig.1 we see the SEM paper of the 1920s (paper sample A), SEM paper from the 1940s (paper sample B), SEM paper from the 1940s of different quality than sample B (paper sample C). In the magnification photographs of 800x, 800x and 400x, various sizes of cellulose fibers and white inclusions are distributed among them. Elementary spot analysis on them and on surface maps, showed the existence of various chemical elements such as Al, Si, Ca, Cl, etc., additionally with the carbon and oxygen predominantly attributed to cellulose, at rates of 0.12 to 5.37%, 0.02 to 0.11% and 0.15 to 4.07% respectively for the three samples. These data are attributed to (i) salts of paper cross-contamination, mainly because of the devastating flood in the building where the historical archive of GCP was kept, and (ii) the salts of the composition of the paper of that period. In Fig.2 we see SEM paper processed from the 1920s (paper sample A1), paper processed from the 1940s (paper sample B1), paper processed from the 1940s of different quality than sample B1 (paper sample C1), paper processed from the 1950s (paper sample D1). In the photos of magnification 800x, 800x, 400x, 300x, the cellulose fibers can be distinguished, and various sizes of white inclusions are distributed among them. Elementary spot analysis on these and on surface maps demonstrated that various chemical elements such as Mg, Al, Si, S, Ca, Fe and others existed, apart from the carbon and oxygen predominantly attributable to cellulose, at rates from 0.02 to 4.48%, 0.14 to 9.72, 0.13 to 14.05%, 0.29 to 7.98% respectively for samples on average. These data are attributed to (i) salts of paper cross-contamination, mainly because the catastrophic flood in the building where the historical archive of the GCP was kept, and (ii) salts of the composition of the paper of that period.

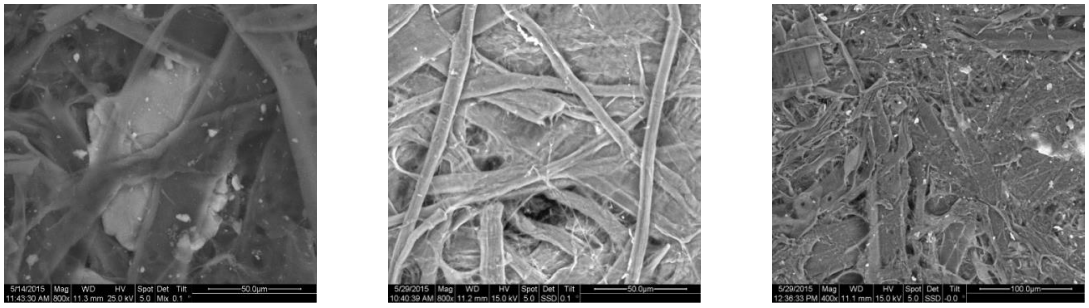

Figure 1: Images of 1920s, 1940s paper samples A (left), B (center), C (right) at 800x, 800x, and 400x magnifications

