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Analytical Investigations of Outdoor Bronze Monuments: EUREKA Project EU 316 EUROCARE-COPAL

The external appearance of metal works of art is impaired by the influence of corrosive substances.

Corrosion of cultural property therefore does not only lead to damage, destruction and – in extreme cases – to the complete loss of the work of art, but also changes its outward appearance in the course of time – a fact that has to be taken into consideration with regard to conservation. Conservation deals not only with the question of arresting the decay, but also with conserving the historical information or historical traces of the object, such as patina etc. Conservation science and research therefore go far beyond the goals of industrial corrosion science in the development of protection strategies.

One of the most important material groups within the production scale of metal artifacts are the copper alloys.

While a lot of research work has been done in the past on the conservation of museum objects, systematical research on the conservation of outdoor bronzes only started a few years ago.

In the meantime much new understanding has been obtained in this field, but there is much still left to be done to close the gap between the basic knowledge about the corrosion processes of the alloys, the formation, constitution and properties of the corrosion patinas and the practical conservation work, the latter often still being carried out on a very empirical and non-scientific basis in the different countries. The EUREKA Project EU 316 EUROCARE-COPAL (VENDL, 1988)[38] aims to close this gap through the practical cooperation of institutions and industry in the following countries: Austria, the Czech Republic, Germany, Hungary, Italy, Portugal, Russia (formerly USSR) and Sweden.

As Marabelli (1987)[17] has already pointed out, studies on the conservation of outdoor metallic monuments must be conducted along three principle lines:
- examination of the structures,
- identification of the corrosion processes, and
- refinement of intervention methods.

The following can only be a short survey of the new scientific approaches of the COPAL project without going into great detail on what has already been carried out during the last years.

In addition to photogrammetry the first step of studying an outdoor monument should be the structural examination of the construction of the monument and the identification of the specific composition and structure of the used alloy. During the last years, some new Non Destructive Methods (NDMs) of examination have been increasingly employed in the field to meet the demands of these investigations:
- ultrasonic control to study thickness, porosity, missing areas of material and structural continuity,
- radiography and endoscopy to define structural defects, restoration inserts and different construction details of large bronze statues,
- thermovision to study homogeneity and dishomogeneity of the cast leading to different thermal signals,
- acoustic emission to investigate structural damage such as plastic deformation and the formation and propagation of microcracks,
- eddy currents to investigate corrosion thickness, soldered joints and dowels,
- interferometry and strain gauges to study structural damages and deformations.

The use of NDMs for the study and conservation of works of art is given in various conference reports.[26]

In the EUREKA Project EU 316 EUROCARE-COPAL two NDMs, used only a few times previously, are going to be developed for routine use in the field of conservation science concerning outdoor statues by our Italian partners:
- A special test head using radar techniques will be developed for analysis of the monument's base and the load bearing structures to replace the more problematical analytical tool of gamma rays.
- A monitoring system for measuring the time of wetness of surface is to be designed and set up. This system will allow to measure conductivity at various relative humidity levels due to microcondensation into the patina layers. The measuring cell will be located on the statue, the data being sent by radio to the monitoring center. From the data, some quantification of the corrosion processes and a damage function, correlated to the period of wetness of the surface as well as to some specific air pollution agents promoting corrosion can be obtained (Marabelli, 1990).[18]

Although a lot of information can be gained by using NDMs, there are still some questions that – at present – can only be answered by taking samples. Therefore, the sampling method is a very important aspect in the field of investigation of cultural property. Samples should be as small as possible, but provide the full scale of information. Within the COPAL project, our partners from Munich developed a simple, but most effective sampling device for taking samples from metal statues (Mach/Mayer, 1988)[14]: A small drilling core of 2 mm diameter is obtained without damaging the statue through perforation of the metal, but leaving just a small cavity only a few millimeters in depth. From these samples not only the exact composition can be studied, but also the metallographic microstructure can be investigated (Fig. 1).

Metallographic examinations of samples from selected outdoor bronze monuments revealed a wide range of polycristalline to cast structures even within one and the same monument.

The influence of microstructure on the corrosion of metals has been neglected for a long time in the field of conservation science.

Recently MacLeod and Pennec (1990)[16] found widely divergent corrosion rates in terms of the metal microstructure and stresses induced – in the absence of any discernable differences in the chemical composition of copper alloys.

