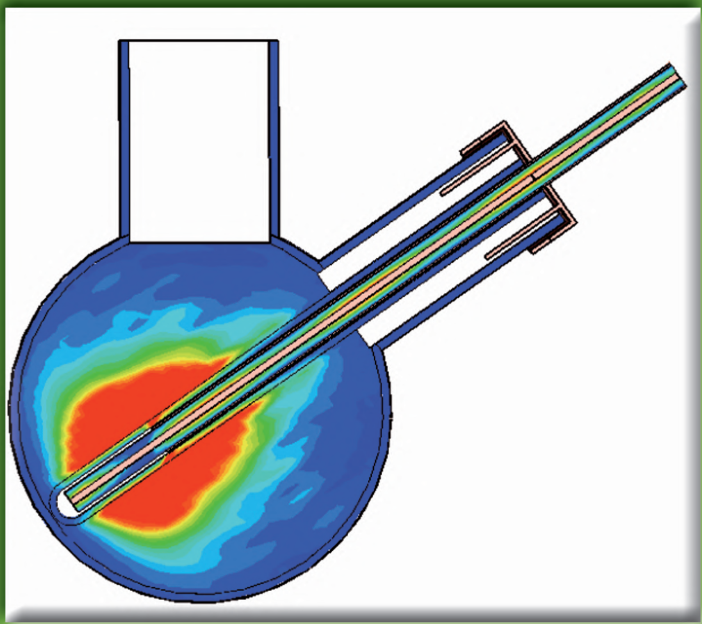
PROCEEDINGS

Microwaves in Italy and France: State of the Art

2008

Edited by Cristina Leonelli and Antonio Colaiuda



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MICROWAVES IN ITALY AND FRANCE: STATE OF ART 2008

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Cover figure: power density distribution produced by a microwave coaxial applicator immersed in a glass reactor filled with water

With permission of G. Biffi Gentili, M. Linari, G. Annino and I. Longo

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MICROWAVES IN ITALY AND FRANCE: STATE OF ART 2008

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CONTENTS

PREFACE

The First Bilateral Italian-French Meeting on Microwaves for Engineering and Applied Sciences (MISA 2008) was held in Salerno, Italy, on 21st to 23rd of May 2008. This meeting combined for the first time Italian and French researchers involved in the Microwave Science and Technology either from industry or academia. Meetings of the Italian community, GIMAMP (Italian Group on Microwaves Applications to Materials and Processes), have been conducted on a regular basis since 1997.

The success of this challenging event organized to enlarge the boundaries of the activity of GIMAMP, was demonstrated by the over 30 talks with delegates from 2 French and 2 Italian industries, 9 French and 8 Italian Research Institutions, 4 French and 26 Italian Universities.

Here are collected the presentations of various groups whose activities cover a multidisciplinary panorama: Dielectric properties measurements, Modelling and Simulation, Medical and Biomedical Applications, Chemical Synthesis and Analytical Applications, Environment and Sustainable Development, Pharmaceutical Applications, Applicators and Control Systems, Materials and Processes.

The 18 contributions in this volume represent a cross section of work presented at MISA 2008 Meeting, and it is hoped that these papers, in addition to being a valuable summary for conference attendees, will be of interest to the entire high power microwave community.

Cristina Leonelli

Antonio Colaiuda

DIBET (Dipartimento di Ingegneria Biomedica Elettronica e Telecomunicazioni) – EMC LABORATORY: ACTIVITY IN THE ELECTROMAGNETIC MATERIAL PROCESSING

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HISTORY

In the last three decades, the group of Università Politecnica delle Marche at Ancona spent particular effort investigating non-communication aspects of electromagnetic fields.

The former aspect is the localized microwave hyperthermia used in the cancer therapy. The analysis of new applicators was performed, [1] [2] and a computer program that includes inhomogeneous tissue was written to simulate them. The simulation gives also the dissipated power into tissues and the temperature distribution. Some anthropomorphic phantoms was build for the experiments and the dielectric constant was measured.

Collaborating with the neurological group of INRCA at Ancona, a magnetic stimulator of nervous tissue was studied. A three-dimensional simulation program was written to find the current distribution in human cortex was written, deriving the head geometry directly from a magnetic resonance image [3].

The Ancona group participated to the European project “CEPHOS” and to the “COST 244” studying the interactions between the human head and the cellular phones. In particular, the absorption of head tissues was simulated with the finite-difference time-domain (FDTD) technique [4].

In the industrial heating, the FDTD technique was applied to simulate microwave and radio-frequency ovens [5], and an industrial induction system was designed and simulated [6].

ACTIVITIES

1. Microwaves heating model for reverberating chambers

A reverberation chamber can be considered as a well designed microwaves oven. An object heated in a microwaves oven, can be analyzed as the same object irradiated and heated by a superposition of plane waves. In particular it is possible to calculate the absorbed power distribution on the object, with the numeric technique Finite Differences – Time Domain (FDTD).

1.1 Description of the method

Drawing on Hill's plane wave model for a reverberation chamber [7], the electromagnetic environment is recreated by a superposition of a finite number of random plane waves [8].

So the chamber was substituted by a superposition of plane waves, each one with statistically variable polarization and phase. The only parameters that describe characteristics of the oven are N and M.

N represents the number of plane waves excited in order to simulate the field distribution in the chamber for a particular position of the stirrer. Then the simulation is repeated M times, where M is the number of independent positions of the stirrer in the chamber.
We choose these parameters as a compromise between the computation time and the statistic convergence of the central limit theorem and of the law of large numbers.
It is not necessary to simulate with the FDTD the entire volume of the chamber and the objects inside it, but only a volume a bit larger than the volume of the analyzed object.[9]
Furthermore, in order to recreate the exact behaviour of the chamber it is necessary to verify a relationship between the total average field in the chamber $<|E_{RC}|>$ and the amplitude of each plane waves $|E_0|$[10]

$$<|E_{RC}|>=\frac{15}{16}\sqrt{\frac{\pi}{3}}\sqrt{N}|E_0| \quad (1)$$

The parameters of each plane wave are generated in the step of FDTD initialization, they are stored and recalled for each FDTD temporal iteration. Referring to Fig. 1 the generated parameters are: the angles φ and θ, the distance d, and the polarization α [9].

The angles φ and θ are, firstly, generated independently. Then we extract only the angles that assure the uniform distribution on a spherical surface of the plane waves.

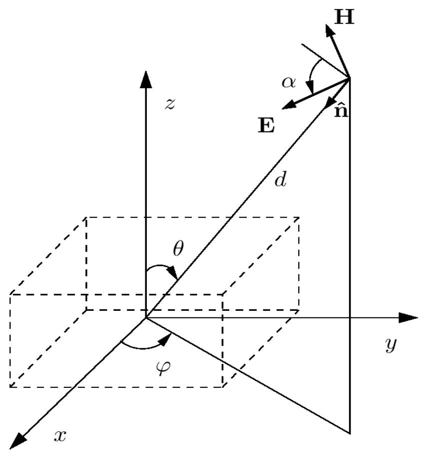


Fig. 1. Geometry of a random plane wave incident on the computation volume

1.2 Results

After a proper analysis, [11] we choose N=100 and M=200.
The amplitude of plane waves $|E_0|$=1 V/m.
In the following Figures there are some of the results obtained with this method.
The first example is a wooden beam with dimensions 0.2 m ×0.2 m × 1.0 m. The discretization was made with a cell size of 0.01 m. Various types of wood were analysed, varying the dielectric constants.
The internal part of the beam in balsa wood shown in Fig. 2 is less heated than the internal part of the beam in birch wood. This depends on the dielectric properties variation.

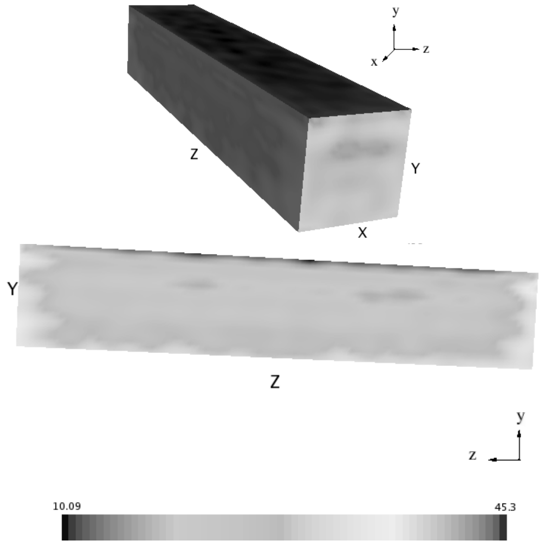


Fig. 2. Absorbed power distribution on the entire volume (on the top) and on a central section on a balsa wood beam expressed in kW/m^3

A second example, shown in Fig. 3, is a package of flour of weight of 1 kg of dimensions 0.1 m × 0.07 m × 0.15 m. The cell size in this case is 0.005 m.

The third and last example concerns to a ream of paper sheets simulated with and without metallic clips, much used in archives. The results are shown in Fig. 4. It is possible to note the clips in the area where the power is greater. Also in this case the cell size is 0.005 m.

The computation time varies on a standard PC with the geometry and shape of the heated object, from 2 minutes for a plane waves set and 3 hours for all simulations to 2 hours for a plane waves set and 400 hours for all simulations.

For all these simulations the heating times are very short, so it is possible to neglect the thermal diffusion. From the absorbed power distribution on these objects, normalizing it to the average total absorbed power on the object, it is possible to recover the temperature distribution in function on the time with the following formula:

$$\frac{\Delta T}{\Delta t} = \frac{P_D}{\rho c_p} \tag{2}$$

Where ΔT is the temperature variation, Δt is the time range, P_D is the absorbed power distribution from the object, ρ is the density and c_p is the specific heat.

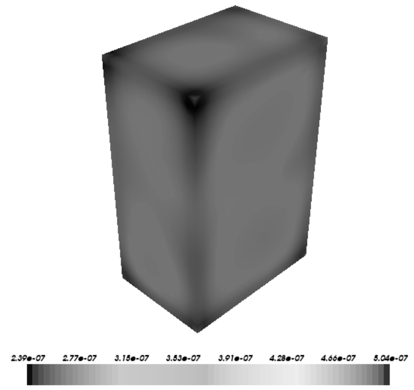


Fig. 3. Absorbed power distribution on a flour package expressed in kW/m^3

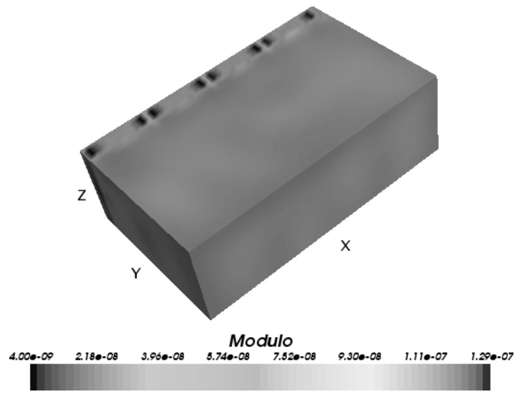


Fig. 4. Absorbed power distribution on a ream of sheets with metallic clips expressed in kW/m^3

1.3 Conclusions

If a microwaves oven is well designed, the heating of an object can be simulated as the same object irradiated by a superposition of plane waves. The volume simulated with the FDTD technique is the same of the analyzed object with the addiction of some cells useful for the field separation and the absorbing conditions. The characteristics of the oven were included in the analysis using N plane waves and making M simulations, reducing in this way the computation time and memory load.

2. Theoretical and experimental analysis of an induction cooking system

Domestic induction cookers become more and more popular because of their high efficiency, safety and ease in use. Due to the present-day state of the art which widely described in existing literature a contemporary induction cooker system consists on following components (Fig. 5): a) an inductor, b) ferrite bars below the coil and c) the load under it (the pan).

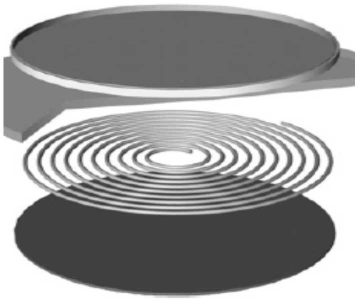


Fig. 5. ***Induction cooker heating system***

Induction coil is winded of Litz-wire which is set of parallel isolated strands with helix transposition (Fig. 6). Up to these days the properties of Litz-wire are researched such as different loss effect, proximity and skin effects [12]. Most of the methods based on finite-element method [13]. Besides the power loss approach there were also developed analytical models, but because of complexity of geometric form all existing models consider litz-wire like bun of strands [14]. The novelty of our approach lies on creating an exact geometry of loop with different shape properties with trajectory description of each single strand and therefore a rigorous electromagnetic model is developed. This method allows also modeling, calculating and analyzing exact behavior of the system in different cases such as load presence with calculation of exact distribution of eddy current in it, shielding with ferrite disc or bars. This model also allows analyzing of input impedance in order to increase efficiency of supplied power. Analyzing the leakage field irradiation gives a characterization of system safety.

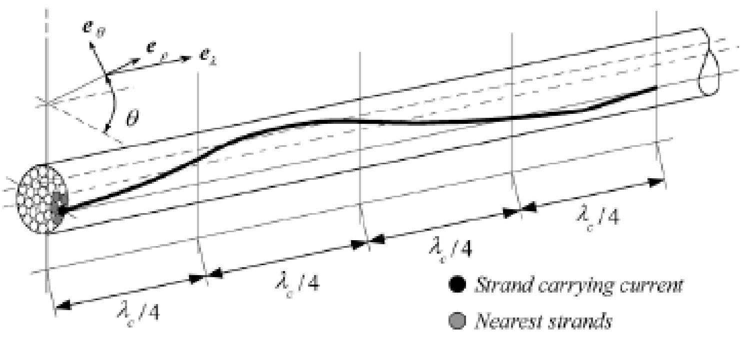


Fig. 6. ***Helix transposition of a strand in Litz-wire***

2.1 Analytical model and numerical solution

The analytical model calculates the impedance coefficients for each single loop and strand. Starting with the potential balance equation for an enclosed wire loop supplied by voltage V_0

$$V_0 = \int_L \frac{\overline{J}}{\sigma} \cdot \overline{dl} + j\omega \int_L \overline{A} \cdot \overline{dl} \tag{3}$$

where $\overline{J}$ is current density, σ is conductivity of the wire and $\overline{A}$ is a vector potential. Having the formulation of vector potential

$$\overline{A} = \int_V \frac{\mu \overline{J} e^{-jk|\overline{R}|}}{4\pi|\overline{R}|} dv \tag{4}$$

where $\overline{R}$ is the distance between source field element to observation point. R is the basic term in following integrations and represent an exact description of integration path i.e. precise trajectory of a strand or loop directly depended on geometry.

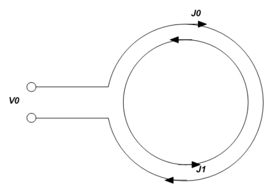
Therefore:

$$V_0 = \frac{J_0 \pi d}{\sigma} + j\omega \frac{\mu J_0 a^2 \pi}{4\pi} \int_L \int_L \left(\frac{1}{|\overline{R}|} - jk\right) dl\, dl' \hat{\phi} \hat{\phi}' \tag{5}$$

In case of the most simple set of single loop of inductor and single load loop (Fig. 7) we can write a system of equations for each element:

$$\begin{cases} V_0 = \int\limits_{L_0} \frac{\overline{J_0}}{\sigma} \cdot \overline{dl} + j\omega \int\limits_{L_0}\int\limits_{L_0} \frac{\mu \overline{J}_0 e^{-jk|\overline{R}|}}{4\pi|\overline{R}|} \cdot dldl' + j\omega \int\limits_{L_0}\int\limits_{L_1} \frac{\mu \overline{J}_1 e^{-jk|\overline{R}|}}{4\pi|\overline{R}|} \cdot dldl' \\ 0 = \int\limits_{L_1} \frac{\overline{J_1}}{\sigma} \cdot \overline{dl} + j\omega \int\limits_{L_1}\int\limits_{L_1} \frac{\mu \overline{J}_1 e^{-jk|\overline{R}|}}{4\pi|\overline{R}|} \cdot dldl' + j\omega \int\limits_{L_1}\int\limits_{L_0} \frac{\mu \overline{J}_0 e^{-jk|\overline{R}|}}{4\pi|\overline{R}|} \cdot dldl' \end{cases} \tag{6}$$

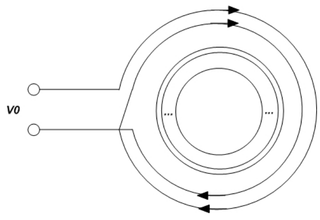
Considering that current density is uniform along all the loop length we can form linear matrix equation (7) made of voltage vector, impedance matrix and current vector



$$\begin{pmatrix} V_0 \\ 0 \end{pmatrix} = \begin{pmatrix} Z_{00} & Z_{01} \\ Z_{10} & Z_{11} \end{pmatrix} \cdot \begin{pmatrix} I_0 \\ I_1 \end{pmatrix} \tag{7}$$

Fig. 7. ***Single source loop and single load loop***

Analogically the description of the full system is given with the following matrix.



$$\begin{pmatrix} V_0 \\ V_0 \\ \dots \\ \dots \\ 0 \end{pmatrix} = \begin{pmatrix} Z_{00} & Z_{01} & Z_{02} & \dots & Z_{0n} \\ Z_{10} & Z_{11} & \dots & \dots & \dots \\ Z_{20} & \dots & Z_{22} & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ Z_{m0} & \dots & \dots & \dots & Z_{mn} \end{pmatrix} \cdot \begin{pmatrix} I_{s0} \\ I_{s1} \\ \dots \\ \dots \\ I_m \end{pmatrix} \tag{8}$$

Fig. 8. *Full system scheme*

Solution of this matrix equation gives us all currents of source coil and in load. So the load disc (pan bottom) can be considered as a set of enclosed circle loops of induced eddy currents (Fig. 9).

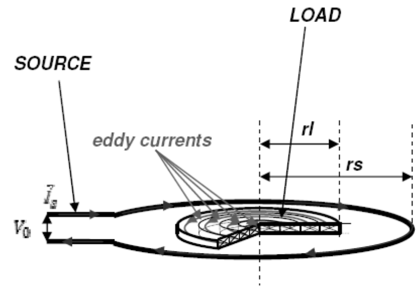


Fig. 9. *Model loaded with a metallic disc*

This approach allows to calculate all the mutual terms of impedance and to simulate magnetic coupling picture and consequently to get distribution of current in the load as well as power distribution and initial thermal heating picture.
The analytical model that has been just described was implemented in program code in Wolfram Mathematica ©. Different cases were calculated and each of them was entailed with appropriate measurements. The results are presented in further tables.

2.2 Results

In this section were shown preliminary results acquired both numerically and experimentally.

set	*Calculated*				*Measured*			
Small single turn (a = 1mm, d = 80mm)	V	2.55mV	R	0.0056	0.006	R	2.55mV	V
	I	0.0025A	X	0.105	0.108	X	0.0022A	I
2 small turns (a = 1mm, d = 75mm)	V	7.34 mV	R	0.011	0.012	R	7.34 mV	V
	I	0.0023A	X	0.314	0.327	X	0.00213A	I
Big single turn (a = 2mm, d = 200mm)	V	6.21mV	R	0.0035	0.007	R	6.21mV	V
	I	0.00224	X	0.276	0.276	X	0.0022A	I
2 big turns (a = 2mm, d = 200mm)	V	20.7mV	R	0.0069	0.016	R	20.7mV	V
	I	0.00218A	X	0.948	0.937	X	0.0022A	I

Table 1

The first test was the comparison between the calculated and measured impedance (R-X) of simple cupper rings (with different rays and sections) in order to characterize an elementary inductor.
Then we added some cupper rings with no fed, so a single ring is used as inductor (d=8.2 mm, a=1 mm) and we considered 3 rings passive (d1=5.5 mm, d2=6 mm, d3=6.5 mm, a1=a2=a3=1 mm).

		X input	
		measured	*calculated*
Single source turn + single load lturn		0,102	0,1015
Single source turn + 2 load tuns		0,097	0,098
Single source turn + 3 load turns		0,094	0,095

Table 2

We tested a cupper disc in order to model the load, while for the inductor we considered again a single cupper ring (d=8 mm, a=1 mm).

		X input	
		measured	*calculated*
Single source turn		0,107	0,1084
Single source turn + load disc (dl=0.032)		0,106	0,1073
Single source turn + load disc (dl=0.067)		0,091	0,0913

Table 3

The eddy current distribution in the load disc were calculated and reported in Fig. 10

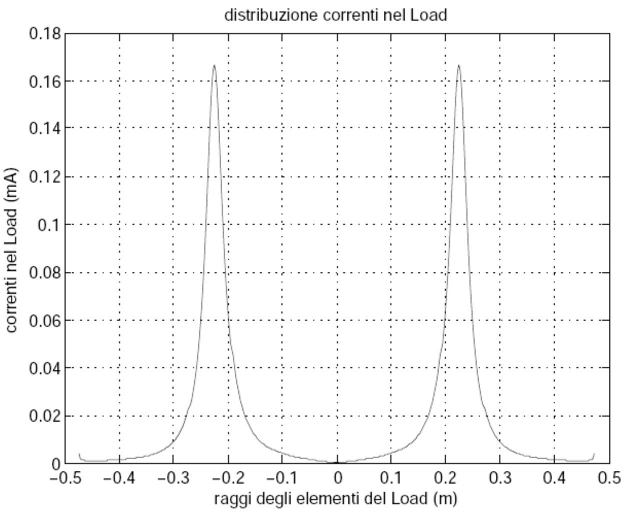


Fig. 10. ***Eddy current distribution in the load disc***

2.3 Conclusions

This approach clearly represent the basic model of induction cooking system work. The numerical solution is based on solving simple linear matrix equation which consist on well-know balance-potential equations for each element of the system. The most significant problem that has been solved is the calculation of impedance coefficients based on calculation of inductance (self and mutual) which for its turn directly depends on geometry of the loop(integration path). Therefore, the R-tracking for complex geometries like litz-wire strand helix transposition has been developed in order to acquire the rigorous model for simulating any kind of wire shape for induction cooking coils. The software program has been developed based on this analytical model which can simulate litz-wire inductors with different parameters. As the next steps are the investigation different load material, particularly ferromagnetic metals in order to research and to model their non-linearity in saturation zone because of hysteresis effect. Another direction to deep in is enhancing our model by including simulation of internal effects in multistrand wires such as proximity effects, skin effects and capacity contribution in power loss.

3. A statistical model of the interaction between reverberation fields and lossy materials

One of the most exciting field of electromagnetic research concerns the study of dielectric properties of materials.

The development of robust and accurate measurement techniques are both theoretical and experimental issues, producing useful and easily employable results for electromagnetic compatibility (EMC) in electronics, aerospace, naval and vehicular

industries. During the past years, a lot of techniques have been developed to retrieve properties of solid materials, using waveguides [15] and free-space environments [16]. More recently, the increasing interest in the reverberation field theory has lead to the analysis of electrically large or small samples of materials using reverberation chambers (RC) [17]. In this kind of electromagnetic problems, a difficult issue concerns the determination of the power absorbed by the material under test: the use of the composite quality factor (Q) seems to be a right choice because of its sensitivity to absorption cross sections of objects inside the RC. In order to facilitate the estimation of the absorbed power and comparison with measurements, it is of fundamental importance

to set up a fully developed random field. Theoretically, this allows for the consistent use of statistical electromagnetism theory [18]. Experimentally, we are able to produce these robust fields in a very easy way, using a mechanically mode-stirred or mode-tuned RC (MS/MTRC) and accelerating the measurements process with the frequency stirring technique [7]. A thermodynamic model for random fields was used to study lossy materials in a reverberation chamber (RC). In particular, angular spectrum (AS) statistics were obtained inside the material and the deterministic alteration of the incidence angle at the boundary was used to find the probability density function (PDF) of the effective refraction angle. The statistical model was validated by a discrete approach and a semi-empirical model was derived to calculate the power transmitted inside a nested RC through an aperture covered by a lossy thin slab. Experimental results are presented for several materials.

3.1 Theoretical model

We are interested in the power transmitted through a (lossy) thin slab inside a nested reverberation environment. To this end, the well-known plane waves spectrum expansion for a fully developed random field ([7] and [19]) has been used

$$E(r) = \iint_{\Omega} F(\Omega) e^{jkr} d\Omega \tag{9}$$

where the harmonic time dependence is suppressed. In (9), the solid angle Ω represents azimuth φ and elevation θ angles with dΩ = sin(θ) dθ dφ, **k** is the free-space vector wave-number and **r** is the location vector. The most interesting feature of (9) is the so-called angular spectrum (AS) $F(\vartheta) = \hat{\vartheta} F_{\vartheta}(\Omega) + \hat{\phi} F_{\phi}(\Omega)$ introduced in [19], [20] [21].

If we consider the ideal situation in Fig. 11, where a perfect random field impinges onto a conductive semi-infinite medium. Each plane wave of the AS is transmitted into the

material, where the local field distribution is modified by the material characteristics.

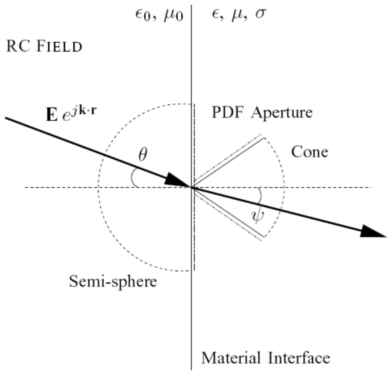


Fig. 11. Incidence plane: random waves are uniformly distributed over a semi-sphere in the reverberation space

We carry on handling only a scalar component $F_m(\Omega) = F_{m\vartheta,\phi}(\Omega)$ where the subscript m refers to a quantity inside the material so that

$$\langle E_m(\mathbf{r}_1)\, E_m(\mathbf{r}_2)\rangle = \\ = \iint_{\Omega_1} \iint_{\Omega_2} \langle F_m(\Omega_1)\, F_m^*(\Omega_2)\rangle\; e^{j(\mathbf{k}_1 - \mathbf{k}_2)\cdot\mathbf{r}}\; \mathrm{d}\Omega_1\, \mathrm{d}\Omega_2\ , \tag{10}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are two different random paths of the "cone" in Fig. 11. If the material is linear and isotropic, it is reasonable to assume that the AS is related to the AS in free space by a function of Fresnel's coefficients, in a separable way, as

$$F_m(\Omega) = F(\Omega)\ \mathcal{H}(\Omega) \tag{11}$$

where $F(\Omega) = F_{\vartheta,\phi}(\Omega)$ is a scalar component of the reverberation AS and H(Ω) is a complex analytic function [22] of the material properties. The angular spectrum F(Ω) changes randomly during the stirrer rotation, while the material function H(Ω) does not. Note that H(Ω) does not exhibit a probability distribution, because it does not change its form during the stirrer rotation. If the rays follow the same path, namely 1 = 2 = , we get the second order moment for the material AS

$$\left\langle |F_m(\Omega)|^2 \right\rangle = \left\langle |F(\Omega)|^2 \right\rangle |\mathcal{H}(\Omega)|^2 \tag{12}$$

Upon substitution of the proper RC field statistics we get [13] [17]

$$\begin{aligned} \langle P_{rm} \rangle = {} & \frac{1}{2} S_c A_m \int_0^{\pi/2} |\mathcal{H}(\theta)|^2 \sin(\theta) \, \mathrm{d}\theta = \\ = {} & \frac{1}{2} S_c A_m \, \mathrm{E}\left[\left\langle |\mathcal{H}(\theta)|^2 \right\rangle \right] , \end{aligned} \tag{13}$$

where η is the free-space impedance, Am the surface of the material, the explicit expression of CE has been introduced, the range of θ is [0, π/2], range of ϕ is [0, 2π], the operator E [·] represents the ensemble average written as an expectation value and the PDF of the angle θ (which solely affects the refraction mechanism) follows from the isotropy property of the RC [23] [24]. The last step in deriving an explicit form for the transmitted power is the definition of H(Ω). From the physical interpretation of (13), it is natural to define $|H(\theta)|^2$ as the power fraction transmitted into the material

$$|\mathcal{H}(\theta)|^2 = \left(1 - |\Gamma_{\theta,\phi}(\theta)|^2\right) \cos\theta \tag{14}$$

where $\Gamma_{\theta,\phi}(\theta)$ is the TE/TM Fresnel's reflection coefficient at the material interface and cos(θ) arises from *Lambert's cosine law*. If the conductive object is electrically large, we can use the Fresnel's coefficients to study the transmission.

Otherwise, for a thin slab, we must take into account the multiple reflections (Fig. 12(a)) at the two interfaces in order to find the transmitted power. This can be done using the lossy transmission line model [25]. We refer to the simplified model of Fig. 12(b), where inner chamber loading effects of the sample were neglected [26]. The so obtained mean transmitted power plays the role of an excitation source for the small RC and can be used to estimate the received power inside the nested chamber.

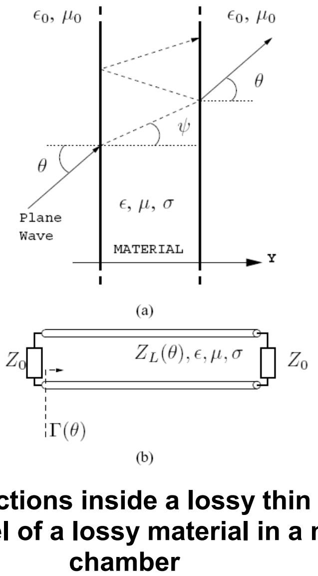


Fig. 12. (a) Multiple reflections inside a lossy thin slab; (b) Simplified Transmission Lines Model of a lossy material in a nested reverberation chamber

Here, we compare the measured power with the calculated one using the formula

$$\langle P_{ri} \rangle = \frac{Q_i \lambda^3 \langle P_{rm} \rangle}{16\pi^2 V_i} \tag{15}$$

where Q_i is the experimental quality factor, V_i the inner chamber volume and P_{rm} is expressed by (13).

3.2 Model Validation

It is possible to obtain the incident isotropic power density S_c using the outer chamber quality factor (Q_o). For example, by a simple power measurement with an antenna inside the working volume, the composite quality factor is given by

$$Q_o = \frac{16\pi^2 V_o}{\lambda^3} \frac{\langle P_r \rangle}{P_t} \tag{16}$$

where V_o is the chamber volume, <Pr> and Pt are the mean received and transmitted power respectively. Since a receiving antenna in RC acts as statistically isotropic, its effective area is $\lambda^2/4\pi$ and we have

$$S_c = \frac{8\pi \langle P_r \rangle}{\lambda^2} \tag{17}$$

Inserting (17) into (13), we obtain the power inside the nested chamber (15). In order to validate the obtained integral model, we compare the result of (13) with the power obtained from the discrete plane wave representation [24], [27], used with success in previous work and experimentally validated in [28]

$$E = \sum_{i=0}^{N} E_i \, e^{-jk_i r + \phi_i} \tag{18}$$

where E_i is the amplitude of the i-th plane wave, r and ϕ_i are the random trajectory and phase of the wave. The average transmitted power is calculated over M sets of N random plane waves (18) to simulate the field stirring process. Used procedure has been described in [8], while the physical framework for an electrically large sample is shown in Fig. 13. As a numerical example, consider an electrically large wall of infinite thickness and A_m = 110 mm × 70 mm, made of a conductor ($\varepsilon_r = 1$, $\mu_r = 1$ and $\sigma = 5000$ S/m) in the frequency range 1 GHz ÷ 4GHz. For E_0 = 1 V/m, N = 100 and M = 2000, Fig. 14 shows the comparison of numerical results with those given by (13). We notice the very close agreement between the two approaches, confirming the correctness of the statistical model. In fact, the numerical discrepancy is about 2-3%.

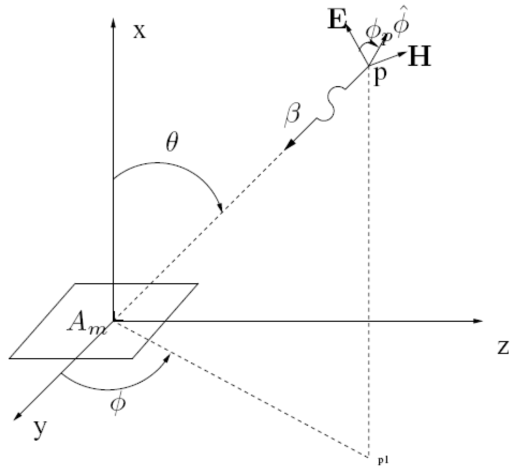


Fig. 13. Incidence of a random plane wave on the material interface

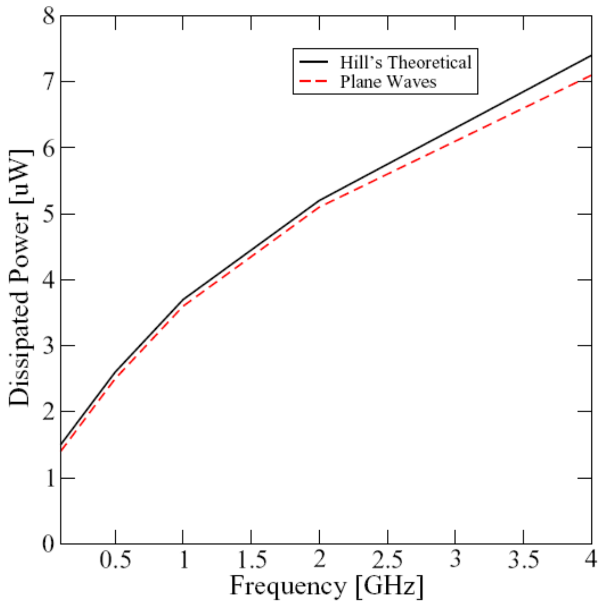


Fig. 14. Comparison of Hill's theoretical and discrete superposition for the power dissipated inside the material, σ = 5000 S/m

3.3 Experimental results

3.3.1 Measurement Set-up

Used experimental set-up is shown in Fig. 15. We employed an automated procedure system to acquire the all scattering parameters by a vector network analyzer (VNA)

AGILENT E5071B. The nested RC geometry, with set-up elements and the material sample under test, have been detailed in [29]. Transmitting and receiving antennas inside the outer chamber are log-periodic Schwarzback USLP 9143, connected to the access panel of the chamber through two cables RG/223 U. The source works in a range between 1 GHz and 4/6 GHz, in which the S_{21} was measured. The fundamental resonance of the outer chamber is f_0 = 64 MHz, so the theoretical LUF is $6 \cdot f_0$ = 384 MHz [8].

Instead, the inner chamber LUF was found to be 1.2.

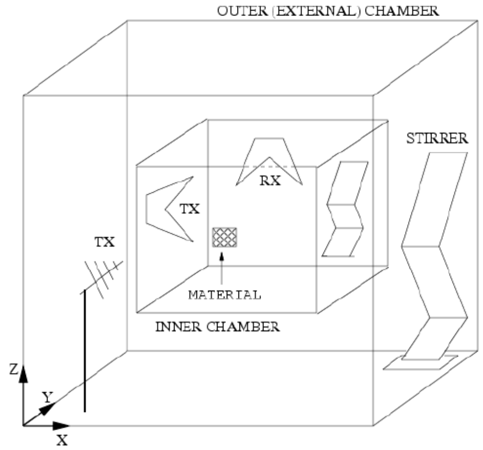


Fig. 15. NRC structure with setup elements and the material sample under test: the inner chamber, of dimensions 1.20m × 0.9m × 0.8m is placed inside a bigger chamber of dimensions 4.01m × 3.00m × 2.48m and working volume 1.58m × 1.20m × 0.54m

At the center of the inner chamber frontal surface, an electrically large aperture of dimensions 138 mm × 86 mm is placed. Inside the inner chamber there are two double ridge antennas EMCO 3115, also connected to the access panel of the outer chamber through two passing connector and two RG/214 U cables. The internal stirrer has a z-folded shape and is 0.6 m high.

3.3.2 Isotropic Materials

The semi-empirical model (13) can be applied to compute the power transmitted through lossy media.We should refine above discussions about the AS distribution: the presence of a conductive unbounded half-space (or thin slab) introduces a squeezing of the transmitted AS and modifies the solid angle distribution in a deterministic way because of the Snell's law. Upon a simple linear variate transform we get the new PDF for θ, thus

$$\mathrm{E}\left[\left\langle|\mathcal{H}(\theta)|^2\right\rangle\right] = \frac{1}{C\,N_\theta}\cdot$$
$$\int_0^{\pi/2} \left(1-|\Gamma_{\theta,\phi}(\theta)|^2\right)\cos\theta\,\tan\theta\sqrt{1-(C\sin\theta)^2}\;\mathrm{d}\theta\ , \tag{19}$$

where $C = \sqrt{(2\omega\varepsilon_1)/(\sigma\mu_2\varepsilon_2)}$ and N_0 is the normalization factor, which depends on frequency and material parameters.

For our test we used an Emerson & Cuming material, the Eccosorb LS-24 already employed in nested RC measurements of shielding effectiveness [29]. Fig. 16 shows the comparison between theoretical and experimental results.

Discrepancies are due to the imperfect working regime of both outer and inner chambers, numerical approximations and measurements uncertainties. The integration in (19) was carried out numerically by means of the MonteCarlo Integration Technique implemented on the GNU Scientific Library (GSL) [30].

