European Journal of Science and Theology, June 2008, Vol.4, No.2, 51-59

THE INDUSTRIAL POLLUTION IMPACT ON RELIGIOUS HERITAGE IN ROMANIA

Nicoleta Melniciuc Puică* **and Elena Ardelean**

University 'Al. I. Cuza', Faculty of Theology, Department of Conservation-Restoration
9 Closca, 700065 Iaşi, Romania

(Received 17 April 2008)

Abstract

This paper is dealing with the old religious heritage resistance to chemical degradation due to the growth of industrial activities in Romania of the 20th century. Air pollutants have a negative influence upon the physical and chemical properties of organic constitutive materials of old books and icons. Influence of one of the most noxious factors -sulphur dioxide- was studied and elements concerning the monitoring of the damages induced by sulphur dioxide are presented.

Keywords: religious heritage, chemical degradation, pollution, sulphur gases, prevention strategies

1. Introduction

Until the beginning of the XIXth century pollution became one of the main causes of the cultural heritage deterioration, due to the degrading action of the air pollutants generated by the industrial activity. Their presence in outdoor atmosphere, museums, libraries, archives, etc. is a permanent threatening to the cultural heritage items, due to complex chemical processes, mainly oxidation reactions, which irreversibly affect the constituent materials structure.

The sensitivity of art works to environmental pollutants effects depends both on the nature of the work's constituent materials and the climatic factors, mainly air temperature and relative humidity.

Materials from which cultural heritage objects are made can be classified as it follows:

- organic materials:
  - of animal origin (leather, ivory, silk, wool, parchment, certain pigments),
  - of vegetal origin (paper, cotton, wood, certain pigments),
- inorganic materials: metals, ceramic materials, glass, stone.

It is known that the damaging action of pollutants is significantly enhanced in environments having the air relative humidity higher than 60 %.

* e-mail: bradeail@yahoo.com

The main air pollutants that affect the constituent materials of the heritage objects are [1 – 5]:

- Smoke resulted from fuels incomplete combustion. Due to its carbonaceous nature, smoke itself is inert but when surrounded by oil or tar-based substances, the carbon particles become sticky and adhere to surfaces; the resulting filth can be removed only by mechanical or chemical mains, which can easily damage the treated support.
- Dust also makes surfaces to become dirty. Initially, a thin dust layer is formed, which grows and is finally included in the host material; it can be removed by mechanical or chemical action which can damage the support. Dust adherence is favoured by rugged or porous surfaces and by oil, waxes or varnish coverings. Metal powders carried by water determine anaesthetic abrasions and can even act as catalysts for unwanted chemical reactions. Organic fine particles (pollen, microorganisms, moulds) can initiate the biotic attack in high relative humidity atmosphere.
- Petrol engine exhaust particulates. Petrol engines using leaded fuels release toxic lead oxide particles.
- Mineral dusts, originating from quarrying or industrial activities, consist of lime, sand or cement. Generally, they do not cause chemical damages, but physical damages. Acidic sulphates bearing these fine dusts arise from coal combustion in electrical plants and cause chemical damages.
- Salts (NaCl, $MgCl_2$), can favour metal corrosion and lead to porous materials disintegration through repeated solubilisation – crystallization cycles.
- Vapours and gases found in the polluted urban atmosphere, such as: oxygen (O_2), water (H_2O), sulphur dioxide (SO_2), oxides of nitrogen (NO_x), ozone (O_3), hydrogen sulphide (H_2S), ammonia (NH_3).
- Oxygen along with ozone, hydrogen peroxide, azotic acid, oxygen is one of the strongest oxidizing agents. For example, oxidizing agents break down the cellulose macromolecular chains and damage the paper-made artefacts.
- Sulphur dioxide (SO_2) is a water soluble acidic gas, originating from the combustion of different fuels. In the presence of water vapours, it slowly turns to sulphuric acid, a strong acid that causes significant damages to archive materials.
- Hydrogen sulphide (H_2S) has the properties of a weak acid and is very active towards silver and lead compounds, which are converted in metal sulphides with black colour.
- Nitrogen oxides, NO_x arise when air is heated at high temperature or from combustion in petrol engines and in furnaces using coal, wood, gas or fuel oil. Nitrogen oxides are water soluble and form nitric and nitrous acids. Nitric acid is a very strong acid and acts as a powerful oxidizing agent towards many archival materials.
- Ozone arises during electrical sparks and discharges and from UV light sources. Ozone undergoes slow breakdown in normal air conditions, but it acts as a strong oxidizing agent and attacks various organic materials, such as polymers, inks, pigments.

