Nuclear Techniques for Preservation of Cultural Heritage Artefacts

Booklet addressability

Given on one hand, the increasing number of laboratory in the world interested to implement these techniques and, on the other hand, the need of references to help to a substantial understanding from conservators who would or could use them, we thought it was necessary to state about main technical and scientific assets. In the light of ethical considerations, we will thus try in this document to identify the conservation issues according to the types of damage encountered, the different materials, but also other considerations such as surrounding of the object after treatment. In this approach, we will review the accumulated experience and the already completed research. Of helpful interest, we will also give some examples of significant treatments done using these techniques.

Though the authors have mostly technical background, they recognized the necessity of interdisciplinary approach and tried to understand problematic and specificity of the conservation – restoration area. That's why chapters related to physics, chemistry and microbiology contain selected information supposed to be helpful for people in charge with decision for radiation conservation. The presentation level of this information took into account the difficulty encountered by conservators, curators or other responsible people in appreciation and foundation of a conservation decision. However especially readers with humanistic background are prompted to read the booklet twice.

For the sake of logical presentation the authors introduced some technical terms like *irradiation dose, Gray, Curie* from the early pages but explained them later. We hope this will not bring another difficulty in understanding this complex domain.

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Content

Foreword

Over the past decades, radiation processing has been used in many sectors of national economies. For example, sterilization, polymer cross-linking (tapes, tubes, cables, etc.), tyre belt vulcanization, and the irradiation of certain food items for hygienization, are well established technologies. Either gamma radiation from isotopic sources or high energy electrons from accelerators are being applied in these processes.

The IAEA, through various mechanisms, including its technical cooperation programme, coordinated research projects, technical meetings and conferences, is promoting the peaceful use of nuclear and radiation technologies.

In response to Member State requests, the Technical Cooperation Department of the European Region launched in 2009 the TC Project RER8015 on **"Using Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the Europe region"** to improve the characterization and preservation of cultural heritage artefacts through the application of nuclear techniques with special emphasis on gamma irradiation treatment, making use of techniques including insect eradication and disinfection in various cultural heritage materials and consolidation of degraded materials with radiation-curing resins.

This working document summarizes some aspects of radiation processing technology for preservation of cultural heritage artefacts. It will be of value to those working in the field of application of radiation technology for preservation of art objects and for conservators and curators to understand this technology and its benefits. Developing Member States with radiation technology programmes will benefit from the rich experience in this area worldwide.

The IAEA wishes to thank to the authors of this booklet for their valuable contributions, and to Mr. Jean Louis Boutaine for his special contribution in the introductory chapter. The IAEA officers responsible for this publication was Ms. Alessia M. Rodrigues y Baena, the Programme Management Officer of the TC Project, and Ms. Maria Helena de Oliveira Sampa, Technical Officer of the Division of Physical and Chemical Sciences.

**Maria Helena de Oliveira Sampa,
in the name of IAEA Team**

Safeguarding the world cultural heritage is a shared, gratifying & important task for the whole technical & scientific community. Among the large palette of techniques used for the examination, the characterization, the analysis, the preservation, the consolidation & the conservation of cultural heritage artefacts, many of them rely on the use of ionizing radiations.

One can obviously mention radiography using X-rays, gamma photons, neutrons or beta particles, X-ray fluorescence analysis, neutron activation & neutron prompt gamma analysis, ion beam analysis like PIXE (particle induced X-ray emission), synchrotron radiation based characterization or analysis techniques.

Many of these techniques are routinely operated, all around the world, in public cultural heritage institutions, universities, museums, libraries, archives institutions, restoration workshops. They greatly contribute to a better knowledge & understanding of the component materials and/or the processes of manufacturing the ancient or modern artefacts & give scientific basis for their optimum safeguarding for the benefit of future generations. Some of them are well recognized, even by a large public.

High intensity gamma radiation (mainly from cobalt-60 sealed sources) has been used for many years for the disinfection or sterilization of collections of cultural artefacts made of wood or other organic materials. It has appeared necessary to establish an assessment of the state of the art of the applications of this technique to wooden artefacts (furniture, statues, archaeological objects, ethnographic collections artefacts, etc.), basketwork, leather, paper, etc. Also, indications of best practices concerning the required radiation dose and facts relative to the return of experience regarding long term behaviour of such treated artefacts are relevant information.

The "Nucleart" technique, developed in the CEA Grenoble nuclear research centre, is based on the impregnation by an adequate resin of altered objects made of dry or waterlogged wood, porous stones or other fragile materials, followed by an in core polymerization under intense gamma radiation (cobalt 60). This technique, used in parallel with other ones like lyophilization or impregnation with high molecular weight organic compounds like polyethylene-glycol is able to consolidate & finally to save heavily altered precious artefacts. So, they can be presented to the public, in long term safe conditions, in museums.

Among the various available consolidation/conservation techniques, the "Nucleart" technique would probably be well fitted to collections kept under equatorial or tropical climates, because the so treated artefacts would be more resistant to mould and/or insect attacks.

It is a real pleasure to see that the IAEA community, after having contributed, through research programmes, training of scientists & technicians, and publications to the development & the mastering of analytical techniques dedicated to the world cultural heritage devotes this booklet to the various intense ionizing radiation based techniques dedicated to the preservation/consolidation/conservation of cultural heritage artefacts.

I wish that the distribution of this publication to curators, conservators/restorers, conservation scientists, and students will enhance the global efficiency of the safeguard of our common cultural heritage.

Jean Louis Boutaine

Introduction

Irradiation technique have been used from the early 70's as treatment to preserve cultural heritage artefacts. Based on the biocide effect of ionizing radiation, the technique was at the beginning developed mostly in Czech Republic and in France, with some resounding success such as the disinfection of the Ramses II mummy. The method have now widened in many countries and became, at different scale, of current use.

In time ionising radiation proved to have other abilities useful for cultural heritage reservation. By initiating polymerisation & crosslinking, radiation may be the clue in consolidation of destructured porous materials.

A treatment is an intervention method applied in order to stop, or at least to reduce the rate of deterioration of an object. As such, it differs definitively from characterization techniques for which the aim is only to collect information, whatever this information could directly help to preserve the object or is only of documental interest. As for any other techniques used in the cultural heritage conservation-restoration context, it has to respect ethical principle in order to keep the artefact "as close to its original condition as possible and for as long as possible".

Regarding to requirements of effectiveness within ethical guidelines such as minimal intervention, non contact irradiation techniques is very attractive. Besides, it is enhanced by the penetration power of gamma rays that provides an interesting way to reach the inside of 3-dimension items.

Ionizing Radiation for Cultural Heritage Preservation - Ethical Perspective

Cultural heritage conservation activities used to include examination, preventive care, documen-tation, stabilization treatment, restoration and any act that could contribute to the perception, appreciation and understanding of the cultural property. All of these activities must be undertaken within special ethics, assuming responsibility of heritage conservation towards the owner, the society and the transfer to future generations. The ethic principle thus defines the stabilization of the object in its significance as the principal goal of any conservation activity.

To reach this goal, cultural heritage conservation is commonly divided into preventive and interventive conservation. Preventive conservation tends mainly to offer protective environment for the collections. It often requires the control of environmental conditions such as temperature, humidity, biological surroundings and exposure to light or ultraviolet, in order to avoid the subsequent degradation. It is also concern with protection against accidental conditions, natural disaster as well as human failure or menace.

It is not the aim of this booklet to discuss about preventive conservation. However, the professionals of cultural conservation should always take into account all aspects of preventive conservation when thinking to undertake physical work on the cultural heritage collections. One has firstly to consider all preventive means that could be sufficient. Then, if nevertheless an interventive method has to be chosen, it must take into account the preventive conservation conditions that will surround the collection after treatment.

At the opposite of preventive conservation, interventive conservation refers to any act that involves a direct interaction with the cultural material. It could include cleaning, treatment, repair, or even more vigorous and definitive action as removal of covering varnish or painting, or replacement of parts of the object for instance.

As it directly interferes with the nature of the cultural property, interventive conservation is the first concerned with ethical considerations. The leading purposes of these ethical considerations can be summarized as follow. It is essential to fully justify any intervention. The level of the intervention must be optimized to keep the artefact "as close to its original" within the efficiency requirements that will ensure that it will be for "as long as possible". Finally, and whatever it may be, it had to be limited to the minimal intervention, "only what is necessary".

Nuclear scientists and technicians will not be surprised as these three fundamentals principles, justification, optimization, limitation, are equal to the ones that preside over any notion of action for which the safety is primary, and among them any "nuclear" activity. However, in terms of environmental, pol-

lution or human security, safety rules include target figures that can easily been implement in regulation. Interventive conservation differs slightly in that this kind of "safety" of cultural heritage artefacts is hardly quantifiable, and its management and control depend more on "valuation" than "monitoring".

Indeed, the "values" that have to be preserved in cultural field are very difficult to define. Conservation comprises the respect of the physical integrity as well as the aesthetic, artistic, documentary, environmental, historic, scientific, social, or spiritual significance. Moreover, the practice could noticeably change according the status of the collection. For instance, replacement of parts of the object could be well accepted in some cases in which the functional is fundamental, as for instance for historical monuments or for furniture while it is almost always out of interest in artistic or archaeological conservation. And beyond the accepted practices, the professional in conservation had also to refer to the uniqueness of any cultural heritage items.

As a result, conservation is an interdisciplinary field. It must associate human sciences (archaeology, history, and art) for the significance of the object, hard sciences (physics, chemistry, biology and materials science) for the characterization of the degradation of the object and its behaviour, and technology of the object itself (fabrication, design, artistic, etc.) as well as of the conservation methods (chemistry, physics) involved in the intervention.

Ethical guidelines such as harmlessness and reversibility of the intervention provide support for decision to the professional workers involved in cultural heritage conservation, quite indifferent if practiced specialty is culture, science or technique related. However, they can not be measured with "absolute binary value" but there is continuity from less to more harmlessness and reversibility. Therefore, any decision to intervene can only be a compromise that has to be the best according the level of knowledge.

The conservator (or restorer) is a professional who has the training, knowledge, skills, experience and understanding to act with the aim of preserving cultural heritage. In classical cases, such a professional is very often self sufficient to accomplish interventive conservation. However, he must undertake only work as he is competent to carry out. If necessary, he may be supported by other professional from human sciences, hard sciences or techniques. This is the case when complex treatments are carried out.

Use non-classical techniques requires at least a high-quality of the dialog between the scientist or technician involved in treatment, and the responsible of the collection that must be treated. This last one, let say the cultural referee, has to describe the object significance, and so on, what characteristics must mainly be subject of maximum care, while the scientist or technician, let say the technical referee, must explain how the method is active, and what can be the consequences.

In this dialog, the main difficulties appear because the cultural referee hardly gives objective boundary to the technical referee, which in turn is hardly able to explain the level of harmlessness with comprehensive words. It is really important that the technical referee can understand that the notion of significance of the object is not only one, and that the cultural referee could accept that total harmlessness does not exist whatever the interventive action, and that it must be described with objective target. It means an important effort from each other to explain, and to understand, a little part of the knowledge of each one.

Applied to nuclear techniques as a means for preservation of cultural heritage, the difficulty to meet the required mutual comprehension is exacerbated because of the reputation of closeness and opacity sometime attached to nuclear science. This image, being or not a reality, often leads to the a priori misunderstanding by non scientist of all concepts related to the physics of radiation. However, concerning the cultural heritage conservation, greatest part of radiation processing technology is mainly one single variable dependent: the dose. Even if this one can vary on very large range, from several orders of magnitude, this is a chance as it becomes really easier to anticipate the behaviour during and after irradiation, "as a matter of dose". This is the responsibility of both cultural and technical referees to initiate a productive dialog that excludes any non rational debate. And it is surely not so difficult.

Justification, optimization, limitation, harmlessness, reversibility are just some of the most general principles that must be respected. They are of course a lot of other ethical considerations. Documentation is, for instance, another very important rule which will be easy for every one: complete reports of the work carried out before, during, and after the treatment, are normal technical standards.

Most ethical issues in conservation, example of codes of ethics and guidelines for professional conduct in conservation and allied fields are provided by associations and professional organizations. UNESCO, International Council Of Museum (ICOM), or European Confederation of Conservator-Restorers' Organisations (E.C.C.O.) furnishes examples of such guidelines of historical, general or practical interest.

By analogy with industrial irradiation, use of both biocide effect and chemical effect caused by ionization are the basis of the treatments for preservation of cultural heritage artefacts.

Radiation treatment of cultural heritage artefacts

1

1.1 Cultural heritage degradation factors

An important part of cultural heritage (CH) inventory is made of wood, leather, textile or paper. All these materials are basically natural polymers vulnerable at environmental aggressors. Water, oxygen, polluting gases from the atmosphere, acids, temperature, and light are physical and chemical agents inducing CH deterioration. Often deterioration of artefacts is mainly due to the biological aggressors: micro-organisms and insects.

There is an important difference between these two deterioration types. Degradation due to physical-chemical factors evolves slowly and seems to be dependant on noxious exposure intensity, while during an active biological attack the artefact degradation evolves with high speed. In the last case, the conservation prime target must be to stop the degradation.

It is important to notice the synergism between improper physical – chemical conditions and development of biological aggressors.

By preventive conservation a plan, including for instance the regulation of microclimate, is efficient in the fight with physical and chemical degradation factors. Usually it is sufficient to control the environment to obtain control on the biological factors if and only if their attack was not started. If the attack is already active each object has to be treated, because the aggressors are present inside the artefact in the active biological form and take it as nutrient.

Laborious way of action is necessary for disinfestations because fungi, bacteria and insects have a complex live cycle, including dormant stages resistant at various biocides and unfavourable living conditions.

1.2 Disinfestation

Classical techniques used in disinfestation

Classical techniques have been borrowed from medicine and agriculture, where huge quantities of goods must be free of micro-organisms or insects. As a matter of fact, equipment and technique used in medicine and agriculture are easily adaptable to CH treatment.

Either sterilization of medical devices or disinfestations of grains used to be performed by gases poisonous for living creatures. Ethylene oxide (ETO) and methyl bromide (CH_3Br) have been the gases most frequently used for these purposes. Anoxia is another issue coming from food technology against insect. However, the efficiency of treatment that involves gas diffusion is hardly predictable, even when most important treatment parameters (gas concentration, temperature and contact time) are accurately controlled. And beyond this problem of reliability, the efficiency has an objective limit given by hard penetration of the gas inside the artefact.

Moreover, when poisonous gases are used, the main concerns are safety and environment related. ETO, which has proved to be very dangerous (carcinogenic, extremely flammable and explosive), must today be employed in approved equipment including a detoxification compartment. CH_3Br, as many halogen compounds that deteriorates the ozone layer, is already prohibited in many countries.

Other chemical treatments such as injection or application on surface of liquid are not very deemed anymore in regards of efficiency and harmlessness, even if, in the other hand, they could have some interesting preventive effects.

As one can easily imagine the side effects, other physical method such as thermal, microwave, low temperature treatments, are not diffused in the cultural heritage conservation community.

Irradiation disinfestation

The biocide effect of irradiation was noticed at the beginning of 20th century, immediately after discovery of natural radioactivity. But irradiation treatment is used in industry from several decades only, especially for sterilization of medical devices. The industrial trend is positive. Irradiation sterilization is used more and more frequently being the alternative recommended by European Pharmacopoeia as final sterilization method. Already in 1993 a half of sterile medical devices produced in the world (~ 10 millions m^3) have been obtained by irradiation.

Irradiation sterilization of medical devices is now a well defined industrial process, including important knowledge on treatment itself and treatment side-effects. All important aspects are known: academic studies focused on influence of irradiation on living organisms established a scientific area called radiobiology; other studies were devoted to radiation qualification of materials exposed to radiation, especially plastics, also some natural polymers (cotton), inscriptions, adhesives; engineering studies gave birth to various facility designs in view of optimizing cost/benefit ratio, improvement the production yield, radiation safety or reliability; normative or guides and standards covered safety design, installation and exploitation, quality assurance, and quality control.

