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THE STUDY OF METAL-OLD WOOD INTERACTIONS UNDER THE INFLUENCE OF PEDOLOGICAL FACTORS

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ABSTRACT

In the manufacture of wood objects, for binding and strengthening were used nails, cramps and other metallic elements, which in the archaeological site suffered degradation and deterioration processes, specific to metal-wood interface. The chemical and physical-structural characteristics of the products resulted from metal-old wood interactions can set up a database that can be used in authentication. For the study were taken wood samples from the Roman and Byzantine era, from Dobrogea and Moldova areas, resulted from the archaeological excavations, after year 2000, which presented in their structure metallic elements. The samples were analyzed with scanning electron microscope coupled with energy dispersion X-ray (SEM-EDX).

KEYWORDS: old wood, degradation, deterioration, corrosion, SEM-EDX.

1.Introduction

One knows the fact that the inorganic materials are much more resistant to exogenous factors as compared to the organic ones. The latest are attacked firstly by the microbiological agents which transform them, by biochemical processes, into humus while the inorganic materials are attacked by erosion and corrosion processes, thus passing into a mineral phase [1-4].

Even from the manufacturing/creation of objects, in the case of complex structures containing organic and inorganic materials, these suffer reciprocal interactions. One also knows that wood, a frequently used material, both in the structure of engineering constructions and for the manufacturing of domestic or art objects, undergoes degradation processes under the influence of some other nature materials with which it chemically interacts. Among these materials we have to mention mortars, concretes and metals. The wood interaction with metals has been very little studied [1-6].

That is why, this paper points out some cases connected to the wood-metal interaction, studied by direct analysis or with magnifying equipment (optical and electronical microscopes) as well as by the SEM-EDX technique.

2. Experimental Part

2.1. Samples

The samples taken for study are pieces of oak-tree wood fixed in iron nails from a Church floor (Zamostea, Suceava County, 1832 A.D.), which had an excessive humidity content and also bronze objects (Nufărul site, Tulcea County, IX-Xth Century and Novium Dunum, Tulcea County, XIIth Century) with monolithised wood on them.

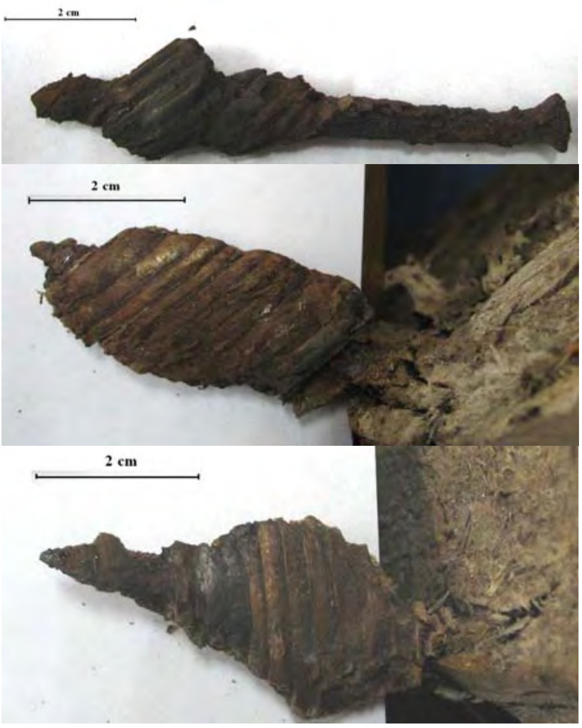


Fig. 1. *Oak-tree wood samples with iron nails (Zamostea Church, Suceava County, 1832 A.D.)*

Fig.2. *Bronze plates (Novium Dunum, Tulcea County) with monolithised wood.*

Fig.3. *Bronze Coins with monolithised wood (Nufărul site, Tulcea County, IX-Xth Century)*

2.2. Optical Microscopy

The samples were optically analyzed with a Motic Microscope with digital camera, having magnifying orders of 10 - 40X.

2.3. Scanning Electron Microscopy and X-ray Spectrometry (SEM-EDX)

The Scanning Electron Microscopy has been done with a TESCAN Vega II LSH electron microscope with a Bruker EDX spectrometer, with two functions:

-The image analysis with secondary electron detector (SE): resolution: up to 4.0 nm;

-The element mapping with energy dispersive X-ray spectrometer (EDX): all elements are simultaneously displayed and automatically overlaid.

-The present study has been done at an accelerating power of 30.0 kV, in the field of magnifying orders of 75-300X, with the distribution mapping of 6 elements from the surface of the old wood.

