ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

Soiling of building envelope surfaces and its effect on solar reflectance – Part II: Development of an accelerated aging method for roofing materials

Mohamad Sleiman, Thomas w. Kirchstetter, Paul Berdahl, Haley Gilbert, Sarah Quelen, Lea Marlot, Chelsea Preble, Sharon Chen, Amadine Montalbano, Olivier Rosseler, Hashem Akbari, Ronnen Levinson, Hugo Destaillats

Environmental Energy Technologies Division

November 2013

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Building Technologies Office of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer

Soiling of building envelope surfaces and its effect on solar reflectance – Part II: Development of an accelerated aging method for roofing materials

Mohamad Sleiman[1], Thomas W. Kirchstetter[1,2], Paul Berdahl[1], Haley E. Gilbert[1], Sarah Quelen[1], Lea Marlot[1], Chelsea Preble[1,2], Sharon Chen[1], Amandine Montalbano[1], Olivier Rosseler[1], Hashem Akbari[3], Ronnen Levinson[1], Hugo Destaillats[1,*]

[1] Heat Island Group, Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.

[2]Department of Civil and Environmental Engineering, University of California Berkeley, Berkeley, CA, USA

[3] Concordia University, Department of Building, Civil and Environmental Engineering, Montreal, Canada

*Corresponding author's E-mail: HDestaillats@LBL.gov

FINAL REVISED DRAFT

Accepted for publication in ***Solar Energy Materials and Solar Cells***

November 18, 2013

Abstract

Highly reflective roofs can decrease the energy required for building air conditioning, help mitigate the urban heat island effect, and slow global warming. However, these benefits are diminished by soiling and weathering processes that reduce the solar reflectance of most roofing materials. Soiling results from the deposition of atmospheric particulate matter and the growth of microorganisms, both of which absorb sunlight. Weathering of materials occurs with exposure to water, sunlight, and high temperatures. This study developed an accelerated aging method that incorporates features of soiling and weathering. The method sprays a calibrated aqueous soiling mixture of dust minerals, black carbon, humic acid, and salts onto preconditioned coupons of roofing materials, and then exposes the soiled coupons to ultraviolet radiation, heat and water in a commercial weatherometer. Three soiling mixtures were optimized to reproduce the site-specific solar spectral reflectance features of roofing products exposed for three years in a hot and humid climate (Miami, Florida); a hot and dry climate (Phoenix, Arizona); and a polluted atmosphere in a temperate climate (Cleveland, Ohio). A fourth mixture was designed to reproduce the three-site average values of solar reflectance and thermal emittance attained after three years of natural exposure, which the Cool Roof Rating Council (CRRC) uses to rate roofing products sold in the United States. This accelerated aging method was applied to 25 products—single ply membranes, factory and field applied coatings, tiles, modified bitumen cap sheets, and asphalt shingles—and reproduced in three days the CRRC's three-year aged values of solar reflectance. It is envisioned that this accelerated aging method will become a useful tool to speed the evaluation and rating of new cool roofing materials.

1 Introduction

Highly reflective roofs can decrease the energy required for building air conditioning, help mitigate the urban heat island effect, and slow global warming. Replacing a conventional dark gray roof with a solar-reflective white roof can reduce a commercial building's annual conditioning energy use in the US by about 20% [1]. Similar effects

have been reported for different European climates [2-4]. Widespread use of cool roofs can help mitigate the urban heat island effect by lowering outside air temperatures. This can further decrease conditioning energy use by another 10%, and reduce the temperature-dependent rate of smog formation [5]. Replacing 100 m^2 of a dark roof (solar reflectance, or "albedo," 0.15) with an aged white roof (albedo 0.55) induces a negative radiative forcing in the global atmospheric energy balance sufficient to offset the emission of 28 t of CO_2, worth US$700 at US$25/t CO_2. This is equivalent to a 7 kg CO_2 per m^2 offset per 0.01 increase of surface albedo. Increasing the albedo of the roofs for all cities between latitudes 45°S and 45°N by an average of 0.25 could offset about 90 Gt CO_2, equal to about three years of global CO_2 emission [6, 7].

Most "cool" roofs can have a very high solar reflectance, but their solar reflectance decreases by soiling and weathering [1, 8]. Soiling processes include deposition of atmospheric black carbon, dust, organic and inorganic particulate matter, as well as microbiological growth. Material weathering results from exposure to moisture and ultraviolet (UV) radiation, and to diurnal temperature cycles. Installed roofing products may take several years to reach a quasi steady reflectance, modulated by the seasonal variability in precipitation, dust deposition, and air pollution, as well as by physical and chemical changes to the exposed materials. These weathering processes have been documented by Berdahl et al. [9].

Part I of our current series on the aging of roofing materials [10] analyzed the initial and aged radiative properties of hundreds of products rated by the Cool Roof Rating Council (CRRC) or by the Energy Star program of the U.S. Environmental Protection Agency (EPA). Part II (this article) details the chemical, physical and microbiological nature of soiling agents, and the transformations that occur on building envelope surfaces. It then describes the application of this information to develop a laboratory method that replicates three years of natural exposure within a few days.

2 Composition of soiling present on urban surfaces

Deposition of atmospheric particulate matter is the dominant source of soiling agents accumulating on exposed building surfaces. Thus, the composition of material deposited on buildings reflects the main constituents of atmospheric particulate matter [11, 12]. Glass substrates exposed in six European cities collected four major constituents of particulate matter emitted from human activities, generated by natural processes, and formed in the atmosphere: dust minerals (28-66 wt%), black carbon (4-12 wt%), organic matter (8-36 wt%) and soluble salts (18-27 wt%) [11]. Black carbon and organic matter are major components of soot particles emitted during the combustion of fossil fuel and biomass. A substantial portion of the particulate organic matter commonly referred to as secondary organic aerosol is formed in the atmosphere. Black carbon, which is largely elemental in composition and thus also referred to as elemental carbon, strongly absorbs solar radiation. Some particulate organic matter, especially that emitted from biomass combustion, also absorbs sunlight, though with much greater wavelength selectivity and lower mass-absorption efficiency than black carbon [13]. Light-absorbing organic matter contains highly polymerized humic-like substances that are brown in color [14]. Windblown dust is a spectrally selective and relatively weak absorber owing to the presence of iron oxides [15]. Particulate salts from evaporated sea spray and secondary aerosol salts such as ammonium nitrate and ammonium sulfate are light scattering [16].

On building surfaces, black carbon is coated with organics and salts [11]. Consistent with the composition of atmospheric particulate matter [17], organic carbon is more abundant than black carbon in urban soiling [11, 18-22]. Deposition of atmospheric SO_2 to urban surfaces is a major source of inorganic soiling (sulfates), leading to the degradation of limestone, granite, metal, and glass surfaces [12, 22-26]. Sulfates and nitrates are the predominant inorganic anions found in building soiling patinas [18, 23]. The principal water-soluble cations found in building surfaces (crusts, patinas and dust) are Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}. The non-water soluble fraction of deposited inorganic constituents remains on surfaces relatively unaltered. The organic fraction of urban soiling undergoes major changes. Evaporation of volatile constituents enriches surface films in semivolatile and non-volatile compounds that experience long-term chemical

transformations, which include photochemical oxidation, hydrolysis, polymerization, oxidation and nitrosation with reactive atmospheric species [11, 12]. The amount of soiling material on surfaces also depends on accumulation or loss of individual constituents due to wind, dissolution in water, and/or runoff [23, 25, 27].

Microbial growth can be a major agent of roof soiling in humid climates. The capacity of roofing materials to capture and retain moisture in porous structures or to leach organic compounds that feed microbial colonies favors the growth of bacteria, fungi, algae and lichen. Deposition of atmospheric particulate matter also promotes microbial growth [28]. The complexity and composition of microbial colonies is site-specific and depends on the nature of the surface material, rainfall, and relative humidity [20, 29]. Lichen colonies excrete oxalic acid that degrade ceramic tiles (biocorrosion) [30]. Green microalgae form biofilms at interfaces in roof tiles, concrete, building façades and other urban surfaces [31-33]. Numerous fungi (*Aspergillus*, *Stachybotrys*, *Epicoccum*) and bacteria (*Streptomyces*) synthesize melanins that are generally dark [34-36]. Cyanobacteria dark crusts have been observed on the surfaces of limestone monuments [37] and building façades [32, 33]. Key chemical constituents of microbiological soiling are complex mixtures of polysaccharides present in the cell wall, capsule and slime, as well as those secreted by algae and cyanobacteria to facilitate adhesion to surfaces [38, 39]. Over time, as colonies die, melanins and polysaccharides become persistent constituents of microbial soiling due to their resistance to photooxidation and other degradation processes.

3 Rating of aged roofing materials

The CRRC product rating program [40] and the US EPA's Energy Star labeling program [41] each report values of solar reflectance and thermal emittance of products in new condition and after three years of natural outdoor exposure. While a roofing product is undergoing this three year exposure, the California Energy Commission’s "Title 24" building energy efficiency standard [42] calculates for compliance a provisional value of aged solar reflectance based on initial solar reflectance. Part I of this series analyzed the

initial and aged solar reflectances of 586 CRRC-rated products exposed at three sites selected by the CRRC: Miami, Florida (hot and humid); Phoenix, Arizona (hot and dry); and Cleveland, Ohio (temperate but polluted) [10]. The analysis concluded that the 2008 Title 24 linear formula for provisional aged solar reflectance over-predicted the CRRC-reported measured aged solar reflectance of up to 30% of the products in certain categories. The rate of overprediction was greatest for field-applied coating and single-ply membrane products, and least for factory-applied coating, shingle, and metal products.

4 Development of an accelerated method to mimic the aged radiative properties of roofing materials

4.1 Selection of tested roofing materials

Initially, nineteen roofing products in seven categories (asphalt shingles, tiles, single-ply membranes, metal roofing, modified bitumen capsheets, factory and field applied coatings) were used to develop the accelerated aging method. Table 1 lists the range of colors and initial solar reflectances of the tested products. These products were selected from more than 100 roofing materials available from 40 US and international roofing manufacturers. Selection criteria included diversity of products and colors, wide range of initial solar reflectance, and significant market share. Also, we included only flat products whose radiative properties could be readily measured using ASTM methods. Since several of these products were not yet rated by CRRC at the time of this study, a second set of 25 rated products (also listed in Table 1) was used to validate the protocol.

4.2 Radiative measurements

Once the roofing samples were selected, we then proceeded to measure their initial radiative properties to have an initial point of comparison, using the following methods:

4.2.1 Solar reflectance

Following ASTM C1549-09 (Standard Test Method for Determination of Solar Reflectance Near Ambient Temperature Using a Portable Solar Reflectometer) [43], the

solar reflectance of each product coupon was measured using version 6 of the Solar Spectrum Reflectometer (Devices & Services; Dallas, Texas). We report the instrument's air mass 1.5 beam-normal solar reflectance output "1.5E," as specified by the ANSI/CRRC-1-2012 Standard [44]. Measurements were made at a minimum of three different spots on each coupon, and then averaged.

