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Smart materials and nanotechnology for energy retrofit of historic buildings

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Abstract – As energy-efficiency standards for buildings become increasingly stringent, using a traditional insulation material often means having to accept increasingly thick layers of insulation in walls, floors, and roofs. In renovation projects, even if it is possible to increase insulation thickness at all, significant aesthetic and functional compromises are often required to fit more insulation on the inside or outside of the building envelope. The article offers an analysis of the use of nanotechnological insulation materials and innovative phase change materials (PCM) in renovation of buildings, illustrating the possibility of integration into the envelope and the benefits achievable in terms of architectural quality, comfort and energy saving, with particular reference to the historic buildings subjected to architectural constraints.

Keywords **– smart materials, nanotechnology, phase change materials, building envelope materials, energy efficiency, energy retrofit, historic buildings, sustainable buildings.**

I. Introduction

The objectives of upgrading the energy efficiency of existing buildings imposed by European legislation – aimed at reducing greenhouse gases emissions by 80-95 % before 2050 – imply the need to identify technological solutions capable of preserving the architectural features of the building. Indeed, the EU Directive 2010/31 expressly provides that Member States may decide to derogate energy performance minimum requirements for "buildings officially protected for belonging to certain areas, or for their special architectural or historic merit". This need is even more felt in Italy, a country rich in historic buildings, subject to the provisions of the Code of Cultural Heritage and Landscape, Decree 42/2004. Due to the need to preserve authenticity and integrity, project proposals should focus on the use of innovative and affordable building renovation solutions that can deliver significant improvements in energy performance while ensuring indoor comfort requirements and architectural quality. The use of nanotechnological insulation materials and smart materials like phase change materials (PCM) in building refurbishment projects could allow to significantly reduce the energy requirements of existing buildings while maintaining their integrity and architectural quality, in order to achieve the goals of reducing primary energy consumption in the building sector.

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II. Energy efficiency and architectural quality

In order to promote energy retrofitting of existing buildings and facilitate the transition to nearly zero energy buildings (NZEB), 2012/27 EU Directive about energy efficiency requires that, by 30 April 2014, Member States shall establish a long-term strategy to mobilize investment towards the restructuring of the residential and commercial national building stock, both public and private. This strategy, to be updated every three years and submitted to the European Commission within the framework of the national action plans for energy efficiency, must include:

- a review of the national building stock based, where appropriate, on statistical sampling;
- the identification of restructuring approaches effective in terms of costs and relevant to the building type and climate zone.

In addition, the aforementioned Directive provides that, as from 1 January 2014, Member States must ensure that 3% of the total floor area of heated and/or cooled buildings owned by central governments, and occupied by them, is renovated each year to meet at least the minimum energy performance requirements set by the concerned Member State.

In this context, Italy has taken steps to approve a specific national plan aimed at increasing the number of nearly zero-energy buildings.

From preliminary studies (conducted in October 2013 on ISTAT 2010 - ENEA - ANCE – CRESME data) emerge significant results concerning the building stock of the country.

On the national territory insist in fact over 13 million buildings, slightly less than 90% of which for residential use and 5% not used.

As for the age of this building stock, about 43% of the buildings was constructed before the year 1972, i.e., has more than forty years, while of the remaining 57%, only 10% of the total is from after 2001.

Another interesting information is related to building types, showing a strong presence of extensive detached housing (26%) or with few floors (21%), with obvious effects on the methodologies to implement to contain overall energy consumption. Equally important is data regarding the characteristics of the buildings structure system with a prevalence of reinforced concrete from the 50s onwards.

III. Technological solutions for energy renovation of the building envelope

Whereas in new constructions energy efficiency starts from a building design aware of the environment and keen on technical solutions where building shape and orientation, room distribution and windows and shading systems positioning can strongly contribute to energy performance (e.g. by exploiting natural lighting and ventilation, winter solar heat gain and renewable energy sources), for existing buildings, in particular those with exceptional historic or artistic value, energy renovation can only focus on building envelope thermohygrometric characteristics, systems efficiency and, where possible, renewable energy use.

Regarding the building envelope, energy renovation aimed at reducing energy requirements during summer and winter may concern:

- the improvement of thermal insulation of opaque components (perimeter walls, floors on the ground or on open spaces, roofs) or transparent components (vertical or horizontal windows) in order to reduce energy loss during winter;
- the improvement of opaque components thermal inertia and external shading systems efficiency in order to reduce overheating during summer.

A. *Thermal insulation*

As regards the thermal insulation of external vertical walls instead, the possibility of intervention concerns installing an inner or outer insulating envelope or, where possible, filling the cavity with insulating material.

With equal insulating material and thickness, in all three cases the thermal resistance of the wall is obviously the same, but the insulating layer position has a strong influence on the dynamic behavior of the wall.

Insulation placed on the outside face of the wall (External Thermal Insulation Composite System) is particularly suitable in the redevelopment of existing buildings. Its application, in fact, does not require the removal of the users and can be performed during the normal course of maintenance works of the facade, thus minimizing installation costs.

