

Influence of gaseous pollutants and their synergistic effects on the aging of reflector materials for concentrating solar thermal technologies

A. García-Segura^{a,1}, A. Fernández-García^a, M.J. Ariza^b, F. Sutter^c, T. C. Diamantino^d,
L. Martínez-Arcos^a, T.J. Reche-Navarro^c, L. Valenzuela^a

^aCIEMAT, Plataforma Solar de Almería, Ctra. Senés, km 4, P.O. Box 22, 04200 Tabernas, Almería, Spain

^bUniversidad de Almería, Física Aplicada, CITE II-A, 04120, Almería, Spain

^cDLR, German Aerospace Center, Institute of Solar Research, Plataforma Solar de Almería, Ctra. Senés, km 4, P.O. Box 39, 04200 Tabernas, Almería, Spain

^dLNEG, National Laboratory of Energy and Geology, Estrada do Paço do Lumiar, 22, E, r/c, 1649-038 Lisbon, Portugal

Abstract

Concentrating solar thermal technologies have experienced an important boost in the last few years. Besides the production of electricity, they are particularly useful for the supply of industrial process heat. The industrial atmospheres affecting these solar plants typically contain gaseous pollutants that are likely to promote corrosion on the components of the solar facility, specifically solar reflectors, thereby compromising their optimal performance and the overall system efficiency. Seven accelerated aging tests were designed to study the effects of three air pollutants (H₂S, SO₂ and NO₂) on the durability of two commercially available reflector types (silvered-glass and aluminum), both in single-gas tests and in multicomponent gas mixtures. Additionally, the same material types were exposed outdoors at five representative polluted sites, including industrial, urban and coastal environments. Reflectance and optical microscope monitoring corroborated which degree of corrosion was developed on a specific type of reflector in the different tests with gaseous pollutants, as well as the synergistic effects of gas combinations. For example, tests with sulfur were harmful for silvered-glass reflectors (up to a total of 16 corrosion spots), whereas aluminum was particularly affected by tests with NO₂ (numerous micro spots of around 50 μm size). Moreover, comparisons of the corrosion patterns found in accelerated-aging and outdoor exposures revealed which laboratory test reproduced the different real polluted atmospheres in the most realistic way, which is the main goal of this work. For instance, the degradation found at Site 2 was reproduced by Test NO₂+SO₂, with an acceleration factor of 27.

Keywords: concentrating solar thermal technology; solar reflector; durability test; multicomponent gas mixture; synergistic effect; acceleration factor.

Nomenclature

¹ Corresponding author. Tel.: +34 950 387 800; Fax: +34 950 365 015. E-mail addresses: agarcia@psa.es (A. García-Segura), afernandez@psa.es (A. Fernández-García), mjariza@ual.es (M.J. Ariza), florian.sutter@dlr.de (F. Sutter), teresa.diamantino@lneg.pt (T. C. Diamantino), lucia.martinez@psa.es (L. Martínez-Arcos), tomasjesus.rechenavarro@dlr.de (T.J. Reche-Navarro), loreto.valenzuela@psa.es (L. Valenzuela).

Acronyms

CASS	Copper-accelerated acetic acid salt spray
CSP	Concentrating solar power
CST	Concentrating solar thermal
IPH	Industrial process heat
NSS	Neutral salt spray
OM	Optical microscope

Symbols

AF	Acceleration factor
k	Degradation rate constant, μm
N	Total number of corrosion spots
N_{extrap}	Extrapolated mean number of micro spots
RH	Relative humidity, %
RH_{av}	Average annual relative humidity, %
$t_{accelerated}$	Testing time in an accelerated laboratory exposure, days
$t_{outdoor}$	Testing time in a real outdoor exposure, days
T	Temperature, $^{\circ}\text{C}$
T_{av}	Average annual temperature, $^{\circ}\text{C}$
$[gas]$	Corrosive gas concentration, ppm
W	Scratch width, μm
ΔW	Mean increment in the scratch width, μm
$\rho_{\lambda,\varphi}(660\text{nm},15^{\circ},12.5\text{mrad})$	Monochromatic near-specular reflectance at wavelength $\lambda=660\text{ nm}$, incidence angle $\theta_i=15^{\circ}$ and acceptance half-angle $\varphi=12.5\text{ mrad}$, -
$\rho_{s,h}([280,2500]\text{nm},8^{\circ},h)$	Solar-weighted hemispherical reflectance in the wavelength range of $\lambda=[280,2500]\text{ nm}$ and at incidence angle $\theta_i=8^{\circ}$, -
τ_l	Characteristic time, days
τ_s	Time scaling factor, -

1. Introduction

The deployment of concentrating solar thermal (CST) technologies has experienced a noteworthy increase in the past few years [1]. Whether for the production of electricity in concentrating solar power (CSP) plants or for the supply of industrial process heat (IPH), CST applications are considered a major renewable and environmentally friendly contributor to the energy mix [2]. One of the main challenges that CST facilities must face is the maintenance of their components' optimal properties over time. Specifically, the reliable performance of solar reflectors is a vital aspect to maintain high conversion efficiency from solar to thermal in a concentrating solar system [3], which may be compromised if the solar facility is located near an industrial site. Corrosive atmospheres typically found near industries are known to interact with the reflective layer of solar reflectors and cause their degradation [4]. Some of the most deleterious gaseous pollutants for the reflective metals of solar reflectors (i.e. silver/copper or aluminum) and their corresponding industrial origins are summarized in Table 1 [5].

Table 1. Main pollutant promoters of solar reflectors degradation and industrial sources of their emission.

The significant influence of airborne pollutants has been previously identified and studied in other materials, such as the metallic absorber components of solar thermal collectors [6-9], and also the main corrosion products resulting from the exposure of both silver [10, 11] and copper [12, 13] to different polluted atmospheres have been recently characterized. Specifically, it has been highlighted the importance of studying the degradation of solar reflectors in industrial sites due to chemical pollutants [14, 15]. Some works have paid careful attention to the degradation of their protective paint coatings in order to correlate accelerated aging with outdoor results, but it has been identified the necessity to better understand the corrosion of the reflective layer [16, 17]. More recent studies have emphasized the need for better degradation models and reliable correlations [18-20], some of the laboratory simulations focusing on the surface damage phenomena [21, 22] and even reproducing some of the most frequent real degradation patterns of solar reflectors [23-25]. The main corrosion mechanisms of silvered-glass and aluminum reflectors have been described in the last few years [26, 27]. In addition, the individual effects of sulfurous pollutant gases on CST reflectors have been already tested in accelerated aging simulations under extreme ambient conditions [28, 29] and humid atmospheres [30]. However, neither the influence of nitrogen dioxide (NO_2) nor the mixture of several corrosive gases on reflector materials has been addressed yet.

Hydrogen sulfide (H_2S) has been long known to be the main responsible for silver sulfidation, given that silver is very sensitive to this gas even at very low concentrations [31]. Also copper tarnishes rapidly when H_2S is present in the atmosphere [32], while aluminum is not apparently affected by this reduced sulfur compound [33]. Sulfur dioxide (SO_2) is also one of the most ubiquitous atmospheric pollutants, which plays a major role in atmospheric acidification [34]. Copper, silver and aluminum are easily degraded in moist sulfurous environments [35-37]. Another frequent gaseous species in both cities and factories is NO_2 , mainly derived from automotive and fossil fuels combustion. Aluminum is strongly corroded by NO_2 , apart from other atmospheric contaminants such as ozone and chlorides [32]. NO_2 can also enhance silver sulfidation significantly [38].

Multicomponent gas mixtures are another scenario that must be taken into consideration, if the complexity of industrial environments is aimed to be simulated in laboratory tests. H₂S and SO₂ is one of the possible combinations in the multicomponent case. It has been stated that there is no synergism between H₂S and SO₂ in the case of silver sulfidation [39]. However, thicker oxide layers were found on copper as a result of the interaction between H₂S and SO₂ [40]. The combination of H₂S and NO₂ has proven to be harmful for many pure metals. For instance, it has been demonstrated that the corrosion resulting from the sulfidation of silver and copper is increased at high NO₂ concentrations [41]. Finally, NO₂ and SO₂ may be another corrosive mixture of pollutants for the pure metals contained in solar reflectors. In fact, copper corrosion in laboratory tests is accelerated when these two gases act together in comparison to their separate action [42]. On the other hand, field experiments with silver and aluminum did not show synergism between NO₂ and SO₂ [32, 43].

