

Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation



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International Atomic Energy Agency

USES OF IONIZING RADIATION
FOR TANGIBLE CULTURAL
HERITAGE CONSERVATION

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FOR TANGIBLE CULTURAL
HERITAGE CONSERVATION

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FOREWORD

Cultural heritage is the legacy of physical artefacts and intangible attributes of a group or society that are inherited from past generations and maintained for the benefit of future generations. Physical or ‘tangible’ cultural heritage includes works of art, artefacts in museum collections, books, manuscripts, drawings, archive documents, musical instruments, ethnographic objects, archaeological findings, natural history collections, historical buildings and historical places, monuments and industrial heritage objects. Museums today have become important institutions not only for culture, but also for tourism, the economy and national identity. Studying and keeping art objects and other cultural heritage artefacts available, in the best condition possible, for future generations is a significant challenge.

The application of scientific methods to art and archaeological materials has a long tradition, and institutions such as the United Nations Educational, Scientific and Cultural Organization (UNESCO), the International Council of Museums — Committee for Conservation (ICOM-CC), the International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM) and the United Nations Environment Programme (UNEP) have promoted the use of natural science techniques by museum curators and cultural heritage researchers. The IAEA, as a leading supporter of the peaceful use of nuclear technology, has assisted laboratories in its Member States to develop and apply nuclear methods in cultural heritage research for socioeconomic development in emerging economies. Ionizing radiation based techniques are now recognized as important tools for the examination, characterization and analysis of art objects or other cultural heritage artefacts and their component materials.

Preservation of existing cultural heritage artefacts continues to pose a serious challenge, as a variety of factors such as improper storage conditions, climate change or adversities like flooding lead to deterioration or loss of cultural heritage worldwide. Both chemical and physical methods have been developed for treatment and restoration of cultural heritage artefacts. However, chemical methods may leave undesirable chemicals, and physical methods generally use extreme conditions which are not suitable for some types of material. The efforts of national and international research programmes dedicated to developing harmonized methodologies for radiation treatment have led to acceptance of radiation technology for treatment of cultural heritage artefacts. The IAEA has also initiated several projects to support the application of nuclear techniques to cultural heritage investigations.

This book results from the cooperative work of a group of experts convened by the IAEA in October 2014. The aim of the book is to provide state of the art knowledge on application of radiation technology for disinfection and consolidation. It is addressed to the conservation community (curators, conservators/restorers, registrars, art historians, archaeologists, conservation

scientists) active in the various fields of cultural heritage (in museums, libraries, archives, archaeological institutions, historical buildings, conservation workshops) and also to the ionizing radiation community (scientists, engineers and technicians working in various disciplines such as radiation technology, radiation chemistry, environmental technology and radiation biology).

The IAEA wishes to thank all the consultants and contributors for their valuable time and their contributions to this manuscript, in particular, C.C. Ponta (Romania) and the late J.B.G.A. Havermans (Netherlands). Mr Havermans's contribution to this book was of great significance, and the IAEA expresses its appreciation to him. The IAEA also wishes to thank the individual contributors who agreed to share their experiences by contributing individual chapters to make this book more comprehensive. It is hoped that this publication will contribute to wider application of radiation technologies for preserving heritage materials. The IAEA officer responsible for this publication was S. Sabharwal of the Division of Physical and Chemical Sciences.

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CONTENTS

CHAPTER 1. INTRODUCTION	1
<i>J.B.G.A. Havermans</i>	
1.1. Background	1
1.2. Objective	5
1.3. Scope	6
1.4. Structure	7
References to Chapter 1	7
CHAPTER 2. BIODETERIORATION OF TANGIBLE CULTURAL HERITAGE	9
<i>C.C. Ponta, J.B.G.A. Havermans</i>	
2.1. Introduction	9
2.2. Major constituents of artefacts and their degradation behaviour	10
2.2.1. The degradation of inorganic artefacts — telluric transformation	10
2.2.2. The degradation of organic artefacts — the biological cycle	11
2.3. The biodegradation phenomenon	13
2.4. Relevant biodegradation agents	14
2.4.1. Microorganisms	15
2.4.2. Insects	16
2.5. Biodegradation of different organic materials	16
2.5.1. Wood	17
2.5.2. Paper	20
2.5.3. Leather, parchment	23
2.5.4. Textiles (fabrics)	26
2.5.5. Other materials	28
References to Chapter 2	29
CHAPTER 3. TRENDS IN DISINFECTION	31
<i>C.C. Ponta, J.B.G.A. Havermans</i>	
3.1. Introduction	31

3.2.	Conventional disinfection techniques	31
3.2.1.	Fumigation	31
3.2.2.	Thermal treatment	32
3.2.3.	Liquids	32
3.2.4.	Anoxia	33
3.2.5.	Dry cleaning	33
3.3.	Radiation disinfection techniques	34
3.3.1.	Radiation sterilization	34
3.3.2.	Radiation treatment of cultural heritage artefacts	34
3.4.	Advantages of radiation techniques	35
	References to Chapter 3	36
CHAPTER 4.	TRENDS IN CONSOLIDATION OF POROUS MATERIALS	39
	<i>Q.K. Tran, J.L. Boutaine</i>	
4.1.	Introduction	39
	References to Chapter 4	41
CHAPTER 5.	FUNDAMENTALS OF RADIATION PROCESSING TECHNOLOGY	43
	<i>P. Vasquez</i>	
5.1.	Introduction	43
5.2.	Absorbed dose and dose rate	44
5.3.	Dosimetry	44
5.4.	Routine product dosimetry	46
	References to Chapter 5	48
CHAPTER 6.	SOURCES AND EQUIPMENT IN RADIATION TECHNOLOGIES	51
	<i>P. Vasquez</i>	
6.1.	Introduction	51
6.2.	Large gamma radiation processing facilities	51
6.3.	Electron beam radiation processing facilities	53
6.4.	X ray irradiation facilities	56
	References to Chapter 6	58

CHAPTER 7. EFFECTS OF IONIZING RADIATION ON MATERIALS	61
<i>C.C. Ponta, J.B.G.A. Havermans, Q.K. Tran, L. Cortella</i>	

7.1. Introduction	61
7.1.1. Biocidal effect and DNA modification	61
7.2. Radiosensitivity of living organisms	63
7.3. Preface to secondary effects	66
7.3.1. DNA of the original artefact	67
7.3.2. ¹⁴ C dating	67
7.4. Secondary effects of ionizing radiation	68
7.4.1. Lignocellulose and cellulose materials including textiles	68
7.4.2. Pigmented and dyed items	75
7.4.3. Varnishes and binders	76
7.4.4. Glasses and gemstones	77
7.4.5. Leather, fur and parchment	77
7.4.6. Mummies and taxidermy specimens	79
7.4.7. Waterlogged archaeological organic material	80
7.4.8. Photographic materials	80
7.4.9. Contemporary art	82
References to Chapter 7	85

CHAPTER 8. DISINFECTION OF CULTURAL ARTEFACTS USING IRRADIATION	93
<i>C.C. Ponta, J.B.G.A. Havermans, J.L. Boutaine</i>	

8.1. Introduction	93
8.2. Recommended treatment doses	94
8.2.1. Insects	95
8.2.2. Mould and overall treatment	95
8.3. Precautions to be taken in deciding the treatment dose	96
8.4. Other precautions and considerations	97
8.5. Comments on particular materials	98
8.6. Radiation disinfection application areas	99
8.7. Radition safety	102
Reference to Chapter 8	103

CHAPTER 9. CONSOLIDATION OF ORGANIC MATERIALS USING RADATION TECHNOLOGY	105
<i>Q.K. Tran, J.L. Boutaine</i>	
9.1. Introduction	105
9.2. Paper and textiles	105
9.3. Consolidation of wooden artefacts by radiation curing resins	106
9.3.1. Monomers and resins	106
9.4. Polymerization under gamma irradiation	107
9.5. Radiation consolidation application areas	109
Reference to Chapter 9	111
 CHAPTER 10. MOULD DISINFECTION THROUGH GAMMA RADIATION IN THE PEACE PALACE LIBRARY	 113
<i>J. Vervliet</i>	
10.1. Introduction	113
10.2. Disinfection through gamma radiation	113
 CHAPTER 11. DISINFECTION OF THE MUMMY OF RAMSES II (FRANCE, 1977)	 117
<i>L. Cortella</i>	
11.1. Introduction	117
11.2. From history to process	117
References to Chapter 11	119
 CHAPTER 12. THE EFFECT OF 8 ± 2 kGy GAMMA DISINFECTION TREATMENT ON MOULD INFECTED PAPER MATERIALS IN THE NETHERLANDS	 121
<i>J.B.G.A. Havermans</i>	
12.1. Introduction	121
12.2. Disaster simulation	121
12.3. Evaluation	123
12.4. Quality of the returned treated and conserved materials	123
12.5. SurveNIR analysis — part 1, material assessment	123
12.6. SurveNIR analysis — part 2, chemometric approach	127
12.7. Conclusions	128

Acknowledgements to Chapter 12	128
References to Chapter 12	129
CHAPTER 13. EMERGENCY INTERVENTION AT THE NATIONAL FILM ARCHIVE.....	131
<i>C.C. Ponta</i>	
13.1. Introduction	131
13.2. Experimental procedures.....	133
13.3. Results and discussion.....	134
13.4. Conclusion.....	134
Acknowledgements to Chapter 13	135
Reference to Chapter 13	135
CHAPTER 14. KHROMA THE FROZEN BABY MAMMOTH.....	137
<i>L. Cortella</i>	
14.1. Introduction	137
14.2. Discussion	137
CHAPTER 15. EMERGENCY INTERVENTION AT A PARISH CHURCH IN ROMANIA	141
<i>C.C. Ponta</i>	
15.1. Introduction	141
15.2. Emergency at Izvoarele Parish Church	141
15.3. Dosimetry	144
15.4. Conclusions	145
Acknowledgements to Chapter 15	147
References to Chapter 15	147
CHAPTER 16. CONSOLIDATION OF AN 18th CENTURY WOODEN POLYCHROME SCULPTURE.....	149
<i>Q.K. Tran</i>	
16.1. Introduction	149
16.2. Impregnation with radiation curing resin and irradiation	150
16.3. Restoration of the sculpture after consolidation.....	152
16.4. Conclusion.....	152

CHAPTER 17. CONSOLIDATION OF PARQUETS	155
<i>Q.K. Tran</i>	
17.1. Treatment of an 18th century parquet in Grenoble, France	155
17.2. Treatment of a 19th century parquet from the city hall of Viviers, France	156
CHAPTER 18. PRESERVATION OF LARGE COLLECTIONS OF ARTEFACTS	159
<i>J. Perkowski, W. Głuszewski</i>	
18.1. Introduction	159
18.2. Prisoners' shoes in the collection of the State Museum at Majdanek	160
18.3. Radiation disinfection of 60 000 shoes	161
18.4. Method of controlling the radiation dose	162
Reference to Chapter 18	162
CHAPTER 19. GAMMA RADIATION FOR MICROBIAL DECONTAMINATION OF CULTURAL HERITAGE: CASE STUDIES WITH PARCHMENT AND CERAMIC TILES	163
<i>S. Cabo Verde, I. Nunes, T. Silva, M. Isabel Dias, M. Isabel Prudêncio, M. Luisa Bothelho</i>	
19.1. Introduction	163
19.2. Parchment case study	164
19.3. Glazed ceramic tile case study	167
19.4. Conclusion	170
Acknowledgments to Chapter 19	171
References to Chapter 19	171
CHAPTER 20. DISINFECTION OF CULTURAL HERITAGE OBJECTS USING ELECTRON BEAM ACCELERATORS	173
<i>W. Głuszewski</i>	
20.1. Introduction	173
20.2. The nature of electron beam radiation	173
20.3. Compatibility of materials with electron beam treatment	174

20.4. Controls for consistent dose delivery	174
20.5. Commercial application of electron beam accelerators at research and development and service centres	176
20.6. Example of employment of accelerator installation for disinfection of objects of historical significance.	176
References to Chapter 20	177
CHAPTER 21. THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN ROMANIA	179
<i>C.C. Ponta</i>	
21.1. Introduction	179
21.2. Research projects.	181
21.3. Decontamination treatments	183
21.4. Decontamination of modern wooden sculptures.	183
21.5. Simultaneous decontamination of artefacts and restoration of museum buildings	184
21.6. Decontamination of the national film archive.	185
21.7. Preventive decontamination of wooden painting supports	187
21.8. International cooperation.	187
21.8.1. Cooperation with the IAEA.	187
21.8.2. Cooperation with ARC-Nucléart.	188
21.9. Recent publications	189
Acknowledgments to Chapter 21	189
CHAPTER 22. MASSIVE PRESERVATION OF WAR-DAMAGED CULTURAL HERITAGE OBJECTS IN CROATIA BY IRRADIATION.	191
<i>B. Katushin-Razem, M. Braun, D. Razem</i>	
22.1. Introduction	191
22.2. Examples of irradiation to preserve cultural heritage objects damaged by war	192
22.2.1. Example 1: The Church of the Blessed Virgin Mary of the Snows in Kamensko near Karlovac (15th century).	192
22.2.2. Example 2: Polychrome sculptures from the destroyed Church of the Assumption of the Blessed Virgin Mary in Gora near Petrinja (12th or 13th century)	193

22.2.3. Example 3: Polyptych of the Virgin Mary from the Church of Saint Francis in Pula (15th century)	194
References to Chapter 20	195
 CHAPTER 23. THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN BRAZIL	197
<i>P. Vasquez</i>	
23.1. Introduction	197
23.2. Public archive of the State of São Paulo: São Luiz de Paraitinga flooding	197
23.3. Control of insects and fungi in a private collection of incunables	198
23.4. Archives of the Secretary of Education for the State of São Paulo: Paper contaminated with sewer water	198
23.5. Gamma irradiation of a restored painting from the 17th century	199
Reference to Chapter 23	201
 CHAPTER 24. THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN TUNISIA	203
<i>M. Kraïem</i>	
24.1. Introduction	203
24.2. The CNSTN's pilot scale gamma irradiation facility	203
24.3. Irradiation process	204
24.4. Cultural heritage artefacts processed at the CNSTN	205
24.4.1. Metal armchairs covered by leather and textile	205
24.4.2. Tapestries, official clothes of the Bey, wooden musical instrument	205
24.4.3. Mummified animals	206
 CHAPTER 25. THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN CROATIA	207
<i>B. Katušin-Ražem, M. Braun, D. Ražem, B. Mihaljević, I. Pucić</i>	

25.1. Introduction	207
25.2. The irradiation facility of the Ruđer Bošković Institute	208
25.3. Acceptance of irradiation treatment	210
25.4. Education and dissemination of knowledge	210
25.5. The visibility of irradiation treatment in publications	212
25.6. National and international cooperation	213
25.7. Research related to cultural heritage irradiation	214
25.8. Example of large scale radiation insect eradication: the Kožarić collection of the Museum of Contemporary Art	215
Acknowledgements to Chapter 25	216
References to Chapter 25	216
CHAPTER 26. THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN FRANCE	221
<i>Q.K. Tran, L. Cortella</i>	
26.1. Introduction	221
26.2. Conservation processes	222
26.2.1. Gamma irradiation for disinfection and consolidation of cultural heritage artefacts	222
26.2.2. Conservation of waterlogged archaeological artefacts	224
26.2.3. Restoration work	226
26.3. Research projects and network	226
26.4. Selected publications	228
ANNEX I: CURRENT APPLICABLE STANDARDS	229
ANNEX II: WEB SITES OF INTEREST	230
ACRONYMS AND ABBREVIATIONS	231
GLOSSARY	233
BIBLIOGRAPHY	239
CONTRIBUTORS TO DRAFTING AND REVIEW	241

Chapter 1

INTRODUCTION

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A unique ancient book or a shipwreck, a statue or a historical building, a leaf from a herbarium or a full archive, a musical instrument or a piece of furniture, an easel painting, a wooden parquet or an archaeological object — different as they are, all can be preserved for the future with proper techniques.

1.1. BACKGROUND

For reasons of ethics, the conservation of cultural heritage is a duty for all countries. Decision makers have only slowly started to understand that conserving cultural heritage, and especially museum, library and archival collections, is a valuable long term investment for the culture of citizens and for the national economy. The accessibility of cultural heritage depends on the conditions under which it is presented to the public, long term conservation actions, any possible restoration actions, and preventive conservation actions. Sensitive materials displayed in an aggressive environment may suffer from chemical attack (from pollutants, inappropriate relative humidity, excessive light, etc.), leading to irreversible damage within only a few weeks (Fig. 1.1).

Under successive European Union Framework Programmes for Research during the last 30 years, more than 150 projects have been dedicated to the conservation of cultural heritage. Tools for stakeholders — to exchange knowledge and improve cooperation — and results of coordinated research programmes can be found on the web sites of some of the organizations that undertook these projects:

- European Cooperation in Science and Technology, which is one of the longest running mechanisms supporting cooperation between scientists and researchers across Europe [1.1];
- European Committee for Standardisation (CEN), where a dedicated technical committee, TC 346, has been established on conservation of cultural heritage [1.2];



FIG. 1.1. An example of damage that can be suffered by sensitive material kept in an aggressive environment.

- The IAEA, which established an international working group on Disinfection and Consolidation of Archived Materials and Cultural Heritage Artefacts by Radiation Processing Techniques and has implemented several technical cooperation projects in this field, including a project on Using Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the European Region [1.3].

International networks improve the impact of research and facilitate the development of recommendations to address needs for future research dealing with both movable and non-movable cultural heritage objects. Cross-fertilization of disciplines strengthens knowledge and application in heritage restoration and conservation. There is broad agreement across networks that although attention is paid to the dissemination of sound scientific developments within the international and national research programmes, improvements can be made in terms of bringing the results to where they have the most impact: the community of curators and conservators/restorers, who need to apply the tools and answers in conservation and restoration. Besides networking (i.e. exchanging knowledge, cooperating and defining research gaps in order to ensure applications of radiation technology are accepted), there is a continuous need for establishing

good practice procedures and standards in the field of safeguarding cultural artefacts.

Degradation of organic and especially cellulose based heritage is caused by endogenous and exogenous factors [1.4]. Endogenous factors include, for example, acidification resulting from the use of certain raw materials in paper making. Exogenous factors include, for example, temperature, moisture and air pollutants. Variation in the equilibrium of the moisture content of the material can initiate the development of mould in the substrate. The threshold of water content in the substrate for mould growth seems to be non-uniformly defined, and therefore different threshold levels of relative humidity can be found in literature: 50–60%, 65–70%, 70 and 75% [1.5]. Moulds are microorganisms that are part of the kingdom of fungi and differ from members of the common plant kingdom by the absence of chlorophyll and the lack of ability to create energy from sunlight. They are incapable of synthesizing organic components from inorganic ones and therefore need carbon as a main source to grow. Most of the mould families are saprophytes (i.e. they are capable of deteriorating plant and animal substrates). The colour of the mould is based on the substrate on which it grows. If the level of moisture in the environment drops, mould species are capable of entering a dormant stage in which they are inactive and are therefore able to survive [1.6].

Mould not only affects archival and library materials, but also affects occupational health through infections (mycoses), allergic reactions and toxic effects (mycotoxicoses). Some families are extremely poisonous and even carcinogenic [1.7]. *Aspergillus flavus* is one such mould. In 1990 a deadly mould species was found in the cellars of the New Museum of Contemporary Art in New York [1.8]. Once killed, mould can still be dangerous because of substances remaining in the substrate. Therefore occupational health aspects remain complex, as was demonstrated during the preservation of the unique library of the Peace Palace in The Hague [1.9].

In terms of degradation, mould, for example, causes an irreversible change to cellulose based substrates. The nutrient matrix for mould in cellulose materials is mainly the amorphous region that also contains polysaccharides such as hemicellulose. Owing to the presence of excess moisture, the fibres swell and become more attractive for mould [1.10]. The enzymes created by the mould deteriorate the cellulose. Mould may also produce radicals which, in the presence of transition metals, will form hydroperoxides [1.11]. It is known that these hydroperoxides stimulate deterioration reactions such as the Fenton reaction [1.12]. The action of light may even stimulate the deterioration reactions presented in Fig. 1.2.

Based on this progression, two treatments are demanded. First the mould has to be made inactive and then the material needs to receive a preventive

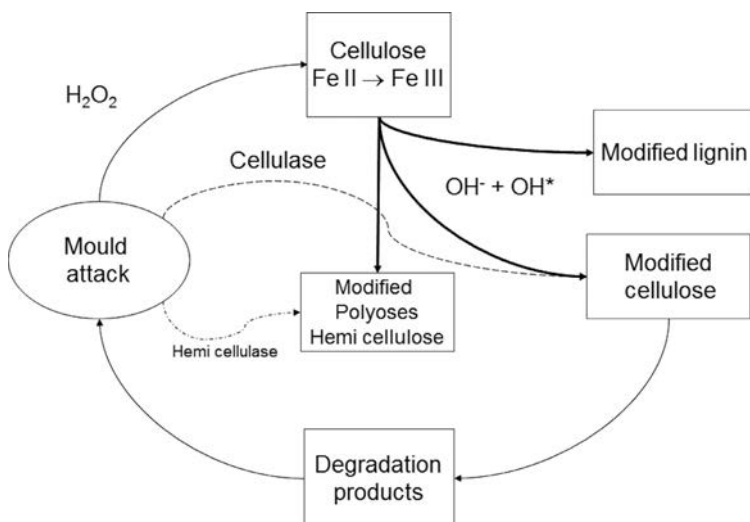


FIG. 1.2. Hypothetical model of paper deterioration by mould according to Ritschkoff and Mahlberg [1.11].

treatment to stop chemical deterioration caused by the waste products remaining from the mould, for example removing the residue of irradiated mould.

An important conclusion can be drawn in advance: doing nothing is not an option, as active mould will severely deteriorate cellulose based heritage.

A variety of curative and preventive measures can be undertaken for preservation and conservation of cultural heritage artefacts. Curative actions include treatment with fumigants such as formaldehyde, ethanol and ethylene oxide. However, these fumigants may be emitted from the objects following fumigation and contaminate the indoor air, resulting in a negative effect on human health. For example, ethylene oxide is a known carcinogen, and the United States Occupational Safety and Health Administration (OSHA) in 1984 specified a standard for occupational exposure to ethylene oxide allowing a permissible exposure level of 1 ppm [1.13].

Preventive measures include healthy storage conditions and a clean environment. Of course when mould is not active and the storage conditions are good, no direct curative action is demanded. However, as mentioned above, mould can be dormant and become active as soon the storage conditions change (e.g. an increase in relative humidity).

The application of ionizing radiation to treat medical devices, pharmaceuticals, food and other materials is well known. Treatment of these products has been carried out for many years and is well accepted. The radiation used can be gamma photons (delivered by sealed sources containing ^{60}Co),

X rays (produced by X ray generators or accelerators) or electrons (produced by accelerators). Such radiation does not induce activation in the treated objects. In addition, the use of X ray or gamma radiography for the non-destructive examination of objects such as easel paintings, statues, archaeological objects and musical instruments is well accepted by the conservation community. The application of ionizing radiation to treat cultural heritage artefacts would therefore appear to be straightforward; however, we have to keep in mind that radiation is capable of deteriorating organic materials, and those materials being irradiated successfully at present have theoretically short lifetimes. Food is quickly consumed, and surgical equipment is used only once. In contrast, heritage materials are to survive for many centuries; therefore the irradiation conditions used for food or surgical equipment cannot simply be copied for use with heritage materials [1.14].

Besides disinfection of artefacts, ionizing radiation can be applied for strengthening extremely weakened materials such as parts from shipwrecks. With the application of a dedicated monomer and radiation, a new polymer can be formed in the weakened substrate and subsequently strengthen the substrate. Research has shown that, depending on their material and on the dose used, objects may react differently upon irradiation. For example, irradiation at a high dose not only kills mould and insects, but also significantly deteriorates the substrate. This leads naturally to the question of whether a high dose is needed. The answer is no, as was demonstrated by, for example, Sinco in 2000. His research showed that books irradiated at a low dose were still in good, consultable condition 10 years later [1.15]. Examples of the application of radiation for treatments such as the effective removal of insects and mould have been reported, though the fundamental backgrounds remain complex, as shown by many researchers [1.6, 1.7, 1.14, 1.16–1.20].

1.2. OBJECTIVE

Application of ionizing radiation for the disinfection of cultural heritage artefacts has been successfully demonstrated in recent years with the participation of museums and libraries. The wider use of this technique requires conclusively establishing that irradiation does not lead to unacceptable changes in the functional or decorative properties of the artefact and its authenticity is not compromised. The technology therefore needs to be applied by professionals at irradiation facilities, ensuring the safety and longevity of the cultural heritage artefacts. Looking at the past decade, many national research programmes worldwide were dedicated to research in the application of ionizing radiation for disinfection. Dissemination of research results to stakeholders — radiation technologists as

well as cultural heritage professionals, is important for the acceptance of the application of radiation technology in the conservation of cultural heritage. This IAEA publication was initiated following two consultants meetings, one on Preparation of Guidelines on the Use of Radiation Technology for Preservation of Artefacts and Cultural Objects (28 October–1 November 2013) and a second on Disinfestation and Consolidation of Archived Materials and Cultural Heritage Artefacts by Radiation Processing Techniques (6–10 October 2014), at IAEA Headquarters in Vienna. The objective of the book is to provide professionals, including radiation polymer chemists and radiation microbiologists who intend to utilize radiation techniques for cultural heritage conservation, with the essential information that will empower them to interact with stakeholders such as conservators and restorers for wider acceptance and use of radiation processing techniques for conservation and consolidation of cultural heritage artefacts.

1.3. SCOPE

Although radiation technology has been successfully utilized in recent years with the participation of museums and libraries for the preservation and consolidation of cultural heritage artefacts, its wider acceptance will depend on scientifically convincing the end users that irradiation does not lead to unacceptable changes in the functional or decorative properties of artefacts and their authenticity is not compromised. This necessitates that the professionals at irradiation facilities possess a deep understanding of the effects of radiation on the basic materials typically used in cultural heritage artefacts, the correct scientific approaches needed to treat the artefacts by radiation to ensure their safety and longevity, and previous documented studies to guide them in designing appropriate treatment methodologies for any new applications. Keeping this in view, this publication focuses on providing fundamental information related to radiation effects on materials typically used in cultural heritage artefacts as well as radiation effects on biocontaminants, characteristics of radiation sources which may be used for treating cultural heritage artefacts, process control procedures and some of the successful applications of radiation technology for cultural heritage preservation and consolidation. The book provides essential information needed to enhance interaction among the stakeholders for wider acceptance and use of radiation processing techniques for conservation and consolidation of cultural heritage artefacts.

1.4. STRUCTURE

The book is divided into the following sections. Chapters 1–6 introduce the essential, fundamental aspects and trends in disinfection of cultural heritage using various techniques. Chapters 7–9 are dedicated to understanding the effects of radiation on the materials typically used in cultural heritage objects and the radiation sources that can be used for treating these artefacts. Chapters 10–26 present actual case studies of the application of radiation technology based techniques for conservation and consolidation of cultural heritage artefacts in collaboration with end users.

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Chapter 2

BIODETERIORATION OF TANGIBLE CULTURAL HERITAGE

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2.1. INTRODUCTION

We know that nothing lasts forever. This is why the idea of eternally conserving the objects that form our heritage is an impossible dream. This impossibility generated such memorable reflections as ‘panta rhei’ (everything flows/changes — Heraclitus). This underscores the fact that prolonging the artefacts’ life is a real challenge because it is a fight against the laws of nature.

There are two scientific branches that study chemical transformation phenomena in nature: thermodynamics and chemical kinetics. Thermodynamics studies the trend in chemical change, while chemical kinetics studies the speed of change. If the trend of degradation cannot be avoided, the speed with which the phenomenon occurs can be influenced within certain limits. In order to better understand how we can control the speed of degradation of objects that are part of our heritage, we will take a closer look at:

- The relation between the materials of which an artefact is composed and its degradation;
- The biodegradation phenomenon;
- Biodegradation causing agents and their mode of action;
- Biodegradation patterns in different organic materials.

2.2. MAJOR CONSTITUENTS OF ARTEFACTS AND THEIR DEGRADATION BEHAVIOUR

Our ancestors could choose raw materials for their artefacts from the three kingdoms: *regnum lapideum* (the mineral kingdom), *regnum animale* (the animal kingdom) and *regnum vegetabile* (the vegetal kingdom), which all make up the *imperium naturae* described by Linnaeus.

2.2.1. The degradation of inorganic artefacts — telluric transformation

Heritage artefacts made of inorganic substances can contain all known chemical elements. Some materials are taken from nature and used in their natural state, after only minor physical modifications. This happens with some pigments and stones such as flint and obsidian. The chemical compounds in these materials are very stable. They appeared over time periods that far exceed the human time horizon, in the process called ‘telluric transformation’. Those events took place hundreds of millions of years ago. The materials we are talking about now result from a process in which the original raw materials, whatever they were, were subjected to extreme temperatures and pressures.

The degradation of inorganic objects of this kind usually requires physical/mechanical damage, caused by water, temperature variations (fire, frost), wind or mechanical stress. All these factors may have destroyed the shape of the object but not its chemical composition. The oldest artefacts of this type date from the palaeolithic era — a historical period which began 2.6 million years ago. For their conservation, any normal indoor environment is sufficient.

Most metals, ceramics and glass, and some mineral pigments, are inorganic materials obtained through human technological intervention upon natural raw minerals. Ceramic and glass are very stable materials. We can find them in artefacts tens of thousands of years old. On the other hand, human-made metals and alloys such as bronze, brass and iron are less stable. In the presence of water, oxygen, sulphur and nitrogen oxides from the air or humic acids from the soil, these metals suffer chemical changes.

Artefacts made of inorganic materials do certainly interact with the living world. Microorganisms have been identified that are able to grow on purely inorganic substrate (lithophilous). They are the pioneers in the establishment of complex colonies comprising organisms ranging from bacteria, algae, lichens and fungi up to macroflora and even animals [2.1]. Biodegradation occurring in such conditions affects buildings and monuments situated in outdoor environments, buried archaeological artefacts and immersed objects. The biodegradation in such circumstances is usually slow. Occasionally, biological degradation has

been incorrectly blamed for damage produced by a physical/mechanical rather than biological action, as in the case of damage produced by plant roots.

As a rule, inorganic artefacts kept in controlled environments in museums, subjected to periodical maintenance operations, are not in danger of biological attack.

Generally, remedial conservation techniques like irradiation are not applied for decontamination and/or consolidation of inorganic artefacts. However, there have nevertheless been some notable scientific experiments. One was a study in Lisbon, Portugal, at the Nuclear and Technological Institute, involving the irradiation of tiles as a biocide against infiltrating microorganisms whose metabolism products induced a pigment colour change [2.2]. In Grenoble, France, Nucléart Regional Conservation Workshop (ARC-Nucléart) consolidated porous structures of some types of gypsum and stone by radiation induced polymerization [2.3].

2.2.2. The degradation of organic artefacts — the biological cycle

Another large category of artefacts consists of those made from organic materials. Carbon prevails in their composition. Organic materials come into the world in a process of transformation that one can call the ‘biological cycle’, in which the main players are plants, animals and microorganisms. The biological cycle refers to the production of organic matter during life, followed by its disintegration as a consequence of death. The remains of this process serve as nutrients for the recommencement of the cycle. The duration of a biological cycle is much shorter than that of a telluric transformation. In most cases, life itself does not last more than 100 years. The duration of disintegration is at least an order of magnitude shorter in natural conditions. There are exceptions, of course, but statistically, this is the approximate average timing.

The artefacts in this category are made of wood, leather, parchment, paper and textiles. From the moment the trunk of a tree becomes a piece of furniture, a musical instrument or a structural element in a building, and from the moment an animal skin becomes parchment, a coat or part of a piece of furniture, the organic matter involved will be kept in conditions more favourable to its preservation than those in nature. As long as it is in use, the degradation of the object is slow. After the period of use has passed, many artefacts go through a period of abandonment (in the worst scenario, being buried in the ground or immersed in water). And then they are rediscovered (in the worst scenario, by an amateur) and often kept in bad conditions. During this stage, degradation advances quickly. From the moment they arrive in a museum, the artefacts become cultural heritage and will evade the natural degradation pattern and its timing. The life cycle in which they are now involved will be purposefully lengthened.

The most important chemical compound present in wood, paper, or textile fibres derived from cotton, flax, hemp or jute is cellulose — a polysaccharide. In materials of animal origin, such as parchment, leather or textile fibres of wool and silk, proteins are dominant (collagen, keratin, sericin and fibroin). Both cellulose and proteins are biopolymers.

The degradation of natural organic materials consists primarily of the breaking of their structural biopolymers. The phenomenon is governed by vulnerabilities, opportunities and preservation conditions.

The vulnerabilities result from the structural characteristics of the biopolymers. The monomer units in cellulose are kept together by glycosidic bonds. These bonds are the vulnerable points in the polymeric chain. In the structure of a protein molecule, peptide bonds dominate, and they are the weak link of the polymeric chain in this case. The degradation products of organic matter are involved in trophic chains. They are the necessary nutrients for the beginning of a new life, and provide the opportunity for resumption of the biological cycle. In this way, the degradation of organic matter plays an essential role in life.

Vulnerabilities and opportunities are the factors leading to the degradation of natural organic materials. However, extreme dryness or perfect isolation from oxygen and water promote conservation even in a natural environment. For instance, coal strata perfectly insulated wooden hunting spears found in good condition at Schöningen, Germany [2.4], and dated to the palaeolithic era. Mummies from the third millennium B.C. and manuscripts on leather and papyrus dated from the 3rd century B.C. were discovered in good condition in similar environments. However, these examples have to be regarded as exceptions from the general rule of quick degradation under natural conditions.

In conclusion, all organic substances participating in the life cycle have low thermodynamic stability in natural conditions. Exceptions are products with a high degree of mineralization: bone, horn and ivory. Proper environmental conditions in museums and frequent hygienic treatments control the development of biodeteriogens (the organisms that degrade cultural artefacts), preserving the artefacts.

Irradiation techniques are applied successfully to preserve artefacts in this category. Irradiation can be used as a method of physical biocide. Polymers obtained through irradiation can strengthen porous, degraded wooden structures or waterlogged wood.

2.3. THE BIODEGRADATION PHENOMENON

The most important feature of the degradation of organic matter is the short time in which the process takes place, compared to the time it takes inorganic artefacts to degrade.

A traditional classification divides the degradation factors into physical, chemical and biological factors. Excess water, the frost/defrost cycle, the temperature and its variation, wind, light and mechanical stress are considered factors of physical or mechanical degradation. Oxygen and other gases, and humic acids from soil are responsible for the chemical degradation of organic artefacts. Fungi, bacteria and insects are factors of biological degradation because they attack organic artefacts that thus become their food source.

A hallmark of the degradation of organic substances is that the process is rarely due solely to physical, chemical or biological factors. They all act synergistically.

This is the reason why certain environmental conditions are necessary for the biological degradation to happen. A fungal attack appears only when excessive moisture is present. Chemical degradation of proteins takes place through hydrolysis. This chemical reaction needs water and is catalysed by acids coming for example from enzymes produced by microorganisms, which are biological degradation factors.

There is still another reason to use the above classification, even if it simplifies the real situation in an excessive and sometimes dangerous way. As long as only physical and chemical degradation factors are present, the degradation will evolve slowly and proportionally to the intensity of exposure to particular noxae. If biological aggressors appear, the degradation will speed up. The identification of a biological attack will alert the conservator, who will then take urgent countermeasures. In the evaluation of the degradation of organic matter it is important to know the history of the artefact.

For example:

- A beam cut from the middle part of the tree trunk is less vulnerable to attack by xylophages (organisms that eat wood) than one that contains the last growth rings.
- Trees that have died in the forest are likely to have been attacked by fungi, even if it is not visible. Wood pieces from these trees preserve fungus spores and are more vulnerable to insect attack.
- Vegetable-tanned leather is more vulnerable to the sulphur dioxide in the air, as well as to fungal attack, than leather tanned with chromium.

Details of biological degradation can be learned based on knowledge of the details of the ecological system. Thus, the chemical reactions of cellulose and protein degradation are catalysed by specific enzymes, generically called cellulase and proteases, respectively. Cellulase is most commonly found in bacteria and fungi, while proteases are produced by all living organisms. It is also important to be aware of the cooperation between aggressors from different species.

The presence of microorganisms (bacteria and fungi) on or in museum artefacts cannot be avoided. Without conditions that promote their development (especially high humidity), fungi or bacteria are found on the artefact in their dormant form (spores) and are not dangerous. However, biodegradation takes place when insects are present. An example is provided by the ecological food chain involving termites. These insects are xylophages par excellence. They destroy the wood, but they do not have the intrinsic ability to break down cellulose. To overcome this lack of ability, termites carry microorganisms in their digestive tract that produce cellulolytic enzymes. The insects do not feed on the cellulose but on sugars resulting from the microorganisms' digestion of cellulose. In this way the termites profit from the metabolic by-products of the microorganisms.

In fighting physical and chemical degradation, a plan using preventive measures that include microclimate control, ventilation and cleaning can be effective. These measures are generally also sufficient to prevent the apparition of biological aggressors. If a biological attack has already begun, each and every object must be treated, because the aggressors may be present in their active biological form. Disinfection action must be very thorough because fungi, bacteria and insects have very complex life cycles, involving dormant stages (spores, eggs) that are resistant to biocides and unfavourable conditions.

2.4. RELEVANT BIODEGRADATION AGENTS

Living organisms capable of destroying organic products important to humans (crops for instance) are called pests. Those that threaten the conservation of cultural artefacts are known as biodeteriogens [2.1]. To successfully fight them, one must know their life characteristics, the optimum conditions for their development and their feeding habits.

Keeping in mind that those artefacts of an organic nature that can be decontaminated by irradiation are mostly to be found in indoor conditions, this publication will focus principally, but not exclusively, on those biodeteriogens that can be found in an indoor environment.

2.4.1. Microorganisms

Microorganisms have a simple internal structure. Their diversity is overwhelming. A simple classification is neither possible nor useful for the purpose of this publication. In addition, traditional taxonomy is often revised, as modern investigative methods involving DNA bring new information regarding the evolution of species. However, to summarize, fungi, bacteria, actinomycetes, yeasts, algae and lichens are the principal classes of microorganisms involved in the destruction of cultural heritage artefacts.

Those most often present in indoor environments are fungi. Bacteria are involved mainly in anaerobic degradation (degradation in conditions with less than normal oxygen). Actinomycetes prefer underground environments. Symbiotic associations, such as algae or lichens, are rarely present in museums.

Cultural artefacts are affected by microorganisms in various ways. The most important degradations are those induced by chemical reactions with certain metabolic products — enzymes, organic acids and other reactive metabolites. Structural biopolymers are broken in this way, with pigments and additives being released. In some cases, the metabolic activity of fungi favours the attack of other deteriogens, such as xylophagous insects in the case of wood. Microorganisms can produce stains on the artefacts' surfaces and can mask or alter the properties of the surface. Their colonization may also fix any dust present to the surface, where it then constitutes a dangerous abrasive element (in the case of paper). Penetration of microorganisms inside the artefacts may produce mechanical stress, cracks or local decay.

People long ago noted that microorganisms grow if there is enough water present. As a result, when parchment, leather or papers are manufactured, they are covered with products that limit the absorption of water.

Apart from humidity, other factors, such as temperature, pH and presence of other nutrients, may favour the apparition and development of microorganisms.

Among fungi, there is a large diversity in morphology and physiology. This diversity might help explain their enormous ability to transform organic matter. Colonies develop very quickly under favourable conditions, leading to a quick breakdown of the substrate. Though the museum environment is far from being favourable to fungus development, in the case of disasters (e.g. flooding) the damage can be considerable. In such a situation, disinfection by irradiation can be an effective measure for preventing a fungal invasion.

Bacteria may be associated with the degradation produced by fungi, or they can be the primary degraders of artefacts in wet environments. Bacteria can play an important role in anaerobic degradation in cases of buried or waterlogged artefacts.

2.4.2. Insects

Insects are the most feared biodeteriogens for organic artefacts in museums and other indoor environments. Approximately seventy very dangerous species are known [2.5]. They use artefacts as sources of nutrition and shelter, and as places to lay eggs.

Insects have a very complex life cycle, which includes various forms of existence (morphs) of the same individual during its lifetime. In the order Coleoptera, the most important biodeteriogen in temperate climates, a complete biological cycle includes the following forms: egg, larva, pupa and adult. The differences between these stages of development are extraordinary, and pertain to appearance, feeding habits, movement, optimal environmental conditions for life and duration. The need for food is different from one stage to another. The egg does not have any metabolic exchanges with the world outside the shell. Its incubation lasts several days and it uses internal resources for feeding. During the pupa stage, lasting several weeks, the insect does not eat and — like the egg — does not move. The adult eats little while accomplishing its essential missions: reproduction and laying eggs. On the other hand, the larva feeds all the time, presenting the real danger for artefacts. A larva can dig galleries for years — up to 5 years, before turning into a pupa.