- Ammonia evolves from decaying organic materials; it is easily dissolved in water and results in alkaline solutions. It reacts with other gases to form salts that deposit on surfaces and change the local acidity.

2. Pollution effects on the works of art constituent materials

Literature reports many degradation cases of the heritage objects constituent materials (paper, leather, textiles, pigments, metals, etc.) by the air pollutants.

Museums, libraries and archives preserve a great number of priceless books, bearing a high artistic and theological value, many of which are affected by internal and external polluting agents. The visible effect of pollutants action is the ageing of paper, accompanied by the brightness reversion. Such changes are obvious on a Pidalion from 1844 (Figure 1).

Figure 1. Aged paper in a Pidalion from 1844, Popăuți Monastery, Botoşani.

2.1. The influence of sulphuric acid and sulphur dioxide upon the bookbinding leather

Veitch, Frey and Leinbach have studied the deterioration of certain bookbinding leathers exposed to polluting gases [6]. Bookbinding leather exposed to air and light exhibited a great content of sulphuric acid originating from the polluting atmosphere. Degradation induced by the absorption of airborne SO_2 is commonly known as the 'red rot', which mainly affects the vegetable bookbinding leathers.

Sulphur dioxide is oxidized by vegetable tannins (pyrocatechine tannins are stronger oxidizer than pyrogallol ones) to sulphur trioxide, which reacts with the air humidity and forms the sulphuric acid, an aggressive leather ageing agent.

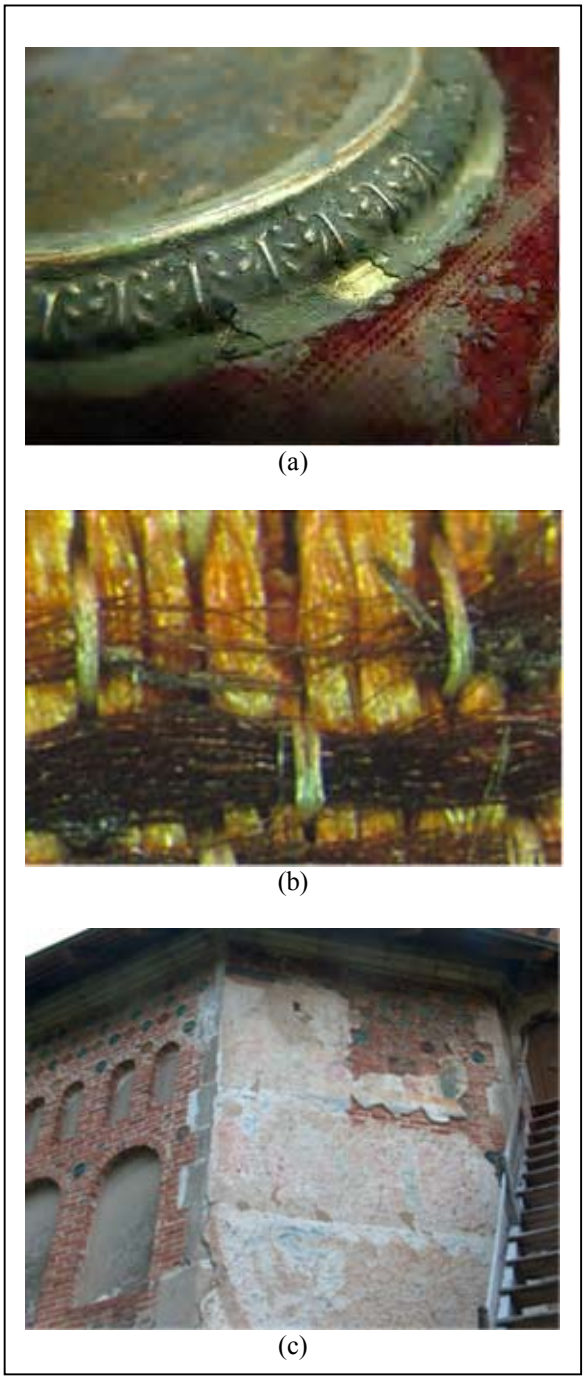
Sulphuric acid breaks down the polypeptide chains to amino acids and ammonium salts – mainly ammonium sulphate, which deposits in leather as a white powder. Under the sulphuric acid action, leather becomes brittle and disintegrates after repeated book openings. Iron salts entered in leather from the contact with metal objects or from the polluted environment oxidize the sulphur dioxide and lead to leather staining. Iron compounds traces in bookbinding act as catalysts to the conversion of SO_2 to SO_3, which results in H_2SO_4 as well.