Given the previously identified state-of-the-art research needs in the field of the durability of solar reflectors used in CST plants near industrial sites, this paper aims to contribute to the study of the effects of different corrosive gases on the aging of reflector materials exposed to accelerated laboratory conditions and to real outdoor sites, in order to identify which accelerated tests better reproduce the characteristic outdoor degradation patterns.

To approach this general objective, three types of commercial solar reflectors (two types of silvered-glass and one type of aluminum-based reflectors, described in section 2.1) were exposed to three atmospheric pollutant gases (H₂S, SO₂ and NO₂), both separately and in binary mixtures, in seven accelerated aging tests at the same temperature, T , relative humidity, RH , and corrosive gas concentration, $[gas]$ (see section 2.2.1 for experimental details). Furthermore, outdoor exposure tests were performed at different polluted locations for a maximum testing time of two years (experimental details in section 2.2.2). Various analytical tools were used to evaluate reflectors' degradation, such as reflectance monitoring and optical microscope (OM) inspections (see section 2.3). First, results of accelerated tests are presented and discussed by the reflector type (see sections 3.1 and 3.2 for Type 1 and Type 2 silvered-glass reflectors, respectively, and section 3.3 for aluminum reflector), and finally the main outdoor results are gathered and compared to the accelerated tests (section 3.4). Conclusions about the most suitable reflector type for a specific atmosphere are drawn according to the degradation level occurring in silvered-glass and aluminum reflectors. Comparisons between accelerated degradation patterns and real outdoor defects allow to determine which accelerated aging tests reproduce the different real outdoor exposures, and to provide their corresponding acceleration factors.

2. Material and methods

This section describes the material and methods used in this study, which are divided into three subsections, namely the description of the reflector materials tested, the experimental design of the accelerated and outdoor exposure tests and the analytical methods employed in the evaluation of the materials.

2.1 Description of materials

Three types of reflectors were tested both in accelerated and in real outdoor experiments, two second-surface silvered-glass reflectors (Types 1 and 2) and a first-surface aluminum reflector

(Type 3), as described in [28, 30]. While silvered-glass are the most commonly used reflectors in CST plants [3], aluminum reflectors are widely employed in solar plants for industrial process heat applications [44, 45]. Consequently, both kinds of reflectors are of interest in this study. Three replicates of each reflector type were used to obtain representative results. Type 1 silvered-glass reflectors constitute the most adverse case because they contain three cut or unprotected edges and an extra initial damage on the paint back coating, namely a scratch. The scratch has been previously described in the literature [28, 30]. Type 2 silvered-glass reflectors represent the undamaged case, with four originally protected edges and no initial defect in the protective coatings. They were specifically manufactured to a 10 x 10 cm² format specification, unlike Type 1 reflectors which were extracted from a real parabolic-trough facet. Type 3 aluminum reflectors include both unprotected edges and a scratch on the front protective coatings, so that the reflective layer is exposed to the testing atmosphere in a similar way as Type 1 silvered-glass reflectors.

2.2 Experimental design

Two types of testing campaigns were performed. On one hand, seven different accelerated aging tests with control of T , RH and $[gas]$ were performed in the laboratory. On the other hand, real outdoor exposures were carried out at several representative sites, which are known to be affected by atmospheric pollutants.

2.2.1 Accelerated aging tests

Six accelerated corrosive tests were designed, three of them testing the single-pollutant case and the other three using mixtures of two corrosive gases. A VCC³ 0034 Vötsch weathering chamber was used for the experiments with gas (Fig. 1 left). A seventh test was performed without gas at the same T and RH values, using an SC340 ATLAS climatic chamber (Fig. 1 right). A summary of the accelerated testing conditions is shown in Table 2. In all cases, conditions of T , RH and $[gas]$ were kept constant inside the weathering chamber for the different accelerated tests.

Fig. 1. Weathering chambers used for the tests with corrosive gases (left) and without gases (right).

Table 2. Experimental conditions of the accelerated aging tests.

Previous experience of the influence of sulfurous gases (H_2S and SO_2) on reflector materials has been reported in a study of the effects of these gases when they act individually [29]. In this previous study, the testing conditions were $T = 60$ °C, $RH = 85\%$ and $[gas] = 15$ ppm. However, these were extreme T and RH conditions for the testing chamber, therefore milder but still accelerated conditions were selected in this case ($T = 40$ °C, $RH = 80\%$), which are also the maximum conditions appearing in ISO 10062 [46]. In addition, $[gas]$ was also optimized and increased to 25 ppm instead of 15 ppm, since 25 ppm is the maximum concentration achievable in the weathering chamber which also appears in an IEC standard [47]. These new conditions are safer than the former ones and they also offer great acceleration of the reflector materials

degradation. Reflector samples were placed at 45° tilt angle on an inert-material tray inside the chamber, and they were optically and microscopically characterized before testing and after 4, 7, 10, 14, and 21 days of the corrosive tests, following the recommendations of various international standards [47-49].

2.2.2 Outdoor exposure tests

Five outdoor sites were selected as representative polluted atmospheres, named Sites 1-5. Sites 1, 4 and 5 are affected by industrial environments, site 3 is characterized by an urban atmosphere of a city and site 2 is a mixture of an industrial and an urban environment of a town. A summary of the outdoor testing conditions is shown in Table 3. Sites with an oil refinery in their surroundings are mainly prone to pollution by H₂S, sites with a coal fired power plant and a cement plant are expected to be affected mainly by SO₂, while urban sites are mostly influenced by NO₂ from traffic origin. Reflector materials were placed at 45° tilt angle on an exposure rack facing South (see Fig. 2), and they were optically and microscopically assessed after every 6 months of outdoor exposure. Apart from the reflector samples, standard coupons of four different pure metals (aluminum, copper, unalloyed carbon steel and zinc) were exposed for one year to determine the corrosivity category of each site according to the ISO 9223 and ISO 9226 standards [50, 51]. There are six possible corrosivity categories, namely very low (C1), low (C2), medium (C3), high (C4), very high (C5) and extreme (CX). Moreover, direct measurements of *T* and *RH* were taken every minute by public meteo stations located in the surroundings of the different sites and then the mean annual temperature (*T_{av}*) and relative humidity (*RH_{av}*) values were calculated at each site, as presented in Table 3.

Table 3. Characteristics and atmospheric conditions of the outdoor exposure sites.

Fig. 2. Exposure racks installed at Site 1 (a), Site 2 (b), Site 3 (c), Site 4 (d) and Site 5 (e).

2.3 Assessment of reflectors degradation

Both monochromatic near-specular reflectance, $\rho_{\lambda,\phi}(660nm, 15^\circ, 12.5mrad)$, and solar-weighted hemispherical reflectance, $\rho_{s,h}([280,2500]nm, 8^\circ, h)$, were monitored along the different tests. The measurement conditions are summarized in Table 4. It has been previously emphasized the necessity to evaluate the performance of reflector materials beyond simply reflectance measurements [28]. For this reason, OM and visual characterization procedures were used to do a complete study of corrosion effects on solar reflectors. Visual characterization was performed with a Panasonic LUMIX model DMC-F745 digital camera, and OM was possible thanks to a Zeiss Axio CSM 700 3D light confocal microscope [52]. Note that the maximum dimension of both the corroded scratch (maximum scratch width, *W*) and the corrosion spots (spot size) found after the tests is considered to be the characteristic length of these defects. Total *N* is defined as the number of corrosion spots counted with the naked eye on a total silvered-glass reflector surface of 300 cm², and *N_{extrap}* is the estimated mean number of micro spots found per aluminum reflector sample.

