

A NEW METHOD TO CHARACTERIZE DEGRADATION OF FIRST SURFACE ALUMINUM REFLECTORS

Florian Sutter¹, Arantxa Fernández García², Peter Heller¹, Cheryl Kennedy³, Stephanie Meyen¹, Robert Pitz-Paal¹, Martin Schmücker⁴

¹ Solar Researcher, DLR German Aerospace Center, Institute for Technical Thermodynamics, PSA, Ctra. Senés Km. 4, P.O.Box 44, 04200, Tabernas, Almería (Spain), +34 950 277684, Florian.Sutter@dlr.de

² Solar Researcher, CIEMAT, Plataforma Solar de Almería, Ctra. Senés Km. 4, 04200 Tabernas, Almería (Spain)

³ Solar Researcher, NREL National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401-3393 USA

⁴ Material Scientist, DLR German Aerospace Center, Institute for Material Sciences, Linder Höhe, D-51147 Cologne, Germany

Abstract

This paper reports the development of a new optical instrument capable of characterizing the aging process of enhanced first surface aluminum reflectors for concentrating solar power (CSP) application. Samples were exposed outdoors at different sites and in accelerated exposure tests. All samples exposed outdoors showed localized corrosion spots. Degradation originated from points of damage in the protective coating, but propagated underneath the protective coating. The degraded samples were analyzed with a microscope and with a newly designed space-resolved specular reflectometer (SR)² that is capable of optically detecting and characterizing the corrosion spots. The device measures the specular reflectance at three acceptance angles and the wavelengths with spatial resolution using a digital camera's CMOS sensor. It can be used to measure the corrosion growth rate during outdoor and accelerated exposure tests. These results will allow a correlation between the degraded mirror surface and its specular reflectance.

Keywords: accelerated and outdoor weathering, aging of reflectors, specular reflectance, reflectometer, filiform corrosion of aluminum, soiling

1. Introduction

Radiation emitted by the sun is focused onto the absorber tube of a parabolic trough collector with solar mirrors if the aperture angle of the reflected beam is less than 20 mrad (half-cone angle (Fig.1a). Including collector tracking, absorber tube position, and mirror slope errors, reflector surface scattering within a 12.5 mrad angle is acceptable for a parabolic trough collector [1].

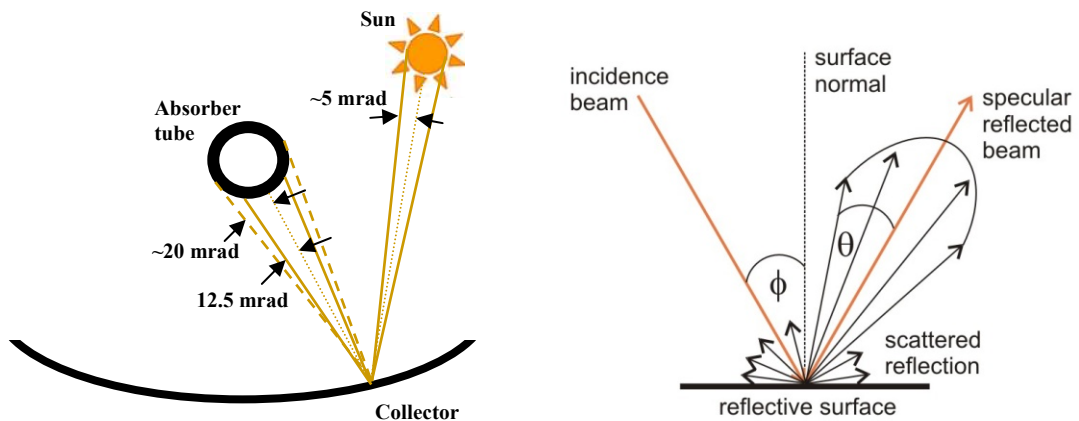


Fig. 1. a) Specular reflectance at a parabolic trough collector and b) definition of terms

Specular reflectance is the amount of light reflected into the acceptance half angle θ shown in Fig.1b. Reflectance is dependent on the wavelength (λ), the angle of incidence (ϕ) that incoming light makes with the mirror surface normal, and the acceptance half angle (θ) that marks the greatest offset of a reflected beam to the ideal specular reflected beam. Hemispherical reflectance can be understood as the reflectance within an acceptance half angle of π . Reflectance is written with all three parameters $\rho(\lambda, \phi, \theta)$. The most important parameter to evaluate if a reflector material is suited for concentrating solar power (CSP) parabolic trough application is its solar-weighted specular reflectance value at 12.5 mrad. Other important parameters for solar mirrors are their cost and their resistance to weathering with a required durability of at least 20 years.