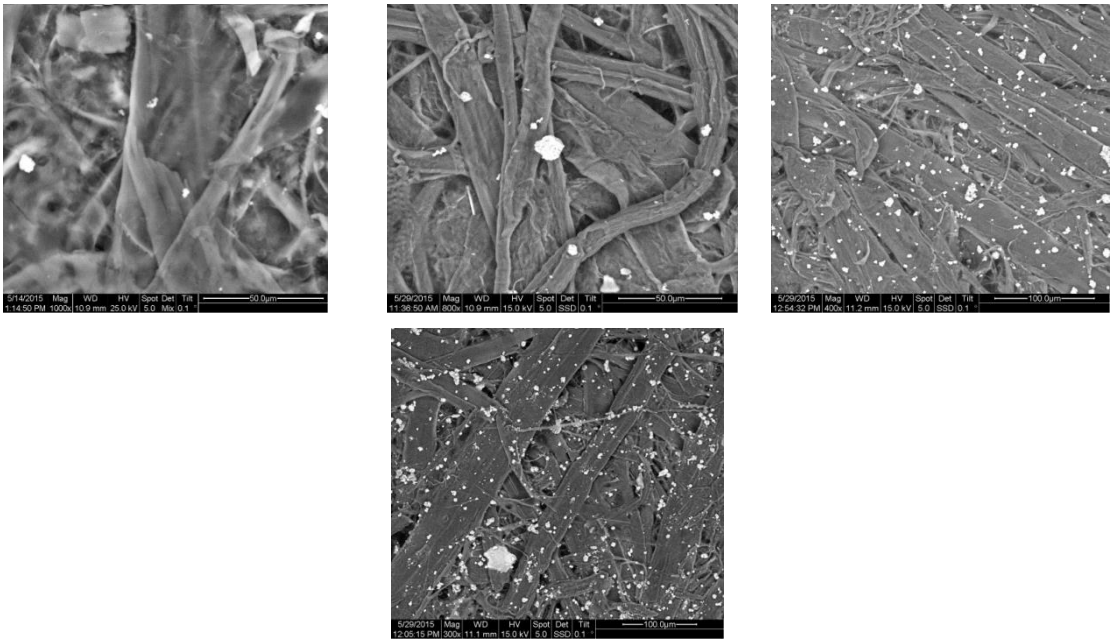

Figure 2: Figures of 1920s, 1940s paper samples A1 (up left), B1 (up center), C1 (up right), D1 (lower) at 800x, 800x, 400x, 300x magnifications

Also, regarding the same sample (A1), it is worth mentioning the differentiation of Ca participation, based on the point where the elemental analysis has focused. In a measure of elemental point analysis on the fiber, the percentage of Ca participation is 0.64%, while on white occlusion is 2.40% on average. Regarding samples B1, C1, D1 compared with the corresponding unpacked paper samples, we observe that the elemental spot analysis on white inclusions shows an increase in the percentage of Ca participation from 0.11% to 9.72 %, 0.15 % to 14.05 %, from 0.29 to 7.98 % respectively (Tables 7, 8). This is because of the treatment of the paper, with $CaCO_3$ for its preservation and restoration. $CaCO_3$ is introduced into the cellulose structure so that it is "sacrificed" when the paper is exposed to "aggressive" conditions.

Table 7: Results of elemental spot analysis on inclusions with respect to at% Ca

Sample	at % Ca
A	0.35
A1	**2.40**
B	0.11
B1	**9.72**
C	0.15
C1	**14.05**
D1	**7.98**

Table 8: Effects of elemental spot analysis on inclusions and a fiber area to at% Ca for processed paper samples.

Sample	at % Ca		
	Map	**Spot in a fiber region**	**Spot in white encapsulation**
A1	0.42	0.64	2.40
B1	0.46	-	9.72
C1	0.79	0.78	14.05
D1	1.28	-	7.98

4.4. XRD data

The samples studied with XRD as well as the parameters of each measurement are presented in Table 9. For different grades of paper, the percentage of crystalline and amorphous structure may vary. For the same paper sample, the crystallinity is increased if the sample is processed for preservation and restoration reasons.

- The sharp peaks (2θ (°) = 12, 20, 25, 28, 48) are attributed to salts such as kaolin having the formula $Al_2Si_2O_5(OH)_2$, which agrees with the results from the samples characterization with Electronic Scanning Microscopy (SEM) and elemental analysis with EDS.
- In the samples that have undergone treatment (B1, C1, E1), the sharp peaks of the salts do not disappear, but their intensity is reduced.

- B1, C1, E1 peaks at 2θ (o) = 30, 40, 50 angles attributed to $CaCO_3$, which has penetrated the amorphous cellulose regions during the paper treatment with a solution of $Ca(OH)_2$ 4%, which is also in accordance with the results from the samples characterization with Electronic Scanning Microscopy (SEM) and with elemental analysis by EDS (Fetisov V., 2020, Klemm et al., 1988; Maxwell et al., 2008).

Table 9 contains the data of the XRD data.