Table 4. Measurement conditions of the reflectance parameters monitoring.

3. Results and discussion

This section sets out the most relevant results obtained for the three reflector types after the corrosion tests, mainly in terms of reflectance and OM changes. A discussion of the results is also provided, first regarding the results obtained in the different accelerated tests (sections 3.1-3.3) and then focusing on the correlations between accelerated and outdoor results (section 3.4). Fig. 3 depicts a flowchart that summarizes the research process developed in this investigation.

Fig. 3. Flowchart of the research process approached to determine the influence of gaseous pollutants on the aging of three types of solar reflectors, by both laboratory accelerated and outdoor tests.

3.1 Type 1 silvered-glass reflectors

Reflectance parameters were monitored in the whole undamaged area of Type 1 silvered-glass reflectors during the 21 days of the different corrosion tests. As can be appreciated in Fig. 4, neither $\rho_{\lambda,\varphi}$ (left) nor $\rho_{s,h}$ (right) underwent significant changes over time. A decrease of -0.002 in $\rho_{\lambda,\varphi}$ was obtained in the test without gas (Fig. 4 left), but this value is considered negligible because it is within the measurement uncertainty of the equipment. In spite of this, some corrosion spots were detected in the reflective layer of the samples. Two prominent corrosion spots are shown in Fig. 5, after 21 days of Test H₂S+NO₂ (left) and Test NO₂+SO₂ (right). Therefore, it is proved that reflectance monitoring is necessary but not enough to prove the existence of corrosion in reflector materials subjected to accelerated aging tests with corrosive gases, and hence the importance of OM inspections.

Fig. 4. Evolution of the mean loss in monochromatic specular reflectance (left) and solar-weighted hemispherical reflectance (right) on the initially undamaged areas of Type 1 silvered-glass reflectors during the testing time of the accelerated aging tests.

Fig. 5. 10x OM appearance of corrosion spots found in the reflective layer of Type 1 silvered-glass reflectors after 21 days of H₂S+NO₂ (left) and NO₂+SO₂ (right) tests.

Table 5 shows a summary of the main parameters evaluated on the undamaged and initially damaged reflective areas at the end of the different tests. The total number of spots in a total reflector area of 300 cm² was not very high (up to $N = 4$ spots) and their characteristic length (maximum dimension) ranged 91-225 μm. Test NO₂ does not produce any corrosion spots in this reflector type, whilst tests containing H₂S and SO₂ contribute to the growing of spots in the reflective layer.

Table 5. Summary of the main parameters evaluated after 21 days of the different accelerated aging tests in Type 1 silvered-glass reflectors.

$\Delta\rho_{\lambda,\phi}$: mean loss in monochromatic specular reflectance on the undamaged reflector surface or in the scratch (-), Total N : sum of the number of corrosion spots visible to the naked eye at the end of testing on a 300 cm² total reflector surface, Spot size: characteristic length of the largest spot (μm), Max. Pen.: maximum penetration of corrosion near the original or cut edge (μm), ΔW : mean increment in scratch width (μm).

The original edges were not corroded in either of the tests, except for Test NO₂ +SO₂, which provoked a maximum penetration of 413 μm (Fig. 6).

Fig. 6. 10x OM image of a corroded original edge of Type 1 silvered-glass reflectors after 21 days of Test NO₂ +SO₂.

As for the cut edges, they were more significantly corroded than the original edges. Examples of these are illustrated in Fig. 7. Especially cut edges in tests containing NO₂ (Figs. 7 c, e, f) were extensively corroded, with a penetration that ranged 534-802 μm . The corrosion pattern in these cases consists in a continuous corrosion progress followed by a dotted corrosion front (Figs. 7 c, f).

Fig. 7. 10x OM images of cut edges of Type 1 silvered-glass reflectors after 21 days of H₂S (a), SO₂ (b), NO₂ (c), H₂S+SO₂ (d), H₂S+NO₂ (e), and NO₂+SO₂ (f) tests.

The initially damaged area of Type 1 reflectors, i.e. the scratch, was also monitored optically and microscopically. The evolution of $\Delta\rho_{\lambda,\phi}$ in the scratch is depicted in Fig. 8. In addition, the mean increment in the scratch width (ΔW) was calculated along the different tests (Fig. 9). According to these results, a fast decrease of $\Delta\rho_{\lambda,\phi}$ and a corresponding increase of ΔW , both followed by a stabilization, were obtained over time for all the tests, and thus a ranking of the tests aggressiveness can be deduced.

Regarding the single-gas tests, H₂S degrades faster and provokes a higher damage level in Type 1 silvered-glass reflectors, since a significant loss of $\Delta\rho_{\lambda,\phi}$ and an increase of ΔW occurs in less than four days. This is in accordance with other authors, who stated that silver is very sensitive to this gas even at very low concentrations [31]. However, in Test NO₂ the $\Delta\rho_{\lambda,\phi}$ starts to be noticeable after 10 days, when ΔW is close to its final plateau value, given that NO₂ can also promote silver corrosion [38]. Finally, Test SO₂ is the weakest test with gas, with a negligible decrease of $\Delta\rho_{\lambda,\phi}$ after 21 days, although it makes a significant difference in terms of ΔW if compared to the test without gas, which does not present any degradation. It must be taken into account that many metals including silver and copper are easily degraded in moist

atmospheres with SO₂ [36]. Therefore, the ranking of aggressiveness in single-gas tests is: SO₂ < NO₂ < H₂S.

Considering the multicomponent tests, the fastest and most harmful one for Type 1 silvered-glass reflectors is Test H₂S+NO₂, followed by Test H₂S+SO₂. Finally, Test NO₂+SO₂ is the slowest and least harmful of the three gas mixtures, as suggested by former studies that found almost no NO₂+SO₂ synergism in field tests with silver [32, 43]. The final damage level after 21 days for the combined tests proves that the ranking of aggressiveness coincides with the one of single-gas tests, but in all gas mixtures the degradation of materials is accelerated, indicating a synergy between the studied gases, as reported in previous publications [39-42].

Fig. 8. Evolution of the mean loss in monochromatic specular reflectance in the scratch area of Type 1 silvered-glass reflectors during the testing time of the accelerated aging tests.

Fig. 9. Evolution of the mean scratch width increment (μm) of Type 1 silvered-glass reflectors during the testing time of the accelerated aging tests.

According to Fig. 9, for the three H₂S tests (blue, green and purple squares), the highest ΔW occurs at the beginning of the tests (between 0 and 4 days), and then the ΔW tendency is to stabilize over time. This similarity between the tests with H₂S (whether single or combined) could be explained because when silver is exposed to high concentrations of H₂S, this gas is the dominant species even in the multicomponent case [58]. The largest ΔW attained at the end of Test H₂S+SO₂ (green squares) is exactly the same as at the end of Test H₂S (blue squares) because of the negligible influence of SO₂ on silver sulfidation in gas mixtures [39]. However, the highest ΔW (up to 900 μm) is achieved after the Test H₂S+NO₂ (purple squares), which is in agreement with previous results that stated the increasing sulfidation rate of silver at high NO₂ concentrations in the presence of H₂S in dry air [39]. Furthermore, the mixture of H₂S and NO₂ provokes higher corrosion than the single-gas tests [41]. Additionally, the other tests with NO₂ (orange and red triangles) present similar ΔW after 21 days, although the mixture of NO₂+SO₂ (orange triangles) implies a slightly higher ΔW than only NO₂ (red triangles), showing the effect of SO₂ molecules. Compared to Test SO₂ (yellow circles), the ΔW achieved with the NO₂+SO₂ combination is more than four times higher than with only SO₂, given that the aggressiveness of NO₂ is much higher than that of SO₂. This has also been previously reported for copper in laboratory tests mixing NO₂ and SO₂ at RH = 90%, where a factor of five relative to SO₂ alone at such a high humidity value was obtained [42, 43].