Furthermore, the insulation reduces the thermal bridges of the structure, does not involve the risk of interstitial vapor condensation and provides protection from atmospheric agents for the exterior walls, as well as decreasing temperature swings with a significant reduction of internal tensions of thermoplastic origin. By maintaining the thermal mass of the inner wall, it is also particularly effective in case of continuous operation of the air conditioning, allowing to minimize air temperature fluctuations. Outside placement of the insulating layer also helps protecting the wall from solar radiation in the summer, slowing heat accumulation within the wall itself.

Inner insulation can be a viable solution in case of energy renovations of existing buildings where working on the external façade is not possible. Compared to external insulation solutions its application is faster, does not require external scaffolding and is cheaper; on the other hand, the insulation of existing buildings from the inside does not allow the elimination of thermal bridges and can often require the application of a vapor barrier to prevent condensation next to the insulating layer, with a consequent reduction of the overall wall permeability. Internal insulation is also more appropriate in environments with discontinuous use in which conditioning systems are frequently turned on and off.

In both insulating solutions, the use of conventional insulation materials, taking into account the minimum thickness needed to achieve the thermal transmittance values required by the regulations (between 6 and 10 cm), may often be incompatible with the building aesthetic and design, or, if placed inside, cause an excessive reduction of space or be incompatible with the finishes (brick molds, jambs, architraves, thresholds, etc.).

As regards, for instance, opaque vertical components of existing Italian buildings established before the application of Legislative Decree 192/2005, depending on thickness and type, their thermal transmittance is between 0,90 and 3,59 W/m^2K (see table 1) against a minimum requirement in the case of restructuring between 0,33 and 0,62 W/m^2K in relation to the climatic zone (see table 2).

TABLE I. U THERMAL TRANSMITTANCE (W/M^2K) OF SOME TYPES OF VERTICAL OPAQUE CLOSURES IN ITALIAN EXISTING BUILDINGS (UNI TS 11300-1)

Thickness [m]	Plastered stone wall	Solid brick wall plastered on both faces	Perforated brick or tuff wall	Non insulated prefabricated concrete panel	Hollow brick cavity wall
0,15	-	2,59	2,19	3,59	-
0,20	-	2,28	1,96	3,28	-
0,25	-	2,01	1,76	3,02	1,20
0,30	2,99	1,77	1,57	2,80	1,15
0,35	2,76	1,56	1,41	2,61	1,10
0,40	2,57	1,39	1,26	2,44	1,10
0,45	2,40	1,25	1,14	-	1,10
0,50	2,25	1,14	1,04	-	1,10
0,55	2,11	1,07	0,96	-	-
0,60	2,00	1,04	0,90	-	-

TABLE II. THERMAL TRASMITTANCE LIMIT VALUES FOR NEW BUILDING ENVELOPE ELEMENTS IN ITALY

Climate Zone	Vertical perimeter walls			Roofs			Floors		
	Dlgs 192/2005		*DM 11.03.2008 (to get tax deduction)*	*Dlgs 192/2005*		*DM 11.03.2008 (to get tax deduction)*	*Dlgs 192/2005*		*DM 11.03.2008 (to get tax deduction)*
	Private buildings	*Public buildings*		*Private buildings*	*Public buildings*		*Private buildings*	*Public buildings*	
A	0,62	0,56	0,54	0,38	0,34	0,32	0,65	0,59	0,60
B	0,48	0,43	0,41	0,38	0,34	0,32	0,49	0,44	0,46
C	0,40	0,36	0.34	0,38	0,34	0.32	0,42	0,38	0,40
D	0,36	0,32	0,29	0,32	0,29	0,26	0,36	0,32	0,34
E	0,34	0,31	0,27	0,30	0,27	0,24	0,33	0,30	0,30
F	0,33	0,30	0,26	0,29	0,26	0,23	0,32	0,29	0,28

Thus, for example, in order to reduce the thermal transmittance of the wall of an existing building, equal to 1.10 W/m^{2}K (empty cavity wall with holed bricks), to meet the requirements of the Decree No. 192/2005 for the climate zone D (0.36 W/m^{2}K), using a good traditional thermal insulator with a thermal conductivity λ of 0.035 W/mK, the minimum thickness to be applied would be at least 6.5 cm.

It is therefore evident that the minimum thickness required can often be incompatible both with the building aesthetic and with the housing needs of the users (reduction of net area or minimum height).

As an alternative to traditional insulation materials, there are now products on the market which, by exploiting the advances of nanotechnology in the field of materials science, are able to provide high levels of thermal protection with low thickness allowing to reconcile the needs for architectural quality with the new requirements for energy efficiency.

Nanotechnological insulating products are suitable for any type of building, but are ideal for external and/or internal interventions of renovation or building restoration, especially of historic buildings subjected to architectural constraints, and in all cases in which it is necessary to increase energy efficiency and comfort with minimum space loss.

B. *Nanotechnology*

Nanosciences and nanotechnologies constitute a new approach to research and development that aims to control structure and fundamental behavior of matter at the atomic and molecular level.

In particular, nanotechnology employs methods and techniques for the manipulation of matter on the size scale of less than a micrometer (μm), normally between 1 and 100 nanometers (nm), aiming to produce materials with new chemical and physical properties that can be used either at macroscopic and microscopic size.