Table 9: Results of radiograms for X-ray diffraction representative radiograms for samples B, B1 and C, C1

2θ (o)	Paper Sample from Archive								Peak in phase
	A	A1	B	B1	C	C1	E	E1	
12	s, i	b, w	-	-	s, w	b, w	s, i	s, i	Salts such as kaolin ($Al_2Si_2O_5(OH)_2$), etc
20	s, i	b, w	-	-	-	-	s, w	s, w	Salts such as kaolin ($Al_2Si_2O_5(OH)_2$), etc
25	s,w	-	-	-	b, w	b, w	s, w	s, w	Salts such as kaolin ($Al_2Si_2O_5(OH)_2$), etc
28	s, i	s, i	-	-	s, i	s, i	s, i	s, i	Salts such as kaolin ($Al_2Si_2O_5(OH)_2$), etc
30	-	-	-	s, w	-	s, w	-	s, w	$CaCO_3$
40	-	-	-	b, w	-	b, w	-	s, w	$CaCO_3$
48	s,w	-	-	-	-	-	s, w	-	Salts such as kaolin ($Al_2Si_2O_5(OH)_2$), etc
50	-	-	-	-	-	-	-	-	$CaCO_3$
14 - 17	+	+	+	+	+	+	+	+	Amorphous cellulose
22 - 23	+	+	+	+	+	+	+	+	Crystalline cellulose
	Where b (broad) broad top s (sharp) acute peak w (weak) weak top (low height) i (intense) strong peak (high altitude)								
	A	A1	B	B1	C	C1	E	E1	% Crystallinity
	-	-	45,8	52,8	61,7	67,4	73,9	75,0	

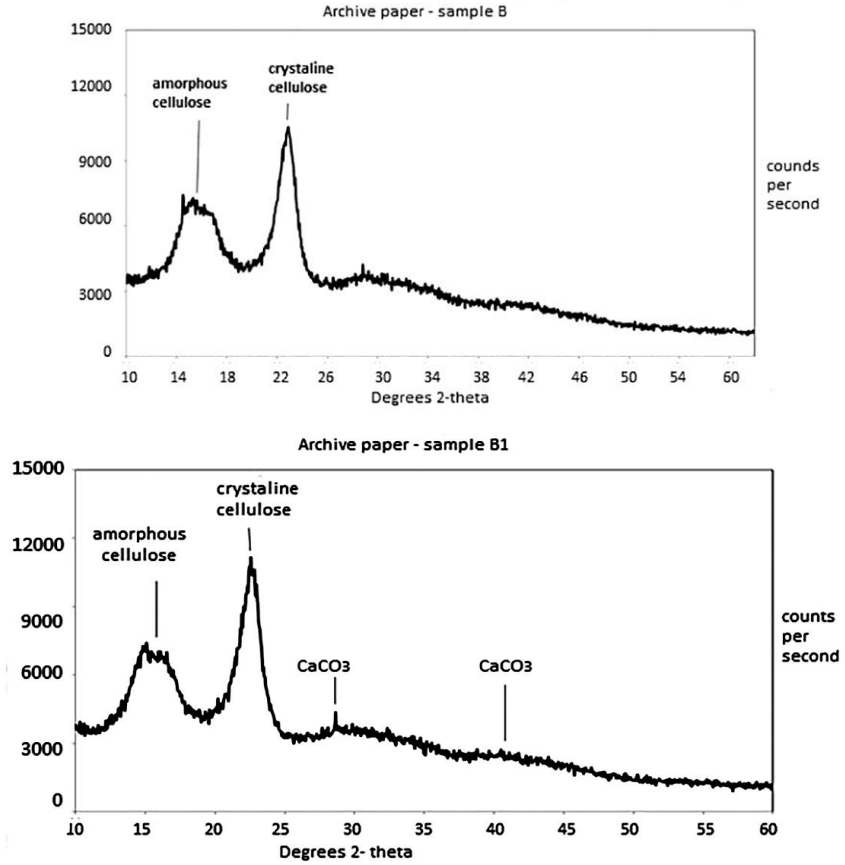

Figure 3: XRD radiograms of Archive paper-samples B and B1. The amorphous areas are smaller in height and range.

