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REVIEW

The Use of Gamma Radiation for the Treatment of Cultural Heritage in the Argentine National Atomic Energy Commission: Past, Present, and Future

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Abstract The use of gamma radiation for treating biodeteriorated cultural heritage on paper has been studied at the Comisión Nacional de Energía Atómica-CNEA (Argentina) since 2001. In order to preserve books, publications, and documents that have been attacked by insects or fungi, gamma radiation techniques have been used at CNEA. The activities include basic research as well as their applications in infected documents and papers currently used in libraries and archives. New papers were subjected to accelerated ageing in order to evaluate the effects of gamma radiation on their physical and mechanical properties. Current studies include resistance to radiation in two batches of highly cellulolytic fungi, associated with indoor environment. They are present in papers and adhesives used for conservation purposes at the Laboratory of Preventive Conservation and Restoration of Documents. A joint study has been started in CNEA with the National University of La Plata.

Keywords Cultural objects preservation · Disinfestation preservation · Fungi in paper · Gamma radiation in paper · Gamma radiation preservation · *Cladosporium cladosporioides* · *Chaetomium globosum*

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1 Introduction

Preservation of books and documents in libraries and archives are hampered mainly by inadequate environmental and infrastructural conditions, as well as by occasional floods, explosions, fire, or extinction methods.

For large amounts of wet and dirty materials, there is a high risk of biodeterioration due to inabilities of immediate drying and cleaning actions. Development of fungi can cause losses of valuable cultural objects [65]. Thus, the necessity of a treatment to eliminate the subsequent infection.

There are different physical and chemical methods in order to avoid biodeterioration. Then it is essential to know their advantages and disadvantages, in order to choose the most effective one. Chemical methods as fungistatic products, ETO, formaldehyde and thymol, among others, leave undesirable residues for documentary material and human health. Gamma radiation is a physical method that leaves no residue on paper. Due to its high penetration capacity, large volumes of packaged documentary material can be treated in a short time.

For decades, radiation processing has been used worldwide in order to preserve, modify, or improve the characteristics [33] of a wide variety of products and materials: sterilization of health care products; food irradiation; polymer cross-linking, tire component curing and conservation of art objects [28]. This technology has been successfully used to reduce biodeteriogene level in infected documents and books to a normal level, contributing to their preservation [8, 27].

In Argentina, libraries and archives have in general conservation problems because of inadequate storage conditions or chemical treatments. In 2001, a multidisciplinary team including a chemist, a conservation expert, and a microbiologist, was integrated in CNEA in order to investigate the benefits and disadvantages of gamma radiation to control fungus on paper documentation. A thesis work on the subject was presented and the CNEA started to assist in the treatment of institutional infected documents, books and magazines, as well as other institution needs [11].

In 2001, the collection of BAP's (Public Administrative Bulletins) documents, which contain institutional administrative historical records since 1951 up to the present, suffered a fungal infection. This was one of the first cases in which gamma radiation was used in CNEA to treat infected paper.

Whenever possible, the effects of the different doses were evaluated by different tests on irradiated and un-irradiated paper. Mechanical physical tests were used to determine:

- mechanical resistance
- optical and electron microscopy for evaluation of fibers of photographic documentation
- pH analysis and accelerated ageing with different methods based on international standards
- UV, moist heat
- dry heat.

Gamma radiation treatments proved to be an effective and safe method, which allowed to deal with large volumes of documents in a short time, leaving no residues on paper. This is the reason why this method was adopted in our Laboratory of Preventive Conservation and Restoration of Documentation (LCRD) for restoration of infected material.

2 Fungi and Their Role in Paper Deterioration

In museums, collections, and libraries, where paper and its derivates are the main organic material, fungi play the most important role in biodeterioration [55]. Although bacteria can also deteriorate paper, the environmental conditions of these buildings are usually more prone to the growth of fungi rather than bacteria, since fungi require less moisture to develop [55].

Fungi that deteriorate paper are mostly air borne, or due to dust accumulation in paper and associated supports. These fungi most frequently belong to the phylum Ascomycota with slow-growing species such as xerophilic ones of the genera *Aspergillus, Paecilomyces, Chrysosporium*, *Penicillium*, and *Cladosporium*. However, there are other fungi, such as some fast-growing species of subphylum Mucoromycotina, as well as ones from the phylum Basidiomycota (Table 1). They can modify the paper substrate or become it in a vector/support for the dispersal of fungal propagules. These fungi colonize paper either by penetrating into the microfibril matrix or growing superficially [57]. Although some data about fungal interaction with substrates and their surface topography exist [57], they are only descriptive and derived from particular cases. Therefore, there is a need to identify the factors that trigger these behaviors, such as those related to limitations or environmental preferences (availability of oxygen, other gases and/or water, among others).

Fungi that colonize documents or art works made of paper can cause structural damage mainly by cellulose decomposition (see Sect. 2.1) and/or by aesthetic detriment (see Sect. 2.2). In addition, handling mould or contaminated paper objects can constitute a serious health risk, because many of them can be pathogenic/toxinogenic, even if they are already dead [47]. Fungi, either airborne and/or deteriorating paper, can cause allergies in people and serious respiratory diseases. In this sense, many fungi available as spores in air, such as those belonging to genus *Cladosporium*, are present at high concentrations in several institutions that conserve heritage documents and are therefore a potential cause of allergic respiratory diseases when inhaled [36].