At the nanoscale level, particles acquire new and surprising properties whose applications may cover virtually all technological sectors. For these reasons, nanoscience is often referred to as "horizontal", "key" or "enabling" since it can reconnect different scientific disciplines together and benefit from interdisciplinary and converging approaches. From medical applications to information technology, from materials science to energy production and storage, nanotechnologies are appearing able to contribute to the solution of many problems of contemporary society, allowing to create products and processes for more specific uses with less environmental impact throughout their life cycle.

The methodological and operational path that leads to the implementation of materials at the nanometer scale is based on two alternative methods.

The first, called top-down approach, is based essentially on assembly processes, involving the miniaturization of materials or devices, and consists of obtaining nanometer-sized structures from the processing of a solid of discernible size.

The second method, called bottom-up approach or "atomic technology", is based on synthesis processes instead and aims to create new structures starting from the atomic and molecular level, completely revolutionizing the existing manufacturing processes.

Regarding the construction sector, nanotechnology applications concern the fields of energy production and storage systems (new fuel cells, hydrogen storage systems, solar paints, thermophotovoltaic cells, LEDs, etc.), environmental protection (nanomaterials for air pollutants and smell reduction or water purification), security (chemical or bacteriological selective detection systems) and materials science.

With regard to materials science, thanks to nanotechnology it is now possible to improve existing materials performance, or to synthesize new classes of nanotech materials with previously unthinkable properties.

Using nanostructures is in fact possible to process the surfaces of the materials to make them, for example, non-slippery, scratch-resistant, corrosion-resistant, hydrofobic, self-cleaning, oil repellent, sterile, reactive, UV-resistant, insulating or reflective to infrared radiation. Also obtainable are: ceramic materials of greater hardness and toughness; metals of increased hardness, with high tensile yield and special electrical properties; polymers with higher mechanical strength, resistance to heat, chemical attacks, weathering and aging, improved gas exchange barring, better transparency and electrical conductivity; paints and varnishes that are mold resistant, heat-insulating (λ = 0.017 W/mK) and reflective to infrared thermal radiation.

Among the new classes of materials that nanotechnology allows to synthesize, of particular interest with regard to energy efficiency in buildings are aerogels, transparent insulating materials that combine unique features of light weight, mechanical strength and thermal insulation.

C. *Aerogel*

Aerogel is a solid nanoporous material with ultra-low density obtained by the dehydration of a gel by replacing the liquid component with a gaseous one.

Also known as frozen smoke, solid smoke or blue smoke due to its transparency, aerogel appears as a solid foam with a tactile feeling akin to foam rubber.

Consisting of more than 99 % air, aerogel is the solid substance with the lowest weight per volume unit known today (the current record is held by graphene aerogel created by researchers at *China's Zhejiang University* with a weight of only 0,16 kg/m^3).

Its high porosity and the very small pore size (diameter less than 100 nm corresponding to 1/10.000 than that of a human hair), give extraordinarily low thermal conductivity values, up to 0.004 W/mK, making aerogel the best material for thermal insulation in the world, capable of operating in a temperature range between -200 and +650 °C (3 mm of aerogel are sufficient to protect humans from temperatures of minus 50 °C).

Despite being extremely friable, its dendritic microstructure, with an internal net up to 800 m^2/g, gives aerogel compression resistance able to bear a load of up to 4000 times its own weight.

Aerogel can be obtained from gels made of materials of different nature such as silicon, aluminum, chromium, tin or carbon. To improve its physical and thermal properties reinforcing fibers or special additives can be added to the matrix, resulting in "composite aerogels" for the most varied applications.

First used only in the highest-tech aerospace, chemical and pharmaceutical sectors, in the last ten years aerogel has been employed at first in the sports sector and more recently in building insulation.

Most used is the silica aerogel (manufactured for the first time in 1931 by Steven Kistler by dehydration of a gel composed of colloidal silica in extreme pressure and temperature conditions), available on the market in loose granular form, or as mats, rolls or fiber-reinforced panels (rigid or semi-rigid).

TABLE III. TECHNICAL PROPERTIES OF SILICA AEROGEL AND GLASS

Properties	Silica Aerogel	Glass
Bulk density (kg/m^3)	5-200	2300
Internal surface area (m^2/g)	500-800	0,1
Refractive index at 632,8 nm	1.002-1.046	1.514-1.644
Light transmission at 632.8 nm	90%	99%
Thermal expansion coefficient at 20-80 °C (1/C)	2x10^{-6}	10x10^6
Thermal Conductivity at 25 °C (W/mK)	0,016-0,03	1,2
Sound speed in the medium (m/s)	70-1300	5000-6000
Acoustic impedance (Kg/m^2/s)	10^4	10^7
Electrical resistivity (Ωcm)	1x10^{18}	1x10^{15}
Dielectric constant 3-40 GHz	1,008-2,27	4,0-6,75

1) Building applications

Aerogel in loose granular form with hydrophobic processing can be used for filling wall cavities or mixed in cement for the construction of internal or external insulating plaster.