Irradiation disinfestation of CH artefacts

At such a matured development level it is not a surprise that radiation treatment has been taken into consideration for disinfestations of CH artefacts. Since the works of Bletchly[about the action of gamma rays on xylophagous insects in the end of the 50's, the use of the biocide effect of ionizing radiation was expected to provide a means of fight against the degradation of organic materials by biological agents in the cultural heritage field. Indeed, two facilities dedicated to conservation of cultural heritage appeared in Europe in the 70's: the irradiator involved in the first "NucléART" program that began in Grenoble, France, supported by Commissariat l'Energie Atomique, in co-operation with cultural institutions at the country. This facility is now just a part of the ARC-Nucléart conservation workshop. The another facility is belonging to the Central Bohemia Museum, near Prague, Czech Republic.

Compared with other classical or not competing techniques, irradiation offers very suitable advantages. The first one is its very high level of effectiveness and reliability. The effectiveness is directly related to the biological effect of ionizing radiation, as the death-rate is effectively controlled according the dose. This dose can range from less than 1 kGy for insecticide treatment to more than 10 kGy for simple microorganism pest. The reliability is just the outcome, as the physical condition leading to the death, i.e. the dose, can be achieved with very high confidence. Moreover, this physical condition can be handled the same way inside large volume and even in closed package. In this, only very simple and truly controllable physical treatments can reach the same level of reliability. However, and it is the second advantage, it also offers a very high level of harmlessness for a large range of materials, including almost every kind of organic material, and so on for the so-called movable cultural heritage (wood, paper, leather, parchment, textile, etc.).

It is of course very important to consider this harmlessness as a matter of dose. For instance, at insecticide doses, only bulk transparent material, which used to rather change colour, must definitely be excluded from such treatment. Indeed, excepting transparent materials, it can be assumed that for insect disinfestation, only anoxia can provide a similar level of harmlessness. But for that last technique, the cost of harmlessness is the well known problem of reliability due to the difficulty to control and to monitor the gas diffusion into the object.

Of course, this very high level of harmlessness has to be moderated when speaking about consequently higher doses. At fungicide dose, chemical effects can be measured in a quite larger range of material. However, for material for which such chemical effects are assessed, it is important to know if and how it can be translated in term of degradation. If not negligible, it has to be sized in order to evaluate a "cost/benefit" balance compared to other techniques or to "doing nothing". Once again, as very few "soft" techniques are efficient against those biological agents, irradiation very often appears as the most respectful for the object that has to be treated.

Other advantages of this curative technique include limited manipulation of the object as the treatment can be completed across a protecting package, and no harm or danger after treatment as there is no residue at all (and of course no creation of radioactivity inside the treated item). On the other hand, the main disadvantage is that there is no preventive effect at all, but this is just the normal consequence of the fact that it leaves no trace. Others limits are of course the incompatibility with some materials, according the dose, and the limiting size of the existing facilities to receive very large objects.

1.3 Consolidation of degraded structures

Use of radiation to consolidate porous material

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 60's in which the aim was to improve mechanical properties of porous material, wood and concrete in particular. The method did already use vacuum impregnation with a liquid resin followed by polymerization controlled by gamma irradiation.

Even if less diffused than disinfestation, this method allows the full consolidation, "in the bulk", of porous part of artefact. After the item has been impregnated, the penetrated resin filling the micro-pores, is cured, controlled by the radiation. This technique is called "densification" in opposition to traditional consolidation techniques using solvent to "convey" the resin into material which only form a film of solid resin after the solvent evaporated.

The mechanical properties are indubitably much better after using densification than any other classical consolidation. The appearance of the object stays unchanged, or at least changed appearance does not exceed the ones that can be encountered with any type of impregnation. However, it is obvious that the material and its physical-chemical properties have been drastically transformed, and that these changes are irreversible. That's why this practice is deliberately limited to the justified cases when mechanical properties must be hugely reinforced.

Derived applications concern archaeological waterlogged wood, using particular and complex impregnation techniques. In addition to the very strong consolidation, it provides excellent results to conserve the initial volume and the surface aspect is very satisfactory as well. But the main advantage is that it allows stabilizing treatment of wood and metal composite objects, while conventional treatments with water-soluble polymers tends to maintain and accelerate corrosion.

2

Particularities of biological aggressors relevant for conservation of cultural heritage artefacts

2.1 CH artefacts and food chains

The carbon based organic matter is in continuous transformation at the time scale of our life. The transformation process is based on relationships of living organisms in nature and is called the food chain or food web. It includes creatures living on the account of other creature substances, being it alive or dead. Any living creature is part of this chain.

Some fungi, bacteria, insects feed themselves with the natural organic matter from which CH artefacts are made. To efficiently fight against them conservators have to know their life characteristics and feeding habits. The living organisms that are able to destroy CH are therefore known as "pest".

Among them, insects and fungi are the major "ravagers" that could be encountered in current conditions storage. However, fungi usually will require humidity while insects are often able to use their own water to degrade organic matter.

Bacteria, whether aerobic or anaerobic, generally need more time to break down artefacts. There is however an important decay process involved in archaeological organic materials.

2.2 Insects

Insects are the most important class of terrestrial animals destroying organic artefacts. There is a very large area of pest insects involved in destroying cultural heritage. It is commonly admitted that more than 70 species are strongly dangerous for cultural heritage items from museum and archives especially for wooden made ones. Among them there are some beetles (Coleoptera), moths (Lepidoptera), bees (Hymenoptera) and termites (Isoptera), but many other xilophagous or polyphagous insects can also be included.

Insects have a complex life cycle including modifications of the same individual during its life. Modifications extend over its shape **(Fig. 1)**, feeding, movement, living conditions (temperature, humidity) et al. A complete biological process (metamorphosis) includes the following morphs: egg–larva–pupa–adult.

Interaction between insects and artefact have to be discussed having in mind the artefact is a food for the insect. Feeding needs are different in different life forms. Being the resistant form, the egg, waiting for proper hatching conditions, has almost no metabolism. During egg incubation the growing embryo is nourished by internal resources. The pupa is not feeding at all and the adult is feeding very few. But larva is feeding all the time and it is the real and big threat. Indeed, aside from the termites and bees, it is usually the larva which is able to extract nutrients and other substances from ingested food in the form of macromolecules and other complex substances. For instance, boring insects' larvae are living all their cycle within the wood, often living in symbiosis with bacteria and fungi that degrade the wood to make it more digestible. They dig galleries until they transform into pupa and adult, leaving the wood by a unique exit hole - **Fig. 2, 3 and 4.**

There are various feeding habits important from CH preservation point of view. Some insects, like cockroach, are eating everything; others are eating selectively only cellulose (wood, paper, and textile), proteins (wool, leather, parchment) or starch (adhesives). Most insects are not able to digest cellulose (they are not xylophages), but being interested in adhesives they destroy the book & paper collections by disintegration.

Focusing on xylophagous insects, some of them start the development in the living tree. Others are living only on manufactured wood. The last are more dangerous because larval activity are going on under the artefact surface and may lasts for several years. They might be discovered only after important damages.

Though there are some species adapted to extreme conditions, the temperature interval proper

Fig. 1: Larva and adult of Hylotrupes bajulus L

for insect development is usually comprise inside 20 to 30°C. Large majority of insect prefers a rather high relative humidity of 60–80 %. For some species, especially for those living symbiotically with mushrooms, humidity is a development condition.

2.3 Fungi and bacteria

Micro-organisms usually have simple structure. Diversity of micro-organisms is overwhelming. Old taxonomy and classification are under revision because DNA based methods revealed new information on their evolution.

Micro-organisms can damage the structure and function of natural or synthetic polymers. The main types of damage include:
  (i)   biological coating masking surface properties,
  (ii) increased leaching of additives and monomers that are used as nutrients,
  (iii) production of metabolites (e.g., acids),
  (iv) enzymatic attack,
  (v)   physical penetration and disruption,
  (vi) water accumulation,
  (vii) excretion of pigments.

Most important micro-organisms related to cultural heritage destruction are fungi, actinomycetes, moulds, yeasts, bacteria, algae, lichens. Fungi, bacteria also animals and plants are classified as separate kingdoms in the group of eukaryotic organisms (having cells with nucleus). Moisture is very often a key for microbial decay to take place, allowing selected microbes to grow and progressively degrade the art objects. In addition to moisture, many other factors influence micro-organism growth, such as temperature, pH, nitrogen, and other nutrients.

Fig. 2: Larvae tracks in wood

Fig. 3: Metabolic waste of the wood boring insects

Fig. 4: Larvae tracks in books

Bacteria may be associated with decay fungi or acts as scavengers to utilize previously decomposed substrates. They may also be primary degraders of artefacts in wet environments.

Fungi are a large kingdom with an important biodiversity in morphology, physiology and an enormous ability to transform organic matter. Some of them are dangerous, producing mycotoxins, and may be pathogens for humans and animals or may directly affect crops. Favourable conditions allow rapid colonization by fungi and fast decomposition. Under aerobic conditions, fungi are the primary decomposers of cellulosic materials, classified into broad categories of white, brown, and soft-rot based on the color and texture of the residual material after decay. White-rot fungi are common degraders, producing extracellular enzymes that degrade all cell wall components. Another group, brown-rot fungi preferentially degrade the polysaccharide components and do not degrade appreciable amounts of lignin.

During incipient stages of decay, extensive depolymerization of cellulose occurs, resulting in significant losses in material strength properties. Soft-rot fungi can be distinguished from other decay fungi by decay patterns they produce in materials. Soft–rot fungi are often associated with wet CH materials, but can also occur in non waterlogged conditions and the advanced stages of decay appear brown and crumbly and may look similar to brown-rotted artefact.

For instance, the type of wood and presence of extractives within the wood cells also influence decay. Woods from cedar, juniper, cypress, redwood, and oak are more resistant to microbial decay than are pine, birch, beech, aspen, and other woods that have fewer extractives.
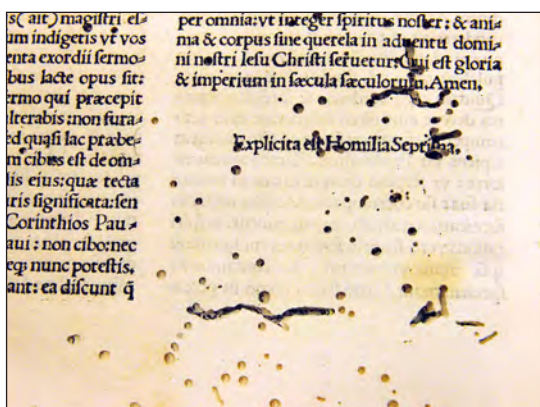
2.4 Radiosensitivity of living organisms

The biocide effect of irradiation was noticed since the beginning of 20th century. Fungal skin disease has been treated with radium salts included in creams and unguents. The initial careless enthusiasm was tempered by discovering the irradiation adverse effects on the skin. However it was noticed that different living organisms have different sensitivities versus irradiation.

Now, after a century, one is able to derive an orientation rule: the more evolved is the living organism the more radiation sensitive is it.

Table 1 – Radiation breakdown of the living organisms

Living organisms	Critical dose	Meaning
Mammals, humans included	4-6 Gy	LD50% (lethal dose)
Insects	0.5 – 2 kGy	reccomanded erradication dose
Fungi	< 10 kGy	max dose for food treatment
Bacteria	25 kGy	sterilization dose (medical devices)

The **Table 1** gives an idea on radiation sensitivity / resistance of living organisms with different position on evolution scale. It is important to note that each value is significant for a specific context, while the assembly may become comprehensive only with some comments.

o Irradiation death is not a sudden blow-up but the finality of morphological and physiological disequilibrium induced by irradiation. The whole picture is similar with a fatal disease not with that of an airplane crash.
o Irradiation death may be quantified only on statistical base. The largest meaning of this term is non-deterministic.
o In the table it is used the term LD50 (Lethal Dose 50%) for the death oh mammals. LD50 means the irradiation dose which proved to be lethal for 50% of irradiated subjects. It is accepted a bad precision of LD50% value because of the bad statistics.
o For micro-organisms more accurate values are available, because a much better statistics was possible to be applied in experiments. For eradication it is used a scientifical established term D_{10} meaning the irradiation dose necessary to reduce the number of microorganisms ten times (with an order of magnitude) – **Fig. 5.** Typical D_{10} values are placed in the interval 0.1 – 2.0 kGy.
o The value of 10 kGy mentioned for fungi eradication is taken from foodstuff treatment.
o In **Fig. 5** the dose of 25 kGy is the value accepted as sterilization dose and is usually related with bacteria eradication. It was calculated taken into account the known most radiation resistant bacteria.

Irradiation induces modifications at the level of chemical components of the microorganism cell. The biological effects are the results of direct interaction of radiation with a significant cell component. The same component may be indirectly damaged by reactive chemical entities produced in the cell by radiolysis, particularly by free radicals produced from water – an important cell component. It is proved that microorganism inactivation is a result of damages produced to DNA molecule. The biological effect is suppression of the reproduction capability. Unable to reproduce the microorganism is considered dead.
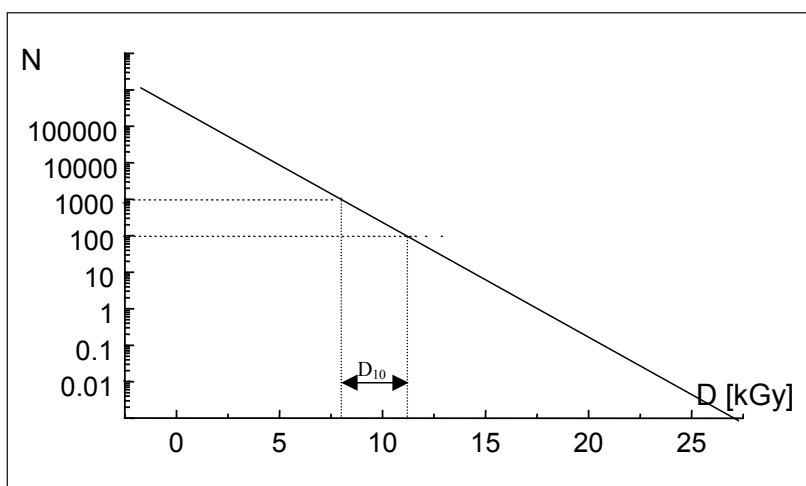
Fig. 5: Irradiation inactivation of microorganisms

Addenda

Insect eradication: lethal doses, minima-maxima doses (Wojtek Gluszewski)

The primary objective was to determine the minimum dose needed to kill the insect larvae. Insect eggs in these conditions which are more sensitive to radiation will also be destroyed. Effective dose against the larvae also causes infertility to beetles.

It was checked in the first stage, the influence of radiation dose up to 1.5 kGy (recommended in the literature) on the survival *of Luctus Brenneus Steph* larvae. It turned out that the intended effect (total elimination of larvae) was achieved, but after a period of 1 to 3 months. For *Ptilinus Penctinicornos L*. insects with a dose of 0.4 kGy was observed after 150 days survival of larvae at 20%. Similarly for variations dose 0.5 kGy eliminate the larvae *Hylotrupes Bajuns, Anobium Punctatum de Deel and Stegobium Penceum L* at the time respectively 90, 200 and 80 days.

In further studies, it was decided to increase the range of doses up to 3 kGy. Test results are summarized in **Fig. 6 and Table 2.**

Fig. 6: Anobius punctatum DEG & Antrenus museorum L – Relation between larva survival and time after irradiation at different dose treatment.

Table 2. *Minimum dose for disinfestations of different kinds of insects*

Species of insect	Recommend doses in Poland	Recommend doses in literature
Anobium punctatum De Gree (Anobiidae)	2 - 3 kGy	France, Czech: 0.25 – 0.5 kGy (Detanger et al 1974, Urban and Justa 1985), Germany: 3.07 kGy (Unger 1984)
Hylotrupes bajulus L	0.5 - 2 kGy	Bulgaria: 3.2 kGy (Michalov 1971)
Stegobium panaceum L.	1 - 3 kGy	No information
Tineidae	2 - 3 kGy	No information
Anthrenus sp.	1 - 3 kGy	No information
Lyctus sp.	No information	Great Britain: 0.72 – 1.5 kGy (Bletchly 1961)

General conclusion is that in order to eliminate the larvae immediately after irradiation should be used doses at 2 to 3 kGy. Doses of 0.5 to 1 kGy, in principle, also lead to disinfection but after a while. Till the death, of course, the wood will be destroyed by the larvae.

Temperature is very important parameter in radiation disinfection. These results indicate that the radio-sensitivity of larvae increases with increasing temperature. Otherwise, speaking with an increase in temperature decreases the survival of larvae at the same dose temperature.