2.1 Fungal Ability to Cause Structural Damage in Paper

Most fungi that infect paper have saprotrophic properties, using the cellulose matrix as a source of carbon and energy. These fungi can involve both enzymatic and non-enzymatic mechanisms to degrade cellulose. The enzyme systems that fungi synthesize in order to depolymerize cellulose include three main types of extracellular hydrolases:

Table 1 Some fungi reported as biodeteriorating agents associated with several paper documents

Substrate/source of isolation	Taxa	References
Laid-paper	*Cladosporium cladosporioides*[a]	[38]
	Cladosporium[a] and *Penicillium*[a]	
Laid-paper	*Toxicocladosporium irritans*[a] and *Chromelosporium carneum*[a]	[38]
Wood-pulp paper	*C. carneum*[a], *Aspergillus versicolor*[a], and *P. chrysogenum*[a]	[38]
Wood-pulp paper	*Chaetomium globosum*[a]	[38]
Wood-pulp paper	*Phlebiopsis gigantea*[b]	[38]
Laid-paper	*Alternaria alternata*[a] and *Toxicocladosporium*[a]	[38]
1920 etching	*Taeniolella* (*Torula*) sp.[a]	[57]
1958 etching	*Chaetomium* sp.[a]	[57]
17th-century paper	*Cladosporium* sp.[a] and *Torula* sp.[a]	[57]
A mold patch in a book	*Aspergillus sclerotiorum*[a]	[18]
Maps	*Aspergillus* sp.[a] and *Penicillium*s sp.[a]	[43]
Indoor air in an archive and one wood-pulp sample	*Aspergillus fumigatus*[a]	[38]
Registry book of councils from the Santa Cruz Monastery (Coimbra)	*Epicoccum nigrum*[a]	[38]
In foxing spots in Leonardo da Vinci's self-portrait	*Eurotium halophilicum*[a]	[49]
Leonardo da Vinci's self-portrait	Lichenized Ascomycota or *Acremonium* sp.[a] as the most dominant taxa	[49]
A degraded paper of a 16th-century book	*Penicillium pinophilum*[a], *Aspergillus versicolor*[a], *Aspergillus nidulans*[a], *Cladosporium cladosporioides*[a], *Epicoccum nigrum*[a], *Debaryomyces hansenii*[a], *Botryotinia fuckeliana*[a], *Rhizopus arrhizus*[c]	[41]

[a] Phylum Ascomycota

[b] Phylum Basidiomycota

[c] Subphylum Mucoromycotina

1. endoglucanases (EC 3.2.1.4);
2. exoglucanases, including cellodextrinases (EC 3.2.1.74) and cellobiohydrolases (EC 3.2.1.91 for the enzymes acting on the non-reducing end and EC 3.2.1.176 for ones on the reducing end); and
3. β-glucosidases (EC 3.2.1.21).

Endoglucanases are the key components in the process since they increase notoriously the number of reducing and non-reducing extremes (including chain ends and oligosaccharides). However, a previous step called amorphogenesis is necessary to open up the fibrillary matrix and increase the access of the enzymes to the glycosidic linkages within the sugar polymers.

Additionally, there is recent evidence that different fungi can also degrade cellulose involving oxidative enzymes such as the polysaccharide monooxygenases

(PMOs or LPMOs; they stand for lytic PMOs), cellobiose dehydrogenases (CDHs), and members of the carbohydrate-binding module family (CBM33), which act complementarily to the hydrolytic cellulase system.

Non-enzymatic mechanisms can also participate in the fungal degradation of cellulose. Such processes are associated with the activity of some Basidiomycota fungi such as the brown-rot ones. Through quinone redox cycling and glycopeptide-based Fenton reactions, they generate small molecular weight oxidants such as the hydroxyl free radical that randomly attack the substrate [20].

Although fungi that deteriorate paper are mostly cellulolytic organisms, the microbiota associated with this substrate can also include fungi with different saprotrophic behaviors, such as non-cellulolytic ones. An example is the fungi from the order Mucorales, which belong to the group called "sugar fungi", which are unable to utilize complex carbohydrates because they lack the extracellular enzyme batteries. However, they can play a role as opportunists on deteriorated paper. If conditions are adequate for spore germination, they develop typical colonies using soluble carbon compounds. They are easily assimilable and derived from the depolymerization of cellulose caused by the activity of extracellular enzymatic systems that have been secreted by cellulolytic fungi.

In addition, fungi developed on paper can nurse themselves from several carbon substrates present on paper other than cellulose or their monomers. They could be either fillers, sizings, or dust, which can be rich in proteins and sugars, or by scavenging CO_2, combined nitrogen, and carbon-rich gases from the atmosphere under stressful conditions [60]. Also, the survival strategy of fungi deteriorating paper under these conditions might also include alternative endogenous carbon sources such as lipids. All of these limitations can lead to the inconspicuous mycelial development on paper, which is associated with the production of fungal secondary metabolites rather than biomass accumulation.

2.2 Fungal Ability to Cause Aesthetical Damage in Paper

Fungal growth on paper can generate colorimetric alterations, whether the substrate degrades or not. However, some changes in the coloration of paper can also result from the physical–chemical transformations of their components such as type-lignin aromatic compounds and the interaction of the cellulose with metal traces that causes deleterious effects on papers. The latter correspond to foxing phenomena by the action of abiotic processes [6].

