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SAVED FROM CORROSION

THE RAILWAY MUSEUM IN WARSAW
NORWEGIAN INSTITUTE FOR AIR RESEARCH

Saved from corrosion – the Polish-Norwegian exchange of experiences to bring rescue to metal historic objects

Supported by a grant from Iceland, Liechtenstein and Norway
through the EEA Financial Mechanism and the Norwegian Financial Mechanism

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About the Project

2nd November 2010 The Railway Museum in Warsaw began the project: S*aved from corrosion – the Polish-Norwegian exchange of experiences to bring rescue to metal historic objects"* which was accomplished 31*th* October 2011. The project was financed by EEA Financial Mechanism and Norwegian Financial Mechanism. The project was estimated for 381.634 PLN. 10 % of it was the Museums input.

The goal of this project was the exchange of knowledge and cooperation between art curators, conservation officers and scientists dealing with the preservation of metal engineering monuments.

This multidisciplinary project merged cutting edge experimental methods with current conservation knowledge and museum practices.

Metal engineering monuments such as steam engines from the Railway Museum collection in Warsaw (some items unique in Europe!) stand in the open air and are susceptible to the effects of the atmospheric conditions, corrode and must undergo frequent conservation.

The project partner was the Norwegian Institute for Air Research NILU. It is a leading European institution in the research of atmospheric pollution, its impact on the environment and historic monuments. NILU experts have been participating in culture-related projects for years, also under the auspices of the Cultural Exchange Fund, and are a reliable partner.

Polish participants in the project included experts from the Military University of Technology and Academy of Fine Arts in Warsaw. They have been successful in the field of research and international project executions.

The expertise of Polish and Norwegian scientists were complementary. The project involved the measurement of the atmospheric pollution, measurement of selected historical samples from the Museum's collection of steam engines as well as identical, artificial metal samples. This analysis will hopefully allow for the diagnosis of the conservation needs and the development of a cutting edge conservation process.

The results were presented in an international workshop on 7-8th October 2011 in Warsaw, in the Muzeum Gazownictwa. In the publication there are texts written by the researchers who participated in the workshop.

During the second day there was a trip by a steam locomotive, which is in the Museum's collection, in the division of the Museum located in Sochaczew.

Project team

The Project leader:	The Railway Museum in Warsaw:
Project coordinator:	Anna Kozelska
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	dr Marek Strzelec
	dr Wojciech Skrzeczanowski
Project Partner:	The Conservation Institute, Warsaw
Researcher:	mgr Anna Zatorska

Biographies:

Anna Zatorska, MA (ASP) – conservation education, majored in conservation and is currently a PhD student at the Academy of Fine Arts in Warsaw. She is the co-author of the analytical methods for metal works of art developed under the MATLAS grant.

Jan Marczak, Ph.D. Eng. (WAT) wrote his doctoral dissertation on quantum electronics and was habilitated in the field of surface engineering. He is a specialist in application of optoelectronics in conservation of works of art. He has been an expert of the Ministry of Culture and National Heritage since 2005.

Wojciech Skrzeczanowski, Ph.D. Eng. (WAT) is an electronic engineer and a specialist in spectroscopy, metrology and management systems.

Marek Strzelec, Ph.D. Eng. (WAT) wrote his doctoral dissertation on quantum electronics and he is a specialist in the field of optoelectronic metrology He has been participating in scientific expert teams under COST, NATO and the EUREKA initiative. He has been assigned to coordinate the works undertaken by the Polish experts.

Janusz Mróz, MA (ASP), conservator qualified to conduct conservation works on historical items in the scope of metal conservation; he has been granted the official expert's authorisation of the Minister of Culture and National Heritage in the field of protection of historical monuments; expert of the Association of Monument Conservators in the scope of conservation of works of art and historical monuments made of iron and metals; collaborates with the Railway Museum in Warsaw by verifying and reviewing the rolling stock conservation works.

Terje Grøntoft, (NILU, Norway) Ph.D. in chemistry, focuses on studying the influence of air pollutants on materials and items of cultural heritage. He has participated in numerous EU projects and published several dozen scientific papers.

Dr Christian Degrigny received a PhD in analytical chemistry from the University of Paris IV in 1990. As an engineer in electrochemistry; he specializes in electrochemical diagnosis and treatment of historic and archaeological metallic objects. He was the coordinator of the ICOM-CC Metal WG in the period 2002-2008, director of studies at the Finnish conservation school in Vantaa in 2001-2002 and director of the diagnostic laboratories at the Malta Center for Restoration from 2003 to 2006. Since 2004 he is part-time professor at the High School of conservation Arc (HECR Arc), Neuchâtel, Switzerland where he carries out applied research on metal conservation. In parallel he is running a historic building: Germolles château, the unique palace of the dukes of Burgundy so well preserved in France.

Peter Brimblecombe is a Professor in Atmospheric Chemistry at the School of Environmental Sciences, University of East Anglia and a director of Postgraduate Study Programme in Science which offers educational training in frames of doctoral Studies at the University of East Anglia. In 1990 he was appointed senior editor of the Atmospheric Environment magazine. He co-worked within the 4th, 5th and 6th Frame Programmes of the European Commission in the field of cultural heritage, among others within the NOAHs ARK programme on the influence of the climate change on the cultural heritage. He received a gold medal from the Italian Chemical Society for contributions in environmental and heritage chemistry and with the NOAHs ARK team the Europa Nostra Grand Prize for research in 2009. Peter Brimblecombe was an advisor to the Council of Europe, the European Parliament and the Chamber of Lords in the field of atmospheric sciences and their effect on the heritage management. He is interested in communicating information about the atmospheric sciences to broader audiences as well as experienced in conducting workshops with students and adults on managing heritage in uncertain future.

Elżbieta Maria Nosek received a PhD in Materials Engineering from the Academy of AGH University of Science and Technology in Cracow in 1979 ("Ferrum oxidixing in high temperatures"). Received a scholarship from the British Council in 1972 r., internship in the British Museum-Research Lab in 1972,1973,1974 and a six-month scholarship in the ICROM Rome. For many years a director of the conservation-diagnostic laboratory in the Archeological Museum in Cracow. From 1973 a professor of applied conservation of metal relics. Postgraduate Studies at the Faculty of Architecture at The Cracow University of Technology. Expert of the Ministry of Culture and National Heritage, Poland. Author of many publications in the field of conservation and ancient metallurgy.

Articles

"Microchemical analyses and Raman spectroscopy in examination of corrosion products on steel and cast-iron samples."

Anna Zatorska, [1]The Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Art, Department of Specialist Analyses and Documentation Techniques

Grażyna Zofia Żukowska, Warsaw University of Technology, Faculty of Chemistry, Inorganic Chemistry and Solid State Technology Department

Introduction

The identification of products of corrosion on steel and cast-iron samples, weathered in open municipal environment, was conducted with the use of three methods: optical microscopy, microchemical analysis and Raman spectroscopy. In result, the images of surface of the samples, their ion composition and thickness of their corrosion layers were determined, as well as chemical compounds comprising them.

Methodology

The research material was constituted by 16 contemporary steel and cast-iron plates. 2 historical samples cut out from two original steam engines exhibited in Sochaczew and Warsaw served as a reference material. The contemporary samples have been exposed to external conditions at the Warsaw Railway Museum and in Sochaczew. Every quarter, the corrosion on samples of steel and cast-iron from each location was analysed (4 plates constituted a full set of samples).

The aim of the research, which was started from making stratigraphic cross-sections, was to observe changes of the surface and to identify products of steel and cast-iron corrosion. Fragments of samples were immersed in acrylic resin, ground and photographed. Photographs were taken using a digital sight camera system for microscopy (Nikon Digital Sight DS.-U2/DS.-Fi1c). The cross-sections served the purpose of determining the layer structure and thickness of the layers. Then, classical examinations were conducted with the use of microchemical method, with the purpose of ion identification. Their aim was to determine the presence of Fe^{2+}, Fe^{3+}, S^{2-}, Ca^{2+}, SiO_3^{2-}, and PO_4^{3-}. The analyses were based on microscopic observation of results of the samples' corrosion reactivity in selected chemical reagents, that is 3M HCl, concentrated HNO_3, 1,5M H_2SO_4, $K_4[Fe(CN)_6]$, $(NH_4)_2MoO_4$, α,α'-dipyridyl and an azide reagent. The observations were conducted with the use of Nikon Eclipse 50i basic polarising microscope. The next stage of research was constituted by analyses of chemical compounds with the use of Raman spectroscopy. They were carried out directly on the steel and cast-iron plates and on cross-sections. A number of measurements were taken on each plate, at sites differing in colour. Spectra were recorded with a dispersive spectrometer (Nicolet Almega) coupled with a confocal microscope that enables precise selection and view of the test site, using the exciting line at 780 nm and a grating of 1200 lines.

Results

1st weathering period. The observation of the surface with stereoscopic microscope revealed that there were sites on the steel on the ground section of the sample weathered in Sochaczew, which were not covered with corrosion products, while the surface of the brushed section and other plates were covered with rust totally. (Fig. 1 A-B). The corrosion on samples exposed in Sochaczew had more sophisticated character (large number of blowholes, corrosion pits and glassy spots) and more diversified colour when compared to samples from Warsaw (Fig. 1 A-B). On the basis of comparison of steel corrosion, it was established that the rust deposited on the plate from Warsaw, on the brushed section, was thinner by 37 µm, while on the ground section it was thicker by more than 30 µm when compared to corresponding areas of the sample from Sochaczew (Fig. 1 D). Corrosion pits

were not large – up to a dozen or so µm. The rust on the cast-iron aged in Warsaw was thinner by approximately 25 µm when compared to the cast-iron aged in Sochaczew. The corrosion pits reached the depth of 25 µm on the Warsaw sample and 87 µm on the Sochaczew sample (Fig. 1 E, table 1-4). During microchemical examinations, the presence of $Fe^{3+}$and small amounts of S^{2-} was ascertained. Examinations of chemical composition with the use of Raman spectroscopy revealed that the dominant corrosion product in all samples is lepidocrocite γ-FeOOH whose main bands are visible at 378 i 250 cm^{-1}. Goethite α-FeOOH occurs in smaller amounts. In addition, magnetite Fe_3O_4 and hematite Fe_2O_3 were found on steel samples. The presence of hematite may be due to local overheating of the sample by laser beam. In the rust on the steel from Sochaczew lepidocrocite, goethite, hematite and magnetite were detected. Figure 2 presents the comparison of Raman spectra typical for corrosion products. The spectrum of orange product is typical for lepidocrocite; goethite was identified in brown deposits, and a mixture of goethite and lepidocrocite in brown-red deposits.

2nd weathering period The observation of the corroded surface of steel and cast-iron from the 2nd weathering period with the use of stereoscopic microscope revealed occurrence of bulges and craters in all four cases. Sample surfaces showed point discontinuities (most often insignificant) in the corroded layer, causing the exposure of non-corroded substrate. Thickness of the rust layer on the steel weathered in Sochaczew was higher even by 65 µm than on the sample of steel exposed in Warsaw. Corrosion pits were deeper by approximately 20-50 µm. The colour of rust on the surface of steel from Sochaczew and Warsaw was orange-brown, whereby on the non-processed area it showed a distinct three-layer structure in cross-section: on the orange-brown layer (situated directly on non-corroded metal), a darker layer was observed, steel-graphite in colour, on which a thin orange layer appeared again. The cast-iron plate weathered in Sochaczew was covered with rather thin, orange-brown layer of rust, which on the ground section was 75 µm deep. The rust on cast-iron plate from Warsaw on the ground section was approx. 50 µm thick, corrosion pits did not exceed 20 µm, and on the brushed section, where the pits reached depth of 35 µm, the rust thickness was more than two times higher. During microchemical examinations, the presence of Fe^{3+} and small amounts of S^{2-} was ascertained in all the cases. In addition, in the case of steel and cast-iron sample (on the ground section) exposed in Sochaczew, the presence of Fe^{2+} ions were ascertained. The Raman spectrum analysis revealed that the main corrosion products are in all cases lepidocrocite and hematite, the latter one may be due to local overheating. In addition, magnetite and goethite were found on the steel samples from Sochaczew and cast-iron samples from Warsaw. Besides, also quartz was present is the samples.

3rd weathering period. A large number of blowholes (bulges), craters, glassy forms and flakes was observed on the surface of all the weathered metal alloy samples with the use of a stereoscopic microscope. Some of the blowholes were oval in cross-section and had star-like cracks at the top. They were observed in particular in all the metal alloy samples subject to grinding. All the samples showed point discontinuities in the corroded layer causing the exposure of deeper, non-corroded strata. The highest number of extensive corrosion pits, reaching 75 µm in depth and 200 µm in width were visible on the cast-iron sample exposed in Sochaczew. The thickness of rust was up to 130 µm and it had a two-layer structure (dark, almost black near the non-corroded metal and more orange on the surface). The rust on cast-iron from Warsaw looked similar, whereby it was even by 50 µm thinner, and the corrosion pits were shallower. Corrosion pits up to 45 µm in depth were revealed on the steel sample from Sochaczew on the ground section, and on the brushed section their depth was between 12.5-35 µm. The steel sample weathered in Warsaw had either no corrosion pits or such pits were less deep and not so frequent, and the corrosion thickness was lower by more than 35 µm. In result of microchemical examinations, the presence of Fe^{3+} and small amounts of S^{2-} ions was ascertained in corrosion products in all the cases. Based on the instrumental analysis, lepidocrocite was identified as the main steel and cast-iron corrosion product. In steel corrosion products also the occurrence of goethite was ascertained, and on brushed sections (aside from lepidocrocite and

goethite) – also of magnetite and hematite. In the cast-iron samples, regardless of whether they were subject to grinding or brushing, only lepidocrocite was identified.

4th weathering period. The observation of corroded surfaces of all 4 plates with the use of stereoscopic microscope showed very uneven surface, numerous flakes revealing internal layers; craters, stratifications and single bulges, and loose encrustations deposited by wind (Fig. 1 G-I). The microscopic observation of cross-sections revealed that the steel samples on the whole section and cast-iron samples on the brushed section were characterised by the most advanced destruction of the substrate (Fig. 1 K). Cast-iron samples which were subject to prior grinding were in a fairly better condition and corrosion pits on them were shallower (Fig. 1 L i J). The steel exposed in Warsaw was covered with corrosion layer which was 180 µm thick, thicker by approximately 30 µm when compared to the rust on sample from Sochaczew. Corrosion pits were observed along the whole cross-sections, independently of the method of processing and place of exposure. Cast-iron from Warsaw was covered with rust which was 80 µm thick, while the corrosion layer on the sample from Sochaczew was thicker by 50 µm (Fig. 1 L). Corrosion pits were more numerous, deeper and wider on the brushed section when compared to the ground one (Fig. 1 J). In result of microchemical examinations, the presence of Fe^{3+} and small amounts of S^{2-} was ascertained in all the cases. Fe^{2+}, Ca^{2+} and SiO_3^{2-}, and PO_4^{3-} ions did not occur. The spectroscopic examinations made it possible to ascertain only the presence of lepidocrocite in steel and cast-iron corrosion products.
The comparison of results of analyses from all the weathering periods as well as examinations of samples from historical steam engines is contained in tables 1-4.

Table 1. Comparison of results of examination of steel exposed to external conditions in Warsaw.

Period	**Corrosion layer thickness [µm]** (method: microscopy)	**Max. depth/max. width of corrosion pits [µm]** (method: microscopy)	**Ion composition** (method: microchemical analysis)	**Identification of compounds** (method: Raman spectroscopy)
1st	10-87	12.5/50	Fe^{3+}, S^{2-}	lepidocrocite, magnetite, hematite
2nd	10-70	45/<200	Fe^{3+}, S^{2-}	lepidocrocite, magnetite, hematite
3rd	15-75	15/190	Fe^{3+}, S^{2-}	lepidocrocite, magnetite, goethite, hematite
4th	10-180	50/320	Fe^{3+}, S^{2-}	lepidocrocite
Historical sample	120	40/85 corrosion under paintwork	Fe^{3+}, S^{2-}	lepidocrocite, goethite, hematite

Table 2. Comparison of results of examination of steel exposed to external conditions in Sochaczew.

Period	**Corrosion layer thickness [µm]** (method: microscopy)	**Max. depth/max. width of corrosion pits [µm]** (method: microscopy)	**Ion composition** (method: microchemical analysis)	**Identification of compounds** (method: Raman spectroscopy)
1st	25-100	12.5/50	Fe^{3+}, S^{2-}	lepidocrocite, goethite, hematite, magnetite
2nd	10-115	75/200	Fe^{3+}, Fe^{2+},	lepidocrocite, goethite,

			S^{2-}	hematite, magnetite
3rd	30-112	45/ok. 300	Fe^{3+}, S^{2-}	lepidocrocite, goethite, hematite, magnetite
4th	more than 150	50/along the whole width	Fe^{3+}, S^{2-}	lepidocrocite
Historical sample	80-338	150/along the whole width	Fe^{3+}, S^{2-}	lepidocrocite, goethite, hematite, magnetite

Table 3. Comparison of results of examination of cast-iron exposed to external conditions in Warsaw.

Period	**Corrosion layer thickness [μm]** (method: microscopy)	**Max. depth/max. width of corrosion pits [μm]** (method: microscopy)	**Ion composition** (method: microchemical analysis)	**Identification of compounds** (method: Raman spectroscopy)
1st	10-75	25/50	Fe^{3+}, S^{2-}	lepidocrocite, goethite
2nd	50-130	35/120	Fe^{3+}, S^{2-}	lepidocrocite, goethite, magnetite, hematite
3rd	25-80	30/110	Fe^{3+}, S^{2-}	lepidocrocite
4th	25-80	50/200	Fe^{3+}, S^{2-}	lepidocrocite

Table 4. Comparison of results of examination of cast-iron exposed to external conditions in Sochaczew.

Period	**Corrosion layer thickness [μm]** (method: microscopy)	**Max. depth/max. width of corrosion pits [μm]** (method: microscopy)	**Ion composition** (method: microchemical analysis)	**Identification of compounds** (method: Raman spectroscopy)
1st	30-100	87/37	Fe^{3+}, S^{2-}	lepidocrocite, goethite
2nd	25-75	25/75	Fe^{3+}, S^{2-}, Fe^{2+}	lepidocrocite, hematite, quartz
3rd	25-130	75/200	Fe^{3+}, S^{2-}	lepidocrocite
4th	10-130	40/170	Fe^{3+}, S^{2-}	lepidocrocite

Summary

The results of corrosion examinations obtained within 11 months make it possible to ascertain that:

-there were no changes observed in the ion composition or such changes were insignificant and concerned only the presence of Fe^{2+} in samples from the 2nd period of weathering in Sochaczew. In all the cases, mainly the presence of Fe^{3+}, and of small amounts of S^{2-} was ascertained;

-from among 16 known iron oxides (Cornell i Schwertmann 2003), four oxides were identified in the corrosion products under examination: the dominant one was orange lepidocrocite, as well as less frequently occurring (and in smaller amounts) – black magnetite, dark-brown goethite and grey hematite, which may be due to local overheating of the sample by laser beam. Measurements with a Raman spectroscope were conducted from the surface of the sample, which means that only its upper layer (most frequently orange one) was subject to examination, while darker products (goethite, magnetite, hematite), which occurred deeper, were possible to analyse just in sites where the external layer came off. As the main component of the rust, lepidocrocite creates a porous

corrosion layer, which does not constitute a good barrier for destructive factors and may easily flake (Głuszko, 2008). It is also known that iron oxides may in specific circumstances transform from one into another, e.g. goethite may be a product of lepidocrocite transformations (Cornell i Schwertmann 2003);

-analyses of rust composition executed in each quarter with the use of Raman spectroscopy made it possible to observe changes in the scope of occurrence of the four oxides indicated above (table 1-4). In the 4th weathering period, only lepidocrocite was identified in all the cases, while in the 1st period, goethite was identified in three cases (on steel and cast iron from Sochaczew), as well as magnetite and hematite on samples from Warsaw;

-chemical composition of corrosion layers from historical steam engines, obtained in result of Raman spectroscopic examination was more sophisticated in comparison to the samples weathered for 11 months (table 1 and 2). Lepidocrocite, goethite and hematite were identified in the historical sample from Warsaw, and in the sample from Sochaczew – also magnetite. In turn, in samples from the 4th weathering period, there was only lepidocrocite found;

-thickness of the corrosion layer and depth and width of corrosion pits on the historical sample from the steam engine from Sochaczew were significantly higher than on the samples weathered for 11 months in Sochaczew (table 2, Fig. 1 F i K). The steam engine from Warsaw had signs of paintwork on the surface, which probably slowed down the process of destruction. Hence, corrosion pits on the sample under examination were smaller and the rust thickness was lower when compared with results from the 4th weathering period (table 1);

-in the 1st period of exposure, the fastest increment of corrosion layer was observed. Within subsequent month, the velocity of rust growth decreased for most samples (table 1-4);
-the biggest changes in the corrosion layer, within 11 months, were observed in depth and width of corrosion pits, and rust thickness;

-after the 4th period of exposure, steel plates were in a more advanced condition of destruction when compared with cast-iron plates, which was observed independently on a place of exposure (Fig. 1 J-L);

-after the 4th period of exposure, the layer of cast-iron on ground section was characterised with a lesser mass loss (lesser number of deep corrosion pits) in comparison to the brushed section (1Fig. 1 J i L).

The applied research methods have certain limitations. Microchemical analyses identify only selected ions. Sensitivity of reaction does not always enable detection of ions, despite their presence in small amounts in the sample. Magnetite, which was identified a number of times, contains iron at oxidation level of 2, which was confirmed by microchemical tests only twice (probably microchemical reaction to identify Fe^{2+} is not sensitive enough). The cross-sections constitute only a part of a larger fragment, in this case - of weathered steel and cast-iron plates. Thus, the obtained image of stratigraphic layers may, but does not have to, be identical for the sample as a whole. The Raman spectroscopy method of identifying chemical compounds is also not sufficient from time to time. In this case, sulphur compounds were not identified (S^{2-}), whose presence where ascertained with the use of microchemical method.

Information obtained in results of the research described above constitutes a supplement for analyses conducted by other institutions taking part in the project, among others SEM-EDS and LIBS.

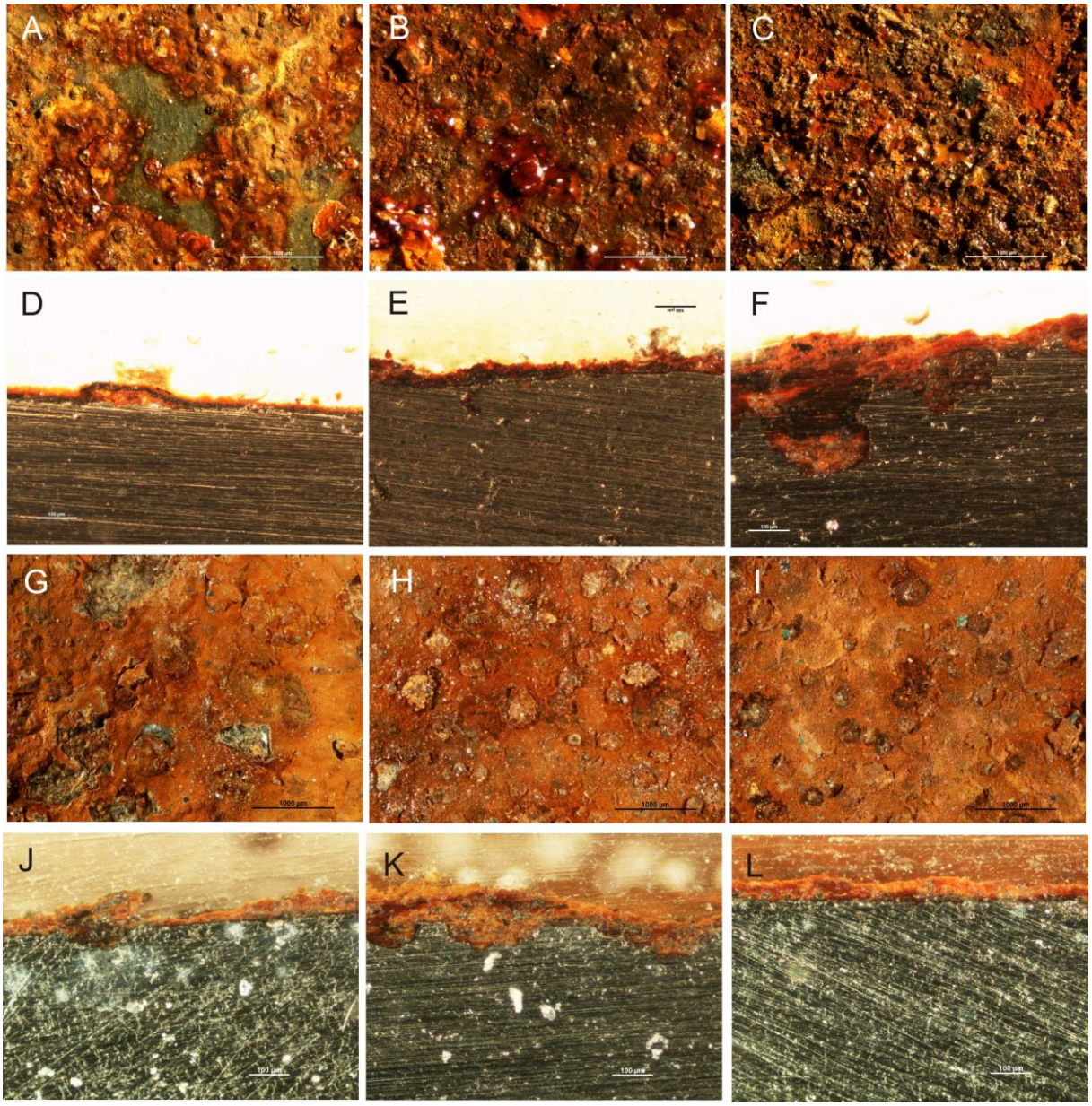

Fig. 1. Corrosion products on contemporary steel and cast-iron plates. Microscopic photographs of surfaces and cross-sections. Photograph A. Zatorska.

