Influence of maritime/industrial atmosphere on solar thermal collector's degradation

M. J. Carvalho[1] S. Páscoa[1] R. Gonçalves[1] N. Mexa[1] T. C. Diamantino[1]

[1] LNEG – Laboratório Nacional de Energia e Geologia, Lisbon (Portugal)

Abstract

Influence of atmospheric corrosivity on solar thermal collector's degradation was studied by exposure of flat plate collectors to two different corrosivity environments, one urban Outdoor Exposure Testing (OET) site with medium corrosivity (C2-C3) and a very high/extreme corrosivity (industrial and marine) (C5-CX) atmosphere highly polluted and simultaneously with highly airborne salinity. This OET site is a natural laboratory and can be considered as an accelerated test site. Results of thermal performance measurements after two years of exposure in the OET site with very high/extreme corrosivity (C5-CX) are presented, as well as the characterization of collectors inside environment with reference materials (zinc) in terms of corrosion rate.

Measurement of thermal performance of the collectors exposed in the OET site with very high/extreme corrosivity (C5-CX) are also presented for 13/14 months and 26 months of exposure. Collectors were dismantled and optical properties of the absorbers were measured.

Keywords: *Solar thermal collectors, atmospheric corrosivity, thermal performance degradation*

1. Introduction

Solar thermal collectors (STC) have to withstand stress conditions like high temperatures, high humidity, ultraviolet irradiance or wind and snow loads depending on the geographic location. Literature points out to dependence on other influences like prevailing wind conditions, contaminants like chlorides, SO_2 and NO_x, global solar irradiation, wetness time and precipitation (Köhl, M., et al, 2004; Slamova, K et al, 2016).

Although for certification of solar thermal collector (e.g. Solar Keymark, SRCC), the testing standards applied, namely ISO 9806:2013, consider a set of tests which address testing of collector resistance to most common adverse conditions when collectors are in use, these tests do not address long term collector durability.

In order to better know how different environmental conditions influence STC, as well as collector components, two OET (Outdoor Exposure Testing) sites were used to expose collectors and collector components. The two OET sites represent an urban climate (Lisboa-Lumiar) and a maritime climate with industrial influence (Sines). The results of full collector exposure will be presented in this work for one of the OET sites where the highest corrosivity levels are present.

In section 2 the collectors exposed are described, as well as the test methodology for thermal performance evaluation of the collector. In this section the method for evaluation of corrosivity inside the collectors is also presented. A short presentation of Sines OET site characterization is given based on detailed work of Diamantino, T. et al., 2016.

In section 3 thermal performances of collectors before and after exposure are presented. In this section the corrosivity inside the collectors is also presented.

Conclusions are presented in section 4.

2. Exposure of STC at OET sites

STC studied were Flat Plate collectors with tempered glass cover. Their main characteristics are described in Table 1.

Tab. 1: Main collector characteristics

Reference of collector model	Main collector characteristics
A *	Aluminum absorber surface with PVD coating (mirotherm ®); Aluminum box.
B	Copper absorber surface with PVD coating (mirotherm ®); Aluminum box.
C *	Aluminum absorber surface with PVD coating (Eta plus ®); Aluminum box.
D *	Copper absorber surface with selective paint coating (SUNCOLOR TS S Black); Stainless steel box.

*one (1) replicate with zinc metal samples (reference materials)

For each collector model, two samples were exposed in each OET site (see Fig. 1).

Fig. 1: Installation of collector in OET- Maritime/Industrial

Thermal performance was measured in one collector of each collector model before exposure. For three of the models, zinc standard samples (reference materials) were installed in one of the collector samples to evaluate the corrosivity inside the collector.

2.1 STC thermal performance evaluation method

Originally it was decided that after two years of exposure, thermal performance would be measured for all collectors. However, considering the need to have a longer exposure period it was decided to measure only the thermal performance of collectors exposed at the Sines OET site since it has the highest corrosivity levels. It was decided to keep the collectors exposed at Lisboa-Lumiar for a longer period, except those with zinc standard samples (reference materials) which will be measured after completing similar exposure time as those in Sines OET site (26 months). The results of the performed measurements for collectors exposed in Sines are presented in this paper.