The specular reflectance is usually measured with a field portable 15R specular reflectometer from Devices and Services Instruments (D&S). Measurements can be taken at different half-cone acceptance angles (3.5, 7.5, and 12.5 mrad), one certain wavelength $\lambda = 660$ nm, and $\phi = 15^\circ$. The solar-weighted specular reflectance value can be approximated using a standard terrestrial solar spectrum [2] and the solar weighting formula described in [2, 3].

The existing instruments used to measure the specular reflectance have several disadvantages in terms of characterizing degradation processes: the measuring spot is usually very small (~ 1 cm in diameter), the measurements can only be taken at one specified wavelength, and the measurements are not spatially resolved. For reflectors that degrade locally, several measurements are necessary to statistically evaluate the influence of degradation on the reflectance properties. Problems associated with the measurement of specular reflectance are also described in [4].

2. Space-resolved specular reflectometer (SR)²

In order to monitor and optically characterize local degradation, the space-resolved specular reflectometer (SR)² was developed (Fig.2) [5]. The major advantage of the (SR)² compared to other reflectometers is the possibility of measuring the specular reflectance on an extended measuring spot of 5.5 cm with a spatial resolution of 12 pixel/mm. Additionally, measurements can be taken at three different acceptance half angles ($\theta = 3.5, 7.5$, and 12.5 mrad) and at three different wavelengths ($\lambda = 410$ nm, 500 nm, and 656 nm).

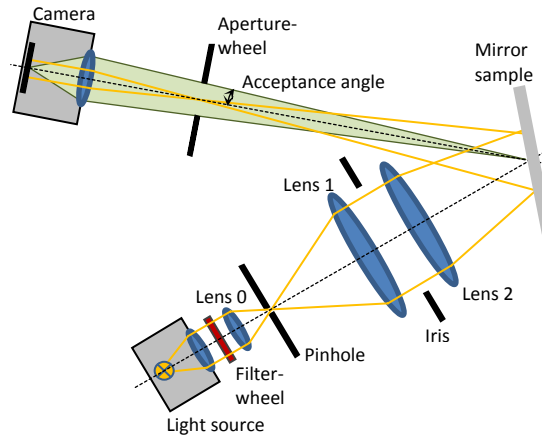


Fig. 2. Space-resolved specular reflectometer (SR)² instrument scheme

The parallel light emitted from a 75W xenon arc lamp is focused onto a 2-mm pinhole. The light passing through the pinhole is collected by two achromatic lenses that focus the beam into the center of the aperture wheel. To measure the specular reflectance, the mirror sample is placed in the optical path and held in place by vacuum suction to a flat plate. The sample holder design reduces the uncertainty due to mirror slope errors. The acceptance angle is changed by rotating the aperture wheel. The instrument is designed so that all of the light passing through the aperture falls onto the complementary metal-oxide-semiconductor (CMOS) sensor of the digital camera. Measurements are taken in a dark room to avoid errors through ambient diffuse light. The prototype of the system is shown in Fig.3a and b.