A. Surface of steel plate after 1st period of exposure in Sochaczew. Ground section; B. Surface of cast-iron plate after 1st period of exposure in Sochaczew. Brushed section; C. Surface of steel plate from historical steam engine from the Warsaw Railway Museum; D. Cross-section of the steel sample from the 1st period of exposure in Warsaw. Brushed section; E. Cross-section of cast-iron sample from the 1st exposure period in Sochaczew. Brushed section; F. Cross-section of steel plate from historical steam engine from Sochaczew; G. Surface of the steel sample after 4th period of exposure in Warsaw. Brushed section; H. Surface of cast-iron plate after 4th period of exposure in Sochaczew. Ground section; I. Surface of cast-iron plate after 4th period of exposure in Warsaw. Ground section; J. Cross-section of cast-iron sample from 4th exposure period in Sochaczew. Ground section; K. Cross-section of steel sample from 4th exposure period in Sochaczew. Ground section; L. Cross-section of cast-iron sample from 4th exposure period in Warsaw. Ground section.

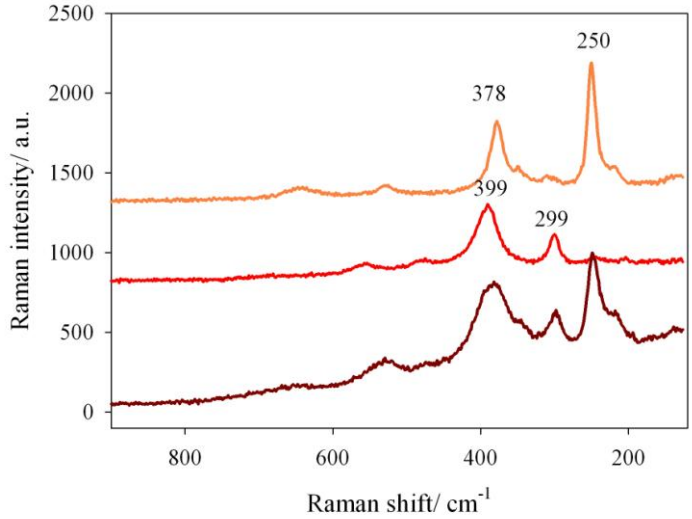

Fig. 2. Raman spectra obtained for various corrosion products on steel from Sochaczew: lepidocrocite Fe(O)OH (orange line), goethite (red line), and goethite and lepidocrocite mixture (brown line).

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"Materials engineering methods in the diagnostics of metal works of art and historical heritage objects."

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INTRODUCTION

Materials research, as a part of a separate scientific discipline called materials engineering, comprises an interdisciplinary field of scientific and technological studies with the aim of analysing the impact of the chemical and physical structure of materials on their electrical, mechanical, optical, chemical, magnetic, thermal and surface properties. Materials are studied with the aid of a variety of physical, chemical and mechanical research methods which enable determining both the structure and properties of materials, and most of all the relations between their structure and properties. The objective of such studies is to identify how the structure affects the properties of materials and what are the options to prevent any undesirable changes in their performance (e.g. by changing the structure). They provide an opportunity to develop ways of preparing, using, protecting (e.g. against corrosion) materials with specific performance characteristics.

One of the essential analytical methods is microscopy, and its basic parameter – resolving power which defines the size of the smallest details discernible in the test sample. Although typical optical microscopes have a resolving power of 100 nm, the application of X-ray radiation (electron beam) extends the measuring range down to sub-nanometers. In general, microscopes with an electron beam can be divided into standard and scanning electron microscopes. Standard microscopes analyse a large area of the sample surface and at the same time generate its image. Scanning electron microscopes (SEM) analyse at a given moment a small area that is processed as if it were a point. The image is generated based on the information gathered for each analysed point. The SEM system can be equipped with a number of detectors. The major key detectors include:

- SE (Secondary Electrons) detector of low-energy secondary electrons, emitted from the sample excited with an electron beam, generates an image of the surface topography;
- BSE (Back-Scattered Electrons) detector of back-scattered electrons generates an image of the elemental distribution on the surface. Darker areas represent lighter elements;
- EDS (Energy Dispersive Spectroscopy) detector of electron energy distribution identifies specific elements on the sample surface.

The more advanced the technology have grown, the more complex and dedicated the X-ray methods for materials studies have become. A selection of such methods, based on the application in the conservation of historical heritage objects, is shown in Table 1 where together with the category of the generated data, the type of the generated image is specified: 2D – surface image and 3D – spatial image.

Table 1 X-ray analysis methods for historical heritage objects and works of art

Method	**Acronym**	**Contrast**	**Information**	**Image**
Electron-beam full-image methods				
Macroscopic X-ray radiography	XRR	absorption	electron density	2D
Macroscopic X-ray computer tomography	CT	absorption	electron density	3D
Microscopic X-ray computer tomography	MCT ?-CT	absorption	electron density	3D
Phase-contrast X-ray computer tomography		refraction	phase transition	3D
X-ray laminography		absorption	electron density	3D

Electron-beam scanning methods				
Method	**Acronym**	**Contrast**	**Information**	**Image**
Microscopic X-ray fluorescence mapping	μ-XRF	elemental	elemental composition	2D
Microscopic XANES mapping *(structure near the edge of X-ray absorption)*	μ-XANES	chemical state	compound composition	2D
Microscopic X-ray diffraction mapping	μ-XRD	crystalline structure	phase composition	2D
Macroscopic X-ray fluorescence scanning	MA-XRF	elemental	elemental composition	2D
X-ray photoelectron spectroscopy	XPS	elements and bonds	elemental and compound composition	2D
Confocal X-ray microfluorescence	CXRF	elemental	elemental composition	3D
Micro-XRF-XRD tomography		elemental crystalline structure	elemental composition phase	3D

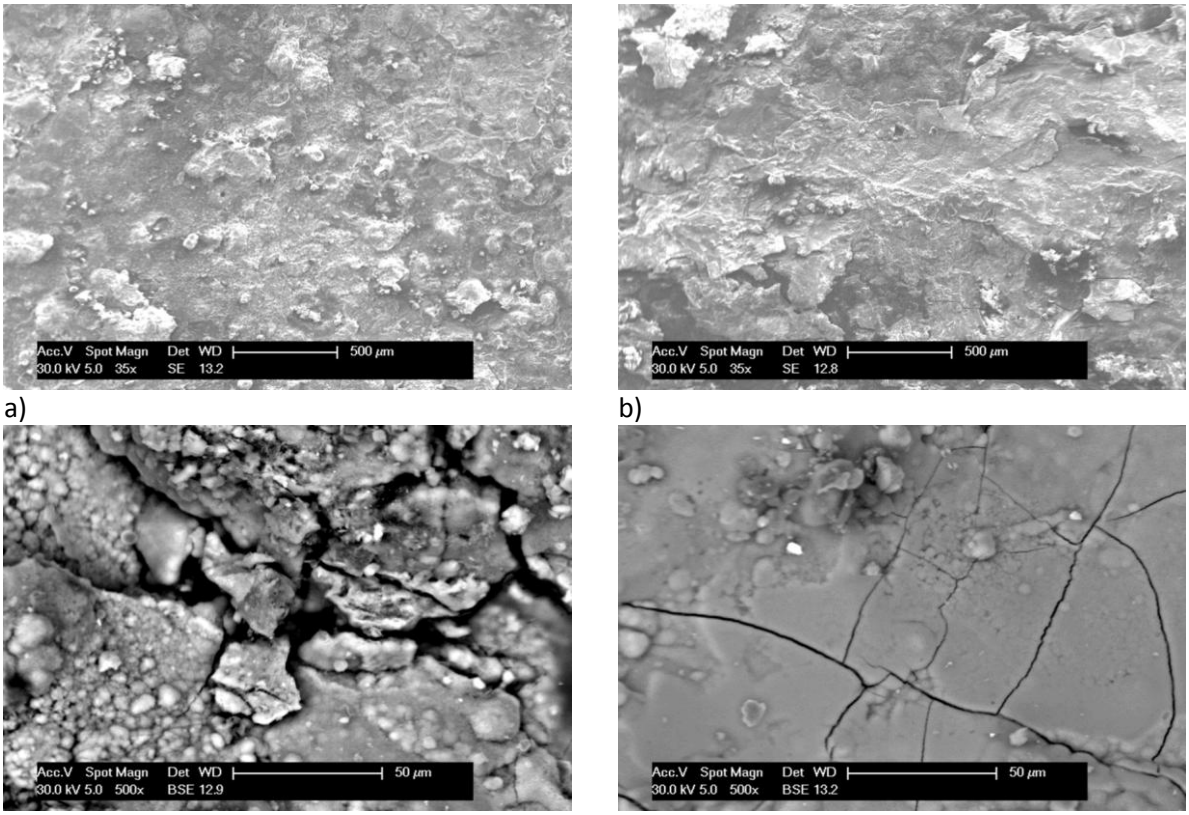
This article presents the results of SEM EDS studies of corrosion build-up layers on the surface of historical and laboratory metal samples exposed to atmospheric conditions at the locations of the Railway Museum in Warsaw and Sochaczew. The studies were carried out using a scanning electron microscope XL30 LaB_6 (Philips). Surface maps (photographs) were recorded based on secondary electron (SE) and backscattered electron (BSE) detection. The microscope has been provided with an energy dispersive x-ray (EDAX) spectrometer with an energy resolution of 138 eV whose essential component is the Si(Li) detector. The SEM–EDAX (SEM-EDS) system enabled qualitative and quantitative micro-scale analysis of the surface. Three readings were taken for random sites on the sample surface.

HISTORICAL SAMPLES

Fig. 1 shows SEM images of the surface of steel samples collected from the steam engines subject to exposure in Warsaw and Sochaczew. Based on the general SEM topography images (SE) it is not possible to distinguish for which locations the surface of the corrosion products is more complex. The topography of corrosion layers and corrosion pits is similar (Fig. 1a, 1b). However, the enlarged BSE images (elemental distribution) show that the surface layer on the samples from Warsaw is much more complex and varied as regards material (Fig. 1c, 1d). This partially confirms the conclusion based on the earlier visual analysis of the optical images of the samples. However, this conclusion does not refer to the thickness of the corrosion layers as it only comprises the surface characteristics of the materials.

Location in Warsaw

Location in Sochaczew

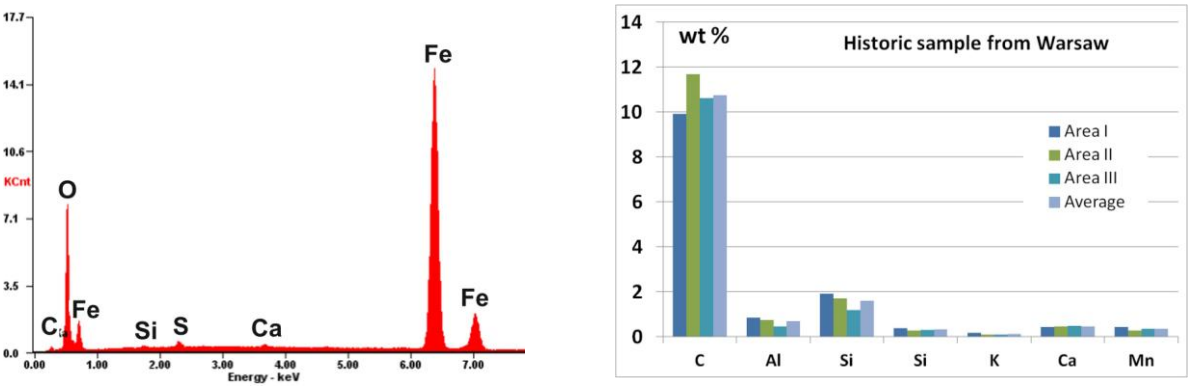


a) b)

c) d)

Fig. 1. SEM images of the surface of historical samples: a, b) SE mode – surface topography; c, d) BSE mode – elemental distribution on the surface.

Fig. 2a shows the standard EDS profile with energy peaks for the specific elements present on the surface of the analysed historical sample. The resulting data distribution for the three analysed points is not large, and the greatest values have been determined for small concentrations of elements (Fig. 2b).

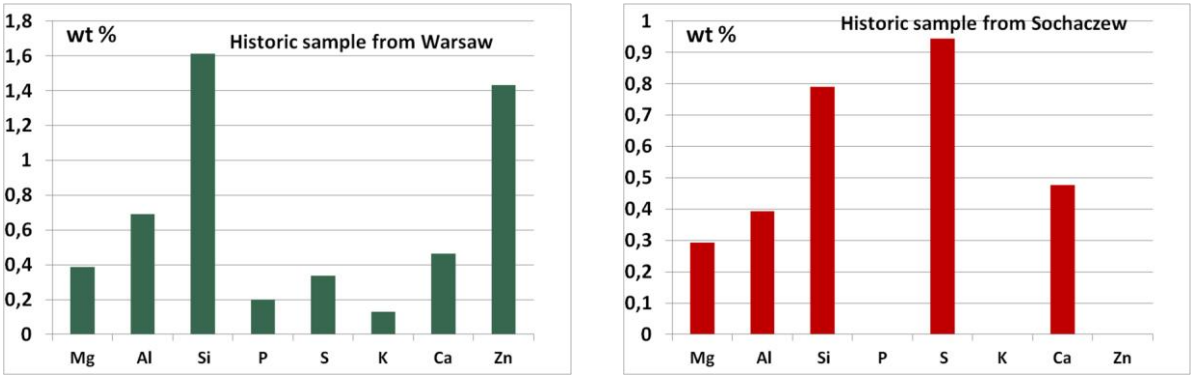


a) b)

Fig. 2. Examples of the SEM EDS concentrations of the specific elements on the surface of the historical metal sample from Warsaw: a) EDS spectrogram; b) data dispersion for three random surface areas.

Fig. 3 shows the results of the concentration analysis of the selected elements on the surface of the samples from Warsaw and Sochaczew. The averaged SEM EDS results show explicitly that the

concentration of such elements as Mg, Al, Si, P, K, Mn and Zn is greater on the surface of the historical samples from Warsaw. The sample from Sochaczew was also identified to have a similar Ca concentration and nearly three times as high S concentration.

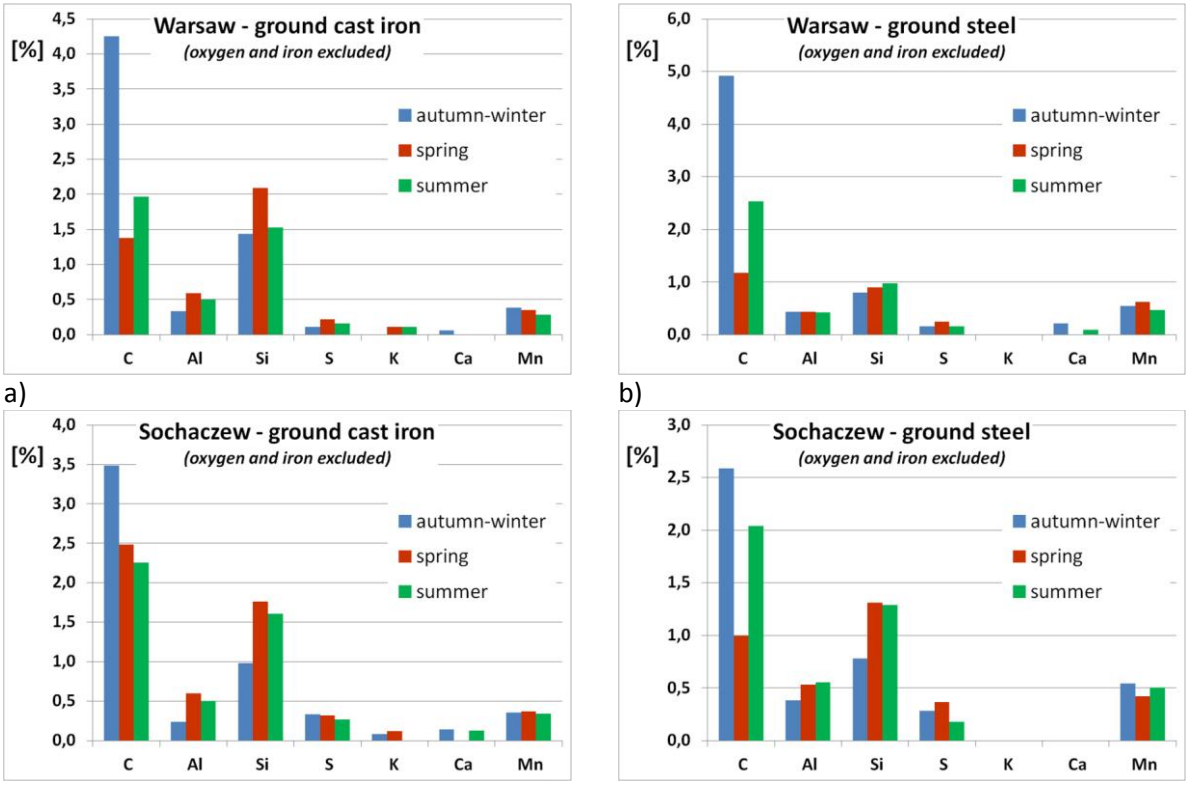


a) b)

Fig. 3. SEM EDS concentrations of the selected elements on the surface of the historical samples: a) from Warsaw; b) from Sochaczew.

LABORATORY CAST-IRON AND CARBON STEEL SAMPLES

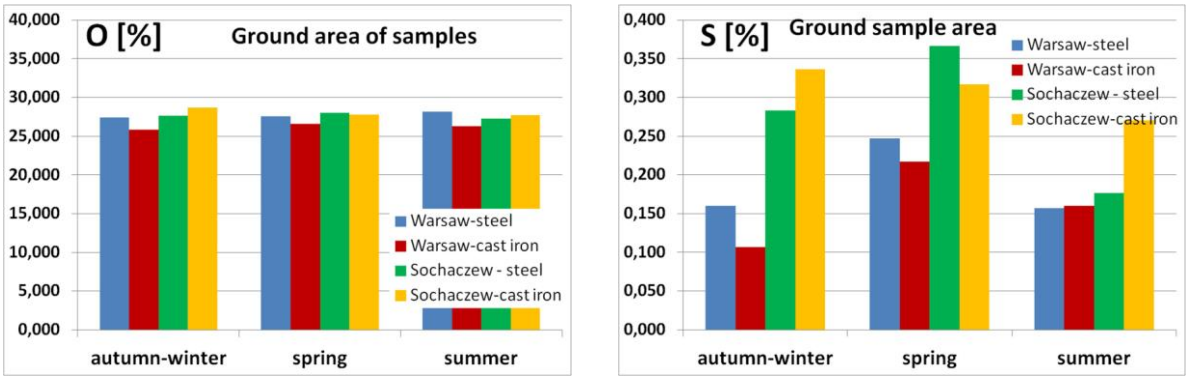
Out of a hundred of images and elemental distribution analyses we have selected the most relevant ones in terms of the sample surface topography and development of corrosion products (Fig. 4, 5).



a) b)

c) d)

Fig. 4. SEM EDS concentrations of the selected elements, excluding large concentrations of oxygen and iron, on the surface of the laboratory samples: a) from Warsaw; b) from Sochaczew.



a) b)

Fig. 5. Concentrations of the selected elements related to the development of corrosion on the samples (ground areas) for different exposure periods: a) oxygen; b) sulphur.

Fig. 4 shows the changes in the concentration levels of the selected elements on the surface of the ground samples where large concentrations of oxygen and iron were excluded for improvement of graph reading. The ground section of the samples was selected as a representative area. The results for the sections subject to brushing did not deviate significantly from the results presented in the graphs, except for only noticeably greater corrosion changes on the brushed sections which have disappeared in time. All the graphs in Fig. 5 show considerably greater carbon surface concentrations in winter, which are additionally higher in Warsaw than in Sochaczew. The concentration of carbon decreases in spring, and then slightly increases in summer. The cast-iron samples have been observed to have a higher concentration of silicon which is related to the presence of this element in the original alloy. The samples subject to weathering in Sochaczew have been observed to have a higher concentration of sulphur. The changes in the elements relevant to the development of iron corrosion were illustrated based on sulphur, a component of all identified corrosion products, and oxygen, for subsequent comparative analysis with the Norwegian results from periodic measurements. As can be seen in the graphs which show periodic oxygen concentrations (Fig. 5a), oxygen is more intensely bonded to the substrate on the carbon steel samples which is evidenced in the microscopic and SEM images, not included in this article due to the limited printing space. On the other hand, Fig. 5b shows considerably larger sulphur concentrations on the samples from Sochaczew. Nevertheless, such differences tend to disappear gradually and level out in summer.

SUMMARY

Despite certain limitations (sensitivity), scanning laser microscopy with an electron energy distribution function (SEM-EDS) proved useful in a series of analyses of the samples of materials used for constructing steam engine components. As a result of the measurement error analysis it was possible to make direct measurements of surface concentrations of the elements present in the encrustation developed in various time frames. The fact that it was impossible to identify any sulphur compounds using Raman spectroscopy might be explained by sulphur concentrations, determined at the level of < 1%, compared to large oxygen concentrations.

The created database contains hundreds of X-ray images of the corroded surface of the samples, comparative material-centred (type and roughness of the substrate) descriptions of elemental concentrations and location of the exposure sites. These data, when combined with the results of the parallel LIBS and Raman spectrometry studies, should provide the basis for the preparation of maintenance procedures.

"Laser-Induced Breakdown Spectroscopy (LIBS) in Qualitative and Quantitative Analysis of Works of Art."

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EXECUTIVE SUMMARY

The work starts with short characteristics of laser-induced breakdown spectroscopy as a quasi-NDE method for art works examination. Attention was paid to the possibility of conducting stratigraphic research and some examples were shown. The objects of studies were: Putto sculpture with laurel branch from the Wilanów Palace Museum, made of a copper-based alloy, metal artefacts from the area of Jasna Góra and Wilanów, as well as historic and contemporary samples made of steel and cast-iron which are prone to corrosion processes. A relative contents of elements and composition of layers at various depths of the objects were determined, as well as authenticity of parts of the sculpture, and the impact exerted by environment on steel and cast-iron items. Also a possibility of analysing spectroscopic data with the use of Principal Component Analysis (PCA) method was presented. The results confirm high usability of the method in examinations of items of cultural heritage and contemporary items made of metal.

INTRODUCTION

In laser-induced breakdown spectroscopy (referred to hereinafter as laser spectroscopy or **LIBS**), the analysis of plasma radiation is used in relation to the plasma created by a laser pulse focused on the surface of the examined item. To put things really short, the LIBS method consists in evaporation of a small amount of examined material with the use of a high-energy laser and in creating plasma which emits continuum and line radiation. The analysis of the line radiation emitted by plasma enables identification of elements contained in the examined sample.

The intensity of plasma-creating radiation should reach at least 0.1 GW/cm^2 (usually 1-10 GW/cm^2) on the surface of the sample. The energy of absorbed laser radiation causes heating, melting, and evaporation of a solid body (but the sample may be also a fluid or gaseous body), and then dissociation of particles and ionisation of atoms. The evaporated and ionised material mixes with gases of surrounding atmosphere, and plasma is created of temperature from 10^4 to 10^6 K. In such temperature, plasma emits radiation with continuum spectrum (bremsstrahlung and recombination radiation) as well as line radiation characteristic for elements (atoms and ions) forming plasma. The analysis of line radiation enables identification of elements contained in the examined sample. Given the assumption that the plasma composition corresponds to the composition of the sample (so-called: stoichiometric ionisation – it is the case for energy density on a sample of 1GW/cm^2), it is possible to obtain quantitative information.

A review of works on LIBS method applications in many fields of science, industry, environment protection, safety, was published in [1]. Essential characteristics of the method and physical phenomena occurring in a typical LIBS experiment were presented by the author in [2], and in [3,4,5] – the results of LIBS examinations of various historical items. In this work, the results of examination of metal items are described. A detailed description and parameters of the experimental system may be found in [2,3,5,6]. A part of results presented in the work is described in more detail in [7].

MEASUREMENT SETUP AND EXAMINED ITEMS

In the studies, a Quantel/BigSky Brio laser was used, with the following parameters (energy/duration, wavelength): 12 mJ/4 ns/266 nm (examination of works of art) and 70 mJ/4 ns/1064 nm (examination of steel and cast-iron plates). The signal was registered with the use of ESA 4000 spectrometer. The measuring range of the spectrometer was 200-780 nm, and resolution $\lambda/\Delta\lambda$~20000. The spectrometer was equipped with a detector – Kodak ICCD 1001 camera. A diagram

of the measurement setup is presented in Figure 1, while pictures of examined items are presented in Figure 2.