The case of termites, the most important biodeteriogen in tropical and subtropical climates, is different. The termites form communities of specialized individuals for reproduction, work and defence. The workers feed the colony using wood as nutrient. These insects avoid light and their attack is usually noticed only when the structure is already ruined.

Although there are species adapted to extreme conditions, the range of temperatures for the development of insects in temperate zones is 20–30°C.

While insects prefer high levels of humidity for their growth, this is not a necessary condition, as it is for fungi. High humidity is necessary for the development of insects which live in symbiosis with microorganisms, such as termites.

2.5. BIODEGRADATION OF DIFFERENT ORGANIC MATERIALS

This section is based on the work of Tiano (Ref. [2.1]), which contains an excellent review providing hundreds of references.

2.5.1. Wood

Wood is the most important natural organic material in human history, as well as the first to be used. It has been used to make such vital objects as shelters, tools, furniture, weapons, boats and coaches, and religious or symbolic works of art. As such, it is of exceptional importance for cultural heritage conservation.

Wood is a complex composite of biopolymers with cellulose as the most important component, making up 40–50% by weight. Cellulose is a linear polymer of glucose with the ability to associate in ordered assemblies (nanoscale crystallites, fibrils, fibres). This high level of organization and its hydrophilic nature qualify cellulose as the main component of the cell structure of wood. Lignin, present at a concentration of 25–30% in wood, is another macromolecule. It is arranged in amorphous form in wood cell walls, and is relatively hydrophobic and aromatic. Hemicellulose, which amounts to 20–25%, is also a polysaccharide, but is ramified and made from many different sugar monomers. It has a random, amorphous structure, providing little strength, and it can be easily hydrolysed. In a simplified model, the cellulose fibrils, which bring resistance to tension, are embedded in a matrix of lignin, which resists compression. The hemicellulose links the lignin and cellulose.

Unfortunately, wood is particularly vulnerable to biological deteriogens. Fungal or bacterial attacks depend on the humidity of the substrate. Studies have established that a minimum of 20% humidity is required for biological deteriogens to act. This level of humidity can be easily found in outdoor environments, where fungi are the primary and most important decomposer of cellulose materials.

Fungi active in biodegradation are generically known by the colour and texture of the material resulting from decomposition:

- White rot, including *Pholiota* sp., *Fomes* sp., *Pleurotus* sp.;
- Brown rot, including *Merulius lacrymans*, *Poria* sp., *Coniophora puteana*;
- Soft rot, including *Chaetomium*, *Xylaria*, *Alternaria*, *Humicola*, *Stemphylium*.

The white rot species produce extracellular enzymes and ruin the whole wood cell, degrading the entire lignocellulose complex. Those in the brown rot category preferentially degrade cellulose and other polysaccharides, but do not attack the lignin. The soft rot species are associated with the degradation of waterlogged wood.

The main insects involved in wood decay are shown in Table 2.1. Members of the Anobiidae family are most frequently found in indoor environments. Those of the Lyctidae family can be found even when the humidity is not high, especially in sapwood.

TABLE 2.1. INSECTS FREQUENTLY FOUND ON WOODEN MATERIALS

Order	Family	Common name	Type of damage
Coleoptera	Anobiidae	Furniture beetle	Winding and circular tunnels; circular egress holes
	Lyctidae	Powderpost beetle	Tunnel with oval section
	Bostrichidae	Wood borer	Circular holes and tunnels
	Cerambycidae	Longhorn beetle	Large, oval tunnels and holes
Isoptera	Kalotermitidae	Termites or white ants	Deep and crater-shaped holes; entire interior of object is destroyed but outer surface is left intact
	Rhinotermitidae		
Hymenoptera	Siricidae	Wood wasp	Circular tunnels and holes of wide dimension

Members of the Cerambycidae family are biodeteriogens of wooden roofs and floors.

Termites are a highly destructive biodeteriogen in the tropics and subtropics.

There are various peculiarities of feeding among the insects which degrade organic artefacts. Some of them selectively eat only cellulose (wood, paper, textile fibres), protein (wool, leather, parchment) or starch (paper adhesives). Others eat anything. Some xylophages are not able to digest cellulose, so they live in symbiosis with microorganisms that produce cellulase. The microorganisms digest cellulose and leave the decomposition residues for the host. Certain insects eat paper adhesives. They destroy books and collections by decreasing cohesion between the components of the objects.

There are xylophagous insects that colonize live trees (Fig. 2.1). Others populate only wooden artefacts (Figs 2.2 and 2.3). The latter are more dangerous because at the larval stage, developing beneath the artefact's surface, they may pass unnoticed.



FIG. 2.1. Insect attack on living wood: DELCROM project, Romania (courtesy of IRASM Radiation Processing Center, Horia Hulubei National Institute for Physics and Nuclear Engineering (IRASM, IFIN-HH)).



FIG. 2.2. Insect attack on wood in an uncontrolled environment: furniture from Izvoarele church, Romania; treated through the DELCROM project (courtesy of IRASM, IFIN-HH).



FIG. 2.3. Insect attack on wood in Aman Museum, Bucharest, Romania; treated through the DELCROM project.

2.5.2. Paper

Paper consists of a relatively random network of mostly cellulose fibres. The origin of papermaking is somewhat obscure, but was almost certainly in China. The first piece of paper, and thus the beginning of papermaking, may be credited to Ts'ai Lun in about 105 AD [2.6]. Until the end of the eighteenth century, white paper could only be made from white rags, as the only method of bleaching was exposure to the sun. After the discovery of chlorine (1774) and hypochlorite (1789), these chemicals were soon used as bleaching agents, enabling coloured materials to be used for the production of white paper. The sizing of paper (the addition of substances to reduce its absorbency) using rosin and alum ($KAl(SO_4)_2$) was introduced by Illig in 1805. Later the alum was replaced by $Al_2(SO_4)_3$, so-called papermakers' alum. Rosin size is a solution or dispersion obtained by treating rosin with a suitable alkali. Unfortunately, the hydrolysis of alum yields sulphuric acid, which deteriorates paper. In 1799, the Fourdrinier machine was invented by Robert in France and was soon extensively developed. This machine produced paper in a continuous process rather than sheet by sheet, and allowed other fibre sources than rags to be used. One of the most promising and inexpensive alternatives was groundwood pulp, as developed by Keller in Germany in 1844. The wood pulp obtained was distinctly inferior, as the

fibres were shorter, less pliable and still contaminated with the cementing lignin, but it was a cheap method and the potential supply was large. But groundwood pulp paper had a much shorter life span and paper made between 1850 and 1880 has yellowed and embrittled to such an extent that books printed on this paper can no longer be used. Since the invention of wood pulping processes, the lignin can be dissolved to release almost pure cellulose fibres. Nevertheless, owing to the change in the origin of the cellulose, paper manufactured after 1850 is less durable than paper produced before 1850 [2.7].

Although the fibre source has changed from cotton or linen rags to wood, its nature is still vegetal. The renewable character of the vegetable kingdom ensures a virtually unlimited supply of raw materials. They differ from type to type, but they all consist to a great extent of cellulose. The fibre structure gives paper not only its strength but also its comfortable feeling. Cotton contains approximately 95% cellulose, linen approximately 80% and wood approximately 45%. Grasses consist of only approximately 30% cellulose.

From the conservation point of view, the consequence of the technological modifications was important: old paper is more resistant to biodeteriogens than modern paper.

Compared to wood, paper is more hydrophilic and thus more vulnerable to microscopic biodeteriogens: bacteria, fungi and actinomycetes.

The most important threat for paper comes from fungi, because for their development they need less water than bacteria and actinomycetes. For instance, ordinary species such as those in the genera *Aspergillus* and *Penicillium* are able to grow on substrates having only 7–8% moisture content. Some paper types are hydrophilic enough to attain this intrinsic humidity just by taking the water from air with relative humidity of 62–65%.

The distinctive sign of paper attacked by fungi is stains of any possible colour: red, violet, yellow, brown, black, etc. (Fig. 2.4).

Sometimes the paper may become feltish and brittle. The cellulose's microbial biodegradation results in formation of oligosaccharides with agglutinant properties. This can result in the pages sticking together. The phenomenon is frequently noticed when the book has been immersed.

Insects are frequently among the detteriogens of paper (see Table 2.2). Cellulose and other paper components are the preferred nourishment of certain insects. Some books are complex artefacts made from paper, glue, textile, leather or wood. For insects eating glue or leather, paper biodegradation could be just a collateral activity.

Damage by insects can include superficial abrasion, surface erosion, and holes and tunnels (Fig. 2.5).



FIG. 2.4. An example of a book infected by mould (courtesy of TNO).

TABLE 2.2. INSECTS RESPONSIBLE FOR PAPER BIODETERIORATION

Order	Family	Common name	Type of damage
Thysanura	Lepismatidae	Silverfish	Small surface erosion with irregular outline
Isoptera	Kalotermitidae Rhinotermitidae Termitidae	Termites	Deep crater-shaped holes and erosion; destruction of the interior of the object while the outside remains intact
Coleoptera	Anobiidae	Furniture beetles	Winding, circular tunnels
	Lyctidae	Powderpost beetles	Tunnels with oval sections
	Dermestidae	Skin beetles	Short blind tunnels with circular sections and irregular perforation
Corrodentia	Liposcelidae	Booklice	Tiny surface abrasion
Blattoidea	Blattidae Blattellidae	Cockroaches	Surface erosion

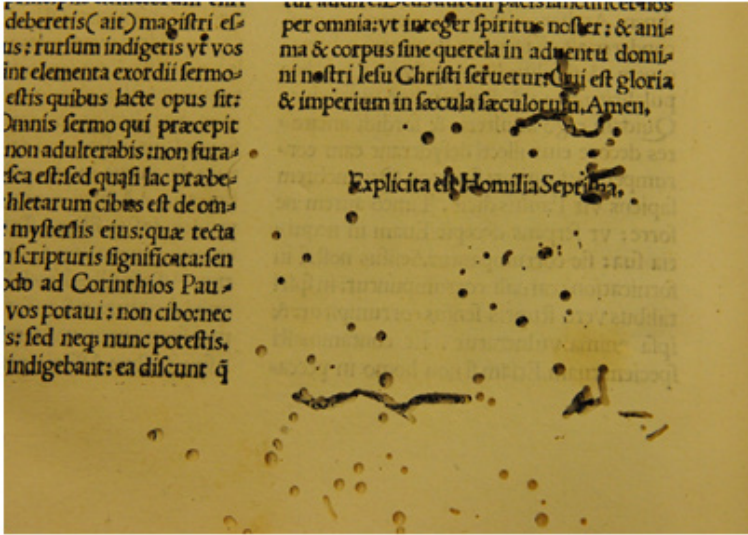


FIG. 2.5. Insect attack on paper: sixteenth century book; treated through the ARCON project, Romania (courtesy of IRASM, IFIN-HH).

2.5.3. Leather, parchment

Leather and parchment are products manufactured from the skin of animals, usually mammals. Unlike wood, animal skin is fast biodegraded if no specific prevention measures (e.g. salting, drying) are taken. The decomposition process begins in a green skin within hours following stripping, unless a preservation method is applied.

Leather artefacts are intended to be used in outdoor environments. On the other hand, parchment was produced as a substrate for writing — therefore for indoor use. The technological processes used to manufacture leather and parchment reflect these two different purposes.

The skin has multiple functions in a living organism; therefore it has an elaborate structure. The main chemical component of the skin is collagen. In its fibril form, this protein is the matrix of animal tissues. Within the skin, it looks like an expanded, unwoven cloth. Skin has three layers: epidermis, dermis and subcutis. Only the dermis is used for leather fabrication, because only it has the collagen fibres in the shape, orientation and consistency needed to produce leather with good mechanical properties.

Transforming the skin into leather is a complicated process which involves several technological steps. These steps include: separating the dermis from the skin assembly, weakening the natural cohesion of the fibres and, most

importantly, tanning. Tanning is a cross-linking process where chemical bonds are formed between tannin and collagen. An important number of hydrophilic chemical groups are blocked in this way, and the assembly becomes much less hydrophilic. After tanning, the skin turns into leather, although there are other steps that finalize the manufacturing process. In the end, the normal water retention in leather is reduced to ~15%. At this level of humidity, the development of microorganisms is not possible.

The most important leather ageing factors are physical, chemical and mechanical. Industrial pollutants such as SO₂ and NO_x catalyse the hydrolytic degradation of the collagen. The same chemical reaction may be helped by metallic ions present in leather from the manufacturing process. Other ageing mechanisms are: oxidative breakdown of the collagen related to ozone and free radicals produced by the UV component of visible light, photochemical degradation of the links between collagen and tannin, and mechanical degradation as a consequence of fluctuations in temperature and humidity combined with the use of the object.

Biological degradation does not play an important role in the larger picture of leather degradation types, as long as the water concentration in the leather stays low. Biological degradation usually appears when the other ageing factors have already modified the water intake. Also, as a result of improper conservation interventions, leather (or parchment) can develop a fatty surface, causing dust retention, which increases the water intake.

Parchment is manufactured by liming, scraping and drying the animal skin, under tension. The manufacturing of parchment does not involve tanning, allowing the opportunity for rehydration. Hence it is much more vulnerable to biological degradation.

Species of bacteria in the *Bacillus* (aerobe), *Pseudomonas* (aerobe), *Bacteroides* (anaerobe) and *Sarcina* (anaerobe) genera attack partially decomposed collagen. Fungi in the *Cladosporium*, *Fusarium*, *Ophiostoma*, *Scopulariopsis*, *Aspergillus*, *Penicillium* and *Trichoderma* genera have also been reported as biodeteriogens of ancient parchment.

Vegetable-tanned leather is more vulnerable to biological attack than chromium-tanned leather. The lipolytic species are among the fungi observed to deteriorate leather. They use the fats present in leather as a source of carbon. The damage is produced in this case by the metabolites of the fungi.

Stained spots and modification of mechanical properties are the main microbial deteriorations in leather and parchment. Biodeteriorated parchment is hard, brittle and deformed, and often has coloured spots affecting the written texts.

Insects also sometimes attack leather and parchment (Figs 2.6–2.8). Dermestidae (skin beetles) and Tineidae (Lepidoptera) are the main families reported to be responsible for this.

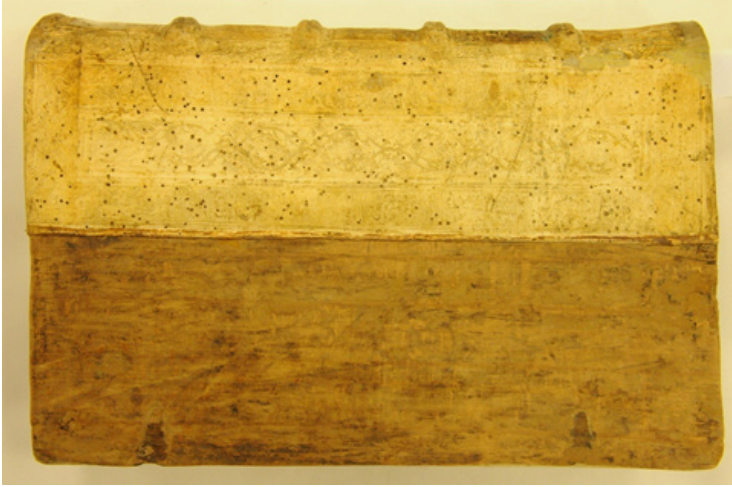


FIG. 2.6. Insect attack on the leather in the binding of a sixteenth century book. The binding was a wood–leather composite; the wooden part had been completely destroyed and was replaced, while the leather was a collateral victim; treated through the ARCON project, Romania (courtesy of IRASM, IFIN-HH).



FIG. 2.7. Insect attack on the leather in the binding of a sixteenth century book, Romania; treated through the TEXLECONS project (courtesy of IRASM, IFIN-HH).



FIG. 2.8. Insect attack on leather, Iasi Museum, Romania; treated through the TEXLECONS project (courtesy of IRASM, IFIN-HH).

2.5.4. Textiles (fabrics)

Many museum artefacts are manufactured from textile fibres, including clothes, carpets, tapestries and easel paintings on canvas. Textiles can be of vegetable or animal origin.

The main component of textiles of vegetable origin is cellulose, extracted from cotton, flax, hemp and a few other plants. This is the reason the biodegradation process for vegetable textiles has many characteristics in common with the processes of wood and paper biodeterioration. However, some aspects specific to textiles must be mentioned. They are related to textile manufacturing characteristics. Fibres with a high content of lignin or wax resist biodeteriogens better than purified cellulose fibres. Fibres containing starch, pectin, dextrin and other low molecular weight carbohydrates are more easily biodeteriorated. Metals such as copper or silver, occasionally present in composite fibres used for high cost clothing, can inhibit microbial growth. Also, loosely woven fabrics have higher ability to attract biodeteriogens than tightly woven fabrics, because they hold more dirt, which is hydrophilic.

In indoor environments, the most frequent biodeteriogens are fungi from genera *Alternaria*, *Aspergillus*, *Fusarium*, *Memmoniella*, *Myrothecium*, *Neurospora*, *Penicillium*, *Scopulariopsis*, *Stachybotrys*, *Stemphylium*, *Chaetomium* and *Mucor*.

Bacteria become active in high humidity, which often characterizes the environment in which archaeological textiles are found. Strains of *Cellvibrio*, *Microspora* and *Clostridium* have been observed in such textiles.

Insects cannot use textiles for shelter as they do with wood. Attack is favoured when the fibres contain glues, like starch or low molecular weight polysaccharides (sugars). In temperate climates and indoor conditions, the main insect families reported to deteriorate textiles are Lepismatidae (e.g. silverfish — *Lepisma saccharina*) and Blattidae (cockroaches). In tropical and subtropical latitudes, the insects responsible for textile deterioration are those in the families Mastotermitidae, Hodotermitidae and Rhinotermitidae (termites).

Biodeterioration produced by fungi on vegetable textiles creates discolouration, staining and loss of strength. Insects may also damage parts of the artefact.

The most important textiles of animal origin are wool and silk, where the main components are proteins. Wool is produced from the hair of sheep and a few other mammals.

The protein in wool is keratin. Keratin is not soluble in water but has a high hygroscopicity (tendency to absorb water from the environment).

Silk contains two proteins: fibroin and sericin. Fibroin is very resistant to chemical agents and insoluble in water. However, sericin is water soluble. Its presence increases the vulnerability of silk. Sometimes the sericin is removed in warm water and soap, as a mean of increasing resistance to microbial deteriogens.

Generally speaking, artefacts made of wool and silk are less deteriorated by microorganisms than artefacts made of cellulose fibres. Owing to their increased hygroscopicity, protein fibres are more easily attacked by bacteria than by fungi.

Bacteria of genera *Bacillus* (*B. mesentericus* and *B. subtilis*), *Proteus* (*P. vulgaris*) and *Pseudomonas aeruginosa*, as well as actinomycetes (*Streptomyces albus* and *Streptomyces fradiae*), are reported among wool bioteriogenes.

Among fungi, those keratinophilic and dermatophytic species from genera *Trichophyton* and *Microsporum* are dangerous because they can produce skin infections. Strains from *Aspergillus*, *Fusarium* and *Trichoderma* genera have been mentioned as deteriogens of silk.

If sericin is removed in the manufacturing processes, silk has good resistance to microorganisms. Fungi may be deteriogens of silk but this has not yet been proven.

Microbial attack rarely appears in museum conditions. However, when it happens, it may cause coloured stains, discolourations and decreased tensile strength in silk.

In indoor environments, insects are the most important biodeteriogens of textiles, as is the case for all organic materials. The most frequently reported

species are those from the family Dermestidae (*Anthrenus erbasci*, *A. museorum*, *Attagenus pellio*), Oecophoridae (brown house moth) and Tineidae (clothes moth — *Tinea pellionella*, *Tineola bisselliella* and *Hofmannophila pseudospretella*).

2.5.5. Other materials

The biodegradation of waterlogged wood is performed by microorganisms that can live in high humidity, low oxygen content and high salt concentration. Algae, wood boring molluscs and shell fish may contribute to biodegradation when the wood is found in a marine environment. Very often, the most important conservation problem with waterlogged wood is to improve the degraded structure, not to stop the biodegradation [2.8].

Some cultural heritage pieces are composed or manufactured from more than one single material. Composite artefacts combine organic and inorganic materials. Examples are mummies, easel and panel paintings, and expensive clothes where pearls, amber and transparent gems have been used together with textile fibres. Some fibres may contain precious metals.

To evaluate the biodegradation of a composite material, one must keep in mind that biodeteriogens act separately on the distinct components. This means that the risk to the most susceptible component must be considered first when an intervention is planned.

When evaluating the use of irradiation for disinfestation, the acceptable dose and the irradiation's side effects on each component must be considered.

Materials used in restoration — animal and vegetal glues, varnishes, temperas and materials used for cleaning and soaking, are of organic origin and have high water content. They increase the risk of a biological attack. This could be confusing in the case of frescos where the substratum is assumed to be completely inorganic therefore not at risk for the development of microorganisms.

Special care is recommended in the case of restored icons. When exposed in churches they are actually kept in a non-controlled environment that could include levels of humidity and temperatures that allow the development of microorganisms.

Photographic film is a sandwich material made of two major layers. The substrate is a plastic material (cellulose nitrate or cellulose acetate for old films, polyester for modern films). The active layer is made of gelatin containing a suspension of microscopic crystals of silver for black and white films or organic dyes for colour films, which makes up the visual information. The plastic layer is a mechanical support that allows the manipulation of the films. As a protein, gelatin is biodegradable if humidity is excessive. The most important

biodeteriogen is fungi. The plastic is hydrophobic and therefore not at risk of biodeterioration.

If decontamination is obtained by irradiation, the possible side effects on both gelatin and plastic material must be taken into consideration [2.9].

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Chapter 3

TRENDS IN DISINFECTION

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3.1. INTRODUCTION

There are several reasons to disinfect cultural heritage artefacts. These include reducing two serious risks: the risk that infection will cause the artefact to deteriorate faster than normal, and the risk that using an infected object will cause negative health effects for the user [3.1]. Traditional disinfection techniques have been borrowed from medicine and agriculture, where huge quantities of goods must be treated to free them of microorganisms or insects. Indeed, equipment and techniques used in medicine and agriculture are easily adapted to cultural heritage treatment [3.2]. Radiation treatment methodologies are also well established for sterilization of medical products as well as for tissue grafts. These methodologies can be effectively used for treatment of cultural heritage objects. A brief description of conventional and radiation disinfection techniques is provided below.

3.2. CONVENTIONAL DISINFECTION TECHNIQUES

3.2.1. Fumigation

Sterilization of medical devices and disinfestation of grains are sometimes performed by fumigation, which is the use of gases poisonous to living creatures. Ethylene oxide ($(\text{CH}_2)_2\text{O}$) and methyl bromide (CH_3Br) are the gases most frequently used for these purposes. However, the effectiveness of fumigation by gas diffusion is hard to predict, even when most important treatment parameters

(gas concentration, temperature and contact time) are accurately controlled. And beyond this problem of reliability, the effectiveness has an objective limit determined by hard penetration of the gas inside the artefact. Moreover, when poisonous gases are used, there are concerns relating to safety and protection of the environment. $(\text{CH}_2)_2\text{O}$, which has proved to be very dangerous (it is carcinogenic, extremely flammable and explosive), must today be used in approved equipment including a detoxification compartment. It has also been demonstrated that ethylene oxide may be emitted over time from the fumigated artefacts and subsequently contaminate the indoor air [3.3].

CH_3Br , like many other halogen derivatives that deteriorate the ozone layer, is already prohibited in many countries [3.4]. 2-phenylphenol is used in ethanolic solution and may cause serious skin irritation. Paradichlorobenzene is a mild fumigant that seems to be effective as a fungicide; however, it is hazardous if inhaled [3.5].

3.2.2. Thermal treatment

As one can easily imagine the side effects, other physical treatments such as thermal treatment and freeze drying are not widely used in cultural heritage conservation. More study is required of their effects on various types of materials.

Also, freeze drying an artefact that contains mould (subjecting it to a temperature below -18°C) can kill active sections of the mould (mycelium); however, spores present inside the substrate may survive the treatment and will remain latently. Mycotoxins cannot be removed by freeze drying as they are not alive like mold spores. For example, it takes treatment at a temperature of 260°C for half an hour to destroy trichothecene mycotoxins [3.6]. Also, by their nature, these processes can only be applied on small batches of goods.

3.2.3. Liquids

Any liquid in prolonged contact with a cultural heritage artefact made of wood, paper, leather or any other organic material produces damage to the artefact. For this reason, the contact time must be short and the expected biocidal action must be limited to the surface of the artefact.

The most precise and accurate information about disinfection properties of chemical substances can be found in medical references. One of the most respected is Guideline for Disinfection and Sterilization in Healthcare Facilities, 2008, published by the United States Centers for Disease Control and Prevention [3.7].

Ethyl alcohol and isopropyl alcohol are fungicidal and bactericidal and act very quickly (for example: 10 s of exposure is sufficient to kill *Escherichia coli* and *Salmonella typhosa*), but these liquids do not destroy any bacterial spores.

Formaldehyde is also used, especially as a 37% water based solution called formalin. It is a bactericide, fungicide and sporicide. Unfortunately, formaldehyde is a carcinogen. Its ingestion can be fatal, and long term exposure to low levels in the air can cause asthma-like respiratory problems while exposure to the skin can cause skin irritation. Additionally, artefacts treated with formalin may emit formaldehyde over time, and formaldehyde in air should be avoided.

Other potential sterilants include glutaraldehyde, hydrogen peroxide, chlorine and chlorine compounds, peracetic acid, iodophors, phenols and quaternary ammonium compounds. Their uses are limited, even under strictly controlled conditions, because severe occupational diseases like asthma have been associated with them.

3.2.4. Anoxia

Insect eradication by dynamic anoxia (flow of nitrogen or carbon dioxide) is currently implemented in museums and conservation workshops, but long exposure times (at least four weeks) are needed, with accurate monitoring and maintenance of very low oxygen content in the treatment chamber (less than 0.1%). Mass treatment or treatment of large volume artefacts could be problematic with this process, owing to the difficulties of the nitrogen reaching the core of the artefacts. Also, fungi and other anaerobic organisms are not eradicated with this method [3.8].

3.2.5. Dry cleaning

It is sometimes mistakenly believed that dry cleaning artefacts infected with mould is sufficient to disinfect them if the artefacts are stored afterwards under good environmental conditions (e.g. at a temperature of 18°C and 45–50% relative humidity). However, dry cleaning only removes mould on the surface, and mould may still exist inside the artefact. Although low humidity may slow down mould growth, it will not stop it. Owing to its presence, other deterioration reactions may continue, and with changing environmental conditions the mould may quickly become active [3.5].

3.3. RADIATION DISINFECTION TECHNIQUES

3.3.1. Radiation sterilization

The biocidal effect of irradiation was first noticed at the beginning of the 20th century, immediately after the discovery of natural radioactivity. But irradiation treatment, especially for sterilization of medical devices, has only been used in industry for the last several decades. Industrial use is growing. Radiation sterilization — the alternative recommended by the European Pharmacopoeia [3.9] — is used more and more frequently as a final sterilization method. Over 260 million m³ of products are sterilized each year using irradiation [3.10]. It is worth emphasizing that when irradiated under typical conditions (using gamma rays or electron beams (EBs) with energies of less than 10 MeV), no radioactivity is induced in the products.

Radiation sterilization of medical devices is now a well defined industrial process, and a large body of knowledge exists on the treatment itself. Important aspects include the following:

- Academic studies focused on the influence of irradiation on living organisms led to establishment of a scientific specialty called radiobiology.
- Other studies were devoted to qualification and testing of materials exposed to radiation, especially plastics and natural polymers (cotton), as well as coatings and adhesives.
- Engineering studies gave birth to various facility designs in view of optimizing the cost–benefit ratio and improving the production yield, radiation safety or reliability.
- Guides and standards have been developed covering safety design, installation and exploitation, quality assurance and quality control.

3.3.2. Radiation treatment of cultural heritage artefacts

Experiments by Bletchly in the late 1950s involving gamma irradiation of xylophagous insects suggested that the biocidal effect of ionizing radiation can be used to stop biodeterioration of cultural heritage artefacts [3.11, 3.12].

Meanwhile, radiation processing became a mature industrial branch involved in vital economic areas (medical, electrical, food industry, etc.). This increased confidence in the use of radiation treatment for decontamination of cultural heritage artefacts.

Two facilities dedicated to conservation of cultural heritage artefacts appeared in Europe in the 1970s:

- (a) An irradiator involved in the first “Nucléart” programme that began in Grenoble, France, at the Atomic Energy Commission (CEA), in cooperation with cultural institutions in the country (see Chapter 26 to read about its successful history of over 40 years);
- (b) An irradiation facility belonging to the Museum of Central Bohemia in Roztoky, near Prague, Czech Republic (at the time Czechoslovakia).

3.4. ADVANTAGES OF RADIATION TECHNIQUES

Cultural heritage preservation using radiation techniques has specific and indisputable advantages over classical procedures.

The first advantage is *harmlessness*. This should be highlighted and explained extensively to counterbalance public resistance to nuclear related areas in general. The nuclear domain is vast, and it is a big mistake to judge radiography (which has undoubtedly improved medical diagnosis), ^{60}Co radiotherapy (one of the few ways to fight cancer) or sterilization by irradiation (a method that brought considerably cheaper medical devices) in the same way as nuclear weapons. Moreover, there are no notable differences between sterilization, food treatment or decontamination of artefacts using ionizing radiation. In all cases, the same technology and the same irradiation equipment can be used.

Radiation decontamination is performed in a confined, protected and well surveyed area. By design, such a facility can only be used under strict safety conditions.

This technology does not leave any residue in the treated artefact or cause any damage to the environment. The artefacts do not become radioactive. Therefore, there is no risk for conservators/restorers, museum curators and registrars, or irradiation facility operators, and there is no risk to the environment.

Validation of recommended treatment doses and detailed evaluation of irradiation side effects are presented in Chapter 7.

Another important advantage is *effectiveness*. This is based on two facts:

- (a) Gamma radiation penetrates any material and is effective up to its penetration depth, which depends on the density of the material and the quantity of the load.
- (b) The biocidal effect is controlled by a single processing parameter — the absorbed dose, commonly called dose. It can be confidently calculated, delivered at a known level, measured and certified. Radiation decontamination can be described as a process that is inherently effective. It does not depend on the material treated. In all other decontamination techniques, effectiveness is conditioned by the diffusion of a gas or the

temperature, and these depend on the type and structure of the treated material.

There is another practical consequence of radiation penetration: the artefacts can be irradiated without being removed from the package or container used for their transportation.

A further advantage is the *reliability* of the treatment. This is based on the fact that decontamination effectiveness depends only on the irradiation dose.

There are international standards, developed by the International Organization for Standardization (ISO), for all dosimetry systems. Additionally, there is an obligation in industrial irradiation facilities to assure the traceability of dosimetry systems to an international reference laboratory. This is a key part of the certification of the quality management system. The composition and structure of the treated artefact do not influence reliability. It is the same for wood, paper, leather, parchment, textile and others, regardless of their degradation stage.

The dose can be accurately calculated at different points in large objects. This makes it possible to irradiate oversized objects as effectively as smaller objects. As a method of remedial rather than preventive conservation, irradiation decontamination is applicable in emergency situations. Industrial radiation processing facilities (designed for sterilization or food treatment) are best suited in such cases. Disinfection using ionizing radiation takes significantly less time than the classical methods. However, at the time of writing, there is no accepted good practice procedure or international standard available for disinfection of heritage materials using ionizing radiation. Within the IAEA and CEN, discussions are ongoing on this subject.

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Chapter 4

TRENDS IN CONSOLIDATION OF POROUS MATERIALS

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4.1. INTRODUCTION

The consolidation of porous artefacts is a second application of ionizing radiation in the field of cultural heritage preservation. It is derived from studies dating from the 1960s in which the aim was to improve the mechanical properties of porous material — wood and concrete in particular [4.1–4.4]. The method uses vacuum impregnation with a liquid resin followed by polymerization under gamma irradiation, called radiation curing. Even if it is less commonly used than disinfestation, this method is useful because it fully consolidates porous parts of the artefact. After the item has been impregnated, the resin filling the micro-pores is polymerized (cured, i.e. solidified) by radiation. This technique is called ‘densification’ (or the ‘Nucléart process’) in opposition to traditional consolidation techniques that use a solvent to convey the resin into the material, which only forms a film of solid resin after the solvent has evaporated. The resin traditionally used for wood is a styrene unsaturated polyester formulation [4.5–4.7].

The mechanical properties of artefacts are indubitably much better after densification than after any other conventional form of consolidation. The appearance of the object remains unchanged, or at least any changes that do occur are no greater than those that can be observed with any other type of impregnation. However, it is obvious that the material and its physicochemical properties have been transformed (enhanced in density and in mechanical strength) and that these changes are irreversible. That is why this practice is deliberately limited to justified cases in which the mechanical properties must be greatly reinforced. In the case of polychrome wood, preliminary tests must be carried out to determine

whether or not there is any interaction (swelling, dissolution) between the liquid resin and the polychrome layers on the artefact.

Derived applications concern waterlogged archaeological wood, and make use of complex impregnation techniques. In addition to very strong consolidation, the technique provides excellent results in terms of conservation of the initial volume, as well as a surface appearance that is also very satisfactory. But the main advantage is that it can be used as a stabilizing treatment for composite wood and metal objects, while conventional treatments with water soluble polymers tend to accelerate corrosion.

The first publications concerning waterlogged wood artefacts were those by de Guichen [4.8] relating to fragments from lakeside towns Switzerland, those by Munnikendam [4.9] in the Netherlands and those by de Tassigny and Ginier-Gillet [4.10] of ARC-Nuléart relating to 11th century artefacts from Lake Paladru near Charavines, France.

The first operations on dry wood artefacts carried out at ARC-Nucléart concerned the parquet floor of the main room of the Stendhal Museum in Grenoble (1970) and the statue of the Virgin of Flavigny (1970) [4.11].

A similar process is applied to enhance the properties of wood as a building or flooring material. The first research programme was initiated in 1956, at the initiative of the Division of Isotopes Development of the former United States Atomic Energy Commission, under the management of the Division's head, E.E. Fowler. The participants in this programme included the Brookhaven National Laboratory, West Virginia University and several industrial companies. The programme was called 'Wood Plastic Composites'. The initial objectives were to improve the qualities of wood such as hardness, compression resistance, dimensional stability, abrasion resistance, toughness, insect repellent properties, low water sorption and attractive appearance. The first public application was for the floor of the United States Pavilion at the New York World Fair in 1965. The industrial coordinator was the Georgia Nuclear Aircraft Laboratory and the parquet was made of yellow pine (*Pinus rigida*) impregnated with the monomer methyl methacrylate (MMA).

More recently, in France, a programme has been dedicated to enhancing the value of wood species such as those in the beech (*Fagus*), hornbeam (*Carpinus*), birch (*Betula*), poplar (*Populus*) and ash (*Fraxinus*) genera, which are of low commercial value but common in western European forests. In this way it is possible to produce high quality parquets that can compete with floors made of oak or tropical species so they can be laid in places where there is intense pedestrian traffic. Some museums in France, such as the Musée de la musique, Museum national d'histoire naturelle and Musée de La Poste, and the Seoul Incheon Airport were equipped with such densified parquets (through technology transfer from CEA to Huot Parquet Company) in the 1990s.

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Chapter 5

FUNDAMENTALS OF RADIATION PROCESSING TECHNOLOGY

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5.1. INTRODUCTION

The ionizing radiation used in industrial processes consists of electromagnetic waves such as gamma and X rays or charged particles such as accelerated electrons. During the irradiation process, electromagnetic waves such as gamma rays interact with the matter (any material or product) in the following five ways: (i) photoelectric effect, (ii) Compton scattering, (iii) pair production, (iv) coherent scattering and (v) photonuclear reactions. The relative importance of each process depends on the photon energy and the atomic number (Z) of the absorbing material. Coherent scattering is of importance for low energy photons (<0.1 MeV), and photonuclear reactions are possible with photons of energies in the range of 2 to 8 MeV for low Z materials and in the region of 7–20 MeV for high Z materials. Thus, for gamma radiation emitted by a ^{60}Co source, only the first three interaction processes are of importance. Through these and subsequent interactions, it transfers energy and thus radiation dose to the product [5.1]. Accelerated electrons, on the other hand, interact with matter via four processes: (i) emission of bremsstrahlung radiation, (ii) inelastic collision, (iii) elastic collision and (iv) Cerenkov emission. The relative importance of these processes depends mostly on the energy of the electrons and to a lesser extent on the nature of the absorbing material. In any case, the transfer of energy to the product by either electromagnetic radiation or accelerated electrons results in breaking of some chemical bonds and leads to formation of free radicals or excited species in the product.

The chemical effect produced in the material owing to irradiation depends on the chemical composition or the type of chemical bonds present in the material. Metallic and ionic bonds in general are unaffected, while covalent bonds typically present in living creatures and organic materials may be greatly affected by radiation; thus this process needs to be well understood. For cultural heritage objects, the material of interest may be wood, paper or any other natural

or artificial/synthetic organic material. The consequences of breaking chemical bonds in these materials by irradiation of cultural heritage artefacts are in large part responsible for side effects, and will be discussed in subsequent chapters.

5.2. ABSORBED DOSE AND DOSE RATE

To quantify the physical, chemical or biological changes produced by ionizing radiation in cultural heritage artefacts, knowledge of the amount of energy absorbed per unit mass and the rate of deposition of the absorbed energy in the absorbing material is necessary. These quantities are defined as follows.

Absorbed dose: The absorbed dose is the amount of energy absorbed per unit mass of the irradiated material. The International Commission on Radiation Units and Measurements has defined absorbed dose (D) as “the mean energy, $\bar{\epsilon}$, imparted by ionizing radiation to the matter in a volume element divided by the mass, dm , of that volume element” [5.2]:

$$D = \frac{d\bar{\epsilon}}{dm} \quad (5.1)$$

The SI unit of absorbed dose is the gray (Gy), 1 Gy = 1 J/kg.

Absorbed dose rate: The absorbed dose rate is the absorbed dose per unit time. Its SI unit is Gy/s.

In practical situations, D is measurable only as an average value in a larger volume than the one specified in the definition, since it is generally not possible to measure it precisely in a very small volume in the material. Then, the absorbed dose is considered an average value, either as measured in the sensitive volume of the dosimeter used if it is relatively large, or existing in its immediate vicinity if the dosimeter is very small and cavity theory can be applicable [5.2]. For any given irradiation conditions, it is necessary to specify the absorbed dose in the particular material of interest because different materials (such as wood, paper or any natural or artificial/synthetic organic material) have different radiation absorption.

5.3. DOSIMETRY

The success of radiation processing of cultural heritage products, like any other kind of product, depends mainly on the capability to accurately deliver the specified absorbed dose to the product and validate it through reliable dose

measurements. The process involves determining the dose distribution patterns in the product package through process qualification procedures and controlling the routine radiation process through process control procedures [5.3, 5.4].

Radiation processing of cultural heritage products involves utilizing intense radiation sources such as high energy EB accelerators, X ray machines or radionuclide based irradiators containing either ^{60}Co or ^{137}Cs sealed sources. Monodirectional scanned beams are generally used for irradiating the artefacts using electrons and X rays, while in the case of radionuclide irradiators, the material is irradiated by isotropic gamma radiation emitted from rectangular plaque or cylindrical sources. Depending upon the specific application, the approximate range of absorbed dose used in processing cultural objects varies from 0.5 to 25 kGy. A variety of dosimetry systems that are currently used in radiation research and processing applications such as polymer modification, sterilization of health care products and food processing are also available for accurately measuring absorbed doses in cultural heritage objects [5.5–5.9]. These dosimetry systems are based on well established physical or chemical changes induced in dosimeters due to absorbed radiation dose which are measured using calibrated instruments for reproducible and accurate results. Standard procedures developed by ASTM and recognized by the ISO are now regularly used in radiation processing applications [5.10]. This section briefly describes the basic characteristics and application areas of these dosimetry systems.