4.2.2 Solar spectral reflectance

Following ASTM E903-96 (Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Spheres) [45], a UV-VIS-NIR spectrophotometer (Perkin-Elmer Lambda 900) equipped with a 150 mm diameter Labsphere integrating sphere was used to measure the solar spectral reflectance of each coupon. Spectral reflectance was measured from 250 to 2500 nm at an interval of 5 nm at a minimum of three different spots on each coupon, and then averaged. To keep the integrating sphere clean, a quartz window was installed at its reflectance port, which separated the vertically mounted sample from the integrating sphere. Since this spectral reflectance is perturbed by the presence of the window[1], we refer to it as "through-window" spectral reflectance.

Our primary measure of solar reflectance was provided by the Solar Spectrum Reflectometer. However, we also used through-window spectral reflectance to calculate through-window solar reflectance $\hat{S}$ (300 – 2500 nm) and through-window visible reflectance $\hat{V}$ (400 – 700 nm). Each through-window broadband reflectance was calculated by weighting through-window spectral reflectance with the beam-normal solar spectral irradiance specified by ASTM E891-87(1992) (Tables for Terrestrial Direct Normal Solar Spectral Irradiance Tables for Air Mass 1.5) [46].

[1] Reflections at the air/window and window/sample interfaces can affect measurement of spectral reflectance. To compare under identical conditions, all spectral reflectance measurements reported in this study are measured through the window.

4.2.3 Thermal emittance

Thermal emittance was measured with a portable emissometer (Devices & Services Model AE1) following ASTM C1371-04a(2010)e1 (Standard Test Method for Determination of Emittance of Materials Near Room Temperature Using Portable Emissometers) [47], as specified in the CRRC Product Rating Program CRRC-1 [48, 49].

4.3 Artificial soiling

While commercial weatherometers are commonly used by industry to simulate the effect of weathering on material durability, widely accepted methods to simulate soiling have not been developed. Various dirt pick-up methods developed by industrial R&D centers are used for in-house testing, but are not intended to mimic the natural soiling required by the above mentioned rating programs [50, 51]. Our goal was to develop an accelerated laboratory method for simulating both soiling and weathering that could reproduce CRRC ratings of products naturally exposed for three years. The accelerated aging method is intended to be (a) applicable to a wide range of roofing products; (b) accurate and reproducible; (c) easy to implement; and (d) tunable to simulate different natural exposure conditions.

4.3.1 Soiling agents

Four soiling agents were selected to mimic natural soiling as described in Section 2: black carbon, mineral dust, inorganic salts, and humic acids (organics). The chemical structure of these acids is comparable to atmospheric oxidized organic particles and to decomposition products and residues from microbiological soiling agents, such as algae, bacteria, and fungi (see Section 2). The four soiling agents were combined in an aqueous mixture and applied as a spray. Spray deposition of the soiling agents was chosen for ease of control, and because soot deposition is typically waterborne [52]. A stock suspension of each soiling component was prepared as follows:

Black carbon. A commercially available self-dispersible hydrophilic black carbon was used (20 wt% carbon pigment in water, AquaBlack 001, Tokai Carbon Co., Ltd). The surfaces of the black carbon particles are carboxylated, which yields an

electrostatically stable suspension in water. The suspension was prepared by mixing 1.25 g of black carbon in 1 L of deionized water.

Mineral dust. A mixture of ferric oxide, Fe_2O_3 (CAS: 1309-37-1) and two natural clays, montmorillonite K10 (CAS: 1318-93-0) and a hydrophilic bentonite (CAS: 1302-78-9), was used to represent the main mineral dust constituents present in soiling. 0.3 g of Fe_2O_3 was mixed with 1 g of bentonite and 1 g of montmorillonite. The mixture was transferred to 1 L of deionized water and stirred for about 30 minutes to prepare a suspension of 2.3 g/L. The mixture was stirred for one hour before use to resuspend settled particles.

Salts. A 1 L solution containing a mixture of inorganic salts was prepared by dissolving 0.30 g of sodium chloride (NaCl, CAS: 7647-14-5), 0.30 g of sodium nitrate ($NaNO_3$, CAS: 7632-00-0) and 0.40 g of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$, CAS: 7778-18-9) in deionized water. The total salt concentration of the solution was 1.0 g/L.

Organics. 1.4 g of humic acid (CAS: 1415-93-6) was dissolved in 1 L of deionized water. Humic acids are good surrogates for light-absorbing particulate organic matter and decomposition products of algae and fungus.

These individual components were mixed in various ratios to simulate soiling in different climates. Three soiling mixtures were optimized to reproduce the site-specific solar spectral reflectance features of roofing products exposed in a hot and humid climate (Miami, Florida); a hot and dry climate (Phoenix, Arizona); and a polluted atmosphere in a temperate climate (Cleveland, Ohio), respectively. A fourth mixture was designed to reproduce the three-site average aged solar reflectance and thermal emittance values that the CRRC requires for the rating of roofing products. This average mixture was prepared by mixing in equal parts the four soiling dispersions described above.

4.3.2 Soiling apparatus and method

We created a prototype apparatus for spraying the aqueous suspensions of soiling agents onto roofing product coupons. As illustrated in Figure 1, a vessel containing the aqueous mixture is pressurized with air and connected to a nozzle that sprays a fine mist

into a soiling chamber. After experimenting with various nozzles, a model producing a hollow cone wide-angle pattern and containing a screen retainer to minimize clogging was chosen (model SF-2, Spraying Systems Co, Wheaton, IL). The following process was developed using a 10 cm × 10 cm coupon of a white single-ply membrane with high initial reflectance and low mass:

a. A dry and clean coupon of a reference sample (white single-ply membrane) is weighed (mass: M_0)

b. The spraying vessel is filled with 1 L of the soiling mixture, then closed and pressurized with compressed air.

c. The spraying is initiated for 10-30 seconds to verify that it is working properly and to attain a stable spraying flow.

d. While the spraying is running, the clean coupon of the reference sample is placed on a flat dry tray and inserted into the soiling chamber (Figure 1). The coupon is left under spray for periods ranging from 10 to 30 seconds depending on the flow rate of the spraying and the position of the coupon .

e. The reference coupon is removed (while spraying is still running to avoid dripping) from the soiling chamber and immediately weighed without the tray (mass: M_1). During this step, it is important to handle the sample delicately to avoid losing some of the soiling droplets.

f. If M_1-M_0 is not between 0.8 and 1.0 g, then steps **d** and **e** are repeated using other dry and clean reference coupons until identifying the optimal position and duration of spraying that lead to 0.8-1.0 g of wet soiling mass. The optimal surface concentration of soiling was determined to be in the range of 8 – 10 mg cm^{-2}, which correspond to a wet soiling mass $M_1 - M_0 = 0.8 - 1.0$ g given that the surface of our reference coupon is about 100 cm^2. This range was determined based on establishing quantitative correlations between the soiling ingredients and the loss of solar reflectance and by comparing with naturally aged samples

retrieved from the three CRRC locations. More details on the optimization are provided below (Section 4.3.3).

g. Once the desired wet soiling mass is obtained, the soiled reference coupon is placed under a heat infrared lamp (250 W) to dry for about 10 - 15 minutes. Surface temperature should not exceed 80 C during the drying process to avoid degradation of the roofing materials.

h. After drying, the uniformity of the soiling is verified visually by taking a picture of the soiled coupon as well as by verifying that the values of solar reflectance measured at three non-overlapping spots (e.g., bottom left corner, center and top right corner) do not differ by more than 0.02. An example of a uniformly soiled coupon is shown in on the right side of Figure 2.

i. Using the same conditions used above, three additional clean reference coupons are sequentially soiled and dried, then measured to determine that the procedure is repeatable with a standard deviation that does not exceed 0.02.

j. Once the wet soiling mass, the uniformity of spraying pattern and the standard deviation conditions are met, conditioned roofing coupons to be tested are soiled one at a time using identical conditions as the reference coupon.

4.3.3 Effects of individual soiling agents on reflectance

As illustrated in Figure 3, black carbon reduced the reflectance of the white single-ply membrane across the entire solar spectrum. Per unit dry mass applied, black carbon reduced the solar reflectance of samples more than other soiling agents. Humic acid and dust surrogates reduced the reflectance in the visible and ultraviolet regions. Inorganic salts did not measurably influence spectral reflectance but were included in the soiling mixture because they can increase the solar reflectance of dark surfaces and also affect the adhesion of soiling constituents to surfaces due to their water solubility. Dose-response relationships between soiling loading and reflectance loss are shown in Figure 4 for black carbon and humic acid using the through-window solar and visible reflectances $\hat{S}$ and $\hat{V}$ defined in Section 4.2.2. These relationships were determined by calculating

the dry coverage rate for each soiling ingredient (dry mass of sprayed soiling agent per unit area, in mg/cm^2), z, as follows:

$$z = \frac{C \cdot m}{\delta \cdot A} \tag{1}$$

where C is the concentration of soiling agent in water [mg/L], $m = (M_1 - M_0)$ is the wet deposition mass [mg], δ is the density of the suspension [mg/L], and A is the coupon area [cm^2]. Since black carbon absorbs over the entire solar spectrum, retention of reflectance after soiling by black carbon was gauged by the ratio of soiled to initial through-window solar reflectance, $\hat{S}/\hat{S}_0$. Spectral changes are illustrated in Figure 4a, and the linear variation of $\hat{S}/\hat{S}_0$ with black carbon deposition is shown in Figure 4b. Humic acid affected the reflectance in the visible region, and retention of reflectance after soiling with humic acid was gauged by the ratio of soiled to initial through-window visible reflectance, $\hat{V}/\hat{V}_0$. Spectral changes with increasing humic acid loading are shown in Figure 4c, and the non-linear variation of $\hat{V}/\hat{V}_0$ with deposited humic acid is shown in Figure 4d. The non-linear trend could be caused by the high surface concentrations of humic acid that lead to a saturation of the signal. Dust surrogates show an effect similar to that observed for humic acid, with changes only in the visible spectrum. Using equal concentrations, the magnitude of change is eight times smaller than that of humic acid. The contribution of salts to the loss of reflectance was negligible. Using the correlations shown in Figure 4, it is possible to predict the loss of reflectance from dry coverage. For example, Figure 4b shows that the ratio of soiled to clean solar reflectance of a light-colored surface with 0.5 µg cm^{-2} of deposited black carbon is about 0.87, which is in good agreement with a previous study reporting a ratio of 0.91 [9].