Therefore, investigation of the correlation of microstructure and the corrosion of copper alloys was made an additional goal of the EUREKA Project EU 316 EUROCARE-COPAL. Since

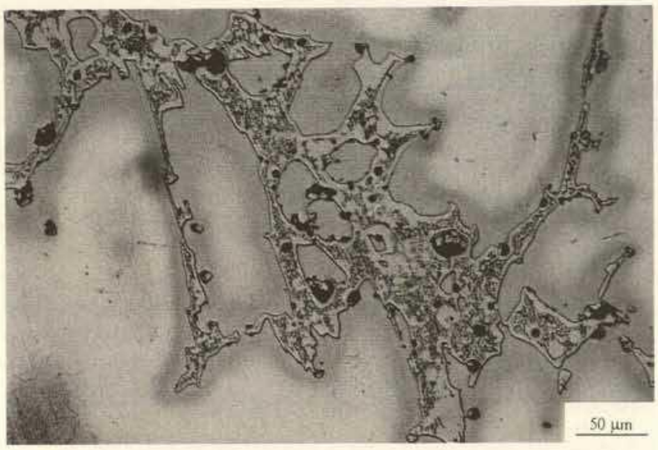

Fig. 1. Microstructure of a sample from the Munich monument of King Maximilian II: dendritic structure consisting of an α– dendritic system with an α + δ– eutectoid infill

all the microstructures mentioned above can occur in a metal statue, the different ways they influence corrosion of the object must be taken into account when considering conservation therapies. In order to study the behaviour of alloys with different microstructures, a special metal-casting device was developed under the COPAL project by the Viennese group in Austria. This can produce alloys with specific microstructures (Vendl/ Pichler,[40] 1990). The alloys used for these experiments are identical in their composition to those of the outdoor bronze monuments (Fig. 2, 3).

Fig. 3. Alloy composition of Marquês de Pombal monument, Lisbon, Portugal

Fig. 2. Alloy composition of two equestrian statues from Millennium monument ensemble, Budapest, Hungary