Paper staining following the activity of the fungi can be due to the de novo synthesis of fungal pigments and to the Maillard reaction of by-products of the fungal metabolism. This is the case of organic acids, oligo-saccharides, and other products derived from cellulose degradation that chemically react together with nitrogen-containing compounds and other additional materials from paper under specific conditions. This latter process forms brown products with the consequent formation of foxing type spots [49]. Although the formation mechanisms of foxing have been studied since 1930, there are still no conclusive results and they are controversial [6]. Therefore, additional studies are required in order to identify the

processes and conditions that contribute to development of foxing due to fungi in paper.

2.3 Chemical Nature of Fungal Pigmentation in Deteriorated Paper

Many fungi that deteriorate paper synthesize different pigments, such as lipophilic ones (e.g., carotenoids), hydrophilic ones (e.g., anthraquinones) and others, which are only soluble in alkaline solutions (melanins). These secondary metabolites may cause extensive color changes in the paper, even if the growth of fungi is limited. These pigments can play different functional roles, such as a protecting agent against environmental stress (including photo-oxidations), or against other organisms (involving an antimicrobial action) or as an intermediary enzyme-related cofactor. In this sense, there are several fungi growing on paper that increase their pigmentation by the establishment of stressful conditions. Llorente et al. [37] reported data about the nature of a dark pigment (1,8-dihydroxynaphthalene (DHN)-melanin) in agar cultures of *Cladosporium cladosporioides* and found that the pigmentation of their colonies was increased under chemical stress imposed by certain fungicides. This fungus is a frequent inhabitant of indoor air of libraries and museums and is an etiological agent that causes paper deterioration. Therefore it is necessary to study the melanization process in this fungus and its relationship with environmental conditions.

Several pigments found in deteriorated paper are produced and accumulated in different structures that fungi can differentiate, which are dependent on the taxonomic group to which they belong and to their ecophysiology. In this sense, the pigments can locate in spores, fruiting structures, and mycelium as well as resistance somatic structures such as the sclerotia. This can be variable, being the physiological state of the fungus a key in the differential effects that might generate on the substrate [48]. Although Szczepanowska and Cavaliere [57] suggested that the staining of several papers deteriorated by *Cladosporium* sp. and *Chaetomium* sp. was confined to the fungal elements, there are several findings that showed fungal pigments can be secreted into the substrate and so spread far away from the origin source. Choi et al. [19] reported the production of 2-methylresorcinol, a diffusible pigment with antimicrobial activity, by the fungus *Helicosporium* sp. (Ascomycota). Also, the pyomelanin, which is a water-soluble brown pigment, has been reported to be synthesized by different fungi under certain culture conditions. This pigment was shown to protect fungi against different stresses such as those generated by reactive oxygen intermediates [5]. Among the pyomelanin producing fungi, there are species from the genus *Aspergillus*, including *A. fumigatus*, which is a typical fungus that deteriorates paper [38]. However, *A. fumigatus* is also able to produce another melanin type, such as one DHN-type, which is insoluble in water and is predominantly present in the conidia and secondarily accumulated in the hyphae and excreted into the medium [52]. On the other hand, Michaelsen et al. [41] postulated that the pinkish to purple-colored spots in the 16th-century book's leaves have their origin in purple exudates from the cellulolytic fungi, *Aspergillus nidulans* and *A. versicolor*. Therefore, fungal staining is a highly relevant process that deteriorates paper and so a problem that conditions the choice of adequate strategies

of restoration. This is compatible with limited results reported in experiments with bleaching agents to eliminate front spots associated with fungal deterioration. Since the mechanical removal of dark fungal elements on paper where the pigments are attached, such as reported by Szczepanowska and Cavaliere [57], is not a minimally invasive restoration procedure, new sustainable strategies must still be developed.

3 Cultural Heritage in Paper: Causes of Biodeterioration and methods for Their Treatment. Benefits and Problems of Various Treatments. Use of Gamma Radiation

A book or document undergoes biodeterioration when it suffers alteration of its physical, chemical, mechanical, and aesthetic properties due to the action of biological organisms. Inadequate infrastructure and environmental conditions, as well as microorganisms on material, are the main causes of deterioration of cultural heritage on paper and a door open to fungal contamination and attack of insects or rodents [14, 17, 44, 56]. Pollution caused by microorganisms is one of the main problems that affect cultural heritage objects because it not only degrades the material but also affects the quality of the air of archives and libraries where they are stored [65–67]. Pollution can cause severe diseases, mainly by inhalation of spores and/or contact with them, so it is essential to proceed to decontaminate prior to restoration [68]. The growth of microorganisms and insect pests that generate biodeterioration are favored by factors such as temperature, high humidity, crowded deposits, dust, and poor air circulation. Thus, it is necessary to control these factors to avoid attack [9].

When we talk about the conservation of cultural heritage on paper, we refer to a wide range of procedures and techniques, which serve both to prevent, correct, and repair the originated damage. Modern scientific and technological advances have supplied fundamental tools to combat biological factors of deterioration and helped to understand if they were caused by physical and chemical elements. There are several effective treatments, to a greater or lesser extent, that have been used worldwide. These pest-control methods can be physical and chemical.

One method of control is based on the use of chemicals to prevent pests or eradicate insects and fungi. Many institutions make periodic fumigations unaware that these products leave residual vapors which, when daily breathed by employees and/or users, may cause severe health problems [25]. Although a wide diversity of chemicals are used–such as fungistatic compounds, for instance thymol or ortophenylphenol—which inactivate some fungi-the two most commonly used methods are ethylene oxide (ETO) and gamma radiation since they are industrially standardized for use.