4.3.4 Soiling mixture formulation

Based on the correlations described in Section 4.3.3, specific soiling mixtures were created to mimic the spectral reflectance and solar reflectance of aged samples in each of the three CRRC-specified locations (AZ, OH and FL). The optimization of the mixtures was performed by comparing the spectral reflectance of laboratory-soiled coupons with naturally aged coupons of the same products retreived from the three CRRC-specified

locations. In addition to site-specific mixtures, a three-site average mixture was prepared to simulate the three-site average solar reflectance after three years of exposure. Figure 5 shows the dry mass fractions within each mixture. Concentrations in the three-site average mixture were 0.575 g/L dust, 0.25 g/L salts, 0.35 g/L humic acid, and 0.0625 g/L black carbon. To obtain the best possible match with the naturally aged samples and to ensure that the soiling is uniform and not excessive, the optimal wet soiling mass was found to be in the range of 0.8 to 1.0 g, yielding a wet coverage rate ω ($\omega = m/A$) of 8 to 10 mg cm^{-2}. This corresponds to a dry coverage rate z of 0.50 – 0.56 μg cm^{-2} for a black carbon concentration of C = 62.5 mg L^{-1} in the average soiling mixture. Considering that measuring z is challenging, the calibration of the soiling method is routinely verified by determining ω via measurement of a reference coupon's weight before and after soiling spraying, as described in Section 4.3.2. When applied as a thick opaque coating over the white single-ply membrane, the solar reflectance of the three-site average soiling mixture was found to be 0.19 (Figure 6), which is very similar to that of an opaque natural soil layer (≈ 0.20) [9].

4.4 Artificial conditioning and weathering

A commercial QUV testing chamber (Q-Lab Corp.; Westlake, OH) was used to condition coupons before soiling and to simulate outdoor weathering after soiling. Conditioning in the QUV was tested to investigate its effect on the subsequent soiling by affecting the surface properties of roofing samples (e.g., roughness, hyrophobicity). On ther other hand, weathering after soiling was studied to evaluate how the soiling applied on roofing samples can be washed, in a manner that simulates the natural weathering where rain and moisture can partially clean soiled roofs. The QUV weatherometer exposes materials to alternating cycles of ultraviolet light (UVA, peak wavelength 340 nm) and moisture at elevated temperatures. It uses fluorescent UV lamps to generate the high energy photons present in sunlight. It also simulates dew and rain with condensing humidity and/or water spray cycles (ASTM G151 and G154) [53, 54]. Our application of the weatherometer to the development of an accelerated aging method that includes soiling is new, as weatherometers are conventionally used to test the durability and light

fastness, but not soil resistance, of coatings, roofing materials and other building surfaces [55, 56].

4.4.1 Conditioning samples before soiling

Conditioning in the QUV instrument was performed following ASTM G154 cycle 1 (8 h of UV 0.89 W/m^2 @ 340 nm, T=60 °C; followed by 4 h water condensation at 50 °C). At 0.89 W/m^2, the QUV delivers an hourly irradiation of 275 kJ/m^2. Thus, accelerated exposure in the QUV for 1,000 hours (about 42 days) is approximately equivalent to one year of Florida sunshine (approximate annual UV dosage = 275 MJ/m^2) [57].

Figure 7a shows the effects of conditioning for 1, 3, 7 and 35 days on the absolute loss of solar reflectance of various roofing products. The absolute loss of solar reflectance with conditioning at 7 or more days was small (-0.03 to 0.03) for all categories of tested roofing materials. At 35 days, only one sample – an initially white modified bitumen that turned light yellow – experienced further solar reflectance loss.

With the exception of asphalt shingles, the solar reflectance of most highly reflective samples slightly decreased during conditioning. UV degradation of oily films covering the granules on the asphalt shingles may have increased shingle solar reflectance [58]. Considering that the change in solar reflectance because of conditioning was in most cases (except for modified bitumen) equally small for one day and longer durations, one day of conditioning was considered sufficient.

Although conditioning alone did not significantly influence the solar reflectance of roofing samples or lead to mechanical failure, we investigated its effect on the adhesion of soiling constituents. As shown in Figure 7b, loss of solar reflectance was slightly more pronounced for most samples if a one-day conditioning step was performed before soiling. Thus, the conditioning step increased the adherence of soiling constituents subsequently added to the surface of roofing samples, probably because water uptake and UV irradiation change the surface roughness and hydrophobicity [59-61]. These findings indicate that a brief conditioning phase is influential in the accelerated aging process.

4.4.2 Weathering samples after soiling

A weathering step after soiling was included to simulate natural exposure to water, UV and high temperatures (Figure 7c). One day of exposure (ASTM G154 cycle 1) partially removed some deposited soiling constituents, thus reducing the loss of solar reflectance. Increasing weathering duration from one day to one week (not shown) did not affect the loss of solar reflectance for 17 out of the 19 products. This suggests that the readily removable fraction of the soil layer is eliminated after one day in the weatherometer, and that longer weathering periods are unnecessary in the simulation of natural cleaning. The two exceptions were modified bitumen and one of the field applied coatings. In both cases, noticeable loss of solar reflectance due to yellowing of the surface was observed, suggesting a poor stability of the polymeric coating during weathering in the QUV.

Given the short sample exposure time during conditioning in the weatherometer before and after soiling, our method is aimed at mimicking natural changes in solar reflectance in the absence of major physical damage, such as coating delamination. Many material durability tests require much longer periods of exposure (> 1000 hours) in order to achieve material degradation [62, 63].

4.5 Accelerated aging process

Based on the results presented above, we developed the three-step accelerated aging process diagrammed in Figure 8:

a. A roofing coupon is conditioned using ASTM G154 cycle 1 for one day.

b. A soiling mixture is deposited on the conditioned coupon under controlled spraying conditions after calibrating the spraying system following . The coupon is then dried under an infrared lamp.

c. The soiled and dried coupon is weathered using ASTM G154 cycle 1 for one day.

4.6 Comparison of accelerated aging to natural aging

4.6.1 Comparison with the three-site average aged values of solar reflectance and thermal emittance

The three-site average values of aged solar reflectance and aged thermal emittance reported by the CRRC for 25 roofing samples were compared with the solar reflectances and thermal emittances obtained using the laboratory accelerated aging process illustrated in Figure 8. Figure 9a shows a very good match between the aged solar reflectances obtained in the laboratory and those reported by the CRRC, suggesting that the accelerated aging method accurately simulates in just a few days the changes due to three years of outdoor exposure in the US. A perfect match (difference equal to zero) was observed for five of the 25 products tested. The values of solar reflectance for 20 out of the 25 products aged in the laboratory were within ±0.03 of the reported 3-year CRRC values.

Figure 9b shows the correlation between the aged thermal emittances obtained in the laboratory and those reported by the CRRC. The range of CRRC 3-year thermal emittance for all products studied is limited to 0.80 – 0.95. On average, the difference between the laboratory aged thermal emittance and CRRC 3-years values is equal to 0.02. The root mean square deviation (*RMSD*) is 0.027 with a mean value of the natural exposure thermal emittance of 0.87, yielding a coefficient of variation $CV = 3.1\%$.

4.6.2 Comparison with the natural exposure results of individual categories of roofing products

Figure 10a illustrates for each product category the average difference (accelerated minus natural) between values of solar reflectance obtained in the laboratory and the 3-year CRRC natural exposure values. The *RMSD* between the laboratory aged and CRRC 3-year solar reflectances was 0.028. This yields a coefficient of variation $CV = RMSD/\text{mean} = 5\%$. The largest difference observed was in the case of modified bitumen samples. In this case, we observed that the surface of naturally exposed sample yellowed more than that of the lab-aged sample likely due to the relatively short accelerated weathering cycles in the laboratory method. Overall, small discrepancies observed between materials exposed in the laboratory and the field may be due to that fact that our

method does not mimic all features of microbial soiling or extreme physical-chemical changes that occur in some materials. For simplicity, our method does not grow microorganisms on the surface of roofing products and thus is unable to gauge resistance of these products to microbial growth. While humic acid can serve as a surrogate for decomposition products of algae and cyanobacteria (e.g., melanin and polysaccarides, as discussed in Section 2), the large variety of microbial species that can grow on roofing surfaces may change their spectral reflectance in ways that our laboratory method does not perfectly mimic.

Figure 10b compares the mean loss of solar reflectance reported by the CRRC for eight single-ply membranes to that obtained using the accelerated aging method. (These membranes are a subset of the 25 samples shown in Figure 9.) In addition to mimicking well the change in solar reflectance for each product, these data illustrate that our method also reproduces the trends of product performance for the eight products. This suggests that our method may be useful in ranking new products during prototyping. Application of the laboratory method of accelerated aging in lieu of lengthy natural exposure may help to identify and speed the development new products.

4.6.3 Comparison with individual CRRC-specified natural exposure locations

Figure 11 compares the through-window solar spectral reflectances of a white field-applied coating soiled in the laboratory with site-specific mixtures to those of white field-applied coatings exposed for three years in each of the three CRRC-specified sites. The spectra match very well for samples exposed in Arizona and Ohio. However, the reflectance spectrum of the laboratory-aged sample is different from that of the sample naturally aged in Florida, particularly in the visible region. This is likely the result of absorption of visible light by microorganisms [64]. Microbial growth on roofing materials exposed in hot and humid climates, such as those in Florida, can be extreme enough to greatly change their appearance and albedo in ways that cannot be reproduced by our method. Other methods have been developed to examine microbial growth on surfaces [65-67].

4.7 Precision of the accelerated aging method

To determine the method's precision, the experimental protocol described in Figure 8 was applied to a sub-set of 12 roofing products (3 single-ply membranes, 2 field applied coatings, 2 modified bitumen capsheet, 1 bare metal, 1 factory applied coating, 2 tiles and 1 asphalt shingle). For each product, four replicate coupons were used. Measurements of the solar reflectance at three non-overlapping spots of the surface were performed. According to ASTM E177-13 [68], the repeatability is precision determined from multiple test results conducted under repeatability conditions, where the test method is conducted by a single, well-trained operator usinf one set of equipment. It is a means for quantifying the uncertainty in the observed difference between identical samples submitted for analysis to a single lab, and can be defined as:

$$\text{Repeatability (\%)} = 2.77 * CV_p \qquad (2)$$

where 2.77 is a constant obtaining by multiplying the inverse of the standard normal cumulative distribution for a confidence interval of 95% (which is equal to 1.96) by the square root of 2. CV_p is the average of coefficients of variation (*CV*) for each of the 12 products (p = 12). For each product, *CV* was calculated by dividing the *RMSD* for the four coupons (n=4) by the mean solar reflectance of those coupons. Results showed that *CV* ranged from 0.4 to 1.6 % with an average CV_p of 0.9%. This yields a repeatability of 2.5%. This means that if identical samples are submitted to the same lab, 95% of the time the observed difference should fall within the repeatability criterion of 2.5%.

An inter-laboratory study following ASTM Standard E691 is underway to determine the inter-laboratory precision of the method (repeatability and reproducibility). The method will be reproduced by a minimum of six laboratories and results will reported separately in a future publication.

