ARC-Nucléart: a workshop for conservation of cultural heritage using gamma irradiation.

Khôi TRAN, PhD
41 Years of Irradiation of Cultural Heritage Artefacts

Mummy of the ancient Painting Museum of Grenoble
• First application of consolidation of cultural heritage item, 1970
• First applications on archeological waterlogged wood

Medieval saddle cradle - Paladru
• The most resounding action that launches definitively the laboratory Nucléart, 1977
Ramses II mummy disinfection
**A workshop and a laboratory**

• A workshop that functions like a small company offering services of conservation and/or restoration for museums, communities or private.

• A laboratory, trying to improve the methods of conservation and proposing new ones for treatment of cultural heritage, but also, if appropriate, for application in more or less industrial field.

• A more and more diverse activity, including removal of large wooden objects from archaeological sites, treatment in all its forms, restoring and museum display.
A very interesting radiation

Cerenkov effect
The $\gamma$-rays nature

Electromagnetic waves ↔ Photonic particles

Radio wave
$10^{-10} - 10^{-6}$ eV

Micro-wave
HF
$10^{-4} - 10^{-5}$ eV

Infra-red
$0.1 - 1.6$ eV

Visible Light
$1.6 - 3$ eV

Ultra-violet
$3$ eV – $100$ eV

X-Ray
$1$ keV - $100$ keV

$\gamma$-Ray
$100$ keV – $2$ MeV

High energy

Croatian National Workshop, Zagreb 4-5 October 2011
The γ-rays nature

An electromagnetic radiation produced by the interaction of nuclear particles in the atomic nucleus
A penetrating radiation

• 2 $\gamma$ photons of the $^{60}$Co
  
  \[ 1.17 \text{ MeV and } 1.33 \text{ MeV}. \]

• Typical penetration (thickness 1/2):
  – 100 m air
  – 11 cm of water
  – 5 cm of concrete, or aluminum
  – 1 cm of lead.

A high penetrating power, it's meaning a radiation that interacts little.
A radiation involving **No radio-activation** in the material.
A biologically active radiation

• The direct and indirect ionization of DNA may lead, according to their number, the non-renewal of cells, which itself can lead to the death of the living organism.

• A biocide effect studied a lot ... and very well known.

• Ididas (International Database on Insect Disinfestation and Sterilization)

www-ididas.iaea.org
Ionization of biological tissues:

*Creation of free radicals*

*Radiolysis of $H_2O$*

*Direct lesions on acid-base pairs on DNA*
A reference method in the food industry and more in the cosmetics industry and the medical field:

- efficiency,
- reliability,
- very good safety,
- no harmful residues,
- processing through packaging.
A 1500 to 3000 TBq 60Co pool Irradiator
(max 100 000 curies)
Co sources

- 20 to 52 standard sealed sources for industrial irradiator
- Double encapsulated in stainless steel 316 L

- No contamination risk
• To get an homogeneous radiation field
Disinfestations and consolidation

- Using the radiobiological effects of $\gamma$-rays to disinfest (fungi and insect)
- Using the radiochemical effects of $\gamma$-rays to consolidate dry porous material or waterlogged organic material
• A matter of dosage:
  - 0.5 kGy for insects,
  - 10 kGy for fungal species,

(- Lethal dose without treatment is 4 Gy (0.004 kGy) for humans).
Irradiation dose for fungi, mould eradication

- Pavon-Flores 1974, 9 kGy => 18 kGy (Stemphylium consortiale)
- Food industrial irradiation ≤ 10 kGy (World Health Org.)
- WHO (1999)