Despite ETO's high toxicity at doses necessary to eradicate fungi, it was used worldwide in the 1980s to treat fungal infections in archives and libraries and it is still used regularly in archives. After this type of treatment, adequate ventilation should be made in order to remove residual gas [4].

In 1984, the U.S. Occupational Safety and Health Agency (OSHA) specified a standard for occupational exposure to ethylene oxide which, among other provisions, lowered the permissible exposure level (PEL) from 50 to 1 ppm [64].

However, the need of appropriateness of a short-term exposure limit has not been evaluated [4]. The World Health Organization (WHO) has given clear guidelines for allowable limits for humans, animals, and the environment. They explained the severe health problems caused by ethylene oxide, such as cancer, abortions, and kidney failure, because of their residual vapors or dermal absorption [68].

Ionizing radiation, in particular, has been and is used worldwide for the elimination of biodeteriorating agents in libraries and archives for the recuperation of large volumes of bibliographic material after disasters, especially those caused by water contact [11, 12, 42, 53].

There are several investigations aimed at the evaluation of the use of gamma radiation as a biocide agent in books or documents affected by fungi and/or insects. Due to its physical character, gamma radiation does not leave any residues and books or documents can be used immediately after treatment [1, 2, 3, 10, 24, 35, 54].

Its high penetration capacity makes it possible to treat large volumes of material in a short time and at room temperature, without vacuum or any other type of additional treatments [1]. Materials are irradiated in their packaging and it is not necessary to air them out after the treatment. Another advantage is that only one parameter has to be evaluated: the delivered radiation dose, which depends only on the time of exposition to radiation.

Chemical reactions induced by gamma radiation on the cellulose molecules include breaking of molecular links and oxidation. The generation of free radicals causes secondary reaction in paper constituent elements [1]. Although the cellulose molecule is broken, reducing its size, the length of the polymeric chain is not affected.

No significant deterioration of mechanical resistance has been reported, even after a 70% reduction in its degree of polymerization. It is highly important to consider that the loss of molecular weight does not concur with observations during practical applications [1, 22, 23, 42, 46].

In case of catastrophical events affecting archives, museums, and libraries, and when the contamination degree is important, the use of gamma radiation is the only way to conserve the material. This technique, followed by appropriate storage, will preserve the material from a definitive loss in a short time [21, 42, 50, 51, 61].

A general acceptability criterion is that materials' properties should not be affected in more than 50% of their original value as a consequence of the treatment. Regarding bibliographical materials, acceptability criteria is the ability to continue its use without significant loss of its functionality. In those cases in which materials could not be recovered for normal use, the procedure consists of treating, cleaning, restoring, and digitalizing them, followed by the appropriate storage of the original [11, 22].

In certain areas, the use of gamma radiation for treatment of books or documents is resisted, without a true knowledge of the advantages of the method. Without a suitable treatment, a book could suffer greater deterioration due to oxidation and/or

acidification from undesirable residues in the paper, with the possibility of total loss in case of lack of adequate measures to revert the situation.

In the USA, during 1980, Nancy McCall, archivist in charge of John Hopkins University Alan M. Chesney, Medical Archives at John Hopkins Hospital, received a donation of 295 boxes with a document collection belonging to Dr. William Horsley Gantt, a psychiatrist disciple of Russian physiologist Iván Pavlov. The material of high heritage value was totally contaminated by microorganisms and had suffered an attack of insects and rodents. After the evaluation of the possible treatment methods, and although there was not enough experience on the use of ionizing radiations, Ms. McCall together with nuclear engineer Walter Chappas of the University of Maryland, decided to irradiate all of the boxes using a cobalt-60 linear accelerator for 45 min at a 4.5-kGy dose [39].

Years later, Ms. McCall explained that after 20 years, no problems have arisen with their irradiated documents, that continue available for normal use, cleaned and restored [40].This experience and its favorable results after many years was in a certain way the starting point for the research and studies, performed at CNEA, in the use of gamma radiation for cultural heritage on paper support treatment.

4 Creation of the Laboratory for Preventive Conservations and Restoration of Documentation (LCRD)

The Laboratory of Preventive Conservation and Restoration of Documentation (LCRD) was created in August 2005, with the main objective of preserving institutional documental heritage on paper support. Gamma radiation was adopted for the treatment and recuperation of documents with a fungal infection because of its strengths (non-contaminating process, highly penetrating).

Desinsectation of cultural heritage objects had already been done at PISI but it was not until 2001 that the evaluation of the effects of gamma radiation on physical and mechanical properties of papers commonly used in libraries and archives was started. Attention was paid to fungi due to the difficulties in their eradication and the highly toxic and contaminating chemical treatments of regular use in the Argentine market.

Thus, it was necessary to face up the great lack of confidence of professionals on cultural heritage conservation especially of paper support to accept the usefulness of this peaceful use of nuclear energy. Although this situation is still present, dissemination and the offer of services to other institutions are very good tools contributing to solve the problem.

