

Preliminary assessment, by means of Radon exhalation rate measurements, of the bio-sustainability of microwave treatment to eliminate biodeteriogens infesting stone walls of monumental historical buildings.

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Abstract. The main purpose of the work described in this paper has been to establish the protocol for a new non-disruptive technique of intervention, based on microwave treatment, for cleaning operations on monumental historical buildings, to eliminate biodeteriogens infesting stones. Non-destructive methods in the cleaning operations, should not only preserve the physical integrity, the chemical-mineralogical and structural identity of materials, but, when the exhalation of pollutant agents (like for example Radon gas) from building materials is considered, also, make the indoor air quality (IAQ) levels healthy. Therefore, one of the main steps of the protocol proposed in this paper is concerned with the assessment of the Radon exhalation rate in order to verify that microwave treatments do not increase the Radon naturally exhaled by building materials. In this paper, the preliminary results of the Radon measurements performed on two different type of tuff samples (grey tuff and yellow tuff), typical of the Italian traditional construction heritage, with the E-PERM passive technique at the Environmental Radioactivity Laboratory (Amb.Ra.), University of Salerno, Italy, ISO 9001:2008 certified, are summarized.

1. Introduction

Cultural heritage is exposed, continuously, to the risk of degradation that may be aggravated and accelerated by the environmental conditions typical of the local context (natural and anthropic). Delaying or reducing its deterioration or, at least, the maintenance and restoration costs is the main goal of many researches, about innovative investigation techniques, new materials and new preventive methods for the conservation.

Any material, when placed in an environment, tend to get in equilibrium with it through long or short transformations that take the name of alterations. The alteration is peculiar for every single rock and can be attributed to three types of phenomena: physical, chemical, and biological.

Biological actions are due, for example, to the attack of algae, musk, lichens, and other living microorganisms that contribute to the decay of materials through a just slightly less effective action



than the physical and chemical ones. Biological deterioration is defined, therefore, as the degradation of the above-mentioned organisms and can be determined directly on the substrate both through chemical processes, consequent to the release of metabolites or acid reactions, either through mechanical processes due to the penetration of the hyphae or the roots in the stone substrate, with a consequent variation of its volume and moisture content.

Generally, cleaning intervention has just the purpose to eliminate the disease responsible of further deterioration and not to improve or change the aesthetic and chromatic aspect of the work. Indeed, cleaning procedures consist in a series of operations that tend to remove, from the surface of the object, substances generating the pathogenic degradation, through mechanical and/or chemical actions which entail problems for the preservation of the original surface, unavoidably.

The adoption of innovative methods in the field of conservation practices can become one of the new goal of industry's development, bringing important economic and practical benefits to the conservation of cultural heritage. An innovative cleaning method to eliminate biodeteriogens from stone materials consists in the application of a delousing procedure based on microwave treatment. The treatment protocol has already been successfully used on paper, wood and cloth (generally affected by mold substrates, fungi and insects) [1]. On the contrary, in the international scientific literature, at the moment of this paper, there are not yet reported other results about disinfestation of stone materials from biological agents, by means of the use of microwaves.

Building materials obtained from the earth's crust, such as tuff, may contain traces of ^{238}U and ^{232}Th . These radionuclides decay to radon (^{222}Rn), a radioactive gas with a half-life of 3.82 days. Due to its long half-life, Radon gas can reach outdoor and indoor air after being produced in the earth crust or from the walls and floors of buildings. The exposure to the inhalation of Radon can turn out to be high especially in buildings with poor ventilation systems, because it can accumulate and reach dangerous concentration for human health. In confined spaces like residential buildings, workplaces, and underground places prolonged exposure to Radon, turns out to be one of the major risk factors for lung cancer, as established by the World Health Organization (WHO). The most significant source of Radon in residential buildings and workplaces, is the soil under foundation. In 1988 UNSCEAR established that this accounts for about 70% of the total Radon emanation. Building materials (e.g. tuff, concrete...), also contribute to increasing the indoor Radon concentration, as they are sometimes produced either from soil rocks or from waste aggregates or industrial wastes. They generate two types of hazards, dangerous for the human beings:

1. Gamma radiation caused by the cumulative concentration of elements from the uranium, thoron and K-40 potassium.
2. Alpha radiation, which is associated with the liberation of radon and thoron decay products [2].