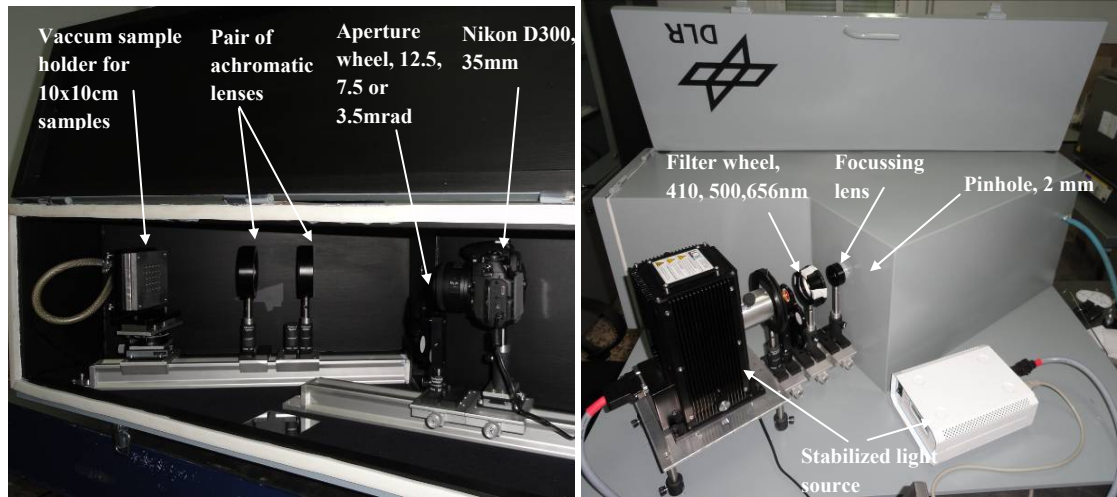


Fig. 3. Prototype at DLR a) interior view of the dark box, b) exterior view

The photographs obtained in RAW-format are linearized and converted to ppm format with the open source software *dcraw*. In the linear photograph, the number of photons that fall on each pixel is proportional to the pixel intensity. The instrument is calibrated with a reference mirror for which the specular and hemispherical reflectance properties are identical ($\rho_{\text{specular},\lambda} = \rho_{\text{hem},\lambda}$). The $\rho_{\text{specular},410\text{nm}}$, $\rho_{\text{specular},500\text{nm}}$, and $\rho_{\text{specular},656\text{nm}}$ can then be determined using the Perkin-Elmer Lambda1050 UV-Vis-NIR spectrophotometer. Measurements taken in the (SR)² are corrected for errors from dust on the optical components or inhomogeneous illumination of the mirror sample by using a reference photograph of the calibration mirror.

The instrument can be employed to evaluate the surface reflectance characteristics of flat mirrors with the creation of a reflectance map. In combination with aging tests, the instrument can monitor gradual changes like the growth of degradation (Fig.4). The fraction of degraded surface relative to the intact surface of the mirror can be evaluated as well. The instrument can also be used to characterize the scattering from soiled mirrors before and after cleaning.

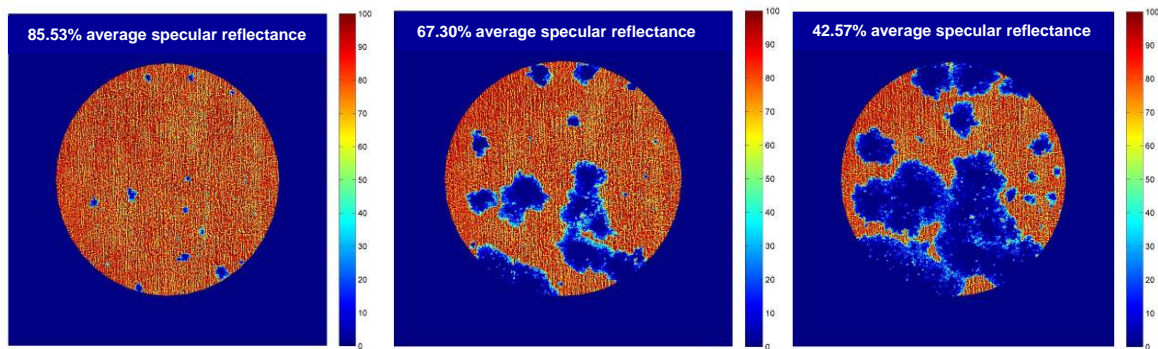


Fig. 4. Corrosion monitoring of accelerated testing to determine the corrosion growth rate and its effect on specular reflectance. (Reflectance map at $\lambda = 656\text{nm}$, $\phi = 15^\circ$ and $\theta = 12.5\text{ mrad}$, blue = 0%, red=100% specular reflectance)

3. Aging analysis of a first surface enhanced aluminum reflector

Aggressive cost reductions and performance improvements in the solar field are required for CSP technologies with thermal storage to produce electricity competitively. This has lead to the study of solar reflector candidate materials with the potential to reduce cost, weight, and installation labor while increasing optical performance and durability.