	Cu	Sn	Pb	Zn	Fe	Ni	Ag	Sb	As	Bi	Cd
H 45 ARPAD	82,10	8,858	5,578	2,8838	0,119	0,1335	0,0281	0,141	0,158	<0,025	<0,001
H 46 ARPAD	82,76	8,338	4,944	3,4063	0,151	0,1426	0,0258	0,118	0,117	<0,025	<0,001
H 49 ARPAD	84,67	7,673	4,789	2,5337	0,071	0,1033	0,0250	0,135	<0,100	<0,025	<0,001
H 51 ARPAD	81,89	8,925	5,581	3,1970	0,112	0,1104	0,0272	0,160	<0,100	<0,025	<0,001
H 52 ARPAD	83,54	8,379	5,446	2,0959	0,065	0,1057	0,0294	0,162	0,150	0,025	<0,001
H 53 ARPAD	83,10	8,330	5,070	2,9530	0,101	0,1151	0,0271	0,158	0,145	<0,025	<0,001
H 55 ARPAD	80,63	7,615	5,131	5,8578	0,323	0,0990	0,0269	0,168	0,128	0,025	<0,001
H 57 ARPAD	87,70	5,722	3,987	2,0814	0,092	0,0953	0,0257	0,162	0,105	0,032	<0,001
H 58 ARPAD	82,70	7,904	5,099	3,7275	0,150	0,1303	0,0274	0,115	0,148	<0,025	0,0010
H 61 ARPAD	81,94	8,986	5,800	2,6768	0,100	0,1108	0,0272	0,193	0,171	<0,025	<0,001
H 63 ARPAD	82,18	8,449	4,869	3,8410	0,156	0,1188	0,0268	0,181	0,176	<0,025	<0,001
H 64 ARPAD	81,52	7,559	4,795	5,3385	0,311	0,1022	0,0272	0,177	0,173	<0,025	0,0012
H 66 ARPAD	81,39	7,313	4,944	5,5466	0,330	0,0997	0,0268	0,168	0,153	0,025	<0,0013
H 101 ARPAD	82,59	8,519	4,876	3,3939	0,070	0,1277	0,0267	0,173	0,188	0,031	0,0010
H 102 ARPAD	82,69	8,542	4,757	3,3887	0,070	0,1281	0,0258	0,173	0,199	0,026	0,0010
H 103 ARPAD	82,56	8,828	4,838	3,1561	0,063	0,1252	0,0284	0,177	0,219	<0,025	0,0010
H 107 ARPAD	82,08	8,560	4,853	3,8285	0,160	0,1175	0,0258	0,166	0,183	0,024	0,0110
H 109 ARPAD	83,00	8,633	5,003	2,7144	0,070	0,1209	0,0425	0,182	0,209	0,027	0,0010
H 68 TAS	80,47	6,213	4,141	8,2733	0,331	0,1922	0,0289	0,166	0,160	0,026	0,0026
H 70 TAS	81,38	6,168	3,750	7,8527	0,337	0,1932	0,0261	0,147	0,140	<0,025	0,0025
H 72 TAS	79,72	6,684	4,303	8,0026	0,322	0,3830	0,0630	0,317	0,205	<0,025	0,0049
H 74 TAS	79,41	7,504	4,311	7,4581	0,208	0,4850	0,0217	0,363	0,239	<0,025	0,0044
H 75 TAS	82,29	7,559	4,121	5,1718	0,219	0,2571	0,0248	0,215	0,144	<0,025	0,0027
H 85 TAS	80,46	6,360	4,360	7,5786	0,299	0,3766	0,0598	0,293	0,208	<0,025	0,0037
H 87 TAS	80,02	7,437	4,935	6,3520	0,229	0,4104	0,0271	0,258	0,224	<0,025	0,0028
H 89 TAS	81,09	6,981	3,699	7,2050	0,371	0,2655	0,0202	0,202	0,162	<0,025	0,0027
H 90 TAS	82,78	4,917	4,888	6,8001	0,292	0,1328	0,0225	0,161	<0,100	0,025	0,0036
H 92 TAS	80,84	6,229	5,376	6,8316	0,241	0,1359	0,0267	0,189	0,124	<0,025	0,0024
H 93 TAS	80,69	7,615	3,855	6,8329	0,039	0,2315	0,0271	0,220	0,130	<0,025	0,0027
H 94 TAS	80,37	7,347	4,162	7,0343	0,404	0,2445	0,0281	0,241	0,166	<0,025	0,0035
H 95 TAS	78,71	6,083	5,942	8,3206	0,368	0,1678	0,0261	0,215	0,165	<0,025	0,0024
H 96 TAS	79,70	6,941	4,638	7,5833	0,432	0,3163	0,0245	0,195	0,165	<0,025	0,0030
H 99 TAS	81,74	6,040	3,667	7,5550	0,410	0,2184	0,0254	0,185	0,152	<0,025	0,0028
H 100 TAS	79,38	6,744	4,505	8,1212	0,249	0,3974	0,0238	0,316	0,258	<0,025	0,0039

Fig. 3. Alloy composition of two equestrian statues from Millennium monument ensemble, Budapest, Hungary

Marquês de Pombal	Cu	Sn	Pb	Zn	Fe	Ni	Ag	Sb	As	Bi	Co	Au	Cd
EU 45	92,49	6,346	0,577	0,1328	0,030	0,1313	0,0887	0,104	0,103	<0,025	<0,005	<0,01	<0,0010
EU 46	94,08	4,900	0,457	0,0631	<0,010	0,1223	0,0743	0,075	0,233	<0,025	<0,005	<0,01	<0,0010
EU 51	90,65	7,633	0,640	0,3771	0,070	0,1157	0,0851	0,101	0,300	0,030	<0,005	<0,01	<0,0010
EU 52	94,29	4,790	0,285	0,1516	<0,010	0,0977	0,0569	0,055	0,274	<0,025	<0,005	<0,01	<0,0010
EU 55	91,44	6,748	0,628	0,1096	0,047	0,0932	0,0863	0,120	0,723	<0,025	<0,005	<0,01	<0,0010
EU 56	92,26	5,965	0,656	0,1135	<0,010	0,1079	0,0811	0,133	0,637	0,042	<0,005	<0,01	<0,0010
EU 57	91,40	7,110	0,616	0,1191	0,013	0,1276	0,0856	0,100	0,386	0,047	<0,005	<0,01	<0,0010
EU 58	92,36	6,478	0,569	0,0417	0,013	0,1730	0,0817	0,089	0,162	0,033	<0,005	<0,01	<0,0010
EU 59	90,57	7,893	0,623	0,0421	0,011	0,1062	0,0831	0,162	0,469	0,039	<0,005	<0,01	<0,0010
EU 60	90,90	7,384	0,706	0,0354	<0,010	0,1099	0,0835	0,146	0,601	0,032	<0,005	<0,01	<0,0010
EU 61	92,52	6,419	0,568	0,1085	<0,010	0,2044	0,0886	0,058	<0,100	0,031	<0,005	<0,01	<0,0010
Maximum	94,29	7,893	0,706	0,3771	0,070	0,2044	0,0887	0,162	0,723	0,047			
Minimum	90,57	4,790	0,285	0,0354	0,011	0,0932	0,0569	0,055	0,103	0,030			
Durchschnitt	92,09	6,515	0,575	0,1177	0,017	0,1263	0,0814	0,104	0,353	0,023			