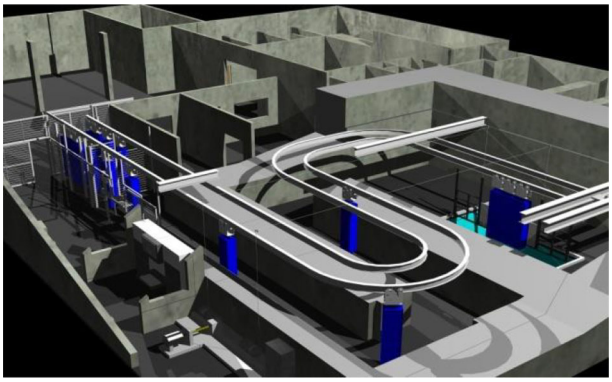
5 Radiation Processing-CNEA's Semi-industrial Irradiation Facility (PISI)

The basic components of irradiation facilities include a

- radiation source (radionuclide gamma or machine source) and the associated systems,
- a product transportation system (in most cases),
- an irradiation chamber with biological shield for protection of personnel and public against radiation,
- storage zones for irradiated and non-irradiated products,
- a dosimetry laboratory,
- a product-handling system and
- the infrastructure for personnel [26].

Argentina's National Atomic Energy Commission has broad experience in radiation processing since the 1960s, mainly in applied research on irradiation of health care products, food polymers, among others. Accompanying this development, Argentina's first irradiation facility—PISI—started operations in 1970, at the Ezeiza Atomic Center. The PISI is a multipurpose facility that uses cobalt-60 sources, with a nominal activity of 1MCi [45].

The process takes place in an irradiation chamber. Products are moved by a conveyor system and exposed to gamma radiation during the time necessary to absorb the proper energy to achieve the objective.



Absorbed dose (sometimes referred to as 'dose') D, is defined as the quotient of the $d\varepsilon$ by dm, $d\varepsilon/dm$. Where $d\varepsilon$ is the mean energy imparted by ionization radiation to matter of mass dm. The unit of absorbed dose is Gray (Gy), where 1 Gray is equivalent to the absorption of 1 Joule per kilogram of specified material (1 Gy = 1 J/kg) (ISO 12749-4 2015).

Absorbed dose is the quantity that relates directly to the intended effect. Prior to the actual irradiation treatment, both the minimum dose required to reduce biodeteriogene level to normal (or treatment dose) and the maximum acceptable dose must be determined. The first one depends on the type of biodeteriogens present on the paper, and the second is related to compatibility of the paper, ink, and to the materials with the radiation process. It is the highest dose the object can absorb without having unacceptable modifications of its properties. This dose range is usually determined by a combination of bibliographical recommendations and

adequate testing. Since absorbed dose is the magnitude of interest, suitable dose measurement techniques are required in order to prevent under- or over-exposure of the product.

The dose measurements required in radiation processing concern characterization of irradiation facilities in installation qualification (IQ), operational qualification (OQ), measurement of dose distribution inirradiated products in performance qualification (PQ), and routine monitoring of the irradiation process [30].

At PISI, routine dosimetry is performed with PMMA dosimetry systems, calibrated with alanine dosimetry systems traceable to NPL.

Although at present there is no specific standard for irradiation of cultural heritage objects, since dosimetry and process validation and control practices are—in general terms-quite similar between different processing applications (except for differences in dose level and package characteristics), dosimetry for biodeteriorated cultural heritage on paper treatment is performed following guidelines of good irradiation practices [26, 31, 32, 34].

6 Studies Performed at the LCRD

6.1 Studies on the Use of Gamma Radiation for Insect and Fungi Control on Paper Support for Conservation Purposes (Magister Thesis, [11])

The ability of this technique was shown to effectively contribute to the conservation of bibliographical material, removing fungi and insects without a significant deterioration of its properties. The study was conducted in three stages. The first two evaluated the seven existing types of paper and cardboard. The third step includes the analysis of paper leafs with advertising from the magazines irradiated at 50 kGy.

The following papers were also analyzed:

- 90 g Permalife paper and 175 g Permalife cardboard, Ecobotanical paper (all of them used in conservation), Epson photographic paper
- Executive Ledesma pulp paper and Fotocopy office paper (acid with pulp fiber),
- leafs from a book and
- a magazine with fungus infection donated for the essay.

These papers were selected due to their regular use in archives and libraries or for having similar characteristics to those used in these places. Samples of irradiated and non-irradiated, aged, and non-aged papers were tested.

First Stage: the papers were irradiated using a single dose of 13.4 kGy, trying to cover the necessary dose range for the treatment applied in case of fungi contamination.

Second Stage: after successful results in the first stage, this was followed by a second one consisting of the irradiation of samples at doses of 3, 5, 10, 15, 20, and 50 kGy, with the aim of getting the different papers' behavior profile under irradiation and the determination of the minimum dose value to reduce microorganisms to their environmental value. The maximum dose each paper could receive

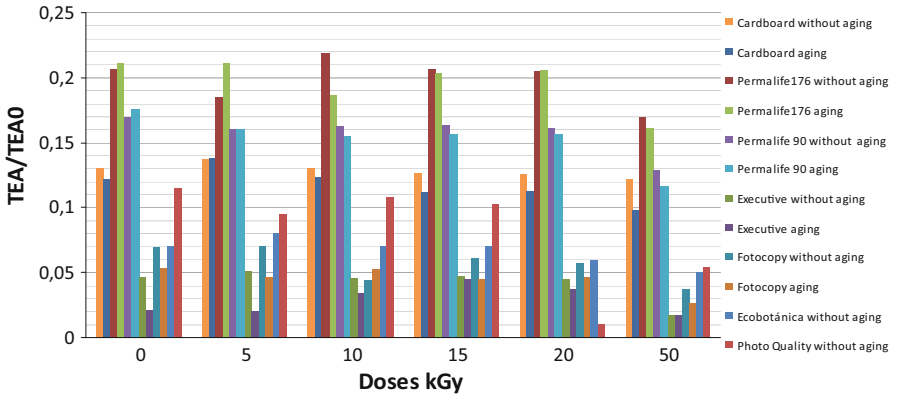


Fig. 1 Behavior of papers irradiating at different doses (5, 10, 15, 20, 50 kGy), aged and without aging