One such promising solar reflector candidate is the enhanced first surface aluminum mirror shown in Fig.5. The polished aluminum substrate is anodized, and a pure aluminum layer is deposited by physical vapor

deposition (PVD). The reflectance of the aluminum is enhanced by $\frac{1}{4}$ wavelength thick, low- and high-index-of-refraction oxide coatings and protected with a sol-gel nanocomposite oxide layer. The initial solar-weighted hemispherical reflectance is 91.8%; initial specular reflectance at 12.5-mrad half angle and 660 nm is 83.7% and at 3.5-mrad is 71.7%.

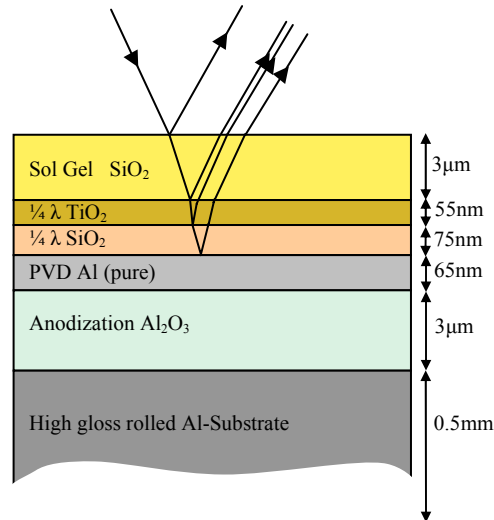


Fig. 5. Composition of the enhanced aluminum reflector

3.1. Outdoor weathering

Samples of the enhanced aluminum reflector were exposed at three outdoor test sites in Phoenix, Arizona (APS), Golden, Colorado (NREL), and Miami, Florida (FLA) in the United States. Outdoor exposure sites in Europe were in Cologne, Germany (KOL) and Tabernas, Spain (TAB). All materials are optically characterized prior to exposure testing and as a function of exposure time to assess optical durability.

3.2. Accelerated weathering

Two accelerated exposure chambers were used at NREL: an Atlas Ci5000 WeatherOmeter (WOM) and a BlueM damp-heat accelerated exposure chamber (BlueM). The Ci5000 WOM uses a two-sun xenon-arc light source with filters designed to closely match the terrestrial AM1.5 global solar spectrum. The Ci5000 operates continuously at 60°C and 60% relative humidity (RH). A single day of testing (24 hours) in the Ci5000 is roughly equivalent to six times outdoors. The BlueM operates continuously without light at 85°C and 85% RH. While the BlueM does not have the same measurable acceleration factor as the WOMs, from experiments, the acceleration factor approaches 25 times outdoors.

The solar-weighted hemispherical and specular reflectance over exposure time at the different exposure sites and in the accelerated exposure chambers is shown in Fig.6.

