Study of the effect of acid atmospheres in solar reflectors durability under accelerated aging conditions

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Abstract

Concentrating solar power (CSP) plants are often located near industrial areas typically affected by high concentration of sulfur dioxide (SO₂). This paper is focused on the influence of acid atmospheres of SO₂ on the durability of solar reflectors, under accelerated aging conditions. A whole test campaign was designed and performed. All types of commercial solar reflectors were included. The accelerated aging tests consisted in applying up to 50 cycles, according to ISO Standard 6988. To quantify the optical degradation, reflectance was measured and a visual assess was done. After exposing the samples to the acid rain atmospheres, the deterioration and reflectance drop was smaller in thick glass mirrors than in the case of thin glass, aluminum and polymer mirrors. The anodized aluminum mirrors showed overall staining and intergranular corrosion, while coated aluminum mirrors did not show any degradation. Although no major reflectance losses were detected in polymer mirrors, a significant degradation, such as pitting corrosion on the reflector and damaged edges, was noticed.

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1. Introduction

At present, the technical development of concentrating solar technologies along with the support of countries and companies has led to the construction of several CSP plants around the world. CSP plants are frequently located near industrial areas and conventional coal power plants to take advantage of the highly qualified staff working on them and the already installed infrastructures (electricity transformers and high-voltage transmission lines, roads, buildings, etc.). These zones are usually affected by high concentration of sulfur dioxide, which is the main gas that contributes to atmospheric acidification. The combination of dry (dust and other acidifying particles, gases and smoke) and wet deposition (rain, snow, sleet, fog, cloudwater and dew) of acids and acid-forming compounds that are present in the atmosphere onto the surface of the earth is known as acid rain or acid deposition.

1.1. Acid deposition phenomena

As a result of the equilibrium with atmospheric carbon dioxide, precipitations are naturally acidic. Natural emissions of SO2 and other species such as nitrogen oxides (NOx) and chlorhydric acid (HCl) further increase precipitations acidity. The most important gas which leads to acidification is SO2 and the main sources of generation are fossil fuel combustion and industry, wildfires and volcanoes [1].

In the absence of human activity, natural long-term mean acidity would be of the order of pH 5.0. Thus, a strict definition of acid rain might be “precipitation which is more acidic than this value”. However, the term refers not only to precipitation but also to other deposition pathways [2]. The deposition of pollutants out of the atmosphere appears in two ways: dry and wet deposition. Dry deposition can be due to adsorption of SO2 on metal surfaces or to impaction of sulfate particles. Wet deposition can be produced by dissolution of atmospheric SO2 into rain or fog. The primary cause of atmospheric corrosion is dry deposition, consisting mainly of the adsorption of SO2. The amount deposited is proportional to the concentration in the atmosphere. Nevertheless, the atmospheric concentration of pollutants is very volatile and, therefore, very difficult to predict [3]. Atmospheric reactions of acid rain generation in which SO2 is involved are equations (1) to (3):

\[
\begin{align*}
\text{SO}_2 + \text{OH}^- & \rightarrow \text{HOSO}_2^- \quad (1) \\
\text{HOSO}_2^- + \text{O}_2 & \rightarrow \text{HO}_2^- + \text{SO}_3 \quad (2) \\
\text{SO}_3(g) + \text{H}_2\text{O}(l) & \rightarrow \text{H}_2\text{SO}_4(l) \quad (3)
\end{align*}
\]

Equations 1 and 2 are reactions in which the sulfur dioxide, in gaseous phase, is oxidized by the hydroxyl radical in an intermolecular reaction. In the presence of atmospheric water or on wet surfaces, sulfur trioxide, SO3, is rapidly converted to sulfuric acid, H2SO4 (equation 3).

1.2. Corrosion processes

In general, corrosion processes of materials can be classified in two major kinds [4]: aqueous corrosion or wet corrosion and gaseous corrosion or dry corrosion. Regarding forms of corrosion, typical defects are [5, 6]: uniform, characterized by corrosive attack proceeding evenly over the entire surface area or a large fraction of the total area;
pitting, localized form of corrosion by which cavities, or “holes,” are produced in the material; intergranular, localized attack along the grain boundaries; exfoliation, often initiated at end grains, edges or holes and whose corrosion products are formed and they force metal away from surface materials; filiform, occurs under some coatings in the form of randomly distributed threadlike filaments; and staining, bright surfaces can be stained in certain aqueous solutions.