Thermal performance tests of solar thermal collectors were performed according ISO 9806:2013, using quasi-dynamic test method. The comparison is made based on the power curve as defined in ISO 9806:2013 for normal incident irradiance of 1000 Wm^{-2} (Direct irradiance = 850 Wm^{-2}; Diffuse irradiance = 150 Wm^{-2}).

Initial thermal performance was measured only in one collector of each reference. Final results of thermal performance were measured for all collectors exposed. The collectors with installed reference materials were dismantled for inspection and for evaluation of the corrosivity in zinc samples.

2.2 Optical properties of absorbers

Optical properties of absorbers were also measured. Information on optical properties of absorbers used in each collector exists and will also be presented and compared with the performed measurements of the absorber samples extracted from collectors.

The optical properties measured were solar absorptance (α_s) and thermal emittance (ε_t). The solar absorption (α_s) was measured using a Perkin Elmer's Spectrophotometer Lambda 950 UV/VIS/NIR with a 150 mm integrating sphere according to equation (1):

$$\alpha_s = \int_0^\infty \frac{[1-\rho(\lambda)]S_\lambda}{S_\lambda}\, d\lambda \qquad\qquad \text{(eq. 1)}$$

where S_λ is the spectral solar irradiance according to ASTM G173 – 03(2012) and $\rho(\lambda)$ is spectral hemispherical reflectance of the absorber coating between 300 and 2500 nm (ISO 22975-3:2014). For measurement of the spectral reflectance a spectralon ® coating reference not calibrated is used.

The thermal emittance (ε_t) was initially determined with a portable emissometer, Devices & Service Company model AE-AD3, which measures a surface emittance at 80°C of temperature and corrected for a temperature of 100ºC based on later measurements using a Spectrophotometer Frontier IR/NIR of Perkin Elmer, with integrating sphere. The thermal emittance is determined according to equation (2):

$$\varepsilon_t = \int_0^\infty \frac{[1-\rho(\lambda)]P_\lambda(T)}{P_\lambda(T)}\, d\lambda \qquad\qquad \text{(eq. 2)}$$

where $P_\lambda(T)$ is the Planck function for the black-body at a temperature T equal to 373 K and $\rho(\lambda)$ is spectral hemispherical reflectance of the absorber coating between 2.5 and 20 μm (ISO 22975-3:2014). For measurement of the spectral reflectance, a diffuse gold coating reference calibrated by Avian Technologies LLC is used.

2.3 STC inside corrosivity evaluation

In the collectors referenced in Table 1 with * five (5) replicates of zinc metal samples were put in the air gap between absorber and glazing according to Fig. 2, to evaluate the corrosivity of the micro-climate after approximately 2 years (26 months). Zinc metal samples are equal to the zinc metal samples placed outdoors to comparatively evaluate the atmospheric corrosivity. The corrosion categories of outdoor exposure test sites were obtained by determination of the corrosivity based on corrosion rate measurement of standard specimens (carbon steel, zinc, copper and aluminum) according to ISO 9226:2012. Three (3) replicates of standard specimens were exposed in support structures fixed with ceramic screws at an angle of 45° facing South (S). After exposure, corrosion products of each metal (inside and outside the collectors) were removed in accordance with ISO 8407:2009 and the corrosion rate was determined by weight loss according to ISO 9226:2012, considering the mass loss, total surface area and exposure period.
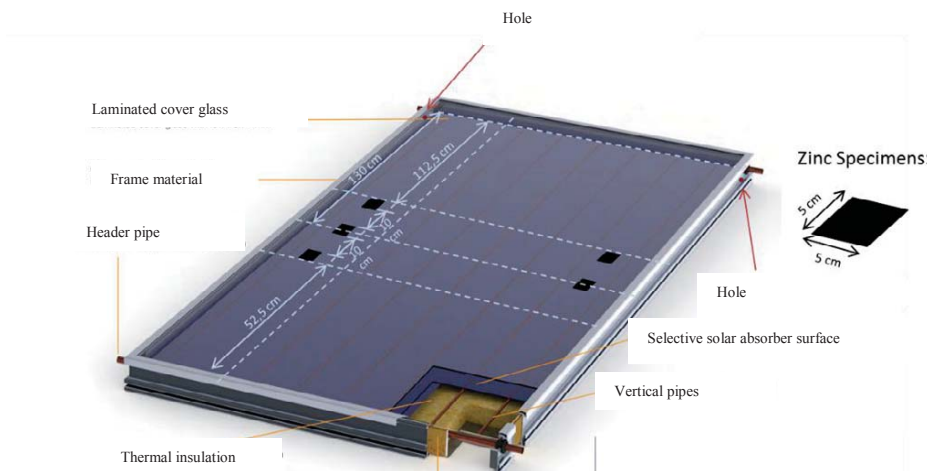