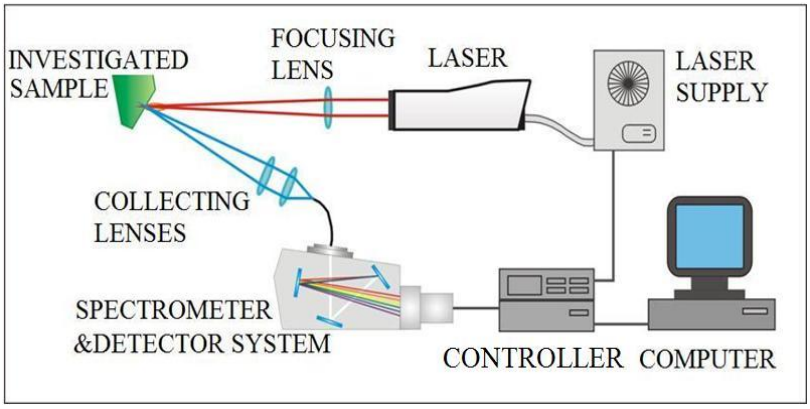


Fig.1 Diagram of the measurement setup

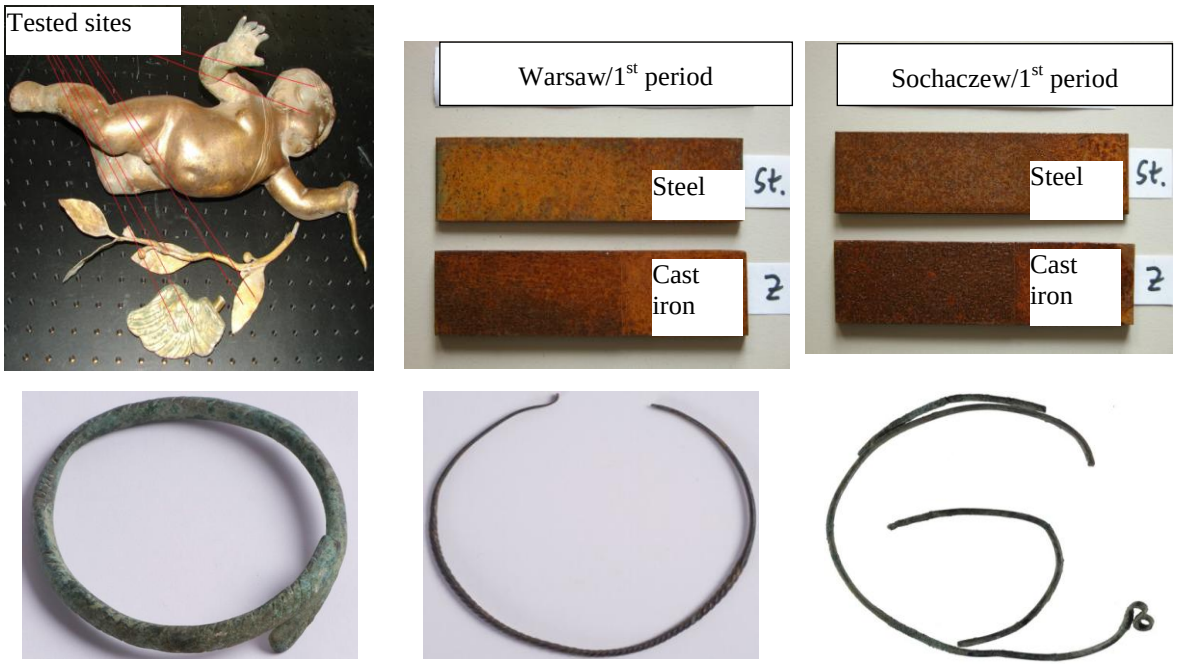


Fig.2 Examined items (from top left corner): Putto with laurel branch, plates from iron alloys exposed to corrosion processes, and medieval jewellery (bracelet, necklace, bow)

METHODOLOGY

The research was conducted in such a way so that from a couple to a couple of dozen laser pulses were fired at the selected sites of the items (at the same spot of a given item), and each time the plasma radiation spectrum was registered. It enabled to determine chemical composition of contaminations, relative thickness of encrustations contaminating surface of the item, and also distribution of the content of matrix elements in the external layer of the item. The results were shown in figures presenting ratios of spectral lines of elements present in the encrustations, and the relative content of matrix components in the outer layer; they were also shown in the form of tables with comparisons of calculated contents of elements creating alloys of which the examined works of art were created. Most LIBS results were also subject to the Principal Component Analysis (PCA) [8-11], the results of which confirmed the conclusions based on LIBS measurements.

RESULTS OF MEASUREMENTS

Examination of the sculpture

The LIBS examination of the PUTTO sculpture (Figure 2) was conducted at many sites of the statue. The measurements were taken at several sites on the sculpture's body (head, temple, right calf and left thigh), on the wing and on the stem and a leaf of the laurel branch. The spectra obtained in result of measurements on the body, wing and some sites of the leaf revealed very similar composition. The sculpture's surface is covered with encrustation (layer) which comprises mostly sodium, calcium, aluminium and lead. It is presented in Figure 3a.

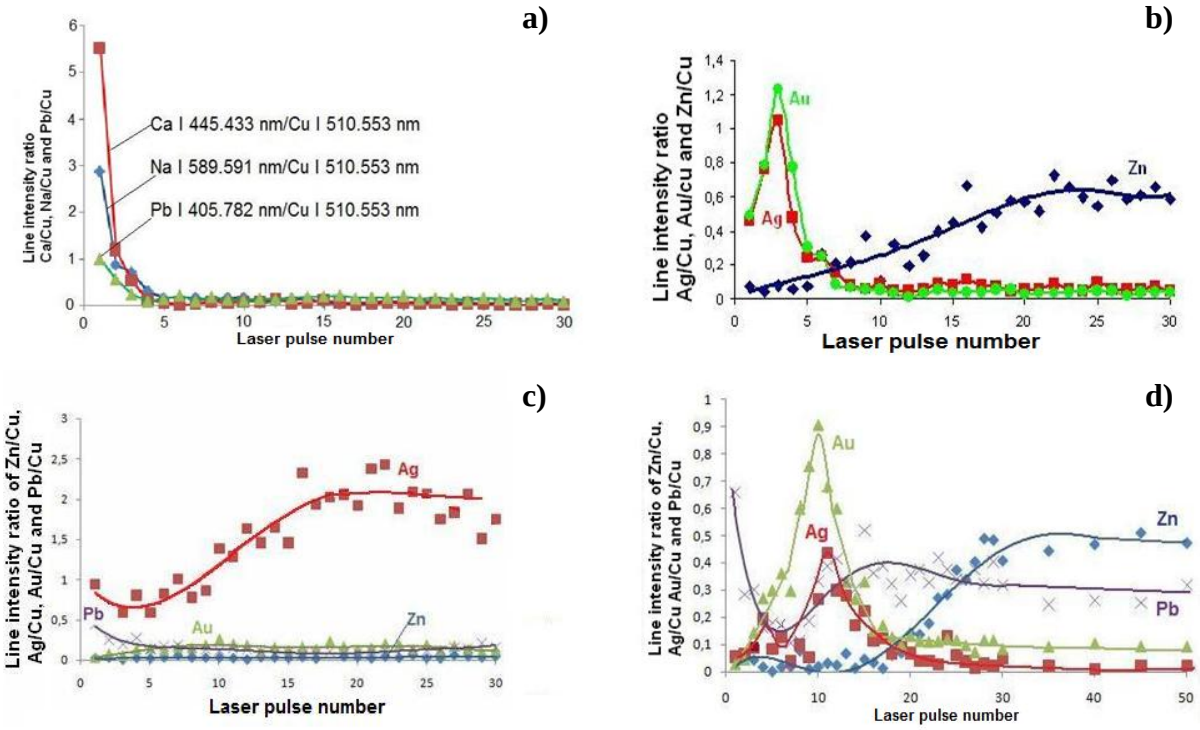


Fig. 3. LIBS of the Putto sculpture. a) Typical stratigraphic distribution of "environmental" encrustation on the surface of the leaf of the laurel branch covered with a painting layer, b) stratigraphic distribution of silver, gold, and zinc in the outer layer of the laurel branch's leaf not covered with a painting layer, c) stratigraphic distribution of zinc, silver, gold, and lead in the outer layer of the cupid sculpture's body (head of Putto),
d) stratigraphic distribution of zinc, silver, gold, and lead in the outer layer of the Putto sculpture's wing.

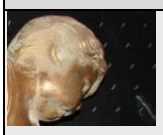
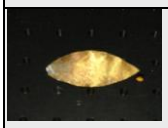
The curves in Fig. 3 were performed within the coordinates composed of the number of laser shots (increasing numbers correspond to the depth measured from the surface of the item) – the ratio of intensity of the spectral line of a given element to the intensity of the Cu I 521.80 mm copper spectral line (copper was selected as reference as it is the main element of the matrix of which the Putto sculpture was made).

In Fig. 3a, the change of relative sodium, calcium, and lead content is presented from the outer layer of the laurel branch's leaf towards its inside at a site covered with a painting layer (that is a mixture of barium and strontium yellow on the substrate of titanium white). Such distribution is typical for all components of the sculpture (the statue's body, laurel branch, cupid's wing) and it concerns such elements as sodium, aluminium, calcium, lead, magnesium. These elements gather in the very thin layer on the very surface (up to 50 µm at average) and influence the stratigraphic distribution of elements which were intentionally placed in the outer area of the sculpture.

It was illustrated in Figure 3b, where diagrams are shown, presenting changes of the relative content of zinc, silver, and gold in the laurel branch's leaf at a site not covered with the painting layer. In the beginning, a growth of relative silver and gold content is visible, the layers being covered by a coating comprised of sodium, calcium, magnesium, zinc, and lead (in Fig. 3a, distributions of Na, Ca and Pb were shown). Since the Ag/Au layer is rather thin, subsequent laser shots at the same spot are accompanied by a decrease of intensity of gold and silver lines. On the other hand, the course of changes of the signal originating from zinc, which constitutes one of the main components of the sculpture's material (brass) evidences the fact that after approximately 30 laser shots (~ 250 - 300 µm), after penetrating layers covering the main material of the sculpture, its original composition is revealed. In Figure 3c and 3d in turn, stratigraphic distributions of zinc, silver, gold and lead are presented in two components of the sculptures – in the outer layer of the cupid's head and in the outer layer of the wing. It stems from these diagrams that individual components of the sculpture were made of different materials (brasses of different composition). It is evidenced first of all by a different course of changes of zinc and lead content, but also by a different signal level originating from gold and silver. The layer of gold on the wing is two or three times thicker that on the statue's body, and there is much more silver in the outer layer of the cupid.

After stratigraphic examination, quantitative measurements of chemical composition of the sculpture's individual components were executed. With the use of calibration curve method and having bronze and brass standards at disposal, the composition of alloys forming the individual components of the sculpture was determined. The result is presented in table 1.

Table 1. Chemical composition of the Putto sculpture, % of mass

Sculpture component	**Cu**	**Sn**	**Zn**	**Pb**	**Ag**
	**23.5±4.8**	**0.3±0.2**	**0.01±0.004**	**0.2±0.01**	**76.0±14.7**
	**85.9±6.5**	**0.9±0.4**	**11.6±1.5**	**1.4±0.2**	**——**
	**81.3±9.73**	**0.4±0.6**	**17.9±2.2**	**0.4±0.1**	**——**

The above chemical composition values were calculated for the depth of approximately 300 µm (30th laser shot at the same site of the sculpture). What attracts attention in data presented in the table is a fairly high uncertainty of the measurement, especially in the case of a little concentrations of a matrix component, e.g. for tin in the wing and the leaf or tin and zinc in the head of the Putto statue.

The results show that individual components of the sculpture were made of different materials. Since there are no exact data related to the history of the sculpture, which many a time left the Wilanów Palace and which belonged to various owners, one may assume that not all components were made in the same time or that they are not original components.

Examination of medieval jewellery

Examinations of items presented in the last row of the Figure 2 were conducted in analogical manner as in the case of Putto sculpture. The components of medieval jewellery were covered with significantly thicker encrustations. The information from before the research suggested that all the

items were made of brass, but initial measurements revealed that various alloys were used to produce them. After stratigraphic research, which revealed that distributions of elements present in the encrustations are similar to distributions from Fig. 3a, chemical composition of alloys comprising the components of medieval jewellery were determined. As in the case of the sculpture, calibration curves for brasses and bronzes were used to calculate the composition. The results of calculations are presented in table 2.

Table 2. Chemical composition of medieval jewellery, % of mass

Item	Cu	Sn	Zn	Pb	Fe
	82.3 ±9.05	16.1±3.39	0.07±0.04	1.47±0.26	0.46±0.01
	84.4±12.67	0.56±0.18	15.1±2.87	0.01±0.003	0.1±0.035
	66.8±8.0	17.5±4.7	12.45±2.7	3.05±0.33	0.22±0.11

From results presented in table 2 it stems that the bracelet was made of bronze, the necklace – from brass, while the bow – from red bronze (an alloy of copper containing comparable concentrations of tin and zinc). Detailed results of examination of the sculpture and jewellery may be found in the work [7], summarising the results of LIBS research conducted for works of art made of metal within the MATLAS project.

The results of analysis of LIBS spectra conducted with the use of PCA method [8] confirmed the conclusions derived from the LIBS research. The idea of the PCA may be explained as reduction of many input variables, which may be sometimes correlated in an unclear way, to a significantly lower number of new, non-correlated variables, so-called principal components. Unfortunately, the reduction of variables takes place at the cost of decreasing the information resources contributed by input data, which means that the first, most important principal components do not describe the overall variability of the input data, while they may describe the resources of the input set in a sound manner. However the total of variances of all principal components is equal to the total of variances of the input set. The transformation procedure to determine the principal components is designed in such a way that the first principle component would explain the broadest part of variability of the input data, the second one would explained somehow lesser part, and so on. It is assumed that in order to correctly describe the input data set, two first principal components should describe approximately 70% of variability (variances) of the input set [9,10,11]. The new variables in the PCA, that is the principal components, do not necessarily need to have a physical interpretation – they create, so to speak, a virtual space where we may describe our variables and input data easier and where their structure and mutual interrelations will be easily detected. The whole PCA and the results presented in subsequent figures were performed with the use of Unscrambler X software [12]. Results for the artworks are shown in Fig. 4.

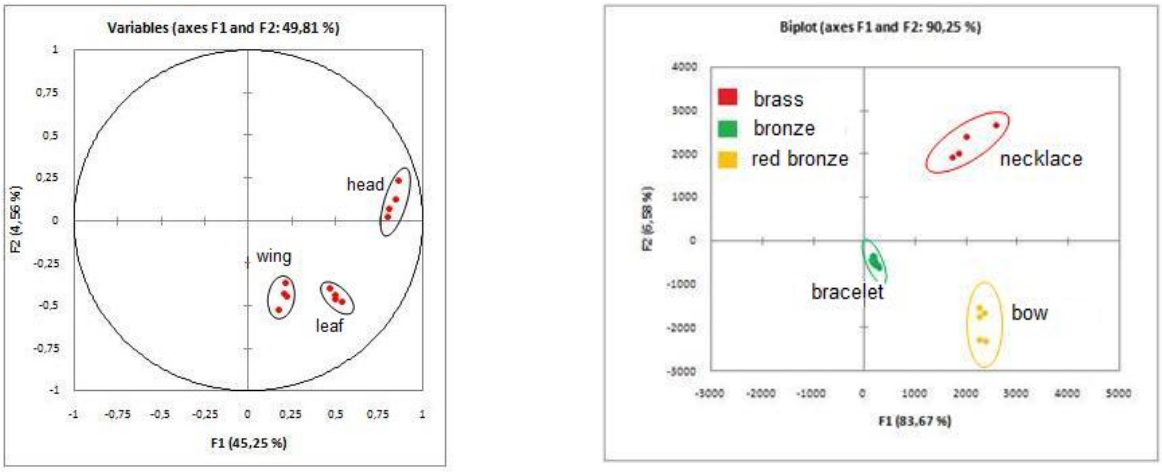


Fig. 4. PCA of the sculpture's component alloys (on the left) and medieval jewellery alloys (on the right).

Examination of steel alloy plates

Examinations of samples made of steel and cast-iron, exposed to environmental corrosion processes in Warsaw and Sochaczew within 4 quarters of the "Save from Corrosion" project (respectively 1st, 2nd, 3rd, and 4th period of research) were conducted within the same experimental setup as in the case of examination of metal works of art. Each of samples had brushed and ground area. Stratigraphic examinations were conducted in both areas of each sample, after exposing the samples to environment influence for 3, 6, 9, and 11 months (for each location).

Typical LIBS spectra of steel and cast-iron samples are characterised by a very large number of iron lines and spectral lines originating from contaminations and encrustations. Differences between subsequent shots in such spectra are difficult to notice. In Figure 5, two sections of LIBS spectra were shown for the area of 390 - 400 nm, obtained from one steel sample exposed for 3 months in Warsaw in 1st and 15th shot at the same spot. Basic differences in both spectra consist in significant growth of intensity of the iron lines in relation to the intensity of the calcium line (red colour in the Figure). An increase of Fe lines intensities is visible on the left side of the calcium line 393.4 nm.

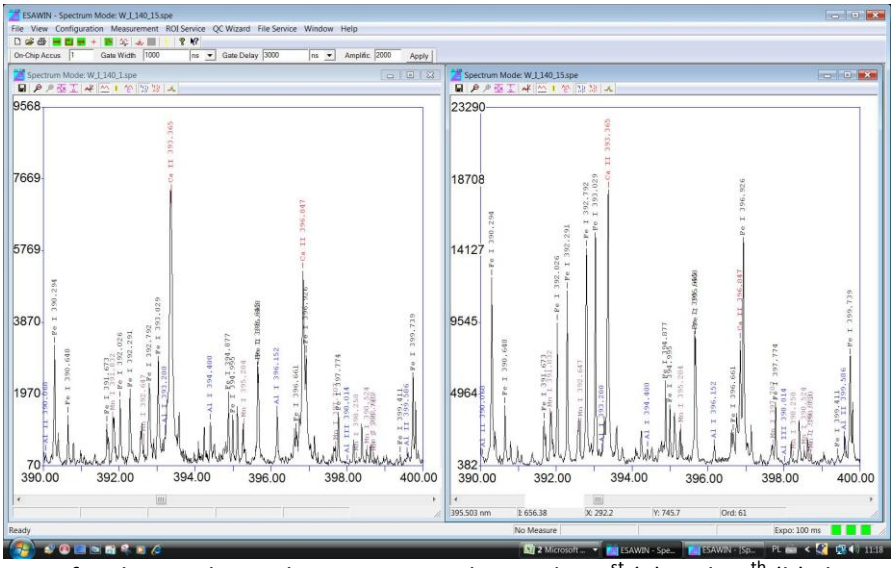


Fig. 5. LIBS spectra for the steel sample in Warsaw, obtained in 1st (a) and 15th (b) shot

After processing hundreds of such spectra (within a range from 200 – 780 nm) obtained from the samples exposed for the almost whole year (11 months), stratigraphic distributions of 15 elements in encrustations created on the surface of the samples were achieved. An example of comparison of

sodium, calcium and barium stratigraphy, which were always present in surface layers, were shown for ground areas of steel samples in Fig. 6.

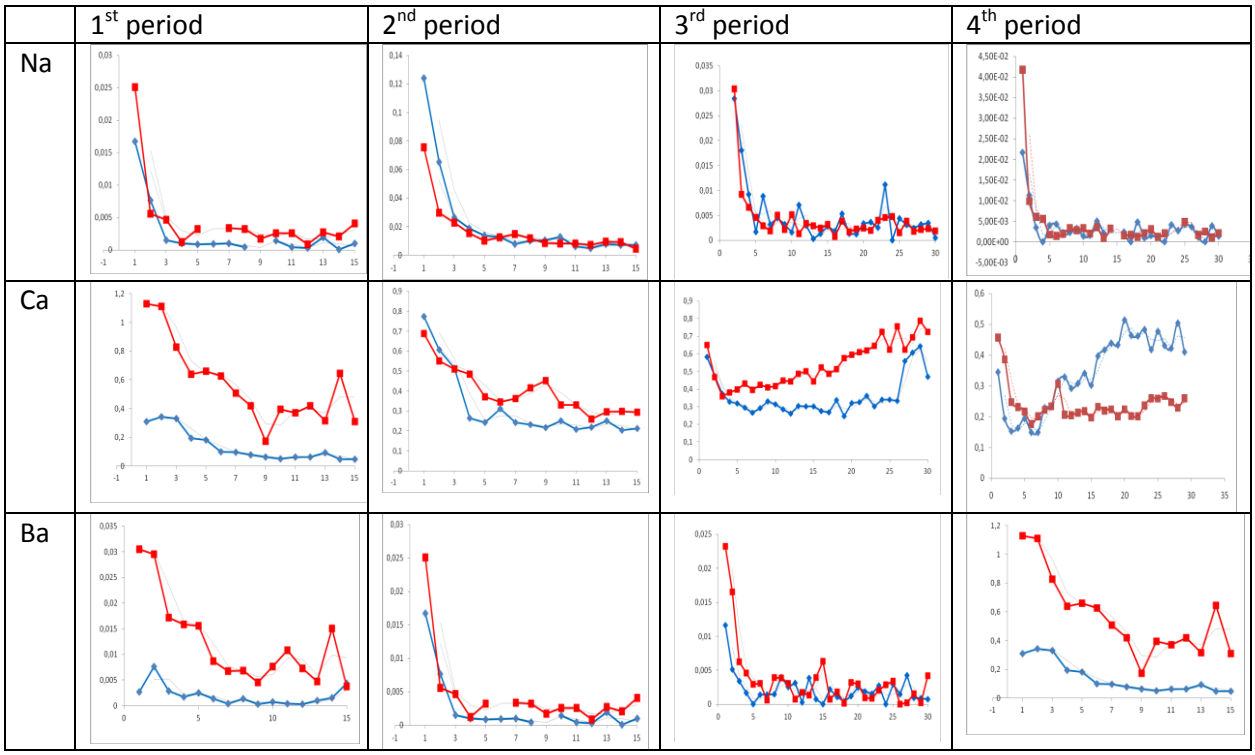


Fig.6 Ratios of intensity of selected lines of sodium, calcium and barium, to the iron line (vertical axis) over subsequent laser shots (horizontal axis) for ground steel samples exposed to environmental influence in 1st, 2nd, 3rd and 4th measurement period (quarter) in Warsaw (red) and Sochaczew (blue)

The analysis for all 15 elements leads to following conclusions (Fig.7):

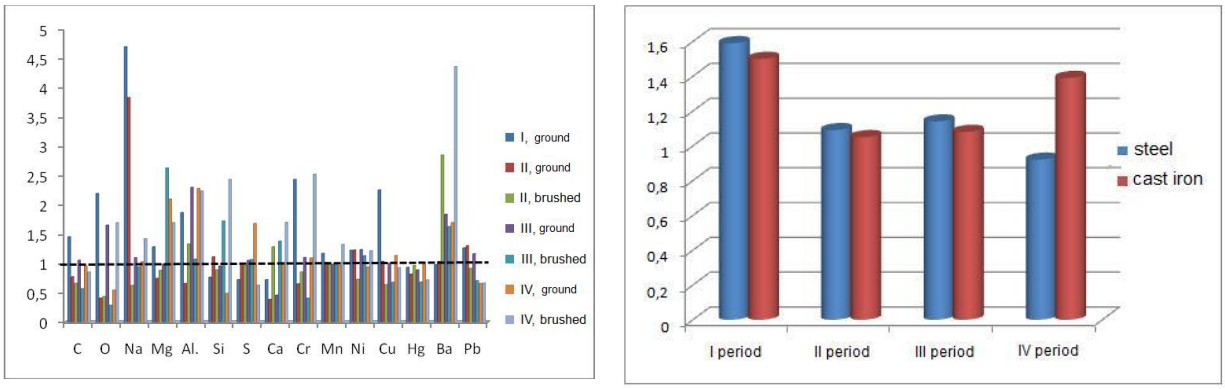


Fig. 7 Comparison of relative encrustation thickness ratios for cast-iron samples and steel samples for Warsaw and Sochaczew: for individual elements (on the left), and in summary (on the right)

- the average thickness of encrustation is higher in brushed area than in ground area,
- In the 1st , 2nd and 3th measurement periods there are thicker encrustations on steel samples but with a tendency to equalizing with time, and in the 4th period we witness a growth of encrustations on cast-iron samples

The PCA applied to LIBS spectra obtained from various samples in subsequent measurement periods clearly evidences that the processes of corrosion and encrustation depositing on the surface of samples proceed in different way in Sochaczew and Warsaw and also within a given sample's ground and brushed areas (despite the fact that the distance between those two areas is a couple centimetres). An example of the above situation was presented in Fig. 8 for samples exposed to environmental influence in Warsaw.

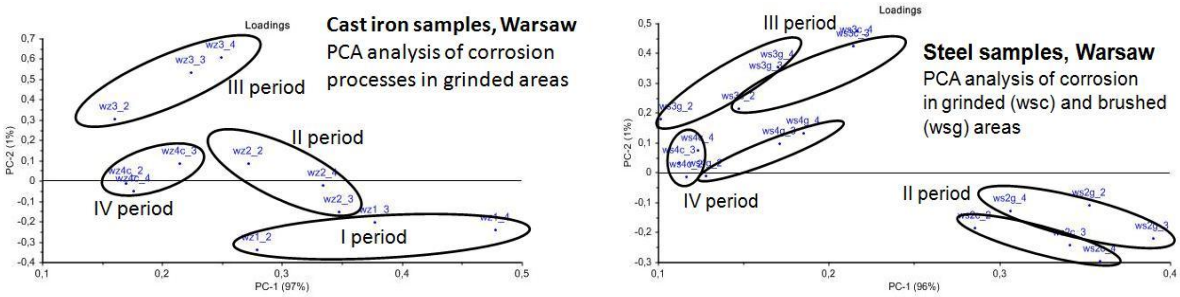


Fig. 8. PCA for samples exposed for 1 year in Warsaw

CONCLUSIONS

The analysis of measurements of historical and contemporary metal items with the use of LIBS method leads to the following conclusions:

- LIBS method is suitable for quick analysis of chemical composition of surface layers of metal objects
- In many cases, a quantitative analysis is possible
- Stratigraphic measurements make it possible to determine distributions of major constituents in the surface layer, in some cases also in quantitative terms.
- In combination with PCA, it is possible to estimate the similarity and diversification of corrosion processes in samples from steel alloys, both in terms of samples' location, as well as the structure of their surface.

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"Summary and analysis of the instrumental examination results under the project "Save from Corrosion"

Marek Strzelec, Military University of Technology in Warsaw

INTRODUCTION

The significant environmental pollution, and in particular air pollution, causes the generation and development of ongoing corrosion of metal heritage objects of technique. Therefore they must undergo periodical conservation treatments which requires in-depth knowledge of the corrosion processes, their origins and effects. This is an interdisciplinary insight into the long-term and ongoing recording of the factors underlying degradation as well as into the types and extent of the changes resulting from the environmental conditions.

This article is an attempt at the analysis and summary of the instrumental examination results for the historical metal samples collected from the actual exhibits at the Warsaw Railway Museum and the laboratory cast-iron and carbon steel samples exposed directly near the objects in two locations: Narrow-Gauge Railway Museum in Sochaczew and Warsaw Railway Museum. The artificial metal samples were exposed to external conditions over a period of one quarter, half-year, 9 months and 11 months, covering all seasons. These studies were performed in addition to the analysis of concentration and deposition of harmful pollutants present in the atmosphere (SO_2) and solid particles (PM10) carried out using passive samplers installed by the Norwegian Institute for Air Research (NILU) from Oslo.

The analyses described in this article were completed based on Raman Laser Spectroscopy, Laser-Induced Breakdown Spectroscopy (LIBS) and Scanning Electron Microscopy (SEM-EDS). Prior to their completion, microscopic surface samples were collected for stratigraphic analysis of the corrosion layers and for microchemical tests of ion composition. This methodology was successfully applied in previous analyses of archaeological objects and historical heritage items exposed to atmospheric conditions prior to their conservation [1-4].

ANALYSIS OF METHODS AND MEASUREMENT CONDITIONS

A detailed description of the applied measurement apparatus, measurement methods and results can be found in other articles in this collection [5-7]. However, the summary and analysis of the obtained results focused on those factors which can have impact on how any data discrepancies or lack of the expected information are evaluated and resolved. This is illustrated below.