1.3. Acid deposition effects on solar reflectors

Acid deposition on solar concentrators can severely damage reflective surfaces [7]. This damage should be a key parameter in the selection of the CSP plant sites and CSP components and it should be considered in order to avoid the unexpected and fast degradation of the materials of the solar field causing a decreasing of the system efficiency and, therefore, important economic losses. The work performed by Coyle et al. in 1982 [7] intends to analyze the effects of accelerated degradation on second-surface silvered-glass mirrors due to exposure of other gases, such as HCl, H2S and SO2. The work is focused mostly on the HCl test which caused a faster degradation than H2S and SO2 exposure. Schutz et al. (1997) studied the effect of acid saline mist on the corrosion of glass mirrors [8]. Other studies are based on the effects of acid rain on unglazed solar absorber surfaces [9] as well as in other type of materials, such as cement concrete [10] and metallic alloys [11, 12], using simulated tests. In the work performed by Graedel (1992), corrosion mechanisms of silver can be found [13]. However, apart from studies of Almanza et al. published in 1995 and 2009 [14, 15] which present the results of testing different solar mirrors for several years under aggressive weather conditions of Mexico City, there is not much information available in the literature about the influence of acid deposition on solar reflectors.

The long-term degradation of solar reflectors can range from a negligible destruction of the mirror to a partial or a total one, and is totally related to the environment which reflectors are exposed to. For this reason, it is interesting to conduct a study with several types of solar reflectors.

2. Methodology

A whole test campaign has been designed and performed in the OPAC laboratory at the PSA. All types of commercially available solar reflectors have been included in the study: second-surface silvered mirrors, first-surface aluminum mirrors and first and second-surface polymer mirrors. Regarding the second-surface silvered reflectors, thin glass, thick glass and laminated glass were tested. The first-surface reflectors studied were anodized aluminum and coated aluminum mirrors. The polymer mirrors were aluminum reflectors protected by polycarbonate and methacrylate and silvered thin film, glued on glass substrate.

2.1. Samples

To assure representative results, 3 identical samples were used, except in Polymer#3. In total, 29 samples of 8 different material types from 8 suppliers were exposed to accelerated aging conditions with acid rain and they were subsequently evaluated. Sample size range is the appropriate for the measurement instruments and for the test chamber. Samples do not have protected edges because they were cut from bigger mirrors. Table 1 shows the main features of all the samples included in the testing. It is assumed that protective paints of samples Glass #1 and Glass #3 are different because they were produced by different manufacturers. However, this information is not available.
Table 1. Description of the samples.

<table>
<thead>
<tr>
<th>Name</th>
<th>Number of samples</th>
<th>Mirror type</th>
<th>Material</th>
<th>Material thickness</th>
<th>Sample size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass #1</td>
<td>3</td>
<td>2nd surface</td>
<td>Thick glass, silver, protective paints</td>
<td>4.0 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Glass #3</td>
<td>3</td>
<td>2nd surface</td>
<td>Thin glass, silver, protective paints</td>
<td>1.6 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Glass #5</td>
<td>3</td>
<td>2nd surface</td>
<td>Glass, silver, glass (laminated glass)</td>
<td>3.6 mm</td>
<td>10x10 cm²</td>
</tr>
<tr>
<td>Aluminum #1</td>
<td>3</td>
<td>1st surface</td>
<td>Aluminum with special protective top coatings</td>
<td>0.5 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Aluminum #2</td>
<td>3</td>
<td>1st surface</td>
<td>Aluminum with special protective top coatings</td>
<td>0.5 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Aluminum #3</td>
<td>3</td>
<td>1st surface</td>
<td>Anodized aluminum</td>
<td>0.5 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Aluminum #4</td>
<td>3</td>
<td>1st surface</td>
<td>Anodized aluminum</td>
<td>0.5 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Polymer #1</td>
<td>3</td>
<td>1st surface</td>
<td>Silvered thin film on glass substrate</td>
<td>0.1 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Polymer #2</td>
<td>3</td>
<td>2nd surface</td>
<td>Methacrylate, aluminum</td>
<td>2.9 mm</td>
<td>8x8 cm²</td>
</tr>
<tr>
<td>Polymer #3</td>
<td>2</td>
<td>2nd surface</td>
<td>Polycarbonate, aluminum</td>
<td>0.85 mm</td>
<td>8x8 cm²</td>
</tr>
</tbody>
</table>