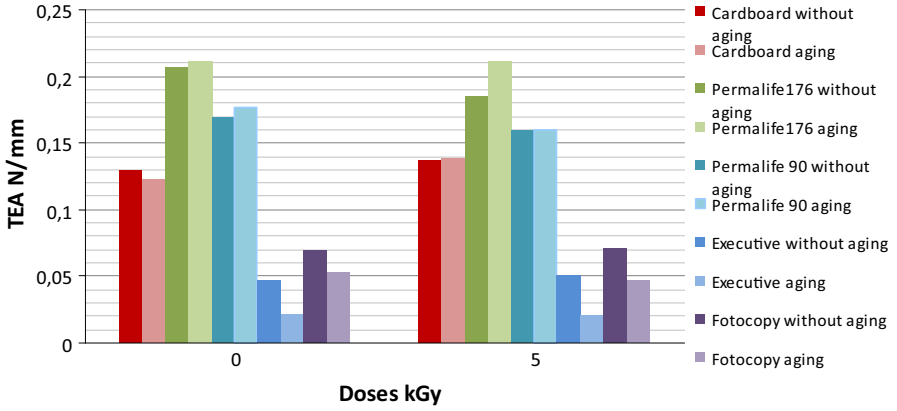


Fig. 2 Behavior of papers irradiating at low doses to reduce microorganisms to their environmental value, aged and without aging

without noticeable deterioration of its mechanical capacity was also determined (Figs. 1, 2).

Third Stage: After the terrorist attack of September 11, 2001, in the USA, all the mail arriving to CNEA was irradiated at the PISI in order to discard any possible attach with filterable virus or other type of etiological agent. Seven boxes of publications containing 125 magazines, coming by post from the USA and Europe, were irradiated at 50 kGy. Three years after their radiation, leafs with publicity were extracted and evaluated under Tappi T494 om96 [59] standard, performing tensile strength tests and pH essays. Although a very high dose was used, five times the necessary to control fungi infections, the material is currently in use without any type of visible deterioration. Physical and mechanical tests of all the material used in the three stages mentioned above were performed in the Laboratory of Polymers, at the Ezeiza Atomic Center. A dynamometer INSTRON model 1122 multipurpose, with a load cell of 500 kg and head speed of 20 mm/

min, was used. Screw grips were used to hold the strips. Tensile strength and percentual stretch were determined according Tappi T494 om 96 standard. Before the tests, all the material was stabilized at 22 °C and 50% RH, for 72 h. Fibers from all the irradiated papers prepared under Tappi T401 om 93 [58] standard were photographically registered and compared against fibers from the unirradiated controls, and the differences were evaluated. Electron micrographs were taken with an optical microscope at 40× and a scanning electron microscope at 800× and 1600×. In this way, it was possible to evaluate the absence of morphological changes in the fibers. The analysis of the fibers by SEM was done with the assistance of the Cellulose and Paper Laboratory of the National Institute of Industrial Technology (INTI), for the determination of the deterioration in fibers and other paper components with a better precision.

Regarding the irradiations of the second stage at different doses, it was possible to confirm that only the biological tests of papers irradiated at 3 kGy presented fungal development. No visible pH changes were observed.

After 3 years of irradiation of magazines at 50 kGy (third stage), samples from these magazines were compared to others taken from unirradiated publications of the same period. It was possible to determine that at this dose there is a 49% loss in the mechanical characteristics of TEA and a 34% loss in the deformation percentage, being both compatible with their normal use.

As a conclusion, it was determined that deterioration of treated materials is not significant, being possible to verify the working hypothesis and the possibility to use gamma radiation or microorganisms and insect control in books and documents [11].

6.2 Treatment of CNEA Public Administrative Bulletins

In 2001, it was found that all leather bindings of the Public Administrative Bulletins (BAPs) collection at the Administrative Archive of CNEA were covered by greenish stains. These Bulletins with the institutional administrative memory suffered a fungal infection due to their storage in a deposit without ventilation (airing) and very high temperature and humidity after cleaning with wet towels during summer [13].

The material was analyzed in the Microbiology Laboratory at the Ezeiza Atomic Center for the determination of the irradiation dose. Three hundred books were put into 50 boxes and irradiated at the PISI at 14.4 kGy and a dose rate of 0.15 kGy/min [23]. In this case, the Microbiology Laboratory only performed the dose analysis as it was irreversible risk destroy the material. After the irirradiation, the books were cleaned and stored in a deposit built under conservation standards established by the International Center for the Study of the Preservation and Restoration of Cultural Property (ICCROM): floor, ceiling, and walls made of fireproof materials, lightning with UV filters, temperature and relative humidity mechanically controlled at 20 °C and 50%, respectively (smoke and temperature change detectors, anti-panic doors).