For this reason, natural radioactivity monitoring in indoor environments and in building materials is strongly recommended by the EURATOM Directive 2013/59 about the protection against the dangers arising from exposure to ionizing radiation, and by the EU Regulation 305/2011, about the hygiene and safety of building materials, that requires that they *"should not have an exceedingly high impact, over their entire life cycle to the environmental quality nor to the climate, [...], in particular due to the emission of dangerous radiation "* [3]. The building materials contribution to indoor Radon levels can be expressed in term of the Radon exhalation rate and the effective Radium content which are the most important parameters for the quality selection of building materials used in bio sustainable design. In the last 20 years, much attention to the measurement of Radon exhalation from building materials has been paid, not only in Europe, but also in many countries worldwide and many methods and techniques have been proposed [4]. Considering all these regulations and the well-known acknowledge that Radon exhalation from natural building materials, like tuff, can reach very high level, potentially dangerous for human health, a preliminary study to measure the effect of microwaves treatment on radon exhalation rate has been carried out at the Environmental Radioactivity Laboratory (Amb.Ra.), ISO 9001-2008 certified, of the University of Salerno (Italy). The preliminary first results for microwave treated building materials are going to be summarized in this paper.

2. Materials and methods

2.1 Microwave treatment

Musk, lichens, and molds are the most diffused pests attacking stone materials and are characterized by having significant amount of water, becoming, therefore, very sensitive to the microwave treatment.

Microwave heating has been already employed, as an innovative method for the disinfestation from biological agents, on some important museum goods like the wooden statue of Saint Leo the Great, in Naples [5]. The procedure and the microwaves treatment protocol, developed exposing samples of a wood very similar to that of the statue, have been applied to a new case study: the restoration of a yellow tuff wall in the historical and cultural site of Paestum (Salerno), UNESCO world Heritage site. In order to avoid damages due to the warming of a specific portion of the wall, two samples of grey and yellow tuff from the nearby geographic area of Nocera-Sarno have been identified and used for preliminary tests, and then for the calibration and validation of the experimental, non-invasive, microwave treatment protocol.

Gray and yellow tuff samples were subjected to ‘disinfectant’ microwaves treatments according to the different attacker biodeteriogen (Table 1).

Table 1. Microwave treatment protocol.

Material	Pest	Power (W)	Time (s)
Grey tuff	musk	700	540
Grey tuff	lichens	500	540
Yellow tuff	musk	500	180



Figure 1. Grey tuff sample attacked by lichens before and after microwave treatment.

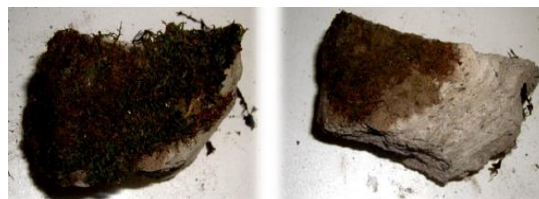


Figure 2. Grey tuff sample attacked by musk before and after microwave treatment.



Figure 3. Yellow tuff sample attacked by musk before and after microwave treatment.

2.2 Physics-chemical analysis

In order to establish whether the microwaves treatment induced aesthetic and structural alterations in the samples, physics-chemical analysis have been carried out. Specifically, nr.6 ‘treated’ samples (nr.3 sample of yellow tuff and nr.3 of grey tuff), of 5x5x5cm size dimension, have been selected and, then,

subjected to colorimetric analysis, thermogravimetric analysis, X-ray diffraction analysis, Fourier transform infrared spectroscopy and scanning electron microscopy (SEM), respectively. Furthermore, the water absorption, the capillarity and the compressive strength were also measured.

Subsequently, the same analysis were carried out on nr.6 'original' samples (nr.3 sample of yellow tuff attacked by musk and nr.3 of grey tuff attacked by lichens) with no treatment, in order to evaluate the effects of the microwaves through a comparison between the two group of samples ('treated', TR and 'not treated', NT) (Fig.4).