Laser-Induced Breakdown Spectroscopy (LIBS) was used in the project to determine the elements present on the surface and carry out a stratigraphic analysis of the corrosion layers on the samples. This method enables identifying the elements present in the analysed material based on the interpretation of the emission spectrum of laser-induced plasma. The qualitative and quantitative analysis of the concentration of the specific components is based on the comparison of the intensity of the characteristic emission spectral lines of each element with the intensity of the strong emission line of the element prevailing in the analysed material. In the described experiments iron, the essential component of cast-iron and carbon steel, was the prevailing element. It should be noted that large fluctuations of the intensity of analytical lines are possible even with small changes in the intensity of plasma-inducing laser radiation, which can be affected by self-absorption of radiation and external measurement conditions, e.g. air humidity and dust level. The concentration of elements in the analysed plasma can be different from that in the matrix sample, as their thermodynamic parameters, such as heat of vaporisation, specific heat or ionisation energy, are different. Furthermore, the intensity of a spectral line depends not only on the concentration and properties of the element emitting the line, but also on the concentration, even trace quantities, of other elements present in the sample. Measurements are frequently subject to such limitations as the spectrum of

wavelengths of the spectrometer detector which is an important factor in UV measurements where strong spectral lines of non-metals are mixed with strong fluorescence of samples. As a result, despite the fact that LIBS measurements are highly sensitive (to a single ppm), its accuracy and precision are usually not greater than several percent.

Scanning electron microscopy with electron energy dispersion (SEM-EDS) has much lower sensitivity than LIBS, in most cases at 0.1% of the composition of the analysed material. The concentration analysis of elements is a direct measurement, which also covers the determination of the iron percentage which was the reference element in the LIBS analysis. This prevents an easy direct quantitative comparison of the quantitative data concerning the concentration of each element present in the surface layers on the samples. If we also take into account different experimental conditions (atmosphere/vacuum) and different probing sites on the samples, the comparative analysis must obviously be carried out with utmost caution. In the analyses referred to in this article the experimental variables were eliminated by comparing data ratios for different materials or exposure locations. Although it was not possible to check the quantitative data, it enabled a successful comparison of qualitative evaluations and determination of trends related to the weathering periods and exposure locations.

The project also involved Raman laser spectroscopic analyses, and in principle its modification – micro-Raman spectroscopy, where a spectrometer coupled with a confocal microscope and micrometric table for accurate positioning of the samples were used. Raman spectroscopy is not a quantitative method and it is not suitable for metal identification, however, it enables identifying chemical compounds formed on the surface of the samples. The major limitation in this method, due to the small intensity of Raman radiation, is the necessity of determining the relevant radiation spectrum against the background of fluorescence emitted by the samples. It often requires greater power of probing laser radiation which causes the heating of sample surface and possibly thermal decomposition of less stable compounds.

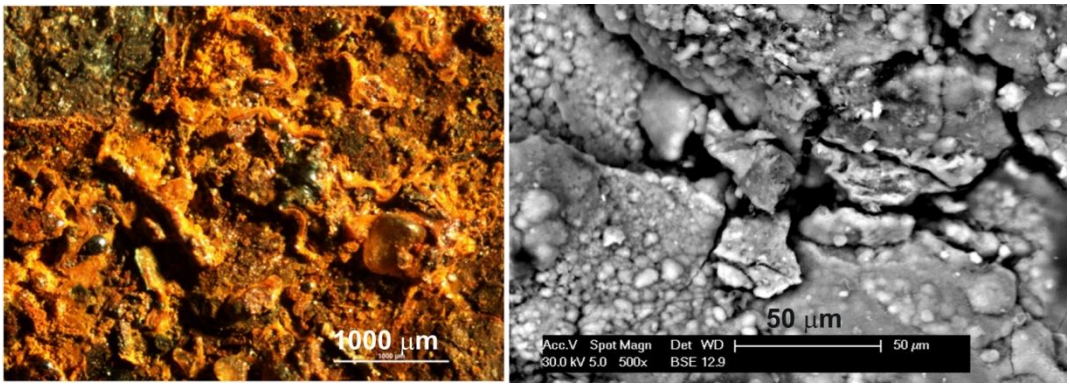
Microchemical tests of the samples provide information about the ions present in the corrosion products on the surface of the analysed samples. Thus, they can be used as a starting point for further, more complex instrumental examination. However, it should be stressed that there are very large differences in the sensitivity of chemical reactions depending on the tested ions which is particularly inconvenient when their percentage in the analysed material is low.

At the same the analyses of the deposition of gas and solid atmospheric pollutants, carried out by NILU specialists, provided a variety of relevant information about the concentration of the corrosion components, mostly sulphur dioxide (SO_2), and ion composition of aerosols. The comparative analysis of the results obtained by the two teams should take into consideration the following two most significant factors. Firstly, the passive samplers applied by NILU were screened from rain, snow and partially from wind. On the other hand, the laboratory metal samples, subject to instrumental analysis, were placed in open air, on the roof of the museum exhibits (steam engine, train car). Secondly, in the NILU laboratories the total build-up within a given period was analysed, while the measurements carried out by the Military University of Technology (MUT) covered only the surface. In the latter case, some comparative data were obtained from the LIBS stratigraphic analysis which enabled tracing the changes in the concentration of each element across the corrosion and deposits layers.

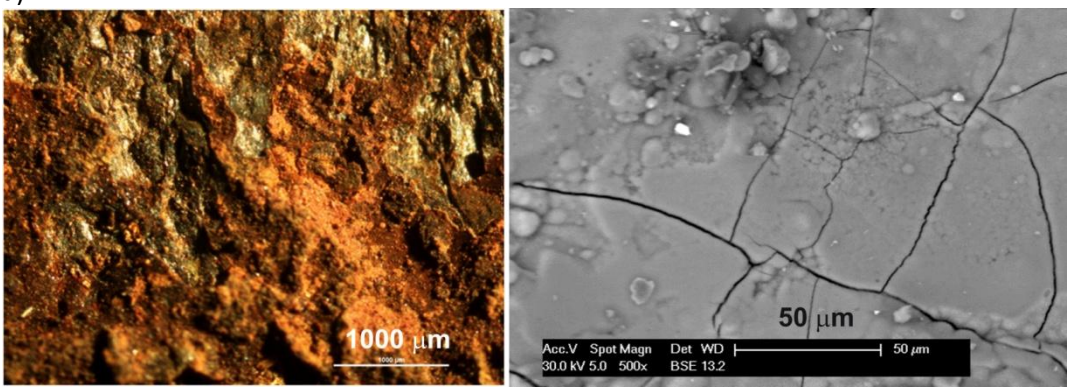
ANALYSIS OF THE RESULTS FOR THE HISTORICAL SAMPLES

Each set of the samples from Warsaw and Sochaczew was collected from the sheet-metal coating of steam engines exhibited in Warsaw and Sochaczew for at least 30 years. There are reasons to believe that these materials were maintained in good condition throughout the operation of the steam engines. The corrosion process progressed during the storage of the steam engines in the museums in Warsaw and Sochaczew in places of losses of the protective paint layer. The type of carbon steel used in the sheet-metal elements should be similar.

The visual assessment of the sample surface, based on the microscopic optical and SEM images (Fig. 1), revealed that the corrosion layers on the samples from Warsaw have more non-uniform surface. However, this provides no evidence as to the thickness of the corrosion products which was estimated based on the sections and scale, and LIBS stratigraphy. The relevant results are shown in Fig. 2. A total of six stratigraphic concentration analyses of the elements specific to the encrustations (Al, Na, Si, Ca, Ba and Pb) were carried out. Fig. 2b shows aluminium which intensely penetrates iron corrosion layers [8]. Both figures show explicitly that the encrustation is thicker on the historical sample from Sochaczew. In the LIBS stratigraphic analysis it corresponds to subsequent (deeper in lateral dimension) saturation of the Al concentration curve in the sample from Sochaczew, as the successive probing laser shots were directed at the same site.

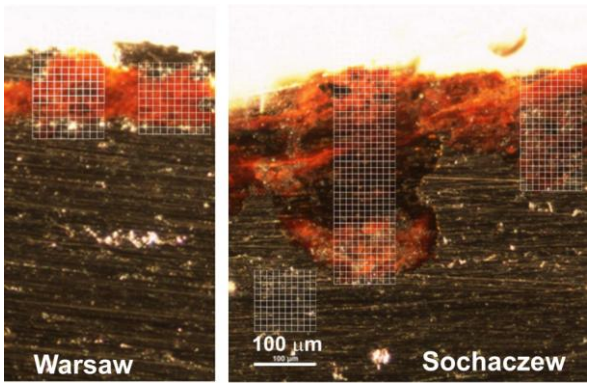


a)

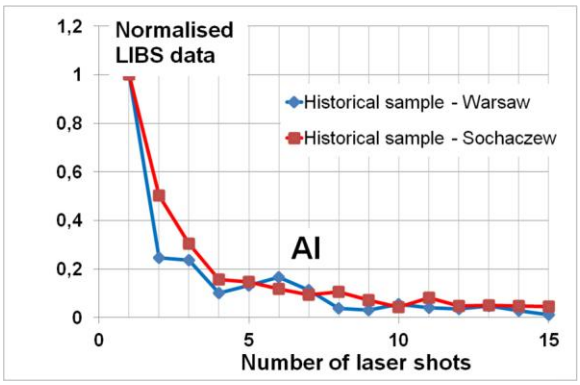


b)

Fig. 1. Optical and SEM surface microimages of the historical samples: a) from Warsaw, b) from Sochaczew. Different areas of the samples were recorded on the SEM and optical images.



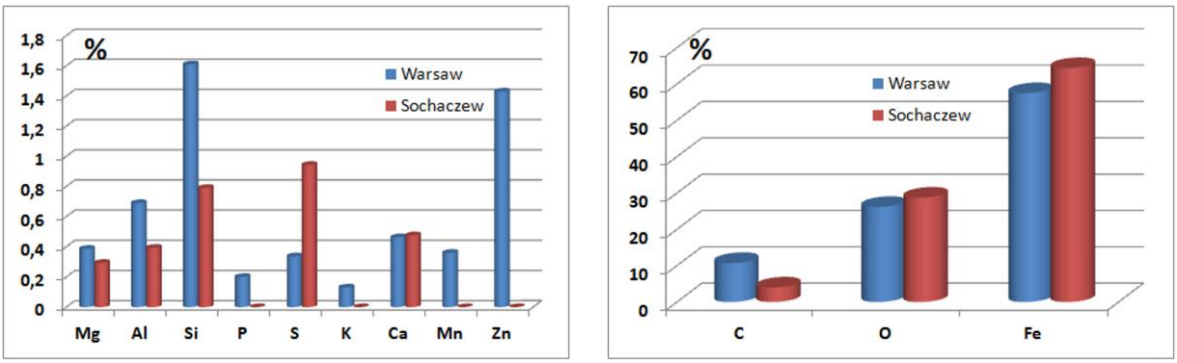
a)



b)

.Fig. 2. Estimation of the thickness of corrosion layers on the historical samples: a) section and the scale, b) LIBS stratigraphy of Al relative concentration.

Other LIBS stratigraphy results, which also provided some relevant information, have not been included in this article due to the limited printing space. With the constant carbon concentration across the profile of the sample from Warsaw, it was observed to decrease down across into the surface structure of the deposits on the sample from Sochaczew. This can support the presence of carbon black on the surface. On the other hand, very irregular stratigraphic profile of oxygen and sulphur can indicate that ionised atoms from the corrosion compounds containing these elements, non-uniformly distributed, quantitatively minimum and different as regards their composition, were registered in the LIBS spectrum. This explains that S^{2-} ions were directly detected microchemically in the corrosion samples in both locations and no iron sulphides were identified in the Raman spectra (sensitivity). With the unknown original composition of the substrate materials in both samples, interesting is the profile of chromium concentration. The increase in the concentration down across the surface layer can indicate its presence in the original alloy of the historical sample from Sochaczew in amounts greater than those resulting from the atmospheric pollution. On the other hand, the slight decrease in the chromium level in the historical sample from Warsaw can indicate the deposition of contamination emitted by the Luccini Steelworks (previously Warsaw Steelworks) [9].



a) b)

Fig. 3. SEM-EDS concentrations of the selected elements on the surface of historical samples: a) less than 2%, b) more than 2% of the composition.

The comparison of the surface concentrations of the selected elements in both locations of the Railway Museum, measured based on the SEM-EDS method and separated with respect to their percentages, are shown in Fig. 3. The results explicitly show the greater surface concentration of Mg, Al, Si, P, K, Mn and Zn on the historical samples from Warsaw. It should be noted that no P, K, Mn and Zn were detected on the sample from Sochaczew, but this can be explained by both the sensitivity threshold of the measurement (<0.1%) and the lack of local sources of industrial pollution, such as the Luccini Steelworks in Warsaw. The sample from Sochaczew was also identified to have a similar Ca concentration and nearly three times as high S concentration which supports the results of the SO_2 concentration analysis from the NILU passive probes.

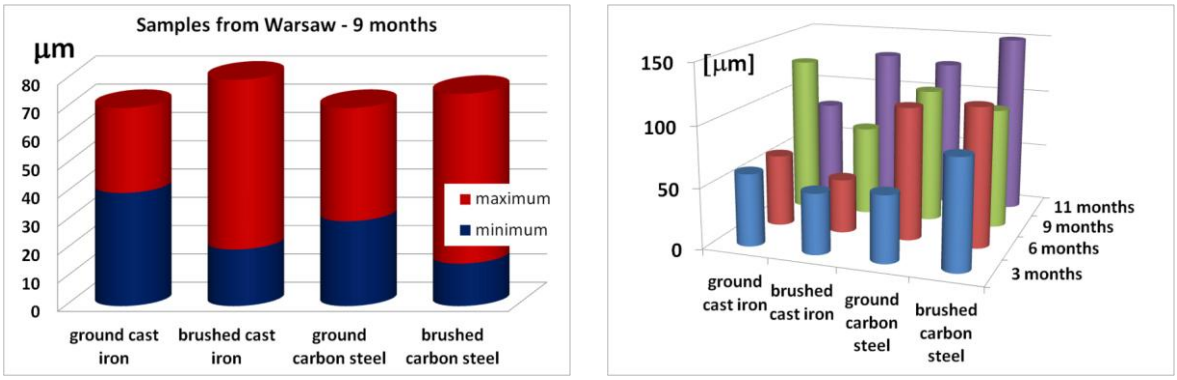
The microchemical tests showed no differences in the ion identification, as the presence of S^{2-} and Fe^{3+} was confirmed for both samples. Such compounds as lepidocrocite [$Fe^{3+}O(OH)$], goethite with the same formula [$Fe^{3+}O(OH)$] and hematite [$Fe^{3+}{}_2O_3$] were identified in both samples based on the Raman analysis. Magnetite [$Fe^{3+}{}_2Fe^{2+}O_4$] was also identified on the historical sample from Sochaczew.

ANALYSIS OF THE EXAMINATION RESULTS FOR THE LABORATORY CAST-IRON AND CARBON STEEL SAMPLES

Each contemporary metal plate was subject to mechanical treatment - one peripheral section was subject to grinding and the other one - central - subject to brushing. One of the sections was used for sample handling, thus fitting, installing in and removing from the measuring apparatus. The metal samples were exposed in two project locations - in Warsaw and Sochaczew - for 3, 6, 9 and 11 months. Following the exposure period, 4x8 mm pieces, intended for stratigraphic grinding (sections)

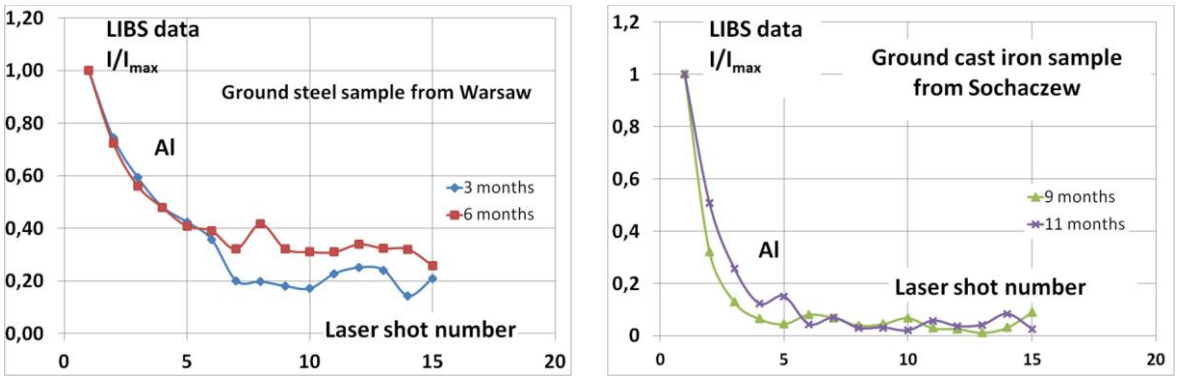
of the surface layers, were cut out using a numerically controlled machine tool from each section subject to mechanical treatment.

The dimensions of the corrosion layers, determined based on the sections, are shown in Fig. 4. The characteristic large range of changes in the layer thickness, corresponding to the surface non-uniformities, is illustrated based on the example of the samples subject to exposure for 9 months in Warsaw (Fig. 4a). The overall maximal dimensions of the corrosion layers are shown in Fig. 4b. However, the sections, underlying the above-mentioned results, are only a small fragment of a larger item, in this case of the weathered steel and cast-iron plates. Thus, the representation and dimensions of stratigraphic layers obtained based on such profiles may, but are not necessarily identical for the whole sample. This causes certain differences in the maximal thickness of the layers, as shown in Fig. 4b. Nevertheless the average thickness of the corrosion layers has been observed to increase - initially more rapidly, and then more slowly. This trend was confirmed by a more precise LIBS stratigraphic analysis as shown in Fig. 5. As in the case of the historical samples, the layer thickness is represented by the observed decrease in Al concentration in the profile.



a) b)

Fig. 4.Analysis of the corrosion layer thickness: a) comparison of the minimal and maximal values on the samples weathered for 9 months in Warsaw, b) summary of the maximal values for the samples from Sochaczew.



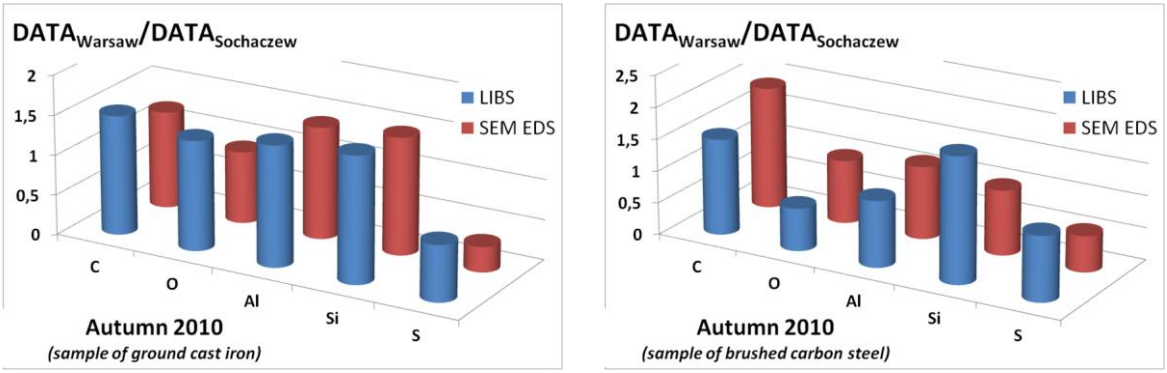
a) b)

Fig. 5.Examples of the normalised LIBS stratigraphic analysis of the corrosion products on the ground metal samples: a) carbon steel exposed in Warsaw in the first two periods; b) cast-iron exposed in Sochaczew in the last two periods.

As can be seen in Fig. 5, the relative changes in the layer thickness in the first weathering periods are noticeably greater compared to the last exposure periods.

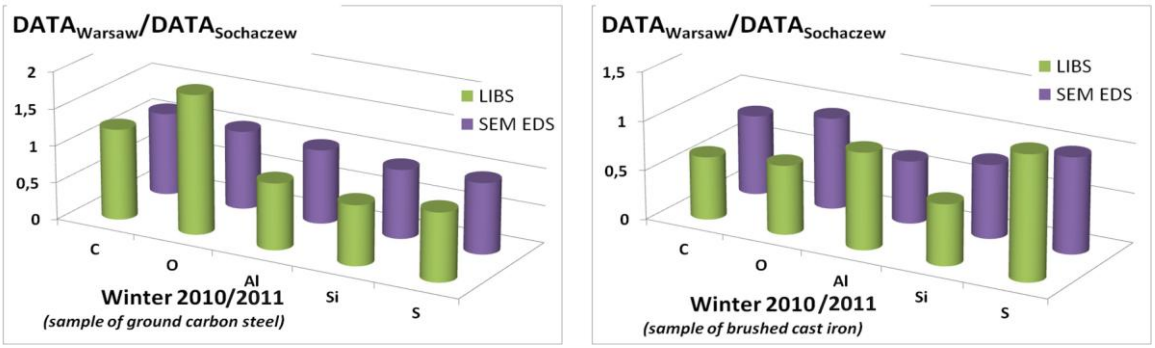
As stressed in the chapter relating to the analysis of methods and measurement conditions, a direct comparison of the LIBS and SEM-EDS concentration levels of the specific elements gave rise to some differences attributable to the principles of measurements. As it was possible to exclude

experimental variables by referring the measurements to the material (steel, cast-iron, mechanical treatment) or the weathering location (Warsaw, Sochaczew), it was decided to compare ratios of the values obtained for each location. Firstly, as the differences in the concentration of the specific elements were greater for both exposure locations than for substrates, and secondly, as it immediately showed the resulting trend (value greater or lesser than one). With several dozen elements detected in LIBS spectra and about 10 elements identified using SEM-EDS (lower sensitivity) it was decided to compare the measurements for two elements highly relevant to the corrosion process, but with significantly different fraction in the build-up - oxygen and sulphur, and three elements present in a majority of solid deposits - carbon, silicon and aluminium. The data for three random sites in the SEM-EDS analysis were compared with the average from the LIBS spectral analysis of 15 probing laser shots. The comparative analysis results for various exposure periods and materials are shown in Fig. 6-8. Conventionally, subsequent exposure periods were matched to the most corresponding seasons.



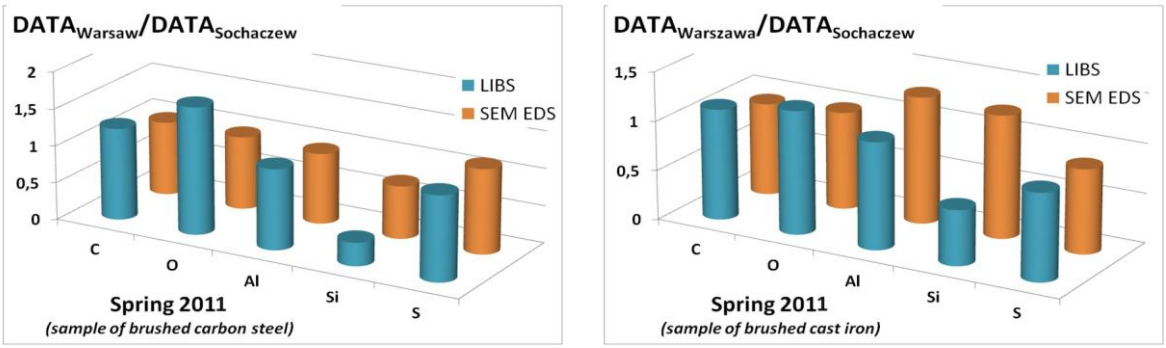
a) b)

Fig. 6. Ratios of LIBS and SEM-EDS results for the samples exposed in autumn 2010. (October – December) in Warsaw and Sochaczew: a) ground cast-iron, b) brushed carbon steel.



a) b)

Fig. 7. Ratios of LIBS and SEM-EDS results for the samples exposed in winter 2011 (January – March) in Warsaw and Sochaczew: a) ground carbon steel, b) brushed cast-iron.



a) b)

Fig. 8. Ratios of LIBS and SEM-EDS results for the samples exposed in spring 2011 (April – June) in Warsaw and Sochaczew: a) brushed carbon steel, b) brushed cast-iron.

When analysing the data shown in Fig. 6-8, the high degree of convergence in most of the compared concentration ratios for the specific elements should be noted. The greatest differences in most diagrams can be observed for oxygen and silicon, and also for carbon and sulphur in autumn 2010. In the case of oxygen it has to be noted that it is present in all the identified corrosion compounds, but in different configurations ($Fe^{3+}O(OH)$, $Fe^{3+}{}_2O_3$, $Fe^{3+}{}_2Fe^{2+}O_4$), which in some point surface measurements and granular structure of corrosion products can be a source of large errors. On the other hand, silicon is present in both metals, and in higher concentration in the cast-iron substrate (greater differences in the diagrams). It is particularly important that each analysis shows the trend in concentration changes for the specific elements as a function of season. It can be seen in Fig. 9 which gives a summary of the analysis and shows the average ratios as defined below.

$$X = \frac{1}{n}(X_1 + X_2 + \cdots + X_n)$$

$$where: X_i = \frac{DATA_{Warsaw}}{DATA_{Sochaczew}}$$

$$i - steel;\ cast - iron;\ subject\ to\ grinding;\ subject\ to\ brushing$$

The highest surface concentration can be observed in autumn for carbon in Warsaw and sulphur in Sochaczew. The data level out in winter and spring, and the carbon concentration in the samples from Warsaw is again higher after summer. The oxygen concentration remains nearly constant in the samples from both locations (ratio ≈ 1) which corresponds to the identification of a single compound - lepidocrocite as the prevailing compound in all the samples throughout the experimental period.

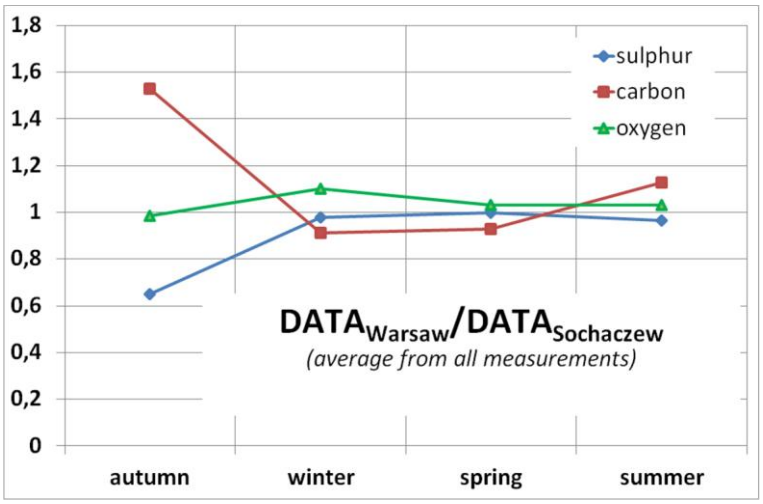


Fig. 9. Ratios of the measurement data for carbon, sulphur and oxygen as obtained from the analysis of the samples subject to exposure in Warsaw and Sochaczew, averaged with respect to both analysis methods and all materials.

