Enhancing the infrared and visible emission properties of calcium silicate hydrate for radiative cooling using metamaterials

Carlos Lezaun[1], Jorge S. Dolado[2,3], Alicia E. Torres[1], José M. Perez-Escudero[1], Iñigo Liberal[1,4], Miguel Beruete[1,4]

[1]Antennas Group-TERALAB, Electric and Electronic Engineering Department, Public University of Navarra, Campus Arrosadía, 31006, Pamplona, Spain

[2]Centro de Física de Materiales (CFM), CSIC-UPV/EHU, 20018, San Sebastian, Spain

[3]Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018, San Sebastian, Spain

[4]Institute of Smart Cities, Universidad Pública de Navarra, 31006, Pamplona, Spain

***Abstract*—Two periodic structures composed of metal cylinders with different orientations are used to improve the solar reflection of calcium silicate hydrate (CSH) while maintaining its atmospheric emission. Interesting effects have been found when the distance between bars is small, suggesting that lattice effects, arising from the interaction between the rods could be leveraged in the design of these metamaterials. The size of the metal bars is selected based on state of the art micromanufacturing techniques. This study limits its scope to a CSH gel model; i.e. the most important component of cement-based materials. Further research will be undertaken to consider a best description of the dielectric function of concrete.**

I. Introduction

GLOBAL warming is more evident every year. Its effects on the environment are leading researchers towards the search of clean energy systems with the maximum efficiency. Cooling systems like air-conditioning are in increasing demand for the excess heat, but they have poor efficiency, hence, they damage the environment with an energy overconsumption [1].

Radiative cooling has emerged as a potential solution to this problem. By combining the blackbody radiation with the atmospheric window allows terrestrial objects to radiate their heat to outer space. The blackbody radiation theory explains that any object with a temperature above 0 K radiates energy in all wavelengths, with the peak and magnitude modulated by temperature. Such peak is located between 8 and 13 µm at ambient temperatures. This band coincides with a spectral region where the atmosphere is transparent to radiation, hence called atmospheric window. This combination allows a direct heat transmission between earth and space, which is a large heat reservoir at a very low temperature.

Different radiative cooling prototypes have been tested in recent years using paints [2], polymers [3], metamaterials [4]–[6] and fabrics [7] to name a few. It is interesting that little research to develop structural materials has been done [8], which could find the most used material in a near future for the so-called zero emission buildings. In this work we present how to improve the emission properties for radiative cooling of a block of calcium silicate hydrate (CSH), which is one of the main compounds of concrete paste. Periodic structures of different construction materials and sizes that are available for current manufacturing methods are used.

II. modelling CSH

The employed atomic structure of CSH gel was the one proposed in [9] corresponding to a very large system whose exact stoichiometry is $(CaO)_{254}(SiO_2)152(H_2O)_{306}$.

The dielectric function of CSH gel is calculated expressing the dielectric function in terms of the oscillator strength as done in [10]. The simulations used a polarizable force field [11] in the GULP code [12] with a damping factor of 25 cm^{-1}.

III. Design

Two different models consisting of a block of CSH with embedded vertical and horizontal metal bars are considered. Such models are shown in Fig. 1(a,b). The metal bars are made of aluminium, whose permittivity is taken from [13], but any other lossy conductor should bring similar results. A parametric sweep study of the parameters of Fig. 1(a,b) has been performed following Table I, considering in all cases to have sizes compatible with current manufacturing technologies [14]. The calculations have been done using GD-Calc, which computes the reflectance (R) and the transmittance (T) using the Rigorous Coupled Wave Method (RCWM) to obtain the diffraction efficiencies of a multilayer structure. Also, it is assumed that no transmittance is observed by considering a semi-infinite CSH block. Considering that emissivity is equal to absorptivity for a body in thermodynamic equilibrium according to Kirchhoff's law of thermal radiation, Eq. 1 computes emissivity:

$$\varepsilon(\lambda) = 1 - R(\lambda) - T(\lambda) \tag{1}$$

Note that for daytime radiative cooling, a strong solar reflection (0.3-4 µm) and large atmospheric emission is desired.