3. Results and Discussions

Fig. 4 presents the section of the wood – metal interaction zone, with the analysed longitudinal section, from which there appears that the part from the floor oak beam placed in the damp soil of the treading level has been preserved under the shape of a lens in a totally rotted beam. The longitudinal section of the lens along the iron nail shows that, on the direction of the fibre, the thickness of the preserved wood is greater than perpendicular on the fibre. The rotting of the beam and partially of the floor (on the beam intrados) has been caused by the *Merulius Lacrimans* mushroom which has attacked extensively all the wooden elements from the respective church.

Therefore, we speak about a preservation process of the wood under the form of a lens due to the different degree of penetration of the Fe oxidihydroxides (II, III) on the two directions along the fibre and perpendicular on it. The test proves that the Fe oxidihydroxides (II, III) have had an antimycotic effect, preserving very well the wood only in the penetration area.

Fig. 4. *Longitudinal section of the wood-metal interaction area: A – the floor; b – joist*

Fig. 5 presents the morphology of the surface from the contact wood – metal area in which one can notice thin traces of iron oxidihydroxides which have represented the impregnation source.

The nails have been better preserved in this area due to the inhibitor components from the oak wood such as, for instance, the tannin, than in the connection beam – floor area which has been directly exposed to the corrosive agents from the soil.

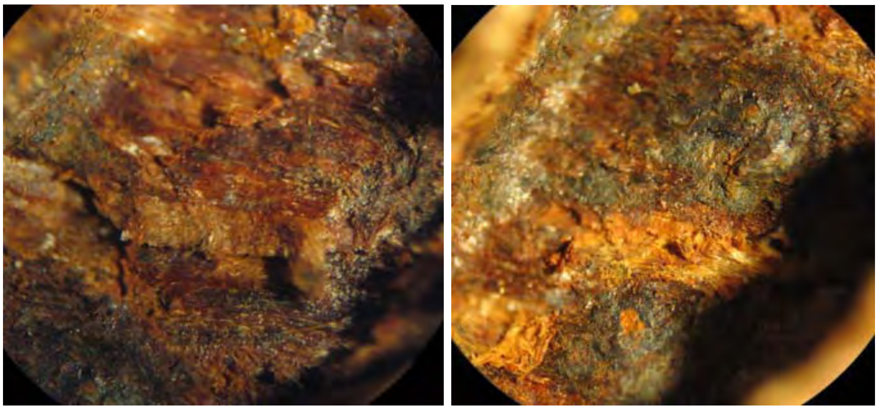


Fig. 5. *Images taken with optical microscope of wood with iron traces non-uniformly distributed*

Table 1 presents the composition of the alloy from which the nail has been manufactured (OL37).

Table 1. *Composition of the iron nail*

Element	Weight percent [%]	Atomic percent [%]	Error in %
Iron	95.849774	87.917083	2.664899
Carbon	0.353141	1.417842	0.558082
Silicon	0.247112	0.424298	0.059891
Phosphorus	0.186209	0.289913	0.051035
Sulfur	0.124372	0.187042	0.043107
Oxygen	3.239392	9.763822	0.884542
	100	100	

Fig. 6 presents the SEM microphotography with the two positions of the vector chosen by the analysis of the variation of the main components from the wood – metal interaction area.

From the EDX spectrum one can point out the continuous and uniform variation of the penetration effect of the Fe oxidihydroxide (II, III) on the two directions in the preservation area of the wood.