5. Conclusions

The high solar reflectance of cool roofing materials typically decreases with natural exposure. This study provided an overview of natural soiling and presented a novel laboratory accelerated aging method that combines soiling and weathering and simulates three years of outdoor exposure. Several features of the proposed method make it a valuable tool to assist industry in developing better-performing cool roofing materials as well as code bodies to help implement cool roof requirements:

a. It is accurate and widely applicable. The method reproduces both the solar reflectance and solar spectral reflectance observed in a wide range of naturally exposed roofing products.

b. It is easy to perform, repeatable, and fast. The method can be performed by different users requiring only a basic training. Unlike outdoor exposure tests that are subject to natural variations in meteorology and air pollution, the laboratory method achieves the same results within a $CV < 3\%$ each time it is applied. While the current outdoor exposure test requires three years to complete, the laboratory method requires only three days.

c. It is tunable. The dose and composition of soiling constituents can be tuned to simulate natural exposure in different climates. While the results described here are intended to simulate the average of the three CRRC sites in the US, the same method may be adjusted to predict aging of materials under other climatic conditions of interest.

At the time that this manuscript is in preparation, the accelerated aging method developed in this study is under consideration as an ASTM standard. No single approach can simulate all possible climates and their effects on the performance of every product. Nevertheless, given the positive attributes summarized above, it is envisioned that this method will be extremely useful for industry to speed prototyping and the development of high performance building envelope materials that resist soiling,

maintain high solar reflectance and save energy. With further tuning, this method may also apply to other building surfaces (e.g., façades) and to photovoltaic systems, including those that are building integrated.

ACKNOWLEDGEMENTS

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Building Technologies Office of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors thank Marc LaFrance, Karma Sawyer, Patrick Phelan and Alexis Abramson of the Department of Energy (Office of Energy Efficiency, Building Technologies Office) for program management and support; and Riccardo Paolini (Politecnico de Milano) and George Ban-Weiss (University of Southern California) for valuable suggestions. The authors also recognize the significant support from several industrial collaborators, who provided the roofing samples for natural exposure and laboratory testing and contributed invaluable feedback and suggestions to improve the accelerated aging method.

References

1. Levinson R., Akbari H., Konopacki S. and Bretz S., 2005. Inclusion of cool roofs in nonresidential Title 24 prescriptive requirements. *Energy Policy* 33, 151-170.

2. Bozonnet E., Doya M. and Allard F., 2011. Cool roofs impact on building thermal response: A French case study. *Energy and Buildings* 43, 3006-3012.

3. Santamouris M., Synnefa A. and Karlessi T., 2011. Using advanced cool materials in the urban built environment to mitigate heat islands and improve thermal comfort conditions. *Solar Energy* 85, 3085-3102.

4. Synnefa A., Saliari M. and Santamouris M., 2012. Experimental and numerical assessment of the impact of increased roof reflectance on a school building in Athens. *Energy and Buildings* 55, 7-15.

5. Rosenfeld A.H., Akbari H., Romm J.J. and Pomerantz M., 1998. Cool communities: strategies for heat island mitigation and smog reduction. *Energy and Buildings* 28, 51-62.

6. Akbari H., Matthews H.D. and Seto D., 2012. The long-term effect of increasing the albedo of urban areas. *Environ. Res. Letters* 7, 024004.

7. IEA, 2012. CO_2 emissions from fuel combustion. Highlights. *International Energy Agency OECD/IEA, Paris, France.* *http://www.iea.org/publications/freepublications/publication/CO2emissionfromfuelcombustionHIGHLIGHTSMarch2013.pdf*

8. Revel G.M., Martarelli M., Bengochea M.A., Gozalbo A., Orts M.J., Gaki A., Gregou M., Taxiarchou M., Bianchin A. and Emiliani M., 2013. Nanobased coatings with improved NIR reflecting properties for building envelope materials: Development and natural aging effect measurements. *Cement & Concrete Composites* 36, 128-135.

9. Berdahl P., Akbari H., Levinson R. and Miller W.A., 2008. Weathering of roofing materials - An overview. *Construction and Building Materials* 22, 423-433.

10. Sleiman M., Ban-Weiss G., Gilbert H.E., Francois D., Berdahl P., Kirchstetter T.W., Destaillats H. and Levinson R., 2011. Soiling of building envelope surfaces and its effect on solar reflectance-Part I: Analysis of roofing product databases. . *Solar Energy Materials and Solar Cells* 95, 3385-3399.

11. Favez O., Cachier H., Chabas A., Ausset P. and Lefevre R., 2006. Crossed optical and chemical evaluations of modern glass soiling in various European urban environments. *Atmospheric Environment* 40, 7192-7204.

12. Ferm M., Watt J., O'Hanlon S., De Santis F. and Varotsos C., 2006. Deposition measurement of particulate matter in connection with corrosion studies. *Analytical and Bioanalytical Chemistry* 384, 1320-1330.

13. Kirchstetter T.W. and Thatcher T.L., 2012. Contribution of organic carbon to wood smoke particulate matter absorption of solar radiation. *Atmos. Chem. Phys.* 12, 6067-6072.

14. Andrae M.O. and Geleneser A., 2006. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. *Atmos. Chem. Phys.* 6, 3131-3148.

15. Kinne S., Lohmann U., Feicher J. and al e., 2003. Monthly averages of aerosol properties: A global comparison among models, satellite data and AERONET ground data. *J. Geophys. Res.* 108 (D20), 4634.

16. Covert D.S., Charlson R.J. and Ahlquist N.C., 1972. A study of the relationship of chemical composition and humidity to light scattering by aerosols. *J. Applied Meteorology* 11, 968-976.

17. Finlayson-Pitts B.J. and Pitts J.N., Chemistry of the upper and Lower Atmosphere. 2000, San Diego, CA: Academic Press. pp.969.

18. Bonazza A., Sabbioni C. and Ghedini N., 2005. Quantitative data on carbon fractions in interpretation of black crusts and soiling on European built heritage. *Atmospheric Environment* 39, 2607-2618.

19. Cheng M.-D., Miller W., New J. and Berdahl P., 2012. Understanding the long-term effects of environmental exposure on roof reflectance in California. *Construction and Building Materials* 26, 516-526.

20. Cheng M.-D., Pfiffner S.M., Miller W.A. and Berdahl P., 2011. Chemical and microbial effects of atmospheric particles on the performance of steep-slope roofing materials. *Building and Environment* 46, 999-1010.

21. Schiavon N., Chiavari G. and Fabbri D., 2004. Soiling of limestone in an urban environment characterized by heavy vehicular exhaust emissions. *Environmental Geology* 46, 448-455.

22. Schiavon N., Chiavari G., Schiavon G. and Fabbri D., 1995. Nature and decay effects of urban soiling on granitic building stones. *Science of the Total Environment* 167, 87-101.

23. McAlister J., Smith B.J. and Torok A., 2008. Transition metals and water-soluble ions in deposits on a building and their potential catalysis of stone decay. *Atmospheric Environment* 42, 7657-7668.

24. Rodriguez-Navarro C. and Sebastian E., 1996. Role of particulate matter from vehicle exhaust on porous building stone (limestone) sulfation. *Science of the Total Environment* 187, 79-91.

25. Monna F., Puertas A., Leveque F., Losno R., Fronteau G., Marin B., Dominik J., Petit C., Forel B. and Chateau C., 2008. Geochemical records of limestone facades exposed to urban atmospheric contamination as monitoring tools? *Atmospheric Environment* 42, 999-1011.

26. Brimblecombe P. and Grossi C.M., 2009. Millennium-long damage to building materials in London. *Science of the Total Environment* 407, 1354-1361.

27. Robert-Sainte P., Gromaire M.C., De Gouvello B., Saad M. and Chebbo G., 2009. Annual Metallic Flows in Roof Runoff from Different Materials: Test-Bed Scale in Paris Conurbation. *Environmental Science & Technology* 43, 5612-5618.

28. Viles H.A. and Gorbushina A.A., 2003. Soiling and microbial colonisation on urban roadside limestone: a three year study in Oxford, England. *Building and Environment* 38, 1217-1224.

29. Thornbush M. and Viles H., 2006. Changing patterns of soiling and microbial growth on building stone in Oxford, England after implementation of a major traffic scheme. *Science of the Total Environment* 367, 203-211.

30. Radeka M., Ranogajec J., Kiurski J., Markov S. and Marinkovic-Neducin R., 2007. Influence of lichen biocorrosion on the quality of ceramic roofing tiles. *Journal of the European Ceramic Society* 27, 1763-1766.

31. Schumann R., Haubner N., Klausch S. and Karsten U., 2005. Chlorophyll extraction methods for the quantification of green microalgae colonizing building facades. *International Biodeterioration & Biodegradation* 55, 213-222.

32. Barberousse H., Ruot B., Yepremian C. and Boulon G., 2007a. An assessment of facade coatings against colonisation by aerial algae and cyanobacteria. *Building and Environment* 42, 2555-2561.

33. Barberousse H., Lombardo R.J., Tell G. and Coute A., 2006a. Factors involved in the colonisation of building facades by algae and cyanobacteria in France. *Biofouling* 22, 69-77.

34. Butler M.J. and Day Can A.W., 1998. Fungal melanins: a review. *J. Microbio.* 44, 1115-1136.

35. Kogel-Knabner I., 2002. The macromolecular organic composition of plant and microbioal residues as inputs to soil organic matter. *Soil Biology and Biochemistry* 34, 139-162.

36. Gomez-Alarcon G., Munoz M., Arino X. and Ortega-Calvo J.J., 1995. Microbial communities in weathered sandstones: the case of Carrascosa del Campo church, Spain. *Science of the Total Environment* 167, 249-254.

37. Bonazza A., Sabbioni C., Ghedini N., Hermosin B., Jurado V., Gonzalez J.M. and Saiz-Jimenez C., 2007. Did smoke from the Kuwait oil well fires affect Iranian archaeological heritage? *Environmental Science & Technology* 41, 2378-2386.

38. Barberousse H., Ruiz G., Gloaguen V., Lombardo R.J., Djediat C., Mascarell G. and Castaing J.-C., 2006b. Capsular polysaccarides secreted by building facade colonisers: characterisation and adsorption to surfaces. *Biofouling* 22, 361-370.

39. Barberousse H., Brayner R., Botelho do Rego A.M., Castaing J.-C., Beurdeley-Saudou P. and Colombet J.-F., 2007b. Adhesion of facade coating colonisers, as mediated by physico-chemical properties. *Biofouling* 23, 15-24.

40. CRRC, 2009. Rated products directory of the Cool Roof Rating Council (CRRC). . Online at http://coolroofs.org/products/search.php

41. EPA, Energy Star Products - Roof Products. Available at: http://www.energystar.gov/index.cfm?fuseaction=find_a_product.showProductGroup&pgw_code=RO (accessed March 2013).