Löwe	Cu	Sn	Pb	Zn	Fe	Ni	Ag	Sb	As	Bi	Co	Au	Cd
EU 48	93,62	5,348	0,496	0,0272	<0,010	0,1367	0,0754	0,090	0,206	<0,025	<0,005	<0,01	<0,0010
EU 49	90,02	8,531	0,699	0,1623	0,013	0,1024	0,0927	0,106	0,275	<0,025	<0,005	<0,01	<0,0010
EU 50	90,01	8,661	0,661	0,0811	<0,010	0,1054	0,0968	0,104	0,250	0,028	<0,005	<0,01	<0,0010
EU 53	90,34	8,218	0,657	0,1825	<0,010	0,0902	0,0885	0,081	0,343	<0,025	<0,005	<0,01	<0,0010
EU 54	92,45	6,294	0,570	0,2412	0,012	0,1163	0,0823	0,082	0,153	<0,025	<0,005	<0,01	<0,0010
Maximum	93,62	8,661	0,699	0,2412	0,013	0,1367	0,0968	0,106	0,343	0,028			
Minimum	90,01	5,348	0,496	0,0272	0,012	0,0902	0,0754	0,081	0,153	0,028			
Durchschnitt	91,29	7,410	0,617	0,1389	0,005	0,1102	0,0871	0,093	0,245	0,006			

Minerva	Cu	Sn	Pb	Zn	Fe	Ni	Ag	Sb	As	Bi	Co	Au	Cd
EU 74	87,79	4,088	2,044	4,9486	0,253	0,0774	0,0506	0,087	0,655	<0,025	<0,005	<0,01	0,0030
EU 76	87,89	4,100	1,686	5,0368	0,150	0,0816	0,0537	0,107	0,893	<0,025	<0,005	<0,01	0,0030
Maximum	87,89	4,100	2,044	5,0368	0,253	0,0816	0,0537	0,107	0,893	0,000			0,0030
Minimum	87,79	4,088	1,686	4,9486	0,150	0,0774	0,0506	0,087	0,655	0,000			0,0030
Durchschnitt	87,84	4,094	1,865	4,9927	0,202	0,0795	0,0522	0,097	0,774	0,000			0,0030