Still in granular form, due its optical properties aerogel is used in manufacturing Transparent Insulating Materials (TIM), placing it in the cavity (10-70 mm thick) between two sheets of polycarbonate, two sheets of glass or within structures of aluminum and glass fiber. While not allowing see-through vision because of its granular form, a thickness of only 16 mm is able to ensure a coefficient of light transmission of 70% and a thermal transmittance U equal to 1 W/m^{2}K. If combined with elements containing phosphorus aerogel TIMs may also constitute a source of light without the use of electricity.

In the form of rolls or FRP panels, possibly pre-coupled with cork slabs, gypsum or gypsum fiber, aerogel can be applied internally or externally for the insulation of roofs, walls and floors, or for thermal bridges correction.

a) Floors

For floor insulation available products consist in rolls of flexible aerogel insulation mats (amorphous silica gel with PTE felted fibers), resistant to compression, breathable and hydrophobic.

This product can be easily cut by conventional tools and can be adapted into any shape, greatly reducing installation time. Thanks to its low thermal conductivity, it allows to obtain a high degree of isolation with low thickness (5-10 mm).

Due to its characteristics the product is suitable for application in all cases in which the use of traditional underfloor insulation would result in an excessive reduction in the height of indoor environments, incompatible with statutory minimum values.

b) External walls

For external insulating envelopes, products are available in the form of panels (700x1400 mm or 720x1440 mm) that are easily applied to existing walls by using glue and dowels, then laying the reinforcement mesh, leveling the reinforcing coat and finishing with colored paste or painting. Resistant to moisture and stresses induced by atmospheric agents, mold and mildew proof, totally breathable, aerogels applied on the outside allow for high levels of thermal insulation with low thickness (16-36 mm) thanks to a thermal conductivity λ of only 0.013 W/mK ensuring consistent performance over a range of temperatures between -200 and +200 ° C.

c) Interior walls

For internal insulation of walls, products in form of rolls, semi-rigid panels or pre-coupled gypsum panels are available.

The last ones are particularly interesting for their ease of installation, mechanical strength and the possibility of combining thermal insulation and air purification.

The panel (1200x1440 mm, 1200x2880, thickness 13 mm) is made from an insulating Aerogel based felt coupled with a gypsum Active-air ® slab (also available in reinforced slabs), and can be indistinctly glued and doweled to the wall or mounted on a suitable structure as a normal plasterboard. The installation is completed with joint sealing. No need for plasters or finishes; once the panel is installed and the joints are leveled simply whitewash the wall.

The presence in the gypsum slab of Activ-air ® (1/1000 of the mass) allows capturing and transforming into inert compounds up to 70% of VOC (Volatile Organic Compounds) such as aldehydes and formaldehyde present in indoor air, with absorption values of 60 μg/m^{2}h.

2) The advantages

Compared to conventional insulation materials, as well as offering greater thermal insulation values (λ = 0.013 W/mK), aerogels have important advantages , including in particular:

- constant thermal performance regardless of operating temperature
- high hydrophobicity values while maintaining high water vapor permeability
- low flammability (Euro Class C: fire-resistant materials)
- mold proofing, UV and weathering resistance
- ease of installation thanks to the lightness and ease of adaptation
- ease of handling and storage
- high environmental sustainability and lack of toxicity .

In view of these advantages, the aerogel insulating materials' cost per square meter is however still high, about 8-10 times higher than traditional insulation.

It is therefore of the utmost importance that research addresses the reduction of manufacturing costs of those materials.

TABLE IV. TECHNICAL SPECIFICATIONS OF INSULATING MATERIALS FROM THE LEADING PRODUCTS ON THE MARKET

Insulating material	*Thermal conductivity λ W/m²K*	*Equivalent thickness cm*	*Reaction to fire Euroclass*	*Resistance to vapour μ*	*Specific heat J/kgK*
Fiber reinforced aerogel	0,013	1,00	C	5	1000
Phenolic resins	0,023	1,77	C	35	1400
Polyisocyanurate foam	0,026	2,00	E	60	1464
Expanded polyurethane	0,027	2,08	E	60	1400
Extruded expanded polystyrene	0,034	2,62	E	150	1450
Molded expanded polystyrene	0,035	2,69	E	60	1450
Stone wool	0,036	2,77	A1	1	1030
Cork	0,042	3,23	F	10	1560
Calcium silicate	0,044	3,38	A1	3	1300
Mineralised spruce wood-wool	0,068	5,23	B	5	1810