Fig. 2: Zinc specimens put in air gap between absorber and glazing.

To avoid contact with the absorber, the zinc samples inside the collector were fixed on the absorber with specially designed polymeric sample holders to ensure that the samples were galvanically isolated.

2.4 Short description of Sines OET site

Detailed description of OET site characterization can be found in Diamantino, T et al. (2016). A short description of Sines OET site is presented in Table 2. The values presented were obtained for one year (2014).

Tab. 2: Climate characterization in Sines OET site (2014) (Diamantino et al, 2016)

Location	Latitude	Longitude	Altitude [m]	Ambient temperature [°C] (average)	Solar irradiance tilt 45° G_h [W/m²]	average relative humidity [%]	Cl⁻ [mg.day⁻¹.m⁻²]	SO₂ [mg.day⁻¹.m⁻²]
Sines, Portugal	37,95°N	8,88°W	17	16,9	351	78,7	191,8	139,1

In Table 3 are presented the results of atmospheric corrosion rates in Sines OET site. Detailed presentation of these results can be seen in Diamantino, T. et al. (2016).

Tab. 3: Corrosion rates of carbon steel, copper, zinc and aluminum and corrosion categories measured after 1 year of exposure for (exposed in 2 orientation – N and S) Sines OET site (Diamantino et al, 2016)

Sines OET site								
Reference materials		**Carbon steel**		**Copper**		**Zinc**		**Aluminum**	
Samples orientation		N	S	N	S	N	S	N	S
Corrosion rate (g/(m².a)*		3535.76	1346.01	82.19	76.06	57.71	89.87	1.31	3.98
Corrosion category	**Category**	**CX**	**C5**	**CX**	**CX**	**C5**	**CX**	**C3**	**C4**
	Corrosivity	**Extreme**	**Very High**	**Extreme**	**Extreme**	**Very High**	**Extreme**	**Medium**	**High**
	Reference values (g/(m².a)*	1500<rcorr ≤5500	650<rcorr ≤1500	50<rcorr ≤90		30<rcorr ≤60	60<rcorr ≤180	0,6<rcorr ≤2	2<rcorr ≤5

*corrosion rates expressed in grams per square meter per year

3. Results of one and two years of exposure in Sines OET.

In Table 4 the periods of exposure of the collectors in Sines OET are listed, as well the exposure time (in months).

Tab: 4 – Exposure dates of STC in Sines OET site

Model (Ref.)	Installation date	Uninstallation data	Exposure time (month)
S_A1	11/04/2014	02-06-2015	14
S_A2 *	11/04/2014	01-06-2016	26
S_B1	11/04/2014	01-06-2016	26
S_B2	11/04/2014	---	Still exposed
S_C1	11/04/2014	01-06-2016	26
S_C2*	11/04/2014	01-06-2016	26
S_D1	16/06/2014	02-06-2015	13
S_D2*	16/06/2014	01-06-2016	26

*one (1) replicate with zinc metal samples

3.1 STC thermal performance results after approximately one and two years of exposure

After approximately one year of exposure (see Exposure time in Table 4) in Sines OET, two collectors were tested for thermal performance and dismantled after. Measurement of optical properties was made in one section of the absorber.

After approximately two years of exposure (see Exposure time in Table 4) in Sines OET, the collectors with zinc metal samples were also tested for thermal performance and dismantled after. Measurement of optical properties was made to one or two sections of the absorber.

One collector of type B was also tested for thermal performance. The other collector is still exposed in Sines.