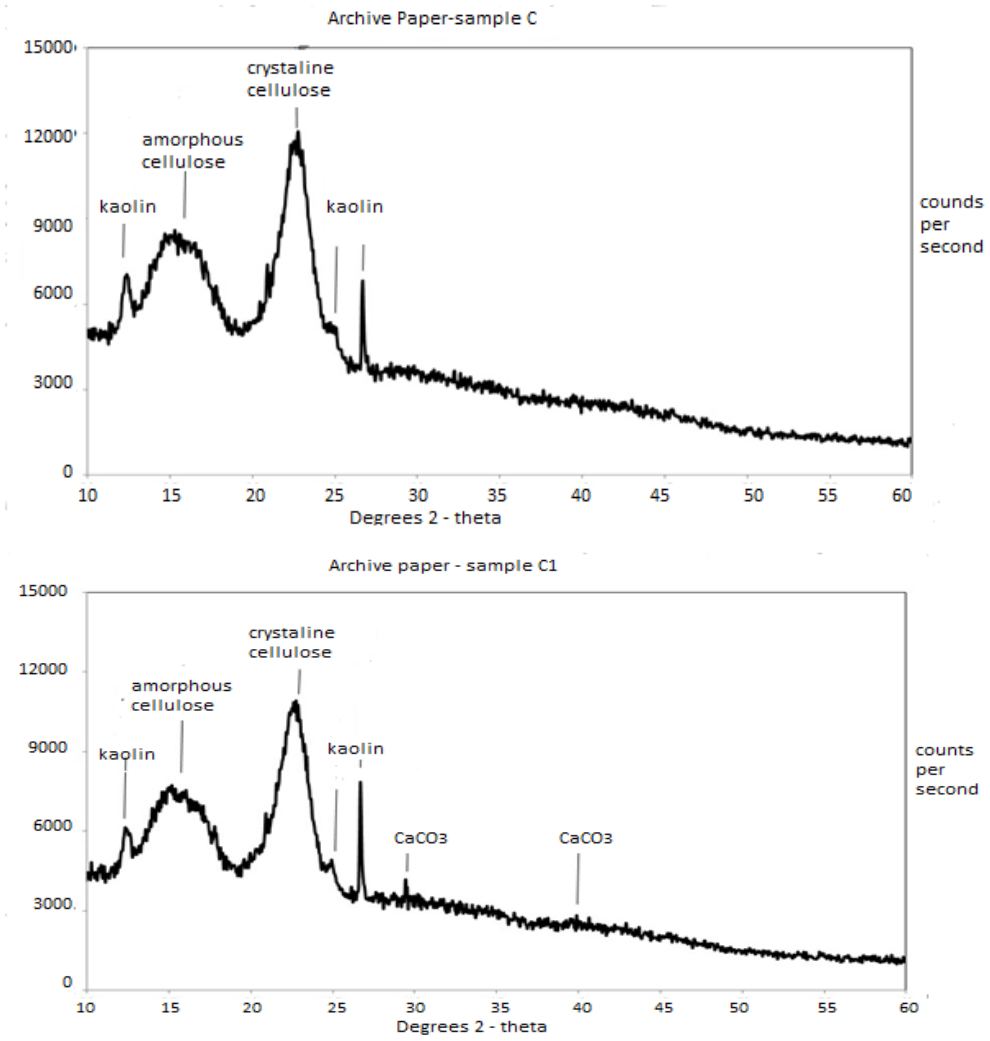

Figure 4: XRD radiogram of Archive paper - samples C and C1 respectively. The amorphous areas are smaller in height and range

5. DISCUSSION

5.1. The disinfection of the archived material

The results on the T-gas efficiency, regarding its fungicide action, based on macroscopic and microscopic observations in cultures of samples infected by mould, prove that in the disinfected material (which is in maintenance conditions), no growth of fungi is observed. In non-disinfected material, in samples infected by fungi, growth is observed in the form of circular green and white colonies. The samples were taken from paper that was not completely infected by fungi, there were only small circular colonies, with a diameter of 1-2 mm or a bit bigger.

