Integrating National Research Agendas on Solar Heat for Industrial Processes

Project Deliverable 3.6: Suitable ageing tests for industrial environment conditions

D 3.6 – SUITABLE AGEING TESTS FOR INDUSTRIAL ENVIRONMENT CONDITIONS		
WP	WP 3: TECHNOLOGY AND APPLICATIONS TO MEDIUM TEMPERATURE SHIP (150° - 400°)	
Due date:	M22	
Submitted	M28	
Partner responsible	FISE	
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Reviewed/supervised by:	CIEMAT	
GA Number	731287	
Start of the project	01 January 2017	
Duration of the project	48 months	
DISSEMINATION LEVEL		
PU	*Public*	
NATURE OF THE DELIVERABLE		
R		
HISTORY		
Author	Date	Comments
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1. Content of deliverable

The main objective of the INSHIP project is "acknowledging both the potential contribution of Solar Thermal technologies towards the development of sustainable industrial production and the need of a coordinated effort tackling the technological challenges still faced by these technologies when applied in industry. INSHIP aims at the definition of a European Common Research and Innovation Agenda (ECRIA) engaging major European research institutes, with relevant and recognized activities on SHIP into an integrated structure" (Horta et al.; 2016).

The Work Package 3 (WP3: Technology and applications to medium temperature SHIP (150ºC to 400ºC) "covers the research topics related to the development of technological solutions aiming at the integration of medium temperature technologies in SHIP applications" (Horta et al.; 2016).

Task 3.3 (Durability and Reliability) from WP 3 will focus on the research topics soiling and corrosion in industrial environment, enhanced reflectors and innovative automated cleaning processes.

Corrosion is one major degradation phenomenon that solar components for Concentrating Solar Power (CSP) collectors are bound to encounter during their service lifetime, especially at those sites near industrial environments, because it may seriously affect the optimal performance of materials. Therefore, the durability study of solar components (in particular reflectors) subjected to industrial atmospheres is a key subject that must be addressed. In this report, a revision of the most significant industrial environmental conditions that play a noteworthy role in solar collector degradation and the prominent parameters for their durability study are presented.

2. Results and discussion

When assessing the ageing behaviour of concentrating solar power (CSP) collectors, two different parts have to be taken into account. These are most prominently the solar mirrors but also the supporting construction. These two parts undergo different stresses during their service life that can be clustered into different load classes like thermal stress, humidity induced stress, stress caused by irradiation and, especially in neighbourhood to industrial sites, corrosive atmospheres. It is stated in the deliverable D 3.3 that the most significant atmospheric contaminants being able to act as corrosive agents are H_2S, SO_2, NO_2 and Cl_2. These molecules may react corrosive to the mirrors as well as to the supporting structure in combination with atmospheric humidity, preferably. Since the concentration of these contaminants may vary with the nature of industrial sites (combustion of fuels, pulp and paper industry, …), it is recommended to determine the corrosiveness of the atmosphere in accordance to the ISO 9223 standard and is has also to be stated that each site has to be evaluated separately.

Within this section, a brief overview of different ageing tests being applied to solar mirrors is provided followed by a short discussion of the suitability of said tests.

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2.1. Ageing tests – state of the art

Tests for mirrors in CSP solar fields can be found in the literature. Summarising the state of the art, García-Segura and co-workers propose the test methods listed in Table 1 as mirror ageing tests. The majority tests are originally established for quality assurance of photovoltaic modules (IEC 62108 and 61214). Therefore, the conditions in terms of temperatures, humidities and cycles or cycle times are not mandatory. Further, the salt spray tests and the acid rain test are suspected to overrate the corrosion since these tests are carried out under unrealistically high humidity of 100 % r.H.

Table 1. Overview of accelerated ageing tests for solar mirrors. (García-Segura et al. 2016)