**Comparison of D10-values of mould spores in aqueous suspensions, irradiated at ambient temperature**

<table>
<thead>
<tr>
<th>Mould</th>
<th>Gamma-irradiated (kGy)</th>
<th>Electron-irradiated (kGy)</th>
<th>Values not significantly different (P&lt;0.005, Student t-test)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Aspergillus echinulatus</em></td>
<td>0.319</td>
<td>0.241</td>
<td></td>
</tr>
<tr>
<td><em>A. fumigatus</em></td>
<td>0.276</td>
<td>0.198</td>
<td></td>
</tr>
<tr>
<td><em>A. glaucus</em></td>
<td>0.250</td>
<td>0.243</td>
<td>x</td>
</tr>
<tr>
<td><em>A. niger</em></td>
<td>0.245</td>
<td>0.199</td>
<td></td>
</tr>
<tr>
<td><em>A. ochraceus</em></td>
<td>0.209</td>
<td>0.198</td>
<td>x</td>
</tr>
<tr>
<td><em>A. versicolor</em></td>
<td>0.282</td>
<td>0.234</td>
<td>x</td>
</tr>
<tr>
<td><em>Penicillium aurantiogriseum</em></td>
<td>0.236</td>
<td>0.194</td>
<td>x</td>
</tr>
<tr>
<td><em>P. cyclopium</em></td>
<td>0.397</td>
<td>0.290</td>
<td></td>
</tr>
<tr>
<td><em>P. granulatum</em></td>
<td>0.239</td>
<td>0.201</td>
<td></td>
</tr>
<tr>
<td><em>P. roqueforti</em></td>
<td>0.416</td>
<td>0.341</td>
<td></td>
</tr>
<tr>
<td><em>P. verrucosum</em></td>
<td>0.266</td>
<td>0.208</td>
<td></td>
</tr>
<tr>
<td><em>P. viridicatum</em></td>
<td>0.333</td>
<td>0.265</td>
<td>x</td>
</tr>
<tr>
<td><em>Curvularia geniculata</em></td>
<td>1.798</td>
<td>1.193</td>
<td></td>
</tr>
<tr>
<td><em>Alternaria alternata</em></td>
<td>2.409</td>
<td>1.099</td>
<td></td>
</tr>
</tbody>
</table>
Irradiation dose for bacteria, virus eradication

Irradiation and food safety (Food Technology, 58, n°1 1)

Table 1—$D_{10}$ values for specific pathogens on meat and egg products. Adapted from Molins (2001).

<table>
<thead>
<tr>
<th>Target organism</th>
<th>Temperature (°C)</th>
<th>Product</th>
<th>$D_{10}$ value (kGy)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Staphylococcus aureus</em></td>
<td>5</td>
<td>Turkey breast meat</td>
<td>0.45</td>
<td>Thayer et al. (1996)</td>
</tr>
<tr>
<td><em>Campylobacter jejuni</em></td>
<td>30</td>
<td>Ground turkey</td>
<td>0.16</td>
<td>Lambert and Maxcy (1984)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>−30</td>
<td></td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td><em>Salmonella Heidelberg</em></td>
<td>0</td>
<td>Poultry (air packed)</td>
<td>0.24</td>
<td>Licciardello et al. (1970)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>Poultry (vacuum packed)</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td><em>Salmonella Enteritidis</em></td>
<td>5</td>
<td>Egg powder</td>
<td>0.6</td>
<td>Matic et al. (1990)</td>
</tr>
<tr>
<td><em>Salmonella spp.</em></td>
<td>3</td>
<td>Ground beef</td>
<td>0.55–0.78</td>
<td>Tarkowski et al. (1984)</td>
</tr>
<tr>
<td><em>Listeria monocytogenes</em></td>
<td>5</td>
<td>Turkey breast meat</td>
<td>0.71</td>
<td>Thayer et al. (1995)</td>
</tr>
<tr>
<td><em>Escherichia coli</em> O157:H7</td>
<td>5</td>
<td>Beef</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Ground beef patties</td>
<td>0.27–0.38</td>
<td>Lopez-Gonzales et al. (1999)</td>
</tr>
</tbody>
</table>

• The most popular application of γ-rays
• Many thousands of cubic meter of wooden objects “desinsectized” since the 70’s (about 100 to 200 m³ a year):
  • Furniture
  • Statues
  • Ethnologic object
  • ...

A modern wood sculpture of Zadkine: “Fauve”
A typical recent insecticide treatment

- Complete collection disinfection (~ 140 m$^3$, mainly wooden objects, transport rotation of 15 to 20 m$^3$ every three weeks)

- As it is only a **curative** method, important care must be taken to avoid re-infestation

*Maison du patrimoine de Villard-de-Lans (local ethnologic museum)*
• A practice limited:
  • because some material cannot be (or better be avoid) irradiated (glass and other transparent materials, white ceramic, marble, mother of pearl ...),
  • because it is not always well accepted (a “nuclear” technique)
• A solution very suitable for volume processing:
  • the penetrating power of gamma radiation gives a excellent efficiency and a excellent reliability, even processing on large volumes,
  • a very good level of harmlessness on a large range of material,
  • no danger at all after treatment.
Fungicide treatments