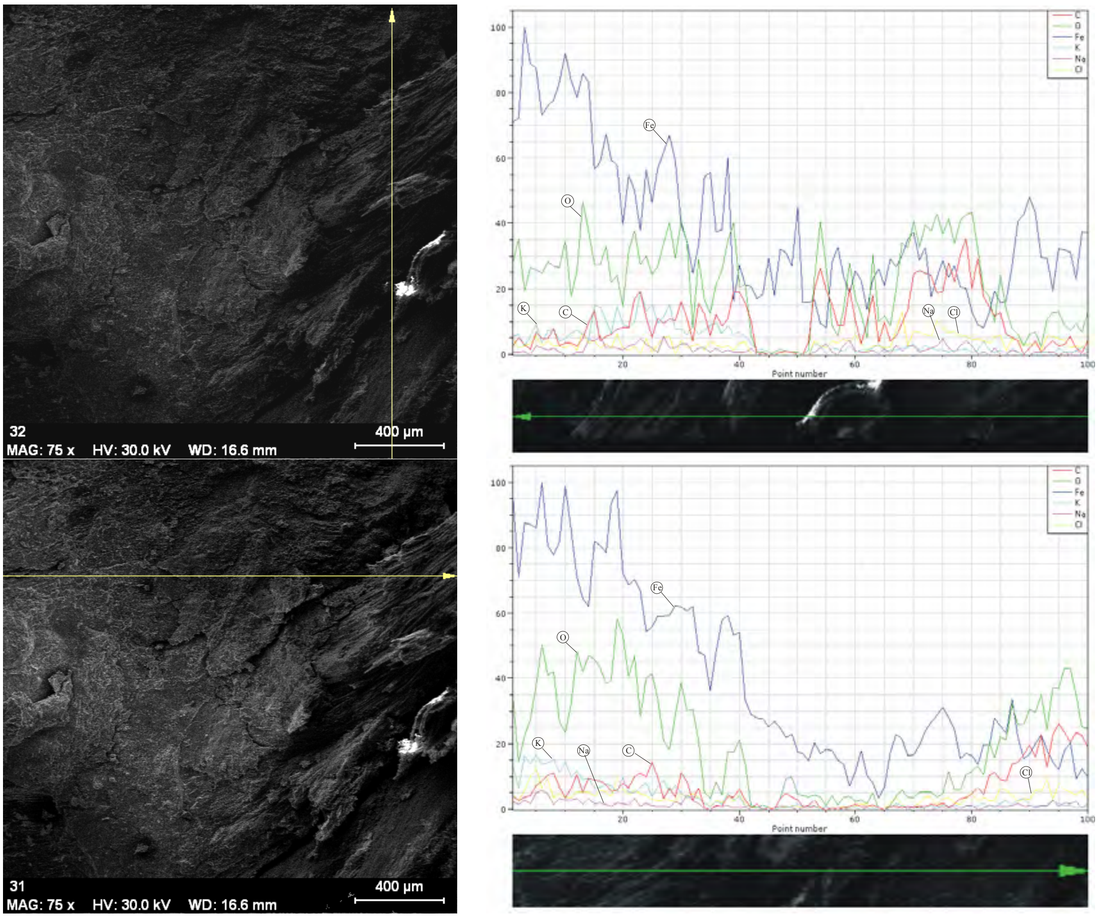


Fig. 6. *SEM Image with EDX spectra of distribution along a line on the sample from wood with iron*

Fig. 7 presents the mapping of the atoms for the area from the microphotography of Fig. 6 which demonstrates the uniformity of the distribution both of the components of the wood (C, O) and of the iron corrosion products (Fe, Cl and K).

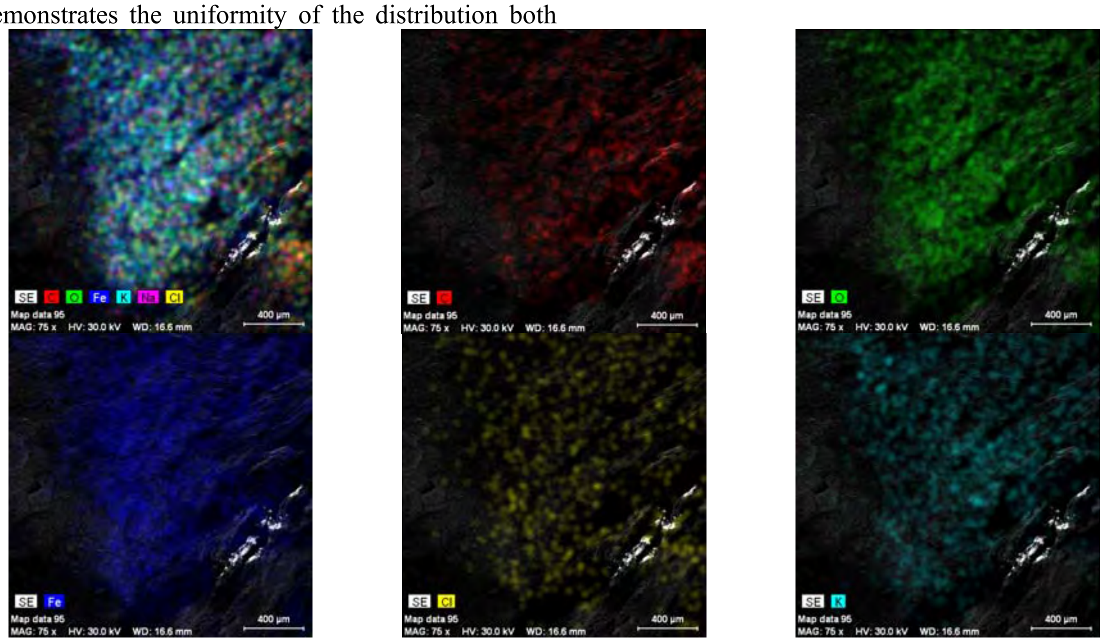


Fig.7. *Element mapping by EDX analyzis of wood-metal interaction.*

Table 2. *Composition of diffused structure surface: wood-iron*

Element	Weight percent [%]	Atomic percent [%]	Error in %
Iron	48.50823	21.5885	1.315599
Carbon	3.876974	8.0227	1.491539
Potassium	2.508171	1.594433	0.121529
Chlorine	0.301288	0.211222	0.046833
Sodium	2.160776	2.33605	0.238743
Oxygen	42.64456	66.24709	5.868803
	100	100	