Reference	**Name of test**	**Proposed conditions**
IEC 62108:2016	Damp heat	T = 85 °C, r.H. = 85 % for 1000 h or T = 65 °C, r.H. = 85 % for 1000 h
ISO 6270-2:2018	Humidity or condensation	T = 40 °C, r.H. = 100 % for 480 h
IEC 61215:2016	Thermal cycling	200 cycles between -40 °C < T < 85 °C
IEC 61215:2016	Thermal cycling + condensation	10 cycles of thermal cycle between -40 °C < T < 85 °C and -40 °C < T < 40 °C at r.H. = 100 %
IEC 62108:2016	Humidity freeze	400 cycles of thermal cycle between -40 °C < T < 65 °C, 20 h at T = 65 °C and r.H. 85 % and 4 h at T = -40 °C
ISO 11341:2004	Weather-ometer (WOM)	Xenon-arc lamp on, cycles of (T = 65 °C, 40 % < r.H. < 60 %; water spray)
ISO 11507:2007-02	QUV or UV + water	250 cycles of UV on (T = 60 °C)/off (T = 45 °C) for 4 h per half cycle
ISO 9227:2017	Salt spray (NSS)	T = 35 °C, cNaCl = 50 g L-1, pH = 6.5 – 7.2 for 480 h
ISO 9227:2017	Salt spray (CASS)	T = 50 °C, cNaCl = 50 g L-1, cCuCl2 = 0.26 g L-1, pH = 3.1 – 3.3 for 120 h
ISO 6988:85	Acid rain	Gas on (T = 40 °C, r.H. = 100 % , SO2 for 8 h) / off (T = 23 °C, r.H. < 75 % for 16 h)

Although several standardizing committees are currently working on a specific standard for solar reflectors, the first standard already finished was recently published (in March 2018) by the AENOR body. This standard (UNE 206016) proposes the set of tests included in table 2.

Table 2. Standard tests proposed by AENOR with minimum durations and main parameters.

Test	**Minimum duration**	**Summary of testing conditions**
Neutral Salt Spray (NSS) ISO 9227	480 h	T: 35 ± 2°C, pH: 6.5 to 7.2 at 25°C Sprayed NaCl solution of 50 ± 5 g/l with condensation rate of 1.5 ± 0.5 ml/h on a surface of 80 cm²
Copper-accelerated acetic acid salt spray (CASS) ISO 9227	120 h	T: 50 ± 2°C, pH: 3.1 to 3.3 at 25°C Sprayed NaCl solution of 50 ± 5 g/l and 0.26 ± 0.02 g/l CuCl2 Condensation rate of 1.5 ± 0.5 ml/h on a surface of 80 cm²
Condensation ISO 6270-2	480 h	T: 40±3°C RH: 100%
Combined thermal cycling and humidity	10 cycles	4 h at 85°C, 4 h at -40°C, Method A: 16 h at T: 40°C and 97±3% RH, Method B: 16 h at T: 85°C and 85±3% RH or

		40 h at T: 65°C and 85±3% RH
UV/Humidity ISO 16474-3	2000 h	1 cycle: 4h at UV exposure at 60±3°C followed by 4h at 100% RH at 50±3°C

Although these are standardised tests, it seems to be questionable if they are able to fully represent the stress caused by atmospheric acidic compounds as well as solid corrosive compounds. Therefore, tests adopted from testing of electronic components as proposed in deliverable D 3.3 might be possible candidates leading to meaningful test results. These are listed in Table 3.

Table 3. Overview of ageing tests under acidic atmospheres

Reference	**Name of test**
IEC 60068-2-42:2003	Sulphur dioxide test for contacts and connections
IEC 60068-2-43:2003	Hydrogen sulphide test for contacts and connections
IEC 60068-2-60:2015	Flowing mixed gas corrosion test
ISO 10062:2006	Corrosion tests in artificial atmosphere at very low concentrations of polluting gas(es)

2.2. Experimental results

Several representative industrial outdoor sites were selected to perform the outdoor exposure tests. These include both inland and coastal locations. In addition, a wide range of accelerated ageing tests were conducted, focusing in the aforementioned main corrosive atmospheric pollutants, both in the single and combined testing modes. Three configurations of reflector materials were weathered in outdoor and accelerated tests, i.e. two second-surface silvered-glass reflectors (Types 1 and 2) and one first-surface aluminium reflector (Type 3). It is worth mentioning that silvered-glass is the most deployed type of reflector in CSP plants, whilst aluminium reflectors are frequently used in solar plants for industrial process heat applications.

The experimental results obtained as a result of these investigations have been published in several high-impact scientific journals and are summarised in the following paragraphs.