Dosimetry systems are classified and defined according to ISO/ASTM 51261:2013 as follows [5.11]:

- (a) Primary standard dosimetry system: “dosimetry system that is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quantity”;
- (b) Reference standard dosimetry system: “dosimetry system generally having the highest metrological quality available at a given location or in a given organization, from which measurements made are derived”;
- (c) Routine/working dosimetry system: “dosimetry system calibrated against a reference standard dosimetry system and used for routine dose measurements including dose mapping and process monitoring”;
- (d) Transfer standard dosimetry system: “dosimetry system used as an intermediary to calibrate other dosimetry systems”.

Calorimeters and ionization chambers are two of the main types of primary standard dosimeters [5.10, 5.12, 5.13]. This type of dosimetry system is generally maintained and operated by national standards laboratories and is used to provide the basic standard for use in each country.

Commonly used reference dosimeters include Fricke [5.14, 5.15], ceric/cerous [5.16], dichromate [5.17], ethanol–chlorobenzene (ECB) [5.18] and alanine dosimeters [5.19–5.23].

Routine dosimeters that are typically used in radiation processing facilities for dose mapping, process monitoring and ensuring quality control include polymethyl methacrylate (PMMA) [5.24–5.28], radiochromic solution and film [5.29–5.37], cellulose triacetate (CTA) film [5.38], ceric/cerous [5.16] and ECB dosimeters [5.18].

Transfer standard dosimeters are used for transferring dose information from an accredited or national standards laboratory to an irradiation facility in order to establish traceability to that standards laboratory. These are normally reference standard dosimeters that have characteristics meeting the requirements of a particular application. Information about the different types of dosimeter is given in Table 5.1.

TABLE 5.1. PRIMARY, REFERENCE, ROUTINE AND TRANSFER DOSIMETERS

Class	Calibration	Uncertainty ($k=1$)	Examples
Primary	No	1%	Calorimeter, ionization chamber
Reference	Yes	2–3 %	Alanine, ceric/cerous, dichromate, ECB, Fricke
Routine	Yes	5%	Ceric/cerous, CTA, ECB, PMMA, radiochromic film
Transfer	Yes	3–5%	Alanine, ceric/cerous, dichromate, ECB, Fricke

5.4. ROUTINE PRODUCT DOSIMETRY

Since dosimetry is the key element in ensuring efficacy and safety of the radiation treatment process, reliable routine dosimeters (traceable to national or international standards) form an essential tool in the control of the irradiation process. For a facility operator to certify the dose applied to the products, routine dosimetry of each and every production run is essential, as specified in the ISO/ASTM 51702:2013 [5.39] and ISO/ASTM 51431:2005 [5.40] standards. This provides a system that relevant authorities worldwide can rely on to ensure

that the products have been treated according to international standards. Table 5.2 presents a list of such dosimeters typically used in radiation facilities. The detailed guidelines for development, validation and routine control of industrial radiation processes can be found in Ref. [5.41].

TABLE 5.2. ROUTINE DOSIMETRY SYSTEMS

Dosimeter	Measurement instrument	Dose range (Gy)
Alanine	Electron paramagnetic resonance spectrometer	$1-10^5$
Amino acids	Lyoluminescence reader	$10^{-5}-10^4$
Cellulose acetate	Spectrophotometer	$10^4-4 \times 10^5$
Ceric/cerous sulphate solution	Potentiometer or UV spectrophotometer	10^3-10^5
Clear PMMA	UV spectrophotometer	10^3-10^5
Dyed PMMA	Visible spectrophotometer	10^2-10^5
ECB solution	Spectrophotometer, colour titration, high frequency conductivity	$10-2 \times 10^6$
Ferrous ferric sulphate solution	UV spectrophotometer	$10^3-5 \times 10^3$
Lithium borate, lithium fluoride	Thermoluminescence reader	$10^{-4}-10^3$
Lithium fluoride (optical grade)	UV/visible spectrophotometer	10^2-10^6
Polymeric plastic (M centre)	Fluorescence reader	$50-5 \times 10^5$
Radiochromic dye films, solutions, optical waveguide	Visible spectrophotometer	$1-10^5$

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Chapter 6

SOURCES AND EQUIPMENT IN RADIATION TECHNOLOGIES

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6.1. INTRODUCTION

The facilities that are used for regular radiation processing applications and can be used to process cultural heritage objects can be divided into two categories [6.1]:

- (a) Gamma irradiation facilities using sealed sources containing radionuclides such as ^{60}Co or ^{137}Cs ;
- (b) Facilities using radiation generators such as EB accelerators with energies up to 10 MeV and X ray generators with energies up to 5 MeV.

The greater penetrating capability of gamma rays and X rays allows processing of relatively thick or dense products, while EBs are suitable for irradiating thin materials but provide a higher throughput at lower cost per unit of product when large amounts are processed. Uniform delivery of radiation dose to the products is a critical parameter in radiation processing applications including disinfestation or consolidation of cultural heritage artefacts, which can sometimes be bulky or of irregular shape. This requires proper treatment methodologies using large industrial gamma irradiators and EB facilities which can provide uniform radiation fields covering large areas. Medical radiation therapy facilities as well as equipment for medical or industrial radiography therefore are not appropriate for treatment of cultural objects because the radiation fields from such sources are non-uniform and not large enough [6.2].

6.2. LARGE GAMMA RADIATION PROCESSING FACILITIES

At the heart of any gamma radiation processing facility is a radiation source that emits high energy gamma radiation. The gamma rays used in radiation

processing, including cultural heritage object processing, are generally obtained from large ^{60}Co sealed sources [6.3]. Cobalt-60 simultaneously emits two photons (gamma rays) per disintegration with energies of 1.17 and 1.33 MeV. In industrial facilities, installed activity is in the range of 10^3 – 10^5 TBq (10^4 – 10^7 kCi).

Besides the radiation source, other essential components of such a facility are:

- A shielded room to house the radiation source;
- A source hoist mechanism;
- Appropriate radiation shielding surrounding the irradiation room;
- Control room housing;
- A product transport system to move in and take out the products;
- Product containers to store the products for transport during irradiation;
- Control and interlocks for safe operation of the facility;
- Loading/unloading areas for storage of products.

Figure 6.1 shows a typical industrial irradiation facility where the irradiation process takes place inside a large chamber. The source assembly (source rack) is a plaque and is moved vertically by a hoist mechanism between a shielded

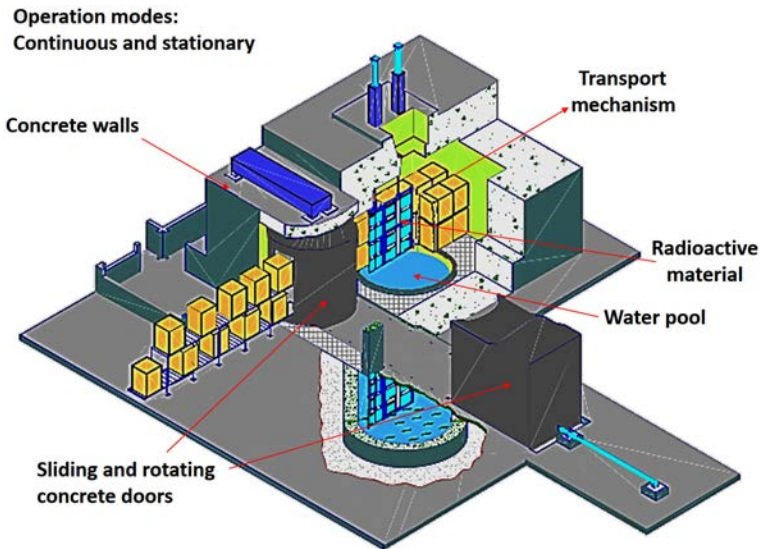


FIG. 6.1. A typical panoramic, wet storage gamma irradiation facility (courtesy of MDS Nordion, Canada).

position inside a water pool and the irradiation position on the chamber level. This kind of facility can be operated in a batch or continuous mode. Products may be moved into the irradiation chamber (where the irradiation will take place) either while the source is fully shielded (batch operation) or while the source is exposed (continuous operation). Uniform irradiation of the product container is achieved by either rotating the product on its own axis during irradiation (suitable for batch operation) or moving the product around the radiation source (more suitable for continuous operation, but also for some batch irradiators).

Depending on the design of the irradiator, the product containers go around a radiation source on a conveyor (or hanging from a track on the ceiling) generally 1–8 times, and may travel at different levels. The principal objective is to ensure that the product absorbs as much radiation energy as possible at a relatively uniform dose. This type of facility is well suited for the treatment of cultural heritage artefacts of any size if they can be brought into the irradiation chamber.

Gamma irradiators have been used commercially for radiation processing since the 1960s. Today, there are over 160 commercial ^{60}Co irradiators for applications such as radiation sterilization and food irradiation operating in many countries worldwide. Some irradiation facilities are also operated in research and development centres. When all uses are taken into account, there are in total over 200 gamma irradiators being operated for a variety of purposes in different countries [6.4]. A Directory of Gamma Processing Facilities in Member States, describing details of locations, geographical distribution and the quality assurance procedures at many of these facilities, was compiled and published by the IAEA in 2004 [6.5].

6.3. ELECTRON BEAM RADIATION PROCESSING FACILITIES

EB accelerators have two important functional parameters: beam energy and beam current. The beam energy determines the penetration depth the beam can achieve, while the beam current controls the throughput that can be obtained. EB accelerators used in radiation processing possess beam energies in the range 0.1 MeV to 10 MeV. An upper energy limit of 10 MeV for EB applications has been set to avoid, with a very high level of confidence, any induction of radioactivity in irradiated products through photonuclear reactions. High beam current is the main distinguishing feature differentiating industrial EB accelerators from equipment that is used for research purposes. While the industrial accelerators have beam currents in the tens of milliampere range (over 10 mA), the research equipment, such as Van de Graaff accelerators, Pelletrons, and many linacs, operates in the microampere range, which is orders of magnitude lower in beam

current than industrial equipment. High beam currents are desired in industry because product throughput rates are proportional to beam current.

An EB accelerator typically consists of the following subsystems:

- Source of electrons: heated cathode which emits electrons;
- Focusing device: electrons are focused into a beam with an extraction electrode;
- Acceleration unit: electrons are accelerated within an evacuated space with a strong electric field;
- Extraction window: electrons pass into the air through a thin titanium foil window.

The electrons are produced through a thermal electron emission effect by an electric device called an 'electron gun'. The emitted electrons are focused and accelerated in a vacuum by different mechanisms to attain the final electron energy. These accelerated high energy electrons then cross a mechanically resistant thin window and are allowed to strike the objects to be irradiated. Accelerators are capable of producing beams that are either pulsed or continuous. Electrons emitted by accelerators have fairly narrow spectral energy limits (usually less than $\pm 10\%$ of the nominal energy). The energy of the electrons reaching the product is further controlled by the bending magnets of the beam handling system, if applicable.

Based on electron energy, EB accelerators used for radiation processing are classified as low, medium or high energy accelerators [6.6, 6.7].

Low energy accelerators: Accelerators in the energy range of 100 keV to 700 keV are in this category. This type of equipment is available with beam widths from approximately 0.5 m up to approximately 1.8 m. Low energy accelerators are generally self-shielded. Their applications are found in areas including surface curing of thin films and laminations, production of antistatic and antifogging films, and wood surface coatings. The maximum range of penetration could be up to 60 mg/cm².

Medium energy accelerators: Scanned beam systems with energies between 1 MeV and 5 MeV fall in this category. This type of equipment is available with beam widths from 0.5 m to 1.8 m. These units are characterized by beam powers from 25 kW to 700 kW. Because of their useful penetration ranges, these accelerators are the workhorses of the radiation processing industry with a range of applications: cross-linking of materials with thicker cross-sections, polymer rheology modification, colour enhancement of gemstones, sterilization of medical products and food irradiation (to a limited extent). Typical penetration depths in unit density material are in the range of 5 mm to 25 mm.

High energy accelerators: Accelerators with an energy range from 5 MeV to 10 MeV provide the highest penetration depth and are best suited to bulk product irradiation. Scanned beams with power levels from 25 kW to 350 kW are available with beam widths up to 1.8 m. With the penetration depth for 10 MeV electrons typically being 50 cm (when irradiated from both sides) for 0.15 g/cm³ product density, this category of accelerator is commonly used for applications such as medical product sterilization, cross-linking of thick section products, disinfestation, wastewater treatment, polymer rheology modification, colour enhancement of gemstones and shelf life extension for food and fruits.

Medium and high energy EB accelerator facilities, like a gamma radiation processing facilities, consist of the following:

- Appropriate radiation shielding surrounding the irradiation room;
- Control room housing;
- Product transport system to move in and take out the products;
- Product containers to store the products for transport during irradiation;
- Control and interlocks for safe operation of the facility;
- Loading/unloading areas for storage of products.

Figure 6.2 shows the layout of a typical EB processing facility designed for processing a high volume of products. The products enter on a conveyer through a labyrinth that permits access but stops radiation from escaping.



FIG. 6.2. Layout of a typical EB irradiation facility (courtesy of IBA, Belgium).

The treatment room houses the accelerator itself and is constructed of thick concrete to protect workers from radiation. In the treatment room, the materials pass under the accelerator for processing. After being irradiated with accelerated electrons, the materials continue on the belt until they exit the irradiation room. The equipment area contains the electrical, electronic and cooling equipment required to run the accelerator. EB processing can provide an extremely fast treatment process with high dose rate that results in faster turnaround times and may be more compatible with a wider range of materials [6.8, 6.9].

For the disinfection of cultural heritage artefacts, high energy EBs are typically required to achieve penetration of the product and packaging. When evaluating EB irradiation for the purpose of sterilization, product density, size, orientation, and packaging must be considered. In general, EB irradiation is most suitable for irradiating low density and uniformly packaged products. It is worth emphasizing that this treatment lasts only several seconds. EBs may very often be sufficient to disinfect or sterilize small cultural heritage objects. In particular, it is useful to use EB irradiation to treat books and documents.

A very conservative market survey indicates that presently there are over 1400 high energy EB units in commercial use. The IAEA published a Directory of Electron Beam Irradiation Facilities in Member States in 2008 [6.10].

6.4. X RAY IRRADIATION FACILITIES

X ray irradiators for industrial radiation processing are based on conversion of high energy electrons from EB accelerators into X rays. In such machines, the EB impinges on the target: an X ray converter made of a material with a high atomic number and refractory properties such as tungsten or tantalum [6.11, 6.12]. The result of this conversion is the emission of a large spectrum of photons combining the characteristic X rays of the target and bremsstrahlung photons with a maximum energy equal to the energy of the impinging electrons. In contrast to the radionuclide sources, which emit nearly monoenergetic photons, this process creates a broad energy spectrum. An extended source of X rays is produced by distributing the primary EB over an X ray converter of sufficient size. An upper energy limit of 5 MeV is often set for X ray applications to avoid, with a very high level of confidence, any induction of radioactivity in the irradiated product through photonuclear reactions. In the future an upper energy limit of 7.5 MeV might become acceptable, as the risk of induced radioactivity is insignificant.

The efficiency of conversion and the spatial distribution of X rays are the main parameters of any target for application in radiation processing. The target construction is optimized to improve its technical and economic features.

Under optimal conditions, only about 7.6% of the total EB power is converted into a forward X ray stream with electron energy of 5 MeV. Up to 76% of EB power has to be removed by a cooling system, while the remaining portion is lost by electron scattering, backscattering, etc., and absorbed in the shielding. Yet, for some radiation processing applications, X rays may offer economic and operational benefits over gamma sources (easy control of radiation, convenience of having easy-on, easy-off electric powered equipment that can operate in step with production demands). Recent developments in high power and high energy accelerators offer an opportunity to produce and use X rays for industrial applications [6.13–6.20].

Layout of an irradiator with an X ray converter is shown in Fig. 6.3. To optimize the irradiation conditions and calculate product throughput, several parameters should be taken into account, such as the density and size of the product package, radiation utilization efficiency, dose required and dose uniformity. In 2010, an EB accelerator with a beam energy of 7 MeV and an

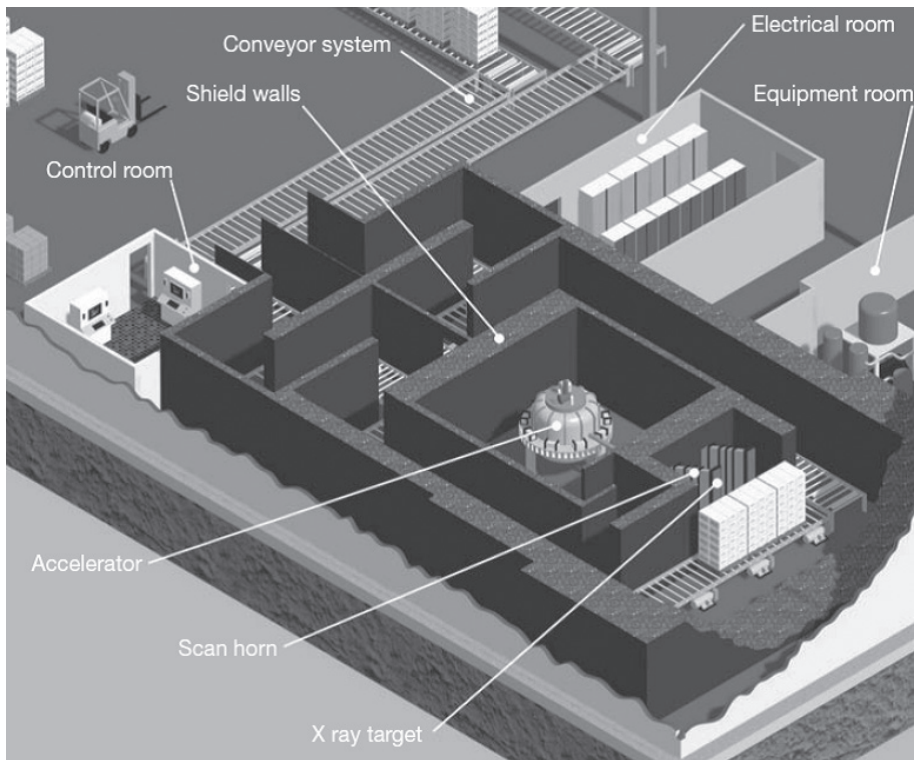


FIG. 6.3. An EB irradiator equipped with an X ray converter (courtesy of IBA, Belgium).

output of 700 kW with an X ray convertor was installed in Däniken, Switzerland. The facility permits treatment of entire pallets of products and is one of the largest systems for sterilizing pallets available today. Installations of this type can be used in disinfection and consolidation of cultural heritage artefacts similar in size to those treated with a gamma irradiator.

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Chapter 7

EFFECTS OF IONIZING RADIATION ON MATERIALS

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7.1. INTRODUCTION

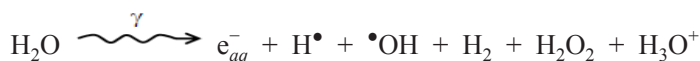
7.1.1. Biocidal effect and DNA modification

Irradiation means transferring energy through radiation to the target material. The target is the artefact, including any biodeteriogens. The primary effect of this transfer is the modification of chemical components of both biodeteriogens and the artefact. The chemical changes that occur in living organisms owing to irradiation produce biological effects. The organic molecules affected are the basic building blocks of a living organism. The most significant and precious of the cell components is the DNA macromolecule. Its function in the cell is directly linked to life as its replication is fundamental in cell multiplication. Its structure permits identification of individuals or taxonomical entities. A structural change that prevents replication of DNA leads to cell death. In the case of unicellular microorganisms (such as bacteria), the impossibility of cell division is equivalent to inactivation. The modifications caused by irradiation are directed at purine and pyrimidine bases — important parts of the DNA double helix structure. These are the most sensitive chemical bonds of the DNA molecule. A drastic DNA modification prevents replication/cell reproduction.

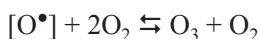
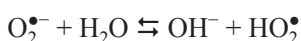
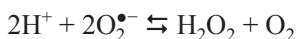
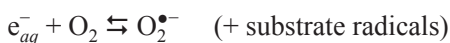
There are several conditions that cause the death of microorganisms by altering their DNA. An example is temperature — which is used in thermal

sterilization. Similarly, the process through which irradiation with ionizing radiation is used to inactivate microorganisms is termed radiation sterilization.

Ionizing radiation can interact with microorganisms in two ways: (i) direct interaction with the cell components such as DNA, and (ii) the indirect modification produced by free radicals resulting from water radiolysis. It is the latter indirect effect that is the predominant pathway of inactivation of microorganisms. Important free radicals like hydroxyl radicals (OH^\bullet) are formed in the hydration shell of the DNA molecule [7.1]. They are responsible for 90% of the DNA damage [7.2–7.5]. Although many other hypotheses have been proposed on the mechanism of cell damage by radiation, it is universally accepted that the DNA in the chromosome represents the most critical ‘target’ for ionizing radiation as damage to it causes inhibition of cell division [7.5].



In the presence of oxygen, other important radicals can be formed [7.6–7.10] according to the following reactions:



These reactions indicate that the ejected electron first is surrounded or captured by the water molecules to produce a hydrated electron, which reacts with oxygen to form the superoxide anion. According to the International Union of Pure and Applied Chemistry (IUPAC), the notation $\text{O}_2^{\bullet-}$ is recommended; however it is frequently written as O_2^- . The superoxide anion subsequently reacts with water, resulting in the formation of hydrogen peroxide. Oxygen, peroxide radicals and ozone also may be formed.

The radicals formed are the cause for the deterioration of organic molecules, as will be discussed in the coming paragraphs. Here the rule of thumb is: the more complex the organic molecule, the less energy is needed to deteriorate it.

We have started with a brief description of the effects of radiation on unicellular microorganisms because these effects are better understood in microorganisms owing to their simple structure. In the case of more evolved life forms, changes at the level of molecules trigger morphological and physiological effects at the higher levels of organization of biotic entities: cells, tissues, organs or the entire organism.

7.2. RADIOSENSITIVITY OF LIVING ORGANISMS

The biocidal effect of irradiation was first noticed at the beginning of 20th century. Mycotic skin diseases were treated with radium salts included in topical unguents [7.11, 7.12]. The initial overenthusiasm was tempered by the observation of the side effects of irradiation, which resulted in the International X-ray and Radium Protection Commission recommending a ‘tolerance dose’ [7.13]. At the same time, the biocidal effect generated important industrial applications of radiation processing: sterilization of medical devices and treatment of food.

A milestone in the basic science related to the biocidal effect of radiation was the observation that different living organisms have different behaviour following irradiation. This led to the concept of *radiosensitivity*. Also, from a pragmatic point of view, an important problem was raised: establishing the most effective treatment dose. Because the diversity of living creatures is vast, it is impossible to perform measurements on every one of them. The number of insect species alone is estimated at 30 million [7.14]. Radiosensitivity has been carefully measured only for the species relevant for or involved in applications. To establish the sterilization dose for medical devices, radiosensitivity of microorganisms, especially bacteria, has been extensively researched. Difficulties in establishing radiosensitivity are enhanced by the fact that a single insect species may have up to four morphs in its life cycle (larva, pupa, adult and egg), each with different behaviour following irradiation.

Microorganisms — fungi and bacteria — also have vegetative forms with explosive development and resistant forms (spores). However, more accurate radiosensitivity values have been obtained for microorganisms because a much better statistical approach was possible in the experiments: radiosensitivity expressed through D_{10} — a scientifically established term meaning the irradiation dose necessary to reduce the number of microorganisms by a factor of ten (an order of magnitude) (see Fig. 7.1).

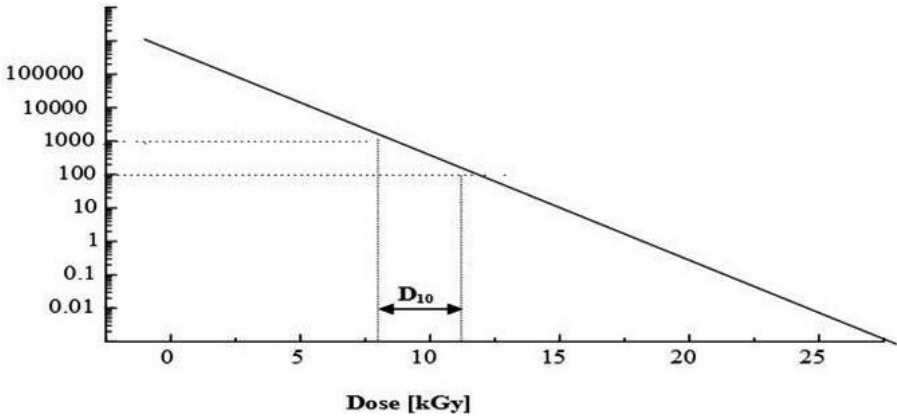


FIG. 7.1. Radiation inactivation of microorganisms; X-axis represents number of microorganisms on a logarithmic scale.

The two important industrial applications — radiation sterilization and food treatment — each have their own approach in terms of establishment and application of the treatment doses. The differences in treatment dose value are due to the different goals of the two applications and not necessarily related to the nature of the pest species (see Table 7.1).

TABLE 7.1. DOSE VALUES SIGNIFICANT FOR IRRADIATION BIOCIDAL EFFECT ON PESTS (BIODETERIOGENS) AND HUMANS

Area of application	Dose	Living organism
Insect eradication dose:		
Prescriptive in disinfestations of cultural heritage artefacts	0.5–2.0 kGy	Insects
Typical dose applied for:		
Food treatment	10 kGy	Microorganisms
Decontamination of cultural heritage artefacts		
Minimum dose applied for sterilization of medical devices	25 kGy	Microorganisms

TABLE 7.1. DOSE VALUES SIGNIFICANT FOR IRRADIATION BIOCIDAL EFFECT ON PESTS (BIODETERIOGENS) AND HUMANS (cont.)

Area of application	Dose	Living organism
<i>D</i> ₁₀ value:		
Radiosensitivity of most microorganisms (fungi and bacteria) found in food, medical devices and cultural heritage artefacts	0.1–1.0 kGy	Frequently found microorganisms
<i>LD</i> _{50/30} :		
Lethal dose 50% for humans within 30 days; important in medicine	4–6 Gy	Humans
Note: For other mammals <i>LD</i> _{50/30} is of the same order of magnitude		

Summarizing the chapter so far:

- Irradiation death is not sudden but is instead the final result of morphological and physiological disequilibrium induced by irradiation. Overall it is better likened to a disease than an airplane crash.
- The irradiation dose needed for effective biocide is best known in the cases of fungi and bacteria, for which good statistics were available.
- In Table 7.1 the term *LD*_{50/30} for the death of mammals signifies the mean value of the dose which proved to be lethal for 50% of irradiated subjects within 30 days. The concept is used in toxicology for chemicals and radiation [7.15].
- Insects are the primary biodeteriogens in museums. For this reason, studies have been pragmatically focused on their eradication. Successful treatment doses between 0.5 kGy and 2 kGy have been reported [7.16, 7.17].
- Typical *D*₁₀ values for common microorganisms found on foodstuffs, medical devices and cultural heritage artefacts are in the range of 0.1–1 kGy [7.7, 7.18].
- Food decontamination is an established radiation processing application [7.19].
- Sterilization is another established radiation processing application [7.20]. As shown in Table 7.2, the dose of 25 kGy is the minimum dose for sterilization of medical devices; it is accepted as the sterilization dose in the European Pharmacopoeia [7.21]. This dose was calculated taking into account the most radiation resistant bacteria known.

- From experiments performed to establish the radiosensitivity of living organisms, it can be noted that more evolved organisms are more sensitive to radiation — the $LD_{50/30}$ for mammals, for example, is at the level of several Gy, compared to hundreds or thousands for pests.

Therefore, radiation decontamination of cultural heritage artefacts is essentially based on similar basic knowledge and can utilize the same equipment used in the two well established industrial areas of food disinfection and sterilization of medical devices.

7.3. PREFACE TO SECONDARY EFFECTS

Despite the similarity of the intended biocidal effect in the case of irradiation decontamination of cultural heritage artefacts to those anticipated from the other applications, one very important difference is that the secondary effects in the cultural heritage artefacts due to irradiation may be unique and specific to each particular artefact. The intended biocidal effect of irradiation may be accompanied by modification of the chemical composition of the disinfected artefact. The treatment is acceptable if it does not lead to unacceptable alteration of the aesthetic and/or functional properties of the artefact. Evaluation and understanding of secondary effects is therefore essential and is discussed below.

Most important secondary effects are related to the changes in the basic polymers that constitute the organic artefacts: cellulose, lignin and proteins. These need to be evaluated for all organic materials that might be subject to irradiation, such as wood, paper, leather and textiles. Other secondary effects are related to modification in the crystalline pattern of materials, for example in gemstones and also some mineral components.

As discussed earlier, the first step in the interaction of radiation with the artefact is the formation of free radicals. These are very reactive chemical species that have a short lifetime of about 10^{-3} sec [7.22]. In this very short time they react, producing all effects — intended and secondary — in the artefact. The interaction of free radicals with polymers leads to both chain scission and cross-linking reactions. Although both modification types are present, one will generally dominate, determining the final effect. The balance between the two reactions may depend on the nature of the substrate as well as irradiation conditions such as radiation dose, dose rate and ambient conditions. Chain scission is associated with weakening of mechanical properties, while cross-linking improves mechanical properties.

Most free radicals produced by irradiation disappear by quick reactions with surrounding substances or with themselves. A small number are trapped,

existing in a 'dormant' form for a time. Trapped free radicals may be detected by electron paramagnetic resonance (EPR), also called electron spin resonance.

Trapping of free radicals is possible in special 'cages' that occur only in crystalline regions of some substances such as cellulose (paper, wood) or hydroxyapatite (bones) [7.23]. Proteins have many fewer crystalline regions. Consequently, leather, parchment, wool and silk have less ability to trap free radicals. Free radicals do not stay trapped forever. In time, they escape and become reactive. This tendency for free radicals to escape over time is cause for concern on the part of conservators/restorers. Although irradiation can degrade artefacts, its effects are less severe than those of mould, for example. Mould also produces radicals and over time will fully degrade the object. Free radicals produced by irradiation are utilized beneficially in irradiation polymerization for consolidation of porous structures.

Besides the above mentioned important reactions responsible for the biocidal and secondary effects, irradiation has important effects on DNA and on ^{14}C dating.

7.3.1. DNA of the original artefact

DNA structure is like a personal signature. For this reason, its analysis is a tool in forensic identification. Before DNA analysis can be undertaken, the raw material for identification frequently has to be disinfected (for example in the case of bodies in putrefaction). Research has shown that DNA analysis is still possible even after irradiation at doses in the range of 50 kGy [7.24–7.26].

Some archaeological findings contain preserved ancient macromolecules (fossil DNA, collagen) which can offer precious information. An important open question is whether irradiation disinfection will modify this information.

'Fossil DNA' is created over time by natural degradation of initial DNA. Analysis may reveal the animal class to which the remains belong. The DNA backbone breaks naturally at its weakest chemical bonds.

No study of effects of irradiation on ancient DNA has yet been presented. However, samples were collected from a baby mammoth before and after irradiation with 20 kGy in Grenoble in 2010 [7.27]. Results of these studies will provide evidence of how ancient DNA has been affected by gamma irradiation.

7.3.2. ^{14}C dating

Collagen extracted from fossil bones is used in accelerator mass spectrometry dating. The dating method is based on measuring the isotopic rate of ^{14}C /total carbon. Neither the ^{14}C content nor the total carbon content is affected by irradiation at any dose.

Pottery has no organic components and therefore it is not necessary to decontaminate it using ionizing radiation. In fact, irradiating ceramics before carrying out any luminescence dating can result in inaccurate results. For example, thermoluminescence dating and optically stimulated luminescence dating are based on measurement of modifications that have been induced by natural irradiation in quartz or feldspar since the artefact was heated. Thus, applying irradiation before this sort of dating would lead to false results. There have been cases in which ceramic fakes were irradiated, resulting in misleading data regarding their origin.

7.4. SECONDARY EFFECTS OF IONIZING RADIATION

From the restorer's point of view, it is essential to understand the beneficial effects of irradiation as well as its effect on the functional properties of the artefact. The following subsections, organized by type of material, summarize the secondary effects of ionizing radiation that may affect the functional or decorative properties of the artefact.

7.4.1. Lignocellulose and cellulose materials including textiles

Lignocellulose materials are materials of several closely related substances constituting the woody cell walls of plants and consisting of cellulose intimately associated with lignin.

Wood is one of the most important products of nature, and has a unique ultrastructure. There are many different kinds of wood, as there are over 30 000 different tree species known. These can be divided into two main groups: hardwoods (angiosperms) and softwoods (gymnosperms or coniferous woods) [7.28, 7.29]. Examples of hardwoods are beech and eucalypt; examples of softwoods are Douglas fir and pine. In the wood cell wall layers there is a matrix consisting of cellulose microfibrils embedded in substances such as hemicellulose and the encrusting material lignin. The primary function of cellulose is to give a high tensile stiffness and strength to the tree. Lignin provides support to the slender cellulose fibrils and prevents them from buckling. Hemicelluloses, or heteropolysaccharides, serve as coupling agents linking cellulose and lignin [7.30].

Wood, paper and textiles made of cotton have cellulose as their main component. Cellulose is a linear, high molecular weight biopolymer, consisting of β -D-glucopyranose units linked by β -(1,4) glycosidic bonds (see Fig. 7.2). The two ends of the polymer are different. On the left end (at C₄ position of the ring structure) is a non-reducing alcoholic hydroxyl group, while on the right

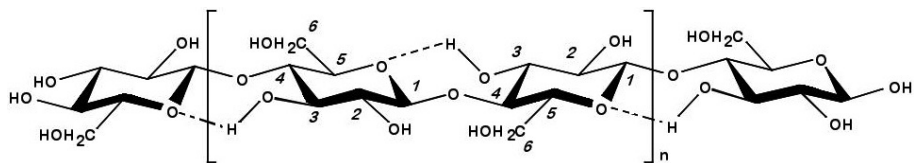


FIG. 7.2. The configuration of cellulose. In the middle the repeating β -glucose units are presented. The dotted lines are so called H-bridges.

end (at C_1 position of the ring structure), a reducing alcoholic hydroxyl group is present. This group is actually a hemiacetal group. The main difference between wood and cotton cellulose is degree of polymerization, or the number of β -glucose units in one polymer, which may vary from 50 000 to 2 500 000 [7.28, 7.29].

As explained above, the principal reactions that may occur are caused by radicals, and therefore oxidation can be seen as the leading factor in degradation, followed by acidification. Radicals may remain stable for a short period of time in the crystalline sections of cellulose [7.31]. According to Young and Rowell, reactions may result in the formation of D-glucose (the leading final degradation product), along with a number of low molecular weight products [7.32]. However, as wood and paper do not contain 100% cellulose, many other reactions may occur, including both oxidation and (acid catalysed) hydrolysis reactions, depending on the degree of crystallinity of the cellulose [7.33, 7.34]. For example, the less crystalline regions are more sensitive to degradation through hydrolysis than the crystalline regions. Cotton cellulose contains more crystalline regions than cellulose from wood [7.28]. Oxidation of cellulose may start at the reducing alcoholic hydroxyl group. On the other hand, if (owing to the irradiation) hydroperoxide radicals are generated in the fibrous structure, lower mass polysaccharides are formed owing to the ionic hydrolytic degradation initiated via terminal groups in cellulose [7.35]. It has been suggested that the main reaction leading to degradation of cellulose involves abstraction of carbon bound hydrogen atoms by hydroxyl radicals. Therefore, hydroxyalkyl radicals should be formed and subsequently converted to the corresponding carboxyl groups by oxygen. The carboxyl groups formed at the C_2 , C_3 and C_6 atoms of the cellulose molecule may result in the cleavage of the glycosidic linkage [7.34, 7.36].

Kořar et al. proved that superoxide radicals have an important role as precursors of a luminescent species, and thus an important role in the oxidative degradation of cellulose [7.37, 7.38]. In addition to being formed as a result of ionizing radiation such as gamma radiation, radicals in (ligno)cellulose materials can also be formed owing to the presence of fungi (Fig. 7.3). Therefore, the deterioration of these materials by radicals should not be attributed only to ionizing radiation [7.39, 7.40]. Exposition of cellulose and other polysaccharides

to sources with a wavelength beneath 330–340 nm may also result in the formation of radicals [7.29, 7.39, 7.41, 7.42].

Lignin is a complex biopolymer consisting of monomeric phenylpropane units. The polymeric structure differs in hardwoods and softwoods. One of the phenylpropane units is coniferyl alcohol (Fig. 7.4). Steelink showed that stable free radicals are present in lignin. He observed using model phenols that α -carbonyl syringol derivatives can be oxidized to remarkably stable radicals in solution. Guaiacol analogues did not form radicals under similar conditions, while disyringylmethane formed a solid, stable free radical, which may be the species responsible for the high radical content of hardwood kraft lignin [7.43]. Studies on the antioxidant activity of 14 lignin samples obtained from apple tree

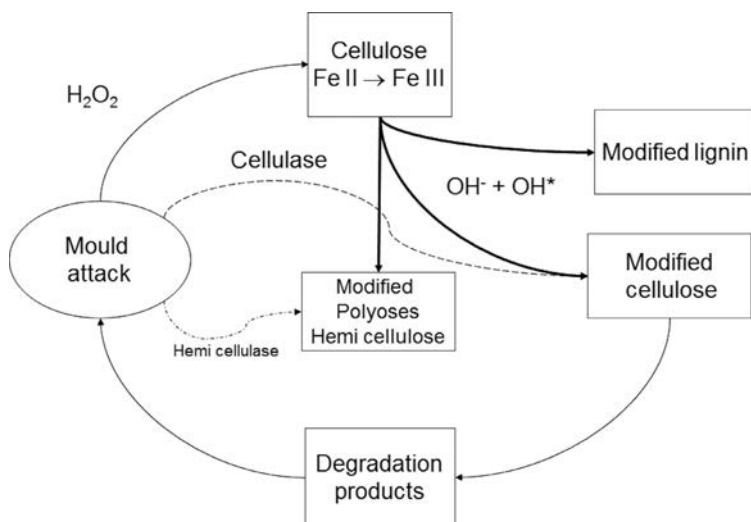


FIG. 7.3. Hypothetical model of the formation of peroxides and radicals by mould initiating paper degradation [7.39].

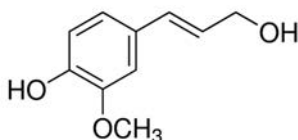


FIG. 7.4. Coniferyl alcohol, one of the building blocks of lignin.

pruning showed that the antioxidant effectiveness of lignin is comparable with that of a powerful natural antioxidant such as catechin [7.44]. Thus, oxidative degradation is reduced in wood and lignin-containing materials, as lignin is able to act as a radical scavenger. Lignin-containing materials may therefore be protected in a natural way from radiation.

Severiano et al. in 2010 concluded that a radiation dose up to 100 kGy did not influence the properties of wood species such as Cedro Rosa (*Cedrella fissilis*) and imbuia (*Ocotea porosa*) [7.45]. In other work, Severiano et al. further suggested that wooden artefacts can therefore be irradiated multiple times if a reinfestation occurs without significant changes in the mechanical properties of the wood. However, some minor chemical changes were observed by Havermans et al. in 2007 [7.46]. They found that pine and redwood became somewhat more acidic after irradiation at 60 kGy, with the pH of pinewood changing from 5.2 before irradiation to 4.8 after irradiation at 60 kGy, and that of redwood changing from 4.4 before irradiation to 4.3 after irradiation at 60 kGy.

More comprehensive research has been focused on the disinfection of paper using gamma irradiation. In 1972, Pavon Flores [7.47] applied gamma radiation as a fungicide and studied its effects on paper. Based on experimental work, the lethal dose for fungus was established, and subsequently this dose was applied to study the effect on modern paper. Doses of 5, 7, 9 and 18 kGy were applied, and it was concluded that these high doses killed the fungus throughout the inside structure of the paper. The evaluation was done using artificial ageing, and additionally it was found that lignin-containing materials showed better resistance to irradiation than those containing only cellulose. It was recommended that the research be repeated using naturally aged and mouldy papers to verify the work, and that this method be applied for the disinfection of certain types of documents. Horakova and Martinek [7.48] applied up to 26 kGy to investigate its effect on mildew affected materials in archival records. They concluded that most of the mould species tested (such as *Aspergillus flavus* and *Aspergillus niger*) could be effectively killed at 8 kGy, and that there were no significant changes in the paper materials tested (Whatman filter paper, rag paper and wood-free calendered paper). A dose of 10 kGy was applied by Butterfield [7.49] in 1987 to investigate the long term effects of irradiation on paper. He concluded that irradiation and thermal ageing have a synergistic effect: in summary, the total decrease in mechanical properties of irradiated artificially aged paper is higher than the sum of those of the samples treated by either irradiation or artificial ageing. In 1992, Hofenk de Graaff et al. [7.50] published research using 10 kGy gamma irradiation and different paper grades. However, data were evaluated after artificial ageing only (so called dry and wet artificial ageing), and although the data presentation suggested that irradiation caused serious degradation, no statistical uncertainty of the analyses was included. A small review was published by Sinco in 2000, in

which different works on gamma irradiation were discussed. Original documents affected by flooding or other phenomena were treated at a dose up to 15 kGy, and after many years the original books were still in good, consultable condition [7.51]. Nevertheless, structural modifications of cellulose do take place owing to irradiation with gamma rays. Baccaro et al. [7.52] investigated molecular changes using thermogravimetry (TG), derivative thermogravimetry (DTG) and Fourier transform infrared (FTIR) spectroscopy. An increase of carbonyl bonds (C=O) was observed owing to breakage of the glycosidic bonds related to oxidative degradation at an extremely high dose up to 500 kGy, and an increase of the crystallinity index was observed, which was attributed to the occurrence of cross-linking reactions. Even at a dose of 4 kGy, they observed the formation of carbonyl groups. Flieder et al. [7.53] also concluded that changes in cellulose occurred at a dose of 3 kGy, but that a dose of 0.5 kGy could be sufficient to kill insects, and resulted in no significant changes in the cellulose matrix.