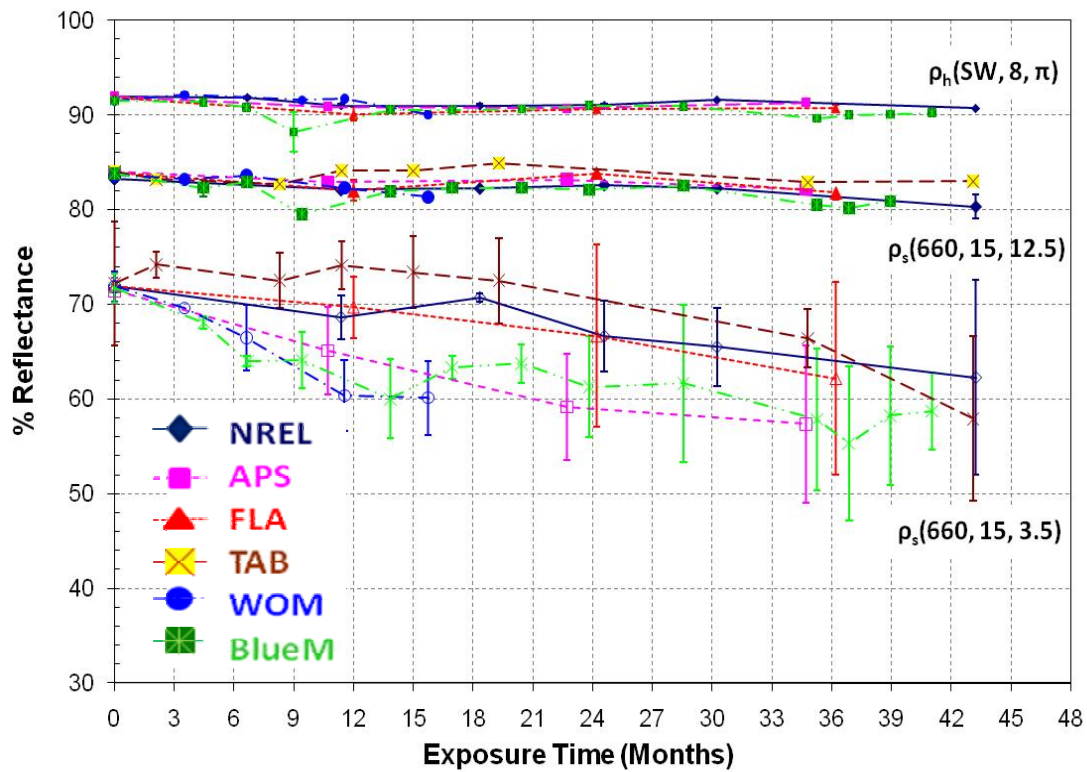


Fig.6: Solar-weighted hemispherical reflectance (SWH) and specular reflectance at $\theta = 3.5$ and 12.5 mrad at $\lambda = 660\text{nm}$ of enhanced aluminum reflectors after accelerated exposure in BlueM (dark / 85°C / $85\%\text{RH}$), WOM (2 sun / 60°C / $60\%\text{RH}$) chambers, and outdoor exposure at NREL, APS, FLA, and TAB.

3.3. Degradation mechanism

After three years of outdoor exposure at the different sites, only slight decreases in the solar-weighted hemispherical reflectance (SWH) can be observed. The specular reflectance at 3.5 mrad shows a maximum loss of 14.1% after 34.7 months of exposure in Phoenix. However, the specular reflectance within the 12.5mrad acceptance angle is more relevant for parabolic trough applications. Here, losses are only in the range of $1\text{-}2\%$ after three years of exposure.

Small corrosion spots were observed by visual or microscopic inspection on all samples exposed at every outdoor site. The corrosion starts at coating defects such as micro-cracks, coating break outs or pinholes (Fig. 7a and 7b).

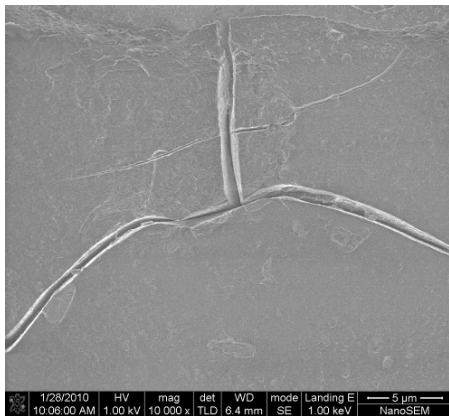


Fig. 7a. Crack in protective coating viewed in the SEM

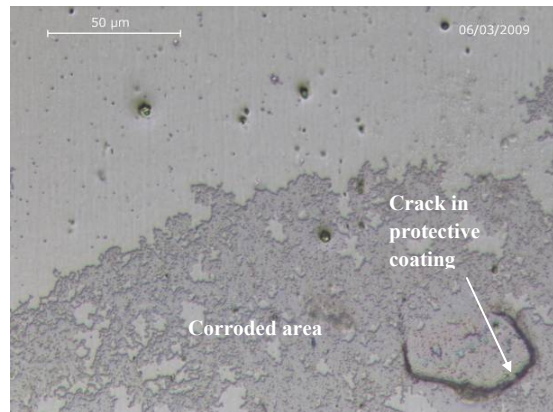


Fig. 7b. Filiform corrosion and crack viewed in the light microscope

A cross section image reveals that the degradation occurs at the pure aluminum layer (Fig.8). The image was produced with a transmission electron microscope (TEM) in Z-Contrast mode (the intensity is proportional to the atomic number Z). The sample preparation occurred by focused ion beam (FIB) to avoid introducing new defects. Other attempts to prepare the sample (like polishing or grinding) were not successful because the blade caused delamination of the sample's coating.