Irradiation of insects: varia (Lorent Cortella)

Biological effects of radiation have been early observed by H. Becquerel and P. Curie since the discovery of radioactivity. In 1906, Bergonié and Tribondeau, predicted that the relative sensitivity of cells or tissues to radiation may be accentuated when cells are immature, they have a long dividing future and they have a high division rate. Furthers works, including M. Curie works on bacteria in 1929, where just the very beginning of a new discipline that will have so many applications: radio-biology.

In living tissues, ionization first caused DNA damage that could be or not repaired, and that may result in a variety of outcomes on the living cells. They are currently divided in determinist and stochastic effects. While the first ones will systematically appears at a certain minimum dose with a severity that will depend on the dose, the seconds will appear with a probability function of the dose but whose severity does not vary with. When biocides effects are sought, deterministic effects on vital function of higher organisms will be researched to cause the dead, while for micro-organisms, generally more radio-resistant, doses will have to be enough to see their populations statistically but drastically decline in proportion to stochastic effects.

Since the first works of Bletchly, insect behaviour after irradiation has been widely studied in order to control it as a pest. Very significant efforts referred for instance to the management of insect damage in harvest (using the Sterile Insect Technique) and food. It leads to an international database in which a very large variety of insects are described in terms of sterilizing and lethal doses.

These works are in good agreement with more dedicated studies for insect pest in the field of cultural heritage. As a matter of fact, most insect species has sterilizing doses comprise between 100 and 200 Gy, and adult lethal doses less than 500 Gy.

Of course, eggs and larvae will have smaller lethal doses, as predicted by the so-called Bergonié and Tribondeau law. However, with these doses, insects will not be killed immediately. In order to eliminate the larvae immediately after irradiation, doses up to 2 to 3 kGy should be used. Doses of 0,5 to 1 kGy, also lead to insect eradication but larvae could survive for duration of a few dozen days. It has to be valued if this is dangerous or not for the collection as in this duration, the larvae see their appetite become increasingly weak.

<div align="right">

Irradiation
side-effects

3

</div>

Irradiation target is to obtain a certain disinfestations level. The radiation efficiency is not contested. To evaluate this biological effect well-known procedures are used.

Instead, there are doubts on evaluation of irradiation side-effects. As the worst approach one may notice a prejudgement based attitude among conservationists which reject a priori CH irradiation treatment. There is also a rational attitude connecting doubts with the lack of reliable R&D experiments eventually extending the doubts on side-effect evaluation methods.

In fact this situation depicts also a bad dialog between scientists and humanists involved in CH preservation.

3.1 Physical, chemical and structural side-effects

Evaluation of irradiation side-effects

Modification of the artefact substance during treatment is considered an irradiation side-effect. Any side-effects consideration has in the background the facts that CH treated objects are mostly made of natural substances having marked variation in structure and properties. One of the consequences is the fact that modification induced by irradiation in treated material is less known than in synthetic material. Indeed, this is similar to other conservation treatments, because there are important methodological difficulties in side-effect evaluation.

A basic premise of this evaluation should be a known relation between degradation state of material and one or several physical, chemical or structural characteristics that can be measured. The first research step is to identify that (those) parameter(s) proper for characterization the material, also the best procedure and equipment to measure them.

Aging may be scientifically studied only if an accelerated aging method is convened and proper equipment is designed and agreed by scientific community. Existing several aging factors, there are several degradation mechanisms. But all properties are modified by aging. That's why side-effect evaluation should be extended in time. Any measurement result is relevant if it is obtained versus a reference material.

It is difficult to obtain references from materials of natural origin. They may be similar but not alike. For instance, wood or leather, produced from living entities, present important variations. Variation is related to:

- particularities, age, feeding history; the same tree species gives different wood in dry and humid conditions or on different soils; cattle leather obtained from a calf skin is different of that obtained from a bull skin;
- sampling place; at wood there is an important radial difference in mechanical and chemical characteristics; the skin sampled from different parts of the same animal have different properties;
- in the case when aged references are necessary, one has to take care that different aging conditions give birth to different aged-related modifications in the same material;

Another obstacle in side-effect evaluation is the fact that most important relevant tests are destructive. Mechanical tests are best example.

3.1.1 Wood
Solid wood

Wood is certainly the most important natural organic material in human story. It has been used for many vital purposes like making shelters, tools, weapons, boats and coaches, religious or symbolical artworks not to talk about fire. As such, it is of exceptional importance for cultural heritage conservation. Unfortunately wood is particularly vulnerable to biological attack **(Fig. 7, Fig. 8)**.

Gamma irradiation, due to its penetration power, is naturally expected to be a very relevant way to oppose to this kind of biodegradation in the "bulk".

Wood is a complex composite of biopolymers with cellulose as most abundant component – around 40 to 50% in weight. Cellulose is a linear polymer of glucose having the ability to associate in ordered assemblies (nanoscale crystallites, fibrils, fibres). Internal order and the hydrophilic nature are proper to assure a functional wood cells structure. Lignin is the other major component in wood, present in a rate of up to 25-30%. Lignin is a cross-linked polymer with an aromatic but not well defined primary structure. It is arranged in amorphous form in the wood cell walls and is relatively hydrophobic. Hemi cellulose, which amounts to 20-25%, is also a polysaccharide, but branched and made from many different sugar monomers. It has a random, amorphous structure with low mechanical strength. On a simplistic model, cellulose fibrils giving resistance in tension, is embedded in a matrix of lignin which resists to compression. Hemi cellulose makes the link between lignin and cellulose.

The major pests are able in short time to destroy important wood quantities. They can transform the macromolecular chains from the wood structure into digestible monomers by the action of specialized enzymes. Enzymes breaking down cellulose prevail but there are also lignolytic enzymes. Because all enzymatic reactions are aqueous reactions, wood degradation is vital related to the presence of water. The enzymatic degradation by fungi must find a source of moisture within the wood itself, while insects have their own source of moisture that enables them to metabolize glucose from dry wood in their digestive tract.

Gamma irradiation has been proposed in the early 1960's as a treatment for wood disinfestations. Even if it never reaches a very large employment for wood industry, it is nowadays used for diverse purposes, including for instance sterilization before laboratory decay test and of course cultural heritage preservation.

Since the 1960's, wood behaviour after gamma irradiation has been intensively studied. Cellulose is the constituent of wood that is most sensitive to irradiation. This polymer can undergo a simultaneous three-dimensional cross-linking and breaks of its chains. While cross-linking tends to reinforce the mechanical properties and stabilize cellulose materials, breaks make them less resistant. As doses increase, this last phenomenon becomes predominant, typically after 10-50 kGy. However, it seems that the coupling of lignin and cellulose on one hand makes it actually less sensitive to irradiation than pure cellulose in amorphous form. As a matter of fact, direct macroscopic properties like mechanical properties of wood are not really affected as long as the dose does not approach 100 kGy (**Fig. 9**).

Fig. 7: Wardrobe, AMAN Museum, Bucharest, Romania, (by IAEA courtesy)

Fig. 8: Ceremonial armchair, Izvoarele Parish Church, Romania

Another dreaded effect would be that some free radicals induced by the irradiation react much later, involving a much more substantial degradation than that observable directly after irradiation. This effect, sometimes observed at high doses for some polymers, is called post-effect. However, it has never been observed either by practitioners of these methods for wood, while their experience exceeds forty years, nor recounted in the scientific literature, despite the very high doses investigated.

As a consequence, it is well accepted that wood disinfestations using gamma ray will not have significant effects, even at the high doses used for fungicide treatment.
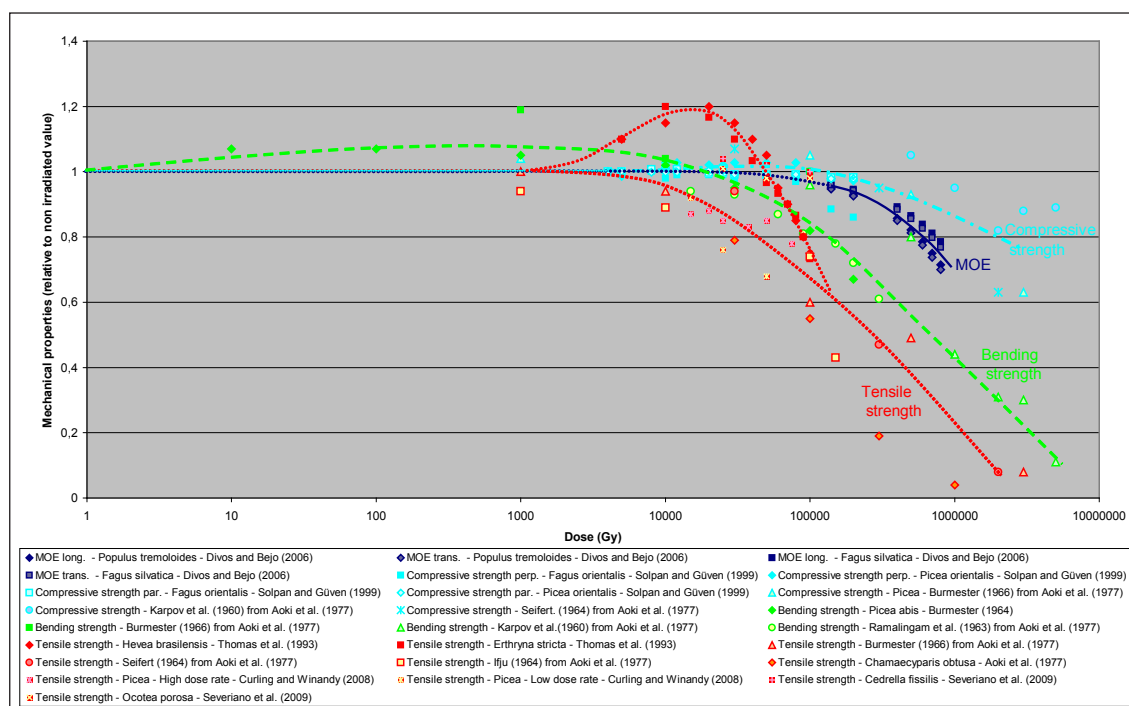

Fig. 9: Some effects of irradiation on mechanical properties of wood (compilation of data found in literature)

Polychromed wood

Wood has also been largely employed with, or as a support of, ornament. It first includes polychromed wood that are of great importance with regards of heritage in many culture. In Europe, wood sculptures have been commonly painted for centuries. Wood panels have also been used as support for "easel painting". The techniques used to apply different layers. They begin with ground, or preparation layer, which received the colored paint by itself. Then, colour layers are made of pigments mixed with binder that provide a transparent matrix, retaining them by surrounding these colored surfaces. Protective layer such as varnish can be added. The constituents and the techniques vary from many historical and cultural considerations, but it is still possible to examine the general behaviour of polychromed layers with gamma irradiation.

As it is a very specific field mostly oriented to cultural heritage conservation interest, the effect of irradiation on painting have not been studied in such accurate way than raw wood. However, it has been the attention of some research teams from the early 1970's until recent years. Other studies were concerned with same painting nature, but applied on canvas.

Attention should firstly focus on the colour that is believed to be easily sensitive to irradiation for instance in transparent material or in very clear or white organic materials.

Among the works done by different teams which cover all the typical irradiation doses, no problem of very sensible painting layers colour have been encountered. Over the amount of more than 30 different pigments that have been studied in paint layer, only lead oxide based pigments (lead white, chrome yellow and minimum) seem to give evidence of some change of colour depending on the dose of irradiation. However, this change were still acceptable, less than 2 CIEL*a*b* units, at he doses used for biocide treatment. No evidence of meaningful post effect has been observed in paint layer any more. In the other hand, when not used in a matrix of binder, colour of pigment can vary more significantly, surely due to oxidation phenomena.

Varnish behaviour could be more delicate as it is a transparent layer. Depending on its thickness, one may fear an activation of colour centre that will become perceptible. Then again, among different varnish and binders that have been explored, only Arabic gum have shown a noteworthy dependence on irradiation, reaching for instance a colour difference of 2 CIEL*a*b* units at 10 kGy when applied in strong thickness (12 layers – 110 μm).

Colour measurement are commonly made in CIEL*a*b* colour space, referring to perceptually uniform orthogonal Cartesian coordinates. In this space, L* is the lightness, ranging from 0 (black) to 100 (white), a* is the red to green antagonist dimension while b* is the yellow to blue antagonist dimensions. Both a* and b* axes have no specific numerical limits, but generally stand within -60 and 60, 0 being the neutral point (grey). Distance between two colours (noted ΔE*) are supposed to correspond to the same perception of colour difference, whatever the position within the space. It is generally assume that colour difference of less than 2 CIEL*a*b* unit are not distinguishable. For instance, in paintings arts, accuracy of 5 CIEL*a*b* units on average is considered for high-quality colour reproduction. Even if more accurate non linear formula have been derived in order to correct some perceptual non-uniformity of the CIEL*a*b* space, we will limit this document to the use of the classical formula of ΔE* in order to not overload the understanding of phenomena.
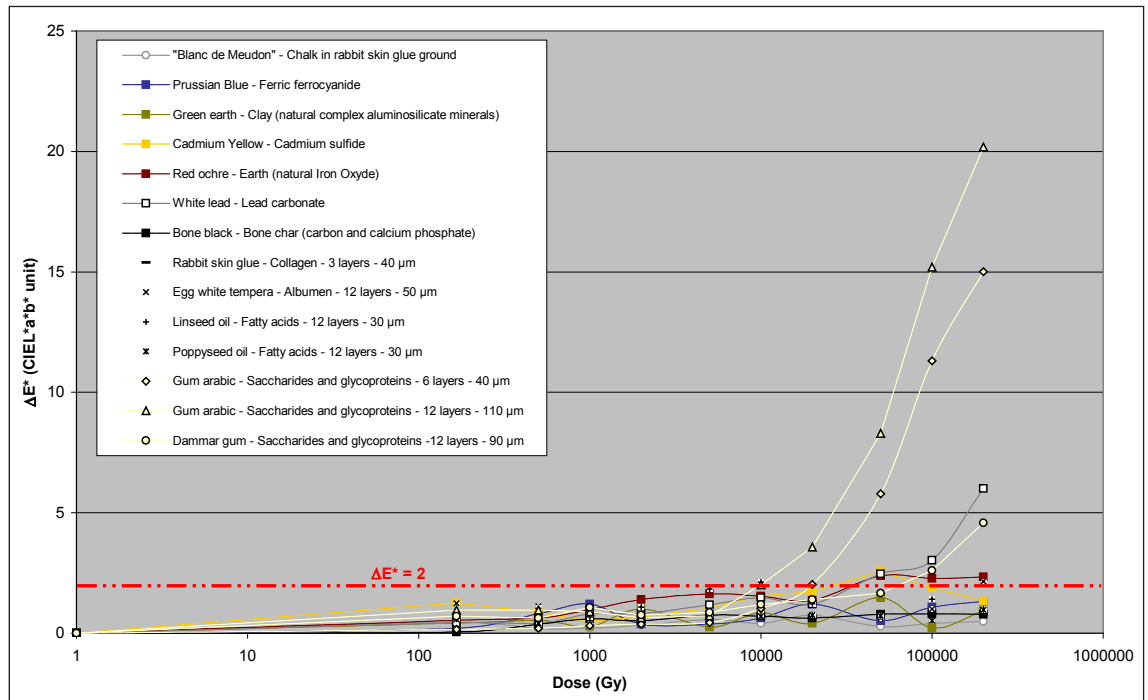

Fig. 10: Some colour effects of irradiation on materials used for polychromy.

Fig. 10 presents original experiments done at ARC-Nucléart, Grenoble (2006-2008). All preparations were applied on "Blanc de Meudon" ground piece of wood. If not specified, pigments were mixed with poppy oil binder.

One must also consider a possible structural weakness of ground layer, binders of varnish after irradiation. But the emergence of such behaviour is not expected before several tens of kGy, widely over the doses used for disinfestations. Only an Italian study in the 70's have revealed that fresh rabbit glue have loss some adhesive power at 10 kGy. No other problem has been reported after treatment for the so many treated materials, neither in the experiments carried out in laboratories. Volume integrity, as well as adhesion, is therefore retained to present good behaviour.

All over again, one have to insist that a relative attention may always be requested when applying very high doses on polychrome items, although studies did not reveal real problem and treatment of many hundred of polychrome wooden items over the world have been successfully applied. As exhaustive studies of any kind of binders and pigments that could be encountered with the different techniques is hard to imagine, adverse behaviour is never completely excluded at such high doses as fungicide ones.