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„Study results obtained within the programme entitled "Save from Corrosion" in the context of anti-corrosion protection of metal objects."

Janusz Mróz – conservator of metal works of art.

The programme "Save from Corrosion" is a result of activity of the museum–scientific community, which would like to counteract phenomena of degradation of metal objects of technological heritage. The degradation phenomena themselves were narrowed down to the corrosion processes, while the types of metals subject to examination were limited to iron alloys: steel and cast-iron. The reason for such selection is simple – the programme was created in the Warsaw Railway Museum and the objects the study relates to are antique steam engines and carriages.

The need to conduct research related with the influence of contaminated environment on the corrosion processes taking place in relation to the technological heritage objects has been growing for many years. What was not noticed however was the specificity of issues of such type, and researchers confined themselves only to transferring conclusions from the general research on the corrosion phenomena. Besides, certain theories persisted in relation to anti-corrosion protection methods even from the 19th century.

Corrosion is a process of environment's influence onto specific material placed in this environment. The environment consists of atmosphere, water, soil, but also the outer space may be regarded as environment for a couple dozen years already. The quantity and quality of contaminations occurring in the ambience influence the impact of one and the same environment.

In order to show the complexity of corrosion processes and the multitude of corrosion forms, one usually lists its numerous types. In connection to metals we talk about: 1/electromechanical corrosion resulting from the potential difference of different metals at their point of contact in the presence of an electrolyte, 2/ chemical corrosion resulting from aggressive chemical reactions between the metal and the environment, 3/intercrystalline corrosion attributed to chromium–nickel steels given too high contents of carbon after occurrence of a temperature above 400 0C, 4/pitting, which causes corrosion pits reaching the substrate's interior, and results most commonly from chloride ions penetrating less resistant oxygen layers, 5/crevice corrosion occurring at the points of contact of metals, where the insufficient oxygen results in creation of an anode, and on the verges – a cathode, which results in metal ion flow, 6/ exfoliation corrosion which destroys screw or rivet joints in result of corrosion products encrustation, 7/ stress corrosion causing intercrystalline or intracrystalline cracks in the presence of electro-chemical agents along with mechanical stress, 8/ fatigue corrosion taking place when cyclical stress occurs in an aggressive environment and causing structural cracks.

Finally, some information should be reminded about the sub-surface corrosion, which is also called the filiform corrosion due to the form of corrosion products created under painting layers (or other protective layers). The sub-surface corrosion leads to de-uniting of the protection layer, loss of its continuity and fast development of corrosion processes. The cause of the phenomenon is an inappropriate preparation of the metal surface before spreading the anti-corrosion protection layers or inappropriate selection of protection type and surface layers.

In connection with metal objects of technological heritage we may also encounter weld corrosion occurring after joining metal fragments with the use of welding. Carbides created along the weld in result of a high temperature become the cause of corrosion processes; in the case of arc welding, the alkaline remnants from electrode jackets may react with the subsequently spread painting layers.

In result of welding fragments of metals we may encounter a variant of intercrystalline corrosion – the so-called knife-line attack. The countermeasures applied in such cases include relevant

preparation of joining spots as well as application of low-carbon steels; also the processing of welding spots in the form of mechanical cleaning, cleaning with hot water and drying is significant here. In the case of welding structures, a complex heat processing of welds is often applied.

The main objective of the programme “Save from Corrosion” was the establishment cooperation and exchange of experiences in the scope of applied and planned restoration methods, and guaranteeing preservation of historical heritage objects related with railway industry in a good condition.

Preservation of technological heritage included into broadly understood cultural heritage has become now a social need. The revolutionary influence of technological achievements on the every-day life of people was finally noticed and appreciated. The development of railway industry in particular enabled realization of dreams of an average man – to experience the world through journeys. Nevertheless, the 19th-century industrial revolution in Europe and the United States would not be possible without mass transport of commodities.

It is worth reminding that the history of railway industry started in the beginning of the 19th century and it proceeded without any competition until the period after the World War II. The crisis of railway industry was caused only by car transport, which was perceived as less costly and more flexible. However the growth of crude oil prices showed that there is also a place for fast, advanced railway transport. Along with the speed fascination, there appeared also a fascination and need of acquainting oneself with predecessors of the modern trains, the latter already reaching velocities of couple of hundreds km/h.

The role of the host and coordinator of the programme was performed by employees of the Warsaw Railway Museum, which also rendered available its site and antique steam engines for the purposes of the planned research. Aside from Warsaw, the corrosion study was also conducted at the Narrow Gauge Railway Museum in Sochaczew – a department of the Warsaw museum.

A foreign partner to the programme “Save from Corrosion” was the Norway Institute for Air Research (NILU) from Oslo, whose representative delivered samplers for examination of atmospheric contaminations, which were installed in Warsaw and Sochaczew. The adopted methodology covered the following examinations:

1/ in a yearly cycle – by way of installing samplers separated from the direct influence of rain and snow; subject to examination were samplers installed in Warsaw (Exhibition of Steam Engines of the Railway Museum) and Sochaczew (Narrow Gauge Railway Museum)

The samplers were placed in the beginning of November 2010 at especially developed measurement stations.

2/ in a quarterly cycle equivalent to seasons of the year occurring in our climate zone; subject to examination were samples exposed a/ for a week in a quarter and b/ for a month in a quarter.

The assumptions for laboratory research proposed by the project participants connected with the Military University of Technology and the Faculty of Conservation and Restoration of Works of Art of the Academy of Fine Arts in Warsaw provided for the execution of examinations of the composition of contaminations on the surface of samplers made of steel and cast-iron and installed in Warsaw and Sochaczew for a determined time of exposure:

1st period – October, November, December – autumn season,

2nd period – January, February, March – winter season,

3rd period – April, May, June – spring season,

4th period – July, August, September – summer season.

- the number of exposed samples as well as exposure periods made it possible to examine the corrosion state of the surface of steel and cast iron within the following time (seasonal) sequences both in connection to Warsaw as well as Sochaczew samples:

1/. after 1st period , 2/. after 1st and 2nd period, 3/. after 1st, 2nd, and 3rd period, 4/. after 1st, 2nd, 3rd and 4th period,

5/. after 2nd period, 6/. after 2nd and 3rd period, 7/. after 2nd, 3rd and 4th period,

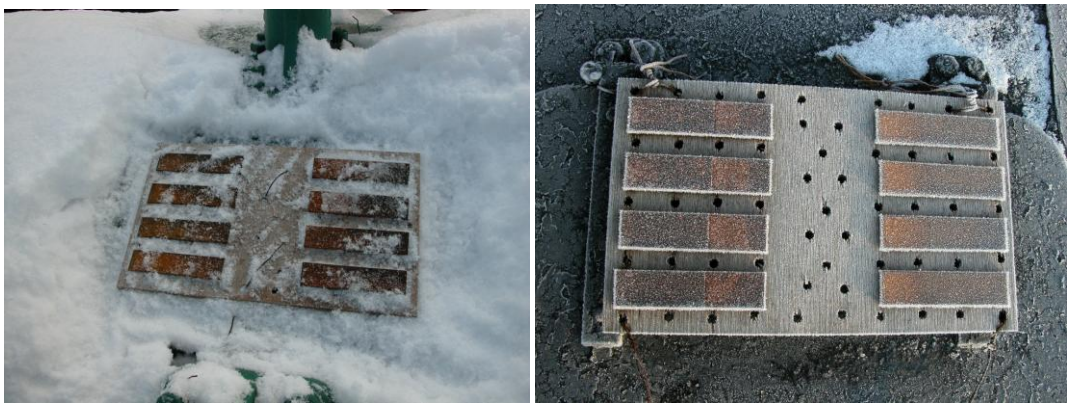
8/. after 3rd period, 9/. after 3rd and 4th period, 10/. after 4th period,

- in addition, all the samples with the size of 10 x 2.5 cm, which were designated for exposure, were divided into three zones: a fragment of surface ground down to the pure metal, a fragment of surface brushed so that the contaminations which had not been permanently tied with the substrate were removed, as well as a fragment without any surface contamination removal processing, which enabled manipulation in the course of the installation and laboratory research.

The above division enabled conducting two times more examinations in the scope of distinction of corrosion processes influence on the steel and cast-iron surfaces in the case of mechanical processing of the surface consisting in grinding and brushing.

- also so-call “historical samples” were subject to examination, that is samples of steel sheets constituting elements of antique steam engines sheeting exposed in Warsaw and Sochaczew.

Photograph 1, 2. Measurement stations containing Norwegian samplers in Warsaw and Sochaczew.



photograph 3, 4. Samplers with cast-iron and steel samplers placed on steam engines in Warsaw and Sochaczew. Period of exposure: October, November, December 2010. State as at January 5th, 2011.

In accordance with the above assumptions, in the end of September 2010, a relevant number of samples of steel and cast-iron were prepared. In the beginning of October, samplers with cast-iron and steel samples attached were placed on steam engines in Warsaw and Sochaczew. In accordance with the schedule, subsequent samples were removed and transferred for examination, and new samples were installed.

photograph 5, 6. Samplers with cast-iron and steel samples placed on steam engines in Warsaw and Sochaczew. After removal of the samples of the 1st period and installing samples of the 2nd period on January 5th, 2011.

A detailed analysis of research results is presented in the articles of Anna Zatorska and Marek Strzelec. The results itself do not leave place for doubts that both conditions in large municipal agglomeration – Warsaw, as well as in a city located away from industrial pollution sources – Sochaczew, independently of the season of the year, cause very fast development of corrosion processes on unprotected steel or cast-iron surface.

The generalized analysis of the research results allows following conclusions:

- encrustation of corrosion products on steel and cast-iron surface shows similar features such as the growth of layer thickness and a similar surface concentration of such elements as oxygen, sulphur, carbon, silicon and aluminium

- distinctly lower growth of corrosion layers occurs on ground steel and ground cast-iron surfaces

- lower encrustation of corrosion layers is also visible on the cast-iron surface in winter season

- the velocity of corrosion layers encrustation in subsequent examination periods decreases, which suggests that thicker layers of rust slow down (?) the corrosion processes.

- analogically to differences in rust encrustation on brushed and ground surfaces, the corrosion pits formed have lesser size in the case of ground surfaces, while they were bigger on brushed ones

- the concentration of large amount of carbon on the sample surface in the autumn season is characteristic for Warsaw due to the type of atmospheric contaminations, while in Sochaczew we observe large amounts of sulphur, probably due to wide usage of carbon stoves heating residential premises in the area.

- the surface oxygen concentration on all the samples is similar, which is a result of the majority of one type of iron corrosion product – lepidocrocite, which in turn makes it possible to confirm an earlier conclusion about the similar character of corrosion processes in all samples subject to examination

- in accordance with data published in the literature, carbon steel samples turned out to be more susceptible to corrosion in both project locations when compared to the cast-iron.

- more developed and thicker corrosion layers occur on the samples of metals from Sochaczew, and the higher surface concentration of sulphur should be considered significant.

- on the samples from Warsaw, there are higher concentrations of carbon and silicon on the surface.

Interesting examination results were obtained in the case of the so-called historical samples. These were samples from the sheeting1 of steam engines, which, after years of service, found rest in museum seclusion. According to information of museum employees, both steam engines have served as exhibits for 25-30 years. It should be assumed then that the corrosion encrustation originates from this very period. The examination results also suggest the following conclusions:

- three times higher concentration of sulphur on the sample from Sochaczew confirms the presence of significant amounts of the element in the atmosphere of the location

- absence of contaminations containing P, K, Mn and Zn on the sample from Sochaczew may indicate absence or unmeasurable amounts of industrial pollution

- the concentration and type of contaminations on both samples seem to confirm the absence of significant changes both in the atmosphere of Warsaw as well as Sochaczew.

It should be stated that thanks to the programme "Save from Corrosion", for the first time ever results were obtained of examinations of basic corrosion processes presently taking place in two environments, which are to a certain degree different in terms of occurring contaminations. The fulfilled research assumptions enable analysis in quarterly periods. A possibility to compare the results of examinations thanks to repeating thereof, on the basis of various methods is an additional value of the programme.

The discussion resulting from the research should last also after its accomplishment, as it enables relevant treatment of the issues related with corrosion processes.

The "Save from Corrosion" is an interdisciplinary programme, and this feature adds value to its substantive assumptions. From the conservatory point of view, the conclusions which were possible to formulate should be divided into two essential groups: 1/ conclusions confirming the hitherto perception of the iron alloys corrosion issues, 2/ detailed results related to protection of metal objects of technological heritage. The conclusions from the latter group should be complemented with suggestions stemming from the executed research, taking into account the influence of moisture (water) on corrosion processes. A serious problem for institutions dealing with metal objects of technological heritage is storage of the objects. Exposition in external conditions, most commonly fates these objects to corrosion threats. A possibility of creation of a friendly atmosphere means "closure" of the objects in pavilions, where we are able to influence the conditions of expositions. Is solution to this problem only a financial issue? Probably in most cases one should start from ensuring relevant funds.

The issue of fundamental importance is anti-corrosion securing of metal surfaces of the objects of technological heritage. The conclusions related to anti-corrosion recommendations in this scope were not subject to programme considerations.

The state of preservation of metal objects of technological heritage in museums dealing with such objects depends on a number of factors: a/ state of preservation of the object at the moment of taking it over by the museum, b/ conservatory – recovery works conducted during the exposition as well as c/ conditions of storage. The issue of storage is fundamental for the purposes of pre-ensuring a relevant conditions for the objects.

It is necessary to determine features of the objects which may influence the necessity of differentiation of storage and exposition conditions.

[1] The jargony term "sheeting" was used to indicate the fact that the samples originated from the steel used in external elements of the steam engines. It was impossible to determine the elements themselves.

The principle of individuality of each of the objects of technological heritage must be constantly adhered to by the administration and substantive employees of museums, which will not enable to duplicate conservation programmes due to a similarity of objects.

For some time already, an important element of designs is anti-corrosion protection of the material. Creators of antique works of art, technological heritage objects or objects being belonging to material culture did not provide for such a need as they simply did not see such a need. The need arose in result of contamination of the environment.

Without conservatory intervention in a short time perspective the nature will do anything to return to its original condition.

The risk the objects of technological heritage are exposed to should be seen as a very real danger of loss of a part of resources. Without relevant anti-corrosion protection, we will be forced to seek remedy in restorations and supplementations, which leads to losing the authenticity of the form and material. And in the case of technological heritage objects, the authenticity is a condition of their exposition and popularization.

Probably it is also the condition of interest on the part of society.

"Measurements of air quality and corrosion risk at the Railway museum in Warsaw."

Terje Grøntoft **-** NILU: Norwegian Institute for Air Research. EEA project "Saved form corrosion"

INTRODUCTION

The "Saved from corrosion" project was performed in cooperation between the Railway Museum in Warsaw and the Norwegian Institute for Air Research. The Railway Museum has many of their important objects; locomotives and carriages, in outdoor storage. Main metals used in historical locomotives are cast iron and steel.

A main objective in the project was to evaluate the corrosion potential of the present ambient atmospheres where the Railway museum objects are stored and the related risk to the preservation of the objects.

To meet this objective NILU is, in cooperation with the Railway Museum, measured the air pollutants that are known to increase steel corrosion and collected information about the climate at two Railway Museum locations. The pollution and climate data were used to evaluate the corrosion potential of the atmosphere and they were correlated with the measured corrosion of steel samples at the locations.

METHODOLOGY

Passive sampling was used to measure and estimate the mass concentration in air of sulphur dioxide, SO_2, and of particulate matter (PM), and the anionic and cationic composition and pH of deposited aerosol. Figure 1 shows the mounting of the NILU passive samplers at the Railway Museum in central Warsaw.

Figure 1: Mounting of the NILU passive samplers at the Railway Museum in central Warsaw.

SO_2 was measured with passive samplers of the badge type (Rosenberg et al. 2009, Ferm, 1991) produced at NILU. The sampler (Figure 2) is cylindrical box with a diameter of 2.5 cm and a height of 1 cm which represents the diffusion length from the top net to the filter in the bottom, which is impregnated with an alkali.

Figure 2: Passive SO_2 sampler

The SO_2 concentration is calculated from the amount of sulphate collected on the filter, which is determined by ion chromatography, from the geometry of the sampler and from the diffusion coefficient of SO_2.

The mass concentration (PM) of aerosol was sampled and estimated with a UNC (University of North Carolina) passive aerosol sampler (Wagner and Leith, 2001). The sampler is cylindrical with a diameter of 15 mm. It consists of a stub and an annular cap with a mesh attached to the top of the stub (Figure 3). The particles are collected by gravity, diffusion and convective diffusion (Leith et al., 2007) and thereafter indentified and their size measured by optical microscopy and the software Image J (2006).

Figure 3: UNC sampler

The mass concentration of aerosol is calculated based on the projected area diameter of each particle, the subsequent estimated aerodynamic diameter and the mass of each particle calculated according to Wagner and Leith (2001).

Field experiments performed by NILU have shown that some underestimation of PM 10 should be expected when using the UNC samplers outdoors in an urban environment.
The badge samplers for SO_2 and aerosol mass concentration were placed during the outdoor exposure in a sample holder as shown in Figure 4.

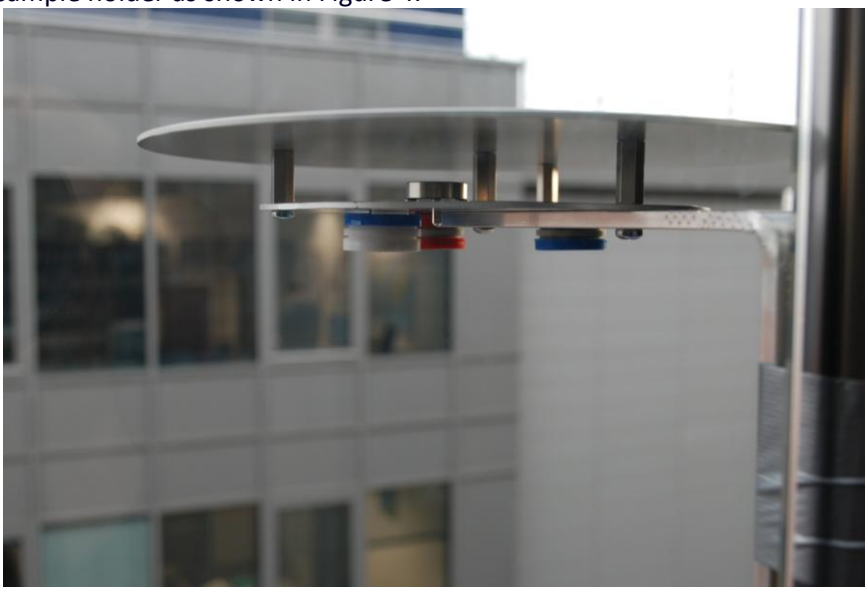


Figure 4: Mounted passive SO_2 and UNC samplers

The anionic and cationic composition of aerosol was measured by passive sampling on a glycerol impregnated Teflon filter with a diameter of 12.5 cm, subsequent washing in deionised water and analysis by ion chromatography. The pH was measured in the washing water with a glass electrode. The filter was fastened horizontally on the lower plate in the larger filter holder shown in Figure 1.
One prepared aerosol filter was stored in the lab in its plastic package during one month and analysed with the same procedure as for the exposed samples.

The four measurement periods started 2nd Nov 2010, 12th January 2011, 30th March 2011 and 29th June 2011. The measurement time was one month for the passive sampling of SO_2 and of aerosol chemical composition, and one week for the passive sampling to estimate aerosol mass concentration with the UNC sampler.

In addition annual sampling of soling and ionic composition of deposited aerosol was performed with IVL Teflon filter samplers, placed in sheltered position inside a box with the dimensions: W = 0.5 m; L = 1.0 m and H = 0.5 m, with a roof with a width of 0.7 m at a distance of 0.2 m above the box (Figure 5). The analysis was performed by the Swedish Environmental Institute, IVL.

Figure 5: IVL passive Teflon samplers, used for annual sampling of aerosol in sheltered position
The passive sampling of all the components: SO_2, aerosol composition, aerosol mass concentration and soiling was performed sheltered from rain. The annual measurement of aerosol composition and soiling was also shielded from wind.

Three parallels of carbon steel, DC01, samples of dimension 15 x 10 x 0.1 cm with the typical reported composition: C = 0.05 %, Mn = 0.20%, P = 0.01%, S = 0.01%, N = 0.003%, Al = 0.04%, were exposed for 10 months at both locations. The steel plates were weighed before exposure and weighed again after exposure, after stripping with Clark's solution. The weight loss due to corrosion was measured as the difference in weight from before exposure to after exposure and stripping.
The measurements were performed on two stations located outdoors, one at the Railway Museum in central Warsaw and one at the Railway Museum location in the small town of Sochaczew 50 km west of Warsaw.

Climate data, relative humidity and temperature, were collected from the Warsaw Targówek meteorological station (Warszawa Targówek meteorological station, 2011) via the internet and were used for bout locations.

MEASUREMENT RESULTS

All the measurement results are given in Appendix no.1, except the results from the eight monthly sampling of aerosol with the IVL samplers, which were not yet available from the laboratory at the time of writing this report.

The average concentrations of SO_2 measured over the four periods was 8.2 µg m^{-3} in Warsaw and 12.9 µg m^{-3} in Sochaczew. The average concentrations of SO_2 measured for the winter, i.e. over the two first measurement periods, were 10.1 µg m^{-3} in Warsaw and 19.1 µg m^{-3} in Sochaczew.

Values of total particulate matter (PM) in the range 20 - 50 µg m^{-3} were measured at both sites in the winter periods, but increasing to values of ~ 100 - 160 µg m^{-3} in April and July, with the lower value of 98 µg m^{-3} being measured in Sochaczew in July. The annual average concentration of particulate matter with a diameter smaller than 10 µm (PM10) was 16.5 µg m^{-3} and 15.5 µg m^{-3} in Warsaw and Sochaczew, respectively. This constituted ~ 20 % of the total annual PM, but ~ 30 % in the winter (November and January) and ~ 15 % in the spring/summer (April and July) at both stations.

Figure 6 and 7 show the measured concentrations of SO_2 and PM for the four measurement periods.

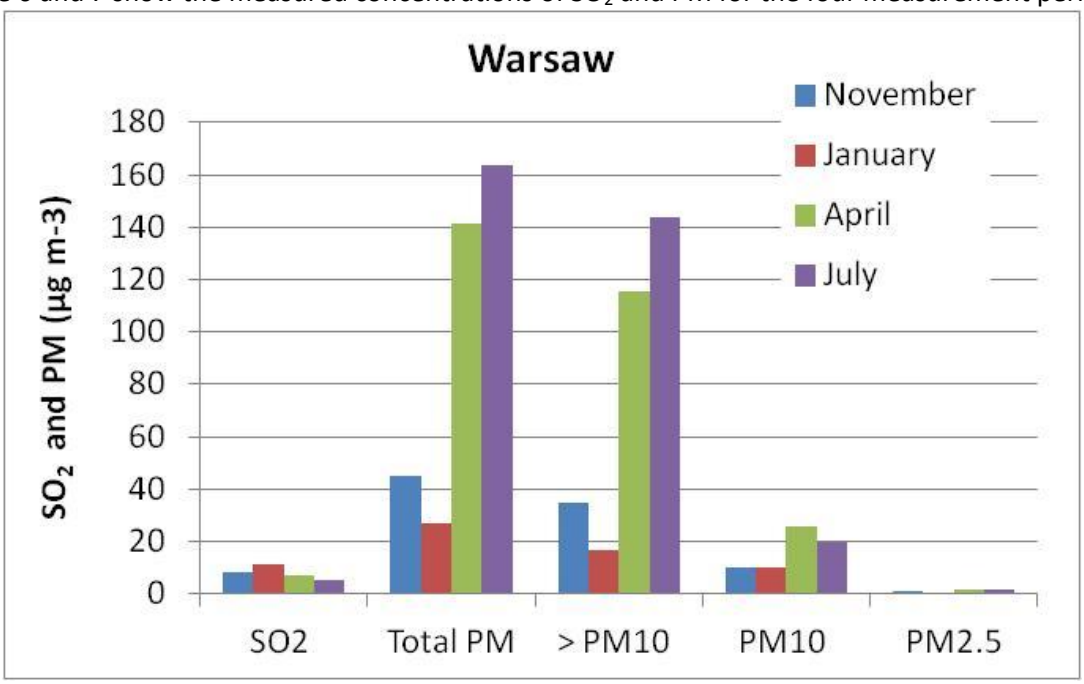


Figure 6: SO_2 and PM concentrations measured in central Warsaw

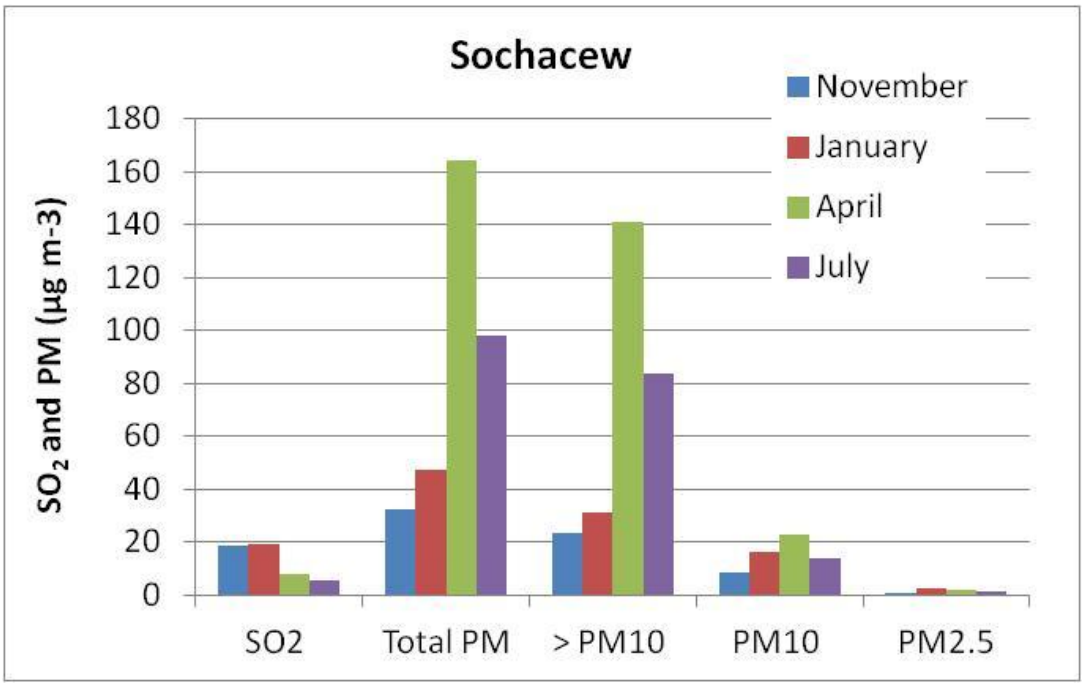


Figure 7: SO_2 and PM concentrations measured in Sochaczew

Figure 8 to 11 show the measured composition of the deposited aerosol at the Warsaw and Sochaczew locations reported as the average milligram (Figure 8 and 9) and the average mol atomic charge multiplied with 1000 (Figure 10 and 11) of the deposited ions in the aerosol per square meter

per day during the one month of measurements. The missing anions in the analysis, necessary to obtain ionic balance, are represented by hydrogen carbonate, HCO_3^- in Figure 10 and 11. Carbonates are expected to be present in significant amount, but cannot be measured by the ion chromatography method used for the elemental analysis. pH values from 5.18 to 5.31 and from 4.89 to 5.09 were measured in central Warsaw and Sochaczew, respectively.