42. CEC, 2009. 2008 Building energy efficiency standards for residential and non-residential buildings. Online at: http://www.energy.ca.gov/title24/2008standards/ ; http://www.energy.ca.gov/2008publications/CEC-400-2008-001/CEC-400-2008-001-CMF.PDF,

43. ASTM, 2009. ASTM C1549-09: Standard Test Method for Determination of Solar Reflectance Near Ambient Temperature Using a Portable Solar Reflectometer. *American Society for Testing and Materials, West Conshohocken, PA.*

44. ANSI/CRRC, 2012. ANSI/CRRC-1-2012 Standard. American National Standards Institute / Cool Roof Rating Council. http://coolroofs.org/product-rating/ansi-crrc-1-standard

45. ASTM, 1996. ASTM E903-96: Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Spheres. *American Society for Testing and Materials, West Conshohocken, PA.*

46. ASTM, 1992. ASTM E891-87(1992): Tables for Terrestrial Direct Normal Solar Spectral Irradiance Tables for Air Mass 1.5. *American Society for Testing and Materials, West Conshohocken, PA.*

47. ASTM, 2010. ASTM C1371-04a(2010)e1: Standard Test Method for Determination of Emittance of Materials Near Room Temperature Using Portable Emissometers. *American Society for Testing and Materials, West Conshohocken, PA.*

48. CRRC, 2012. CRRC Product Rating Program CRRC-1, October. Cool Roof Rating Council, Oakland, CA. http://www.coolroofs.org/documents/CRRC-1_Program_Manual_100412.pdf

49. Moore C., 2011. Model AE1 emittance measurements using a port adapter, Model AE-ADP. Technical note 11-2. *Devices and Services, Dallas, TX. http://www.devicesandservices.com/TechNotes/TN11-2.pdf* In November 2011, the CRRC-1 Product Rating Program was updated to require the use of a "slide method" when using the portable emissometer to measure the thermal emittance of nonmetal products. However, the reported values of aged thermal emittance in the CRRC's Rated Product Directory being used for validation were made following ASTM C1371, without the slide method. .

50. Japanese standard of accelerated test method for building materials exposed to exterior pollution. *http://www.jtccm.or.jp/library/jtccm/hyojyun/jstm/201205/J7602.pdf*

51. DowConstructionChemicals, Elastomeric roof coatings. *http://www.dowconstructionchemicals.com/na/en/pdfs/832-00209.pdf*

52. Jacobson M.Z., 2004. Climate response of fossil fuela dn biofuel soot, accounting for soot's feedback to snow and sea ice albedo and emissivity. *J. Geophys. Res.* 109(D21), D21201.

53. ASTM, 2010. ASTM G151-10 Standard Practice for Exposing Nonmetallic Materials in Accelerated Test Devices that Use Laboratory Light Sources.

54. ASTM, 2012. ASTM G154-12a Standard Practice for Operating Fluorescent Ultraviolet (UV) Lamp Apparatus for Exposure of Nonmetallic Materials.

55. Samui A.B., Patankar A.S., Rangarajan J. and Deb P.C., 2003. Study of polyaniline containing paint for corrosion prevention. *Progress in Organic Coatings* 47, 1-7.

56. Decker C., Masson F. and Schwalm R., 2004. Weathering resistance of waterbased UV-cured polyurethane-acrylate coatings. *Polymer Degradation and Stability* 83, 309-320.

57. Q-Lab, 2013. Florida exposure is an international benchmark for durability testing of materials: http://www.q-lab.com/test-services/florida.aspx.

58. Berdahl P., Akbari H., Levinson R., Jacobs J., Klink F. and Everman R., 2012. Three-year weathering tests on asphalt shingles: Solar reflectance. *Solar Energy Materials and Solar Cells* 99, 277-281.

59. Bachmann J. and McHale G., 2009. Superhydrophobic surfaces: a model approach to predict contact angle and surface energy of soil particles. *Eur. J. Soil Sci.* 60, 420-430.

60. Maatta J., Piispanen M., Kymalainen H.R., UUsi-Rauva A., Hurme K.R., Areva S., Sjoberg A.M. and Hupa L., 2007. Effects of UV radiation on the cleanability of titanium dioxide-coated glazed ceramic tiles. *J. European Ceramic Soc.* 27, 4569-4574.

61. Piispanen M., Kronberg T., Areva S. and Hupa L., 2011. Effect of mechanical and chemical wear on soil attachment and cleanability of sanitary ware with additional coatings. *J. Amer. Ceramic Soc.* 94, 951-958.

62. Cocuzzi D.A. and Pilcher G.R., 2013. Ten-year exterior durability test results compared to various accelerated weathering devices: Joint study between ASTM International and National Coil Coatings Association. *Progress in Organic Coatings* 76, 979-984.

63. Mehta G., Mohanty A.K., Drzal L.T., Kamdem D.P. and Misra M., 2006. Effect of accelerated weathering on biocomposites processed by SMC and compression molding. *J. of Polymers and the Environment* 14, 359-368.

64. Levinson R., Berdahl P., Berhe A.A. and Akbari H., 2005b. Effects of soiling and cleaning on the reflectance and solar heat gain of a light-colored roofing membrane. *Atmospheric Environment* 39, 7807-7824.

65. ASTM, 2009. ASTM D3274 - 09e1. Standard test method for evaluating degree of surface disfigurement of paint films by fungal or algal growth, or soil and dirt accumulation. *http://www.astm.org/Standards/D3274.htm*

66. ASTM, 2009. ASTM G21 - 09. Standard practice for determining resistance of synthetic polymeric materials to fungi. *http://www.astm.org/Standards/G21.htm*

67. ASTM, 2010. ASTM E2149 - 10. Standard test method for determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions. *http://www.astm.org/Standards/E2149.htm*

68. ASTM, 2013. ASTM E177 - 13. Standard practice for use of the terms precision and bias in ASTM test methods. http://www.astm.org/Standards/E177.htm.

Table 1. Roofing products used for laboratory-accelerated aging.

Category	No. products used in method development	No. products used in method validation	Color	Range of initial solar reflectance
Single-ply membrane	2	8	blue, tan, white	0.26 – 0.88
Factory-applied coating	3	6	black, grey, red, white	0.25 – 0.76
Field-applied coating	6	5	white	0.82 – 0.91
Asphalt shingle	2	2	light brown, grey	0.26 – 0.28
Modified bitumen	1	2	white	0.27 – 0.75
Tile (clay and concrete)	4	1	White, red	0.29 - 0.76
Metal	1	1	bare	0.67

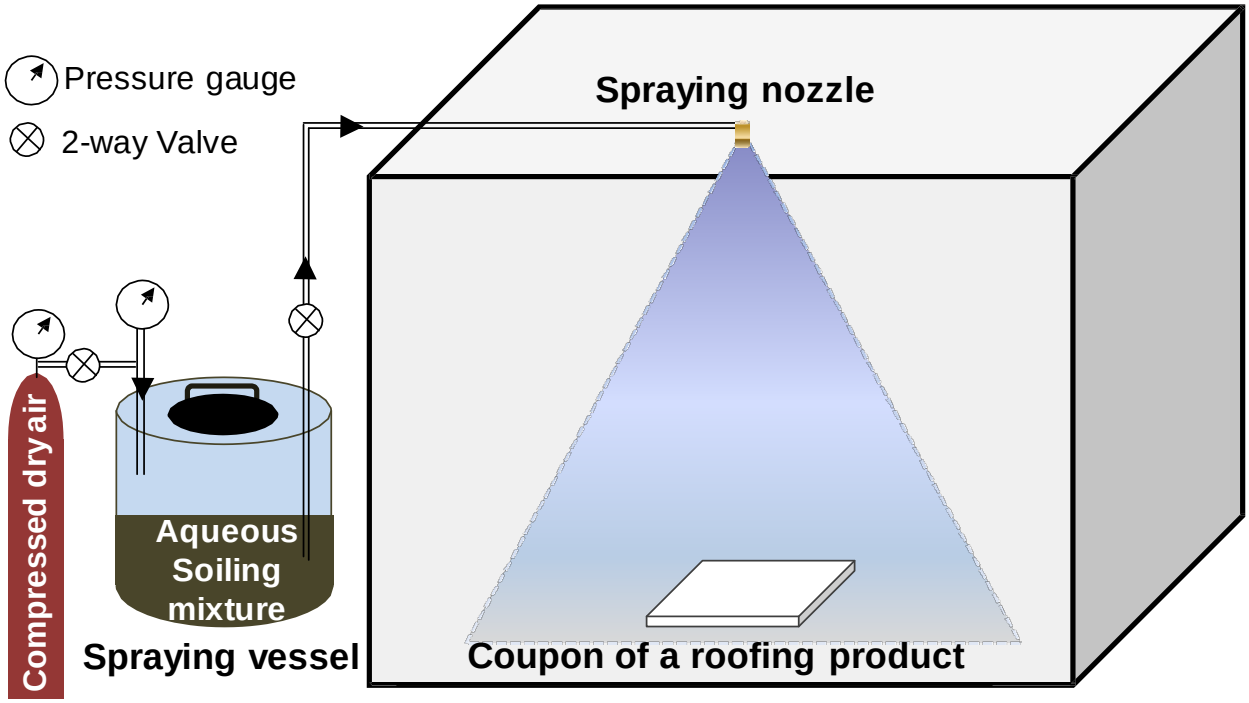


Figure 1. Apparatus used for laboratory-accelerated soiling of roofing materials.

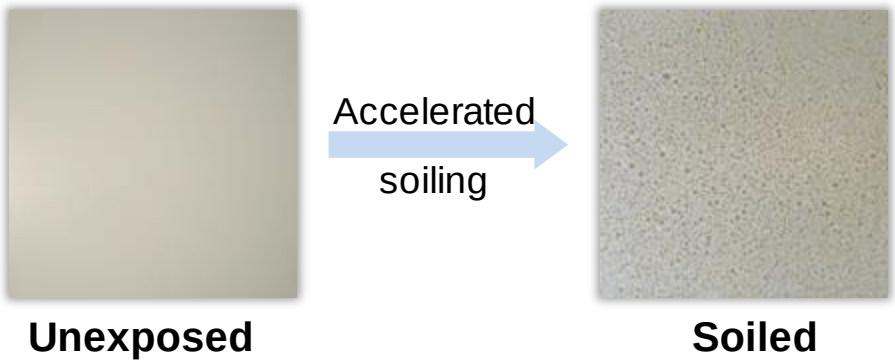


Figure 2. Photograph of unexposed and laboratory-soiled single-ply membrane coupons.

