Research and Investigation of Historic Materials in Latvia

L.Krage

Faculty of Materials Science and Applied Chemistry, Riga Technical University, Azenes Str. 14/24, Riga LV-1048, Latvia, E-mail: linda@ktf.rtu.lv

1. Introduction: Legislation system of cultural heritage in Latvia

System of legislation and normative acts on cultural heritage in Latvia is founded by the Law on the protection of cultural monuments adopted by Saeima in 1992, Regulations On Enumeration, Protection, Use and Restoration of Cultural Monuments adopted by the Council of Ministers, Statute of State Inspection for Heritage Protection adopted by the Cabinet of Ministers in 1996 and 37 other legal instruments concerning preservation of cultural heritage.

The Cabinet of Ministers insures state administration on protection and use of cultural heritage and it is implemented by the State Inspection for Heritage protection which is subordinated by the Ministry of Culture. Administrative acts – directions – on use and preservation of every single cultural monument – issued by the Inspection are binding to every owner and landlord of the cultural monument. State Inspection for heritage Protection appoints an inspector for heritage protection directly subjected to the Inspection in every region and city of republic (in total 33 administrative units). Municipalities have been called to found local services for cultural heritage.

The main tasks and rights of the Inspection:

1. To implement state control on protection of cultural monuments.
2. To carry out state enumeration of cultural monument, to register and to research cultural monuments.
3. To examine documentation on works connected with cultural monuments.
4. To issue directions for owners of cultural monuments on the use and preservation of the corresponding cultural monument.
5. To issue licences of a definite pattern for works on conservation, restoration, repair and reconstruction of cultural monuments.
6. To carry out examination of objects of art and antiquity, to issue licences to export them abroad.
7. To finance works on research, preservation and restoration of cultural monuments from specially allocated resources.
8. To suspend economic activity if regulation on protection of cultural monuments have been violated and the cultural monument is endangered; to fine with an administrative punishment; to file a petition on remedies.

8 voluntary boards of experts are working at the Inspection:

Board of Organ Experts

Board of Architecture Experts

Board of Restoration Certification

Board of Archaeology Experts

Board of Art and Antiquity Experts

Board of Architectural and Art Values

Board of Registration of Architectural and Art Values

Board of Experts of Restoration of Art Monuments

There are 8 departments in the State Inspection for Heritage Protection:

Management and Administrative Department

Expert's Department

Archaeology Centre

Department of Architecture and Art

Department of Historical Environment

Information Centre

Centre of Monument Documentation

Latvian Museum of Architecture

The owner (landlord) carries out conservation, maintenance, repair and restoration of cultural monuments from his own resources. Resources from the sate budget may be allotted for research of cultural monuments and conservation and restoration of cultural monuments of state significance with no economic value; resources from the budget of local governments are allotted for conservation and restoration of cultural monuments of local significance with no economic value. Financing resources of municipalities received from lease or economic use of cultural monuments and fines for damage of cultural monuments may be employed for research, conservation, repair and restoration of cultural monuments only.

Tax privileges are established for owners of cultural monuments in connection with restrictions on use of land or object. Real estate tax is not imposed on land on which economic activity is forbidden by the law, as well as property that is recognised as cultural monument, except cultural monument used for economic activities.

Works of restoration of cultural monuments are allowed to carry out by licensed specialists – restorers and licensed companies. Restoration projects are worked out by architects and building engineers certified in restoration. Certification is carried out by corresponding professional organisations.

2. Educational Programmes

2.1 Riga Technical University

Riga Technical University (RTU) is the oldest and at present the second largest higher educational institution in Latvia, founded under the name of Riga Polytechnic in 1862. There are 8 faculties in RTU now: Faculty of Architecture, Faculty of Civil Engineering, Faculty of Materials Science and Applied Chemistry, Faculty of Mechanical Engineering, Faculty of Electrical and Power Engineering, Faculty of Computer Science and Computer Engineering, Faculty of Radio engineering and Telecommunication, Faculty of Engineering Economics.

