

## Solar cooling with aluminium pillared clays

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### ABSTRACT

Aluminium modified clays were prepared, characterised and tested for their potential application as solar coolers of roof surfaces. The water adsorption isotherm of the samples with restored cation exchange capacity was of hydrophilic type II, indicating multilayer adsorption with large heat of adsorption and pore condensation of water vapour at the pressures of the proposed application. In addition, high moisture adsorption capacity (more than 0.1 g of moisture per g of material at 60–70% of relative humidity) and fast kinetics for night sorption (comparable to silica gel) were determined for the freeze-dried pillared sample. In cyclic experiments with low irradiation during the day and night relative humidity of 55%, the maximum temperature inside the pillared montmorillonite was 6.5 °C lower than the corresponding temperature inside a typical soil sample. The primary mechanism for the reduced temperature elevation at aluminium modified clays was evaporative cooling and desorption with minor influence of solar reflection. These results indicate the suitability of aluminium pillared clays for lowering the roof surface temperatures.

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## 1. Introduction

Microclimate changes with increased temperatures especially during the summer time are among the major energy and environmental problems of big cities [1]. The intensity of the phenomenon, known as urban heat island (UHI) effect is defined as the maximum temperature difference between the urban and rural environments [2,3]. Urban areas of more than 10 °C warmer than their surrounding rural areas have been observed in Athens, like an “island” of heat surrounded by cooler rural areas [4].

During the last years, because of the severe consequences of the UHI effect (increase of the electricity generation due to the demand for cooling energy, deterioration of the living environment due to higher pollutants emission, increase of the chemical weathering of building materials and increase the discomfort and even the mortality rates), there has been an impetus in research aiming in understanding its origin and developing the appropriate mitigation measures [1,5–8]. Roof temperatures of up to 70 °C due to solar radiation during the summer time are a major heat source for the formation of the UHI effect or the urban microclimate change [9].

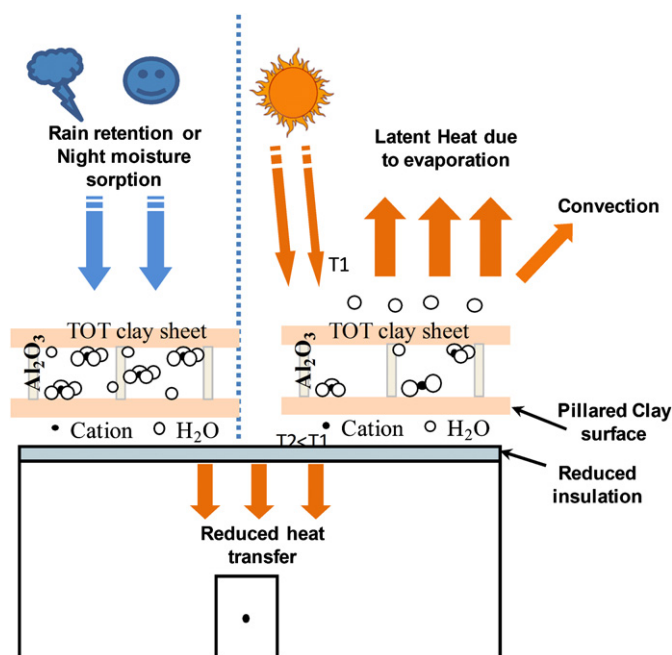
In order to alleviate the UHI adverse effects, several mitigation measures have been proposed like the reduction of the thermal and pollutants emissions of human origin, the increase of the green

spaces in the urban environment, the use of cool materials as construction and roof materials and more specialized designs like those associated with humidification and albedo increase, photovoltaic canopies, super-hydrophilic photocatalyst-coated building surfaces with water film [1,10–13]. Since 20% of the urban surface is roofed, the use of cool roofing materials can save energy, mitigate urban heat islands and slow global warming [13].

The proposed mitigation strategies have a limited ability for temperature reduction with both advantages and disadvantages [8]. As an example, the characteristic disadvantage of the humidification techniques is the outdoors humidity increase and the subsequent increase of the discomfort index. Albedo increase with cooling materials has been found to be an effective mitigation measure [7], but it also reduces the surface temperature in the winter while the measure is reduced up to 15% in the first year of its use due to weathering [14].