5.2. Chemical processing - deacidification of the paper

A low pH means a cellulose carbon chain with a high degree of degradation. The physicochemical wear is stopped by deacidification. The endogenous chain disintegrators are inactivated, which effectively neutralizes the phenomenon where it is found. There is a slight improvement of the mechanical properties of the paper, however, this is not the dominant one, since regarding historical papers the daily use of the actual historical document is strictly forbidden, and to safeguard it as electronic form and use is something imperative. Under no circumstances, does the chemical treatment improve, rejuvenate, or re-join the cellulosic chain. The pH after chemical treatment is increased to a slightly alkaline range (8.5-9.5). When the paper is more acidic, the less pH rises. The initial pH of the bath should be 11.5-12 so that the pH of the paper does not rise greatly, more than 10, which is not desirable. Calcium carbonate is the most compatible paper material for this procedure and still is the first choice for chemical treatment (Kolar, 1997; Sistach, 1996). The slower the alkaline reserve is produced, the more evenly is settled in the different regions of the cellulose bonds while at the same time the amount of its formation is maximized.

5.3. Characterization of paper with electronic sensor microscope (SEM-EDS

From the SEM figures and the elemental analysis of both spot and surface, the conclusions are the following:

- Depending on the quality of paper, year and composition, we notice different amounts of inclusions.
- Depending on the above elements, we notice different encapsulation.
- All paper samples that have undergone process for their restoration and maintenance (A1, B1, C1, D1) have high percentages for Ca.
- The results of elemental spot analysis on paper samples processed for their restoration and maintenance (A1, B1, C1, D1) show a great variation in the Ca percentages which varies on where the analysis has been conducted (on a white background or in the fiber region) (Table 7).
- The results from the SEM photographs as well as from the elemental analysis of both spots and maps reflect the results obtained from XRD. To be more specific, (i) the elevated percentages of Ca in the samples that have undergone treatment for their maintenance and repair as this is determined by the elemental analysis in the SEM, is also confirmed in the XRD X-rays, where the peaks of $CaCO_3$ (Table 9 and Figs 3,4) and (ii) the presence of other chemical elements (e.g Al, Si, S, Cl etc.) as determined by elemental analysis in SEM is confirmed in the XRD radiograms and is attributed to various salts that originate either from the composition of paper, or from the cross-contamination of the paper (Glezos, 2012; Koui et al., 2003; Oxenkioun, 2008; Skoog et al., 2002).

5.4. X-ray (XRD) pattern characterization

Cellulose is a very significant natural polymer. In any chemical reaction, the accessibility of cellulose molecules related with the reagent is particularly important in the process and effectiveness when dealing with maintenance problems. Most cellulosic materials consist of crystalline and amorphous areas, in proportions that may vary, depending on the origin and the way of construction. The cellulose's physical properties, as well as its chemical behavior and activity, are intense and they are influenced by the arrangement of cellulose molecules in relation to the fiber axis. The chemicals reacting with cellulose and eventually leading to the degradation of the cellulosic chain, penetrate only the amorphous regions (low order domains) and the reactions take place on the surface of these areas, where the presence of crystallites is observed, leaving the intra-crystalline amorphous areas unaffected. The amorphous areas in the XRD analysis (Figs 3,4) are smaller in height and range (Maxwell et al., 2008).

6. DISCUSSION & CONCLUSION

In fact, the elements that rescued the archive material were the placing of the archived material in low temperature fridges, the great and immediate mobilizations on behalf of Universities, archives and scientists that offered their scientific knowledge, the disinfection, the configuration of a space with humidity and temperature conditions based on the international literature, the set-up of a maintenance and restoration laboratory, with specialized personnel (in a very small period of time).