The question becomes would it be more guarantee for the same results using other techniques. Depending on the context of the treatment for each particular collection, further studies could be undertaken to insure a good treatment. However that may be, it is worth mentioning that insecticide doses between 0,5 and 2 kGy stay very sure, even in presence of poorly known or exotic polychrome layers.

3.1.2 Leather, parchment

Origin, structure, manufacturing process

The leather raw material is the animal skin, usually from the mammals. The skin has multiple functions in a living organism and by consequence an elaborated structure. The main chemical component is the collagen. In its fibrilar form this protein is the matrix of animal tissues. In the skin it looks like an expanded unwoven cloth. Three skin layers could formally be considered: epidermis, dermis and subcutaneous layer. Only dermis counts for the leather fabrication, because only here the collagen fibers are present in the shape, orientation and consistency proper to obtain leather with good mechanical properties.

Transforming the skin into leather is a complicate process and involves several technological steps. *Unhairing, liming, fleshing, scudding* are related to the separation of dermis from the skin assembly. The natural cohesion of fibers has to be weakened, chemically – *liming*, mechanically – *scudding* or enigmatically – *bating*, so as to facilitate an efficient and bulky *tanning*.

Tanning is a cross linking process where chemical bond 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 turned into leather.

Other stages like *lubricating, dyeing* or *coating* are particular related to specific final destination. But *drying* is a must, because after tanning (or dyeing) the water content is 65-70%. It must be reduced at ~15% that is normal water retention in leather. A higher water % favours the development of proteolyses bacteria that compromises the leather durability.

Aging and degradation pattern

Most important leather aging factors are industrial gaseous pollutants – SO_2, NO_x which catalyze *hydrolytic degradation* of the collagen. The same chemical reaction may be assisted by metallic ions present in the leather from manufacturing process. Other aging mechanisms are: *oxidative breakdown* of the collagen related to ozone and free radicals produced by UV component of the visible light; *photochemical degradation* of the links between collagen and tannin; *mechanical degradation* which is the consequences of fluctuation in temperature and humidity, combined with object functionality.

Biological degradation is mentioned in this approach because irradiation can control only biodegradation. It is found more often in ethnographical collections (**Fig. 11 and Fig. 12**). However biological degradation does not play an important role in the vast picture of leather degradation types. This is strange indeed because any protein is an excellent food for microorganisms like proteolytic bacteria. The decomposition process is installed in a green skin in a few hours after stripping if a preservation method is not applied (e.g. salting, drying). In the manufacturing process, during tanning – the key-stage, it is drastically reduced the water uptake in the leather and in this way it is avoid the microorganism development.

Parchment – an untanned skin is more vulnerable to biological degradation. It should be added that proper conditions for fungi (moulds) development – RH > 70% and T > 22 °C – are seldom found in places where precious objects like parchments, books bound in leather or ethnographical artefacts
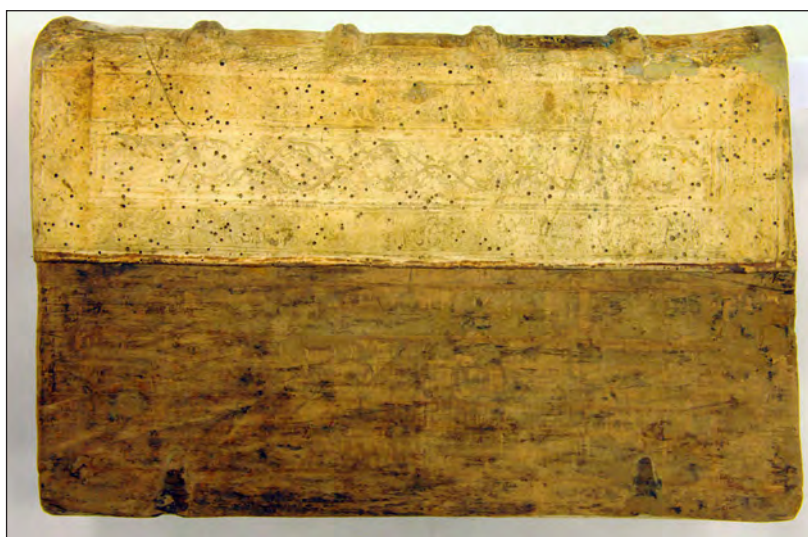

Fig. 11: Leather clothe with insect attack

Fig. 12: Book binding with flying holes

are sheltered. Even when humidity and temperature are correctly chosen and maintained, moulds may appear in case of improper finishing layers or in case of early conservation intervention that made leather (or parchment) too fat and by consequence proper to retain dust which is hydrophilic.

Irradiation disinfestations and side effects

Irradiation disinfestations were seldom applied on leather artefacts. It has been treated:
  - clothes – Ethnographical Museum Iasi, Romania (**Fig. 13**),
  - furniture with leather parts – Severeanu Museum Bucharest, Romania (**Fig. 14**),
  - books with leather bindings – private collection Ana Sofia, Romania (**Fig 15**) and (most probably) archive of Allen Mason Chesney Hospital, USA.
  - shoes and suitcases – Majdanek Museum, Poland (**Fig 25**).

Fig. 13:
Ethnographical cloth,
Museal Center, Iasi,
Romania

Fig. 14: Armchair
with Cordoba leather,
Severeanu Museum
Bucharest, Romania

Fig. 15: Liturgical book, private collection Ana Sofia, Romania

Applied doses were under 10 kGy in most cases. The target was insects and fungi eradication. The artefacts from Holocaust Museum were considered possible contaminated with pathogenic bacteria and have been treated with 25 kGy – the sterilization dose.

No treated artefact has been unique. No side-effects were performed on the treated artefacts. As we know, there was no notable R&D project focused on irradiation side-effects on leather CH artefacts. This strange situation may be a result of the lack of need. Precious CH leather artefacts – especially leather bounded books – are usually kept in proper storage conditions where development of biological aggressors is under control.

However irradiation of collagen – leather basic component - was studied. It was an interest stimulated early in the '60 by "preservation of animal skins and elimination of anthrax infection". As in the case of other proteins only doses greater than 50 kGy proved to modify somehow the collagen structure. Related to the utilization of collagen in cosmetics and medicine appeared the necessity of sterilization (catgut, artificial arteries and heart valves, composite biovitroceramics). Irradiation sterilization is the unique acceptable method. This intensified research on collagen modification by irradiation and expanded the investigated the dose range.

Of coarse extrapolation of side-effects from collagen irradiation to leather irradiation side-effects has to be done with precaution. But for this approach two ideas are important and relevant. First, it was confirmed that side-effects are dose dependant. For CH disinfestations the recomanded dose for fungi eradication is 10 kGy. The experiments on collagen revealed marked modifications only at huge doses of 50-1000 kGy. The other approach is that collagen cross-linked with glutaraldehyde is much less influenced by irradiation than native collagen. The first is similar to leather and the second is similar to parchment.

3.1.3 Paper, archives

The major concern for the using radiation treatment in paper conservation is the large decrease of the degree of polymerisation (DP) of cellulose. The main effect is the scission of β-glycoside bonds **(Fig. 16)**. These scissions are reducing the average length of the polymeric chain in the amorphous region of cellulose and will reduce the strength of cellulose fibbers. Macroscopically, this can be observed as a reduction of zero-span strength.

Fig. 16: Scission of β-glycoside bonds of cellulose

Despite all other paper properties are less or not affected, the degradation of cellulose chain gives a major break of the conservation principles when it is important to preserve not only the written information and morphological characteristics of the paper, but also the information revealed by the composition of the paper (raw materials, technology, etc.).

The number of scissions (which can be roughly described through DP) it is traditionally the most important parameter used for characterization of paper degradation in accelerating ageing studies. All the irradiation studies showed that DP, evaluated by viscometer method, is highly affected by irradiation and other physical and chemical methods may satisfy better the conservation principles. However, the viscometer method it has some limitations and is affected by errors and the results reported may be reviewed through Size Exclusion Chromatography (SEC), which has been developed latter and gives better accuracy. But even in the case of paper for conservation, there are situations when restorers may choose irradiation: if the biological attack is so destructive than no other physical or chemical methods can give the same efficiency in short time, as in **Fig. 17**, where attack started from wooden cover and spread quickly to paper and leather covers.
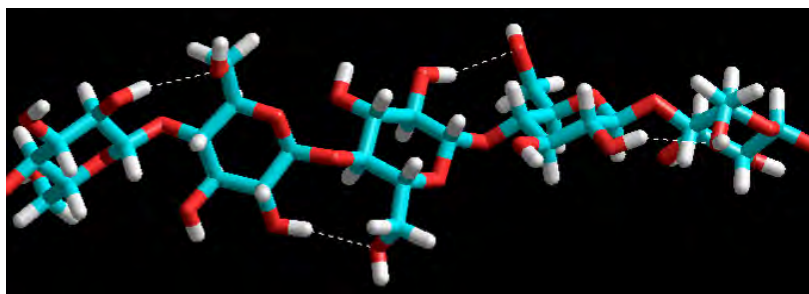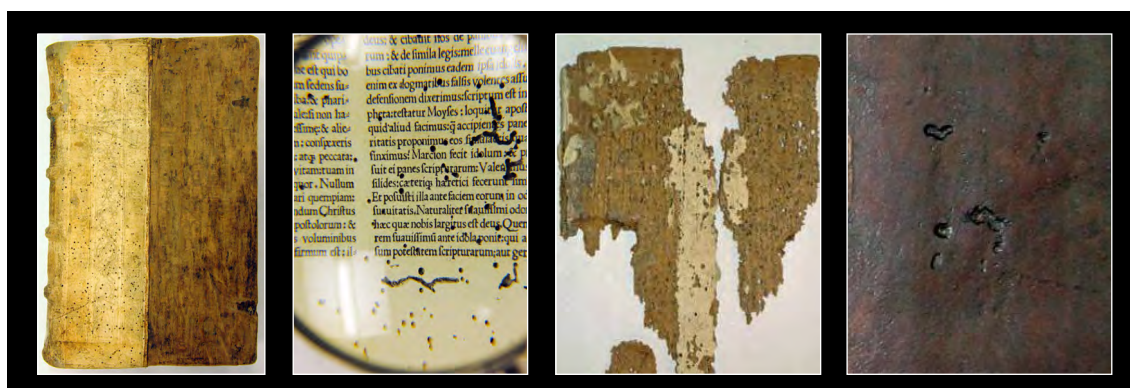

Fig. 17: Books after xylophages insect's heavy attack

When the information stored on paper is much important than the paper itself (archives, libraries or memorial collections), the ionizing radiation treatment it may be the choice. Archives have a primary goal of preserving the information but also to make it available for administrative or research purposes. Both paper and users must be protected against the biological threats. The radiation induced degradation should be evaluated taking into account the usually well defined life-time of the archive documents and the actual trend for digitisation.

Library collections may not include unique items and ionizing radiation it may be used not only to stop the biological attack but also to stop spreading to other collections or in a new (refurbished) location. It is widely accepted that paper has a limited life-time ("acid paper" inherited from the last century is rapidly degrading in normal storage conditions) and the removal of biological contaminants can only extent the life of the books until digitization issues will be solved.

Memorial collections brings together various documents (books, files, manuscripts, notes) which may have less individual importance (information or morphological properties) but the cultural value is given by the whole assembly, which may offer a snapshot of a certain historical period of time or life of a certain character. These kinds of collections are usually recovered after a period of time of unknown/improper storage conditions and to bring them in a museum or archive it may be a threat to other collections (**Fig. 18**).

Outside the conservation/restoration environment, the archives and library collections (administrative, private) might be the main candidate for the irradiation treatment. Large quantities of rather uniform load of paper (**Fig. 19**) can be treated in industrial irradiators and often there are not reported in the literature.

Other kind of paper items may have only decorative purposes (for example, wallpaper) and the acceptance of the irradiation treatment may be considerably higher (**Fig. 20**).

One of the first reports on the irradiation of a large quantity of paper documents is the treatment of Dr. Gannt' Collection (medical files, manuscripts and photos, dated from beginning of XX century). The collection belonging to John Hopkins Hospital from Baltimore, Maryland, USA was stored in really improper conditions (infested not only with fungi and insects but with rats!). The irradiation treatment (using Co-60, 4.5 kGy) seemed to be the only solution recovering documents. The only tests performed at that time where microbiological and colour tests but after 20 years from the treatment there was no complaints against the properties of the paper.

Most of the studies developed from the '60s to '80s did not recommend the irradiation for conservation of paper because of the decrease in DP, increase of CO and COOH groups and increase of solubility in alkaline solution for cellulose. The non-correlation between the high decrease of DP and the much lower decrease of mechanical strength (tensile, shear, burst) it was related to the formation of new bonds after cellulose scission. From the beginnings, for the dose range required for paper treatment, it was stated that colour modification and crystallinity changes (CI) are insignificant. Mechanical properties are less or not affected, excepting the strength after double bending and only for the synergistic effect of irradiation and artificially ageing (thermal methods).

Fig. 18: Collection Dumitru S. Panaitescu - Perpessicius (Braila Museum, Romania)

Fig. 19: Archive materials treated by ionizing radiation at IRASM Facility, Romania

The good results on mechanical and optical properties together with a new approach in the estimation of the biological efficacy (*D10 value*) encouraged the researchers to continue the studies and to find new arguments for the irradiation treatment of paper items.

One of the most documented irradiation treatment for paper it was developed in Italy. The works where developed in cooperation by ENEA –Entity for New Technology, Energy and Environment, the Central Institute for Book Pathology, and the National Imprimery. The results obtained by the Italian group are in good agreement with all other previous reports and therefore are summarized bellows.

An interesting and complex study was performed in Italy with the purpose of showing that low dose irradiation (5 kGy) will not affect the integrity of permanent paper (low lignin content) and Whatman No 1 (pure cotton cellulose without additives and fillers), irradiated (2 and 5 kGy, 14.7 kGy/h) and/or artificially aged (ISO 5630-3 – moist heat). Also where tested three possible methods for reducing the decrease of DP (vacuum, nitrogen atmosphere and water saturation). The tests included: mechanical properties (ISO 1924-2 - tensile, ISO 1974 – tear), optical properties (ISO 2470 – brightness, ISO 9416 – Kubelka-Munk and CIE L*a*b*), pH (ISO 6588 – cold water), Kappa index (ISO 302), IR spectra (5000–350 cm^{-1}), DP (AFNOR NF 12005 – viscosity). Microbiological test where performed by inoculation of a population of strains recovered from contaminated paper (mainly *Penicillium spp*).

Fig. 20: Highly affected wallpaper from Aman Museum, Bucharest, Romania

Excepting DP (which decreased up to 50% after irradiation, as expected from previous literature results, and synergistically for combined irradiation and ageing), there was observed statistically significant changes of other paper properties only for 5 kGy (less than 10% after irradiation and less than 20% after irradiation and ageing). Neither vacuum nor nitrogen did not reduced the negative effects of irradiation upon paper. Water saturation modified significantly the paper properties.

IR spectrometry observations showed that the studied papers do not present substantial structural changes and that the various associated treatments had no relevant influence on the irradiation effects. The increase of the kappa number and of the light absorption coefficient (up to 50%), proportional to the absorbed dose, can be related to the DP decrease. The ISO brightness and the light scattering coefficient slightly decreased (less than 10%). It was stated that "relatively low irradiation doses (2–3 kGy) decontaminate a paper, until the microbial presence reaches levels comparable, or even lower, to those found on the "blank" samples". It was observed the synergetic effect of presence of the water during the irradiation.

Taking into account the complexity of the "classical" testing of paper degradation (physical and chemical methods), the Italian group worked for developing alternative methods based on the "biological degradability" of the paper. It was revealed a proportionality between fungi growth (*Penicillium chrysogenum*) and the decrease of DP but different susceptibilities to insect attack for different sort of paper.

The Italian group also described in detail the irradiation process, the measurement of absorbed doses and the perspectives of using the treatment for historical and cultural heritage paper.

Not only paper, but inks (colour or fastness) may be affected by irradiation. The Italian group tested a number of inks according to ISO 2834 on irradiated and/or artificially aged samples. The experiment showed no significant change of inks at the doses taken into consideration for the treatment of the paper. A significant change was recorded only for synergistic effect of irradiation and accelerating aging procedure.