Moise et al. [7.54] applied a dose of 10 kGy to study the structural changes using thermal and calorimetric studies. They concluded that changes in the cellulose structure owing to irradiation are mainly driven by modifications in the hydrogen bond structure. At low dose (e.g. 10 kGy), they observed that the original hydrogen bond structure remained in the irradiated filter paper cellulose; however there was some decrease in the degree of polymerization. By means of these two observed phenomena they explained why the mechanical properties of filter paper cellulose were not changed by low dose irradiation.

In the last 15 years, Adamo et al. have published much work dedicated to the effects of gamma irradiation on paper stability. In 2001 [7.55] they concluded that significant changes could be observed in paper materials when they were irradiated using a dose higher than 10 kGy. Additionally, they concluded that these high doses (up to 200 kGy) are not necessary for killing mould and insects in archives and libraries. They also found that at extremely high doses of 100–200 kGy, paper became more susceptible to mould owing to polymeric changes. This was not observed at lower dose (i.e. 10 kGy) [7.56]. They reached similar conclusions in a study in 1998 [7.57]. Cellulose filter paper was irradiated with a dose up to 10 kGy. No significant effect on the mechanical properties was observed. Also, no significant change in acidity was observed owing to irradiation. Studies on the effects of a dose up to 10 kGy on cellulose degradation and stabilization were also carried out by Area et al. [7.58] and Havermans [7.59, 7.60], and they concluded similarly that no significant chemical and physical changes could be observed owing to a treatment using a dose up to 10 kGy. The principal changes observed that could be attributed to the gamma irradiation concerned the degree of polymerization and the formation of smaller molecules, but did not affect the daily use of the artefact.

Havermans et al. [7.61] reported that irradiation at 10 kGy slightly increased the emission of volatiles, and in particular acetic acid and n-pentanal, suggesting oxidative deterioration.

The work of Moise et al. in 2012 [7.62] confirmed that the uncertainty of the mechanical property measurements was higher than the degradation induced by 15 kGy of gamma radiation and that in the case of original papers affected by mould, this could be even higher. They concluded that a dose range of 5–7 kGy can ensure a significant decrease of bioburden and minimize the negative effects (i.e. paper degradation). This range is in agreement with results presented by Havermans in 2011 [7.59]. In the Netherlands, therefore, the effective average dose has been set to 8 ± 2 kGy owing to scattering of the observed dose in bulk original paper materials treated on pallets.

Based on the research described above, it is clear that irradiation causes radicals to be formed in the (ligno)cellulose matrix. These radicals are able to initiate oxidative degradation reactions similar to those caused by living mould that is present in the substrate. Most studies are carried out using highly crystalline filter paper. These materials are able to ‘hold’ radicals for a short period of time, and therefore it is suggested that materials that are naturally aged and contain less crystalline cellulose should be less affected by these radicals. It is to be kept in mind that mould causes severe degradation of paper. This degradation is more severe than that caused by killing the mould at an early stage (e.g. by gamma irradiation), as will be demonstrated later in the case studies (Chapters 10–26). Michaelsen et al. [7.63] compared freeze drying, gamma rays, and ethylene oxide fumigation and monitored samples to assess the short and long term effectiveness of these techniques in inhibiting fungal growth by studying both DNA and RNA changes after treatment. They concluded that gamma rays can be used to treat large amounts of paper simultaneously and without subsequent chemical hazard and should be considered as a decontamination treatment to remove biodeteriogenous microorganisms or reduce them to a controllable level. Freeze drying, on the other hand, can be applied only to stop heavy mould before further treatment.

7.4.1.1. Textiles

Natural textile fibres can be classified into cellulosic fibres such as cotton, flax and hemp, and protein fibres such as wool and silk. These fibres are made of linear long chain polymers, the macromolecules being aligned with the long axis. In general, the higher the degree of orientation and the molecular length in these fibres, the stronger they are. Molecular symmetry of the linear molecule enhances the possibility of the formation of crystalline areas within the fibre structure. There are areas where the molecules may not be aligned and where no

crystallinity exists; such parts are referred to as amorphous areas, and elongation characteristics are primarily associated with this part of the fibre structure. Because of its penetrating ability, high energy radiation does not concentrate its effects on any particular portion of the fibre — the attack is a random one. Radiation effects on fibres can be determined in several ways; tensile strength, elongation at break and modulus are used as the critical physical properties. A decrease in strength is indicative of a decrease in average molecular length or of chain scission; an increase in modulus is regarded as evidence of cross-linking. Oxidation reactions may also occur at irradiation and may influence fibre properties. The major structural changes that occur in cotton cellulose during gamma irradiation in addition to chain cleavage are the formation of carbonyl and carboxyl groups. The dose curves for these changes are all similar in shape. Thus the cellulose chain is not significantly affected chemically until it receives a dose greater than 10 kGy. After this, the number of depolymerizations, the number of carboxyl groups formed and the number of carbonyl groups formed increase rapidly with further increases in dose [7.64].

High dose gamma irradiation (21–74 kGy) used for quarantine treatment of cotton does not have significant impact on the yarn's evenness and imperfection values, but the effect on yarn strength and elongation, as well as fabric strength and abrasion resistance, is important [7.65].

Research carried out in the 1960s showed that when wool is subjected to radiation in a nuclear reactor, the first noticeable change in its properties is in its susceptibility to damage by alkali [7.64]. At radiation doses above 100 kGy, the increase in susceptibility to alkali was accompanied by a decrease in the 30% index, which is defined as the ratio of the work necessary to extend a single treated fibre by 30% in water to the work necessary to extend an untreated fibre. Thus, a number less than 1 indicates damage to the fibre. The shape of the stress–strain curve of the exposed fibre, however, was identical to that of unexposed fibre, and the long term elastic recovery was not lost. This indicated that irradiation did not disrupt the folded chain configuration of keratin molecules that is believed to account for the long range recovery properties of wool. Low doses of radiation do not appreciably damage the fibre, and a dose of about 50 kGy was required to produce a perceptible change [7.64].

More recent research combining thermal analysis (TG and DTG), infrared spectroscopy (attenuated total reflectance FTIR spectroscopy) and mechanical tests on samples of silk and wool fabrics subjected to accelerated ageing and then irradiated with gamma ray doses of 10 and 25 kGy emphasized that increasing the irradiation dose above 10 kGy produces loss of elasticity and affects the mechanical resistance of the yarns [7.66].

Silk is less stable than wool under the same conditions of exposure, as evidenced by changes in strength, but it is slightly more stable than cellulosic

fibres. There is evidence that some molecular change other than chain scission does occur because exposed fibres are insoluble in zinc chloride solution under conditions where the unexposed fibres are soluble [7.64, 7.67–7.69].

Textiles are frequently dyed, and ancient fibres are often coloured with water soluble natural dyes extracted from plants or some animal species. The secondary effects of irradiation on textile dyes are discussed elsewhere and have to be carefully considered. It is suggested that the highest practical level of gamma radiation exposure should not exceed 10 kGy for cotton, silk and wool [7.64, 7.66].

7.4.2. Pigmented and dyed items

In easel or wood paintings, and even in cave paintings, the colour is given by inorganic, crystalline substances called pigments, which consist of oxides, hydroxides, salts and charcoal. Textiles, leather and paper are sometimes coloured with water soluble substances called dyes.

The pigment is ground into a fine powder and mixed with a binder. A pigment is not soluble in the binder. It forms a uniform suspension called paint. The colour of the paint is the colour of the pigment. Chemical composition of pigments is not affected by irradiation, as is the case with all inorganic substances. An assessment of possible colour changes produced by irradiation was made on paints — pigment and binder blends. No specific colour was substantially changed by irradiation up to the rather high dose of 36 kGy [7.70]. Pigments' behaviour under irradiation is similar to that of opaque gems such as lapis lazuli and turquoise.

Unlike pigments, dyes are of organic origin. Dyes are extracted from plants and animals such as insects and gastropods. They are also called biological pigments. The chemical composition and colour of dyes may be modified by irradiation. For this reason, tests are necessary before radiation decontamination. Care must be taken with dyed artefacts. While the low doses needed for insect eradication seem innocuous, recent research has reported a notable discolouration from red to yellow of henna dyed cotton, measured in ΔE at around 5 to 10 at doses between 5 and 25 kGy [7.71]. However, it is important to note that some dyes are reported to change colour at the same order of magnitude following treatment with the alternative anoxia disinfestation method, which in turn is only effective for insect eradication [7.72–7.74].

Special care has to be taken with carmine — a pigment which is also a dye. It is a lake pigment that is very expensive and of organic origin, produced from insects. Although there are no known specific tests, theoretically its colour could change as a result of irradiation.

For the same reasons, increased attention should be given to modern paintings, which may contain pigments of organic origin. In the 1950s, acrylic paints appeared on the market, containing only synthetic organic colourants. As far as the authors of this book know, no scientific publications on secondary effects of irradiation on acrylic paints exist.

7.4.3. Varnishes and binders

The behaviour of varnishes under irradiation may be more complex, as they are transparent layers. Depending on their thickness, it may be feared that colour centres in the varnishes will be activated and become perceptible. Among different varnishes and binders that have been tested, only gum Arabic has shown a noteworthy dependence on irradiation, with for instance a colour difference of 2.48 CIEL*a*b* units observed at 20 kGy when applied thickly (12 layers, 110 μm). The same binder applied more thinly shows no detectable change ($\Delta E = 1.50$ for 6 layers, 30 μm at the same dose). The same results (i.e. no visible effects) were obtained in a study in 2012 involving gum Arabic with animal glue and egg yolk irradiated at doses up to 25 kGy [7.75].

Furthermore, possible structural weakness in ground layers, binders or varnishes after irradiation must also be considered. However, such behaviour is not expected to appear with doses less than several tens of kGy, which is well higher than the doses we are interested in. An Italian study in the 1970s [7.76] revealed that fresh rabbit glue lost some adhesive power following irradiation at 10 kGy. No other problem has been reported for the many materials treated, or in experiments carried out in laboratories.

Another family of materials has to be investigated in terms of radiation effects: natural or synthetic materials used as varnishes or adhesives/consolidants in restoration and conservation (Fig. 7.5). Most of these constituents have been designed to be highly stable, and this is the case with regard to biocidal doses. No loss of their mechanical functions has been reported after irradiation in the case of adhesives, sealants, mastic coatings, consolidants or other filling materials. A significant case of colour change, however, was detected with a special filling coating: white Modostuc [7.77]. Tests on other materials commonly used in conservation, such as Paraloid B72 and Plextol B500 resin, Toupret filler and Lefranc & Bourgeois synthetic 'gesso', did not reveal any colour problems. Retouching colours such as acrylic Liquitex also demonstrate excellent stability after irradiation. Interestingly, the reversibility of colour changes in four conservation products (Paraloid B72, ketone-N resin Laropal K80, polyvinyl acetate Mowilith 30 and polyethylene glycol) has been confirmed after irradiation with doses of up to 50 kGy [7.78].

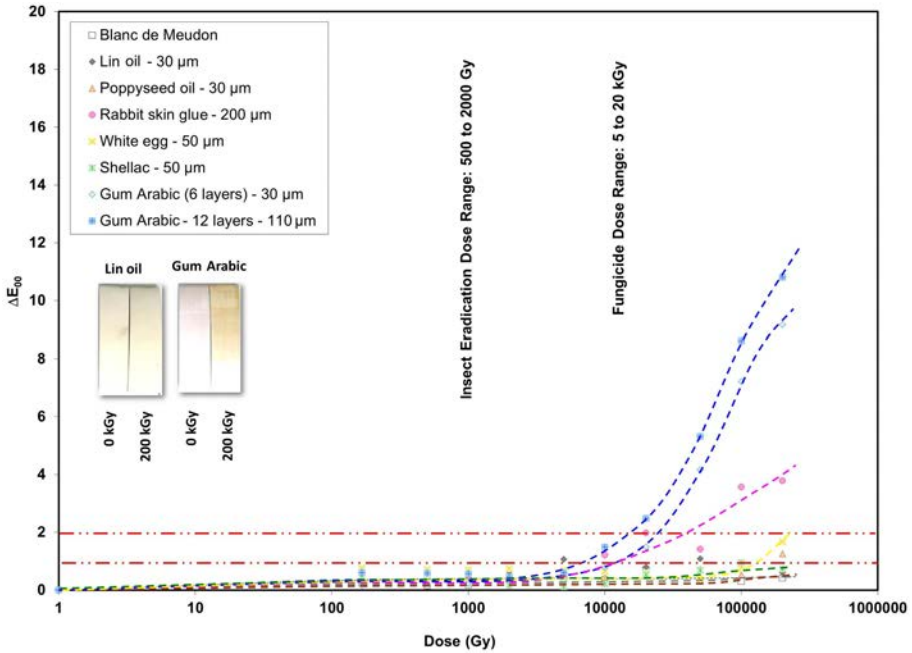


FIG. 7.5. Colour changes of some binders and varnishes as a function of gamma ray doses.

7.4.4. Glasses and gemstones

Under irradiation at doses of even less than 1 kGy (insect eradication dose), glasses [7.79, 7.80] and gemstones [7.81] may undergo partially reversible changes in colour, due to modifications in optical absorption after the creation of colour centres, which involve one electron missing from a normally occupied position. Colour centres are activated to give colour to transparent colourless gems such as natural white topaz [7.82], but huge irradiation doses are needed [7.83]. Glass usually becomes dark brown after irradiation at sterilization dose levels. The results of colour change measurements for some transparent materials (glass, silica, quartz and fluorite) after irradiation are presented in Fig. 7.6.

On the other hand, coloured opaque materials are rarely affected by irradiation. Opaque gems such as lapis lazuli, jasper, jade, turquoise and tiger's eye can be irradiated at 10 kGy without any modification.

7.4.5. Leather, fur and parchment

There are few scientific papers focused on leather and parchment decontamination by irradiation. This may be explained by the fact that leather, fur

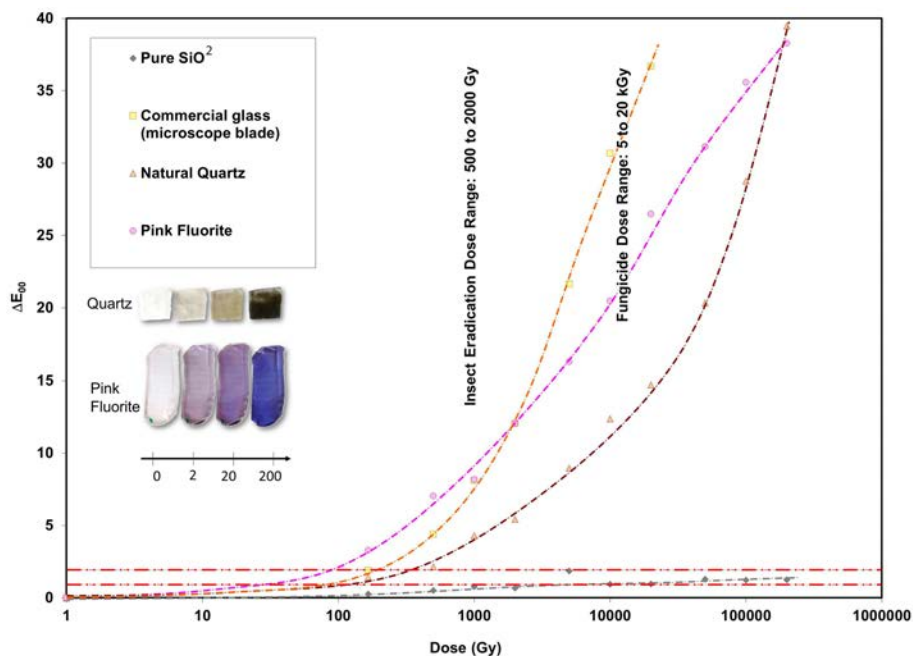


FIG. 7.6. Colour changes of some transparent materials as a function of gamma ray doses.

and parchment do not contain enough water for the growth of microorganisms. Only a small number of insects feed on leather and parchment. However, leather in book bindings, especially in wood–leather book bindings, is sometimes a collateral victim of insects that eat glue and/or wood and therefore also deteriorate the leather book binding.

More studies were focused on irradiation of pure collagen because of its use for medical purposes. Pure collagen proved to be very resistant to irradiation. Collagen sponges (a medical product used in wound treatment) are sterilized by irradiation at doses between 25 and 50 kGy. The same sterilization process and doses are used for allogeneic tissue grafts kept sterile in tissue banks [7.84, 7.85].

In light of the favourable conclusions obtained by studying the irradiation of pure collagen, some papers dedicated to leather and parchment reported using radiation doses far beyond those necessary for decontamination. The two experiment groups offered complementary information related to modification of collagen solubility, crystalline phase structure, shrinkage temperature and mechanical properties of leather and parchment. In 1988, Chahine and Vilmont [7.86] presented a pertinent review of the above information. More recent studies have shown that there is a direct relation between leather degradation and

the shrinkage temperature [7.87]. Measuring extractable monomers, including tannins, is among the accepted methods of degradation evaluation [7.88]. In an attempt to identify new relevant methods for investigation of secondary effects on leather due to irradiation at 10–25 kGy, attenuated total reflectance FTIR spectroscopy was used [7.89]. In another recent paper, irradiation effects on the colour and texture of parchment were evaluated (doses: 10 kGy to 30 kGy). A texture analyser was used to determine hardness and springiness. The colour modification was evaluated with an electronic colorimeter [7.90]. Based on these studies, it has been concluded that the functional properties of leather and parchment, including the aesthetic properties, are insignificantly affected by decontamination using radiation at doses up to 10 kGy.

7.4.6. Mummies and taxidermy specimens

Mummies are dead human or animal bodies whose soft tissues have been preserved from decomposition thanks to conditions that prevent normal biodegradation. This may be intentional, for instance owing to the use of chemicals, or natural, because of extreme conditions such as frost, very low humidity or lack of air, as in the case of mummies found in bogs. Such conditions, however, are usually fragile. Biodegradation can quickly resume if the equilibrium is broken. Irradiation is one way to stop further infestation. However, as irradiation has no preventive effect, conservation will depend on finding ways of establishing a new equilibrium to prevent further active contamination.

Furthermore, gamma irradiation has been recognized as a benchmark for disinfection since the mummy of Ramses II was treated in this way [7.91]. An extensive study was conducted before this mummy received gamma treatment, involving many laboratories and using more than a hundred samples from other mummies. The characteristics of many components were studied after irradiation, such as hair, skin, muscle, bone, teeth and even other organs such as the liver, kidney and heart. Two less prestigious ‘study’ mummies were also wholly irradiated. Mechanical and chemical tests were carried out directly on fragments and hair belonging to the mummy of Ramses II. All these studies concluded that an 18 kGy gamma ray treatment was effective and would not modify any components of the mummy. It should be noted, however, that the effects of irradiation on genetic information were not considered at that time. This particular problem has been discussed in this section and it was noted that information can still be extracted from irradiated DNA. It may therefore be accepted that gamma irradiation at fungicide and up to bactericide doses is a treatment suited to mummies. But these conclusions can also be extended to many other areas, for example disinfection of archaeological bones and naturalized furry animals.

Even taxidermic feather specimens have been treated successfully. Over more than 40 years of experience in France, the only problem ever encountered concerned a tortoiseshell specimen that browned slightly after irradiation. However, care must be taken in particular with disinfection doses of the order of 10 kGy and more, because the resins used in taxidermy and other sizing or filling materials used in both modern and older processes may, paradoxically, be more sensitive than animal components.

Lastly, the conditions in which the mummies or specimens are kept are an element of decisive importance. Such fragile items must only be irradiated with the aim of stopping a proven infestation. And as this will not modify the appetite of invasive organisms for these materials, preventive conservation is necessary after the current infestation has been stopped by curative irradiation.

7.4.7. Waterlogged archaeological organic material

Once excavated from archaeological sites, waterlogged organic materials are very susceptible to microorganism growth when in contact with air. Gamma irradiation has been applied to prevent biological growth in timbers while they are stored in plastic bags [7.92]. This type of treatment is only undertaken in some complex cases. This may involve items whose sources of biological contamination are located inside the artefact and are therefore difficult to reach by conventional means.

The absorbed dose necessary to inactivate all wood decay organisms tested in the wet wood study was established as 15 kGy. However, large items are difficult to treat. It is necessary to reach high doses in a short time, while keeping the wood wet. The density of the waterlogged wood material itself generates a significant shield against gamma radiation. No adverse effects on the physical properties of slightly or heavily degraded waterlogged archaeological wood were detected at doses up to 100 kGy. The appearance of slightly and heavily degraded waterlogged wood samples was not affected by gamma irradiation at doses up to 250 kGy. Treated wrapped timbers require no special storage environment; however, the wrapping must remain intact to prevent recolonisation by biodeteriogens.

7.4.8. Photographic materials

In classic photographic papers and films, the image is made up of silver particles or colourants, finely distributed in one or more layers of gelatin.

Gelatin is a hydrophilic, transparent and colourless substance, obtained from the collagen in skin, bone and other animal tissues. Owing to very poor

mechanical properties, gelatin was placed on a support of paper in the case of photos or on plastic in the case of film.

An example of the different layers of photographic materials is given in Fig. 7.7. In general, these include the substrate or carrier layer, an adhesive layer and the image holding layer. For synthetic polymer films, an anti-halo layer is also included.

Under normal storage conditions, photographic materials are stable. However, the gelatin's hygroscopicity makes these materials susceptible to biodegradation, particularly fungal attack. An emergency situation can be triggered by a flood for instance. This was the case with the National Film Archive of Romania, a story detailed in Chapter 13. Tests for evaluation of secondary effects were undertaken on this occasion. They targeted both characteristics of the gelatin layer (colour changes, ageing), as well as those related to the plastic support (mechanical tests, the distance between the holes for presentation, identification of trapped free radicals). They proved that decontamination by irradiation using an exceptional high dose (lower dose limit (D_{\min}) = 25 kGy; upper dose limit (D_{\max}) = 50 kGy) produced acceptable side effects (e.g. mechanical changes <6%). Experiments and decontamination treatment were conducted only on film with polyester support [7.93].

To study the effects of gamma radiation on the stability of photographic materials, different experiments were carried out by Havermans and Abdul Aziz [7.94].

Image layer: 5–20 μm
Adhesive layer
Carrier (cellulose acetate): 80–300 μm
Anti-halo layer

FIG. 7.7. An example of the different layers of photographic materials.

It was expected that delamination could occur owing to irradiation, and therefore delamination tests were carried out as shown in Fig. 7.8. Tensile tests were carried out by pulling the ‘tongue’ from the carrier layer, in this case a paper based carrier. Colour printed artefacts were made and subjected to a gamma irradiation dose of 0, 6, 10 and 60 kGy. The materials and techniques used to create the photos that were tested were chosen according to the internal guidelines of the conservation workshop of the Nederlands Fotomuseum in Rotterdam.

The results showed that the tensile strength needed to pull the tongue from the carrier increased with increasing dose, showing that instead of being degraded, the bonding of the layers actually improved, owing to possible cross-linking reactions. At no dose the tensile strength needed was 11 N, while at a dose of 10 kGy it was 15 N.

The effect of ageing following irradiation was investigated. Samples of colour images were stored in the dark for two years after treatment, after which the colour density was investigated using a Macbeth TR-900 series densitometer as used at the conservation workshop in the Nederlands Fotomuseum. It was remarkable that only for the high dose (i.e. 60 kGy) was discolouration observed between irradiated and non-irradiated artefacts.

For a dose up to 10 kGy, no significant changes of the colours (white, blue, light blue, red, pink, yellow, light yellow, grey and black) could be observed between irradiated and non-irradiated artefacts [7.95].

7.4.9. Contemporary art

Contemporary art is art created by artists living today. Humans have always tried to improve natural materials, resulting in ceramics, glass, bronze, iron, tanned leather, paper, Roman concrete and many others. Thus it can be

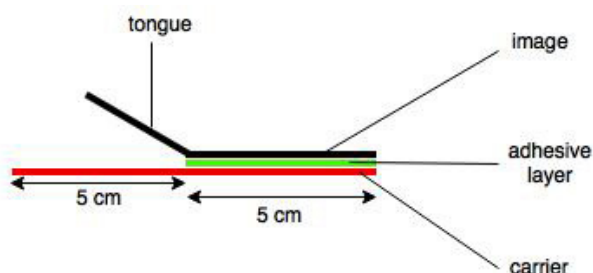


FIG. 7.8. Set-up for testing the delamination of film materials. The tensile test equipment was put on the tongue (artificially created on the sample of the photographic materials) and on the carrier, which was a paper based layer.

said that humans have produced and used new materials continually. In the 1920s–1930s, significant advances occurred in several industries, leading to development of modified natural materials or synthetic materials like rubber, plastics, fibres, coatings and adhesives [7.96]. An increasing number of novel materials, mainly synthetic polymers, have been introduced in all areas of life, including art. Synthetic polymers are not biodegradable; therefore there is no need to decontaminate them by irradiation. However, they can be subjected to irradiation when they are part of composite objects. Examples include motion picture film materials (discussed in Section 7.4.8) and acrylic paints (mentioned in Section 7.4.2). Table 7.2 contains some general information about polymeric materials frequently identified in modern or contemporary art objects.

TABLE 7.2. POLYMERS APPEARING FREQUENTLY IN MODERN OR CONTEMPORARY ART OBJECTS

Polymer	Classical abbreviation	Main trade names
Cellulose triacetate	CTA	
Nitrocellulose		Celluloid
Phenol formaldehyde	PF	Bakelite
Polyamide 11	PA 11	Rilsan
Polyamide 12/12	PA 12/12	
Polyamide 6/12	PA 6/12	Nylon 6/12
Polyamide 6/6	PA 6/6	Nylon, Technyl, Ultramid, Amilan, Durethan, Akulon, Technyl, Zytel
Polycarbonate	PC	Lexan, Makrolon
Polyethylene	PE	Tyvek
Polyethylene terephthalate	PET	Estar, Dacron, Terylene
Polyimide	PI	Kapton
Polymethyl methacrylate	PMMA	Lucite, Perspex, Plexiglas, Altuglas, Acrylite

TABLE 7.2. POLYMERS APPEARING FREQUENTLY IN MODERN OR CONTEMPORARY ART OBJECTS (cont.)

Polymer	Classical abbreviation	Main trade names
Polyoxymethylene	POM	Delrin, Celcon
Polyparaphenylene terephthalamide		Kevlar, Twaron
Polypropylene	PP	Hostalen
Polystyrene	PS	
Polytetrafluoroethylene	PTFE	Teflon, Gore-Tex, Fluon, Halon, Hostaflon
Polyurethane	PUR	
Polyvinyl chloride	PVC	
Regenerated cellulose	RC	Viscose, Rayon, Cellophane, Lyocell, Tencel
Urea formaldehyde	UF	

Some polymers can be affected by irradiation and therefore should preferably not be treated [7.97, 7.98]. These polymers are:

- Cellulose nitrate, as this polymer may become etched [7.99].
- Fluoropolymers such as polytetrafluoroethylene, as their mechanical properties may be drastically affected through chain scission reactions that may occur even at low doses.
- Polyvinyl chloride, as transparent pieces may become yellow because of free chlorine molecules that appear in the system. However, mechanical properties are not affected, even at the sterilization dose (i.e. 25–50 kGy).
- Polypropylene and phenol formaldehyde, as cross-linking reactions may occur and therefore these polymers may become brittle at the sterilization dose.

The most radiation resistant polymers are polystyrene, polyethylene, polyimide and polyethylene terephthalate (PET), which can be irradiated

at up to 100 kGy without notable secondary effects. With the exception of polytetrafluoroethylene, all other plastics can be irradiated safely at decontamination doses of up to 10 kGy [7.100].

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Chapter 8

DISINFECTION OF CULTURAL ARTEFACTS USING IRRADIATION

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8.1. INTRODUCTION

The disinfection, or decontamination, of cultural heritage artefacts by means of irradiation has been discussed extensively in the previous chapters. In this chapter, more pragmatic information is given to help choose the right methods for disinfection. Some fundamental aspects are discussed briefly below in the form of questions and answers so that the reader may become more familiar with the terminology.

Question: What is irradiation?

Answer: Irradiation is a transfer of energy from ionizing radiation to the irradiated material.

Question: Is radiation dangerous to health?

Answer: Ionizing radiation has potential to cause damage in living organisms if they are exposed to excessive levels. It has been scientifically established that biological response is proportional to dose.

Question: So materials will not become radioactive after treatment?

Answer: Indeed, materials remain the same as they were before the irradiation treatment, only decontaminated. Treated materials do not retain radiation and therefore cannot irradiate people handling them. In

addition to being used to disinfect cultural heritage artefacts, ionizing radiation (e.g. X rays and gamma rays) is used in radiotherapy (medical) and for non-destructive testing of objects such as cultural artefacts (gamma radiography).

Question: What happens to materials that undergo an irradiation treatment?

Answer: The energy transferred modifies the material's structure only at the molecular level. The irradiation effects depend on the chemical bonds existing in the irradiated material. In metals and inorganic materials, where there are either metallic or electrostatic bonds, the primary effect of irradiation is warming; in certain situations colour changes may occur. This effect is comparable to heating food in a microwave oven. In organic substances, characterized by covalent bonds, irradiation leads mainly to the breaking of the chemical bonds. The more complex the molecule, the more easily the bonds can break. Therefore, for example, bonds in DNA may be broken more easily than those in cellulose.

Question: Will irradiation only break bonds in mould and insects?

Answer: Organic substances are present in both artefacts and their living contaminants; therefore, degradation is expected in both of them.

Question: For ancient and/or already degraded artefacts, will irradiation degrade them more severely?

Answer: This depends on the radiation dose, and therefore the dose should be limited to a maximum of 10 kGy to destroy mould. For many materials, irradiation contributes less to deterioration than mould.

Question: How are radiation units expressed, so I can discuss these with the people at the treatment facility?

Answer: The radiation dose (D) quantifies the transfer of energy during the irradiation. It is measured in units called grays (Gy). The multiple kGy (kilogray) is often used.

Question: What about the side and secondary effects?

Answer: The intensity of all effects — disinfection and side effects, is dose dependent. The irradiation disinfection of cultural heritage is an acceptable intervention method, because doses for disinfection are lower than doses producing significant side effects.

8.2. RECOMMENDED TREATMENT DOSES

There are two different levels of dose that can be recommended for irradiation treatment: one for insects and another for mould. The dose for

disinfection of insects is lower than that for mould. This is based on the complexity of the DNA structure of the species; complex DNA is more easily degraded than simpler DNA.

8.2.1. Insects

The recommended treatment dose in the case of an insect attack is preferably 0.5 kGy, but can be up to 2 kGy. This dose is also effective for eradication of insect eggs.

There are some elements to bear in mind when irradiation treatment is used for insect removal:

- Treatment with 2 kGy can be recommended for furniture that was stored under improper conditions for a relatively short period of time, located in geographic areas with a temperate climate.
- If the environmental conditions are uncontrolled, a fungal attack can occur simultaneously with an insect attack. A dose of 2 kGy is too low for disinfection of all kinds of fungi; some fungi may remain and even form a basis for a new infestation by insects. Thus, the use of 2 kGy is not recommended if the artefacts are reintroduced after treatment into a non-controlled environment. Churches are an example of this kind of environment.
- There is a serious risk that a 2 kGy treatment may be ineffective in warm and wet climatic conditions. This is because termites' feeding system is based on a symbiotic relationship with certain microorganisms.

8.2.2. Mould and overall treatment

The treatment dose of maximum 10 kGy can be seen as a reference dose for overall disinfection of cultural heritage artefacts. At this level of dose, eradication of fungi occurs.

There are some elements to bear in mind:

- The dose given to a batch of materials should be seen as an average dose. The final dose depends on the homogeneity of the density of the batch. Therefore it is preferable that denser materials not be combined in the same batch with light (in density) materials. Thus, if possible, materials should be sorted into batches by density.

- The dose of 10 kGy has to be treated as a maximum. Based on research, an average dose of 8 ± 2 kGy should be set. This dose is sufficient to eradicate most fungi and will have minor side effects on the materials irradiated.
- Recommended doses exist; however, based on their experience, the conservator and the staff of the irradiation facility may decide to use another average dose. This dose can be lower or higher than the recommended dose.

In the case of artefacts subjected to flooding, there are some additional considerations:

- Microorganisms, and fungi in particular, develop explosively in conditions of excessive moisture. This happens frequently in the case of artefacts that have been subjected to flooding and have remained after the flooding in an environment with a high moisture content. Also, the conditions of storage between the time of the flood and treatment may encourage the growth of mould. Therefore, a dose of 10 kGy has to be considered.
- A dose higher than 10 kGy could be taken into consideration in special situations.

The examples presented in the case studies (Chapters 10–26) demonstrate the exceptional utility of irradiation disinfection in special cases (floods, war, poor storage conditions) and for very complex artefacts such as mummies.

8.3. PRECAUTIONS TO BE TAKEN IN DECIDING THE TREATMENT DOSE

In many cases, artefacts are handed over to the vendor (the facility that carries out the radiation treatment) in batches. A batch may contain artefacts made from different materials, and different parts in a batch of artefacts receive different doses, no matter what kind of irradiator is used for disinfection. This is unavoidable and is due to the distance between the radiation source and different parts of the artefacts, which obviously varies by artefact. Additionally, the density of the artefacts individually or as a batch has to be considered. The larger the object is, the larger the difference between D_{\min} and D_{\max} . Effective disinfection should be ensured by D_{\min} , and D_{\max} must not exceed the dose value at which side effects become unacceptable.

Dose can be measured by means of dosimetry. The dosimetrist can estimate the geometric parts of the artefact that get D_{\min} and D_{\max} , respectively. The values D_{\min} and D_{\max} are dependent on each other for any given radiation geometry. The irradiation time is chosen in order to obtain the D_{\min} (disinfection effectiveness).

This will result in a value of D_{\max} which cannot be independently modified. It is compared with the value of the acceptable dose in terms of side effects. In the best case, the resulting D_{\max} does not exceed the value at which side effects become unacceptable.

When the artefact is oversized and/or when its density is high (e.g. a composite with metal), D_{\max} may be unacceptably high. In these situations, the irradiation should be scheduled in two or more irradiation geometries. The estimates, calculations and decisions to be undertaken before irradiation therefore require some time and effort.

It is important that dosimetry calculations be confirmed by dosimetry measurements. Of course dosimeters will remain attached to the geometrical points of the artefact during irradiation. After any intermediate readings, dosimeters will be replaced at the same points. The measured values are recorded in the final dosimetry bulletin.

In all cases, irradiation treatment involves three stages:

- Estimation of the dose;
- Irradiation;
- Verification of the final dose received.

In general, no quantitative microbiological tests can be performed on cultural heritage artefacts as they may destroy the artefact. This is the main reason why previous results available in the literature, derived from the relation between the applied dose and the biocidal effect, have limited usefulness. In spite of this limitation, for all practical purposes, when choosing the appropriate dose for a treatment it is sufficient to know that the D_{10} value for most microorganism pests affecting cultural heritage artefacts lies within the interval of 0.1 to 1.0 kGy.

8.4. OTHER PRECAUTIONS AND CONSIDERATIONS

Once a decision has been made to irradiate batches of cultural artefacts, the following items have to be considered:

- *Knowledge of the irradiation facility.* The person responsible for the irradiation must know the facility's technological capabilities well and should be able to consider all technical limitations of the irradiator. Only in this way can an irradiation plan (geometry, irradiation time and number of stages) dedicated to the batch of artefacts be developed, resulting in the most effective D_{\max}/D_{\min} ratio.

- *Dosimetry*. The dosimetry system should be reliable and be part of a certified quality management system. The dosimetrist is considered part of the dosimetry system. The dosimetrist's skills are very important for carrying out the dosimetry.
- *Curator's/restorer's role*. It is important that curators/restorers NOT place the irradiated artefacts back in the repository where they originated, as the source of infection may still be present in that repository. The irradiated artefacts are to be placed preferably in a controlled — or at least clean — environment. If the artefacts are placed in a poor environment (dirty, moist), recontamination may occur. This recontamination may also occur when other treatments, such as anoxia, fumigation or freeze drying, are performed.

8.5. COMMENTS ON PARTICULAR MATERIALS

Certain considerations relate to treatment of particular materials:

- *Mould residue*. Fungi and microorganisms often produce residues on the substrate. People can be allergic to some of these residues, and in the worst case the residues can be carcinogenic (depending on the mould family). Therefore, the surfaces of the artefacts should be cleaned carefully after irradiation.
- *Wood*. Irradiation using a dose up to 10 kGy (effective in ensuring eradication of insects and fungi) improves the mechanical properties of wood, owing to cellulose cross-linking. At a higher dose, both mechanical and chemical properties of wood may change. The level of change is dependent on the wood origin and the size of the artefact. In practice, it is not dangerous for the object when oversized objects receive doses greater than 10 kGy, in the case of panoramic irradiation.
- *Polychromy*. The colour of inorganic pigments is practically not modified by the recommended treatment dose. For organic pigments, colours may change; however, this is also the case when objects with organic pigments are being exhibited.
- *Paper*. The development of fungi and microorganisms in archives creates serious health problems for the people who use or take care of them. The dimensions of books allow their treatment by conveyor irradiation. This is the best radiation treatment procedure, permitting a small and controlled D_{\max}/D_{\min} (overdose ratio). The average dose for safe irradiation of paper artefacts is 8 ± 2 kGy.

- *Leather, parchment, fur, hair, feathers or skin in composite artefacts.* Composite artefacts are artefacts that consist of different materials, such as mummies. For these materials, treatment with a maximum dose of 10 kGy can be seen as being safe. In this case no additional tests are necessary.
- *Textiles, fabrics.* The maximum dose of 10 kGy can be used safely in textiles, especially when cellulose fibres are present in the textile. The 10 kGy has to be the maximum (D_{\max}); an average dose of 8 ± 2 kGy can be considered. Unfortunately, the behaviour of dyes present in textiles and fabrics has not yet been extensively studied.
- *Binders, varnishes, gums and resins in easel or wood paintings.* A dose of 10 kGy does not normally affect this group of materials. However, it is wise to carry out tests to determine side effects in advance of any scheduled treatment.
- *Amber.* Amber is a natural resin found in many colours. Amber is not attacked by biodeteriogens. Sometimes amber beads are sewn on clothes or added to other artefacts. Because some types of amber may be turned brownish by irradiation, it is best to remove the amber beads before irradiation of the artefact.
- *'Grey' materials (mother-of-pearl, mica, opaque gems (lapis lazuli, turquoise, jasper, jade)).* Like amber, these materials are not biodegradable by themselves. They may be part of a composite object (e.g. furniture or clothes). A dose of 10 kGy does not affect their structure or appearance.
- *'White' materials (including ivory, horn and bone).* These materials are added to composites, where they fulfil an aesthetic role. Even the slightest change in colour should be avoided. As there is not enough experience with the irradiation of this group of materials, it is recommended that they be removed from the artefacts before carrying out any irradiation treatment.
- *Glass and transparent gems.* Glass and transparent gems are inorganic materials and should not be irradiated for disinfection. They change colour when irradiated. However, these materials may be irradiated with the aim of changing their colour. In this case, the process is known as material modification.

8.6. RADIATION DISINFECTION APPLICATION AREAS

Much research has been performed in the last decade on how to apply irradiation techniques to various types of cultural artefacts. This work is continuing in response to new questions from both the cultural heritage field and

conservation science. Table 8.1 contains a summary of the current state of the art of radiation disinfection and sterilization in France by artefact type.