• A very efficient method
• As chemical treatments tends to be prohibited in Europe, the only competitive method to stop fungi is drying
• Must be done when drying can not be undertaken … or is not sufficient
• Few but sometimes very relevant examples

Virgin and the Son
XVIIIth century
stolen and abandoned
in a canal
for several month.
Baby mammoth Kroma in the irradiation Chamber (July 2010)

Minimum dose : 20 kGy after 50 hours of irradiation
**Doses ARC-Nucléart**

- 10 kGy: Désinfection (dose fongicide)
- 500 Gy: Désinsectisation

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Other facilities for gamma irradiation of cultural heritage artefacts
A conservation radiation laboratory was founded at the Museum of Central Bohemia in 1981. The conservation irradiation laboratory accepts objects made of all kinds of organic materials for treatment: wood, leather, textiles, paper, etc. For more detailed information contact ozarovna@muzeum-roztoky.cz.
Other gamma irradiation facilities worldwide

- IRASM – Bucharest (Romania)
- MITR – Lodz (Poland)
- ENEA – Casaccia (Italy)
- Ruder Boskovic Institute – Zagreb (Croatia)
- KAERI ARTI – Jeongeup (Korea)
- CNSTN – Tunis (Tunisia)
- IPEN- Sao Paulo (Brazil)

- Peru, Chili, Mexico, Morocco, Turkey, Argentina, Malaysia, UK, …
• More than 100 industrial facilities worldwide.
• Application for disinfection of archives or furniture in France, Germany, USA … and surely in numerous other countries.
Disinfection of **Archive materials** and **Art objects** by
Gamma Service GmbH
Radeberg(Dresden), Germany

Archive materials as well as art and sacred objects, which are infested with micro-organisms (e.g. mould) and/or pests (e.g. woodworm), can be saved from further destruction by treatment with ionizing radiation and used again after a possible restoration. Dose range: **10-12 kGy**, at dose rate **5-7.5 kGy/h**

The applied energy dose is carefully determined after a professional examination of the degree of infection (e.g. by germ count) and by considering experience and the results of preliminary test irradiations on samples, in order to minimize possible adverse effects caused by the irradiation process.

Address:
http://www.casaccia.enea.it/

Research on insect species *Periplaneta americana* and micro-fungi species *Penicillium*
For insects: dose 0.2 – 0.5 kGy
For fungi: 3-8 kGy: no significant harmful effect on mechanical and physical properties of pure cellulose. But significant de-polymeriation of cellulose already at 5 kGy dose!
Question: Neglectable effect or not?
Testing of 3 cellulose/paper types contaminated by mould.
Irradiation at 8 kGy
No significant differences were found based on Near Infra-Red and Chemometric analysis

At dose \( \leq 10 \) kGy
No significant change

At dose \( > 10 \) kGy
Decrease strength

Future research:
Compare radiation treatment at 8 kGy with:
- Doing nothing
- Conventional methods

TNO Netherlands
Built Environment & Geosciences
Study on disinfection of cellulosic materials by gamma irradiation
John Havermans, Built Environment & Geosciences
The first irradiation dose of 6 kGy was not sufficient to eradicate the fungi. The second irradiation (6 years later) with 9 kGy did not affect the polychromy of the painting.

Hard contamination of mould growing on 70% of its area. Species *Aspergillus* and *Penicillium*

The painting was put in an hermetic acrylic box for irradiation.
ININ-Mexico 2006
Conservation of a Maya sculpture
Dry porous “Nucléart” consolidation

- Gamma irradiation process for dry wood (or other porous material) consolidation by impregnation with radiation-curing resin
- Vacuum pressure impregnation of unsaturated polyester-styrene resin
- Crosslinking-controlled thanks to irradiation
Dry porous “Nucléart” consolidation

- Historically, the first application for cultural heritage at Grenoble
- A very efficient but irreversible method

Must be justified:
- The last chance for very degraded artifacts (polychromed sculpture)
- When the function of the artifact have to be preserved.
Effects of γ-rays and new improvements for consolidation techniques
The research activity around the irradiator