Figure 4. Tuff samples used for the comparison of the physics-chemical analysis.

2.3 Radon Activity Concentration Measurements

Measurements of the time-integrated Radon activity concentration have been carried out by using a passive technique[6] on nr.8 samples of yellow tuff and nr. 8 of grey one (nr.4 'treated' and nr.4 'not treated'), according to the internal protocols established by the ISO 9001:2008 Quality Management System of the Environmental Radioactivity Laboratory of the University of Salerno.



Figure 5. E-Perm® system for Radon activity concentration measurements[7].

This passive approach, for Radon activity concentration measurements, uses an electret ion chamber for monitoring Radon and consists of a stable electret (electrically charged Teflon disc) mounted inside an electrically conducting chamber. The electret serves both as a source of the electric field and as a sensor. The ions by Radon decay produced inside the chamber are collected by the electret. The reduction in charge of the electret is related to total ionization achieved during the period of exposure. This charge reduction is measured using a battery operated electronic electret reader. Using appropriate calibration factors, taking into account the sample mass, the exposure time (10

days), and by means of convenient algorithm provided by the manufacturer company [7], the Radon activity concentration in air, C_{Rn0} and the Radon Exhalation Rate, E, were calculated (Table 2) for each sample. Then a mean characteristic value for each group of four samples was obtained. The detailed description of the E-Perm[®] method is contained in a previous paper by the authors [8].

Table 2. Radon exhalation rate E [Bq/h] on different samples.

Grey tuff sample	M [Kg]	C_{Rn0} [Bq/m ³]	ΔC [Bq/m ³]	E [Bq/h]	ΔE [Bq/h]
1 (TR)	0,130	42,82	30,99	0,0012	0,0008
2 (TR)	0,142	96,18	32,88	0,0027	0,0009
3 (TR)	0,131	85,80	32,49	0,0024	0,0009
5 (TR)	0,141	158,42	35,90	0,0045	0,0010
Mean	0,136	95,81	33,07	0,0027	0,0009
1 (NT)	0,135	53,62	31,33	0,0015	0,0008
2 (NT)	0,117	88,68	33,11	0,0025	0,0009
3 (NT)	0,137	55,30	31,77	0,0015	0,0009
5 (NT)	0,114	122,42	34,78	0,0034	0,0009
Mean	0,126	80,01	32,75	0,0022	0,0009
Mass (M); C_{Rn0} Radon concentration without leakage (CR_{n0}); uncertainty [Δ]; Radon exhalation rate (E); treatment with microwaves (TR); No-treatment with microwaves (NT)					
Yellow tuff sample	M [Kg]	C_{Rn0} [Bq/m ³]	ΔC [Bq/m ³]	E [Bq/h]	ΔE [Bq/h]
1 (TR)	0,125	442,78	56,65	0,0125	0,0016
2 (TR)	0,123	388,19	52,19	0,010	0,0014
3 (TR)	0,133	679,89	78,31	0,019	0,0022
5 (TR)	0,128	347,50	48,86	0,009	0,0013
Mean	0,127	464,59	59,00	0,012	0,0016
1 (NT)	0,135	659,4	76,20	0,018	0,0021
2 (NT)	0,124	578,64	69,20	0,0163	0,0019
3 (NT)	0,121	486,16	60,75	0,0137	0,0017
5 (NT)	0,124	614,01	72,01	0,0173	0,0020
Mean	0,126	584,55	69,54	0,0163	0,0019
Mass (M); C_{Rn0} Radon concentration without leakage (CR_{n0}); uncertainty [Δ]; Radon exhalation rate (E); treatment with microwaves (TR); No-treatment with microwaves (NT)					

3. Results and discussion

This first preliminary experimental results demonstrate that the microwaves treatment for pest control in stone materials, like tuff, does not produce evidence or alterations of color type or chemical-structural characteristics of the material (fig.6 and 7). About Radon exhalation rate measurements, results don't show a particular evident increase in yellow tuff after the microwaves treatment. Instead, in grey tuff a little increase of Radon exhalation rate is registered, as shown in the graphic comparison between treated and not treated samples in fig.8.