Evaporative cooling is the oldest technique of cooling and several methods are being studied for direct or indirect evaporative cooling systems [15]. In the last few years, the use of porous materials for the evaporative cooling of building has been started to be studied as an alternative and sustainable way to cool the roof surface of a building or the pavement of outdoor spaces by taking advantage of the properties of porous materials [10,11,16–19]. The principle of evaporation cooling of buildings (either as a stand-alone roof material or as an additive in green roofs or roofs covered by gravel stones) is the same as in the solar heat energy storage (Fig. 1); the night or the rainy days are the period of cold and the day of sun irradiation is the period of hot. Stored water or night sorbed

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**Fig. 1.** The principle of solar cooling of buildings with the use of aluminium pillared montmorillonite (TOT represents the tetrahedral/octahedral/tetrahedral sheet structure).

moisture are evaporated during the hot day and the porous surface temperature is reduced due to the release of the latent heat. Lower surface temperatures contribute to the reduction of air temperature since the intensity of heat transfer through the cold surface is lower while the heat flow inside the building is reduced. The method of roof evaporative cooling is considered to be the most effective method for roof and indoor temperature reduction [20]. In countries with very hot summers like Greece, reduced surface temperatures lead to the reduction of the cooling load. Complementary, in cases of dry summers with reduced water sources where the use of hydro-electric energy is forbidden, the reduced demand leads to reduced imports and the subsequent associated reduced costs.

So far, the few studies in the building integrated evaporation cooling have been mainly focusing in natural materials (silica sand, volcanic ash, pebbles, siliceous shale) [16,20] with the absence of similar studies with inorganic materials like zeolites, clays and more complex structures like modified clays and mesoporous molecular sieves. In this frame, aluminium modified montmorillonite was tested in the present work as an application material for solar cooling of buildings in addition to materials like natural soil and bentonite. The primary objective was to explore some of the basic relations between the composition and the structure of clays upon aluminium modification, the sorption properties of moisture such as the sorption rate and capacity, the water evaporation rate under controllable conditions in a specially developed chamber (wind tunnel), the water/moisture sorption–desorption under simulated solar radiation and the associated surface temperature reductions with the contributing factors.

## 2. Experimental

### 2.1. Synthesis and characterisation of the modified clays

The aluminium pillared montmorillonite samples were prepared according to the methods described by Karamanis and Assimakopoulos [21]. In order to simplify and reduce the required amount of energy and water for an industrial perspective of the materials

preparation process, the as-received bentonite was used with no fractionation or purification pre-treatment. The preparation conditions and labelling of the tested modified porous clays are summarised in Table 1.

Characterisation of the aluminium modified clays included elemental analysis, which was performed with the spectrometric methods of proton induced gamma-ray emission (PIGE) and X-ray fluorescence (XRF) [22]. X-ray diffraction (XRD) patterns, nitrogen adsorption–desorption isotherms (pore size distributions were calculated via the Kelvin equation), thermogravimetry (TG) and differential thermogravimetry (DTG) measurements were also performed. The characteristics results of some of the prepared materials are shown in Table 2. Finally, the spectral reflectance of the samples was measured using UV/vis/NIR spectrophotometer (Varian Carry 5000 fitted with a 150 mm diameter, integrating sphere (Labsphere DRA 2500) that collects both specular and diffuse radiation) over the solar spectrum (200–2500 nm).

### 2.2. Water sorption experiments

#### 2.2.1. Sorption isotherms

Water vapour sorption isotherms (kinetics and capacity) were determined by applying a modified version of the discontinuous method ASTM E96-80 [23]. According to the method, samples were placed in an array of four sealed desiccators with saturated salt solutions for controlling relative humidity while temperature was air-conditionally controlled at 25 °C. Temperature and humidity inside the desiccator were continuously monitored with a TFA Dostmann/Wertheim sensor. The measured humidities of the saturated salt solutions are shown in Table 3. Prior to measurements, samples were dried to constant mass in an air-circulated oven at 105 °C. In order to determine the sorption isotherms and kinetics, the samples were periodically weighed and the moisture content was calculated as the

**Table 1**  
Preparation conditions and labelling of the studied modified clays and materials.

Code	Material
ZN	Zenith-N Raw Bentonite (used as-received)
NaM	Montmorillonite in Na form
Na-FPM	Freeze-dried pillared montmorillonite with restored cation exchange capacity (CEC)
Na-APM	Air-dried pillared montmorillonite with restored CEC
Na-APZ-500	Air-dried bentonite calcinated at 500 °C with restored CEC
Na-APZ-200	Air-dried bentonite calcinated at 200 °C with restored CEC
Al13-FPM	Freeze-dried uncalcinated montmorillonite precursor with Al13 intercalant (keggin ion)
H-FPM	Freeze-dried pillared montmorillonite with unrestored CEC
Al13-APZ	Air-dried uncalcinated bentonite precursor with Al13 intercalant
Soil	Typical soil material (wet sieved and grains < 500 μm)

**Table 2**  
Characteristics of the starting montmorillonite and the pillared samples.

Samples	XRD interlayer spacing $d_{001}$ (Å)	Pore size distribution		TGA—total mass reduction at 100 °C (%)
		Micropores (%)	Mesopores (%)	
NaM	15.5	–	–	7.0
Na-FPM	17.4	75	25	4.2
Na-APM	17.8	100	0	5.9
Na-APZ-500	17.5	80	20	5.8

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