IV. Results

It should be noted that raw CSH is a great emitter in the computed range (0.3-25 µm) with an emissivity higher than 0.8, as shown in Fig. 1 (c). Regarding the metamaterial of Fig. 1 (a), the radius and length parameter sweeps bring a linear variation of the emissivity, nearly like an offset with no selectiveness. However, when the radius and length are close to the periods P_1

Table I

Horizontal bars (Fig. 1 (a))		***Vertical bars (Fig. 1 (b))***	
P1	[9, 12, 15, 18] µm	P	[9, 12, 15, 18] µm
P2	[15, 18, 24, 30] µm	r	[3, 4, 5, 6] µm
l	[4, 8, 12, 18, 24] µm	h	[2, 5, 8, 11, 14] µm
r	[3, 4, 5, 6] µm	o	0.5×P

Table 1.Parameters sweep for both periodic structures

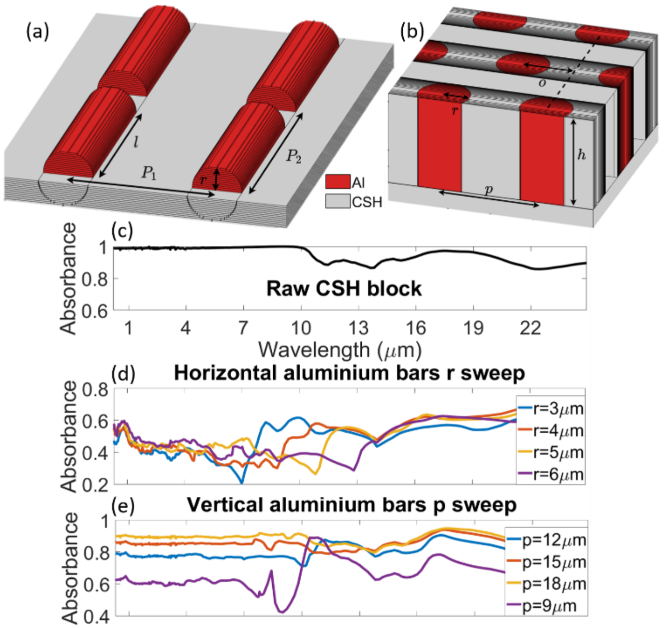

Fig. 1. Periodic structures made of (a) horizontal semi-embedded bars and (b) vertical vars embedded. (c) depicts the absorbance or emissivity of a raw CSH block, (d) shows the absorbance for the radius sweep of (a) when the distance along the axis of P_1 between bars is 1 µm with l = 12 µm and P_2 = 14 µm. Finally, (d) shows the results of the period sweep of (b) with r = 3 µm, h = 5 µm and $o = 0.5{\times}p$.

and P_2 of the structure, lattice effects arising from the interaction between the rods like in Fig. 1(d) emerge, where $P_1 = 2r + 1$ µm. When periods get smaller, collective effects appear for both structures, as it is shown in Fig. 1(e), where the minimum period value happens to have an emission peak in the atmospheric window nearly as strong as the other options, but with a much higher solar reflectance. In general, smaller dimensions tend to enhance solar reflection but, for Fig. 1(b) the emission is largely independent of the height of the cylinders and the radius alone only brings an offset constant in frequency to the emissivity curve, without selectiveness. Then, the solar power absorption reduction is nearly 50% for the best case, which will bring a huge increase in the cooling power for radiative cooling. Although it is still insufficient for daytime radiative cooling, combining this method with modifications in the substrate composition may help achieve such effect.

V. Conclusions

A large improvement in the emission spectrum of CSH for radiative cooling has been obtained using simple structures with state of the art dimensions and materials. Embedding periodic metal bars in CSH have non-linear effects in the emissivity and reflectivity spectrum. From these results it seems feasible to optimize such structures to reflect the solar radiation and enhance atmospheric emission at the same time. A study of different materials and the possibility of having different cylinder sizes in a macro unit cell is now ongoing. Also, a permittivity model for concrete is being developed to obtain more realistic computations. This involves accounting for additional phases like Portlandite ($Ca(OH)_2$), unreacted cementitious phases like Alite (Ca_3SiO_5) along with porosity related effects.