2.2. Testing procedure

Tests were carried out following the procedure established in ISO Standard 6988 [16]. A weathering chamber for Kesternich corrosion tests were used in the test campaign. This chamber had an inner capacity of 300 dm³ and was designed according to the standard mentioned above (see Fig. 1). Before each cycle, 2 ± 0.2 dm³ of demineralized water with a conductivity lower than 500 μS/m and 0.2 dm³ of SO₂ gas were introduced inside the chamber. Every cycle lasted 24 hours and were divided into two phases: a first stage of 8 hours in which samples were exposed to a corrosive atmosphere of SO₂, keeping a constant temperature of 40 ± 3 °C and a relative humidity of 100 %, followed by a second stage of 16 hours in which samples were exposed to a new atmosphere at room temperature (23 ± 5 °C) and a relative humidity lesser than 75 %. The test campaign consisted of 50 cycles. After a given number of cycles (15, 20, 30, 40 and 50), samples were taken out of the chamber and assessed using the following criteria: appearance after the test, amount and distribution of corrosion defaults, time elapsed before the appearance of the first signs of corrosion, reflectance measurement and microscopic inspection.

![Fig. 1. Acid rain chamber installed in the OPAC laboratory at the PSA during the tests.](image-url)

2.3. Measurement procedure and measurement instruments

The following instruments were used to quantify the solar reflector optical degradation:

- A portable specular reflectometer model 15R-USB, manufactured by Devices and Services. This instrument measures monochromatic specular reflectance in a wavelength range between 635 and 685 nm, with a peak at 660 nm. The measurements were taken with 12.5 mrad of acceptance angle.
A spectrophotometer model Lambda 1050 manufactured by Perkin Elmer. This instrument measures spectral hemispherical reflectance with a 150-mm diameter integrating-sphere accessory. Wavelength range measured was from 250 nm to 2500 nm, using 5 nm intervals and an incidence angle of 8°. Solar-weighted hemispherical reflectance was calculated following ISO Standard 9050 [17] and using solar direct spectrum from ASTM G173-03 [18].

A 3D light microscope model Axio CSM 700 manufactured by Zeiss. This microscope allows 5, 10, 50, 100x and measures roughness, defect features (size and depth) and surface profiles.

In the three samples of each material were made three measurements at different points of the reflector with the portable specular reflectometer and three measurements with the spectrophotometer, in this case, trying to measure the same point and rotating the sample. Solar-weighted specular reflectance is the key optical parameter commonly employed to quantify the optical quality of solar reflectors. It was calculated by means of the equation in [19], using results obtained from the reflectometer and spectrophotometer measurements.

3. Results

All tests campaign results are presented in this section and consist of a visual assessment with the eye and the optical microscope, solar-weighted specular reflectance and solar-weighted hemispherical reflectance. These parameters are used in this work to evaluate the reflector degradation.

In this section, results shown in all graphs are the average of the measurements of all the samples studied for each material. Results are organized by material types.

3.1. Glass based samples

3.1.1. Corrosion effects on glass based samples

It was found that the deterioration of glass reflectors is much slower than other types of reflectors also studied (aluminum and polymer mirrors). Glass #1 sample (4 mm-silvered thick glass) does not show early corrosion defects until the cycle number 15. These defects consist of cavities or holes located in different parts of the silver reflector (pitting corrosion), probably as a result of the reaction between the SO₂ and the silver layer. Also, it was observed that the number of isolated defects increased as more cycles were applied. The SO₂ attack is likely to have begun with the penetration of the gas through micro defects in the back paints. This affirmation was confirmed after the tests because most of this type of defects observed in the samples corresponds with visible holes in the back paints.