Scientific research is one of the predominant activities at RTU and it is carried out in each faculty, and also in several independent structural units. Research program of RTU covers a broad spectrum from the natural sciences to all areas of engineering and technologies. It also includes architecture, engineering, economics, ergonomics and environmental engineering. RTU scientists are widely involved in different international projects financially supported by European Union (TEMPUS, COPERNICUS, PECO, LIFE, EUREKA) and International Science Foundation. There are also many joint projects with partner universities of different countries (Denmark, Finland, Germany, Italy, Norway, Russia, Spain, Sweden, Ukraine, United Kingdom, United States and another) supported by their universities or local foundations.

2.2 Faculty of Material Science and Applied Chemistry

There are several departments (13) within the Faculty of Material Science and Applied Chemistry – Organic Chemistry, Material Science, Institute of Polymer Materials, Institute of Silicate Materials etc.

In reply to the request of Latvian libraries, museums and archives in September 1990 an academic group of students in conservation/restoration chemistry and technology was formed for the first time at the Faculty of Chemical Technology (now – Faculty of Materials Science and Applied Chemistry) (FMSAC) at the Riga Technical University (RTU). Beginning with autumn 1996, alongside with engineer's programme, a master's degree programme was introduced for logical continuation of specialisation studies after acquisition of bachelor's degree.

With an aim to prepare all-round specialists, particularly for potential conservators/restorers in smaller museums, libraries and archives, wood, paper, textiles, leather, metal, natural stone and ceramics, glass, porcelain were chosen as specialisation directions. A model of close collaboration between the Faculty and specialist employers was put in the basis of students education and training, accentuating academic studies at the FMSAC, but acquiring practical skills in the restoration centre and laboratories of libraries, museums and archives during 3 weeks long summer practice. It is necessary to emphasise that degree programmes in conservation/restoration chemistry and technology were formed on the basis of chemistry and chemical technology of the Faculty, discarding a part of technical and technological subjects and introducing instead of them cultural and historical courses as well as those associated with student's specialisation.

Lecture courses, incorporated in the programmes, conditionally could be subdivided into 4 groups: the first group contains basic subjects, such as mathematics, physics, a full spectrum of chemistry course, compulsory for all students of the Faculty, the second – history of civilisation and courses introducing in conservation/restoration art and science, the third – materials for conservation and restoration, methods of investigation and identification, the fourth – material science course of 7 possible specialisation directions. Such a structure of degree programmes gives students a possibility to acquire the basic course of chemistry, partially of chemical technology and material science, opening a broader access to labour market.

Remarkable decrease of the number of enrolled students in the last few years is one of the principal problems for further existence and development of the Faculty and the specialisation as the number of students in it is limited.

In such conditions on the one hand there is a greater possibility to work in close contact with students, even individually. On the other hand just from the number of students in the faculty salaries of the teaching staff and assignment of other resources depend.

If academic education of students in general is ensured today, that cannot be entirely assigned to laboratory and practical work carried out at the Faculty. Not in all lecture courses the necessary proportion between hours of lectures, practical and laboratory work is kept. Anyway for the last two positions the number of hours must be greater. Acquiring of practical skills in conservation/restoration is more complicated and still remains the main problem of the training process and incorporates such factors as:

Practical training bases and the number of working places their, equipment, supply with instruments and tools, chemicals and materials. They are gradually formed in the restoration centres and laboratories of the Latvian History Museum, Latvian National Library, Riga History and

Navigation Museum as well as at the Central Microphotocoping and Documents Restoration Laboratory of the Latvian archives system, Scientific Research laboratory of the Centre for Conservation and Restoration of Stone Materials, established in 1995 at the Silicate Materials Institute of the FMSAC.