In the table:

- *Well accepted* means that the application is being carried out frequently and successfully.
- *Work in progress* indicates that these fields are still being explored and/or investigated.
- *Potential* means that the application is well suited to the material, however some questions need to be answered (in most cases relating to natural and synthetic dyes).
- *Not recommended* indicates that the application is not well suited to the material.
- *No interest* means that although irradiation can be applied successfully, there is no need to irradiate these materials.

TABLE 8.1. APPLICATION OF RADIATION FOR DISINFECTION AND INSECT ERADICATION IN FRANCE

Collection	Radiation for disinfection/insect eradication				
	Well accepted	Work in progress	Potential	Not recommended	No interest
Easel paintings (on canvas)			X		
Easel paintings (on wood panel)	X				
Easel paintings (on stone, metal)					X
Paper, drawings, manuscripts, prints, books	X				
Parchment, vellum, leather		X	X		

TABLE 8.1. APPLICATION OF RADIATION FOR DISINFECTION AND INSECT ERADICATION IN FRANCE (cont.)

Collection	Radiation for disinfection/insect eradication				
	Well accepted	Work in progress	Potential	Not recommended	No interest
Canvas, textiles, tapestries			X		
Basketwork	X				
Furniture	X				
Decorative art objects (composites)	X				
Musical instruments			X		
Wooden elements of constructed structures (buildings, ships, etc.)	X				
Waterlogged archaeological wooden artefacts	X				
Wooden (dry) statues (raw)	X				
Wooden (dry) statues (polychrome or gilded)	X				
Bone, horn, ivory, tortoiseshell, amber			X		
Porous stone statues					X
Porous stone (or brick) elements of constructed structures					X
Plaster, staff, stucco objects			X		

TABLE 8.1. APPLICATION OF RADIATION FOR DISINFECTION AND INSECT ERADICATION IN FRANCE (cont.)

Collection	Radiation for disinfection/insect eradication				
	Well accepted	Work in progress	Potential	Not recommended	No interest
Ethnographic collections (clothes, textiles, ceramics)			X		
Composite ethnographic collections (organic and non-organic materials)	X				
Natural history collections	X				
Mummies	X				
Photographs and film stock (classical silver halide emulsion layers on paper, or a polymeric substrate such as PET)	X				
Photographs and film stock (cellulose nitrate or acetate substrate) ^a				X	
Glass, gemstones, amber				X	X

^a Photographic and film materials based on cellulose nitrate and acetate require special care, as these materials may be severely naturally deteriorated.

8.7. RADIATION SAFETY

In the use of nuclear techniques for peaceful purposes, the first step is to evaluate whether applications employing ionizing radiation are justified. If it is decided that an application is justified, the next step is to define the means and measures to control exposure arising from the irradiator, which is

a licenced facility that is established with approval of the regulatory authority. Regulatory requirements cover engineering and administrative measures for safety. Necessary radiological protection must be in place in proportion to the degree of hazard. The possible source of hazard at the irradiation facility is mainly external exposure due to gamma radiation. The required amount of shielding is defined in the radiological safety assessment, undertaken during the licensing or authorization process. The process of gamma irradiation does not generate any radioactivity in the irradiated materials or any radioactive residues on their surface. Radiation is an effective tool to inactivate pathogens, as is evident from successful applications such as sterilization of medical equipment used for surgery. Activities such as food irradiation and medical sterilization are performed by this well regulated industry that has been operating safely for more than 60 years in commercial and business parks and in a considerable number of research and developments centres. All activities performed in these facilities are very safe and reliable. IAEA Safety Standards Series No. SSG-8 (published in 2010) [8.1] provides comprehensive information and guidance regarding the design and safe operation of irradiation facilities. In addition, other safety regulations (local, national or international) covering areas other than radiation safety may be implemented in these facilities. The process of irradiation is a safely managed activity with many potential applications for humankind.

REFERENCE TO CHAPTER 8

- [8.1] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiation Safety of Gamma, Electron and X Ray Irradiation Facilities, IAEA Safety Standards Series No. SSG-8, IAEA, Vienna (2010).

Chapter 9

CONSOLIDATION OF ORGANIC MATERIALS USING RADIATION TECHNOLOGY

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9.1. INTRODUCTION

Owing to the length and/or conditions of their storage, cultural artefacts are subject to deterioration, frequently resulting in difficulties handling these materials. A well known result is enhanced brittleness of paper manuscripts. Another example is the softening of wood by waterlogging. Brittle materials may crumble easily, with the result that they cannot be consulted anymore and may even be lost forever. This section describes the use of radiation based methods for consolidation of heritage materials. The main application involves the use of radiation curing resins.

9.2. PAPER AND TEXTILES

Paper and textile materials may become brittle and extremely fragile over time. The process of degradation depends not only on the storage environment, but also on the production process. Existing methods for strengthening paper and textiles do not involve the application of radiation technology. One method was developed in the late 1980s at the British Library to strengthen paper with a so called graft polymerization process; however, this method was not developed beyond the experimental stage [9.1].

At present, there are no known processes to improve the strength of paper or textiles using radiation technology.

9.3. CONSOLIDATION OF WOODEN ARTEFACTS BY RADIATION CURING RESINS

Consolidation of porous materials such as wood or concrete was implemented during the 1960s in the United States of America, Japan and Europe by first impregnating these materials with acryl and vinyl monomers under pressure and then causing in situ polymerization or solidification using gamma irradiation. Wood–plastic composites were developed during that period for flooring in public areas. Very hard surfaces were obtained because the resin completely fills the empty spaces in the wood, giving a densified wood which is much less sensitive to relative humidity. Applications in the field of cultural heritage were initiated in the 1970s in France and the Czech Republic (at the time Czechoslovakia). In 1970, the ARC-Nucléart laboratory in Grenoble undertook a project to consolidate the 19th century mosaic parquet from the old Grenoble city hall by dismantling the wooden panels, impregnating them with the monomer MMA and curing them with radiation. During the late 1970s, the consolidation of very degraded wooden artefacts was carried out using radiation curing of resin based on unsaturated polyester and styrene. This was also implemented in conservation of waterlogged archaeological artefacts which require additional liquid phase exchange steps with the solvent acetone. At present, the ARC-Nucléart laboratory is the only laboratory in Europe able to implement the consolidation treatment.

9.3.1. Monomers and resins

Radiation polymerization is initiated by free radicals; hence, monomers and resins to be cured by this process must have a chemical structure containing carbon–carbon double bonds or reactive unsaturated bonds such as acrylic, methacrylic, vinylic or unsaturated sites in polyester oligomers. The acrylic monomer currently used most often is MMA (Fig. 9.1), which polymerizes to

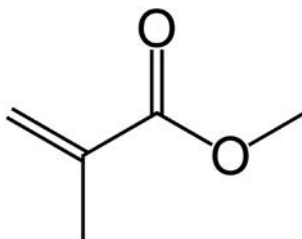


FIG. 9.1. The chemical structure of the monomer MMA.

form the thermoplastic polymer PMMA (Plexiglas), with a shrinkage in volume of about 20%. Although it has the advantage of very low viscosity for good penetration in porous materials, MMA presents two main disadvantages in this application: very high volatility, resulting in product loss on artefact surfaces, and sensitivity to oxygen inhibition of the radiation curing in air, resulting in surface layers that are sticky or not completely cured.

Standard unsaturated polyester resins are currently used in the composite material industry (boats, containers) and are composed of the monomer styrene (mass ratio 30–50% in the resin) and the unsaturated polyester prepolymer. They are much more viscous and polymerize to form a three dimensional network through the cross-linking of the polyester chains by the styrene radicals (thermoset type resins). The shrinkage in volume is only 10%, and after curing the polyester resin forms an insoluble hard material, even at the surface. For this reason, polyester resins of isophthalic (recommended for durability) or tetrahydrophthalic types have been used successfully for more than 30 years.

Some of the trade names of unsaturated polyester resins in Europe are Norsodyne, Ludopal, Palatal, Synolyte and Atlac. A trade name in North America is Norpol.

9.4. POLYMERIZATION UNDER GAMMA IRRADIATION

Acrylic monomer and unsaturated polyester resin are polymerized by a free radical mechanism through irradiation (gamma rays, EB) or through addition of chemical catalysts such as peroxides (the conventional process in the composite industry). When irradiation is used, the resin is free from any chemical additives (peroxides, accelerators) because the gamma rays initiate the free radicals necessary for the first step of polymerization. This occurs at room temperature. The second step is the propagation of the chain of polymers, which is always done with irradiation — the ‘gel effect’ with heat buildup. The last step is the formation of the solid polymer after reaction of all the free radicals present. Thanks to the fact that the polymerization reaction rate is proportional to the irradiation dose rate (i.e. the intensity of the radiation), one can control the heat buildup during curing by varying the dose rate, the highest rate usually being around 1–2 kGy/h. The total dose for complete polymerization of the resin is in the range of 20–30 kGy.

The resin impregnation of degraded wooden artefacts in dry condition is carried out in steel tanks suitable for vacuum and pressure applications. Inside the adapted tank, the artefact is fixed to its support to keep it from floating in the resin bath, and then a low vacuum (around 1 mm Hg) is set-up during several hours to extract the air from the wood pores. Liquid resin then fills the tank by

vacuum suction until the complete immersion of the artefact in the resin bath. In order to ensure the diffusion of the resin in the core of the artefact, nitrogen pressure is then applied in the tank, in the range of 1 to 3 bars depending on the state of decay of the wood, during a period ranging from several hours for thin artefacts to more than 24 hours for large ones. At the end of impregnation, the excess resin flows back to the storage tank for further use. This feature is one of the main advantages of the irradiation process: the resin, without any catalyst as mentioned previously, can be reused and stored for a long period at room temperature. Once it is returned to atmospheric pressure, the artefact is left to drain inside the tank until no further resin flows from it. Outside the tank, the object is cleaned with textile to absorb any resin residue on the surface and then is wrapped entirely with textile and plastic film prior to irradiation.

In the Grenoble irradiation chamber, the artefact is placed 10 cm from the panel ^{60}Co source to start the in situ resin polymerization after putting thin thermocouples inside the object to monitor the temperature, which must not exceed 50–60°C. The other advantage of radiation curing, as mentioned above, is the ability to control the temperature by varying the dose rate; for instance, increasing the distance between the artefact and the panel source will lower the wood temperature. It is important to be able to vary this parameter to suit the artefact's surface area or its internal structure. Thanks to the penetrating power of the gamma rays, the polymerization is performed at each point on and inside the object, resulting in a homogeneous and complete reaction. During the first 48 hours of irradiation, it is crucial to clean the surface of the artefact with textile and replace the wrapping textile, to ensure that there is minimal residual resin on it, which could cause the surfaces to become glossy. The two sides of the artefact are exposed to the source to ensure homogeneity of the absorbed irradiation dose, which is around 30–40 kGy after many days of treatment. This dose range is not harmful for the wood structure. Finally, the consolidated artefact is placed in a ventilated chamber during many weeks to eliminate any residual styrene monomer trapped in it.

The quantity of resin absorbed by the wood increases its weight correspondingly and gives it a composite wood–polymer structure. The material obtained is hard throughout, and its mechanical strength is considerably increased. This gives it greater resistance to abrasion and friction at the surface and improves solidity and resistance to shocks. The densified wood is also unaffected by temperature variations and only slightly sensitive to changes in climatic conditions when it is displayed or manipulated indoors. Impregnation slightly darkens the colour of the wood, depending on its species (broad leaved species darken more than conifers).

Regarding polychromic sculptures, it is important to carefully test the interaction of pigment layers with the monomer or resin. The method is obviously to be avoided if any dissolution of pigment by the resin is detected. In some cases, the pigment layer can be protected by applying wax prior to impregnation.

Undoubtedly, this process, using an insoluble cross-linked polymer and maximum resin content, is at the opposite end of the spectrum from conventional application of diluted solutions of polymers that form a film on the surface of the wood, which is theoretically reversible. Nevertheless, it should be considered as a 'last chance method' for preserving heavily degraded artefacts.

9.5. RADIATION CONSOLIDATION APPLICATION AREAS

Much experience has been gained at the ARC-Nucléart laboratory and conservation workshop in applying irradiation techniques to consolidate various cultural artefact collections. The work on the applications continues as the polymer industry develops new monomers. Of course, questions from both the cultural heritage and conservation science fields have to be answered before an application is accepted. Table 9.1 contains a summary of the current state of the art of radiation consolidation of heritage materials in France by collection type.

In the table:

- *Well accepted* means that the application is being carried out frequently and successfully.
- *Work in progress* indicates that these fields are still being explored and/or investigated.
- *Potential* means that the application is well suited to the material, however some questions need to be answered.
- *Not recommended* indicates that the application is not well suited to the material.
- *No interest* means that although irradiation can be applied successfully, there is no need to consolidate these materials.

TABLE 9.1. APPLICATION OF RADIATION FOR CONSOLIDATION OF HERITAGE MATERIALS IN FRANCE

Collection	Impregnation, consolidation				
	Well accepted	Work in progress	Potential	Not recommended	No interest
Easel paintings (on canvas, wood panel, stone, metal)					X
Paper, drawings, manuscripts, prints, books					X
Parchment, vellum, leather			X		
Canvas, textiles, tapestries					X
Basketwork				X	
Furniture	X				
Decorative art objects (composites)			X		
Musical instruments			X		
Wooden elements of constructed structures (buildings, ships, etc.)	X				
Waterlogged archaeological wooden artefacts	X				
Wooden (dry) statues (raw)	X				
Wooden (dry) statues (polychrome or gilded)			X		

TABLE 9.1. APPLICATION OF RADIATION FOR CONSOLIDATION OF HERITAGE MATERIALS IN FRANCE (cont.)

Collection	Impregnation, consolidation				
	Well accepted	Work in progress	Potential	Not recommended	No interest
Bone, horn, ivory, tortoiseshell, amber				X	
Porous stone statues			X		
Porous stone (or brick) elements of constructed structures			X		
Plaster, staff, stucco objects			X		
Composite ethnographic collections (organic and non-organic materials)			X		
Natural history collections					X
Mummies					X
Photographs and film stock (classical silver halide emulsion layers on paper, cellulose nitrate or acetate substrate, or PET substrate)					X

REFERENCE TO CHAPTER 9

- [9.1] FOOT, M., “The reinforcement of papers by graft copolymerisation”, *Sauvegarde et conservation des photographies, dessins, imprimés et manuscrits, Actes des journées internationales d’études de l’ARSAG, ICCROM, Paris (1991) 228–230.*

Chapter 10

MOULD DISINFECTION THROUGH GAMMA RADIATION IN THE PEACE PALACE LIBRARY

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10.1. INTRODUCTION

In 2003, the Peace Palace Library, which holds a unique homogeneous international law collection and serves the International Court of Justice and The Hague Academy of International Law, had the opportunity to construct a new environment for its reading room, offices and storage in stacks. The pre-2003 storage spaces were spread out over the entire complex, which was not practical from the point of view of logistics. There were stacks, mainly containing material that was used less often, such as government documents, under the central entrance of the Peace Palace itself, a space that was not built for archival storage or to hold a library collection. This room was too humid, as it was next to a ditch, and did not have proper air-conditioning. As a result, the stack area was too hot and moisture appeared on the walls. No other depots in the library met the requirement for a repository (some of them flooded frequently). Moreover, the stacks were unhealthy and dusty. Figure 10.1 shows part of the contaminated collection.

10.2. DISINFECTION THROUGH GAMMA RADIATION

The original stacks contained old and open racks, and therefore the books were dusty (because there were no slabs in the stepped shelving system) and mouldy (as a consequence of the humidity, which also entered the building because windows to the garden were always open). Everything was contaminated with fungal spores — even the walls. Organic paper, dust and humidity form an ideal breeding environment for mould. In addition, the library was forced to move collections regularly to make efficient use of space, circulating the fungi to areas that were not yet infected. Mould also caused serious health problems for employees, including dry or watery eyes, rashes on the skin and even blisters. It



FIG. 10.1. Every book in the pre-2003 Peace Palace Library stacks contained mould.

is known that mould can cause allergic reactions in addition to heart problems and cancer.

Measurements and investigations showed the presence of *Aspergillus*, *Cladosporium* and *Penicillium*. Before the collection could be moved back into the newly constructed premises, the mould problem had to be solved. By coincidence, in 2006, J.B.G.A. Havermans of TNO invited the Peace Palace Library to participate in a newly launched initiative to clean mould infected collections using gamma radiation. The contribution of the Peace Palace Library would mainly be to provide book material for the research and to provide information on the logistics of processing about 15 shelf km of materials (books, magazines, etc.) for irradiation treatment.

A moving company with particular skills in moving and storing library collections was hired to move the materials to a temporary location and to the decontamination facility. Part went to a non-accessible storage area and another part went to an accessible complex (a third part, containing the books and journals consulted the most often, was placed in the above described basement under the Peace Palace). It was important to measure the contamination levels during the temporary storage in the three locations. The measurements revealed that *Aspergillus* and *Cladosporium* were rampant. These measurements were important in choosing the radiation methodology to be used. A maximum dose of 10 kGy was applied over 150 consecutive days. Specially designed boxes 1 m

long (the old shelves were 1 m long and the new ones would be 1 m long as well) on 12–16 pallets of 8–10 boxes arrived daily in the Peace Palace to be stored in the new stacks.

Eventually, the Peace Palace Library collections were moved back into the storage space, which was built in accordance with the regulations for archival repositories, with air filtration, air circulation, a temperature of 18°C and relative humidity of about 45%. The books seemed to be well cleaned — with fungi and mould killed — after the gamma treatment. But the dust that was such a great breeding place for mould was still on the books. Obviously, that dust had to be removed before the collection was placed in the new stack area. The Italian Depulvera machine, developed at the request of an Italian moving company specializing in museum, archive and library collections (in essence a ‘book vacuum cleaner’), offered a way to remove the dust, which also contained the contaminating particles killed by the treatment, from the exterior of the books.

The last stage comprised the vacuum cleaning: all books, piece by piece, went through the vacuum cleaner. Along with other tests frequently executed, research on the indoor air quality and collection undertaken in 2010 (two years after the gamma treatment and the renovation of the storage rooms) concluded that thanks to the gamma disinfection and removal of book dust, as well as good collection management (e.g. climate conditions, handling of books), the rooms were still free of mould and spores (Fig. 10.2). Moreover, all materials in this unique homogeneous international law collection are easily accessible and are thus once again frequently consulted.



FIG. 10.2. Samples were taken from unique and rare books two years after the gamma disinfection. It was concluded that there was still no living mould present and that the books could be consulted safely.

Chapter 11

DISINFECTION OF THE MUMMY OF RAMSES II (FRANCE, 1977)

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11.1. INTRODUCTION

While it was on display at the Cairo Museum, the mummy of Ramses II began to present signs of pest infestation due to the hot and humid environment, and the unsealed glass cover used to protect it (1975). In the framework of an exhibition held in Paris (1976) on the subject of Ramses II and numerous artefacts relating to his reign, the mummy was transferred to France for examination by the French National Museum of Natural History. Having been damaged in the past by insect larvae, the mummy was also found to be infested by a dense population of various types of fungi, though without any pathogenic bacteria. In agreement with the Egyptian authorities, it was therefore decided to disinfect the mummy by gamma irradiation, a process that had been used for many years at the Nucléart laboratory (renamed ARC-Nucléart in 1987) located in the CEA's Grenoble Research Centre.

11.2. FROM HISTORY TO PROCESS

A consortium of laboratories and museums was set-up in Paris (Anthropology Museum, Musée de l'Homme) and Grenoble, coordinated by a research laboratory in Paris, in order to manage the different steps of the project: preliminary studies and testing, the treatment itself, and the return of the mummy to the Cairo Museum. Indeed, more than four hundred samples were taken from other mummies for testing under gamma irradiation in order to determine the irradiation dose to be applied; this had to be effective enough to eradicate all the fungi (of which there were more than sixty species) but not harm the components of the mummy such as the hair, textiles, skin and teeth. No sampling of the actual mummy of Ramses II was authorized, except for some fragments of hair and textile that were lying on the linen or on the Plexiglas plate placed under it. It was

very important to design the cover under which the mummy would be kept during irradiation, and even after, to ensure a sterile atmosphere around it and thus avoid any recontamination (Figs 11.1 and 11.2).

Due to the length (1.72 metres) and uneven shape of the mummy (especially the arrangement of the arms), as well as the presence of the sarcophagus and various other materials inside it, it was necessary to design dosimetry software based on simple geometric forms representing the whole artefact to be treated in order to determine the irradiation dose in each part of the mummy. As the density of the materials could not be estimated accurately, equivalent data were obtained from other mummies. Thanks to the calculus model, the gamma ray source was designed in a way that satisfied the irradiation parameters, which included a 18 kGy disinfection dose at an average dose rate of 1.5 kGy/h. It was possible to determine the dose rate at each point of the mummy model, depending on its position with respect to the ^{60}Co source and the presence or absence of absorbing materials. The challenge was to apply this minimum dose of 18 kGy to all parts of the mummy. The model was validated by irradiating two mummies dedicated to the studies, one from the Museum of Fine Arts in Grenoble and the other from the Anthropology Museum in Paris. Good agreement between the calculated and measured irradiation doses was obtained [11.1].

During irradiation, it was necessary to keep the mummy, the sarcophagus and various materials in a sealed plastic envelope similar to a glove box, so

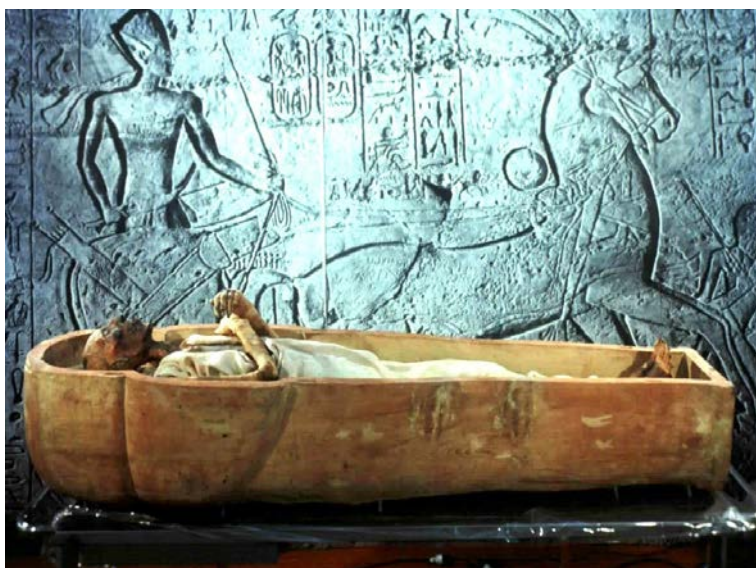


FIG. 11.1. The mummy of Ramses II at the Musée de l'Homme, Paris.



FIG. 11.2. The mummy of Ramses II.

the artefact could be manipulated afterwards in a sterilized atmosphere. The irradiation phase could then be started in the facility at the CEA Research Centre at Saclay, near Paris, which at the time (May 1977) had a radiation activity of 5.92×10^{15} Bq. Irradiation lasted 12 hours and 40 minutes, with the mummy being rotated halfway through this period. The ratio between the maximum and minimum gamma ray dose was 1.33, and the measurement uncertainty was around 10%. The disinfected mummy is displayed in its sealed transparent Plexiglas cover in which the sterilized atmosphere is permanently maintained thanks to a pumping and filtering system located in the base supporting the covered sarcophagus.

Many factors contributed to the success of the operation, which preserved the mummy of Ramses II in excellent conditions that are still maintained after almost forty years. The irradiation process proved to be highly effective in handling this complex case. Last but not least, the skills of the different partners involved as well as the perfect coordination between them were key factors in meeting the challenges in applying such a unique treatment process in such a short period of time [11.2, 11.3].

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Chapter 12

THE EFFECT OF 8 ± 2 kGy GAMMA DISINFECTION TREATMENT ON MOULD INFECTED PAPER MATERIALS IN THE NETHERLANDS

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12.1. INTRODUCTION

One of the most common disasters to befall paper based heritage is damage caused by moisture and water. Poor building conditions can result in damp interior environments, and floods can also affect repositories. When a repository has been affected by moisture or flooding, quick action is usually taken to rescue the collection. However, wet collections are highly subject to mould growth, especially if the environment remains humid. An explosion of mould can only be prevented if the wet collection is dried immediately and subsequently stored in a dry, mould free environment. This is not usually the case, and therefore wet collections often become infected with mould that has to be removed afterwards. One of the methods to disinfect a collection is based on the application of radiation technologies. Previous studies in the Netherlands have indicated that gamma disinfection treatment at 8 ± 2 kGy causes insignificant material degradation [12.1]. To further establish this, a research project was undertaken to study and evaluate gamma disinfection treatment using real mould infected materials. Previous studies dedicated to the effects of gamma disinfection of cellulose materials have been mainly carried out on new paper materials such as Whatman filter paper or other types of new or artificially aged paper materials and not using defined mould infected materials [12.2].

12.2. DISASTER SIMULATION

Three different paper grades were subjected to a cocktail of mould and subsequently stored under conditions with a relative humidity higher than 65%. The paper materials used were a cotton linter paper (chloride bleached), a softwood pulp paper and a groundwood-containing writing paper (acid sized). The cocktail, sprayed on sheets of the above mentioned papers, contained a

mixture of *Aspergillus niger*, *Chaetomium globosum*, *Aspergillus versicolor* and *Eurotium herbariorum*. The choice of these mould species was based on the recommendation of the National Archives in The Hague, which found that they were detected frequently in archival materials. The materials were stored in standard archival boxes under the conditions described above. Once the papers were fully covered with mould, the boxes were removed from their storage location and placed in a drier environment. Two conservation workshops were asked to evaluate the level of damage and apply a conservation treatment to make the materials accessible again. The quality of the materials can be seen in Fig. 12.1.

Both conservation workshops tested the mould activity using agar test tubes [12.3]. A small part the paper surface was touched with a cotton swab and the swab was put in contact with the agar. After the test tubes had been in a warm oven (35°C) for 5 days, the growth of the mould colonies was evaluated. It was concluded that the mould was alive and active. Both conservation workshops recommended applying gamma disinfection and then cleaning the paper surface. After cleaning, the surface was to be flattened and strengthened, for example with Japanese paper. Considering the aim of this work, strengthening was not undertaken; otherwise no strength analyses could be performed.

In total, three batches of materials were obtained. One batch was manually dry cleaned and not disinfected, and two batches were disinfected with gamma radiation at 8 ± 2 kGy. The disinfected batches were sent to the two workshops (one batch to each workshop) to remove the mould residues and flatten the paper according to their own process.



FIG. 12.1. An overview (left) and a close up (right) of the artificially infected materials. Here it can be seen that mould significantly damaged the paper materials. On the left, the test tubes can also be seen; these were filled with agar for testing the activity of the mould.

12.3. EVALUATION

In practice, evaluation of the quality of materials cannot be done by just taking a piece of material from each original document or book. Non-destructive analyses are therefore needed for evaluating the quality and/or damage level of an object. Based on the damage level observed, conservation action can be taken. For example, if a material is acidic, deacidification is recommended. If a material is weak, leaf casting or strengthening is recommended. One of the methods used to evaluate the quality of paper materials non-destructively is the SurveNIR method [12.4]. SurveNIR is an entirely non-destructive characterization tool and survey methodology using near infrared spectroscopy. By building a large database of historical samples and by detailed characterization, chemometric calibration can be performed to characterize the state of degradation of paper. SurveNIR can evaluate the following parameters within 1 second: acidity (pH), tensile strength, degree of polymerization and yellowing risk (lignin content) [12.5].

12.4. QUALITY OF THE RETURNED TREATED AND CONSERVED MATERIALS

Restoration workshop H performed conservation work on both irradiated and non-irradiated samples, while restoration workshop S performed conservation work only on the irradiated samples. The non-irradiated samples were only dry cleaned. The irradiated samples were surface cleaned. Both types of materials were flattened. Figure 12.2 shows some of the materials after all treatments. Initially, all samples had a dry and brittle feeling; however, the non-irradiated samples took on a wetter feeling after two months of storage in the dark and at room conditions similar to those in which the irradiated samples were stored.

12.5. SurveNIR ANALYSIS — PART 1, MATERIAL ASSESSMENT

Before the SurveNIR analysis was performed, the following criteria were established for evaluating the treated materials: acidity (pH), risk of yellowing and risk of brittleness. Weight factors were given to the near infrared (NIR) correlated values for pH, tensile strength, tear after folding strength and the presence of lignin. As one of the three samples indeed contained lignin, degree of polymerization was not included in this evaluation stage. Maximum and minimum values were assigned to calculate the need for conservation.



FIG. 12.2. Left: a sheet of mould infected groundwood paper after dry cleaning. Right: a sheet of mould infected groundwood paper after disinfection with 8 kGy of gamma radiation and removal of the mould dust.

Based on the results presented in Table 12.1, it is obvious that for all papers, severe degradation was observed as a result of the serious mould infection. For both the softwood and cotton-containing paper, the overall qualification was 'poor', while for the groundwood-containing paper it was 'critical'. This qualification is in agreement with the recommendation of the restoration workshops to have the papers strengthened after the irradiation treatment.

After the disinfection by irradiation, using 8 ± 2 kGy, no serious changes were found in the evaluation by SurveNIR. These observations suggested that the paper degradation caused by up to 10 kGy of gamma radiation is minor compared to the degradation caused by mould.

Looking at the SurveNIR evaluation of the acidity of the groundwood paper after irradiation and flattening, it is observed that the acidity is lower after all treatments than before them. This might be due to the small amount of pH neutral water used for flattening the curled paper leaves.

As SurveNIR is based on a large database of original correlated characteristics, the SurveNIR software is able to estimate the characteristics of the paper, for example, the degree of polymerization, or the tensile strength index. The degree of polymerization of both cellulose types is presented in Figs 12.3 and 12.4. The values presented in these figures represent an average of 30 measurements; nevertheless, the estimated error in the presented mean value is about 10% due to non-homogeneity of the samples. It is demonstrated that mould degrades cotton cellulose paper less than softwood cellulose, probably owing to the higher degree of crystallinity of the cotton cellulose, while softwood cellulose contains more amorphous fractions that can easily be hydrolysed by factors such as mould, enzymes and acids. After irradiation with a maximum of 10 kGy of gamma radiation, no significant changes were observed in the

TABLE 12.1. RESULTS OF THE SurveNIR ASSESSMENT

Code	Restoration workshop	Material type	Treatment	SurveNIR assessment		
				pH	Yellowing risk	Brittleness risk
P1	None	Softwood cellulose	No mould, reference	Fair	Fair	Fair
P1 M	H	Softwood cellulose	Mould, dry cleaned, flattened	Poor	Fair	Poor
P1 M G	H	Softwood cellulose	Mould, irradiated, flattened	Poor	Fair	Poor
	S	Softwood cellulose	Mould, irradiated, flattened	Poor	Fair	Poor
P2	None	Cotton cellulose	No mould, reference	Fair	Good	Fair
P2 M	H	Cotton cellulose	Mould, dry cleaned, flattened	Poor	Good	Fair
P2 M G	H	Cotton cellulose	Mould, irradiated, flattened	Poor	Good	Fair
	S	Cotton cellulose	Mould, irradiated, flattened	Fair	Good	Fair
P3	None	Groundwood	No mould, reference	Poor	Poor	Critical
P3 M	H	Groundwood	Mould, dry cleaned, flattened	Critical	Critical	Critical
P3 M G	H	Groundwood	Mould, irradiated, flattened	Critical	Critical	Critical
	S	Groundwood	Mould, irradiated, flattened	Poor	Critical	Critical

Note: ‘Good’ indicates that the material is in good condition and does not need any conservation action; ‘fair’ indicates that conservation action is recommended but not necessary; ‘poor’ indicates that there is a need for conservation; and ‘critical’ indicates that conservation action is necessary to avoid total loss of the material.

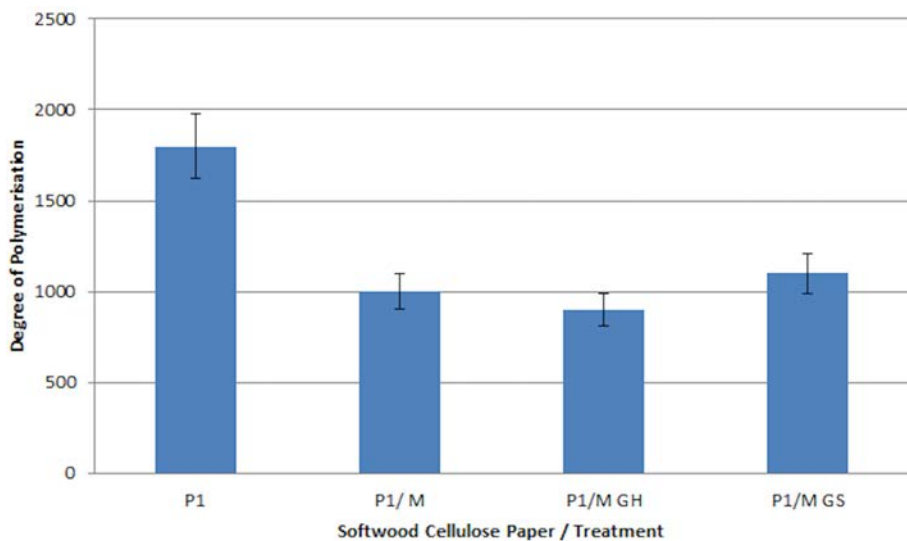


FIG. 12.3. The degree of polymerization of the softwood cellulose paper before mould and irradiation (P1), after infection by mould and dry cleaning (P1/M), and after infection by mould and irradiation using maximum 10 kGy and subsequent surface cleaning and flattening (P1/M GH and P1/M GS).

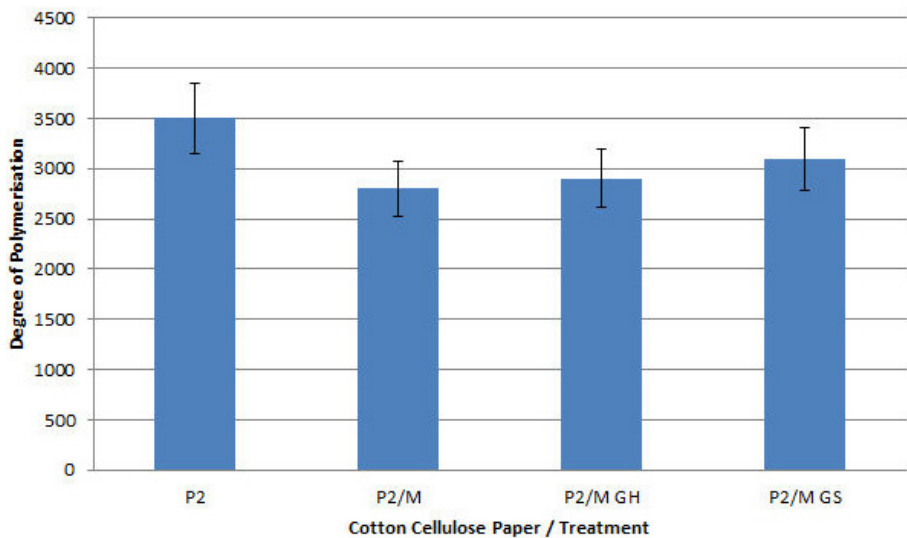


FIG. 12.4. The degree of polymerization of the cotton cellulose paper before mould and irradiation (P2), after infection by mould and dry cleaning (P2/M), and after infection by mould and irradiation using maximum 10 kGy and subsequent surface cleaning and flattening (P2/M GH and P2/M GS).

degree of polymerization for either the cotton or softwood cellulose-containing papers.

12.6. SurveNIR ANALYSIS — PART 2, CHEMOMETRIC APPROACH

Another approach to measuring the effects of irradiation on paper is the application of principal component analysis (PCA). PCA is a statistical multivariate analysis to evaluate and describe a large amount of data using a small number of relevant variables. This application was first established by the European research project on the effect of air pollutants on the ageing of paper (STEP CT 90-0100) [12.6]. Experimental data can often be arranged as a table, a data matrix with p variables measured on n objects. In this case the objects are the paper samples and the variables are the measurements. PCA can be used to obtain an overview of the data structure in the data matrix. PCA reduces the dimensionality of data matrices that contain intercorrelated variables. A plot based on the two most significant components can be found in Fig. 12.5. The measurements are presented in a 2-D component weight plot. The further a method is away from zero on the axis, the better the method can be applied for determining the ageing effect. The two most significant components (component 1 and 2) are calculated based on a co-variance matrix using a statistical software program. In this analysis, the calculation of the component weights was done by means of a software program. The parameters for ageing used in the EU project

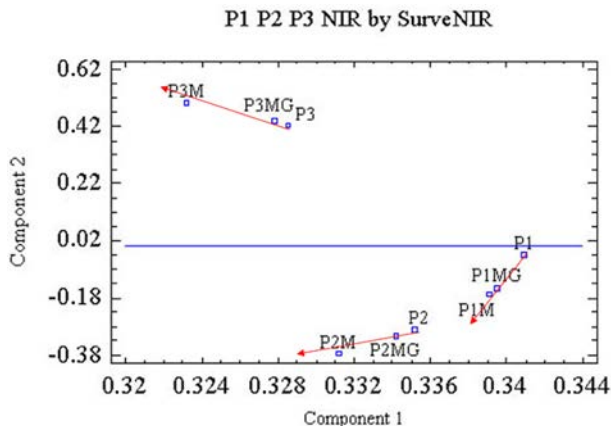


FIG. 12.5. PCA of the NIR spectra of the original samples, the mould infected samples (M) and the samples that were surface cleaned and flattened after irradiation with up to 10 kGy of gamma radiation (MG).

were comparable to those used by the SurveNIR project, and the PCA can be established based on these data, although the SurveNIR project did not generate a large quantity of data. The original NIR spectra of the samples were used for the evaluation. The results of the PCA evaluation are shown in Fig. 12.5.

Figure 12.5 shows not only components 1 and 2 for each sample, but also the direction of ageing (red arrow), which has been put into these graphs starting from the original least aged sample (e.g. paper P1, the softwood cellulose-containing paper). For the three samples it is clear that the arrow points from 1 to MG to M, and that the main deterioration of the materials is caused by mould (M) as this point lies farthest from the original point. This method of evaluation demonstrates again that irradiation using 8 ± 2 kGy of gamma radiation (which therefore has a maximum dose of 10 kGy) causes less degradation than mould.

12.7. CONCLUSIONS

The research described in this chapter demonstrated that the SurveNIR assessment method can be applied even to samples that contain mould. Nevertheless, care should be taken in choosing the location for sampling the NIR spectrum, as papers with mould are extremely inhomogeneous. The sampling locations used for this research appeared visually identical.

Based on the SurveNIR assessment method, it can be concluded that mould caused the highest degree of degradation of the paper materials and that there was no significant difference between mould infected samples irradiated with 8 ± 2 kGy of gamma radiation followed by manual flattening and mould infected samples that were dry cleaned only.

ACKNOWLEDGEMENTS TO CHAPTER 12

SynergyHealth Netherlands (previously Isotron B.V.), Conservation Workshop Helmond, Conservation Workshop Sterken, Preservation Technology Netherlands, the Nederlands Fotomuseum, the National Archives of the Netherlands and the Peace Palace Library are gratefully acknowledged for their financial contributions.

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Chapter 13

EMERGENCY INTERVENTION AT THE NATIONAL FILM ARCHIVE

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13.1. INTRODUCTION

At the end of 1990, the long neglected National Film Archive of Romania began a modernization effort. A new building was built, with a controlled atmosphere and a modern storage system. Before relocation to the new building, the film reels showing fungal traces (Fig. 13.1) were cleaned using a special machine. The procedure included brushing and washing with a detergent.



FIG. 13.1. A film reel showing serious effects of fungal attack (courtesy of National Film Archive, Romania).

The structure of film favours fungal attack. Photographic film is made of a transparent support on which is applied a gelatin emulsion that includes silver atoms (black and white film) or organic dyes (colour film). Gelatin is a hydrophilic protein that remains dry in normal humidity, but can take water from the air if the relative humidity is high. Gelatin emulsion is an excellent source of food for fungi. As a consequence of contamination, part of the gelatin disappears. Instead, fungal metabolic by-products appear. They can chemically interact with the dyes or the support. Of course, the degradation is in direct proportion to the development of fungal attack. In a dry environment, fungi do not develop further and films can be considered stabilized.

It was believed that the fungal attack on film reels in the National Film Archive was not active and that the traces of previous attacks would be washed away by the cleaning action. It was thought that there was no need for emergency action. The discovery of several hundred reels where contamination was active and had developed disastrously was a very unpleasant surprise (Fig. 13.2).