Some of the most important defects in the reflector surface were observed with the optical microscope. Fig. 2 shows as a pitting corrosion defect has evolved after exposing the sample to several cycles.

![Fig. 2. Microscopic view of a pitting defect detected in sample 2 of Glass #1 material after (a) 15 cycles (b) 40 cycles.](image-url)
Regarding thin glass mirrors, Glass #3 material has resisted very well the accelerated aging cycles, presenting after 50 acid rain cycles a slight deterioration in the sides and the bottom edge. Glass #5 material is a laminated mirror, composed by glass, silver as reflector, and glass, and has not presented any deterioration after 50 cycles. The glass layers on both sides of the reflector protect it from the attack of SO₂.

3.1.2. Solar-weighted hemispherical and specular reflectance
As can be seen in Fig. 3a, solar-weighted hemispherical reflectance average values for the three tested materials have declined very little after being exposed to acid rain conditions. Fig. 3b shows the solar-weighted specular reflectance average value for each glass based material: Glass#1 (thick glass), Glass#3 (thin glass) and Glass#5 (laminated glass). In general terms, the solar-weighted specular reflectance of glass based material slightly decreases after being exposed to a greater number of acid rain cycles.

To calculate the solar-weighted specular reflectance is necessary to measure previously the monochromatic specular reflectance with the reflectometer. These measurements are done manually. Three measurements are made on the three samples of each material, resulting in nine values. Any alteration in the instrument, the room temperature, the cleaning of the sample after each cycle and the heterogeneity of the samples surface have an influence on the measurements and this is reflected in the standard deviation. This is what happens, for example, in the case of measures for cycle 30.

The strongest diminution has been experienced by Glass#3, with a 0.015 points fall. Although initial solar-weighted specular reflectance values of Glass#1 were lower, the diminution was smaller, only 0.004 points fall. Glass#5 had higher initial solar-weighted specular values than the other two materials and the decrease was smaller, of 0.003 points.

As hemispherical reflectance kept constant while the specular reflectance decreased, the degradation suffered by the samples involved an increase in the scattering phenomenon.

3.2. Aluminum samples
3.2.1. Corrosion effects on aluminum samples
Samples of the two types of coated aluminum, Aluminum #1 and Aluminum #2, did not show any deterioration on the reflecting surface. On the contrary, samples of anodized aluminum, Aluminum #3 and Aluminum# 4, have
shown an important deterioration from early exposure stages (from cycle 15). These materials exhibit a corrosion defect of staining with appearance of bright spots over the entire surface (Fig. 4).

![Fig. 4. Staining corrosion in sample 1 of Aluminum #3 (anodized aluminum) after (a) 15 cycles; (b) 30 cycles and (c) 50 cycles.](image)

In addition, after each cycle, it has been detected saline sediments on the reflector surface (Fig. 5), which could not be analyzed in this study, but it will be identified and presented in future works.

![Fig. 5. Saline deposits on (a) sample 1 and (b) sample 2 of Aluminum #3 (anodized aluminum).](image)

This product is likely to be an aluminum salt produced in the reaction of SO2 with aluminum, taking advantage on the deterioration on the protective anodized layer, but still cannot say with certainty. On the other hand, the backside of the aluminum mirror is not sealed so it could be assumed that the back surface is also responsible for this salt sediment.

Samples of both coated aluminum and anodized aluminum were observed in the microscope and the damage detected seems like intergranular corrosion, which starts at grain boundaries.

### 3.2.2. Solar-weighted hemispherical and specular reflectance

As can be seen in Fig. 6a, solar-weighted hemispherical reflectance values of Aluminum #3 material has shown a very significant decline, reaching until 0.200 point drop after 50 cycles. Aluminum #1 and Aluminum #2 values have remained almost constant and for Aluminum #4 solar-weighted hemispherical reflectance has slightly decreased (although this decrease is not really noticeable in the graph due to the scale).

In the case of the aluminum reflectors studied, initial values of solar-weighted specular reflectance are very similar (Fig. 6b). Anodized aluminums have suffered stronger deterioration than coated aluminum samples during the tests. In fact, solar-weighted specular reflectance of coated aluminum mirrors has remained virtually unchanged throughout the experimental campaign.