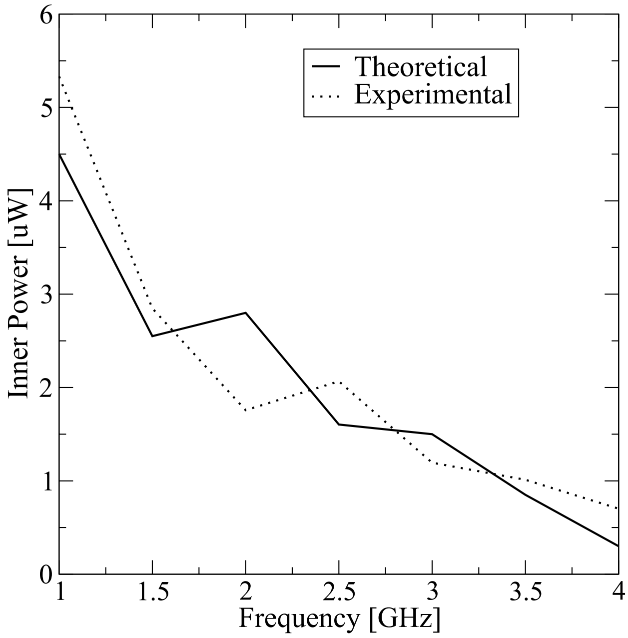


Fig. 16. Power inside the inner chamber with the altered-AS: comparison between measurement and theoretical estimation for Eccosorb LS-30

3.3.3 Random Materials

Derived semi-empirical model can even be applied to study the electrical properties of random materials, starting from SE measurements. Although, the inverse electromagnetic problem must be formulated beforehand. This topic will be developed in the future improving of previous theoretical findings and will be applied to the measurements hereafter. In this subsection, an experimental investigation of Densified-Small-Particles (DSP) cement composite is detailed and discussed [31] [32]. From the electromagnetic point of view, the DSP composite is a random media with isotropic metal particles embedded into an host dielectric.

This last one is weakly-lossy, because there are fluid components - such as water - that increase the electric polarizability. It is possible to estimate the complex permittivity in a theoretical way, applying the well known Maxwell-Garnett formalism [33], which is a generalization of the Clausius- Mosotti formula. Fig. 17 shows a cement sample installed to the inner chamber fixture. Since we used a VNA for measurements, it is useful to formulate the SE expression given in [34] as follows:

$$SE = -10\log\left(\frac{\left\langle |S_{21}|^2_{ns}\right\rangle \left\langle |S_{41}|^2_{s}\right\rangle \left\langle |S_{43}|^2_{s}\right\rangle}{\left\langle |S_{21}|^2_{s}\right\rangle \left\langle |S_{41}|^2_{ns}\right\rangle \left\langle |S_{43}|^2_{ns}\right\rangle}\right) \tag{20}$$

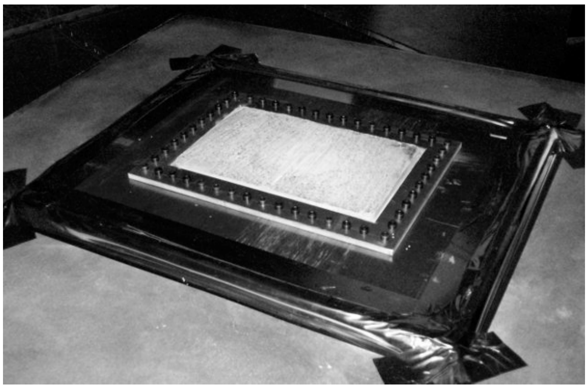


Fig. 17. A cement sample installed to the inner chamber aperture

where physical quantities are evaluated with (s) and without (ns) the sample. This requires the acquisition of four scattering parameters, hence the application of mechanical stirring process inside both the chambers. In order to reduce the measurement time and increase frequency resolution we used the frequency stirring technique (FS) inside the inner chamber, which relies on the presence of (at least) 60 modes – i.e., well overmoded regime. The computation of the SE has been done applying the following equation:

$$SE = -20\log\left(\frac{\langle|S_{41}(f_k)|_s\rangle}{\langle|S_{41}(f_k)|_{ns}\rangle}\right) \tag{21}$$

which arises as a special case of (20) when it is assumed that wall losses are dominant in both cavities (see (22) in [34]). Furthermore, the operator h·i means the averaging over a prefixed frequencies number (SL) – i.e., the FS process [35]:

$$\langle|S(f_k)|\rangle = \frac{1}{S_L}\sum_{n=k-S_L/2}^{k+S_L/2}\frac{1}{18}\sum_{m=1}^{18}|S_{nm}(f_k)| \tag{22}$$

This strategy allows for a strong reduction of the measurements variability: it has been viewed, by some experimental evidences, that the frequency stirred SE averaged out over the tuner positions is very close to the mechanical stirred one. In our test we chose 18 tuner steps spaced of 20 deg. SE values for the cement composite, calculated from (21), are shown in Fig. 18. Measurements were performed after one month, allowing the complete drying of the samples. Results were obtained using the scattering parameter S_{41}. The SE curves are obtained using the same concentration in weigh of particles and the difference are due to their different screening effect. All the curves growth up with the frequency, indicating that the screen behaviour is essentially continuous.

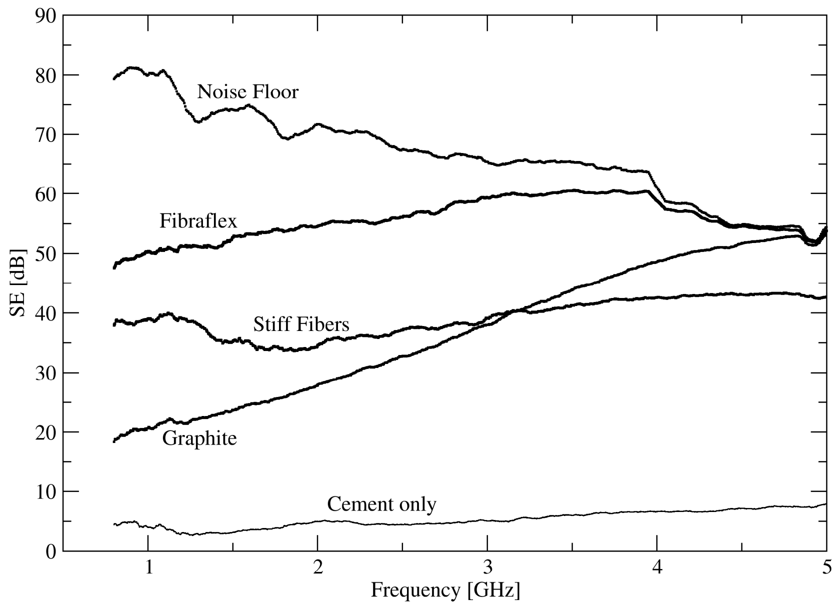


Fig. 18. Measured SE for the cement composite with different particles at 20% concentration, post-processed with the FS technique

Evaluating the SE from (20), involving every scattering parameters and without the FS technique, gives similar results.

The latter strategy gives stronger (frequency) fluctuations, of course within the NRC fixture uncertainty [36]. It must be pointed out that expressions like (21) are already employed in classical standards even if the measured parameters are taken without ensemble averaging [37].

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LABORATORIO DI ANTENNE E MICROONDE

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[2] *ASK Industries S.p.A., 42100 Reggio Emilia, Italy*

HISTORY

Antenna and Microwave Laboratory (LAM) [1] was founded in the mid-90s at the Department of Electronics and Telecommunications of the University of Florence, under the scientific responsibility of Prof. Guido Biffi Gentili, with the purpose to contribute to and promote the creative research in modern electromagnetics, antennas, sensors and microwave power applications by addressing the needs of industry government agencies and scientific community.

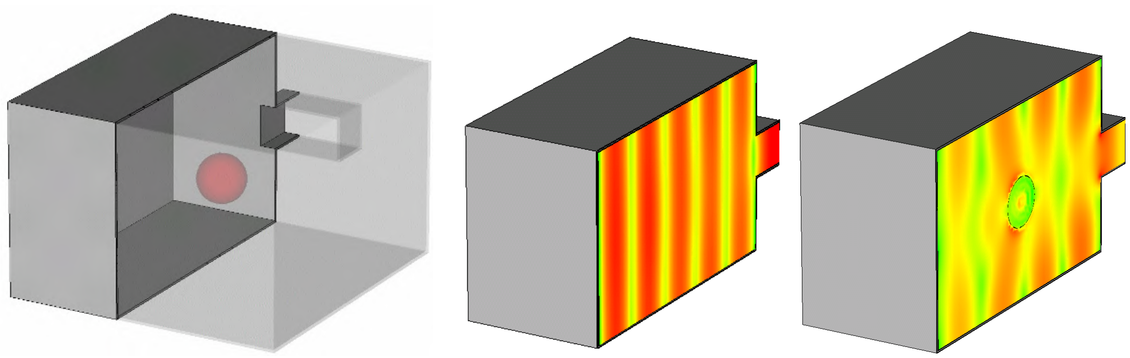
ACTIVITIES

In the fields of the energetic applications of microwave the LAM research and professional activity is focused on the following topics:

1. Radiofrequency and Microwave heating systems

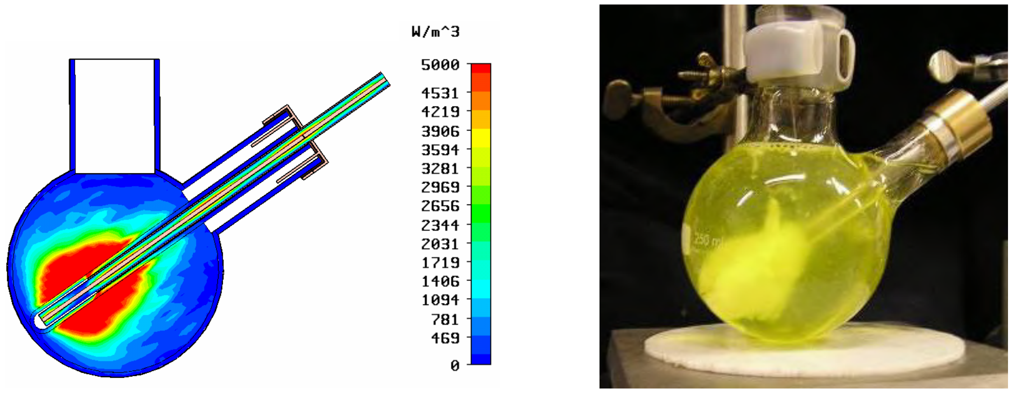
Research activity is focused on the EM and thermal modeling of industrial high power microwave heating processes and microwave reactors for laboratory usage.

- Granular ceramic materials EM modeling [2-3]
- High temperature dielectric spectroscopy
- Mono and multimodal resonant cavity EM modeling
- Microwave Reactors
- Insulated microwave coaxial applicators [4-6].



(a) (b) (c)

Fig. 1. EM analysis of a multimode cavity (a): electric field distribution of resonant modes for a empty cavity (b) or for a cavity containing a meat sphere (c)



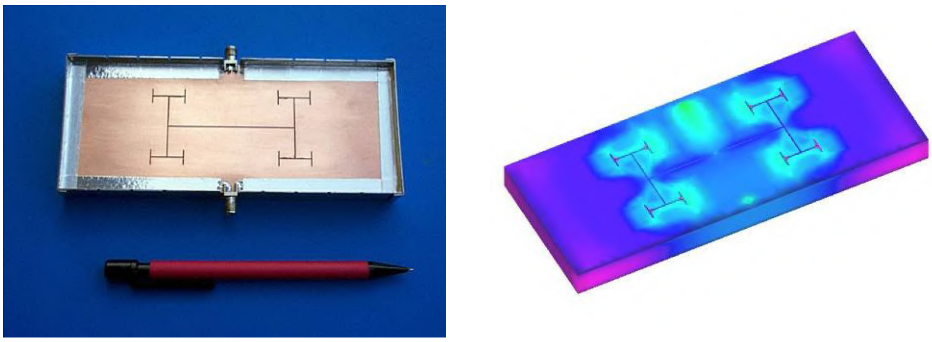
(a) (b)

Fig. 2. Microwave Chemical Reactor filled with egg white: power density distribution (a); coagulation of egg white when 85 W input power is applied for 60 s (b) [4-6]

2. Microwave Sensors

Research activity covers topics addressing industrial, scientific, medical and environmental heritage sensing needs as [7-16]:

- Microwave aquametry
- Dielectric spectroscopy
- Surface and sub-surface planar sensors
- High temperature microwave sensors
- Near-field anisotropy sensors
- Sensor-MUT electromagnetic interaction modeling
- Material moisture sensing
- Calibration and inversion techniques
- Smart sensor networks
- Microwave plethysmography

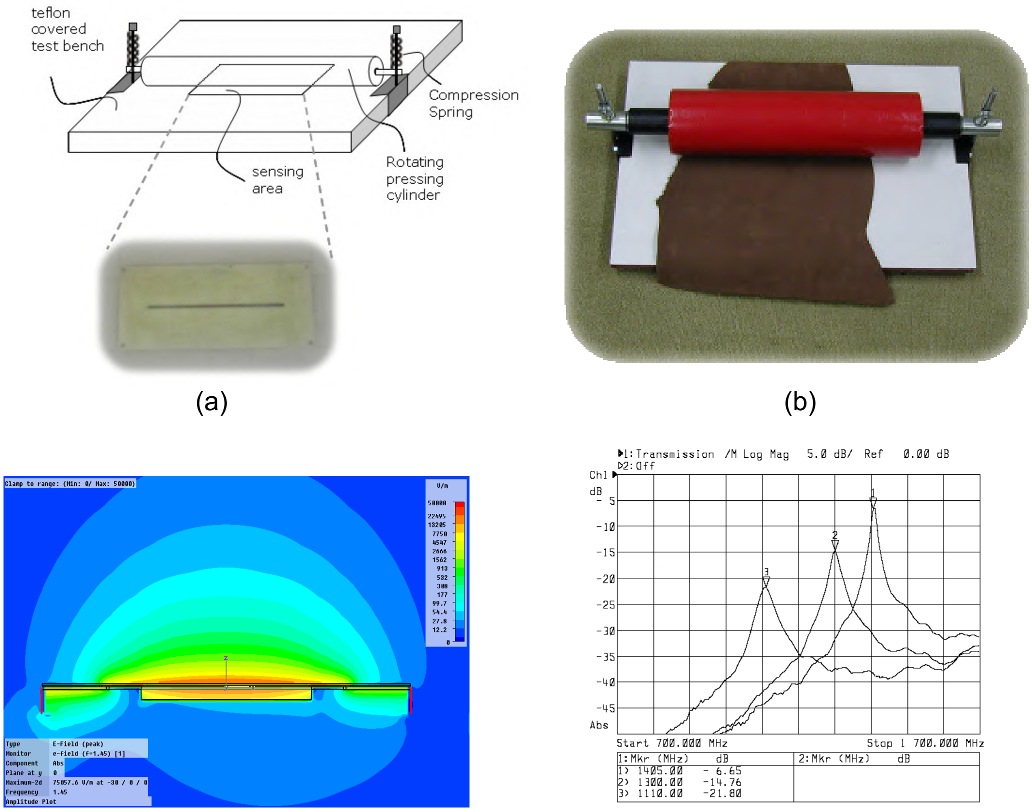


(a) (b)

Fig. 3. Microwave Sensor for Moisture Content Measurement in Paper Milling Industry (a); electric field distribution on the sensing area (b) [7]

(a) (b)

Fig. 4. (a) Microstrip ring sensor (surface planar sensor) [10]; (b) Cavity-backed meander slot sensor (sub-surface planar sensor) [12]



(a) (b)

(c) (d)

Fig. 5. A cavity backed microstrip sensor for leather moisture measurement in continuous industrial processes: (a) placement along the line of contact between the driving cylinder and the basement where the leather slides (a); test bench for continuous measurement of leather moisture (b); electric field distribution (c); measured $|S_{21}|$ parameter vs. frequency (d): 1. unloaded sensor, 2. dry leather (7% moisture content), 3. wet leather (53% moisture content) [14]

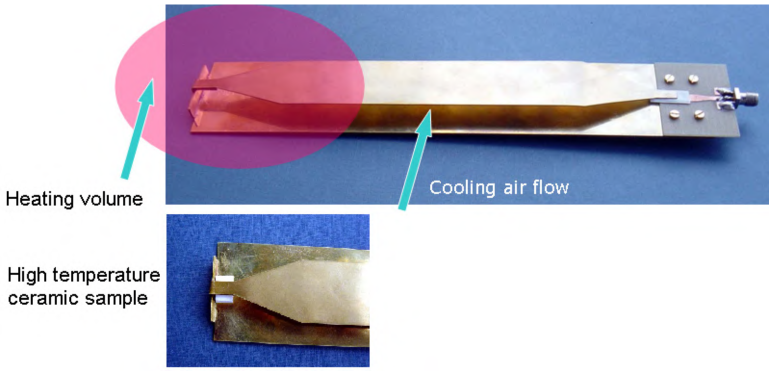


Fig. 6. Reflection microwave TEM Cell Sensor for ceramic materials characterization at very high temperatures [15]

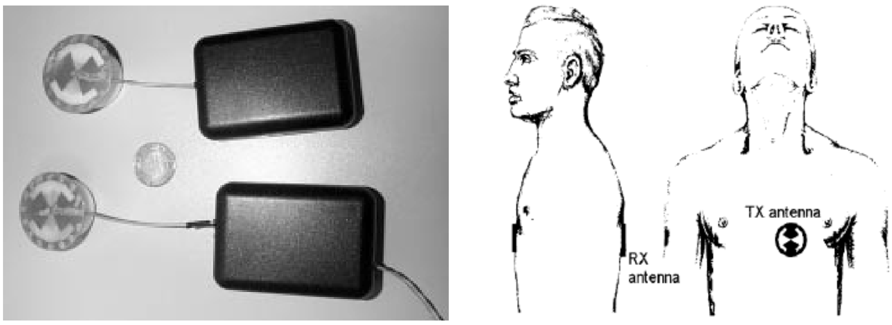
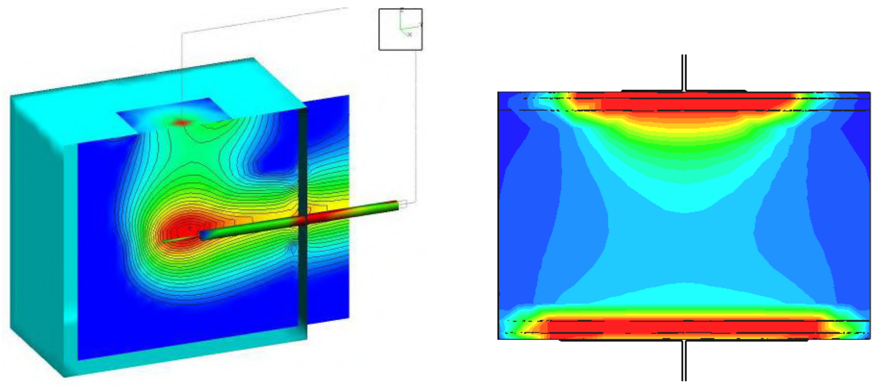


Fig. 7. Microwave Plethysmograph for the monitoring of physiological parameters: prototypes of the transmitter (upper) and receiver (lower) used for measurements(a); TX/RX antenna positions for cardiac monitoring (b) [16]

2. Biomedical Applications

Research activity covers topics addressing microwave applicator modeling and optimization, RF heating of biological tissues (hyperthermia) and temperature monitoring [17-21]:

- Loco-regional microwave applicators
- Endocavitary microwave applicators
- Minimally invasive microwave interstitial applicators
- RF magnetic applicators
- Magnetic nanoparticles assisted hyperthermia
- Magnetic targeting
- Transponder-based temperature monitoring

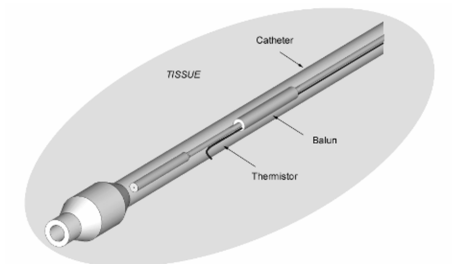


(a) (b)

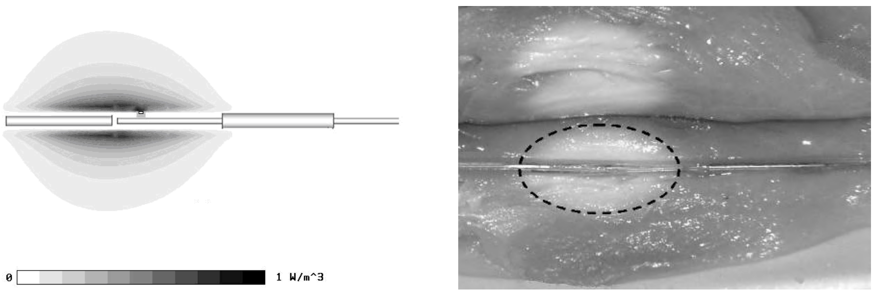
Fig. 8. Simulated electric field distribution inside a simplified human thoracic model for RF loco-regional hyperthermia: invasive electrode (a) and external electrodes (b) [17]

(a) (b)

Fig. 9. Flexible applicator (a) and applicator with bolus (b) for physiotherapic MW hyperthermia



(a)



(b) (c)

Fig. 10. A minimally invasive microwave hyperthermic applicator with an integrated temperature sensor (a); SAR distribution (b); thermal pattern in a splitted chicken tissue obtained by applying 20 W CW power for 20 minutes (c) [18-21]

INSTRUMETATION

LAM is equipped with:

- HP8713B RF Automatic Network Analyzer (300 kHz to 3 GHz)
- HP8720 RF Automatic Vector Network Analyzer (130 MHz to 20 GHz)
- HPE4408B Spectrum Analyser (9 kHz to 26.5 GHz)
- MW generator (Sairem @2.45 GHz, 0-300W adjustable output power)
- Commercial MW ovens
- MW/RF sources, amplifiers, power meters and sensors
- Oscilloscopes and standard electronic equipments
- Computer controlled milling machine for microwave circuits and planar passive/active antenna prototypes fabrication
- Anechoic chamber (1 GHz to 30 GHz)

Software:

- The most advanced EM and MW circuit simulators are used for the design and optimization phases and for the analysis of transient and stationary induced thermal effects.
  - FEKO
  - CST Studio Suite
  - ENSEMBLE
  - MW OFFICE
  - ADS
  - Proprietary EM CAD Framework

EDUCATIONAL ACTIVITY

Prof. Guido Biffi Gentili held the following courses:

- Microwave and Millimeter waves theory and technique
- High frequency system and circuits

at the University of Florence, Faculty of Engineering, Information Engineering Degree Course.

- Ph.D. courses
- Post-Doctoral/Postgraduated courses
- Master's courses

in information and electromagnetic engineering are also organized at the University of Florence with the scientific support of the LAM.

Seminary activity on EM topics are held by the LAM team at the University of Florence, at public or private research institutes and at industrial companies on specific invitation.

COLLABORATION

National Research Institutes

- IPCF-CNR - Institute for Chemical-Physical Processes of the National Research Council, Pisa
- IFAC-CNR - "Nello Carrara" Institute for Applied Physics of the National Research Council, Firenze
- University of Siena
- University of Messina
- University of Pisa
- ASI (Italian Space Agency)
- National Institute for Cancer Research and Therapy, Milano
- Careggi Hospital, Firenze
- Meyer Pediatric Hospital, Firenze
- AUSL 11 Hospital, Empoli (Firenze)
- CNIT - National Inter-University Consortium for Telecommunications
- INSTM - National Inter-university Consortium for the Science and Technology of Materials
- Italian Ministry of Defence

International Research Institutes

- Thayer School of Engineering, Dartmouth College, NH, USA
- Radiation Oncology Department, University of California at San Francisco, USA
- Laboratoire d'Electromagnetique, Université de Nice-Antipolis, France
- ESA (European Space Agency)

Industrial collaborations

- Finmeccanica - Centro Ricerche Radar
- Galileo Avionica Spa
- ASK Industries Spa
- Centro Laser Spa
- Cristini Spa
- Saima Spa
- AME – Advanced Microwave Engineering Srl
- Gruppo Colorobbia - Colorobbia Italia S.p.A.

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BIOLOGICAL EFFECTS AND BIOMEDICAL APPLICATIONS OF ELECTROMAGNETIC FIELDS

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HYSTORY

The Institute for Electromagnetic Sensing of Environment (IREA) is part of the Italian National Research Council. The scientific program of the Institute aims to cover the fundamental aspects of remote sensing, electromagnetic diagnostics, as well as biological and dosimetric aspects of the electromagnetic risk control.
The interaction between electromagnetic fields (EMF) and biosystems has been investigated at IREA since 1983 and the main field of expertise is the evaluation of biological effects induced in vitro. Other investigations, more recently launched, are related to biomedical applications of electromagnetic fields and mainly focused on the use of such radiation to control biological processes. The research activities are carried out in cooperation with national and international research groups, often within the framework of international programmes.

The Bioelectromagnetic research group, composed by three research scientists and two research assistants, is joint to the Interuniversity Center on Interaction between EMFs and Biosystems (ICEmB) that has its legal seat in Genova (Italy) and combines the expertise of many Italian researchers involved in this field.

ACTIVITIES

1. In vitro studies to investigate the biological effects of electromagnetic fields

This activity is devoted to the evaluation of effects induced in vitro following exposures to: a) high frequencies in the band of radiofrequencies with particular concern to those employed for mobile communication devices (900-2000 MHz); b) extremely low frequencies (ELF) mainly related to the transmission and use of electric energy at the industrial frequency (50 Hz); c) THz frequencies, employed for new applications in biomedical area.

Biological samples are exposed to EMFs to evaluate the possible “non thermal” effects. EMF exposures are performed in exposure systems designed and constructed to expose biological samples under controlled conditions. To assure the reproducibility of the experiments the main requirements of exposure systems are: to guarantee the optimal environmental conditions for cell cultures in terms of temperature, CO_2 and humidity; to achieve controlled field distribution inside the biological sample. Mammalian cell cultures are employed, and the main interest is in the alteration of cellular endpoints involved in carcinogenesis. Moreover, due to the high environmental pollution and the large diffusion of EMF sources, a very interesting but scarcely investigated aspect of the interaction between EMF and biological systems is the evaluation of cooperative effects induced by combined exposures to well known chemical and physical environmental pollutants. In this context, following EMF exposures/co-exposures, the attention is focused on 1) the evaluation of DNA damage (genotoxic effects), 2) alteration of cell viability and proliferation, 3) alteration of both cellular redox state and mechanisms involved in detoxification (oxidative stress) and apoptotic processes.

The above described activities are also devoted to evaluate the interaction mechanisms between EMFs and biological systems and to the definition of safety standards for EMFs-exposed population. In this context a researcher of the group is consulting expert of ICNIRP (the International Committee on Non Ionising Radiation Protection).

1.1 Biological effects of EMFs related to mobile communication devices

To evaluate the biological effects of either radiofrequency radiation alone and cooperative effects when the exposure is given in combination with well known environmental pollutants, cell cultures are exposed to EMF at frequencies in use for mobile communications. In particular, the attention is focused on the effects of frequencies related to the first and second generation systems (800-2000 MHz; GSM signal) and recently to the third generation (1950 MHz; UMTS signal). The EMF applicators used are waveguides, transverse electromagnetic (TEM) cells and wire patch cells (WPCs). They can be easily hosted in cell culture incubators to guarantee the optimal environmental conditions. The exposures are carried out in strictly controlled conditions of temperature and dosimetry. They have different duration on the bases of the biological target investigated, and are performed at both continuous and modulated waves at SAR values comparable to the threshold value suggested by the ICNIRP for human exposures. The systems allow the exposure of several biological samples at the same time. The temperature inside the samples is maintained constant by a forced circulating water, and is monitored during the exposure by a fiber optic thermometer.

In Figure 1 and 2 the exposure systems employing waveguides and WPCs, respectively, are reported.

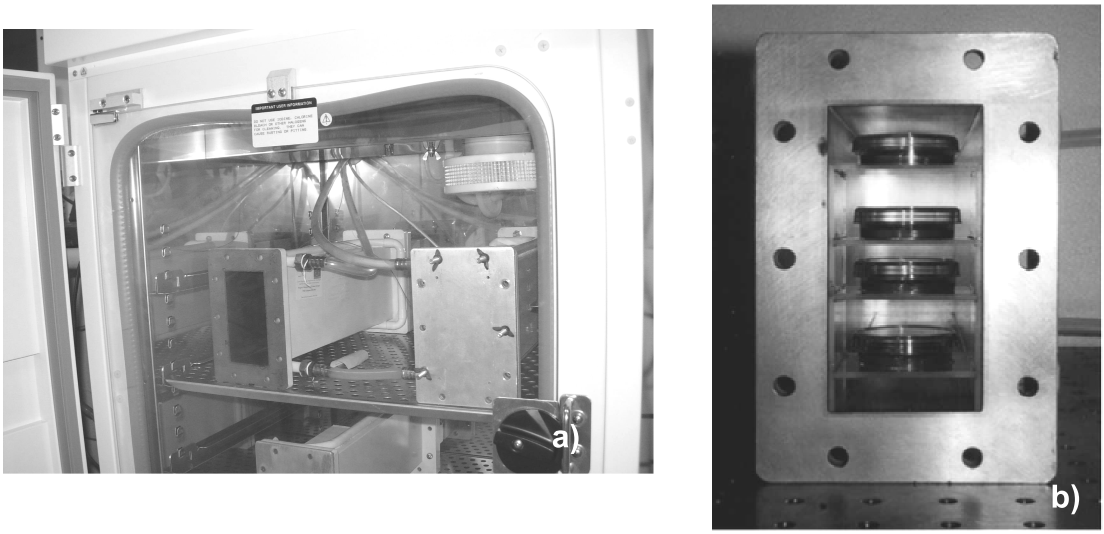

Fig. 1. (a) **Exposure system operating at cellular phone frequencies (1800-2500 MHz), designed and realized in cooperation with the Department of Electronic Engineering and Telecommunication (DIET), University Federico II of Naples. It employs short-circuit waveguides as exposure chambers; (b) waveguide hosting four biological samples**

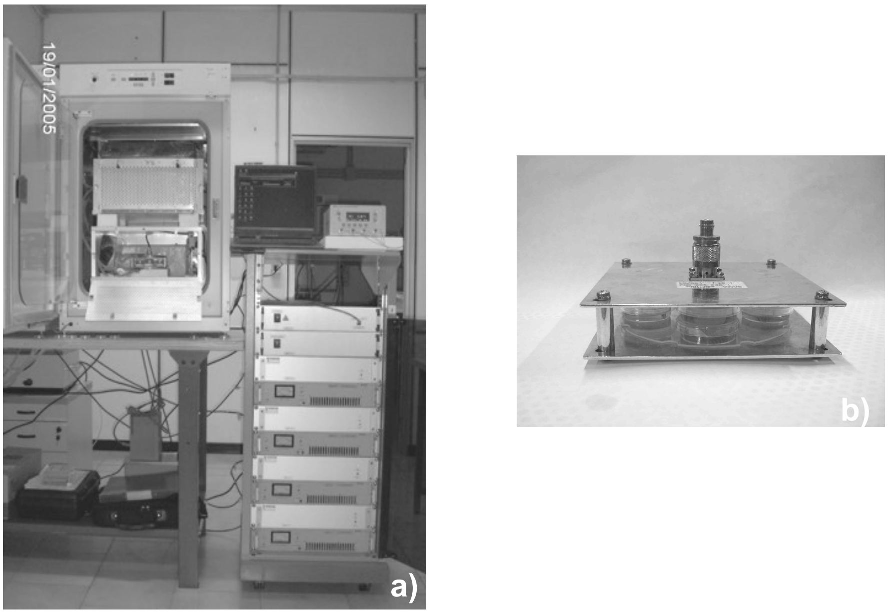

Fig. 2. **(a) Exposure system for cell cultures operating in the frequency range of 895-905 MHz. It employs four WPCs as exposure chambers and has been designed and realized in cooperation with the Section of Toxicology and Biomedical Sciences of ENEA-Casaccia (Rome) in the framework of a project funded by Cellular Telecommunication and Internet Association (CTIA), with the scientific supervision of the US Food and Drug Administration; (b) WPC hosting four biological samples**

The main results are summarized below, on the bases of the frequency and signal employed.

Exposures to 900 MHz, GSM signal - Effects on DNA have been evaluated in cultured human lymphocytes by applying classical (micronucleus, chromosomal aberration and sister chromosome exchanges) and molecular (alkaline comet assay) cytogenetic techniques. The results, obtained at different exposure durations and applied SARs, do not indicate induction of DNA damage. At the moment, to evaluate if different cell types show different sensitivity, experiments are in progress on human fibroblasts [1-3].

Moreover, in comparable experimental conditions it has also been detected lack of oxidative stress in murine fibroblasts exposed and co-exposed to an environmental carcinogen [4] and a time dependent increase in caspase-3 activity, not related to apoptotic events [5].

Exposures to 1800 MHz, GSM signal - Exposures at SAR values lower than 5 W/kg induced neither DNA damage nor alterations of cell cycle kinetics in human lymphocytes from healthy donors. On the contrary, when SAR values higher than 5 W/kg were applied, DNA damage was detected in cultures exposed to a phase-modulated field (GMSK modulation) but not in the case of continuous wave exposure [6].

Exposures to 1950 MHz, UMTS signal - Absence of genotoxicity and production of reactive oxygen species have been detected in human lymphocytes following different exposure duration and SAR values (from 0.2 to 2.2 W/kg) [7-8].

1.2 Biological effects of extremely low frequency electromagnetic fields

Human lymphocytes and cultured cell lines are exposed to magnetic fields, both sinusoidal and pulsed, at the frequency of 50 Hz. For this purpose Helmholtz coils are designed and constructed to be hosted in cell culture incubators and to guarantee the magnetic field homogeneity (Fig.3). The induction of genotoxic effects and apoptosis are investigated in exposed samples. Moreover, to evaluate possible cooperative effects, in some cases co-exposures with physical or chemical agents are also carried out. Of particular interest are the cooperative effects detected following exposure of: a) human lymphocytes from subjects occupationally exposed to low doses ionising radiation and co-exposed to pulsed magnetic fields [9]; b) human lymphoblastoid cell cultures exposed to sinusoidal magnetic fields and co-exposed to well known inducers of apoptosis [10].

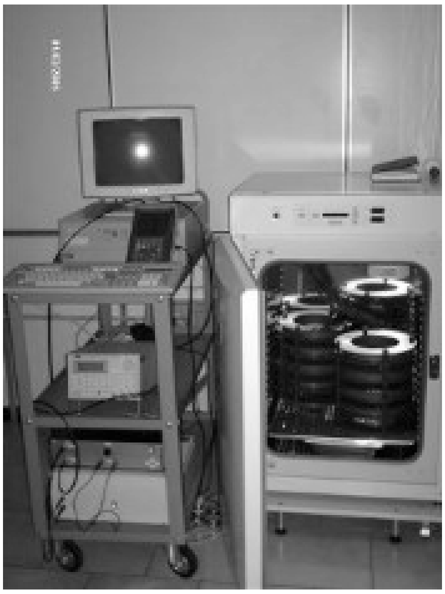

Fig.3. ELF exposure system designed and realized in cooperation with the Department of Physics, University of Bologna. It allows double blind exposures of biological samples. Helmholtz coils are hosted inside a cell culture incubator

1.3 Biological effects of THz radiation

Human peripheral blood lymphocytes from healthy subjects are exposed to 120 - 130 GHz to evaluate the induction of direct DNA as well as chromosomal damage. The experiments are carried out in strict collaboration with ENEA-Frascati, where a free electron laser (FEL), that generates coherent radiation in the frequency range 90-150 GHz, is available. At moment absence of any effect has been detected [11-13]. This result is particularly interesting taking into account that the technologies based on the use of THz frequencies are very recent, and a large number of applications, especially in biomedical area, has been developed.

2. Use of electric fields to control biological processes.

This research activity is devoted to employ pulsed electric fields (PEF) to control cellular processes. In fact, experimental support exists on the efficiency of such PEF for gene and drug delivery, cancer therapy, induction of apoptosis, modification of intracellular structures and trans-membrane transport. The basic mechanism of such process consists in the capability of ultra short electric pulses (nanoseconds) to selectively modulate cellular functions without damaging plasma membranes. In particular, selective intracellular membrane permeability can be induced and the related effects are dependent either from pulse duration and intensity and from the cell type investigated, although action mechanisms determining the selective interaction need further studies. The objective of the activity is the investigation on the effects of high voltage ultra short pulses on selected cellular processes related to carcinogenesis [14]. For this purpose an experimental set up has been constructed for the generation of high voltage ultra short PEF (60 nanoseconds; 60 KV/cm); several cell types will be investigated to study the induction of apoptosis, direct DNA damage and effects on cell viability.

3. Use of electromagnetic fields as promoters of osteogenesis.

The electric field inside the bone is calculated to modelling the electromagnetic behaviour of the biological tissue examined under osteogenic EM signal.

INSTRUMENTATION

The laboratory is equipped with the instruments for cell cultures set up and maintenance such as sterile room, laminar flow cabinet, CO_2 incubators and facilities for the storage of cells (- 80° C and liquid nitrogen dewar). Optical microscopes, inverted microscopes, flow cytometer, spectrophotometers and fluorometer are available. A fluorescence optical microscope, equipped with a computerized image analysis system and specific software devoted to the analysis of comet assay slides is also available. The laboratory is also equipped with electromagnetic field generators and measurement instruments at both ELF and microwave frequencies, to realize exposure systems for cell cultures.

For ELF, the following instruments are available: function generators (0.2 Hz - 2.0 MHz), ELF amplifiers, Helmholtz coils, thermocouple thermometers, Gaussmeter and probes (DC-10kHz), oscilloscope.

For high frequencies, the main instruments are: signal generators (250 kHz-3 GHz) able to reproduce signals employed for mobile communication systems (GSM, UMTS and WiFi), amplifiers (900 MHz - 2,5 GHz), spectrum analyzer, coaxial cable components, waveguides, TEM cells and Wire Patch Cells (900 MHz), power meters (200kHz-4GHz, 0.7mW-30W), fiber optic thermometer

EDUCATIONAL ACTIVITIES

Teaching at the International School of Bioelectromagnetics “Alessandro Chiabrera” (Centre for Scientific Culture E. Majorana, Erice, Italy)

Teaching at the post-degree course on “Electromagnetic fields: risks and protection” (University of Naples Federico II)

Supervision of degree and PhD thesis on several interdisciplinary aspects of EMF interaction with biological systems (students of electronic engineering, physics, environmental science, biological science and medicine).