Fig. 3 to 6 show the collector's power curve according to the definition of ISO 9806:2013, comparing the
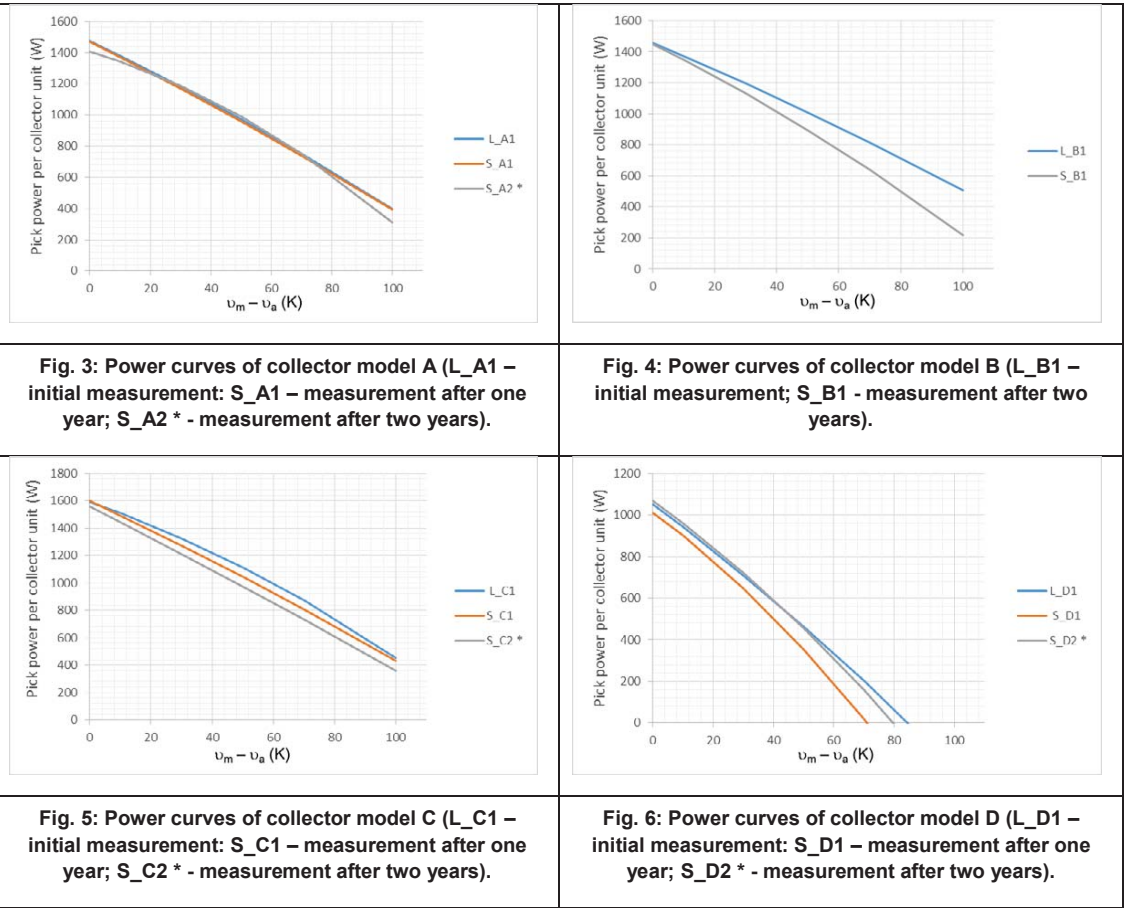
thermal performances after exposure with the initial thermal performance, measured in collectors of the same type before exposure.

Fig.3 and 5 show the thermal performance after one and two years for collectors with aluminum absorbers and PVD coatings (Mirotherm ® and Eta plus ®, respectively) (Models A and C). After one year there was almost no change in thermal performance. After two years, a difference can be observed mainly due to change in optical efficiency.

Fig. 4 shows the impact of two years of exposure on a collector with copper absorber and PVD coating (Mirotherm ®) (Model B). In this case, optical efficiency does not show differences but thermal losses are higher and a loss in power for higher temperatures is visible. The collector was not dismantled and no information is yet available on optical properties of the absorber or on other degradation factors that can explain this behavior.