Currently, in the maintenance and restoration laboratory of the GCP, the experience of the rescue is utilized to the maximum, the wear factors are weighed, and interventions take place to neutralize the factors that wear out the paper, to thus ensure its longevity. The location where the archive material is kept, is on a high floor to avoid any natural disasters and especially a possible flood, stable humidity and temperature conditions are ensured within the limits $T= 18 \pm 2\ ^0C$ and $RH= 50 \pm 5\%$, which is a big step for the physicochemical course of the material. In this way, 2% - 3% of humidity of its weight is ensured for the material, which does not allow the paper expansions and contractions (and as a result to a less extent the "breakage" - degradation of the cellulosic chain) and do not favor the growth of fungi-mould. It should be stressed that for the growth of mould, high ratios of humidity and temperature, as well as acidic microenvironment are required. The total of the archived material has been disinfected - sterilized, eliminating the possibility of mould growth in the already infected papers, a disinfection or preventive disinfection closed of 1 m^3 has been set up, to deal with cases of infection of the archived material.

Most of the archived material has undergone chemical treatment, the paper has an alkaline stock of $CaCO_3$ and PH of 7,5 -8, limiting to a great extent the action of endogenous and exogenous paper degradation factors. The alkaline microenvironment along with the stable values of humidity and temperature that are ensured in the archive location, eliminates the possibility of fungi growth even in material where the mould spores are genetically active. The restoration procedures continue with the use of Japanese papers which finalize the maintenance procedure. The controlled ventilation limits the action of external gas contaminants on the paper, since these are held, to a great extent by specialized activated carbon filters. The high standards folders and boxes (antiacid with an alkaline stock) where the documents are finally

stored is the final additional protection shield (Havermans, 1997; Whitemore et al., 1995; Daluka 1991). Digitalization has proceeded to a great extent. Quite often, in cooperation with institutions and Universities, qualitative and quantitative measurements are conducted in the archived material, utilizing Scanning Electron Microscopy (SEM) - micro-analysis (EDS), X-Ray Diffraction (XRD), FTIR spectroscopy, the fungi cultures and measurements with X-ray photoelectron spectroscopy (XPS). At the same time, experience is exchanged with other archives. The whole Archive of the GCP protection system is supported by fire extinguishing, fire detection, activation of the alarm in case of temperature or humidity rise, as well as by a power generator supporting the operations, in case of power cuts. All the above ensure the best possible longevity of the archived material.

AUTHOR CONTRIBUTIONS

Conceptualization: P.M.; methodology: P.M.; formal analysis, P.M.; resources: P.M.; data curation: P.M.; writing—original draft preparation: P.M.; writing—review and editing: P.M.; supervision: L.Z. All authors have read and agreed to the published version of the manuscript.

REFERENCES

Ballard, M., Baer, N. (1986), Ethylene Oxide Fumigation: Results and Risk Assessment, *Restaurator,* Vol.7, 4, pp. 143-168.

Bansa, H (1998), Aqueous Deacidification - with Calcium or with Magnesium? R*estaurator*, Vol. 19, 1, pp 1-40.

Barrow W, (1974). *Physical and Chemical properties of the book papers*. Research Laboratory Publications, Richmond, USA, No 7, pp 1507-1949.

Bos A (1972). The UV spectra of cellulose and some model compounds. *Journal of applied polymer science,* Vol. 16 pp. 2567-2576.

Calvini P, Grosso V, Hey M, Rossi L, Santucci L. (1988) Deacidification of paper: a more fundamental approach. *The Paper Conservator*, Vol.12, pp. 35-39.

Craig R (1986). Alternative approaches to the treatment of mould - biodesterioration - aninternational problem. *The Paper Conservator,* Vol 10, pp. 27-30.

Daluka T (1991). Preventive Maintenance in the Library of the Holy Synod of the Church of Greece. Diploma thesis. Technological Educational Institute in Athens, Department of Preservation of Antiquities and Works of Art, pp 1-188 (in Greek).

Dupont A- L (1996b). Degradation of Cellulose at the Wet/dry Interface: An Approach to the Identification of the Oxidation Compounds, *Restaurator*, Vol 17, 3, pp. 145-164.

Dupont A-L., Tetreault J. (2000). Cellulose Degradation in an Acetic Acid Environment, *Studies in Conservation*, Vol. 45, pp. 201-210.

Fetisov V (2020). X-ray diffraction methods for structural diagnostics of materials, progress and achievements. *Turpion Journal*, Bristol, UK, Vol.63, No 1, pp 2-32.