GRANTS AND CONTRACTS

Italian Ministry of University and Scientific Research (MIUR) - Protection of human being and environment from electromagnetic emissions - (2001-2004)

EU Commission–VFP - Combined Effects of Electromagnetic Field and Environmental Carcinogens (CEMFEC) - (2001-2004)

EU Commission–VFP - THz radiation in Biological Research: Investigation on Diagnostics and study of possible Genetic Effects(THz-BRIDGE) – (2001-2004)

Consorzio Elettra 2000 – Evaluation of genotoxic effects in mammalian cell cultures exposed to 900 MHz, GSM signal, and co-exposed to environmental mutagens - (2002-2006).

CTIA–FDA – Micronucleus induction in human lymphocytes following exposures to Radiofrequency Radiation – (2001-2005)

Telecom Italia Lab – Biological effects of electromagnetic fields in use for mobile communication systems (GSM and UMTS) in human cell cultures – (2004-2008)

EU-Campania Region Center of Competence on Information and Communication Technologies, project "Wireless Technology Health Risks (2002-2005)

APAT – Evaluation of biological processes related to genotoxic and not genotoxic carcinogenesis in mammalian cell cultures exposed to electromagnetic fields at frequencies in use for mobile communication devices – (2005-2007)

Campania Region – Use of electromagnetic fields for the control of cell viability in cells treated with metallic nanocrystals (2004-2005)

Campania Region – Development and characterization of an integrated microflowcytometer (MCFI) for in situ analysis (2007-2008)

COLLABORATION

University of Naples Federico II (Italy), Department of Electronics and Telecommunication
Second University of Naples, Department of Information Engineering, Aversa (Italy)
University of Bologna (Italy), Department of Physics
University of Basilicata (Italy), Department of Animal Sciences
University of Salerno (Italy), Department of Information and Electric Engineering
University of San Antonio, Texas, Department of Radiation Oncology
University of Kuopio (Finland), Department of Environmental Sciences
CNR - Institute for Protein Biochemistry, Naples (Italy)
CNR – Institute for Biostructures and Bioimaging, Naples (Italy)
CNR - Institute for Neurobiology and Molecular Medicine, Rome
ENEA, Casaccia, Toxicology and Biomedical Sciences Section, Rome (Italy)
ENEA, FIM-FISACC, Frascati (Italy)
TILab, Torino (Italy)
IGEA, Carpi (Italy), Clinical Biophysics Lab

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EXPOSURE TO ELECTROMAGNETIC FIELDS: BIOLOGICAL EFFECTS AND MATERIALS TREATMENT

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HISTORY

The University of Salerno has very ancient origins as it is one of the oldest universities in Europe together with Paris and Bologna. The Salerno School of Medicine was founded in the 8th century and was the principal institution in Europe for the study of medicine, reaching its utmost splendour during the Middle Ages. "From the 10th to the 12th century the *licentia docendi* awarded by the Universities of Paris, Bologna and Salerno was recognised universally and enabled the holder to teach *ubique locorum ac per universum terrarum orbem*, a privilege which did not apply to other universities." Léo Moulin (Student Life in the Middle Ages). The School remained active until 1811, when it was closed by royal decree under the Napoleonic government of Joachim Murat. In 1944 the university was re-opened by king Vittorio Emanuele II, and the Istituto Universitario di Magistero "Giovanni Cuomo" was founded, which became Facoltà di Magistero of the University of Salerno in 1968. In 1988, the University, which now has over 43,000 students, moved to the village of Fisciano, a few miles from Salerno. Its structure is that of a university campus and its modern buildings offer many efficient services for teaching, research and student life in general.

ACTIVITIES

1. Effects of LF electromagnetic fields on the bone tissue regeneration

LF (Low Frequency) electromagnetic fields are currently used for clinical therapies of several bone diseases. These treatments are given with the goal to increase bone regenerative processes, but their efficacy is based only on limited clinical evidences. To identify possible molecular mechanisms accounting for *LF* fields ability to stimulate bone regenerative processes, we evaluated at a biochemical level the effects on cell cultures of the signal of currently used clinical apparatus. Two different human cell lines, bone *SAOS-2* and liver *HepG2*, were used for *LF* field stimulation, representing a considerable model of patient tissues, since they allow a strictly controlled experimental condition and a precise effect analysis. Moreover, these cell lines are particularly functional for analyzing the expression of Alkaline Phosphatase (ALP), which is generally considered a typical enzymatic activity associated with the bone tissue regeneration and activation of cells forming the mineral matrix of the involved tissues. *LF* fields significantly increased alkaline phosphatase enzymatic activity within both cell lines after 1 hour of stimulation. The increase was of about 35% in *SAOS-2* and of 80% in *HepG2* cells. No temperature variations were detected during *LF* fields exposure.

2. Microwave (2.45 *GHz*) exposure of *Saccharomyces cerevisiae*: effects on growth and thermal stress tolerance

Saccharomyces cerevisiae is the common yeast used in baking (baker's yeast) and brewing (brewer's yeast). It is a popular model organism in the laboratory because it can be cultured easily and it grows rapidly. Saccharomyces cerevisiae, by virtue of its rapidly fluctuating environment, has developed effective stress sensing and response mechanisms. Recent studies take care of mutagenicity of static and timevarying magnetic fields highlighting that the existence of possible non-thermal biological effect of *MW* is still matter of concern.

Analysis of the samples treated at 55 °C highlights that yeast cultures grown under MW exposure exhibit ability to tolerate thermal stress greater than the unexposed ones. Such a difference is more pronounced in the case of the samples treated at 55°C using MW exposure (about 10-20%) with respect to the samples treated at 55°C using conventional heating. Samples treated at 65 °C do not show a similar behaviour, the temperature being lethal in both cases.

3. Microwave disinfestations of works of art

Many objects made up of wood as well as paper and cloth with artistic or cultural value are seriously damaged by a variety of pests and often such damages are irreversible. The current technologies employed in disinfestations of works of art present risks of pollution both for the operator and for the environment and possible damages for the treated objects. Due to specific Microwave treatment of works of art represents an innovative and promising technique for disinfestations. Many biological forms do not survive over the *lethal temperature*. This technology could be applied to objects of historical-artistic interest made up of: wood (furniture, frames, musical instruments, etc.), paper (books, documents, etc.), cloth (carpets, tapestries, canvas, etc.), which are generally subjected to the attack of bugs (woodworms), moulds, funguses. The exposure system consists in a Reverberating chamber or a free space irradiator for *in situ* treatment.

4. Electromagnetic Band Gap (EBG) microwave applicators

Electromagnetic Band-Gap (PBG) structures, exhibiting forbidden frequency bands, can be realized as layered dielectric structures either periodic or aperiodic. Among the various types of aperiodic structures the ones characterized by fractal morphology show attractive features for devices in the optical regime as well as in the microwave frequency band (frequency selective surfaces, filters, sensors, etc…). Fractals are self-similar structures characterized by invariance property with respect to a change of scale. They can be obtained from a starting set (*initiator*) by performing a basic operation (*generator*) on a smaller and smaller scale. Triadic Cantor fractal multilayers are one of the most simplest and feasible one-dimensional fractal morphology. They are layered structure consisting of alternate layers of two different dielectric media whose optical or geometrical lengths are chosen according to the triadic Cantor procedure. The transmission spectrum of a Cantor multilayer exhibits forbidden bands in which narrow transmission peaks occur. At frequencies where these peaks reach their maximum value the field localization phenomenon is observed, i.e. in some regions of the multilayers the field intensity reaches values significantly greater than the incident one. This behavior is observed for Cantor multilayers whether as volume structures or filling a rectangular waveguide. If a Cantor multilayer is perturbed (e.g., inserting an extra lossy dielectric layer at its midpoint) the field localization phenomenon still occurs.

It is possible to localize the field just inside the lossy extra layer, introducing the idea of fractal applicators.

INSTRUMENTATION

HP 8510 Network Analyzer
HP 85070B Dielectric Probe
Reverberating enclosure (dimensions 120×120×120 cm^3)
Microwave Power sources
Laser sources
Printed-Circuit Board Prototyping Machine

COLLABORATIONS

Dipartimento di Scienze Farmaceutiche, University of Salerno, Fisciano (SA), Italy.

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MICROWAVES AND ECOFRIENDLY PROCEDURES IN THE COSMETIC AND PHARMACEUTICAL SCIENTIFIC RESEARCH

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HISTORY

The research activity of the operative unit is carried out at the Department of Pharmaceutical Sciences of the University of Genoa, focusing the studies on bioactive compounds interesting in the cosmetic and pharmaceutical fields.

In the 1990's the attention has been addressed towards the study and application of microwave irradiation in chemical processes with the main goal of assessing the potential of microwave dielectric heating in organic synthesis.

The development of several research projects supported by CNR grants (CNR Strategic project 1997-1999), MIUR (PRIN 2001 and PRIN 2004) and University of Genoa (Athenaeum projects 2000-2008) allowed to highlight the advantages of microwave irradiation over conductive heating in several applications.

Actually the unit carries out the research on the application of microwave irradiation as an alternative energetic source to solvent-free reactions in organic synthesis, to hydrothermal processes for the preparation of inorganic and hybrid organic-inorganic compounds and to extractive procedures for the recovery of botanical bioactives. The studies are developed in a Green Chemistry context, following different strategies: use of innocuous reagents and solvents or elimination of the toxic ones, development of alternative reaction conditions and reduction of energy consumption. The research unit is a part of the Interuniversitary Consortium INCA - Chemistry for the Environment.

The skills developed in a microwave context are updated thanks to the involvement in national and international microwave networks (GIMAMP - Gruppo Italiano Microonde Applicate ai Materiali ed ai Processi; AMPERE - Association for Microwave Power in Europe for Research and Education)

ACTIVITIES

1. Microwave-mediated solvent-free organic synthesis

In the field of organic synthesis, the research is mainly focused on the development of microwave-mediated solvent-free procedures as improvement and simplification of the synthesis of potential cosmetic and pharmaceutical compounds as well as well-known ingredients.

The coupling of microwave technology with solvent-free conditions in organic synthesis represents a new and particularly efficient, powerful and attractive strategy. Significant enhancements of the reaction rate can be achieved, together with considerable simplification of work-up and low environmental impact in comparison with conventional procedures.

Different kinds of solvent-free techniques are considered:

- *Reactions on solid mineral supports* such as acidic and basic Al_2O_3, *p*-toluenesulfonic acid (PTSA)/Al_2O_3, KF/Al_2O_3, KOH/Al_2O_3.

- *Solvent-free phase transfer catalysis (PTC)* using tetraalkylammonium cations as trasfer agents (i.e. TBAB - tetrabutyl ammonium bromide; Aliquat 336 - Methyltrioctylammonium chloride) and bases.

- *Simple mixture of neat reagents* using as catalysts PTSA, graphite bisulfate, K_2CO_3.

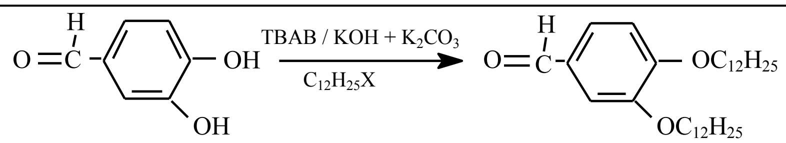
These microwave-mediated (MW) procedures in dry media have been successfully applied as alternatives to several conventional methods.

1.1 Alkylation and Knoevenagel condensation

PTC was applied for the synthesis of new benzylidene derivatives of 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-one as potential UV sunscreens[1].

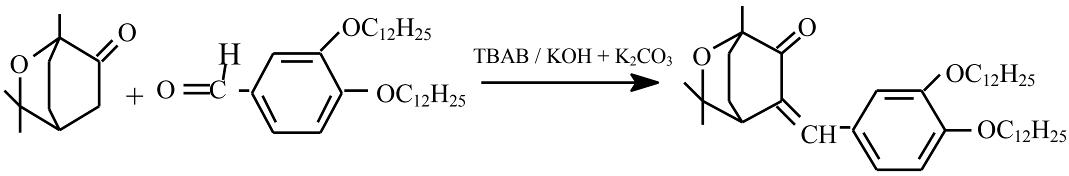
In Scheme 1 and 2 an example with the most significant results in dry media under microwave activation (MW) and conventional heating (Δ) in comparison with the classical method are reported.

Scheme 1 - Alkylation of 3,4-dihydroxybenzaldehydes



MW - PTC	10 min	130°C	86%
Δ - PTC	10 min	130°C	18%
Classical method (Acetone/K_2CO_3)	720 min	Reflux	66%

Scheme 2 - Knoevenagel condensation

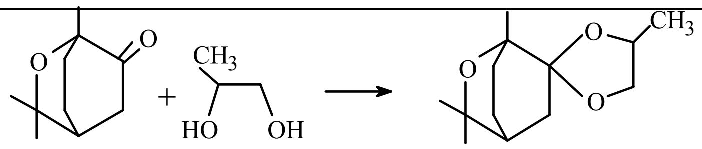


MW - PTC	60 min	140°C	80%
Δ - PTC	60 min	140°C	13%
Classical method (THF/CH_3ONa)	1440 min	Reflux	51%

1.2 Ketalization

Solid supports with acidic catalysis have been used for the synthesis of 1,3 dioxolanes and 1,3 dioxanes of (+)1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6 one (new cosmetic fragrances)[2] . In Scheme 3 an example is reported.

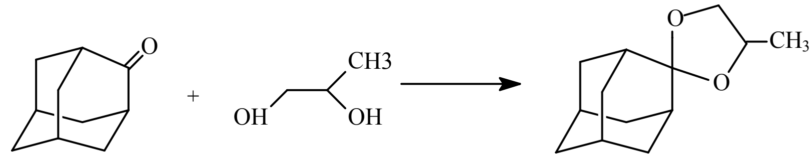
Scheme 3



MW - Acidic Al_2O_3/PTSA	30 min	110°C	78%
Δ - Acidic Al_2O_3/PTSA	30 min	110°C	25%
Classical method (Toluene/PTSA)	360 min	Reflux	30%

The simple mixture of neat reagents under acidic catalysis has been applied for the synthesis of spiro[1,3-dioxolan]2,2'tricyclo[3.3.1.13,7]decanes (new cosmetic fragrances)[3] . In Scheme 4 an example is reported.

Scheme 4



MW - catalyst: PTSA	15 min	110°C	94%
Δ - catalyst: PTSA	15 min	110°C	41%
Classical method (Toluene / PTSA)	360 min	Reflux	57%

1.3 Esterification

Three kind of reactions have been considered (Scheme 5):

Scheme 5

$$RCOOH + R'OH \xrightleftharpoons{\text{Acidic catalysis}} RCOOR' + H_2O$$

$$RCOCl + R'OH \xrightarrow{\text{Basic catalysis}} RCOOR' + HCl$$

$$RCOO^- X^+ + R'Y \xrightarrow{\text{Phase transfer catalysis}} RCOOR' + X^+Y^-$$

A number of long chain aliphatic esters (Table 1) derived from mono and dicarboxylic acids, lipophilic ingredients (emollients, solubilizers, conditioning agents), were synthesized under mild conditions, in high yields and short reaction times using PTC (with Aliquat 336/K_2CO_3) and the simple mixture of reagents under acidic catalysis by neat PTSA [4]. In Table 2, as examples, the most significant results related to the synthesis of two studied esters are reported.

Table 1 - Mono e dicarboxylic lipophilic esters

RCOOR'	R	R'
2-Ethylhexyl pivalate	$(CH3)_3C$	$CH_3CH(C_2H_5)(CH_2)_4$
Isopropyl myristate	$CH_3(CH_2)_{12}$	$(CH_3)_2CH$
Isopropyl palmitate	$CH_3(CH_2)_{14}$	$(CH_3)_2CH$
Isobutyl palmitate	$CH_3(CH_2)_{14}$	$(CH_3)_2CHCH_2$
Butyl palmitate	$CH_3(CH_2)_{14}$	$CH_3(CH_2)_3$
2-Ethylhexyl palmitate	$CH_3(CH_2)_{14}$	$CH_3CH(C_2H_5)(CH_2)_4$
Octyl palmitate	$CH_3(CH_2)_{14}$	$CH_3(CH_2)_7$
$R'OOC(CH_2)_8COOR'$		
Diisopropyl sebacate		$(CH_3)_2CH$
Dibutyl sebacate		$CH_3(CH_2)_3$
bis(2-ethylhexyl) sebacate		$CH_3CH(C_2H_5)(CH_2)_4$

Table 2

BUTYL PALMITATE			
MW - PTC (Aliquat/K_2CO_3)	5 min	140°C	97%
MW - PTSA	10 min	160°C	94%
Classical method (H_2SO_4)	120 min	Reflux	73%
Classical method (Pyridine)	180min	Reflux	87%
DIBUTYL SEBACATE			
MW - PTC (Aliquat/K_2CO_3)	5 min	140°C	91%
MW - PTSA	10 min	160°C	87%
Classical method (H_2SO_4)	120 min	Reflux	69%
Classical method (Pyridine)	1080 min	Reflux	76%

The research was then extended to the synthesis of some aromatic esters, widespread bioactive ingredients: UV absorbers and antimicrobial agents (Table 3) [5]. In spite of the importance of these compounds as raw materials in different industrial applications, only few example of innovative (but not eco-friendly) synthetic procedures are reported in the literature.

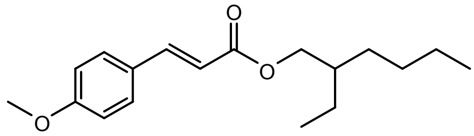
Table 3 – Aromatic esters

NAME	FUNCTION
3-methylbutyl 4-methoxycinnamate	UV filter
2-ethylhexyl 4-methoxycinnamate	UV filter
2-ethylhexyl 4-(dimethylamino)benzoate	UV filter
2-ethylhexyl salicylate	UV filter
4-isopropylbenzyl salicylate	Potential UV Filter
propyl 4-hydroxybenzoate	Antimicrobial agents
butyl 4-hydroxybenzoate	Antimicrobial agents

Several methodologies in dry media were assessed and the most performing results were achieved using PTC for the synthesis of UV filters, acidic catalysis by PTSA for the synthesis of parabens. In Table 4 as examples the most significant results related to a UV filter (2-ethylhexyl-4-methoxycinnamate) and an antimicrobial agent (butyl 4-hydroxybenzoate) are reported

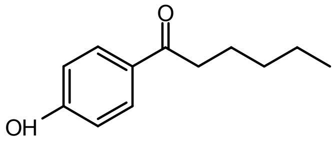
Interesting results were arised studying the esterification of 3,3,5-trimethyl-cycloexanols to obtain new compounds of potential cosmetic application, such as the cyclopropionic ester (potential new fragrance) and the 10-undecenoic ester (potential lipophilic ingredient), and well-known pharmaceutical and cosmetic ingredients such as Cyclandelate (mandelic ester, pharmaceutical hypolipidemic agent) and Homosalate (salycilic ester, UVB filter) (Table 5) [6].

Table 4



2-ethylhexyl-4-metoxycinnamate

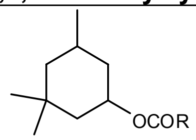
MW - PTC (Aliquat 336/K_2CO_3)	160°C	10 min	92%
MW - PTC (Aliquat 336/K_2CO_3+KOH)	160°C	10 min	81%
MW - PTC (TBAB / K_2CO_3)	160°C	10 min	80%
MW - PTSA	160°C	10 min	45%
MW - Graphite bisulfate	160°C	20 min	73%

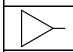


butyl 4-hydroxybenzoate

MW - PTSA	160°C	5 min	77%
MW - PTSA	180°C	5 min	73%
MW - Graphite bisulfate	160°C	20 min	81%
MW - PTSA/Al_2O_3	160°C	5 min	25%

Table 5 - 3,3,5-trimethylcycloexyl esters

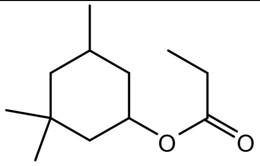


R	
CH_3CH_2	3,3,5-trimethylcyclohexyl propanoate
$CH_3(CH_2)_2$	3,3,5-trimethylcyclohexyl butanoate
$CH_3(CH_2)_6$	3,3,5-trimethylcyclohexyl octanoate
CH_2=$CH(CH_2)_8$	3,3,5-trimethylcyclohexyl undec-10-enoate
	3,3,5-trimethylcyclohexyl cyclopropanecarboxylate
$C_6H_5CH(OH)$	Cyclandelate
2-(OH)C_6H_4	Homosalate

In order to develop the best performing reaction conditions several experiments were carried out. In Table 6 the most significant results related to 3,3,5-trimethylcyclohexyl propanoate are reported. These results can be considered representative for all compounds except for Homosalate.

Homosalate, whose classical synthesis is very difficult, is obtained in good yield only using a basic catalyst on a solid mineral support (Table 7).

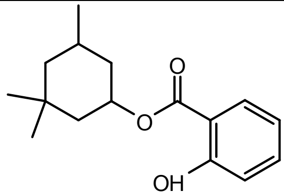
Table 6



3,3,5-trimethylcyclohexyl propanoate

MW - PTSA	130°C	30 min	98%
MW - PTSA/ Al_2O_3	130°C	30 min	40%
MW - PTSA/mesoporous silica	130°C	30min	45%
MW - Graphite bisulfate	130°C	40min	85%
MW - KF/Al_2O_3	100°C	20min	94%
MW - KOH/Al_2O_3	100°C	20min	93%

Table 7



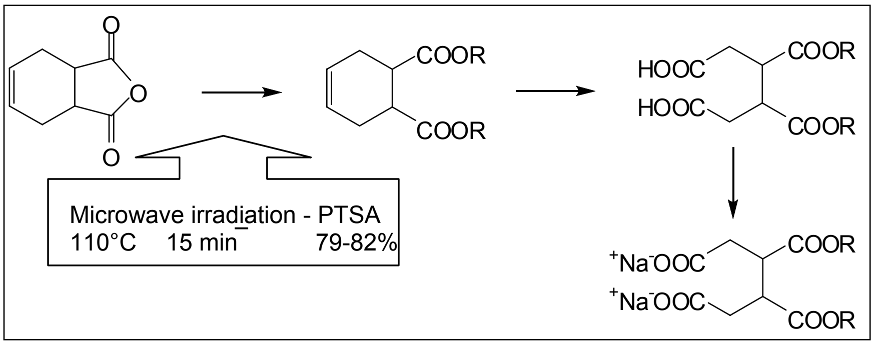
Homosalate

MW - KF/Al_2O_3	100°C	20min	72%
MW - KOH/Al_2O_3	100°C	20min	65%
MW - PTSA	130°C	30 min	11%
MW - Graphite bisulfate	150°C	40 min	11%

1.4 Synthesis of Gemini surfactant

At present, with the aim of studying new eco-sustainable compounds of cosmetic interest, a research project is addressed towards the synthesis under mild conditions, of different Gemini surfactants, compounds with low environmental impact due to the high efficiency for the improved surface-active properties[7]. Microwave activation is applied in the first step of the synthetic pathway (Scheme 6) for the preparation of dialkyl-cyclohex-4-en-1,2-dicarboxylates starting from the opportune anhydride.

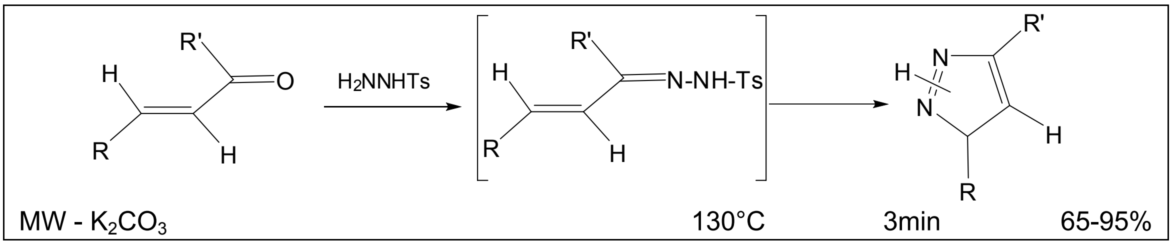
Scheme 6



1.5 Synthesis of pyrazole derivatives

In a pharmaceutical context, a novel green approach to the synthesis of pyrazole derivatives from α,β-unsaturated carbonyl compounds with α,β hydrogen, has been also studied[8]. A “one-pot” microwave-mediated cycloaddition reaction was developed, starting directly from the ketones as the precursors, via tosylhydrazones generated *in situ* (Scheme 7).

Scheme 7



2. Microwave-mediated hydrothermal processes

The hydrothermal process, in line with the Green Chemistry principles due to the use of mild conditions and water as the solvent, can be considered one of the most efficient methods to obtain nanoparticle and it is suitable to be coupled with MW activation. MW technology can contribute significantly to the development of new processes for the synthesis of nano-sized materials due to its advantages in terms of reaction conditions such as heating rapidity and selectivity, and volume reduction.

Within our studies focused on the development of alternative processes for the synthesis of cosmetic ingredients, microwave-hydrothermal methodologies have been applied for the manufacture of nano-sized materials such as mineral oxides[9] and natural or synthetic organoclays.

2.1. Titanium dioxide

Nanosized titanium dioxide in the polymorphic phase rutile is applied in cosmetic formulations as an effective UVB filter, due to its triple action – absorption, scattering and reflection of UVB radiations. Furthermore, TiO_2 possesses interesting dielectric and catalytic properties, which result in manifold industrial applications; in particular anatase, more efficient than rutile as an eco-friendly photocatalyst, may be employed in water decontamination for the degradation of pollutants.

In our research, nanosized TiO_2 was prepared with good results under different reaction conditions by a microwave-mediated hydrothermal process[10-12].

2.2. Organoclays

Organophilic clays are rheological additives frequently used in cosmetics and toiletries; moreover, they are exploited to absorb organic pollutants in soil remediation programs.

Organoclays are classically prepared from natural smectites, but organophilic derivatives of synthetic clays might represent more performing technological materials in order to prepare pure and reproducible hybrids featuring specific properties. In our research, a fast and efficient MW procedure was developed for the preparation of organophilic derivatives of various synthetic sodium fluorophlogopite micas[13], characterized by different layer charge.

All syntheses were also carried out by a conventional-hydrothermal procedure under the same reaction conditions for comparison. In most cases microwave heating has proved to be more efficient than conventional one, yielding a higher extent of intercalation. Microwaves resulted particularly superior in the treatment of high-charged clays, with significant energy and time savings.

3. Microwave-mediated extractive procedures of natural bioactives

Our research is focused on the use of SFME - Solvent-free microwave extraction, an original combination of microwave heating and dry-distillation, performed at atmospheric pressure that provide e new idea in the extraction of essential oils from fresh aromatic plants. This green methodology was successfully applied to the recovery of essential oil from *Salvia Somalensis* Vatke, whose potential cosmetic use we are studying.

The results seem to indicate several advantages in terms of efficiency, speedinesss, easy work-up, substantial energy and solvent saving when comparing this methodology with hydro-distillation and steam distillation[14],

INSTRUMENTATION

Prolabo Synthewave TM S402 - Single mode microwave reactor (specific for organic synthesis): open vessels, control and monitoring of temperature by IR detector, power control up to 300W, mechanical stirring with adjustable rotation speed.

Discover^{TM} CEM - Single mode microwave reactor: open or closed vessels, control and monitoring of temperature by IR detector and optical fiber sensor, power control up to 300W, pressure control in closed vessel up to 200 psi, magnetic or mechanical stirring, possibility of cooling with compressed air during the process.

EDUCATIONAL ACTIVITY

The Unit cooperated to the draft of an educational book edited by INCA as regards its specific knowledge in the field of microwave application to chemical processes[15].

Several students of the Faculty of Pharmacy have attended the unit lab for the developed of master theses on a “microwave activation” subject.

The members of the Unit are components of the teacher council of the Doctorate School in “Sciences and Technologies of Chemistry and Materials” and of the single Doctorate Course in “Medicinal, Food and Cosmetic Sciences” belonging to the Doctorate School itself. They hold a theoretical/pratical course of “Microwave technology applied to chemical processes” for PhD students attending the Doctorate School in “Sciences and Technologies of Chemistry and Materials”. The lab is attended by the PhD student also for the development of PhD Dissertations.

GRANTS and CONTRACTS

1997-1999 CNR grants for the research project: “Application of microwave ovens to the synthesis of compounds of potential cosmetic interest” - CNR strategic project “Industrial application of microwave technology”

2001 PRIN research project co-financed by MIUR (Italian Ministry of Education, University and Research): “Microwave assisted syntheses of nanoparticles for cosmetic applications” *(National research project:* “Microwave assisted syntheses of nanoparticles”).

2004 PRIN research project co-financed by MIUR: “Microwave-mediated ecofriendly methodologies for the synthesis of biactive compounds” *(National research project:* Chemical processes under electromagnetic field irradiation for a sustainable chemistry*)*

University of Genoa: Athenaeum projects 2000-2008.

COLLABORATIONS

Department of Materials and Environmental Engineering - University of Modena e Reggio Emilia.

Department of Physical Chemistry - University of Palermo.

Material Research Laboratory – Penn State University (USA)

Department of Ophthalmology and Visual Sciences, Department of Pharmaceutical Sciences - University of Kentucky, Lexington, USA.

Laboratoire des Réactions Sélectives sur Support - ICMMO - Institut de Chimie Moléculaire et des Matériaux d’Orsay - University of Paris-Sud (from 1997 to 2005)

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USE OF MICROWAVES TO SYNTHESIZE SOLID ACID CATALYSTS: ABOUT AN HIDDEN EFFECT ?

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HISTORY

The LMSPC lab belongs to the CNRS and the University of Strasbourg, as UMR 7515 CNRS. Its localisation is at the Strasbourg - Cronenbourg Campus, 25 rue Becquerel 67087 Strasbourg cedex 2. Web : www-lmspc.u-strasbg.fr

The activities in the frame of the LMSPC cover the different field of heterogeneous catalysis and nanomaterials development: electrocatalysis, carbide and nanostructures, depollution, energy and bio-ressources valorisation, as well as acid catalysis. In a green chemistry context, LMSPC researchers tend to develop nanomaterials which both suit aforementioned applications and being environmental friendly (non toxic, highly selective and reusable).

The use of microwaves also enters in a concept of green chemistry with a gain in energy, and enhanced atom economy. Their application in the laboratory remains (so far) in the solid acid catalysis group, either for the preparation of novel generations of catalysts, or for the application of solid acids in the synthesis of fine chemicals.

ACTIVITIES

1. Development of solid acids with peculiar properties

The synthesis of solid acids, and particularly zeolites, may be accelerated by order(s) of magnitude when exposed to microwaves (MW) [1]. However, the reasons for MW reaction enhancements in the field of zeolite science are rather speculative, and often conflicting.

We therefore focus our efforts on the development of novel methods to control the morphology of zeolite crystals using a MW. One method consists in an assisted solvothermal synthesis based on the use of an alcohol as co-solvent [2]. Two types of dipolar alcohols were used as co-solvents for both conventional heating (CH) and micro-waved assisted (MW) procedures for the synthesis of zeolites.

The zeolite synthesis mixture was prepared by adding at room temperature sodium aluminate, sodium chloride, tetrapropylammonium hydroxide in demineralized water. Afterwards, TEOS, followed by co-solvent, were added dropwise under vigorous stirring.

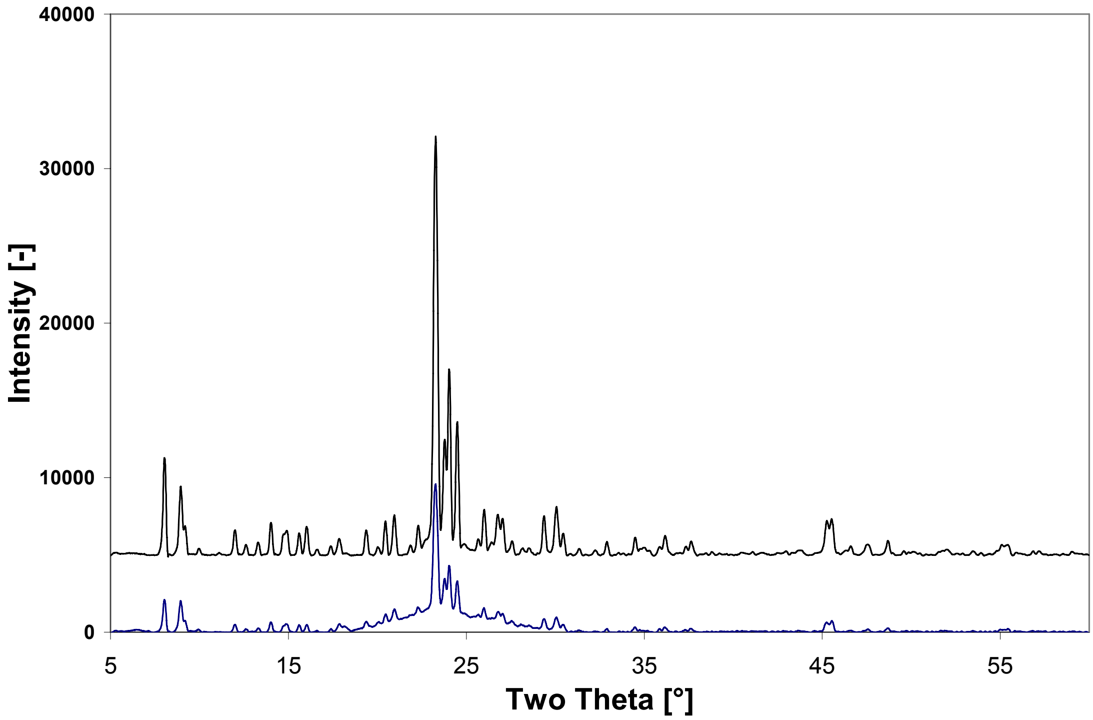


Figure 1. **XRD of ZSM-5 obtained via conventional heating in octanol as co-solvent (black); and after a pre-activation under MW (blue)**

The mixtures were prepared in the following molar ratio, TPA-OH : TEOS: NaCl : $NaAlO_2$: H_2O : alcohol = 9 : 23 : 14 : 1 : 4030 : 1815. Ageing and homogenisation of the mixture were performed during 2h. In the case of the MW procedure, the aged solution was pre-activated during 5 min in CEM Discover 35mL reactor. This MW pre-activation was carried out at 363 K under a fixed power of 250W. Finally, the gel was poured in a 70 mL Teflon-lined autoclave. The zeolite synthesis was carried out for 24h at 443 K under autogeneous pressure.

Figure 1 shows the powder diffractogram of MFI zeolites obtained via the two procedures. Surprisingly, the zeolite pre-activated under MW exhibits a lower crystallinity (40%) when compared to the one prepared under CH. Such unexpected effect observed after micro-wave irradiation is difficult to explain. Further studies are under progress to relate the size and the stacking of zeolite crystals with the mode of heating.

Besides, novel ways of zeolite synthesis were also developed in our group, as a promising way to tailor the properties of such materials at a molecular level, together with a defined (and desired) size of the crystals and shape [3]. Figure 2 shows a microscopic assembly of zeolite crystals which was achieved while using a supramolecular mediated path.

Based on supramolecular chemistry concepts [4,5], we were also able to synthesize polyoxometalate crystals which are known as strong solid heteropolyacids. The self-assembly process has not been fully understood yet without MW use, and is further complicated by the MW irradiation.

Figure 3 presents a last example where umbedded Ti-promoted zeolite crystals where grown, thus being assembled into each other like primary building blocks.

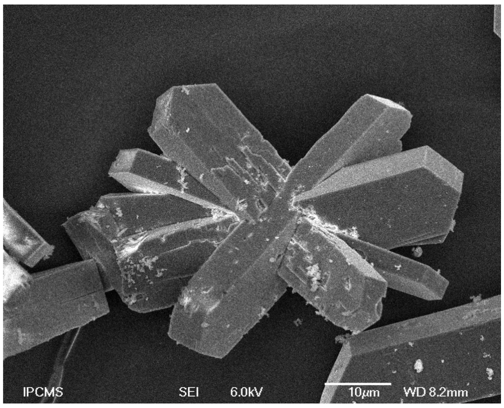


***Figure* 2. Self-organization of MFI-type zeolite crystals at a microscopic level**

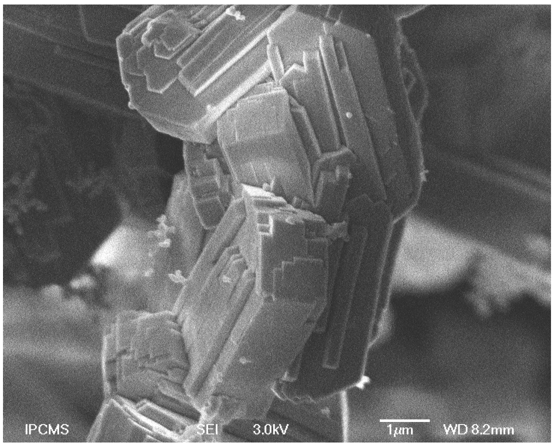


***Figure* 3. Titano-zeotype crystals assembly promoted by MW irradiation**

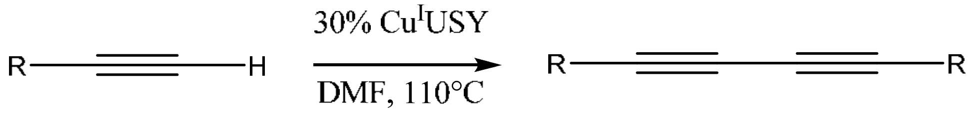
These primary studies started current 2007 are still at early stages of investigation, and many questions are left without answers. Our methodology is based on a simple comparison between a conventional heating procedure and MW. Based on our sol-gel chemistry knowledge, we hope to achieve significant outcome in the coming years.