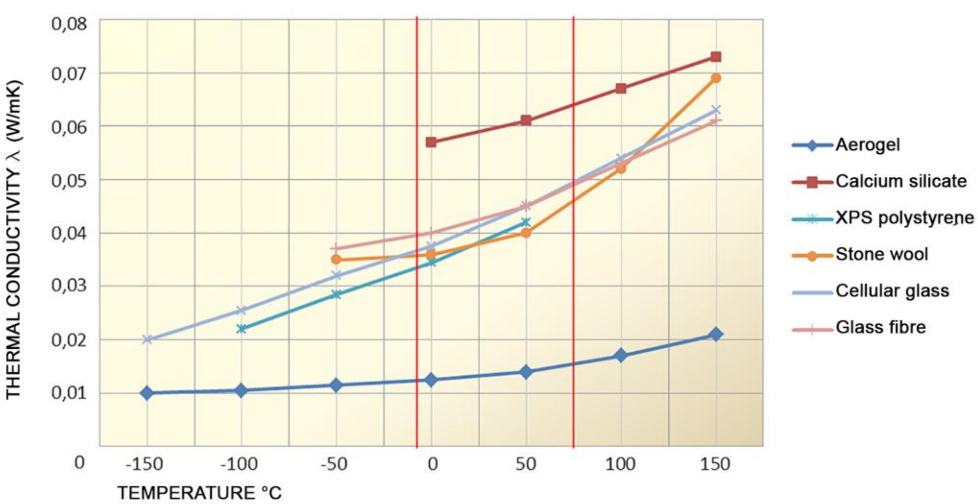

Figure 1. Insulating materials temperature ranges from the leading products on the market

D. Thermal inertia and energy efficiency

In order to limit energy requirements for air conditioning during summer and to contain rooms internal temperature, the Presidential Decree 59/2009, implementing Decree No. 192/2005, requires the building envelope opaque components (perimeter vertical walls and roof) to have a sufficient thermal inertia, i.e. that their temperature can vary slowly over time even in the presence of rapid changes in the temperature of the environment.

In particular, the DPR states that in all Italian climatic zones, with the exception of the F area (degree-days > 3000), for places in which the irradiance value on the horizontal plane in the month of maximum insolation is greater or equal to 290 W/m2:

- the surface mass value Ms of opaque vertical walls (with the exception of those included in the Northwest/North/Northeast sector) of new or to be renovated buildings must be greater than 230 kg/m^2 or, alternatively, the value of the periodic thermal transmittance modulus (Y_{IE}) must be less than 0.12 W/m2K;
- the value of the periodic thermal transmittance modulus Y_{IE} for all horizontal and inclined opaque walls must be less than 0.20 W/m^2K.

The legislator's goal is to ensure that the building envelope hit by the heat of summertime solar radiation is able, through its thermal inertia, to attenuate and shift the interior temperature fluctuations over time.

During summer, in daytime, the building envelope must be able to slowly accumulate external heat, releasing it inside the environments attenuated and delayed during nighttime, when the air temperature is lower and cooling the rooms via natural ventilation is possible. Furthermore, since thermal comfort depends on radiant temperature too, thermal inertia also plays a positive role in this case, keeping walls surface temperature lower than that of air during daily peak times.

Although the energy and environmental benefits provided by high thermal inertia are particularly acute during summer, they also relate to the winter period. In winter, during the day the thermal mass of the building envelope may in fact contribute to store heat from solar radiation then release it in the evening and at night when it is most needed. Furthermore, high thermal inertia can prevent the rapid lowering of the temperature in living quarters with nighttime heating setback, or heat loss in areas subject to frequent air changes and without heat recovery devices.

As an alternative to compliance with the opaque walls surface mass requirements, Presidential Decree 59/2009 allows for the positive effects of building envelope thermal inertia to be achieved by using innovative techniques and materials, i.e. green roofs, as long as they may limit temperature fluctuations of the environment following solar radiation. In this case, proper documentation and certification of technologies and materials must be produced, to certify compliance with the requirements above.

1) Smart materials

"Smart Materials" constitute a new class of highly innovative materials, able to perceive stimuli from the external environment (such as mechanical stress or temperature variations of humidity, pH, electromagnetic fields or solar radiation) and to react accordingly by autonomously and reversibly changing their mechanical, physical-chemical or electrical properties or their geometrical characteristics, adapting to the new environmental conditions.

Smart materials applications today still refer primarily to the aerospace, medical, bioengineering and biotechnology, transport and telecommunications sectors, but are also of great interest in the fields of design and architecture, in view of the numerous advantages their use can provide: self-cleaning materials, shape memory materials, piezoelectric, photovoltaic, electrochromic, photochromic or thermochromic materials, etc.

Among the different types of smart materials, particularly interesting towards energy efficiency of buildings are phase change materials (PCM), able to react to thermal stimuli with a reversible transition between solid, liquid and gaseous states.

Using PCM, the ability to attenuate and time shift air temperature fluctuations in a room does not depend on the more traditional building envelope thermal capacity to accumulate external sensible heat without warming rapidly (capacity given by the product between body mass itself and the specific heat capacity of the material), but on the material ability to accumulate the external heat in the form of latent heat to undergo a phase transition. During phase transition PCM are able to accumulate a quantity of thermal energy between 100 and 250 kJ/kg in the form of latent heat, compared with the specific heat capacity of building materials which varies from a maximum of 1.5-2 kJ/kg (wood and compact plastics) to a minimum of 0.8-0.3 kJ/kg (bricks and metals).

This way it is possible to split thermal inertia from body mass, in order to obtain the same beneficial effects with lighter materials and a significantly reduced thickness. Ultimately, through the use of PCM the building envelope tends to assume even more the characteristics of the human body skin, whose main thermoregulation mechanism to maintain a constant body temperature is precisely subtraction of heat as latent heat through evapotranspiration and sweating.