Supplementary information of the inks' radiation resistance can be found in another application: irradiation of mail in fighting with bio-terrorism threats when where tested more than 100 ink specimens! The review of the entire study, aimed at receiving the authorization for ionizing radiation treatment for deteriorated books and archive documents revealed the following conclusions:

- the ionizing radiation treatment is extremely efficient for the disinfestations against harmful insects and for disinfection against micro fungi;

- using the necessary dose for an efficient treatment (roughly 0.2–0.5 kGy – thousand of Grays - for insects; 3–8 kGy for micro-fungi), no significant harmful effect has occurred on the mechanical and physical properties of pure cellulose and of paper or on printing inks.

Other recent studies on irradiation of paper where reported in Brazil and Argentina The results obtained for different sorts of paper and different microbial contaminants are in agreement with those discussed above. The main result reported from Brazil it is the treatment of the archive of a bank (including 1700 manuscripts, 3400 xylograph matrices and 850 printouts) highly affected by fungi and xylophages insects due to improper storage after flooding. The radiation treatment was performed at a dose lower than 5 kGy.

A similar research program is under development in Romania [ARCON project]. Two major problems should be solved in order to have a reliable quantification of the irradiation effects on paper:

- the large non-uniformity of the material to be tested: micro-structural differences in paper, different sorts of paper (more than 1000 additives and fillers are used in the present) and different stages of biological and/or chemical degradation – there was observed differences up to 30% for the mechanical properties of the pages of the same book;

- the use of testing methods which are consuming large quantities of samples, not always available or not available with the desired uniformity (see above).

One solution to overcome this it may be to establish correlations between properties tested by destructive tests and parameters that can be evaluated by non-destructive or micro-analytical techniques, such as thermal analysis and FT-IR / FT-Raman.

The long term stability of the paper after irradiation ((including the free radicals issue) it may be evaluated through the usual testing for paper permanence but the results of artificial ageing are still questionable.

Taking as a fact the depolymerisation of cellulose with less significance on the functional properties of the paper (support for written information), the ultimate goal it will be to provide the owner of the large quantities of paper with a testing programme (designed according to the actual knowledge

and the magnitude of the risk of total degradation), which can provide the arguments supporting the decision for irradiation treatment and the choose of the right irradiation dose.

As final remarks on the paper treatment with ionizing radiation it should be mentioned:
- The irradiation treatment can be designed such a way that the desired effect (biological decontamination) it is achieved and undesired effects (degradation) are minimized;
- Due to the worldwide spread of radiation technology the irradiation treatment is now both accessible and cost-effective;
- Among other cultural heritage applications, due to the large quantities a small size of the items, paper irradiation it is most appropriate to be performed in industrial irradiators;
- Certain quantities of paper treated by irradiation until now (with or without reporting in scientific publications) may prove the need of the users for this kind of technology.

3.1.4 Mummies and taxidermy specimen

Mummy is human or animal dead body whose soft tissues have been preserved from decomposition thinks to conditions that avoid the normal biodegradation. It could be intentional, for instance due to use of chemical, or natural, because of extreme conditions, frostiness, very low humidity, or lack of air like mummies found in bogs.

Such conditions, however, are commonly fragile. Biodegradation can quickly resume if the equilibrium is broken. Irradiation is one way to stop again a new infestation. However, as it has no preventive effect, conservation will need to find again a new equilibrium to avoid new active contaminations. Nevertheless, gamma irradiation is recognized as a reference for disinfection since the Ramses II mummy underwent this intervention (see success story).

An extensive study was conducted before gamma treatment of this mummy, involving many laboratories and using more than hundred samples of other mommies. Characteristics of many components have been studied after irradiation. It mentions hair, skin, muscle, bone, tooth and even other organs like liver, kidney, heart. Two less prestigious mommies, said "studies mummies", were also wholly irradiated. Even, mechanical and chemical controls have been carried out directly on fragments of strips and hair belonging to the mummy of Ramses II. All these studies have concluded that the 18 kGy treatment was efficient "without modifying any mummy's components". It should be noted however that at this time, the problem of conservation of the genetic information was not considered. This particular problem will be discussed in the further section "others effects".

Therefore, one may retain that gamma irradiation at fungicide and up to bactericide doses is a treatment adapted to mummies. But these conclusions can also extend too many other areas: disinfestations of archeological bones and naturalized furry animals. Even feathers taxidermy specimens were treated successfully. After more than 40 years of experience, the only problem ever encountered in ARC-Nucléart workshop concerned a tortoiseshell that slightly browned after irradiation.

However, one has to stay careful in particular with doses of disinfections of the order of 10 kGy and more, because resins used in taxidermy and other materials sizing or filling, both for modern or old processes, can be paradoxically more sensitive than animal constituents.

The last, but definitively decisive, considerations must regard the conditions that conservators will be able to achieve around the mommies or specimens. On such fragile items, irradiation must be employed only with the aim to stop a proven infestation. And as it will not modify the appetite of pest organism for so attractive artefact, preventive conservation is finally the only issue after the current infestation has been stopped by curative irradiation.

3.1.5 Other materials

Many others materials could be involved in treatment of disinfestations. There is, for instance, a wide variety of ornaments, being directly or not subject to infestations, but being often associated with organic materials that requires such biocide treatment. As a principle, one must be very careful before use of irradiation on this kind of material, for which the singular aspect is primary. However, depending on the applied dose, it can be possible to irradiate them.

All transparency materials can suffer irradiation that causes activation of colour centre even at doses less than 1 kGy. Glass can hardly darken and obscure. Gems can change colour, for instance from rose to blue (this is use in jewellery). Vitreous enamel could follow the same behaviour, depending on the charge in solid colour. All these phenomena are more or less reversible and are closely linked to the amount of impurity that could be activated as color center (pure silica quartz, either glass or crystal, shows no tendency to become opaque).

Horn, bone, ivory, nacre, white ceramic and even marble could also be slightly sensitive. Depending on the initial whiteness, it could darken or yellow at fungicide doses. For instance, white nacre quickly yellow after 1 kGy while grey nacre remains stable until 20 kGy. Once again, and strange though it may appear, all these light materials tend to exhibit an inverse post-effect, i.e. irradiation induced yellowing or darkening partially disappear after some month. However that may be, if insecticide treatment can be carried out in some case with such materials, it had to be implemented with maximum care, controlling rigorously the over dosage, and avoiding strictly any repeats treatment.

Coloured opaque materials are rarely affected. For instance opaque gems like lapis lazuli, jasper, jade, turquoise, tiger's eye, can be irradiated at 10 kGy without any problem. Finally, metals appeared with the best behaviour, which is not affected at all at the doses that can be used even for repeated disinfestations treatment.

Another family of materials has to be investigated in terms of irradiation effects: the modern synthetic materials used in restoration-conservation. Most of these constituent have been designed to be very stable, and thus they are with regards to biocide doses. No loss of their mechanical function have been reported after irradiation for adhesive, sealants, mastic coating, consolidant or other filling materials. A significant case of colour change, however, was detected with a special filling coating: the white Modostuc®. Other tested classical materials used in conservation field like Paraloid® B72 and Plextol® B500 resin, Toupret® fillier and Lefranc & Bourgeois® synthetic "gesso" did not revealed any problem of colour. Retouching colours like acrylic Liquitex® also demonstrate excellent stability after irradiation. Interesting enough, the reversibility of four conservation products (Paraloid B72, ketone-N resin Laropal® K80, polyvinyl acetate Mowilith® and Polyethylene Glycol) has been confirmed after irradiation to doses of 100 kGy.

Addendum on leather (Wojtek Glushevski)

The problem of radiation resistance of collagen, the main component of skin, was examined from the viewpoint of tissue grafts. Studies have shown that the dose of 25 kGy is acceptable from the medical standpoint. It may be assumed that the dose needed to get rid of insects or even mold and fungus will not affect significantly the mechanical properties of historical objects.

There is a review on the degradation of the skin in the radiation preservation: "Chahine C., Vilmont L. B., Effect du rayonnement gamma sur le cuir et le parchemin. Patrimoine culturel et alterations biologiques. Actes des journees d'etudes de la S.F.I.I.C. 1988". The authors examined the effect of gamma radiation on mechanical properties of the parchment for a dose of 36 kGy. Work contains an overview of the basic literature on radiation preservation of historical objects made of leather. Modifications for the 10 kGy dose are around a few percent. So are comparable with the radiation modifications of the paper. A very good recommendation for using radiation techniques in skin preservation was the sterilization of mammoth Khroma – see success stories.

Addendum on paper (W.Glusevski)

The paper matter is a subject to degradation due to natural processes of ageing as the degradation caused by physical-chemical; mechanical and microbiological factors like fungi, mould and insects. The microorganisms, part of them pathogenic, negatively affect books; the destruction of fungi and mould is the first and most basic intervention before further processes of conservation of books and old prints can take place. The fungi and mould are resistant to high and low temperatures, they need little moisture and their resistance to chemical substances increases with time.

Methods of disinfection applied by the paper conservators usually narrow in the liquid form (bath, spray or tissue-paper saturated with a fungicide and inserted among the infected pages), or gas. These methods are time-consuming and laborious. They are not friendly to the people and environment. The chemical means are insufficient when we deal with, large collections infected with microorganisms. While the disinfection of one part of the books takes place, the fungi freely develop, infecting other volumes.

This situation occurred in Leipzig in 1992 where 15 000 – 20 000 books were infected with a fungus due to the inadequate storage in humid crypts. Disinfection on a large scale became necessary and disinfection was made by irradiation of the books with Co-60 gamma rays. According to the published report the intervention was successful and rescued of the collection.

Literature review on issues of radiation preservation of paper was made on the occasion of work done in Poland on the effects of gamma radiation and E-beam on two grades of paper. There is a comparison between Whatman's paper no. 1 (almost pure cellulose) and newspaper (aromatic blend

of cellulose and lignin).

In all previous work only gamma radiation Co-60 was used. Research performed in Poland confirmed the radiation dose of 8 kGy recommended by most authors as sufficient to combat fungi and moulds. Ionizing radiation can also be used to combat insects and the radiation doses are then reduced by various authors between 0.5 and 3 kGy.

As a general conclusion the radiation degradation of paper at 20 kGy dose is ~ 2%. This is small change taking into account that this dose is three times greater then the dose needed for disinfection procedure.

Simultaneously, it is noted that changes of chemical properties of paper are much lower when applying the electron radiation. Very fast treatment with electron beam (several seconds) is limited post oxidation degradation. Long treatments in the sources of gamma irradiation favour the oxygen diffusion processes in the irradiated paper. The recommended dose of 8-9 kGy is consistent with the results received by German, Italy, Polish and Dutch groups dedicated to preservation of paper with gamma radiation. The work has also drawn attention to the protective effect of lignin in the process of radiation degradation of paper. It is of course debatable whether the 1% degradation of paper is acceptable in the case of objects of historical significance. For objects that may be very valuable, however, not in a situation where it quickly to save a large harvest is acceptable.

In the year 1995, the Facility of Art Conservation at the Academy of Fine Art in Warsaw, in cooperation with Institute of Nuclear Chemistry and Technology and Warsaw University of Technology and the National Library undertook a research dealing with the effect of ionizing radiation coming from Co-60 gamma radiation and fast E-beam on paper matter. Exploration made so far included paper resistance changes as copper-number and pH-water extract. The mechanical (double fold number, tear resistance, breaking length), physical-chemical (copper-number, pH water extract) properties, as well as the degree of whiteness in paper (Whatman`s paper No1 - pure cellulose and Wood pulp paper – cellulose + lignin) were investigated. Part of the samples were studied for a second time, after six months of natural and 25 years of artificial ageing process of ageing. Results are presented in **Table 3, 4 and 5.**

Table 3: The pH-water extract from Whatman`s paper Modified: cooper-number for Whatman`s paper depending of kind of radiation

Kind of radiation	D [kGy]	0	1	5	10	20
Γ	x,l,Cu	0,194	0,226	0,38	0,581	0,960
EB	x,l,Cu	0,194	0,21	0,30	0,436	0,60
		0,065	0,065	0,065	0,065	0,065

Table 4: Whitening and yellowing Whatman`s paper depending of dose and kind of radiation

Dose [kGy]	Whitening R457 (%)	
	EB	γ
0	92,12	92,12
1	92,34	93,34
5	92,14	91,84
10	91,13	90,61
25	89,83	90,02

Table 5: Whiting and yellowing Whatman`s paper depending of dose and kind of radiation after six months ageing

Dose [kGy]	Whitening R457 (%)	
	EB	γ
0	91,34	91,34
1	91,44	90,97
5	90,54	89,86
10	88,69	87,79
25	87,03	86,55

The microbiological studies carried out on two strains of fungi (*Aspergillums Niger* and *Chaetomium globulum*), proved that both types of radiation are similar effective. The study confirmed a slight influence of radiation on the strength of paper (2% at the rate of 20 kGy, thus the dose three times greater than the "mortality rate" for most microorganisms). The chemicals results, picturing the radiolysis state proved the electron beam radiation to be more beneficial.

3.2 Other side-effects

Physical integrity and appearance of cultural heritage are not the only characteristics to be conserved. Heritage artefacts are also sources of information, some of them being not accessible by observation but only from analysis. Such analytical investigations include a very large panel of methods, from chemical to physics through biological analysis. Before undertake any treatment, It must be asked if this kind of information could be affected.

It is first obvious that gamma irradiation will not modified radiometric dating results, using ^{14}C or other natural radioactive isotopes, as it can not product artificial radioactivity, even in traces.

In the other hands, thermo-luminescence dating will not be possible after irradiation, as it use directly the natural radiation absorbed dose from its environment that will of course be drastically modified by gamma treatments. Fortunately, organic materials are poorly concerned with this method.

DNA is another very important source of information that has been more and more accessible since the development of DNA analysis using PCR amplification. As the biocide effect is due directly to DNA induced lesion, one may retain that irradiation will affect widely the DNA information. However, once again, this has to be considered as a matter of dose. Indeed, in well conserved DNA, the order of magnitude of gamma irradiation biocide treatment effect is only one lesion for one thousand base pairs. It has also been proven that such irradiation will not prevent forensic identification.

About ancient DNA, which is characterized by its low quality, and the modified surrounding environment, with presence or not of free water, no study of irradiation effect has been presented. The length of the available sequences in ancient DNA rarely exceed a few hundred pair of bases, and the number post mortem mutations increase with time. These are two factors that should make insignificant the number of errors due to irradiation at biocides doses. Samples of old baby mammoth specimen Khroma have been collected before and after irradiation and will give some evidence of how the ancient DNA is really affected by gamma irradiation. Whatever, it is reasonable that random single irradiation-induced error in DNA sequence could easily be statically identified and removed after repeated analysis.

At the end, we have no idea of what our successors will be able to implement as new method for characterize cultural heritage. As present-day scientists, we must remain humble. Nobody can argue that our action of irradiation is definitively not damaging some properties that could interest the scientists of the future, just as nobody can say it for any other methods.

Irradiation consolidation of porous structures

4

The consolidation in the whole volume of porous materials such as wood or concrete was implemented during the sixties worldwide (USA, Japan and Europe) by using the process impregnating these materials by acrylic, vinylic monomers under pressure, and then their in-situ polymerising or solidifying by gamma irradiation.

Wood plastic composites were developed in that period for the main industrial application which was flooring in public areas. Very hard surfaces were obtained because the resin fills completely the wooden vessels, giving a densified wood which is much less sensitive to relative humidity. Application in the field of cultural heritage was initiated in the seventies in Europe by France and Tcheque Republic.

In 1970, the Grenoble laboratory took the challenge to consolidate the 19th century mosaic parquet from the ancient Grenoble city hall by dismantling the wooden panels which were impregnated by the monomer methy-methacrylate. During the late seventies, the consolidation of many degraded wooden artefacts was carried out by using more appropriated radiation-curing resin based on unsaturated polyester and styrene. This latter was also implemented in conservation of waterlogged archaeological artefacts which require additional liquid phase exchange steps with the solvent acetone. ARC-Nucléart is the unique laboratory in the world to implement currently so far both treatment of disinfection and consolidation.

Monomers and resins

Radiation polymerization being initiated by free radicals, monomers and resins which can be cured by this process must have in their chemical structure double bonds carbon-carbon or unsaturated bonds enough reactive such as acrylic, methacrylic, vinylic or unsaturated sites in polyester oligomers.