A vertical energy-dispersive X-ray spectroscopy (EDX) line scan with high spatial resolution detected a loss of the aluminum in the degraded areas. The void is able to propagate underneath the SiO_2 and TiO_2 enhancing layers, while they themselves remain unharmed. This effect is also known as filiform corrosion. The natural corrosion mechanism observed in samples exposed outdoors was not reproduced in the accelerated weathering chambers. More germane accelerating test methods are still being developed.

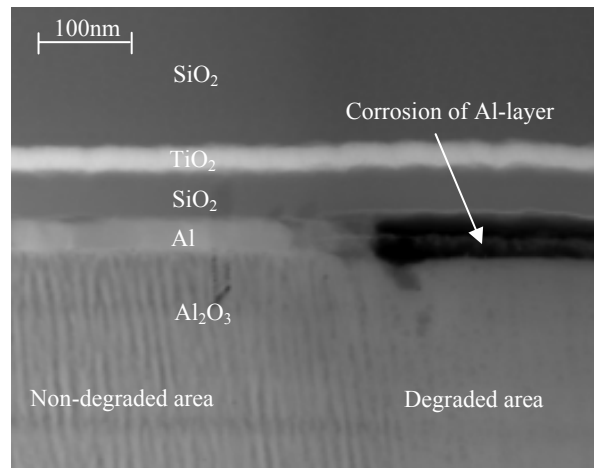


Fig.8: Cross section of a corrosion spot

4. Optical characterization of corrosion processes with the space-resolved specular reflectometer (SR)²

The new instrument measures the following parameters through image analysis:

- Average specular reflectance of the measurement spot of the sample
- Fraction of area with specular reflectance below a boundary value (selected by user)
- Detection of local corrosion spots and evaluation of their area and specular reflectance
- Specular reflectance of non-corroded area.

The new instrument has been used to measure samples of the enhanced aluminum reflector exposed for 57 months outdoors in Tabernas and for 36 months in Miami. The specular reflectance, the corroded mirror area, the number of corrosion spots, and the specular reflectance of the non-corroded area are shown in Fig. 9 for both sites. The given values are mean values averaged from two samples per site. The initial specular reflectance was $\rho_s(660\text{nm}, 15^\circ, 12.5\text{mrad}) = 83.7\%$ measured with the D&S. Samples measured after 36 months of exposure in Miami, $\rho_s(660\text{nm}, 15^\circ, 12.5\text{mrad}) = 81.8\%$ with the D&S and with the (SR)² $\rho_s(656\text{nm}, 15^\circ, 12.5\text{mrad}) = 81.8\%$. After 57 months of exposure in Tabernas, $\rho_s(660\text{nm}, 15^\circ, 12.5\text{mrad}) = 81.2\%$ for samples measured with the D&S and $\rho_s(656\text{nm}, 15^\circ, 12.5\text{mrad}) = 81.4\%$ measured with the (SR)². The results show that Miami is a more aggressive environment than Tabernas because the corroded mirror surface area is almost twice as big in a shorter period of time. Local corrosion accounts for a loss in specular reflectance of 0.4% in Tabernas and 1.1% in Miami.

In future work, samples exposed at Köln, Germany and in salt spray chambers will be evaluated for the influence of climatic conditions on corrosion kinetics. The corrosion growth rates will be determined as a function of climatic conditions through periodic monitoring.