2. Synthesis of fine chemicals via acid catalysis

Tightening environmental legislation is driving the fine and speciality chemical industries to consider alternative processes that avoid the use of conventional mineral acids. Solid acids such as zeolites represent an excellent alternative. A wide range of important organic reactions can be efficiently catalyzed by these materials, which can be designed to provide different types of acidity as well as high degrees of reaction selectivity.

The combination of material design at the molecular level with microwaved-assisted reactions offers exciting opportunities for future innovative green chemicals manufacturing. The second main part of our activities relies on the catalytic application of as-prepared solids in the synthesis of fine chemicals. We restrict essentially our reactions to the broad domain of acid catalysis. Furthermore, we mostly deal with C-C bond coupling formation and partial oxidation of aromatics, which are essential in organic chemistry and drug design.

To illustrate the importance of MW, we have perfomed acetylenic coupling reaction as follows:



Whereas starting with phenylacetylene, a yield toward diyne of 30% was achieved after 3 days [6], 15 min only were necessary to reach the same yield under MW heating with the discover apparatus (in sealed batch reactor). Moreover, the reaction was performed under clean conditions with a close to 100% selectivity. This opens new doors for performing fine organic synthesis under microwaves.

INSTRUMENTATION

The instrument used for our studies is a Discover S-Class CEM reactor (Figure 4). This mono-mode MW cavity can operate up to 300W in a temperature range 30-300°C and pressures below 20 bars. Working set-up and acquisition are operated manually or automatically via Synergy Software.

Figure 4. **CEM Discover S-Class reactor**

COLLABORATIONS

Universidade Federale Rio de Janeiro, Laboratoire de Physico-Chimie des Hydrocarbures (Prof. J. Sommer, Strasbourg), Laboratoire de Synthèse et Réactivité Organique (Prof. P. Pale, Strasbourg), Ecole Polytechnique Fédérale de Lausanne, Center for Future technology (Dr. Y. Huisuk, Korea), Fritz Haber Institut Berlin (Dr. J.P. Tessonnier).

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GERM - GROUPE D'ETUDES ET DE RECHERCHE SUR LES MICROONDES

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HISTORY

The pioneering period: At the beginning of the 80s, Pr. M. Lallemant belonging to the LRRS (Laboratoire de Recherche sur la Réactivité des Solides) from University o Burgundy used microwave heating as a tool to activate endothermic transformations as evaporation. Several studies devoted to hydrodynamic instabilities induced by microwave heating came after. These investigations induced several European grants in relation to ESA (European Spatial Agency). The PhThesis of D. Stuerga in 1989 was the last in hydrodynamics in Dijon. Head of laboratory and CNRS decided to stop studies upon microwave hydrodynamics. Many papers resulting from this work were awarded specifically by IMPI (International Microwave Power Institute) in 1994 [1,2,3,4]. Furthermore, Prof. Lallemant and Dr. Stuerga attended ESA Expert Working Group (EWG Capillarity directed by Pr. A. Sanfeld).

The growing period: D. Stuerga has been appointed *Maitre de Conférences* in 1990. The microwave heating was not only a tool but an investigation field itself. Several PhD theses had been defended in area of electromagnetic field calculus (free propagation, waveguide and cavity). D. Stuerga was appointed as *Professor* (Physical Chemistry) in 1997. In the meanwhile, P. Pribetich from IEMN (Institut d'Electronique et Microélectronique du Nord, Lille) was appointed *Professor* (Electronics) in University of Dijon (LIESIB). They created together a transversal operation called GERM (Groupe d'Etudes et de Recherches sur les Microondes). Then, Pr Pribetich founded LME (Laboratoire Microonde et Electromagnétisme) for a short period. Indeed, this laboratory was winded up in 2000. The transversal operation GERM was finally validated by laboratory head of LRRS in 1999. Several new researchers joined GERM: C. Bousquet-Berthelin (*Materials chemistry* 1999), D. Chaumont (*Chemical physics* 2001) and J. Rossignol (*Electronics* 2002). Finally, this transversal operation GERM has been confirmed by laboratory head of LRRS as a new research team in 2005 managed by Pr. D. Stuerga. LRRS has merged with LPUB (Laboratoire de Physique de l'Université de Bourgogne) to found the ICB (Institut Carnot de Bourgogne) in 2007. Consequently, GERM is one of the research team of the Nanoscience Department of ICB.

The start-up period: A start'up project called *Naxagoras Technology SAS* was founded in 2005. The Naxagoras Technology Company started on July 2007. This start-up develops GERM microwave research success. It has an operating licence of a patent upon microwave process for preparing nanomaterials. The managing team is constituted by C. Lohr (manager and shareholder) and Pr. D. Stuerga (consultant and shareholder). C. Lohr holds his PhD in physical chemistry from GERM in 2004.

ACTIVITIES

The studies of interaction microwaves-matters and electrothermal coupling developed since twenty years lead to current fruitful results. Numerical tools were set up to forecast electromagnetic fields within dielectric lossy media. They allow design and development of laboratory microwave reactors straightforward usable on industrial scale. Originality of GERM approach is an transdisciplinary approach of microwave processes including lossy electromagnetics, hydrodynamics, thermal and chemical processes. Studies combine sophisticated experimental approach with numerical and analytical modelling and systemic simulations.

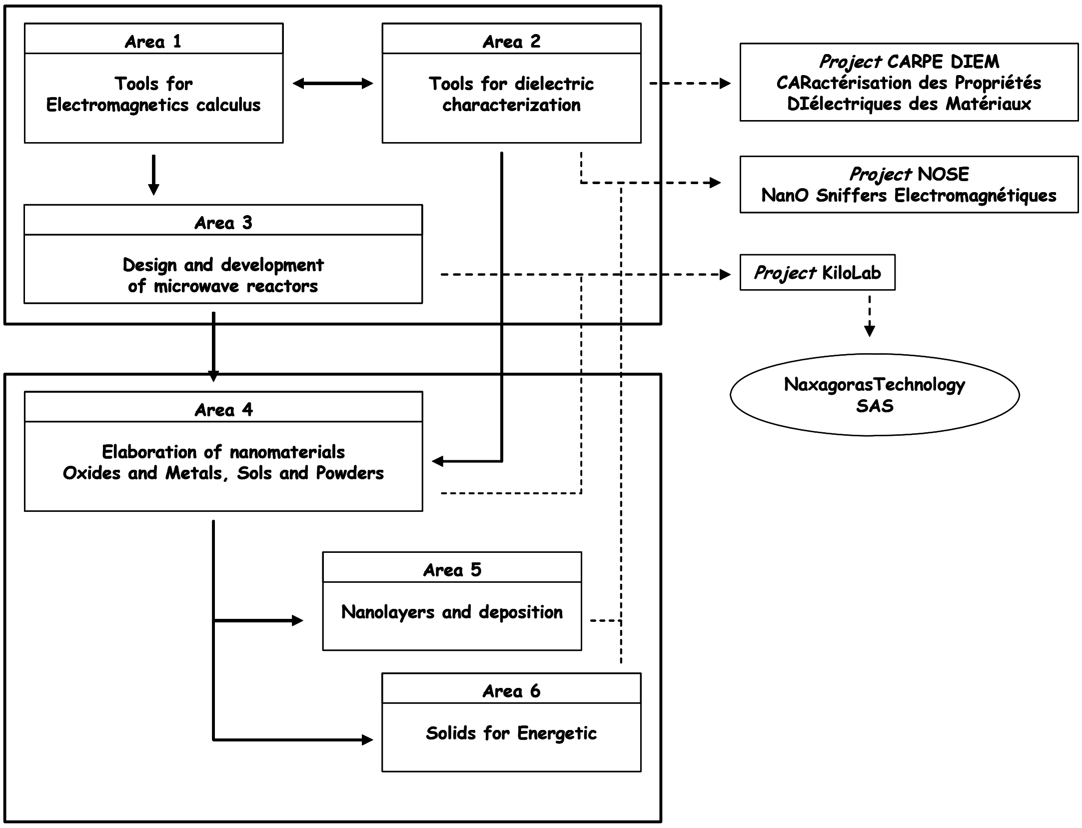

Figure 1. Flow chart of research areas of GERM [5]

Seven research areas constitute GERM activities. Tools for electromagnetic calculus (*Area 1: D. Stuerga, P. Pribetich, J. Rossignol*) associated with those for dielectric characterisation (*Area 2: J. Rossignol, D. Stuerga*) lead to microwave energy harnessing. These two areas imply theoretical approach, experimental protocol, instrumentation and microwave metrology. These tools allow laboratory reactors and pilot plant design (*Area 3: D. Stuerga*). These reactors allow design of original microwave processes called Thermal Initiated Nucleation (*Area 4: D. Stuerga, D. Chaumont*).

Microwave induced thermohydrolysis leads in one step to oxides nanoparticles even as stable colloid suspensions. This new route is a direct route to oxide from metal salts without precipitation of hydroxide. Nucleation could be induced by microwave heating. Moreover, core heating can induce a homogeneous nucleation. The symbiotic association between thermohydrolysis and hydrothermal microwave heating allow obtaining monodisperse nanoparticles within only a few minutes.

These products are used to obtain layers by deposition (*Area 5: D. Chaumont*) or densified materials for energy (*Area 6: D. Stuerga, C. Bousquet-Berthelin*). Area 7 corresponds to projects around dielectric characterization (*CarpeDiem*), new gas sensors founded upon microwave broadband measurements (*Nose*) and pilot plant for nanomaterials (*Kilolab*). Naxagoras technology is a startup which develops GERM microwave research success. The flowchart described by the Figure 1 gives interaction between the different research axes.

1. Tools for electromagnetic calculus

Microwave heating offers the ability to realize high power densities due to core thermal conversion of electromagnetic energy. The electric field is one of the crucial parameter in microwave heating and design of microwave applicators or ovens. If electric field distributions within empty microwave ovens or cavities are well-known, the problem is totally different if loaded microwave applicators are considered [6]. Moreover, dielectric properties of most materials vary with temperature. This temperature dependency of dielectric properties may influence process significantly. Such dielectric change of the load must be taking into account in the design of the applicator. However, microwave applicator (traveling wave, multimode and single mode cavities) are often designed by a trial and error procedure. However, industrial in-line processing calls for the design of specific applicators, which enables high power densities and hence rapid heat-up rates to be achieved.

GERM has demonstrated advantages of cylindrical applicators. Information has been published regarding the design of such applicators with taking into account the loading effect of the pipe (lossy dielectric rod) and the tuning due to thermal dependency of the dielectric properties of the heated fluid. Modes established for lossless structures have been extended to high-loss systems and limits of classical perturbations approaches can be completely avoided. The advantage of cylindrical applicators is that the field is at its highest value at specific regions into which the loads are normally inserted.

The aspect of energy profiles within lossy media is more complicated. Resonant devices and especially dimensional resonance according to author's terminology can induce electric field focusing effects. The Figure 2 describes thermal dependency of electric field radial distributions within water pipe.

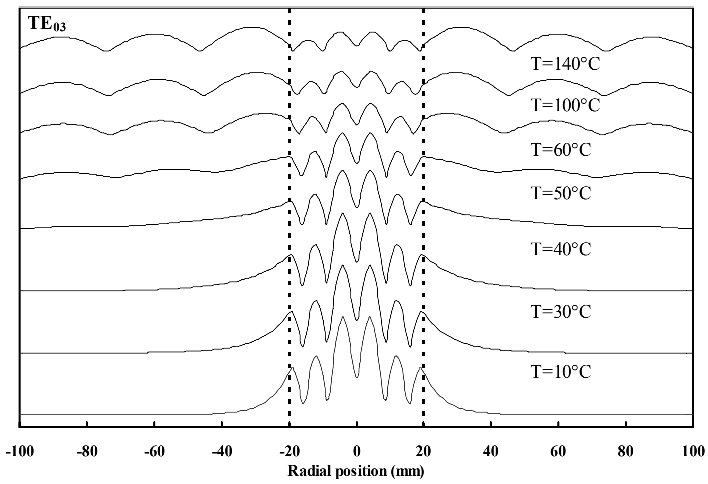

Figure 2. Radial electric field profile within a water pipe in relation to temperature [7]

Different radial distributions within air and water are observed. Whatever the temperature, a ring distribution is obtained in air. For the water pipe, 40°C appears as a critical value. Three rings are observed for temperature below 40°C and two rings for temperature higher.

The development of models for such applicators would improve the understanding of microwave processing and heating. It would enables the rapid design of optimized microwave devices.

Taking into account dielectric losses is a key goal for the design of optimized microwave industrial applicators for microwave heating of fluids within pipes. Moreover, dielectric tuning due to thermal dependency of dielectric properties must be took into account. It has been shown that our approach provides an accurate means of trapping modes for lossy loaded cylindrical applicators. Moreover, our approach should make predictive control and design of optimized travelling waves applicators [7,8]. According to authors, a viable alternative to the trial and error methods currently used for designing microwave applicator for industrial heating applications has been set up.

2. Tools for dielectric characterizations

The specificity of microwave heating results from the thermal dependency of dielectric properties. The complex dielectric permittivity is strongly dependent on temperature and the dynamic behavior of microwave heating is governed by this thermal change. Moreover the electric field amplitude depends on the real and imaginary part of the dielectric permittivity which depends themselves of temperature The Figure 3 describes the thermal feedback induced by thermal dependency of dielectric properties.

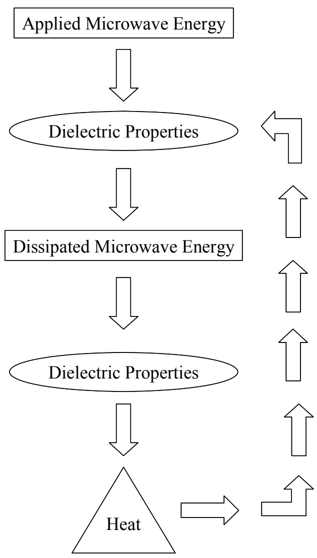

Figure 3. Scheme of dielectric thermal feed-back [9]

The applied microwave energy gives dissipated microwave energy in relation to dielectric properties. The heating rate is controlled by thermal properties (thermal diffusivity, specific heat). However, thermal dependency of thermal properties is very slight compare to thermal dependency of dielectric properties. Contrary to conventional heating techniques, heated medium acts as an energy converter.

Consequently, thermal change of dielectric properties causes changes in the dissipated energy during heating. Depending on the nature on the thermal changes, this may result in thermal runaway, even in some cases reduced material heating. The thermal runaway is a catastrophic phenomenon in which a slight change of microwave power causes the temperature to increase rapidly. Futhermore the electric field depends on the spatial location in relation to the wavelength within the heated material and thus inhomogeneous heating causes the deleterious effect of inhomogeneous material properties (e.g. in ceramics densification and sintering or polymers curring and reticulation).

Hence, a precise knowledge of the dielectric properties is essential for any study of microwave heating or design of microwave applicator. However, the thermal behavior of the heated material is generally dependent not only on the dependence of dielectric losses but on the strength of the electric field applied. Both of these two parameters have to be known to optimize operating conditions and microwave thermal processes. Consequently, the basis understanding of the microwave heating processes still remains somewhat empirical and speculative due to its highly non-linear character [10,11].

3. Design and development of microwave reactors and processes

Design of chemical microwave processes, especially scale-up of operating conditions, involve knowledge and control of several non-linear feed-back loops. The Figure 4 gives a description of chemical microwave processes according to concepts of systemic theory or theory of system in cybernetic modelling. This theory studies systems in relation to feed-back and coupling loops.

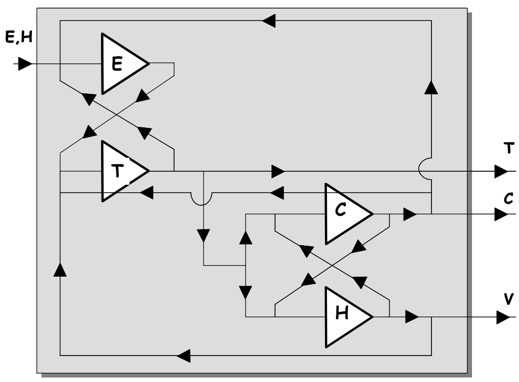

Figure 4. Scheme of Chemical Microwave Process [9]

The microwave process includes the microwave oven, the reactors and the reactants. The inputs of the system are microwave energy (E,H) and reactants whereas the outputs are heat (T), products (C), and convection motions of fluids for solutions (V). A processor is associated to each process. They are schematized by triangle upon the Figure 4. In systemic theory, the meaning of a processor is a function linking input and output. These processors could be expressed by partial differential equations. The two first processors to be considered are the electromagnetic (E) and the thermal processors (T) leading to heating. The heating processor can supply the chemical (C) and hydrodynamical (H) processors. The chemistry can modify hydrodynamical conditions (viscosity, superficial tension, etc) whereas the convection motions affect yield of reactions.

Moreover, convection motions and chemical reactions can modify thermal and dielectric properties. Hence, four coupling loops could be defined. Moreover, most of these coupling loops have highly non-linear character. Since 1990, the authors have studied separately all these coupling and now the general problem of chemical microwave process could be solve with optimized devices and plants.

The importance of these phenomena cannot be overemphasized because they exert significant influence over the yields and the quality of the products. The characteristics and limitations of these systems which affect the reactor performance should be well understood to ensure successful design and operation of the plant.

Consequently, microwave plant could be optimized for several given composition (i.e. dielectric properties and thermal dependency). An optimized microwave plant cannot be a versatile device in term of dielectric properties or in other words chemical composition.

3.1 The Athermal and specific effects of electric field

Many authors claimed athermal and specific effects of microwave heating. Five criteria or arguments (in mathematical sense) relating to existence of microwave athermal effects have been formulated by the author [12]. More details could be found in this comprehensive paper which analyses and quantify the likelihood of non-thermal effects of microwaves. This paper provides some guidelines to clearly define what should characterize non-thermal effects. Hence, according to these five criteria there are no doubt that an electric field cannot have any molecular effect for solutions. Firstly, the orienting effect of electric field is small compared with thermal agitation, which results from the weakness of the electric field amplitude. Even if the electric field amplitude should be sufficient, the presence of dielectric loss expresses a delay of dipole moment oscillations in comparison with electric field oscillations. The medium heating expresses the stochastic character of molecular motions induced by dissipation of the electromagnetic wave. The third limitation is the annihilation of molecular rotations in condensed phases as liquid state. According to our demonstration, in usual operating conditions, it will be proved that the frequently propounded idea that microwaves rotates dipolar groups is, mildly speaking, misleading.

3.2 Hot spots effects and heterogeneous kinetic

Effect of temperature upon reaction rate and heterogeneous character of microwave heating are well-known. The wavelength of microwaves used is equal to 12.2 cm (2.45 GHz). Within dielectric medium, the wavelength is in first approximation equals to wavelength in air divided by square root of real part of relative dielectric permittivity. Therefore, for very polar solvents as alcohol or aqueous solutions several local electric field maxima could be obtained within the heated sample. For solid reagents or materials, microwave heating can lead rapidly to fusion in relation to thermal dependency of dielectric properties and especially with increase of conduction with temperature. Consequently, most of local thermal fluctuations can be amplified and temperature close to 1000°C could easily reaches in a few seconds. The author has made real time infra-red video of powder under microwave heating (alumina, oxides, zéolithes, water gels [13]). Evidences of strong thermal gradients have been obtained (for ferrites, 50°C.mm-1). The author has shown that these hot spots or areas could induce localized rate enhancement [13].

These results have shown that a very small density of superheating areas is sufficient to induce a consequent rate enhancement (2% of hot spots are sufficient to increase yield of 60% !), even if their effects are not detectable on averaged temperature.

3.3 The thermal path effect: anisothermal conditions

According to the author, before claiming microwave heating effects over collisional or mechanistic term, it is necessary to estimate effect of strong heating rates induced by microwave heating. Energy density used in domestic oven are sufficient to raise temperature from ambient to 200°C in less than one minute, and so cause the total reaction is reduced by a factor close to 10^3. This natural tendency for thermal racing is accentuated by these implicated energy densities which are generally different from those used with water or oil bath, particularly for sealed vessels and autoclaves as used by organic chemists. The temperature and especially the thermal path T(t) appears as a crucial variable. The authors have shown theoretically and experimentally that strong heating rates (up to $5°Cs^{-1}$) can induce selectivity or inversion between two competitive reactions [14]. The author has illustrated experimentally theses selectivity effects with a very classical reaction However, to observe such kinetic effects of microwave heating, it is necessary to have reactions with reaction time close to heating time. In fact, in most operating conditions reactions times are close to several tenths of minutes and anisothermal effects could be neglected. The use of sealed vessels and autoclaves should permit to take advantages of strong heating rate induced by microwave heating (heating time close to reaction time). Then, the microwave heating strictly appears as an easy way to impose very fast heating rates and kinetic control of reactions.

In conclusion, is it needed to obtain microwave athermal effect in order to justify microwave chemistry ? Obviously no, it is not necessary to present microwaves effects in a scientific disguise. There are many cases where microwave heating gives particular time-temperature histories and gradients which cannot be achieved by other means especially with solids materials. Hence, rather than claiming non-thermal effects it is better to claim a way or a tool to induce a specific thermal history.

3.4 A new route for nanomaterials

The main objective of the GERM is to design and develop microwave processes able to produce nanomaterials in an efficient and selective way. Soft Solution Processing (SSP) without firing, sintering or melting step could be defined as environmentally friendly processing compare to vapour or solid processes. Microwave heating appears as a fourth route to nanomaterials called Microwave Soft Solution Process (MSSP). Microwave appears as an overwhelming tool to induce nucleation of monodisperse nanoparticles. Contrary to conventional ovens, where heating goes up by diffusion through reactor surface and diffuses to bulk, microwave heating leads instantaneously to spatial distribution of thermal sources within the heated solution. The main benefits for thermally activated processes as nucleation stem from volumetric or core heating induced by thermal conversion of electromagnetic energy. Consequently, microwave heating is very attractive for chemistry applications and material processing, especially for nucleation and growing processes, due to its in situ mode of energy conversion able to allow decoupling between nucleation and growing processes [15].

INSTRUMENTATION
1. The RAMO System

Since seven years, D. Stuerga have designed an original microwave reactor the *RAMO* system (french acronym of *Reacteur Autoclave MicroOnde*). This microwave applicator and the reactor are original. The resonant frequency of the cavity can be controlled by varying the position of a plunger. The effective cavity power could be increased by three orders of magnitude. The autoclave is made with polymer materials which are microwave transparent, chemically inert and sufficiently strong to accommodate the pressures induced. The reactants are placed in a Teflon flask inserted within a polyetherimide flask. A fiber-optic thermometry system, a pressure transducer and a manometer allow to measure simultaneously temperature and pressure within the reactor. The system is controlled by pressure.

The reactor is described by Figure 5.

The microwave power could be adjusted in order to allow constant pressure within the vessel. An incorporated pressure release valve permits to use this experimental device routinely and safely. Furthermore, an inert gas as argon could be introduced within the reactor to avoid sparking risk with flammable solvents.

This experimental device is able to raise temperature from ambient to 200°C in less than 20 seconds (pressure is close to 1.2 MPa and heating rate is close to seven degrees per second). The RAMO system has been designed for nanoparticles growing and elaboration. The RAMO system is a batch system. It has been adapted to continuous process with industrial scale (several hundred kilograms by seconds, *Kilolab project*).

Figure 5. General view of RAMO system [16,17]

2 The Coconut reactor :

D. Stuerga and P. Pribetich have designed an egg-shaped microwave reactor. Its name has been chosen in relation to its appearance (a black egg which reveals after opening a white core). The coconut reactor is described by Figure 6.

Figure 6. General view of the coconut reactor [16,17]

The origin of this project is the classical observation of egg explosion during microwave cooking. Spheroidal objects act as dielectric lenses focusing electromagnetic energy. The difference between sphere and egg is the level of focusing. The authors don't want to focus all the microwave power within a small area. The most important point is to control the shape and volume of the focusing spot. This focusing spot is named caustic in geometrical optic. The focusing effect obtained allows heating rates five times higher than those obtained with the RAMO system (close to 35°C/sec).

GRANTS and CONTRACTS

Among our industrial partners, Kodak Eastman Company has participated to growing with several founding and contracts. Furthermore people from Kodak were detached to work within GERM. Several trainees of Burgundy University have been remunerated by Kodak Eastman Company.

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INSTITUT DE RECHERCHES SUR LA CATALYSE ET L'ENVIRONNEMENT DE LYON « IRCELYON »

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HISTORY

Our Lab. (LACE created in 1992) Laboratory of the Application of Chemistry to the Environment merged with the Institute of Catalysis (IRC created in 1959) into the new lab "IRCELYON", a CNRS/Univ. LYON-1 joint Unit on Jan. 1st , 2007.
IRCELYON brings together all competences in heterogeneous catalysis over the Lyon area and forms the largest laboratory of catalysis in France. It includes a permanent research staff of 115 members from CNRS and University and as many PhD students, post-docs, and invited scientists from all over the world.
IRCELYON includes *eight research groups* supported by a platform of state-of-the-art equipments. The research activities, at the very heart of sustainable development, are essentially devoted to energy, environment and green chemistry.

ACTIVITIES

1. Activity 1

The activity of our group "*Clean and Renewable Energies*" is focused on the synthesis, physico-chemical characterisation and catalytic activity of solid catalysts (mixed oxides and /or supported metal).
These solids are prepared both using conventional and non conventional methods:

- Coprecipitation in basic or acid medium, sol-gel process, impregnation, hydrothermal treatment.....etc,
- Microwaves irradiation at atmospheric pressure or under pressure (30 atm),
- Ultrasounds.

Different catalytic reactions are studied:

- Methane combustion for energy production
- Methane traces elimination (NGV post treatment)
- Diesel soot combustion (Diesel post treatment)
- Ammonia traces elimination
- Biogas valorisation

In the last few years we studied the activity of several family of solids (Perovskites, Pyrochlores, Garnets, Magnetoplumbites,.......etc. The perovskite family lanthanum manganites are promising for a variety of applications. They have been widely studied because of their high electronic conductivity and good chemical stability. They are also known to be active catalysts for waste gas purification and catalytic combustion. Previous studies have focused on the effects of A or B site substitution (different ratios and different metals), rather than the effects of different synthesis conditions. The purpose of our investigations was to differentiate between differently synthesised perovskites doped or not with different actives species based upon their catalytic activity in methane combustion, and relates the differences back to the microstructure each inherited from their respective modes of synthesis.

We have recently performed a series of studies on the synthesis of undoped and Ag-, Sr- and Ce-$LaMnO_3$ perovskites using a microwave process by comparing the heating time and reaction temperature with the same factor under conventional thermal process. Experiments have been conducted using the hydrothermal method at medium pressure (T = 200 °C, P = 20 atm).

Structural and physico-chemical properties of the solids were investigated using X-ray diffraction (XRD), BET sorption, temperature-programmed reduction or desorption, mass spectrometry (TPR-MS and TPD-MS), and X-ray photoelectron spectroscopy (XPS).

We have found that while both conventionally (CH) and microwaves-prepared powder catalysts (MW) exhibited similar XRD patterns indexed as pure perovskite structure, their surface physico-chemical properties are strongly influenced by the preparation method.

The catalytic properties of the synthesised solids in methane combustion were found to be strongly dependent on the nature of oxygen species, their amount and mobility (Fig.1). MW catalysts were found to exhibit a much better performance in methane combustion together with higher resistance to sulphur poisoning than CH catalysts (Fig. 2).

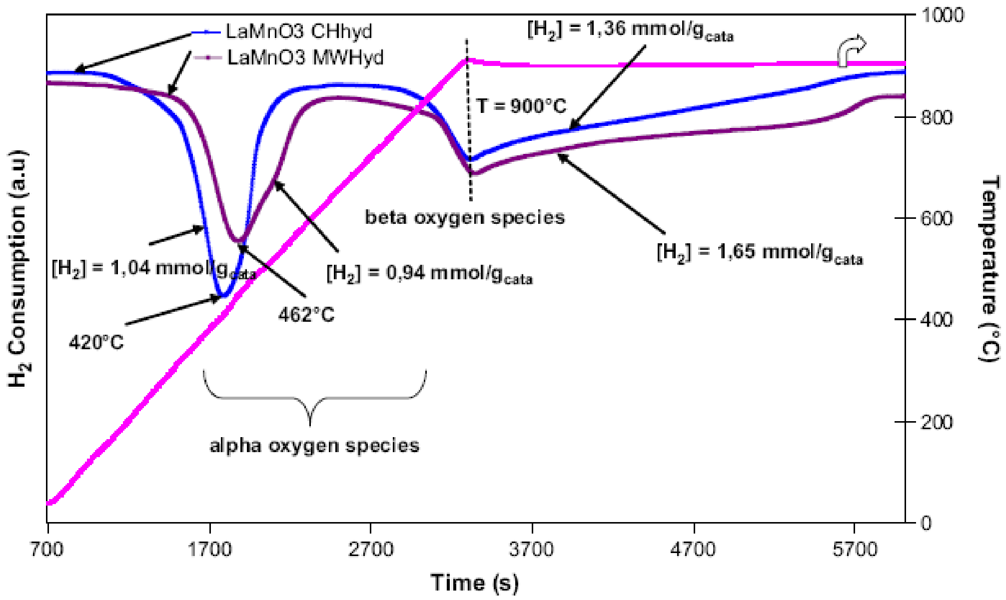


Figure 1: TPR profiles of microwave and conventionally prepared $LaMnO_3$ perovskite

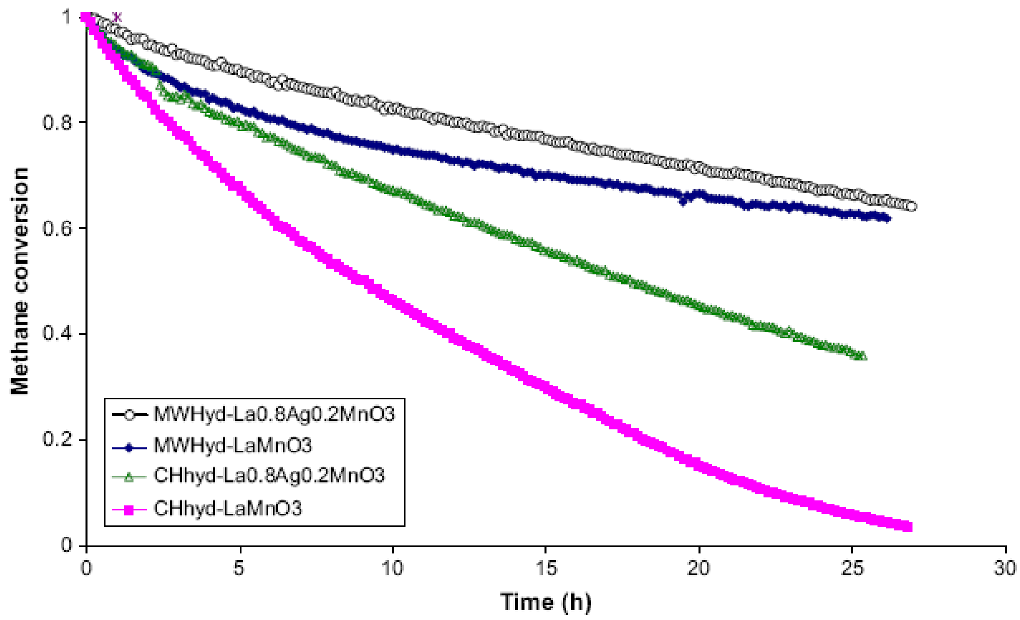


Figure 2: Catalysts poisoning with H_2S during CH_4 combustion over MW- and CH- $LaMnO_3$ and Ag-doped $LaMnO_3$ perovskites

2. Activity 2

Another topic that we have recently developed in collaboration with the Politecnico di Milano (*Dipartimento di Chimica, Materiali ed Ingegnieria Chimica "G. Natta")* was the use of microwave irradiation for the preparation of materials that can be used for the confinement of nuclear elements.

Some pyrometallurgical processes generate chloride salt waste containing alkaline metal- fission products. Due to the presence of chloride, this waste is not easily vitrifiable. Besides, a high leaching rate of material immobilised in glass and a consequent increased risk of release of nuclear elements into the geosphere have been observed. Therefore other solutions have to be found. Crystallised natural minerals have been reported as materials able to stock and isolate nuclear waste from the geosphere for a long period of time. For instance it appears that apatite has remarkable properties for the confinement of actinides.

Sodalite $Na_8(Al_6Si_6O_{24})Cl_2$ because it is a water insoluble halide salt with high structural stability. This material can also exchange its sodium ions with others while keeping its structural stability. These specific properties can be exploited and sodalite could be considered as a potential host structure for the confinement of chloride salt waste.

Sodalite synthesis can be generally carried out in several ways, among which the dry process and the hydrothermal method. The hydrothermal synthesis requires high temperatures, high pressures and long reaction times. In order to develop high-quality sodalite crystals some authors operated at 450°C and at high pressures for a reaction time varying from 48 to 96 h, using ultra-fine silica powder, aluminium metal, sodium hydroxide and sodium chloride of high purity.

In this investigation, we have reported the synthesis by the soft hydrothermal process, starting from two natural materials, kaolinite and metakaolinite, and the characterisation of $Na_8(Al_6Si_6O_{24})Cl_2$ sodalites. Experiments have been conducted using the hydrothermal method at atmospheric pressure. The results showed that the reaction is more significantly hastened under microwave irradiation than under conventional heating. The structural change induced by the kind of thermal treatment i.e. conventional or microwave irradiation has been studied and the effect of starting materials on the sodalite yield has particularly been evidenced.

Crystalline, fine powders of sodalite were produced in a short time due to the effective microwave coupling of slurries containing natural material precursors, while when using conventional heating only zeolite A is formed under the same operating conditions (Fig.3). The good thermal stability (Fig.4) of the microwave synthesised sodalite is an essential property for confinement of nuclear wastes based-halide salts.

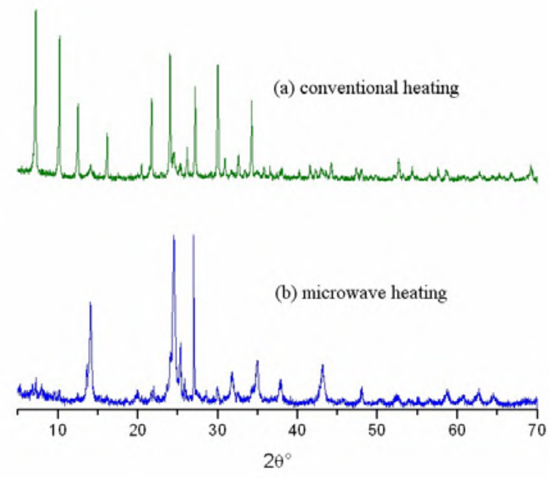


Figure 3: XRD patterns of solids obtained from metakaolinite at 80°Cafter a heating period of 180 min, a) conventional heating b) microwave irradiation (100W)

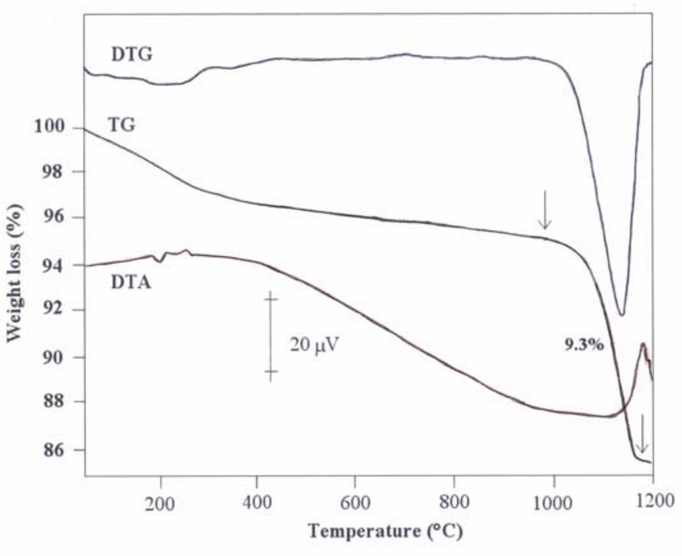


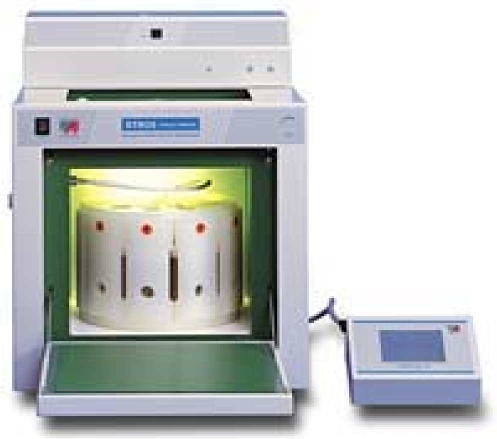
Figure 4: TG-DTA-DTG analyses of sodalite prepared from metakaolinite

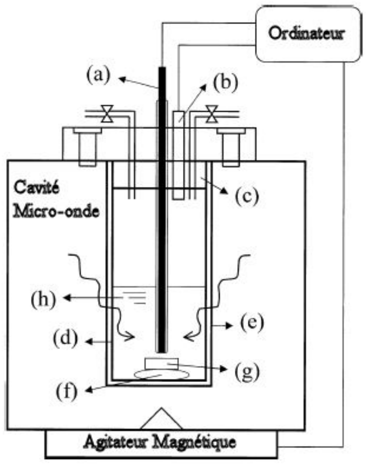
3. Activity 3

- Bio-ethanol steam reforming for hydrogen production
- Internal steam reforming of methane in solid oxide Fuel cells (SOFC)

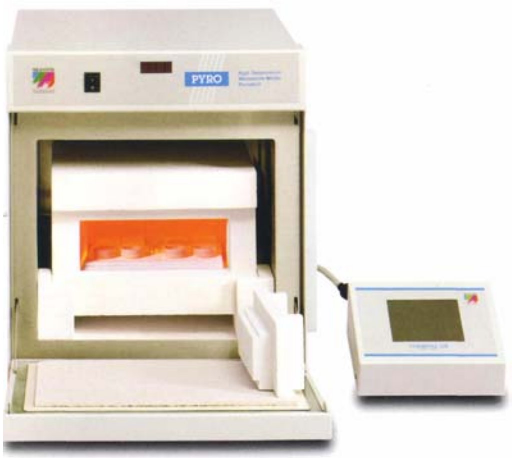
INSTRUMENTATION

An advanced Microwave Model Microsynth Labstation microwave operating at 2.45GHz with a power supply of 1000 W. The instrument is multimode and equipped with temperature and pressure monitoring device.