Fischer DJ (1977) Conservation research: Fumigation and sterilization of flood-contaminated library, office, photographic, and archival materials. In: Williams JC (ed) *Preservation of paper and textiles of historic and artistic value.* Advances in chemistry series, vol 164. American Chemical Society, Washington, DC, pp 139–148.

French AD, Roughead WA, Miller DP (1987) X-Ray diffraction studies of ramie cellulose I. In: Atalla RH (ed), *The structures of cellulose.* ACS Symposium Series 340. American Chemical Society, pp 15–38.

Glezos, P. (2012). Analysis, morphology, surface with SEM. Diploma Thesis.Technological Educational Institute of Heraklion Crete, Department of Technological Agriculture, pp.5-6, 64-69 (in Greek).

Guerra, R., Vives, J., Monmany, J., Carrido, J. (1998). The Effect of Aqueous Solutions of Alkoxypolyethyleneglycols (ALKPG) on the Mechanical Properties of Paper. *Restaurator*, Vol. 19, 4, pp.187-211.

Havermans A., Dufour J (1997). Photo Oxidation of Paper Documents – A Literature Review, *Restaurator*, Vol.18, 3, pp. 103-114.

Hengemihle F (1995). *Desorpion of Residual Etylene Oxide from Fumigated Library Materials*, library of Kongress Washington USA, FIG 1.3.L.

Hengemihle, F.H., Weberg N, Shahani C.J. (1995). *Desorption of Residual Ethylene Oxide from Fumigated Library Materials.* Preservation Research and Testing Series, No. 9502, pp.1-13.

Hon D. N.-S. (1981). *Preservation of Paper and Textiles of Historic and Artistic Value II*. Advances in Chemistry Series, 193, Washington DC, American Chemical Society, pp. 119-142.

IOS (International Organization for Standardization) (2013) ISO 18928:2013, Imaging Materials – Unprocessed

Photographic Films and Papers – Storage Practices. Geneva, Switzerland: International Organization for Standardization.

Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W (1998). Comprehensive Cellulose Chemistry. Fundamentals and Analytical Methods. Vol. 1, pp. 1-25, 42-50.

Kolar J (1997). Mechanism of Autoxidative Degradation of Cellulose. *Restaurator,* Vol. 18, 4, pp. 163-176.

Kolar J, Gabrijela N (1996). Effect of Various Deacidification Solutions on the Stability of Cellulose Pulps. *Restaurator*, Vol 17, pp. 25-31.

Koui M (2005). Methods and Techniques of Analysis and Characterization of Materials. Notes for the course and the laboratory of the 8th semester of the Department of Materials Science and Engineering of the NTUA, Department of Chemical Engineering, Structure of Atoms and Molecules - Spectroscopy, Compulsory Course of Materials, Athens, pp. 1- 169 (in Greek).

Koui M, Moropoulou A, Anastasopoulou I, Bati G, Karagianni X, Simitzis I, Yfantis D, Dimitlikali D, Zoumboulakis L (2003). Inorganic and Non-Destructive Material Testing Methods. Undergraduate notes Course, Materials Science and Technology, 7th semester, National Technical University, Department of Chemical Engineering, Athens, pp.100-153 (in Greek).

Kyriakidis G, Binas V (2014) *Introduction to Electronic Microscopy*, University of Crete. University of Grete, Greece, pp. 39-44, 95-101.

Lienardy A, Van Damme P (1990). Practical deacidification, *Restaurator,* Vol.11, pp.1-21.

Lienardy, A., Van Damme, P (1990a). Paper washing. *The Paper Conservator*, Vol.14, pp.23-30.

Margaret H, (1979). The Washing and Aqueous Deacidification of Paper. *Restaurator,* Vol.4, pp. 66-80.

Maxwell C,Kennedy C, Wess T, Knuutinen U (2008). X-RAYdiffraction analysis of paper samples – investigation into the effects of water, deacidification treatments and artificial ageing process on cellulose crystallinity. In: *Durability of paper and writing*, 2nd International Symposium and Workshops Ljubliana 2008, Book of abstracts, pp. 48-50.