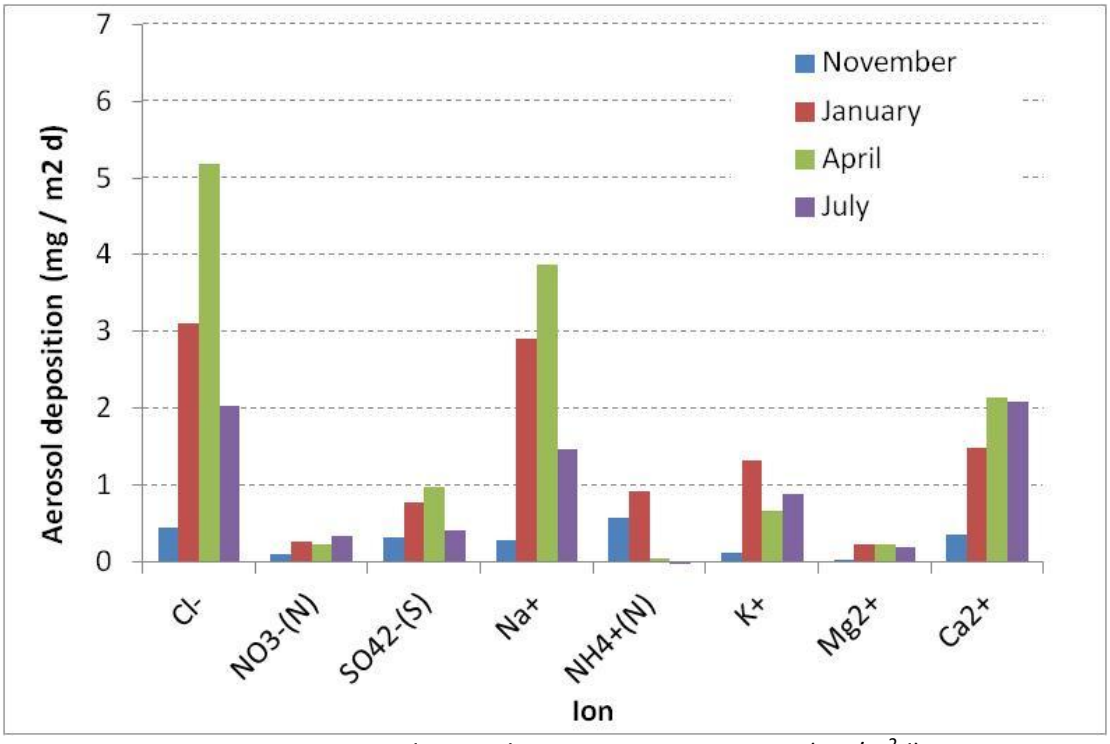


Figure 8: Measured aerosol composition in Warsaw (mg/m^{2}d)

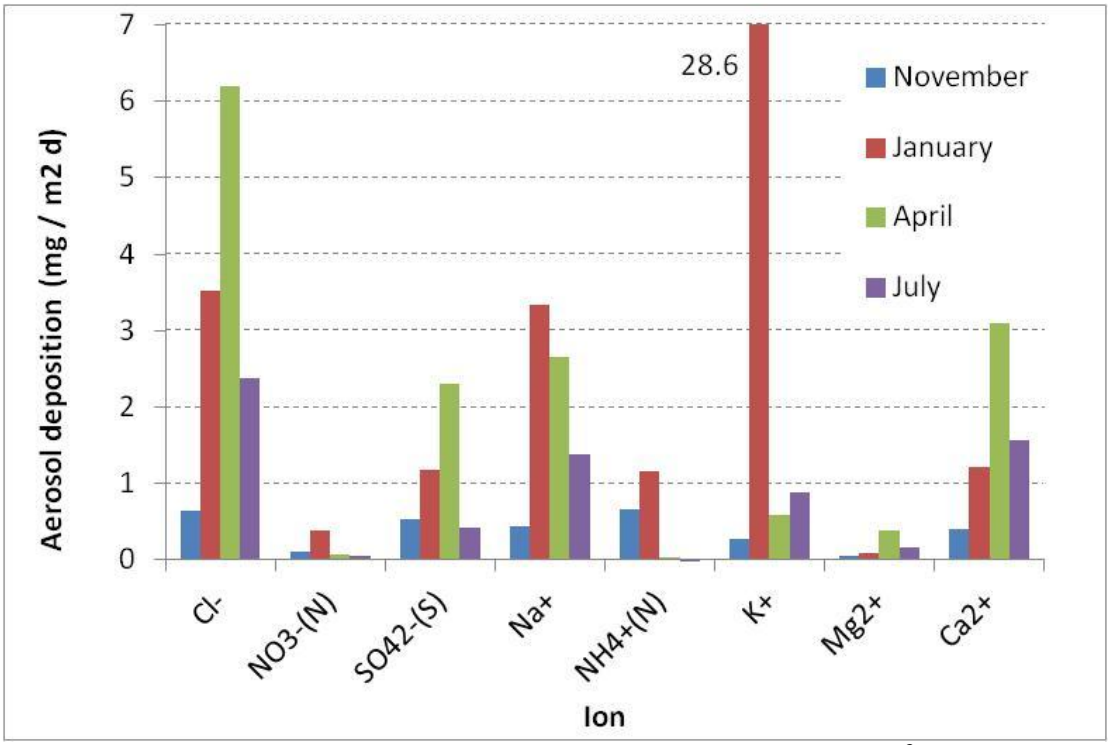


Figure 9: Measured aerosol composition in Sochaczew (mg/m^{2}d)

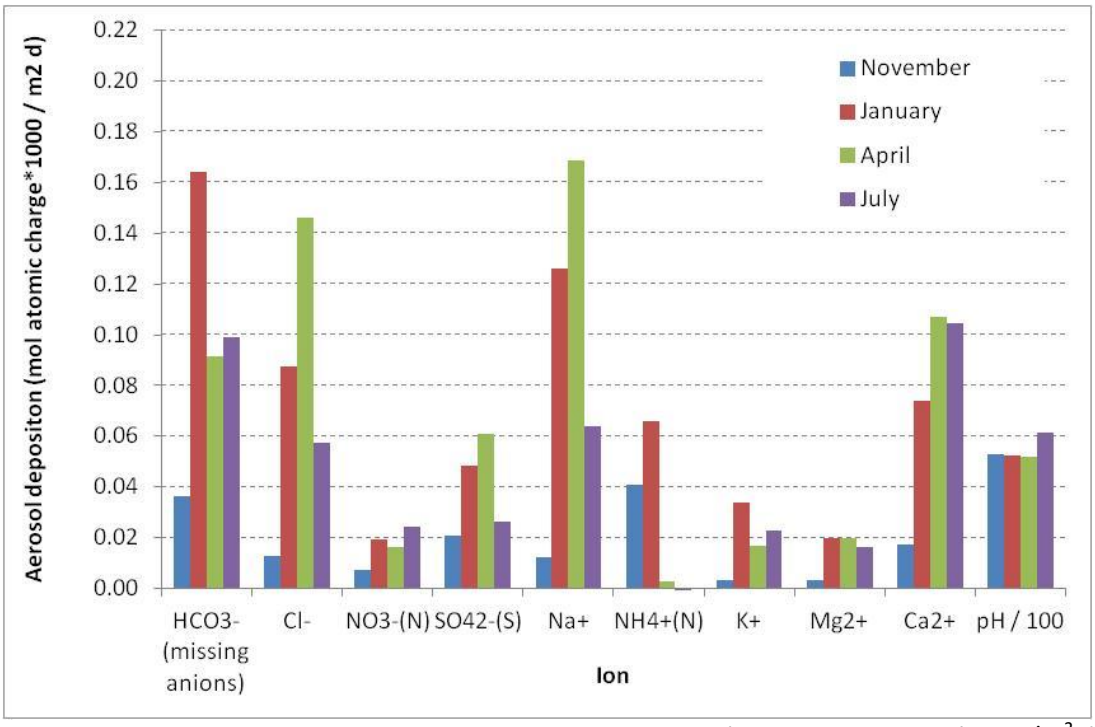


Figure 10: Measured aerosol composition and pH in Warsaw (mol atomic charge*1000/m^{2}d)

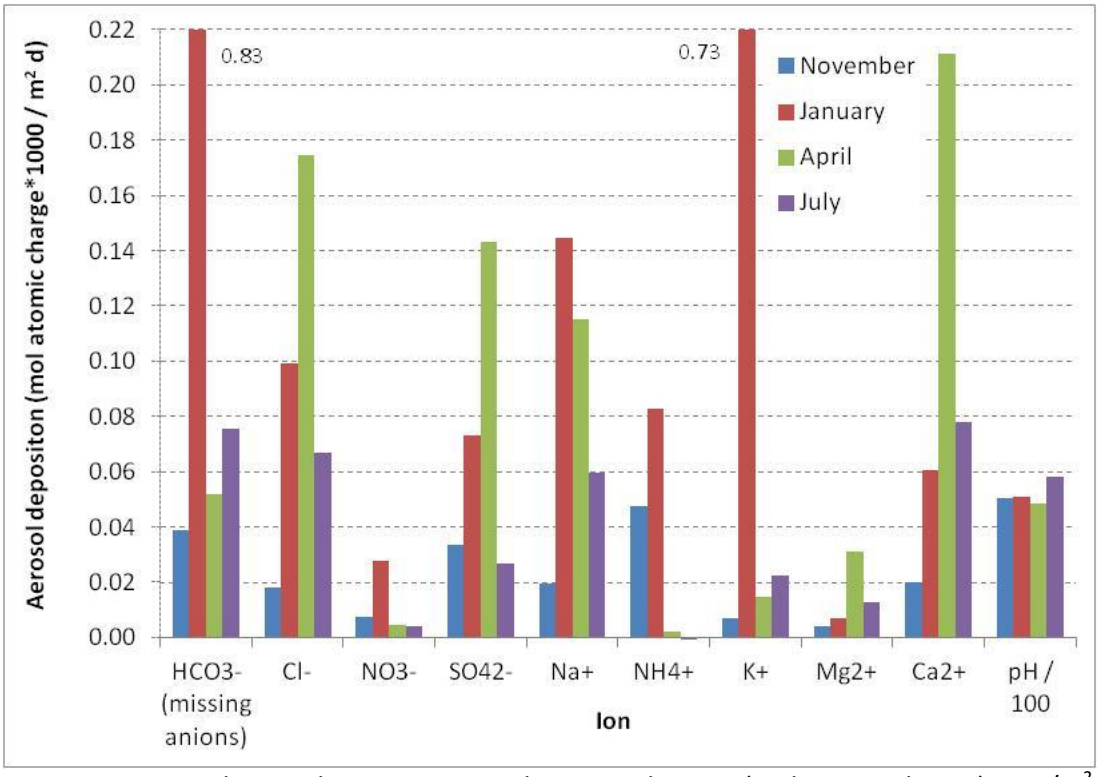


Figure 11: Measured aerosol composition and pH in Sochaczew (mol atomic charge*1000/m^{2}d)

Table 1 and 2 show the correlation coefficients between all the ion deposition rates measured red as mol atomic charge*1000/m^{2}d, for the four monthly measurement periods, for the central Warsaw and Sochaczew locations, respectively. Coefficients higher than 0.8 are marked in bold.

	HCO3-	Cl	NO3-N	SO4-S	Na	NH4-N	K	Mg	Ca
HCO3-	1.00	0.48	0.67	0.55	0.62	0.37	**0.99**	**0.81**	0.51
Cl		1.00	0.39	**0.96**	**0.98**	-0.30	0.45	**0.84**	0.76
NO3-N			1.00	0.24	0.41	-0.35	0.78	0.79	**0.85**
SO4-S				1.00	**0.98**	-0.03	0.47	0.78	0.58
Na					1.00	-0.13	0.57	**0.88**	0.72
NH4-N						1.00	0.26	-0.19	-0.61
K							1.00	**0.83**	0.58
Mg								1.00	**0.89**
Ca									1.00

Table 1: Correlation coefficients between ion deposition rates for four monthly measurement periods at the Warsaw station.

	HCO3-	Cl	NO3-N	SO4-S	Na	NH4-N	K	Mg	Ca
HCO3-	1.00	0.10	**0.98**	0.04	0.72	**0.81**	**1.00**	-0.37	-0.25
Cl		1.00	0.01	**0.93**	0.76	-0.30	0.10	**0.88**	**0.94**
NO3-N			1.00	0.01	0.64	**0.90**	**0.99**	-0.46	-0.34
SO4-S				1.00	0.65	-0.18	0.05	**0.84**	**0.89**
Na					1.00	0.29	0.72	0.37	0.49
NH4-N						1.00	**0.82**	-0.68	-0.59
K							1.00	-0.37	-0.25
Mg								1.00	**0.99**
Ca									1.00

Table 2: Correlation coefficients between ion deposition rates for four monthly measurement periods at the Sochaczew station.

Good correlation between an anion and cation shows that this is a probable salt composition. Good correlation between two cations or anions show that their salts are likely to have the same source or that their emission is affected by the same process. The correlation between four different months through the year gives approximate annual averages for the correlations. There is likely to be different sources for, and compositions of, salts through the year. This will reduce the correlations coefficients.

For the blank aerosol filter that was stored in the laboratory a pH of 4.76, a chloride, Cl^-, value of 0.36 mg/m^{2}d (mol atomic charge*1000/m^2 d = 0.01) and a calcium, Ca, value of 0.02 mg/m^{2}d (mol atomic charge*1000/m^2 d = 0.0006) were measured. Zero values were measured for the other ions.
Table 3 gives the results for the weight loss due to corrosion of the carbon steel plates exposed at the two stations.

Station	Sample	Weight loss(g)	Recession (µm)	Recession (µm) - adjusted to one year
Warszawa	W1	2.46	10.5	12.6
Warszawa	W2	2.45	10.4	12.5
Warszawa	W3	2.45	10.4	12.5
Average		**2.45**	**10.4**	**12.5**
Station	**Sample**	**Weight loss(g)**	**Recession (µm)**	**Recession (µm) - adjusted to one year**
Sochaczew	S1	3.58	15.2	18.3
Sochaczew	S2	3.05	13.0	15.6
Sochaczew	S3	3.32	14.1	16.9
Average		**3.32**	**14.1**	**16.9**

Table 3: Weight loss and recession due to corrosion during 10 months, and estimated annual recession, at the Warsaw and Sochaczew stations.

DISCUSSION - THE CORROSION POTENTIAL OF THE ATMOSPHERE

The average annual urban concentration of SO_2 in Poland decreased from ~ 25 µg m^{-3} in 1993 to ~ 10 µg m^{-3} in 2001 (Mitosek 2004). The measured average value of SO_2 for the four monthly measurement periods during 2010-2011 at the two Railway museum locations in Warsaw and

Sochaczew are close to this value, but slightly higher in Sochaczew due to higher concentrations in the winter.

The measured total PM values are much higher in the spring period, April, at both locations, and also in the summer period, July, in Warsaw, than in the winter period, November and January. The fraction of larger than PM10 particles (Total PM/PM10) is larger in the spring and summer than in the winter. The reason for this difference between spring/summer and winter may be resuspension of dust that has accumulated during the winter or possibly increase in biological or agricultural (Sochaczew) or other human activity. A general trend of increasing aerosol deposition in January and then in April can be observed for most of the measured ions, except nitrate, ammonium and potassium. The highest deposition of nitrate, ammonium and potassium was in January, except for nitrate in Warsaw, which was slightly higher in July than in April. Especially, there was very little ammonium deposition in April and July, both in Warsaw and in Sochaczew, and very high potassium deposition in Sochaczew in January. The trend in the changes in the deposition of the ions over the periods is very similar in central Warsaw and in Sochaczew, except for the reduction in sodium deposition that was measured in Sochaczew from January to April. The amounts of and changes in the chloride and sodium deposition is very similar, especially in central Warsaw, which point to the presence of sodium chloride, possibly used for de-icing of the streets during winter. The larger presence of nitrate, ammonium and potassium in January, especially in Sochaczew, could be due to use of fertilizers in agriculture in winter.

In Warsaw there is very high correlation between sodium and chloride and between sodium and sulphate and also between chloride and sulphate. This indicates the deposition of sodium chloride and sodium sulphate. The presence of magnesium chloride that can originate from the same source or process as the sodium chloride is indicated by the high correlation between magnesium and chloride and magnesium and sodium. Both magnesium and potassium have high correlation with missing anions which are likely to be mainly carbonates, suggesting the presence of potassium- and magnesium carbonate. The nitrate seems most likely to be calcium nitrate.

In Sochaczew the correlations indicate the presence of calcium and magnesium chlorides and sulphates, and the presence of potassium and ammonium carbonates and nitrates. The best correlation for sodium is with chloride, which indicates that this is the major sodium salt.

The correlations for Warsaw and Sochaczew supports the suggestion that sodium chloride, possibly from de-icing in the winter, is more present in Warsaw, where as potassium and ammonium nitrates, possibly related to agriculture, are more present in Sochaczew. The sulphate in Warsaw seems most likely to be sodium sulphate where as the sulphate in Sochaczew seems most likely to be calcium and magnesium sulphate. The amounts of the various salts should correspond to the measured amounts as shown in Figure 7 to 10.

The annual average pH is slightly lower and the sulphate deposition higher in Sochaczew than in Warsaw. The pH is slightly lower in April in both Sochaczew and Warsaw when also the sulphate deposition is highest in both locations.

More detailed understanding of the emissions affecting the two locations is needed for a better understand of the sources for the ion and salt composition.

Tolerable values for SO_2 of 11 mg m^{-3} for “average European locations” and of 6 µg m^{-3} for “urban European locations” were recommended for the protection of immovable cultural heritage to the Clean Air For Europe Programme (CAFÉ, 2011) by the EU project Multi Assess (Kucera, 2005). A similar evaluation of tolerable levels performed for the PM10 effect on the corrosion of carbon steel (Grøntoft, 2007; Kucera, 2005) gave tolerable levels of 110 µg m^{-3} and 22 µg m^{-3} for the average and urban European situation. The measurements that were performed at the Warsaw and Sochaczew locations indicate that the annual average SO_2 concentrations are slightly higher, but that the annual average PM10 concentrations are lower, than these levels.

It has been found that different corrosion dose - response functions for the degradation of materials due to air pollution should be used for a situation with high SO_2, the so called SO_2 dominating situation, and for a situation with low SO_2, the so called multi-pollutant situation. The ICP mapping manual (Kucera, 2007) states that; "it is not possible to give an absolute SO_2 level below which the multi-pollutant functions should be used since the level is depending also on temperature and relative humidity, but such a level would be in the order of 10 µg m^{-3}." The annual average concentration at Sochaczew was higher than this level, and the concentration in the winter was about the twice this level.

The data for the air pollutants and for climate were used to estimate the ISO 9223 corrosivity category, which varies from 1 (very low) to 5 (very high), for the environments at the locations (ISO, 1992), and the expected corrosion rates in µm loss of material.

The estimation is based on pollution values for the four monthly periods when measurements were performed, with the average for the four periods used as the "annual average", and on climate values of relative humidity and temperature that represent 77 % of the whole year, from 2nd November 2010 until 9th August 2011, extrapolated to the value for the whole year (i.e. multiplied with 77/100).

If the autumn 2011 will be somewhat wetter than the rest of the year this is not likely to affect the estimated corrosion category as the ISO limit between the t4 and t5 categories for time of wetness is 5500 hours, as compared with the 2755 hours estimated for Warsaw in 2011 in Table 4. Table 4 shows the values used in the estimation of the corrosivity category.

Station	Railway museum – central Warsaw	Sochaczew
Time of wetness (hours where RH > 80 %, Temp > 0°C) - Warsaw Targowek met. station	2755 (t4)	2755 (t4)
SO_2 concentration (µg/m^{-3})	8.2 (P0)	12.9 (P1)
Cl^- depositon (mg/m^2d^{-1})	2.7 (S0)	3.2 (S1)
Expected corrosivity category	**3 (Medium)**	**3 (Medium)**
Expected corrosion rate of carbon steel (µm/year)	25 - 50	25 - 50
Measured corrosion rate (µm/year)	13	17
Measured corrosivity category	**2 (Low)**	**2 (Low)**

Table 4: Environmental data, expected and measured corrosion rates and ISO corrosivity categories for the central Warsaw and Sochaczew locations.

CONCLUSION

The environmental measurements at the Warsaw Railway Museum indicate a low to medium corrosivity for the atmospheres, which is typical for northern European inland environments with low chloride concentrations and relatively low SO_2 concentration.

At the central Warsaw location both sulphur dioxide, SO_2, and chloride, Cl^-, are in the category 0, which is considered background concentration by ISO 9223, on a scale from 0 to 4. The category 1 assigned to these pollutants in Sochaczew indicate a significant contribution to the corrosion from anthropogenic sources.

The measurements indicate that sulphur dioxide SO_2 is the main pollutant that gives increased corrosion at the sites, especially in Sochaczew, and that the presence of chloride, Cl^-, and sulphate, SO_4^{2-}, in the aerosol at significant levels contributes to the corrosion. Higher concentration or deposition of these pollutants, were measured in Sochaczew than in central Warsaw, and a lower pH was measured in Sochaczew.

The values for SO_2 are slightly higher, but the PM10 values are lower, than the European wide assessment performed for CAFÉ of the tolerable levels for immovable (i.e. outdoor) cultural heritage. Still, the main factor that increases the corrosion to a higher ISO category (2-3) at the locations is the relatively humid climate. A further reduction of air pollutants should further reduce the corrosion, but the largest potential protection effect would be from measures to shelter the objects form rain and reduce the humidity in the air around the objects, e.g. by moving vulnerable smaller objects or particularly valuable objects to the indoor or applying other options for sheltering.

If aims to further reduce pollutant concentrations can be met and it is at the same time becoming rainier due to climate change (Sabbioni et al. 2010) the effort to protect cultural heritage, such as the objects at the Railway Museum in Warsaw, against the ambient climate will be more important.

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Appendix no.1

Warszawa		Time	Gas (µg m-		Particle mass (µg m-3)								Particle composition (mol atomic charge*1000 /m2 d)									pH
Periods:			SO2	stdv	Total PM	stdv	>PM10	stdv	PM10	stdv	PM2.5	stdv	HCO3- (missing anions)	Cl-	NO3-(N)	SO42-(S)	Na+	NH4+(N)	K+	Mg2+	Ca2+	pH / 100
November	1	2/11-2/12,2010	8.61	0.42	45.00	4.70	34.63	3.04	10.36	1.66	0.94	0.22	0.037	0.013	0.007	0.021	0.012	0.041	0.003	0.003	0.017	0.053
January	2	12/01-11/2,2011	11.50	0.20	26.85	14.26	16.79	13.24	10.06	1.03	0.72	0.04	0.164	0.088	0.019	0.049	0.126	0.066	0.034	0.020	0.074	0.053
April	3	30/03-28/4,2011	7.15	0.39	141.28	64.41	115.32	58.29	25.96	6.12	1.78	0.18	0.092	0.146	0.016	0.061	0.169	0.003	0.017	0.020	0.107	0.052
July	4	29/06-02/08,2011	5.37	0.67	163.45	107.44	143.82	99.37	19.63	8.07	1.94	1.06	0.099	0.057	0.024	0.026	0.064	-0.001	0.023	0.016	0.104	0.061
Average			8.16	0.42	94.14	47.70	77.64	43.48	16.50	4.22	1.34	0.38	0.098	0.076	0.017	0.039	0.093	0.027	0.019	0.015	0.076	0.055

NILU Carbon steel plates				
Station	**Sample**	**Weight loss(g)**	**Recession (µm)**	**Recession (µm) - adjusted to one year**
Warszawa	W1	2.46	10.5	12.6
Warszawa	W2	2.45	10.4	12.5
Warszawa	W3	2.45	10.4	12.5
Average		**2.45**	**10.4**	**12.5**

BLANK	Particle composition (mol atomic charge*1000 /m2 d)							pH
HCO3 (missing anions)	**Cl-**	**NO3-(N)**	**SO42-(S)**	**Na+**	**NH4+(N)**	**K+**	**Mg2+**	**Ca2+**	**pH / 100**
-0.008713362	0.01	0.00071	0.00031	0.0004	0.00071	0.0003	0.00041	0.00055	0.048

Table A.1: Aerosol, including blank, and corrosion measurement results from the central Warsaw station

Sochaczew			Gas (µg m-		Particle mass (µg m-3)								Particle composition (mol atomic charge*1000/m2 d)									pH
Periods:			SO2	stdv	Total PM	stdv	>PM10	stdv	PM10	stdv	PM2.5	stdv	HCO3- (missing anions)	Cl-	NO3-(N)	SO42-(S)	Na+	NH4+(N)	K+	Mg2+	Ca2+	pH / 100
November	1	3/11-6/12,2010	18.79	0.22	32.24	14.88	23.51	12.20	8.73	2.68	0.73	0.06	0.039	0.018	0.008	0.034	0.020	0.048	0.007	0.004	0.020	0.051
January	2	12/01-11/2,2011	19.45	0.14	47.49	30.15	31.13	30.72	16.36	0.57	2.39	1.14	0.825	0.099	0.028	0.074	0.145	0.083	0.730	0.007	0.061	0.051
April	3	30/03-28/4,2011	7.68	0.27	164.36	84.47	141.25	78.08	23.10	6.39	1.73	0.11	0.052	0.175	0.005	0.144	0.115	0.002	0.015	0.031	0.211	0.049
July	4	29/06-02/08,2011	5.55	0.24	97.99	68.10	84.03	60.80	13.96	7.30	1.70	1.70	0.076	0.067	0.004	0.027	0.060	-0.001	0.023	0.013	0.078	0.059
Average			12.87	0.22	85.52	49.40	69.98	45.45	15.54	4.23	1.64	0.75	0.248	0.090	0.011	0.069	0.085	0.033	0.194	0.014	0.093	0.052

NILU Carbon steel plates				
Station	**Sample**	**Weight loss(g)**	**Recession (µm)**	**Recession (µm) - adjusted to one year**
Sochaczew	S1	3.58	15.2	18.3
Sochaczew	S2	3.05	13.0	15.6
Sochaczew	S3	3.32	14.1	16.9
Average		**3.32**	**14.1**	**16.9**

Table A.2: Aerosol and corrosion measurement results from the Sochaczew station

"Corrosion of historic iron and copper based artefacts in uncontrolled atmospheres and new achievements in protection systems."