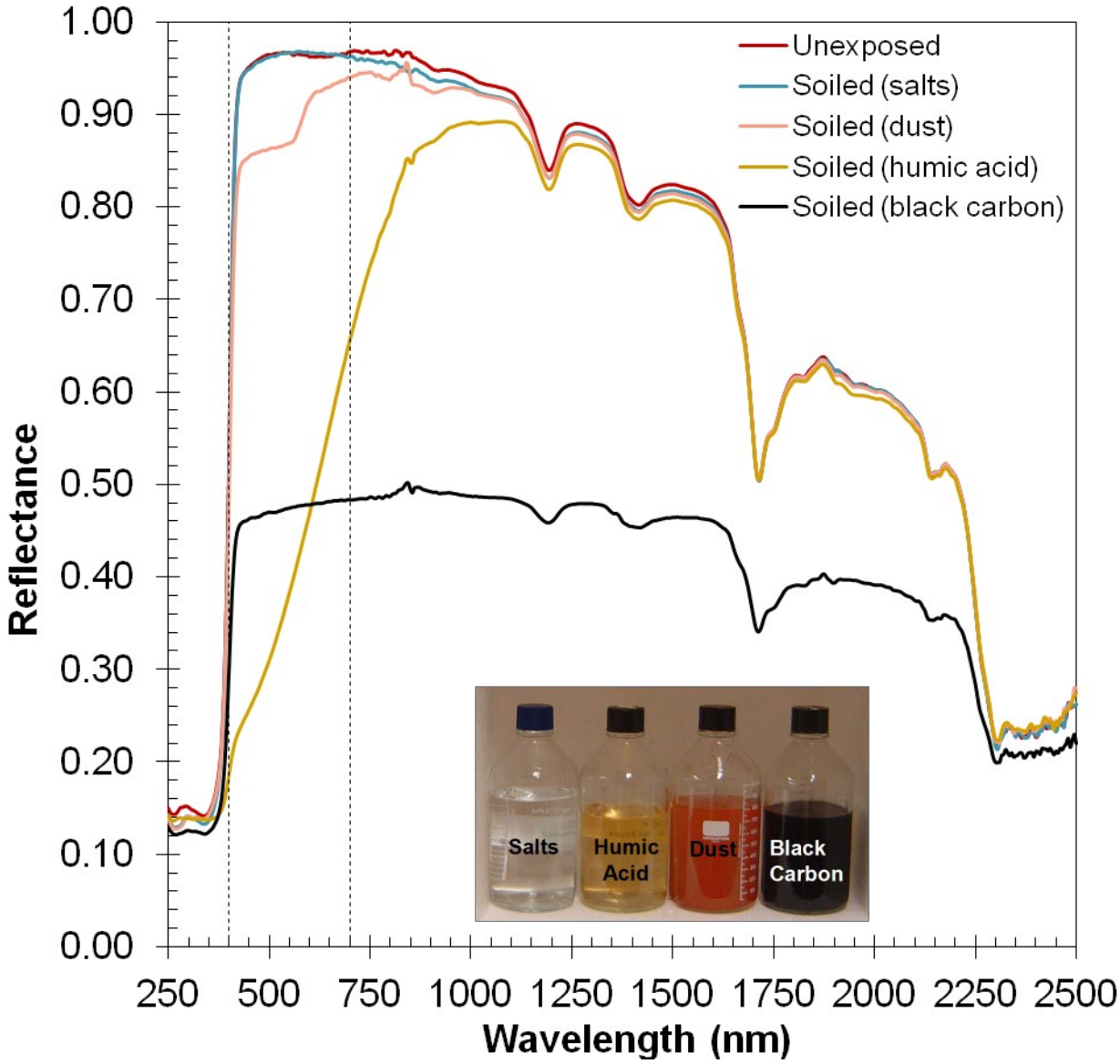


Figure 3. Effect of individual soiling agents on the spectral reflectance of the reference specimen (a white single-ply membrane). The dashed lines represent the limits for the visible region at 400 nm and 700 nm. Dry coverage rate *z* was 4 μg/cm^2 for black carbon and 30 μg/cm^2 each for salts, dust and humic acid. The inset shows each soiling agent dispersed in water.

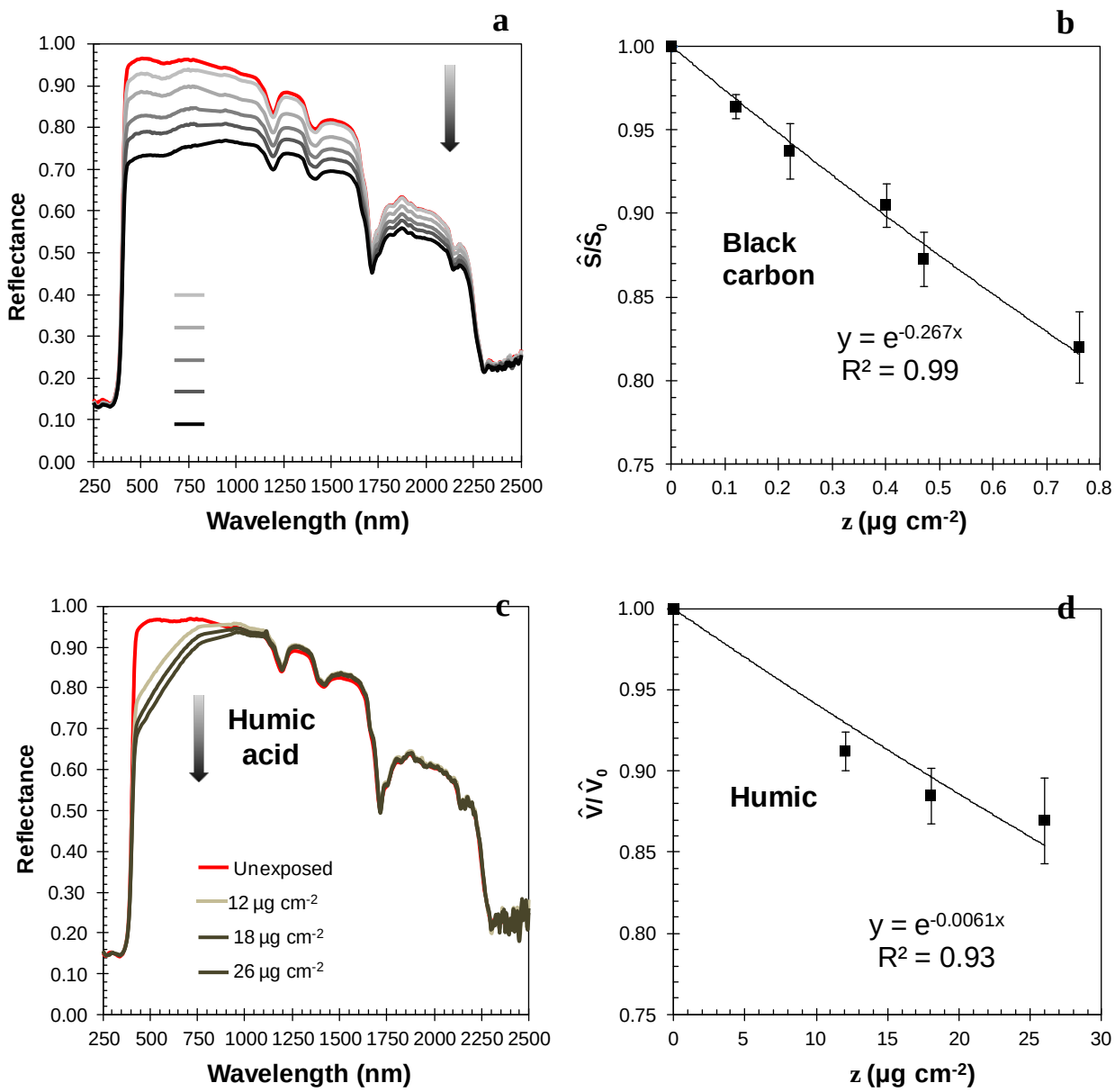


Figure 4. Effect of increasing dry coverage rate *z* (retained mass of sprayed soiling agent per unit area) of black carbon (top) and humic acid (bottom) on the reflectance spectrum (left) and on relative changes in reflectance (right) of a soiled white single-ply membrane. $\hat{S}/\hat{S}_0$ is the ratio of soiled to initial through-window solar reflectance (250 – 2500 nm), while $\hat{V}/\hat{V}_0$ is the ratio of soiled to initial through-window visible reflectance (400-700 nm). Each through-window broadband reflectance was calculated by weighting through-window spectral reflectance with the beam-normal solar spectral irradiance specified by ASTM E891-87(1992).

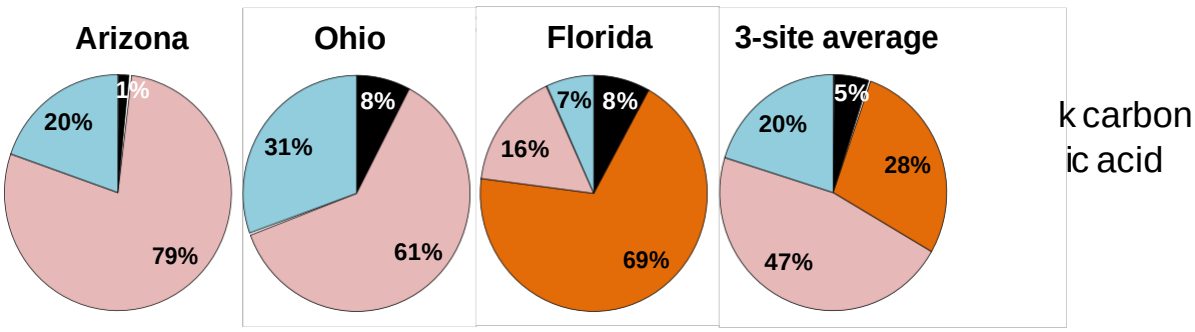


Figure 5. Dry mass fractions of soiling mixtures used to mimic the solar reflectance of roofing materials naturally exposed for three years in Arizona, Ohio and Florida, and to mimic the three-site average.