A first set of experiments was devoted to the degradation of solar reflectors exposed to atmospheres containing 15 ppm of H_2S in accelerated ageing tests based on IEC 60068-2-43 standard (García-Segura et al., 2018a). Both, standard (T = 25 °C and RH = 75%) and extreme (T = 60 °C and RH = 85%) conditions were explored. Reflectance parameters were monitored in the reflective area of silvered-glass reflectors and no significant changes were obtained, although optical microscope inspections revealed the presence of some corrosion spots that grew over time. The reflective area intentionally damaged at the beginning of tests, i.e. the scratch, was deeply analyzed in Type 1 silvered-glass reflectors and it was demonstrated that the reduced sulphur gas enhances corrosion, with a monochromatic specular reflectance loss of -0.076 and -0.011 after 21 days of the extreme and standard tests, respectively, while no decrease was noticed in the tests without gas. Preliminary EDS results showed the main role of the H_2S gas in the corrosion process of the reflective layer, since all the observed silver and copper atoms might have been sulphured. Type 2 silvered-glass reflectors also featured defects after the corrosive tests, being more developed than in Type 1 reflectors, especially in terms of edge corrosion penetration (almost double length of corrosion penetration in protected edges after the extreme test). Finally, reflectance and microscopic analyses performed in the reflective area of Type 3 aluminium reflectors corroborated that the corrosive gas employed in the tests (H_2S) hardly affects aluminium reflectors.

Humid atmospheres containing high concentrations of SO_2 (acid rain) were tested in a subsequent study (García-Segura et al., 2018b). Reflectors were subjected to a number of accelerated ageing tests based on the current Kesternich test methods (DIN 50018 and ISO 6988 standards), exploring different T (T = {25, 40, 50} °C) and corrosive gas concentrations ($[SO_2]$ = {666.7, 3333.3, 6666.7} ppm) at RH = 100%. The reflective area of Type 1 silvered-glass reflectors did not show any significant loss in reflectance parameters at the end of the ageing tests. However, a major decrease in both specular and solar-weighted hemispherical reflectance (up to -0.635 and -0.301, respectively) was found in the reflective area of Type 2 silvered-glass reflectors at the end of the most harmful corrosion tests, i.e. those tests with SO_2 at the highest T (T = 50 °C) and at the highest gas concentration ($[SO_2]$ = 6666.7 ppm). Numerous corrosion defects (up to 370 spots on a 300 cm^2 total reflector surface of Type 2 reflectors) and significant corrosion penetration near the edges (up to cm order) were also found in the silver reflective layer, particularly at the end of the most deleterious corrosion tests. On the other hand, aluminium reflectors were generally not as corroded by the Kesternich tests as silvered-glass reflectors. The two high corrosion tests at the highest T and SO_2 concentration caused numerous visible corrosion spots on the reflective surface of aluminium (up to 681 spots on a 300 cm^2 total reflector surface), but this degradation was difficult to be detected by reflectance measurements, with a maximum average monochromatic specular reflectance loss in the whole reflective surface of -0.008. Furthermore, results of the most aggressive Kesternich test were compared to real data from corroded facets exposed at a commercial CSP plant near an industrial site, and it was possible to derive a correlation between the Kesternich testing time and the real on-site exposure time, being 57 the acceleration factor of the first in relation to the second.

The comparative analysis of the performance of solar reflectors in two accelerated ageing tests using two different sulphur compounds (H_2S and SO_2) at the same concentration (15 ppm) and weathering conditions (T = 60 °C and RH = 85%) was studied in another investigation (García-Segura et al., 2018c). Silvered-glass reflectors were more degraded by H_2S than by SO_2. For instance, both protected and cut edges were significantly corroded by H_2S, unlike in the rest of tests. Corrosion spots were also more numerous when the experiment was performed in an H_2S atmosphere, with an average of 24 spots per sample. In addition, aluminium reflectors were not corroded in either of the tests but some defects in the protective coating layer were detected after the SO_2 test, which implies a slightly worse performance of this reflector type when exposed to SO_2 in comparison to H_2S at the studied conditions.

A final work (García-Segura et al., Under Revision) compared the effects of H_2S, SO_2 and NO_2 pollutant gases individually at the same testing conditions (T = 40 °C, RH = 80%, $[gas]$ = 25 ppm). Moreover, it addressed the effects of combining these three gases in binary mixtures, and results were compared to real outdoor exposure sites. Type 1 silvered-glass reflectors underwent no reflectance decrease at the end of any test. However, corrosion defects were found by optical microscope inspections, especially after tests containing H_2S and SO_2. Also tests with NO_2 were responsible for extensive corrosion penetration in cut edges (up to 802 μm). Analyses in the area of the scratch informed about the ranking of the tests aggressiveness, which is as follows (from highest to lowest): H_2S+NO_2, H_2S+SO_2 and H_2S, NO_2+SO_2, NO_2, SO_2, no gas. The three tests with H_2S caused similar effects because when silver is exposed to high concentrations of H_2S, this gas is the dominant species even in the multicomponent case, although a synergistic effect between H_2S and NO_2 was observed. Then, the mixture of NO_2+SO_2 is more powerful than the use of only NO_2, and about four