• Research about effects of gamma ray at disinfestations doses
  – Paper and leather behavior by Ramiere (in collaboration with the Center for Research on the Conservation of Graphic Documents - 90s)
  – Color behavior of decorative and ornamental material
  – Varnishes, pigments and binders color behavior
  – Textile mechanical behavior
  – …
  – Ancient DNA information ??
• Research for use of new resin for polymerization or crosslinking under irradiation
Pigments

- No noteworthy change even after 200 kGy

- Only silver white presents $\Delta E_{2000}$ significantly higher than 2
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Textile

Dose (Gy)

Fibers from animal origin

Fibers from vegetal origin

Traction rupture loads

Fibers from animal origin

Fibers from vegetal origin

Relative behavior

Cotton

Laine

Lin

Soie
Wood

Evolution relative (rapport à la valeur originale pour l'échantillon non irradié)

- Module d'élasticité du tremble (Populus Tremuloides)
- Degré de cristallinité de la cellulose dans le pin (Picea Abies)
- Compressibilité perpendiculaire au fibres pour du hêtre (Fagus Orientalis)
- Compressibilité perpendiculaire au fibres de bois pour du sapin (Picea Orientalis)
- Resistance à la flexion du pin (Picea Abies)

Dose (Gy)
Glass, quartz, silica

**Graph:**
- **X-axis:** Dose (kGy)
- **Y-axis:** $\Delta E_{\text{2000}}$

- **Points and Labels:**
  - Natural Quartz
  - Glass (Microscope Blade)
  - Glass (Microscope Blade x 3)
  - Pure SiO2

**Legend:**
- ▲ Natural Quartz
- □ Glass (Microscope Blade)
- ○ Glass (Microscope Blade x 3)
- ○ Pure SiO2

**Axis Ranges:**
- X-axis: 0 kGy to 200 kGy
- Y-axis: 0 to 50

**Additional Information:**
- Croatian National Workshop, Zagreb 4-5 October 2011
- Slide N°47
• A matter of dose:

<table>
<thead>
<tr>
<th>Material</th>
<th>Desinsectisation (500 Gy)</th>
<th>Fungus Disinfection (10 kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood, wicker</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Resin and binder</td>
<td>Yes</td>
<td>Yes ... but</td>
</tr>
<tr>
<td>Pigments</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Mummy</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Leather</td>
<td>Yes</td>
<td>To be justified</td>
</tr>
<tr>
<td>Fur, plucks, hair</td>
<td>Yes</td>
<td>Yes / To be justified</td>
</tr>
<tr>
<td>Textile, rope</td>
<td>Yes</td>
<td>To be justified</td>
</tr>
<tr>
<td>Paper</td>
<td>Yes</td>
<td>??</td>
</tr>
<tr>
<td>Gray Mother-of-Pearl, Tine</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Amber</td>
<td>yes</td>
<td>No</td>
</tr>
<tr>
<td>“White” mother-of-pearl, Ivory, Horn, Bone, Scale</td>
<td>To be justified</td>
<td>To be avoid</td>
</tr>
<tr>
<td>Marble, Porcelain</td>
<td>To be avoid, if possible</td>
<td>To be avoid</td>
</tr>
<tr>
<td>Glass</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Transparent gems</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Mica, opaque gems (lapis lazuli, turquoise, jasper, jade ...)</td>
<td>Yes</td>
<td>Yes, if necessary</td>
</tr>
</tbody>
</table>
Research to improve the « Nucléart » technique

- Attempts to limit the quantities of resin for dry wood simple object

- Attempts to introduce plastic additive to make the cured resin less brittle.

- Tests of elastomers resins in order to consolidate leather or other soft materials (acrylic resin).

- Research of new water-soluble polymer that may be cured by irradiation, to used them for archaeological waterlogged artifact (crosslinked hydrogel HEMA like contact lenses …)

- Development of a mixed treatment for waterlogged wood: freeze-drying of the object slightly impregnated with PEG followed by vacuum pressure impregnation of styrene polyester resin and crosslinking under irradiation (dry wood "Nucléart").
Using Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the Mediterranean Region

The Irradiation Group:
Romania, Croatia, Poland, France
Our Objectives in the IAEA Technical Project:

Effects of irradiation on various materials of Cultural Heritage, both for disinfection/insect eradication and consolidation

- Edition of a guide-book on conservation of cultural heritage by radiation techniques: on-going work

- Transfer of treatment protocols to other participant country through cooperation or scientific visits:
  
  *my mission this week in Croatia!*
Hvala vam na pozornosti!