2.3 Financial guarantee and funding possibilities

Organisation and arrangement of students practical training bases, remuneration of lectures, practical and qualification work supervisors are connected with investments and consumption of large or smaller funds, which are very restricted. To find them is a common task of the Faculty and employers of the specialists. The same relates to the provision of studies with lectures, improvement of syllabus and curricula, acquisition of books and journals etc. There is a range of important and necessary study courses which still are not included in the degree programme as in Latvia there are not specialists in this field. To invite lecturers from abroad or find people who would like to prepare such course is not possible for one and the same reason. It must be taken into account that education and training of conservation/restoration specialisation students is specific and expensive and differs from other traditional specialisations of the Faculty.

Funding possibilities for the research and scientific investigation are mainly restricted to Grants of Latvian Science Council – in the year of 2001 the sum obtained for one project was about 3300 USD per year. There are also several contracts between CCRSM and the City Council not exceeding several hundreds of USD per year.

2.4 Co-ordination of the study process and other arrangements

Along with education and training, research work, as an intermediate stage between the other two must take a remarkable place in the study programmes. Up to now investigations in the field of cultural heritage conservation/restoration are poorly developed in both the conservation/restoration centres and laboratories, and in the FMSAC, other Universities and institutes. Besides research work is not always connected with needs and actual problems of conservation/restoration. It is a very essential drawback, which remarkably decreases effectiveness of studies. For the time being academic studies and practical training prevail in the study process while research work has a case disposition.

To improve the quality of studies more attention must be paid to collaboration with other Universities. This position has been very weak up to now. Starting with the academic year 1999/2000 broader possibilities opens for the specialisation students to study abroad.

3. Research institutions

There are very few laboratories and institutions working in the field of scientific investigation of historical materials. Main of them are:

- Latvian Academy of Art (LAA)
- Restoration Centre of Latvian History Museum (RC-LHM)
- The Centre for Conservation and Restoration of Stone Materials of Riga Technical University (CCRSM-RTU)

3.1 Latvian Academy of Art

There are no large laboratories or research centres in the LAA as the institution is oriented to education. The students of Restoration Department, which is specialised in the restoration of paintings, are touched to make documentation and some diagnostics of the paintings, which they are restoring during the study process. First of all the analysis of object from the viewpoint of history of art is carried out. The main activities of documentation and diagnostics are following:

- studies of archive and illustrative materials;
- photo fixation;
- simple chemical analysis of pigments, binding media, varnish etc., more complicated analysis are carried out in collaboration with RTU;
- investigation with visible UV light ;
- microscopy (x 1200 magnitude);

In order to obtain wider information and data, Department of LAA collaborates with RTU (chemical analysis, XRD), Latvian University (mycological investigation), Restoration Centre of Latvian History Museum.

Personnel involved – teaching stuff and students.

3.2 Restoration Centre of Latvian History Museum

The Restoration Centre of Latvian History Museum started its activities in 1988. The Centre is specialised in practical restoration of archaeological material, textile, drawings, documents, books, ceramics and polychrome wood. At the moment there are working 25 specialists, 13 of them are certified by the Board of Restorers Attestation. Investigation and analysis are carried out by certified restoration chemist (one person).

The diagnostics of cultural heritage materials involve the following:

- stratigraphic research of paint
- termocontrolle of samples
- micro chemical research
- hystochemical reactions
- microscopy
- thin layer chromatography

The RC-LHM collaborates with:

- Institute of Organic Synthesis - IR spectroscopy, gase-licquid mass spectroscopy
- Latvian University – emition spectral analysis, mycological research
- Riga Technical University – XRD
- Centre of Criminalistics – Fourier transmition IR spectroscopy.

RC-LHM collaborates also with Restoration Centre of State Archive and in special cases with Medical Centre of Catastrophes.

3.3 The Centre for Conservation and Restoration of Stone Materials

The Centre for Conservation and Restoration of Stone Materials of the Institute of Silicate Materials (Riga Technical University) was founded in the 1995 summarising the knowledge obtained during researches devoted to the investigation of corrosion processes of stone materials, and practical skills of restoration.