A MILESTONE Pyro Touch control microwave heating oven.



BET surface area and porosity measurement apparatus (Micromeritics)
FTIR spectrophotometer (Nexus Thermo Nicolet)
Perkin Elmer *Pyris Diamond* TG/DTA analyser.

EDUCATIONAL ACTIVITY

Physical, Surface and Theoretical Chemistry,
Heterogeneous and Environmental Catalysis,
Materials Processing.

COLLABORATION

With :
- Dipartimento di Chimica, Materiali ed Ingegnieria Chimica “G. Natta”, Politecnico di Milano P.zza L. Vinci, 32, 20133 Milano.
- Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Universita' degli Studi di Modena e Reggio Emilia Via Vignolese 905/A 41100 Modena.

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MICROWAVE APPLICATIONS IN THE SYNTHESIS OF NANOSTRUCTURED MATERIALS AND IN ORGANIC EXTRACTIONS

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HISTORY

The research of this group focuses on the structural investigation of dispersed systems such as micelle solutions and microemulsions, using techniques such as X-ray and Neutron Small Angle Scattering. Recent research has concentrated on the synthesis and characterization of nanostructured materials, and specifically, the preparation of nanoparticles, nanopowders, nanocomposites and mesoporous materials. The characterization of these materials has been performed using structural (XRD, SAXS, SANS, DLS), spectroscopic (Uv-vis, Raman, NMR, Photoluminescence), and microscopic (SEM, HR-TEM) techniques.

The group includes 2 professors, 1 researcher, 1 postdoc and 2 Ph.D. students.

Microwave applications on the synthesis of nanostructured materials started in 1999 with a COFIN Project "Microwave assisted synthesis of nanoparticles".

Prof. Caponetti has recently founded the Centro Grandi Apparecchiature (CGA) which is an integral part of a network of laboratories called "UniNetLab" at the University of Palermo. CGA is a research and service operations centre working in several areas of chemical sciences, with particular reference to cultural heritage and environmental issues, but also with an eye to areas such as pharmaceuticals, the food industry and the science and technology of materials.

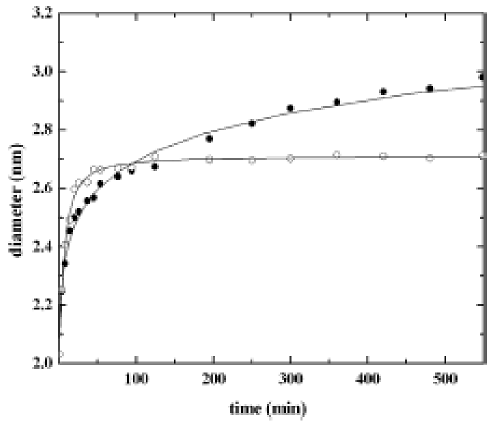
ACTIVITIES

The activities related to the use of microwaves will be presented in what follows. These activities include the synthesis of nanoparticles (CdS, ZnS and $Y_3Al_5O_{12}$), of mesoporous materials MCM-41, and the dehydration of microemulsions. In addition, microwave irradiation has been used in the extraction of essential oils and in the purification process of Carbon Nanotubes (CNT).

1. The synthesis of nanoparticles

1.1. *Calcogenide.* Interest in CdS nanoparticles is related to their photophysical properties which make them useful in applications such as optoelectronic, photocatalysis, solar energy conversion and photodegradation of water pollutants. CdS has been prepared in a microemulsion in order to obtain nanoparticles with very small dimensions (1–5 nm). This is because microemulsions can stabilize clusters and thus inhibit their indefinite growth. Water in oil microemulsions are thermodynamically stable systems in which spatially separated, polar and non-polar microregions coexist. Since reaction rates in microemulsions are appreciably different from those observed in water, these systems have often been used as microreactors. Nanoparticle size is regulated by the concentration of the reactant, the water to surfactant molar ratio and the temperature.

1.2. *The ripening phenomenon* (growth of the biggest particles at the expense of the smaller ones) takes place as a consequence of the dynamics of the system. Bare thermodynamically unstable nanoparticles tend to lose their specific properties, due to their tendency to coalesce. Several researchers have attempted to passivate the nanoparticles surface using suitable capping agents such as thiols, ammines and pyridines, i.e. electron donor or acceptor species that bond to the nanoparticles' surface, thus avoiding coalescence. Unfortunately, capping molecules influence the nanoparticles' surface characteristics such as, for example, luminescence properties. A limitation of microemulsion synthesis becomes apparent when bare nanoparticles are required. In dealing with microheterogeneous systems such as microemulsions, microwaves interact powerfully with water molecules as a consequence of the coupling of the electromagnetic field by the rotational dynamics of polar water molecules and by the head-group counterions, whilst they do not interact with the non-polar moieties such as surfactant tails and oil. It follows that microwave irradiation causes a rapid and localized heating of the reversed micelle "core" (the inner part containing water molecules) with a very steep and transient thermal gradient between the core and the outer oil phases.
The CdS nanoparticle synthesis was performed using a microwave exposure set-up which is described in the instrumentation section below. This exposure set-up allows irradiation of the reactor whilst maintaining the temperature constant.
It has been found that, compared to conventional thermostatic conditions, microwave irradiation influences the growth of nanoparticles, affecting both their final size and surface properties. These effects were found to be microwave frequency dependent [1,2]. The growth in nanoparticle size irradiated at 2.45 GHz and at a power value ranging from 22 up to 30 W is reported in Figure 1 as a function of time. The growth in non-irradiated particle size is reported in the same Figure for comparison.



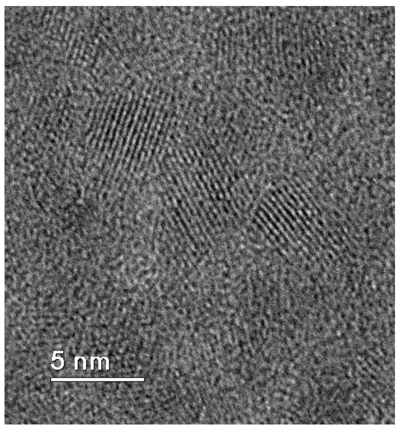


Figure 1. left) CdS nanoparticle diameter for irradiated (●) and non-irradiated (○) samples as a function of time; right) TEM micrograph of irradiated sample

The irradiated nanoparticles grew faster than non-irradiated ones, but, after less than an hour, growth was inhibited, while nanoparticle size continued to increase in the non-irradiated sample. The initial faster growth has been attributed to the more rapid reactant exchange caused by the heating of water within the aqueous core of the reversed micelles. The growth inhibition has been attributed to a decrease in water content in the reversed micelles slowing down the material exchange between micelles.

The significant decrease in the water content caused by microwave irradiation improved the CdS luminescence proprieties [6]. Some results have been obtained in the synthesis of ZnS nanoparticles [5]. Irradiated ZnS nanoparticles displayed a slow nucleation rate compared to that of the same material in conventional thermostatic conditions but, the nanoparticle size also tended to a smaller constant value in this case as well.

1.2.1. Microemulsion dehydration. Microwave irradiation has been discussed as an alternative to traditional methods for the dehydration of microemulsion systems and, consequently, for the stabilization of nanoparticles in microemulsions [10]. It has been shown that microwave irradiation of a water/sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/n-heptane microemulsion containing CdS nanoparticles, at constant temperature, causes a progressive dehydration of the system leaving the other components unchanged. Dehydration stabilizes the nanoparticles against indefinite growth. This procedure offers some advantages over traditional treatment with phosphorous pentoxide. The latter process leads to surfactant molecule degradation, although it is the most rapid one. The microwave irradiation method can be considered safe for the environment because it avoids the use of substances extraneous to the system and circumvents treatments that can damage the system itself and/or increase pollution.

1.3. *YAG.* Yttrium Aluminum Garnet (YAG, $Y_3Al_5O_{12}$), with a cubic structure and space group Ia-3d, doped with neodymium atoms, has received considerable attention because of its interesting technological applications. Nd:YAG single crystal is widely used in the four–level solid state laser.

Many studies have recently focussed on producing transparent ceramics by Nd:YAG nanopowder sintering, which can advantageously substitute single crystals because single crystals entail considerable production costs and long preparation times. The production of high-quality ceramics is conditional upon the use of a fine, low-agglomerate powder of pure garnet phase. Several chemical routes such as sol-gel, co-precipitation [11,12], ball milling [6], and microemulsion [8] have been used. All of these methods require a relatively long calcination step involving temperatures higher than 900°C depending on dopant quantity, and thus produce powder composed of nanoparticle agglomerates. Only a few authors have prepared YAG using microwave irradiation. The majority of papers report samples prepared in domestic microwave ovens and lack a comparison with conventional preparations. In particular, Vaidhyanathan and Binner obtained an un-doped YAG nanopowder using a microwave assisted citrate gel process at reduced calcination temperature. They compared results with those obtained using the conventional heating process.

In our laboratory, Nd:YAG nanopowders have been prepared using a sol-gel Pechini method assisted by microwaves [15]. It has been shown that this procedure entails certain advantages such as simplicity, a short reaction time and a short calcination time. The conventional method using the same calcination time leads to the formation of YAG face, accompanied by the YAH hexagonal phase. Many additional hours of thermal treatment were necessary in order to obtain the single YAG phase. In both preparations the samples were obtained in nanosizes, and a similar average particle size was measured, even though microwave irradiation causes a narrower distribution of particle sizes and a smaller surface area.

2. Synthesis of mesoporous MCM-41

Mesoporous materials known as MCM (Mobile Composition of Matter) constitute one of the most interesting discoveries in the field of material chemistry. These materials can be depicted as arrays of pores with sizes in the range between 2 and 50 nm, organised in hexagonal (HMS and MCM-41), cubic (MCM-48) or lamellar (MCM-50) structures. Such materials are characterised by a long range order, a surface area larger than 700 m^2g^{-1} and easy pore accessibility. These features have enabled the use of MCM materials in the catalysis of many petrol-chemical processes, of redox processes in liquid phase, of heteropolyacid supports, and highly efficient adsorbents. Among the others, MCM-41 can be considered the most important mesoporous material. It is constituted by cylindrical pores (3-5 nm), whose length is in the range of microns, separated by amorphous silica walls and organised in a hexagonal long range structure.

The MCM-41 synthesis procedure, first proposed by Kresge et al. in 1992, is based on the acid (or basic) hydrolysis of silicate precursors and the use of ionic surfactant liquid crystals as templates. Pore diameter and wall thickness can be modulated by opportunely changing the surfactant and silicate precursors, their concentration, temperature and reaction time. A final calcination process destroys the surfactant aggregates inside the pores. Most of the reported MCM-41 microwave preparations involve the use of microwave ovens in which the temperature reaches up to 150 °C.

Our work has focused on the microwave assisted synthesis of MCM-41 at room temperature [9]. The material thus obtained has been structurally and morphologically characterised using X-ray diffraction and Scanning Electron Microscopy. Results have been compared with those obtained from the same material produced using a conventional method. MCM-41 synthesis assisted by microwave irradiation gives rise to the formation of a material with a weaker structure that changes after calcination. This material has a structure similar to that of mesoporous HMS with a smaller pore size than that prepared using the traditional method.

3. Carbon Nanotube purification

Carbon nanotubes (CNT) have super/semiconductive properties, powerful resistance to stress, optic limitation and other advantages, depending on their structural characteristics, but they also have severe limitations because they are insoluble in all solvents and have very low reactivity. The CNT obtained by current ordinary syntheses contain amorphous carbon and growth in catalyst metallic clusters in their extremities. Different purification and functionalization methodologies have been proposed regarding both single-wall (SWNT) and multi-wall (MWNT) nanotubes to permit better manipulation whilst maintaining their properties unvaried. Strong oxidative acid treatments or high temperature annealing, long treatment times and extreme environments are generally required. In particular, the purification of SWNT has been obtained using concentrated nitric acid and a commercial microwave oven.

In our laboratory, a new methodology was employed to cut and purify MWNT. MWNT were provided by Prof. Carlo Mazzocchia, (Polytechnic of Milan, Italy). MWNT in a sulphonitric mixture has been irradiated with microwave at 200 W to cut and make an initial purification. The use of sulphonitric mixture enables selective attachment to the more reactive sites (big bending and wall defects). The use of microwaves drastically reduces treatment times from 4 hours (ultrasonic assisted method) to 10 minutes.

Purification is applied to remove the carbon residues and metallic clusters, as well as to open fullerenic tips. This is the first step to start the CNT functionalization process.

4. Essential oil extraction

The essential oils of *Calamintha nepeta* [13] and *Ferulago campestris* have been obtained by solvent-free extraction as well as microwave-assisted hydrodistillation extraction (SFME and MAHD, respectively), and by classical hydrodistillation (HD). A comparative qualitative/quantitative study into the composition of the oils was carried out. The use of microwaves causes fewer chemical changes in the original plant components of *C. nepeta*, i.e. less rearrangement and dehydration, as well as fewer isomerization processes occur with the conventional HD method. A total of 38 compounds, constituting 97.6% of the oil, were identified in the oil obtained by SFME, whereas 46 compounds, representing 95.4% of the oil, were identified in the HD oil. Furthermore, larger amounts of oxygenated monoterpenes and sesquiterpenes and a smaller quantity of hydrocarbon monoterpenes were recovered from C. nepeta by SFME. HD oil seems to be affected by more chemical changes than SFME oil. Similar results were obtained by MAHD with *F. campestris*. Lightly oxygenated monoterpenes are the main contributors to the aroma of many essential oils. SFME could therefore be a suitable method for producing an oil with more aromatic properties, using a simple apparatus which is less expensive than SFE.
This methodology has also been applied to the extraction of organic compounds in resins and materials which are of interest in the field of Cultural Heritage. An experimental protocol is currently under development.

INSTRUMENTATION

Two microwave devices are available in the group laboratory: one is a commercial CEM Discovery 1 in single-mode cavity and working at atmospheric pressure in standard glassware to perform the organic synthesis, the other is a SAIREM assembled apparatus interfaced with a Beckmann spectrophotometer. A diagram and a photograph of the microwave apparatus used to irradiate all samples previously presented are shown in Figure 2.

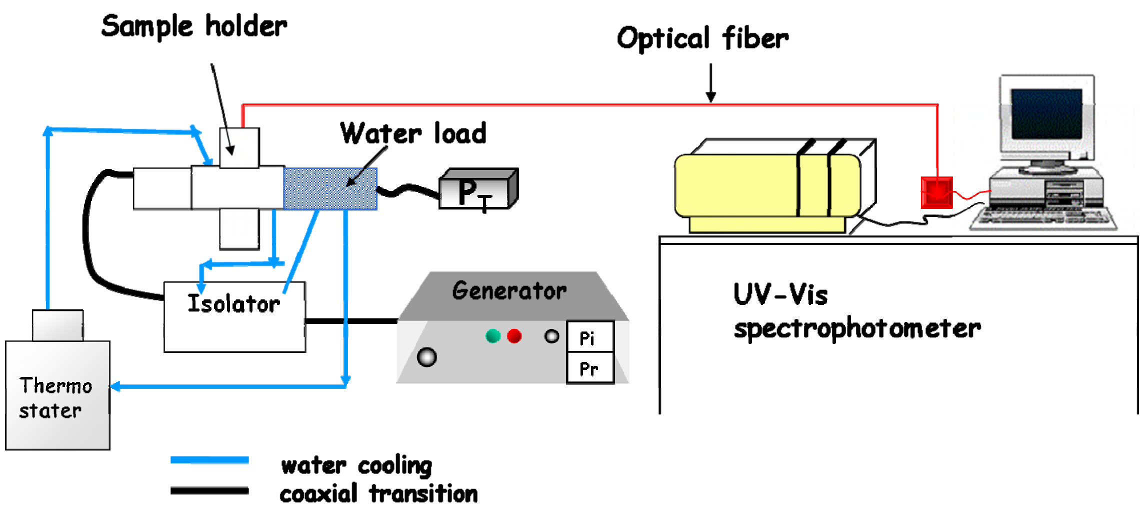


Figure 2. Schematic diagram of Microwave Apparatus SAIREM

The instrumentation consists of a SAIREM GMP 03 K/SM high power single frequency generator operating at 2.45 GHz and variable power, an insulator which avoids damage to the generator by mismatching, a sample holder constituted by a rectangular waveguide connected to two cylindrical waveguides, and a water load to absorb transmitted power. The temperature was controlled by a cooling applicator with an external coil where thermostated water flowed. The incident, the reflected and transmitted power, as well as the sample temperature can be controlled and recorded during irradiation [2]. Further details about this apparatus and its field dosimetry have been reported in ref [3]. Two different samples and various volumes were considered to evaluate efficiency and electromagnetic field homogeneity. The device was modelled by means of a commercially available tool, CST microwave studio-4, which is based on the Finite Integral Technique. Numerical simulations indicated that low or medium loss materials are more suitable.
Taking into account the cavity dimension, sample volumes shouldn't be either too large or extremely small to achieve a satisfactory homogeneity and efficiency. An example, the S- parameter of the electric field in the middle plane calculated when the sample holder contains 42 ml of water/AOT/n-heptane microemulsion is reported in Figure 3.

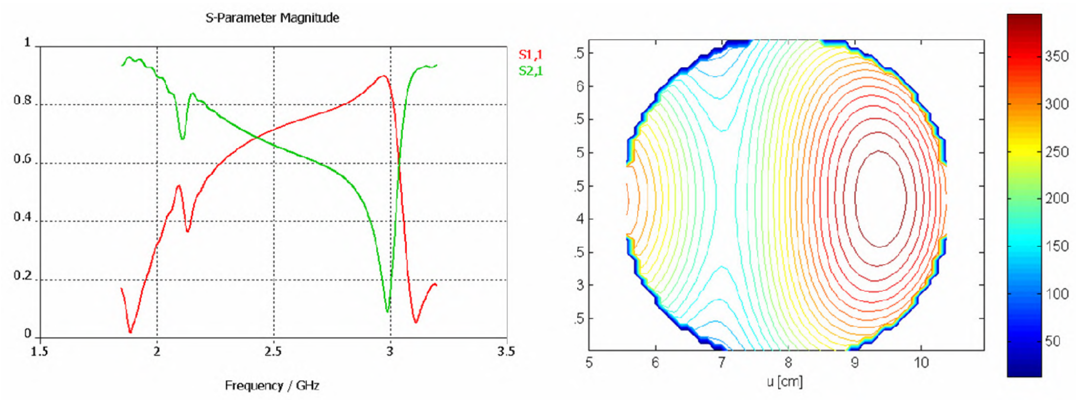


Figure 3. left) The amplitude of the reflection (S11) and transmission (S21) coefficients; right) the amplitude of the electric field in the middle plane calculated when the sample holder contains 42 ml of water/AOT/n-heptane microemulsion

Finally, a UV-Vis spectrophotometer Beckmann-Coulter DU 800 operating in the 200-800 nm range is interfaced with the microwave apparatus. The evolution of the reaction under investigation has been monitored by one of the following methods:

- UV-Vis spectra from aliquots taken from the irradiated sample were recorded at various times until the reaction was completed;
- an immersion probe connected to the spectrophotometer by means of optical fibres was used to record the UV-Vis spectra in situ;
- the reaction mixture flowed through the spectrophotometer cell by using a peristaltic pump.

It can be concluded that the main characteristics of this exposure setup are homogeneous field distribution inside the sample holder, the ability to measure the microwave power absorbed by the sample, and the simplicity of using it.

EDUCATIONAL ACTIVITY

Prof. Eugenio Caponetti was on the Scientific Committee of:

- MISA 2002: *1° National Meeting MISA 2006-Microwave in Engineering and Applied Sciences*, Cetara, 7-9 November 2002;
- MISA 2004: *2° National Meeting MISA 2006-Microwave in Engineering and Applied Sciences*, Ancona, 6-8 October 2004;
- *MISA 2008: The First Bilateral Meeting Italy-France: The Microwave: New technology for productive activity*, Salerno, 21-23 May 2008.

In addition, the group has organized:

- *3° GIMAMP School, Palermo, 23-24 may 2006.*
- *3° National Meeting MISA 2006-Microwave in Engineering and Applied Sciences, Palermo, 24-26 May 2006.*

GRANTS and CONTRACTS

Three contracts have been financed using funds from two PRIN projects. The first grant dealt the "Preparation of sulphurs and oxides nanoparticles" in the COFIN "Synthesis of nanoparticles assisted by Microwave" (2002-2003, Maria Luisa Saladino).The other grants dealt the "Preparation of mesoporous silica" and the "Dispersion of mesoporous silica in polymeric matrix", in the COFIN " Synthesis of mesoporous materials using conventional methods assisted by microwave" (2006, Alberto Spinella and Antonio Zanotto).

COLLABORATIONS

Some of the results presented were obtained in collaboration with other groups from Italian Research Institutions.

- Prof. Cristina Leonelli, University of Modena
- Prof. Carlo Mazzocchia, Polytechnic of Milan
- Prof. Lia Mariani, University of Genoa
- Prof. Domenico Acierno, University of Naples
- Prof. Matteo D'Amore, University of Salerno
- Prof. Mario Castiglioni, Polytechnic of Turin
- Prof. Rita Massa, University of Salerno

Acknowledgments. *The authors would like to thank MIUR for supporting this research through the PRIN-COFIN 2001 "Synthesis of nanopowders assisted by microwaves" and the PRIN 2004 prot. 2004033823: "Chemical processes under magnetic field irradiation for sustainable chemistry". TEM experimental data were provided by Centro Grandi Apparecchiature - UniNetLab - Università di Palermo funded by P.O.R. Sicilia 2000-2006, Misura 3.15 Azione C Quota Regionale.*

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CMIC (Dipartimento di Chimica, Materiali ed Ingegneria Chimica "Giulio Natta") – POLIMI SCT (Special Chemical Technologies) LABORATORY: ACTIVITY IN THE MW ASSISTED SYNTHESIS OF COMPOUNDS

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HISTORY

POLIMI SCT Unit has a large and supported experience in inorganic compounds (specifically catalysts and catalyst supports) preparation sector. The usually adopted methods are the precipitation, the hydrothermal method, the sol-gel method [1-8]. In the last years, in relation with these techniques, microwaves were employed [5] [16]. So the Unit developed experience in MW assisted synthesis of inorganic oxides nanoparticles (AlOOH, γ-Al_2O_3, TiO_2, γ-Fe_2O_3, ZrO_2) for application in the polymers composites field (PRIN 2007).

The research group has also experience in metallic oxides MW assisted sintering processes (ZrO_2 sintering).

It is rather recent the study of the textiles drying, dyeing and printing by the use of MW. The Unit in fact is studying the drying process of clothes in collaboration with Indesit Company, and the dyeing and dyestuff fixation in collaboration with Loro Piana Company and Emitech Company. The Unit is studying a continuous dyeing process cooperating with a research group at the ENSAIT of Roubaix and with AMP Company.

The POLIMI group also studied the process of production of biodiesel and FAMEs (Fatty Acid Methyl Esters) from triglycerides assisted by MW [9-13].

In addition, the Unit has a proved experience of chemical-physical characterization methods of prepared materials (like DRX, FTIR, UV, TG-DTA, SEM-TEM, XPS, BET, acid-basis analysis, chemisorption, porosimetry, spectrophotometry). POLIMI Unit carries out some important kinetic studies, related to heterogeneous and homogeneous catalytic processes, that allow, in some cases, the drawing up of Patents with societies, like Arkema (ex Atofina) and Cognis (ex Henkel) [14] [15].

ACTIVITIES

1. Microwave assisted synthesis of mesoporous alumina

A microwave assisted technique is proposed for the preparation of a mesoporous alumina (bohemite, AlOOH) using a surfactant as templating agent (Brij® 56, a polyethylene glycol hexadecyl ether). By microwave assistance the reaction time is drastically reduced (30 minutes) compared with conventional hydrothermal synthesis (24 hours). Pore size, surface area and pore structure can be controlled by adjusting the surfactant/aluminium ratio and changing the surfactant removal technique (Soxhlet extraction, combustion in a controlled atmosphere of nitrogen and air). The produced aluminas show a pore size distribution ranging between 1 to 10 nm in diameter and a specific surface area of 300-400 m^2/g, The controlled porosity, high pore volume (325-370 mm^3/g) and low content of micropores, which could hinder the diffusion of reactants and products, make this alumina particularly suitable as a catalyst support.

The aim of this work is to develop a monomodal support for the platinum based catalyst used in the hydrogen iodide decomposition section of the sulphur-iodine cycle (S-I cycle). This cycle is at present widely studied for the hydrogen production by the thermochemical water splitting.

1.1 Description of the method

In a typical synthesis, 53.63 g of surfactant Brij® 56 (Sigma Aldrich) was dissolved in a H_2SO_4 aqueous solution of 566 mL (pH = 2) under magnetic agitation for 3 h at 70 °C, followed by the addition of 33.95 g of aluminum *sec*-butoxide (Fluka). After 1 hour further stirring, the mixture was then transferred into a Teflon-lined autoclave and was microwave treated at 80 °C for 30 min.

Microwave heating was carried out in a Milestone Ethos 1600 microwave oven with a temperature-control program, operating at a constant output power of 300 W.

After cooling, the resulting product was filtered, washed by Soxhlet extraction with ethanol (3633 ml) for 36 h to remove the surfactant species, and dried at 40 °C. The theoretical yield is equal to 7.02 g of alumina. Calcination was carried out at 350°C (for 1 h), 500°C (for 1, 2, 3, 4 h), 600°C (for 2 h) and 700 °C (for 2 h) to investigate the structural stability of the product. The material was more accurately analyzed at 500°C because some studies, reported in literature [17], show that the mesoporous alumina reveals its major structural thermal instability at this temperature value.

For comparison, other alumina samples were prepared by a conventional hydrothermal method (at 80 °C under magnetic agitation). The overall procedure is similar to the procedure described above with the exception of the microwave irradiation and the synthesis time (24 h).

During the microwave assisted synthesis some operative parameters, like the stirring action into the reaction vessels (that can affect the interaction between alumina and surfactant and the *in fieri* mesoporous structure) and the presence of the thermocouple (a probe that, because of its metallic structure, could affect the electro-magnetic field) were investigated. It was also examined the polyethylene glycol hexadecyl ether role in the synthesis and how its presence affects the morphological properties of the aluminas producing different samples with different BRIJ56/aluminium ratios. At last it was studied the step of surfactant removal, modifying the post synthesis treatment (Soxlhet extraction, calcination in air or pyrolysis under controlled atmosphere).

1.2 Results

During the microwave assisted synthesis some operative parameters into the vessels were varied: the presence of the stirring (*ALMS*), the absence of the stirring (*ALMN*). The texture properties of these samples (as-synthesized, calcinated at 350°C (1 h) and calcinated at 500°C (1 h)) are provided in Table 1. The pore size distribution of as-synthesized *ALMS* and *ALMN* samples are also indicated in the Table 1.

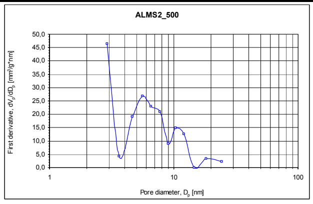
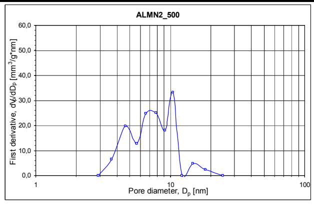
Sample	**Thermal treatment**	**S_{BET} [m²/g]**	**$V_{micropores}$ [mm³/g]**	**V_P [mm³/g]**	**Desorption pore volume plot**
ALMS	As-synthe-sized	261,33	55,92	225,70	
	Calcinated at 350°C	360,07	80,75	318,59	
	Calcinated at 500°C	302,83	43,66	292,23	
ALMN	As-synthe-sized	256,47	61,31	216,33	
	Calcinated at 350°C	349,24	105,58	349,07	
	Calcinated at 500°C	299,19	76,47	268,14	

Table 1

It was then studied the surfactant importance on the substrate final morphological properties (after a calcination at 500°C for 1 h). For this reason some samples were produced without Brij® 56. In the following tableare reported the texture properties of one of these (*ALM_no Brij56*).

Sample	**S_{BET} [m²/g]**	**$V_{micropores}$ [mm³/g]**	**V_P [mm³/g]**
ALM_no Brij 56	145.30	25.68	94.96

Table 2

In order to investigate the influence of the surfactant amount on the alumina morphology, some sample with different Al-precursor/surfactant ratio were prepared. In particular the surfactant amount were reduced as shown in the table 3. BET and porosity analysis of these samples explain the surfactant role: a higher amount of surfactant provides a well-ordered structure, while a lower amount of surfactant lead to higher BET areas with a less regular pore size distribution. The results of this study are reported below:

1.classical preparation (Soxlhet extraction followed by calcination in air at 500°C) (Table 3).

1.classical preparation (Soxlhet extraction followed by calcination in air at 500°C) (Table 3).

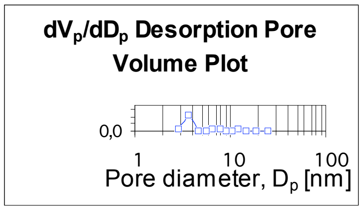
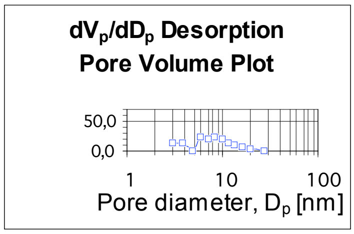
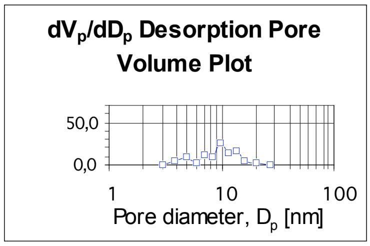
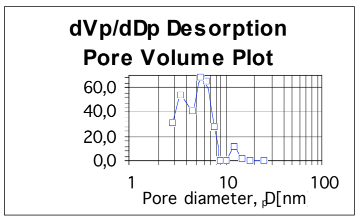
Sample	R = BRIJ56 moles / Al moles	S_{BET} [m^2/g]	$V_{micropores}$ [mm^3/g]	V_P [mm^3/g]	Ratio $V_{micropores}$ /V_P	Desorption pore volume plot
ALM_no Brij 56	0.00 *without BRIJ56*	145.30	25.68	94.96	0.27	
ALM6_500	0.191 *1/3 of the typical amount*	415.79	141.39	370.60	0.38	
ALM7_500	0.381 *2/3 of the typical amount*	379.21	173.58	307.74	0.56	
ALM3_500	0.572 *typical amount*	320.97	80.85	305.76	0,26	

Table 3

2. degradation protocol in controlled atmosphere nitrogen-air (Table 4).

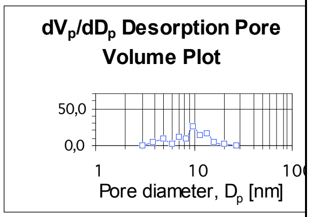
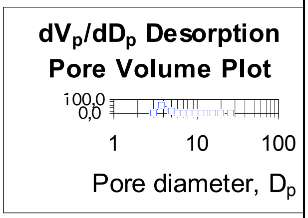
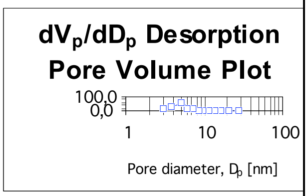
Sample	R = BRIJ56 moles / Al moles	S_{BET} [m^2/g]	$V_{micropores}$ [mm^3/g]	V_P [mm^3/g]	Ratio $V_{micropores}/V_P$	Desorption pore volume plot
ALMN6_N_2	0.191 (*1/3 of the typical Brij 56 amount)*	359.86	30.09	234.06	0.13	
ALMN7_N_2	0.381 (*2/3 of the typical Brij 56 amount)*	321.87	78.96	182.06	0.43	
ALMN3_N_2	0.572 (*typical Brij 56 amount)*	313.07	52.73	254.91	0.21	

Table 4

The classical surfactant removal protocol, *via* extraction and calcination, produced aluminas with a high S_{BET} value (> 300 m^2/g) and without any Brij® 56 residual or products of its decomposition (fig. 1). The material appeared completely white, with a not well-ordered and scarcely reproducible porous structure (Table 1). The ethanol extraction step is too long and very energetically expensive, but it allows the surfactant recovery (after a distillation operation), an important step into the scale-up of the HI decomposition catalyst preparation. The surfactant degradation route in controlled atmosphere of N_2 produced aluminas with a high S_{BET} value (> 300 m^2/g) and with a well-ordered (D_{pores}~4 nm) and more reproducible porous morphology (fig. 2). Moreover it results possible and advantageous to work with a surfactant amount equal to 1/3 of the typical amount, producing a Brij® 56 free material. The surfactant removal is faster and energetically less onerous, but it isn't possible to recover the Brij® 56, that is completely destroyed.

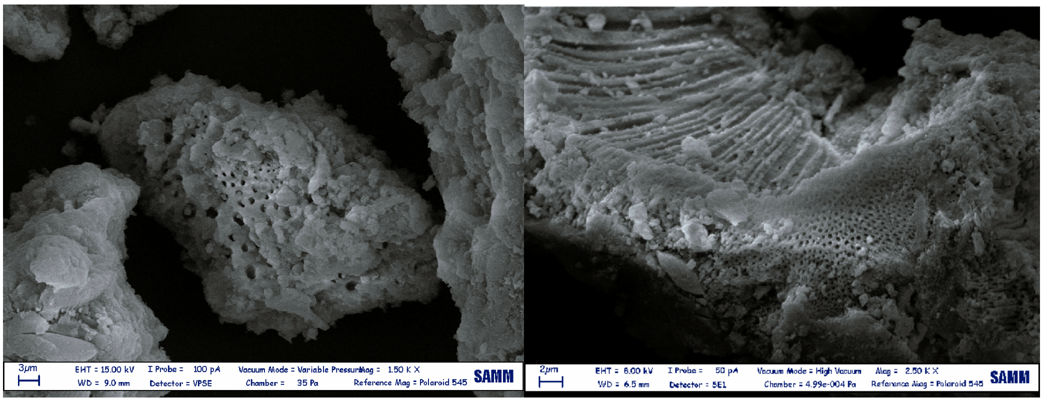


Figure 1. ***Scanning electron microscopic images of the product obtained via classical preparation***

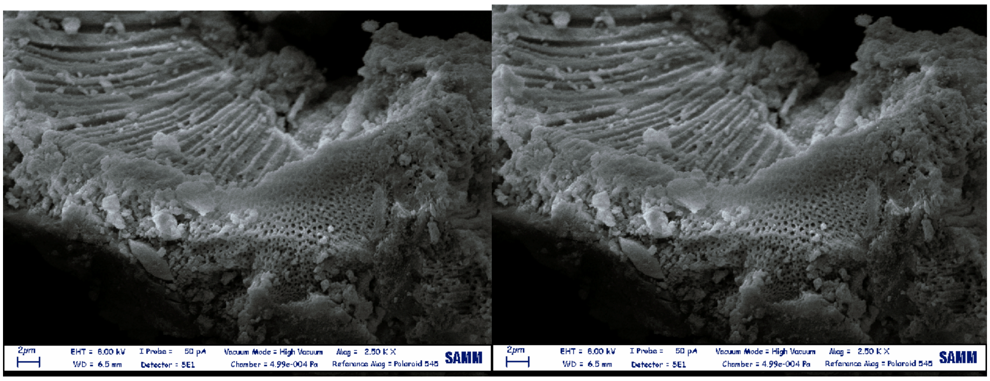
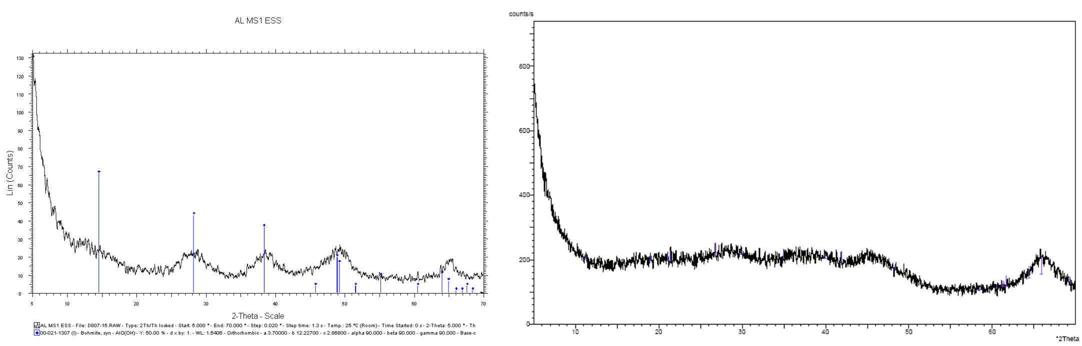


Figure 2. ***Scanning electron microscopic image of the ALM7_N_2 product obtained via degradation protocol in controlled atmosphere (scale bar is 2 μm)***

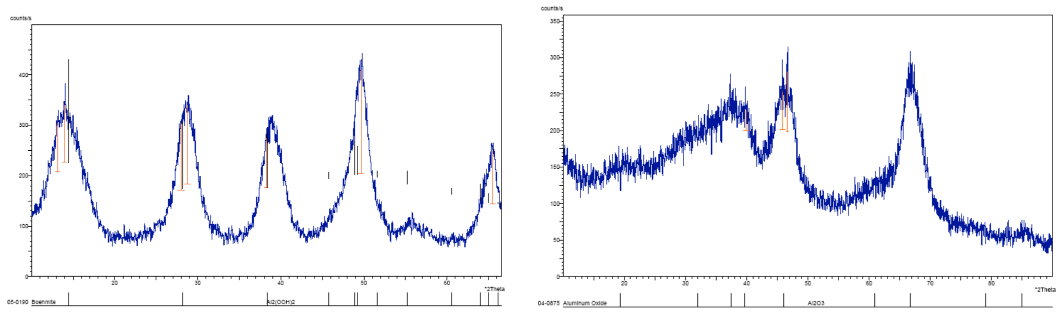
Figure 3(a) shows the X-ray diffraction (XRD) pattern of the as-synthesized products (*ALMS*). The as-synthesized samples obtained from microwave heating exhibit diffraction lines assignable to the bohemite phase AlOOH (JCPDS card no. 21-1307). The structure of bohemite can be kept after calcination at 500°C (Figure 3(b)). After calcination at a temperature higher than this value, the bohemite structure turns to *γ*-alumina (JCPDS card no. 10-0425), which is in agreement with a previous report which shows that the *γ*-Al_2O_3 phase is formed upon the dehydratation of aluminium oxyhydroxide bohemite at temperatures ranging from 400°C to 700°C [17].