The signs of a potential disaster were obvious:

- The presence of very aggressive contamination on a large number of reels;
- The imminent destruction of the films if the biological attack was not stopped immediately;



FIG. 13.2. Active fungal attack on film reel (courtesy of National Film Archive, Romania).

- The impossibility to act by the usual means, because the treatment capacity of the cleaning equipment was far below that needed for the intervention.

Radiation decontamination was chosen. In Romania, this was the only available method for the decontamination of large volumes in a short time. The literature did not indicate any antecedent, and there was no information regarding irradiation side effects on films. Given these circumstances, the action was preceded by a programme of exploratory tests.

13.2. EXPERIMENTAL PROCEDURES

The intensity of the fungal attack prompted the use of the sterilization dose of 25 kGy for decontamination, applied by a tote box irradiator. In these conditions, D_{\min} is 25 kGy and D_{\max} is assumed to be 50 kGy.

The microbiological tests evaluating the effectiveness of decontamination were performed on spores of the identified fungi, and on the infected film samples, after treatment at 25 kGy. All tests related to the assessment of side effects were performed at radiation doses of 25 and 50 kGy.

Mechanical degradation refers to the degradation of the film support made of plastic. This makes it impossible to use the film. It consists of changes in the distance between the perforations, and/or mechanical strength parameters. Both lead to film breakage during screening. Tests searched for irradiation induced modifications of the distance between perforations, tensile strength and elongation at break. These tests were also performed on samples of new motion picture film produced by Azomures (a Romanian company that produced Fuji type film) and the National Film Archive. Test equipment and procedures belonging to these two institutions were used in this research. The plastic support of the films was made of polyester.

The degradation of the visual information contained on the film is a result of the emulsion losing its coherence or even disappearing. These phenomena occur because the gelatin is used as a nutrient by fungi. In colour films, even dyes (organic substances) can be sources of food for fungi. To assess the degradation of visual information, the changes in the basic colours (yellow, magenta, cyan) were measured in a sensitogram¹. Colour tests were performed on Kodak film, by a Kodak laboratory approved by the National Film Archive, using a sensitogram

¹ A sensitogram is a quantitative tool for the calibration of colour films. It consists of a piece of film containing film frames in the same colour but having different intensities.

for both negative and positive films. Densitometry values were measured before and after irradiation for each colour layer.

Theoretically, after irradiation, subtle changes may appear in the structure of the dyes that are not detectable by tests performed immediately after irradiation, but that could lead to an increased rate of ageing of the film. Ageing manifests itself by weakening the image. Unfortunately, there is no standardized test for artificial ageing of motion picture films. In order to evaluate these effects, a novel artificial ageing test was used. At the same time, free radicals trapped in the film were measured. A thermal procedure used for accelerated ageing of paper was adopted as a test for films. Temperatures up to 75°C and exposure times up to 6 hours were used. Sensitograms were performed on negative and positive, and irradiated and non-irradiated test samples. An EPR spectrometer built at IRASM, IFIN-HH was used to identify free radicals in the film. Measurement was made one day after irradiation.

13.3. RESULTS AND DISCUSSION

All tests — mechanical, colour and artificial ageing tests — indicated irradiation induced modifications of no more than 6% for the highest irradiation dose. No trapped radicals were identified, which is not surprising. The cages where free radicals are trapped are the microcrystalline regions of the polymer. The polyesters used as film support have no microcrystalline component.

Detailed information about the project, the irradiation facility, the testing programme and the decontamination were published in Ref. [13.1].

13.4. CONCLUSION

The results justified the radiation decontamination of the infected film reels. The tests lasted for two months and the treatment of several hundred reels lasted two days. Thus, biodegradation was quickly and effectively stopped and the films were out of danger while they waited for complete cleaning. After the cleaning they were stored in the modern building (Fig. 13.3).



FIG. 13.3. Motion picture film reels stored in modernized building (courtesy of National Film Archive, Romania).

ACKNOWLEDGEMENTS TO CHAPTER 13

Thanks go to the management of the National Film Archive of Romania for the collaboration and support, and for their trust in science and their openness to new approaches that the nuclear domain can offer to society.

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Chapter 14

KHROMA THE FROZEN BABY MAMMOTH

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14.1. INTRODUCTION

In autumn 2008, a frozen specimen of a baby mammoth was discovered in Siberian permafrost in the Sakha Republic, Russian Federation. It was named Khroma, after the river on the edges of which it was found. It proved to be the oldest baby mammoth ever recovered (at least 50 000 years), but surprisingly, it is the best preserved judging by the exceptional condition of some of the almost fresh tissues. The top of its body, however, was partially dried, as if mummified, while the back and belly were torn and the proboscis and hump of fat were lacking, having been eaten by polar foxes.

Before being studied by scientists and being presented to the public in a special refrigerated chamber during an exhibition in a French museum (Fig. 14.1), it required sanitary treatment to inactivate the traces of bacteria or other potentially pathogenic organisms it might be carrying. Thanks to its power of penetration, gamma radiation quickly emerged as the only technique able to guarantee non-destructive biocidal treatment of the entire volume of the specimen. As a matter of fact, it was possible to fulfil a double requirement, on the one hand of effectiveness and reliability for sanitary handling and, on the other, of harmlessness with regard to this unique example of biological heritage.

14.2. DISCUSSION

The selected dose was 20 kGy, with reference to *Bacillus anthracis* that may be present in the soil and in the remains of dead animals, in particular those of herbivores. ‘Cold’ treatment was carried out with the baby mammoth in its frozen state and in its packaging (a plastic wrapping barrier plus insulating container with dry ice) in July 2010, in Grenoble, France. To reach this dose, the specimen was irradiated for 50 hours, being turned over halfway through in order to homogenize the dose. The maximum dose, on its flanks, was no more



FIG. 14.1. Khroma in its special refrigerated chamber after the irradiation treatment, during the exhibition at the Musée Crozatier, Le Puy-en-Velay, France.

than 40 kGy, which is consistent with preserving the properties of organic materials, and in particular the protein structure of tissue of animal origin.

Beyond protecting the health of researchers and the public, this treatment significantly improved the conservation of the specimen. Indeed, the bactericidal action of radiation inactivated germs already present inside it, limiting natural soft tissue decay mechanisms triggered during thawing. It certainly helped the scientists by ensuring good conditions during thawing for the examinations ‘in the flesh’ carried out in August 2010. And it will also enhance the taxidermy that will be undertaken after the scientific programme of studies on the fresh tissues has been completed.

Just before the irradiation, samples were collected in the irradiation chamber at the ARC-Nucléart facility (Fig. 14.2) to preserve the living information (i.e. old bacteria) that could be the subject of biological studies and the quality of the DNA information. Indeed, gamma irradiation causes lesions in DNA, although, theoretically, only a small number of lesions would occur with the applied dose of 20 to 40 kGy, and these would not interfere with access to the DNA information.



FIG. 14.2. Collection of samples from Khroma in the irradiation chamber at ARC-Nucléart, just before treatment. For this operation, the baby mammoth, confined in a double plastic envelope, was installed on its insulating container. Palaeo-geneticists had to incise through these envelopes to collect the samples.

Chapter 15

EMERGENCY INTERVENTION AT A PARISH CHURCH IN ROMANIA

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15.1. INTRODUCTION

Sometimes a monument has only local relevance. In such cases, the local community has to assume the responsibility for conservation/restoration. Limited resources and lack of expertise make it a difficult task, especially in emergency cases.

The church in Izvoarele, a village in Romania, was constructed in 1935. Internal decoration consisting of wooden pieces, furniture and painted panels was created by people from the village. Some of them had links with the royal family of Romania. Especially for this reason, the church was important for the local community. The inventory consisted of a 6 m × 8 m × 0.8 m iconostasis (great painted wooden wall separating the altar and narthex in Orthodox Christian churches), a balcony, holy chairs and other religious pieces. Most pieces were made of linden wood. Although the decoration is beautiful, the church is not among the special heritage sites under the care and surveillance of the Ministry of Culture.

15.2. EMERGENCY AT IZVOARELE PARISH CHURCH

Over time, the church has been contaminated more than once with xylophagous insects. Each time, it was cleaned using the local remedy — wiping the surface with a cloth soaked in petrol. The petrol enters the larvae holes and acts as a biocide. The effectiveness of this treatment was low, but it had the advantage that the church could continue to function during the treatment. After a while, no further attacks were recorded. However, larvae holes and a decaying structure remained. The petrol is in contact with painted surface for a very short time, which reduces the risk of polychromic deterioration.

A new attack of *Anobium punctatum* appeared in the fall of 2002. This time the attack was present on several pieces. It was extremely virulent on the iconostasis, whose structure was already decayed (Fig. 15.1). An experienced biologist detected an old fungal infection that had been present since the wood was harvested in the forest. This weakened the wooden structure, making xylophage infestation easier. Using the traditional treatment again would have been too risky. A quick and total destruction of the insects and a thorough restoration of the wooden pieces were required.

It was also known that the flight season for *Anobium punctatum* in Romania is in May. To avoid the presence of another insect generation, decontamination had to be completed before this time.

After costly and unsuccessful tests using conventional methods, the priest considered irradiation decontamination. This required transporting the whole wooden inventory, including the large iconostasis, balcony, holy chairs and other religious pieces 120 km to the IRASM Radiation Processing Center (Fig. 15.2).

The IRASM facility is a category IV gamma irradiator. Industrial sterilization of medical devices — the main purpose of the facility, is performed using a tote box type conveyor.

When not in use, the ^{60}Co source is sheltered in a water pool 6 m deep (Fig. 15.3). During irradiation, the source is lifted out of the pool. As it is

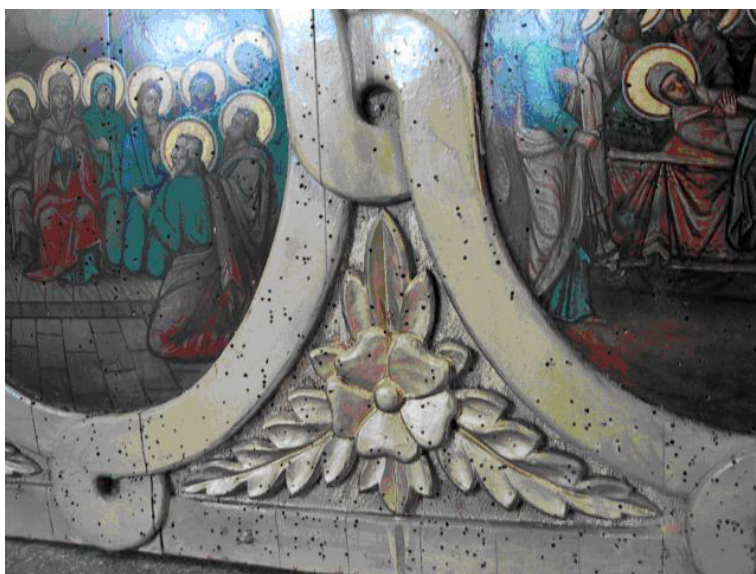


FIG. 15.1. *Anobium punctatum* attack on part of the iconostasis.



FIG. 15.2. Disassembled iconostasis and other wooden pieces in IRASM storage.

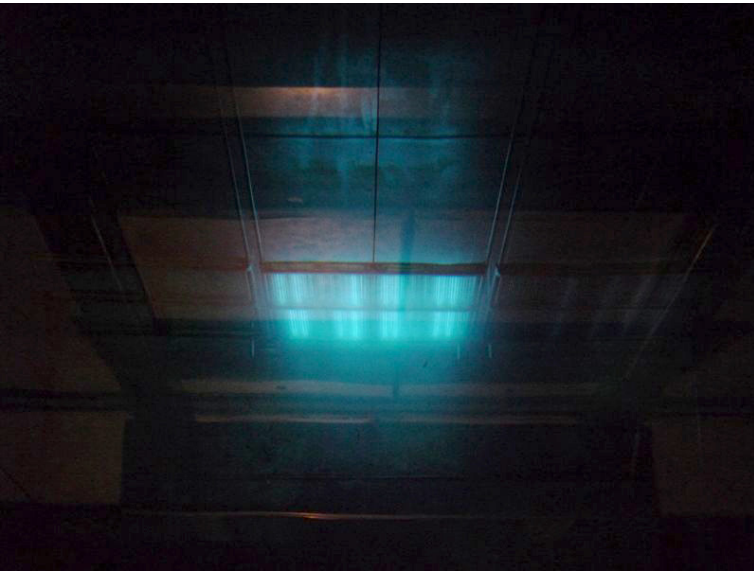


FIG. 15.3. The IRASM ^{60}Co source in its water pool. Cerenkov radiation causes the water to glow.



FIG. 15.4. The IRASM tote box conveyor. Left: the storage facility. Right: the irradiation room. (Courtesy of IRASM, IFIN-HH.)

considered an activity of national importance, irradiation decontamination of cultural heritage artefacts is undertaken cost free. It is performed outside the conveyor path without any inconvenience for the main industrial activity (Fig. 15.4). Large pieces may be treated.

15.3. DOSIMETRY

The pieces to be treated were placed in the irradiation chamber in positions with known 3-D dose mapping. One can expect a variation in the dose received by different parts of the treated object. The chosen irradiation geometry was characterized by a ratio between maximum dose and minimum dose of less than 2.

A dose of 2 kGy is considered to be sufficient for eradication of any insect morph (egg, larva, pupa or fly) [15.1]. Fungi are destroyed by a total dose of 10 kGy [15.2]. Mechanical properties of wood are not affected at doses less than 10 kGy [15.3]. Irradiation doses were chosen based on experience and taking into account the above information. No supplementary tests on possible modifications of treated materials were performed.

ECB dosimetry was used. The dosimeter is a sealed ampoule. The solution conductivity is measured by oscillometry. ECB ampoules do not lose information during reading. Irradiation may be stopped to check the accumulated dose. If it is not sufficient, irradiation is restarted. The IRASM ECB dosimetry system is traceable to Risø High Dose Reference Laboratory in Denmark. To follow the

accumulated minimum and maximum doses, up to 10 dosimeters were attached to the treated items. Doses between 4.4 and 7.6 kGy were applied [15.4].

15.4. CONCLUSIONS

Gamma irradiation is used for decontamination based on its biocidal effect. Irradiation treatment has important advantages:

- It carries no risk for the operator; it is performed only in the irradiation room, which is a confined and protected area.
- It carries no risk for restorer, visitor or environment; no toxic or radioactive residues remain in the treated item.
- It is very effective through the entire volume of each object thanks to the deep penetration of gamma radiation. Conversely, the effectiveness of gas treatment (anoxic or poisonous gases) is limited by diffusion.
- Its effectiveness is correlated with absorbed dose, which is a parameter that is easy to measure and control.
- It has excellent reliability based on the fact that the irradiation field is always the same.
- Large amounts of material can be treated simultaneously.
- Treatment in industrial facilities is performed in a short time.
- It has a low cost.

Irradiation decontamination is chosen especially when at least one of the following circumstances is present:

- Emergency intervention (e.g. Alan Mason Chesney Medical Archive or anthrax — United States of America [15.5]);
- Intervention on objects with complex structure (e.g. Ramses II mummy — France [15.6]);
- Intervention on large objects/assemblies (e.g. Romanian Film Archive [15.7]);
- Classical methods cannot be applied (e.g. a gas chamber is not available);
- The process is cost effective.

In the case of Izvoarele church, all the above circumstances were present.

The irradiation decontamination was applied to the entire wooden inventory of the parish church. The iconostasis was disassembled and transported together with the rest of the inventory to the IRASM irradiation facility. Approximately 10 m³ of wood items of various shapes and dimensions were treated. The largest

piece was 3.2 m long and 1.5 m wide. The treatment lasted 4 days. As expected, there was no evidence of colour modifications in the paint. After treatment, the pieces were reassembled, insect holes were filled following a proper procedure, and paintings were restored. After 12 years, no sign of reinfestation appeared (Fig. 15.5).

Although irradiation treatment is an excellent method of decontamination in well defined situations, it is rarely used. This is mostly because of erroneous associations with nuclear weapons and radioactive contamination. The emergency decontamination of Izvoarele church demonstrated the utility of this approach and the excellent outcome it makes possible.

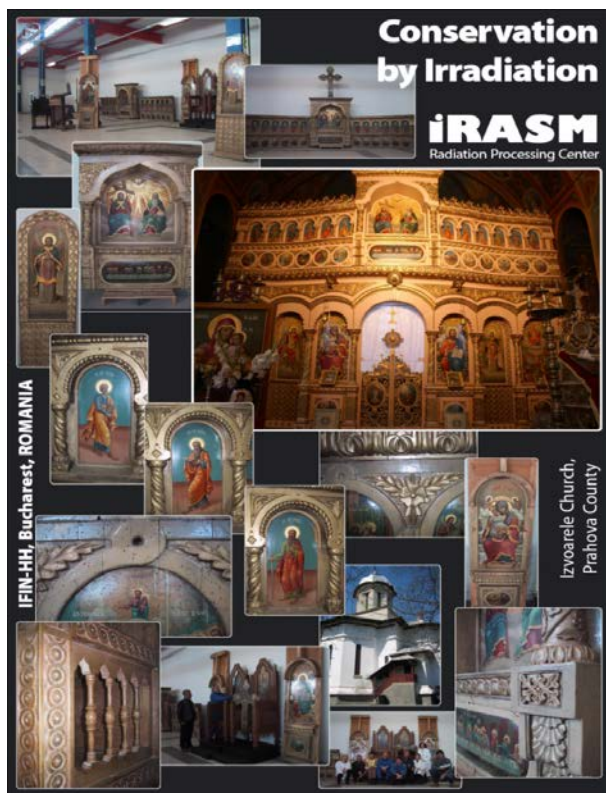


FIG. 15.5. Poster showing the wooden objects from Izvoarele church that were treated by irradiation.

ACKNOWLEDGEMENTS TO CHAPTER 15

Priest I. Barat was the key force behind this project. He evaluated with accuracy the irradiation decontamination method, took the unconventional decision of disassembling/reassembling the iconostasis, and assumed responsibility for the transportation and the final restoration. His dedication is gratefully acknowledged.

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Chapter 16

CONSOLIDATION OF AN 18th CENTURY WOODEN POLYCHROME SCULPTURE

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16.1. INTRODUCTION

A polychrome sculpture dated from the 18th century representing Saint Vincent was located in the church Sainte Croix at Suzannecourt, France. Its dimensions were 117 cm × 36 cm × 20 cm and it presented a very important degree of deterioration, with powdery wood in some parts (Fig. 16.1). The most appropriate method to save the sculpture was determined to be in-depth full consolidation using radiation curing resin. This was recommended by a conservator who studied the sculpture's condition (taking into consideration any interaction between the resin and the polychrome, among other factors). Owing to the fragility of the polychrome layer, it was necessary to fix it to the surface before the resin impregnation. This was carried out using an aqueous solution of gelatin at 5 to 10%, after the dust removal operation.

It was also necessary to remove the powdery wooden parts of the sculpture to get access to the degraded areas, to ensure high quality consolidation. A preconsolidation of the surface layers, with Paraloid B72 acrylic resin dissolved at 10% first in ethyl acetate for deep penetration, then in acetone for the surface,



FIG. 16.1. Before treatment, the 18th century polychrome wooden sculpture of Saint Vincent showed a very high degree of wood deterioration by larvae and xylophagous insects.

was necessary for the mechanical stabilization of the sculpture during the next phase of its transfer into the impregnation tank (Fig. 16.2).

16.2. IMPREGNATION WITH RADIATION CURING RESIN AND IRRADIATION

The preconsolidated sculpture was then introduced into the tank for the total impregnation of the porous wooden structure with the styrene unsaturated polyester resin without any solvent (Fig. 16.3). In this process, any void within the artefact is filled by the resin, resulting in the densification of the material. After a night of impregnation under a nitrogen pressure of 3 bars, the artefact was taken out of the tank, and its surface was then cleaned with cloth to remove any excess liquid resin on the sculpture. It was transferred into the irradiation chamber for the polymerization of the resin, which involves volume shrinkage of around 10% from the liquid to the solid state (Fig. 16.4). The moderate heat buildup (maximum of 40–50°C) during the polymerization reaction was controlled



FIG. 16.2. Preconsolidation procedures before immersion in the resin bath.



FIG. 16.3. Impregnation with the resin in a vacuum/pressure tank.



FIG. 16.4. The impregnated sculpture in front of the gamma ray source for the in situ solidification of the resin.

by varying the irradiation dose rate (from 0.5 to 1 kGy/h). The total radiation dose for the complete polymerization was in the range of 30–40 kGy. Thorough ventilation (over many weeks) of the artefact after irradiation was crucial in order to remove the residual styrene component in the wood structure.

16.3. RESTORATION OF THE SCULPTURE AFTER CONSOLIDATION

Traditional restoration work was carried out on the consolidated sculpture: fixing the head on the body and filling some areas with epoxy mastic (red colour), covered afterwards by white mastic for final colour application. Overall stability for the sculpture was obtained by mechanical modelling, especially on the base support (Figs 16.5 and 16.6).

16.4. CONCLUSION

In conclusion, saving this highly degraded sculpture was made possible by totally impregnating it with a radiation curing resin. The strong consolidation of the different parts of the artefact facilitated the restoration of delicate areas, such as the head, ensuring good stability in the overall structure. The polyester resin has enhanced or touched up the polychrome aspect of the sculpture, and the densification of the wood sculpture with this hydrophobic resin will make the artefact much less sensitive to variations in relative humidity in its display place in the church. The success of this operation was possible only through discussion, studies and agreement between cultural heritage authorities, conservators and irradiation scientists.



FIG. 16.5. Restoration steps after consolidation: attaching the head, filling gaps and applying mastic for colour retouching.



FIG. 16.6. The restored sculpture on its metallic support, ready to be displayed (October 2014) in the church at Suzannecourt, France.

Chapter 17

CONSOLIDATION OF PARQUETS

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17.1. TREATMENT OF AN 18th CENTURY PARQUET IN GRENOBLE, FRANCE

In 1969, the city of Grenoble planned to restore an 18th century parquet from the old city hall, which was to become the Stendhal Museum in 1970. The parquet was degraded by wood worm attack, and the consolidation by radiation curing resin was proposed by Louis de Nadaillac, an engineer from the CEA Grenoble gamma irradiation laboratory, which at the time was studying the development of new materials (wood, stone) by impregnation with acrylic monomers to be hardened in situ when exposed to gamma irradiation. Louis de Nadaillac pioneered the use of ionizing radiation for cultural heritage preservation in France.

The surface of the mosaic parquet is around 155 m², composed of five species of wood, and the areas subjected to public traffic were very altered: the 9 mm initial thickness of the panels was reduced by half by both biological and mechanical erosion. After various types of testing using the monomer MMA as consolidant (the thermoplastic polymer formed is PMMA, Plexiglas), and agreement from the cultural heritage organizations, the parquet was dismantled, resulting in 750 wooden panels weighing 2 tonnes. Maintained in metallic frames, the wooden panels were impregnated under pressure and then irradiated during many days for complete polymerization of the monomer inside the wood. The consolidated panels were returned to the city hall and successfully reassembled (Figs 17.1 and 17.2).

Forty years later, the parquet is still in very good condition and is appreciated by numerous visitors during exhibitions or cultural events in the building.



FIG. 17.1. The 18th century parquet, 40 years after the consolidation treatment (Stendhal Museum, Grenoble, France).

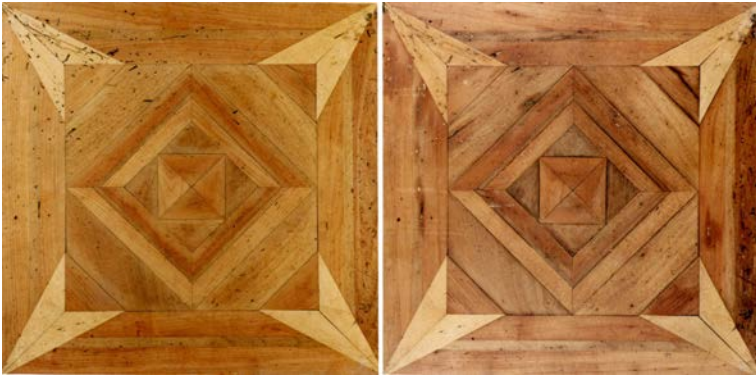


FIG. 17.2. A wooden panel before the consolidation treatment (left) and after it (right).

17.2. TREATMENT OF A 19th CENTURY PARQUET FROM THE CITY HALL OF VIVIERS, FRANCE

The city hall in Viviers, France, has a parquet inlaid with geometrical designs that was created at the beginning of the 19th century. The 4 to 7 mm thick veneer consists of several wood species (walnut, cherry, maple) and is glued to a support consisting of planks of chestnut, walnut or others. This 86 m² parquet in a room dedicated to cultural events in the city hall (the former bishop's palace) needed disinfection and consolidation.

In cooperation with a local artefact restoration company, and under the supervision of a senior architect for historical monuments from the Ministry of Culture, the parquet was dismantled into 76 rectangular panels measuring 97 cm × 103 cm each, and a central panel measuring 194 cm × 206 cm (Fig. 17.3). Optimization of the treatment conditions was carried out in 1997, and it was decided that a plywood plank would be glued onto the back of each panel and the panels put under stress in metallic frames during irradiation, to avoid any dimensional changes in the panels due to the radiation curing of the resin (Fig. 17.4). Since the 1970s, acrylic monomer (a thermoplastic resin) has been replaced by styrene unsaturated polyester (a thermosetting resin), resulting in less shrinkage and better complete polymerization in air. The treatment was carried out in the first half of 1998, and the parquet was reassembled at the original site at the beginning of 1999 (Fig. 17.5).



FIG. 17.3. Left: an example of a parquet panel before consolidation treatment; right: impregnation of a series of parquet panels.



FIG. 17.4. Impregnated parquet panels maintained in steel frames inside the irradiation chamber.



FIG. 17.5. After the consolidation treatment, the parquet was reassembled in the city hall of Viviers, France.

Chapter 18

PRESERVATION OF LARGE COLLECTIONS OF ARTEFACTS

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18.1. INTRODUCTION

Historical objects are exposed to a number of adverse factors: chemical (corrosion and chemical reactions of various types), physical (atmospheric agents, e.g. changes in humidity, temperature), mechanical (vibration, shock, impact, etc.) and, perhaps the most dangerous, biological agents. Biological degradation of historical objects is done by both the smallest and simplest organisms (bacteria, fungi, moulds) and more complex organisms (mostly insects). Destruction can also be caused by birds and mammals (particularly rodents), but these phenomena are rather marginal and much easier to control.

The physical factors which can be used to combat pests in historical objects include temperature, ultrasound, ultraviolet radiation and ionizing radiation (X ray, gamma, EB). Radiation techniques are ideal for situations when there is a need to disinfect a very large number of objects. Ionizing radiation may be the only method of conservation that ensures control of bacteria and mould contamination in a short time. Other advantages of gamma radiation are its high penetration and the fact that its effectiveness does not depend on the shape and structure of the material, which allows disinfection of objects with large dimensions and complex shapes.

Described below is an example of radiation disinfection of a large collection of artefacts carried out by the Institute of Applied Radiation Chemistry (IARC) at the Faculty of Chemistry of the Technical University of Lodz, Poland, for the State Museum at Majdanek. The project involved the disinfection of 60 000 shoes

that belonged to camp prisoners. The museum was founded in November 1944 on the grounds of a former concentration camp. It is an institution managed by the Ministry of Culture and National Heritage in Poland. Its main duties include keeping the area of the former camp at Majdanek with its buildings and appliances in proper condition, as well as substantiating the history of the camp.

18.2. PRISONERS' SHOES IN THE COLLECTION OF THE STATE MUSEUM AT MAJDANEK

In the early post-war years, the shoes found in the camp were sorted into several categories depending on their origin, material, finish and size. The categories included civilian shoes for adults and children, clogs made in the camp, wooden soles for use in the camp shoemaker's workshop, and shoes made of straw. Most shoes were adults' and children's shoes that belonged to Majdanek prisoners. According to estimates, the collections of the museum include approximately 280 000 civilians' shoes: approximately 245 000 for adults and approximately 35 000 for children. These are made of leather, cloth, rubber and wood. The exact time of their origin is unknown, but it can be assumed that most of them were made in the 1930s. Different styles and models are represented, among them both high quality shoes (the work of shoemakers throughout Europe, as evidenced by preserved labels) as well as simple shoes made by artisans who supplied peasants in Poland, Ukraine and Belarus. The condition of the shoes varies. The vast majority have heavily worn soles and heels as a result of intensive use by their owners (especially the men's shoes, with numerous traces of repeated repair and patching) or deliberate disruption in search of valuables and notes, often hidden by the deportees in their shoes (see Fig. 18.1).



FIG. 18.1. Example of the condition of the shoes.

In 1998, the museum received funding from the Foundation for Polish-German Cooperation for renovations on barracks 53 and 54. Thereafter, efforts were initiated to obtain funds for the preservation of footwear, temporarily kept in 2 571 jute bags in one of the barracks (Fig. 18.2). Assistance was sought from the Council for the Protection of Struggle and Martyrdom Sites, the Society for the Protection of Majdanek and the Ministry of Culture and National Heritage. In 2001, the museum received a grant from the Ministry of Culture and announced a tender for partial preservation of 150 000 units of prisoner footwear. The IARC, which had proposed the implementation of non-invasive radiation disinfection and mechanical cleaning, was selected to carry out the work [18.1]. Owing to financial constraints, it decided to reduce the number of shoes to be treated to 60 000.

18.3. RADIATION DISINFECTION OF 60 000 SHOES

The 60 000 shoes were packed into 500 bags (the size of the bags was 60 cm × 100 cm × 35 cm) and transported to the IARC gamma irradiation facility. Based on a preliminary microbiological analysis, an absorbed dose of 20 kGy was chosen as the minimum dose required for achieving the desired degree of removal of microorganisms. The shoes were irradiated in the bags, which were laid centred in the irradiation chamber in four layers of 14 pieces. In order to



FIG. 18.2. The 60 000 treated shoes on display at the barracks.

improve the uniformity in the absorbed dose, the bags were moved and rotated in the middle of the exposure period. Under the irradiation conditions, the absorbed dose variation observed was about 7.5%. The microbiological analysis looked at the total number of bacteria and fungi on the surface of the shoe before and after irradiation. A reduction of bacteria in the range of 95 to 99.9% was obtained, while the reduction in fungi was between 80 and 97%. Shoes, like any disinfected object, should be protected from secondary infection. One way to ensure this is to store and display them under the right conditions.

18.4. METHOD OF CONTROLLING THE RADIATION DOSE

The prime technical concern with irradiation of museum artefacts is to ensure the highest homogeneity of absorbed dose to ensure that the process results in the desired microbiological control. This is very challenging as these objects may be made of various types of material and have varying sizes, shapes and other special features that require individual treatment in the radiation disinfection process. The method of treatment may also include optimizing the irradiation geometry as well as the geometry of the radioactive sources.

The existing IARC irradiation chamber with dimensions of 414 cm × 350 cm × 220 cm was equipped with 20 sources located in a circle with a total activity of about 0.74×10^{15} Bq. It enabled the irradiation of large objects, but with significant differences in the dose rate in different parts of the object. A computer simulation program was used for calculating the distribution of dose rate. The program allowed the user to make quick calculations of dose distribution depending on the location of the object in the chamber and the thickness and type of radiation absorbing material. The results obtained made it possible to develop an optimal plan for conducting the irradiation process.

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Chapter 19

GAMMA RADIATION FOR MICROBIAL DECONTAMINATION OF CULTURAL HERITAGE: CASE STUDIES WITH PARCHMENT AND CERAMIC TILES

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19.1. INTRODUCTION

Today, increased concerns regarding the safeguarding of heritage result in constant evolution of the conservation and restoration fields as new challenges arise. Besides the deterioration that occurs with the passing of time, most of our cultural and artistic heritage can be damaged by environmental factors as well as by organisms and microorganisms that attack and may induce aesthetic changes [19.1]. Microbial deterioration is related to environmental conditions and also to the physicochemical properties of the objects' constituent materials [19.2, 19.3]. Microorganisms can cause alterations to material surfaces through a variety of mechanisms, including biofilm formation, chemical reactions with the material, physical penetration into the substrate and production of pigments [19.4–19.6]. To diagnose biodeterioration processes and design effective biocontrol measures, the microbial communities and the material need to be investigated.

Research into biodeterioration of cultural heritage objects is important for the development and optimization of methodologies that help prevent their degradation. Different preventive and corrective measures have been developed to decontaminate and preserve cultural heritage artefacts. Some of these procedures are chemical based, such as the use of pesticides and fumigants [19.7]. In spite of their unquestionable decontamination potential, the chemicals used (e.g. ethylene oxide, methyl bromide and sulphuryl fluoride) are toxic to humans. Non-chemical treatments include modified atmospheres [19.8], oxygen deprivation, temperature treatments or exposure to ionizing radiation [19.9, 19.10]. There are, however, some limitations to these procedures; for example, modified atmospheres can still

be toxic to the working staff, cold treatments have to deal with humidity problems in the chambers and high temperature can lead to oxidation and artificial ageing. Development of new approaches in restoration, preservation, conservation and decontamination procedures is needed.

Gamma radiation has proven to be a clean and safe alternative for the treatment of biodeteriorated objects. Its high penetration capability, along with the possibility to apply it to a broad range of materials (in contrast with temperature treatments), make it an attractive alternative in art preservation, conservation and decontamination [19.11, 19.12]. However, despite the fact that it has been used for over 50 years in the decontamination of archives and library materials [19.9, 19.13, 19.14], there are still reservations about its applicability for some materials, of which parchment is a successfully resolved example, and glazed ceramic tiles are a still non-resolved one. A multidisciplinary approach for each case must be tailor made for a correct application of radiation technologies as an alternative treatment for cultural heritage objects.

The assessment of gamma radiation as an alternative preservation treatment for parchment and glazed ceramic tiles will be discussed further below. The methodology was based on the evaluation of the microbial inactivation patterns and potential irradiation side effects on the art objects resulting from gamma radiation. This work was accomplished by the multidisciplinary team and equipment from Centro de Ciências e Tecnologias Nucleares (C2TN), Portugal. The team's major resources include irradiation facilities (^{60}Co experimental equipment and linear accelerator) and microbiology and material characterization laboratories.

19.2. PARCHMENT CASE STUDY

Parchment was, along with papyrus, one of the most important ancestors of paper. It is a natural organic material consisting of specially treated animal (goat, cow or sheep) skin. Parchment is rich in compounds such as collagen, keratin, elastin, albumin and globulin that turn it into an excellent biological substrate, especially for fungal communities [19.3].

A study was conducted with the aim of evaluating the feasibility of decontaminating parchment by gamma radiation treatment, as a conservation method to provide an alternative to the current toxic chemical and non-chemical decontamination methods. The specific objectives were to estimate: (i) the minimum gamma radiation dose (D_{\min}) for the microbial decontamination of parchment and (ii) the maximum gamma radiation dose (D_{\max}) that could guarantee the decontamination of parchment documents without significant alteration of their physical properties. To achieve these goals, the microbial

inactivation patterns and the effects on the colour and texture of parchment were assessed after exposure to different gamma radiation doses.

Parchment samples (Fig. 19.1) from the Archive of the University of Coimbra were irradiated in normal atmospheric conditions, at room temperature with a ^{60}Co experimental source (Precisa 22; Graviner, United Kingdom) located at C2TN. Dosimetric studies using the reference Fricke dosimeter were carried out in the gamma facility in order to determine the best geometry and dose rate for the irradiation process. The doses applied were 2 to 30 kGy at a maximum dose rate of 3.1 kGy/h. The absorbed dose was monitored using calibrated routine dosimeters (Perspex, Harwell) to assess the doses absorbed by the material.

The microbial inactivation patterns of parchment microbiota and of *Cladosporium cladosporioides* were evaluated using a validated destructive method [19.15]. The texture and colour of samples were measured before and after the irradiation using a texture analyser (Fig. 19.2) and an electronic colorimeter.

Based on the methodology applied, parchment samples presented bioburden values lower than 5×10^3 colony forming units (CFU)/ cm^2 for total microbiota, and lower than 10 CFU/ cm^2 for fungal propagules. Considering the low initial contamination of the parchment samples, no inactivation trend was observed for the natural parchment microbiota, especially regarding the fungal community. However, following artificial contamination, microbial inactivation efficiencies higher than 90% (corresponding to a microbial population decrease of 1 log) were obtained for all parchment samples, with doses above 4 kGy [19.15].

In order to propose a minimum gamma radiation dose for decontamination, parchment samples artificially contaminated with *C. cladosporioides* (strain isolated from parchment and archive indoor air) [19.17] were used, since

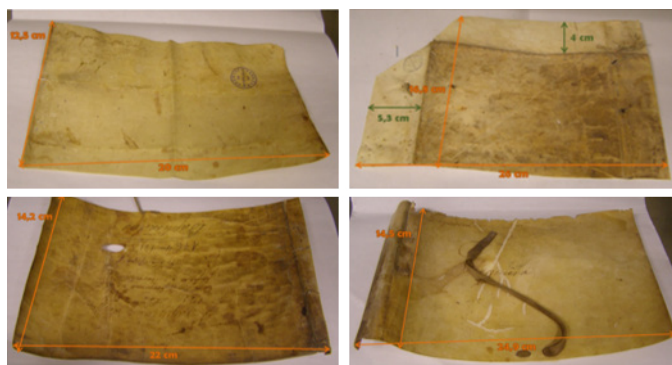


FIG. 19.1. Parchment samples used in the study from the archive of a Portuguese university.

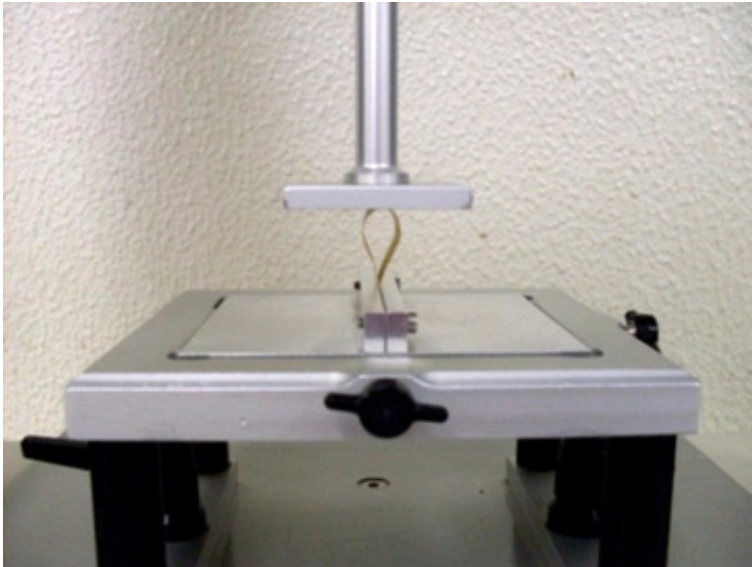


FIG. 19.2. Texture analyser used to test parchment samples. This method allows determination of the compression and decompression energies, peak force and springiness of the tested material. An aluminium sample support was custom designed to fit the texture analyser, while holding the sample to determine its hardness and springiness [19.16].

the natural contamination levels did not allow a clear definition of the inactivation response to gamma radiation. The survival curve obtained for *C. cladosporioides* is presented in Fig. 19.3.

For all the gamma radiation doses tested in this work, no substantial changes in the hardness, springiness or colour of parchment samples were found [19.16]. There were some significant differences in colour observed between samples at different irradiation doses; however these differences may also have been related to intrinsic variability in sample colour. Our results highlight the complexity and the natural non-uniformity of parchment documents, which are the main difficulties found in parchment texture and colour analyses [19.16].

In view of the results obtained in this study, a dose of 30 kGy is considered to be harmless, and it was therefore proposed as the maximum irradiation dose to be applied in the decontamination treatment of parchments. Based on the inactivation efficiencies achieved for the spiked natural microbiota of parchment and the inactivation kinetics of *C. cladosporioides*, our results suggested a dose of 5 kGy as a minimal decontamination dose for the analysed parchment documents.

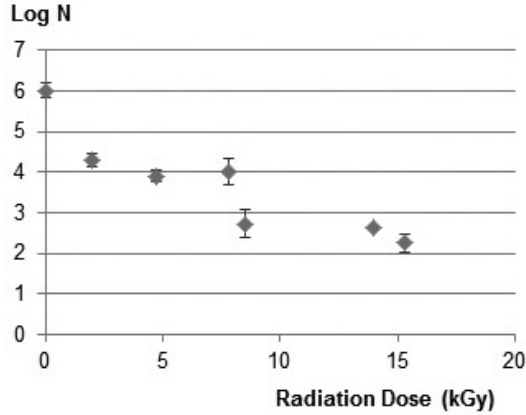


FIG. 19.3. *Cladosporium cladosporioides* gamma radiation survival curve in parchment. Error bars correspond to 95% confidence intervals regarding mean values ($1 < n < 50$; $\alpha = 0.05$). The *C. cladosporioides* strain revealed a sigmoidal survival curve with gamma radiation. A 2 log decrease (inactivation efficiency of 99%) was obtained for *C. cladosporioides* after exposure to a 5 kGy dose.