The most current acrylic monomer used is methyl-methacrylate (MMA) which polymerizes to give the thermoplastic polymer polymethyl-methacrylate Plexiglass, with a volumic shrinkage of about 20 %. Besides its advantage of very low viscosity for good penetration in porous materials, MMA presents two main disadvantages in our application: very high volatility resulting in product loss on surface area, and sensitivity to oxygen inhibition of the radiation-curing in air resulting in sticky or uncompleted cured surface layers.

Standard unsaturated polyester resins are currently used in composite material industry (boats, containers) and are composed of the monomer styrene (mass ratio from 30 to 50 % in the resin) and the unsaturated polyester prepolymers. They are much more viscous (at least one hundred times, oil consistency) and polymerize to form a three dimensional network through the crosslinking of the polyester chains by the styrene radicals (thermoset type resins). With a volumic shrinkage reduced to 10 %, the polyester resin gives after curing an unsoluble hard material even at the surface. For this last reason, the polyester resin with chemical nature such as isophtalic (recommended one for durability) or tetrahydrophtalic types is used since more than thirty years by the Grenoble conservation laboratory. Following the country producers, the main trade names of unsaturated polyester resins are Norsodyne, Ludopal, Palatal, Synolite, Atlac, Crystic in Europe and Norpol in North America.

Polymerisation under gamma irradiation

Acrylic monomer and unsaturated polyester resin are polymerised by a free radical mechanism by irradiation (gamma rays, electron-beam) or also by addition of chemical catalysts such as peroxides (conventional process in composite industry). By irradiation, the resin is free from any chemical additives (peroxides, accelerators) because the gamma rays initiate the free radicals necessary for the fist step of polymerisation, and that at room temperature. The second step is the propagation of the chain of polymers always under irradiation, the "gel effect" with heat build-up, and the last one, termination, is the formation of the solid polymer after total reaction of the free radicals in pres-

ence. Thanks to the fact that the polymerisation reaction rate is proportional to the irradiation dose rate, i.e. the intensity of the radiation, one can control the heat build-up during curing by varying or lowering the dose rate, the highest being usually around 1-2 kGy/h. The total dose for complete polymerisation of the resin is in the range of 20-30 kGy.

Impregnation of wooden artefacts and irradiation

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 must be wedged on its support to avoid the floating in the resin bath, and then low vacuum is set up (around 1 mm Hg) during some hours to extract the air from the wood pores. Liquid resin fills then 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 afterwards applied in the tank, in the range of 1 to 3 bars following the decay state of the wood, during some hours for thin artefacts to more than 24 hours for large size ones. At the end of impregnation, the excess resin is flowed 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 long period at room temperature.

Back to atmospheric pressure, the artefact is left to drain inside the tank until no more flowing of resin from the object. Out of 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 at 10 cm from the panel cobalt 60 source to start the in-situ resin polymerisation after putting thin thermocouples inside the object to monitor the temperature which must not exceed 50-60 °C.

The other advantage of radiation-curing is the temperature control by varying the dose rate, for instance increasing the distance between the artefact and the panel source will result in lowering the wood temperature. This parameter is important for the behaviour of the artefact in terms of dimensional variations of the surface area or its internal structure. Thanks to the penetrating power of the gamma rays, the polymerisation is performed at each point on and inside the object, resulting in a homogeneous and complete reaction.

During the first 48 hours of irradiation, cleaning of the surface with textile and the styrene monomer, putting new wrapping textile, are crucial for the wood aspect without the minimum of residual resin on it or glossy surfaces.

The two faces of the artefact are exposed to the sources for the 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 the object.

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 it bulk and its mechanical strength is considerably increased. This gives 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 hardly sensitive to changes in climatic conditions when it is displayed or manipulated indoors. Impregnation darkens slightly the colour of wood, depending on its species (broad-leaved species darken more than conifers).

Regarding polychromic sculptures, much care must be put in testing the interaction or not of pigment layers with the monomer or resin. The method is obviously avoided if any dissolution of pigment by the resin is detected. In some cases, protection of the pigment layer could be realized by wax application prior to impregnation.

Undoubtedly, this process, using insoluble cross-linked polymer and its maximum resin content, is at the opposite of conventional application of diluted solutions of polymers which are theoretically reversible and film forming in the wood structure. Nevertheless, it could be considered as a useful method for the preservation of many degraded artefact, the "last chance method", and the forty year experience of the Grenoble laboratory in this field is there to prove it.

Radiation processing technology and facilities

5

Irradiation dose is the decisive parameter in disinfestations of CH artefacts. Proper treatment doses (order of magnitude of kGy), may be obtained in reasonable time only in industrial gamma and electron beam facilities.

Other irradiation facilities like equipment for defectoscopy or medical radiography are not proper for CH disinfestations. The obtained doses here are extremely non-uniform and not big enough.

5.1 Radiation process for cultural heritage

Interaction between radiation and substance

Interaction between a ray (or radiation) and a substance is called irradiation. It is basically a process of energy transfer from the radiation to the substance. The physical main characteristic for this process is called "absorbed dose" (or simpler "dose"), is symbolized by D and represents the energy transferred to the mass unit.

$$D = energy / mass.$$

The measuring unit is called gray, is symbolized by Gy and represents the energy of 1 Joule (J) transferred to 1 kg.

$$1Gy = 1J / kg$$

We talk about a certain process by indicating the "bullet": *gamma* irradiation, irradiation with *e-beam* (electron beam), *laser* irradiation etc. This is happened because interaction of each radiation type has particularities.

In industrial processes are used three types of ionizing radiation: gamma, accelerated electrons and X ray. An ionizing radiation is a bullet with the energy greater (kiloelectronvolts - keV, mega-electronvolts – MeV) than energy of chemical bonds (electronvolts – eV). In this way some chemical bonds may be broken.

Substance sensitivity to irradiation depends on the type of chemical bonds: metallic and electrostatic bonds are inert and irradiation do not modify at all metals and salts; covalent bonds (also known as true bonds) might be broken. This bond is typical for all substances present in living creatures.

The consequences of braking chemical bonds by irradiation of cultural heritage artefacts are of greatest importance for disinfestations as final target and for irradiation side-effects as well. They will be considered in extenso in this booklet.

Irradiation disinfestations of cultural heritage – state of the art

Irradiation sterilization of medical devices is now a well defined industrial process, including important knowledge on treatment itself and treatment side-effects. All important aspects are known:

- academic studies focused on influence of irradiation on living organisms established a scientific area called radiobiology;
- other studies were devoted to radiation qualification of materials exposed to radiation, especially plastics, also some natural polymers (cotton), inscriptions, adhesives;
- engineering studies gave birth to various facility designs in view of optimizing cost/benefit ratio, improvement the production yield, radiation safety or reliability;
- normative or guides and standards covered safety design, installation and exploitation, quality assurance, quality control et al.

When irradiation treatment is applied for cultural heritage disinfestations, important advantages can be mentioned in its favour. They are connected to:

SAFETY:
- o The treatment associates no risk for restorer, curator, visitor or environment;
- o It associates no risk for the operator; it is performed only in the irradiation room which is a confined and protected area;
- o The treated artefacts do not become radioactive; no other toxic residue remains in the treated item;

EFFICIENCY AND RELIABILITY
- o The efficiency is extended on the whole inner volume based on excellent and predictable penetration of gamma radiation; alternatively, any gas efficiency (including anoxic treatment) is limited by diffusion;
- o Efficiency is only related to absorbed dose which is a parameter easy to measure and control;
- o Reliability of the treatment is very good due to the fact the irradiation parameters are inherently the same all the time;

TIME
- o Irradiation simultaneously acts on all biological aggressors;
- o Large amount of objects can be treated simultaneously;
- o Treatment in industrial facilities is performed in short time – days or hours;

HARMELESSNESS AND SIDE-EFFECTS
- o When irradiation is properly applied, the modification of basic properties of wood, paper, leather, parchment, hay, silk, cotton, wool and other textiles, moving film peliculles are negligible;

OTHERS
- o Oversized objects may be treated;
- o Composite artefacts may be treated without precautions;
- o Raw materials for restoration may be treated;
- o The treatment is performed at room temperature;
- o Artefacts can be treated in the transport boxes, avoiding any inconvenient that may result from manipulation.

In spite of advantages, up to now, the cultural heritage conservation method is not wide spread. Acting separately or synergistically several reasons imposed this state of the art:

- Irradiation of cultural heritage needs facilities as costly as facilities for industrial sterilization, which means important investment and unattractive capital cost.
- Though the investment level is high, the activity can not follow the business philosophy. Instruments like planning, profit, schedule, risk, provisions are not applicable or have total different meanings. Cultural heritage artefacts can not be considered "goods", being priceless in a way. Responsibility is the key-word and entire activity, procedures, knowledge and the people quality is acting around this idea. Pragmatically speaking this approach brings high operation costs.
- There is a basic contradiction connected to the place where the artefact meets the irradiation equipment. On one way the irradiation facility is not transportable. On the other way in cultural heritage domain the artefacts movement, for any reason, is considered a risky, expensive and even dangerous step, being generally avoided by curators or other decision makers in conservation.
- Another difficulty is the need for a complex team capable to manage a high-tech also to apply deontological principles proper for completely other human area of activity.
- It is well known that people without technical knowledge, establish subliminal connections between words like irradiation or radioactivity and Hiroshima, Nagasaki or Chernobyl disasters. This catastrophic perception is often shared by the decision makers in cultural heritage area that usually have a humanistic background.
- Having not the same economical motivation as sterilization, cultural heritage treatment gathered less R&D studies on specific side-effects and almost no norms.

Being the chosen alternative most frequently in emergency cases, irradiation treatment of cultural heritage artefacts is practiced in facilities constructed for medical supply sterilization.

Acceptance of irradiation disinfestations

Advantages of utilization of irradiation as disinfestations method are obvious and indisputable. The method is recommendable without hesitation in the following situations:

- the intervention time must be short (e.g. in case of an active attack)
- the volume of piece(s) to be treated is large
- the treatment price must be low
- there is no alternative - e.g. for mummies or in cases when technical equipment for alternative methods is missing.

Usually the chosen treatment doses followed the values empirically established and in most of the cases, side-effects are only evaluated from theoretical analogy with model material and according manipulators.

5.2 Gamma facilities

In gamma facilities the irradiation field is produced by Cobalt-60 (Co-60) radioisotopes. In industrial facilities, installed radioactivity is in the range of 10^3 - 10^5 TBq (10^4 – 10^7 kCi). The main purposes of such facilities are sterilization of medical devices or foodstuff disinfestations.

The known irradiator types will be described together with particular limitations for cultural heritage treatment. Irradiation facilities are usually classified in relation with radiation safety, in two types – SELF-CONTAINED and PANORAMIC irradiators and four categories (I to IV).

Self-contained irradiators of Category I

Particularities: it is considered self-contained because the sources – placed in fixed positions in a solid container, have permanent shielding; equipment is delivered with sources already installed providing a defined and unchangeable irradiation field; only the irradiation chamber is moving between the irradiation position and loading/unloading position.

Irradiation chamber: irradiation chamber is cylinder-shaped and has volume limited at a few liters; the irradiator configuration and the chamber volume do not permit human access in the irradiation field.

Dose-rate non-uniformity: is quite good being an irradiator for research or for special applications.

Utilization: it is useless for cultural heritage treatment having very small volume.

Panoramic irradiators of Category II

Particularities: irradiation field is temporary constituted in a large chamber; source assembly is usually of a cylinder form and has a vertical moving between a "shielded position" (in a water pool or in a dry container placed underground) and "irradiation position" (in the irradiation chamber); irradiation chamber door may be opened for introducing / taken out the goods only when sources are in shielded position;

Irradiation chamber: has a great volume of tens m^3;

Shield: concrete;

Dose rate non-uniformity: is important but may be easy counteracted by changing object place in the irradiation field; a careful three dimensional dose mapping or proper software is necessary;

Utilization: it is suited for the treatment of CH artefacts of any size if they may be brought into the irradiation chamber.

Self-contained irradiators of Category III

Particularities: the sources are placed in a water-pool which permanently acts as shielding; the irradiation field is constituted in the water; as in the case of Category I irradiators only the irradiation chamber is moving penetrating the water.

Irradiation chamber: it is water-proof; its configuration and volume do not permit human access in the irradiation field; its volume is of tens litres; sometimes there is a rotation device for irradiation dose uniformization;

Shield: concrete during irradiation; water or lead during non-utilization;

Dose rate non-uniformity: is accentuated, but could be improved by chamber rotation;

Utilization: theoretically could be used for small CH artefacts but intensive dosimetry exercises have to be performed on dose distribution.
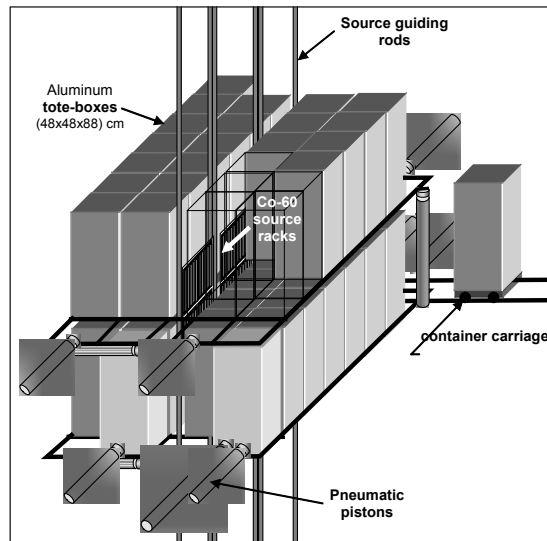
Panoramic irradiators of Category IV (**Fig. 21**)

Fig. 21: Category IV irradiator IRASM – IFIN-HH, Romania. Irradiation in conveyor boxes - conveyor pass and source plate in irradiation position.

Particularities: this is the typical industrial irradiation facility; irradiation field is temporary constituted in a large chamber; source assembly is a plate and has a vertical moving between a "shielded position" (in a water pool) and "irradiation position"; the goods to be treated may be continuously introduced / get out from irradiation chamber during irradiation process through a conveyor penetrating the concrete shield;

Irradiation chamber: has a great volume of tens m3; there are two irradiation possibilities: a) small objects are placed in the conveyor boxes; irradiation is performed during the movement; b) oversized artefacts may be placed outside the conveyor pass in panoramic position;

Shield: concrete during irradiation; water during non-utilization;

Dose rate non-uniformity:

- for irradiation in conveyor is minimized by the conveyor pass around the source plate; an overdose ratio = max. dose / min. dose is defined with a typical values < 1.5;
- for irradiation in panoramic position may be minimized by placing the artefacts parallel with source plate; no uniformity is better at greater distance between source and object; a dose-mapping is necessary;

Utilization: it is suited for the treatment of CH artefacts of any size if they may be brought into the irradiation chamber.

5.3 Electron beam facilities

The Nature of Electron-Beam Radiation (E-beam)

E-beam radiation is a form of ionizing energy that is generally characterized by its low penetration and high dosage rates. The beam, a concentrated, highly charged stream of electrons, is generated by the acceleration and conversion of electricity. The electrons are generated by equipment referred to as accelerators which are capable of producing beams that are either pulsed or continuous.

As the product/material being sterilized (disinfection) passes beneath or in front of the electron beam, energy from the electrons is absorbed. This absorption of energy alters various chemical and biological bonds within the product/material. E-beam radiation is similar to gamma processing in that, upon contact with the exposed product, electrons alter various chemical and molecular bonds, including the reproductive cells of microorganisms.

Electron beam radiation was introduced in the 1950s as a means of sterilizing single-use, disposable healthcare products. The process, however, was not widely accepted due to the unreliable nature of the e-beam equipment. By the 1970s, advances in technology brought improved operating efficiency and e-beam irradiation became an acceptable method of sterilization for healthcare products. The EB process is ideal for low-density products. In electron beam processing, electrons are accelerated to very high speeds (near the speed of light) in order to increase their energy. These high speed, high energy electrons then penetrate products to achieve sterility by damaging the DNA strands of the microorganisms.

Once damaged, these microorganisms are unable to reproduce, and are therefore considered sterile. For many applications, particularly low density packed boxed goods, electron beam processing can provide an extremely fast, economical alternative to other sterilization technologies. The comparatively higher dose rate may result in faster turn times and be more compatible with a wider range of device materials.