(a) **(b)**

Figure 3. **(*a) as-synthesized AMLS X- ray diffraction pattern, (b) AMLS X- ray diffraction pattern after the calcination (500°C, 1 h)***

The alumina hydrothermal synthesis was made under continuous stirring at 80°C for 24 hours. The surfactant was removed by the classical protocol of Soxlhet extraction with ethanol (36 hours). The X-ray powder pattern of the extracted product shows five well defined peaks (Figure 4), that indicates a crystalline structure of the material.



(a) (b)

Figure 4 ***(a) as-synthesized alumina X- ray diffraction pattern, (b) hydrothermal alumina X- ray diffraction pattern after the calcination (500°C, 1 h)***

Sample	**Thermal treatment**	S_{BET} **[m^2/g]**	$V_{micropores}$ **[mm^3/g]**	V_P **[mm^3/g]**
ALM$_{hydro\text{-}thermal}$	As-synthe-sized	288.87	116.47	
	Calcinated at 350°C	240.09	71.39	
	Calcinated at 500°C	276.57	48.44	205.69

Table 5

1.3 Conclusions

In this study, it is demonstrated that the microwave radiation in the synthesis of the alumina exhibits the significant effect on shortening of its synthesis time and control of its morphology and superficial area. The short preparation time could be ascribed to relatively fast dissolution of the gel upon microwave irradiation as compared to conventional heating system. The short synthesis time in microwave heating is explained by two different mechanism: the rapid heat-up of the sample and a better heat transfer which results in rapid and sufficient heating of the synthesis mixture [18]. An essential difference between conventional and microwave heating is the enhancement of the Brownian motion and the rotation dynamics of the water molecules [19]. In the case of the rotational motion, far more hydrogen bridges of water molecules are destroyed, resulting in so-called active water molecules. The active water molecules have a higher potential compared to the hydrogen-bonded water molecules to dissolve gel because the lone pairs and OH groups of the active water molecules are available to attack gel bondings [19].

The 24 hours hydrothermal synthesis, on the contrary, leads to a material with a crystalline structure better adjusted and so with a superficial area lower than that of the microwave treated material. Similarly to SBA-16 synthesis in presence of a non ionic surfactants, we think that the formation of the bohemite depends also on the premixing conditions, probably to determine short range ordering. Hydrothermal synthesis required a much longer stirring time, at last 24 hours, in the premixing stage than microwave synthesis to obtain a regular structure.

Relating to the macrokinetics, the microwave role on the bohemite formation is well pointed out by following results:

1. after the surfactant removal, work working with different reaction time (30' *vs* 24 hours), it is obtained the same crystalline phase (XRD);
2. after the surfactant removal, the S_{BET} are 320 m^2/g (30', in presence of microwave) and 290 m^2/g (24 hours). The superficial area difference (10%) results consistent with the higher cristallinity of the phase obtained *via* classical hydrothermal preparation.

2. Thermal stability of sodalite synthetized from zeolite 4A

This work describes the reactions taking place in a mixture of zeolite 4A and sodium chloride with increasing temperature In the nuclear energy research one of the most important aims is to develop a method to stabilize HLW (High level radioactive Waste) using a suitable matrix with strong leaching resistance, thermal stability and mechanical resistance. A proposed matrix is sodalite. In order to verify sodalite's thermal stability, we explored the solid state reactions of a mixture of zeolite 4A and sodium chloride. Zeolite 4A was treated, in presence of NaCl, from 500°C to 900°C, in a traditional oven and in a microwaves oven.

2.1 Description of the method

The reaction inside the microwave oven is conducted at 900°C to assure the complete zeolite A decomposition and to obtain melted NaCl with an higher reaction rate (melting temperature=801°C). Salt quantity is higher than stoichometric value; because the objective of this research is to verify sodalite formation, without focusing on material balance and optimal reaction conditions. More tests were made varying time in order to conduce a kinetic study of the reaction. At the end of every reaction the product is washed with hot water, in presence of mechanical agitation for 1 hour with the purpose of melting the excess of non reacted salt. At last, the dust is recovered by vacuum filtration. Before conducting the reactions, a test , called ZEOCAL, is performed. In this test, starting zeolite A is thermally treated at 900°C for 5 hours inside the microwaves oven in NaCl absence, for evaluating the salt influence on the reaction.

To make a comparison between the conventional heating method and the microwaves one, some tests inside a tubular traditional furnace are made. In this case the reaction is conducted at 900°C and the reactants are weighted in a way that there is a NaCl excess, too. The test are made varying their duration to verify the kinetic (the fixed temperature is reached in 15-20 minutes).

2.2 Results

It is possible to conclude that a zeolite A thermal treatment at 900°C produces the nepheline ($NaAlSiO_4$) (Figure 5). This compound probably represents the more stable phase obtainable under these conditions.

Thermodynamically, under the above mentioned operative conditions, on the contrary, it shall obtain either the sodalite, if chloride ions are present in the reaction ambient , or the hydroxyapatite (or basic sodalite, in that OH^- ions substitutes the Cl^- ones), like more stable phases.

During the test ZEOCAL, the two possible sodalites doesn't form on account of chloride ions and hydroxylic ions source absence into the reaction ambient (water absence).

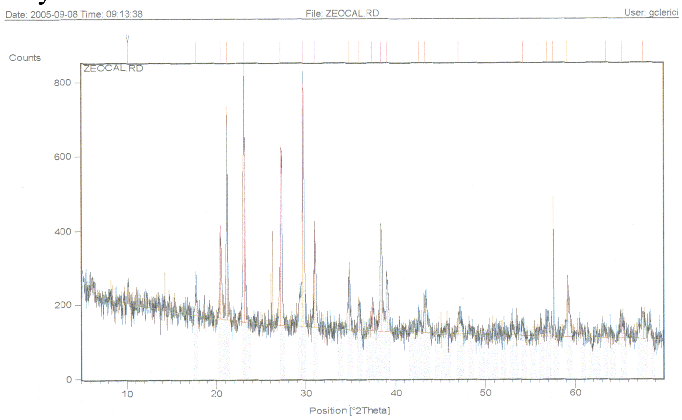


Figure 5. ***ZEOCAL test XRD spectrum. The red stripes indicate the nepheline presence***

In the table 6 the tests conducted to obtain sodalite are reported.

Sample	Zeolite A [g]	NaCl [g]	T [°C]	t*	product [g]
ZOS 01	2 (uop 7007)	3	900	1h30' R (+) 1h40'	1,91
ZOS 02	2,02 (uop 7007)	3,02	900	1h R (+) 2h	2,02
ZOS 03	2,1 (uop 7007)	3,02	900	1h30' R (+) 3h	2,1764
ZOS 04	2,045 (uop 7007)	3	900	1h30' R (+) 5h	2,26

*the reaction time is given from a phase, R, in that the oven reached the set temperature and from a second phase in that the temperature is mantained constant

Table 6

Observing Figure 6 it can be noted that, in all the tests, the starting zeolite peaks aren't present: this data confirms the zeolitic structure instability at high temperatures.

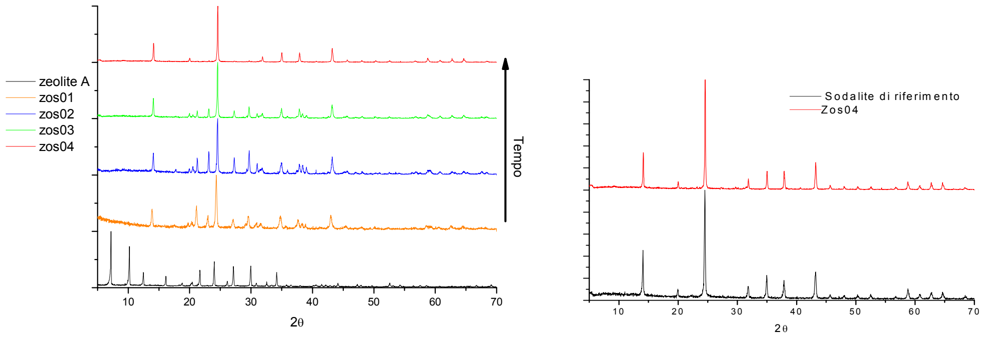


Figure 6. ***XRD patterns comparison***

It is possible to conclude that the zeolite A and NaCl starting reaction brings to sodalite production, yet the reaction advances through the formation of nepheline, like intermediate phase. This aspect confirms the metastable nature of zeolite A and nepheline , compounds that, inside an opportune reaction ambient, tend to transform themselves into the more stable phase: the sodalite. It just is the sodalite stability at high temperatures that makes this material very interesting on the point of view of nuclear waste inertization, because the nuclear decadence reactions present a very high energetic release, that can wears away the containing material resistance. This resistance must obviously be the higher possible. The Zos04 test is the one that has produced pure and crystalline sodalite (Figure 7).

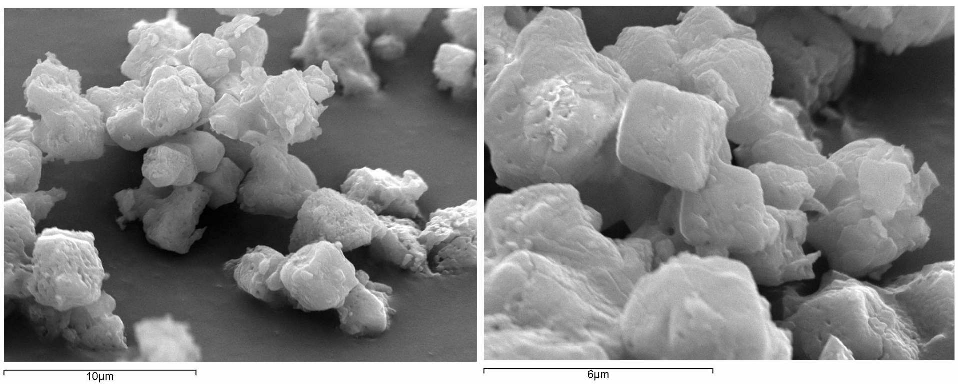


Figure 7. ***Zos04 sample SEM images***

The tests in a tubular conventional oven are made varying their duration to verify the kinetic (the fixed temperature is reached in 15-20 minutes).

Sample	Zeolite A [g]	NaCl [g]	T [°C]	t [h]	prodotto [g]
ZOST 02	1,01	1,514	900	5	0,99
ZOST 03	1,03	1,52	900	8	1,08
ZOST 04	1	1,51	900	10	1,0424

Table 7

The Figure 8 shows the XRD spectra of the 3 samples prepared. Rising the reaction time, keeping all other conditions equal, the reaction evolves to form sodalite , even if in spite of the 10 hours of reaction of the test ZOST04, the desired purity of the product is not reached.

The extraneous peaks of sodalite diminish in intensity when the reaction time rises and they represent an intermediate phase between starting zeolite A and sodalite.

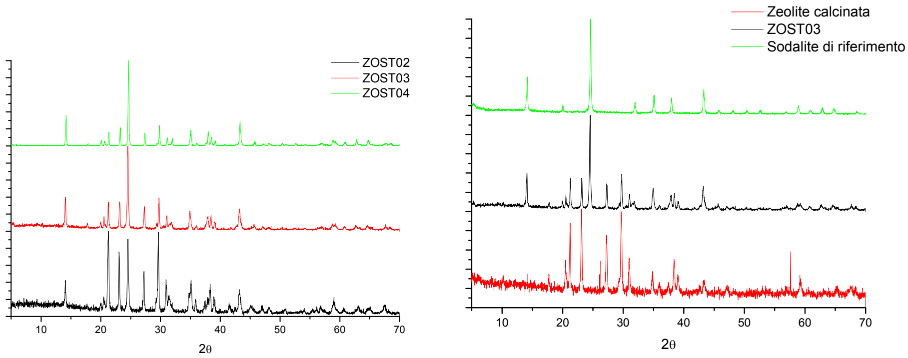


Figure 8. ***Comparison between ZOST03 test and thermally treated zeolite (red pattern) and sodalite of reference (green one)***

2.3 Conclusions

Comparing the microwave assisted reaction with the one made in the tubular oven it's possible to remark again the microwave effects on the reaction. In fact the reaction made with traditional heating usually requires longer reaction times. Zos04 test has produced a pure sodalite in a reaction time equal to 5hours in constant temperature plus 1 hour and a half of heating to reach 900°C. The reactions in the tubular oven, instead, haven't produced a pure sodalite not even after 10 hours of reaction. This effect is due to microwaves, probably NaCl in the reaction mixture, being a polar compound, gets the microwaves to reach high temperatures. Because of the salt being uniformly distributed into the mixture, different zones are created in which the temperature locally surpasses 900°C and this phenomena highly increases the reaction rate.

3. Clothes drying assisted by microwaves

This work is focused on the study of a microwaves assisted drying process of different nature clothes after they have been washed in a washing machine with the aim of reduce treatment time, and save energy.

The work has been divided in two step: the study of the interaction between microwaves and clothes and the realization of a microwaves assisted washer drier prototype studying the process variables.

The research has been developed in collaboration with the Indesit Company, leader in the production of electrodomestic devices.

3.1 Description of the method

The first step has been the study of the interaction between microwaves and clothes During is phase of the project, it has been studied the effect that the microwaves field produces on different types of standard cotton fabrics at different temperature and different degrees of residual moisture.

It has been exactly conducted a preliminary study of drying of cotton tissue specimens provided by various nature provided by Indesit using a thermobalance (Smart 5 produced by CEM company) and treating 5-20 g. of standard specimens in each test.

The cotton specimens have been soaked with water and then placed on a horizontal perforated support in order to drain the excess water.

The tests analyzed some parameters of the drying process in presence of a MW field (nature of tissues, temperature and final level of moisture) and during them it has been monitored the loss of water from the tissues under the action of MW until a programmed remaining moisture degree. Finally, it has been mapped the MW field into the oven SMART 5 to check the homogeneity of the field distribution in the support area, where samples are placed to be studied.

To make the mapping of the MW field inside the oven Smart 5 it has carried out with a card produced by DCMIC at Polytechnic of Milan, which, when hit by the MW, has a black colour. The intensity of the electromagnetic field is controlled by the intensity of colour that takes the paper.

The second step has been the realization of a microwaves assisted washer drier prototype studying the process variables.The objective of the second phase of the work has been studying and pointing out the operative parameters of the drying process of different various clothes types. The load consisted of several brightly coloured cotton items.

The tests has been carried out in multimodal MW oven Mars Xpress model produced by CEM company at 2.45 GHz. The used load for the experimental dryer has been about 0.3 – 2.5 kg. The clothes have been soaked with water and then placed on a perforated support in order to remove the excess of water and to obtain uniformly wet and ready for drying clothes. The amount of water added to the clothes has been measured and varied between 0.3 – 1 Kg, depending on the composition of the load.

There were two thermal probes to check the input and the output of air.
For the control of the tissues temperature, during the drying tests, a sapphire probe and a remote optical pyrometer have been used.

3. 2 *Results*

The preliminary study demonstrated that a complete tissue drying process produces (fabrics totally dried without residual moisture) irreversible on the tissues folds, browning and streaking effects on them. These phenomena didn't occur leaving in the tissues more than 5% residual moisture It has been also determined the maximum temperature that allows to remove the water from samples ensuring their maintaining its integrity (102°C). The tests during the second step of the work have been showed that the extraction fan into the oven is completely insufficient to remove the water vapour released during the textiles drying and the cold water that condensated on the walls of the oven. This leaded to a slowdown in the rate of clothes drying because a part of irradiated microwaves was absorbed by condensed water. The result of the specific power consumption to drying (W/Kg of clothes) was therefore heavily distorted by excess.

For these reasons the oven has been properly amended with a system of adjustable release of hot air. The regulation provides for two flow rate and two powers of heating.

During the tests, the following variables has been monitored:
- temperature inside the oven;
- moisture and temperature of air flow in and out the oven;
- textile temperature;
- textiles residual moisture;
- drying time;
- power input;

- textiles integrity after the microwaves irradiation.

Clothes	power MW (Watt.)	Convective heat	Warm air (T °C)	Drying time (minutes)	Air flow outlet (T°C)	Moisture (%) air flow outlet	MW Energy (kWh)
wool 1	1200	NO	-----	24	27.2	90.5	0.64
wool 2	1200	SI	47,4	17	35.3	72.6	0.427
wool 3	1200	SI	77,4	14	41.1	51.5	0.373
wool 4	1200	SI	68,7	11	42,3	49.5	0.293
wool 5	1200	SI	98.6	8	52.6	27.3	0.213

Table 8

Table 8 shows the operative parameters and the outputs of 5 different drying process. An hybrid drying system (microwaves and hot air flow) leaded to a reduction of the treatment time compared with a MW drying system. It has been studied the effect of the MW field on some non tissue materials, present in the clothes.

The load has been made of jeans with some metallic objects (buckles, buttons, zippers). The tests that the presence of metal object may create some problems due to the uncontrollable phenomena of local overheating and arcing discharge.

These phenomena have been particularly evident when the clothes drying has been complete leaving a residual moisture content less than 10%.

The repeated tests have shown that to preserve the integrity of the tissue avoiding over heating phenomena it has been necessary to achieve a more soft drying of the clothes.

So to remove the residual moisture from clothes in presence of metallic parts it has been used a flow of hot air. The tests have been made by an hybrid heating system (microwaves and hot air).

This system allowed:

- the remotion of the moisture present in the oven;
- an outgoing air temperature higher than the ingoing one.
- the decrease of the processing time;
- the decrease of the condensation phenomena inside the oven;
- the treatment time reduction with saving in energy consumption.

During the tests it has been also evaluated the temperature reached in correspondence of various points of fabrics collected one on the others.

For this purpose have been used various sapphire temperature sensors placed between the layers of tissue in order to monitor the thermal gradient inside a group of clothes along the vertical axis.

The test has been carried out under static conditions (the tissues inside the oven have been not moved) and in dynamic conditions, (the tissues inside the oven have been rotated).

It has been found that in a static system there was a non uniform temperature distribution inside the oven around the metal accessories there has been an higher temperature than around the other tissues area.

Some test independently of the metal accessories presence, showed some damages of different areas samples due to uneven distribution of the MW field in the resonant cav-

ity. In fact the temperature measured by the sensors presented some gradients from one area to another one inside the oven.
These experiments clearly showed that, during the microwaves irradiation it is fundamental that the clothes are shuffled to avoid local overheating and that it is carefully controlled the remaining moisture. It has been considered the possibility of using the hot air from the cooling system of the magnetron, which is usually dispersed. The temperature of the air flow is about 50°C. Its use in drying of tissue occurred without any extra energy consumption. The tests have been carried out in the MW oven Milestone Ethos 1600 FKV, in which it has been possible to intercept cooling air of magnetron and convey it inside the oven. So the oven has been turned into a system with an additional input of hot air
The tests showed that this system reduced the drying time, compared to a drying system with only MW but the tests have not been successful because the hot air recuperated from the magnetron's cooling in addition to a convective flow air was higher than the air's output of the oven and this led to the formation of condensation on the walls of the oven. It was therefore decided to postpone tests with the drying air intake from the magnetron in a system designed for this purpose.

3.3 Conclusions

The inlet of convective heat into the microwave oven improves the mass and heat transfer.

If microwave power is combined with hot air for clothes drying, the energy consumption and drying time can be reduced to about 30 %.
The use of a rotating plate as samples support permits an uniform drying.
It is not clear if about the utilization of the input air from magnetron (if the oven doesn't contain an appropriate fan for residual moisture extraction.) is suitable for the purpose to facilitate the microwaves assisted drying process.

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BETTER CONTROL AND PROCESS INTENSIFICATION BY IN SITU MICROWAVE HEATING

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HISTORY

The Institute for Physical and Chemical Processes (IPCF) is a multidisciplinary institute where theoretical, computational and experimental approaches are fruitfully combined in specific fields of physical and chemical disciplines, namely New Models and Devices, Environment and Soft Matter. Their expertises cover a wide variety of disciplines including synthetic chemistry, analytical and spectroscopic techniques, thermodynamics and calorimetry, lasers, modelling and computational chemistry, molecular design and nanotechnologies. At IPCF, the laboratory research activities can be effectively supported by technological workshops of high quality, including high precision mechanical workshop, advanced electronics, surface polishing and coating, free-standing thin foil preparation, laser optics design and optimisation, chemical preparations.

Experience and skill acquired by scientists and technicians at IPCF in the study and use of microwave (MW) circuits and techniques has led to the development of experimental methods and devices useful for research work. More recently, efforts have been made also in view of industrial and civil applications of MW power. An innovative methodology was developed consisting essentially in the use of a MW emitter placed directly inside a material with dielectric losses, to activate a process of physical or chemical interest [1]. That way, MW power heats the materials with maximum efficiency enabling to obtain fast and reproducible results without the need of an oven or a closed metal cavity. CNR Industrial Patents are pending regarding the MW chemistry, the production of visible, UV or IR radiation with a MW lamp without electrodes and the construction of a miniaturized MW applicator for minimally invasive surgery [2, 3, 4, 5].

ACTIVITIES

1. The MW chemical reactor

Microwave assisted chemistry (MAC) is an invaluable tool within chemistry research and many remarkable advantages make this methodology very attractive. The benefits, though, are obtained at the expense of relevant drawbacks. At the state of the art the chemical process occurs by introducing a non metal MW-transparent reaction vessel into a microwave cavity. As a consequence, the shape and the size of the sample is important because the microwave source and the oven cavity itself react differently to loads of the same volume placed in different vessels or in different positions.

The use of auxiliary metal devices is severely limited by the presence of microwave electric fields of high amplitude generated by electromagnetic resonances of the metal enclosure. For the same reasons hot spots, arching and unpredictable explosions of closed reactors are not rare events, particularly when looking for new experimental procedures or routes. The impossibility of direct manual, visual and/or instrumental access to the reaction vessel is another limitation for the operator. The use of glassware directly connected to the reactor is not straightforward and other useful devices or tools must be placed outside the oven. The simultaneous application of optical radiations, and/or ultrasounds, is not so easy. Control of temperature using circulating cooled water is not feasible. On the other hand, the use of mono-mode metal waveguides or cavities, i.e. the focused applicators, permits to treat only samples of small volume.

To overcome the aforementioned difficulties, IPCF has proposed a novel method in which the chemical activation is better obtained using an immersed insulated coaxial antenna working at 2450 MHz [1]. In situ microwave heating enables to obtain safe and reproducible results. The apparatus and the experimental procedures are very simple and easy to handle and the obtainable advantages are of general interest in chemistry. A metal walled reactor enables fast MAC operations at high pressures. When using ordinary glass reactors fed with high MW powers, safety measures are easily adopted in presence of stray radiation by wrapping the walls with metal foil, tape, paint or netting.

1.1 Applications

The MW chemical reactor is useful in all cases, specially when flexibility, control and simultaneous application of experimental techniques of different disciplines are of concern.

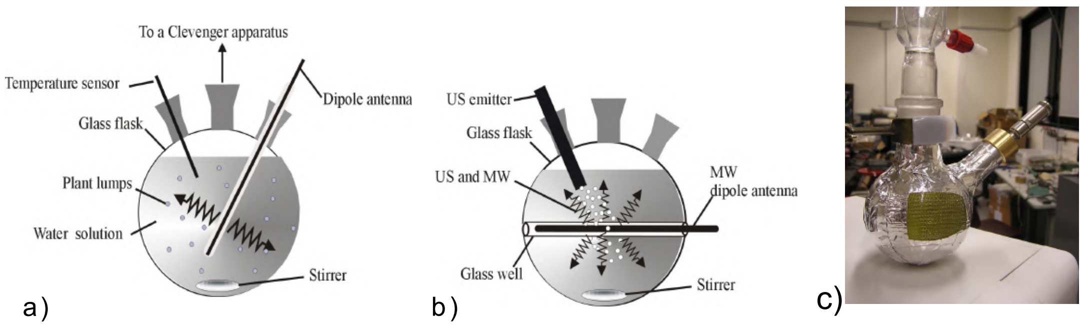


Figure 1. a) The 1000 ml flask reactor is fed with MW power (up to 1 kW, at 2450 MHz) for the extraction of essential oils from plants using a Clevenger apparatus at reflux; b) the 3 neck glass flask reactor features simultaneous US and MW treatments and both forms of energy can be applied in pulsed or in continuous wave regime; c) using this reactor metal nanoparticles are prepared by solvothermal or polyol methods at reflux, using MW power densities of 10 W/ml on the sample. The picture shows the coaxial antenna with choke and with a type N standard connector

In Fig. 1 we show some representative examples in which the MW chemical reactor was successfully applied at IPCF. The drawing in a) represents the scheme utilized for the extraction of essential oils from plants [6]. The scheme of a MW reactor useful for the simultaneous application of US and MW in an ordinary glass flask [7] is depicted in b). In Fig. 1 c) we show a MW reactor wrapped in aluminium tape, utilized for the preparation of metal nanoparticles by solvothermal or polyol method, by applying to the sample a MW density of power as high as 10 W/ml for better control of particle sizes and morphology [8]. The same scheme of reactor can be used for nanoparticle preparation by photo-reduction. In this case the applicator is made out of a dual MW/UV source, as described in section 2.

1.1 Advantages

The thermal activation using a MW antenna (probe) presents a number of relevant economical, practical and technical advantages in MAC:

1. Use ordinary vessels, also with metal walls, of whatsoever geometry and shape, of small or large volume. Samples in a glass cuvette or in a 1 ton steel reactor can be activated with the same efficiency.
2. Apply microwave power in existing complex chemical apparatus or systems or in pilot plants without or with minor modifications.
3. Select at will the position, the power, the polarization and the number of the microwave probes to be used for the activation of the process.
4. Have direct manual, visual and instrumental control of the chemical reaction using ordinary glassware on the bench.
5. Use metal components or devices in proximity of the microwave probe, taking advantages of the absence of electric field antinodes, since the microwaves emitted by the probe are absorbed by the material without giving rise to electromagnetic resonances.
6. Break the scale-up barrier in industrial processes and increase the capability of control of the local temperature by applying many independent microwave probe. It was found that one probe emitting more than 1 kW of microwave power at 2450 MHz can be placed at about 5 cm of distance from another one, in the same continuous or batch reactor.
7. Activate chemical processes strongly dependent from the geometry and from the wall of the reactor.
8. Enter effectively into multidisciplinary applications taking advantage from the extreme versatility of the in situ heating technique. Optical radiations, UV, X-rays, electron beams, magnetic/electric fields of high-amplitude can be applied simultaneously to the microwave assisted reaction/process. Microwave effects on biological specimens placed under the microscope lens are feasible using a 0.5 mm dipole coaxial probe.
9. Reduce substantially the investment costs getting rid of cumbersome closed metal cavity applicators.
10. Use dipole coaxial radiators featuring wide band impedance matching characteristics, easy to operate, cheap, long lasting, safe and, most of all, featuring highly reproducible thermal effects both in homogeneous and in multiphase materials.
11. Produce a conformable microwave power density distribution in the volume of the material, taking advantage from the interference phenomena presented by an array of microwave probes fed with the same source.
12. All these advantages are *unique* and cannot be obtained using the traditional metal cavities.

The IPCF method is a valuable achievement in the field of MAC, for applications of laboratory, for civil and industrial interest.

Key-words : *microwave assisted chemistry; microwave chemical reactor;*

2. The electrodeless MW/UV dual source

Electrodeless lamps are commonly excited with microwaves to obtain visible, IR or UV radiation, with increased life span and better control capability. Wide-band or spectral line emission is possible with good efficiency featuring continuous or pulsed output regimes.

Microwave electrodeless lamps, made out of sealed-off glass bulbs filled with metal vapour and noble gas at suitable working pressure, are usually excited using a metal enclosure, typically a microwave resonant applicator. The innovative aspect of the IPCF invention consists in the excitation of the gas discharge from the inside, utilizing a microwave coaxial antenna protruding in the glass bulb without being in contact with the gases and/or metal vapours. Using this method a metal cavity resonator is not necessary, and metal electrodes or walls around the lamp can be totally absent. The microwaves are emitted continuously or in pulsed regime by a short dipole coaxial antenna. Accordingly the emitted microwaves in the near region field accelerates free electrons giving rise to and sustaining a plasma discharge which emits optical radiation and, within limits, microwaves not absorbed by the plasma discharge. Atoms or molecules emit UV-vis radiation by decaying spontaneously from excited states or during shocks with other gaseous particle, with selectable spectral distribution. In Fig. 2 details of the lamp are reported, showing in panel a) a 3 cm diameter quartz bulb filled with Ar (5 Torr) and sulphur (1 mg) , excited by a 3 mm semirigid coaxial open tip dipole antenna.

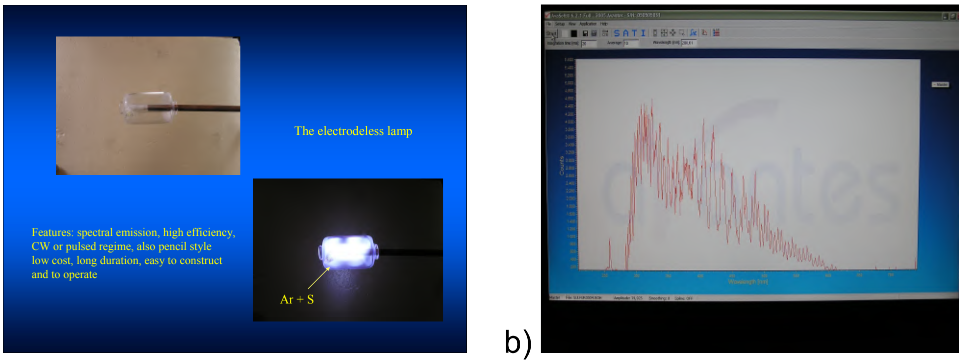
a) 

Figure 2. a) the 3 cm x 5 cm glass bulb is shown when MW was off (left) and when it was excited by a open end coaxial dipole antenna made out of a 3.5 mm semirigid coaxial cable (right). The bulb was filled with Ar gas (5 Torr) and 1 mg solid sulphur; b) the spectral emission of the lamp in the UV-vis wavelength range is shown, in arbitrary units

The working frequency is 2450 MHz, and the applied power is 20 W. The recorded spectral emission of the molecular S_2 bands are shown in b), in arbitrary units.

2.1 Applications

The MW electrodeless lamps are utilized for the construction of powerful MW/UV-vis sources with selected spectral emission. They can be applied for the treatment of polymers and biological materials, sterilization, excitation of photochemical or photocatalytic reaction, laser optical pumping, and other applications in which a pulsed or continuous source, with controlled emission is at a premium.

At IPCF a microwave photochemical reactor was utilized for the oxidative decomposition of Acid Orange 7 azo dye by MW/UV/H_2O_2 process [9]. The reactor was constructed using a low pressure Hg/Ar filled quartz bulb emitting both MW and UV (mostly at 254 nm) radiation (Fig. 3). The temperature inside the reactor was easily controlled within 0.5 ^oC using a cooled water bath (not shown). The new method, in comparison with other MW electrodeless lamp operating inside a MW oven, enabled to measure and control the MW and optical power, leading to a greater and more realistic knowledge of the energetic aspects of the photochemical process, which as far as we know has not been possible before with this degree of accuracy. From a general point of view, the use of a dual source placed inside the reagents was in itself mostly efficient, especially if synergetic effects are important In fact, in this experimental configuration, the MW available power was completely utilised to produce UV-vis radiation and volumetric heating, both contributing to the decoloration process, with no energy loss to the ambient or to the walls of an oven. The possibility of recording the spectroscopic data during the process without the need for periodic sample withdrawals and using ordinary auxiliary techniques were additional advantages. Working on the bench without needing an oven a substantial reduction in the time spent in preparing and performing each reaction was obtained saving time and chemicals in the oxidative decomposition of Acid Orange 7. Compared to other MW commercial equipments currently in use our method is more versatile and useful for the construction of MW/UV photo reactors of industrial interest.

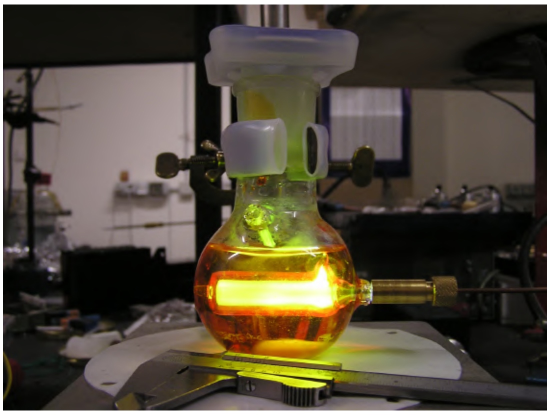


Figure 3. The fully integrated 100 mL quartz photo reactor is working on the bench for the photoreduction of Acid Orange AO7 azo dye in water solution (30 mg/l) by MW/UV/H_2O_2 process. Applied power: 10 W at 2450 MHz; optical emission (UV-vis): 2 W

2.2 Advantages

The new technique enables the construction of MW/UV-vis source of low cost, since no electrodes nor metal cavities are necessary. Furthermore, the possibility of complete electronic control of the microwave applied field enables pulsed operation (typically, 1 microsecond of duration) and higher repetition frequencies (up to 20 kHz), with advantages with respect to other commercialised technologies. Experiments dedicated to the preparation of metal nanoparticles by MW/UV photoreduction are ongoing at IPCF.

3. The MW surgical applicator

A miniaturized interstitial applicator of new design was constructed at IPCF. It essentially consists in a microwave coaxial antenna of small diameter, suitable to be introduced inside a steel biopsy-needle and inserted into a deep solid lesion of a perfused tissue, under sonographic guidance, to obtain the coagulative necrosis of a solid tumor by focal thermal treatments (thermo-ablation) of short duration. The novel antenna features a sleeve choke (to impede unwanted heating of nearby tissues due to reflected microwave power) completely integrated with the introductory needle, so that the antenna can be constructed in a highly miniaturized version. The device compares favourably with all other commercial MW choked devices for minimally invasive thermo-ablative surgery [10].

3.1 Applications

The miniaturized choked antenna can be introduced inside a biopsy-needle of smaller diameter, reaching the lesion not only using intraoperatory techniques, but also utilizing percutaneous, laparoscopic and endoscopic procedures, to apply coagulative microwave therapy. It can be used for the treatment of lesions in liver, kidney, prostate [11], brain, etc., taking advantage presented by microwave heating with respect to all other thermo-ablative techniques.

3.2 Advantages

The extreme grade of miniaturization enables the operator to apply the percutaneous microwave coagulative therapy to a greater number of cases, with less invasiveness and greater precision, also in lesions nearby vital organs. The technical solution indicated by IPCF is very simple and reduces drastically the applicator size and cost, enabling its industrial production in disposable version for outpatient applications.

An international Patent is pending on the miniaturized applicator. Clinical trials are ongoing and the number of treatments in which the MW miniaturized applicators are utilized for the thermoablation of liver, lung, kidney and prostate continuously is increasing in Italy and in other countries. H.S. Hospital Service (Aprilia, Latina) is producing the complete microwave system, state of the art of microwave applicators for minimally invasive surgery all over the world. Fig. 4. shows the MW system produced by H.S. Hospital Service, comprehensive of a fully programmable solid state source at 2450 MHz, 100 W output power, with water cooled applicators, actually as small as 17 G (external diameter <1.5 mm).

More informations about usable MW sources, coaxial cable technology, costs and scale up can be obtained by the authors [12].