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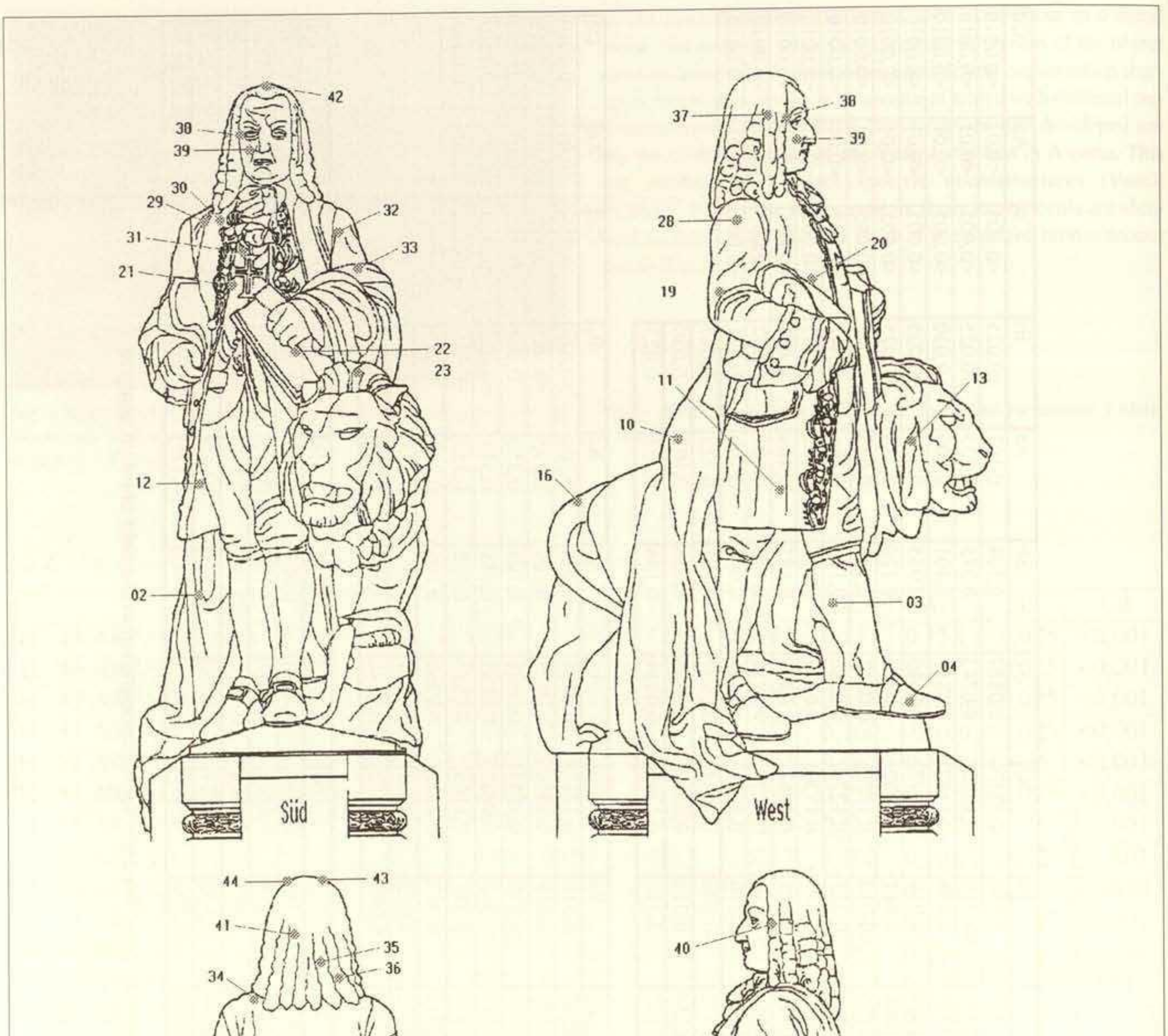
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Corrosion tests on these alloys are being carried out by the Swedish group in Göteborg, using a special sensitive artificial weathering chamber. This experimental set-up allows the use of pollutants at ppb concentration range.

One of the outstanding advantages of this corrosion exposure system is the fact that concentrations of SO_2, NO_x etc. can be used as they occur in the real environment.

First results show that various microstructures – dendritic, recrystallized, mechanically stressed, reheated mechanically stressed structure – exhibit different types of corrosion behaviour.

Before the cleaning of a statue a detailed investigation of the patina layers has to be carried out:

Extensive studies of the patina layers (using XRD and light microscopy) of some of the most outstanding outdoor bronze monuments, i. e. the memorials of King Gustav II Adolf (Göteborg, 1854), Minin and Pozharsky (Moscow, 1818), Peter the Great (St. Petersburg, formerly Leningrad, 1782), King Max II (Munich, 1875), Emperor Josef II (Vienna, 1807), the Millennium Memorial (Budapest) or the Marquês de Pombal Memorial (Lisbon) have been performed (e. g. Pichler/Sauer)[25] with the aim of developing special conservation treatments, some of which have already been implemented (Fig. 4, 5, 6).

Copper oxide, cuprite, and basic copper sulfates are the predominant crystalline corrosion products found on outdoor bronze and copper monuments.

◁ Fig. 4. Positions of investigated patinas from the Marquês de Pombal Memorial (Lisbon)