6.3 Publications Belonging to the Constituyentes Atomic Center Biodeteriorated Due to a Flood Event

In 2001, several boxes with periodical publications at the Information Center of the Constituyentes Atomic Center got wet due to a flood in the area. Drying activities begun immediately after the problem had been detected. However, due to high temperature and humidity, a great part of the material was severely infected. After evaluating the degree of the damage, the most adequate solution was selected.

The material was analyzed at the Microbiology Laboratory for the determination of their radiation dose and was irradiated at the PISI at 15 kGy. After irradiation, the material was returned to the Information Center including a report indicating the procedure for its conservation, cleaning, and storage.

6.4 Documentary Fund Declared by UNESCO Memory of Humanity

In 2006, the LCRD received an offer to work with a documentary Collection included in the UNESCO Memory of the World Register. The collection consisted of 36 boxes with 100–120 records of 1–20 pages each, in plastic envelopes. Due to a flood, the documents were kept wet in these envelopes for over 2 months. The archivist of the institution where the collection was kept asked the LCRD for an evaluation of the material and of its recuperation. Samples were collected for the determination of the irradiation dose (9 kGy) at the Microbiology Laboratory. An important amount of the material was recuperated by hand. In this case, due to the paper acidity degree (acid papers with ferrogallic inks), calcium carbonate was used to increase alkalinity in the document restoration. The method consisted of the addition of 5 mg of calcium carbonate per liter of 2% methylcellulose solution to stick Japanese paper to the documents after their cleaning. Tests were done for the determination of pH of the irradiated and un-irradiated documents as well as on the aged ones.

In order to verify the degree of improvement, essays were done for accelerated aging using dry heat [62] and wet heat [63] and IRAM ATIPCA P3118 [29] standard for UV aging. Papers treated with methylcellulose and with methylcellulose plus calcium carbonate were compared.

Tensile tests were done and the results compared to those obtained from wet heat aged probes treated with Japanese paper and methylcellulose (A) and with Japanese paper plus methylcellulose plus calcium carbonate (B). Preliminary results showed an increase of about 40% in mechanical resistance to tensile strength for B papers as compared to A papers. It was found that accelerated aging at 80 °C and 65% RH for 24 h did not cause noticeable changes in the tested samples. Mechanical properties of the restored samples were examined in order to evaluate their tolerance to handling for their digitalization or direct reading. As no identical material was available for control purposes, a common office paper of known tolerance to handling and accelerated and natural aging was used. In relation to this control sample, resistance of the paper fibers was about 37% for samples restored using methylcellulose and about 51% for those treated with calcium carbonate. In the direction perpendicular to the fibers, samples treated without calcium carbonate

showed the same resistance as the control samples, and the ones treated with calcium carbonate 45% less. Elongation capacity was slightly higher than that of the control sample for samples restored without calcium carbonate and about 50% for the ones with calcium carbonate—in the direction perpendicular to the fibers and in the sense of the paper fibers, values were 60—68% of the control values. It is interesting to notice that dispersions, expected when working with restored material coming from highly deteriorated originals, were well above the results from samples treated with calcium carbonate, probably due to problems in the carbonate dispersion in the methylcellulose solution. Thermal aging did not cause any important fall of tensile strength and elongation capacity. Irradiated paper, restored with and without carbonate, resulted with enough mechanical resistance for handling in the different studies performed [22].

6.5 Influence of the Irradiation Dose and Dose Rate on the Physical Properties of Commercial Papers Commonly Used in Libraries and Archives

The objective of this study was the evaluation of the dose and dose rate in papers commonly used in libraries and archives for their optimization. Doses between 2 and 11 kGy and dose rates between 1 kGy/h and 11 kG/h were used. Physical and mechanical properties, intrinsic viscosity, tear resistance, and brightness were analyzed.

The three different brands of paper with different pulp compositions were:

- soda-anthraquinone pulp from sugar cane bagasse (author),
- bleached eucalyptus kraft pulp with an elemental chlorine free bleaching sequence (Boreal), and
- a specialty paper with a 25% of cotton fiber in use for paper conservation (Capitol Bond).

Gamma radiation is a valid option for removing mold from books and documents because it has no residual toxicity, is highly penetrating, does not pollute the environment, and large volumes of material can be processed in a short time. Although a lot of research has been conducted about adequate doses, no recent works have been found on the effect of dose rate or on its combination with dose. The aim of this study was to evaluate the effects of dose and dose rate of gamma radiation on the physical properties of commercial papers commonly used in libraries and archives in order to optimize the irradiation conditions for each one.

Three different brands of paper with different fiber composition were used, and a 3^2 factorial design with four replicates of the center point with doses ranging from 2 to 11 kGy and dose rates between 1 and 11 kGy/h were applied. Chemical, mechanical, and optical properties were determined on the samples. With some difference between kinds of paper, tensile strength, elongation, TEA, and air resistance were in general unaffected by the treatment. The lowest loss of intrinsic viscosity, tear resistance, and brightness were obtained with doses in the range of 2–3 kGy for all the papers, where dose rate was different for each paper: 11, 10, and

3 kGy/h for papers A, B, and C, respectively. These conditions are ideal for removing insects. If the irradiation is performed at 10 kGy to remove a mass fungal attack, the additional loss of viscosity would be of about 40% and the loss of tear strength would be about a 10% approximately for all the papers [7, 15].