Theoretical background: the base of theoretical and practical work of the CCRSM is formed of:

- International principles and standards of restoration/conservation
- Legal requirements of the State Inspection for Heritage Protection
- Scientific research
- Co-operation with colleagues from abroad

Activities:

The main areas of activities include:

- Research of stone materials of Latvian monuments
- Evaluation, photo fixation, cartography of cultural heritage monuments
- Analysis of corrosion of stone materials; composition of corroded materials, determination of structure and mechanical properties
- Elaboration of restoration/conservation methods
- Stone repair and masonry grout composition design
- Design of restoration program's, recommendations
- Practical conservation and restoration of stone materials
- Supervision of restoration activities
- Systematisation of information and literature, elaboration of a database of corrosion and restoration of monuments of Latvia
- Theoretical and practical training of new specialists (bachelors, M.Sc. and doctors)
- Participation in the International projects

Laboratory facilities available:

The composition and structure of stone materials is investigated with the help of following techniques:

- XRD, DTA
- Petrography
- Flame photometry
- Gravimetric analysis
- Complexonometric titration

Personnel involved:

- Dr.Sc.ing., certif. stone restorer (II^{nd} category)
- Dr.Sc.ing., certif. restoration chemist (I^{st} category)
- Ing., certif. restoration chemist (II^{nd} category)

- M.Sc. certif. stone restorer (IIInd category)
- M.Sc., stone restorer
- Certified restoration architect

Stone restorers and chemists are certified by the Board of Restoration certification of the State Inspection for Heritage Protection, the restoration architect - by the Sate Association of Architects.

4. Joint Projects

Related to the 5th Framework project just launched: Bioremediation for Building Restoration of the Urban Stone Heritage in European States (BIOBRUSH). Co-ordinating Organisation: University of Portsmouth.

Partner names:

- University of Portsmouth, UK
- Stiftung Institution für Werkstofftechnik, Germany
- DISTAM – University of Milan, Italy
- Riga Technical University - CCRSM, Latvia
- National Technical University of Athens, Greece
- Syremont (Montedision Group), Italy

BIOBRUSH is a research consortium of experienced scientists, industrialists and end-user conservators formed to study the feasibility of using bioremediation to restore buildings in cities. This innovative approach will select appropriate, safe microorganisms and delivery systems so that treatment combinations can be tested in the laboratory and then on buildings where performance and risk will be assessed under the different climatic conditions of Northern and Southern Europe.

Project objectives:

1. To investigate bioremediation for conservation of stone and brick in heritage buildings through Europe.
2. To use microbes to remove salts by crust mineral destroying processes and consolidate by mineral-forming bio calcification.
3. To screen, select and test suitable stone materials, safe microorganisms and practical delivery systems.
4. To carry out performance and durability tests and risk assessment for innovative treatment combinations on stone and brick in the laboratory and then on heritage buildings in European cities and urban environment.
5. To identify the environmental constrains imposed by climate within Europe so that the treatment process can be adapted for use through Europe.
6. To work closely with industry and conservators to recommend practical treatment strategies based on bioremediation for conservation practice to protect European cultural heritage.

5. Case story: Riga Brethren's Cemetery – investigation of the stone materials

Riga Brethren's Cemetery – the symbol of Latvian national identity – is dedicated to the worriers fallen during the First World War and national independence struggles from 1915 to 1920. It was constructed between 1920 and 1936. The choice of material for this object was based on artistically/architectural and nationalistic considerations as at that time geologists in the area of Allazi found the local freshwater limestone deposits. As the quarry was rather small the limit of stone material was exhausted already during the construction. Thus in object the stone blocks of different quality could be observed, as there were no possibilities to select more qualitative material. Deterioration processes of limestone due to external factors proceeds faster and has more destructive activity. During the last six years the intensive restoration works *in situ* have been carried out (1).