The initial stages of the 'red rot' development consist of superficial cracks and a pink coloration, which darkens as the attack progresses. Over time, the cracks extend, the materials looses its integrity and may even turn into a reddish – brown powder [7], in the final degradation stages (Figure 2).

Figure 2. Red rot, bookbinding, XIXth century.

Unfortunately, damages produced by the 'red rot' in leather are irreversible and no effective conservation-restoration methods are known by now [8]. The red rot prevention can be achieved by adequate microclimate parameters in the storage places and by preventive conservation policy, properly put into practice.

Silver objects in contact with airborne sulphur gases blacken, due to the silver sulphide formation (Figure 3a) [9]. Natural polymers from old textiles are also affected by the polluting agents, mainly through depolymerisation and reticulation [10] which contribute to the ageing process; silk is the most sensitive to such unwanted processes (Figure 3b). Mural paintings, mainly the outdoor ones, have suffered significant degradation beginning with the industrial age. One example is the fading of the painted decoration from the Bălineşti – Botoşani church (Figure 3c).



(a)

(b)

(c)

Figure 3. (a) silver objects attacked by the hydrogen sulphide; (b) fragment of an aged silk material, ecclesial textiles, XIXth century; (c) degradation exterior paintings.

2.2. The effects of sulphur gases pollution at 'D. Stăniloae' Library from Iaşi

'D. Stăniloae' Library from The Metropolitanate of Moldavia and Bukovina hosts valuable old books collections, preserved in optimum microclimate conditions. Nevertheless, specialty literature reports certain effects of the air pollutants upon the preserved books.

The 'red rot' damages mainly the exposed parts of the books stored on shelf, *i.e.* the corners and upper edges, which can easily adsorb the sulphur dioxide that reacts with the air humidity to produce sulphuric acid, as described above (Figure 4).