3.2 Type 2 silvered-glass reflectors

Reflectance parameters were also monitored in the reflective area of Type 2 silvered-glass reflectors. As shown in Fig. 10, no noticeable changes in $\rho_{\lambda,\varphi}$ (left) or $\rho_{s,h}$ (right) can be observed in either of the tests. Only a decrease of -0.002 in $\rho_{s,h}$ is appreciated in the test without gas (Fig. 10 right), but this value is considered negligible because it is within the measurement uncertainty of the equipment.

Fig. 10. Evolution of the mean loss in monochromatic specular reflectance (left) and solar-weighted hemispherical reflectance (right) on the undamaged areas of Type 2 silvered-glass reflectors during the testing time of the accelerated aging tests.

Like in the previous reflector type, the reflective surface of reflectors was visually and microscopically inspected to corroborate the presence or absence of corrosion defects, given that reflectance monitoring has proven not to be sufficient to wholly evaluate corrosion in solar reflectors. As summarized in Table 6, corrosion defects were found in the undamaged reflective surface in the form of corrosion spots and edge penetration. The largest and/or most numerous corrosion spots were found after 21 days of H₂S ($N = 3$ spots with a maximum size of 248 μm), NO₂ ($N = 4$ spots with a maximum size of 347 μm) and H₂S+NO₂ ($N = 16$ spots with a maximum size of 155 μm). Examples of these defects are shown in Figs. 11 left, center and right, respectively. This may be due to the powerful sulfidation of silver by H₂S, as well as the synergistic effect of the H₂S+NO₂ combination, as has been previously discussed in section 3.1 for Type 1 silvered-glass reflectors. Concerning original edge corrosion, the most harmful tests were those containing NO₂, either single or combined (Fig. 12). In fact, a maximum corrosion penetration of 400 μm was obtained at the end of Test NO₂+SO₂ (Table 6). As illustrated in Fig. 12, the initial stage of a dotted front of corrosion can be observed near these edges.

Table 6. Summary of the main parameters evaluated after 21 days of the different accelerated aging tests in Type 2 silvered-glass reflectors.

$\Delta\rho_{\lambda,\varphi}$: mean loss in monochromatic specular reflectance on the undamaged reflector surface (-), Total N : sum of the number of corrosion spots visible to the naked eye at the end of testing on a 300 cm² total reflector surface, Spot size: characteristic length of the largest spot (μm), Max. Pen.: maximum penetration of corrosion near the original edge (μm).

Fig. 11. 10x OM appearance of corrosion spots found in the reflective layer of Type 2 silvered-glass reflectors after 21 days of H₂S (left), NO₂ (center) and H₂S+NO₂ (right) tests.

Fig. 12. 10x OM images of original edges of Type 2 silvered-glass reflectors after 21 days of NO₂ (left), H₂S+NO₂ (center) and NO₂+SO₂ (right) tests.

3.3 Type 3 aluminum reflectors

Type 3 aluminum reflectors were studied following the same methodology as for the previous reflector types (sections 3.1 and 3.2). First, both $\rho_{\lambda,\varphi}$ and $\rho_{s,h}$ were measured in the undamaged reflective area of samples throughout the different tests (Fig. 13). In this case, $\rho_{\lambda,\varphi}$ (Fig. 13 left) decreased at the end of three corrosion tests, namely Test NO₂ (red line), Test H₂S+NO₂ (purple line) and Test NO₂+SO₂ (orange line), with reflectance decrease of -0.012, -0.006 and -0.005,

respectively. This was also noticed in $\rho_{s,h}$ (Fig. 13 right), with reflectance diminutions of -0.005, -0.006 and -0.004 after 21 days of the aforementioned tests with NO₂. Therefore, the presence of NO₂ appears to enhance the degradation of aluminum reflectors, which is in agreement with former publications [32, 37]. In the rest of tests, no changes in reflectance parameters were detected. This is also in accordance with other studies, which highlighted that aluminum is barely affected by reduced sulfur compounds such as H₂S [33].

Fig. 13. Evolution of the mean loss in monochromatic specular reflectance (left) and solar-weighted hemispherical reflectance (right) on the initially undamaged areas of Type 3 aluminum reflectors during the testing time of the accelerated aging tests.

OM inspections were performed on the aluminum reflective surface to confirm the reflectance results. Fig. 14 exhibits examples of the kind of corrosion that appeared in aluminum reflectors after being exposed to the tests containing NO₂. This type of corrosion consists in small (40-60 μm) micro spots that uniformly scatter the whole reflective surface of samples. They are smaller than typical corrosion spots appearing, for instance, in acid-rain and CASS tests [24, 30] but larger than micropitting corrosion occurring in outdoor sites without the influence of corrosive gases [45]. In addition, they look white at naked eye but black in the OM images. It is therefore a new type of corrosion defect in aluminum reflectors. No degradation was found in the rest of tests without NO₂, and as a result no OM images of either corrosion spots or edges penetration can be shown.

Fig. 14. 10x OM appearance of corrosion spots found in the reflective layer of Type 3 aluminum reflectors after 21 days of NO₂ (left), H₂S+NO₂ (center) and NO₂+SO₂ (right) tests.

Table 7 gathers the information related to the main corrosion defects found in Type 3 aluminum reflectors in the different accelerated aging tests. As can be deduced, the total number of micro spots could not be counted because they are too small to the naked eye. However, the total number of micro spots could be extrapolated from the OM images. A minimum of three images per reflector sample were evaluated to obtain the extrapolation figures (N_{extrap}). Values ranged 2.8-4.8·10⁵ micro spots.

Table 7. Summary of the main parameters evaluated after 21 days of the different accelerated aging tests in Type 3 aluminum reflectors.

$\Delta\rho_{\lambda,\varphi}$: mean loss in monochromatic specular reflectance on the undamaged reflector surface or in the scratch (-), Mean N_{extrap} : extrapolated mean number of micro spots found per aluminum reflector sample, Spot size: characteristic length of the largest micro spot (μm), Max. Pen.: maximum penetration of corrosion near the cut edge (μm), ΔW : mean increment in scratch width (μm).

Cut edges were also microscopically inspected and some penetration of corrosion developed after the NO₂-containing tests (around 250 μm), as shown in Fig. 15. The relevant influence of NO₂ on aluminum has been identified by other authors. NO₂ is one of the factors that most strongly corrode aluminum, along with ozone, chlorides, etc. [32, 37]. It was found that the preferential areas where NO₂ attacks the aluminum surface are defect-ridden sites [33], resulting in a uniform, local corrosion attack [59]. These reported findings are similar to the degradation in the form of micro spots that has been obtained in the tests with NO₂ (see Fig. 14).

Fig. 15. 10x OM images of cut edges of Type 3 aluminum reflectors after 21 days of NO₂ (left), H₂S+NO₂ (center) and NO₂+SO₂ (right) tests.

Similarly to Type 1 silvered-glass reflectors (section 3.1), the scratch was analyzed in aluminum reflectors. First, $\rho_{\lambda,\phi}$ was monitored during the testing time, as represented in Fig. 16. The largest decrease in $\rho_{\lambda,\phi}$ in the scratch area (-0.014) occurred at the end of Test NO₂, while negligible losses in this parameter were obtained in the rest of tests. Only Test NO₂+SO₂ provoked a slight reduction of -0.004 in $\rho_{\lambda,\phi}$. This tendency was also confirmed by the measurement of the scratch width increment over time. As shown in Fig. 17, no significant changes in the scratch width were observed in any of the tests, except slight increments in the tests containing NO₂, being the largest ΔW of only 8 μm at the end of Test H₂S+NO₂. Results of the reflective area of the scratch are also summarized in Table 7. According to the authors' previous experience, Test NO₂ is more aggressive for aluminum reflectors than the most deleterious Kesternich test, which uses $[SO_2] = 6666.7$ ppm at $T = 40$ °C and $RH = 100\%$ [30]. Although corrosion spots are bigger and more numerous in the Kesternich test than the micro spots found with NO₂, corrosion penetration in cut edges is similar and even $\rho_{\lambda,\phi}$ undergoes a larger decrease both in the scratch and the whole reflective area in Test NO₂.