Fig. 6 shows the impact of two years of exposure of a collector with copper absorber and Paint coating SUNCOLOR TS S Black (Model D). Two collectors were tested after two years. The collector with installed zinc metal samples does not show significant decrease in the power curve. This collector was dismantled and information on optical properties are available in Table 5.

The collector without zinc samples was not dismantled but shows a difference on the power curve. Further analyses will be made to this collector.

Fig. 3: Power curves of collector model A (L_A1 – initial measurement: S_A1 – measurement after one year; S_A2 * - measurement after two years).	**Fig. 4: Power curves of collector model B (L_B1 – initial measurement; S_B1 - measurement after two years).**
Fig. 5: Power curves of collector model C (L_C1 – initial measurement: S_C1 – measurement after one year; S_C2 * - measurement after two years).	**Fig. 6: Power curves of collector model D (L_D1 – initial measurement: S_D1 – measurement after one year; S_D2 * - measurement after two years).**

In Table 5 the average relative difference between the power curves is presented.

Tab. 5: Average difference of power curve relative to initial peak power (%) in the temperature range 0-100 K.

Collector sample	Exposure time (month)	Average difference of power curve relative to initial peak power (%) in the temperature range 0-100 K
S_A1	14	0,6
S_A2 *	26	1,8
S_B1	26	7,7
S_C1	13	2,2
S_C2 *	26	6,2
S_D1	26	12,4
S_D2 *	26	0,0 (temp. range 0-70 K)

In Table 6 the optical properties of the absorber of the four collector models are listed. Initial values were obtained from measurement of thirty samples of the absorber used in each collector. The values after one and two years of exposure were measured in section of the collector absorber after dismantling.

The initial values of the optical properties correspond to average values of thirty samples with corresponding standard deviation. The values after 13/14 months correspond to only one measurement in one sample of the absorber of the collector dismantled. The values after 26 months correspond to values of measurements made on two different samples of the absorber (side and bottom) and, when more than one measurement was made, the standard deviation is given.

For collectors A with aluminum substrate and PVD coating, the variation in the solar absorptance is in agreement with the change in peak power (see Fig. 3). The thermal emmitance shows a higher change and after two years the bottom part of the absorber has higher thermal emittance values. For collectors C the solar absorptance does not show significative difference although some change in peak power measured (see Fig. 5) is observed. A change in glass transparency may be the reason for this. Also in this case a higher change in thermal emmitance can be observed and this change is not uniform. The bottom part of the absorber shows higher thermal emmitance values.

Tab. 6: Optical properties of collector absorber coatings.

Note: Figures in parentheses indicate that the standard deviation observed is lower than the measurement uncertainty.

Collector sample	Exposure time (month)	Location inside collector	α	σ_α	ε	σ_ε
	Initial	---	0,96	0,00(1)	0,11	0,00(2)
S_A1	14	---	0,95	---	0,11	----
S_A2 *	26	side	0,94	0,00(1)	0,13	0,01
		bottom	0,94	0,00(1)	0,12	0,00(2)
	Initial	---	0,96	0,000(2)	0,11	0,00(3)
S_C1	13	---	0,95	---	0,14	---
S_C2 *	26	side	0,95		0,11	
		bottom	0,95		0,14	
	Initial		0,95	0,00(1)	0,72	0,02
S_D2 *	26	side	0,93		0,56	
		bottom	0,93	0,00(1)	0,56	0,00(4)

The high difference of initial thermal emittance of collector D absorber when compared with the thermal emittance of absorber sections measured may result from different application procedures in initial samples and collector absorber.

3.3 Corrosivity rates

After dismantling the collectors with zinc specimens installed, the determination of the corrosivity based on corrosion rate measurement was obtained according to ISO 9226:2012 and ISO 8407:2009.

The results are presented in Table 7. Although five samples were installed, only three were used for corrosion rate measurement. The two additional samples will be used for morphological and chemical characterization of corrosion products formed. The average corrosion rate obtained inside each collector is presented in the Table below, as well as the categories obtained according to the classification described in ISO 9223:2012.