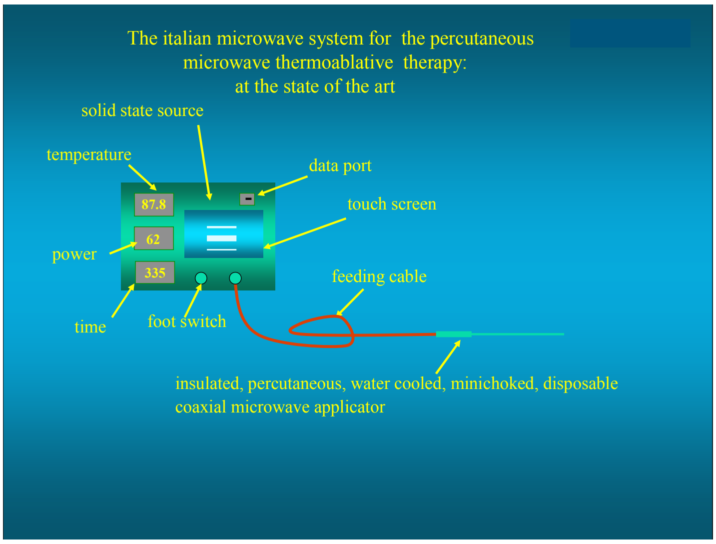


Figure 4. A programmable solid state source at 2450 MHz, with 100 W maximum output power is schematically shown, connected to a water cooled insulated disposable applicator through a flexible coaxial cable. A complete MW thermo-coagulation system is actually produced by H.S. Hospital Service S.p.A. (Aprilia, Latina)

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LAB FOR MICROWAVE PROCESSING OF POLYMERS AND COMPOSITES

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HISTORY

The Institute of Composite and Biomedical Materials (IMCB) of Italy National Research Council (CNR) is officially active from the 12^{th} October of 2001.
In the field of Microwave (MW) polymer processing, the research activities are developed and performed in collaboration with Department of Materials and Production Engineering (DIMP) of University of Naples "Federico II".
The Institute carries out research, development and training activities and technological transfer about the following topics: *polymeric and composite materials with programmed structural and functional characteristics, processing technologies of polymers and composites, conventional and nano-composite, polymeric and composite materials for tissue engineering.*
The various research topics have generated elevated interdisciplinary competences, renowned nationally and internationally through many collaborations with universities, research centres and industries. During the last years the institute developed innovative knowledges for the synthesis of new materials. Advanced methodologies for materials analysis and for improving their chemical properties (bulk and surface) have been tuned. The institute has studied new technologies for design and engineering aimed to development of advanced multi-functional materials for aerospace, automotive, marine, building consolidation, electronic packaging, optoelectronic functional material, food packaging and biomaterials.

ACTIVITIES

In the following the most recent activities developed by IMCB/DIMP in the field of MW processing of polymers and composites, focused on characterization of chemical-physical, rheological, spectroscopic and calorimetric properties of polymeric materials, with particular emphasis on adhesives, resins, conventional and nano-composites are reported.

1. Comparison between Conventional and MW thermosetting curing

1.1. Calorimetric Characterization

One of the most important activities is the determination of calorimetric properties of thermosetting polymers and composite materials.

DSC measurements enable the determination of total cure energy and glass transition temperature of thermosetting resins and the evaluation of fractional conversion of samples conventionally or microwave cured. The enthalpy of polymerization is measured through linear integration of specific heat flow vs. temperature signal.

1.2 Kinetic Analysis

An investigation of the reaction mechanism and kinetic parameters of thermosetting curing process is another important activity.

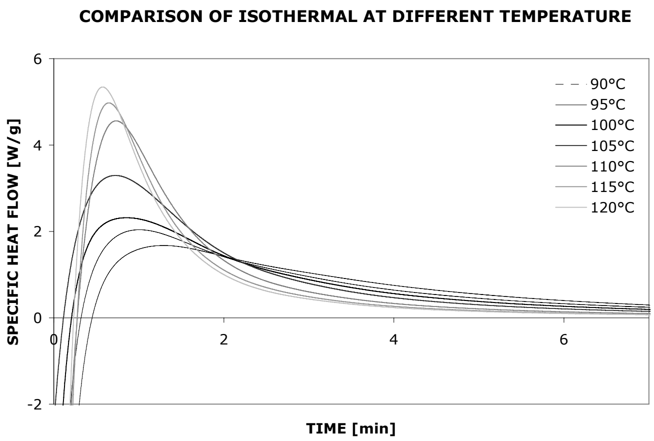

Fig 1. Comparison of isothermal DSC at different temperatures for an epoxy resin

This purpose is accomplished through analysis of isothermal DSC at various temperatures, selected on the basis of preliminary dynamic scans. As an example, in Fig. 1 the results of isothermal DSC at various temperatures of an epoxy resin is illustrated.

The rate of heat generation during these tests, is related to the reaction rate. In this way the integration of the signal enables the determination of fractional conversion and therefore the reaction rate. The analysis of this curve allows the identification of the appropriate phenomenological kinetic model. The non-linear regression of these data with a suitable algorithm enables the determination of kinetic parameters. Activation energy E_a and preexponential factor k_0 can be determined using Arrhenius law.

1.3 Comparison between DSC and MW Reaction Time

Another very important activity is the comparison of degree of conversion and reaction time of thermosetting resins microwave sensitive such as epoxides, cured alternatively in conventional DSC and in microwave field.

For this purpose a laboratory scale microwave oven, operating in static conditions with immobile sample-holder tray, has been chosen.

For investigating the existence of a “specific microwave effect” the selection of a comparable thermal profile between a dynamic scan in DSC and under microwave radiations has been verified. After each microwave curing process the degree of conversion of the sample has been measured through evaluation of residual enthalpy with dynamic scans in DSC.

As an example, Fig. 2 shows the comparison between the degree of conversion against time in MW and DSC for the same epoxy system. The degree of cure achieved in MW field is always higher than that obtained with conventional DSC heating.

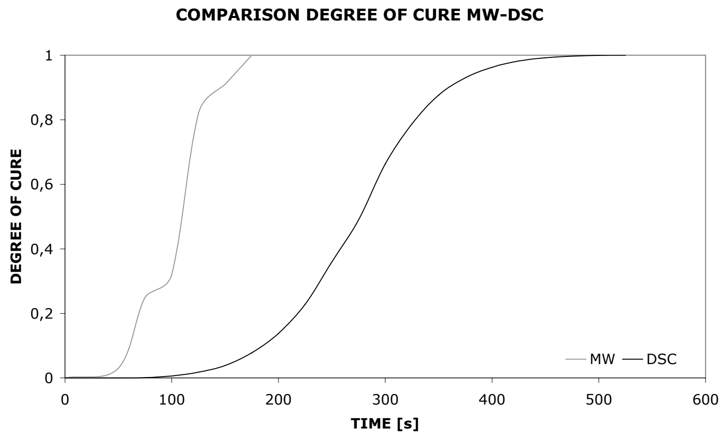

Fig. 2. Comparison of fractional conversion between DSC and microwave curing process of an epoxy system

2. Dynamical-Mechanical Characterization

Another activity is the comparison of the final dynamical-mechanical properties between thermosetting samples conventionally and microwave cured.

For this purpose three parameters have been selected: the storage modulus at room temperature measured during a dynamical analysis, glass transition temperature T_g e.g. the abscissa corresponding to the maximum value of tanδ during the same test and the flexural strength obtained through a static measurement.

As an example, Fig. 3 illustrates the curves of storage modulus obtained by dynamical-mechanical test of an epoxy resin conventionally and microwave cured.

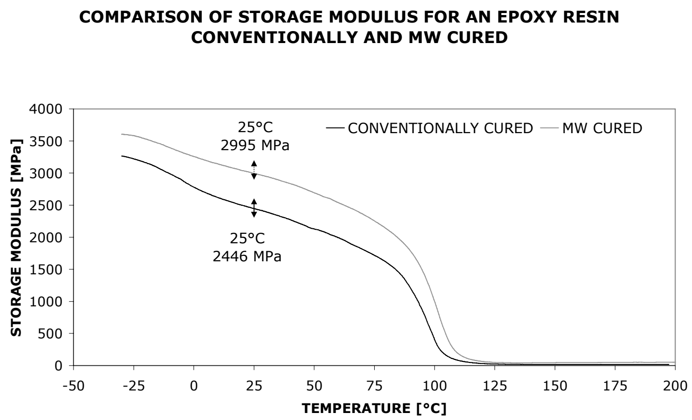

Fig. 3. Comparison of storage modulus during dynamical-mechanical test of an epoxy resin conventionally and microwave cured

Fig. 4 shows a comparison of stress-strain plot during flexural test performed on the same epoxy resin samples conventionally and microwave cured, according to ASTM D 790-03 standard.

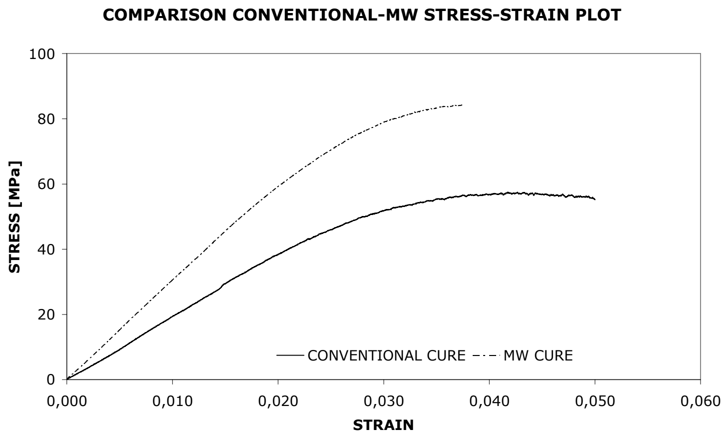

Fig. 4. Comparison of flexural strength of an epoxy resin conventionally and microwave cured

3. Kinetic analysis during MW exposure

MW exposure cycles at various irradiation powers, and consequently with different thermal profiles, have been tuned. After each microwave activated curing process the fractional conversion of thermosetting systems at different time have been estimated measuring residual enthalpy by DSC dynamic scans. The thermal profiles have been detected by an electronic device specifically designed for in situ real-time monitoring of temperature and density of electromagnetic field of the sample.

The elaboration of these data through isoconversional method enable the determination of kinetic parameters and an estimation of reaction mechanism.

4. Microwave-absorbing materials and sensitizers development

Organic oligomers and metallic nanopowders have been chosen for improving the microwave absorption of polymeric resins.

Organic oligomers are affected by electromagnetic field for the presence of polar groups, while metallic nanopowders increase the thermal conductivity of the system. Moreover, magnetic loss is a very effective mechanism for MW absorption of ferromagnetic particles embedded into a polymeric matrix.

It is possible to control the temperature heating by changing the Curie Temperature of ferromagnetic particles, which is related to the composition and morphology of synthesized particles.

A study of the thermal profile of polymeric and composite material containing these substances has been performed using the electronic device previously described. A number of technological application can be based on such phenomenon (e.g. hot melt adhesives, EMI/RF absorber, RADAR shields).

5. Spectroscopic Characterization

The conversion of thermosetting resins is studied through spectroscopic analysis (infrared, near infrared and UV-Vis region).

The disappearance of functional groups can be detected through spectroscopic analysis.

As an example, in Fig. 5 the region of infrared spectrum between 750 and 1000 cm^{-1} of an epoxy resin microwave cured is illustrated.

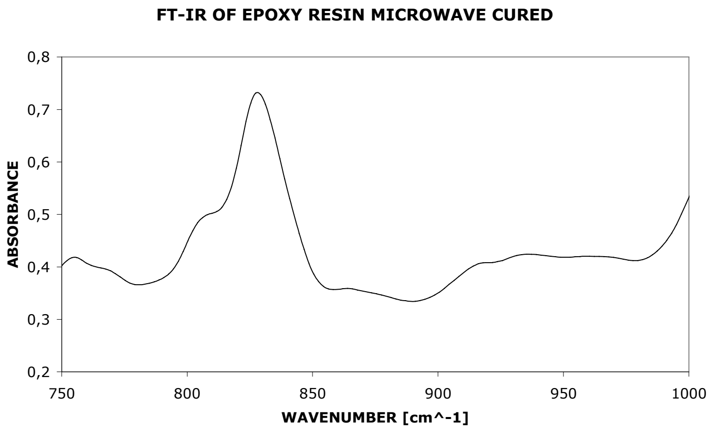

Fig. 5. Zoom of FT-IR spectrum of an epoxy resin microwave cured

No peaks corresponding to epoxy group are evident in the wavenumber region of 916 cm^{-1}.

INSTRUMENTATION

Laboratory scale microwave oven, equipped with infra-red and hot-air pre heating, with moving or static sample holder tray, Microglass s.r.l.;

Modulated Differential Scanning Calorimeter, TA Instruments;

Thermogravimetric Analyser, TA Instruments;

Dynamical Mechanical Analyser, TA Instruments;

Static dynamometer, Alpha Technologies;

Infrared Spectrometer, Nicolet,

UV-Vis Spectometer, Perkin Elmer.

EDUCATIONAL ACTIVITY

Assistance for PhD and graduation thesis.

COLLABORATION

Regional Competence Centre of Campania “New Technologies for Production Activities”.

Technological District on polymeric and composite materials and engineering and structures (IMAST).

Department of Materials and Production Engineering of University of Naples “Federico II” (DIMP).

Fiat Research Center (CRF), Orbassano, Torino (IT)

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MICROWAVE APPLICATION GROUP (MAG)

MICROWAVE
APPLICATION
GROUP

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HISTORY

The idea of applying microwave heating to inorganic materials was initially developed in Modena by the group of Applied Chemistry in 1995. At that time the group was guided by Prof. Gian Carlo Pellacani (Faculty of Engineering), who strongly supported this research both at local and national level. This was the beginning of a first nation-wide research program funded by CNR (National Research Center) and co-ordinated by Prof. Pellacani himself and his staff in Modena. "Industrial application of the microwave technology" - this was the program title - seemed to open new and interesting perspectives on materials processing, involving many different fields. The activity of the Modena research group mainly focused on providing high temperature treatment of ceramics and oxides to be employed in structural applications and glazing.
The base research, inspired to the quest for a non thermal effect, was accompanied by a plethora of short-time research programs focused on finding new and potential microwave industrial applications. Many industrial partners joined the group activities and proposed new research fields. Thanks to these new inputs, the Microwave Application Group interest evolved towards the simulation and design of specific microwave systems and the optimisation of manufacturing cycles.
Over the years the group successfully managed to gather Italian researcher involved in microwave application to chemical reactions involving solids in the framework of five national biannual projects funded by the Ministry of University and Technological Research (PRIN 1999, PRIN 2001, PRIN 2002, PRIN 2004, PRIN 2007) and one COST Action funded by the European Community: D32-CHEM (Chemistry in High Energy Microenvironments) (FP6, 2003-2009).

ACTIVITIES

The several applications of microwave (MW) energy performed by the Microwave Application Group (MAG) research team can be divided on the basis of the temperature range involved. In this way it is possible to distinguish low temperature ($T<200°C$), medium temperature ($200<T<800°C$), and high temperature ($T>800°C$) applications.

1. Low temperature applications

In the temperature range from ambient to 200°C, the main processes investigated are: drying of pigments and extruded ceramics, processing of gels, MW hydrothermal synthesis, MW assisted organic synthesis, heat treatment on textiles fibres, drying of water-based paints, gluing and sterilisation.

1.1 Drying of pigments and ceramics

The use of microwaves to dry powders is well known, however it can be further exploited considering the "milling effect" that microwaves have due to rapid evaporation of solvents. In the case of pigments, using microwaves it is possible to speed up the drying process and to obtain precursors having smaller particle size [1, 2]. For the drying process of ceramics the volumetric heating and the moderate moisture leveling effect of the microwaves can be usefully applied when pre-heating extruded ceramic items [3] as well as in the drying of low water content products, such as ceramic pressed tiles.

1.2 Processing of gels

Sol-gel preparation of catalytic powders can benefit of the use of microwave power, since it can be conveyed directly inside the material. By accurately controlling the forward power, small monolithic pieces can be obtained as well as samples to be easily reduced to mesoporous powders [4].

1.3 Microwave hydrothermal synthesis of inorganic nanoparticles

Hydrothermal syntheses of inorganic nanoparticles can offer several advantages when microwave heating is applied. This is principally due to the uniform and fast heating as well as high purity conditions of the process [5].
The Microwave Application Group particularly focused its efforts in the microwave assisted hydrothermal synthesis of different inorganic oxides such as ZrO_2 [6,7], Pr doped ZrO_2 [8], CeO_2 [9], TiO_2,[10] perovskites [11] phosphates/monazite [12] and carbonates/aragonite [13].
The possibility of scaling up these syntheses to an industrial level, developing continuous manufacturing and collection processes, can give access to mass scale production of inorganic materials. At this scope we also optimised a synthetic procedure of silica nanoparticles in a continuous-flow microwave reactor [14].

1.4 Microwave assisted organic synthesis

Microwave heating was also applied to increase yields and speed of some organic reactions. In particular, starting from 2004 the activities were focussed on a particular kind of organic compounds, i.e. p-toluenesulfonylhydrazones [15]. These intermediates are generally used in organic reactions to protect the carbonyl function, but they are also useful starting compounds for the obtainment of heterocycles derivatives such as pyrazoles. Microwave heating was used to obtain both the de-protection of the hydrazones and their conversion into heterocycles adducts [16]. An interesting application of microwaves to organic synthesis involves the use of dielectric heating coupled with solvent-free conditions in order to accomplish a green chemistry procedure. In figure 1 is reported a typical set up realised in MAG laboratories to perform organic syntheses in a single mode applicator. It consists of a magnetron operating at 2.45 GHz, with power output in the 30-300 W range, a WR 340 waveguide and impedance matching devices. With this versatile set up it is possible to reach the full control of all reaction parameters, such as temperature (measured by pyrometers and by multi-channel fibre optic system), direct, reflected and absorbed power. It is of course particularly useful prior to a possible scale-up, to evaluate the specific energy consumption of the process under study.

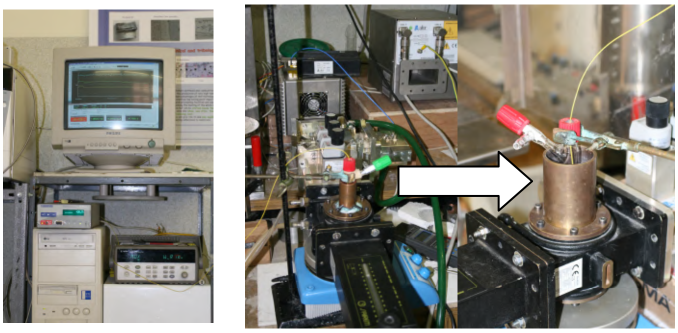

Fig. 1: Photos of the single mode experimental set up for organic synthesis (arrow indicate the insertion of the optical fibre)

1.5 Drying of water-based paints

Water-based paints allow to reduce the VOC emissions, but usually they require longer production cycles, compared to conventional paints. Microwaves can effectively dry the water-based paints, without significantly heating the underlying substrate, provided the applicator is well-designed. This proved to be particularly useful for wood boards, MDF panels and composite wood structures.

Electromagnetic field modelling of the multi-feed continuous applicator helped in designing the prototype, in particular as far as the microwave inlet waveguides position and inclination is concerned. Two different air blowing system were examined, showing better results in case of "percussion air" systems, rather than simple counter-current ones. Dimensions of the prototype, shown in figure 2, are approximately 14 x 1 x 2 meters, and the belt speed can be varied from 10 to 50 m/min. This allows the continuous treatment of up to 30 m^2 of boards per minute. Compared to conventional treatments, this leads to a throughput increase of more than one order of magnitude [17].

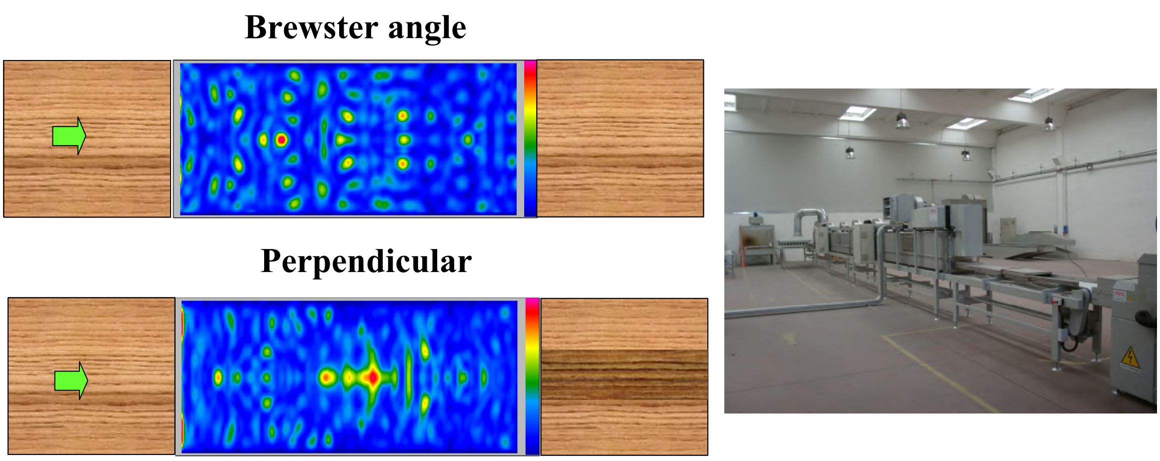

Figure 2: Simulation (left) of the SAR distribution in the boards plane in case of two different feeding waveguide geometries for the 14 meter-long furnace, shown on the right

1.6 Gluing cellulose products

Microwave assisted gluing was successfully performed using large applicators fed by slotted waveguides. Preferential microwave absorption by the glue allows a only moderate heating of the assembled cellulose products (MDF, HDF, paperboard honeycomb, wood). A modified glue composition, especially designed for microwave application, allows the complete gluing of 2 m^2 composite boards (MDF, honeycomb, wood) in less than 20 seconds, using an overall 16 kW power [18]. In some cases, additional cooling after gluing was required due to the thermoplastic nature of the glue. The glued boards, exiting from the applicator (Figure 3), already possess enough mechanical strength to be further processed (sawing, conveying, lifting …).

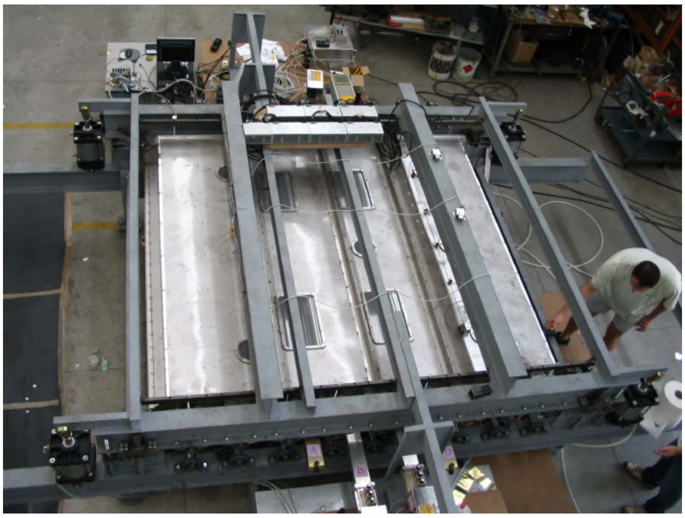

Figure 3: Top view of the 6 x 2 x 1.5 m gluing machine showing inspection windows, pyrometers ports and conveying system (rollers)

1.7 Sterilisation

In the field of non-incineration of hospital wastes MAG has been working in order to apply microwave irradiation to rapidly increase temperature and pressure (up to 8 bars) of a closed vessel containing shredded and properly moisturized waste. Microwave direct heating can involve only some species of the pathogens contained in the waste, while more resistant species (spores, in particular), require an indirect heating provided, for instance, by the vapor generated in the applicator. The microwave generator and applicator is part of a modular system including a loading and unloading station, a shredder and a device to recover water and control emissions (Figure 4) [19].

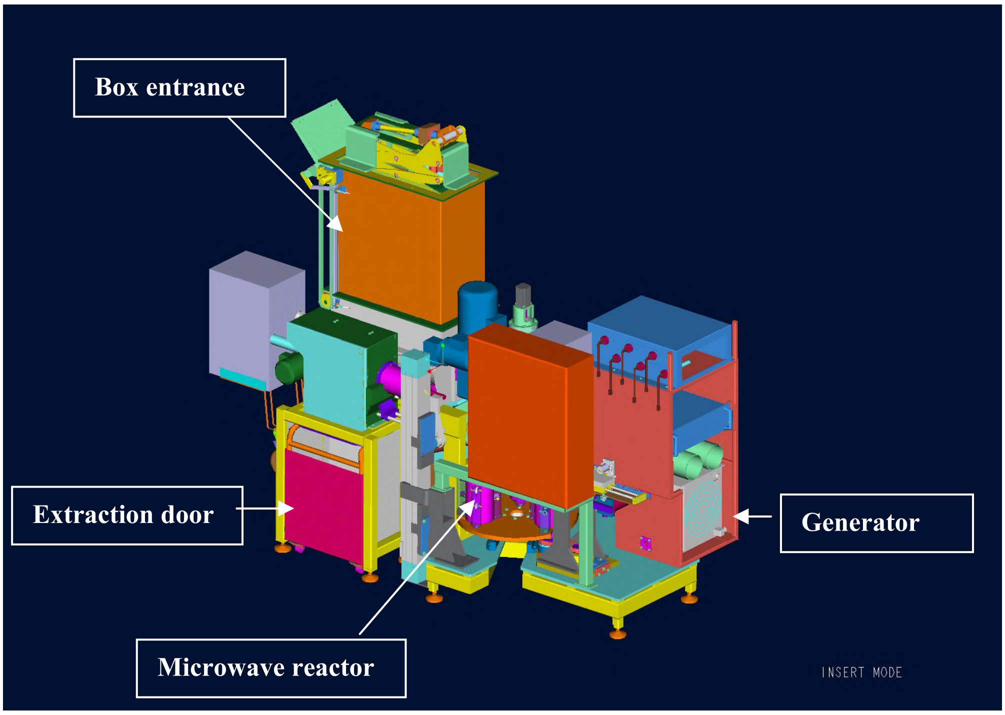

Figure 4: Microwave high temperature sterilising apparatus for hospital waste

2. Medium temperature applications

This group of applications includes debinding of technical ceramics and MIM parts, post combustion of ashes, recovery of exhausted alumina catalysts and ion exchange on silica glasses.

2.1 Debinding of technical ceramics and MIM parts

Microwave assisted binder removal of thick ceramic samples has been optimized with several laboratory tests, lowering processing time to 20 hours instead of the 5-7 days typical of the industrial cycles, without significant detrimental effects on the surface quality (Figure 5). A multimode furnace was used for this purpose after performing a proper numerical simulation to determine sample arrangement within the cavity [20]. For special purpose components, like supports for textile use, the surface quality of the material after sintering is not satisfactory, but the process can be used to speed up the design and testing of new moulds. Similar rapid debinding cycles performed by conventional heating lead to samples cracking, deformation and cause superficial defects not suitable for any kind of technical application.

In case of powders which can absorb microwaves, or possessing a higher thermal conductivity than ceramic green parts, the debinding process becomes less critical and the use of microwaves can further accelerate the removal of the binder, even in case of parts obtained by Metal Injection Molding (MIM). The combination of chemical debinding (rinsing in warm water) and microwave assisted thermal debinding allowed to decrease the binder removal time of stainless steel green parts to less than 150 minutes.

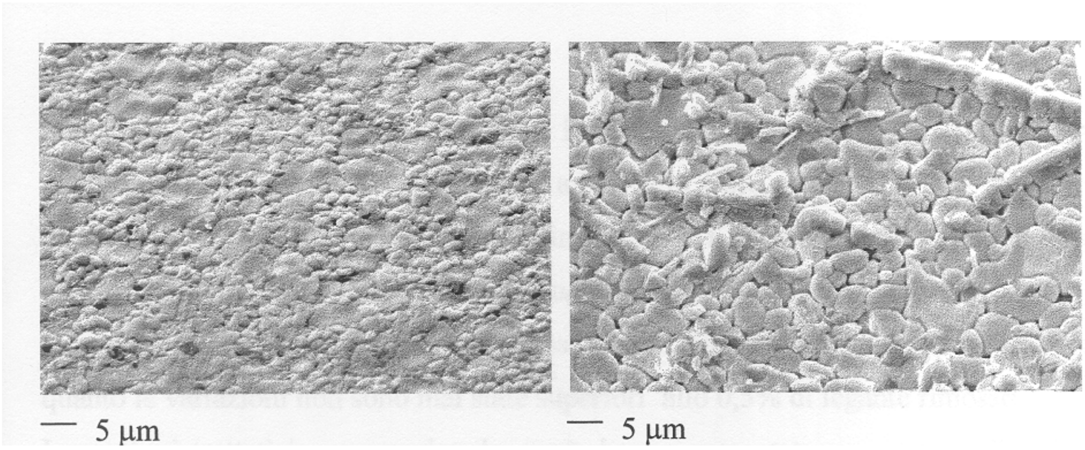

Figure 5: SEM micrograph of the surface of the conventionally sintered parts previously subjected to conventional debinding (6 days, on the left) and microwave assisted debinding (20 hours, on the right)

Figure 6 shows the SAR distribution in the green parts subjected to microwave assisted thermal debinding on a SiC plate, in the optimized conditions determined by coupling numerical simulation and Design of Experiment (DoE) techniques.

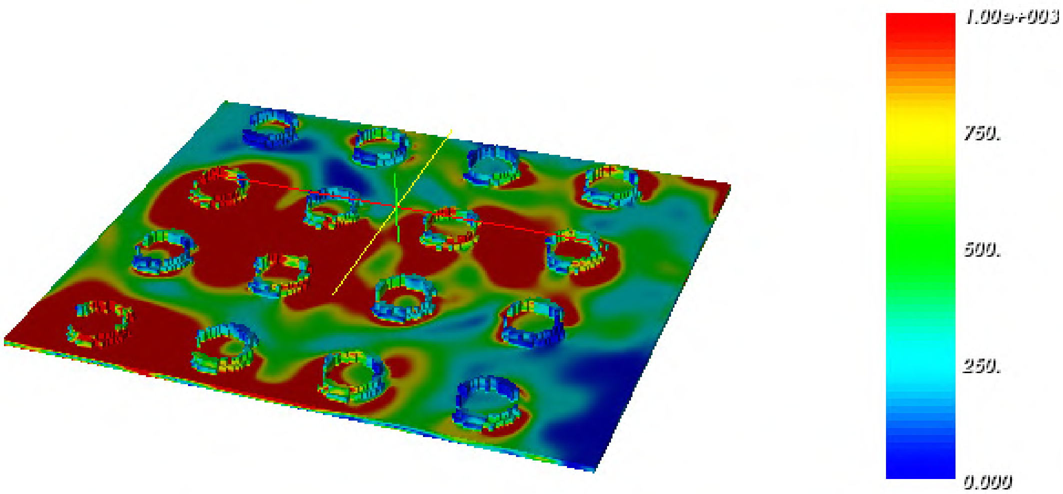

Figure 6: SAR distribution in the green parts and in the underlying SiC plate used for microwave-assisted thermal debinding of stainless steel rings obtained by MIM

The obtained brown parts possess a compressive strength much higher than what achievable by conventional heating, due to the occurrence of pre-sintering triggered by discharge phenomena induced by the electric field concentration in the space between the conductive particles [21].

2.2 Post combustion of ashes

Drying and rapid heating of ashes resulting from the combustion of lignite for large scale production of electrical power were laboratory performed in order to develop a prototype microwave furnace [22, 23]. Such an apparatus is capable of recreating the temperature and atmospheric conditions existing at the end of the combustion process by operating a 750 W magnetron at 2.45 GHz in an air-tight applicator (Figure 7).

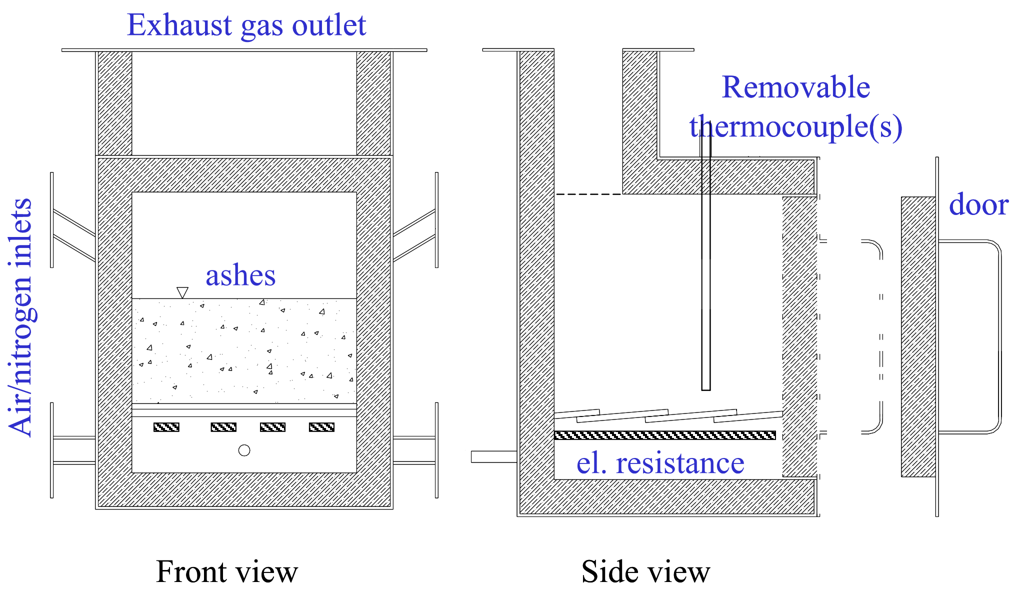

Figure 7: microwave applicator for studies of post-combustion of ashes: 4+1 gas inlet/outlet ports, resistance heating of the bottom of the applicator, temperature measurements at three different levels of the load

2.3 Recovery of exhausted alumina catalysts

Polluted alumina porous spheres, 2.0-2.5 mm in diameter, used as catalyst in organic reactions, can be successfully restored by fast microwave heat treatment in 2.45 GHz multimode cavity. A complete recovery of few grams of spheres was accomplished in 6-8 minutes at 600°C, which is from two to four times faster when compared to conventional heating [24]. The microwave selective and volumetric heat treatment allowed the transfer of power mainly towards the organic part, which has been rapidly decomposed, maintaining the alumina support unaltered as far as pore size and interconnectivity is concerned.

Figure 8 shows a comparison between conventional and microwave heating cycles.

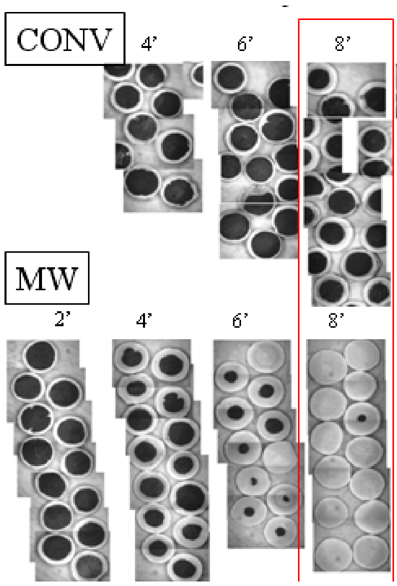

Figure 8: Comparison between conventional (CONV) and microwave (MW) heating of the porous spheres, showing how the pollutants, in black, are progressively removed (T= 600°C, time is indicated in minutes)

2.4 Ion exchange

Microwaves at the ISM frequency of 2.45 GHz have been applied to heat the molten potassium salt bath used for ion exchange of silicate glasses. A commercial soda-lime silicate glass has been used in order to investigate the processing time and the exchange depth resulting from the microwave assisted treatment, compared to the conventional one. Provided the molten salt, having a high electrical conductivity, does not shield the glass sample from microwave exposure, there is evidence of an increased ion mobility under microwave irradiation. In particular, this is confirmed by the two times higher measured diffusion coefficient and by the increased potassium concentration in the exchanged layers [25].

3. High temperature applications

All the following applications involve temperature higher than 800°C. For these MAG laboratory has a number of dedicated furnaces and refractory containers and shields. The preferred temperature measurement device is a sapphire fibre which allows contact temperature measurements without affecting the electromagnetic field distribution inside the applicators. However, optical pyrometers are used as well, but providing information only on the surface temperature.

3.1 Sintering of ceramics

Powders tendency to densify can be accelerated and somehow controlled to obtain porous materials by microwave treatments. Depending on the nature of the powders (conductive, dielectric) and their dimension and arrangement, direct microwave heating and localised overheating can occur due to electric field concentration in the space between the particles, as well as due to the presence of the magnetic field.

This can trigger more efficient transport phenomena (breakdown phenomena promotes the existence of liquid d phases or evaporation/condensation) which enhance sintering [26]. So for sintering is proved to be faster under microwave heating than without electromagnetic field presence

3.2 Crystallization of glass ceramics

Glass transforms spontaneously into the corresponding crystalline form/s once the temperature is high enough to allow atomic movements towards reorganization. The crystallization path of complex glassy composition has been proved to be altered by the presence of microwave, some metastable phases can be skipped, purer materials can be obtained in the case of silicate glasses. In many cases the rapid devitrification produced unusual microstructure, and the inverse temperature profile favored bulk nucleation instead of surface nucleation [27].

3.3 Processing of glass matrix composites

The application of microwave energy at 2.45 GHz frequency, can be exploited for the fabrication of glass matrix composites containing SiC fibres [28], metallic particles [29, 30] and metallic fibres [31, 32] in the particular case of glass powders. Metallic inclusions dispersed in a dielectric matrix led to the preparation of light-weight materials with controlled porosity, which present a peculiar microstructure generated by the inverse temperature profile present in the body heated by microwave irradiation. Figure 8 shows an example of a borosilicate glass matrix loaded with Hastelloy X fibres, which tend to concentrate the electric field at their tip, locally overheating the glass matrix and improving adhesion or promoting bubble formation. A different pore size and distribution is encountered if the samples are heated in the maximum of the electric or magnetic field.