Fig. 16. Evolution of the mean loss in monochromatic specular reflectance in the scratch area of Type 3 aluminum reflectors during the testing time of the accelerated aging tests.

Fig. 17. Evolution of the mean scratch width increment (μm) of Type 3 aluminum reflectors during the testing time of the accelerated aging tests.

3.4 Comparisons between accelerated aging tests and outdoor exposures

The results obtained in accelerated aging tests can be compared to those extracted from real outdoor exposures. Comparisons will be established according to OM images of highly informative parts of the samples, such as the area of the scratch and the corrosion spots.

3.4.1 Comparisons with the industrial inland sites (Sites 1 and 2)

Sites 1 and 2 are inland locations affected by some pollution sources (such as oil refinery, coal power and cement plants, etc.) that are characterized by not very high RH_{av} values (maximum of

$RH_{av} = 54.8\%$). The corrosivity categories range from low (C2) to high (C4), therefore a mild level (C3) can be considered in average (see Table 3).

OM images of Type 1 silvered-glass reflectors in the area of the scratch at these sites were compared to the images obtained in the different accelerated aging tests. Fig. 18 shows similar corrosion patterns in the scratch between Site 1 (left) and those accelerated tests containing sulfur, i.e. Test H₂S (center) and Test SO₂ (right). As can be observed, Test H₂S is more aggressive than Test SO₂ because similar effects are achieved after 1 and 21 days of the tests, respectively. This could agree with the type of pollution expected in the atmosphere of Site 1, which is mainly affected by sulfurous gases. The corrosion patterns depicted in Fig. 18 consist in small, black defects that start developing on both sides of the scratch in a scattered way. In the course of the tests, these scattered defects become more numerous, so that the reflective surface near the scratch ends up being uniformly covered by corrosion. This is confirmed after 12 months of Site 1 exposure (Fig. 19 left) and after 10 days of Test H₂S (Fig. 19 right).

Fig. 18. Scratch appearance of Type 1 silvered-glass reflectors after 6 months of Site 1 exposure (left), after 1 day of Test H₂S (center) and after 21 days of Test SO₂ (right).

Fig. 19. Scratch appearance of Type 1 silvered-glass reflectors after 12 months of Site 1 exposure (left) and after 10 days of Test H₂S (right).

Furthermore, Fig. 20 exhibits some similarities between the corrosion defects found in the scratch after 6 months of exposure at Site 2 (left) and after 21 days of Test NO₂ (center). However, the uniform development of corrosion found near the scratch of Site 2 seems to be qualitatively closer to the one observed in Fig. 20 right, corresponding to 7 days of Test NO₂+SO₂. The comparability between Site 2 and Test NO₂+SO₂ is confirmed with the passing of time, as shown in Fig. 21. Note that the atmosphere surrounding Site 2 is expected to be mainly characterized by the presence of NO₂ due to the urban traffic, but the cement plant may additionally contribute to the emission of SO₂.

Fig. 20. Scratch appearance of Type 1 silvered-glass reflectors after 6 months of Site 2 exposure (left), after 21 days of Test NO₂ (center) and after 7 days of Test NO₂+SO₂ (right).

Fig. 21. Scratch appearance of Type 1 silvered-glass reflectors after 12 months of Site 2 exposure (left) and after 10 days of Test NO₂+SO₂ (right).

Therefore, in polluted inland environments like Sites 1 and 2 the industrial influence seems to prevail over the rest of atmospheric factors, since the morphology of corrosion defects is completely different from the rest of exposure tests (see sections 3.4.2 and 3.4.3). For this

reason, it could be concluded that these environments would be more suitably reproduced in accelerated aging tests containing corrosive gases, as illustrated in Figs. 18-21.

Apart from the resemblance in OM inspections, the evolution of ΔW over time in Sites 1 and 2 can be graphed and compared to the one from the accelerated aging tests to estimate acceleration factors. The tendency of ΔW over time in Site 1 (Fig. 22, red triangles) is to grow and then stabilize and form a plateau, like the ones observed for the accelerated aging tests containing H_2S (Fig. 9), with the difference that the plateau is achieved at higher ΔW values than in Site 1. Consequently, despite the probable influence of this sulfurous gas at Site 1, the degradation mechanisms could differ from those obtained in the accelerated aging tests and thus, an optimization of the laboratory conditions of tests containing H_2S should be pursued in future investigations.

Fig. 22. Evolution over time of the mean increment in the scratch width (μm) of Type 1 silvered-glass reflectors during their exposure in Site 1 and Site 2.

However, the evolution of ΔW over time in Site 2 (Fig. 22, blue circles) is different from the one observed in Site 1. As can be observed in Fig. 23 a, the curve shape at Site 2 is very similar to that of the Test NO_2+SO_2 , precisely the accelerated aging test which shows similar degradation patterns by OM analysis to this outdoor exposure, being the time scaling factor

$\tau_s = \frac{t_{outdoor}}{t_{accelerated}} = 27$. Additionally, the evolution of ΔW in these two experiments can be fitted with the logarithmic function of Eq. (1):

$$\Delta W = k \ln\left(\frac{t}{\tau_l} + 1\right) \quad (1)$$

where ΔW is the scratch width increment, t is the testing time, and k and τ_l are fitting parameters that represent the degradation rate constant and the characteristic time, respectively (see Fig. 23 b and Table 8). Although the data sets of these experiments could be also fitted with other mathematical functions, a logarithmic one has been selected because it reminds of the common tendencies in oxidation kinetics of metals. An exponential behavior, which is typical in natural processes such as the kinetics in electrochemical reactions [60], can be also valid, but a logarithmic function fits these two data sets better because the long-time plateau of exponential functions is not observed in the time interval studied.

Table 8. Fitting parameters of the temporal evolution of the scratch width increment for Site 2 and Test NO_2+SO_2 , according to Eq. (1).

The characteristic times obtained in the logarithmic fitting (τ_l in Table 8) can be used to calculate the acceleration factor (AF), which is defined by Eq. (2):

$$AF_{(Site\ 2/NO_2+SO_2)} = \frac{\tau_{Site\ 2}}{\tau_{NO_2+SO_2}} = 27.0 \quad (2)$$

In consequence, both the manual scaling and the mathematical fitting indicate that the Test NO_2+SO_2 reproduces similar degradation as the one occurring in Site 2 with an acceleration of 27 times. In a recent publication, an AF of 26 was derived for the copper-accelerated acetic acid salt spray (CASS) test with regard to an outdoor exposure site of CX corrosivity level [20].

Fig. 23. Evolution over time of the mean increment in the scratch width (μm) of Type 1 silvered-glass reflectors during their exposure in Site 2 and time-scaled Test NO_2+SO_2 (a), and logarithmic fitting of these two data sets (b).

3.4.2 Comparisons with the polluted coastal sites (Sites 3 and 4)

Sites 3 and 4 are coastal sites characterized by urban (Site 3) and industrial (Site 4) atmospheres. They present slightly higher RH_{av} values than Sites 1 and 2, with RH_{av} of nearly 60%. The corrosivity categories are also higher than in the previous inland sites, ranging from medium (C3) to very high (C5), thus a high category (C4) would be the representative average category (see Table 3).

Comparing the OM images of Type 1 silvered-glass reflectors in the area of the scratch (Fig. 24), the development of corrosion appears to have a similar pattern in both Sites 3 (left) and 4 (center), with a continuous advancement of corrosion in the form of ring-like circles. These ring-like formations are not observed in none of the accelerated tests of this study, but they remember of the typical degradation obtained in the neutral salt spray (NSS) test according to ISO 9227 [24, 61] (Fig. 24 right). Fig. 25 also illustrates that corrosion spots found at Sites 3 and 4 are very similar to those of NSS test. Consequently, in polluted coastal environments like Sites 3 and 4 the corrosion effects caused by high salinity and humidity would be dominant over the possible impact of corrosive gases. Therefore, these environments would be more suitably reproduced in the NSS test or even in the more aggressive CASS test, as demonstrated in Figs. 24 and 25.