As an outcome of this study, a conservation and restoration procedure using a decontamination treatment dose of 5 kGy was successfully applied to a parchment book from the university archive (Fig. 19.4).

19.3. GLAZED CERAMIC TILE CASE STUDY

Among cultural assets, ceramics, and particularly glazed tiles ('azulejos' in Portuguese and Spanish, from the Arab designation 'al-zuléija' or 'al-zulaiju'), deserve special attention in the Mediterranean region, where they have long been used to decorate buildings. Azulejos are present in many historical Portuguese buildings of the 17th to the 19th centuries. Most of these ceramic tiles present various signs of degradation, mainly due to exterior exposure in a range of different environments [19.18]. The main goal of this study was to assess the applicability of gamma radiation as a decontamination treatment for glazed ceramic tiles. Microbial inactivation studies were carried out using as object of study the ceramic panel Quinta de Santo António (17th century, National Tile Museum, Portugal) (Fig. 19.5), which was originally part of a well and was presenting signs of deterioration.

Tile samples from the panel were irradiated in normal atmospheric conditions, at room temperature using a ^{60}Co experimental source (Precisa 22; Graviner, United Kingdom) located at C2TN [19.10]. The tile samples were



FIG. 19.4. Parchment book restored and treated using a decontamination dose of 5 kGy.



FIG. 19.5. Glazed ceramic tile samples used in the study.

placed individually in sterilized plastic bags and irradiated at the doses of 1, 2 and 4 kGy at a dose rate of 1.7 kGy/h. The absorbed doses were monitored by routine dosimetry (Harwell dosimeters).

The non-destructive swab method was used to estimate the samples' initial bioburden and the number of survivors after each irradiation dose. The survival curve (Fig. 19.6) suggested that the inactivation kinetics for glazed ceramic tile microbiota do not follow an exponential pattern. Although it was not reasonable to determine a D_{10} value, a significant microbial population decrease of approximately 25% ($p < 0.05$) was observed for irradiation doses higher than 2 kGy.

The morphological profile of the microbial population, before and after irradiation, was analysed in order to understand how it varied with the applied gamma radiation dose. The results show that with increasing dose, the initial major morphological type — non-spore forming rods (61%) — disappears, with filamentous fungi prevailing starting at 4 kGy (86%) [19.10]. The low efficiency of inactivation obtained might be due to the heterogeneity of the microbial population and its constitution, since filamentous fungi are usually considered more resistant to gamma radiation than bacteria.

Beyond the limited microbial inactivation, the applied gamma radiation doses caused changes in visual characteristics of glazed ceramic tiles, namely an increase in the glaze opacity and darkening of areas without pigment (Fig. 19.7), which could not be reversed.

The results obtained in this case study showed gamma radiation to be inappropriate as a decontamination treatment for glazed ceramic tiles. Further

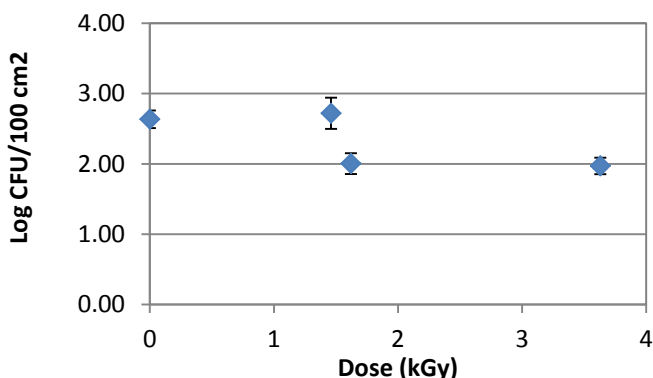


FIG. 19.6. Gamma radiation survival curve for the microbial population of glazed ceramic tile samples from the panel Quinta de Santo António ($3 < n < 12$; $\alpha = 0.05$).



FIG. 19.7. Visual appearance of glazed ceramic tile samples before irradiation (left) and after irradiation at 4 kGy (right).

studies will be performed to elucidate the gamma radiation side effects on ceramic tiles.

19.4. CONCLUSION

Improved knowledge of the agents of deterioration is essential for an accurate evaluation of the damage caused or for the correct planning of restoration measures. Microorganisms can cause damage to material through a variety of mechanisms, including biofilm formation, chemical reactions with the material, physical penetration into the substrate and production of pigments. Ionizing radiation technologies can be used successfully as an alternative treatment method for some artefacts. However, to design effective control measures, the microbial communities, the material and their interactions need to be characterized and evaluated. Therefore, only when a multidisciplinary approach based on these aspects is tailor made for each case can an appropriate treatment strategy be designed for a correct application of radiation technologies as an alternative treatment for cultural heritage objects.

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Chapter 20

DISINFECTION OF CULTURAL HERITAGE OBJECTS USING ELECTRON BEAM ACCELERATORS

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20.1. INTRODUCTION

A unique feature of radiation techniques is the possibility of disinfection of a large number of objects in a short time. Gamma radiation is generally used for this purpose, but sometimes an EB can be used [20.1, 20.2]. For gamma radiation, the irradiation time can vary significantly depending on the dose rate [20.3]. When EB accelerators are used, treatment time for an individual object under the EB is of the order of few seconds. Depending on the number of objects, the procedure typically takes from several minutes to several hours (for very large collections of artefacts). EB accelerators have been successfully used for treating low density material and relatively thin objects. The use of an EB for disinfecting artefacts from the Polish Army Museum is described below.

20.2. THE NATURE OF ELECTRON BEAM RADIATION

EB treatment is generally characterized by high dose rates but low penetration. The high energy electrons are generated by accelerators which are capable of producing EBs that are either pulsed or continuous. As the product/material being treated (disinfected) passes beneath or in front of the EB, energy from the electrons is absorbed by the material. Upon interaction with the exposed products, EB radiation causes ionization and excitation of the molecules, resulting in alteration of various chemical bonds. As with gamma radiation, secondary electrons play a major part in bringing about these transformations, and they cause the same ionizing effect.

While commercial medium and high energy range EB accelerators range in energies from 0.7 to 10 MeV and usually operate at a single energy, advances in technology have resulted in the development of select EB equipment capable of operating at varying energies. For the disinfection of cultural heritage objects,

high energy EBs are typically required to achieve penetration of the product and packaging. When evaluating EB irradiation for the purpose of disinfection, product density, size, orientation and packaging must be considered. In general, EB irradiation performs best when used on low density, uniformly packaged products. Electrons from EB accelerators have a usable penetration of about 3.5 mm in water for each million volts of accelerating potential. A 10 MeV beam will therefore penetrate about 3.5 cm. In lower density materials, the penetration will be correspondingly higher.

20.3. COMPATIBILITY OF MATERIALS WITH ELECTRON BEAM TREATMENT

Most materials making up cultural heritage objects that must be disinfected are not formulated for radiation stability. Some materials have demonstrated less degradation when processed with EB radiation as compared to gamma radiation. This is due to a significant difference in dose rate between the two radiation technologies. In general, products processed with EB radiation experience shorter exposure time, which could result in a lower oxidative effect on certain materials [20.4]. Some cellulose materials, for example, experience less breakdown and fewer long term ageing effects from processing with accelerated electrons (see Table 20.1).

TABLE 20.1. RADIATION EFFICIENCY OF HYDROGEN EVOLUTION AND OXYGEN UPTAKE FOR CELLULOSE AND CELLULOSE + LIGNIN AT DIFFERENT DOSE RATES

	EB (18 000 kGy/h)		γ (7 kGy/h)	
	Cellulose	Cellulose + lignin	Cellulose	Cellulose + lignin
GH ₂ [μ mol/J]	0.334	0.211	0.219	0.206
GO ₂ [μ mol/J]	0.942	0.532	1.72	0.842

20.4. CONTROLS FOR CONSISTENT DOSE DELIVERY

EB disinfection requires the simultaneous control of the beam's current, scan width and energy, as well as the speed of the conveyor transporting the product through the beam. The speed of the conveyor is usually regulated with

feedback circuitry from the beam current. If the beam current changes during processing, the conveyor speed correspondingly changes to ensure that the delivered dose is held constant (Fig. 20.1). After extensive research, it has been established and internationally accepted that keeping the energy of machine sources below the well defined threshold of 10 MeV will ensure that no induced radioactivity is produced in the irradiated object.



FIG. 20.1. Conveyor and aluminium boxes under the scanner of the EB accelerator (Institute of Nuclear Chemistry and Technology (INCT), Warsaw, Poland).

20.5. COMMERCIAL APPLICATION OF ELECTRON BEAM ACCELERATORS AT RESEARCH AND DEVELOPMENT AND SERVICE CENTRES

In a typical EB facility designed for high volume processing, products enter on a conveyer through a labyrinth that permits access but stops radiation from escaping (Fig. 20.2). The treatment room houses the accelerator itself and, like the whole installation, is constructed of thick concrete to protect workers from radiation. In the treatment room the materials pass under the accelerator for processing. Once the materials have been ‘sprayed’ with electrons, they continue on the belt until they exit the installation. The equipment area contains the electrical, electronic and cooling equipment required to run the accelerator.

20.6. EXAMPLE OF EMPLOYMENT OF ACCELERATOR INSTALLATION FOR DISINFECTION OF OBJECTS OF HISTORICAL SIGNIFICANCE

In the summer of 1991, a significant number of objects were brought to Poland after exhumation from mass graves in Kharkov and Miednoje. There were: fragments of uniforms, shoes, distinctions, photos and everyday objects.

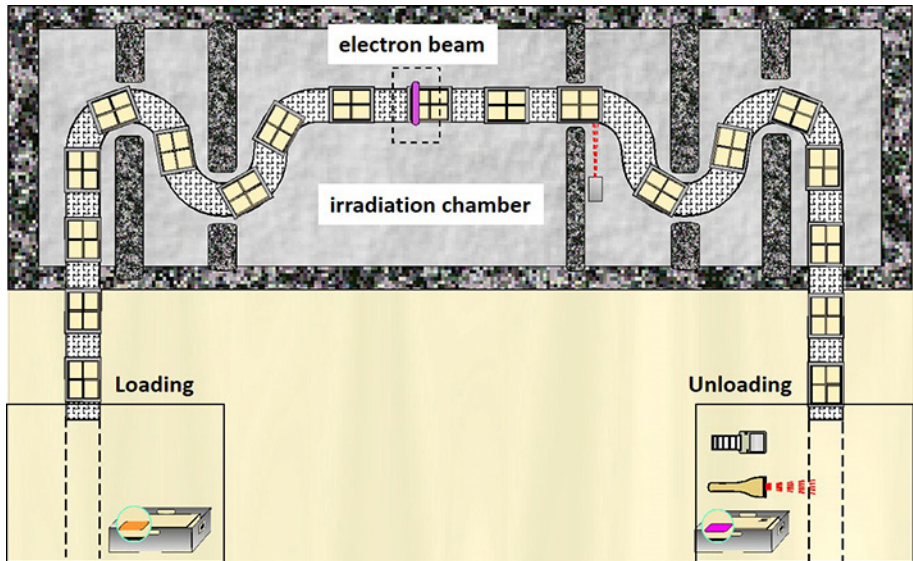


FIG. 20.2. Block diagram of the accelerator installation at the facility for radiation sterilization.

It was decided that the items would be transferred to the Museum of the Polish Army, where they would be maintained and the records would be kept. These collections were to be shown in the exhibition of 25 November 1991. In this situation, it was necessary to quickly sterilize the objects so that they could be subjected to research work in the Central Forensic Laboratory of the Police Headquarters in Warsaw and the Institute of Police in Legionowo. The Institute of Nuclear Chemistry and Technology (INCT) in Warsaw was asked to carry out radiation sterilization treatment on the artefacts. After assessment of the size of the objects and the types of materials from which they were made, INCT decided to use an EB for disinfection. The artefacts were brought in bags, arranged in a single layer in aluminium boxes and passed under the EB accelerator (approximately 10 MeV energy and power of 10 kW) using a conveyor system. A typical radiation sterilization dose of 25 kGy was applied. Since the installation is routinely used for sterilization of medical devices, the procedure was carried out after normal working hours (at night) and care was taken to ensure that there was no contact between the medical devices and the historical artefacts. After radiation treatment, the artefacts were taken to the Museum of the Polish Army and the Police Headquarters, where they were subjected to necessary conservation work.

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Chapter 21

THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN ROMANIA

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21.1. INTRODUCTION

In Romania, radiation processing takes place at the IRASM Radiation Processing Center (Fig. 21.1), a department of the Horia Hulubei National Institute for Physics and Nuclear Engineering (IFIN-HH), the most important research and development institute in Romania. IRASM was founded in 2001 with the help of the IAEA, which partially funded the irradiator. It was designed to promote the use of radiation technology in industry and agriculture and the preservation of heritage for public benefit. To be able to fulfil its mission, the



FIG. 21.1. IRASM Radiation Processing Center.

irradiation facility is surrounded by analytical laboratories. The work of these laboratories is to measure and certify the beneficial effects of the irradiation.

IRASM's structure is presented in Fig. 21.2. On the premises are a Dosimetry Laboratory which has a mini-irradiator and a microbiological laboratory which validates irradiation sterilization. A laboratory for physical and chemical tests is located in a nearby building. It is able to conduct tests for the identification of irradiated foods, mechanical, structural and colorimetric tests, and others. A biocompatibility laboratory works in close cooperation on some IRASM activities related to medical devices. The activities performed at IRASM are certified by DQS Germany as being compliant with ISO 9001, ISO 13485 and ISO 11137. The laboratories received proof of their competence through licensing and accreditations, both domestic and international. The dosimetry lab is traceable at the National Physical Laboratory, United Kingdom, through Risø High Dose Reference Laboratory, Denmark.

Decontamination of cultural heritage objects by irradiation has been considered an activity of national interest since the design of the IRASM facility. The category IV irradiation facility includes a tote box conveyer and allows industrial irradiation at high doses to be delivered in a short time. In the irradiation room of the facility, there is a space next to the conveyor where oversized artefacts may be placed for irradiation. Paper and other smaller artefacts can be irradiated in containers. Since the construction of the facility (in the 1990s), IRASM staff held periodic meetings with conservators/restorers, presenting information on the irradiation method and establishing relationships of trust with museum staff.

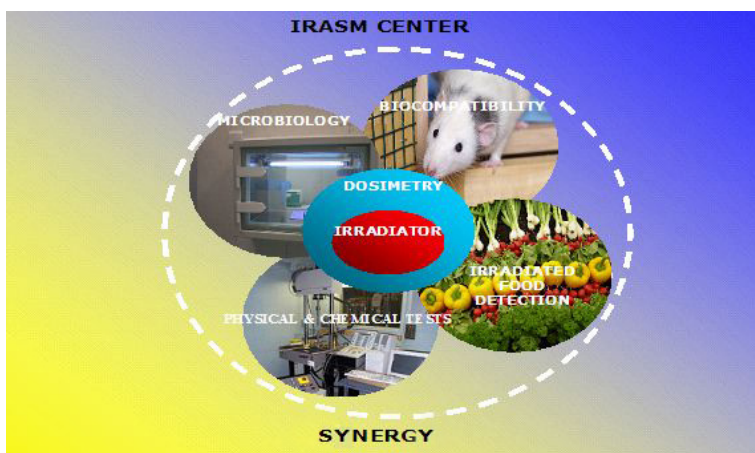


FIG. 21.2. IRASM's structure.

There were also several cases in which small artefacts were decontaminated with an existing irradiator.

The activities mentioned above have brought end users from museums since 2001, the year the IRASM centre was commissioned. The first activity was furniture decontamination for the Cotroceni Museum, Bucharest (Fig. 21.3).

The purpose of the treatment was to remove fungi before restoration. The next year, in 2002, the entire wooden inventory (~10 m³) of a parish church in Izvoarele village was treated (see Chapter 15). Also in 2002, an important project for the National Film Archive took place. It included the treatment of several dozen film reels severely contaminated with fungi (see Chapter 13). The treatment was preceded by several tests.

IRASM activity related to the preservation of cultural heritage has developed continuously and now comprises undertakings ranging from research projects and doctoral theses to international cooperation.

21.2. RESEARCH PROJECTS

Radiation decontamination brings about the intended effect of destroying biodeteriogens as well as side effects consisting of modifications of the materials from which the artefacts are built. The useful biocidal effect is well known and does not require further study. Further research is still needed to learn more about the insufficiently studied area of side effects. This insufficiency is unusual for



FIG. 21.3. Wardrobe from Cotroceni Museum, Bucharest (courtesy of IRASM, IFIN-HH).

the scientific world today, when it is difficult to find an unexplored area. Certain characteristics make this an unattractive research area. These features lead to weak relevance for the tests performed and may even disqualify the research activity. Some specific drawbacks are presented below:

- To evaluate the physical and chemical properties of a material, scientists need to make repeated measurements to counteract the inaccuracy of the measuring method. The samples tested must be identical. Wood, paper, leather or textile samples cannot be identical, as their basic raw materials are not homogeneous. There are not two perfectly alike wooden pieces, sheets of paper or leather pieces. The value measured by the investigator will include variation resulting from the inaccuracy of the measuring method in addition to that resulting from the lack of homogeneity in the samples. Selecting testing samples that fall within a defined reasonable range of homogeneity is difficult and expensive even for new materials. For aged materials, it is almost impossible. This is the reason such tests are unreliable.
- Many relevant mechanical or chemical testing methods are destructive. Sacrificing a cultural heritage artefact for a test defies the purpose of such an action. Even when samples can be taken from the artefact for such tests (e.g. textiles), the resulting statistics are poor.
- Extrapolation of results obtained in tests performed on new materials to draw conclusions for aged materials is not relevant.
- Artificial ageing does not follow the same pattern as natural ageing. Indeed, in the United Kingdom an experiment on naturally ageing leather has been going on for several decades. After several more decades, leather samples naturally aged in different environmental conditions will become available for experiments. A similar experiment intended to last 100 years is being conducted in the United States of America on natural paper ageing.

The main consequences of these drawbacks are:

- There are very few standards applicable to the treatment of cultural heritage artefacts. For this reason, different experiments cannot easily be compared to confirm or invalidate them.
- The experiments are often presented at cultural heritage meetings and then published in conference proceedings, not in peer reviewed journals that guarantee high scientific standards. Such papers carry no recognition in the scientific area to which they belong, but sometimes are taken as references by conservators/restorers who do not have any alternative option.

IRASM has been involved in research and development projects focused on evaluating the side effects of irradiation, keeping in mind the above mentioned difficulties. The drawbacks were minimized by working in complex teams that included museums and other research institutes with complementary profiles. There have been three projects, one focused on irradiation's side effects in each of the following areas:

- Wood and polychrome wood;
- Paper, archives;
- Leather, parchment and textiles (ongoing project).

The scientific results may be found in the publications listed in Section 21.9.

All research projects included treatment of compromised artefacts hosted in partner museums or other cultural institutions or by private persons. Each project provided an opportunity to promote the most important advantage of irradiation decontamination by proving it to be the proper method for emergency situations, when large volumes have to be treated quickly.

21.3. DECONTAMINATION TREATMENTS

IRASM has treated more than 200 m³ of wood, paper, leather and textile artefacts for museums like the Aman, Severeanu, Cotroceni and Mogosoia museums and the National Museum of Romanian History (all in Bucharest); museums in other cities in Romania such as Braila, Iasi and Sibiu; religious institutions like Manastirea Dintr-un Lemn (monastery); two parish churches in Izvoarele; the National Film Archive; the Radio Archive; the National University of Arts; the IFIN-HH archives; private institutions and persons and others. Conveyor irradiation was preferred for the treatment of archives, books, small icons (polychrome wood), small carpets and leather clothes. For furniture and any other oversized artefacts, static irradiation was used. The minimum dose (D_{\min}) was ~6 kGy and the maximum dose (D_{\max}) was less than 10 kGy in most cases. The dosimetry system used was ECB with oscillometric readings. Several details on these treatments are presented below.

21.4. DECONTAMINATION OF MODERN WOODEN SCULPTURES

The sculptor Laurentiu Mogosanu carves works out of decayed wood (Fig. 21.4). Hosting these artefacts in a museum would be like accepting a Trojan horse — bringing them inside could contaminate the indoor environment with



FIG. 21.4. Sculpture in rotten wood by Laurentiu Mogosanu entitled *Time Direction* (courtesy of Laurentiu Mogosanu).

fungi and insects. Irradiation decontamination is a fast and reliable solution that can get artefacts into the museum circuit.

Nicapetre (real name P. Balanica) was a well known Romanian artist who lived his last 30 years in Canada. He donated to his native town of Braila an important art collection including 85 wooden sculptures. To protect and enhance the donation, the Braila town council and museum dedicated a splendid building to the collection, establishing the Nicapetre Cultural Centre. The most impressive pieces are carved in oak trunks. These sculptures were severely attacked by fungi. It was necessary to disinfect them before placing them in the centre's controlled environment. Irradiation decontamination was the only solution because it was the only method that could effectively penetrate the wooden pieces with large dimensions and weight — up to 2.5 m and ~300 kg. The treatment was performed in October 2014 (Fig. 21.5).

21.5. SIMULTANEOUS DECONTAMINATION OF ARTEFACTS AND RESTORATION OF MUSEUM BUILDINGS

In the case of the Aman and Severeanu museums, the buildings were restored at the same time the collections were decontaminated. This approach is considered a model because only this kind of action makes it possible to capitalize on the benefits of irradiation decontamination and avoid rapid recontamination. The institutions had their entire inventory disinfected by irradiation. The artefacts in the museums were removed and stored in another



FIG. 21.5. Monumental wooden sculpture by Nicapetre, before shipment to IRASM for decontamination (left) and after treatment (right). (Courtesy of Braila Museum and IRASM, IFIN-HH.)

location during the restoration. These were then decontaminated and placed in the clean and controlled environment of the restored buildings. Also included in this category were the decontamination of the IFIN-HH archive (housed in a separate building), the Perpesiccius collection from Braila Museum (separate building) and the archives of the Museum Mogosoaia (limited space in the museum's building). The treated pieces were hosted at the IRASM premises until the completion of the repair and restoration of their original locations (Fig. 21.6).

21.6. DECONTAMINATION OF THE NATIONAL FILM ARCHIVE

Dozens of film reels had been neglected, flooded and then further neglected, resulting in a serious fungal attack in the National Film Archive of Romania (Fig. 21.7).

In this catastrophic situation, the treatment of choice was irradiation disinfection. No alternative intervention was known, although the side effects of radiation on cinematographic film were undefined. The treatment was therefore preceded by an investigation into the side effects. The research focused on the changes in the mechanical support and the colour of each layer, on ageing and on the accumulation of free radicals in the irradiated material. Microbiological tests



FIG. 21.6. Furniture from Aman Museum packaged for irradiation.



FIG. 21.7. Fungal attack on a movie film reel (courtesy of National Film Archive, Romania).

were performed as well, because the fungal attack was very severe. The decision was made to apply the treatment using the conveyor irradiator at $D_{\min} = 25$ kGy. The corresponding D_{\max} was 50 kGy.



FIG. 21.8. Wooden paintings from the cycle Martyrdom of the Brancovan Saints by E. Murariu. Left: irradiated wooden support; right: polychrome icons (courtesy of E. Murariu).

21.7. PREVENTIVE DECONTAMINATION OF WOODEN PAINTING SUPPORTS

Sometimes it is profitable to be a restorer and also a painter. As a restorer, E. Murariu knew very well that wood dried in the forest or in uncontrolled conditions may be attacked by fungi and become more vulnerable to xylophagous insects. For this reason, as a painter, she took a preventive measure in her important project on the Martyrdom of the Brancovan Saints. In the preparation of the support for the wooden polychrome icons, she included irradiation treatment (Fig. 21.8).

21.8. INTERNATIONAL COOPERATION

21.8.1. Cooperation with the IAEA

Cooperation with the IAEA has developed continuously since 2005, within the outlines of the regional (European) projects dedicated to the study and conservation of cultural heritage: RER 1006 (2005–2008), RER 8015 (2009–2011) and RER 0034 (2012–2013). Regional projects are dedicated to sharing knowledge, networking and promotion.

The following important activities were organized by IRASM or carried out with IRASM specialists:

- Organizing and hosting a workshop in 2007 and a regional training course in 2011;
- Organizing and hosting a group fellowship in 2013;
- Undertaking expert missions to France (2007, 2009), Greece (2008), Azerbaijan (2009), Hungary (2011) and Portugal (2012).

21.8.2. Cooperation with ARC-Nucléart

The main aim of the bilateral project bringing together IRASM and ARC-Nucléart (2013–2015) was networking and to transfer to Romania the technology of irradiation consolidation of porous objects. The method has been used in Grenoble for more than 30 years.

The first object consolidated in Romania using Nucléart technology was an ethnographic object belonging to the Golesti Museum (Fig. 21.9).



FIG. 21.9. Photographic presentation of the first series of experiments on irradiation consolidation of porous artefacts at IRASM under the assistance of ARC-Nucléart specialists.

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ACKNOWLEDGEMENTS TO CHAPTER 21

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We also wish to thank the French team from ARC-Nucléart for their open and efficient cooperation since our collaboration began in 1993.

We acknowledge the IAEA for its long term interest in the study and conservation of cultural heritage, expressed by supporting regional (European) technical cooperation projects RER 1006 (2005–2008), RER 8015 (2009–2011), RER 0034 (2012–2013) and RER 0039 (2014–2015). Cooperation with the IAEA has been consistently helpful and stimulating for the IRASM team.

Chapter 22

MASSIVE PRESERVATION OF WAR-DAMAGED CULTURAL HERITAGE OBJECTS IN CROATIA BY IRRADIATION

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22.1. INTRODUCTION

The war in Croatia, from 1991 to 1995, put many objects of cultural significance in great peril.

As part of an organized effort to save these objects, the collections of many museums and galleries, churches, libraries and archives were moved to previously determined, sometimes improvised, storage spaces [22.2–22.5]. About 5000 objects, comprising about 3000 altars, with polychrome sculptures, altar parts and other wooden objects, were evacuated by the spring of 1992 [22.2, 22.6].

The evacuation and other protective actions could not prevent vast injuries to cultural heritage. According to the final report of the State Committee for Inventory and Estimate of War Damages, about 40% of immovable — mostly architectural — heritage was destroyed or damaged. The list of lost, destroyed or damaged objects from 162 churches, monasteries and other sacral buildings affected by the war comprises 3098 paintings, sculptures and pieces of church furniture [22.7]. The losses from museums and galleries recorded by the Museum Documentation Centre comprise 3178 destroyed and 2283 damaged objects [22.8, 22.9].

Although a large fraction of evacuated cultural heritage — mostly wooden objects — escaped direct damage, it faced another serious problem related to storage: biodeterioration.

The sheer number of the objects requiring attention threatened to overwhelm the effort of conservators and restorers to mitigate the problems of

massive biodeterioration in a timely and effective way. Fortunately, technical means and considerable experience in treating large numbers of items against biological contaminants were already available in the country. Thanks to the panoramic gamma irradiation facility operated by the Radiation Chemistry and Dosimetry Laboratory of the Ruđer Bošković Institute (RBI) in Zagreb, in use since 1984 [22.10], it was feasible to quickly treat a large quantity of cultural heritage objects at risk of biodegradation.

Under the supervision of the Croatian Conservation Institute, more than one third of cultural heritage objects evacuated from northern Croatia, mostly polychrome sculptures, parts of altars and other wooden pieces, comprising almost 1500 complete altars, were transported to the RBI for radiation insect eradication or, if necessary, disinfection [22.11]. In addition to stopping degradation, irradiation was used as the first step of conservation to enable safe storage of objects without the risk of cross-contamination before final conservation and restoration [22.5].

22.2. EXAMPLES OF IRRADIATION TO PRESERVE CULTURAL HERITAGE OBJECTS DAMAGED BY WAR

22.2.1. Example 1: The Church of the Blessed Virgin Mary of the Snows in Kamensko near Karlovac (15th century)

Pauline monastery in Kamensko near Karlovac was destroyed in 1991 [22.12]. However, before its destruction, 29 sculptures and paintings were removed from its Church of the Blessed Virgin Mary of the Snows and placed in temporary shelters. Some parts were hidden in the crypt, but the main parts of the three altars were left in place inside the church. The church roof was later destroyed, exposing the interior to further degradation. While the main altar survived, lateral altars, especially the Holy Cross Altar from 1685, were subjected to heavy damage and decay (Fig. 22.1). In 1995, the walls of the church and the remaining unburnt parts of the altars were found to be overgrown with microflora, especially the objects hidden in the crypt. In the process of recovery, the remains of the altars were collected and at first stored in a temporary shelter in the monastery itself. In 2002, after all the parts needed to assemble the altars were sorted out, the material underwent preliminary conservation work in a workshop improvised on the spot.

All packages underwent irradiation treatment: some parts were irradiated with 2 kGy for insect eradication, strongly infested parts were irradiated with 5 kGy for disinfection and heavily infested remains recovered from the crypt were irradiated with 20 kGy. The altar sculptures evacuated in 1991 were taken out of



FIG. 22.1. *Left and middle: war destruction — remaining parts of the altar choked with microflora; right: Holy Cross Altar after conservation and restoration, re-erected in 2008 (courtesy of the Croatian Conservation Institute) [22.13].*

their temporary shelters and irradiated with 2 kGy for insect eradication before joining the rest of the materials. As the elements of all ornaments were found, complete reconstruction of the Holy Cross Altar was possible. The reconstructed altar was re-erected in the repaired church in 2008 [22.13–22.15].

22.2.2. Example 2: Polychrome sculptures from the destroyed Church of the Assumption of the Blessed Virgin Mary in Gora near Petrinja (12th or 13th century)

At the beginning of the war, polychrome wooden sculptures from the Church of the Assumption of the Blessed Virgin Mary in Gora near Petrinja, dating from the 12th and 13th centuries, were hidden in the crypt. The destroyed church superstructure soon collapsed, burying them for 6 years. Seven sculptures were recovered in 1997 from under the rubble in a very poor state, covered with dirt and fungi (Fig. 22.2).

In coordination with several other specialists, the restorers of the Croatian Conservation Institute started the lengthy treatment involving cleaning, drying, climate stabilization, partial chemical treatment and repeated irradiation. Identification of contaminating moulds and bacteria was performed in the process [22.16]. Immediately upon recovery, the heavily contaminated objects were treated with a decontamination dose of 20 kGy.

In the course of a lengthy drying process at the Croatian Conservation Institute the infection reappeared and the sculptures were irradiated again with



FIG. 22.2. Left: destroyed Church of the Assumption of the Blessed Virgin Mary in Gora; middle: sculpture of an angel from the church immediately after excavation in 1997; right: sculpture of the same angel in 2011, after conservation work in 2006 (courtesy of the Croatian Conservation Institute) [22.13].

5 kGy in 1998. The sculptures have been stored after initial conservation and partial restoration work at the Croatian Conservation Institute in Ludbreg, waiting in a stable state for further restoration [22.13, 22.16–22.18].

22.2.3. Example 3: Polyptych of the Virgin Mary from the Church of Saint Francis in Pula (15th century)

A polyptych from the Church of the Franciscan monastery in Pula is considered one of the finest late Gothic works of art in Croatia. The influence of the Venetian artistic family Vivarini, active towards the end of the 15th century, has been strongly suggested. The polyptych was dismantled and stored in a safe place in late autumn 1991. When conditions allowed for its reinstallation in the church, this was not deemed possible owing to the poor condition of the polyptych resulting from it being repositioned several times over the last 200 years. All parts of the polyptych were transported for radiation insect eradication with 2 kGy to the RBI, and further conservation and restoration work was carried out at the Croatian Conservation Institute in Zagreb. In December 2004, the polyptych was re-erected in the Church of Saint Francis (Fig. 22.3) [22.13, 22.19].

In conclusion, irradiation has proven to be an effective and very useful method for protecting cultural heritage artefacts endangered by massive biodegradation [22.20].

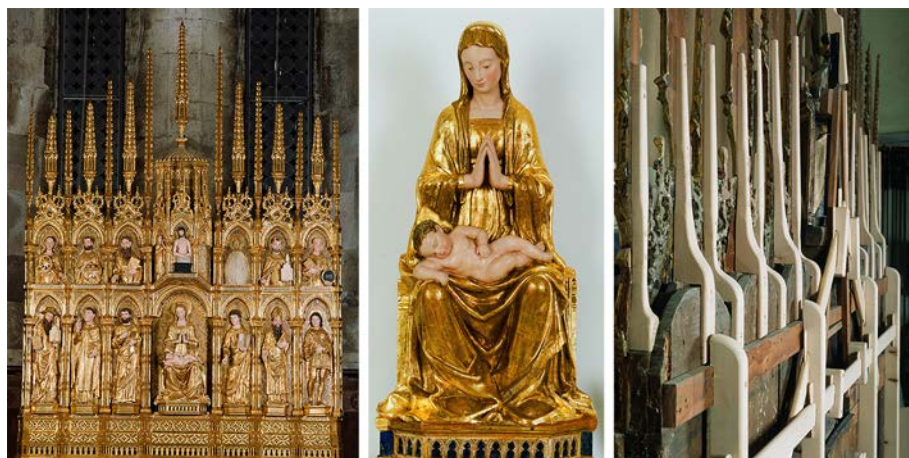


FIG. 22.3. *Left: polyptych of the Virgin Mary from the Church of Saint Francis in Pula; middle: the central sculpture of the Virgin Mary with infant Jesus after conservation; right: backside supports of the polyptych (courtesy of the Croatian Conservation Institute) [22.13].*

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Chapter 23

THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN BRAZIL

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23.1. INTRODUCTION

The climate of Brazil comprises a wide range of weather conditions across a large area and varied topography, but most of the country is tropical. High temperature and humidity levels favour the growth of mould and other fungi in works of art and books. Another big problem found in the conservation of cultural heritage is related to xylophagous insects, especially termites and wood boring beetles. The Multipurpose Gamma Irradiation Facility at the Nuclear and Energy Research Institute (IPEN) of the National Nuclear Energy Commission (CNEN) in São Paulo has been used for disinfestation, disinfection and sterilization of many kinds of cultural heritage materials made of paper, wood, leather, textiles and other materials. These activities have had a significant social impact, and museums, libraries, collectors, conservators and others have benefited from this use of radiation technology. A few these activities are described below.

23.2. PUBLIC ARCHIVE OF THE STATE OF SÃO PAULO: SÃO LUIZ DE PARAITINGA FLOODING

In 2010, São Luiz de Paraitinga, a colonial city popular with tourists, was affected when a nearby river flooded as a result of weather conditions. Archives containing significant data on public buildings as well as identity records, retirement records, contracts and other records were destroyed or heavily damaged. The Public Archive of the State of São Paulo established a partnership with the National Service for Industrial Training to recover the damaged archives. Part of the affected archives was treated by traditional recovery methods such as drying, interleaving and cleaning. A considerable number of documents were infected by fungi, mainly owing to inappropriate storage and incomplete drying. Traditional recovery methods failed, including after drying. The material was

processed by the gamma irradiation facility at the IPEN with an average dose of 8–10 kGy (Fig. 23.1).

23.3. CONTROL OF INSECTS AND FUNGI IN A PRIVATE COLLECTION OF INCUNABLES

Incunables or incunabula are books printed before 1501 in Europe. The owner of a private collection of incunables covering fields such as wine and viticulture had a collection of approximately 5000 ancient books which were attacked by several pests including mould and other fungi. The National Service for Industrial Training referred the problem to the IPEN. The fungi were very resistant to traditional control treatments. The collection was irradiated at the Multipurpose Gamma Irradiation Facility at the IPEN with 2 kGy and 10 kGy for insects and fungi respectively (Fig. 23.2). Cleaning and related additional services were performed by a commercial book restoration company.

23.4. ARCHIVES OF THE SECRETARY OF EDUCATION FOR THE STATE OF SÃO PAULO: PAPER CONTAMINATED WITH SEWER WATER

In 2011, archives containing significant personal data of the Secretary of Education for the State of São Paulo were contaminated with sewer water. The flooding was a consequence of pipe breakages. Drying operations were performed



FIG. 23.1. Public Archive of the State of São Paulo: flood, damage and conservation in São Luiz de Paraitinga.



FIG. 23.2. Private collection of incunables: control of insects and fungi.

on the damaged documents. A temporary storage space was selected to avoid additional problems. The Basic Sanitation Company of the State of São Paulo proposed various approaches to disinfection including gamma irradiation. The material was packed using plastic boxes (Fig. 23.3). The processing was carried out by the Multipurpose Gamma Irradiation Facility at the IPEN. The average processing dose was approximately 15 kGy. The recovered documents will be digitized and stored under proper conditions.

23.5. GAMMA IRRADIATION OF A RESTORED PAINTING FROM THE 17th CENTURY

It is important to study the material composition and behaviour of any art work which will be treated by gamma radiation before beginning the treatment, as well as to use complementary procedures to prevent recontamination after the treatment, because this method has no residual effects. As an example, the object of study is a Peruvian painting from the 17th century (Fig. 23.4), which was restored, contaminated by mould, treated with gamma rays and put in a hermetically sealed acrylic box, and which showed microorganism growth after



FIG. 23.3. Archives of the Secretary of Education for the State of São Paulo: paper contaminated with sewer water, before and after gamma disinfection.



FIG. 23.4. A contaminated 17th century Peruvian painting was irradiated at the IPEN.

six years [23.1]. A new treatment was performed using the same process and a complementary treatment was also performed using cloistering with anoxic atmosphere to prevent recontamination. The results related to the stability of the painting's materials obtained before the first irradiation made it possible to increase the applied dose with no changes in those materials.

REFERENCE TO CHAPTER 23

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Chapter 24

THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN TUNISIA

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24.1. INTRODUCTION

Since 2005, the Tunisian National Centre for Nuclear Science and Technology (CNSTN) has been using gamma radiation technology to conserve cultural heritage objects from different national museums. Thanks to a multidisciplinary team including physicists, biologists and chemists, the efforts were focused on:

- Carrying out research in order to study materials and develop best practices adapted to the radiation treatment of the objects and collections: determination of irradiation dose, dose rate and homogeneity ratio and establishment of dose cartography of products.
- Carrying out the necessary treatments for insect eradication and disinfestation of tapestries and other objects made of organic materials such as wood or leather.
- Informing professionals and the general public of the new techniques developed for conservation of cultural heritage.

24.2. THE CNSTN's PILOT SCALE GAMMA IRRADIATION FACILITY

The CNSTN's pilot scale gamma irradiation facility has the following characteristics:

- Irradiator type: pilot.
- Commissioning year: 1999.
- Location: CNSTN, Tunis.
- Radiation source: ^{60}Co .
- Activity: 3.7×10^{15} Bq.

- Dry source storage.
- Product handling system:
 - Position 1: for pallets (automatic system) — 5 carriers ($\sim 7.5 \text{ m}^3$) per batch.
 - Position 2: for samples.

The facility (Fig. 24.1) is mainly used for enhancing research and development work and delivering services to businesses in the areas of food irradiation (in accordance with the relevant national decree), sterilization of medical devices (in accordance with the relevant national decree and ISO 11137), conservation of art objects and radiation processing of materials.

24.3. IRRADIATION PROCESS

The first step is to determine the necessary irradiation dose to eradicate insects without causing modifications such as changes in the colour of substances including varnishes, glass and ceramics, tissue and wood. In general, sterilization and disinfection aiming to eliminate fungi and other microorganisms require more significant doses.

Whereas 0.5 kGy (minimum dose) is sufficient for example to eliminate xylophagous insects, a dose of 2 kGy is needed to kill certain fungi, and a dose of 10 kGy or more is needed for sterilization.

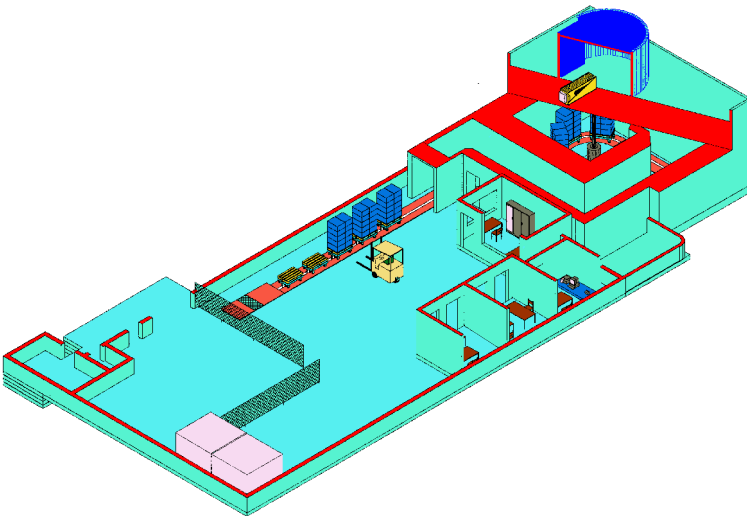


FIG. 24.1. Schematic of the CNSTN's pilot scale gamma irradiation facility.