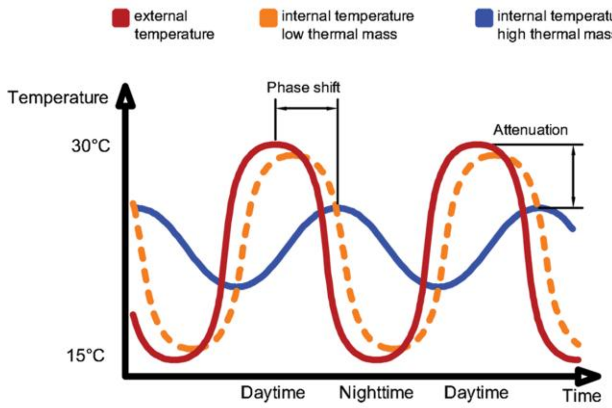

Figure 2. Thermal inertia and internal temperature diagram

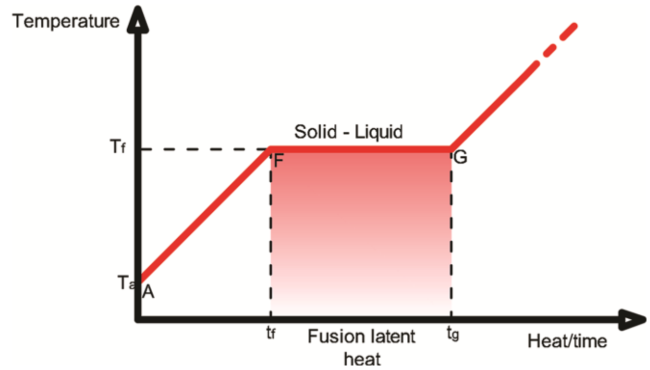

Figure 3. Solid-liquid state diagram

TABLE V. THERMAL INERTIA: BUILDING STRUCTURE PERFORMANCE CLASSES IN ITALY (DM 26 JUNE 2009)

Phase shift S (h)	Attenuation f_a	Performance	Performance class
S >12	f_a< 0,15	Excellent	I
10 < S <12	0,15 < f_a< 0,30	Good	II
8 < S <10	0,30 < f_a<0,40	Sufficient	III
6 < S <8	0,40 < f_a<0,60	Poor	IV
S <6	f_a> 0,60	Bad	V

2) Phase change materials

As we have seen, PCM are materials that exploit the phenomenon of phase transition to absorb or release heat (called latent heat) without increasing their internal temperature. The energy supplied or subtracted from the material during the phase transition is in fact used to break or form chemical bonds while keeping the kinetic energy of the body constant and hence its temperature stable.

During daytime, when air temperature exceeds a certain value (the so-called operating temperature at which the PCM begins the phase change, typically between 23 and 26° C), the excess heat is used by the PCM to undergo the phase transition (for example from solid to liquid state) and thus subtracted from the environment. At night, when the temperature drops below the set point, the PCM returns the accumulated heat to the environment undergoing the reverse phase transition (liquid - solid). This way it is possible to damp the temperature oscillations of an indoor environment and maintain a state of comfort. Obviously, in order for PCM to perform their function, daily temperature must exceed the melting point to allow phase transition, then drop below the melting point in order to start a new cycle the following day.

PCM in the building can be used for internal and perimeter walls, floors or false ceilings (with operating temperatures between 20 and 35° C). The benefits resulting from their use in the building envelope regard, as mentioned, the possibility to obtain with thinner materials a decrease in summer thermal loads and a reduction of internal temperature oscillations and air conditioning energy requirements, increasing at the same time the internal microclimatic comfort.

a) Classification

The phase transition of a material may be through solid - solid, solid - gas, solid-liquid or liquid-gas transformations.

PCM used in building construction generally exploit solid-liquid transition as, even if characterized by a lower exchange of latent heat than that achievable in the liquid-gas phase changes, it involves a smaller change in volume resulting in more simplicity in the accumulation management system and greater affordability.

Depending on the type of material used for latent heat accumulation, PCM are divided into two main categories: organic PCM, including paraffin waxes (C_nH_{2n+2}), non-paraffin waxes (fatty acids ($CH_3(CH_2)_{2n}COOH$) and other organic non-paraffinic PCM); inorganic PCM, including hydrate salts (M_nH_2O) and metallic materials with low melting temperatures. To both categories belong eutectic PCM, which consist of mixtures of different substances (organic and/or inorganic) whose overall melting point is lower than that of the individual substances.

b) Technical specifications

Each category has its own advantages and disadvantages for use in building construction from the thermal, physical, chemical, environmental and economic points of view. Regarding the thermal aspects, in general, for effective use in buildings PCM should have a melting point ranging within a particular temperature span, high fusion latent heat per unit mass, high specific heat capacity, fusion congruence and limited, if not absent, supercooling phenomenon. From a physical point of view, PCM should be characterized by high density, reduced volume changes during phase transitions and sufficiently high crystallization rates.