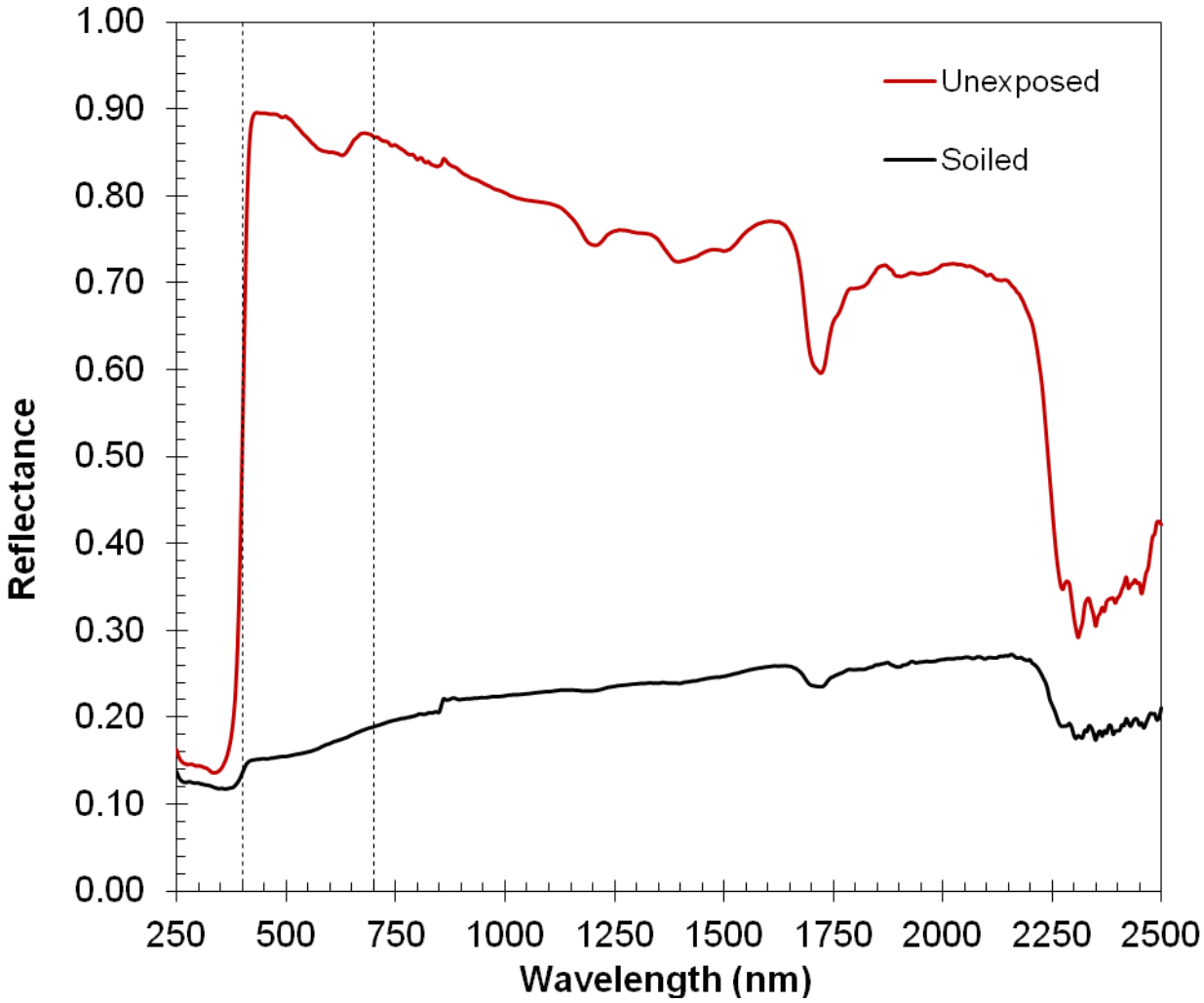


Figure 6. Solar spectral reflectances of an unexposed white single-ply membrane and of a thick opaque layer of the three-site average soiling mixture on this membrane. The blue dashed lines represent the limits for the visible region, between 400 and 700 nm.

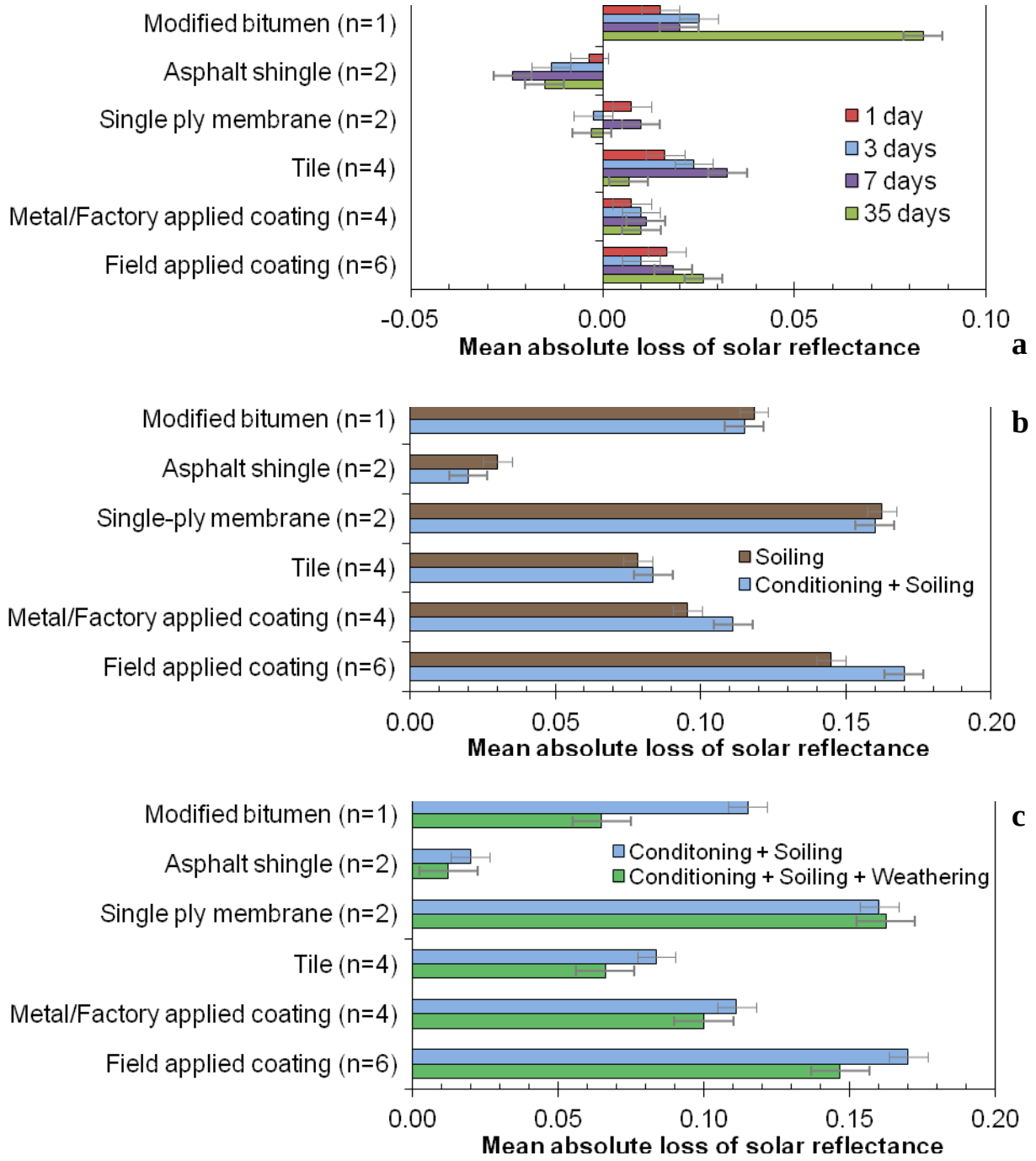


Figure 7. Effects of weathering and soiling on the loss of solar reflectance of various roofing materials, including (a) effect of conditioning cycle duration on solar reflectance loss from conditioning; (b) solar reflectance loss after soiling, shown with and without pre-conditioning; and (c) solar reflectance loss after conditioning and soiling, shown with and without weathering after soiling.

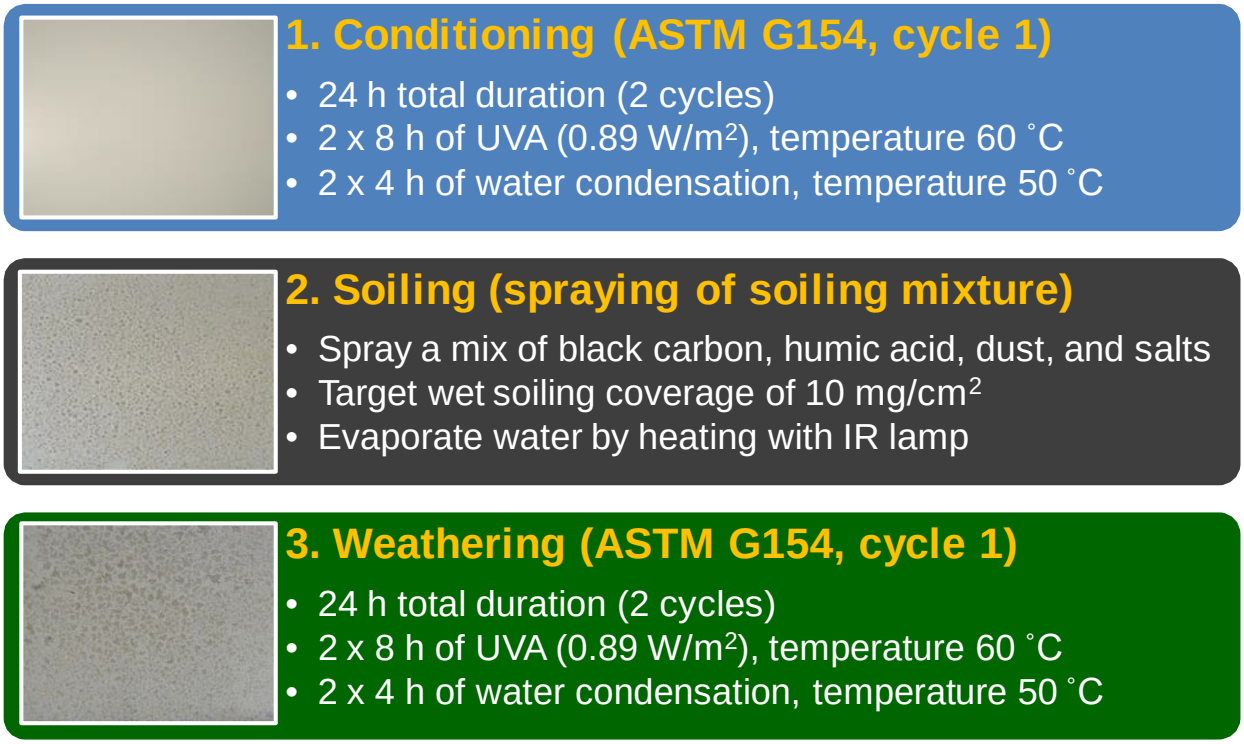


Figure 8. Summary of the laboratory-accelerated aging protocol to mimic the three-year outdoor exposure of roofing materials.