McCabe, C., (ed.) (2005) *Coatings on Photographs: Materials, Techniques, and Conservation.* Washington, D.C.: Photographic Materials Group, American Institute for Conservation.

Modgi S, McQuaid M. E, Englezos P. (2006). SEM/EDX analysis of Z-direction distribution of mineral content in paper along the cross direction. *Pulp and paper Canada*, pp. 48-51.

Moropoulou A (2003a). Characterization, quality control, wear diagnosis and maintenance building materials, methodology of instrumental & non-destructive techniques. Teaching notes of the course, Material wear and protection, 9th semester, National Tehnical University, Department of Chemical Engineering, Athens, pp.271-302 (in Greek).

Moropoulou A., Zervos S., Mavrantovis, P (2001). Quality control and optimization of the conservation treatments applied to the material of the archives of KKE (Greek Communist Party), *Restaurator*, Vol. 22, pp. 146-163.

Oxekionou Petropoulou M (2008). Physical Methods of Analysis. Publicasion Simetria, Athens, pp.21-26 (In Greek).

Peltikoglou V (1995). Thoughts and suggestions for intervention in case of flood-related disasters. *Archival News,* April, Vol. 11, pp. 14-18 (in Greek).

Roberts J.C (1996). *The Chemistry of Paper*, The Royal Society of Chemistry, Cambridge, UK.21-24.

Rushdya Rabee Ali Hassan (2015) Behavior of archaeological paper after cleaning by organic solvents under heat accelerated aging. Mediterranean Archaeology and Archaeometry, Vol. 15, No 3, pp. 141-150 DOI: 10.5281/zenodo.18365.

Silverman R et al (2008) *Comparing mass drying and sterilization protocols for water-damaged books.* National Center for Preservation Technology and Training, Natchitoches.

Sistach Anguera, M.C. (1996), Structure of Paper Fibres in Ancient Manuscripts: Acidic Decomposition and Deacidification, *Restaurator*, Vol. 17, 2, pp. 117-129.

Skoog, Holler, Nieman (2002). Principles of Instrumental Analysis, Kostarakis press, pp. 331-332, 350-352, 633-638 (in Greek).

Stephanis E (2002). Physicochemical identification, Conservation and restoration of artwork on paper. Postgraduate Work. Interdepartmental postgraduate program, maintenance, and restoration of works of art and mechanisms, Polytechnic School of Thessaloniki, Department of Chemical Engineering, pp. 41- 88 (in Greek)

Stillings R. A, Van Nostrand R. J (1994). The action of ultraviolet light upon cellulose. I. Irradiation effects. II. Postirradiation effects. *Am. Ceram. Soc.* 66, pp. 753-760.

Whitmore P. M, Bogaard J. (1995), The Effect of Oxidation on the Subsequent Oven Aging of Filter Paper,

Restaurator, Vol.16, 1, pp. 10-30.
Williams, R.S. (1994) *Display and Storage of Museum Objects Containing Cellulose Nitrate*. CCI Notes 15/3. Ottawa, ON: Canadian Conservation Institute.
Wilson R, Riley D (1988). *Mould*. National preservation office, the British Library, Preservation policies, London, pp.1-5.
Wilson W.K, Ogden S (1999b). Storage Methods and Handling Practices in Preservation of Library and Archival Materials. A Manual of Northeast Document Conservation Center, UK, Antover. Third edition, seaction four, leaflet 1.
Yasin Zidan, Ahmed El-Shafei, Wafika Noshy and Eman Salim (2017). A comparative study to evaluate conventional and nonconventional cleaning treatments of cellulosic paper supports, *Mediterranean Archaeology and Archaeometry*, Vol. 17, No 3, pp. 337-353. DOI: 10.5281/zenodo.1005538.
Zervos, S., Alexopoulou, I. Paper conservation methods: a literature review. *Cellulose* 22, 2859–2897 (2015). https://doi.org/10.1007/s10570-015-0699-7.