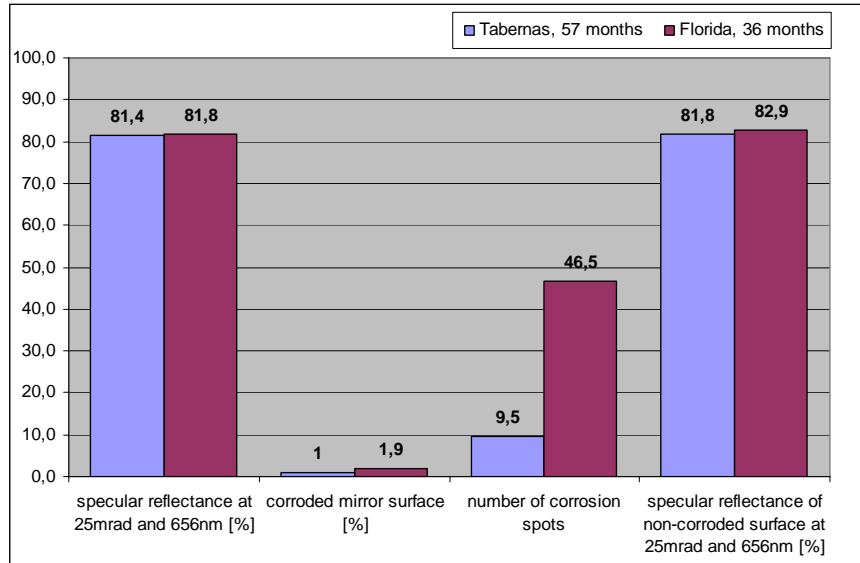


Fig.9: Optical characterization of four samples of the enhanced aluminium reflector exposed for 57 months in Tabernas, Spain and 36.1 months in Miami, USA. (Initial specular reflectance was 83.7%)

5. Optical characterization of soiling processes of a glass mirror with the space-resolved specular Reflectometer (SR)²

The new instrument can also be employed to determine the cleanliness factor of mirror samples and to characterize the scattering due to soiling. The device was used to measure a new glass mirror exposed for 22 days in Tabernas, Spain both in soiled condition and after being cleaned. The mirror surface area whose reflectance is less than a defined boundary value can be determined from the curves in Fig.10. For example, it can be seen that 91.4% of the mirror surface has a reflectance less than 70% when soiled, whereas after being cleaned, only 0.001% of the surface has a reflectance less than 70%.

The average specular reflectance of the soiled surface was $\rho(656\text{nm}, 15^\circ, 12.5\text{mrad}) = 52.3\%$; after being cleaned it was $\rho_s(656\text{nm}, 15^\circ, 12.5\text{mrad}) = 95.2\%$. Thus the cleanliness factor χ (as ratio of ρ_{soiled} to ρ_{clean}) is $\chi = 0.55$. The measurements show good agreement with D&S readings. The larger measurement spot (5.5cm in diameter for the (SR)² compared to 1cm for the D&S) has benefits because inhomogeneous soiling requires a statistical evaluation of the surface.

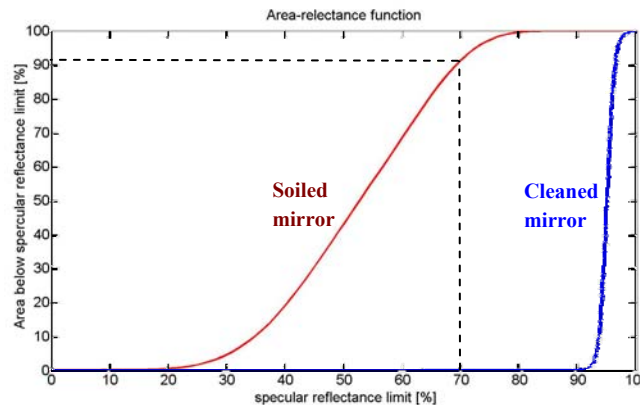


Fig.10: Area-reflectance dependency for a new glass mirror (soiled in Tabernas, Spain for 22 days and cleaned afterwards; measurements at 656nm, 15° incidence angle, and 12.5mrad)

6. Conclusion and Outlook

A new instrument has been designed to measure spatially resolved specular reflectance. The method is suited to characterize local corrosion and soiling processes of solar reflectors. Analysis of an enhanced aluminum reflector with the new (SR)² instrument showed that the reflectance loss of the mirror is mainly due to local corrosion and scattering. Microscope analysis showed that the pure aluminum layer corrodes underneath the unharmed protective and enhancing coatings. Samples exposed in Miami, United States corrode faster than samples exposed in Tabernas, Spain.

In future work, samples exposed in the United States and Europe will be periodically monitored in order to determine corrosion growth rates as a function of climatic conditions. With this data, simplified service lifetime prediction models can be derived to predict the reflectance losses during long-term exposure.

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