Both solar-weighted hemispherical and solar-weighted specular reflectance of Aluminum #1 and Aluminum #2 kept constant. On the other hand, Aluminum #3 and Aluminum #4 showed a very interesting behavior. In the case of Aluminum #3, the trend of both variables was decreasing which means that the effect of absorption phenomenon of the radiation is present, although also an increase in the scattering is detected because the fall of solar-weighted specular reflectance is massive (reaching values lower than 0.100). In Aluminum #4 was observed that solar-
weighted hemispherical reflectance kept constant while solar-weighted specular reflectance decreased, indicating that the degradation of reflective surface involves an increasing on the scattering mechanism.

![Graphs showing solar-weighted hemispherical and specular reflectance](image)

Fig. 6. (a) Solar-weighted hemispherical reflectance and (b) Solar-weighted specular reflectance of aluminum mirrors before the test and after 15, 20, 30, 40 and 50 cycles.

### 3.3. Polymer samples

#### 3.3.1. Corrosion effects on polymer samples

Polymer mirrors differ in the structure from the other materials used in this study. In this kind of materials, the reflective layer is protected by several polymeric coatings on its front, such as polycarbonate and methacrylate. In the case of polymeric films, the reflector is protected, on the front and behind, only by polymeric layers. For ease of handling, in this study the polymeric film has been glued to a glass substrate. In these experiments, edges have not been protected.

![Images of polymer samples](image)

Fig. 7. Samples of (a) Polymer #1, (b) Polymer #2 and (c) Polymer #3, after 50 cycles.

Polymer #1 samples present deterioration at the edges, as these have not been protected. It is assumed that this deterioration will not take place when the edges are properly protected. Therefore, this edge protection represents a key aspect in the employment of this type of solar reflectors. Also, they show defects in the reflector as pitting corrosion as well as blisters, as it can be observed in Fig.7a. These defects have increased with the number of cycles applied.
In the case of Polymer #2, the reflector has not suffered a large deterioration. Only it shows that the reflector is peeling on the right edge (Fig. 7b). Polymer #3 samples have suffered important degradation (Fig. 7c). Cavities and holes have appeared in the center of the reflective layer. Blisters and roughness have acted in the upper right corner. Edges are also damaged.

3.3.2. Solar-weighted hemispherical and specular reflectance

Solar-weighted hemispherical reflectance of Polymer #1 and Polymer #2 remained constant, while Polymer #3 shows a significant decline in its values.

Polymer #2 and Polymer #3 solar-weighted specular reflectance decreased as the samples were exposed to the acidic atmosphere.

In Polymer #2 material was observed that the degradation resulting from exposure to acid rain cycles caused an increase in the scattering phenomenon, whereas Polymer #3 material, the absorption phenomenon is also present.

![Graphs](image)

Fig. 8. (a) Solar-weighted hemispherical reflectance and (b) Solar-weighted specular reflectance of polymer mirrors before the test and after 15, 20, 30, 40 and 50 cycles.

4. Conclusions

An accelerated aging testing under acid rain atmospheres was successfully applied to 29 samples of 8 different materials types, including all the currently commercial reflectors. Test campaign consisted of up to 50 cycles of acid rain.

After the completion of the testing, it was observed that the deterioration and reflectance drop was smaller in thick glass mirrors than in the case of thin glass, aluminum and polymer mirrors. Glass mirrors exhibit localized defects, known as pitting corrosion, in the reflector surface.

The anodized aluminum showed overall staining corrosion, reaching specular reflectance practically nulls. Furthermore, salt deposits were detected in these samples. Another corrosion defect identified in this kind of aluminum mirror is intergranular type, starting in the grain boundaries. The coated aluminum mirrors maintained initial reflectance after the testing, without showing any degradation.

Polymer mirrors kept their reflectance which did not experience a significant decrease. However they suffered degradation because the edges of the samples were unprotected. The most common defects were the detachment of the reflecting surface from the polymeric support, blisters, holes and staining of the reflector.

Both anodized aluminum samples and polymer samples showed that the degradation of the reflective surface has led to the appearance of absorption and scattering mechanisms.

Much of the degradation observed in most of the samples could have been avoided with proper edge protection.
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References