Shorter Exposure Time for Favourable Material Compatibility

Most materials manufactured for use in disinfection, disinfection or sterile Cultural Heritages are formulated for radiation stability. Although not formulated exclusively for gamma or e-beam sterilization, some materials have demonstrated less degradation when processed with e-beam radiation. This is due to a significant difference in dose rate between the two radiation technologies.

In general, products processed with e-beam radiation experience shorter exposure time, which could result in less oxidative effects on certain materials. Some cellulose materials, for example, experience less breakdown and long-term aging effects from processing with accelerated electrons. However, reports published by material experts with leading manufacturers of plastics and resins demonstrate that the vast majority of other materials commonly used in medical and packaging applications perform equally well, assuming treatment with the same dose of radiation.

Excellent Controls for Consistent Dose Delivery

E-beam sterilization 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. In the public mind there is an unclear association between irradiation and radioactive materials (which if leaked or spread would be a health hazard) leading to the erroneous conclusion that irradiation is dangerous.

Radioactive materials can be created when very high energy particles (as created in nuclear reactors and very high energy electron accelerators) bombard a target. In this case, the radiation energy entering the target material can not only ionize it, it can transform a stable element into an unstable one. This is called induced radioactivity. After extensive research, it has been established and internationally agreed, that keeping the energy of machine sources below certain well defined thresholds will ensure that any such induced radioactivity will be negligible.

Typical Electron Beam Plant

In a typical sterilization plant (**Fig. 22**) designed for high volume processing, products enter on a conveyer through a labyrinth that permits access but stops radiation from escaping. 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.

Fig. 22: Facility with an LAE 13/9 electron accelerator (Institute of Nuclear Chemistry and Technology, Warsaw Poland)
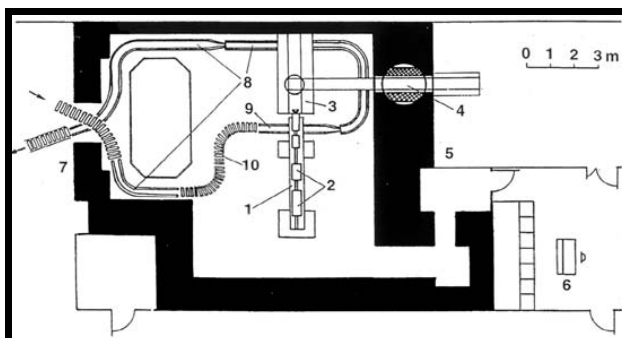
1. LAE 13/9 electron accelerator
2. Accelerating sections
3. Irradiation zone for horizontal beam
4. Gate
5. Measurement room
6. Control room
7. Technological room for radiation processing
8. Input and output conveyors
9. Conveyor with controlled speed
10. Rollers

Irradiated objects are placed on the conveyor, which transfers the sweeping them under the electron beam. Time treatment is very short - a few seconds. *Elektronika 10/10 electron accelerator (Institute of Nuclear Chemistry and Technology, Warsaw Poland)*

There is a significant difference in the distribution doses in the radiation processes using electron beam and gamma radiation **(Fig. 23)** In the case of EB occurs characteristic going up doses inside materials the booster of reaching the tens of percent. There is adverse phenomenon from the point of view of radiation degradation of material.

Dose range in the material can become more uniform by using double-sided irradiation **(Fig. 24)**. It belongs to add that maximum energy EB it can not surpass 10 MeV. So the maximum range of EB on a material with a density 1 g/cm3 may reach 10 cm. Electron beam very often enough to disinfestations and sterilisation small historical objects. In particular, it is useful, use electron beam to irradiate the books and documents. It is worth to emphasize again that this treatment several seconds. Currently produced in the world commercial installations for radiation sterilization of mail.

High-Energy Beams for Reliable Penetration

The total number of accelerators installed all over the world exceeds 13,000, among them the number of units applied for radiation processing being close to 1200. Direct, transformer accelerators, single resonant cavity accelerators and microwave source powered linear accelerators have been found to be the most suitable for radiation processing. The industrial accelerators' development is

still in progress, not only due to new areas of application but also because of demands of lower cost and more compact size machines. While commercial e-beam accelerators range in energies from 3 MeV to 12 MeV (million electron volts) and usually operate at a single energy, advances in technology have resulted in the development of select e-beam equipment capable of operating at varying energies.

For the sterilization of *Cultural Heritage*, high-energy electron beams are typically required to achieve penetration of the product and packaging. When evaluating e-beam irradiation for the purpose of sterilization, product density, size, orientation, and packaging must be considered. In general, e-beam irradiation performs best when used on low-density, uniformly packaged products.

Electron beam units equipped in e/X converters

The different forms of radiation penetrate items to quite different degrees. Electrons are much less penetrating than X-Rays and gamma rays. Most electrons collide with the product irradiated within a few atomic distances of the surface but each collision creates secondary electrons under the surface. These continue to create more electrons in a shower effect. Radiation is scattered forward and the peak dose actually lies a short distance below the surface. Thereafter it diminishes quite quickly. If the electrons are converted to X-Rays, the penetration of the X-Rays is an order of magnitude higher but there is a considerable loss of useful radiation power.

Application of X-rays for radiation processing based on X-ray tubes is quite popular in the case of blood irradiation. Commercial irradiators are offered on the market. The concept of e^-/X conversion is known for years, a lot of R&D was performed in the field and some units were installed.

In 2010, the company Däniken (Switzerland) - LEONI Studer Hard AG has launched as the world's first x-ray sterilisation plant that uses IBA's new Rhodotron TT-1000 system. The Rhodotron is an electron particle accelerator that was designed primarily for industrial application. The system enables especially efficient sterilisation of medical products, decontamination of packaging materials as well as modification of other materials.

The new Rhodotron TT-1000 is, with an energy reading of 7 MeV (million electron volts) and output of 700 kW, the world's most powerful electron accelerator of this kind. It permits entire pallets of product to be either treated or sterilised. The new Rhodotron TT-1000 x-ray sterilisation line is one of the largest systems for sterilising pallets available anywhere in the world. Installations of this type of radiation can sterilize and consolidate the historic buildings of similar size as the source of gamma.
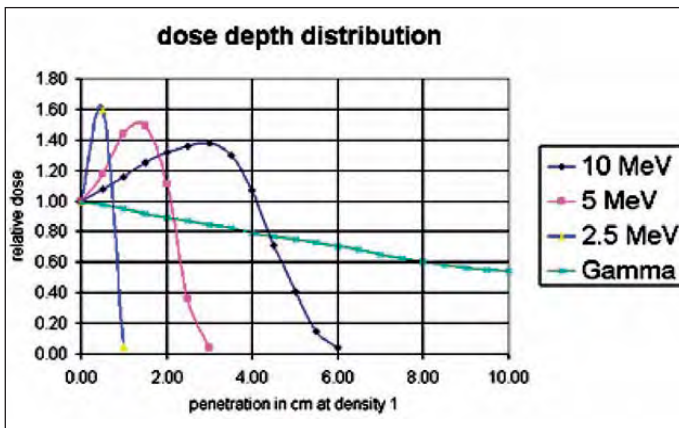

Fig. 23: Depth–dose distribution for electrons of various energies and for ^{60}Co gamma rays (courtesy of Studer Hard, Switzerland)
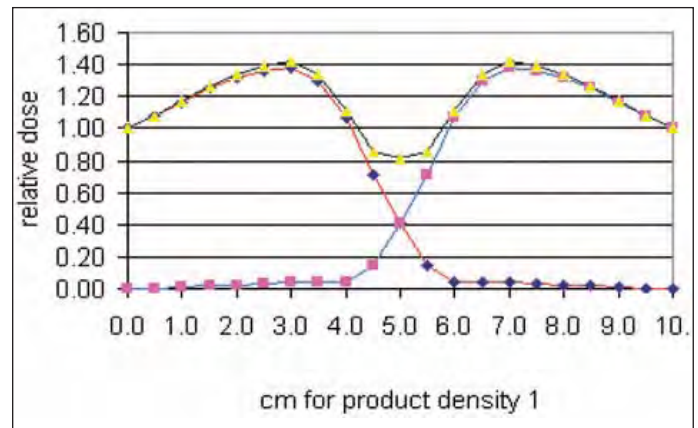

Fig. 24: Dose distribution for two-sided irradiation with 10 MeV electrons (courtesy of Studer Hard, Switzerland).

Success stories

6

The disinfection of the Mummy of Ramses II (France, 1977)

During its display at the Cairo Museum, the Ramses II mummy presented already infestation by larvae, insects and fungi, due to the tropical environment, and the non-sealed glass cover for its protection (1975). In the frame of an exhibition in Paris (1976) on Ramsès II and numerous artefacts relating to its reign, the mummy was transferred in France for examination of its condition by the French National Museum of Natural History. Degraded in the past by larvae insect, the mummy was also found during this investigation infested by a dense and various fungi population, without any pathogen bacteria. In agreement with the Egyptian authorities, it was therefore decided to disinfect the mummy by gamma irradiation, process which is carried out since many years at the Nucléart laboratory (called ARC-Nucléart in 1987) located in the Grenoble Research Center of the French Atomic Energy Commission (CEA).

A consortium of laboratories and museums in Paris (Anthropology Museum, Musée de l'Homme) and Grenoble was set up, coordinated by a research laboratory in Paris, in order to manage the project in its different steps: previous 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, which must be effective to eradicate all the fungi (more than sixty species) and also not harmful to the components of the mummy such as the hair, textiles, skin, teeth,...No sampling was authorized on the Ramses II mummy, except some fragments of hair and textile that were laying on the linen or on the Plexiglas plate placed under mummy. It was very important to design the covering element in which the mummy will be kept during irradiation and even after, to ensure the sterility of the atmosphere around it, avoiding thus any further recontamination.

Due to the length (1.72 meter) and the uneven form of the mummy (especially the disposition of the arms), as well as the presence of the sarcophagus and various other materials inside it, the determination of the irradiation dose in each part of the mummy necessitated the design of dosimetry software based on simple geometric forms representing the whole artefact to be treated. Furthermore, the density of the materials could not be estimated accurately, and equivalent data was obtained from other disposable mummies. Anyway, thanks to the calculus model, the gamma ray source was designed satisfying the irradiation parameters such as the 18 kGy disinfection dose at an average dose rate of 1.5 kGy/hour. It could be (was ?) possible to determine the dose rate at each point of the mummy model, depending on its position regarding the cobalt 60 sources and the presence or not of absorbing materials. The challenge was the application of this minima dose of 18 kGy on all parts of the mummy.

The validation of the model was carried out by irradiation of two mummies dedicated for studies, one coming from the Museum of Fine Arts in Grenoble and the other from the Anthropology Museum in Paris. Good agreement between calculated and measured irradiation doses was obtained.

In order to be able to manipulate after irradiation, in a sterilized atmosphere, the mummy, the sarcophagus, the Plexiglas cover, the dosimeters, and the various materials used for maintaining the mummy, it was necessary to keep all these items in a sealed plastic envelope during irradiation, similar to a glove box. The irradiation phase could then started in the facility of the CEA research center at Saclay, near Paris, having a radiation activity at this time of 160 000 curies (May 1977). The duration of irradiation was 12 hours and 40 minutes, with a rotation of the mummy at mid-irradiation. The ratio between the maxima and minima gamma ray dose is 1.33, and the uncertainty of the measurement is around 10%.

The disinfected mummy is displayed in its sealed transparent plexiglass 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, preserving the Ramses II mummy in good conditions, still nowadays after thirty tree years. The irradiation process (is has revealed to be) quite effective to solve complex case studies. Las but not least, the skills of the different partners involved, as well as their perfect coordination was the key factors to accept the challenge of such unique treatment in such short delay.

Alan Mason Chesney Medical Archive – stolen book collection (USA, 1982)

In 1982 Alan Mason Chesney Medical Archive belonging to John Hopkins Medical Institution, Baltimore, USA – 10 m³ - has been stolen and later abandoned in miserable conditions: street cats and dogs cohabitating with insects, fungi, other micro-organisms among animal remains and dead bodies. To recuperate the book collection the first mandatory step was its radiation disinfestation.

Radiography of the case:

Preliminaries: The whole operation was elaborated by a hygienist which indicated the microbiological tests, packaging procedures (remove dust, placing the book in sealed plastic bags), safety measures of the packaging team (complete protection suit including special shoes, mask and gloves). The actions were design having in mind the elimination of contamination risk of the people, transport car and irradiation facility. For packaging 8 people worked 7 days preparing 295 standard packages. The transportation was straight to the irradiation facility without any intermediate manipulations.

Irradiation: Irradiation facility was not mentioned, but most probably was of category IV. Irradiation was performed in the conveyor and declared treatment dose was 4.5 kGy. Most probably it is the value of the medium dose. Taking a probable overdose of 1.5 the books have been treated at doses between 3.6 and 5.4 kGy. This is in accordance with insecticide and fungicide doses.

Post-treatment actions: Treated books have been kept in quarantine in plastic sealed bags for one week waiting for all insect death. Microbiological tests also proved treatment efficiency. A conservator noticed no evident (visible) modification of the paper characteristics. A monitorization file has been established. At 8 years after treatment (in 1990) "the project has to be considered a success"

Fig. 25: Shoes packed for transport to IARC

Fig. 26: Concentration camp - museum

Mass sterilization of artefacts from Majdanek Nazi Camp (Poland)

An example of radiation sterilization of large amounts of artefacts is the work done by the Institute of Applied Radiation Chemistry (IARC - the Faculty of Chemistry of Technical University of Lodz, Poland) for the Museum at Majdanek, regarding the disinfection of 60 thousand pieces of shoes camp prisoners **(Fig. 25 and Fig. 26)**. **The State Museum at Majdanek** was founded in November 1944 on the grounds of the former Nazi concentration camp. It is an institution directly subordinated to the Ministry of Culture and National Heritage in Poland. Its main duties include keeping the post-camp area with its buildings and appliances in proper condition, as well as substantiating the history of the camp at Majdanek.

Shoes (60 000) were packed into bags (size of the bags were 60x100x35 cm), and then were transported to IARC gamma irradiation facility for their disinfection at a dose around 20 kGy, eradicating the Bacillus (*Bacilus subtilis*), the efficiency rating from 95 to 99 %.

E-Beam disinfection of artefacts from Katyń massacre (Poland)

Electron radiation was used for disinfection of historic object of Katyń Museum in Warsaw. There were fragments of uniforms, footwear, dignity, distinctions, photos and other objects. Items were placed in aluminum boxes and irradiated with E-beam of 10 MeV at a dose of 25 kGy. It was used a graphite calorimetric dosimeter. Normally a thickness of 4 g/cm² was not surpassed. In case of more heavy objects two-sided radiation was used (**Fig. 27**).
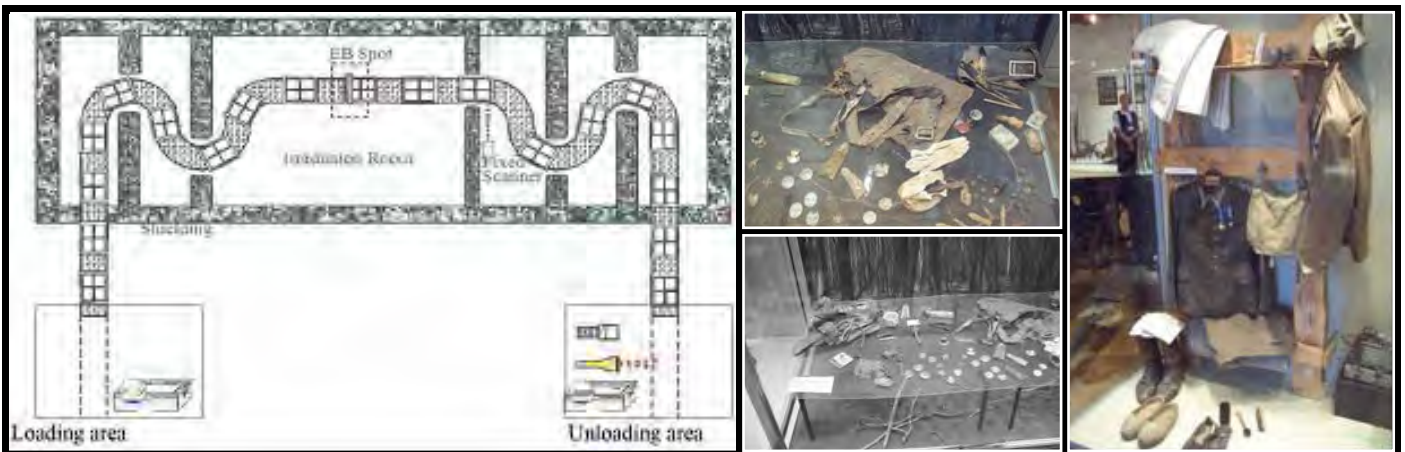

Fig. 27: Elektronika 10/10 electron accelerator (INCN Warsaw, Poland) and Katyn objects after E-beam treatment

National Film Archive (Romania, 2001)

The gelatin present in the film emulsion is a hydrophilic protein sensitive to humidity in the air. As a consequence it is a favourable media for fungi development. Immediately after the 1989 revolution, the preservation conditions of a part of Romanian Film Archive became very bad. Impressive development of fungi appeared.