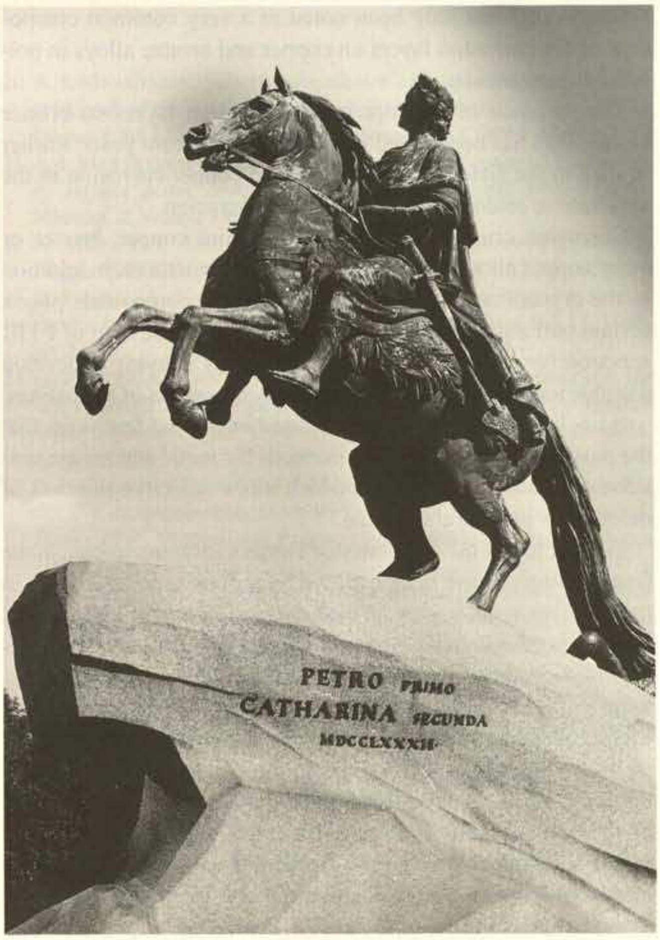
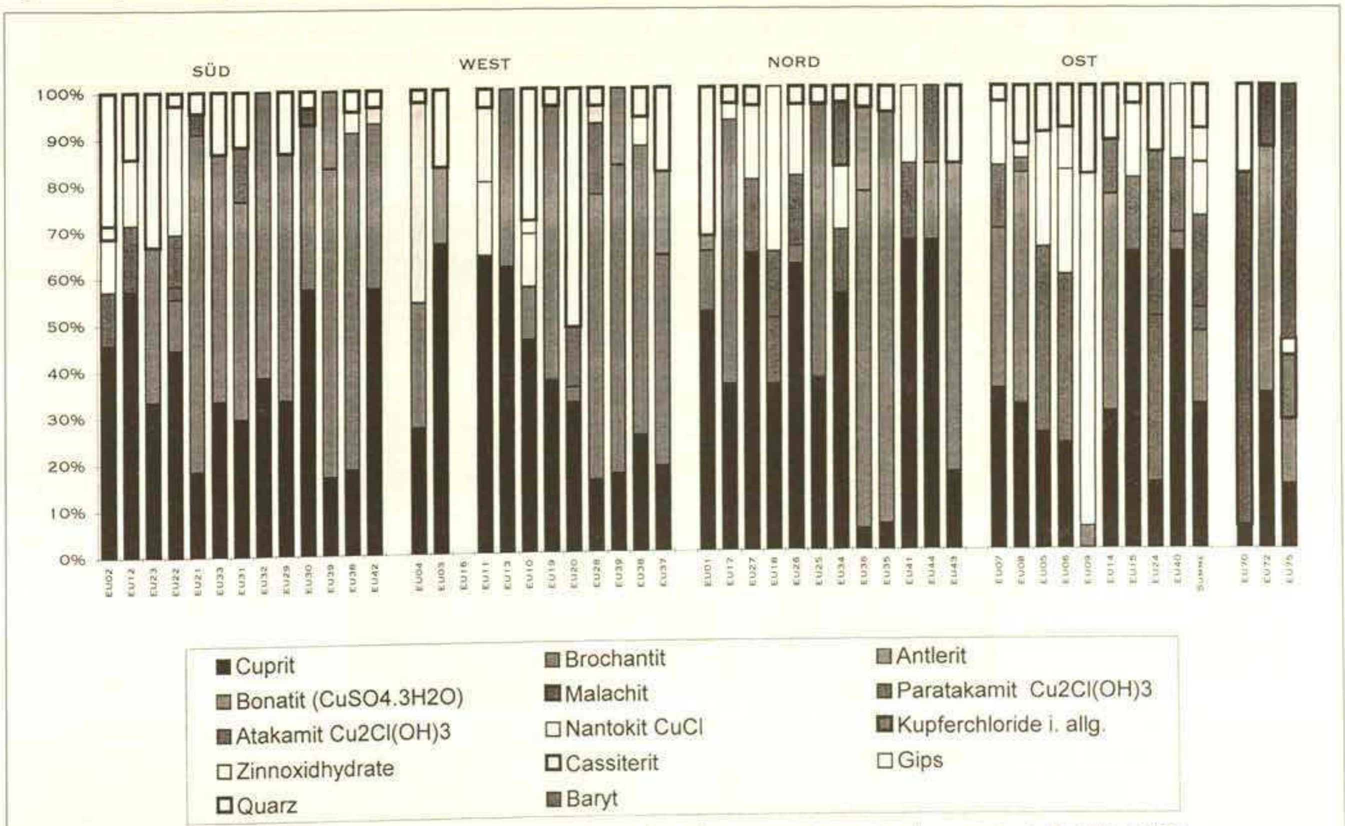