The composition of stone materials used in the construction and restoration of Riga Brethren's Cemetery as well the products of corrosion were investigated with the help of the following techniques: X-ray powder diffraction (XRD), differential thermal analysis (DTA), petrography (carried out in the State Geology Survey of Latvia), scanning electron microscopy (SEM) and mercury porosimetry. The latest two were carried out in the University of Erlangen (Germany).

Chemical analyses were carried out determining the heating loss of samples at 400^0 and 1000^0 C; for the solution of sample H_2SO_4 and HF were used. Soluble SiO_2, Al_2O_3 and SO_3 by sedimentation; CaO and MgO – by complexonometric titration; Fe_2O_3 by photocolorimetry; Na_2O and K_2O – by flame photometry.

5.1 Characterisation of material

According to chemical analyses (tab.1.) Allazi limestone is practically pure calcite rock: calcium carbonate ($CaCO_3$) – 97.7 %, magnesium carbonate ($MgCO_3$) – 0.56 %. A small amount of organic substances (1.53 %) and iron trioxide (Fe_2O_3) ca 0.1 % are responsible for the yellowish colour of stone. This type of tufa consists of microcrystalline (0.001-0.2 mm) and macro crystalline (0.25-0.7 mm) calcite aggregates.

Table 1. Chemical composition of freshwater limestone (heat loss at 1000^o C – 42.96 % of mass)

Components	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3
Amount (% of mass)	0.71	54.74	0.27	0.16	0.10	0.12	0.07	0.18

Due to inhomogeneous structure and texture of stone the physical-mechanical properties of freshwater limestone are inconstant and variation could reach wide range even in the area of one stone block (ca 60x30 cm) (see tab.2.)

Table 2. Physical-mechanical properties of freshwater limestone (1).

Density (g/cm^3)	Mass by volume (g/cm^3)	Water absorption (%)	Porosity (%)	Compressive strength (MPA)	Frost resistance (cycles)
2.63-2.7	1.48-2.40	5.5-21.0	11.1-43.0	4.5-20.5	10-25

Due to the high porosity and large pore sizes the water uptake of limestone is very high and evaporation is long lasting. Laboratory measurements of water absorption by capillarity show that maximum of water content is reached already during the first 30 minutes of testing. On the other hand the evaporation dynamics shows that the drying up process of limestone occurs very slowly. In conformity with laboratory measurements the stone is completely dry only after 72 hours.

Electron microscopy shows the grained shape of fine freshwater limestone crystals.

Obtained mercury porosimetry data allow to conclude that freshwater limestone is frost resistant as the pore content with diameter 0.04-0.1 μm is insignificant – only 1.2 mm^3/g by volume.

5.2 Corrosion of material

It has to be admitted that for over 10 years the limestone in Brethren's Cemetery had been exposed to the pollution generated by a super phosphate manufacturing plant. This plant was closed down in seventies. Today the object is exposed to the decay due to increase of the city traffic emitting large amounts of dangerous pollutants into the atmosphere. Although Brethren's Cemetery is located 5 km from the centre of the city, there is a quite dense traffic near the cemetery. There is no question that the polluting gases must have attacked the calcareous stone leaving it more susceptible to further damage.

Main causes of corrosion of Allazi limestone are (i) bad quality of stone material, (ii) porosity and inhomogeneous structure of material, (iii) environmental pollution, (iv) influence of soluble salts, (v) migration of water, (vi) impact of biological growth.

Main deterioration processes observed in Riga Brethren's Cemetery are (i) darkening of the surface and final formation of black crusts, (ii) efflorescence, (iii) cracks, (iv) disintegration of the stone, (v) open joints and joints with poor mortar, (vi) open caverns and mendings from previous restoration , (vii) bio corrosion.

Darkening of the stone surface and black crusts. The surface of the limestone is coated with a black or grey film due to the polluted environment – motor exhaust fumes, soot, dust etc. On the areas, such as parts of ornamental and sculptural groups and structural elements, which are not directly exposed to the strong rain bearing, the severe black crusts are being formed since these places have not been washed away by the rainwater.