Construction of a new building having proper environmental control was only one of the necessary measures to save the archive. Equipment for wet cleaning of the peliculle was procured. It was still not enough because the rolls that must be saved outnumbered the treatment possibility of the machine.

Irradiation disinfestations were chosen as emergency intervention for stopping the peliculle destruction. The action was preceded by several tests types taking into consideration the peliculle structure and mechanical characteristics for film presentation.

Identified microorganisms were from the following families: Penicilium, Mucor, Aspergillius, Tricoderma and Claviosporum. As can be seen from **Fig. 28** it would have been useless to estimate the number of microorganisms. The contamination was terrible and it was thought the treatment at the sterilization dose of 25 kGy. This was the guiding dose for estimation the possible mechanical and colour side-effects. Taking into account the inevitable overdose ratio tests at 50 kGy were also performed.

The following mechanical tests have been performed using testing equipment and procedures applied for AZO industrial peliculle manufacturer (Romania) or in use at Romanian Film Archive:

a) The contraction of the distance between two perforations. This is the most dangerous modification and most frequent sign of pelicule aging. An excessive contraction value does not permit film presentation. On statistical base the registered contraction was zero in comparison with non treated peliculle.

b) Other mechanical characteristics – thickness, tensile strength, elongation at break were also not visible modified by irradiation.

Colour tests have been performed by a Kodak Laboratory using sensitograms for both negative and positive films. It was measured the densitometric value before and after irradiation for each color layer. No modification has been registered.

It was imagined a test to identify if irradiation induces an accelerated aging of the peliculle by adapting a procedure used for paper aging. The test materials were irradiated and non-irradiated, negative and positive sensitograms. No modification was registered at any applied temperature (50, 60, and 75 C).

Using EPR spectrometry and an equipment manufactured at IFIN-HH, Romania, it was proved that the peliculle do not have trapped free radicals.

The presented results legitimated the successful treatment of several tens of film peliculle rolls. The biological degradation was stopped and the time was gained in waiting for the final wet cleaning.

Fig. 28: Contaminated pelicule, Romanian Film Archive

Izvoarele Parish Church (Romania, 2002)

The church from Izvoarele – Prahova, Romania, was constructed in 1935. Internal decoration – wooden pieces, furniture and painted panels – was performed by people living in the village. Some of them used to have engagements with royal house. Especially for this reason the church was important for local community. The inventory consisted of 6 x 8 x 0.8 m "iconostasis" (great painted wooden wall separating the altar and narthex in Christian Orthodox churches), balcony, holly chairs and other cultic pieces. Most pieces were linden made.

Facing an active attack and an advanced biodegradation stage, the priest and local council decided for a conservation / restoration intervention. The identified enemy was the insect Anobius punctatum. An experienced biologist detected old fungi infestation since the wood was into the forest.

After unhappy and costly tests using conventional methods, the priest took into consideration irradiation disinfection. The *iconostasis* was dissembled and transported together with the rest of inventory to IRASM irradiation facility. The largest piece was 3.2 m long.

Irradiation: IRASM facility is a category IV gamma irradiator. Due to geometrical restrictions it was applied panoramic irradiation procedure. The wooden pieces were placed against the inner wall of irradiation chamber to not interfere with conveyer pass.

Dosimetry: Irradiation doses were chosen to be efficient for both insect and fungi. By changing piece position during irradiation overdose ratio was limited. Doses between 4.4 – 7.6 kGy were applied. The wooden pieces were placed in the irradiation chamber in positions with known 3-D dose mapping. Ethanol – chloro benzene dosimetry system (ECB) was used. The dosimeter is a sealed ampoule. The solution conductivity is measured by oscillometry. ECB ampoules do not loose information during reading. Irradiation may be stopped for accumulated dose checking and than restarted. IRASM ECB dosimetry system is traceable to High Dose Reference Lab RISO – Denmark. Up to 10 dosimeters were attached to the items to follow the accumulated minimum and maximum doses.

Intervention moment: insects have 4 living stages: egg – larva – pupa – fly. Anobius punctatum is dangerous for wood in larval stage. In this stage it is also radiation sensitive. Most insects have a flying season. After this moment the insect lays eggs. Being a resistance stage, eggs are more radiation resistant than larvae and pupae. In Romania Anobius punctatum flying season is in the month of May. The treatment was performed in December.

Conclusions: It was applied an emergency treatment for disinfestations of the entire wooden inventory of a parish church (**Fig. 29**). Approximately 10 m^3 of wood items of various shapes have been treated. The treatment lasted 4 days. There was no subjective evidence of some colour modifications on paintings. No supplementary tests on possible modifications of treated materials have been performed. After radiation disinfestations the pieces were reassembled, insect holes filled following a proper procedure and paintings restored. The treatment was efficient. After 9 years no sign of re-infestation appeared.

Fig.29: Wooden inventory from IZVOARELE Church

IFIN-HH, Bucharest, ROMANIA

Conservation by Irradiation

iRASM
Radiation Processing Center

Izvoarele Church, Prahova County

KHROMA – a frozen baby mammoth specimen irradiated for sanitary reasons and conservation (2010, France)

In autumn 2008, a frozen specimen of baby mammoth was discovered in the permafrost of Siberia, Sakha Republic, Russian Federation. It has been named Khroma, after the river on the edges of which it was found. It's revealed to be the oldest baby mammoth ever recovered (at least more than 50,000 years), but surprisingly, the best conserved according to the exceptional conditions of some fresh-like tissues it did preserve. The top of its body, however, was partially dried, as mummified, its back and belly were torn and its proboscis and its hump of fat were lacking, eaten by polar foxes.

Before to be studied by scientists, and to be presented to the public in a special refrigerated chamber during an exhibition in a French museum, it needed a sanitary treatment to inactivate the traces of bacteria or other potentially pathogenic organisms it could carry. Thanks to its power of penetration, gamma radiation quickly emerged as the only technique that agrees with a non-destructive biocide treatment of the entire volume of the specimen. As a matter of fact, it was possible to meet the double constraint, on the one hand of efficiency and reliability for sanitary handling and, on the other hand, of harmlessness with regards of this unique witness of biological heritage.

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. The "cold" treatment of the baby mammoth has been achieved in its frozen state, and through its packaging (plastic wrapping barrier plus insulating container with dry ice) in July 2010, at Grenoble, France. To reach this dose, the specimen was irradiated for 50 hours, being returned after half irradiation to homogenize the dose. The maximum dose, on its flanks, was no more than 40 kGy, consistent with the preservation of properties of organic materials, and in particular the protein structure of tissue of animal origin.

Beyond health care issues, this treatment significantly improves the conservation of the specimen. Indeed, the bactericidal action of radiation allows to inactivate the germs already present therein, limiting soft tissues natural decay mechanisms that trigger during thawing. It certainly helped scientists, ensuring good conditions during its thawing for the examinations "in the flesh" carried out in August 2010. And it shall also enhance its future taxidermy that will surely be undertaken as the ultimate conservation project after the scientific program of studies of fresh tissues has been completed.

Nevertheless, gamma irradiation causes lesions in the DNA. Although their number remains *a priori* low for the applied dose of 20 to 40 kGy, samples were collected, in the irradiation cell of ARC-Nucléart, just before treatment, in order to not compromise the quality of the analyses of such exclusive information. This will be the occasion to compare irradiated and non-irradiated samples in order to assess full-scale effect of irradiation on the ancient DNA (**Fig. 30 and Fig. 31**)

Fig. 30: Sampling on 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. Paleo-geneticists had to incise these envelopes to collect the samples.

Fig. 31: Khroma in its special refrigerated chamber, after the irradiation treatment, during the exhibition at the Musée Crozatier, Le Puy-en-Velay, France

5 Aide-memoire for curators-conservators

Irradiation means an injection with energy on the artefact. The intensity of the intervention is appreciated and measured by *irradiation dose* which is energy quantity transferred to the matter. All effects – disinfestation also side-effects are dose dependant.

Treatment dose of 10 kGy is a formal upper limit and a guiding dose for overall disinfestation of cultural heritage artefacts found in emergency situation. It takes into consideration fungi infestation – the great danger appearing in case of drastic modification of environmental preserving conditions, especially flooding or excessive humidity in deposits.

If only an insect active attack is present the recommended dose is 2 kGy which is efficient also for eggs – insect resistant form. The most important recommendation for curators is to place the artefacts after irradiation treatment in controlled or at least clean environment. Disinfestation is acting only in the moment of irradiation. Nothing is left in the artefact to protect it after treatment.

The problem of free radicals

During irradiation some energetic and unstable chemical species appear in the treated matter. They are called free radicals and usually have a very short live (10^{-3} second). They disappear in different ways. Some of them interact with the artefact matter being responsible for disinfestation and irradiation side-effects. An important number interacts each other.

Materials having crystalline structure may trap a few free radicals in electrostatic cages prolonging their presence in the matter. In this way free radicals may be present in the artefact long time after irradiation. When they are released from the traps they disappear following of course the described mechanisms.

As conclusion trapped free radicals may induce irradiation post-effects. It is true. But structure-modifications that may appear in time are not and may not be significant because as it was noticed all effects are dose-dependant.

Brief comments on particular materials

Wood

Irradiation with efficient doses for insects and fungi eradication (up to 10 kGy) improves mechanical properties due to the cellulose cross-linking. Over this dose mechanical properties slightly decrease. That's why there is no danger 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 at the recommended treatment dose.

Paper

Development of fungi and micro-organisms in archives brings serious healthy problems for people that use or take care of them. Books dimensions permit their treatment by conveyor irradiation. This is the best treatment procedure permitting a small and controlled overdose radio. Irradiation disinfestation is a good solution for the treatment of books or administrative archives at recommended doses.
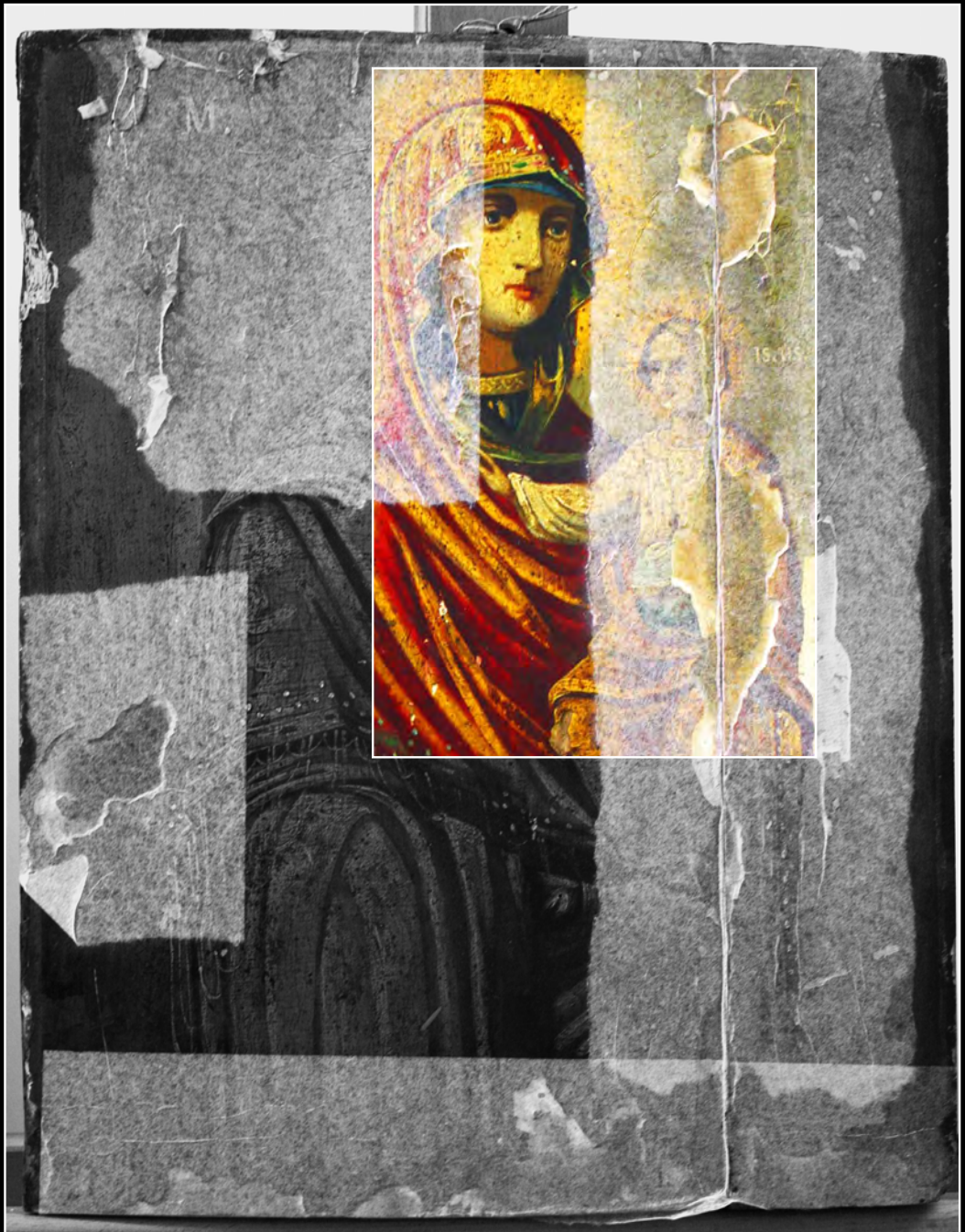
Leather

Ethnographical artefacts also leather bookbinding may be treated without hesitation at recommended doses.

In the **Table 6** there is a summary of different materials to be treated by radiation.

Table 6: Radiation disinfestation of the main CH materials

Material	Insecticide treatment (from 0.5 to 2 kGy)	Fungicide treatment (up to 20 kGy)	Remarks
Wood	yes	yes	
Binder, varnish, gum, resin,	yes	yes	Arabic gum in strong thickness (> 100 μm) may slightly perceptibly darken at doses higher than 20 kGy.
Pigments	yes	yes	Pb oxide based pigments may present some slightly perceptible yellowing at doses higher than 20 kGy.
Mummies	yes	yes	Even if made of sensible material, mummy's disinfestation using irradiation must be undertaken if fungi and bacterial contamination are degrading the mummy.
Leather, skin, parchment, fur, hair, feathers	yes	yes	Anoxia is a relevant alternative for insecticide treatment if the artefact can be isolated and considered as a two dimensional item (small thickness).
Textile, fiber	yes	yes	Anoxia is a relevant alternative for insecticide treatment if the artefact can be isolated and considered as a two dimensional item (small thickness). Particular care must be taken to avoid fungicide overdose in order to not depolymerise cellulosic based fibers. Dye behaviour has not been widely studied and may cause problems at fungicide doses.
Paper	yes	yes, but …	Anoxia is a relevant alternative for insecticide treatment if the artefact can be isolated and considered as a two dimensional item (small thickness), as for instance a graphic document as a simple sheet. Particular care must be taken to avoid fungicide overdose in order to not depolymerise cellulose. France cultural authority does not recommend irradiation of paper as a common one.
Grey mother-of-pearl, tine	yes	yes	
Amber	yes	NO	
"White" nacre, ivory, horn, bon, flake, marble, porcelain, enamel	to be avoided	NO	For white or very clear such material, a slight variation in colour, whether or not perceptible, is feared even for insecticide doses. The irradiation may be only considered if it is justified for example by an active contamination and / or the difficulty to undertake a technique of anoxia. For furniture, the practice is to take apart the marble before irradiation.
Glass	NO	NO	
Crystals (transparent gems)	NO	NO	
Mica, opaque gems (lapis lazuli, turquoise, jasper, jade…)	yes	yes	

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