Table 2 presents the average composition for the surface of the preserved area of the wood by impregnation with the Fe oxidihydroxides. One can notice a very high concentration of the Fe ions (II, III). In spite of the fact that in the structure we can find the chloride anion (the main corrosion agent of iron and the most active one, a real catalyst) due to the inhibitor components from the oak wood, the iron nail has been pretty well preserved. Fig. 8 presents a cross-section through the coin from Fig. 3 which preserves well a small wooden area from a box in which the coins have been once kept, an area which is now rotted. This trace of the preserved wood allows the archaeologists to establish the method of keeping the coins at abandon, the type of the abandon (hiding and forgetting) and their preservation state.

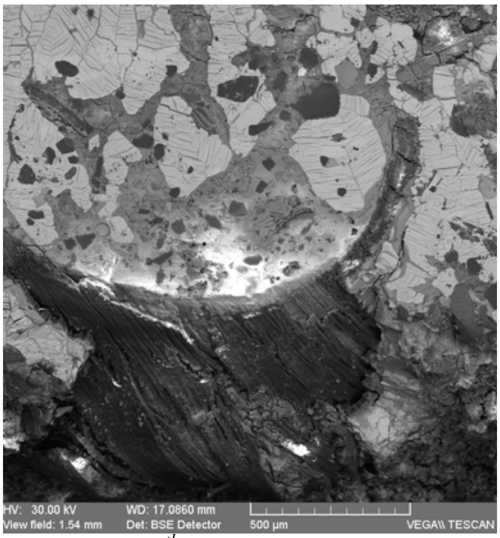


Fig. 8. *SEM image of a bronze coin (Xth Century) in cross-section: on first line is visible the Liesegang Effect in a non-disturbed archaeological site; on the second line there are complex monolith structures with wood*