Other measurements should be, of course, carried out in order to obtain a more accurate evaluation about the possible tendency of the materials to release Radon after a microwaves treatment .

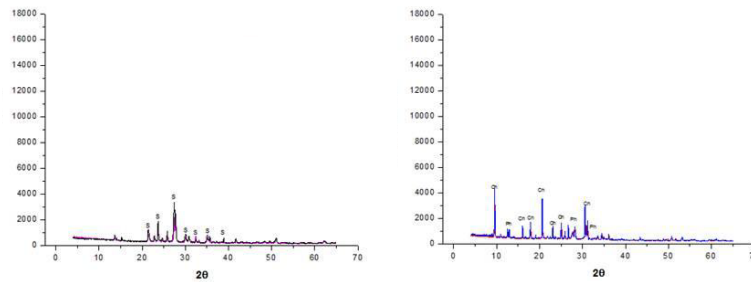


Figure 6. Results from grey tuff (left side) and yellow tuff (right side) samples after the X-ray diffraction analysis.

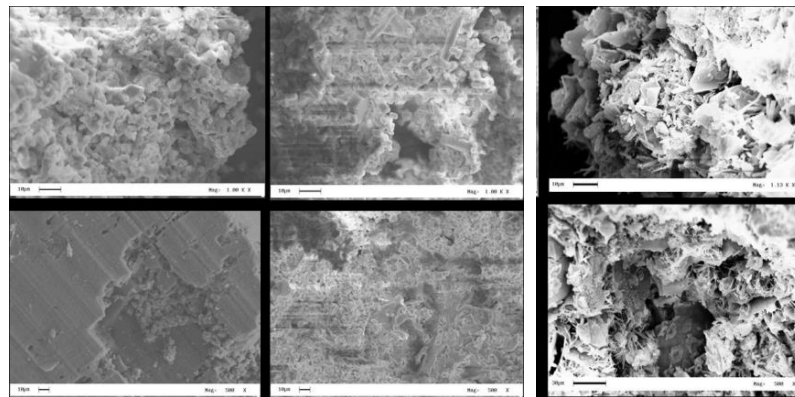


Figure 7. Results from grey tuff (left side) and yellow tuff (right side) samples after the SEM analysis.

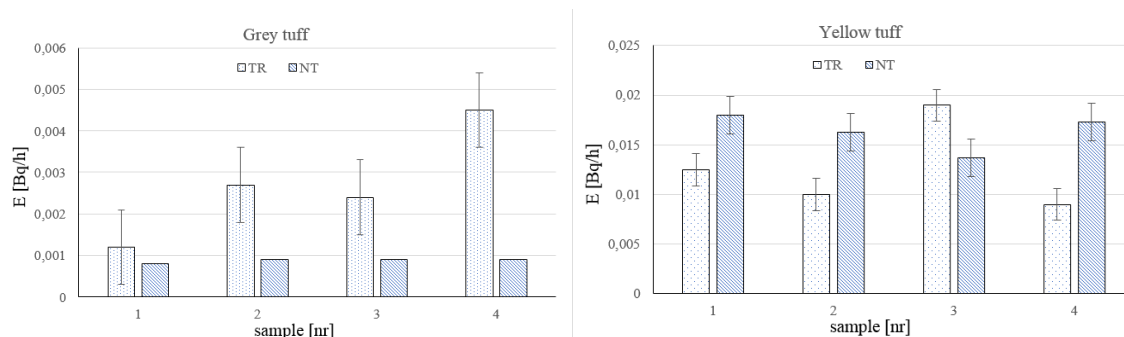


Figure 8. Radon exhalation rate results comparison between treated (TR) and untreated (NT) samples of grey tuff and yellow tuff.

4. Conclusion

The results represent, therefore, a starting for developing and establishing of a procedure to preserve historical buildings from the biological degradation of stone substrates with an innovative treatment, based on microwaves that combine aesthetic results and the benefits of the exhaustive removal of pests from surfaces, without the risk of inducing chemical and structural alterations that may, over time, affect the durability of the material and produce negative consequences on the Indoor Air Quality (IAQ) levels, harming human population, with a particular referring to Radon.

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