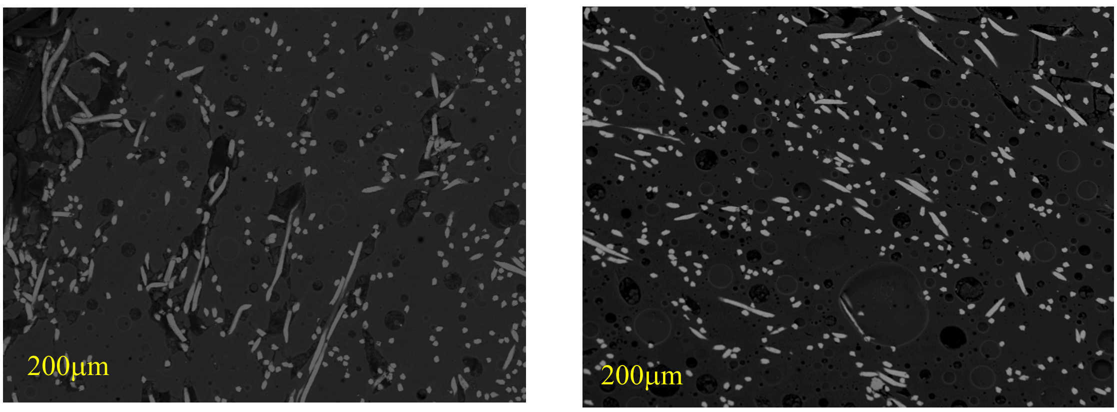

Figure 8: 10vol % Hastelloy X fibres dispersed in a borosilicate glass matrix, subjected to microwave heating in the maximum of the magnetic field (left) or of the electric field (right) in a single mode applicator

3.4 Melting and vitrification

Powders and bulk materials can be vitrified by microwave heating, benefiting from the reduced thermal capacity of the system, which roughly corresponds to the load itself, without involving the furnace, which is kept substantially colder. Thermal runaway, on the other hand, assures a rapid increase in temperature which culminates in the melting process itself. Moreover trough microwave heating was also reached the rapid inertisation, vitrification and the consequent recycling of asbestos containing materials [33, 34].

3.5 Microwave metallurgy

In this particular field, MWs were applied in the sintering, melting, surface treatments and intermetallics synthesis.

3.5.1 Microwave assisted combustion synthesis of high performances materials

Combustion synthesis (CS) exploits the energy generated by highly exothermic reactions between loose powder mixtures. These mixtures have to be ignited by an external energy source and when the ignition temperature is reached, no other energy is required and the reaction spontaneously proceeds thanks to the heat generated by the exothermic reaction itself. Among the many different techniques of initiation of CS processes, it was recently demonstrated that microwave (MW) heating is probably the most attractive one, due to its possibility of transferring energy, and not heat, directly to the reacting powders [35]. This kind of electromagnetic activation is generally referred as microwave assisted (or activated) CS (MACS). This leads to the possibility of conveying energy to the reacting powders, not only during, but also after the CS occurred, thus allowing to control the heating behavior at the reaction front, which becomes no longer affected by the inversion of the heat flow, typical of conventional heating.

CS is currently exploited by our group for the obtainment of a wide variety of high performances materials such as intermetallic compounds (NiAl [36], CoAl), CERMET composites (NiAl-SiO_2) and for joining high temperature ceramics [37]. This process is also exploited to realize high performances coatings, where a controlled reaction between the substrate and the intermetallic coating provides excellent adhesion and influences the coating thickness. [37].

3.6 Microwave plasmas

Microwave have been used to promote plasma formation in reactors dedicated to high temperature materials processing [38] or to PVD/CVD [39]. Numerical simulation allowed to maximize energy efficiency of the system and, in case of plasma sources for coating technology, to provide a homogenous generation of plasma. A prototype of the novel microwave plasma source is shown in figure 9, comprehensive of impedance matching devices and generator.

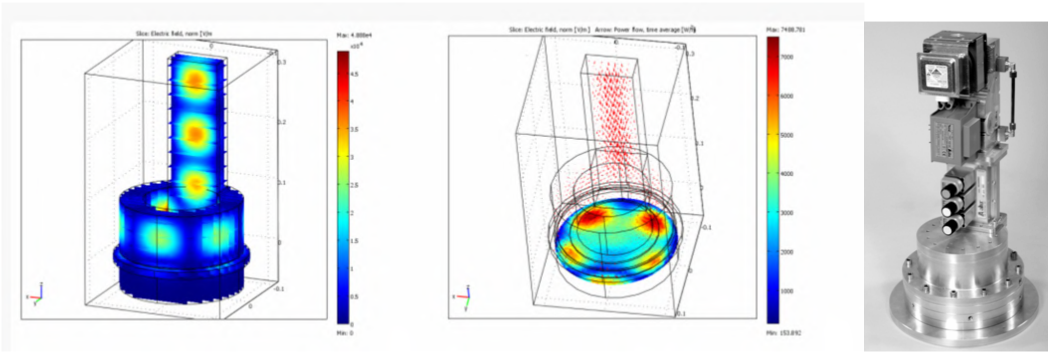

Figure 9: Microwave plasma source[40]: (from the left) numerical simulation of the electric field intensity in the empty applicator, 2.45 GHz excitation at port – slice plot; electric field intensity in the upper part of the cylindrical cavity of the loaded applicator; prototype (courtesy of Alter Srl)

4. Modeling and applicators design

The use of numerical simulation, in fact, allows to better design applicators, as well as to shorten time to market, or to help understanding what is happening to a material when exposed to microwaves.

Two commercial software are currently used by our group for these purposes: Concerto (Vector Fields, U. K.) and Comsol Multiphysics.

INSTRUMENTATION

The instruments available at MAG's laboratories include commercial multimode applicators, self constructed multimode systems, different kinds of single mode systems and several devices for temperature and dielectric properties measurements.

Commercial multimode applicators are used for a wide range of applications especially in the materials heating treatment and in the digestion of materials before elemental analyses.

The main systems available for experimental activity and materials processing are:

- TE_{103} applicator, up to 3kW power, 2.45 GHz
- TE_{103} applicator, up to 3kW power, 2.45 GHz, with ports for treatments in maximum of E or H field
- WR340 waveguide based applicator for fibres, filaments and small extruded products, up to 3kW power, 2.45 GHz
- Horn applicator (open or as feed in closed cavity), up to 3kW power, 2.45 GHz
- Cylindrical applicator, up to 3kW power, 2.45 GHz, up to 8 bars, controlled atmosphere
- 2 m^3 rectangular applicator, fed by slotted waveguide, up to 3kW power, 2.45 GHz, port for continuous processing of up to 1 m large products
- Multi-pass meander applicator, up to 1.2kW power, 2.45 GHz, combined with hot air, for paper and thin boards
- Microwave plasma torch, up to 3kW power, 2.45 GHz
- Tapered microwave plasma torch, up to 0.3kW power, 2.45 GHz
- MLS ETHOS TC, Milestone, 100 ml, up to 1.6 kW power, 2.45 GHz
- CEM MAS 7000, up to 1kW power, 2.45 GHz

- Milestone MicroSynth CFR Continuous Flow Reactor, 400 ml,1.6 kW power, 2.45 GHz
- Circulators, directional couplers, power meters, impedance matching devices

An update of the available equipment is visible on the website www.mag.unimore.it

EDUCATIONAL ACTIVITY

MAG is active in organizing national schools on high power microwave irradiation as well as participating with seminar to AMPERE Short Course or teaching activities organized by other institutions/association.
Personnel from MAG are particularly dedicated to spread out results to industrial associations and other Italian universities.
They have two representative in the Italian Electromagnetic Committee for regulations.

COLLABORATION

MAG is currently involved in several collaboration with universities and industries institutions. In Italy with Politecnico di Torino, Politecnico di Milano, Università di Trento, Università di Genova, Università di Napoli “Federico II”, Università di Salerno, Università di Palermo In Europe with Polish Academy of Science (PL), Institute of Geotechnics-Slovak Academy of Sience, Kosice, Slovakia. Universidad de Valencia (E), University of Oradea (ROM), Imperial College (U.K.). Worldwide with Inha University (South Korea), Kasertsart, Bangkok, Thailand, Yunnan Normal University, Kunming People’s Republic of China.
Many industrial partners have been collaborating with MAG, developing new equipment, products or processes.

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NAXAGORAS TECHNOLOGY SAS

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HISTORY

The Naxagoras Technology company started on July 2nd, 2007. This start-up develops GERM (Groupe d'Etudes et de Recherches sur les Microondes) microwave research success. Three shareholders constitute the company (SAS) with capital amounts of 60 KEuros. The managing team is constituted by Dr. C. Lohr (manager and shareholder) and Pr. Didier Stuerga (consultant and shareholder). C. Lohr holds PhD in physical chemistry (University of Burgundy). D. Stuerga is full Professor at the University of Burgundy. He is the manager of the GERM of the Institute Carnot of Bourgogne. They have both patented their original process for elaboration of functional nanomaterials. Naxagoras technology has an operating licence of this patent which is a University of Burgundy property. For the time being, the operational premises (pilot plant) of the company are located at the University of Burgundy. The company is member of the Allisé-Plasturgie network. Naxagoras technology team is considered as expert in the field of new materials as nanomaterials. The canvassing has been initiated. The technological validations of our products are in progress. These technological validations are mandatory to convince our future customers that our products are compliant with their requests: to guarantee and to improve one or several functions.

ACTIVITIES

Naxagoras Technology offers two kinds of services: nanomaterials production on demand and custom-made research and development. The nanomaterials are commercialized as active bases ensuring innovative and adapted functions. Nanomaterials with catalytic properties and especially those dedicated to purification, disinfection and cleaning up are targeted. The marketed products are nanometre active bases (single and complex oxides) provided as slurries for coating or casting slip (from few cubic centimetres to hundred of litters).

The active bases ready to use are proposed instead of raw nanomaterials. Indeed, the base actives slurry in ethanol makes easier the nanoparticles trapping during a manufacturing process. Such slurries reduce the level of handling and nanomaterials loss. These active base slurries ensure turnkey nanoformulations. Consequently, customers gain in efficacy and process safety for their final products. Naxagoras Technology is aimed at producing innovative nanomaterials with original characteristics and functionalities.

1. Nanomaterials and environmentally friendly applications

Nanomaterials have become a magic word in our technologic society and they dominate science and science-funding today. They present great promises and opportunities for a new generation of materials with improved properties for many applications as sensors, optoelectronics, energy storage, separation and catalysis.

The field of nanomaterials is very large and includes any material having nanometer dimension as nanopowders, colloids but also monolayers, thin films and multilayers. When crystalline dimensions are reduced to nanometer sizes (ranged between 1-500 nm), new properties result and surface effect dominate particles behaviour. For example, a body-centered cubic Ag particle of 100 nm in diameter has 2% of all the constituent atoms at the surface, the one of 10 nm has 16%, and the one of 1 nm has 88% constitute. The mechanical properties of nanostructures such as strength are dominated by the interfacial properties and it was established that materials with smaller grain size are stronger. The electric and magnetic properties can be unusual. Some multilayer and granular materials exhibit specific magnetic properties as gigantic magnetoresistance effect required for non-volatile memory devices and magnetic recording and reading heads. In chemistry, catalysts being mostly nanoparticles are typical nanomaterials, perhaps the first nanomaterials to be widely used in applications.

Photocatalytic properties of titanium nano-oxides are the most amazing applications. When photocatalyst titanium dioxide absorbs ultraviolet radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. The titanium dioxide photocatalyst has been found to be more effective than any other antibacterial agent due to long-term anti-bacterial effect (three times stronger than chlorine, and 1.5 times stronger than ozone). On the deodorizing application, the hydroxyl radicals accelerate the breakdown of VOCs (Volatile Organic Compounds) to produce water carbon dioxide not harmful to humans thus enhance the air cleaning efficiency.

2. Economic breakthrough of nanomaterials

Nanomaterials present a tremendous opportunity for chemical industry to introduce a host of new products that could energize economy, solve major societal problems, revitalize existing industries, and create entirely new businesses. Improved catalysts, primarily in the chemicals industry and for improved diesel engine combustion in the trucking industry, provide the most significant opportunities for energy reduction. Nanomaterials will have positive impacts beyond energy savings in waste reduction. The use of more selective catalysts in refining will reduce the production of wastewater and toxic emissions. The use of improved hard coatings can lead to elimination of the substantial amounts of anti-corrosion additives currently used. In the shipping industry more environmentally friendly antifouling coatings can eliminate pollution abatement costs for ship-owners.

After more than twenty years of basic and applied research, nanomaterials are gaining in commercial use. Nanoscale materials could be found in specific applications of electronic, cosmetics, automotive and medical products. According to several commercial inventory 800 manufacturer-identified nanomaterial-based consumer products are now currently on the market [1]. Companies based in the USA have the most products, with a total of 426, followed by companies in Asia (227), Europe (108), and elsewhere around the world (38). Up to now, many efforts are being devoted to fabricating nanomaterials in order to exploit their specific properties. Unfortunately, commercial utilization of these new nanosized materials still stays quite limited.

The absence of cost-effective nanopowder production methods is responsible for this lack of industrial use.

3. Nanomaterial routes

Uniform-sized nanopowders and colloids of metals, metal oxides and other compounds could be prepared by a great variety of methods. They can be classified into three principal routes:

Solid Route (SR) uses solid precursors. In fact, this way could be the first step of the high temperature ceramic processing followed by shape forming, firing and sintering of the powders or melting in the case of glasses. Both steps usually require high temperatures and consume a lot of energy. Among solid state ways, we find mechanical methods as ball milling and mechanical attrition. The main drawbacks of these methods are powder contamination due to balls and low production rates (1-5 g/h) depending on the materials and size of mill.

Vapor Phase Routes (VPR) with vapour condensation, plasma induction, electrical spraying, thermal decomposition and chemical reaction. Conceptually these are the simplest methods for nanopowders preparation. If these methods are well adapted for high purity metals and alloys nanopowders, the agglomeration level, the wide size distribution and an expensive device are the drawbacks which limit considerably their use. New variant using gaseous phase like CVD, MOCVD or vacuum systems such as laser ablation, sputtering, MBE, requires more energy than standard high temperature processing without showing a satisfying enhancement of size distribution control.

Soft Solutions processes (SSP) may be also regarded as similar to soft or mild chemistry. These methods (decomposition, oxidation, reduction, hydrolysis of metal salts, homogeneous precipitation, micro emulsion) lead to a great variety of compounds with tailored size and morphology. The size distributions obtained are the narrowest between the three classes of methods. Soft Solution Processing (SSP) without firing, sintering or melting step could be defined as environmentally friendly processing compare to solid or vapour phases routes.

4. Microwave soft solutions processes

Microwave heating has become a very popular and useful technology in organic chemistry but it is still an emerging technology nanomaterials processing. The number of publications on organic chemistry is growing rapidly with almost more than two thousand papers since the pioneering work of Gedye in 1986. A general overview of microwave organic reactions could be found in Loupy [1]. Most of these publications describe strong time saving and conversion enhancement for a wide range of organic reactions especially when carried out under solvent-free operating conditions. These environmentally friendly operating conditions are called *Microwave Green Chemistry*.

Among inorganic and microwave processing of materials, an important place is occupied by ceramics processing. This kind of process is called high temperature processing (1000-2000°C range). It refers primarily to the process of inorganic materials by activating mass transport phenomena based on diffusion. In solid state reactions, species diffusion controls the kinetics and reaction rates are unworkably slow below this temperature range. These ceramics processing cannot lead to nanomaterials.

Inorganic compounds could be also obtained by solution chemistry from soluble precursors. Specific operating conditions can reach nanosized materials. Several authors have used microwave heating of inorganic precursor solutions in order to produce nanomaterials and specially nanoparticles. The publications number is close to one hundred but the progress is regular since fifteen years. Various methods have been used as decomposition, oxidation, reduction, hydrolysis of metal salts, homogeneous precipitation, and micro emulsion. They lead to a great variety of compounds with tailored size and morphology. The size distributions obtained are the narrowest between the three conventional classes of methods (solid, vapour and solution routes). Many inorganic products with nanometric size have already been synthesized by these microwave processes. These products will be described and classified from usual species such as oxides, hydroxides, carbonates, to highly complex ion exchangers, hybrid fluorides, ceramic phosphates and nanocomposites. Various criteria as size distribution, particles morphology, side products, cristallinity, crystalline and formation mechanism will be compared between the different microwave operating conditions. A general overview of products [3] and microwave processes [4,5] has been published.

Soft Solution Processing (SSP) without firing, sintering or melting step could be defined as environmentally friendly processing. Moreover, the total energy consumption among the three processing routes (solid, vapours phases routes and solutions) should be the lowest one in solutions systems. Thermodynamic data demonstrated that soft solution processes allows one to fabricate in aqueous solutions shaped/sized/oriented particles in only one step without excess of energies for firing, sintering melting and without expensive equipment, providing an environmentally friendly route for the preparation of advanced materials. Hence, the thematic of nanomaterials, especially from solutions, appears as the most significant example of microwave heating advantages within inorganic chemistry. Naxagoras Technology only develop nanoparticles soft solutions processes specifically devoted to growing and crystallization of nanomaterials. Even within this limited area a fourth route to nanomaterials called *Microwave Soft Solution Process* (MSSP) could be considered.

5. Microwave induced thermohydrolysis

5.1 The conventional basic route

The *basic route* is the operating conditions mostly used. The *basic route* uses water solutions with high values of pH. Water and metallic salts are the reagents. Water is a good solvent with high dielectric losses. Anions could be chloride, nitrate, or sulphide. The first step is the addition of sodium hydroxide. A basic solution is obtained with precipitation of hydroxide. The second step is microwave heating with or without hydrothermal conditions. Hydroxides, oxohydroxides or oxides are produced. Finally the third step is washing to eliminate anions and recover powder. These operating conditions don’t lead to good control of particles size distribution. Moreover, several oxides are only obtained after thermal treatment of the powder. This step induces growing of crystal size and it is difficult to keep the nanometric size.

5.2 The conventional thermal hydrolysis route

Thermal hydrolysis by conventional heating has been used for about three decades. This technique leads to narrow size distribution powders from precipitation in homogeneous solutions, by adjustment of precursor concentration, temperature and pH. Colloidal metal hydrous oxides and basic metal compounds could have been prepared by forced hydrolysis. This method is really time-consuming as it can be seen from the following example: 100°C heating for seven days was required to obtain well defined hematite micrometer sized particles. Thermal hydrolysis consists in enhancing deprotonation of hydrated metal cations in aqueous solution by increasing temperature. This treatment is driven in very acidic conditions even without acid addition because metallic cations show high acidity in aqueous solutions.

5.3 The microwave induced thermal hydrolysis route

Microwave thermal hydrolysis has been studied and optimized by the author. The advantages of using microwaves for thermal hydrolysis, compared to conventional heating are the attainment of higher rates of heating and the avoidance of conduction phenomenon due to core heating of reactants. Moreover, microwave synthesis can be done in autoclave, allowing hydrothermal conditions (higher temperature, under pressure syntheses) to be reached. By enhancing heating rate, microwave thermal hydrolysis is greatly more efficient than conventional process and particles of equivalent qualities can be obtained with a treatment time reduced by one or two orders of magnitude.

This *microwave induced thermohydrolysis* leads in one step to oxides nanoparticles even as stable colloid suspensions. This new route is a direct route to oxide from metal salts without precipitation of hydroxide. Nucleation could be induced by microwave heating. Moreover, core heating can induce a homogeneous nucleation. The symbiotic association between thermohydrolysis and hydrothermal microwave heating allow obtaining monodisperse nanoparticles within only a few minutes.

6. From laboratory to industrial scale

According to these results and in order to scale up the process, a pilot plant has been designed by GERM. This pilot plant uses 6 KW microwave source coupled with an original microwave applicator with high level of electric field. Typical batches are closed to 100 liters of salts aqueous solutions. Specific surfaces of powder are close to several hundred of square meter by gram. In fact, colloidal solution ready to use could be produced. Nanomaterials could be single or complex oxides (Fe, Ti, Zr, Y, Ce) produced by microwave treatment without any further treatment. This original process for elaboration of functional nanomaterials has been patented by the University of Burgundy.

According to these results and due to specificities of microwave heating a fourth route to nanomaterials called Microwave Soft Solution Process (MSSP) could be now considered. Microwave appears as overwhelming tools to induce nucleation of monodisperse nanoparticles. Oxide nanoparticles (Fe, Ti, Zr, Y, Ce) are produced with only few seconds of microwave treatment without any further treatment. These straightforward operating conditions lead to nanoparticles suspension without any further treatment or work-up. Contrary to conventional ovens, where heating goes up by diffusion through reactor surface and diffuses to bulk, microwave heating leads instantaneously to spatial distribution of thermal sources within the heated solution. The main benefits for thermally activated processes as nucleation stem from volumetric or core heating induced by thermal conversion of electromagnetic energy. Consequently, microwave heating is very attractive for chemistry applications and material processing, especially for nucleation and growing processes, due to its in situ mode of energy conversion able to allow decoupling between nucleation and growing processes.

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ENEA MICROWAVE LABORATORY

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HISTORY

During 2007, the FIS-NUC (Nuclear Fission) group at ENEA, had to relocate the the microwave (MW) laboratory from Bologna to Brasimone the site of cleared experimental nuclear reactor PEC of ENEA.

With the help from ANSTO, ENEA personnel started the laborious process of setting up the laboratory and collecting together in one site the technology for dielectric heating with MW and with the cold crucible operated at radiofrequency (RF). The aim was that of implementing a joint ENEA/ANSTO agreement for applied research in the confinement of pyrometallurgical waste form containing caesium and strontium with matrixes similar to **SYNROC (SYNthetic ROCk)** for which ANSTO holds patents, within the frame of **EUROPART**, **EUropean Research On Partitioning** integrated project.

Large areas available on the ground floor (with separate vehicle entry) and on the floor above in the south-west wing of the building that housed the PEC "control room", have been allocated for the MW laboratory. The electric switchboard installed was designed to a power supply of 100 kW in view of future expansion of the equipment of the laboratory.

The group is ready to promote the transformation of the exPEC "CHILLED WATER BUILDING" into a Technological Hall since the building is suitable for hosting the facilities aimed to scale up new laboratory processes to faisibility demonstration level.

INSTRUMENTATION

Major equipment at ENEA Microwave laboratory, and now fully operating, include:

- **1 microwave oven**, model Panasonic PRO II NE 1880, variable power microwave furnace, multimode chamber (Internal dimensions WxHxD mm 535 x 250 x 330), operating at 2.45 GHz, M/W Output Power 1800W, Power Requirement 14.8 Amp, cycle counter,16 touch control programmable programs,
- **1 open field microwave applicator** box made of stainless steel (750x850x750 mm) hermetically sealed containing 3 magnetrons National YJ1600, each of 6 kW nominal power, operating at 2,45 GHz frequency. installed on a remotely operated caterpillar
- **1 radio frequency apparatus** with 20 kW power supply, pulse width at 50-60Hz 22μS, pulse train frequency 25KHz.

ACTIVITIES

The experimental activities are performed by ENEA personnel together with MAG group at the Department of Materials and Environmental Engineering of the University of Modena and Reggio Emilia, and taking advantage of the collaboration with ANSTO.
Research has been undertaken in the following fields:

- Production of biofuel by MW enhanced heating and familiarization of the technological advances associated with the European objectives in "*green chemistry*".
- Enhancing surface characteristics of plastic and cellular laminates with MW devices developed by industry and certified at the laboratory.
- Testing open field MW applicators for the treatment of contaminated sites and for transforming asbestos into harmless silicate glass with a process developed and patented jointly by ENEA and UNIMORE.

Fig 1
ENEA PEC nuclear experimental reactor at Brasimone (BO)

Fig 2
South-west wing of the building: first and second floor are occupied by MW labs

Fig 3
View of exPEC
"CHILLED WATER BUILDING"

Fig 4
MW oven Panasonic PRO II

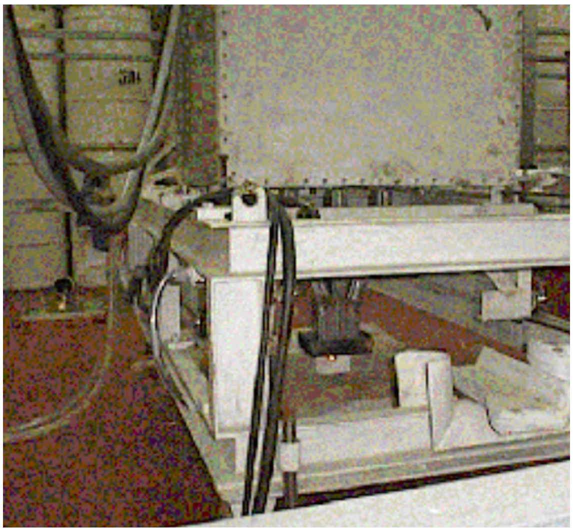

Fig 5
Open field MW applicator

Fig 6
Specimen melting in crucible in MW oven

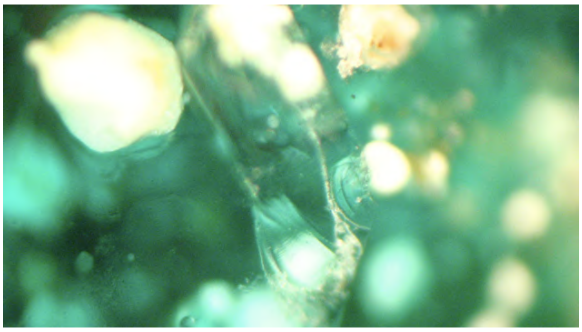

Fig 7
Green glass formed showing what appears to be pollucite crystals.

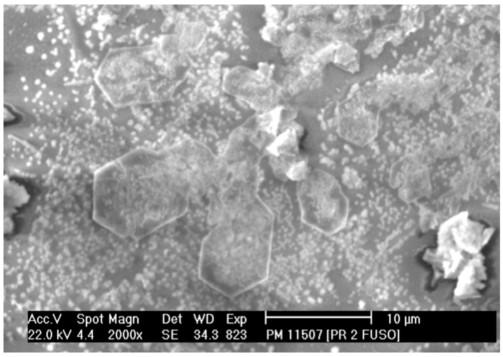

Fig 8
SEM analysis of glass-ceramics from EUROPART WASTE

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C. Mazzocchia, G. Modica, F. Martini, R. Nannicini, D. Venegoni
"Biodisel and fame triglicerides over acid and basic catalysts assisted by microwave"

M. Annibali
"*Asbestos's degradation bi microwaves: application to a real cas*e"

F. Martini, G. Modica, C. Mazzocchia, R. Nannicini
" Effetto delle microonde sull'esterificazione dell'oleina con etanolo"

ALTER POWER SYSTEMS

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HISTORY

Alter Ltd company was established in 1986 and its main activity is to design and produce microwave generators, magnetron power supplies, microwave sources and waveguide components for industrial microwave heating, microwave plasma coating or scientific processes.

From its foundation Alter's mission has been: "To promote the utilization of the microwave energy with proficiency, innovation and quality."
To reach such goal Alter invests significant resources in R&D to meet demands of customized solutions.

ACTIVITIES

During these 20 and more year, the attention dedicated to the R&D activities allowed Alter to have today one of the most extensive product range in magnetron power supply ranging from 300W for small laboratory chemical reactor, to the multiple power supply MPS series for magnetron up to 100KW for high technological CVD processes.

Alter has not limited R&D activities on the power supply side, but it also invests energy on design of custom microwave applicators and, in recent time, on developing its line of microwave triggered plasma source, culminating with the design of the "TORPLA" a toroidal plasma source (patent pending).

Thanks to the know-how acquired over the years and to an highly skilled technical structure Alter is able to develop and manage complex projects from the assembling to the final tests.

1. Adjustable power microwave generators

Adjustable power microwave generators in switching technology, with power ranging from 300W to 30 kW for the 2.45 GHz frequency, from 5 to 90 kW for 915 MHz (US) or 896 MHz (UK) frequency.

This kind of microwave generators are suited for critical application like semiconductor industry or microwave plasma application.

This product line includes also pulsed microwave sources developed for plasma coating application.

2. Fixed power microwave generators

Fixed power microwave generators with traditional L-C unit (ferro-resonant), with power ranging from 1 to 3 kW and relative complement accessories.

Latest addition to this product line is the new family of fixed power microwave generators in switching technology, that combines the technical advantages of a switchmode power supply to the cost effectiveness of the traditional ferro-resonant design.

This kind of microwave generators are suited for application where the control of the output power is non critical, like industrial microwave heating and industrial microwave drying application.

3. Accessories and waveguide components

Accessories and waveguide components such as: Connecting cables, Isolator, Magnetron, Tuner 3 stubs, Waveguides supplied in standard bars or on Customer specs.

4. Microwave-triggered plasma generator

Microwave-triggered plasma generator for processes in forced vacuum and for processes in atmospheric pressure.

CERTIFICATION

Since May 2000 Alter has obtained by DNV authority the certification of its Quality System according to UNI EN ISO 9001/2000.

COLLABORATION

A long term co-operation with the Material Engineering Department of the University of Modena and the National Institute for Physic of Matter of Modena enhances Alter's technical capability.

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SAIREM, MICROWAVE & RADIO FREQUENCY

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HISTORY

1978:	Foundation of SAIREM by Mr. Jean-Marie JACOMINO presently President of SAIREM. From the beginning SAIREM specializes in microwave and radio frequency systems for laboratory and industry.
1990:	Starting of export sales.
1997:	SAIREM exports 40 % of its production, turnover is 3 M€ and the company employs 20 people.
1998:	Construction of new buildings in Neyron near Lyon covering 1,600 m².
1998:	Creation of a Spanish subsidiary SAIREM IBERICA in Barcelona. The target is to develop SAIREM sales in Spanish-speaking countries. Creation of SAIREM web site: http://www.sairem.com.
2007-2008:	Development on the world market, turnover: 6.2 M€ (50 % export sales).
2009:	Building of a 2nd production hall and extension of the electronic department.

ACTIVITIES

1. Plasma

SAIREM offers a large choice of microwave and radio frequency generators in the following frequencies and powers:

a) 2.45 GHz: 300 W to 15 Kw, (Figure 1)

b) 915 MHz: 5 to 100 kW,

c) 27.12 MHz: 400 W to 100 kW,

d) 13.56 MHz: 400 W to 100 kW.

SAIREM also offers all related cavities (Surfaguide, Evenson, etc.) and wave guide components (tuners, sliding short-circuits, etc.).

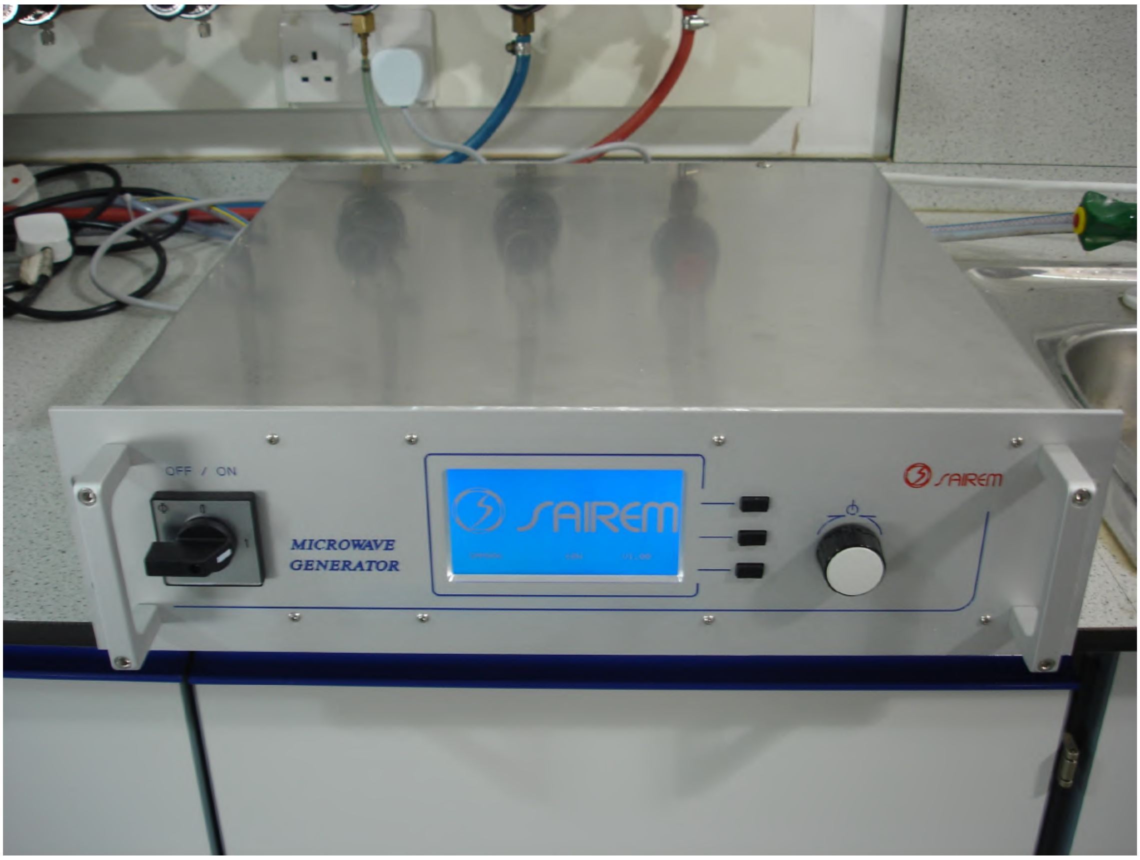

Figure 1. Solid state generator at 2.45 GHz

2. Food processing

During the last 15 years SAIREM has developed a complete range of microwave and radio frequency machines for food processing. It can be used for the following applications:

- tempering/thawing,

- cooking/pasteurisation,

- heating.

3. Chemistry

SAIREM is developing micro-wave systems for synthesis, extraction and analysis (laboratory and industrial equipments) (Fig. 2).

Figure 2. Vegetable oil extraction laboratory reactor

INSTRUMENTATION

SAIREM has a number of measuring devices such as spectrum analyser, network analyser, wattmeter… and a whole range of microwave or radio frequency demo machines for laboratory or industry (powers : 1.2 to 10 kW).

GRANTS and CONTRACTS

SAIREM participates in European contracts such as ICARE. It has also a number of contracts in the food processing industry.

REFERENCES AND PATENTS

1. Microwave U-reactor, Sairem's patent pending.

2. Coaxial reactor, Sairem's patent pending.

EMitech

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HISTORY

EMITECH s.r.l. (Electro Magnetic Innovative Technologies) is a company boasting a consolidated know-how in industrial applications of electromagnetic energy.

EMitech's mission is the design and manufacturing of microwave technology based systems to replace obsolete and highly polluting technologies.

In order to achieve its objectives, EMitech invests many economic and human resources in research and development activities and by participating to national and international research and development projects.

Thanks to these activities, EMitech enhances the competence of its staff, a multidisciplinary team composed of professionals with proficiency in various fields like engineering, chemistry, electronics, food science etc.

ACTIVITIES

Today EMitech has a leading position in the construction of shielded reverberation chambers thanks to its particular know-how, which is the outcome of long experience and an attentive research on the effects of microwave dielectric heating.

EMitech's first achievement and main product line is called Mi.Sy.A. (Microwave System for Art). It is a system using microwaves for carrying out pest control treatments of artistic objects of wood, paper and cloth (including antiques, furniture, tapestries, archival documents etc.) with evident advantages in terms of effectiveness, efficiency and safety.

Mi.Sy.A. is composed of a shielded treatment chamber (Faraday Cage) operating at a frequency of 2,45 GHz. The electromagnetic field which is generated at its interior is uniform and isotropic thanks to an electro-mechanical apparatus (stirrer) enabling a constant electromagnetic modes mixing. Access to the treatment chamber is possible through a shielded door provided with all necessary safety devices.

The electromagnetic generation system is composed of a three-phase generator of microwaves whose power depends on the particular application requirements.

Mi.Sy.A. is endowed with sophisticated devices like fiber optic sensors, infrared pyrometers, electronic balances, programmable logics for control and monitoring of the process parameters.

The successful application of Mi.Sy.A. in the field of conservation and restoration of precious ancient objects and sometimes of real works of art led EMitech's research activities to further developments in those sectors where efficacious alternatives to the use of toxic and polluting gases are urgently sought, such as disinfestation and drying of foodstuff, disinfestation of wood packaging materials (mainly pallets), sterilization and biological sanification.

As regards the agro-food sector, EMitech's microwave technology enables to disinfest foodstuffs of vegetable origin (mainly cereals and legumes) and also products for animal nourishment. Products are treated before the storage phase through this physical method which is totally compatible with organic farming. During the treatment the electromagnetic field into the reverberation cavity is opportunely controlled so that the energy spreads uniformly in the cavity's portion where products pass through.

The method is efficacious in terms of both the product's quality preservation and the mortality of pests in all life stages (eggs, larvae, pupae and adults). Pests, infesting food, are readily destroyed by overheating because of the microwave effects that make increase their inner temperatures up to the lethal values ranging from 56 to 60°C.

CERTIFICATIONS

The need to reach good quality and efficiency levels in all productive processes and a significant reduction of environmental hazards led EMitech to an unavoidable engagement, the implementation of Quality and Environmental Management Systems.
EMitech has achieved the following certifications:

- Quality Management System in conformity with UNI EN ISO 9001;
- Environmental Management System in conformity with ISO 14001.

COLLABORATION

EMitech's main partners in research projects are scientific laboratories and academic institutions such as: the Marche Polytechnic University, the Department of Electronic Engineering and Telecommunications - Polytechnic of Bari, the University of Naples "Federico II"; IVALSA (Institute studying the valorization of wood and arboreous species); IFAC (Institute of Applied Physics); CRB - research centre "Bonomo"; Laboratory of Diagnostics for the Preservation and the reuse of materials - Polytechnic of Milan; Faculty of Engineering - University of Sannio, Faculty of Agricultural Sciences - University of Bari; Faculty of Agricultural Sciences - University of Foggia, CRA-ABP (Research centre for Agrobiology and Paedology); the Scientific Laboratory (GRS) of the VATICAN MUSEUMS; C2RMF – Research Centre of the French Museums (Versailles); LRMH – Research Centre of Historical Monuments (Paris); GIFruits - Tunisian Department for Environment, Food, and Rural Affairs.

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