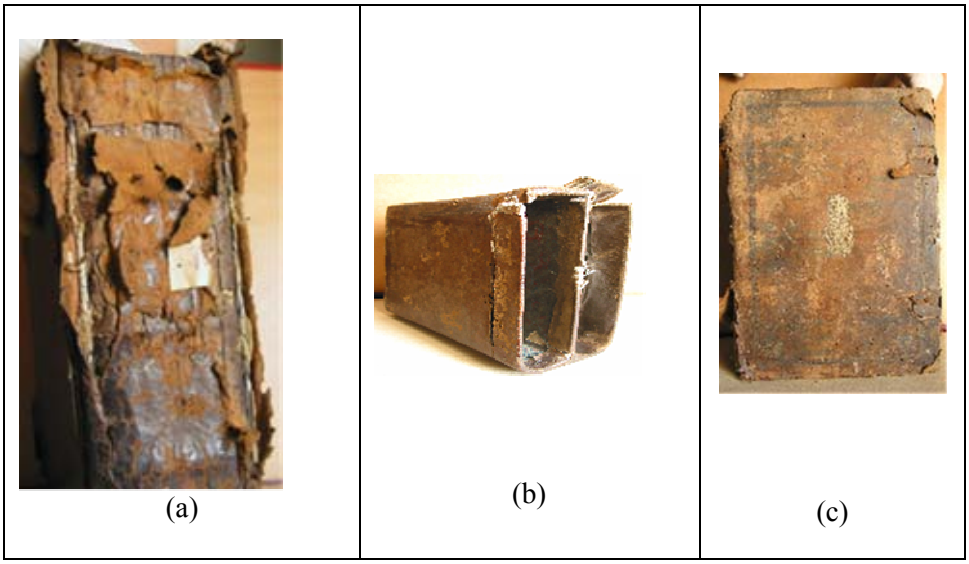


Figure 4. Old bookbinding with red rot degradation: a) Octoih, 1774; b) Box XIXth century; c) Pravila 1834.

3. Strategies for the minimisation of the pollution effects upon the cultural heritage

Specific strategies for the reduction of the pollution impact upon the cultural heritage are applied worldwide. Further on, we'll present the strategies for old books and documents, some of which being identical to those used for the constituent materials of other kinds of patrimony objects [11, 12].

Taking in account the specificity of each archive, the UNESCO programmes have established long term anti-pollution strategies for the documentary heritage, which can be classified as it follows:

- the reduction or elimination of the pollution sources;
- the prevention against the entry of pollutants into the archives and exhibition spaces;

- the removal or deactivation of pollutants within the archives and exhibition spaces;
- the protection of records by air-conditioned small enclosures;
- the promulgation of measures for the outdoor air pollution abatement, which takes long time and high costs.

Amongst the actions for the abatement of the outdoor air pollutants, the most important are:

- use of fuels (coal, oil) with low sulphur content;
- washing of combustion exhaust gases for the solid particulates removal, followed by release at high altitudes;
- use of leadless oil;
- the replacement of actual fuels with alcohol or liquefied gases;
- banning of wastes and wood incineration ;

Depending on the nearest pollution source, changes of the direction, place and air admission, schedule can be made; for example, air ventilation can be stopped during the maximum pollution periods. All the activities generating pollution (such as building maintenance/restoration sites) and wastes disposal must be taken in account. All the inflammable materials, such as cellulose nitrate films, negatives or colloidal prints etc., must be stored away from museums, archives, libraries.

The prevention against the entry of pollutants into the archives and exhibition spaces implies a good knowledge of the ventilation systems construction and control, identification of the main pollutants, a proper storage of the brittled documents etc. No matter the type of the ventilation system, the polluting agents must be removed: the capital costs for an air purification system is lower than those required by a full air-conditioning system. Forced air ventilation systems are more expensive if HEPA filters are included (HEPA - high efficiency particulate air filter).

Air scrubbing with alkaline solutions is an effective method for the acidity removal, but has a great disadvantage: it increases the air relative humidity and can be used only when the climate is naturally very dry, or along with a dehumidification system, which significantly increases the capital and operation costs.

The extent to which dusts can actually be removed requires careful consideration, especially where dusts are raised by activities within an archive, such as different movements and cleaning operations. Conservators can not entirely remove dust from the old documents, because ultra fine particulates, such as acid sulphates, have a great penetration power and can not be removed by filtration. These particulates soil the documents and embed abrasive hygroscopic materials within the support. Coarse filterable particles arise from smoke, ash, dust, fungi, leather and fibbers fragments, and from marine salts as well.