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INTRODUCTION

The study of corrosion mechanisms on historic metals exposed to uncontrolled atmospheres has benefited from new developments in the past years that have been used by conservation professionals to test innovative protection systems. This paper is reviewing important results obtained up to now and presents some current research projects.

CORROSION OF HISTORIC IRON AND COPPER BASED ARTEFACTS IN UNCONTROLLED ATMOSPHERES: AN OVERVIEW OF PAST AND RECENT KNOWLEDGE

Before being important materials of the industrial field, iron and copper alloys have been used in historic buildings, either as reinforcing structures or protection materials. Some are still surviving like the iron reinforcing bars at 14th c. Vincennes royal château situated on the border line of Paris. After their first use at Versailles in the 17th c., copper sheets were extensively used in the 19th c. as roofing materials. The copper patina is appreciated worldwide and copper is still recommended in France to protect historic buildings [1]. Although industrial heritage movable artefacts are made of the most appropriate materials, they are generally suffering from the absence of any preventive conservation strategy. Conserved often in the worse environmental conditions (figure 1), they have lost their original surface treatment and corrosion is extensive.

Reference to corrosion can be traced back to Antiquity when Pline suggested the use of oil or asphalt to protect bronze and gypsum or ceruse (a lead carbonate) to protect iron [2]. But it is only in the 19th c. that scientific concepts of corrosion and its prevention were developed. Corrosion is inevitable. Most metallic artefacts are produced artificially and when exposed to aggressive conditions they transform back to the stable mineral state. We evaluate the loss of steel per year through the "corrosion cycle" to 150 millions of tons! [3]. If in the industrial field, corrosion is accepted and the damaged materials are constantly replaced by new ones, in the field of heritage it is our task to prevent or slow down the corrosion processes to preserve the artefacts under study. Understanding and monitoring of corrosion processes are therefore required and conservation professionals can intervene at two levels: while the object is still in use or stored in uncontrolled atmospheres through preventive conservation policies and by stabilising the corrosion processes when they have developed (interventive conservation). The regular protection with paint of the Eiffel Tower, built for the International Exhibition in Paris, in 1889 and made of puddle iron is a good example of an effective but costly (3 millions € are spent every 7 years) preventive conservation strategy [4]. Another way to improve the corrosion resistance of iron alloys is the addition of elements such as Cu and Cr (Corten steels developed in 1933).

Parameters affecting atmospheric corrosion of metals and more particularly iron are [5]: relative humidity (RH) - iron does not corrode below 60% but corrosion quickly increases above 80% RH; pollution – dust, salts deposited on the metal surface as well as gas affect the corrosion processes - SO_2 and Cl^- are the major aggressive pollutants for iron alloys and time of wetness (TOW) that is related to fluctuations of RH and temperature [6].

Three groups of corrosion forms are found on copper and iron based artefacts depending on the nature of the material: starting as pitting corrosion, it might further develop as intergranular corrosion, exfoliation or dealloying; the environment: general, galvanic, filiform corrosions are of that type as well as corrosion in concrete and external stress: stress corrosion cracking and the more developed fatigue corrosion are of that type as well as fretting corrosion [7].

The initiation process requires an electrolyte and the simultaneous presence of anodic and cathodic half reactions given below [8,9]:

Fe èFe^{2+} + **2e**$^-$ for iron (for copper: Cu ® $Cu^+ + e^-$) Anodic reactions

$O_2 + 2H_2O$ + **4e-** è $4OH^-$ Cathodic reaction (in aerated neutral solutions)

After combination we obtain:

$2Fe + O_2 + 2H_2O$ è $2Fe^{2+} + 4OH^-$ è $Fe(OH)_2$ for iron

$4Cu + O_2 + 2H_2O$ ® $4Cu^+ + 4OH^-$ for copper

Iron hydroxide $Fe(OH)_2$ / green rust is highly unstable and transforms in rust. Rust is a mixture of complex oxides and hydroxides and develops in a different way when an existing corrosion layer is already present on the metal surface than on bare metal. Green rust is first oxidised in lepidocrocite (γ-FeOOH) or magnetite (Fe_3O_4). γ-FeOOH might further develop in maghemite (γ-Fe_2O_3) or an amorphous FeIII oxy-hydroxide such as ferrihydrite while Fe_3O_4 is transformed in γ-Fe_2O_3. Eventually all corrosion products get transformed in stable goethite (α-FeOOH) [10]. As regards copper, cuprite (Cu_2O) formed indoor is more stable than rust on iron alloys. Still it is often transformed outdoor in brochantite ($CuSO_4$,$3Cu(OH)_2$) and in the presence of chlorides in nantokite (CuCl) and atacamite ($Cu_2(OH)_3Cl$)). Black crusts often occur. Their composition is not well established yet [11]. The stability of corrosion layers (CLs) can be appreciated theoretically through thermodynamics. Pourbaix diagrams are commonly used to determine the field of stability of the different compounds involved [12]. The real stability of these compounds depends on kinetics aspects related to their electrochemical reactivity (green rust and ferrihydrite are more reactive than γ-FeOOH, itself more reactive than α-FeOOH) and solubility: of all corrosion products $Fe(OH)_3$ is the more soluble while ferrihydrite is the less [13].

CLs formed on iron during short, medium and long exposure times are made of two sub-layers. Macroscopic analyses show that the inner dense product layer (DPL) is constituted mainly of α-FeOOH and a multilayer system made of γ-Fe_2O_3 / Fe_3O_4 /amorphous phase while the outer porous and cracked transformed layer (TL) is constituted mainly of γ-FeOOH with a mixture of a-FeOOH and/or Fe_3O_4 / β-FeOOH. The proportions of both sub-layers depend on the environmental conditions. Often to describe the CL we define a protection ratio α/γ where α corresponds to the proportion of α-FeOOH (passive) while γ corresponds to the proportion of γ-FeOOH (reactive). We consider that the CL is stable if this protection ratio is superior to 2 [13]. Similarly the different CLs found on copper based alloys such as bronzes exposed outdoor have been studied by Robbiola and divided in two possible structures (I corresponding to stable patina and II corresponding to active corrosion). The patina forms in non polluted atmospheres while active corrosion develops in atmospheres contaminated with Cl, dirt or/and biological compounds [14].

The corrosion mechanism for iron artefacts already covered with a corrosion layer is based on the wet-dry cycle (figure 2) presented by Stratmann [15] and modelled by Hoerlé et al. [16]. Corrosion can be divided in 3 steps: wetting (Fe is oxidised while FeIII oxy-hydroxide (γ-FeOOH) is reduced in conductive γ-FeII hydroxide), wet stage (Fe is oxidised while O_2 is reduced on γ-FeII hydroxide) and drying (precipitation of $Fe(OH)_2$ followed by the re-oxidation of γ-FeII hydroxide in FeIII oxy-hydroxide (γ-FeOOH)). As indicated above analysis of historic iron CLs formed on the long term clearly shows that γ-FeOOH is not in contact with the metal surface. Therefore the Stratmann / Hoerlé model has to be revised [13].

To correct this model, micro-focused analytical techniques (such as micro-Raman spectroscopy) were required to study the complex CLs considered as well as a reference site, clearly dated and where a large number of samples could be taken and analysed. The reinforcing iron chains placed in 1497 in the triforium of Amiens cathedral offered that possibility [13]. The microscopic analysis of the DPLs of the 25 samples showed that they are mainly constituted of α-FeOOH with marblings of amorphous FeIII oxy-hydroxide (ferrihydrite) and γ-FeOOH as a top layer [17]. Monnier could then propose a corrected representation of the CL depending on the orientation of the marblings (connected or not to the metal) that was further studied all around the Amiens cathedral. It shows that α-FeOOH and

ferrihydrite are prominent (respectively 20 to 58% and 26 to 65%) while γ-FeOOH and β-FeOOH are more discrete (respectively 2 to 19% and 5 to 13%). These corrected data enabled to suggest a modified corrosion mechanism for historic iron based artefacts exposed to uncontrolled environments [13]:

- Wetting: oxidation of Fe and reduction of amorphous ferrihydrite (FeIII oxy-hydroxide) to form conductive $Fe(OH)_2$;
- Wet stage: oxidation of Fe and reduction of O_2 on conductive $Fe(OH)_2$;
- Drying process: precipitation of $Fe(OH)_2$ followed by re-oxidation of conductive $Fe(OH)_2$ in amorphous FeIII oxy-hydroxide (ferrihydrite).

The application of this approach to armour elements of the Palace Armoury (PA), Valletta, Malta, enabled the 3-years EU PROMET project consortium to propose a phase distribution in the CLs of iron based materials of the collection [18]. Based on this knowledge, artificial coupons were manufactured to simulate the behaviour of real artefacts and evaluate the performance of new and innovative protection systems [19]. Steel coupons were positioned on an exposure rack during 3, 6, 9 and 12 months in the PA, Valletta, Malta so to obtain different degrees of corrosion state. Micro-Raman spectrometry of the coupons showed that when the CL was slightly cleaned (with cotton swabs) γ-FeOOH was analysed and when it was cleaned mechanically to remove all powdery corrosion products, the expected mixture of ferrihydrite, α-FeOOH and γ-FeOOH was found.

NEW ACHIEVEMENT IN PROTECTION SYSTEMS

If transparent protection systems (varnishes, waxes) are often applied on historic metal artefacts exposed to controlled and uncontrolled environmental conditions, some damaging side effects are observed in the latter case. Indeed filiform corrosion develops and leaves irreversible marks on the metal surface. The repeated interventions on historic metal surfaces can cause further damage due to the lack of reversibility of the coatings applied, use of inappropriate tools that mark the original metal surface, non respect of the appropriate environmental conditions (T,RH) for the application of the new protection systems. Therefore we need to develop a new approach to protect historic metal surfaces in uncontrolled environments. The protection systems to use should cover the following requirements: compatible with existing oxidised surfaces, reversible and/or retreatable, effective over several months, transparent, dry and non-tacky, easy to apply (by non-conservators) and non-toxic.

Some research has been carried out in the past years to develop protection systems responding to these needs. From the 1990's onwards, the organic-inorganic Ormocer compounds have been developed as coatings for outdoor monuments and large industrial structures [20-22]. Although they give good results, they are still not available on the market and rather expensive. Cheap, non toxic and easy to produce non-toxic corrosion inhibitors such as carboxylates and carboxylatation solutions seem more promising [23]. The PROMET EU project was the occasion to assess their efficiency for the short-term protection of historic copper and iron based artefacts in parallel to polyethylene Poligen ® wax emulsion recommended for long-term protection as a replacement to varnishes (such as Paraloid B72) [19]. Time was too short to cover important issues related to the practical use of the protection systems in real conditions such as the level of surface preparation before the application of the protection systems, the number of layers to apply, the influence of alloying elements of the metal and original surface treatments, the need of a careful monitoring of the protection systems, their long-term efficiency and the level of reversibility / retreatability with time. The Swiss POINT project was setup to respond to some of these questions. More specifically we carried out field tests with carboxylates and carboxylatation solutions for the temporary protection of copper and iron alloy artefacts, assessed their efficiency and precised their maintenance (removal and retreatment) [24].

After the preparation of metal coupons aged artificially to simulate the appearance of historic iron and copper alloy artefacts in a similar way than in the PROMET project, half of these coupons were used to optimise the conditions of application of the protection systems considered through

accelerated corrosion tests and examination by means of destructive analytical techniques. The other half was used to further optimise the formulation of the best rated protection systems and application protocols. In parallel the efficiency of these protection systems as well as their reversibility and retreatability were assessed on real artefacts from the Historical Swiss Army Material (HSAM) Foundation.

A military carriage and cartridge cases were selected to represent the materials and alteration of iron and copper alloy artefacts of the HSAM Foundation collection. Based on the analysis of fragments sampled from the artefacts metal sheets of similar composition (building steel - 0.2% carbon and 1.5% Mn by weight - to simulate historic steel and leaded brass - CuZn39Pb2 - to simulate historic brass) and available on the market were cut in coupons. After surface preparation (degreasing and/or chemical cleaning), the 100 coupons were artificially aged in a humidity chamber (cycles of 16h at 40°C and 100% relative humidity and 8h at 20°C and 60% RH) and mechanically cleaned to remove all powdery corrosion products. Sodium decanoate (NaC_{10}) adapted to clean metal surfaces and carboxylatation solution ($HC_{10} + H_2O_2$) more adapted to highly oxidised surface, applied by brush (1 to 3 layers) or by spray, were tested on these coupons. The following protection systems and application methods were selected for steel : NaC_{10}-3 layers-by brush, NaC_{10}-1 layer-by spray, HC_{10} + H_2O_2-3 layers-by brush, HC_{10} + H_2O_2-1 layer-by spray and HC_{10} + H_2O_2-1 layer followed by 2 layers of NaC_{10}-by brush and brass : NaC_{10}-1 layer-by brush and by spray; NaC_{10}-3 layers-by brush and NaC_{10}-4 layers-by brush.

The efficiency of the protection systems was assessed on 50 metal coupons exposed to accelerated corrosion tests in a humidity chamber (cycles of 16h at 40°C and RH=100% and 8h at 20°C and RH=60%) over 3 weeks, using visual examination (macro) and observation under binocular (micro) on a weekly basis, destructive examination and reversibility / retreatability testing. The following protection systems gave the best results for further testing: NaC_{10}-3 layers-by brush, NaC_{10}-1 layer-by spray, HC_{10} + H_2O_2-3 layers-by brush (for steel) and NaC_{10}-1 layer-by brush as well as NaC_{10}-3 layers-by brush (for brass).

They were applied on real artefacts and a second series of metal coupons exposed next to the artefacts. Two sites of the HSAM Foundation were chosen for field testing: Burgdorf (humid storage area with rather stable T and RH) for iron alloy materials and Seftigen (storage area with uncontrolled environmental conditions) for copper alloy materials. The iron based artefacts selected were the heavily corroded military carriage already mentioned and a steel spacer having a similar surface appearance as the steel metal coupons. The copper alloy artefacts selected were cartridge cases. Some areas of these artefacts were mechanically cleaned and protection systems were applied using the same protocols as for the metal coupons. The 2nd series of metal coupons used to optimise the formulation of the protection systems and the application protocols were positioned on an exposure rack. Comparative exposure tests were carried out on other protection systems selected by the HSAM Foundation: a coating currently in use at HSAM Foundation: Carnauba wax and a polyethylene wax, Poligen 91009 ®, tested in the PROMET project but not used yet at HSAM Foundation. The materials were monitored on a regular basis during the 1-year exposure time on a monthly basis on site (through high resolution pictures of groups of coupons and artefacts – figure 3) and on a quarterly basis in the laboratory (using macro-photographs on both sides of the coupons and microphotographs of specific areas). Series of coupons (non protected, protected with corrosion inhibitors and waxes) were removed after 3, 6 and 9 months and were used for additional examination, reversibility and retreatability tests.

Only slight modifications of the copper based materials were observed on the aggressive Seftigen site. Coupons protected with corrosion inhibitors darkened slightly like unprotected coupons while Carnauba wax favoured the development of localised corrosion and Poligen wax darkened the metal surface. As regards steel materials exposed on the more stable Burgdorf site, almost no alteration of the coupons and the spacer areas unprotected or protected with corrosion inhibitors was observed. Slight whitening (excess of compound?) of the metal surface was observed on the

military carriage areas treated with the corrosion inhibitors as well as discoloration phenomena (attributed to the formation of an iron carboxylate with carboxylatation solution). Coupons treated with Carnauba wax developed after less than 3 months some localised corrosion that expanded with time while darkening of the metal surface was observed with Poligen wax ®.

Reversibility tests were carried out with cotton swabs impregnated with ethanol. The removal of corrosion inhibitors was possible and left no mark on the coupons all along the 1-year exposure time but was slightly more difficult after 6 months of exposure. Marks were left on the heavily corroded surfaces of the military carriage. The removal of waxes on coupons with ethanol was more difficult and left a clear mark in the case of Poligen ®. The half cleaned metal coupons were retreated with the same protection systems and protocol of application. Some defaults in the protection systems newly applied were observed: stains (excess of compound? or application marks) on steel and brass covered with the corrosion inhibitors that could further develop in localised corrosion (steel coupons). Waxes reapplied left overlaying lines on both steel and brass coupons that disappeared with time.

Upon completion of this work, we have further evaluated the properties of carboxylates and carboxylatation solutions as corrosion inhibitors of iron and copper based materials exposed to uncontrolled atmospheres. Not only these solutions are non toxic, but NaC_{10} gives a transparent film that whitens heavily oxidised surface when applied in excess while HC_{10}+H_2O_2 provokes a slight but still acceptable discoloration of the same oxidised surfaces. Both corrosion inhibitors can be applied at temperatures between 5 and 25°C and RH of 50-60%. The protection seems efficient for a 1-year period on the sites tested (no definitive conclusion can be done yet due to the absence of corrosion on unprotected coupons). Spraying is a simple mode of application but seems less efficient than with brushes (3 layers). The monitoring of treated surfaces, using high resolution macro-photographs taken on monthly basis in standardised conditions, is recommended to detect any failure of the protection systems. The reversibility with ethanol is possible at least after one year of application and local retreatment can be carried out but with care to avoid the formation of unaesthetic stains. The comparative work carried out on coatings (waxes) tested in parallel is not so promising: Carnauba and Poligen 91009 ® should not be recommended for the short-term protection of slightly corroded steel and brass surfaces in uncontrolled atmospheres.

CONCLUSION

Current research on corrosion mechanisms of historic artefacts exposed to uncontrolled atmospheres continues to further understand the reactivity of specific CLs (containing chlorides or other aggressive species). Similarly field tests still continue to precise the properties of carboxylates and carboxylatation solutions as corrosion inhibitors of iron and copper based materials. Today more collaborative work is required between scientists and end-users (curators, conservators) to transfer the scientific knowledge acquired to conservation professionals, define the limits of application of the current corrosion models and precise the conditions of application of the innovative protection systems tested according to different uncontrolled environments.

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Fig. 1: Bern, Historischer Autofriedhof Gürbetal, 1930-1970 – 2008 (ã HECR Arc).

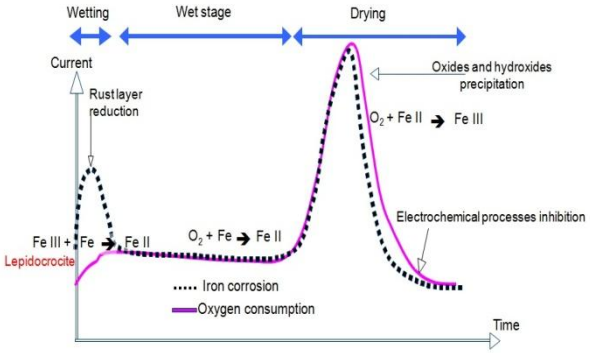
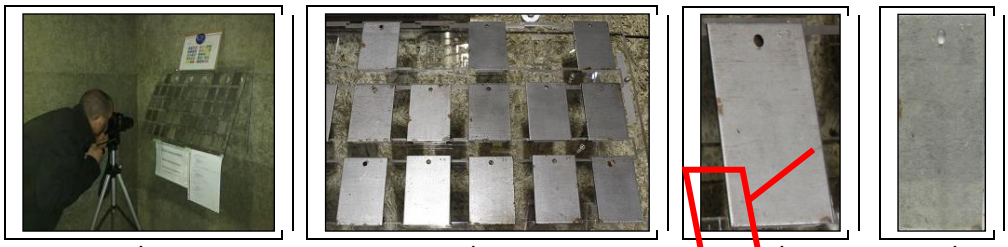


Fig. 2: Wet-dry cycle taking place during atmospheric corrosion (from Stratmann [15]).



a/ b/ c/ d/

Fig. 3: Monitoring of steel coupons on an exposure rack at Burgdorf site (POINT project) through high resolution macro-photographs (a/&b/). The coupon under study is magnified (c/) and the development of corrosion is assessed by comparison to the original state (ã HECR Arc).

"Practical aspects of treatment of artifacts made of ferrous metal for indoor and outdoor exposure."

Elżbieta Maria Nosek

THE CONSERVATION OF THE GOTHIC DOOR FROM HETMAN HOUSE.KRAKÓW

The building of the Hetman house also called the old mint is one of the brick house in Krakow. It is dates to XII and XIVc. At the end of the XIVc, the house belonged to Piotr Bork, the superior of the royal mint. At that time the stone portal and the wooden/iron door was formed. At the end of the XVc. the building belonged to the Beer family, who made their fortune on a silver mine, at that time this led to a treasury.

In 1980 the final renovation program began, during which the elevation was made. During renovations , a few secrets were revealed : the foundation from the XIIIc., the gothic portal with a door, gothic cellars, and the first floor wall with three niches, with the arches are supported with stone heads and renaissance columns between the windows.

During complex renovation work conducted in the 1980's the condition of the walls was routinely checked. During this work, the existence of a niche with relatively well preserved iron door was discovered, On the archival photographs, a gothic door is visible immediately after the removal of the brick wall (Fig,1-2) . Lower fragments of the door showed deterioration of both wood and metal. The reasons for walling up the door are not known ; perhaps it is connected with the change in function of the chamber.

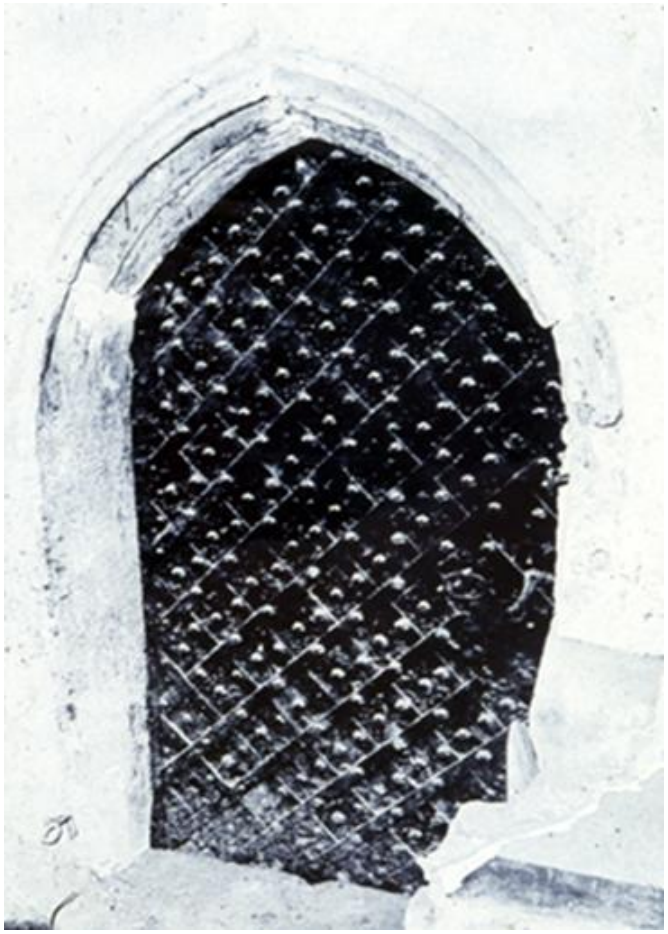


Fig.1 The gothic door. Archive photography

Description of the door

The door was done on the wood panel. The upper part of the door has an arch shape, typical for medieval doors. The door borders from the outside were reinforced by wrought iron strips of 90mm width and 6mm thick. In the arch part of the strip there are visible sections of arches. In the outside part of the door there are several diagonal narrow strips, running from two opposite directions, creating a chess –board, The interiors of chess –boarder squares are filled up by two square plates ; one is plain and fits close to wood, and outside ones is decorated with convex geometrical ornamentation. Its borders are carved out in geometrical pattern. Inside the plate there is a convex rose bump, surrounded by the circle consisting of a small half sphere. These plates were additionally covered by tin .All elements (Fig.2-3) were fixed to wooden panel by decorative hobnails.