Fig. 24. Scratch appearance of Type 1 silvered-glass reflectors after 12 months of Site 3 exposure (left), after 18 months of Site 4 exposure (center) and after 21 days of Test NSS (right).

Fig. 25. Corrosion spots appearance of Type 1 silvered-glass reflectors after 24 months of Site 3 exposure (left), after 18 months of Site 4 exposure (center) and after 125 days Test NSS (right).

3.4.3 Comparisons with the heavy industrial and coastal site (Site 5)

Site 5 is regarded as a heavy industrial location near the coast, which can be deduced from its high RH_{av} value of 78.3% and its extreme corrosivity level (C5-CX), as shown in Table 3. It is therefore the most aggressive site of all the outdoor tests implemented in this study.

The main issue of the OM results in Type 1 silvered-glass reflectors at Site 5 is that after only 6 months of exposure, the scratch is too corroded to be able to establish comparisons with other tests (see Fig. 26). The corrosion spots found at this site are also larger than in the previous exposures and have similar features to those obtained in CASS tests (Fig. 27), as reported in [24]. Therefore, high salinity and humidity would be the dominant factors over corrosive gases, as was the case for Sites 3 and 4, but with a higher development of corrosion in Site 5.

Fig. 26. Scratch appearance of a Type 1 silvered-glass reflector after 6 months of Site 5 exposure.

Fig. 27. Corrosion spots appearance of Type 1 silvered-glass reflectors after 6 months of Site 5 exposure (left) and after 20 days of Test CASS (right).

Finally, note that corrosion defects related to the presence of corrosive gases in outdoor-exposed aluminum reflectors were not detected. However, typical corrosion spots, also known as pitting corrosion [45], were found in coastal Sites 3, 4 and 5 because of the effect of salinity, as illustrated in Fig. 28. It can be concluded that, in spite of the considerable exposure times gathered in the outdoor tests (up to 24 months), aluminum reflectors need longer exposure times to degrade in industrial atmospheres. In fact, a previous study highlighted the high endurance of laminated and lacquered aluminum reflectors in industrial outdoor exposures, mainly because of the protection offered by their coating layers against moisture and pollutants [62]. However, in terms of near-specular reflectance loss, silvered-glass reflectors still perform better than aluminum reflectors during outdoor exposure at the different sites (Table 9). For example, the maximum loss of specular reflectance achieved in silvered-glass reflectors was only 0.006 ± 0.001 after 12 months of exposure at the coastal Site 3, whilst the same exposure time at the coastal Site 4 provoked a significant loss of 0.043 ± 0.006 in aluminum reflectors.

Fig. 28. Corrosion spots appearance of aluminum reflectors after 24 months of Site 3 (left), after 18 months of Site 4 (center) and after 12 months of Site 5 (right) exposures.

Table 9. Mean loss in monochromatic specular reflectance on the undamaged reflector surface (-) for the three reflector types after 12 months of exposure at Sites 1-5.

4. Summary and conclusions

The degradation of three types of solar reflectors for CST applications caused by typical atmospheric contaminants of industrial and urban environments was studied in accelerated aging tests and real outdoor sites. Comparisons of the corrosion patterns found in both types of tests were discussed to determine which accelerated aging tests would be more suitable to reproduce the different real outdoor exposures, in order to obtain the corresponding acceleration

factors. These investigations are of interest to select the most suitable type of solar reflector for a certain CST location, since both IPH and CSP facilities are usually located in industrial environments that may seriously compromise the optimal performance of solar reflectors. Laboratory corrosion tests are able to simulate and reproduce in shorter times and at a lower cost the reflectors' aging, but correlations with outdoor tests are necessary to identify the accelerated experimental conditions that suitably reproduce the real outdoor degradation. Therefore, this study offers prospect solutions for the better installation and operation of CST plants.

Reflectance parameters were monitored throughout the corrosive tests for the three reflector types and it was concluded that reflectance is a helpful parameter but still not sufficient to evaluate corrosion. For this reason, OM inspections are vitally important to fully assess reflectors aging.

Type 1 silvered-glass reflectors were microscopically inspected in the whole reflective surface, and the initially damaged areas (cut edges and scratch) were also carefully examined. ΔW was a key parameter to establish a ranking of the corrosive tests' aggressiveness. The most harmful test is Test H_2S+NO_2 , followed by H_2S+SO_2 and H_2S tests, both of which producing very similar effects (ΔW around $720 \mu m$). Next, Test NO_2+SO_2 can be considered more deleterious than Test NO_2 , in terms of the evolution of ΔW and $\Delta\rho_{\lambda,\varphi}$ over time. Finally, Test SO_2 is the weakest corrosive test, but it still provokes more degradation than the test without gas. Therefore, H_2S , whether single or combined, is the gas responsible for the most significant effects on silvered-glass reflectors. These effects are boosted if NO_2 is added, whereas SO_2 does not contribute significantly to the sulfidation reaction of silver, which has been also reported by other authors that studied the sulfidation of silver and other metals. Additionally, the synergistic combination of NO_2 and SO_2 accelerates more than four times the reflective layer degradation with respect to the use of only NO_2 or SO_2 .

Despite representing the initially undamaged paradigm, Type 2 silvered-glass reflectors also exhibited noteworthy degradation patterns in the originally protected edges and the rest of the reflective surface after the corrosive tests. Corroded edges were obtained in tests containing NO_2 , whether single or combined. The maximum corrosion penetration in original edges took place at the end of the Test NO_2+SO_2 , as occurred in Type 1 silvered-glass reflectors and with a similar degree of development ($400 \mu m$). However, Type 2 reflectors exhibited more and larger corrosion spots than Type 1 reflectors (up to $N = 16$ spots with a maximum size of $350 \mu m$ versus up to $N = 4$ spots with a maximum size of $225 \mu m$). The poorer performance of Type 2 silvered-glass reflectors probably stems from their special manufacturing process at small scale. On balance, the most deleterious tests for this reflector type are H_2S , NO_2 and H_2S+NO_2 tests, which can be explained by the main role of H_2S in silver sulfidation and the important synergism between H_2S and NO_2 , as previously identified in the literature.

Unlike silvered-glass reflectors, Type 3 aluminum samples did undergo reflectance decrease in their undamaged reflective area. This was evidenced in the three tests with NO_2 , with specular reflectance losses of up to -0.012 ± 0.004 . The degradation of aluminum by NO_2 tests was corroborated by OM inspections. A new type of degradation defect was detected, consisting in microscopic spots (micro spots) of around $50 \mu m$ average size that uniformly scatter the whole reflective surface of reflectors and are different from the other corrosion spots of aluminum reflectors previously found in the accelerated and outdoor tests of other studies.

Degradation results of reflector materials exposed at the five outdoor tests were compared to OM images of the accelerated corrosive tests. Firstly, it was found that silvered-glass reflectors exposed in the polluted inland environments (Sites 1 and 2) featured different degradation patterns from those reflectors weathered in polluted coastal regions (Sites 3, 4 and 5). Then, according to the morphology of defects in OM images, it was concluded that the accelerated aging tests that most suitably reproduce the defects found in Sites 1 and 2 are those containing H_2S and NO_2+SO_2 , respectively. Degradation found near the scratch area of silvered-glass reflectors at Site 1 consists in small, black defects that initially scatter the reflective surface and then, in subsequent stages of the test, develop in a continuous and uniform way. Tests with H_2S are responsible for similar damages in the silver layer as the ones found in Site 1. In addition, their curves are similar and have a tendency to stabilize with time, but the accelerated conditions with this gas should be optimized to achieve a similar damage level in both tests. Conversely, Site 2 can be compared to Tests NO_2 and NO_2+SO_2 , being the uniform development of corrosion near the scratch at Site 2 more identifiable with the multicomponent case. In consequence, the evolution of ΔW over time at Site 2 can be compared to the Test NO_2+SO_2 (in both cases fitted with a logarithmic function), and the corresponding AF obtained is $AF = 27.0$. In another work, a similar AF value has been obtained for the CASS test with respect to a more aggressive atmosphere.