Fig. 5. Peter the Great Memorial, St. Petersburg (formerly Leningrad) ▷

Fig. 6. Semiquantitative presentation of crystalline substances found in the Marquês de Pombal Memorial patina layers (dependent on wind direction)



Acknowledgement: I am deeply indebted to Dr. Roman Sauer for permanent support and cooperation in the field of XRD

Brochantite has long been noted as a very common component of the corrosion layers on copper and bronze alloys in polluted environments.

The presence of antlerite in the corrosion layers on bronze monuments has been noted several times in recent years. Earlier studies in the field of copper alloy and copper corrosion in the atmosphere seldom cited this form of corrosion.

Corrosion crusts on artifacts made from copper, bronze or other copper alloys may display complex structures. In addition to the crystallized components, amorphous compounds play a certain part and should not be forgotten. With the help of FTIR spectroscopy the Munich group in Germany is trying to develop a usable tool to check the amorphous components of the patinas.

It has been repeatedly demonstrated in the last few years that the most appropriate cleaning methods for metal statues are sensitive mechanical treatments which allow selective removal of deleterious parts of the patina.

In order to test the efficiency of conservation treatments in the future, samples have been exposed at various exposition sites in the last five years under defined exposition and environmental conditions. Racks with Rg5 and Cu test plates (exposed to unhindered weathering) have been installed in Europe in St. Petersburg (formerly Leningrad), Moscow, Göteborg, Copenhagen, Munich, Vienna (exposition also on freely rotating carousels, the Mank Carousel), Venice and in the Algarve, in Australia in Fremantle, in the USA in New York, San Francisco and Honolulu. Prior to exposure some samples at USA sites were patinated artificially with antlerite, brochantite and antlerite / brochantite mixtures. Some of the sites have a meteorological station in the immediate vicinity (e. g. Göteborg, Venice etc.). Recent results (Pichler/Vendl)[24] indicate that specially produced dense brochantite and / or antlerite layers seem to protect the metal substrate as much as 10 times more effectively than the organic coatings currently being used for the routine conservation of outdoor sculptures.

Therefore, present investigations carried out at the ISCA are concentrating on the formation of artificial cuprite, brochantite, antlerite, and brochantite / antlerite mixtures on pure copper and the Rg5 alloy.

Some of the structural details may be dependent on the microstructure of the metal which is attacked by corrosive agents (Fig. 7). Their formation may also be influenced by a variety of growth mechanisms relating to the development and morphology of the corrosion products themselves (correlation of patina colours versus condition of crystal growth, deposition medium etc.). A variety of colours and surface finishes have already been obtained by developing different patinating procedures.

Still the question of an evaluation method concerning efficiency of protecting outdoor bronzes against metal loss (patinated and coated objects) has not been able to be answered so far. Once developed this could radically question the quality of present routine conservation measures.

Within the COPAL project (chairman from 1988-1996 Alfred Vendl, since late 1996 Martin Mach) a quantification of the efficiency of treatments by using statistical methods for the evaluation of results, obtained from non-treated and treated exposed sample plates, will be worked out.

The following monuments are investigated within the frame of COPAL:

King Max II (1875) in Munich, Bartolomeo Colleoni (1497) in Venice, Tsar Peter I (1782) in St. Petersburg, Minin and Pozharskij (1818) in Moscow, Josef II (1807) in Vienna, King Gustav II Adolf (1854) in Göteborg, the Millennium Memorial in Budapest and the Marquês de Pombal Memorial (Lisbon).

Fig. 7. SEM micrograph: artificial antlerite on Rg5 alloy

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