Tab. 7: Corrosion rates and corrosion categories obtained inside collectors

Collector	Corrosion rate inside collectors r_{corr} (g/m^2.a) (SD)	Corrosion category according to ISO 9223:2012
A	90,31 (9,53)	CX
C	99,91 (10,63)	CX
D	4,56 (0,55)	C2

Collector model A and C show corrosivity levels almost equal to outdoor (89,87 g(m^2/a) (category CX). Collector D shows low corrosivity values. These differences may be explained by different ventilation rates and higher temperatures in the collectors A and C. Further investigation will be performed on this aspect.

4. Conclusions

A first evaluation of STC exposure impact to a very high/extreme corrosivity (C5-CX) (Maritime/Industrial) was performed after one year and two years of exposure by measuring thermal performance of four collector models and comparing it with the initial thermal performance measured. Simultaneously measurement of the absorbers optical properties after dismantling of the collectors was performed. The change in thermal performance was evaluated based on the power curve of each collector for normal incidence with 1000Wm^{-2}.

In one replicate of each collector model, zinc metal samples (reference material) were installed in the air gap between absorber and glass cover. These zinc metal samples were collected after the two years of exposure of the collectors and allowed measurement of corrosion rate inside collectors.

For two of the collector models, the thermal performance was measured after one year of exposure of each collector model and did not show high impact. The average difference in the power curve relative to initial peak power (%) in the temperature range 0-100 K was of the order of 0,6 and 2,2 % for collector samples S-A1 and S-C1, respectively. The reduction in thermal performance after two years was higher for collector model C (6,2%) than for collector model A (1,8%). These differences can be correlated with the measured optical properties of the absorbers.

Collector model B showed a higher difference (7,7%) which is related with higher change in thermal losses. Future dismantling of the collector will help to identify causes for this change in thermal performance.

Collector model D showed low and high differences for the same exposure period. Also in this case for the collector showing higher difference, future dismantling of the collector will help to identify causes for the change in thermal performance.

The corrosion rate inside collectors and evaluation of the corrosion category according to ISO 9223:2012 showed for models A and C corrosion rates very close to atmospheric corrosivity measured at Sines OET site

(89,87 g(m^2/a) (category CX). For model D the corrosion rate was much lower. These differences may be explained by different ventilation rates and higher temperatures in the collectors A and C. Further investigation will be performed on this aspect.

The corrosion rates inside the collectors installed in Lisboa-Lumiar OET site will be measured for approximately the same time as for Sines OET site and will allow comparison between corrosion category inside the collectors and atmospheric corrosion for this test site.

5. Acknowledgements

6. References

ASTM G173 – 03, 2012. Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface

Diamantino, T. C. , R. Gonçalves, A. Nunes, S. Páscoa, M. J. Carvalho, 2017. Durability of different selective solar absorber coatings in environments with different corrosivity. Solar Energy Materials & Solar Cells, Volume 166, July 2017, Pages 27–38, (https://doi.org/10.1016/j.solmat.2017.03.004)

ISO 8407:2009 Corrosion of metals and alloys - Removal of corrosion products from corrosion test specimens. 2009

ISO 9223:2012 Corrosion of metals and alloys - Corrosivity of atmospheres - Classification, determination and estimation. 2012

ISO 9226:2012 Corrosion of metals and alloys - Corrosivity of atmospheres - Determination of corrosion rate of standard specimens for the evaluation of corrosivity. 2012

ISO 9806:2013(E), Solar Energy – Solar Thermal Collectors – Test Methods

ISO 22975-3:2014, Solar energy- collector components and materials – Part 3: Absorber surface durability, ISO 2014

Köhl, M., Carlsson, B., Jorgensen, G. J., Czanderna, A. W. (Editors), Performance and Durability Assessment. Optical Materials for Solar Thermal Systems. 2004, Elsevier (ISBN 0-08-044401-6)

Performance and Durability Assessment. Optical Materials for Solar Thermal Systems. Köhl, M., Carlsson, B., Jorgensen, G. J., Czanderna, A. W. (Editors), 2004, Elsevier (ISBN 0-08-044401-6)

Slamova, K., I. Duerr, T. Kaltenbach, M. Köhl, 2016. Degradation effects of maritime atmosphere on metallic components of solar collectors. Solar Energy Materials & Solar Cells 147, 246–254 (http://dx.doi.org/10.1016/j.solmat.2015.12.011)