The organic materials provide a source of food for micro-organisms. Activated carbon filters are very effective for the removal of pollutant vapours and gases. Nitrogen oxides seem to be more difficult to remove than sulphur dioxide. The rapid variations of the pollutants concentration make the research of the polluting action of acid gases very difficult.

Deactivation is the ultimate defence against the pollutants negative effects. It is known that the buildings constituent materials play an important role in the pollutants deactivation: buildings themselves reduce the sulphur dioxide concentration by about one half; it is absorbed by the stone, cement, concrete, woodwork and furnishings. Ozone concentration is reduced in the same way – due to its instability and it gradually turns into oxygen.

Consequently, measures for the increase of the building absorption capacity must be considered, along with the assessment of the materials with polluting gases release capacity. It is important that alkaline building materials (such as cement and lime plasters) are used, due to their absorption capacity towards the acid pollutants, but one must have in mind that such materials can generate noxious dusts.

Cellulose retains the sulphuric acid as well and therefore the use of renewable, fire proofed (if needed) wallpapers are recommended. Impregnation with sodium borate (borax) is of assistance.

Prevention of fine dusts spreading by surface sealing may create more pollution when paints and varnishes are over dehydrated.

Protection of documentary heritage by small enclosures and air-conditioning systems; exhibition showcases, cupboards, shelves, boxes and boards provide some degree of protection against pollutants of all kinds. Conservators and archivists should carefully consider each enclosure, as it concerns the records exhibition, storage, transportation and handling damages, general security precaution and the hazards associated with fire and floods.

Conclusions

Air pollutants, i.e. sulphur gases, have a negative influence upon the physical and chemical properties of organic constitutive materials of old books and icons. The effects are visible to old book, old icon, silver object, mural painting, etc.

Old book collections of 'D. Stăniloae' Library from The Metropolitanate of Moldavia and Bukovina are preserving in optimum microclimate conditions but the effects of pollution, like red rot, are also presented. Here we implemented the UNESCO programmes long term anti-pollution strategies for the documentary heritage.

References

[1] A. Moldoveanu, *Conservarea preventivă a bunurilor culturale,* Editura Ministerului Culturii, Bucureşti, 1999, 129.
[2] G. Thomson, *The museum environment*, London IIC Butterworths, London, 1986, 268.
[3] H.J. Plenderleith, *The conservation of Antiquities and Works of Art*, Oxford University Press, London, 1971, 160.
[4] P.M. Whitmore, G.R. Cass and J.R. Druzik, Journal of the American Institute for Conservation, **26(1)** (1987) 45.
[5] R.G. Derwent and H.N.M. Stewart, Atmos. Environ., **7** (1973) 385.
[6] V. Dirksen, Journal of Conservation and Museum Studies, **3** (1997), available at http://www.jcms.ucl.ac.uk/issue3/dirksen.html.
[7] J.W. Waterer, *A Guide to Conservation and Restoration of Objects Made Wholly of Part in Leather,* Drake Publishers Inc, New York, 1971, 107.
[8] M. Graham-Bell, *Leather*, in *Preventive Conservation: A Manual.* 2nd Edition, M. Graham-Bell (ed.), British Columbia Museums Association, British Columbia, 1986, 28.
[9] N. Melniciuc-Puică European Journal of Science and Theology, **1(1)** (2005) 77.
[10] N.S. Baer and P.N. Banks, Int. J. Museum Management & Curatorship, **4** (1985) 9.
[11] J. Tétreault, Bulletin de ICC, **31** (2003), available at http://www.cci-icc.gc.ca/publications/newsletters/news31/pollutants_f.aspx.
[12] W.W. Nazaroff, M.P. Ligocki, L.G. Salmon, G.R. Cass, T. Fall, M.C. Jones and I.H. Liu, *Airborne particles in museums,* The Getty Conservation Institute, New York, 1993, 121.