6.6 In-vitro Attack of Paper by Selected Fungi and its Control by Gamma Radiation

At the beginning of 2015, an agreement was signed with the National University of La Plata, in order to work on the following subjects:

(a) Resistance of abaca paper to attack by *Chaetomium globosum* LPSC 259 and gamma radiation.
(b) Resistance of Capitol Bond paper to attack by *Cladosporium cladosporioides* LPSC 1088 and gamma radiation.
(c) Resistance of an adhesive, methylcellulose, to attack by both *Chaetomium globosum* LPSC 259 and *Cladosporium cladosporioides* LPSC 1088 and gamma radiation.

The papers were exposed to the inoculation with biodeterioration causing fungi as *Chaetomium globosum* LPSC 259 y *Cladosporium cladosporioides* LPSC 1088. In this sense, two experiments were done:

(a) Inoculation of sexual spores of *Chaetomium globosum* LPSC 259 on circle probes of abaca paper (8 cm in diameter) that were incubated axenically under two humidity levels (65 and 95%) at 28 °C. Paper probes free of spores were incubated under the same conditions.
(b) A suspension of conidia from *Cladosporium cladosporioides* LPSC 1088 was applied to probes (20 mm × 250 mm) of Capitol Bond paper according to Tappi T494 om96 test, which were then incubated at 75% humidity and 28 °C during 5 months. No signs of fungal deterioration were found in the Capitol Bond probes. This is possibly due to the presence of antifungal compounds in the composition of paper, which might have limited the fungal growth and its effect on the paper quality. However, the spores of *Chaetomium globosum*, when inoculated in abaca paper, germinated both under 65 and 95% of humidity. They showed pigmented sexual structures after 1 month of incubation (Fig. 3). These last probes were exposed to gamma radiation at 3 and 8 kGy. They were then characterized by Fourier transform infrared (FTIR) spectroscopy. Although the results obtained are still preliminary, the FTIR analysis upon the irradiated abaca paper, as compared to non-irradiated sample, suggests that the chemical structure of paper was not affected. However, additional analyses are still necessary in order to evaluate whether their behavior is affected by the absorbed dose. At present, the effects on methylcellulose of fungal alteration and gamma radiation are being analyzed.

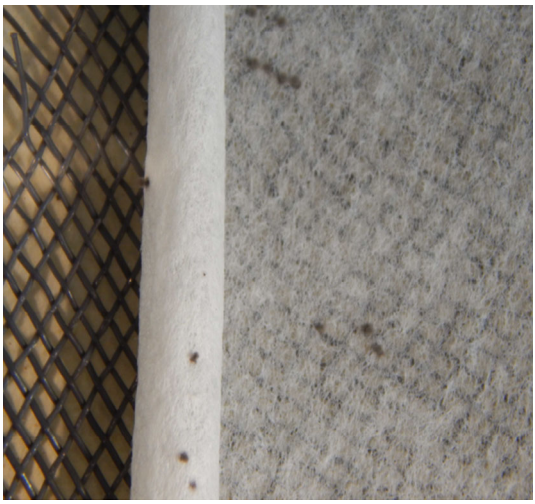


Fig. 3 Probes of abaca paper colonized by *Chaetomium globosum* LPSC 259, showing several pigmented peritecia

6.7 IAEA Technical Co-operation Project RLA/0/058

The laboratory is currently taking part in the International Atomic Energy Agency (IAEA) Technical Co-operation Project RLA/0058 on the 'Use of nuclear techniques for conservation and preservation of cultural heritage objects'. Twelve Latin American countries: Argentina, Bolivia, Brazil, Chile, Costa Rica, Cuba, Ecuador, Mexico, Panama, Peru, Dominican Republic, and Uruguay are participating in the project, Argentina being the project leader. Its objective is to promote and harmonize the use of nuclear techniques in support of cultural heritage preservation and characterization.

The LCRD experience on the benefits of the technique was presented at the IV International Conference on Intervening and Preventing Conservation of Cultural Heritage, Buenos Aires, Argentina, April 4–7, 2016. Particular cases as well as loads of infected material were analyzed.

6.8 Dissemination of the Use of Gamma Radiation for the Treatment Of Fungal Infections

Given the low acceptance of the technique, principally due to limited knowledge, the LCRD has faced up to its dissemination. Regarding the general public, the laboratory has been present at scientific fairs for 3 years and spread general information by means of leaflets, institution Web sites, Facebook, etc. The laboratory has participated in a Conference of Preservation of Cultural Heritage objects at Roffo Hospital, especially aimed at museum curators, librarians, archivists, and other potential users of the technique.

Recuperation of wet bibliographical material on paper support [16] was also presented in national and international seminars and conferences. In addition, some workshops were organized for other institutions.

7 The Future

For the near future, it is expected to continue with the dissemination of the results obtained in our laboratory. As a complement of the activities done so far, we will deepen our study of the effects of gamma radiation on photographs and different inks.

8 Conclusions

Gamma radiation treatments were systematically applied to several heritage documents in CNEA for more than 10 years. They have contributed to solve biodeterioration problems caused by inadequate handling or storing conditions or by natural factors.

Similarly to what happens with alternative methods of preservation or conservation, radiation technology has both strengths and weaknesses, which always have to be taken into account. It is considered that the main difficulty for a generalized use of these techniques is certainly the resistance that conservation professionals have towards radiation technology. This is attributed mainly to misconcepts or preconception emerging from insufficient knowledge in the matter. Designing a communication strategy is mandatory in order to reverse this situation.

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