Soluble salts. In the object the presence of soluble salts is stated and the main kinds of salts are established: sodium and potassium sulphates, in less quantities – nitrates.

Copper stains. Rainwater contains more or less quantities of dissolved sulphur and nitric oxides and other chemical compounds. Due to chemical reaction between copper containing products and rainwater components and washing down the reaction products by water, the bluish-green stains are formed on the surface of the stone. Thus decay pattern mainly affects the aesthetics of the object and does not cause any serious damage to the stone. In Riga Brethren's Cemetery such stains could be observed on the stone blocks contacted with roof and on sculptural groups, where both limestone and copper containing elements were used.

Cracks. There are cracks in the stone blocks of the object. The formation of cracks could be explained with the settlement and deformation of ground, vibration due to traffic, thermal expansion of constructions and materials, water and frost attack.

Disintegration of stone. It is mainly due to the effects of natural weathering, including chemical corrosion caused by air pollution on Allazi limestone of poor quality. The stone surface gradually disintegrates into powder and loses its mechanical strength and artistic form. Such powdered stone material could be observed in the object.

Open joints and joints with poor mortar. One of the problems is the high incidence of deteriorated joints or even missing joints. This situation had resulted in the infiltration of water and succeeding frost attack.

Open stone caverns. Deteriorated previous mendings. Mendings of inappropriate material. Freshwater limestone is very porous and besides this there are a lot of open caverns (ca 0.5-10 cm) in the stone. Such caverns, especially if placed on the horizontal surfaces, accumulate water after rain events. A lot of mendings made during the construction and previous restoration works are being deteriorated. In most cases the powdered stone material could be observed behind these mendings. Some mendings from previous restorations were made of mortar with high quantity of cement. These mendings are more compact and stronger than Allazi limestone. This leads to cracking of Allazi limestone.

Biocorrosion. Being very porous material limestone favours the establishment of micro flora, especially in view of its great ability to retain water. Outdoor surfaces of tufa are colonised in different ways by micro flora and plant communities. Bio corrosion attacks the stone by: (i) chemical action – producing organic acids, (ii) mechanical action growing into the stone pore system with roots and other parts, (iii) providing regular moisture.

5.3 Practical restoration program

According to the physical-chemical analysis of stone material and corrosion products as well as taking into account the experience in practical stone restoration in the Cemetery, the new restoration program of freshwater limestone was elaborated. Basically it consists of maintenance, cleaning, consolidation, desalination, mending and jointing. Regular maintenance – mainly includes the removal of organic growth from the surface of stone, what should be done at least twice in season. General cleaning – washing with low pressure water jet (ca 50 atm). Mechanical cleaning of black crusts using micro abrasive – air blaster. As abrasive fine corundum or aluminium powder with diameter of particles 37 μm, p=6 Ba, could be used. Cleaning of copper stains with the help of clay and NH_4OH poultice. Consolidation of disintegrated limestone using lime-water (saturation 40 times). Desalination using clay poultices. Mending of tufa using porous mortar of ground tufa and lime with small hydraulic lime or cement additives. Tufa aggregates consisting of different fraction – 40 % 1mm, 33 % 0.5mm, 27 % > 0.2mm. Ration of aggregates and binder 1 : 1. Depending on colour 50 % burned lime and 50 % white cement or 85 % hydraulic lime and 15 % white cement could be chosen as a binder. For jointing – the mortar of lime – cement – sand (1 : 2 : 10-12 by mass) mixture is preferable.

6. References

[1] I.Sidraba, L.Krage, I.Graudums *Problems and solutions in practical restoration of freshwater limestone – tufa*. 9th International Congress on Deterioration and Conservation of stone. Vasco Fassina edited. ELSEVIER SCIENCE B.V., ISBN:0444-50517-2: Vol.2., pp 175-178.