From a chemical point of view PCM should be characterized by high long-term stability and building materials compatibility. Moreover, they should be non-toxic, non-flammable and non-explosive. From an environmental point of view PCM should have low impact throughout the entire life cycle, from production to decommissioning. From an economic point of view they should, finally, be characterized by wide availability on the market, easy procurement and low cost.

There is not, today, a material capable of fully covering all of the above characteristics. Most used materials are, as already said, paraffin (organic materials), hydrated salts (inorganic materials) and fatty acids (organic materials). Regarding applications in very cold accumulators ice is also widely used.

Hydrated salts are among the cheapest PCM, have a good latent heat value, high thermal conductivity, a fixed value for phase transition temperature, are not flammable and are biodegradable and recyclable (sodium sulfate decahydrate $Na_2SO_4 10\ H_2O$, commonly called Glauber's salt from the name of its discoverer Johann Rudolf Glauber, is the most used; it has a melting point of 32.4° C). However, hydrated salts need careful preparation and additives for long-term stability, undergo considerable volume change during phase transition, can be corrosive to certain metals and are prone to incongruent melting and subcooling phenomena.

The incongruent melting occurs when water released in the crystallization process is not sufficient to dissolve all the solid-state material present. Because of their lower density, less hydrated salts end up in the lower part of the accumulation making the phase transition increasingly irreversible over time. Sub-cooling is instead caused by the rate of nucleation of hydrated salt crystals, which is generally very low. This means that the latent heat, instead of being released at the melting temperature, is released at a lower temperature.

Organic PCM are typically more expensive than inorganic ones, have a lower latent heat value, have often a larger fusion range, can cause reactions with the concrete and may be combustible (the latter problem can be solved through the use of appropriate containers). On the other hand they have the advantage of being simple to use, chemically stable, non-corrosive, having a more limited volume change in the phase transition, being free from of undercooling phenomena and nucleation agents and being recyclable.

Eutectic PCM have finally a higher density than organics and allow to obtain a compound with a single melting temperature. However, data on their thermal and physical properties are still limited in relation to their still recent introduction.

TABLE VI. PCM: LATENT HEAT AND FUSION POINTS (A.SHARMA ET AL.)

Material	Fusion temperature (°C)	Latent Heat (kJ/kg)
Paraffin	6 - 76	170 – 269
Non paraffin	8 - 127	86 – 259
Fatty acids	17 - 102	146 – 242
Salt hydrates	14 - 117	68 – 296
Eutectics	15 - 82	95 – 218
Water	0	333

c) Encapsulation

PCM must be encapsulated. The encapsulation process main objectives are, in addition to material containment in the liquid and solid state, to prevent changes in its chemical composition, to avoid interactions with the environment, to increase compatibility with surrounding materials inside the accumulator, and to improve handling and reduce possible variations of the external volume.

There are two types of encapsulation: macro-encapsulation and micro-encapsulation.

The first includes the enclosure of PCM in containers such as tubes, spheres, panels and other housings, which can act directly as heat exchangers or in turn be incorporated into other elements. It is the most used form of encapsulation and involves containers larger than 1 cm.

In microencapsulation, spherical particles are enclosed in a thin polymer film and with high molecular weight. The coated particles (less than 1 mm in diameter) can then be incorporated in a matrix compatible with the film. The microcapsules, due to their size, are virtually indestructible and extremely safe from the risk of harmful substances release, and feature a remarkable heat exchange surface (1 g encapsulated product nets about 30 m^2).

This technique appears to have considerable development scope as an innovative form of encapsulation, although at the moment it can only be applied to hydrophobic PCM, or materials that do not absorb or retain water on the surface, such as paraffin, and not hydrated salts. The microencapsulation also helps to improve the stability of the fusion - solidification cycle since phase separation is confined to microscopic distances. The microcapsules can then be included in the mix of building products such as plaster, screed, concrete, gypsum, wood products such as MDF and OSB, or even in acrylic paints.

Among the microencapsulated PCM on the market, BASF Micronal is particularly interesting; it is made out of globules of highly refined formaldehyde free paraffin wax (Ø = 2-20 μM) coated with an extremely rigid polymer layer (polymethyl methacrylate), usable in many construction products. The special coating protects the PCM inside keeping it in a pure state and guaranteeing unchanged performance for a period of over 30 years (300 cycles/year for a total of 10000 cycles). The very small size of the capsules (diameter of approx. 1/500 mm) also protects the material from any risk of breakage by impact or crushing.

According to the need, BASF Micronal is supplied as a liquid dispersion or powder with three different operating temperatures: 26° C for overheating protection during summer; 23° C for internal temperature stabilization in the comfort zone; 21° C for use in surface cooling systems.

d) Functional model and building applications of PCM

Inside buildings, PCM can find different applications, depending on building type and energy and microclimate objectives, and can be used in both new constructions and renovations of existing buildings.