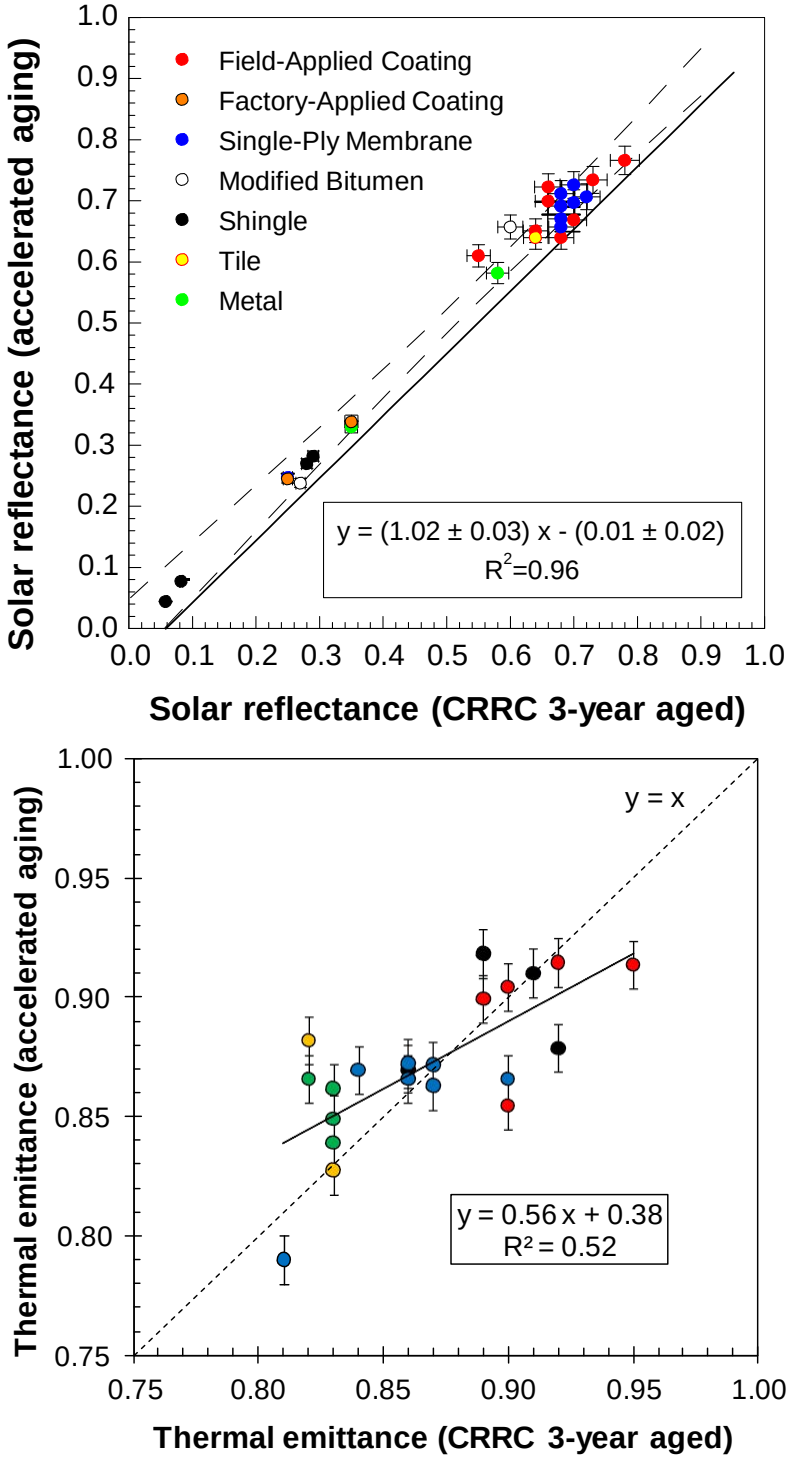
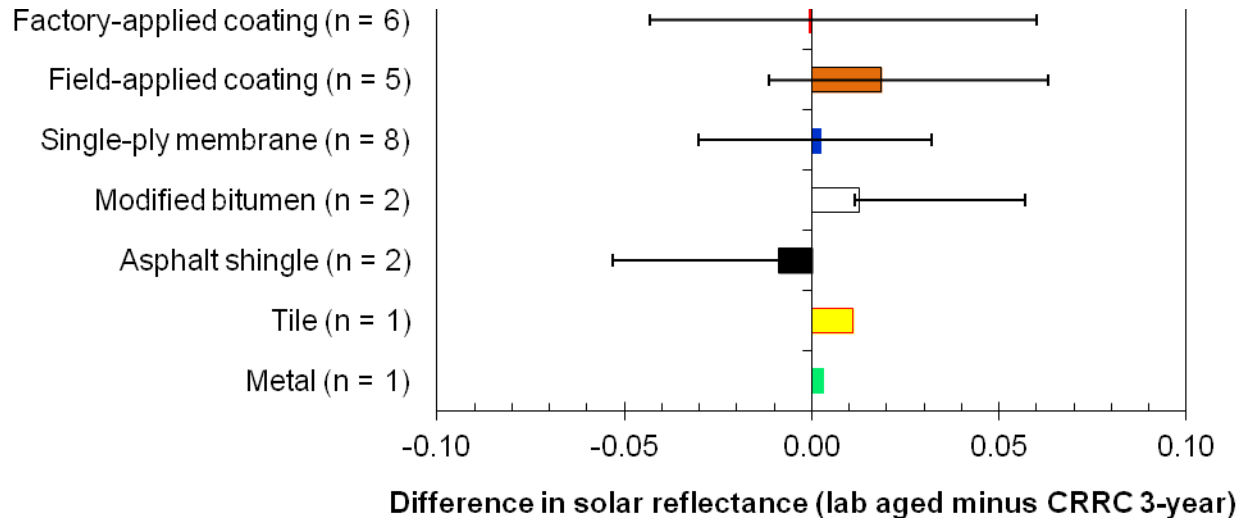
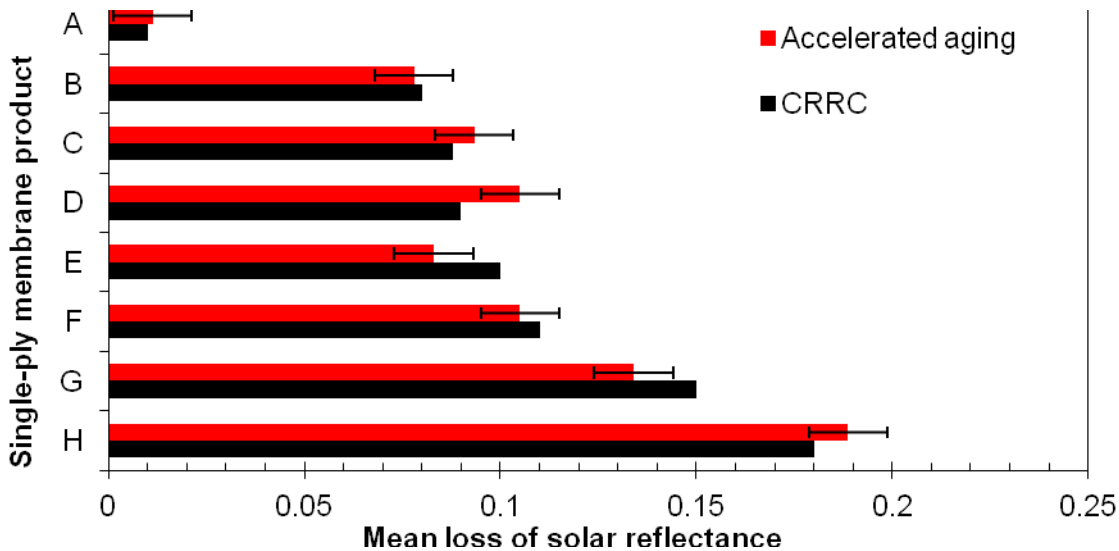


Figure 9. (a) Correlation between solar reflectance of roofing products aged using the laboratory method developed in this study and during three years of natural exposure (CRRC 3-site average). (b) Correlation between thermal emittance of roofing products aged using the laboratory-accelerated method and 3-year CRRC natural exposure.

a





b

Figure 10. (a) Mean difference in solar reflectance for each roofing category (laboratory accelerated aging minus CRRC 3-year natural exposure). The error bars on Figure 9b illustrate the minimum and maximum difference for each roofing category). (b) Comparison of the loss of solar reflectance (initial minus 3-year aged) between accelerated aging and CRRC 3-year natural exposure for eight single ply membrane products.

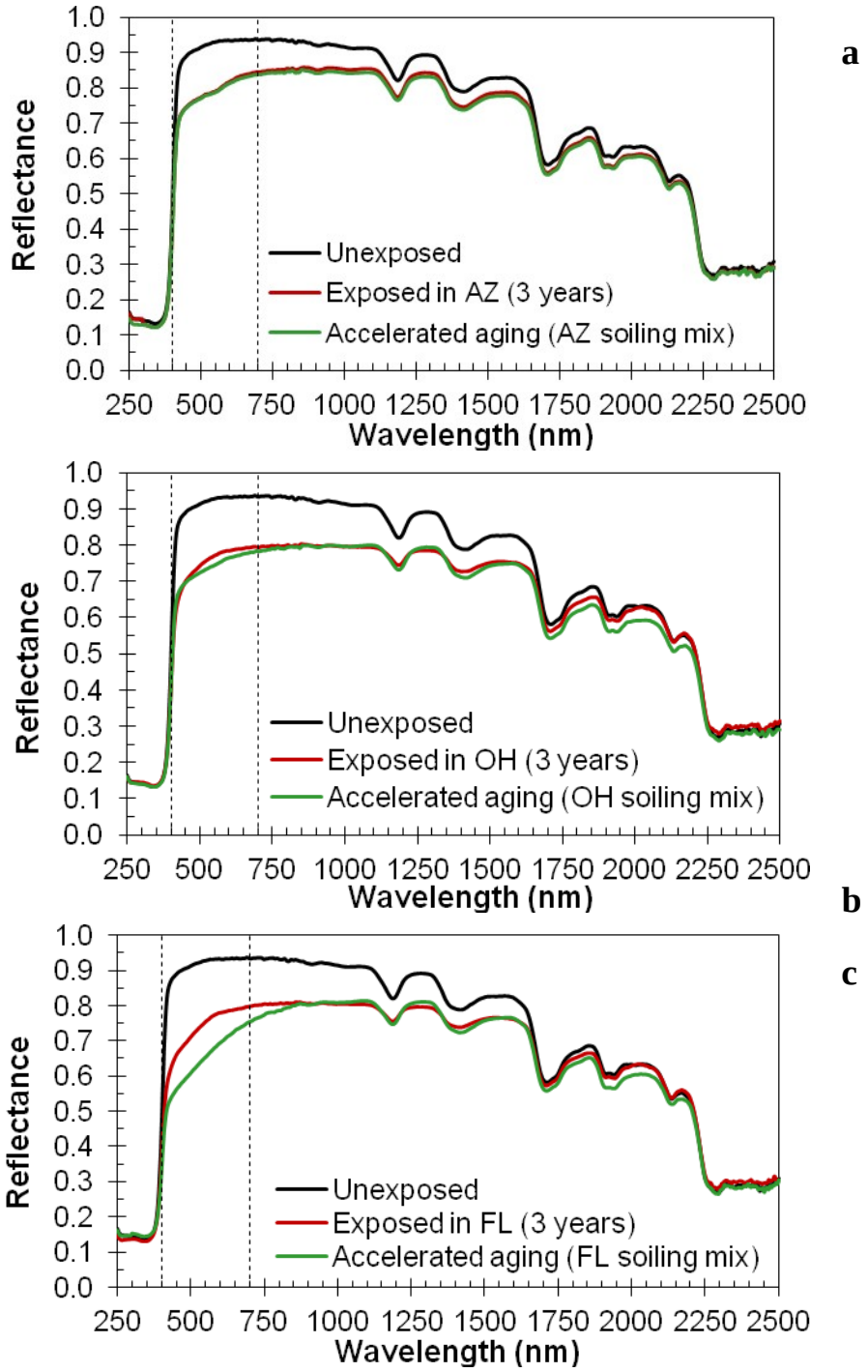


Figure 11. Comparison between the spectral reflectance of laboratory aged white field-applied coating and those exposed for three years in Arizona (a), Ohio (b), and Florida (c). The dashed lines represent the limits for the visible region at 400 nm and 700 nm. Laboratory aging was performed using site-specific mixtures described in Figure 5.