Fig.2 The gothic door
Before conservation

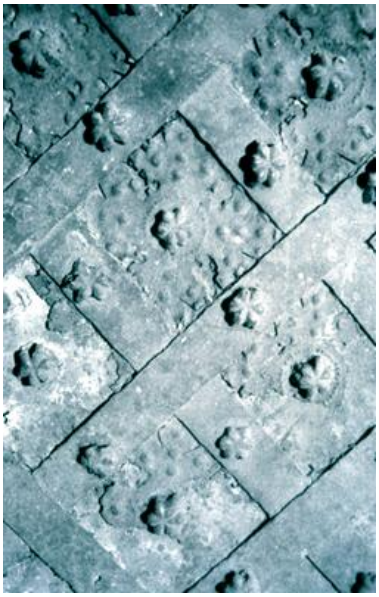
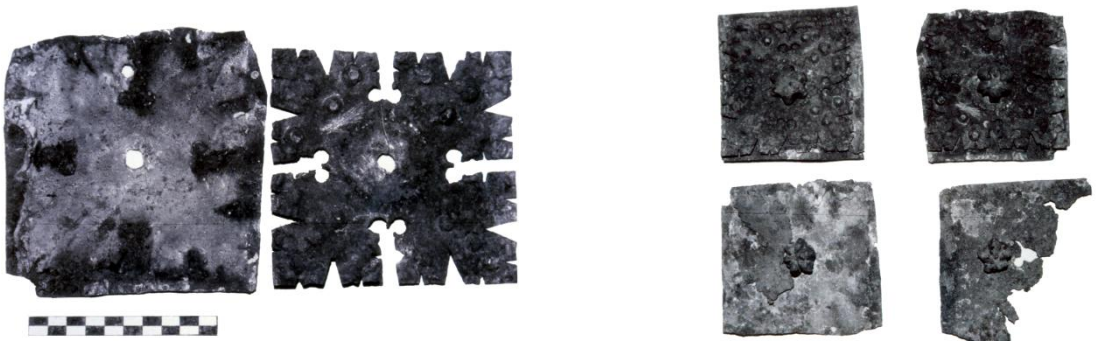


Fig.3 The gothic door ,detail
Before conservation

The view- finder was fixed , which was opened by taking off the bump. Its shape is shown on the Fig.4 The door –knocker and iron bars (Fig.5) were also fixed to the iron side of the door. In the place where the handle was located, an iron plate was there. Probably the handle was destroyed earlier.
On the wooden side of the door are the strips finished with hinges, fixed by the iron hobnails with simple round heads. There are two beautiful gothic locks and a bigger iron plate in the place of the previously installed lock .Each lock's element was additionally decorated with engraved geometrical and floral motifs. It is typical for all gothic and renaissance locks.

Fig.4 The view-finder

fig.5 The door-knocker



a b

Fig.6 a-b The plain and decorative plates. Before conservation

The door was transported to a conservation workshop, but work was held off until final renovation of the whole building was completed .Unfortunately, the changing climate conditions of temperature and humidity caused huge destruction of the metal, speeding up corrosion as well as destruction of wooden panel. Plates placed between diagonal strips also crushed and crumbled the lower part of the wooden base. It caused warping of the diagonal strips. its breaking off and total destruction.

The investor wish the door was repaired in such way the door would be again practical and functional. In 1984 the conservation work began. My team task was conservation of iron part, the another conservation team did the wooden panel conservation.

Preliminary tests

Before beginning work, X-rays tests were done for the purpose of determination the actual condition of particular iron elements. The chemical analysis were done as well as stratygraphical tests .X-rays showed the large destruction of the square plates due to corrosion process, reach up even 90percent.

The condition of diagonal and surrounding strips was much better. The presence of tin was discovered on the decorative plates .The internal plates were painted red .Such a color should not surprise anybody. In medieval times, it was the preferred color for door finishing.

Fig.7 The lock before conservation

Fig.8 The decorative plate
After reduction

Fig.9 The view-finder
After treatment

Conservation of iron details

Very advanced corrosion of several plates caused the biggest problem. None of the methods of iron conservation so far used was successful, especially since the door should be very stable to use and easy to open and close after conservation. We decided to use the method of rust reduction with hydrogen and argon gas, Such an operation is done in temperature of nearly 800° C. This method was first used in Stockholm to conservation iron objects found a wrecked warship Wasa ,extracted from the sea bottom. In that situation it was very effective.

After a lot complications, we succeeded in cooperating with Rolling Cooper Mills in Gliwice. The management made its furnace accessible to us to heat up the iron elements in hydrogen atmosphere. We created a special program for our door's elements.

The first stage of conservation consisted of very precise cataloguing ,taking photographs and documentation ,for the sake of ease in door assembly afterwards .On the following figures, particular elements before and after conservation are shown.

The next stage consisted of heating the iron element in hydrogen atmosphere In the meantime the conservators had consolidated the wooden panel with acrylic resin and completed a space in the lower part of the door by a special seasoning wood.

After reduction procedure and removing the black magnetite layer by a soft brush the shining metallic surface had appeared .On the decorative plates and hobnail head the tin layer was visible .We protected the flat internal plates by minium (red lead) and red oil paint .The rest of elements were protected by acrylic resin and wax. The lost parts (plates and strips) were reconstructed following the existing original pattern.

The last step was to fix all elements together to the wood. It was difficult and many problems came up because the wood in some parts was not hard enough to assemble the hob nails and bend them on the other side .We had to do an additional strengthening of the wood parts. Finally we succeeded .The result of our work is shown on the next figures. Since its conservation 27 years ago, the door can be inspected in the Cepelia shop located in the Hetman house. The meta is still in perfect condition .The wood does not stand the changing humidity condition and required some conservation treatment.

Fig.10 The gothic door after conservation treatment

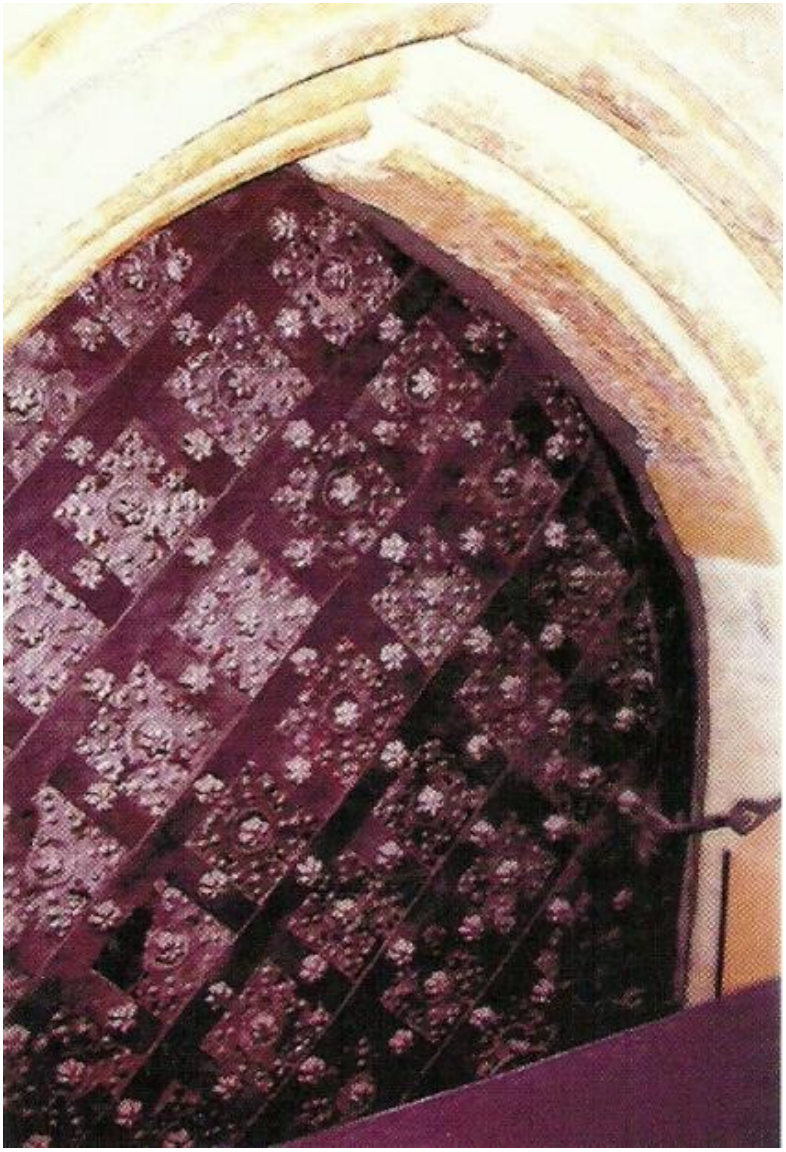


Fig.11 The gothic door after mounting to the wall

CONSEVATION OF IRON OBJECTS FROM THE ANCIENT SALT MINE WIELICZKA

The historic salt mine of Wieliczka is one of the oldest mines in Europe . It is also the most popular tourist sites in Poland. Every year, it is visited by 900 thousand tourists from all over the word who can admire the well preserved mining chambers, historical mining tools and machines.

The Saltworks Museum on the level III (135 m below the surface) boards up valuable exhibits illustrating well the development of different mining technique. The origin of Salt Mine reaches back to 13th century.

The climate in the mine is extremely aggressive as far as corrosion is concerned. The relative humidity varies from 75%RH in winter to 100% in summer, while the temperature shows more stability and oscillates around 12°C. The air is saturated with salt.

This kind of environment presents creates a lot of conservation problems. The problem being not only the removal of the products of corrosion but also creating the required stability for metallic objects which have be exhibited in condition of the salt mine .Metal exhibits found in salt mine could be divided into three groups:

The first one comprise items relating to mining techniques such as pumps, ventilators, carts and utensils made entirely of iron. More ancient mining equipment is made of puddled iron.

The second group includes wooden mining equipment and machines used for transport, both horizontal and vertical. These items are made partly of iron elements such as bands, rims, hoops, wheels, screws, nails etc.

The most ancient exhibits belong to the third group. They are the archaeological excavations which are made of wrought iron.

State of preservation of exhibits

Most exhibits when recovered were in poor state of preservation .Surfaces were usually covered with a thick corroded layer while the smaller iron objects were very frequently corroded right through. The working surfaces of different machines reveal varied stages of advances corrosion depending on whether they were in contact with salt or not.

In order to illustrate better the actual state of preservation some objects have been chosen and shown. The first object (Fig.19,20) illustrates a horse-drawn train car used by tourist in the mine, mainly by eminent Poles as well as kings and emperors of neighbouring countries ,who have visited Poland.

Due to economic reasons in1925 horse transport was replaced by cheaper in exploitation batter-powered locomotives. In 1931 electric traction was introduced on level IV. After the Second World War, the locomotives were used to carry miners. The traction locomotives (Fig.) displayed in the chamber was manufactured by Siemens in 1950.

The following examples are metal bands and mining tools. They were previously conserved by electrochemical method. After some months droplets of sweep iron appeared on their surface. The maximal concentration of chloride in corroded metal was reached about 1,2 by weight while in corrosion layer about 10%. Puddled iron tools were particularly affected by corrosion because they contained a great deal of non metallic inclusions .Disintegration of metal delamination along the nonmetallic inclusion and cracks, are visible on the Fig. The pickaxe was made of puddled iron.

The conservation treatment

In the early stage of conservation work the electrochemical method were applied which proved ineffective .Recently the alkaline-sulphite reduction process and electrolysis methods are used in conservation lab in the Museum .In the case of large objects some elements are dismantled and treated in lab by electrolytic reduction. The large objects had to be treated in situ in mine. After

removing the old protective layer ,the surface are treated mechanically. The machines are covered with the protective paints.

Air circulation was changed while its humidity was lower to 65% (wherever possible).The microclimate conditions were create for the exhibits.

Fig.12 The Cracow Saltworks Museum

Fig.13 A horse-drawn train used by tourist in the mine (19th century)

Fig.14 A horse-drawn train car used by tourist in the mine (19th century)

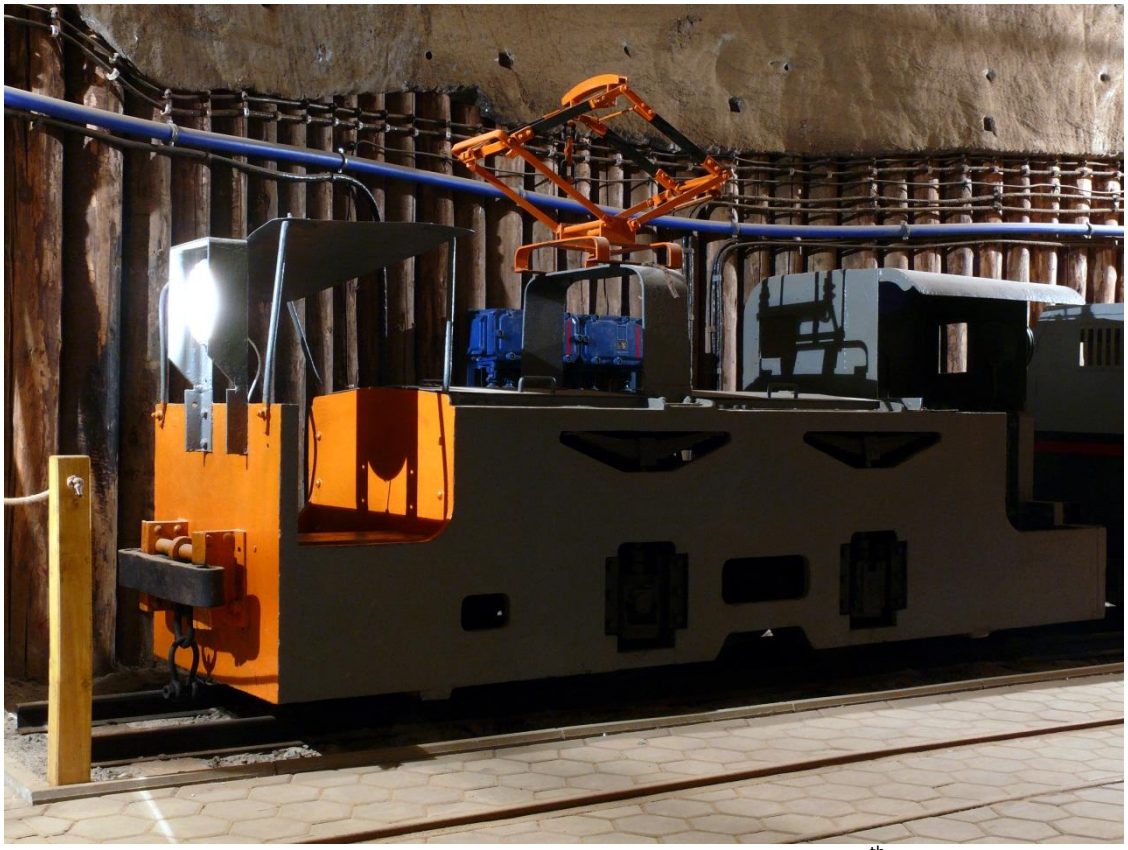


Fig.15 The electrical locomotive with a passenger car, mid 20th century

Fig.16 The electrical locomotive with miners car

a

b

c

d

Fig.17 a-d The machines used for salt transport

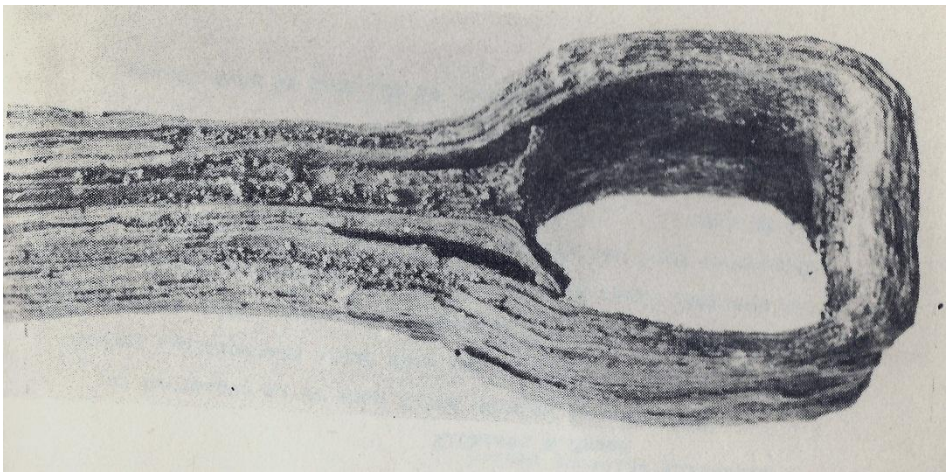


Fig.18 The fragment of the pickaxe with the droplets of ferric chlorides

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"CLIMATE MYTHS AND METAL HERITAGE."

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The attendees at the international workshop were introduced in a short lecture to key factors that are likely to affect metal heritage in our changing world. These pressures, not only included those which arise from a changing environment, but the lecture also touched on potential social and economic changes affecting the management of heritage. After this introduction participants were introduced to five objects likely to be affected by the changing global environment. These were:

1.A Class B Shay locomotive in poor condition that German railway enthusiasts had purchased from the Philippines for restoration.
2. Carnley station, a sheep farm complete with a traction engine on a sub-Antarctic island that has long been abandoned.
3 An abandoned tubular railway bridge across the River Don.
4. The Sklodowska-Curie monument constructed from stainless steel and erected outside Paris
5. The wreck of the prototype Arado-560 four jet bomber, under restoration after recovery from a barn near its crash site in Denmark.

After introducing the exercise, three groups formed to undertake the task of planning a management strategy for the objects. Each of these items and their sites pose particular problems for conservation and display, so the groups of participants were asked to develop a strategy for the presentation and preservation of the objects in a changing world. They were obliged to consider physical issues (pollution, climate), along with sociological ones (cultural importance, visitor behaviour). The climate and environmental threats to the objects were considered first. From these considerations a plan was developed, that included economic considerations, for conservation, maintenance and presentation, such that long term protection was ensured.

The plans for the objects and sites and the ideas that developed from group discussion are outlined in the sections below. The sections first give a brief description of the object followed by the discussion points made within the three groups and then some comments that arose during subsequent discussion.

SHAY LOCOMOTIVE FROM PHILIPPINES

Introduction to the object: Ephraim Shay's concept of a geared steam locomotive led to the development of a whole series of steam locomotives in the late 19th century. These were widely used in the United States and the Pacific; many on narrow gauge and forest railways. This particular Class B Shay engine was purchased by a group on enthusiasts in Germany who bid for it on Ebay. They have shipped it back from the Philippines. It is an interesting example, but has been much neglected in the jungle over the past twenty years. The enthusiasts have received a grant to restore it.

The view of the participants was that the Type B Shay should be brought back to working condition, as that is the optimum way to appreciate the locomotive. Although this class of steam engine is not known in Germany, they are so unique there would be a great interest in restoring one to its original condition. Documentation should be easy to recover from the United States as there is a great interest in these locomotives, but this will involve travel to archives and to meet with knowledgeable American engineers. The Silesian boiler works would provide an excellent location for rebuilding the boiler, that has long been out of commission. There are a large number of railway enthusiasts in Germany which should mean that they will be able to get plenty of financial help, to rebuild the engine, from individuals and local industry. The running locomotive might best be located in Saxony as there is an excellent facility there with a good storage shed for working engines. The steam locomotive should be maintained within a context that is as close as possible to its original working

life. Each year there should be a number of thematic events that reflect its origins in the Pacific forests. There should be events where hauls wooden logs to a mill. Additionally there should also be Philippine-days where food and drinks are served and everyone is encourage to dress in the national costume. The steam engine should also be used to carry the Philippine culture more widely through Germany.

Perhaps the Philippine embassy would be interested in supporting these events. Broader audiences might be attracted by with wider ranges of activities such as forest trips that emphasized other aspects of the event and encouraged forest picnic, berry collections and access to nature trails for those who were not primarily committed to railway history. Available rolling stock might not be totally realistic, so there should be an attempt to buy some examples that come available from the Philippines.

CARNLEY SHEEP STATION

Introduction to the object: The site lies on a New Zealand Sub-Antarctic Island exploited first for sealing and whaling and later sheep farming. It was never an economic success, but the abandoned site is rich in 19th century relics and probably represents one of the most complete 19th sheep stations in its original condition. A particularly important item is a complete example of a late 19th steam traction engine built in Christchurch, New Zealand. This engine was derived from a model created by the firm of *Ransomes, Sims and Jeffries* in Great Britain, and although in the traction engine is in parts it is certainly capable of being restored to running condition. There are increasing numbers of tourists who visit the island, while en-route to the Antarctic. The island also boast an interesting ecology, which has put pressure on preserving the station ruins. The major problem is that government policy for these Sub-Antarctic Islands favours a return to their natural state and often demands the removal of any signs of earlier occupation or economic activities. Additionally climate change is making the islands warmer and wetter.

There is considerable importance in restoring this sheep station as so many of these have already been removed from sub-Antarctic Islands by the Australian Government in line with their desire to return then to their natural state. The New Zealand government should be encouraged to reflect on the uniqueness of the remaining signs of occupation, perhaps using the not-so-subtle pressure of a suggestion that the neighbouring "Australian government may have got it wrong" The small number of tourists who come to the island en-route to the Antarctic might find some relief to see the hint of human settlement in the vast remoteness of the Southern Ocean. The sheep-station should be testimony to human desire and spirit that struggled to use the island.

The desolation, solitude and serenity should not be disturbed by running this engine so it should not be displayed in running condition. Furthermore it would be costly to maintain in this condition. Nevertheless the complete traction engine should be disassembled and restored. The boiler is probably in reasonable condition, but many of the components have rusted so these will have to be restored using modern techniques of rust replacement or rust prevention.

The large shearing shed, which still stands although in a damaged state, should be restored as a kind of pavilion. The galvanized iron sheets in many cases will have to be replaced as they are badly corroded and torn away by strong winds, but these do not have a particular notable heritage significance. The building could be painted in its original muted red colour, rendering it as close as possible to its original appearance. Once restored and weather-proof it could become a centre for displaying the steam traction engine. This presentation should be accompanied by photographs and objects that represent the lives of the sheep farming families that occupied the island so long ago. This would give a sense of of daily life and the way the wool was handled before transfer to New Zealand.

It would be important to improve the dock facilities that handle the tourists and perhaps also tidy up some of the debris relating to the early 19th century whaling efforts based on the island. These would present an additional point of interest for visitors. The increased corrosion that is likely to arise from

warmer conditions in the sub-Antarctic needs to be addressed by a careful maintenance programme. It is possible that soil structure will be disturbed by longer periods of thawing in a warmer world, the tourists could further damage the soils. Well formed paths are needed to direct the tourists in a way that minimize damage and to some extent encourage walking along the sand and pebbles of the beach where possible.

The fact that this is an unoccupied island means a minimalist intervention. The tour-ships should visit with a tour-leader who also has received some training in conservation, so that anything that has become a problem since the previous visit can be documented and set right. Security can be at a minimum there are few visitors who might damage the relics or venture unsupervised onto this remote island.

MIKHAIL VOROSHILOV'S TUBULAR BRIDGE ACROSS THE DON

Introduction to the object: The town of Voronezh represents an important rail link and the first attempt to bridge the River Don at this point. The bridge was an imaginative design of the little known engineer Mikhail Voroshilov, which led to this almost unique tubular structure of the 1870's, the only such bridge in Russia. Other examples, would have been the lost Menai Strait bridge in Wales. Voroshilov's bridge has been poorly maintained and has now been replaced by a more conventional bridge nearby. Although the iron box structure of the old bridge is superficially complete, the cast iron structural elements are suffering from years of neglect.

This object was mentioned in the workshop, but not discussed or developed in detail.

SKLODOWSKA-CURIE MONUMENT

Introduction to the object: Marie Curie monument near Paris is near completion with its assembly on site. There has been some enthusiasm over incorporate a small polonium insert into the stainless steel structure. The radioactive metal has been extracted from samples of polonium found by Marie Sklodowska-Curie in 1898, which led to her first Nobel Prize. The monument is already tarnishing, perhaps related to the deposition of diesel particles and there is growing corrosion around the polonium insert and at metal welds.

This object was mentioned in the workshop, but not discussed or developed in detail.

ARADO-560

Introduction to the object: The Arado-560 is a four-engined jet that was developed from the Arado Ar 234 *Blitz* . The Blitz was the world's first operational jet-powered bomber. The sole Arado-560 prototype crash landed in a field in Denmark during trials late in World War 2 and was thought to be lost. Recently much of the aircraft, including the BMW 003E jet engines, has be re-discovered in an isolated barn and shipped for restoration and display at the nearby aviation museum near Åbenrå, Southern Denmark. The metal has suffered much from the marine environment, although one of the jet engines has been fully restored.

The key idea of the participants was not to over-restore the Arado 560. The plans were to present this aircraft, as if it has only recently crashed. This is somewhat reminiscent of the restoration of the DC3/C47 from the *Catalina Incident* (Grisell, 2007; Anon, 2011), which is now on display in Sweden. Although the Arado 560 has spent much of the time since it crashed in a barn there is still much soil attached, so the partial burial and initial recovery has led to some damage particularly to the wooden parts. Wood was typical of Arado aircraft and increasingly common in German aircraft towards the end of the World War 2 as aluminium was in short supply; hence the widening use of glued wood.
The conservation approach for this aircraft, so long in a barn with less than idea storage conditions, was driven from a desire for minimum intervention. There is a potential for pollutant attack as the future summers will perhaps have higher ozone concentrations and hence a threat to aluminium. Additionally as it is so near the sea that deposited chlorides might be a problem. An aircraft hanger style building will house the aircraft along with additional displays to broaden the interest at this

single-object museum. This would detail the lives of the crew and the development of local issues surrounding the recovery. A full scale mockup will incorporate a simulator, so you can fly the prototype and even attempt to prevent the crash that destroyed it. Funding from BMW will hopefully to assist conservation as the engines are from this manufacturer.

CONCLUSIONS

The participants worked very hard to develop plans for their objects and sites and showed considerable breadth in their approaches to management of the problems. They often emphasized aspects of presentation of the object and funding, more than concerns for changing physical and climate pressures. The short verbal presentations were imaginative and conveyed a sense of excitement to the audience.

At the end of the exercise we had to reveal that all the sites were mythical and sadly none of the objects exist, rather in the vein of exercises run previously (Brimblecombe, 2010). The objects were fictitious reflecting an approach akin to the imaginary geography of Manguel and Guadalupi (1999). Such a mythological approach was adopted to prevent prior knowledge from distorting the need for an innovative evaluation or attempts by participants to download a proposed solution from the Internet.

However, the objects were not without some realism. We realize that there are a number of Far Eastern Shays to be found in various states of repair in mountain forests, most notably Alishan, of Taiwan. There were some unsuccessful attempts at sheep farming on some Australian sub-Antarctic islands, but these islands have been returned to their natural state and few traces of the pioneering activities remain. There may be parallels with the need to preserve some of the recent Arctic heritage, such as that from mining on Spitsbergen. The Arado 560 was planned, but never built, although its parent the Arado 234 was the last German aircraft to fly over England during World War 2. The participants accepted the imaginary sites with good grace, many being sorry that they did not really exist as they all seemed so fascinating.

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