As for the polluted coastal environments of Sites 3, 4 and 5, the prospective corrosion defects of silvered-glass reflectors caused by corrosive gases must have been overlapped by the effects originating from the high salinity and humidity conditions that are characteristic of coastal regions. Therefore, they are not comparable to the corrosive tests performed in this study, but they are proven to be suitably reproduced in NSS and CASS tests.

Finally, aluminum reflectors were mostly corroded in coastal Sites 3, 4 and 5 in the form of corrosion spots (pitting corrosion). However, degradation associated with the influence of corrosive gases was not detected for aluminum reflectors in the outdoor tests. Although the testing time of the outdoor exposures was not negligible, longer periods of time render necessary to obtain significant deterioration by industrial atmospheres in aluminum reflectors. The main degradation found on aluminum reflectors originates from the high salinity and humidity present at the coastal exposure sites.

As a concluding remark, this study has shown which gaseous pollutants may be determining when studying the durability of silvered-glass solar reflectors in inland environments. Conversely, aluminum reflectors appear to be more stable than silvered-glass materials in this type of atmosphere, being other factors such as humidity and salinity more harmful for this reflector type. As a result, gaseous pollutants might have a significant economic impact on the installation and operation of CST facilities. Therefore, it would be advisable to take this factor into consideration to ensure the profitability of a prospect solar plant.

Acknowledgments

The research work leading to this article received ERDF funds from the Spanish government within the framework of the SOLTERMIN project (Ref. ENE2017-83973-R) of the Ministerio de Economía, Industria y Competitividad (Spanish Ministry of Economy, Industry and Competitiveness). Additionally, research leading up to this study also received funding from the EU Horizon 2020 – H2020-LCE-2016-2017 under grant agreement n° 731287 (Integrating National Research Agendas on Solar Heat for Industrial Processes, INSHIP).

References

- [1] IEA, Technology roadmap: solar thermal electricity. <https://webstore.iea.org/technology-roadmap-solar-thermal-electricity-2014>, 2014 (accessed 10 September 2018).
- [2] Protermosolar. www.protermosolar.es, 2018 (accessed 10 September 2018).
- [3] A. García-Segura, A. Fernández-García, M.J. Ariza, F. Sutter, L. Valenzuela, Durability studies of solar reflectors: a review, *Renew. Sustain. Energy Rev.* 62 (2016) 453-467.
- [4] P. Schissel, A.W. Czanderna, Reactions at the silver/polymer interface: a review, *Sol. Energy Mater.* 3 (1980) 225-245.
- [5] R.H. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, seventh ed., McGraw-Hill, New York, 1999.
- [6] B. Carlsson, K. Möller, U. Frei, S. Brunold, M. Köhl, Comparison between predicted and actually observed in-service degradation of a nickel pigmented anodized aluminum absorber coating for solar DHW systems, *Sol. Energy Mater. Sol. Cells* 61 (2000) 223-238.
- [7] K. Slamova, I. Duerr, T. Kaltenbach, M. Koehl, Degradation effects of maritime atmosphere on metallic components of solar collectors, *Sol. Energy Mater. Sol. Cells* 147 (2016) 246-254.
- [8] T.C. Diamantino, R. Gonçalves, A. Nunes, S. Páscoa, M.J. Carvalho, Durability of different selective solar absorber coatings in environments with different corrosivity, *Sol. Energy Mater. Sol. Cells* 166 (2017) 27-38.
- [9] J.C.S. Fernandes, A. Nunes, M.J. Carvalho, T.C. Diamantino, Degradation of selective solar absorber surfaces in solar thermal collectors – An EIS study, *Sol. Energy Mater. Sol. Cells* 160 (2017) 149-163.
- [10] C.E. Sanders, D. Verreault, G.S. Frankel, H.C. Allen, The role of sulfur in the atmospheric corrosion of silver, *J. Electrochem. Soc.* 162 (2015) C630–C637.
- [11] L. Yan, K. Xiao, P. Yi, C. Dong, J. Wu, Z. Bai, et al., The corrosion behavior of PCB-ImAg in industry polluted marine atmosphere environment, *Mater. Des.* 115 (2017) 404-414.
- [12] F. Samie, J. Tidblad, V. Kucera, C. Leygraf, Atmospheric corrosion effects of HNO₃– Influence of temperature and relative humidity on laboratory-exposed copper, *Atmos. Environ.* 41 (2007) 1374-1382.
- [13] L. Mariaca, D. de la Fuente, S. Feliu Jr., J. Simancas, J.A. González, M. Morcillo, Interaction of copper and NO₂: Effect of joint presence of SO₂, relative humidity and temperature, *J. Phys. Chem. Solids* 69 (2008) 895-904.
- [14] M. Brogren, A. Helgesson, B. Karlsson, J. Nilsson, A. Roos, Optical properties, durability, and system aspects of a new aluminium-polymer-laminated steel reflector for solar concentrators, *Sol. Energy Mater. Sol. Cells* 82 (2004) 387-412.
- [15] J. Wette, F. Sutter, A. Fernández-García, R. Lahlou, P. Armstrong, Standardizing accelerated aging testing conditions for silvered-glass reflectors, in: *Proceedings of the SolarPaces Conference 2017*, Santiago de Chile, 2017.

- [16] O. Raccurt, C. Delord, C. Bouquet, R. Couturier, Correlation between solar mirror degradation and colorimetric measurement of protective back layer, *Energy Procedia* 49 (2014) 1700-1707.
- [17] R. Girard, C. Delord, A. Disdier, O. Raccurt, Critical constraints responsible to solar glass mirror degradation, *Energy Procedia* 69 (2015) 1519-1528.
- [18] C. Avenel, O. Raccurt, J.L. Gardette, S. Therias, Review of accelerated ageing test modelling and its application to solar mirrors, *Sol. Energy Mater. Sol. Cells* 186 (2018) 29-41.
- [19] F. Sutter, J. Wette, F. Wiesinger, A. Fernández-García, S. Ziegler, R. Dashbach, Lifetime prediction of aluminum solar mirrors by correlating accelerated aging and outdoor exposure experiments, *Sol. Energy* 174 (2018) 149-163.
- [20] F. Sutter, A. Fernández-García, J. Wette, T.J. Reche-Navarro, L. Martínez-Arcos, Acceptance criteria for accelerated aging testing of silvered-glass mirrors for concentrated solar power technologies, *Sol. Energy Mater. Sol. Cells* 193 (2019) 361-371.
- [21] M. Karim, S. Naamane, I. El Amrani El Hassani, C. Delord, S. Belcadi, P. Tochon, et al., Towards the prediction of CSP mirrors wear: Methodology of analysis of influencing parameters on the mirrors surface degradation: Application in two different sites in Morocco, *Sol. Energy* 108 (2014) 41-50.
- [22] M. Karim, S. Naamane, C. Delord, A. Bennouna, Laboratory simulation of the surface erosion of solar glass mirrors, *Sol. Energy* 118 (2015) 520-532.
- [23] A. Fernández-García, M.E. Cantos-Soto, M. Röger, C. Wieckert, C. Hutter, L. Martínez-Arcos, Durability of solar reflector materials for secondary concentrators used in CSP systems, *Sol. Energy Mater. Sol. Cells* 130 (2014) 51-63.
- [24] F. Sutter, A. Fernández-García, P. Heller, K. Anderson, G. Wilson, M. Schmücker, et al., Durability testing of silvered-glass mirrors, *Energy Procedia* 69 (2015) 1568-1577.
- [25] F. Wiesinger, F. Sutter, A. Fernández-García, J. Reinhold, R. Pitz-Paal, Sand erosion on solar reflectors: accelerated simulation and comparison with field data, *Sol. Energy Mater. Sol. Cells* 145 (2016) 303-313.
- [26] F. Sutter, S. Ziegler, M. Schmücker, P. Heller, R. Pitz-Paal, Modelling of optical durability of enhanced aluminum solar reflectors, *Sol. Energy Mater. Sol. Cells* 107 (2012) 37-45.
- [27] K.A. Folgner, Environmental durability of silver mirrors with nanostructured protective coatings, M Sc thesis, University of California (2016).
- [28] A. García-Segura, A. Fernández-García, M.J. Ariza, F. Sutter, L. Valenzuela, Effects of reduced sulphur atmospheres on reflector materials for concentrating solar thermal applications, *Corros. Sci.* 133 (2018) 78-93.
- [29] A. García-Segura, A. Fernández-García, F. Buendía-Martínez, M.J. Ariza, F. Sutter, L. Valenzuela, Durability studies of solar reflectors for concentrating solar thermal technologies under corrosive sulfurous atmospheres, *Sustainability* 10 (2018) 3008.