There are several products on the market to buy in bulk for mechanical systems use, micro-encapsulated, liquid dispersed or in powder, to add in plasters or screeds, microencapsulated in bags, balls, rusticated mats to place in wall cavities or above suspended ceilings, or already integrated within the building products (pre-mixed plasters, gypsum boards and plasterboards, concrete blocks, wall cavity panels, etc.). A premixed plaster with microencapsulated PCM has a capacity to absorb, at its operating temperature (melting/solidification range), a quantity of heat 4.5 times higher than that of a traditional plaster (1.5 cm equal to 7 cm plaster or 14 cm brick).

Most interesting applications of PCM in building construction include:

- inner lining of perimeter walls or partitions through the use of plaster, gypsum boards or plasterboards with added Micronal PCM or panels to be placed behind finish;
- integration within counter ceiling using prepackaged panels or bags to be placed above the plates;
- insertion beneath the floors (especially if radiant) as screed or panels;
- external lining of perimeter walls (also ventilated), through the use of plasters or panels or directly concrete blocks containing PCM; or roofs;
- integration into passive solar systems, such as Trombe walls or solar greenhouses to increase heat gain (screeds, panels);
- use inside insulating glass glazing.

e) Use within the building

Using PCM within the internal environment allows to increase the thermal capacity of walls, reducing temperature fluctuations throughout the day. The surface temperature is stabilized around the melting temperature of the material, to be chosen close to that of comfort; this solution allows reducing dispersion and thus heating energy requirements and the storage capacity allows reducing cooling energy requirements. The most suitable use of PCM in the building industry is in combination with lightweight or dry construction systems, characterized by low thermal inertia, such as gypsum panels or slabs. Thanks to the material micro-encapsulation such systems do not require special care in setting up and, like traditional panels, can be used in internal counter walls, ceilings and partitions. This way it is possible, for example, to intervene on existing buildings by applying an internal insulation, preferably using Aerogel, with a superimposed PCM lining, thus allowing to reduce dispersion and at the same time maintain a good thermal inertia to support the air-conditioning system. In fact, the application of thermal insulation panels inside the building to reduce energy loss during winter, especially in the energy upgrading of historic buildings where working with an external insulation system is not possible, often determines the exclusion of the preexisting thermal mass. This results in a quicker drop of the internal temperature during winter after turning the heating system off and in a possible overheating of the environment during summer because of the inability to dispose of excess heat through the mass of the walls.The application of the PCM lining above the Aerogel insulation would just allow to overcome these drawbacks and at the same time to minimize the total additional thickness. With only 2.75 cm (1 cm aerogel + 0.5 cm PCM panel + 1.25 cm gypsum wall board), you can have the equivalent in terms of insulation and thermal inertia of an additional 25 cm thick counter wall comprised by 3 cm of traditional insulating material and about 20 cm brick wall plus 2 cm of plaster.

f) Use outside the building

PCM can also be positioned on the outer side of the perimeter walls or the roof. In this position they are able to reduce the building envelope heat load during summer due both to the solar radiation and the high outside air temperature. Using PCM allows to attenuate and shift the incoming heat wave over time and to reduce the radiating temperature of walls, improving interior microclimate and reducing the envelope cooling requirements during summer ($EP_{e,\ housing}$).

External positioning is therefore particularly suitable in hot areas or in all cases in which the existing wall does not have a thermal mass sufficient to cope with the problems of summer overheating. PCM can be applied as lining of a thermal insulation system or inside ventilated walls, either next to the slab or next to the insulation, furthering heat dissipation towards the outside.

g) Use in glass walls

Another interesting use of the PCM is inside glazing systems. A Swiss company has developed a triple glazed glass with a selective layer that allows the reflection of solar radiation in the summer when the sun is high and its storage during winter in slabs of translucent hydrate salts, embedded within the glazing, that allow the diffusion of light giving the effect of a translucent wall.

This way it is possible to obtain a thermally insulated transparent wall that allows light radiation to pass through and increase the luminance levels of internal rooms and that is able, thanks to the presence of PCM, to accumulate the heat of the incident solar radiation in the winter and to release it during the night, maintaining a high environmental comfort.

IV. Conclusions

In this research, evaluation of application of insulating nanotechnology and smart materials in the building envelope is discussed and compared to traditional insulation materials. The analysis shows that the use of insulating nanotechnology and smart materials for renovation of historic buildings is an effective solution to improve the hygrothermal performance of the envelope by allowing you to reconcile the objectives of reducing energy consumption with the need to preserve their integrity, authenticity and architecture quality. The combined use on opaque components (perimeter walls, floors on the ground or on open spaces, roofs) of nanotechnology insulation and phase change materials can allow to improve thermal insulation, in order to reduce energy loss during winter, and thermal inertia, in order to minimize air temperature fluctuations and to reduce overheating during summer. Nanotechnological insulating products and Phase Change Materials (PCM) are suitable for any type of building, but are ideal for external and/or internal interventions of renovation or building restoration, especially of historic buildings subjected to architectural constraints, and in all cases in which it is necessary to increase energy efficiency and comfort with minimum space loss. In view of these advantages, the application cost per square meter of these new materials is however still higher than traditional materials. It is therefore of the utmost importance that research addresses the reduction of manufacturing costs of those materials in order to allow their application on a large scale and achieve the energy efficiency targets set by the European Union.

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