The products are then forwarded to the irradiation room and a cartographic study is carried out to determine the dose distribution in the product (maximum and minimum dose, and homogeneity ratio).

According to the result of the cartography, the irradiation of products is carried out by category (according to the nature and geometry of the product) and continuously (to avoid radioresistance in insects or microorganisms).

24.4. CULTURAL HERITAGE ARTEFACTS PROCESSED AT THE CNSTN

The CNSTN signed a convention with the National Heritage Institute for the restoration of art objects. The following sections present the CNSTN's activities treating some categories of objects from the different national museums.

24.4.1. Metal armchairs covered by leather and textile

Musée Habib Bourguiba in Monastir (2012): treatment of metal armchairs covered by leather and textile at 2 kGy to eradicate insects (Fig. 24.2).

24.4.2. Tapestries, official clothes of the Bey, wooden musical instrument

National Bardo Museum (2008): insect eradication in tapestries, official clothes of the Bey and a wooden musical instrument. Irradiation dose applied was 2 kGy to eliminate xylophagous fungi and insects (Fig. 24.3).



FIG. 24.2. Left: packed metal armchairs with leather and textile covers; right: the products being irradiated in the gamma irradiation facility.



FIG. 24.3. Left: official clothes of the Bey; centre: wooden musical instrument; right: products being irradiated in the gamma irradiation facility.

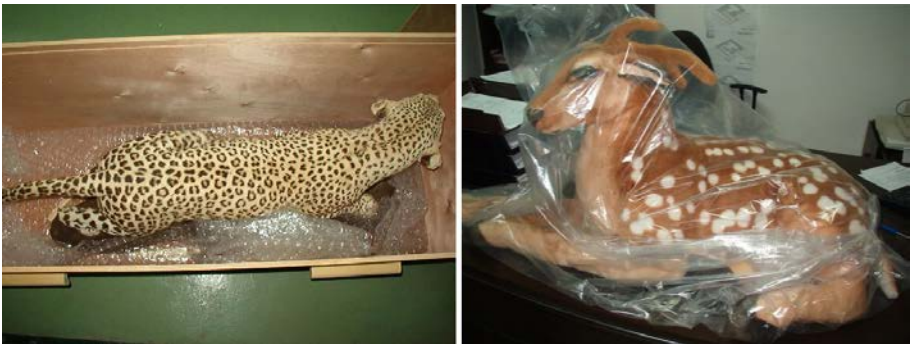


FIG. 24.4. Mummified animals from the Presidential Museum of Carthage treated by irradiation.

24.4.3. Mummified animals

Presidential Museum of Carthage (2009): insect eradication and disinfection of mummified animals for elimination of keratophagous insects (biodecomposers able to degrade keratin in the hair and cuticles of many animals) (Fig. 24.4).

Chapter 25

THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN CROATIA

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25.1. INTRODUCTION

The only irradiation facility in Croatia capable of providing irradiation services to interested parties, including conservators and restorers, is the panoramic ^{60}Co gamma irradiation facility at the Radiation Chemistry and Dosimetry Laboratory (RCDL) of the Ruđer Bošković Institute (RBI) in Zagreb. The RBI was established in 1950 as the Institute for Atomic Physics. Its scope was soon expanded to include chemistry and biology, thereby reinforcing its multidisciplinary character, which it has been fostering ever since. Today, the RBI is Croatia's leading scientific institute. It has over 550 scientists and researchers in more than 80 laboratories pursuing research in a variety of areas related to theoretical and experimental physics, materials science, electronics, physical chemistry, organic chemistry and biochemistry, molecular biology and medicine, marine and environmental research, information and computer sciences, and lasers [25.1]. The RCDL was established in 1958 and has remained until the present day the only laboratory in the country pursuing both basic and applied scientific research in the fields of radiation chemistry and dosimetry and radiation processing [25.2].

The panoramic gamma irradiation facility of the RCDL was constructed in 1963. Although only an experimental facility at the beginning, it was designed with the future role of a multipurpose pilot scale irradiation facility in mind, with a capacity of more than 3.7×10^{15} Bq of ^{60}Co . The facility was upgraded into a pilot scale irradiation facility and loaded with 1.85×10^{15} Bq of ^{60}Co in 1983. However, the application of irradiation treatment to the protection of cultural

heritage became possible only after some proficiency in radiation processing procedures at the larger scale was acquired. Performing commercial scale irradiations for sterilization, pasteurization, decontamination and disinfection of various materials — medical supplies, pharmaceuticals, cosmetics, toiletries and foods — provided the necessary understanding of practical aspects of irradiation processes and dosimetric control methods [25.3, 25.4]. At the same time, increasing experience regarding radiosensitivity of various biological contaminants, side effects of radiation on materials and dosimetry [25.5] made the operators more competent to deal with new challenges posed by the preservation of cultural heritage artefacts. Indeed, over the past 25 years, protection and conservation of cultural heritage objects by irradiation has been successfully carried out in Croatia [25.6, 25.7].

25.2. THE IRRADIATION FACILITY AT THE RUĐER BOŠKOVIĆ INSTITUTE

The irradiation facility is a panoramic type dry storage irradiator. The source of radiation consists of 90 pencils of ^{60}Co arranged in 24 rods so that 18 rods contain 4 pencils each and 6 rods contain 3 pencils each. The rods are arranged in the shape of a cylindrical cage, with a diameter of 32 cm and a height of 32 cm (Fig. 25.1). The rods are suspended on cables, each within its own guide tube inside which it can be moved between the safe and the operating positions. The safe position is inside a lead container at the bottom of a storage well dug into the floor of the irradiation chamber. In the operating position, the radiation sources are lifted above the floor of the irradiation chamber, but each source rod remains within its guide tube for safety reasons. The irradiation room is a rectangular chamber, $4.9\text{ m} \times 3.9\text{ m} \times 3.5\text{ m}$, in which there is room for $4\text{--}6\text{ m}^3$ of material in each batch. When the radiation source is in the operating position, its centre is 0.7 m above the floor of the irradiation room. The topography of the radiation field in the room was measured using the ethanol–chlorobenzene dosimetry system [25.8].

Because the radiation source has the form of a cylinder, the radiation field around it also has a cylindrical symmetry. Dose rate at all points at a given height depends only on the distance from the axis of the source; that is, in all horizontal planes, isodose curves have the shape of circles. In vertical planes at any distance from the axis of the source, dose rate varies with the height from the floor of the chamber, reaching a maximum at the height of the centre of the cylinder, 0.7 m above the floor. The closer the vertical plane is to the axis of the source, the more this maximum is pronounced. In the horizontal plane at 0.7 m above the floor, dose rate decreases inversely with $r^{1.96}$. If all radioactivity were concentrated in



FIG. 25.1. Irradiation facility at the RBI (courtesy of RCDL archive, RBI).

the centre of the source cylinder, dose rate would decrease inversely proportional with the square of the distance (i.e. with r^2).

These details of the radiation field should be taken into account when planning the irradiation of larger items, such as certain cultural heritage objects, to ensure more even dose distribution throughout the irradiated volume. The objects are generally positioned so that larger objects are placed away from the axis of the source, where the curvature of isodose curves is smaller. Smaller objects can be placed closer and put one atop another, especially if packed in boxes, so that the total height does not exceed 1.4 m (i.e. $2\text{ m} \times 0.7\text{ m}$). After the first half of the prescribed irradiation time has elapsed, the objects must be rotated around a vertical axis by 180° , and those above 0.7 m must be replaced by those below. Larger objects, such as sculptures, can only be rotated by 180° . In this case, the parts that are at 0.7 m receive the highest dose, and parts at the bottom and at the top receive the smallest dose. Care must be taken that the minimum dose is still sufficient to achieve the desired effect. So, for example, the nominal dose for insect disinfestation at this facility is set at 2 kGy, although 0.5 kGy would be sufficient if that dose were homogeneously distributed.

25.3. ACCEPTANCE OF IRRADIATION TREATMENT

After the gamma irradiation facility was upgraded in 1983, irradiation treatment of infested cultural heritage objects could be undertaken for the first time. At first, occasional insect eradication in antique furniture was the main service sought. However, the demand for radiation treatment of cultural heritage objects of some significance grew considerably during the war in Croatia (1991–1995), when an increasing number of cultural heritage objects damaged directly or indirectly in the war were brought to the RCDL badly in need of restoration and conservation. The irradiation was a meaningful step towards preservation, especially of polychrome wooden sculptures. Their treatment with gamma rays in the RCDL irradiation facility played a significant role in the prevention of massive biodeterioration. Under the supervision of the Croatian Conservation Institute (CCI), hundreds of objects, mostly polychrome wooden sculptures, parts of altars and other wooden artefacts, comprising about 1500 complete altars, were transported to the RBI for radiation insect eradication or, if necessary, disinfection, to arrest biodegradation and to enable them to be accommodated in safe depots until restoration [25.9]. This contribution to the preservation of cultural heritage objects has been recognized internationally [25.10]. In Croatia, this activity helped promote radiation treatment among national conservators and led to its gradual acceptance.

The doses applied for irradiation treatments at the RCDL have been those that are generally accepted in the professional literature: 0.5 to 2.0 kGy for control of insects, 5 to 10 kGy for control of fungi and 5 to 20 kGy for control of bacteria.

It is estimated that over the past 25 years more than 8000 wooden sculptures, parts of altars, furniture pieces, tools, musical instruments and other objects made of wood, paper, straw, textile and leather have been treated in cooperation with the CCI and other interested parties. Almost 95% of all treated objects were subject to insect eradication. Most often, single cultural heritage objects were treated, but irradiation has been proved an especially appropriate method when a complete dismantled altar or iconostasis, or an entire museum collection, had to be treated simultaneously to avoid cross-contamination. Presently about 20 m³ of objects, comprising mainly wooden heritage objects, are treated annually at the RBI facility.

25.4. EDUCATION AND DISSEMINATION OF KNOWLEDGE

The acceptance of the irradiation method and its correct application depend on the understanding by conservators/restorers of its advantages and limitations. The need to disseminate this kind of knowledge and to provide basic information

on the irradiation method to potential users in a systematic manner has led the RCDL to take an active part in the education of conservators/restorers at all levels.

For ten years, students of the carpentry division of the secondary technical school for wood technology in Zagreb have been making annual visits to the irradiation facility and receiving information on irradiation for the preservation of antique furniture. A national seminar for their teachers was organized by the Centre for Continuous Professional Education in November 2012 at the RBI.

The Academies of Fine Arts of the three Croatian universities in Zagreb, Split and Dubrovnik offer graduate studies in conservation/restoration. The lectures on the application of nuclear techniques, including irradiation, are often accompanied by a demonstration of the irradiation facility. As a practical part of the study and in preparation for graduate work (theses) requiring hands-on experience in restoration, real heritage artefacts are often irradiated as a first step in the complex process of conservation and restoration [25.11]. The scientists of RCDL are co-mentors for graduation theses of particularly interested students.

However, working conservators and restorers remain the principal target of activities aimed at dissemination of knowledge. Several lectures on irradiation treatment of cultural heritage objects were held at CCI seminars and conferences in Zagreb: Destruction of Cultural Monuments by Microbiological Decay in 2000 [25.12], The Most Important Procedures for Preserving and Improving the State of Textile Artworks in 2008 [25.13] and Ethical Approach to Works of Art Made of Textiles in 2013 [25.14–25.17].

A national seminar covering irradiation treatments for conservators and related specialists, titled Irradiation Methods in the Protection of Cultural Heritage, was jointly organized by the RBI and CCI in October 2011 in Zagreb and Zadar [25.18]. The seminar gathered 150 participants, indicating the timeliness of the forum and the opportunities it provided to learn about and discuss prospects for irradiation methods. Several experts in the application of irradiation from the RBI covered radiation chemical and radiobiological aspects of the method and shared their experience in insect eradication and disinfection. Q.K. Tran from the ARC-Nucléart Laboratory, France, an expert appointed by the IAEA, provided additional information on the application of radiation for consolidation. The accompanying exhibition of posters: Examples of Successful Applications of Irradiation in Croatia, presented by the members of the profession, reinforced the impact.

Lectures on irradiation methods were presented by members of the RCDL at the international scientific conference on the Protection of Cultural Heritage from Natural and Man-made Disasters, held in Zagreb and Šibenik in May 2014, organized by the National and University Library, Zagreb [25.9, 25.19].

In addition to irradiation services, the RCDL has been providing consultations to interested parties on demand.

25.5. THE VISIBILITY OF IRRADIATION TREATMENT IN PUBLICATIONS

According to the Venice Charter, all treatments, including irradiation, to which a cultural heritage object has been subjected in the process of conservation/restoration, have to be recorded in a database and kept for future reference. Consequently, the irradiation of all artefacts within the framework of the cooperation between the RBI and CCI is recorded in the CCI database called BREUH (Base of Croatian Artefacts Recorded for Restoration) [25.20].

There are two main periodicals for conservators/restorers in Croatia: *Preservation of Cultural Heritage in Croatia* (the journal of the Ministry of Culture) and *Portal* (the annual of the CCI). Both publish reports on conservation/restoration work involving irradiation.

In the open access domain, the web sites of institutes, academies, museums, archives and libraries offer user friendly insights into the activities of the respective institutions, also covering work related to conservation and restoration of relevant cultural heritage materials, which often involves the use of irradiation.

The CCI web site, in the section presenting its activities in conservation, provides some extensive descriptions of conservation/restoration work, including radiation treatments [25.21]. An example is the polyptych by Girolamo da Santa Croce from Vis (Fig. 25.2) [25.22].

The web site of the International Conference of Conservation and Restoration Studies, the student conference of Croatian and international art restoration students, includes lectures and posters, results of students' workshops and theses.

The use of irradiation is increasingly seen as one of the important approaches to conservation [25.23]. The visibility of the successful application



FIG. 25.2. A panel of the predella from the polyptych by Girolamo da Santa Croce from Vis after conservation (courtesy of the Croatian Conservation Institute archive).

of irradiation was enhanced by appropriate acknowledgement of this fact at a number of exhibitions of restored cultural heritage objects.

25.6. NATIONAL AND INTERNATIONAL COOPERATION

The cooperation between the RBI, the CCI and the Department of Restoration of the Academy of Fine Arts, University of Zagreb, has been essential for the successful application of irradiation treatment to objects of cultural heritage. The lasting cooperation between the CCI and several laboratories of the RBI was made formal in 2006 by a memorandum of understanding between the Ministry of Science and the Ministry of Culture.

The cooperation between the RCDL and the Croatian State Archives mostly involved radiation treatment of books and old book covers to eradicate insects [25.18]. In 2010 the two institutions joined efforts in the conservation of The Book of Statutes of the town of Dubrovnik from 1272. The codex, a 15th century transcription on parchment with wood–leather covers, was heavily damaged by insects and mechanical injuries. In the process of conservation, the book's covers were treated by irradiation with a disinfection dose of 5 kGy. Mutual agreement to extend the cooperation to radiation disinfection/insect eradication in historical paper led to a formal collaboration agreement between the RBI and Croatian State Archive in 2013.

The RCDL also cooperates with the National and University Library in Zagreb, a number of Zagreb museums (Museum of Arts and Crafts, Museum of Contemporary Art, Ethnographic Museum, Croatian History Museum, Mimara Museum) and many museums and galleries outside Zagreb.

Good cooperation and confidence has been established with religious institutions of the principal denominations, the Zagreb archdiocese, the Serbian Orthodox Church parish and the Jewish community in Zagreb.

The RBI, the CCI and the Academy of Fine Arts in Zagreb have been involved in international cooperation through IAEA regional projects RER 1006 (2005–2008): Nuclear Techniques for the Protection of Cultural Heritage Artefacts in the Mediterranean Region; RER 8015 (2009–2011): Using Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the European Region; and RER 0034 (2011–2014): Enhancing the Characterization, Preservation and Protection of Cultural Heritage Artefacts. All participating parties have been active in the respective project activities, as evident from the activity reports [25.24, 25.25].

Cooperation between the RCDL and the (then) Institute of Isotopes of the Hungarian Academy of Science took place during 2010–2011 under the Agreement of Scientific and Technical Cooperation between the Croatian

Academy of Sciences and Arts and the Hungarian Academy of Science on the subject of Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts.

Bilateral cooperation between Croatia and Slovenia has brought together the RCDL and the Restoration Centre, Institute for the Protection of Cultural Heritage of Slovenia, Ljubljana, since 2011. The subject of cooperation, Irradiation Methods in the Preservation of Historic Museum Textiles, is a part of the Slovenian national project Microbiological and Structural Investigations of Biologically Damaged Textiles from Slovenian Museums.

Another bilateral cooperation project focused on the transfer of knowledge has been established with the Serbian Central Institute for Conservation in Belgrade. The irradiation of some cultural heritage objects is planned within the context of this cooperation.

25.7. RESEARCH RELATED TO CULTURAL HERITAGE IRRADIATION

In almost 95% of cases, wooden cultural heritage objects are treated for insect eradication with a dose of 2 kGy. In a field somewhat related to irradiation of cultural heritage, a cooperative project with the Faculty of Forestry, University of Zagreb aimed at evaluating a standard for determination of efficacy of chemical wood preservatives against wood destroying microorganisms. According to European Standard EN 113: 1996 (Wood preservatives — Test method for determining the protective effectiveness against basidiomycetes — Determination of the toxic values), toxicity testing had to be carried out on substrates consisting of wood samples rendered sterile by irradiation with 25 to 50 kGy. Although there is often an underlying concern by conservators and other users for the integrity of wooden cultural heritage objects irradiated with only 2 kGy, it was shown that prescribed sterilization doses 10 to 20 times the insect eradication dose did not interfere with the substrate; only at much higher doses, about 90 kGy, does the wood substrate become detectably deteriorated and digestible to test organisms [25.26].

Thanks to the generally smaller dimensions of textile artefacts, control of insects therein could be effectively achieved by 1 kGy instead of a flat nominal dose of 2 kGy, and at a more favourable ratio of D_{\max} to D_{\min} . Successful examples include:

- Liturgical textiles from the Franciscan monastery in Slavonski Brod dating from the 19th and 20th centuries [25.15, 25.27];

- Historic church textiles which are no longer in use but are stored in a special depot for preventive maintenance (textile collection of the CCI, Ludbreg) [25.15, 25.17];
- Garments of the tilters of Sinj, part of the collection of costumes, accessories and weapons of the Alka annual knightly equestrian contests, which have been running for 300 years [25.15, 25.28].

The application of higher doses for the control of fungi on textile fibres has to be justified to avoid undesirable changes. Some of the results of experiments performed in the context of Croatian–Slovenian cooperation at the RBI irradiation facility are included in Ref. [25.29].

Ongoing research at the RCDL on thermal properties of textiles using differential scanning calorimetry and thermogravimetric analysis shows that irradiation itself and post-irradiation storage induce changes in properties of fibres that are comparable to or smaller than those resulting from artificial ageing itself and subsequent irradiation [25.16, 25.30].

Another research project in progress deals with radiation effects on some ornamental materials making up cultural heritage objects (e.g. nacre) and some pigments to establish their response to irradiation [25.23].

25.8. EXAMPLE OF LARGE SCALE RADIATION INSECT ERADICATION: THE KOŽARIĆ COLLECTION OF THE MUSEUM OF CONTEMPORARY ART

In 2007 the City of Zagreb purchased the entire inventory of the atelier belonging to one of the most significant contemporary Croatian artists, sculptor I. Kožarić (b. 1921), and gave it to the Museum of Contemporary Art for future permanent exhibition, management and maintenance. The Kožarić Studio, assembled over 50 years of the artist's activity, contains more than 6000 items: sculptures, reliefs, assemblages, installations, objects, paintings, prints, drawings, sketches, ready-mades and many everyday items (Fig. 25.3).

While still in their original location, as well as during the relocation, transportation and handling, the objects were not kept under appropriate conditions, and they could not be protected against infestation. Consequently, the entire collection had to be checked and treated before being moved into the new museum building. The majority of the objects of organic origin were treated with an insect eradication dose of 2 kGy at the RBI irradiation facility for preventive and curative purposes [25.31].



FIG. 25.3. Left: part of the Kožarić Studio inventory; right: graphic map from the Kožarić collection.

ACKNOWLEDGEMENTS TO CHAPTER 25

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Chapter 26

THE STATE OF THE ART IN RADIATION PROCESSING FOR CULTURAL HERITAGE IN FRANCE

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26.1. INTRODUCTION

ARC-Nucléart is located in the CEA's Grenoble Technology Research Centre and was set-up jointly by the CEA, the Ministry of Culture, the Grenoble city council, the Rhône–Alpes regional council and the association Pro-Nucléart. This consortium was created in 1989 and was awarded administrative status as a 'Public Interest Group for Culture' in 1997, enabling it to be managed independently like a small company. ARC-Nucléart offers services in the conservation/restoration of cultural heritage artefacts, mainly those made of wood, using various processes that will be described later. Its origin goes back to the creation of the Nucléart laboratory in 1969 by Louis de Nadaillac, an engineer studying the applications of gamma processing in industry and in the field of cultural heritage at the CEA's Grenoble centre.

During those pioneering days, in 1970, the small group of scientists and technicians took up the challenge of consolidating the old parquet of the Stendhal Museum in Grenoble by using a radiation curing resin (see Section 17.1). The success of this operation led to the technique being applied to disinfect and consolidate dry wooden cultural heritage objects such as sculptures, furniture and ethnographic artefacts. At the same time, archaeological artefacts excavated from underwater sites in the Grenoble area were given conservation treatment using the radiation curing resin process following requests from local archaeologists and curators. In 1997, the mummy of Ramses II was successfully disinfected by gamma irradiation in the CEA centre at Saclay, near Paris (see Chapter 11). During the 1980s, the conservation of waterlogged archaeological wood was enhanced by the creation of a dedicated centre, jointly supported by the CEA, the Grenoble city council and the Ministry of Culture. This initiative allowed the Nucléart laboratory to develop another process, which is now used worldwide, for the conservation of waterlogged wood of different sizes, from small pieces to large objects such as boats or shipwrecks. This technique, the polyethylene glycol

(PEG) process, was then used to treat an 11th century canoe excavated from lake Paladru, near Grenoble. The Nucléart laboratory became ARC-Nucléart in 1989, when the Rhône-Alpes regional council joined the consortium. This was followed by the adoption of private law status in 1997.

The agreement linking the five partners for a renewable period of 5 years clearly defines ARC-Nucléart's aims:

- Conservation/restoration treatment of organic cultural heritage materials such as dry and waterlogged wood, leather, ropes and basketry;
- Studies and research projects to develop analysis methods as well as conservation processes to tackle new issues;
- Training for undergraduate and graduate students involved in national or European research projects;
- Communication activities targeting cultural heritage partners and the public.

In fact, ARC-Nucléart offers a full spectrum of conservation/restoration services, ranging from services at excavation sites to assistance with the display of artefacts in museums, thanks to a multidisciplinary staff of around 20 people (permanent and under contract) from the CEA (nine persons for management and scientific activities), Grenoble city council (two technicians), the Ministry of Culture (one museum curator and one technician) and ARC-Nucléart itself (which is authorized to hire seven permanent conservators/restorers under contract). The various conservation/restoration tasks are performed in dedicated facilities covering a total of 3000 square metres. The facilities consisted in the 1970s of only the irradiation facility (Figs 26.1 and 26.2); then in the 1980s and 1990s the PEG impregnation facilities were built (Fig. 26.3), followed by addition of restoration workshops and air-conditioned storage facilities. This entire infrastructure exists today thanks to the confidence and continued support of the State, the CEA and the other partners in developing ARC-Nucléart's activities.

26.2. CONSERVATION PROCESSES

26.2.1. Gamma irradiation for disinfection and consolidation of cultural heritage artefacts

Insect eradication and bacteria or fungus disinfection are carried out by exposing the artefacts to gamma rays at the corresponding radiation doses: 0.5 to 1 kGy for larvae or wood boring insects and 10 to 20 kGy for microorganisms. The highest dose rate applied in the irradiation chamber is



FIG. 26.1. The ARC-Nucléart irradiation facility.



FIG. 26.2. Irradiation of polychrome statues for insect eradication.



FIG. 26.3. Large (12 m × 6 m) PEG impregnation tank.

around 1 kGy/hour. In 2010, a frozen baby mammoth from Siberia, Khroma, was disinfected at the ARC-Nucléart irradiation facility with a total dose of 20 kGy.

Consolidation of degraded wooden artefacts (dry state) is undertaken through a two-step process consisting of impregnation by an unsaturated polyester resin in pressurized steel tanks (Fig. 26.4) followed by in situ polymerization of the resin by gamma irradiation with doses ranging from 30 to 40 kGy. The first step lasts around 24 hours, while the second one requires many days for the resin inside the object to polymerize completely.

26.2.2. Conservation of waterlogged archaeological artefacts

One technique for conservation of waterlogged archaeological artefacts is with a widely known and used process. First, the wet wood is impregnated with an aqueous solution of the polymer PEG (2000 g/mol), followed by controlled air drying for large objects such as boats or shipwrecks, or freeze drying for smaller collections. Depending on the dimensions of the artefacts, the PEG impregnation phase can last from a few months to more than a year, while freeze drying



FIG. 26.4. Stainless steel resin impregnation tank.

can take almost a month and air drying a year or more. The concentrations of PEG in the impregnation baths depend on the drying method: 30–40% PEG in solutions for freeze drying and up to 70% PEG for air drying. A large Roman period shipwreck (30 m long divided into 10 sections) from the Rhône River at Arles was treated by PEG/freeze drying, and has been displayed in the Arles Archaeological Museum since 2013.

Another technique uses a combination of the two processes described above for conservation of waterlogged composite archaeological artefacts (mainly iron compounds in wood). First, the object is freeze dried after impregnation with a minimally concentrated 20% PEG solution, and then the dried object is impregnated with the radiation curing polyester resin. This hydrophobic resin has a twofold action: it consolidates the wood, and it stabilizes or protects the ferrous parts against further corrosion during display. For instance, the prow and the mast of the Arles Roman shipwreck were treated with this so-called mixed



FIG. 26.5. Installing the prow of the Arles Roman shipwreck in the irradiation cell.

Nucléart process, associating freeze drying with a minimum content of PEG, followed by impregnation with styrene polyester resin and irradiation (Fig. 26.5). The bow was in fact rimmed with metal that it was important to preserve, despite the risk of corrosion and acidification reactions in the presence of iron, sulphur and PEG. The high content of extremely hydrophobic resin is expected to ward off corrosion and protect the wood from aqueous acid diffusion. With regard to the mast, a high level of consolidation was needed in order to be able to present it in a vertical position (Fig. 26.6).

26.2.3. Restoration work

Classical restoration work (cleaning, gluing, varnishing, assembling, etc.) for historical artefacts (furniture, polychrome wooden sculptures, etc.) as well as for consolidated and dried archaeological collections is carried out by a team of permanent conservators. When necessary, wooden or metallic supports are designed to hold the items for display in museums.

26.3. RESEARCH PROJECTS AND NETWORK

ARC-Nucléart cooperates internationally (e.g. through European research projects) on cultural heritage conservation. Examples are:



FIG. 26.6. The Roman shipwreck (with its prow consolidated by radiation curing resin) in the Arles Archaeological Museum.

- The European Commission Joint Programming Initiative on Cultural Heritage’s Heritage Plus Call project ‘ARCO’, Ageing Study of Treated Composite Archaeological Waterlogged Artefacts, which aimed to develop original characterization protocols to assess the most appropriate treatments for composite archaeological artefacts. Four countries (Norway, Denmark, Italy and France) were involved in this collaborative research during 2013–2015.
- Bilateral cooperation between Romania and France in using gamma irradiation for cultural heritage artefact conservation (2013–2015), supported by IFIN-HH (Romania) and the CEA (France). The main aims of the cooperation were the following: scientific visits, research on the effects of irradiation on cultural heritage materials, and technology transfer relating to the CEA consolidation process to IFIN-HH.
- The IAEA technical cooperation project on Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the European Region. ARC-Nucléart staff K. Tran and L. Cortella participated as expert consultants in projects RER 1006 (2005–2008), RER 8015 (2009–2011), RER 0034 (2012–2013) and the organization of a regional training course in Grenoble in 2007.

26.4. SELECTED PUBLICATIONS

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Annex I

CURRENT APPLICABLE STANDARDS

This annex lists the principal standards that are currently applicable.

Standards applicable to cultural heritage

EN 15898:2011. Conservation of cultural property — Main general terms and definitions

ISO 21127:2014. Information and documentation — A reference ontology for the interchange of cultural heritage information
www.iso.org/iso/catalogue_detail?csnumber=57832

Standards applicable to radiation processing

ISO 14470:2011. Food irradiation — Requirements for the development, validation and routine control of the process of irradiation using ionizing radiation for the treatment of food
www.iso.org/iso/catalogue_detail?csnumber=44074

ISO 11137-1:2006. Sterilization of health care products — Radiation — Part 1: Requirements for development, validation and routine control of a sterilization process for medical devices
www.iso.org/iso/catalogue_detail?csnumber=33952

ISO 11137-2:2013. Sterilization of health care products — Radiation — Part 2: Establishing the sterilization dose
www.iso.org/iso/catalogue_detail?csnumber=51238

ISO/ASTM 51702. Standard practice for dosimetry in a gamma facility for radiation processing (2013)

ISO/ASTM 51431. Standard practice for dosimetry in electron beam and X-ray (bremsstrahlung) irradiation facilities for food processing (2005)

Annex II

WEB SITES OF INTEREST

The following web sites may be useful for readers.

International organizations in conservation and preservation

ICOM-CC (International Council of Museums — Committee for Conservation)
www.icom-cc.org

ICCROM (International Centre for the Study of the Preservation and Restoration of Cultural Property)
www.iccrom.org

ECCO (European Confederation of Conservator-Restorers' Organisations)
www.ecco-eu.org

CAMEO (Conservation and Art Materials Encyclopaedia Online — Museum of Fine Arts, Boston)
<http://cameo.mfa.org>

International organizations dedicated to standardization

ISO (International Organization for Standardization)
www.iso.org

CEN (European Committee for Standardization)
www.cen.eu

ICRP (International Commission on Radiological Protection)
www.icrp.org/

ICRU (International Commission on Radiation Units and Measurements)
www.icru.org

ACRONYMS AND ABBREVIATIONS

CEA	Commissariat à l'énergie atomique
CTA	cellulose triacetate
<i>D</i>	absorbed dose (or simply dose)
D_{\max}	upper dose limit
D_{\min}	lower dose limit
D_{10}	dose decimal reduction value (the irradiation dose necessary to reduce the number of microorganisms by a factor of ten)
DNA	deoxyribonucleic acid
DTG	derivative thermogravimetry
EB	electron beam
ECB	ethanol-chlorobenzene
EPR	electron paramagnetic resonance
FTIR spectroscopy	Fourier transform infrared spectroscopy
NIR	near infrared
IUPAC	International Union of Pure and Applied Chemistry
keV	kilo electron volt
$LD_{50/30}$	lethal dose 50% (the dose lethal for 50% of irradiated subjects) within 30 days
MeV	mega electron volt
MMA	methyl methacrylate
PCA	principal component analysis
PEG	polyethylene glycol
PET	polyethylene terephthalate
PMMA	polymethyl methacrylate (Altuglas, Lucite, Perspex, Plexiglas, etc.)
TG	thermogravimetry
UV	ultraviolet

GLOSSARY

dose limit ratio. For each product or process, the ratio $(D_{\max})/(D_{\min})$ defines the acceptable dose window; every part of the product should receive a dose within that range.

dose rate. Absorbed dose delivered per unit time, for instance in Gy/h.

dosimeter. Device that, when irradiated, exhibits a quantifiable change that can be related to absorbed dose in a given material, using appropriate measurement instruments and procedures.

dosimetry. Measurement of absorbed dose by the use of a dosimetry system.

dosimetry system. System used for measuring absorbed dose, consisting of dosimeters, measurement instruments and their associated reference standards, and procedures for the system's use.

electron. One of the elementary particles, characterized by its light mass and its negative electrical load. It is one of the fundamental components of an atom. It can be generated by the disintegration of radioactive atomic nuclei (beta particle) or produced by an electronic vacuum tube.

electron beam (EB). The basic components of a typical EB are an electron gun (source of thermal electron emission) and a high voltage generating device which accelerates the primary EB. This use of a direct high voltage to produce a high energy EB allows the conversion of input AC power to beam power at efficiency greater than 95%, making EB material processing a highly energy efficient technique. After exiting the gun, the beam passes through an electromagnetic lens and deflection coil system for producing either a focused or defocused beam spot on the treated object. The system can deliver a stationary beam spot or provide an oscillatory motion. Electron energies typically vary from the keV to MeV range, depending on the depth of penetration required.

equivalent dose. Radiation weighted dose quantity which takes into account the type of ionizing radiation producing the absorbed dose. Equivalent dose is used in radiological protection to measure the biological effects of ionizing radiation. The equivalent dose is calculated by multiplying the absorbed dose by a radiation weighting factor appropriate to the type and energy of radiation. To obtain the equivalent dose for a mix of radiation types and

energies, a sum is taken of all types of radiation energy doses. This takes into account the varying biological effect of different radiation types. The SI unit for equivalent dose is the Sievert (Sv). For X and gamma radiation, an absorbed dose of 1 Gy delivers an equivalent dose of 1 Sv.

equivalent dose rate. Equivalent dose delivered per unit time, for instance in Sv/h.

gamma radiation. Electromagnetic radiation produced in the disintegration of radioactive atomic nuclei. The energy range of gamma radiation is between several keV and several MeV. Cobalt-60, used for irradiation of cultural heritage artefacts, emits gamma radiation of 1.17 and 1.33 MeV.

ionizing radiation. Electromagnetic radiation or particles that carry enough energy to liberate electrons from atoms or molecules, thereby ionizing them. Gamma rays, X rays, and the upper vacuum ultraviolet part of the ultraviolet spectrum are ionizing, whereas the lower ultraviolet, visible light (including laser light), infrared, microwaves, and radio waves are non-ionizing forms of radiation.

irradiation. The process by which an object is exposed to radiation. The exposure can originate from various sources. Most frequently the term refers to ionizing radiation, and to a level of radiation that will serve a specific purpose, rather than exposure to normal levels of background radiation. The term irradiation usually excludes exposure to non-ionizing radiation, such as infrared, visible light, microwaves, or electromagnetic waves emitted by radio and TV receivers and power supplies.

irradiation biocidal effect. Degradation of the DNA in the cells of microorganisms, insects, or fungi under ionizing radiation exposure, resulting in the eradication of these organisms.

irradiator. Any device producing ionizing radiation designed to irradiate objects for different purposes (e.g. sterilization, chemical modification). The process does not leave radioactive residue or cause the treated products to become radioactive. The radiation can come from a sealed source containing a radioactive isotope (such as ^{60}Co), an X ray generator or an EB.

lower dose limit (D_{\min}). This value sets the minimum dose required to achieve the desired sterility level in the product.

maximum equivalent dose rate. The 2007 Recommendations of the International Commission on Radiological Protection¹ distinguish between two categories of exposed individuals: workers (informed individuals) and the public (general individuals). For those two categories, the maximum equivalent dose rate (for 2000 h of annual exposure) is:

- 0.010 mSv (10 μ Sv) for workers;
- 0.0005 mSv (0.5 μ Sv) for the public.

microorganism. Microscopic organism, which may be a single cell or a multicellular organism. Microorganisms are very diverse and include all bacteria, viruses and protozoa, and some fungi, algae and others. Many macroorganisms and plants have juvenile stages which are also microorganisms.

preventive conservation. All measures and actions aimed at avoiding or minimizing future deterioration or loss. They are carried out within the context or on the surroundings of an item, or more often a group of items, whatever their age and condition. These measures and actions are indirect; they do not interfere with the materials and structures of the items. They do not modify their appearance.

Examples of preventive conservation are appropriate measures and actions for registration, storage, handling, packing and transportation, security, environmental management (light, humidity, pollution and pest control), emergency planning, education of staff, public awareness and legal compliance.

process load. Volume of material with a specified product loading configuration irradiated as a single entity.

quality [ISO 9000]. Degree to which a set of inherent characteristics fulfils requirements.

quality assurance [ISO 9000]. Part of quality management focused on providing confidence that quality requirements will be fulfilled.

¹ INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, The 2007 Recommendations of the International Commission on Radiological Protection, Publication 103, Elsevier, Amsterdam (2007).

quality control [ISO 9000]. Part of quality management focused on fulfilling quality requirements.

quality management system [ISO 9000]. Management system to direct and control an organisation with regard to quality.

quality manual [ISO 9000]. Document specifying the quality management system of an organisation.

radiation processing. Intentional irradiation of products or materials to preserve, modify or improve their characteristics.

radiation shielding. Material that protects people from ionizing radiation. As radiation passes through matter, its intensity is diminished. Materials commonly used for shielding against gamma radiation, X rays and electrons are concrete (including barite or lead loaded concretes), lead or any dense and high atomic number material.

remedial conservation. All actions directly applied to an item or a group of items aimed at arresting current damaging biodegradation processes or reinforcing the structure of the items. These actions are only carried out when the items are in such a fragile condition or are deteriorating so quickly that they could be lost in a relatively short time. These actions sometimes modify the appearance of the items.

Examples of remedial conservation are disinfestation of textiles, desalination of ceramics, deacidification of paper, dehydration of wet archaeological materials, stabilization of corroded metals, consolidation of mural paintings and removing weeds from mosaics.

restoration. All actions directly applied to a single stable item aimed at facilitating its appreciation, understanding and use. These actions are only carried out when the item has lost part of its significance or function through past alteration or deterioration. They are based on respect for the original material. Most often such actions modify the appearance of the item.

Examples of restoration are retouching a painting, reassembling a broken sculpture, reshaping a basket and filling losses on a glass vessel.

routine dosimetry system. Dosimetry system calibrated against a reference standard dosimetry system and used for routine absorbed dose measurements, including dose mapping and process monitoring.

sealed radioactive source. Container enclosing radioactive material that is permanently bonded or fixed in a capsule designed to prevent release and dispersal of the radioactive material under the most severe conditions which are likely to be encountered in normal use and handling. Generally, the radioactive material is encapsulated in a tight, double walled, welded stainless steel capsule.

side effects. In the context of radiation treatment of cultural heritage artefacts, side effects are non-desired effects — such as colour alteration, mechanical strength degradation, surface aspect modification and introduction of new compounds that may interact negatively with the original substrate — induced by radiation treatment to consolidate, conserve or restore artefacts. These effects cannot always be stopped in the short or medium term.

sterility. Sterility can be defined as the freedom from the presence of viable microorganisms. It is generally defined for an object in functional terms. As an example, in pharmaceutical practice, a container is defined as sterile when the probability is less than one in one million that it is contaminated with replicating microorganisms.

sterilization. Validated process used to render a product free of all forms of viable microorganisms.

sterilization process. Process leading to sterilization of a load. It includes preconditioning (if used), the sterilization cycle and aeration.

Note: in a sterilization process, the level of microbial death is described by an exponential function. Therefore, the presence of viable microorganisms on any individual item can be expressed in terms of probability. While this probability may be reduced to a very low number, it can never be reduced to zero. This probability can be expressed as a sterility assurance level.

upper dose limit (D_{\max}). This value is set to ensure that radiation will not adversely affect the quality of the product.

X radiation. Ionizing electromagnetic radiation that can ionize atoms and disrupt molecular bonds. Note: X ray is a common term used for X radiation.

X ray generator. A device used to generate X rays. X ray generators are commonly used by radiographers to acquire an X ray image of the inside of an object (as in medicine or non-destructive testing), but they are also used in sterilization or X ray fluorescence analysis. Such a device contains an X ray tube, a vacuum tube consisting of a cathode that emits electrons through the thermoelectron effect and an anode or anticathode generally made of tungsten (owing to its refractory properties and its high electron/X ray photon conversion ratio) sealed to copper to evacuate the heat generated by the collision. Anode and cathode are connected to a high voltage power supply (in the range of several hundred kV to several MV). When the accelerated electrons collide with the target, only a small percentage of the resulting energy is emitted as X rays, with the remaining energy released as heat. A cooling system is necessary to cool the anode; many X ray generators use water or oil recirculating systems.

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