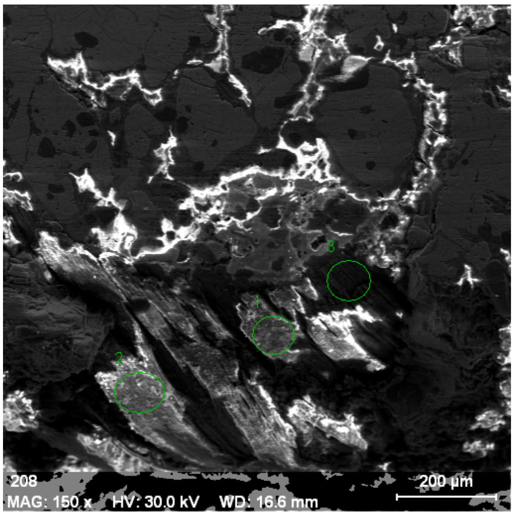
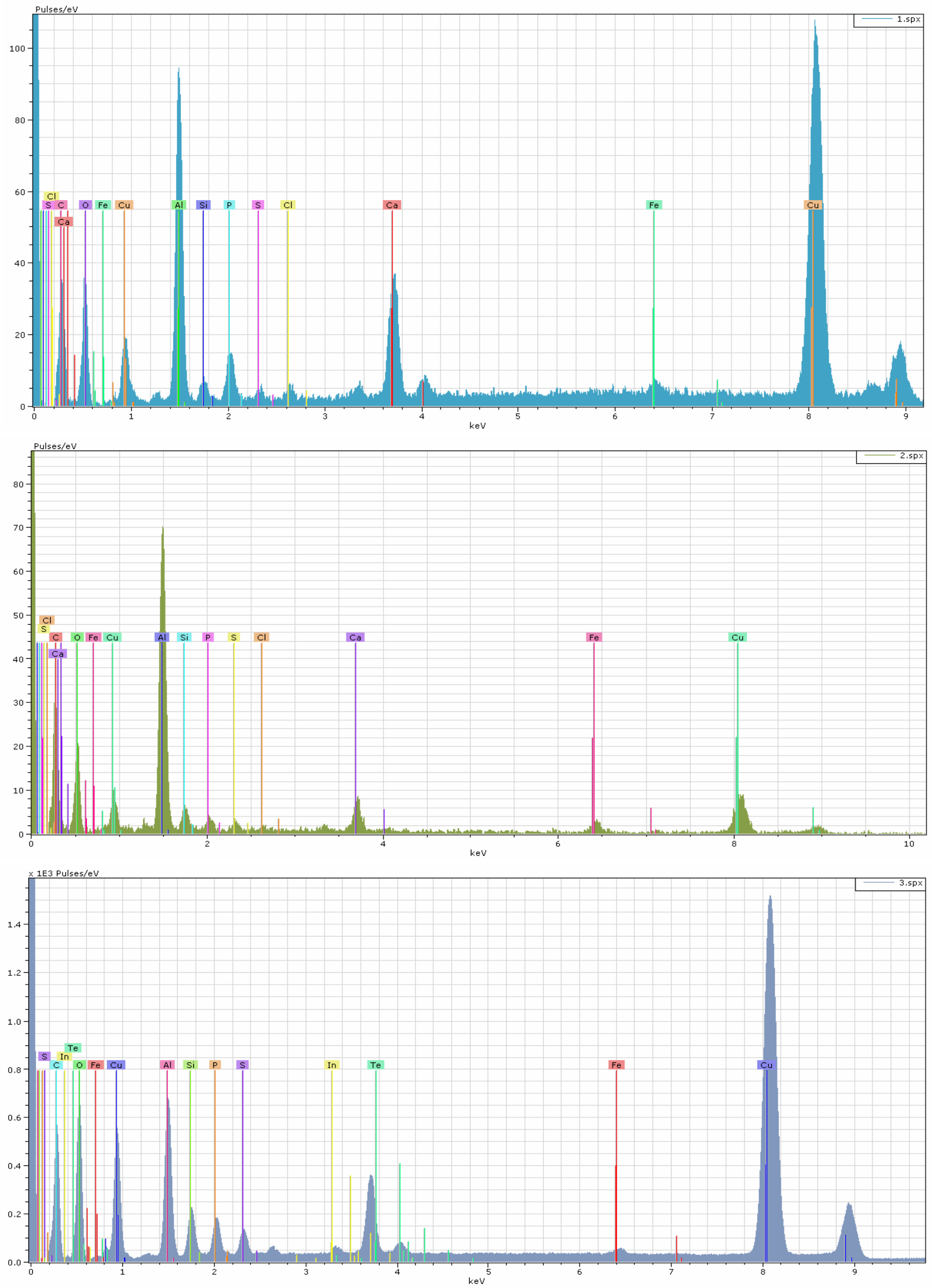


Fig. 9. *SEM image of the coin with the analysis areas*



a.

b.

c.

Fig. 10. *Composition of area 1 (a), 2 (b) and 3 (c)*

The data from table 3 confirms the presence of the wood partially carbonized with visible dendrological elements (micro-fiber, annual rings). The wood was conserved by the copper compounds.

Table 3. *Composition of area 1, 2 and 3*

Area	1		2		3	
Element	Weight percent [%]	Error in %	Weight percent [%]	Error in %	Weight percent [%]	Error in %
Carbon	6.389193	1.814477	12.18501	3.529135	7.733482	1.041857
Oxygen	35.33253	4.72851	38.85173	9.277283	30.78189	4.009206
Copper	29.53714	0.570017	11.50144	0.487489	43.06152	1.164948
Aluminium	18.78719	0.742615	26.78328	1.655008	9.274744	0.529978
Calcium	6.117853	0.176049	2.901968	0.185975	3.847487	0.154689
Iron	0.689548	0.048993	1.934821	0.149728	0.592968	0.043224
Silicon	0.864429	0.075672	2.991724	0.267102	2.065661	0.127574
Chlorine	0.155296	0.037845	0.477909	0.080947	0.627806	0.050521
Sulfur	0.110234	0.036185	0.87741	0.11058	0.668576	0.053926
Phosphorus	2.016597	0.108595	1.494708	0.159937	1.345867	0.086249

Conclusions

The paper deals which two important aspects in the field of artifacts conservation, which have wood and metal elements in contact and had been interacting in time, offering reciprocal conservability.

Therefore, in the case iron – oak-tree wood interaction, the Fe (II, III) ions conserved very well (for a long time - 200 years) the wood where they diffused. At the same time, the tannin from wood conserved the iron nail, in condition of an aggressive environment with chlorine ions.

Regarding the role of copper ions which protected the pieces of ancient wood for a very long time (1000 years).

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