Acknowledgments

This work has been funded by the research and innovation program Horizon 2020 of the European union. Project MIRACLE, Grant Agreement 964450.

References

[1] K. Lundgren and T. Kjellstrom, "Sustainability challenges from climate change and air conditioning use in urban areas," *Sustain.*, vol. 5, no. 7, pp. 3116–3128, 2013, doi: 10.3390/su5073116.

[2] A. W. Harrison and M. R. Walton, "Radiative cooling of TiO2 white paint," *Sol. Energy*, vol. 20, no. 2, pp. 185–188, 1978, doi: https://doi.org/10.1016/0038-092X(78)90195-0.

[3] Y. Zhai *et al.*, "Scalable-manufactured randomized glass-polymer hybrid metamaterial for daytime radiative cooling," *Science (80-.).*, vol. 355, no. 6329, pp. 1062–1066, 2017, doi: 10.1126/science.aai7899.

[4] M. M. Hossain, B. Jia, and M. Gu, "A Metamaterial Emitter for Highly Efficient Radiative Cooling," *Adv. Opt. Mater.*, vol. 3, no. 8, pp. 1047–1051, 2015, doi: 10.1002/adom.201500119.

[5] D. Wu *et al.*, "The design of ultra-broadband selective near-perfect absorber based on photonic structures to achieve near-ideal daytime radiative cooling," *Mater. Des.*, vol. 139, pp. 104–111, 2018, doi: 10.1016/j.matdes.2017.10.077.

[6] C. Zou *et al.*, "Metal-Loaded Dielectric Resonator Metasurfaces for Radiative Cooling," *Adv. Opt. Mater.*, vol. 5, no. 20, pp. 1–7, 2017, doi: 10.1002/adom.201700460.

[7] J. K. Tong, X. Huang, S. V. Boriskina, J. Loomis, Y. Xu, and G. Chen, "Infrared-Transparent Visible-Opaque Fabrics for Wearable Personal Thermal Management," *ACS Photonics*, vol. 2, no. 6, pp. 769–778, 2015, doi: 10.1021/acsphotonics.5b00140.

[8] T. Li *et al.*, "A radiative cooling structural material," *Science*, vol. 364, no. 6442, pp. 760–763, 2019, doi: 10.1126/science.aau9101.

[9] E. Duque-Redondo, "Atomistic simulations of confined species in 2D nanostructures: Clays and C-S-H gel," Ph. D dissertation, UPV/EHU, San Sebastián, 2018.

[10] J. S. Dolado, G. Goracci, E. Duque, P. Martauz, Y. Zuo, and G. Ye, "THz fingerprints of cement-based materials," *Materials (Basel).*, vol. 13, no. 18, 2020, doi: 10.3390/MA13184194.

[11] H. Manzano, J. S. Dolado, and A. Ayuela, "Elastic properties of the main species present in Portland cement pastes," *Acta Mater.*, vol. 57, no. 5, pp. 1666–1674, 2009, doi: 10.1016/j.actamat.2008.12.007.

[12] J. D. Gale, "GULP: A computer program for the symmetry-adapted simulation of solids," *J. Chem. Soc. Faraday Trans.*, vol. 93, no. 4, pp. 629–637, 1997, doi: 10.1039/A606455H.

[13] M. A. Ordal, R. J. Bell, R. W. Alexander, L. A. Newquist, and M. R. Querry, "Optical properties of Al, Fe, Ti, Ta, W, and Mo at submillimeter wavelengths," *Appl. Opt.*, vol. 27, no. 6, pp. 1203–1209, Mar. 1988, doi: 10.1364/AO.27.001203.

[14] L. Borasi *et al.*, "3D metal freeform micromanufacturing," *J. Manuf. Process.*, vol. 68, no. March, pp. 867–876, 2021, doi: 10.1016/j.jmapro.2021.06.002.