- [30] A. García-Segura, A. Fernández-García, M.J. Ariza, F. Sutter, L. Valenzuela, Degradation of concentrating solar thermal reflectors in acid rain atmospheres, *Sol. Energy Mater. Sol. Cells* 186 (2018) 92-104.
- [31] B.H. Chudnovsky, Degradation of power contacts in industrial atmosphere: silver corrosion and whiskers, *Proc. Forty-Eighth IEEE Holm Conf. Electr. Contacts*, 2002, 1-22.
- [32] S. Syed, Atmospheric corrosion of materials, *Emirates J. Eng. Res.* 11 (2006) 1-24.
- [33] T.E. Graedel, Corrosion mechanisms for aluminum exposed to the atmosphere, *J. Electrochem. Soc.* 136 (1989) 204C-212C.
- [34] A. Fernández-García, R. Díaz-Franco, L. Martínez-Arcos, J. Wette, Study of the effect of acid atmospheres in solar reflectors durability under accelerated aging conditions, *Energy Procedia* 49 (2014) 1682-1691.
- [35] W.H.J. Vernon, A laboratory study of the atmospheric corrosion of metals. Part I.-The corrosion of copper in certain synthetic atmospheres, with particular reference to the influence of sulphur dioxide in air of various relative humidities, *Trans. Faraday Soc.* 27 (1931) 255-277.
- [36] C. Kleber, U. Hilfrich, M. Schreiner, In situ QCM and TM-AFM investigations of the early stages of degradation of silver and copper surfaces, *Appl. Surf. Sci.* 253 (2007) 3712-3721.
- [37] M. Morcillo, B. Chico, D. De La Fuente, J. Simancas, Looking back on contributions in the field of atmospheric corrosion offered by the MICAT ibero-american testing network, *Int. J. Corros.* 2012 (2012).
- [38] H. Kim, Corrosion process of silver in environments containing 0.1 ppm H₂S and 1.2 ppm NO₂, *Mater. Corros.* 54 (2003) 243-250.
- [39] L. Volpe, P.J. Peterson, The atmospheric sulfidation of silver in a tubular corrosion reactor, *Corros. Sci.* 29 (1989) 1179-1196.
- [40] B.I. Rickett, J.H. Payer, Composition of copper tarnish products formed in moist air with trace levels of pollutant gas: hydrogen sulfide and sulfur dioxide/ hydrogen sulfide, *J. Electrochem. Soc.* 142 (1995) 3723-3728.
- [41] C.O. Muller, Multiple contaminant gas effects on electronic equipment corrosion, *Corros.* 47 (1991) 146-151.
- [42] V. Kucera, Influence of acid deposition on atmospheric corrosion of metals: a review, in: R. Baboian (Ed.), *Materials Degradation Caused by Acid Rain*, ACS Symposium Series 318, American Chemical Society, Washington, DC, 1986, pp. 104-118.
- [43] C. Arroyave, M. Morcillo, The effect of nitrogen oxides in atmospheric corrosion of metals, *Corros. Sci.* 37 (1995) 293-305.
- [44] A. Fernández-García, L. Valenzuela, E. Zarza, E. Rojas, M. Pérez, Q. Hernández-Escobedo, et al., SMALL-SIZED parabolic-trough solar collectors: development of a test loop and evaluation of testing conditions, *Energy* 152(C) (2018) 401-415.

- [45] J. Wette, F. Sutter, A. Fernández-García, S. Ziegler, R. Dasbach, Comparison of degradation on aluminum reflectors for solar collectors due to outdoor exposure and accelerated aging, *Energies* 9 (2016) 916.
- [46] ISO 10062:2006, Corrosion tests in artificial atmosphere at very low concentrations of polluting gas(es), International Organization for Standardization (ISO), Geneva, 2006.
- [47] IEC 60068-2-42:2004, Environmental testing – Part 2–42: Tests – Test Kc: Sulphur dioxide test for contacts and connections, International electrotechnical commission (IEC), Geneva, 2004.
- [48] IEC 60068-2-43:2003, Environmental testing – Part 2–43: Tests – Test Kd: Hydrogen sulphide test for contacts and connections, International electrotechnical commission (IEC), Geneva, 2003.
- [49] IEC 60068-2-60:2016, Environmental testing - Part 2–60: Tests – Test Ke: Flowing mixed gas corrosion test, International electrotechnical commission (IEC), Geneva, 2016.
- [50] ISO 9223:2012, Corrosion of metals and alloys – Corrosivity of atmospheres – Classification, determination and estimation, International Organization for Standardization (ISO), Geneva, 2012.
- [51] ISO 9226:2012, Corrosion of metals and alloys – Corrosivity of atmospheres – Determination of corrosion rate of standard specimens for the evaluation of corrosivity (ISO), Geneva, 2012.
- [52] Zeiss 3D light microscope model Axio CSM 700 Operating Manual, Carl Zeiss MicroImaging GmbH., Jena, 2010.
- [53] A. Fernández-García, F. Sutter, L. Martínez-Arcos, C. Sansom, F. Wolfertstetter, C. Delord, Equipment and methods for measuring reflectance of concentrating solar reflector materials, *Sol. Energy Mater. Sol. Cells* 167 (2017) 28-52.
- [54] C. Sansom, A. Fernández-García, P. King, F. Sutter, A. García-Segura, Reflectometer comparison for assessment of back-silvered glass solar mirrors, *Sol. Energy* 155 (2017) 496-505.
- [55] A. Fernández-García, F. Sutter, M. Montecchi, F. Sallaberry, A. Heimsath, C. Heras, et al., Parameters and method to evaluate the solar reflectance properties of reflector materials for concentrating solar power technology, *SolarPACES Official Reflectance Guideline Version 3.0*, Almería, 2018.
- [56] ISO 9050, Glass in Building, Determination of Light Transmittance, Solar Direct Transmittance, Total Solar Energy Transmittance, Ultraviolet Transmittance and Related Glazing Factors, International Organization for Standardization (ISO), Geneva, 2003.
- [57] ASTM standard G173-03, Terrestrial Reference Spectra for Photovoltaic Performance Evaluation, American Society for Testing and Materials (ASTM), West Conshohocken, 2003.
- [58] Y. Fukuda, T. Fukushima, A. Sulaiman, I. Musalam, L.C.Yap, L. Chotimongkol, et al., Indoor corrosion of copper and silver exposed in Japan and ASEAN 1 countries, *J. Electrochem. Soc.* 138 (1991) 1238-1243.

[59] S. Oesch, M. Faller, Environmental effects on materials: the effect of the air pollutants SO₂, NO₂, NO and O₃ on the corrosion of copper, zinc and aluminum. A short literature survey and results of laboratory exposures, *Corros. Sci.* 39 (1997) 1505-1530.

[60] N. Sato, Basics of Corrosion Chemistry, in: S.K. Sharma (Ed.), *Green Corrosion Chemistry and Engineering: Opportunities and Challenges*, Wiley, Hokkaido University, 2011, pp. 1-32.

[61] ISO 9227:2017, Corrosion tests in artificial atmospheres -Salt spray tests, International Organization for Standardization (ISO), Geneva, 2017.

[62] M. Brogren, B. Karlsson, A. Roos, A. Werner, Analysis of the effects of outdoor and accelerated ageing on the optical properties of reflector materials for solar energy applications, *Sol. Energy Mater. Sol. Cells* 82 (2004) 491-515.