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times more deleterious than only SO_2. Type 2 silvered-glass reflectors did not undergo reflectance losses but also featured numerous corrosion spots after 21 days of H_2S+NO_2, H_2S and NO_2 tests (up to 16 spots on a 300 cm^2 total reflector surface). This is explained by the powerful sulphidation of silver by H_2S, as well as the meaningful synergistic effect of the H_2S+NO_2 combination. Unlike silvered-glass reflectors, reflectance parameters of aluminium reflectors decreased at the end of the corrosion tests with NO_2, with an average loss in monochromatic specular reflectance of -0.012 in the whole reflective area. The degradation of aluminium by NO_2 was confirmed by optical microscope inspections in the form of micro-spots that uniformly scattered the whole reflective surface of samples, whereas no defects were found in the rest of tests without NO_2. Finally, some comparisons between the accelerated ageing tests with pollutant gases and the real outdoor exposures at sites near polluted industrial environments were made. According to optical microscope comparisons of the degradation defects detected in Type 1 silvered-glass reflectors, similar corrosion patterns were found in a site affected by pollution from an oil refinery and a coal-power plant and in the accelerated tests containing sulphur, i.e. Test H_2S, Test SO_2 and Test H_2S+SO_2. In addition, similarities between the corrosion defects found in the scratch at an urban-industrial site with a cement plant and in Test NO_2+SO_2 were also observed. The acceleration factor of this test in relation to the urban-industrial site was estimated at a value of 27. Finally, aluminium reflectors exposed at outdoor sites developed pitting corrosion only in the coastal environments due to the effect of salinity, whilst defects related to the presence of corrosive gases were not detected. Therefore, aluminium reflectors need longer exposure times to degrade in industrial atmospheres. However, in terms of near-specular reflectance loss, silvered-glass reflectors still perform better than aluminium reflectors during outdoor exposure at the different sites.

2.3. Discussion of a suitable test routine

Literature comparing outdoor exposure and indoor ageing experiments and including acidic species can scarcely be found. Therefore, a strategy to investigate the influence of said species is described here that has to be verified experimentally.

First, outdoor exposure stress can be clustered in load classes. Afterwards, different combinations of tests have to be carried sequentially including temperature cycles, humidity exposure, UV-tests and ageing tests comprising acidic compounds.

A standard procedure should always comprise temperature cycles as described in the IEC 61215:2016.

As reported in literature, a good agreement between indoor and outdoor ageing can be achieved by following the thermal stress with subsequently altering a NSS and a UV+water test – at least, when no corrosive agents are present (Sutter et al. 2014). Further, it has been shown, that parallel testing is not sufficient, especially when corrosive species may be present (Sutter et al. 2015). Therefore, the second load class should consist of altering NSS and UV+water tests on samples that have been preaged by a thermal cycling test.

If corrosive species might be present in the atmosphere the second tests should be modified by replacing the NSS by a CASS test or to an additional test according to the tests described in *Table* 3. Herein it is important to choose the test according to the investigated industrial site in terms of composition of contaminants.

Last but not least, in a fourth load class, additional soiling tests should be included using test sands according to the investigated site. (Klimm et al. 2016)

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However, it is noteworthy, that there are far too less results available for outdoor exposure tests in industrial sites and also in accelerated ageing tests under corrosive conditions and that there is therefore a huge demand in further development of such tests.

3. Conclusion

- A variety of different standardised tests is shown.
- Literature lacks of sufficiently broad data to conclude a defined test routine for industrial sites.
- A first approach to define a test routine for industrial sites has been successfully carried out, and significant implications regarding the most suitable reflector materials and testing conditions for industrial atmospheres with pollutant gases have been derived.
- A test strategy based on loading classes is proposed to be verified experimentally consisting of four load classes: Thermal cycling, altering UV+water and NSS tests, additional tests with corrosive agents and soiling tests.

4. Dissemination

(García-Segura et al., 2018a) García-Segura, A., Fernández-García, A., Ariza, M.J., Sutter, D., Valenzuela, L. Effects of reduced sulphur atmospheres on reflector materials for concentrating solar thermal applications. Corrosion Science, 133, 78–93, 2018. Doi: 10.1016/j.corsci.2018.01.021.

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5. Appendix

References

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